PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL

[ ] REVISION NO. ____

Project No. __E-19-648__   DATE: __4/10/81__

Project Director: __Dr. A. S. Teja__   School/XXX __Chemical Engineering__

Sponsor: __National Science Foundation; Washington, D. C. 20550__

Type Agreement: __Grant No. CPE-8104201__

Award Period: From __3/1/81__ To __8/31/82* 84__ (Performance) __----__ (Reports)

Sponsor Amount: __$31,688__   10/31/84   Contracted through:

Cost Sharing: __$1,766 (E-19-357)__   GTRI

Title: __Collaborative Research: Generalized Corresponding States Principle Using Two__
__Nonspherical Reference Fluids__

ADMINISTRATIVE DATA   OCA CONTACT Duane Hutchison   x 4820

1) Sponsor Technical Contact: __Mr. David O. Cooney, NSF Program Officer; Thermodynamics__
__and Mass Transfer; Division of Chemical and Process Engineering; Directorate for Engineering__
__and Applied Science; NSF; Washington, D. C. 20550 (202/357-9606)__

2) Sponsor Admin./Contractual Contact: __Ms. Karen L. Sandberg, NSF Grants Official; Section I,__
__AAEO/EAS Branch; Division of Grants and Contracts; Directorate For Administration;__
__National Science Foundation; Washington, D. C. 20550 (202/357-9626)__

Reports: __See Deliverable Schedule__   Security Classification: __None__

Defense Priority Rating: __None__

RESTRICTIONS

See Attached __NSF__ Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval - Contact OCA in each case. Domestic
travel requires sponsor approval where total will exceed greater of $500 or
125% of approved proposal budget category.

Equipment: Title vests with __GIT__

COMMENTS: * Includes the usual six (6) month unfunded flexibility period. Two (2)
additional years are contingent upon the availability of funds.

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GEORGIA INSTITUTE OF TECHNOLOGY　　　　　OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date___April 23, 1985___

Project No.___F-19-648_____　School XXXXX　Chemical Engineer

Includes Subproject No.(s)___N/A_____

Project Director(s)___Dr. A.S. Teja_____ GTRC / XXX

Sponsor___NSF_____

Title___Collaborative Research: Generalized Corresponding States Principle Using Two

___Nonspherical Reference Fluids._____

Effective Completion Date:___October 31, 1984_____ (Performance)_January 31, 1985_(Reports)

Grant/Contract Closeout Actions Remaining:

☐ None

☐ Final Invoice or Final Fiscal Report

☐ Closing Documents

☒ Final Report of Inventions　for our records.

☐ Govt. Property Inventory & Related Certificate

☐ Classified Material Certificate

☐ Other_____

Continues Project No._____　Continued by Project No._____

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FORM OCA 69.285

Georgia Institute of Technology

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING
(404) 894- 3098

November 17, 1981

Dr. Mary Anne Farrell Epstein
Program Director, Thermodynamics and
  Transport Phenomena,
National Science Foundation
Washington, D.C.   29550

Dear Dr. Epstein,

Re: NSF Grant No. CPE 8104201 Collaborative Research: Generalized
Corresponding States Principle using two non-spherical reference fluids.

Thank you for your letter of September 25, 1981. I enclose the
following:

(1) A summary of scientific progress

(2) A statement to the effect that no funds will remain unobligated
     by the end of the first year of the grant period.

(3) Four copies of the proposed budget for the second year

(4) Current information about other research support.

Yours sincerely,

Dr. Amyn S. Teja

AST/kh

(1) SUMMARY OF SCIENTIFIC PROGRESS ON GRANT # CPE 8104201

"Generalized Corresponding States Principle Using Two Non-spherical

Reference Fluids"

Throughout this progress report we will presume that the reader has a
copy of our proposal (# CPE8104201). Research work on the use of the Gener-
alized Corresponding States Principle has progressed during the initial year
of this grant and we are pleased to report achievements in a number of areas.
For convenience, this report will be divided into sections corresponding to
the tasks listed in the proposal.

Task A: Choice of reference substances, equations and mixing rules. (Grant Years 1, 2 and 3)

We have shown that the proper choice of reference fluids leads to im-
provements in the accuracy of prediction of vapor-liquid equilibria, and vapor
and liquid densities. Three classes of mixtures have been studied (i) CO_2 +
hydrocarbon mixtures, with CO_2 and a hydrocarbon as the reference fluids.
(ii) water + hydrocarbon mixtures with water and a hydrocarbon as the reference
fluids and (iii) alcohol + hydrocarbon mixtures with an alcohol and a hydrocar-
bon as the reference fluids. We have also begun our study of the mixture
models suitable for the various classes of systems mentioned above. In par-
ticular, we have developed new mixture models applicable to each of the
aforementioned classes of mixtures. A paper describing this work will be pre-
sented to the Spring National Meeting of the AIChE in March 1982. During the
coming year we plan to continue our studies of asymmetric mixtures and, in
particular, of mixture models suitable for such systems over wide ranges of
temperatures, densities and compositions.

Task B: The prediction of vapor-liquid equilibria. Grant years 1 and 2.

We have developed a computer package for the implementation of the Generalized Corresponding States Principle to vapor-liquid equilibria. Indeed, this program package has been used to test the effect of reference fluids and mixing rules on the predictions described under Task A. Currently, the package allows the user flexibility in the choice of one-fluid mixing rules and reference fluid equations of state. The following reference equations are available:

(a)   The Bender equation of state for methane, ethane and n-pentane

(b)   The BWRS equation of state for n-octane and n-decane.

(c)   The Teja-Patel equation of state for the hydrocarbons, carbon dioxide, water, methanol and inorganic gases.

(d)   The Soave and Peng-Robinson equations of state for the hydrocarbons and inorganic gases.

(e)   The Won-Walker equation of state for polar substances.

At present, the computer package permits calculations of bubble points (P or T), dew points (T only) and isothermal flash vaporizations. During the coming year, work will proceed on improvements of the programs and the inclusion of additional subroutines for other phase equilibrium calculations.

Task C: Calculation of enthalpy and entropy deviations. Grant Year 1.

It was decided that the calculation of critical states represented a more severe test of the Generalized Corresponding States Principle than enthalpy and entropy calculations. Work on this task has therefore been deferred until the second grant year.

Task D: Calculation of critical states and critical end points. Grant years 2 and 3.

Since critical point predicitions provide a severe test of thermodynamic theories, we initiated the study of critical phenomena this year in place of Task C, instead of waiting until the second year as originally proposed. The field of critical phenomena has undergone resurgence recently because of interest in reservoir simulation and oil recovery calculations. We have concentrated on three aspects of these calculations: (i) alternative forms of the Gibbs criteria for describing singular points; (ii) critical state calculations using equations of state; and (iii) critical state calculations using a four-parameter Corresponding States principle. In particular, we have examined various mixture models and their suitability for asymmetric mixtures such as those which are used in supercritical extraction processes. A paper on the extension of the four-parameter Corresponding States Principle to asymmetric mixtures was presented to the Annual Meeting of the AIChE in November 1981 in New Orleans. During the coming year, we aim to apply these ideas to equations of state and to the Generalized Corresponding States Principle.

Task E: Liquid-liquid and Vapor-liquid-liquid equilibria. Grant year 3.

Although work on this task is not scheduled to begin for another year, initial data gathering and the formation of a data bank has already begun.

STATEMENT OF FUNDS

Graduate Students supported on NSF grant at Georgia Tech.

(i)   Mr. R. L. Smith

Undergraduate student supported on NSF grant at Georgia Tech.

(i)   Mr. D. Pittaluga (summer 1981)

Faculty (PI):

(i)   Dr. A. S. Teja (2 months)

Funds obligated: Nil

OTHER RESEARCH SUPPORT

Dr. A. S. Teja: None.

3/1/82 TO 2/28/83
SUMMARY
PROPOSAL BUDGET

	FOR NSF USE ONLY		
GANIZATION	PROPOSAL NO.	DURATION (MONTHS)	
GEORGIA TECH RESEARCH INSTITUTE		Proposed	Granted
NCIPAL INVESTIGATOR/PROJECT DIRECTOR	AWARD NO.		
A. S. Teja			

SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates List each separately with title; A.6. show number in brackets)	NSF FUNDED PERSON-MOS.			FUNDS REQUESTED BY PROPOSER	FUNDS GRANTED BY NSF (IF DIFFERENT)
	CAL.	ACAD	SUMR		
A. S. Teja, Associate Professor		1	1	$ 7460	$
) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)					
( ) TOTAL SENIOR PERSONNEL (1-5)					
OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
) POST DOCTORAL ASSOCIATES					
) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)					
1) GRADUATE STUDENTS 2100 / qtr.				8400	
1) UNDERGRADUATE STUDENTS				1075	
1) SECRETARIAL-CLERICAL				550	
) OTHER					
TOTAL SALARIES AND WAGES (A+B)				17485	
RINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 11.59% of A and B-5				928.	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				18413.	
ERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $1,000; TEMS OVER $10,000 REQUIRE CERTIFICATION)					
TOTAL PERMANENT EQUIPMENT					
RAVEL 1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)				1000	
2. FOREIGN					
ARTICIPANT SUPPORT COSTS					
. STIPENDS $					
. TRAVEL					
. SUBSISTENCE					
. OTHER					
TOTAL PARTICIPANT COSTS					
OTHER DIRECT COSTS					
. MATERIALS AND SUPPLIES					
. PUBLICATION COSTS/PAGE CHARGES				500	
. CONSULTANT SERVICES					
. COMPUTER (ADPE) SERVICES				1200	
. SUBCONTRACTS					
. OTHER					
TOTAL OTHER DIRECT COSTS				1700	
OTAL DIRECT COSTS (A THROUGH G)				21113	
NDIRECT COSTS (SPECIFY)					
OTAL INDIRECT COSTS 55%				11612	
OTAL DIRECT AND INDIRECT COSTS (H + I)				32725	
ESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS GPM 252 AND 253)					
MOUNT OF THIS REQUEST (J) OR (J MINUS K)				$ 32725	$

TYPED NAME & SIGNATURE*	DATE	FOR NSF USE ONLY	
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. REP. TYPED NAME & SIGNATURE*	DATE	Date Checked / Date of Rate Sheet	Initials - DGC
			Program

The Correlation and Prediction of Critical States of Mixtures
Using a Corresponding States Principle

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School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Ga.   30332

ABSTRACT

The calculation of critical states using a Corresponding States Principle is described. It is shown how a correlation of binary critical T^c - P^c behavior can lead to predictions of high pressure as well as low pressure phase equilibria and PVT properties. Critical states (including V^c - X^c behavior) of hydrocarbon systems as well as systems containing polar components have been successfully correlated using this method. The applicability of the method to asymmetric mixtures which are typical of supercritical extraction processes is examined.

INTRODUCTION

The PVT behavior of mixtures in the critical region is of practical importance in the petroleum and energy industries and also in processes involving supercritical gas extraction. Indeed, a knowledge of phase equilbria in the critical region is necessary for assessing the feasibility of supercritical gas extraction processes.

The calculation of critical lines of mixtures is also of theoretical interest, since the topology of these lines in the PVTx space is complex and it may be argued that their calculation provides a most severe test of any theory.

In this work, we outline an extended Corresponding States method which has been used with considerable success for the calculation of densities [1-3], vapor-liquid equilibria [3-5] and critical and azeotropic states [6,7] of mixtures when the components of the mixture do not differ too greatly in size. The applicability of the method to asymmetric mixtures (such as ethylene + napthalene, which are typical of supercritical extraction processes) is examined.

THE EXTENDED CORRESPONDING STATES METHOD:

A large number of methods for the calculation of thermodynamic properties make use of extensions of the (two parameter) Corresponding States Principle. These extended Corresponding States methods may be divided into two broad categories. The first, and by far the largest, category involves a perturbation of a thermodynamic (configurational) property about that of a spherical reference fluid. The theoretical justification for this perturbation was presented by Pitzer [8] who showed that the compressibility Z_{ii} of fluid i at reduced temperature T_R and pressure P_R is given by the sum of the compressibility $Z^{(0)}$ of a spherical reference fluid at the same reduced temperature and pressure and a deviation $\omega_{ii} Z^{(1)}$ which is proportional to the acentric factor ω_{ii} of substance i. Thus:

$$Z_{ii}[T_R, P_R] = Z^{(0)}[T_R, P_R] + \omega_{ii} Z^{(1)}[T_R, P_R] \tag{1}$$

Teja et al. [9] later showed that the perturbation may be carried out about the property of a nonspherical reference fluid.

The second category of extended Corresponding States methods involves a perturbation of the variables T_R and V_R (or P_R) and has been termed the shape factor approach by Leland [10]. It is this approach that is described below. For convenience, the shape factor approach will be desribed in terms of the configurational Helmholtz energy rather than compressibility, as the former is more suited to the calculations performed in this study.

Two pure substances i and o are defined to be in corresponding states if the configurational Helmholtz energy of substance i at temperature T and volume V may be obtained from the configurational Helmholtz energy of substance 0 at temperature $T/f_{ii,o}$ and volume $V/h_{ii,o}$ as follows:

$$A_{ii}[T,V] = f_{ii,o} A_o[T/f_{ii,o}, V/h_{ii,o}] - RT \ln h_{ii,o} \tag{2}$$

where the subscripts ii,o signify a property of i relative to substance o. The parameters $f_{ii,o}$ and $h_{ii,o}$ are related to the critical constants of substances i and o by

$$f_{ii,o} = (T_{ii}^c/T_o^c) \, \theta_{ii,o} \tag{3}$$

$$h_{ii,o} = (V_{ii}^c/V_o^v) \, \phi_{ii,o} \tag{4}$$

where the shape factors $\theta_{ii,o}$ and $\phi_{ii,o}$ are unity for simple spherical fluids and are slowly varying functions of reduced temperature T_{Ri} and reduced volume V_{Ri} in the general case. They may be thought of as small perturbations of the reduced temperature and volume. Analytical expressions for the shape factors have been reported by Leland and Chappelear [10] and are of the form:

$$\theta_{ii,o} = 1 + (^{\omega}_{ii} - ^{\omega}_{o}) F_1[T_{Ri}, V_{Ri}] \qquad (5)$$

$$\phi_{ii,o} = (Z^c_o/Z^c_{ii}) \{1 + (^{\omega}_{ii} - ^{\omega}_{o}) F_2 [T_{Ri}, V_{Ri}]\} \qquad (6)$$

where F_1 and F_2 are functions of the reduced temperature and volume. Although the shape factor correlations were originally obtained for the n-alkanes (upto about n-decane) relative to methane, the utility of this method lies in the fact that they have been used successfully for other hydrocarbons and for polar and quantum fluids [3,7]. Deviations from experiment are small for the n-alkanes and somewhat larger for polar and quantum fluids, as expected [7]. It should be noted that the deviations of the shape factors from unity are proportional to the differences in the acentric factors as well as to the ratio of the critical compressibility factors of the two substances i and o. For normal fluids, the critical compressiblity factor Z^c is a linear function of the acentric factor and a three-parameter form of the Corresponding States Principle results. For fluids for which Z^c is no longer a linear function of ω, a four-parameter Corresponding States Principle is obtained.

Given the properties of a reference substance (these may, for example, be obtained from an accurate equation of state or from tabulated PVT properties) and the shape factor correlations, then the calculation of the thermodynamic properties of any substance i requires a knowledge only of its critical constants T^c_{ii}, V^c_{ii}, Z^c_{ii} and ω_{ii}.

Equation (2) may be extended to mixtures by assuming that the configurational Helmholtz energy of a mixture, after subtraction of a combinatorial term, is equal to that of a single hypothetical equivalent substance. This is the so-called one-fluid model for mixtures.

$$A_{mixture} [V,T,x] = A [V,T,x] + A_{comb} \qquad (7)$$

The configurational Helmoltz energy of the equilvalent substance A[V,T,x] may then be obtained from that of the reference substance using eqn. (2):

$$A(V,T,x] = f A_o[T/f, V/h] - RT \ln h \qquad (8)$$

where the parameters f and h depend on the composition of the mixture. Various prescriptions may be written for these parameters. A convenient form of these prescriptions is as follows:

$$f\,h^{\delta} = \Sigma\Sigma\; x_i x_j f_{ij} h_{ij}^{\delta} \qquad (9)$$

$$h = \Sigma\Sigma\; x_i x_j h_{ij} \qquad (10)$$

When $\delta=0$, these equations reduce essentially to the modified Kay's model proposed by Prausnitz and Gunn [11]; setting $\delta=1$ leads to the van der Waals one fluid model [10], and setting $\delta=0.25$ leads to the model proposed by Plocker et al. [12] for mixtures in which the molecular sizes of the components differ by a factor of 3 or more. It should be added that the critical temperatures and volumes used in the original one-fluid models described above are "weighted" by the shape factors in equations (9) and (10).

In using eqns. (9) and (10), the like terms (i=j) may be obtained from pure component properties, but the unlike terms (i≠j) require mixture data for their evaluation. The usual procedure is to transfer the problem of evaluating f_{ij}, h_{ij} to the problem of evaluating the binary interaction coefficients ξ_{ij} and η_{ij}, where:

$$f_{ij} = \xi_{ij}\,(f_{ii} f_{jj})^{1/2} \qquad (11)$$

$$h_{ij} = \eta_{ij}\{(h_{ii}^{1/3} + h_{jj}^{1/3})/2\}^3 \qquad (12)$$

Values of ξ_{ij} and η_{ij} are generally close to unity and no further information is required to predict the properties of ternary and higher mixtures [7].

For nonpolar mixtures in which the molecular sizes of the components differ by a factor of 3 or less, it is usually sufficient to use one adjustable co-efficient to characterize each binary system and it is common to assume η_{ij} = 1.0, with ξ_{ij} being calculated from experimental data. Values of ξ_{ij} estimated from the correlation of various thermodynamic properties and phase equilibria agree very well with each other [7], but depend on the particular mixture prescription (eqns. 9-10) chosen.

The combinatorial contribution to the Helmholtz energy for an ideal mixture is given by:

$$A_{comb} = RT \sum_i x_i \ln x_i \qquad (13)$$

When the molecules differ appreciably in size, this equation is known to be in-adequate. The Flory-Huggins equation was derived for monmer-polymer mixtures (ie. for molecules made up of like segments), but it has been applied to many different

asymmetric mixtures. This equation is given by:

$$A_{comb} = RT\Sigma\, x_i \ln \psi_i \tag{14}$$

where the volume fraction ψ_i is given by:

$$\psi_i = x_i\, V_{ii} \Big/ \sum_j x_j V_{jj} \tag{15}$$

In the binary case, we may write the two volume fractions by:

$$\psi_1 = x_1/(x_1 + r\, x_2) \tag{16}$$

$$\psi_2 = rx_2/(x_1 + rx_2) \tag{17}$$

where

$$r = V_{11}/V_{22} \tag{18}$$

is the ratio of molar volumes (or the ratio of semiarbitrarily defined segments). Since the systems considered in this study are not polymer solutions, we have treated r as an empricial parameter in this study. Previous studies have shown [7,13] that r = 1 when the components of a mixture do not differ appreciably in size.

CRITICAL STATES OF BINARY MIXTURES:

Critical states of binary mixtures satisfy the following equations [6]:

$$A_{2x} \cdot A_{2v} - A_{xv}^2 = 0 \tag{19}$$

$$A_{3x} \cdot A_{2v}^3 - 3\, A_{2xv} A_{xv} A_{2v}^2 + 3\, A_{x2v} A_{xv}^2 A_{2v} - A_{3v} A_{xv}^3 = 0 \tag{20}$$

where the subscripts denote derivatives eg.

$$A_{2xv} = \partial^3 A/\partial x^2\, \partial V$$

It should be noted that these equations contain second and third derivatives of the Helmholtz energy (and, therefore, of the one-fluid model-eqns. 9, 10 and 17) with respect to composition. It may therefore be argued that the calculation of critical states represents a severe test of the mixture model chosen, since errors will tend to increase with successive differentiation of the function.

Solution of the two equations at a given critical composition gives the critical temperature and volume (and hence the critical pressure) of the system. Details of the procedure are given elsewhere [6].

RESULTS

Methane was chosen as the reference substance, since an accurate analytical equation of state is available for this substance and shape factor correlations relative to methane are also available. The results of the calculation of critical states are discussed below.

Figures 1-3 show typical results for a nonpolar hydrocarbon mixture (methane + propane) in which the components do not differ appreciably in size. It is seem that P^c vs T^c, T^c vs. X^c as well as V^c vs X^c curves can be correlated with $\xi_{12} = 1.0$ and $\eta_{12} = 1.04$ when the van der Waals one-fluid prescription ($\delta=1$) and the ideal combinatorial term (r=1) are used for this system. In general, only one binary interaction coefficient - close to unity- is required for such systems [6,7]. Moreover, Barber et al. [14] have shown that the single binary interaction coefficient calculated from the critical states of mixtures can be used to predict vapor-liquid equilibria and second virial coefficients of the system. This is shown in Figs. 4 and 5 which show the azeotropic locus and second virial coefficients of propane + perfluorocyclobutane mixtures calculated with $\xi_{12} = 0.89$ which was obtained from the correlation of the critical states of the system [14]. A number of authors [1,5,7] have used two binary interaction coefficients to characterize each binary mixture. Our studies have shown that the use of two adjustable coefficients leads to values which are not unique and which do not necessarily show a regular trend for a series of binary mixtures with a common component. The latter is usually true when only one adjustable coefficient is used in the calculations.

Figures 6-10 show the results of our calculations for three asymmetric mixtures (methane + n-decane, CO_2 + n-decane and ethylene + napthalene) in which the components differ in size (as measured by the ratio of their critical volumes) by a factor of 3 or more. These systems are typical of those found in supercritical extraction. In general, there is a great deal of uncertainty in the available values of the critical volumes of large molecules (indeed, the critical volumes of many single and multi-ring aromatic compounds are not known). For asymmetric mixtures, we have therefore replaced eqn. (4) with

$$h_{ii,o} = \{(T_{ii}^c/P_{ii}^c)/(T_o^c/P_o^c)\} \phi_{ii,o} \tag{21}$$

This equation has the advantage that critical volumes are not required and is equivalent to a slight modification of the mixture model (ie. of multiplying $h_{ii,o}$ in eqns. (9) and (10) by Z_{ii}^c/Z_o^c). We have found that this modification leads to better predictions than the original model (There is of course little change for mixtures of small molecules since $Z_{ii}^c \approx Z_o^c$). Figs. 6-10 show that upto two adjustable binary interaction coefficients are required for the correlation of the critical properties of asymmetric mixtures.

The use of the Flory-Huggins combinational term did not lead to a reduction in the number of adjustable coefficients required. It would therefore appear that only a small contribution to the Helmholtz energy can be attributed to the combinatorial term. The use of r as an additional empirical constant in the methane + n-decane system is shown in Figs. 6-8. The major effect of varying r appears to be on the critical pressure of the system, with critical temperature remaining practically unchanged. However, the accuracy of critical data in practice does not warrant the use of three adjustable constants in any method and r was set to unity in all other systems reported here. Use of the Plocker et al [12] one-fluid model ($\delta=0.25$) did not also lead to a reduction in the number of adjustable constants required. Hence the van der Waals one-fluid model ($\delta=1$) was used in all calculations presented in this work. Our calculations lead us to believe that only slight modifications of the van der Waals one-fluid model are required for the treatment of asymmetric mixtures.

It may be argued that part of the errors that arise in the treatment of asymmetric mixtures may result from the fact that the properties of large molecules (such as n-decane or n-hexadecane) cannot be obtained from the properties of methane using the shape factor correlations. That this is not so is demonstrated conclusively in Figures 11 and 12, which shown P^c vs T^c curves for n-hexane + n-tridecane and n-hexane + cis-decalin mixtures. These systems can be well correlated with the extended corresponding states method, although the components of the mixture are large. The relative size differences in these systems are, of course, less than 3.

A final observation that should be mentioned is that T^c vs X^c behavior of many systems (including asymmetric mixtures can often be correlated equally

well by various models. This is shown in Fig. 7, where the T^c-X^c behavior of the methane + n-decane system is correlated with three different one-fluid models. It is obvious that this behavior is not sufficient to distinguish between the various models and that the simultaneous fit of $P^c-V^c-T^c-x^c$ data is a much more severe test of the models. The van der Waals one-fluid model (with a maximum of two adjustable binary interaction coefficients) appears to be the best amoung the models tested.

CONCLUSIONS

We have examined the applicability of an extended Corresponding States Method using shape factors to the calculation of critical states of asymmetric mixtures which are typical of systems used in supercritical extraction. Various modifications of the method have been evaluated. In general, the van der Waals one-fluid model with two adjustable constants appears to yield results which compare well with experiment, although there remains room for improvement. The method provides a means for the quantitative prediction of the behavior of interest in supercritical extraction.

ACKNOWLEDGEMENT

NOMENCLATURE

A	Helmholtz energy
F	functions in eqns. (5) and (6)
f	Corresponding States energy parameter
h	Corresponding States size parameter
P	pressure
R	gas constant
r	adjustable constant
T	temperature
V	volume
x	mol fraction
Z	compressibilty factor

Greek Symbols

δ	exponent in mixture model (eqn. 9)
ξ	binary interaction coefficient
η	binary interaction coefficient
ω	acentric factor
θ	shape factor for energy (temperature)
ϕ	shape factor for size (volume)
ψ	volume (or segment) fraction

Subscripts

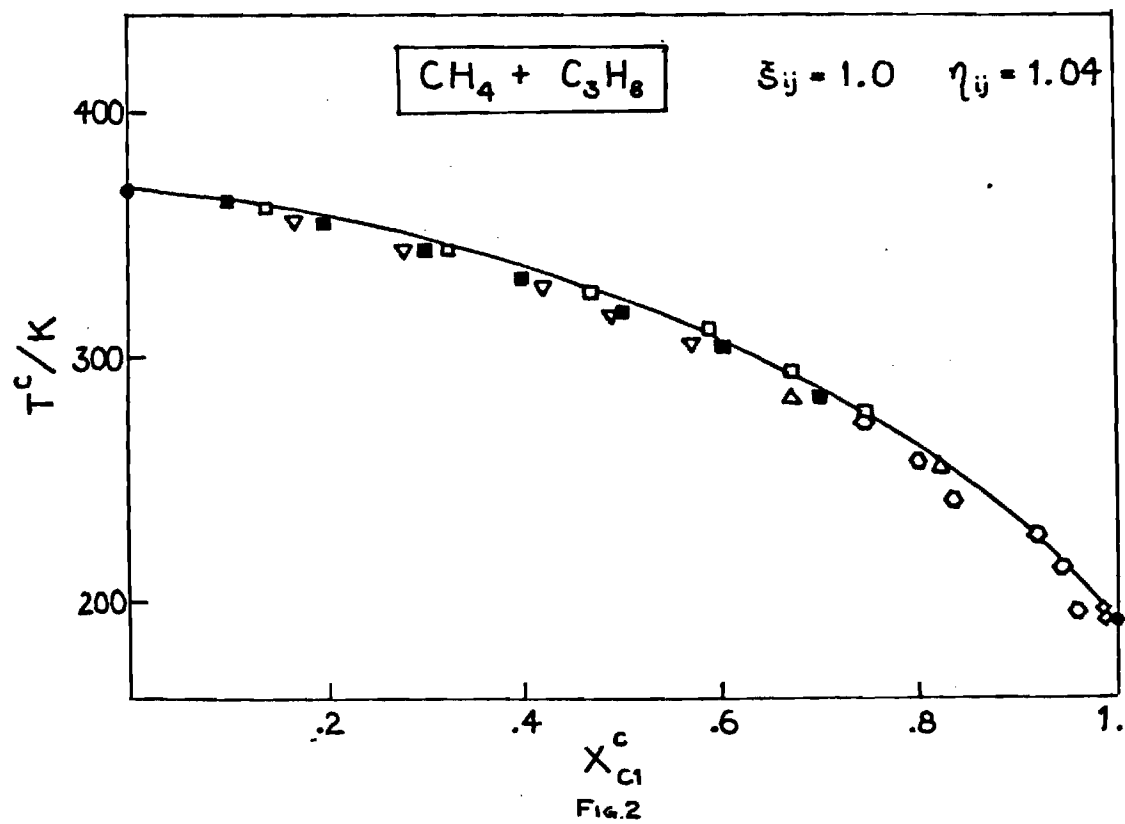|	
comb	combinatorial
i,j	components i,j
o	reference fluid
1,2	components 1,2

Superscripts

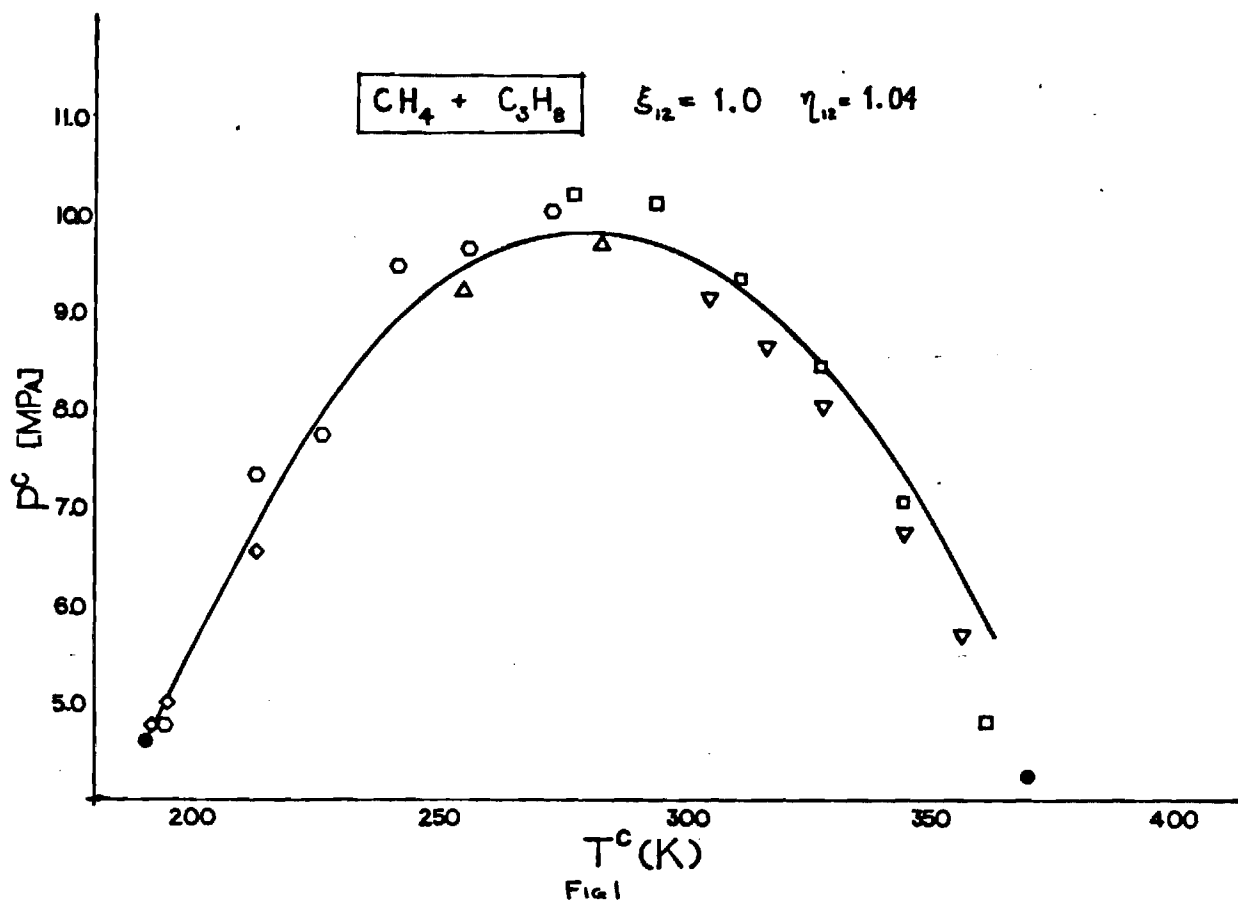|	
c	critical
(o)	spherical reference fluid

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(11)

FIGURE CAPTIONS

Fig 1. P^c vs T^c behavior of the methane + propane system with ξ_{12} = 1.0 and η_{12} = 1.04.

Fig 2. T^c vs x^c behavior of the methane + propane system with ξ_{12} = 1.0 and η_{12} = 1.04.

Fig 3. V^c vs x^c behavior of the methane + propane system with ξ_{12} = 1.0 and η_{12} = 1.04.

Fig 4.   The azeotropic locus of propane + perfluorocyclobutane mixtures predicted with ξ_{12} = 0.89, η_{12} = 1.0.

Fig 5.   Second virial coefficients of propane + perfluorocyclobutane mixtures predicted with ξ_{12}=0.89, η_{12} = 1.0

Fig 6. P^c vs T^c behavior of the methane + n-decane system

Fig 7. T^c vs x^c behavior of the methane + n-decane system

Fig 8. V^c vs x^c behavior of the methane + n-decane system

Fig 9. P^c vs T^c behavior of the CO_2 + n-decane system.

Fig 10. P^c vs T^c behavior of the ethylene + napthalene system.

Fig 11. P^c vs T^c behavior of the n-hexane + n-tridecane system.

Fig 12. P^c vs T^c behavior of the n-hexane + decalin system.

Fig.1

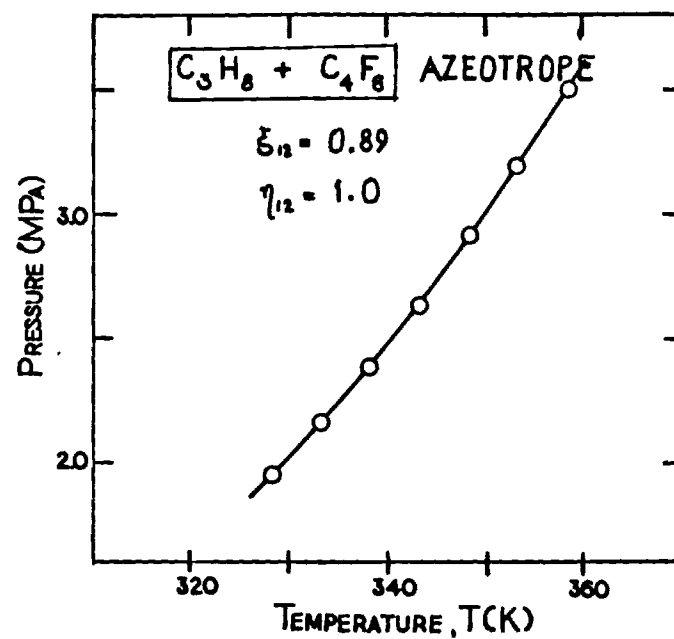Fig.2

FIG 3

$CH_4 + C_3H_8$

$\xi_{ij} = 1.0$ $\eta_{ij} = 1.04$

V^c $m^3 mol^{-1} \times 10^6$

X^c_{C1}

$C_3H_8 + C_4F_8$ AZEOTROPE

$\xi_{12} = 0.89$

$\eta_{12} = 1.0$

PRESSURE (MPa)

TEMPERATURE, T(K)

FIG 4

FIG 5.

FIG 6

$CH_4 + n\,C_{10}H_{22}$

$\xi_{12} = 1.0 \qquad \eta_{12} = 0.81$

FIG 7

$CH_4 + n\,C_{10}H_{22}$

$\xi_{12} = 1.0 \qquad \eta_{12} = 0.81$

FIG 8

$CO_2 + n\,C_{10}H_{22}$

$\xi_{12} = 1.0 \qquad \eta_{12} = 0.81$

Fig 9

$CO_2 + n\,C_{10}H_{22}$

$\xi_{ij} = 0.81$

$\eta_{ij} = 1.0$

Fig 10

CO₂ + n C₁₀H₂₂

$\xi_{ij} = 0.81 \qquad \eta_{ij} = 1.0$

Vertical axis: $V^c \ \ m^3 \, mol^{-1} \times 10^6$

Horizontal axis: X_{C10}

Fig II

C₂H₄ + C₁₀H₈

$\xi_{12} = 0.9, \ \eta_{12} = 1.0$

Vertical axis: $P^c / MPa.$

Horizontal axis: T^c / K

$n\,C_6H_{14}\ +\ n\,C_{13}H_{28}$

$\xi_{12} = 1.0 \qquad \eta_{12} = 0.9$
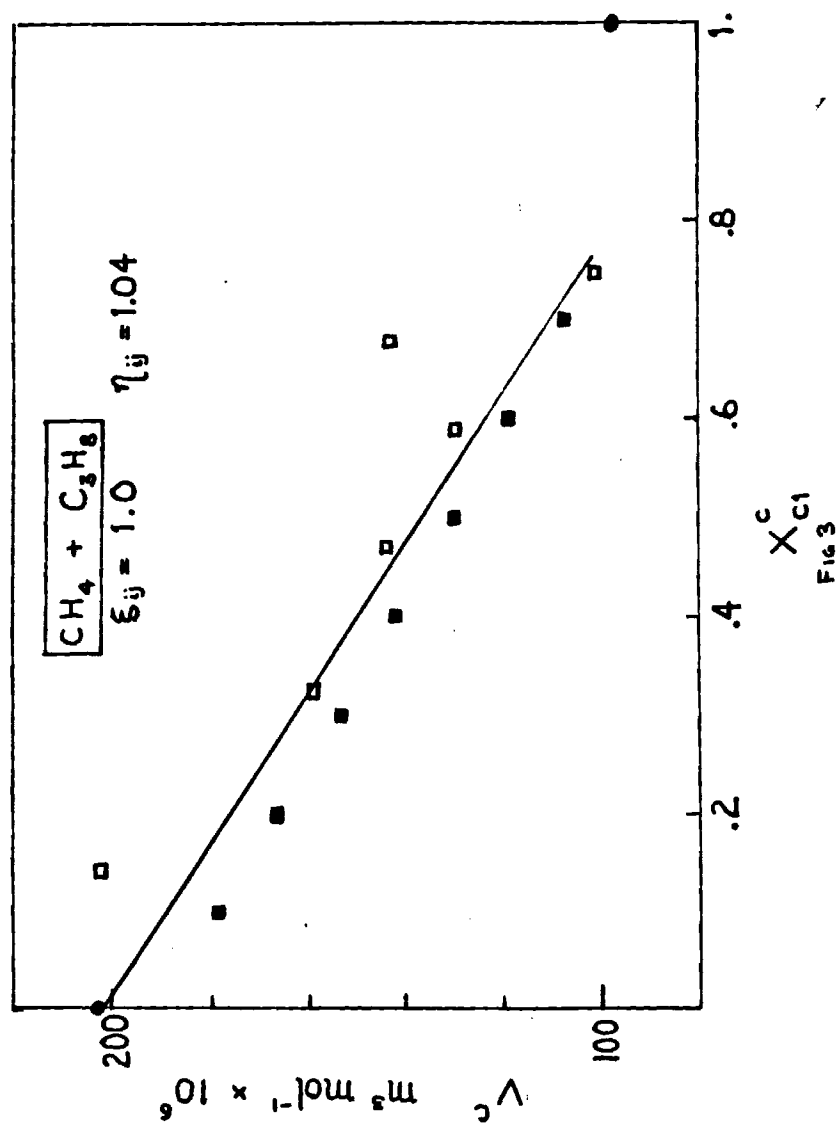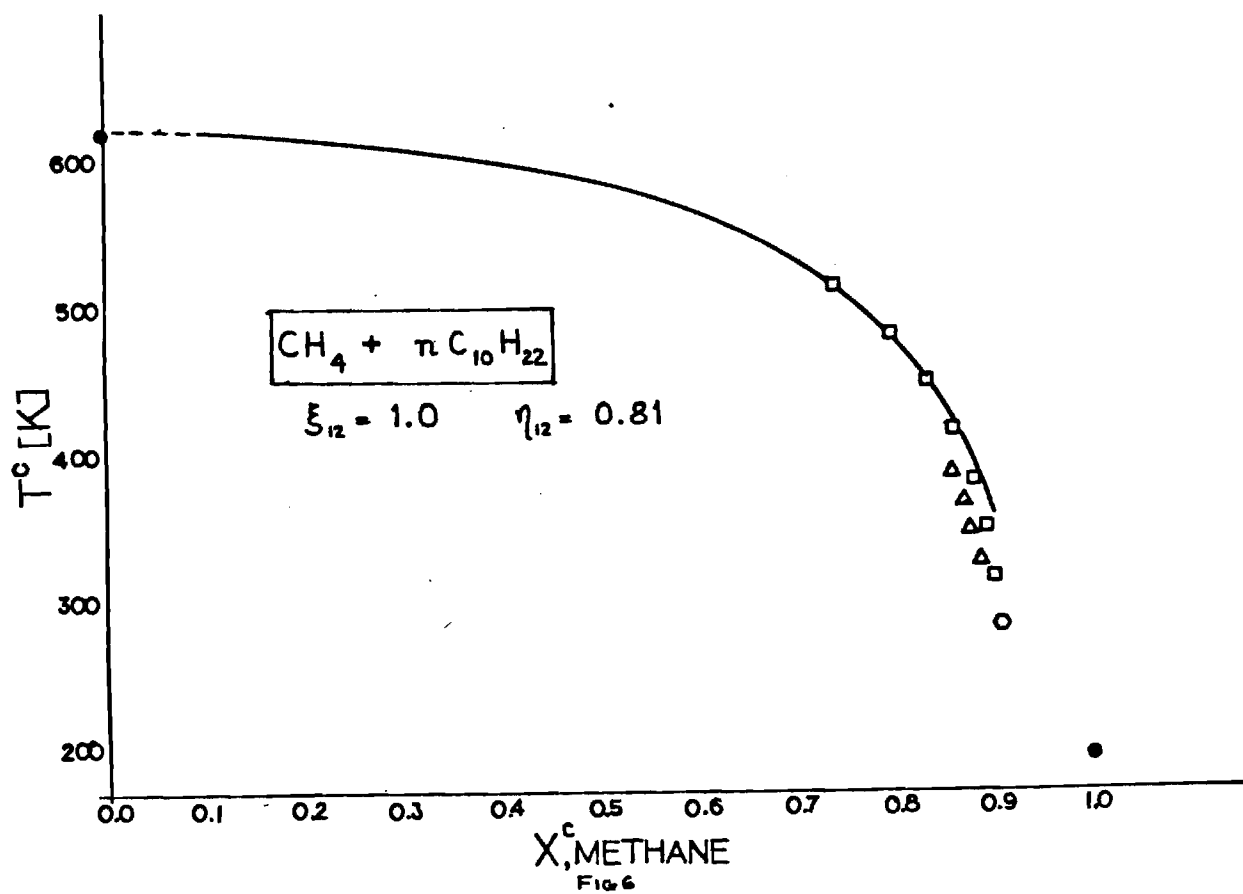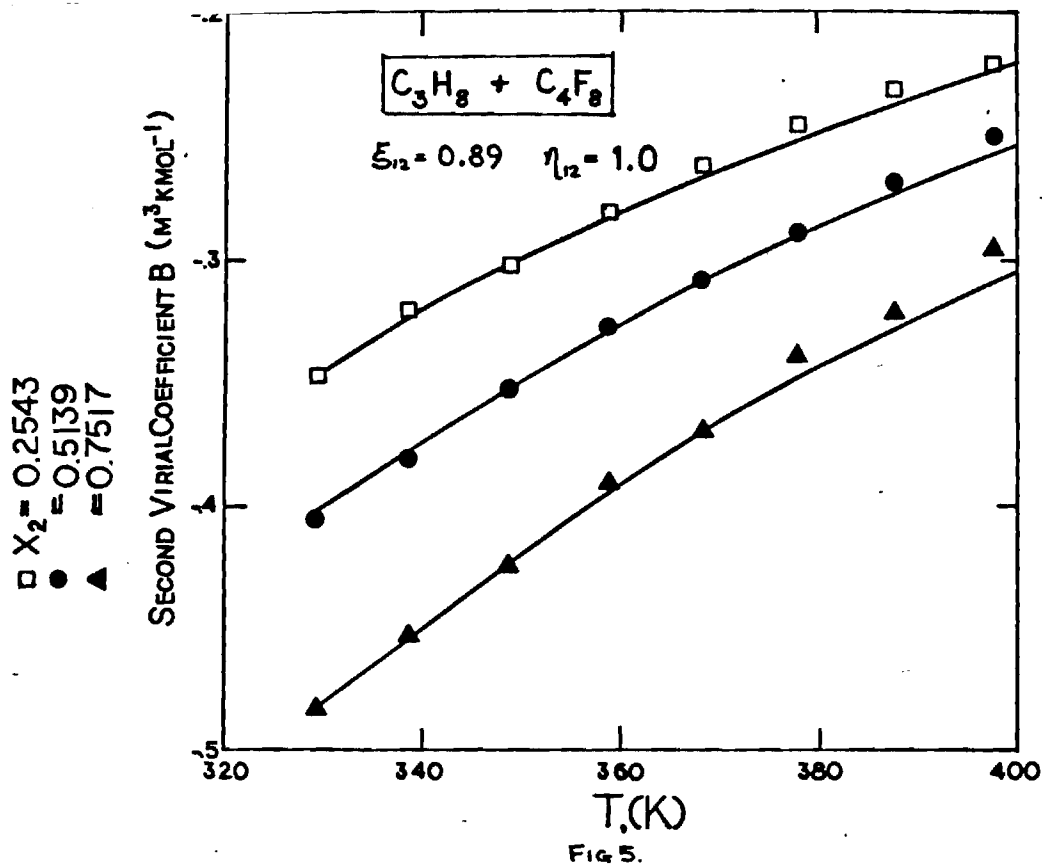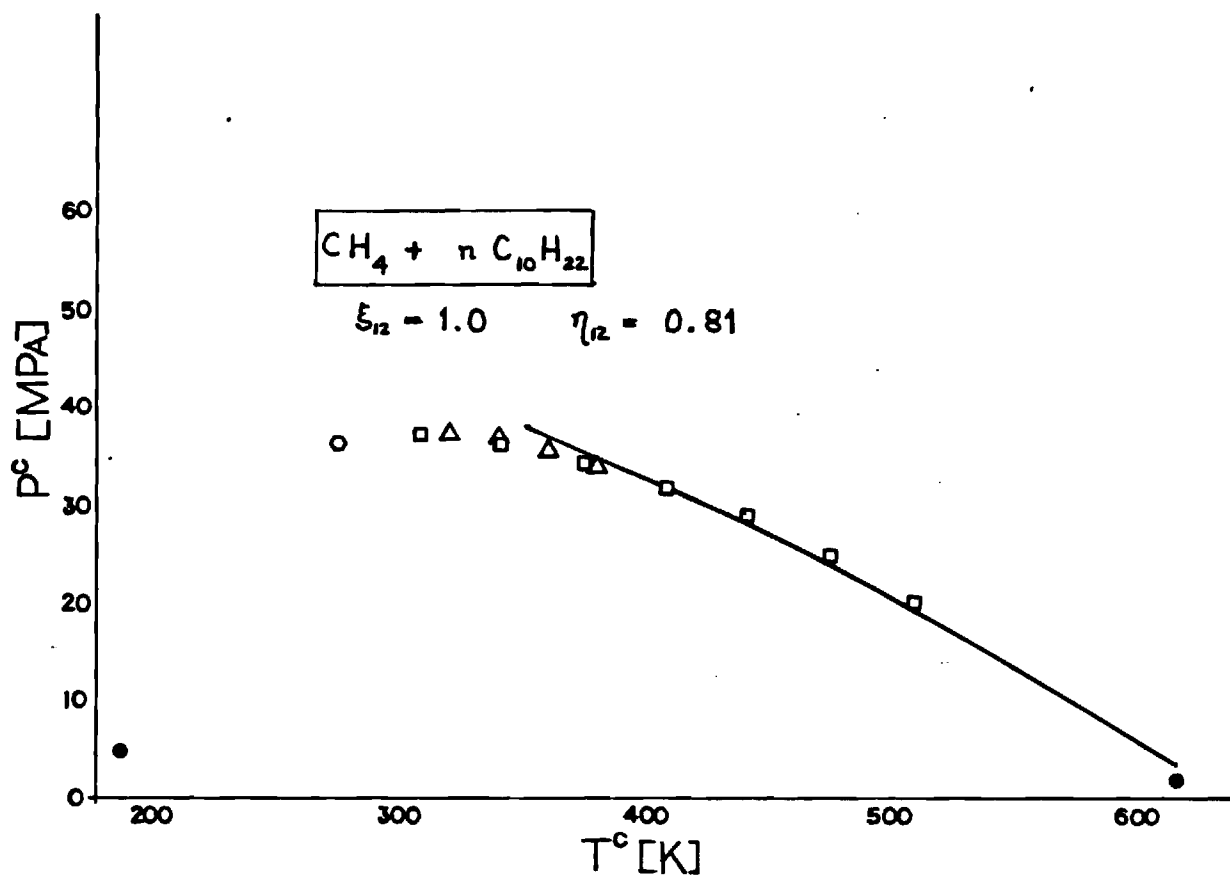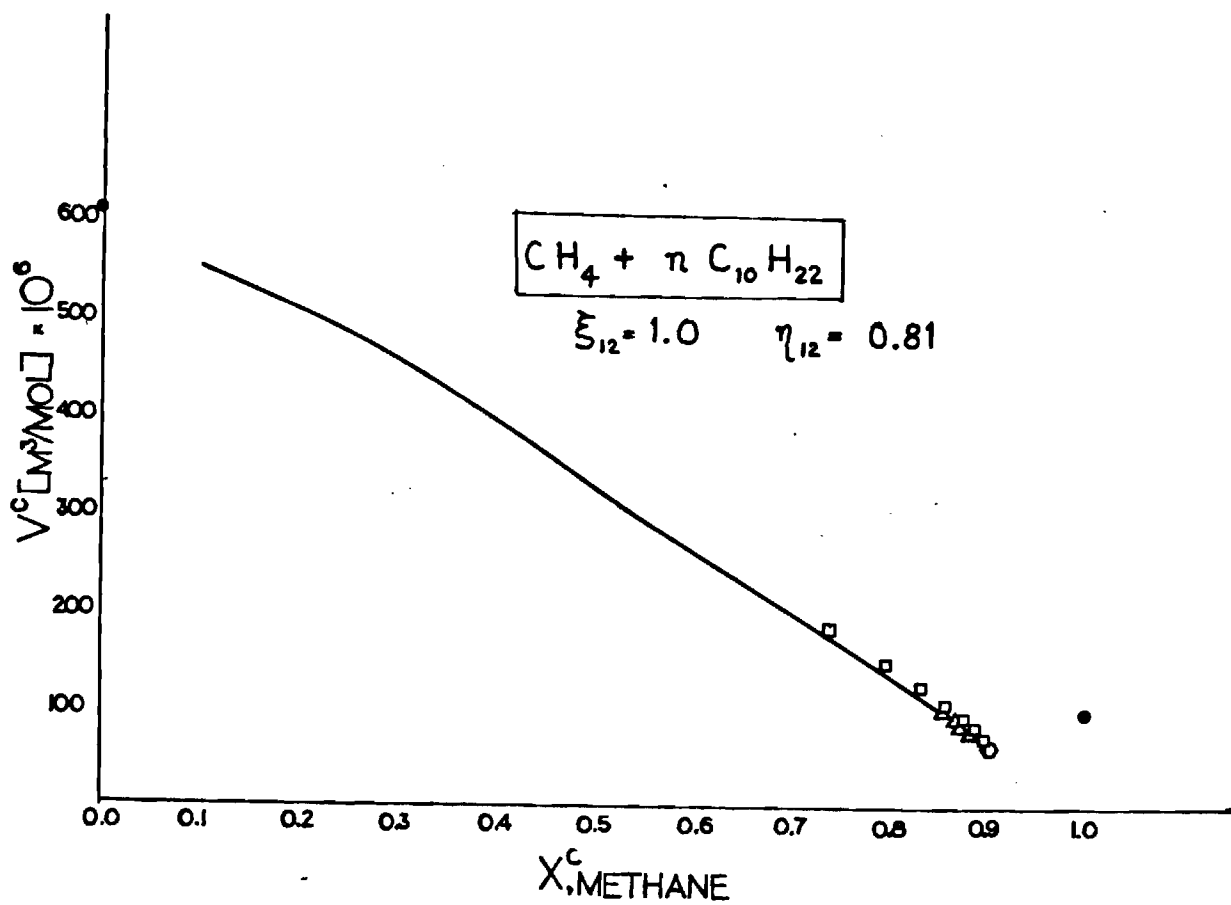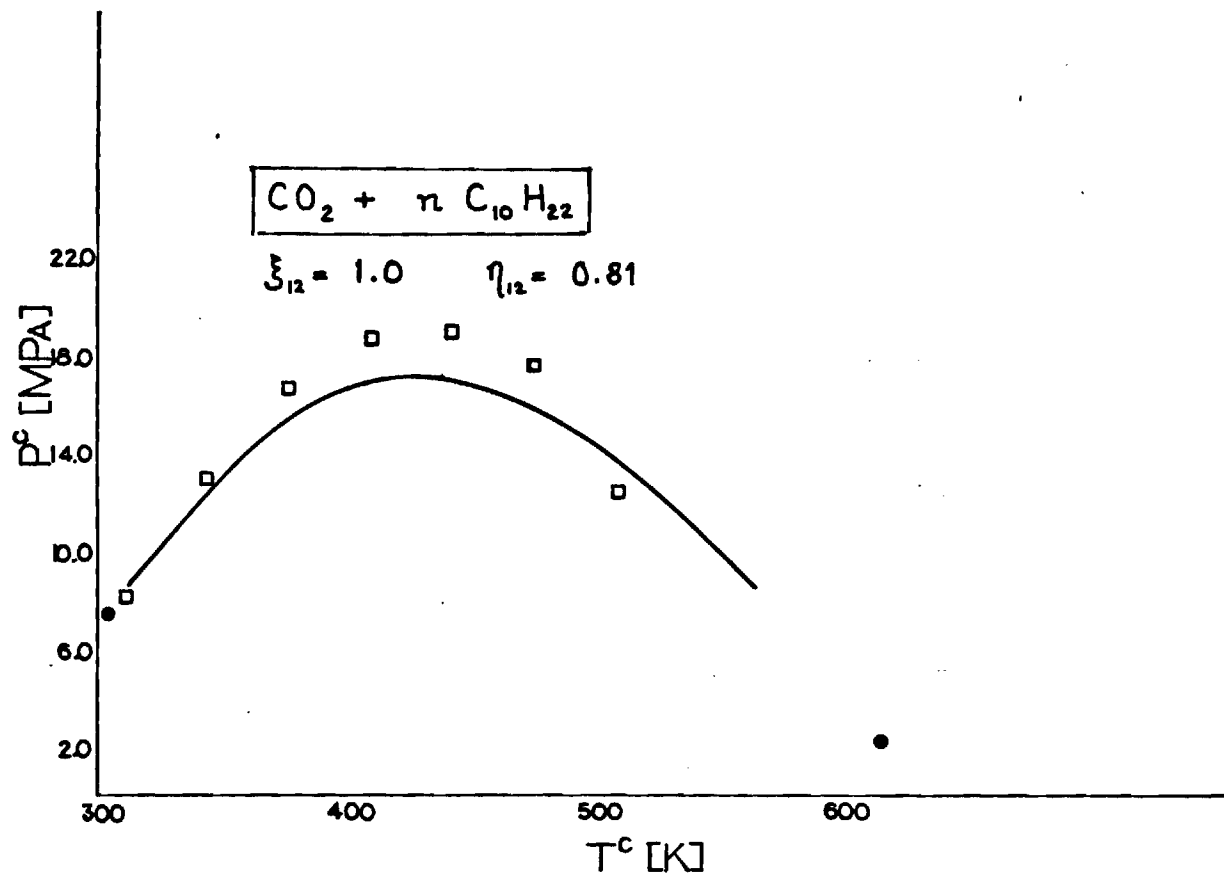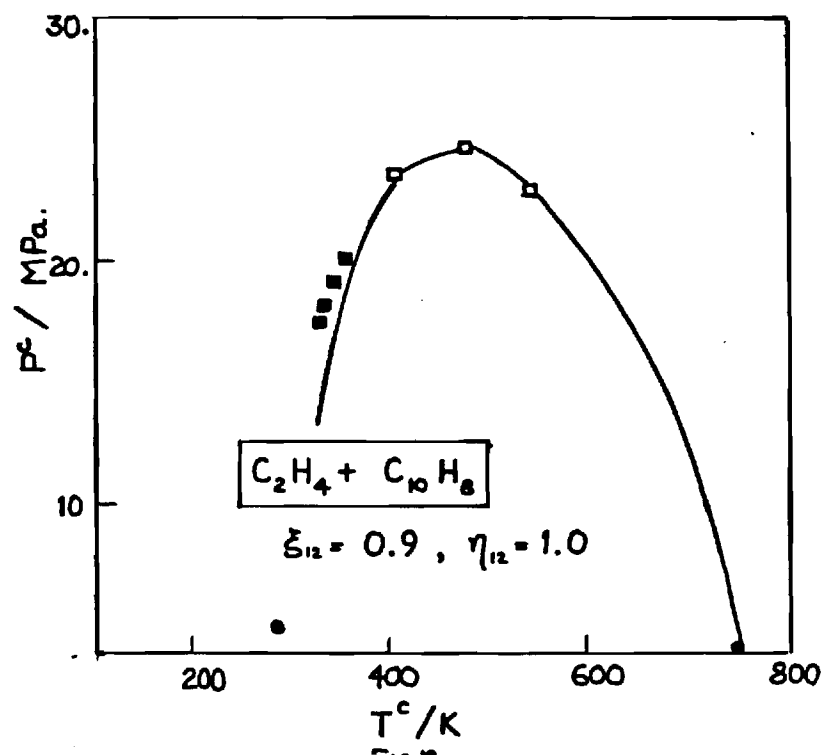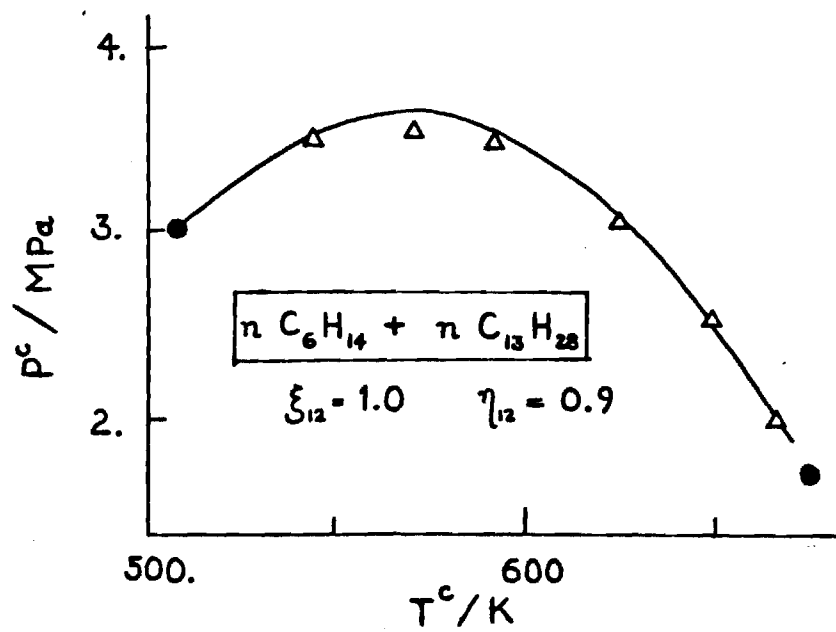
FIG 12

SUMMARY OF SCIENTIFIC PROGRESS ON GRANT # CPE 8104201

"Collaborative Research: Generalized Corresponding States Principle Using
Two Non-Spherical Reference Fluids"

We are pleased to report significant progress in a number of areas con-

cerned with the applications of the Generalized Corresponding States Principle.

For convenience, this report will be divided into sections corresponding to

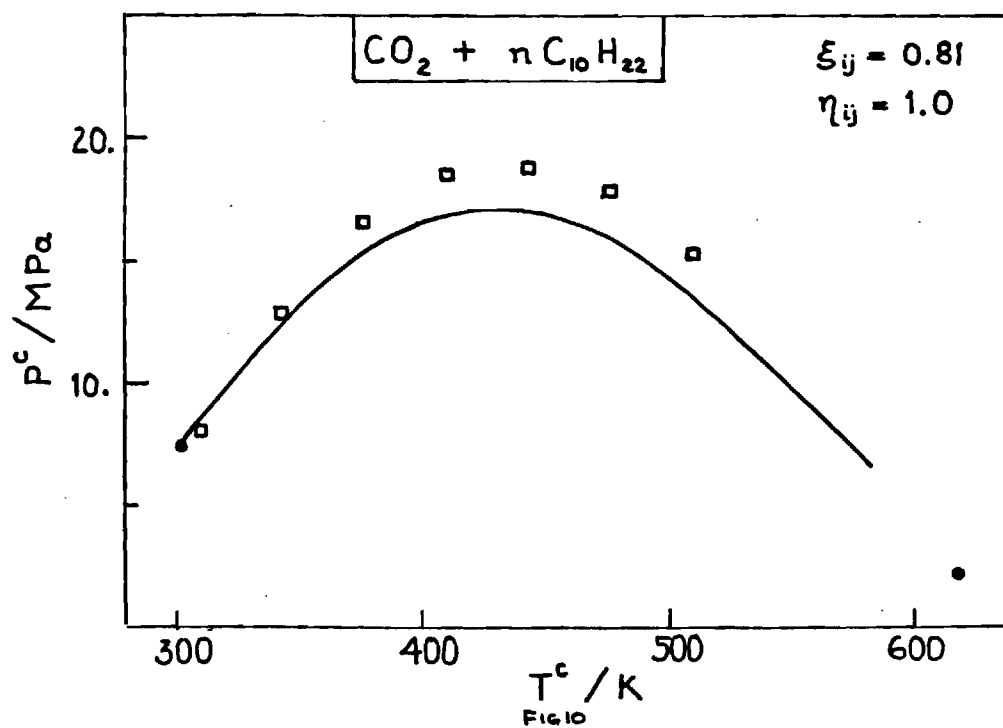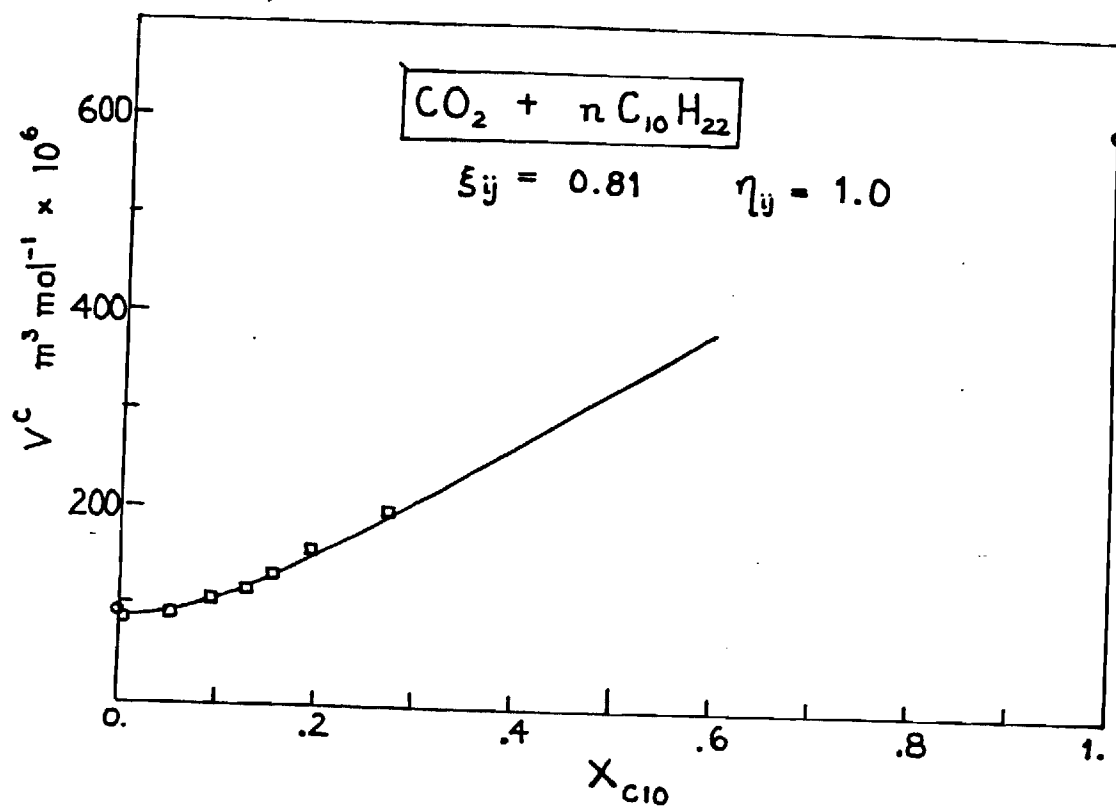the tasks listed in our proposal (# CPE 8104201). Moreover, this report will

deal with tasks that were primarily carried out at Georgia Institute of Tech-

nology (Tasks C, D and two new tasks). It is assumed that the reader will

have access to the report by Dr. Stanley I. Sandler on other tasks (A, B and

E) which were primarily (although not entirely) carried out at the University

of Delaware.

Task C: Calculation of enthalpy and entropy deviations. Grant Year 1.

This task was postponed from Year 1 pending our results on the effects of reference fluids and mixing rules on vapor-liquid equilibria. Extensive values of the experimental enthalpy and entropy deviations of pure fluids and fluid mixtures are presently being compiled and we expect the results of our calculations to be available in the early part of Year 3. Calculations using cubic equations of state for the reference fluids have confirmed that the GCSP method is as good as the quation of state method for the calculation of enthalpy deviations but requires less data. We have examined the calculation of the temperature derivative of the enthalpy (i.e. heat capacity) and shown how this may be predicted using the GCSP method [Ref. 1].

Task D: Calculation of critical states and critical end points. Grant Years 2 and 3

Since critical point predictions provide a severe test of thermodynamic theories, we initiated the study of critical phenomena in Year 1 of the Grant. This study has made considerable progress and is still continuing.

We have identified a need for a method for the rapid calculation of critical points of multicomponent systems for reservoir simulations and have developed an empirical method for such calculations based on the excess critical property concept [Ref. 2]. We believe that this method can be further extended using a group contribution approach and this would make it extremely powerful for mixtures where little data exist.

Our rigorous calculations of critical points in binary mixtures using cubic equations of state are now complete. We have applied this method to simple systems, asymmetric systems, azeotropic systems and to systems containing polar species [Ref. 3]. The limitations of cubic equations of state for density predictions in the critical region are well known. We have shown how these limitations can be overcome by introducing a simple composition dependence of the pseudocritical compressibility in our calculations [Ref. 3]. We have also shown that, with this modification, a simple equation of state predicts all critical properties as well as, and often better than, a more complex corresponding states approach with shape factors. [Ref. 4,6]

Our calculations of critical curves using a generalized corresponding states principle are in progress.

New Task: Calculation of Henry's constants

The solubility of gases in liquids represents a special case of vapor-liquid equilibrium in which the solute is supercritical. Such equilibria are often described using Henry's constants. Our calculations have shown that we can use the Generalized Corresponding States Principle to predict Henry's constants of a gas in a given solvent provided we know the Henry's constants of two similar substances in the same solvent at the same reduced conditions. This technique of keeping the solvent constant in the calculations has enabled us to correlate an interaction property such as Henry's constant in spite of the fact that we cannot use pure substances as our reference fluids. These calculations are in progress and a data bank of Henry's constants is being compiled.

New Task: Calculation of Diffusion Coefficients

Although the calculation of transport properties is beyond the scope of the present grant, the technique of using a common solvent in all calculations (used in the calculation of Henry's constants) can easily be extended to the calculation of diffusion coefficients. We have shown [Ref. 5] how the self diffusion coefficients of a fluid can be calculated from the self-diffusion coefficients of two reference fluids using the GCSP method. We have further shown how the infinite dilution diffusion coefficient of a given substance in a given solvent can be predicted from the infinite dilution diffusion coefficient of two reference substances in the same solvent. Finally, we have shown how this approach can be extended to the calculation of the composition dependence of mutual diffusion coefficients [Ref. 5].

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3. Smith R. L. and Teja A. S., "Phase diagrams in the critical region using equations of state," paper to be presented to PACHEC 83, May 1983.

4. Smith R. L., Sandler S. I. and Teja A. S., "Calculation of critical points using equations of state," paper to be presented to the 3rd Int. Conference on Thermodynamics Properties and Fluid Phase Equilibria in the Chemical Industry, Callaway Gardens April 1983.

5. Teja A. S., "A Correlation and Prediction of Diffusion Coefficients using a Generalized Corresponding States Principle," paper presented to the Annual Meeting of AIChE, Los Angeles, November 1982.

6. Smith R. L., "Application of a Corresponding States Principle to the Calculation of Critical Curves," M.S. Thesis, Georgia Institute of Technology, (1982).

These references do not include three papers by Wong, Sandler and Teja which describe the applications of the Generalized Corresponding States Principle to vapor-liquid and liquid-liquid equilibria. These latter are included in the report from the University of Delaware.

FINAL REPORT

COLLABORATIVE RESEARCH:
GENERALIZED CORRESPONDING STATES PRINCIPLE
USING TWO NON-SPHERICAL REFERENCE FLUIDS

By

Dr. Amyn S. Teja

Prepared for

NATIONAL SCIENCE FOUNDATION
WASHINGTON, D.C. 20550

Report Period from 3/1/81 to 10/31/84

Under

NSF Award No. CPE8104201

February 1985

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF CHEMICAL ENGINEERING
ATLANTA, GEORGIA 30332

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program Thermodynamics and Transport Pheno.	3. NSF Award Number CPE8104201
Georgia Tech Research Institute Georgia Institute of Technology	4. Award Period From 3/1/81 To 10/31/84	5. Cumulative Award Amount $106,694

6. Project Title
Collaborative Research: Generalized Corresponding States Principle Using Two Non-Spherical Reference Fluids.

PART II–SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The ability to predict the thermodynamic properties of fluid mixtures is of central importance in the design of separation equipment, reactors and heat exchangers. One of the more successful methods of prediction of these properties has been the three parameter corresponding states principle proposed by Pitzer et al. and later modified by Lee and Kesler. We have proposed a Generalized Corresponding States Principle (GCSP) using two non-spherical reference fluids which reduces to the Pitzer and Lee-Kesler formulations when one of the fluids is spherical. Moreover, we have carried out a wide-ranging study of the GCSP for predicting properties of industrial importance (vapor-liquid and multifluid phase equilibria, critical states, densities, enthalpies and entropies of hydrocarbon + hydrocarbon, hydrocarbon + alcohol and hydrocarbon + water mixtures). We have further extended the GCSP to the prediction of transport properties (viscosities, thermal conductivities and diffusion coefficients) of these mixtures. Our results should be useful to design engineers dealing with mixtures of present industrial interest and mixtures likely to be of interest in future energy-related technologies.

PART III–TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM Check (√)	Approx. Date
a. Abstracts of Theses		XX			
b. Publication Citations		XX	XX		
c. Data on Scientific Collaborators	XX				
d. Information on Inventions	XX				
e. Technical Description of Project and Results		XX	XX		
f. Other (specify) Two Detailed Annual Reports			XX		

2. Principal Investigator/Project Director Name (Typed) Dr. Amyn S. Teja	3. Principal Investigator/Project Director Signature	4. Date 2/20/85

FINAL REPORT

Title: Collaborative Research: Generalized Corresponding States Principle Using Two Non-Spherical Reference Fluids

Principle Investigators: Dr. Amyn S. Teja (Georgia Tech)
Dr. Stanley I. Sandler (University
of Delaware)

Graduate Research Assistants:

Richard Lee Smith, Jr.   (Georgia Tech)
Sohail Siddiqi   (Georgia Tech)
Paul Thurner   (Georgia Tech)
David Wong   (University of Delaware)
Glenn Shealey   (University of Delaware)

Undergraduate Research Assistants:

Daniel Pittaluga   (Georgia Tech)
Laurel Kleven   (Georgia Tech)
Tim Barnette   Georgia Tech)
Meet Tucker   (Georgia Tech)
Russell Carter   (Georgia Tech)

Summary:

The ability to predict the thermodynamic properties of fluid mixtures has always been of central importance in Chemical Engineering practice.   One of the more successful methods of thermodynamic properties and phase equilibrium predictions has been the three parameter corresponding states principle proposed by Pitzer et al (1) which was put in an analytic form for digital computation by Lee and Kesler (2). In our initial work, we proposed a Generalized Corresponding States Principle (GCSP) using two non-spherical reference fluids (3-5) and showed that the Pitzer et al and Lee-Kesler formulations were special cases of the more general GCSP. This work was concerned with a wide-ranging study of the GCSP for predicting properties of industrial importance (vapor-liquid and multifluid phase equilibria, critical states, densities, enthalpies and entropies) as well as a study of the effect of using different reference fluids, reference equations, and mixtures models. As will be seen, all tasks originally proposed have been completed. In addition, considerable success has been achieved with the extension of the GCSP to transport properties. A summary of the achievements is presented below.

(a) Choice of Reference Substances, Equations and Mixing Rules

An importnat characteristic of the Generalized Corresponding States Principle is the freedom to choose reference substances which are similar to the fluid or mixture of interest. We have established that this ability to choose the reference substances leads to very accurate, easy-to-apply corresponding states theory. We have further shown that the ability to vary the reference substances is more important than providing a highly accurate representation of fixed substances, as has been current practice. Thus, for example, using the GCSP with a simple cubic equation of state description for one hydrocarbon and one alcohol (the reference fluids) yields very good equilibrium predictions for alcohol-hydrocarbon systems. Further, these predictions are much more accurate than the Lee-Kesler corresponding states method, which uses very accurate (11-constant) equations of state for two fixed reference fluids.

The choice of mixing rules is a problem which is of special importance in corresponding states theory and we have developed an appropriate set of mixing rules for the GCSP. These mixing rules have been tested and found to yield good predictions for hydrocarbon-hydrocarbon, hydrocarbon-alcohol and hydrocarbon-water systems. The mixing rules appear to work well for both thermodynamic and transport properties.

The results of this work appear in all our publications, but are summarized in references 5-9.

(b) The Prediction of Vapor-Liquid Equilibria

We have developed the GCSP and its mixing rules to a point where it can routinely be used in engineering calcualtions for the prediction of vapor-liquid-equilibria for hydrocarbon-hydrocarbon (of both similar and dissimilar sizes), hydrocarbon-alcohol and hydrocarbon-water systems. This work is described in detail in references 6, 7, and 9.

(c) Calcualtion of Enthalpy and Entropy Deviations

We have shown that the GCSP can also be used for the prediction of enthalpy and entropy deviations fo both pure fluids and fluid mixtures. This work is detailed in reference 10. We have also examined the prediction of the temperature derivative of the enthalpy (ie. the heat capacity) and shown how this may be predicted using the GCSP (ref 11).

(d) Calculation of Critical States

Critical point predictions provide a severe test of thermodynamic theories since they require a knowledge of the second and third derivatives of the Gibbs energy with respect to composition. We have identified a need for a rapid method for the calculation

of critical points of multicomponent mixtures for reservoir simulation studies and have developed an empirical method for such calcualtions based on the excess critical property concept (ref 12). We have also carried out rigorous calculations of critical points using cubic equations of state, later using these calculations for the reference fluids in the GCSP method. The limitations of cubic equations of state for density predictions in the critical region are well known. We have shown how these limitations can be overcome by introducing a simple composition dependence for the critical compressibility (ref. 13). We have also shown that, with this modification, a simple equation of state can predict all critical properties of simple mixtures, asymmetric mixtures, azeotropic mixtures and mixtures containing polar species with quantitative agreement between experiment and calculations (ret 13-15). Our calculations of critical curves using the GCSP are detailed in ref. 16.

(e) Prediction of Liquid-Liquid and Vapor-Liquid-Liquid Equilibrium.

We have shown that the GCSP method leads to reasonably accurate predictions of liquid-liquid and vapor-liquid-liquid equilibria for systems of hydrocarbons and hydrocarbons with inorganic gases. An important characteristic of the prediction method is that it is thermodynamically consistent in that a single set of binary interaction coefficients is used in all phases. This work is described in ref. 8.

We have also prepared a user friendly computer package that implements the GCSP for density, vapor-liquid and vapor-liquid-liquid predictions. Separate packages have been prepared for density, enthalpy and entropy predictions and for the prediction of critical states.

In addition to the above tasks, which were outlined in our original proposal, the following additional tasks were also completed in this work.

(f) Measurement and Prediction of the High Pressure Densities of Coal Chemicals.

We have shown that the GCSP leads to accurate correlations of the densities and excess volumes of coal chemicals at high pressures. Because of lack of data for mixtures of interest in coal processing, we have measured the high pressure densities of seven model coal compounds and their binary mixtures. Our results are detailed in reference 17.

(g) Prediction of Transport Properties

Some of our earlier work (refs. 18-21) showed that the GCSP can be extended to the correlation and prediction of the transport properties of liquid mixtures. We have now shown that the GCSP based on two non-spherical reference fluids can be used to

predict the viscosities and thermal conductivites of mixtures of interest in synfuels process design (ref. 22). Moreover, we have shown that an appropriate choice of reference fluids leads to good predictions of the transport properties over a range of pressures and temperatures for both defined and undefined mixtures (refs 22-23). Finally, we have shown how the method can be extended to self-diffusion coefficients, infinite dilution diffusion coefficients and mutal diffusion coefficients (ref. 24).

In conclusion, we have shown that the Generalized Corresponding States Principle using two non-spherical reference fluids is a powerful method for the calculation of the thermodynamic and transport properties of pure fluids and fluid mixtures. The freedom to choose reference fluids and reference fluid representation offers flexibility and reliability and can lead to very accurate predictions of properties with a minimum of experimental information.

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2. B. I. Lee and M. G. Kesler, AIChEJ, 21, 510 (1975).

3. A. S. Teja, AIChEJ, 26, 337 (1980).

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6.* D. Wong, S. I. Sandler and A. S. Teja, Ind. Eng. Chem. Fundamentals, 23, 38 (1984).

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9.* D. Wong, S. I. Sandler and A. S. Teja, Fluid Phase Equilibria, 14, 79 (1983).

10.* R. L. Smith and A. S. Teja, paper to be presented at the 9th Thermophysical Properties Symposium, June 1985 and to appear in Int. J. Thermophysics.

11.* A. S. Teja, J. Chem. Eng. Data, 28, 83 (1983).

12.* A. S. Teja, K. B. Garg and R. L. Smith, Ind. Eng. Chem. Process Des. Dev., 22, 672 (1983).

13.* A. S. Teja, S. I. Sandler and R. L. Smith, Fluid Phase Equilibria, 14, 265 (1983).

14.* R. L. Smith and A. S. Teja, Proc. Third Pacific-American Chem. Eng. Conf., Vol. II, 315 (1983).

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16.* R. L. Smith and A. S. Teja, paper presented at the AIChE Meeting, Houston, March 1985.

17.* S. Siddiqi and A. S. Teja, paper presented at the AIChE Meeting, Atlanta, March 1984.

18. A. S. Teja and P. Rice, Ind. Eng. Chem. Fundam., 20, 77 (1981).

19. A. S. Teja and P. Rice, Chem Eng. Sci., 36, 417 (1981).

20. A. S. Teja and P. Rice, J. Colloid and Interface Sci., 86, 158 (1982).

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22.[*]   A. S. Teja, P. Thurner, B. Pasumarti, <u>Ind. Eng. Chem. Process Des. Dev.</u>, <u>24</u> (1985), in press.

23.[*]   P. Thurner and A. S. Teja, <u>Chem. Eng. J.</u>, submitted for publication.

24.[*]   A. S. Teja, <u>Ind. Eng. Chem. Fundam.</u>, <u>24</u> 39 (1985)

[*]   A total of 15 papers (refs. 6-17 and 22-24) have resulted from this project.

CONFERENCE PRESENTATIONS

1. A. S. Teja and R. L. Smith, "The Correlation and Prediction of the Critical States of Mixtures using a Corresponding States Principle", Annual Meeting of AIChE, New Orleans, November 1981.

2. D. Wong, S. I. Sandler and A. S. Teja, "New Mixing Rules for Phase Equilibrium Calculations Using a Generalized Corresponding States Principle", Spring National Meeting of the AIChE, Orlando, March 1981.

3. A. S. Teja, "The Correlation and Prediction of Diffusion Coefficients in Liquids Using a Generalized Corresponding States Principle", 75th Annual Meeting of the AIChE, Los Angeles, November 1982.

4. D. Wong, S. I. Sandler and A. S. Teja, "Corresponding States, Complex Mixtures and Mixing Rules", Third International Conference on Phase Equilibria and Fluid Properties for Chemical Process Design, Callaway Gardens, Georgia, April 1983.

5. A. S. Teja, R. L. Smith and S. I. Sandler, "The Calculation of Critical States - Effect of Improved Pure Component Critical Point Representation", Third International Conference on Phase Equilibira and Fluid Properties for Chemical Process Design, Callaway Gardens, Georgia, April 1983.

6. R. L. Smith and A. S. Teja, "Phase Diagrams in the Critical Region Using an Equation of State", Pacific-American Chemical Engineering Congress III, Seoul, Korea, May 1983.

7. A. S. Teja, P. Thurner and B. Pasumarti, "The Calculation of Transport Properties of Mixtures for Synfuels Process Design", Diamond Jubilee Meeting of the AIChE, Washington, November 1983.

8. S. Siddiqui and A. S. Teja, "High Pressure Densitite of Coal Derived Chemicals", national Meeting of the AIChE, Atlanta, March 1984.

9. R. L. Smith and A. S. Teja, "Critical Point Prediction Using a Generalized Corresponding States Principle", National Meeting of the AIChE, Houston, March 1985.

10. R. L. Smith and A. S. Teja, "Prediction of Enthaply and Entropy Deviations Using a Two-Fluid Corresponding States Principle", Ninth Symposium on Thermophysical Properties, Denver, June 1985.

In addition, seminars on the Generalized Corresponding States have been presented at Clemson University, University of Alabama at Tucaloosa, National Bureau of Standards, Cleanese Chemical Company and King Saud University.

THESES

1. Richard Lee Smith, Jr., M.S. Thesis, Georgia Institute of Technology, December 1982.

2. Sohail Siddiqi, M.S. Thesis, Georgia Institute of Technology, June 1983.

3. Paul Thurner, M.S. Thesis, Georgia Institute of Technology, March 1984.

4. David S-H Wong, Ph.D. Thesis, University of Delaware, March 1984.

5. Richard Lee Smith, Jr., Ph.D. Thesis, Georgia Institute of Technology, expected completion date June 1985.

7. Glenn Shealey, Ph.D. Thesis, University of Delaware, expected completion date, June 1985.

ABSTRACTS OF THESES

A STUDY OF THE THERMODYNAMIC PROPERTIES

OF SYNTHETIC FUELS AND COAL DERIVED

LIQUID MIXTURES

A Thesis
Presented to
The Faculty of the Division of Graduate Studies
By
Sohail Azeem Siddiqi

Approved:

_____

Amyn S. Teja, Chairman

_____

P. Durbetaki

_____

Ronald. T. Gibbs

Date approved by Chairman 5/6/83

Georgia Institute of Technology
May 1983

SUMMARY

This study reports measurements of the densities of seven
model coal compounds and their binary mixtures at three different
temperatures (298.16 K, 318.16 K and 338.16 K) and pressures
upto 5000 psia (34.5 MPa). The model compounds included single-
ringed aromatic hydrocarbons such as Benzene, Toluene and M-Cresol,
as well as polycyclic aromatic hydrocarbons such as Tetralin,
Quinoline, Bicyclohexyl and 1-Methylnapthalene.

The results for the seven binary mixtures studied were
correlated using a Generalized Corresponding States Principle
with the pure components being used as the reference fluids.
The pure component densities were correlated within the experimental
accuracy by means of a modified Tait equation with temperature
dependent constants.

One of the important conclusions is that with an appropriate
set of mixing rules, the GCSP method proved to be an excellent
correlation for the densities/specific volumes of mixtures of
model coal compounds over a range of temperature and pressure.

While there is much room for further work on the GCSP,
this study establishes its accuracy, applicability and utility
for the prediction of thermodynamic properties of aromatic
hydrocarbons and possibly of real coal liquids.

A CORRESPONDING STATES APPROACH FOR THE CALCULATION OF

VISCOSITY OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE

A THESIS

Presented to

The Faculty of the Division of Graduate Studies

By

Paul Alan Thurner

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

Georgia Institute of Technology

March, 1984

SUMMARY

The Generalized Corresponding States Principle is applied to mixtures over a wide range of temperature and pressure. The following binary hydrocarbon mixtures were examined: methane + n-butane, methane + n-decane, ethane + ethylene, benzene + n-hexane, benzene + n-decane, and hydrogen + nitrogen. The viscosities of four coal liquids were successfully predicted using benzene and decane as reference fluids. The coal liquids were treated as single pure pseudo-components. The characterization parameters (T_c, P_c, and ω) were obtained from correlations of Starling or Wilson.

The overall average absolute deviation between predicted and experimental viscosity values was less than ten percent. When a single binary interaction coefficient is introduced in the critical temperature mixing rule, errors can be reduced to less than five percent. Predictions for coal liquids were within ten to fifteen percent of experimental results.

The generalized corresponding states principle has been demonstrated to be a powerful technique for the correlation and prediction of the transport properties of mixtures of interest in synfuels processing. The generalized corresponding states principle requires only that data for two reference fluids be available over the range of reduced temperatures and pressures of interest.

APPLICATION OF A

CORRESPONDING STATES PRINCIPLE

TO THE CALCULATION OF CRITICAL CURVES

A THESIS

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SUMMARY

Critical curves are successfully predicted for binary mixtures using the Teja-Patel equation of state for a select group of mixtures made up of simple, similarly shaped molecules, slightly asymmetric molecules, asymmetric molecules, and polar molecules. Also examined is the methane + n-alkane homologue and the carbon dioxide + n-alkane family. Spatial critical phase diagrams are presented along with their plane projections for each system. Comparisons are also shown using the Peng-Robinson equation of state and using the Vennix equation of state as a reference equation with the Leach shape factors.

It is found that the anomaly of cubic equations failing to predict volumetric properties in high concentrations of one component may be alleviated by forcing the equation of state to reproduce the pure component critical compressibilities. Pressure errors result and high binary interaction coefficients are required for correction. A suitable modification of the Teja-Patel equation of state is suggested such that the pure component critical compressibilities are reproduced and high interaction coefficients are unnecessary.

CALCULATION OF PHASE EQUILIBRIA USING

A GENERALIZED CORRESPONDING STATES PRINCIPLE AND

A CUBIC EQUATION OF STATE

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ABSTRACT

Correlation and prediction of phase equilibrium behavior are very important in solving chemical engineering problems. In this research, a generalized corresponding states principle (GCSP) has been developed for correlating vapor - liquid and vapor - liquid - liquid equilibria. A new set of mixing rules to be used with this (and other) corresponding states method has also been developed. This combination has been found to be comparable to traditional corresponding states methods in correlating vapor - liquid equilibria of mixtures of small nonpolar molecules. However, with this mixing model and the appropiate choice of reference fluids, we are able to extend the application of corresponding states principle to calculate vapor - liquid equilibria of asymmetric mixtures and mixtures with moderate polar - nonpolar interactions.

The GCSP is also found to be able to produce results similar to the cubic equation of state method in calculating vapor - liquid equilibria. However, as the generalized corresponding states principle requires less information on the components in the mixture, it is more useful in calculations of vapor - liquid equilibria of fluids containing a large number of components each of which is only

characterized by a few parameters.

The GCSP is also found to be equilvalent in phase equilibrium calculation accuracy to activity coefficient models such as UNIQUAC at low pressure, but much better when being extended into high pressure region. Further, the GCSP has the advantage of being able to calculate all thermodynamic properties (i.e., density, enthalpy, etc.), not only phase equilibrium.

Prediction of liquid - liquid - vapor equiliria of ternary nonpolar molecule mixture using information obtained from binary vapor - liquid equilibria is, in general, not possible with all the phenomenological thermodynamic models discussed. The cubic equation of state and the GCSP with higher order reference equations are, however. able to correlate liquid - liquid - vapor equilibria using binary interaction parameters that are different from those obtained from binary vapor - liquid equilibria. The GCSP using only cubic equation of state as equation of state for the reference fluids, is not able to predict liquid - liquid - vapor equilibrium in all the regions in which experimental three phase equilibrium is observed. This indicates that both the mixing model and the pressure - volume - temperature relation are not accurate enough for this more complicated phase behavior.

REPRINTS AND PREPRINTS OF PAPERS

Vapor–Liquid Equilibrium Calculations by Use of a Generalized Corresponding States Principle. 1. New Mixing Rules[†]

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A recently developed generalized corresponding states principle based on the properties of two nonspherical reference fluids is used for the calculation of vapor–liquid equilibria in homogeneous mixtures, in asymmetric mixtures, and in heterogeneous mixtures containing polar components such as water and alcohols. New semi-empirical mixing rules are proposed for these mixtures, and comparisons with conventional mixing rules are shown. In a companion paper, the combination of generalized corresponding states method and new mixing rules is compared with other corresponding states and equation of state methods.

Introduction

A generalized corresponding states principle (GCSP) based on the properties of two nonspherical reference fluids has been proposed by Teja and co-workers (1980, 1981) to calculate the densities of liquefied natural gas, the swelling factors of crude oil fractions with dissolved carbon dioxide, and viscosities of liquid mixtures. There are certain advantages of the use of the GCSP approach. First, the reference fluids chosen can be pure fluids (or even mixtures) which are similar to the component or components of interest. Thus, the corresponding states method can be extended to mixtures containing molecules that are very different in nature. Second, the GCSP method requires few fluid characterization parameters (usually only critical properties and acentric factors of the pure components). Therefore, it is especially suited for poorly characterized fluids such as oil fractions. Third, only a small number of mixing rules and binary interaction coefficients are needed in the calculations regardless of the complexity of the equation of state of the reference fluids. Thus, complicated equations of the type proposed by Benedict and co-workers (1951) or Hassar and co-workers (1977) can be employed for accurate calculations without the use of arbitrary mixing rules.

Patel and Teja (1982) have recently proposed a cubic equation of state that accurately predicts the saturation density of a variety of fluids including paraffinic and aromatic hydrocarbons, water, and alcohols. In this work, we use the Teja and Patel cubic equation of state for the reference fluids in the GCSP method and several semiempirical mixing rules to investigate phase equilibria of a variety of binary mixtures. In particular, we consider homogeneous mixtures containing small hydrocarbon molecules and/or carbon dioxide, asymmetric mixtures containing both large and small molecules, and heterogeneous mixtures containing polar and/or nonpolar species (such as alcohol + alcohol, alcohol + hydrocarbon, and water + hydrocarbon). Our results include mixing rules

for various classes of mixtures and an examination of the advantages and limitations of the GCSP method. It should be stressed that the Teja–Patel equation of state representation for the reference fluids was used here merely for convenience; any equation of state could be used in the GCSP method. In a companion paper, we compare correlative ability of the GCSP method using the new mixing rules with other corresponding states methods that use other fixed reference equations, and with the cubic equation of state method.

Corresponding States Theory

The three-parameter corresponding states theory of Pitzer and co-workers (1955) uses critical temperature T_c, critical pressure P_c, and acentric factor ω as fluid characterization parameters. It is based on the assumption that the compressibility factor Z of a fluid is a universal function of the reduced temperature T_r ($= T/T_c$), reduced pressure P_r ($= P/P_c$), and the acentric factor ω as follows

$$Z = Z^{(0)}[T_r, P_r] + \omega Z^{(1)}[T_r, P_r] \qquad (1)$$

In Pitzer's formulation, the functions $Z^{(0)}$ and $Z^{(1)}$ are given in graphical form. Lee and Kesler (1975) replaced the graphical representation with the following equation

$$Z = Z^{(0)}[T_r, P_r] + \omega\{Z^{(r)}[T_r, P_r] - Z^{(0)}[T_r, P_r]\}/\omega^{(r)} \qquad (2)$$

where $Z^{(0)}$ is the compressibility factor of a spherical reference fluid (essentially argon, for which ω is zero), and $Z^{(r)}$ is that for a nonspherical reference fluid (essentially n-octane). These reference fluid compressibility factors were represented by the modified Benedict–Webb–Rubin equations of state (Benedict and co-workers, 1951).

The generalized corresponding states principle is based on the choice of two nonspherical reference fluids, denoted r1 and r2, that are representative of the fluid or fluid mixture of interest, and for which the equations of state are known. The corresponding states relation of the compressibility is then written as

$$Z = Z^{(r1)}[T_r, P_r] + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \{Z^{(r2)}[T_r, P_r] - Z^{(r1)}[T_r, P_r]\} \qquad (3)$$

The theoretical basis of eq 3 is the same as that of eq 1 and 2. To see this we note that by considering the com-

pressibility factor Z to be a function of T_r, P_r, and ω, Z can be expanded in the form of Taylor series about any point $(T_r, P_r,$ and $\omega_0)$

$$Z = Z(\omega_0) + (\partial Z/\partial\omega)(\omega - \omega_0) + O(\omega^2)$$

If we approximate the partial derivative by its finite difference

$$(\partial Z/\partial\omega) = [Z(\omega) - Z(\omega_0)]/|\omega - \omega_0|$$

we obtain eq 3. If, as a special case, ω_0 is zero, eq 2 is recovered.

It seems reasonable that a better estimate of the properties of a fluid can be obtained if the reference substances are similar to the fluid of interest. Therefore, eq 3 enables us to extend the corresponding states approach to more complicated systems such as those containing long chain or aromatic hydrocarbons, and/or even polar components like alcohols, and water by the appropriate choice of reference equations.

One of the most important applications of the corresponding states principle is the calculation of mixture properties. The extension of the corresponding states method to mixtures is generally based on replacing the characterization parameters T_c, P_c, and ω with appropriate pseudocritical parameters T_{cm}, P_{cm}, and ω_m, which are dependent on composition. Note that T_{cm} and P_{cm} do not correspond to any mixture critical properties but are coordinates of the critical point of the isotherm with fixed composition at which

$$\left(\frac{\partial P}{\partial V}\right)_{T,x} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,x} = 0$$

The compositional dependence of the pseudocritical parameters are generally computed a priori with a mixture model. Leland and co-workers (1962) have presented the statistical mechanical basis of the most commonly used one-fluid model. The underlying assumption of the one-fluid model is that the interaction potential between a molecule of species i and a molecule of species j in a fluid is of the following form

$$u_{ij}(r) = \epsilon_{ij}F(r/\sigma_{ij}) \tag{4}$$

where F is the same function for all i–j pairs. Using this assumption, a consistent set of effective parameters for the mixture is

$$\sigma_m^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{5}$$

$$\epsilon_m \sigma_m^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3 \tag{6}$$

Equations 5 and 6 are commonly known as the van der Waals one-fluid mixture model for molecular parameters.

The relationship between the potential parameters and the pure component critical or mixture pseudocritical parameters is

$$\sigma^3 = k_1 V_c \tag{7}$$

$$\epsilon = k_2 T_c \tag{8}$$

where k_1 and k_2 are numerical constants which depend on the specific form of F. Substituting these into eq 5 and 6 leads to the van der Waals mixing rules for the pseudocritical properties

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{9}$$

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{10}$$

There are various ways to define the cross coefficients ϵ_{ij},

σ_{ij} (or equivalently T_{cij} and V_{cij}). The most common approach is to introduce binary interaction coefficients ξ_{ij} and η_{ij} which characterize the nonideality of interaction between the binary pair. (We retain the conventional usage of the word "parameter" in this study. Thus, the two-parameter corresponding states principle refers to the two *constants* T_c and P_c, which are required for the application of the principle to any fluid. These constants are obtained from critical properties and are not adjusted in the application of the method. In contrast, the mixture model has two *adjustable constants* which are chosen to fit binary data. Although these are parameters of the model in a mathematical sense, we call then *binary interaction coefficients* to avoid confusion with the previous usage of the word "parameter"). Binary interaction coefficients are introduced into the GCSP as follows

$$\sigma_{ij}^3 = \eta_{ij}[(\sigma_i + \sigma_j)/2]^3 \text{ or } V_{cij} = \eta_{ij}[((V_{ci}^{1/3} + V_{cj}^{1/3})/2]^3 \tag{11}$$

and

$$\epsilon_{ij} = \xi_{ij}(\epsilon_i \epsilon_j)^{1/2} \text{ or } T_{cij} = \xi_{ij}[T_{ci}T_{cj}]^{1/2} \tag{12}$$

Equations 5–12 constitute the van der Waals one-fluid model for use with the two-parameter corresponding-states principle. Its extension to a three-parameter corresponding states principles requires an additional equation to determine the mixture acentric factor. Lee and Kesler (1975), Joffe (1971), and Plocker et al. (1978) used a simple linear combination rule

$$\omega_m = \sum_i x_i \omega_i \tag{13}$$

Plocker et al., however, have noted that the three-parameter model is successful only for mixtures containing small nonpolar molecules.

Starling and co-workers (1979) have outlined a three-parameter extension of the work of Leland et al. that uses an additional molecular corresponding states parameter, the anisotropic strength parameter δ^2 which is analogous to the acentric factor ω. Using a perturbation technique, they were able to derive the following mixing rules for the mixture parameters σ_m, ϵ_m, and δ_m^2

$$\sigma_m^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3$$

$$\epsilon_m \sigma_m^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3$$

$$\delta_m^2 \epsilon_m^2 \sigma_m^3 = \sum_i \sum_j x_i x_j \delta_{ij}^2 \epsilon_{ij}^2 \sigma_{ij}^3$$

However, the results of calculating vapor–liquid equilibria for a number of methane and hydrocarbon mixtures led them to replace these mixing rules with the empirical equations

$$\sigma_m^{4.5} = \sum_i \sum_j x_i x_j \sigma_m^{4.5}$$

$$\epsilon_m \sigma_m^{4.5} = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^{4.5}$$

$$\delta_m^2 \sigma_m^{3.5} = \sum_i \sum_j x_i x_j \delta_{ij}^2 \sigma_{ij}^{3.5}$$

We have chosen not to consider this model further since it was obtained for a specific equation of state. However, we show these equations here to demonstrate that both theory and practice require a nonlinear mixing rule that weights the averaging of the acentric factor (or δ^2) with the other parameters.

One of the major inconveniences in using the van der Waals one-fluid model is that it gives mixing rules for T_{cm}, V_{cm}, and ω_m, while the corresponding states theory is

Table I. Comparisons of Pseudocritical Pressure Calculated by Model II and Model I for the Carbon Dioxide + Methane Binary

mole fraction CO_2	P_{cm}, bar	
	model II	model I
0.1	70.64	70.70
0.2	67.58	67.70
0.3	64.61	64.76
0.4	61.72	61.89
0.5	58.91	59.08
0.6	56.19	56.34
0.7	53.54	53.67
0.8	50.97	51.07
0.9	48.48	48.53

formulated in terms of T_{cm}, P_{cm}, and ω_m. Therefore, an additional relation is necessary between T_{cm}, P_{cm}, and V_{cm} (i.e., a mixing rule for Z_{cm}). One example of such a rule is

$$Z_{cm} = \sum_i x_i Z_{ci} \qquad (14)$$

Joffe (1971) has shown that the use of eq 14 implies eq 13 and vice versa, and Teja (1979) has shown that eq 14 is valid only for mixtures of molecules of equal size. Therefore, if a nonlinear mixing rule is to be used for the acentric factor, as suggested by Starling et al., eq 13 and 14 cannot be used.

These problems and inconsistencies of the one-fluid model motivated us to reformulate the problem of calculating pseudocritical parameters for the generalized three-parameter corresponding states theory. Three mixture parameters, namely T_{cm}, P_{cm}, and ω_m, can be determined from pure component properties using the following set of mixing rules

$$\omega_m{}^{a_{h1}} T_{cm}{}^{a_{h2}} P_{cm}{}^{a_{h3}} = \sum_i \sum_j x_i x_j \omega_{ij}{}^{a_{h1}} T_{cij}{}^{a_{h2}} P_{cij}{}^{a_{h3}} \qquad (15)$$

for $h = 1, 2, 3$ with

$$T_{cij} = \xi_{ij}(T_{ci} T_{cj})^{1/2} \qquad (16)$$

$$P_{cij} = 8 T_{cij}/\{\eta_{ij}[(T_{ci}/P_{ci})^{1/3} + (T_{cj}/P_{cj})^{1/3}]^3\} \qquad (17)$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 \qquad (18)$$

where a_{hk}, with h, k, equal to 1, 2, and 3 are nine constants and ξ_{ij}, η_{ij} are two binary interaction coefficients that are characteristic of each i-j binary pair. As a result, the problem of finding a general mixing model becomes the problem of determining a set of suitable a_{hk} that is applicable to the different types of mixtures in which we are interested. Owing to the theoretical basis and empirical success of the van der Waals mixing rules, their analogues, represented by the following equations, are used as two of the three equations of our model

$$T_{cm}/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}/P_{cij} \qquad (19)$$

$$T_{cm}{}^2/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}{}^2/P_{cij} \qquad (20)$$

Equations 19 and 20 are equivalent to the van der Waals mixing rules of eq 9 and 10 if we consider V_c to be proportional to $Z_c T_c/P_c$ and Z_c to be a quantity that only changes slightly from species to species so that V_c is replaceable by T_c/P_c. Table I shows that the pseudocritical pressure of a carbon dioxide + methane mixture calculated by eq 9, 10, and 13 and by eq 19 and 20 are almost identical.

An additional mixing rule is needed to determine the acentric factor for the mixture. The following equation is proposed

$$\omega_m(T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j x_i x_j \omega_{ij}(T_{cij}/P_{cij})^{2/3} \qquad (21)$$

This mixing rule for ω_m may be justified by noting that the acentric factor characterizes the nonsphericity of a molecule, and T_c/P_c is proportional to the molecular size. Since the orientation and packing of molecules of different sizes and shape plays an important role in characterizing the mixture, one should expect that ω and (T_c/P_c) should be interrelated. Further, Starling and co-workers (1979) have shown that coupling the calculation of the shape parameter of the mixture with the calculation of the size parameter has a theoretical basis. Therefore, it seems reasonable that an equation of the following form be chosen as the mixing rule for the acentric factor

$$\omega_m(T_{cm}/P_{cm})^\alpha = \sum_i \sum_j x_i x_j \omega_{ij}(T_{cij}/P_{cij})^\alpha \qquad (21a)$$

The value $\alpha = {}^2/_3$ has special significance, since $(T_c/P_c)^{2/3}$ is essentially a characteristic surface area of the molecule (Patterson, 1976) and the total interaction between molecules of different sizes is proportional to the surface area (Flory, 1970; Henderson and Leonard, 1971).

Our complete model, which is an extension of the two-parameter van der Waals model, consists of eq 16–21 and will be denoted as model I in later discussions. This model has two adjustable coefficients for each binary pair, ξ_{ij} and η_{ij}. In many cases, η_{ij} may be set equal to one; this special version of model I is called model IA. In some cases, it is necessary to use a different value of the binary interaction parameter ξ_{ij} for each phase; this variation of model I will be designated as model IB. The two-parameter van der Waals model of eq 13 and 16–20 will be called model II. For asymmetric mixtures, Plocker et al. (1978) suggested the replacement of eq 10 in the van der Waals model with the following equation

$$T_{cm} V_{cm}{}^{0.25} = \sum_i \sum_j x_i x_j T_{cij} V_{cij}{}^{0.25} \qquad (22)$$

We call this model of Plocker et al. (eq 9, 22, and 11–14) model III. Each of the mixing models used in this work is summarized in Table II. In the following discussions, we consider the application of the generalized corresponding states theory and the various mixing models to the calculation of vapor–liquid equilibria for various types of mixtures.

Application to Homogeneous Mixtures

In this study, mixtures that contain species that are similar in size and in the nature of their intermolecular forces are termed homogeneous mixtures. The accuracy of correlations of vapor–liquid equilibrium data for a number of homogeneous binary systems using the generalized corresponding states principle and mixing models IA and II are shown in Table III. It is found that only one binary interaction coefficient ξ_{ij} is necessary to give satisfactory correlations of experimental data for these systems and Table III also contains the values of this binary interaction coefficient. The columns headed REF1 and REF2 denote the reference fluids that have been used in the GCSP calculations. The equation of state constants for the reference fluids were obtained from the work of Patel and Teja (1982). Note that for these homogeneous mixtures it is found that two mixing models, IA and II, are very similar in correlating vapor–liquid equilibria of homogeneous mixtures.

It should be noted that eq 13 and 21 are identical if the values of T_c/P_c of all components in the mixture are equal. Figure 1 compares the mixture acentric factors calculated from these equations for a methane + ethane binary sys-

Table II. Summary of the Mixing Models Used in This Work

model name	equations	features
I	$\omega_m (T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j x_i x_j \omega_{ij} (T_{cij}/P_{cij})^{2/3}$ $T_{cm}/P_{cm} = \sum_i \sum_j x_i x_j (T_{cij}/P_{cij})$ $T_{cm}^2/P_{cm} = \sum \sum x_i x_j T_{cij}^2/P_{cij}$	$\xi_{ij} = T_{cij}/T_{ci}T_{cj} \neq 1$ $\eta_{ij} = 8T_{cij}/P_{cij}[(T_{ci}/P_{ci})^{1/3} + (T_{cj}/P_{cj})^{1/3}]^3 \neq 1$
IA	as above	$\xi_{ij} \neq 1; \eta_{ij} = 1$
1B	as above	$\xi_{ij}^L \neq \xi_{ij}^V; \eta_{ij} = 1$
II	$\omega_m = \sum_i x_i \omega_i$ $T_{cm}/P_{cm} = \sum_i \sum_j x_i x_j (T_{cij}/P_{cij})$ $T_{cm}^2/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}^2/P_{cij}$	$\xi_{ij} \neq 1, \eta_{ij} = 1$
III	$\omega_m = \sum_i x_i \omega_i$ $Z_{cm} = \sum_i x_i Z_{ci}$ $V_{cm} = \sum_i \sum_j x_i x_j V_{cij}$ $V_{cm}^{0.25} T_{cm} = \sum_i \sum_j x_i x_j V_{cij}^{0.25} T_{cij}$ $P_{cm} = Z_{cm} R T_{cm}/V_{cm}$	$\xi_{ij} = T_{cij}/T_{ci}T_{cj} \neq 1$ $\eta_{ij} = 8V_{cij}/[V_{ci}^{1/3} + V_{cj}^{1/3}]^3 = 1$

Table III. Comparison of Bubble Point Pressure Correlation of Homogeneous Mixture by Use of GCSP and Mixing Models 1A and II

mixture	T, K	max P, bar	ref1	ref2	model IA ξ_{12}	model IA $\Delta P\%$	model II ξ_{12}	model II $\Delta P\%$	data ref
CO_2 + methane	242	79	nC_4	CO_2	0.989	2.707	0.989	2.703	Donnelly and Katz (1974)
CO_2 - ethylene	232	10			0.957	1.066	0.956	1.061	Nagahama et al. (1974)
CO_2 + ethane	253	21			0.905	0.944	0.904	0.969	Nagahama et al. (1974)
CO_2 + propane	254	59			0.888	1.106	0.887	1.258	Reamer et al. (1951)
CO_2 + n-butane	273	32			0.884	3.473	0.883	3.931	Nagahama et al. (1974)
methane + ethylene	150	9	C_1	nC_2	1.010	1.712	1.011	1.430	Miller et al. (1977)
methane + propane	273	97			1.021	2.428	1.022	1.522	Reamer et al. (1950)
ethane + propene	278	24			1.001	0.321	1.001	0.324	McKay et al. (1951)
ethanol + 1-propanol	323	0.727	C_2OH	nC_3OH	0.998	0.967	0.988	1.021	Gmehling and Onken (1977)
1-propanol + 1-butanol	353	0.49			1.001	0.299	1.001	0.295	Gmehling and Onken (1977)

Table IV. Comparisons of Bubble Point Pressures of Methane + Heavy Hydrocarbon Mixtures Calculated by Use of Different Mixing Models and the Lee-Kesler Corresponding States Method with Experimental Values

mixture	T, K	model II ξ_{ij}	model II $\Delta P\%$	model III ξ_{ij}	model III $\Delta P\%$	model IA ξ_{ij}	model IA $\Delta P\%$	data ref
methane + n-pentane	176.3	1.032	9.57	1.249	4.25	0.978	3.79	Chen et al. (1976)
	280.0	1.014	7.56	1.239	3.31	0.980	2.18	Berry and Sage (1970)
	370.0	1.023	1.32	1.243	0.74	0.995	0.50	Berry and Sage (1970)
	450.0	1.021	1.18	1.238	1.06	1.010	0.49	Berry and Sage (1970)
methane + n-hexane	223.2	1.033	16.10	1.305	3.56	0.962	1.63	Shim and Kohn (1962)
	273.2	1.021	10.15	1.297	1.83	0.962	0.59	Shim and Kohn (1962)
	323.2	1.011	5.10	1.294	0.69	0.966	0.47	Shim and Kohn (1962)
	373.2	1.007	2.85	1.289	0.64	0.966	0.71	Shim and Kohn (1962)
	423.3	1.004	0.99	1.285	2.28	0.968	2.65	Shim and Kohn (1962)
methane + n-heptane	255.4	1.043	15.40	1.371	5.60	0.973	2.59	Chang et al. (1966)
	310.9	1.035	8.25	1.364	1.84	0.976	0.34	Reamer et al. (1956)
	377.6	1.029	4.60	1.356	0.96	0.978	0.14	Reamer et al. (1956)
	444.3	1.029	2.17	1.355	1.23	0.987	0.62	Reamer et al. (1956)
methane + n-octane	273.2	1.052	8.54	1.419	5.36	0.960	2.27	Kohn and Bradish (1964)
	373.2	1.045	6.85	1.411	3.12	0.962	1.63	Kohn and Bradish (1964)
	423.2	1.028	1.47	1.397	1.99	0.965	1.50	Kohn and Bradish (1964)
methane + n-decane	310.9	1.110	17.92	1.521	12.15	0.968	0.70	Reamer et al. (1942)
	377.6	1.099	11.50	1.511	6.84	0.975	0.68	Reamer et al. (1942)
	444.3	1.078	6.30	1.501	4.57	0.975	0.88	Reamer et al. (1942)
	510.9	1.084	3.90	1.520	6.21	1.000	2.64	Reamer et al. (1942)

tem and a methane + n-eicosane system. It can be seen that the two mixing rules are virtually identical for the methane + ethane binary, but they are very different for the asymmetric methane + n-eicosane system.

Application to Asymmetric Mixtures

Although the linear van der Waals model is satisfactory for homogeneous mixtures, it is not adequate for asymmetric mixtures (i.e., mixtures of molecules that differ appreciably in size). This limitation was observed by Plocker and co-workers (1978) among others. To correct

for this failure, they suggested use of the mixing rules that we have designated as model III (eq 9, 22, and 11-14). In Table IV, the results of bubble point pressure correlations for several asymmetric systems obtained by corresponding states theory and model IA are compared to those obtained using models II and III. In these calculations the reference equations proposed by Lee and Kesler (1975) have been used because model III was proposed for these reference equations. We find that model IA is superior to the other two models. Since T_c/P_c is representative of the characteristic size of molecules, model II (the van der Waals

Table V. Comparisons of Bubble Point Pressure Correlations of Mixtures Containing Aromatic Hydrocarbons by Use of GCSP and Mixing Models II and IA

mixture	T, K	max P, bar	ref1	ref2	model II ξ_{ij}	model II $\Delta P\%$	model IA ξ_{ij}	model IA $\Delta P\%$	data ref
methane + benzene	339	137.9	CH₄	C₆H₆	0.999	3.245	1.081	0.930	Lin et al. (1979)
	501	145.6			1.096	3.842	1.000	2.434	Elbislawi and Spencer (1951)
ethylene + benzene	348	91.2			1.030	2.517	1.028	4.046	Ellis et al. (1968)
ethane + benzene	298	38.0			1.025	3.560	1.022	4.728	Ohgaki et al. (1976)
	333	48.3			1.027	2.914	1.025	3.908	Kay and Nevens (1952)
	393	68.9			1.019	0.946	1.018	1.102	Kay and Nevens (1952)
	433	82.7			1.014	1.154	1.013	1.156	Kay and Nevens (1952)
	513	68.9			0.981	0.823	0.981	0.818	Kay and Nevens (1952)
propane + benzene	377	41.4			1.013	2.047	1.012	2.167	Glanville et al. (1950)
	411	51.7			1.010	0.893	1.010	0.982	Glanville et al. (1950)
	477	58.6			1.001	0.572	1.000	0.540	Glanville et al. (1950)
methane + toluene	462	152.0			1.043	3.071	1.033	1.447	Lin et al. (1979)
	543	115.1			0.990	1.040	0.991	0.308	Lin et al. (1979)
methane + 1,3-trimethylbenzene	311	142.7			1.167	15.14	1.112	2.049	Knapp et al. (1982)
	394	145.9			1.144	8.923	1.104	1.981	Knapp et al. (1982)
	477	141.3			1.115	5.923	1.092	1.486	Knapp et al. (1982)
methane + m-xylene	394	144.8			1.140	15.24	1.093	4.453	Knapp et al. (1982)
	477	139.1			1.122	8.442	1.075	1.806	Knapp et al. (1982)
	541	153.7			1.088	4.854	1.029	2.684	Simnick et al. (1979)

Table VI. Bubble Point Pressure Correlations of Mixtures of Low Molecular Weight Alcohols and Small Nonpolar Molecules by Use of GCSP

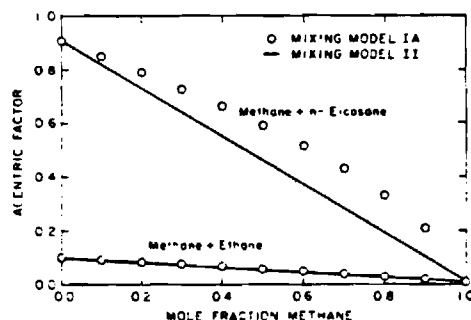| mixture	T, K	max P, bar	ref1	ref2	model IA ξ_{ij}	model IA $\Delta P\%$	model I η_{ij}	model I ξ_{ij}	model I $\Delta P\%$	data ref
methanol + CO₂	298	61.3	CO₂	EtOH	1.089	4.02	1.090	1.020	1.34	Ohgaki and Katayama (1976)
methanol + ethane	373	60.8	C₂H₆	EtOH	1.074	5.46	1.077	1.078	1.46	Ma and Kohn (1964)
	348	60.8			1.092	4.71	1.095	1.068	1.10	Ma and Kohn (1964)
ethanol + propane	350	27.6			1.066	6.75	1.063	1.066	1.93	Gomez-Nieto and Thodos (1978)

Figure 1. Comparison of acentric factor of methane + ethane and methane + n-eicosane calculated by mixing models IA and II.

model) can be viewed as a special case of model IA that is satisfactory only for homogeneous mixtures.

It should be noted from Table IV that the difference between the various models decreases as the temperature increases. This may be because the movement of molecules increases with increasing temperature so that the effect of orientation and molecular packing becomes less important. Also, the difference between model I and model III increases as the size difference between the components of the mixture increases. Since the study by Plocker and co-workers included data only for the methane + n-pentane and methane + n-heptane systems, it may be that model III is suitable for mixtures with intermediate size differences only.

As in the case of homogeneous mixtures, only one binary interaction coefficient ξ_{ij} was needed to correlate the data for the mixtures studied here. The optimal values of ξ_{ij} obtained using model IA are, in general, closer to unity than those obtained using the other two models. This indicates that model IA is probably a better representation for this class of systems. In practice, a smaller range of values of ξ_{ij} is better since fewer errors in prediction result if slightly inaccurate values of ξ_{ij} are used.

The behavior of mixtures containing aromatic compounds is becoming more important as the chemical and energy industries use more coal as a raw material. Model IA is not limited to mixtures of aliphatic molecules; it may also be used for aromatic mixtures. Table V shows the results of the bubble point pressure correlations for several systems that contain a small hydrocarbon molecule with an aromatic hydrocarbon using GCSP and models IA and II. It is found that, as in the case of aliphatic mixtures, the two models are nearly the same if the size difference between the two types of molecules in the binary mixture is not too great. However, as the size difference increases, model IA is clearly better than model II.

Application to Mixtures Containing Low Molecular Weight Alcohols and Nonpolar Molecules

In this section we demonstrate the extension of our model to binary mixtures in which the unlike pair interactions are significantly different from the like pair interactions, i.e., to heterogeneous mixtures. Low molecular weight alcohols such as methanol, ethanol, and propanol form such heterogeneous mixtures with nonpolar molecules such as the hydrocarbons and carbon dioxide. Table VI illustrates the application of the GCSP with the new mixing model to three binary systems representative of this class of mixtures. It is seen that mixture model I (with two adjustable constants ξ_{ij} and η_{ij}) is successful in correlating the data whereas model IA (with only one adjustable constant ξ_{ij}) leads to less accurate correlations. The values of the additional binary interaction coefficient η_{ij} are found to be greater than one, and the values of ξ_{ij} found using model I are only slightly different from those obtained using model IA. If we consider T_{cij}/P_{cij} to be a measure of the closest distance of approach between two unlike molecules, than values of η_{ij} greater than one would indicate that there is a certain degree of exclusion between the two types of molecules. A possible explanation for this

Table VII. Comparisons of Experimental and Calculated Azeotropic Pressures and Compositions of Alcohols + Heavy Hydrocarbon Systems (Data Taken from Gmehling and Onken (1977))

mixture	exptl values			model IA			model I			
	T, K	P, bar	x	ξ_{ij}	P	x	η_{ij}	ξ_{ij}	P	x
methanol + n-hexane	318	0.840	0.504	0.926	0.840	0.627	0.175	1.028	0.840	0.504
n-hexane + ethanol	298	0.254	0.753	0.909	0.257	0.552	0.100	1.374	0.260	0.742
	318	0.608	0.703		0.593	0.563			0.593	0.707
n-heptane + 1-propanol	348	0.713	0.560	0.926	0.713	0.419	0.225	1.064	0.713	0.560

Table VIII. Dew Point Pressure Correlations of Water + Hydrocarbon Systems by Use of GCSP and Mixing Model IA

mixture	T, K	max P, bar	ξ_{ij}	ΔX	data ref
water + methane	511	690	1.035	0.0050	Olds et al. (1942)
water + ethane	511	690	0.743	0.0027	Olds et al. (1943)
water + n-butane	511	690	0.629	0.0071	Reamer et al. (1952)

is that the interaction between unlike species is still essentially dispersive in nature and the size and polarizability of the nonpolar molecules are not enough to disrupt the hydrogen bonding between the alcohol molecules. However, because of the hydrogen bonding between alcohol molecules, the nonpolar molecules cannot get as close to the alcohols as normally would be the case for two molecules of comparable size.

Application to Mixtures Containing Low Molecular Weight Alcohols and Heavy Hydrocarbons

Mixtures of low molecular weight alcohols with medium size (C_5–C_8) hydrocarbons are sufficiently different from the previous class of heterogeneous systems to require separate treatment of their behavior. In fact, the vapor–liquid behavior of these mixtures is highly nonideal and often results in the formation of azeotropes.

Table VII contains the smoothed experimental values of azeotropic pressures and compositions of three binary mixtures, and values predicted using the GCSP method with models I and IA. Experimental data for these binary systems can be found in the vapor–liquid equilibrium data collection compiled by Gmehling and Onken (1977). The Teja–Patel equations of state for ethanol and n-octane were used as the reference fluid equations. The GCSP method with model IA did not give good prediction of the azeotropic composition. This is probably due to the existence of strong unlike pair interactions between molecules in these mixtures that are of dipole–induced dipole nature. Unlike the case of mixtures containing alcohols and small nonpolar molecules, the size and polarizability of these medium size hydrocarbon molecules is great enough to disrupt hydrogen bonding between the alcohols. Instead of forming aggregate species with themselves, alcohol molecules interact with the hydrocarbon molecules in these mixtures. Since the environment of the alcohol molecules undergoes a substantial change in going from the pure component to the mixture, a simple mixture model like model IA is not likely to work. With model I (and two adjustable constants), however, there is a substantial improvement in predicting the azeotropic compositions. Figure 2 compares the experimental x–y curve of the binary system n-heptane + methanol at 348 K with that calculated using GCSP with models I and IA. Mixture model I was also found to yield more accurate calculations of vapor–liquid equilibria away from the azeotropic point than model IA. However, instead of η_{ij} being greater than one, as in the case of mixtures of alcohols and small nonpolar molecules, here we found η_{ij} to be less than one and very small. This may due to the strong interaction between the alcohol and the hydrocarbon molecules, so that the closest distance of approach between unlike species is much smaller than normal. Consistent with this is the
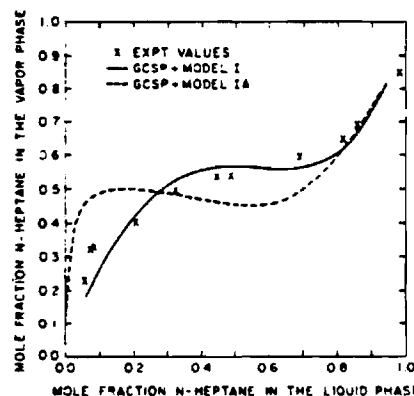
Figure 2. Experimental and correlated vapor–liquid equilibrium data of n-heptane + 1-propanol at 348 K.

observation that values of ξ_{ij} were found to be greater than one, indicating that there is strong interaction between unlike molecules.

Application to Water–Hydrocarbon Systems

Water–hydrocarbon systems are of great importance in hydrocarbon processing operations. Because of the polar nature of the water molecules and their strong hydrogen bonding tendency, the miscibility of water and hydrocarbons in the liquid phase can be very low.

Table VIII gives the experimental and calculated compositions of the vapor phase for three water + hydrocarbon systems at pressures up to 700 bar. It was found that model IA gave good correlations of these data. However, for the water + n-butane system, this model failed to predict the proper order of magnitude for n-butane in the aqueous (liquid) phase that has been observed by Reamer and co-workers (1952). The introduction of a second binary interaction coefficient (i.e., use of model I rather than model IA) leads to some improvement, but agreement with the experimental results is still not as accurate as desired.

Peng and Robinson (1979) considered similar systems using their cubic equation of state and a one-fluid model that is analogous to the van der Waals model and suggested that different binary interaction coefficients are used in the different phases. Significant improvement in the prediction of hydrocarbon mole fraction in the aqueous phase results in using this idea in model IA, that is, allowing the binary interaction coefficient ξ_{ij} to take different values in the liquid and vapor phases; this model is denoted as model IB. Experimental P–x and P–y curves are compared with those calculated using model IB in Figure 3. Reasonable agreement between correlation and experiment is obtained if the value of ξ_{12} is taken to be 0.882 for the liquid phase and 0.629 for the vapor phase in the water + n-butane system.
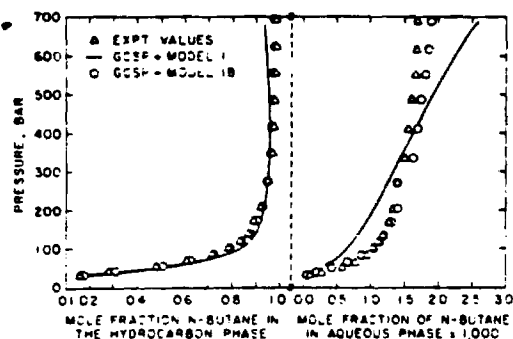
Figure 3. Experimental and correlated vapor-liquid equilibrium data of n-butane + water at 511 K.

Both models I and IB contain two adjustable parameters. Model IB, however, gives a more accurate correlation of experimental data for the water + hydrocarbon system as illustrated in Figure 3. The success of model IB implies that the interaction between the water molecules and the hydrocarbon molecules changes as the composition and/or density of the mixture changes. It should be noted, however, that the use of different values of ξ_{12} for the two coexisting phases means that model IB is unable to properly describe the continuity of the liquid and gaseous phases at a gas-liquid critical point—unless the two ξ_{ij}'s converge to the same value in the critical region.

Conclusions

We have studied the role played by mixing rules in three-parameter corresponding state calculations of vapor-liquid equilibria for various types of binary mixtures. While this work was done within the context of the generalized corresponding states principle, we expect that the conclusions should be more generally applicable. It was found that the usual van der Waals model has limited application except for simple homogeneous mixtures. One of the reasons, is the inadequacy of the linear combination rule for the acentric factor to represent the effect of orientation and packing of molecules. A new mixture model was developed which contains the van der Waals model as a special case. This model retains the mixing rules derived from the van der Waals two-parameter corresponding states theory for T_{cm} and P_{cm}, but modifies the mixing rule for the acentric factor. It is found that this newly proposed model results in accurate predictions and correlations for a wide range of mixtures, including those for which the van der Waals model is not applicable. The generality and simplicity of this new mixing model are great advantages in engineering applications.

We have also established that the generalized corresponding states principle, using adjustable reference equations, can be used for a wide variety of mixtures, including those not usually candidates for correlation by corresponding states methods.

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Vapor–Liquid Equilibrium Calculations by Use of a Generalized Corresponding States Principle. 2. Comparison with Other Methods

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We have correlated vapor–liquid equilibrium data for a variety of mixtures by use of a generalized corresponding states principle (GCSP) with two nonspherical reference fluids and compared the results with other corresponding states and equation of state methods. We conclude that, given a set of mixing rules, the GCSP with only cubic equations as reference fluid equations of state is, for nonpolar fluids, as good as conventional corresponding states methods that use more complicated but fixed reference equations, and better for mixtures containing polar compounds. The GCSP is as accurate as the direct use of the cubic equations of state and may be more useful for mixtures containing substances for which equation of state constants are not available. The GCSP, with the proper choice of reference fluids, is also found to be of comparable accuracy to an activity coefficient model in low-pressure vapor–liquid equilibrium calculations for polar mixtures; it is, however, a much more general model for thermodynamic properties.

Introduction

In part 1, we used a generalized three-parameter corresponding states principle (GCSP) that allows the use of two nonspherical reference fluids and different types of reference equations to correlate vapor–liquid equilibrium data for a wide variety of mixtures. A mixing model, which is an extension of the van der Waals one-fluid model of the two-parameter corresponding states theory, was developed. Here, we discuss the advantages and disadvantages of the GCSP by comparing it to other commonly used methods of correlating vapor–liquid equilibrium data.

Comparison with the Cubic Equation of State Method

One of the thermodynamic models most commonly used in vapor–liquid equilibrium (VLE) calculations is the cubic equation of state. Patel and Teja (1982) have recently proposed a cubic equation of state that accurately predicts the saturation density of a variety of fluids including paraffinic and aromatic hydrocarbons, water, and alcohols. They have demonstrated the advantages of their equation of state over other cubic equations of state (e.g., Peng and Robinson, 1976; Soave, 1972) for VLE calculations. In this work, therefore, we have compared our calculations using GCSP with calculations using the Teja–Patel equation of state (TPES).

The Teja–Patel equation of state is given by

$$P = RT/(v - b) - a/[v(v + b) + c(v - b)] \qquad (1)$$

where a, b, and c are obtained from the critical point, the vapor pressures, and the saturation liquid densities of the fluid of interest. The mixing rules adopted for the parameters a, b, and c in this work are

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad (2)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \qquad (3)$$

$$c_m = \sum_i \sum_j x_i x_j c_{ij} \qquad (4)$$

with

$$a_{ij} = \xi_{ij}(a_i a_j)^{1/2} \qquad (5)$$

$$b_{ij} = \eta_{ij}(b_i + b_j)^{1/2} \qquad (6)$$

$$c_{ij} = \eta_{ij}(c_i + c_j)^{1/2} \qquad (7)$$

Since the effect of molecular size and shape on the equation of state parameters is included through the dependence of the parameters a, b, and c on the acentric factor, eq 2–7 are considered to be a general two-parameter mixture model that is analogous to model I (see part 1) in the generalized corresponding states principle. We refer to these equations as model I for the cubic equation of state method. A special version of model I is to set η_{ij} equal to unity; this one-parameter model is denoted as model IA for the cubic equation of state method (and is analogous to model IA of the GCSP in part 1). Model IA was used by Soave (1972), Peng and Robinson (1976), and Patel and Teja (1982) in their equations of state methods.

Table I contains the results of bubble point correlations using the TPES method and the GCSP with Teja–Patel equations of state as references. Again we emphasize that equations of state of any form and complexity can be used as reference equations; cubic equations have been used here only for comparison and because the parameters for such equations of state are available for many substances. In these calculations model IA appropriate to each method has been used. We see from this table that for these hydrocarbon–hydrocarbon and carbon dioxide–hydrocarbon systems, the results of the GCSP are very similar to those of the TPES despite the fact that the GCSP contains both the errors due to the cubic equation of state representation of the reference fluids and to the corresponding states assumption.

One of the most important advantages of the corresponding states method is the ability to extend the information for a relatively small number of reference sub-

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Table I. Comparisons of Bubble Point Pressure Correlations of Nonpolar Mixtures by Use of Teja–Patel Equation of State (TPES) and the Generalized Corresponding States Principle (GCSP)

		TPES				GCSP		
mixture	T, K	ξ_{ij}	ΔP %	ref 1	ref 2	ξ_{ij}	ΔP %	data ref
methane + CO_2	242	0.899	1.89	C_1	nC_8	0.998	2.69	Donnelly and Katz (1974)
ethane + CO_2	253	0.869	0.76			0.905	1.12	Nagahama et al. (1974)
methane + n-pentane	370	1.007	1.45			1.032	2.20	Berry and Sage (1970)
methane + n-hexane	273	0.981	0.93			1.048	0.97	Shim and Kohn (1962)
methane + n-heptane	311	1.103	0.73			1.068	1.05	Reamer et al. (1956)
methane + n-octane	273	1.004	1.31			1.066	1.42	Kohn and Bradish (1964)
methane + n-decane	444	1.067	1.39			1.074	2.14	Reamer et al. (1942)
methane + n-eicosane	313	1.098	1.036			1.217	2.39	Kohn and Puri (1970)
CO_2 + n-decane	411	0.925	1.75	CO_2	nC_8	0.884	1.01	Reamer and Sage (1963)

Table II. Comparison of Bubble Point Pressure Correlation of Binary Systems Containing Alcohols by Use of Teja–Patel Cubic Equation of State (TPES) and Generalized Corresponding States Principle (GCSP)

		TPES					GCSP			
mixture	T, K	η_{ij}	ξ_{ij}	ΔP %	ref 1	ref 2	η_{ij}	ξ_{ij}	ΔP %	data ref
methanol + CO_2	298	0.980	0.952	2.54	EtOH	C_2	1.030	1.091	1.16	Ohgaki and Katayama (1976)
methanol + ethane	373	1.089	1.019	1.13			1.093	1.078	1.18	Ma and Kohn (1964)
ethanol + propane	350	1.000	0.976	2.27			1.066	1.063	1.93	Gomez-Nieto and Thodos (1978)
ethane + 1-propanol	323	1.000	0.991	1.24	EtOH	nC_5OH	1.000	0.999	0.99	Gmehling and Onken (1977)
1-propanol + 1-butanol	363	-	-	-			1.000	1.001	0.30	Gmehling and Onken (1977)

Table III. Comparisons of Prediction of Azeotropic Points of Alcohol + Hydrocarbon Mixture by Use of Teja–Patel Equation of State (TPES) and the Generalized Corresponding States Principle (GCSP)[a]

	exptl values				TPES				GCSP		
mixture	T, K	P, bar	x	η_{ij}	ξ_{ij}	P	x	η_{ij}	ξ_{ij}	P	x
methanol + n-hexane	318	0.840	0.504	0.075	0.099	0.840	0.505	0.175	1.028	0.840	0.504
n-hexane + ethanol	298	0.254	0.753	0.050	0.102	0.254	0.721	0.100	1.374	0.260	0.742
	318	0.608	0.703	0.050	0.102	0.593	0.680	0.100	1.374	0.593	0.707
1-propanol + n-heptane	348	0.713	0.560	0.190	0.219	0.714	0.560	0.225	1.064	0.713	0.560

[a] Data taken from Gmehling and Onken (1977).

stances to a large number of systems containing similar species. In Table I, we correlated the VLE data for a large number of nonpolar mixtures by using reference equations of methane, carbon dioxide, and n-octane only. Although generalized correlations of equation of state parameters for the Teja–Patel equation of state are available for each of the substances in this table, their determination requires much more data than that needed to determine the parameters of the three reference fluids used in the generalized corresponding states principle. This advantage of the corresponding states theory is more obvious in the correlation of VLE data of systems containing alcohols, since generalized correlations of the equation of state constants using the acentric factor are inaccurate for alcohols. In Table II, we demonstrate that given only equation of state constants for ethanol, 1-pentanol, and ethane, we can use the GCSP to accurately correlate VLE data of a number of alcohol + alcohol and alcohol + hydrocarbon systems. The results of the GCSP are comparable to those of the equation of state method when equation of state constants specific to each component are used, though to calculate such constants accurate vapor pressure and saturation liquid density data are needed, and these data may not be available for all substances of interest in chemical engineering. For example, equation of state calculations could not be done for the 1-propanol + 2-methyl-1 propanol mixture since the constants for 2-methyl-1-propanol have not been reported. Instead of determining these constants with vapor pressure and saturated liquid density data, a good correlation of the VLE data was developed by using the GCSP and already
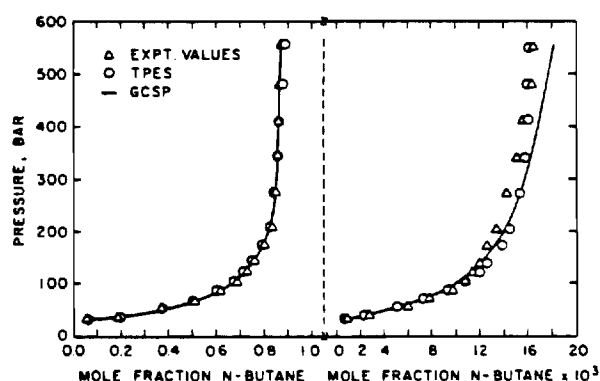
Figure 1. Experimental and correlated vapor–liquid equilibrium data for n-butane + water system in the hydrocarbon-rich and water-rich phases, respectively at 511 K. Experimental data are those of Reamer and Sage (1952).

available information on ethanol and 1-pentanol.

The similarity between correlations obtained with the GCSP and the TPES is not limited to simple VLE behavior. Table III illustrates that both methods are of comparable accuracy in predicting the azeotropic compositions of mixtures containing alcohols and hydrocarbons. In this case the mixture models I with two binary interaction coefficients are used in both the TPES and GCSP to fit experimental azeotropic pressures and compositions. The binary interaction coefficients obtained in the two methods are very different; for the TPES, both ξ_{12} and η_{12} are quite small, while for the GCSP, η_{12} is found to be small, and ξ_{12} is close to unity.

Table IV. Comparisons of Bubble Point Pressure Correlations of Nonpolar Mixtures by Use of Generalized Corresponding States Principle (GCSP) and Lee-Kesler Corresponding States Method (LKCS)[a]

| | | GCSP | | | LKCS | | |
mixture	T, K	ref 1	ref 2	ξ_{ij}	ΔP %	ξ_{ij}	ΔP %
methane + n-pentane	370	C_1	nC_5	1.032	2.20	0.995	0.50
methane + n-hexane	273			1.048	0.97	0.962	0.59
methane + n-heptane	311			1.068	1.05	0.976	0.34
methane + n-octane	323			1.066	1.42	0.962	1.63
methane + n-decane	444			1.074	2.14	0.975	0.88
CO_2 + n-decane	411	CO_2	nC_{10}	0.884	1.01	0.809	3.86

[a] See Table I for sources of experimental data.

Figure 1 shows the results of using the GCSP and TPES to correlate VLE data of the water + n-butane system. For both methods we have used different values for the binary interaction coefficient ξ_{12} in different phases, as suggested by Peng and Robinson (1979) (see model IB in part 1). For the liquid phase ξ_{12} was found to be 0.927 for the TPES and 0.882 for the GCSP; for the vapor phase it was 0.552 for the TPES and 0.629 for the GCSP. The two methods lead to very similar results, though at the higher pressures, the amount of n-butane in the aqueous phase predicted by the GCSP is slightly greater than both the experimental values and the TPES results.

From these calculations and others we have done, we have established that there is no significant difference between the cubic equation of state method and the generalized corresponding states principle in correlating binary vapor-liquid equilibria, provided that comparable mixture models are used in both methods. The advantage of a cubic equation of state method is that it is faster computationally, since only one density calculation is necessary for each fugacity calculation, while two such density calculations are necessary in the GCSP. However, more data are needed to obtain all the parameters for the direct application of the equation of state; this may not always be possible as with the alcohol systems considered here. For the GCSP, equation of state parameters for only a few reference fluids are needed to calculate properties of a large variety of pure and mixture fluids. This advantage of the GCSP can be especially important in the modeling of vapor-liquid equilibrium behavior of complicated mixtures such as coal liquid and petroleum reservoir fluids, which contain a large number of components that are incompletely identified and for which pure component data may be unavailable.

Comparisons with the Lee-Kesler Corresponding States (LKCS) Method

There are two important elements in any corresponding states theory: the mixture model and the reference fluid representation. We have hitherto used cubic equations of state to represent our reference fluids. The limitations of cubic equations are well-known (Abbott, 1979). Therefore, we compare our method with corresponding states calculations that use more accurate PVT representation for the reference fluids. In particular, we have compared our method with the corresponding states method (LKCS) proposed by Lee and Kesler (1975), which essentially uses argon and n-octane as fixed reference fluids but represents these reference fluids by eleven-constant Benedict-Webb-Rubin equations. In essence, we are comparing the advantages gained by using a changing reference fluid vs. those of using an improved, but fixed reference fluid representation. It should again be emphasized here that the GCSP is not limited to cubic equations of state. We can use more accurate equations of state for the reference fluids if necessary, though cubic equations are sufficient in many cases as we shall see. In fact, an important advantage of
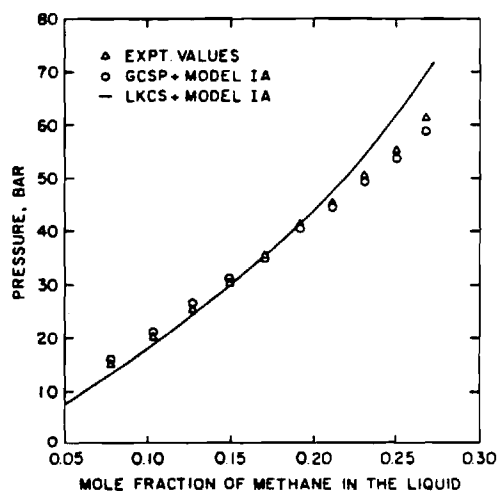

Figure 2. Experimental and correlated solubility of methane in n-eicosane at 313 K.

the GCSP is its ability to use an equation of state for any fluid, and of any complexity in the reference representation.

Table IV contains the results of bubble point pressure correlations for a number of nonpolar mixtures using the GCSP with the Teja-Patel cubic equation as the reference fluids representation and the LKCS method. In the original version of the LKCS method, a linear mixing rule for the acentric factor was used. This equation has been demonstrated to be inadequate for many mixtures (see part 1) and therefore was replaced by mixture model IA of part 1 in this study. The same mixture model was also used for the GCSP. It is evident from Table IV that the use of a more complicated reference equation does not improve VLE correlations to any significant extent. This is not unexpected since the composition dependence of the fugacity coefficients in the corresponding states method, which is so important in phase equilibrium calculations, arises from the derivatives of the pseudocritical parameters. Therefore a small change in the mixing rules or the binary interaction coefficients affects VLE calculations significantly as we have already seen in part 1. Conversely, the fugacity coefficients depend on the integral of the PVT relation of the reference fluids. Therefore, the VLE calculations will not be strongly dependent on the accuracy of the equation of state used. Indeed, any small inaccuracy of the equation of state can be compensated for by an adjustment in the interaction coefficients.

Although accuracy of the VLE calculation is largely determined by the mixture model, the effect of choosing the proper reference fluid is not negligible in all cases. Figure 2 shows the experimental (Kohn and Puri, 1970) and calculated values of solubility of methane in n-eicosane using the GCSP with cubic equation of states for methane and n-eicosane as references, and the LKCS method using mixture model IA in both cases. There we see that the
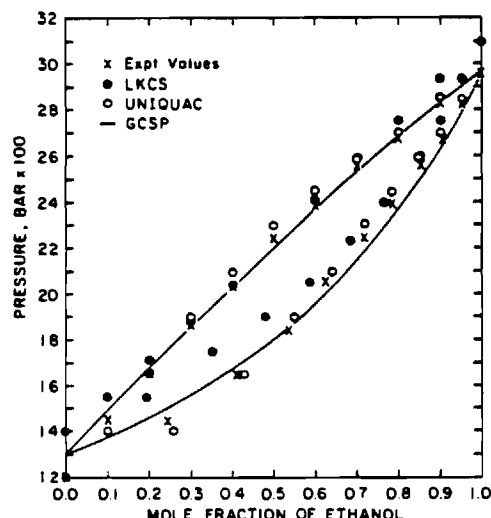
/ /

Figure 3. Experimental and correlated vapor–liquid equilibrium data for ethanol + 1-propanol at 323 K.

Figure 4. Experimental and correlated vapor–liquid equilibrium data for n-heptane + 1-propanol at 348 K.

GCSP leads to more accurate correlations as a result of the better selection of reference fluids.

The importance of choosing representative reference fluids is further illustrated by examining the results in Figure 3 comparing the experimental P-x-y data for the binary system ethanol + 1-propanol (taken from Gmehling and Onken, 1977) with values calculated by LKCS and GCSP. Again mixture model IA is used in both cases. The LKCS method is unable accurately to predict pure component vapor pressures for these components because of the use of argon and n-octane as reference fluids. It therefore fails to yield accurate values of mixture bubble point pressures, irrespective of the mixture model used. The GCSP, on the other hand, leads to successful correlation of the data because it allows the use of reference fluids, ethanol and 1-pentanol in this case, that are more representative of the components in the mixture.

Thus, we have demonstrated that the GCSP yields accurate phase equilibrium calculations for mixtures containing nonpolar as well as polar molecules by the use of different, appropriately chosen reference fluids. Calculations of equivalent accuracy for such a wide variety of mixtures are not possible with the LKCS method, or any other corresponding states method with fixed reference fluids. However, even for nonpolar systems, there is an important advantage of being able to change reference fluids, rather than being constrained to fixed reference fluids.

Comparisons with Activity Coefficient Models

Methods of calculating VLE based on the corresponding states principle and the equation of state method are similar in that they use the same equations to calculate species fugacity in both the vapor and liquid phases. Another way of modeling VLE is to use activity coefficient models, such as the universal quasi-chemical theory (UNIQUAC) proposed by Abrams and Prausnitz (1975), for the liquid phase, and an equation of state for the vapor phase. Activity coefficient methods are generally applied to low pressure VLE where pressure corrections are unimportant. Here we compare the correlations of low-pressure VLE data for alcohol + alcohol and alcohol + heavy hydrocarbon mixtures using the GCSP and the UNIQUAC model; both models contain two adjustable coefficients. In Figure 3, the experimental P-x-y data of the ethanol + 1-propanol binary are compared with the values calculated by the GCSP and UNIQUAC. In Figure 4, experimental x-y data of an n-heptane + 1-propanol (Gmehling
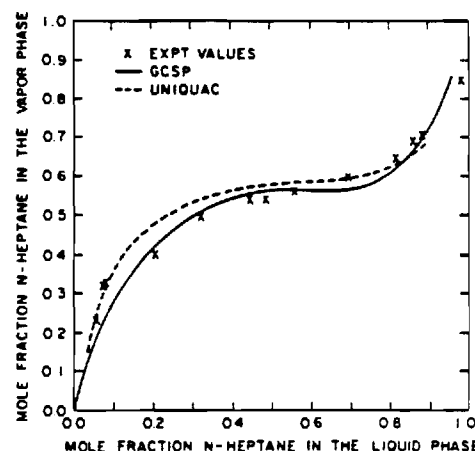
and Onken, 1977) system are compared with the calculated values. In both cases, the GCSP is able to fit the data about as well as the UNIQUAC method. The most important conclusion that can be drawn from these results is that the GCSP, given appropriately chosen mixing rules and reference fluids, can be used to predict/correlate VLE for systems that hitherto have been described using activity coefficient models. In addition, the GCSP can be used to calculate other thermodynamic properties, whereas the activity coefficient models can be used to calculate fugacity only.

Conclusion

In this study, we have demonstrated that the GCSP is of comparable or better accuracy than many existing thermodynamic models for calculating VLE. In particular, the methods considered include cubic equations of state, the Lee–Kesler corresponding states method, and the UNIQUAC activity coefficient method. However, the GCSP has many advantages. First, it requires less information on the components in the mixture than either the cubic equation of state method or the UNIQUAC model. Second, unlike the LKCS method, it is also able to correlate the VLE of systems containing polar species. Also, even for nonpolar systems, more accurate results can be obtained than with the LKCS method by appropriate choice of reference fluids. Third, the GCSP can be used over the whole pressure range for the calculation of all thermodynamic properties, whereas UNIQUAC is a model for activity coefficients at low pressure only. Though far from complete, the testing done here establishes that the GCSP is a versatile tool for modeling of phase equilibrium and other thermodynamic properties of many different mixtures over large ranges of temperature and pressure.

Acknowledgment

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Calculation of Vapor–Liquid–Liquid Equilibrium with Cubic Equations of State and a Corresponding States Principle

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Vapor–liquid–liquid equilibrium data for three ternary systems are correlated by use of two cubic equations of state and a generalized corresponding states method with the same binary interaction coefficients in all phases. It is found that vapor–liquid–liquid equilibrium cannot be accurately predicted with interaction coefficients obtained from binary vapor–liquid equilibrium data, though accurate correlation is possible with a set of interaction coefficients fitted to the three-phase data. For the systems studied, the same value for the interaction coefficients for a binary pair can be used in the calculation of vapor–liquid–liquid equilibrium when this pair occurs in different ternary systems.

Introduction

While multicomponent, multiphase equilibria are important in chemical processing, the prediction and correlation of vapor–liquid–liquid equilibria (VLLE) and other multiphase behavior are not as well studied as vapor–liquid equilibria (VLE). Several algorithms for the isothermal isobaric VLLE calculations have been proposed, and Peng and Robinson (1976a) have used their cubic equation of state (1976b) to study VLLE in heterogeneous water + hydrocarbon systems. Since the coexisting phases in water + hydrocarbon systems are of very different composition and character, different binary interaction coefficients, as defined below, were used for each liquid phase in that study. This is equivalent to describing each of the phases by a different thermodynamic model and in principle introduces two thermodynamic inconsistencies. First, with different interaction coefficients for a pair of components in different phases, the critical point of the system may not be properly described. Second, since the liquid phase fugacity coefficients are obtained by an integral of the equation of state from low pressure into the liquid region, it is not clear what expressions should be used when the interaction coefficients change with density, phase, or composition. Further, for the liquid phases, the binary interaction coefficients change discontinuously with composition.

In this study we consider the thermodynamic correlation of VLLE data for three ternary mixtures recently reported by Kohn and co-workers (1982): methane + ethane + n-octane, methane + propane + n-octane, and methane + carbon dioxide + n-octane. One characteristic of these systems is that each has a very small three-phase envelope which exists over a range of temperatures of only a few degrees Kelvin and pressure range of only one or two bar. Another is that the compositions of the coexisting liquid phases are of similar orders of magnitude, unlike the heterogeneous water + hydrocarbon systems. Therefore, predictions or correlations of VLLE for these simple, nonpolar mixtures is a stringent test of the accuracy of a thermodynamic model. Here we consider two classes of thermodynamic models: the cubic equations of state and the corresponding states principle.

Computational Procedure

In an isothermal three-phase flash a feed of composition $(z_1, z_2, ..., z_n)$, where n is the total number of components

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in the mixture, undergoes an equilibrium separation at constant temperature T and pressure P to a liquid phase L of composition $(x_1, x_2, ..., x_n)$, a second liquid phase L′ of composition $(x_1', x_2', ..., x_n')$, and a vapor phase V of composition $(y_1, y_2, ..., y_n)$. The fractional amount of the two liquid phases and the vapor phase will be denoted by L, L', and V, respectively. The material balance equations are

$$z_i = x_i L + x_i' L' + y_i V \tag{1}$$

$$1 = L + L' + V \tag{2}$$

The equilibrium relations between the compositions of each phase are

$$y_i/x_i = K_i = \phi_i^L/\phi_i^V \tag{3}$$

$$y_i/x_i' = K_i' = \phi_i^{L'}/\phi_i^V \tag{4}$$

where ϕ_i^j is the fugacity coefficient of species i in phase j. In this work the fugacity coefficients were calculated by using the thermodynamic models to be discussed in the next section. The phase compositions also have to satisfy the following normalization constraints

$$\sum_i x_i = 1 \tag{5}$$

$$\sum_i x_i' = 1 \tag{6}$$

$$\sum_i y_i = 1 \tag{7}$$

There are $3n + 3$ equations in the set above, and $3n + 5$ variables. Therefore, if we specify the temperature and pressure, the equilibrium composition of each phase can, in principle, be found by an iterative procedure similar to that used by Peng and Robinson (1976a).

To correlate VLLE data, a feed composition within the experimental three-phase envelope at the given temperature and pressure is chosen and, upon using the three-phase flash algorithm and a thermodynamic model for the fugacity coefficients, the compositions of the equilibrium phases are computed. This procedure is repeated, varying the adjustable parameters in the model until the best agreement between theory and experiment is obtained. However, since the three-phase region is very small for the systems we are considering, the feed composition so chosen may be outside the three-phase region predicted by the thermodynamic model, in which case the flash calculation will not converge to a three-phase solution. In such cases the feed composition is varied until a three-phase solution

Table I. Binary Interaction Coefficients Obtained by Fitting VLLE Data with the TPES and GCSP Models

binary pair	TPES		GCSP	
	η_{12}	ξ_{12}	η_{12}	ξ_{12}
methane + n-octane	1.036	0.985	0.994	0.964
methane + ethane	0.984	1.032	1.024	1.022
methane + propane	1.017	1.035	1.114	0.994
methane + carbon dioxide	0.990	0.991	1.012	1.089
ethane + n-octane	1.030	1.000	1.018	0.985
propane + n-octane	1.012	1.008	1.129	1.006
carbon dioxide + n-octane	0.929	0.994	0.990	0.892

is obtained, if indeed there is such a solution for the thermodynamic model chosen.

Thermodynamic Models

In this study we considered three thermodynamic models: the three-constant cubic equation of state proposed by Teja and Patel (1982) (hereafter referred to as TPES), the two-constant cubic equation of state of Peng and Robinson (1976b) (PRES) and a generalized three-parameter corresponding states principle developed by Wong et al. (1984) (GCSP). Each model was used to compute the thermodynamic properties and species fugacity coefficients for the VLLE calculations.

The TPES method uses the following equation for the compressibility of a fluid

$$Z = v/(v - b) - av[v^2 + (b + c)v - bc] \quad (8)$$

For a pure fluid the parameters a, b, and c were obtained from the generalized correlations of Teja and Patel (1982). For a mixture the equation of state parameters a, b, and c were obtained from the pure component constants using the following mixing rules

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (9)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (10)$$

$$c_m = \sum_i \sum_j x_i x_j c_{ij} \quad (11)$$

$$a_{ij} = \xi_{ij}(a_i a_j)^{1/2} \quad (12)$$

$$b_{ij} = \eta_{ij}(b_i + b_j)/2 \quad (13)$$

$$c_{ij} = \eta_{ij}(c_i + c_j)/2 \quad (14)$$

where η_{ij} and ξ_{ij} are the binary interaction coefficients for the i–j pair. The expression for the fugacity coefficient of species i in a mixture for this equation of state and mixing rules is given by Wong (1982).

If the constant c is set equal to b in eq 8, the two-parameter Peng–Robinson equation of state is obtained. Generalized correlations for the two equation of state constants a and b are given by Peng and Robinson (1976b), and the expression for the species fugacity for the mixing rules of eq 9, 10, 12, and 13 is given by Wong (1982).

The corresponding-states method we used is based on the following assumption for the compressibility of a fluid (Wong et al., 1983)

$$Z = Z^{(r1)}[T_r, P_r] +$$
$$(\omega - \omega^{(r1)}) \{Z^{(r2)}[T_r, P_r] - Z^{(r1)}[T_r, P_r]\}/(\omega^{(r2)} - \omega^{(r1)}) \quad (15)$$

where $Z^{(r1)}$, $Z^{(r2)}$, $\omega^{(r1)}$, and $\omega^{(r2)}$ are the compressibilities and the acentric factors of two reference fluids. In this study we have, in fact, used the spherical reference fluid (essentially argon for which ω is zero) and the nonspherical reference fluid (essentially n-octane for which $\omega = 0.398$) proposed by Lee and Kesler (1975) together with their equation of state constants. Thus, 11 constant equations

of state of the Benedict–Webb–Rubin type were used to represent the reference fluids. For pure fluids the reduced temperature T_r and reduced pressure P_r are defined as

$$T_r = T/T_c \quad (16)$$

$$P_r = P/P_c \quad (17)$$

where T_c and P_c are critical properties for pure fluids. For mixtures, T_c and P_c are replaced by the pseudocritical parameters T_{cm} and P_{cm} calculated as follows

$$T_{cm}/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}/P_{cij} \quad (18)$$

$$T_{cm}^2/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}^2/P_{cij} \quad (19)$$

$$\omega_m (T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j x_i x_j \omega_{ij}(T_{cij}/P_{cij})^{2/3} \quad (20)$$

$$T_{cij} = \xi_{ij}(T_{ci} T_{cj})^{1/2} \quad (21)$$

$$P_{cij} = T_{cij}/\{\eta_{ij}[(T_{ci}/P_{ci})^{1/3} + (T_{cj}/P_{cj})^{1/3}]^3\} \quad (22)$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 \quad (23)$$

The calculation of the fugacity coefficient of any species i in a mixture using the above equations is summarized in the Appendix and given in more detail in Wong (1982).

Results and Discussions

In both the cubic equation of state and the corresponding states methods, there are two adjustable binary interaction coefficients ξ_{ij} and η_{ij}. Ideally, the values of these interaction coefficients obtained from binary vapor–liquid equilibrium data could also be used to predict multicomponent, multiphase equilibrium. However, in both methods we found that using interaction coefficients obtained from binary VLE data led to the prediction of a three-phase region only for the methane + ethane + n-octane ternary system, and even in this case the predicted compositions of the equilibrium liquid phases were substantially different from the experimental results. This is illustrated in Figure 1. For the other two ternary systems, no three-phase regions could be found using the interaction coefficients obtained from binary VLE data.

To proceed, we attempted to correlate the three-phase data by using the equation of state and GCSP methods by adjusting the binary interaction coefficients so as to minimize the following objective function

$$F = \sum_j^M \sum_i^3 [(1 - x_i^C/x_i^E)^2 + (1 - x_i'^C/x_i'^E)^2]_j \quad (24)$$

where x_i^C, and $x_i'^C$ are calculated compositions of the equilibrium liquid phases, x_i^E, and $x_i'^E$ are corresponding experimental values, and summation index j is over the number of experimental observations. Since only estimated methane vapor compositions have been reported (Kohn and Luks, 1982), they were not used in the regression procedure. The optimal values of the interaction coefficients for each binary pair obtained by regressing the VLLE data are given in Table I.

Table II contains the experimental and calculated compositions of the equilibrium liquid phases at various temperatures and pressures for the methane + ethane + n-octane ternary system. The agreement between the experimental results and the values calculated by both the three constant Teja–Patel and the two-constant Peng–Robinson equations of state is very good, with the average deviation in mole fraction being less than 0.01 for all species in both of the liquid phases. The correlation using the GCSP was almost as good, being slightly less accurate

Table II. Comparison of Experimental and Correlated Equilibrium Liquid Phase Compositions of VLLE of Methane (1) + Ethane (2) + n-Octane (3)

T, K	P, bar	exptl n-octane lean phase x_1	x_2	exptl n-octane rich phase x_1	x_2	PRES n-octane lean phase x_1	x_2	PRES n-octane rich phase x_1	x_2	TPES n-octane lean phase x_1	x_2	TPES n-octane rich phase x_1	x_2	GCSP n-octane lean phase x_1	x_2	GCSP n-octane rich phase x_1	x_2
200	46.61	0.806	0.158	0.682	0.187	0.808	0.158	0.680	0.181	0.809	0.154	0.688	0.177	0.818	0.158	0.646	0.192
	47.62	0.840	0.137	0.657	0.173	0.842	0.136	0.652	0.170	0.844	0.133	0.657	0.169	0.847	0.130	0.625	0.183
	48.64	0.865	0.118	0.641	0.161	0.869	0.117	0.632	0.157	0.870	0.115	0.637	0.158	0.870	0.114	0.609	0.173
	49.65	0.888	0.100	0.625	0.152	0.895	0.097	0.612	0.143	0.896	0.094	0.613	0.144	0.892	0.097	0.592	0.160
202	48.63	0.803	0.162	0.683	0.192	0.802	0.163	0.682	0.187	0.805	0.158	0.688	0.184	0.808	0.157	0.663	0.196
	49.65	0.835	0.142	0.657	0.181	0.836	0.142	0.654	0.177	0.838	0.138	0.658	0.176	0.839	0.137	0.632	0.189
	50.66	0.861	0.123	0.642	0.169	0.863	0.123	0.637	0.166	0.865	0.120	0.639	0.166	0.864	0.119	0.611	0.179
	51.68	0.885	0.104	0.629	0.158	0.888	0.104	0.619	0.154	0.890	0.101	0.619	0.154	0.884	0.104	0.600	0.169
	52.69	0.907	0.085	0.616	0.147	0.912	0.083	0.599	0.139	0.915	0.080	0.594	0.139	0.901	0.091	0.591	0.159
	53.70	0.924	0.071	0.600	0.136	a	a	a	a	a	a	a	a	0.918	0.077	0.582	0.149
204	50.66	0.800	0.166	0.685	0.196	0.798	0.167	0.686	0.192	0.801	0.163	0.687	0.190	0.800	0.163	0.676	0.196
	51.68	0.831	0.147	0.656	0.188	0.831	0.147	0.657	0.183	0.835	0.142	0.655	0.182	0.831	0.144	0.642	0.194
	52.69	0.856	0.128	0.641	0.179	0.856	0.129	0.641	0.174	0.860	0.125	0.639	0.174	0.855	0.128	0.624	0.187
	53.70	0.879	0.109	0.629	0.169	0.879	0.111	0.625	0.164	0.884	0.107	0.620	0.163	0.875	0.113	0.610	0.179
	54.72	0.901	0.091	0.613	0.157	0.904	0.091	0.605	0.151	0.906	0.089	0.602	0.152	0.893	0.099	0.600	0.170
	55.73	0.922	0.074	0.576	0.144	a	a	a	a	a	a	a	a	a	a	a	a
206	52.69	0.796	0.171	0.683	0.202	0.792	0.173	0.684	0.197	0.797	0.168	0.687	0.195	0.779	0.175	0.680	0.203
	53.70	0.827	0.153	0.655	0.196	0.828	0.151	0.659	0.190	0.832	0.146	0.656	0.189	0.819	0.153	0.653	0.200
	54.72	0.853	0.133	0.645	0.186	0.854	0.132	0.642	0.181	0.857	0.129	0.644	0.182	0.844	0.136	0.634	0.194
	55.73	0.878	0.111	0.632	0.176	0.876	0.115	0.627	0.172	0.879	0.112	0.625	0.173	0.866	0.121	0.621	0.187
	56.74	0.902	0.090	0.619	0.167	0.894	0.100	0.617	0.164	0.903	0.092	0.607	0.161	0.884	0.107	0.609	0.180
208	54.72	0.794	0.175	0.692	0.200	0.777	0.183	0.690	0.203	0.791	0.174	0.686	0.201	a	a	a	a
	55.73	0.824	0.157	0.663	0.192	0.821	0.157	0.659	0.197	0.828	0.151	0.660	0.196	0.801	0.166	0.678	0.203
	56.74	0.847	0.139	0.652	0.187	0.846	0.140	0.649	0.190	0.850	0.136	0.648	0.190	0.833	0.146	0.649	0.200
210	56.74	0.770	0.185	0.717	0.199	0.764	0.192	0.709	0.207	0.768	0.189	0.713	0.204	a	a	a	a
	57.76	0.815	0.162	0.665	0.203	0.811	0.166	0.667	0.204	0.816	0.161	0.666	0.204	a	a	a	a
	58.77	0.842	0.144	0.648	0.201	0.840	0.146	0.652	0.198	0.845	0.141	0.653	0.198	0.817	0.158	0.668	0.205
	59.78	0.866	0.126	0.628	0.199	0.865	0.126	0.639	0.191	0.874	0.118	0.631	0.190	0.841	0.142	0.651	0.202

a Indicates that no three-phase solution could be found.

Table III. Comparisons of Experimental and Predicted Liquid Molar Volumes of Vapor-Liquid-Liquid Equilibrium Points of the Ternary System Methane (1) + Ethane (2) + n-Octane (3)

T, K	P, bar	exptl v_1^a	exptl v_2^a	P-R v_1	P-R v_2	TPES v_1	TPES v_2	GCSP v_1	GCSP v_2
200	46.61	0.0630	0.0588	0.0615	0.0544	0.0642	0.0594	0.0630	0.0562
	47.62	0.0657	0.0594	0.0655	0.0555	0.0677	0.0608	0.0652	0.0568
	48.64	0.0683	0.0610	0.0688	0.0573	0.0706	0.0628	0.0673	0.0577
	49.65	0.0708	0.0638	0.0725	0.0605	0.0743	0.0664	0.0697	0.0592
202	48.64	0.0629	0.0588	0.0611	0.0550	0.0641	0.0600	0.0618	0.0566
	49.65	0.0658	0.0600	0.0648	0.0561	0.0673	0.0615	0.0646	0.0572
	50.66	0.0678	0.0620	0.0676	0.0580	0.0699	0.0638	0.0669	0.0583
	51.68	0.0694	0.0645	0.0708	0.0611	0.0729	0.0672	0.0685	0.0598
	52.69	0.0713	0.0677	0.0744	0.0662	0.0768	0.0730	0.0700	0.0616
	53.70	0.0740	0.0719	b	b	b	b	0.0716	0.0644
204	50.66	0.0610	0.0594	0.0606	0.0556	0.0640	0.0606	0.0610	0.0571
	51.68	0.0648	0.0605	0.0642	0.0568	0.0673	0.0624	0.0637	0.0578
	52.69	0.0676	0.0629	0.0667	0.0587	0.0695	0.0647	0.0656	0.0587
	53.70	0.0697	0.0658	0.0694	0.0616	0.0723	0.0682	0.0674	0.0602
	54.72	0.0726	0.0684	0.0729	0.0667	0.0752	0.0732	0.0688	0.0622
	55.73	0.0790	0.0781	b	b	b	b	b	b
206	52.69	0.0624	0.0608	0.0606	0.0561	0.0640	0.0613	0.0608	0.0575
	53.70	0.0652	0.0624	0.0637	0.0576	0.0670	0.0633	0.0628	0.0580
	54.72	0.0670	0.0643	0.0662	0.0599	0.0687	0.0659	0.0646	0.0590
	55.73	0.0688	0.0670	0.0686	0.0630	0.0712	0.0695	0.0661	0.0606
	56.74	0.0734	0.0725	0.0705	0.0665	0.0740	0.0754	0.0676	0.0626
208	54.72	0.0635	0.0601	0.0600	0.0565	0.0640	0.0618	b	b
	55.73	0.0654	0.0626	0.0633	0.0582	0.0665	0.0642	0.0612	0.0582
	56.74	0.0659	0.0656	0.0649	0.0605	0.0679	0.0666	0.0634	0.0593
210	56.74	0.0618	0.0595	0.0586	0.0570	0.0626	0.0619	b	b
	57.76	0.0642	0.0621	0.0623	0.0585	0.0657	0.0643	b	b
	58.77	0.0648	0.0668	0.0642	0.0612	0.0672	0.0676	0.0621	0.0593
	59.78	0.0666	0.0706	0.0661	0.0651	0.0698	0.0732	0.0635	0.0607
% av dev				1.97	6.30	3.15	3.08	2.88	7.55

a v_1 and v_2 are volumes of the n-octane rich and the n-octane lean phase, respectively. b Indicates three phase region not found.

I

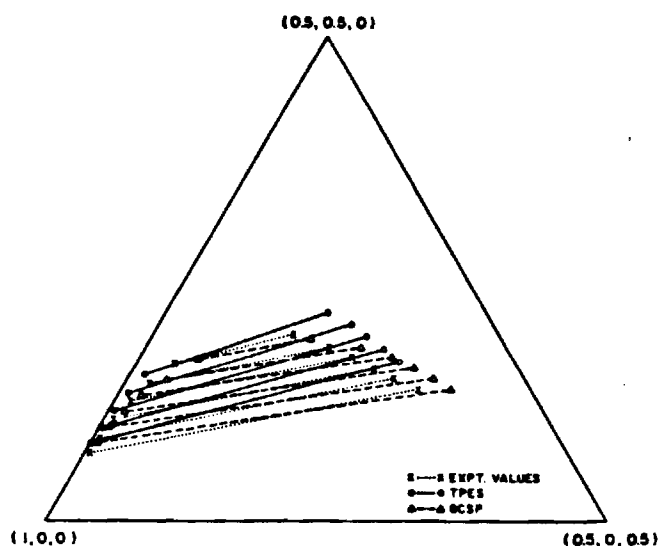Ind. Eng. Chem. Fundam., Vol. 23, No. 3, 1984 **351**

Figure 1. Experimental and predicted liquid-liquid tie lines of VLLE for the ternary system methane (1) + ethane (2) + n-octane (3).

Table IV. Comparison of Raw Experimental and Predicted Methane Vapor Phase Compositions for Methane (1) + Ethane (2) + n-Octane (3)

	est exptl	TPES	GCSP
T, K	y_1	y_1	y_1
200	0.950	0.969	0.970
202	0.938	0.964	0.967
204	0.931	0.959	0.961
206	0.925	0.954	0.955
208	0.914	0.946	0.949
210	0.918	0.938	0.940

only for the composition of the liquid phase which is rich in n-octane. The molar volumes predicted by use of the PRES, TPES, and GCSP methods are compared to experimental results in Table III. All methods give very accurate values of the molar volume of the n-octane-rich liquid phase. However, the GCSP and PRES underestimate the molar volumes of the n-octane lean phase as shown in Table III. Since there were no essential differ-

ences between the Peng-Robinson and the Teja-Patel equations of state, and the latter leads to slightly more accurate predictions, the Peng-Robinson equation will not be considered further.

The raw experimental data of Kohn and Luks (1982) show that the vapor phase methane compositions in the methane + ethane + n-octane system varies slightly with temperature and little with pressure. Table IV lists the estimated raw experimental data, together with the results from TPES and GCSP. These two predictions are close to each other, and consistently higher than estimated data of Kohn and Luks.

For the methane + propane + n-octane ternary, as mentioned earlier, no three-phase region could be found using the interaction coefficients obtained from binary VLE data. The results of correlating VLLE data are found in Tables V to VII. The overall agreement is similar to that for the methane + ethane + n-octane system.

The ternary system methane + carbon dioxide + n-octane exhibits VLLE behavior which is similar to the two systems considered above. Correlations of the data for this system using the TPES and GCSP methods were found to be less accurate than the previous system, but still acceptable, as shown in Tables VIII to X. Presumably, the lower accuracy here is due to the presence of carbon dioxide which, as a pure component, is not as well represented by either the equations of state with generalized constants or the corresponding states method as are hydrocarbons.

It should be noted that there is one common pair in the three systems studied, methane and n-octane. The interaction coefficients obtained for this binary pair by fitting the three different sets of VLLE data were found to be the same at similar temperatures and pressures. This suggests that while interaction coefficients from VLE data cannot be used to predict accurate ternary VLLE, interaction coefficients for a particular binary pair obtained from VLLE data can be used to predict VLLE for other multicomponent systems involving the same binary pair at similar temperatures and pressures.

While good correlations of the compositions of the coexisting liquid phases in VLLE equilibrium can be ob-

Table V. Comparison of Experimental and Correlated Equilibrium Compositions of the Liquid Phases of VLLE Data for Methane (1) + Propane (2) + n-Octane (3)

		exptl				TPES				GCSP			
		n-octane rich phase		n-octane lean phase		n-octane rich phase		n-octane lean phase		n-octane rich phase		n-octane lean phase	
T, K	P, bar	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
204	56.74	0.782	0.141	0.894	0.066	0.766	0.151	0.881	0.099	0.783	0.134	0.892	0.088
	57.25	0.741	0.152	0.915	0.074	0.724	0.159	0.912	0.078	0.724	0.148	0.905	0.079
	57.76	0.706	0.154	0.930	0.062	0.703	0.159	0.929	0.064	0.711	0.147	0.914	0.072
	58.26	0.680	0.153	0.944	0.050	0.685	0.159	0.942	0.054	0.703	0.146	0.923	0.066
202	54.21	0.752	0.146	0.898	0.084	0.747	0.152	0.883	0.096	0.735	0.144	0.897	0.084
	54.72	0.718	0.151	0.914	0.073	0.717	0.155	0.910	0.077	0.711	0.146	0.910	0.075
	55.22	0.698	0.152	0.928	0.062	0.694	0.155	0.927	0.065	0.699	0.145	0.929	0.061
	55.73	0.683	0.149	0.939	0.053	0.677	0.153	0.940	0.054	0.689	0.142	0.934	0.054
	56.24	0.673	0.145	0.949	0.045	0.669	0.151	0.947	0.048	0.682	0.140	0.945	0.048
	56.74	0.661	0.140	0.966	0.031	a	a	a	a	0.675	0.137	0.961	0.034
200	52.18	0.726	0.148	0.910	0.074	0.720	0.151	0.903	0.082	0.702	0.145	0.910	0.073
	52.69	0.703	0.149	0.923	0.064	0.697	0.151	0.921	0.068	0.693	0.142	0.921	0.066
	53.20	0.683	0.146	0.935	0.055	0.677	0.148	0.935	0.057	0.684	0.139	0.930	0.059
	53.70	0.670	0.139	0.946	0.047	0.652	0.144	0.951	0.044	0.674	0.135	0.940	0.052
	54.21	0.659	0.133	0.955	0.040	a	a	a	a	0.667	0.132	0.947	0.046
	54.72	0.652	0.128	0.967	0.030	a	a	a	a	0.658	0.127	0.955	0.040
198	49.14	0.737	0.145	0.885	0.089	0.738	0.147	0.875	0.098	0.715	0.143	0.900	0.079
	49.65	0.713	0.145	0.908	0.074	0.708	0.147	0.905	0.078	0.706	0.141	0.911	0.072
	50.16	0.700	0.141	0.926	0.061	0.685	0.145	0.925	0.065	0.683	0.138	0.926	0.061

Table VI. Comparisons of Experimental and Predicted Molar Volumes (L/g-mol) of the Liquid Phases of Vapor-Liquid-Liquid Equilibrium Points of the Ternary Methane (1) + Propane (2) + n-Octane (3)

T, K	P, bar	exptl		TPES		GCSP	
		$v_1{}^a$	$v_2{}^a$	v_1	v_2	v_1	v_2
204	56.74	0.0612	0.0612	0.0628	0.0627	0.0637	0.0592
	57.25	0.0624	0.0628	0.0653	0.0660	0.0641	0.0597
	57.76	0.0639	0.0654	0.0670	0.0695	0.0650	0.0604
	58.26	0.0655	0.0711	0.0686	0.0730	0.0657	0.0611
202	54.21	0.0616	0.0610	0.0636	0.0620	0.0631	0.0587
	54.72	0.0636	0.0630	0.0658	0.0646	0.0648	0.0592
	55.22	0.0655	0.0652	0.0678	0.0673	0.0658	0.0599
	55.73	0.0668	0.0678	0.0695	0.0705	0.0667	0.0607
	56.24	0.0677	0.0721	0.0705	0.0726	0.0674	0.0618
	56.74	0.0700	0.0808	b	b	0.0681	0.0631
200	52.18	0.0624	0.0617	0.0656	0.0627	0.0653	0.0585
	52.69	0.0647	0.0635	0.0676	0.0649	0.0661	0.0591
	53.20	0.0668	0.0654	0.0696	0.0675	0.0669	0.0598
	53.70	0.0687	0.0676	0.0723	0.0721	0.0680	0.0609
	54.21	0.0705	0.0704	b	b	0.0687	0.0620
	54.72	0.0719	0.0748	b	b	0.0696	0.0638
198	49.14	0.0634	0.0601	0.0640	0.0600	0.0640	0.0574
	49.65	0.0645	0.0609	0.0665	0.0618	0.0648	0.0578
	50.16	0.0660	0.0618	0.0689	0.0640	0.0668	0.0585
% av dev				3.95	2.95	1.60	8.78

$^a v_1$ and v_2 are the molar volumes of the n-octane rich phase and the n-octane lean phase, respectively. ^{b}VLLE calculation did not converge.

Table VII. Comparison of Raw Experimental and Predicted Methane Vapor Phase Compositions for Methane (1) + Propane (2) + n-Octane (3)

T, K	est exptl y_1	TPES y_1	GCSP y_1
204	0.976	0.982	0.987
202	0.979	0.986	0.990
200	0.982	0.989	0.992
198	0.985	0.992	0.994

tained as shown above, the binary interaction coefficients so obtained do not lead to accurate predictions of VLE behavior. Figure 2 compares the experimental VLE data of the binary mixture methane + n-octane at 220 K with the values predicted using the TPES and the binary interaction coefficients from ternary VLLE data. It can be seen that there is substantial disagreement. Therefore, at

present, it is not possible to use VLE data to make VLLE predictions using the thermodynamic models considered here or vice versa. It was found that although the amount of n-octane in the vapor phase is very small, its presence is essential for the existence of VLLE. Had vapor composition been accurately measured and used in the regression procedure, the accuracy and generality of resulting interaction coefficients might have been improved.

Conclusion

In this work, we have studied the VLE of three ternary systems containing only nonpolar molecules. We have found that vapor–liquid–liquid phase equilibria can be predicted with both cubic equations of state and a generalized corresponding states principle by using a single set of binary interaction coefficients for all phases. However, it was found that both the cubic equations of state

Table VIII. Comparison of Equilibrium Liquid Phase Composition of VLLE Data for the Ternary System Methane (1) + Carbon Dioxide (2) + n-Octane (3)

| T, K	P, bar	exptl n-octane rich phase		exptl n-octane lean phase		TPES n-octane rich phase		TPES n-octane lean phase		GCSP n-octane rich phase		GCSP n-octane lean phase	
		x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
212	62.31	0.562	0.259	0.791	0.200	0.598	0.246	0.811	0.176	0.585	0.253.	0.791	0.183
	61.81	0.572	0.265	0.760	0.224	0.597	0.250	0.783	0.196	0.594	0.254	0.773	.0.194
	61.30	0.575	0.273	0.737	0.241	0.605	0.252	0.761	0.210	0.605	0.255	0.752	0.206
	60.79	0.588	0.283	0.709	0.260	0.617	0.255	0.735	0.225	0.619	0.254	0.724	0.220
208	58.77	0.558	0.220	0.826	0.167	a	a	a	a	0.545	0.239	0.845	0.141
	58.26	0.565	0.228	0.805	0.185	0.582	0.225	0.841	0.149	0.552	0.243	0.831	0.152
	57.76	0.566	0.238	0.787	0.200	0.593	0.230	0.822	0.164	0.559	0.246	0.816	0.162
	57.25	0.567	0.249	0.770	0.213	0.601	0.234	0.800	0.180	0.564	0.249	0.802	0.172
	56.74	0.573	0.258	0.753	0.226	0.604	0.238	0.778	0.195	0.574	0.252	0.787	0.182
	56.24	0.583	0.268	0.730	0.242	0.613	0.241	0.755	0.208	0.588	0.253	0.771	0.192
	55.73	0.620	0.278	0.692	0.265	0.647	0.244	0.722	0.226	a	a	a	a
204	55.22	0.564	0.178	0.858	0.136	0.558	0.187	0.893	0.103	0.528	0.218	0.878	0.113
	54.72	0.564	0.187	0.843	0.149	0.566	0.195	0.878	0.116	0.531	0.224	0.867	0.121
	54.21	0.564	0.196	0.829	0.161	0.573	0.201	0.864	0.128	0.534	0.228	0.857	0.129
	53.70	0.563	0.206	0.814	0.174	0.580	0.207	0.849	0.140	0.537	0.232	0.846	0.137
	53.20	0.564	0.217	0.798	0.187	0.589	0.212	0.831	0.154	0.541	0.237	0.836	0.146
	52.69	0.568	0.228	0.781	0.201	0.596	0.218	0.811	0.168	0.546	0.241	0.824	0.154
	52.18	0.579	0.240	0.763	0.215	0.606	0.223	0.789	0.183	0.554	0.244	0.811	0.163
	51.68	0.581	0.252	0.741	0.230	0.620	0.228	0.767	0.197	0.559	0.248	0.797	0.173

^{a}VLLE calculation did not converge.

Table IX. Comparisons of Experimental and Predicted Molar Volumes of Liquid Phases of Vapor-Liquid-Liquid Equilibrium Points of the Ternary Methane (1) + Carbon Dioxide (2) + n-Octane (3)

T, K	P, bar	exptl		TPES		GCSP	
		v_1	v_2	v_1	v_2	v_1	v_2
212	62.31	0.0645	0.0685	0.0632	0.0639	0.0589	0.0543
	61.81	0.0630	0.0630	0.0630	0.0603	0.0582	0.0536
	61.30	0.0612	0.0613	0.0620	0.0585	0.0574	0.0532
	60.79	0.0591	0.0602	0.0608	0.0573	0.0564	0.0531
208	58.77	0.0682	0.0698	a	a	0.0630	0.0563
	58.26	0.0668	0.0658	0.0661	0.0653	0.0621	0.0552
	57.76	0.0653	0.0626	0.0648	0.0622	0.0612	0.0543
	57.25	0.0639	0.0609	0.0636	0.0596	0.0604	0.0536
	56.74	0.0625	0.0594	0.0629	0.0578	0.0594	0.0531
	56.24	0.0608	0.0581	0.0618	0.0567	0.0583	0.0527
	55.73	0.0582	0.0569	0.0587	0.0561	a	a
204	55.22	0.0711	0.0713	0.0725	0.0729	0.0659	0.0574
	54.72	0.0701	0.0680	0.0708	0.0684	0.0652	0.0563
	54.21	0.0690	0.0654	0.0695	0.0653	0.0644	0.0554
	53.70	0.0678	0.0630	0.0680	0.0627	0.0637	0.0546
	53.20	0.0666	0.0608	0.0665	0.0603	0.0630	0.0540
	52.69	0.0652	0.0589	0.0652	0.0583	0.0623	0.0534
	52.18	0.0637	0.0575	0.0638	0.0568	0.0612	0.0529
	51.68	0.0619	0.0563	0.0620	0.0559	0.0605	0.0524
% av dev				2.25	1.57	5.57	13.04

Table X. Comparison of Raw Experimental and Predicted Methane Vapor Phase Compositions for Methane (1) + Carbon Dioxide (2) + n-Octane (3)

T, K	est exptl y_1	TPES y_1	GCSP y_1
212	0.825	0.895	0.928
208	0.861	0.915	0.943
204	0.890	0.936	0.957
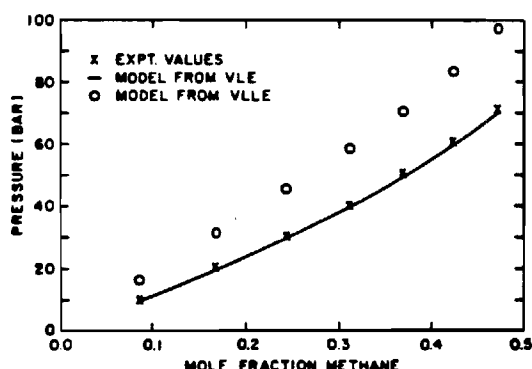
Figure 2. Solubility of methane in N-octane at 220 K; (×) denotes experimental points; (—) denotes calculated results by use of the Teja-Patel equation of state with binary interaction coefficients obtained from VLE data; (O) denotes as above with coefficients obtained by regression of VLLE data.

and the generalized corresponding states method cannot predict accurate VLLE with interaction coefficients obtained from binary VLLE data. It is possible to develop VLLE correlations by using interaction coefficients which are different from those obtained from binary VLE data. This failure of the thermodynamic models to accurately predict both VLE and VLLE without varying parameters may be attributed to several factors. First, it may be that the cubic equations of state and the GCSP are not sufficiently accurate in calculating species fugacities, especially the fugacity of a trace component (e.g., n-octane in the vapor phase). Second, it may be that the mixing model is inadequate under these conditions, though since only nonpolar substances are involved, complex mixing models would be difficult to justify. It was also found, however, that the binary interaction coefficients obtained for one binary pair using VLLE data of a multicomponent system may be used for the same binary pair in correlating VLLE

data of another multicomponent system. Finally, we note that the relatively simple three-constant cubic equation of state of Teja and Patel did as well as, or better than, the Lee-Kesler corresponding states method, which uses 11-constant equations of state, in predicting phase compositions and densities.

Acknowledgment

Fugacity Coefficient Expression for the Generalized Corresponding States Principle. The fugacity coefficient $\phi = f/p$ for a pure fluid is

$$\ln \phi = \int_0^P (Z - 1) \frac{dP}{P} \tag{A1}$$

when using eq 15 becomes

$$\ln \phi = \ln \phi^{(r1)}[T_r, P_r] + \frac{(\omega - \omega^{(r1)})}{(\omega^{(r2)} - \omega^{(r1)})} \{\ln \phi^{(r2)}[T_r, P_r] - \ln \phi^{(r1)}[T_r, P_r]\} \tag{A2}$$

The fugacity coefficient for a species in a mixture $\phi_i = \bar{f}_i/x_iP$ is gotten from the fugacity coefficient for the mixture ϕ_M (which is also calculated from eq A2) as follows

$$\ln \phi_i = \left(\frac{\partial(N \ln \phi_M)}{\partial N_i} \right)_{T,V,N_{j,i}} =$$

$$\ln \phi_M + \frac{\partial \ln \phi_M}{\partial x_i} - \sum_j x_j \frac{\partial \ln \phi_M}{\partial x_j} \tag{A3}$$

where the partial derivatives with respect to x_i are taken holding all other mole fractions constant. Using eq 15 we obtain

$$\frac{\partial \ln \phi_M}{\partial x_i} = \frac{\partial \ln \phi^{(r2)}}{\partial x_i} + \frac{\omega_M - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \left\{ \frac{\partial \ln \phi^{(r2)}}{\partial x_i} - \frac{\partial \ln \phi^{(r1)}}{\partial x_i} \right\} + \frac{\ln \phi^{(r2)} - \ln \phi^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \frac{\partial \omega_M}{\partial x_i} \tag{A4}$$

where, further

$$\frac{\partial \ln \phi^{(r_j)}}{\partial x_i} = \frac{\partial \ln \phi^{(r_j)}}{\partial T_r} \frac{\partial T_r}{\partial x_i} + \frac{\partial \ln \phi^{(r_j)}}{\partial P_r} \frac{\partial P_r}{\partial x_j} \qquad (A5)$$

Finally

$$\frac{\partial \ln \phi^{(r_j)}}{\partial T_r} = \frac{1}{T_r} \frac{\Delta H^{(r_j)}}{kT} \qquad (A6)$$

$$\frac{\partial \ln \phi^{(r_j)}}{\partial P_r} = \frac{(Z^{(r_j)} - 1)}{P_r} \qquad (A7)$$

and

$$\frac{\partial T_r}{\partial x_i} = \frac{-T_r}{T_{cm}} \frac{\partial T_{cm}}{\partial x_i}; \quad \frac{\partial P_r}{\partial x_i} = \frac{-P_r}{P_{cm}} \frac{\partial P_{cm}}{\partial x_i} \qquad (A8)$$

Here, $\Delta H^{(r_j)}$ is the known enthalpy deviation from ideal gas behavior for the reference fluid.

Thus the fugacity coefficient for a species in a mixture depends upon the two reference fluid equations of state and upon the pseudocritical constant mixing rules through the values of T_{cm}, P_{cm}, and ω_m and, more importantly, their derivatives with respect to mole fraction.

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CORRESPONDING STATES, COMPLEX MIXTURES AND MIXTURE MODELS

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ABSTRACT

A three parameter Generalized Corresponding States Principle (GCSP) which allows a choice of reference fluids is reviewed. When combined with a new set of mixing rules proposed here, the GCSP method is shown to lead to accurate calculations of vapor-liquid and vapor-liquid-liquid equilibria in mixtures containing paraffinic hydrocarbons, aromatic hydrocarbons, alcohols and water. The new method is also shown to work well for asymmetric mixtures (i.e., mixtures of large and small molecules). Our studies have established the accuracy and utility of the method for complex mixtures not heretofore treated by the method of corresponding states.

INTRODUCTION

The corresponding states principle (CSP) was suggested by van der Waals (1890) based on the observation that his two-parameter equation of state

$$(P + \frac{a}{V^2}) \, (V-b) = RT \tag{1}$$

could be written in the form

$$(P_r + \frac{3}{V_r^2}) \, (3V_r-1) = 8T_r \tag{2}$$

where the reduced properties (denoted by a subscript r) are given by $T_r = T/T_c$, $P_r = P/P_c$ and $V_r = V/V_c$, and the subscript c denotes a critical property. Since the critical compressibility Z_c predicted from the van der Waals equation is

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} \tag{3}$$

for all fluids, eqn. (2) is a two (independent) parameter corresponding states principle.

There are a number of shortcomings of CSP based on the van der Waals equation. First, as eqn. (1) is not very accurate--particularly in the liquid and critical regions--a corresponding states principle based on it will not be

of high accuracy. Second, the van der Waals equation, as well as other two-parameter cubic equations of state predict a single value of Z_c, even though common fluids have values of this parameter in the range of 0.23 to 0.32 (Reid et al, 1977).

These shortcomings have led to a number of modifications to the two-parameter CSP. Generally, these modified CSPs use additional characterization parameters, and more accurate P-V-T (equation of state) relations for the reference substance(s). For example, Lydersen, Greenkorn and Hougen (1955) proposed the following CSP relation for hydrocarbons

$$Z(T_r,P_r,Z_c) = Z^0(T_r,P_r,Z_c = 0.27) + (Z_c-0.27)Z^1(T_r,P_r) \qquad (4)$$

in which the critical compressibility Z_c was taken as the third parameter. In this equation Z^0 is the compressibility factor based on experimental data for hydrocarbons with $Z_c = 0.27$, and Z^1 is the departure function. Equation (4) may be thought of as a first order Taylor series expansion of the compressibility of a fluid around that for a fluid with $Z_c = 0.27$. That is

$$Z(T_r,P_r,Z_c) = Z(T_r,P_r)\Big|_{Z_c=0.27} + (Z_c-0.27) \frac{\partial Z(T_r,P_r)}{\partial Z_c}\Big|_{Z_c=0.27} \qquad (5)$$

where clearly the derivative term above is equal to the departure function $Z^1(T_r,P_r)$. In the work of Lydersen et al, both Z^0 and Z^1 were presented as tables.

More popular has been the corresponding states relation of Pitzer and coworkers (1958)

$$Z(T_r,P_r,\omega) = Z^0(T_r,P_r) + \omega Z^1(T_r,P_r) \qquad (6)$$

using as the third parameter the acentric factor ω defined by

$$\omega = -1.0 - \log_{10} \frac{(p^{vap}(T_r=0.7))}{P_c} \qquad (7)$$

with p^{vap} being the vapor pressure. Again, $Z^0(T_r,P_r)$ and $Z^1(T_r,P_r)$ were presented in tabular form. For nonpolar molecules the acentric factor increases with nonsphericity, being approximately zero for methane. Equation (7) may be viewed as a first-order Taylor series expansion of the compressibility factor about its value for a spherical molecule, that is,

$$Z(T_r,P_r,\omega) = Z(T_r,P_r)\Big|_{\omega=0} + \omega \frac{\partial Z(T_r,P_r)}{\partial \omega}\Big|_{\omega=0} \qquad (8)$$

To adopt the Pitzer et al corresponding states principle for easy use on digital computers, Lee and Kesler (1975) replaced the derivative in eqn. (8) with its finite difference approximate,

$$\frac{\partial Z(T_r,P_r)}{\partial \omega}\bigg|_{\omega=0} = \frac{Z(T_r,P_r,\omega_1) - Z(T_r,P_r,\omega=0)}{\omega_1} \tag{9}$$

where ω_1 represents the acentric factor of some appropriately chosen reference fluid. Thus, eqn. (8) becomes

$$Z(T_r,P_r,\omega) = Z^0(T_r,P_r) + \frac{\omega}{\omega_1}\{Z^1(T_r,P_r,\omega_1) - Z^0(T_r,P_r)\} \tag{10}$$

They then used the eleven constant Starling (1972) modification of the Benedict-Webb-Rubin equation for essentially argon (for which $\omega=0$) to represent Z^0, and for essentially n-octane (for which $\omega_1 = 0.3978$) to represent $Z^1(T_r,P_r,\omega_1)$. The result was an accurate, analytic CSP for nonpolar fluids.

While the Lee-Kesler corresponding states method leads to good predictions for hydrocarbons, it is much less accurate for molecules with permanent dipoles and/or quadrupoles. This is because the method is an expansion in nonsphericity only; the acentric factor was meant to measure the departure from spherical behavior and, more importantly, both reference fluids (argon and n-octane) are nonpolar.

THE GENERALIZED CORRESPONDING STATES PRINCIPLE

Real molecules can be both nonspherical and polar. To develop a corresponding states principle for such fluids, it is useful to consider the insights obtained from statistical mechanics. Smith (1973) and Flytzani-Stephanopoulis, et al (1975) in statistical mechanical perturbation theory have used a multi-dimensional Taylor series expansion in nonsphericity, dimensionless electrostatic moment and other appropriately chosen parameters as the expansion variables. The results of such calculations have shown that these series can be slow to converge, and, as shown by Sandler (1974), the synergistic effects between nonsphericity and dipole or quadrupole moment do not appear in the first order term, which is all that has been used in most corresponding states methods.

Further, the accuracy of any perturbation theory calculation is greater, and the convergence more rapid, if the reference fluid for the expansion is very similar to the fluid under study. This suggests that the reference fluids for a corresponding states theory: (1) should not be restricted to a spherical fluid and a nonpolar hydrocarbon, as has been the case in the past; and (2) need not be the same for all substances or mixtures of interest, but

should be allowed to change so that the reference fluids and the substances under study are similar.

Therefore, we have recently proposed the following generalized corresponding states principle (GCSP) of Teja et al (1980a, 1980b, 1981a)

$$Z(T_r,P_r,\theta) = Z^{r1}(T_r,P_r,\theta^{r1}) + \tag{11}$$

$$\frac{\theta-\theta^{r1}}{\theta^{r2}-\theta^{r1}} \{Z^{r2}(T_r,P_r,\theta^{r2}) \quad -Z^{r1}(T_r,P_r,\theta^{r1})\}$$

Here r1 and r2 refer to appropriately chosen reference fluids, and θ is some characterizing property: in the work to be discussed below θ was taken to be the acentric factor, though other properties could have been chosen. In the following section we consider the use of the GCSP of eqn. (11) and the results obtained with the computer package of Wong (1983) to implement it. In this package, the user can select the two reference fluids to be used from the list given in Table 1.

TABLE 1

Reference Substances Available in Present
Generalized Corresponding State Principle Program Package

Lee-Kesler Spherical Reference Fluid
Lee-Kesler Nonspherical Reference Fluid
Methane
Ethane
N-Butane
N-Octane
N-Dodecane
N-Eicosane
Methanol
Ethanol
N-Pentanol
Benzene
Carbon Dioxide
Water

Notes:
1) The three constant Teja-Patel cubic equation of state has
   been used for all reference fluids save the first two.
2) Additional reference fluids and reference equations of state
   of complexity may easily be added.

The use of eqn. (11) in calculating high accuracy liquid densities has been described previously by Teja et al (1980a,b), as have its analogs for the calculation of vapor pressure (Teja et al, 1981) [12], heat capacity (Teja, 1983) and other properties. Here we will only consider its use in vapor-liquid and vapor-liquid-liquid phase equilibrium calculations. Of course, when applying corresponding states theory to mixtures, one question that arises is the appropriate choice of mixture pseudocritical properties. We have shown (Wong,

1983), based on semitheoretical and semiempirical arguments, that the mixing rules given by:

$$\omega_m(T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j x_i x_j \omega_{ij}(T_{cij}/P_{cij})^{2/3} \tag{12}$$

$$T_{cm}/P_{cm} = \sum_i \sum_j x_i x_j T_{cij}/P_{cij} \tag{13}$$

$$T^2_{cm}/P_{cm} = \sum_i \sum_j x_i x_j T^2_{cij}/P_{cij} \tag{14}$$

with

$$T_{cij} = \xi_{ij}(T_{ci}T_{cj})^{1/2} \tag{15}$$

$$P_{cij} = 8T_{cij}/\{n_{ij}[(T_{ci}/P_{ci})^{1/3}+(T_{cj}/P_{cj})^{1/3}]^3\} \tag{16}$$

$$\omega_{ij} = (\omega_i+\omega_j)/2 \tag{17}$$

are especially useful for a large range of mixtures. We denote eqns. (12-17) with two adjustable parameters ξ_{ij} and n_{ij} as Model I; the special case in which n_{ij} is set equal to unity will be referred to as Model IA. These mixing rules are somewhat different from the commonly used van der Waals' one-fluid rules (Leland et al, 1962). For comparison, we also consider a variation (denoted as Model II) to the one-fluid rules in which V_{cij} is replaced by T_{cij}/P_{cij}. This model consists of eqns. (13 to 17) together with:

$$\omega_m = \Sigma x_i \omega_i \tag{18}$$

RESULTS

To illustrate the advantage of the mixing rules we have proposed, we compare, in Table 2, the predictions for the bubble point of binary mixtures of methane with C_5 and heavier hydrocarbons using the corresponding states principle and the Lee-Kesler reference fluids with Models IA and II (each with $n_{ij}=1$) and, for comparison, selected values computed using the three parameter cubic equation of state of Teja and Patel (1981b, 1982) with their mixing rules for the equation of state constants. There we see that the average mean error for these hydrocarbon mixtures is approximately one-fifth as great using the new mixing rule as when using Model II. Though not shown in the table, the error in using the new mixing rule is only about 40% of that which results from using the mixing rules proposed by Plocker, Knapp and Prausnitz (1978) for asymmetric hydrocarbon mixtures, i.e. mixtures of molecules with large differences in size.

The real advantage of our generalized corresponding states principle (and its mixing rules) is that it can, by the appropriate choice of reference fluids, be applied to polar as well as nonpolar mixtures. This is demon-

TABLE 2

Comparison of Bubble Point Pressures of Methane + Heavy Hydrocarbon Mixtures
Calculated Using Different Mixing Models in the Corresponding States Method
and the Teja-Patel Equation of State with Experimental Values

Mixture	T (K)	Model IA ξ_{ij}	ΔP%	Model II ξ_{ij}	ΔP%	TPES ξ_{ij}	ΔP%	Data Ref.
METHANE +	176.3	0.978	3.79	1.032	9.57			a
N-PENTANE	280.0	0.980	2.18	1.014	7.56			b
	370.0	0.995	0.50	1.023	1.32	1.007	1.45	b
	450.0	1.010	0.49	1.021	1.18			b
METHANE +	223.2	0.962	1.63	1.033	16.10			c
N-HEXANE	273.2	0.962	0.59	1.021	10.15	0.981	0.93	c
	323.2	0.966	0.47	1.011	5.10			c
	373.2	0.966	0.71	1.007	2.85			c
	423.3	0.968	2.65	1.004	0.99			c
METHANE +	255.4	0.973	2.59	1.043	15.40			d
N-HEPTANE	310.9	0.976	0.34	1.035	8.25	1.013	0.73	e
	377.6	0.978	0.14	1.029	4.60			e
	444.3	0.987	0.62	1.029	2.17			e
METHANE +	273.2	0.960	2.27	1.052	8.54	1.004	1.31	f
N-OCTANE	373.2	0.962	1.63	1.045	6.85			f
	423.2	0.965	1.50	1.028	1.47			f
METHANE +	310.9	0.968	0.70	1.110	17.92			g
N-DECANE	377.6	0.975	0.68	1.099	11.50			g
	444.3	0.975	0.88	1.078	6.30	1.067	1.39	g
	510.9	1.000	2.64	1.084	3.90			g

(a) Chen, T. C., Chen, R. J. J., Chappelear, P. S. and Kobayashi, R., 1976, J. Chem. Eng. Data, 21, 41;
(b) Berry, V. M. and Sage, B. H., 1970, NSRDS-NBS 32; (c) Shim, J. and Kohn, J. P., J. Chem. Eng. Data, 1962,
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Sage, B. H., and Lacey, W. N., 1956, Ind. Eng. Chem. Data Ser., 1, 29; (f) Kohn, J. P. and Bradish, W. P.,
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1526.

strated in Table 3, where the bubble point pressures for binary mixtures of low molecular weight alcohols with carbon dioxide, ethane and propane are considered. There we see that by using mixture Model I (two interaction parameters for each binary pair) the accuracy of the corresponding states predictions for these mixtures is equivalent to that obtained for simple hydrocarbon mixtures. Similarly, in Table 4, we have shown that when using ethanol and n-octane as the reference fluids, accurate azeotropic compositions and pressures can be obtained for mixtures of alcohols and heavy hydrocarbons, mixtures not usually treated by corresponding states methods.

In Table 5 are the results for bubble point correlations of low molecular weight hydrocarbon-aromatic hydrocarbon mixtures using methane and benzene as the reference fluids and mixing Model IA. There we see that with only one adjustable parameter (ξ_{ij}), excellent predictions are obtained for such systems.

Further, in Figure 1, we show the experimental data for the compositions of the two coexisting liquid phases of the n-butane and water system at 511 K, as well as the predictions using the GCSP with water and n-butane as the reference fluids. There we see that using mixing Model I (two adjustable parameters, n_{ij} and ξ_{ij}) leads to reasonably accurate compositions of both coexisting liquid phases (and, though not shown, the vapor phase as well), even though the phase compositions differ by several orders of magnitude . A slight improvement in these predictions could be made by using two different parameters, one for each of the liquid phases, as suggested by Peng and Robinson (1979). However, this latter method is not thermodynamically consistent.

The prediction of vapor-liquid-liquid equilibrium in simple hydrocarbon systems, such as the ternary methane + ethane + n-octane system as measured by Hottovy, Kohn and Luks (1981) and shown in Fig. 2, is a severe test of any thermodynamic model because the three phase envelope exists over a range of only a few degrees Kelvin and several bar. We show, in Fig. 2, that the predictions which result from the GCSP using the Lee-Kesler reference fluids and mixing Model I (two parameters for each binary) are quite good. However, the binary parameters used have been fitted to the three phase data, and are somewhat different than those obtained from the regression of binary vapor-liquid equilibrium data.

As a final example of the use of the generalized corresponding states principle and the mixing rules we have proposed, we consider the low pressure vapor-liquid equilibrium for the n-heptane and 1-propanol system at 348 K. We show, in Fig. 3, the experimental x-y data for this system together with correlations of the data using the UNIQUAC activity coefficient model of Abrams and Prausnitz (1981) and the GCSP with mixing Model I (two binary para-

TABLE 3

Bubble Point Pressure Correlations of Mixtures of Low Moleculer
Weight Alcohols and Small Nonpolar Molecules Using GCSP

Mixture	T (K)	Max.P (BAR)	Ref1	Ref2	n_{ij}	Model I ξ_{ij}	$\Delta P\%$	Data Ref.
METHANOL + CO_2	298	61.3	CO_2	EtOH	1.090	1.020	1.34	a
METHANOL + ETHANE	373 348	60.8 60.8	C_2H_6	EtOH	1.077 1.095	1.078 1.068	1.46 1.10	b b
ETHANOL + PROPANE	350	27.6			1.063	1.066	1.93	c

(a) Ohgaki, J. and Katayama, T., 1979, J. Chem. Eng. Data, 21, 53; (b) Ma, Y. H. and Kohn, J. P., 1964, J. Chem. Eng. Data, 9, 3; (c) Gomez-Nieto, M. and Thodos, G., 1978, AIChE J., 24, 672.

TABLE 4

Comparisons of Experimental and Calculated Azeotropic Pressures and
Compositions of Alcohols+Heavy Hydrocarbon Systems
(Data Taken from Gmehling et. al. [1977])

Mixture	T (K)	Expt. Values P (BAR)	x	n_{ij}	ξ_{ij}	Model I P	x
METHANOL + N-HEXANE	318	0.840	0.504	0.175	1.028	0.840	0.504
N-HEXANE + ETHANOL	298 318	0.254 0.608	0.753 0.703	0.100 0.100	1.374 1.374	0.260 0.593	0.742 0.707
N-HEPTANE + 1-PROPANOL	348	0.713	0.560	0.225	1.064	0.713	0.560

TABLE 5

Comparisons of Bubble Point Pressure Correlations of Mixtures
Containing Aromatic Hydrocarbons Using GCSP and Mixing Models IA and II

Mixture	T (K)	Max.P (BAR)	Ref1	Ref2	Model IA ξ_{ij}	Model IA $\Delta P\%$	Oata Ref.
METHANE +	339	137.9	CH_4	C_6H_6	1.081	0.930	a
BENZENE	501	145.6			1.000	2.434	b
ETHYLENE + BENZENE	348	91.2			1.028	4.046	c
ETHANE +	298	38.0			1.022	4.728	d
BENZENE	333	48.3			1.025	3.908	e
	393	68.9			1.018	1.102	e
	433	82.7			1.013	1.156	e
	513	68.9			0.981	0.818	e
PROPANE +	377	41.4			1.012	2.167	f
BENZENE	411	51.7			1.010	0.982	f
	477	58.6			1.000	0.540	f
METHANE +	462	152.0			1.033	1.447	a
TOLUENE	543	115.1			0.991	0.308	a
METHANE +	311	142.7			1.112	2.049	g
1-3-5-TRI-	394	145.9			1.104	1.981	g
METHYLBENZENE	477	141.3			1.092	1.486	g
METHANE +	394	144.8			1.093	4.453	g
M-XYLENE	477	139.1			1.075	1.806	g
	541	153.7			1.029	2.684	h

(a) Lin, H. M., Sebastian, H. M., Simnick, J. J. and Chao, K. C., 1979, J. Chem.
Eng. Oata, 24, 146; (b) Elbislawi, M. and Spencer, J. R., 1951, Ind. Eng. Chem.,
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Progr. Sym. Ser., 48, 108; (f) Glanville, J. W., Sage, B. H. and Lacey, W. N.,
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lished data as reported in H. Knapp et al, "Vapor-Liquid Equilibrium Oata
Collection", published by OECHEMA, Frankfurt, Germany; (h) Simnick, J. J.,
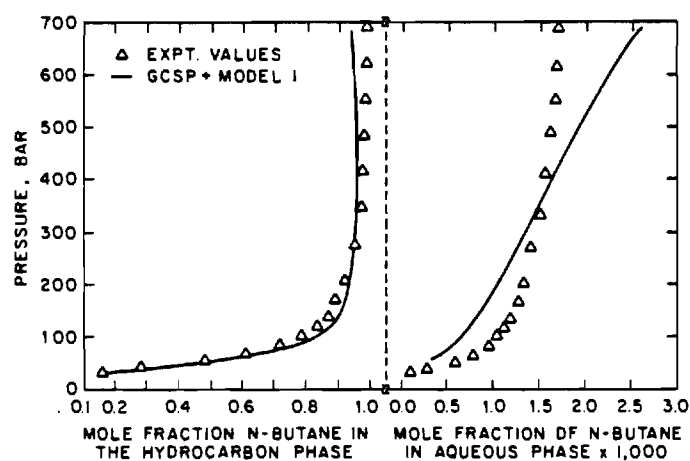Sebastian, H. M., Lin, H. M. and Chao, K. C., 1451, Fluid Phase Equil., 3, 1,
979.

Fig. 1. Experimental and Correlated Vapor-Liquid Equilibrium Data for
n-Butane + Water System in the Hydrocarbon-Rich and Water-Rich Phases,
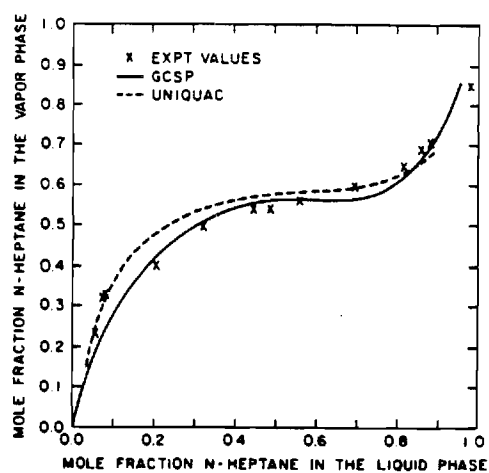Respectively.

Fig. 3. Experimental and Correlated Vapor-Liquid Equilibrium Data for
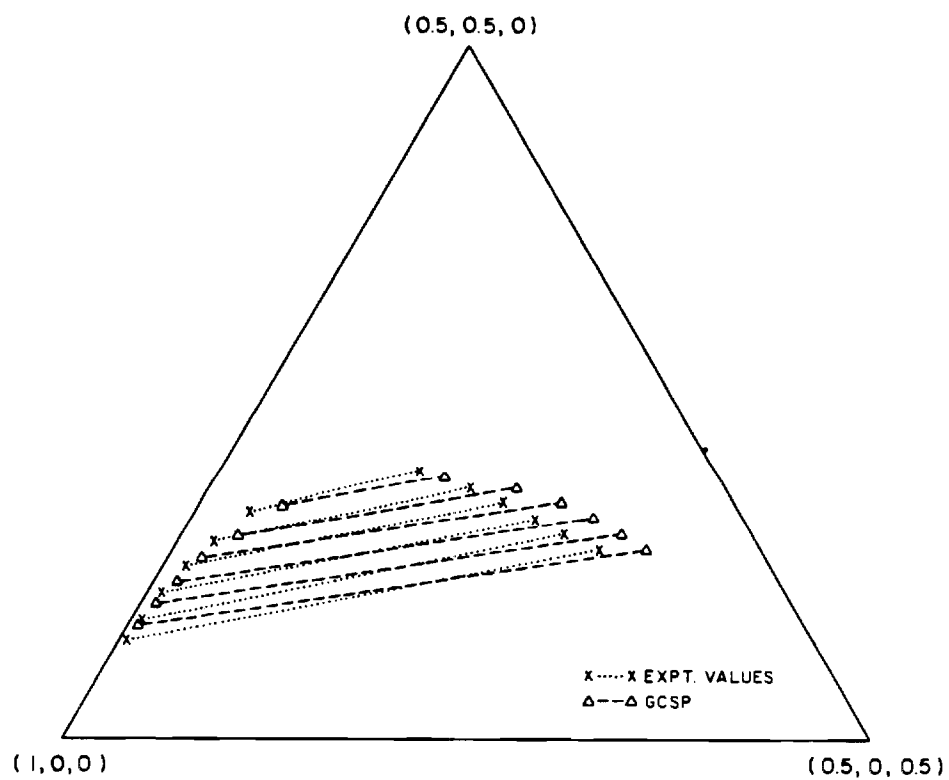n-Heptane + 1-Propanol at 348 K.

Fig. 2. Experimental and Correlated Liquid-Liquid Equilibrium for the Methane + Ethane + n-Octane System at 202 K.

meters). While we do not want to dwell on this result, it is interesting to note that with appropriately chosen reference fluids and mixing rules, the GCSP leads to predictions about as accurate as those obtained with the best fitting two-parameter activity coefficient model for this system.

CONCLUSIONS

In this communication we have suggested a three-parameter Generalized Corresponding States Principle that allows choice of the reference fluids, and also a set of mixing rules, which leads to accurate phase equilibrium calculations. Most importantly, this single method results in accurate predictions for mixtures containing paraffinic hydrocarbons, aromatic hydrocarbons, alcohols, large and small molecules, and water over a large range of pressures and temperatures. While there is much room for further work on the generalized corresponding states principle, the studies already completed establish its accuracy and utility for systems not heretofore treated by the method of corresponding states.

A computer program for phase equilibrium predictions using the Generalized Corresponding States Principle and the mixing models discussed here is available from the authors.

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Simple Method for the Calculation of Heat Capacities of Liquid Mixtures

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A simple method based on the corresponding state principle is proposed for the calculation of the heat capacities of liquid mixtures. The method requires a knowledge of the heat capacities of two pure liquids as a function of temperature. For the 16 binary liquid mixtures studied in this work, average absolute deviations (AADs) between experimental and calculated heat capacities were found to be 3.03% when only the pure-component heat capacities were used in the calculations and 1.44% when binary data at a single temperature were used. The method is simple to use and can easily be generalized to multicomponent mixtures.

The heat capacity of liquids and liquid mixtures is important in many heat-transfer calculations (appearing, for example, in the Prandtl number and in enthalpy expressions). Although there are a number of heat capacities in common use, the heat capacity at constant pressure C_p is of greatest interest in heat-transfer work. The heat capacity of the saturated liquid C_{sat} is also of interest, but the difference between C_p and C_{sat} is usually negligible.

There are a number of estimation methods for the heat capacities of pure liquids (1). However, very few specific correlations have been suggested for mixtures. Normally, the use of an arithmetic mole or weight fraction average of the pure-component values is recommended (1) although this neglects any contribution due to the temperature variation of the enthalpy of mixing. Thus

$$C_{pm} = w_1 C_{p1} + w_2 C_{p2} \tag{1}$$

or

$$C_{pm} = x_1 C_{p1} + x_2 C_{p2} \tag{2}$$

Recently, Jamieson and Cartwright (2) assessed the effective-

ness of eq 1 and 2 using data for both aqueous and nonaqueous mixtures and concluded that, although the equations were moderately successful in predicting heat capacities of liquid mixtures, improvements were required to meet the higher-accuracy needs of industry. They therefore proposed the following equations for nonaqueous mixtures

$$C_{pm} = (w_1 C_{p1} + w_2 C_{p2})(1 + \alpha + \beta) \qquad (3)$$

where

$$\alpha = (0.00141|\Delta H_1 - \Delta H_2|^{0.86} - 0.08)w_1 w_2 \qquad (4)$$

$$\beta = (5 \times 10^{-5}|\Delta H_1 - \Delta H_2|) \sin(360 w_2) \qquad (5)$$

and for aqueous mixtures, they proposed

$$C_{pm} = (w_1 C_{p1} + w_2 C_{p2})(1 + Dw_1 w_2) \qquad (6)$$

where ΔH is the enthalpy of vaporization at the boiling point and D is a constant which was optimized for each system.

Jamieson and Cartwright (2) found that for 215 nonaqueous mixtures and a total of 1083 data points, eq 1 gave a maximum error of 12.5%, whereas the use of eq 3 reduced this maximum to 9.1%, with 95% of values lying within ±5%. For 52 aqueous systems and a total of 503 points, eq 1 gave a maximum error of 16.9%, whereas the use of eq 6 reduced this maximum to 10.2%, with 95% of values lying within ±7%.

We have recently proposed a generalized corresponding state principle (GCSP) for the thermodynamic (3) and transport (4, 5) properties of liquids and liquid mixtures. The applications of the method to heat capacities at constant pressure are shown below. It is also shown that, under certain assumptions, the GCSP reduces to a simple mole fraction average of the heat capacities of the pure components at the *same reduced temperature*.

Generalized Corresponding State Principle for Heat Capacities

A generalized corresponding state principle (GCSP) for thermodynamic and transport properties has recently been proposed (3–5). According to the GSCP, a reduced property X of any pure fluid (with critical constants T_c, P_c, V_c, molecular weight M, and acentric factor ω) can be obtained from the known properties of two reference fluids (denoted by superscripts r1 and r2) at the same reduced temperature and pressure as follows:

$$X = X^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}}[X^{(2)} - X^{(r1)}] \qquad (7)$$

where X is a property such as compressibility, reduced viscosity, or reduced thermal conductivity. We may write an analogous expression for the dimensionless residual heat capacity as follows:

$$\left(\frac{C_p - C_p^{\,\circ}}{R}\right) = \left(\frac{C_p - C_p^{\,\circ}}{R}\right)^{(r1)} +$$
$$\frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}}\left[\left(\frac{C_p - C_p^{\,\circ}}{R}\right)^{(r2)} - \left(\frac{C_p - C_p^{\,\circ}}{R}\right)^{(r1)}\right] \qquad (8)$$

The two reference fluids r1 and r2 are chosen so that they are similar to the pure fluid of interest or, in the case of mixtures, to the key components of interest. If r1 is a simple fluid of zero acentric factor, then eq 8 reduces to the equation proposed by Lee and Kesler (6). Equation 8 states that, given the residual heat capacities of two reference fluids as functions of T_R and P_R (or V_R), we may predict the residual heat capacities of any (similar) fluid of interest as a function of T_R and P_R (or V_R).

Equation 8 may be extended to mixtures using, for example, a one-fluid model to replace T_c, V_c, M, and ω of a pure fluid

by the pseudocritical properties T_{cm}, V_{cm}, M_m, and ω_m of a hypothetical equivalent substance as follows:

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \qquad (9)$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \qquad (10)$$

$$M_m = \sum_i x_i M_i \qquad (11)$$

$$\omega_m = \sum_i x_i \omega_i \qquad (12)$$

There is some theoretical justification (7) for using the van der Waals one-fluid model (eq 9 and 10) for mixtures of nonpolar molecules which do not differ greatly in their sizes. Equation 11, on the other hand, arises naturally from a mass balance. However, eq 12 is completely arbitrary—its only justification being the success with which it has been applied in our previous studies.

The one-fluid model can be used to obtain the properties of mixtures provided values can be assigned to the cross-parameters T_{cij} and V_{cij} when $i \neq j$. Various mixing rules have been tried in this study including a geometric mean rule for T_{cij} and an arithmetic mean rule for V_{cij}. However, there was little improvement over the mixing rules used in our previous studies, viz.

$$T_{cij} V_{cij} = \xi_{ij}(T_{ci} V_{ci} T_{cj} V_{cj})^{1/2} \qquad (13)$$

$$V_{cij} = \tfrac{1}{8}(V_{ci}^{1/3} + V_{cj}^{1/3})^3 \qquad (14)$$

and results for these rules are reported below. In eq 13, ξ_{ij} is a binary interaction coefficient which must be calculated from experimental data. An advantage of using appropriate reference fluids is that a single value of the binary interaction coefficient is often sufficient to characterize each binary mixture. Its value reflects, in part, our inability to represent intermolecular forces by means of eq 9–14.

For the special case when the two pure components of a binary mixture are used as the reference fluids, use of eq 12 leads to the simplification

$$\left(\frac{C_{pm} - C_{pm}^{\,\circ}}{R}\right) = x_1\left(\frac{C_{p1} - C_{p1}^{\,\circ}}{R}\right) + x_2\left(\frac{C_{p2} - C_{p2}^{\,\circ}}{R}\right) \qquad (15)$$

and, since $C_{pm}^{\,\circ} = x_1 C_{p1}^{\,\circ} + x_2 C_{p2}^{\,\circ}$, we may write

$$C_{pm} = x_1 C_{p1} + x_2 C_{p2} \qquad (16)$$

The difference between eq 2 and eq 16 is that, by convention, eq 2 refers to heat capacities at the same temperature whereas the derivation of eq 16 requires that the heat capacities be evaluated at the reduced temperature and pressure of the mixture. Since pressure has little effect on the heat capacities of liquids, we may write eq 16 as

$$C_{pm}[T_R] = x_1 C_{p1}[T_R] + x_2 C_{p2}[T_R] \qquad (17)$$

Predictions using eq 17 are shown below. It should be added that, in the general case, the heat capacities are functions of both T_R and P_R.

Reference-Fluid Calculations

The heat capacities of the pure-component reference fluids were correlated by means of the relationship

$$\ln(C_p/R) = A - B/T_R \qquad (18)$$

where A and B are constants and pressure effects have been neglected. The choice of the reference equation is arbitrary. Other, more accurate and/or more complex expressions could equally have been used (a four-constant polynomial in T_R was

.Table I. Constants of Eq 18 for the Reference Fluids for Each System

no.	system	A_1	B_1	A_2	B_2
1	$(CH_3)_2CO + CS_2$	3.1506	0.2438	2.5450	0.1616
2	$(CH_3)_2CO + CHCl_3$	3.1506	0.2438	2.9470	0.1830
3	$C_6H_6 + CCl_4$	3.6107	0.4400	3.2316	0.2637
4	$C_6H_6 + c\text{-}C_6H_{12}$	4.4651	1.1085	4.6450	1.0824
5	$C_6H_6 + CH_2ClCH_2Cl$	3.3498	0.2985	3.1038	0.1906
6	$C_6H_6 + C_6H_5CH_3$	3.6760	0.4770	3.5225	0.3094
7	$CCl_4 + CHCl_3$	3.0826	0.1826	3.1808	0.3008
8	$c\text{-}C_6H_{12} + C_2H_5OH$	3.7769	0.4568	4.0193	0.8259
9	$n\text{-}C_6H_{14} + C_2H_5OH$	3.8983	0.3336	3.9368	0.7733
10	$c\text{-}C_5H_9CH_3 + C_2H_5OH$	3.5910	0.2553	3.2197	0.3583
11	$C_6H_5CH_3 + C_2H_5OH$	3.6152	0.3425	4.2453	0.9565
12	$n\text{-}C_6H_{14} + i\text{-}C_3H_7OH$	3.5353	0.1375	3.6269	0.4278
13	$n\text{-}C_7H_{16} + C_2H_6$	3.6524	0.4241	4.5219	1.5152
14	$CH_3OH + H_2O$	2.8410	0.3315	2.1492	−0.0258
15	$n\text{-}C_3H_7OH + H_2O$	3.6893	0.4673	2.1473	−0.0268
16	$(CH_2OH)_2 + H_2O$	3.5212	0.2988	2.2178	0.0065

Table II. Summary of Results

system no.[a]	no. of data points	temp range, K	AAD, % $\xi_{12} = 1.0$	AAD, % $\xi_{12} = \xi_{opt}$	ξ_{opt}
1	18	293.2–313.2	2.17	0.45	0.781
2	24	293.2–323.2	2.48	0.58	0.737
3	25	293.2–333.2	0.98	0.85	0.958
4	9	453.2–473.2	0.42	0.05	1.019
5	36	293.2–343.2	0.57	0.56	1.007
6	35	293.2–333.2	0.78	0.62	0.976
7	20	293.2–323.2	0.66	0.46	1.046
8	30	303.2–343.2	5.06	2.63	0.803
9	36	293.2–343.2	3.53	2.09	0.836
10	35	223.2–303.2	2.38	1.43	0.886
11	37	303.2–346.2	8.14	2.27	0.711
12	35	205.4–304.7	3.10	1.64	0.839
13	18	294.2–327.2	3.06	0.79	0.911
14	9	275.7–313.2	5.75	3.73	0.625
15	9	275.7–313.2	9.73	6.33	0.413
16	9	293.2–351.5	1.35	1.25	0.920
	385		3.03	1.44	

[a] The system no. corresponds to that used in Table I.

also used but did not yield significantly better results). The choice of the reference substances is also arbitrary. However, the use of the simple relationship given by eq 17 requires that the two pure components be used as the reference substances for each binary mixture. Constants A and B for various reference substances are given in Table I and are applicable in the temperature range given in Table II. In the general case, the actual heat capacities of the reference fluids at the same reduced conditions may be used. The data were taken from the compilation of Jamieson and Cartwright (2).

It should be added that eq 8 does not require that the pure components be used as the reference substances. In fact, the expression may be used to predict the (unknown) heat capacities of the pure components given the (known) heat capacities of two (similar) fluids at the same reduced conditions.

Results

Sixteen binary systems and a total of 385 data points were examined using eq 17. Only those systems where a single investigator had measured the heat capacities at three or more different temperatures were selected for study. The systems included nonpolar mixtures, mixtures containing polar molecules, and aqueous mixtures. The results are shown in Table II. The

experimental data used in the comparisons were taken from the compilation of Jamieson and Cartwright. Table II shows average absolute deviations between experimental and calculated heat capacities both with the binary interaction coefficient ξ_{12} set equal to 1.0 (i.e., using pure-component data only) and with the binary interaction coefficient optimized by using the binary mixture data at the lowest temperature. To a good approximation, ξ_{12} was found to be independent of temperature and composition. Thus, the use of the same value of ξ_{12} over a 100 °C range of temperature in some cases did not lead to any significant decrease in accuracy of the predictions. The average absolute deviation between calculation and experiment was found to be 3.03% with all $\xi_{12} = 1.0$. The average deviations could be reduced to 1.44% if a single binary interaction coefficient (independent of temperature and composition) was included in the calculations. As expected, the method works best for nonpolar mixtures and is least accurate for aqueous mixtures. The larger than average deviations for aqueous systems are in part due to the inadequacy of the reference-fluid equation (eq 18) for water and in part due to the fact that water is strongly associated in solution. Nevertheless, the method compares favorably with available methods for all systems. An additional advantage is that eq 17 can easily be generalized to multicomponent systems and requires, at most, only binary information at a single temperature for the prediction of heat capacities of multicomponent mixtures.

Glossary

A, B	reference-fluid-equation constants
C	heat capacity
D	constant in eq 6
H	enthalpy
M	molecular weight
R	gas constant
T	temperature
V	molar volume
w	weight fraction
x	mole fraction

Greek Letters

α, β	constants in eq 3
ω	acentric factor
ξ	binary interaction coefficient

Subscripts

c	critical value
i, j	component i, j
m	mixture value
p	constant pressure
R	reduced value, e.g., $T_R = T/T_c$

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A Method for the Calculation of Gas–Liquid Critical Temperatures and Pressures of Multicomponent Mixtures

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The critical properties of 75 binary systems have been correlated by use of a modified two-parameter Wilson equation. The great advantage of using the Wilson equation is that its generalization to multicomponent systems is straightforward and requires binary parameters only. Extensive tables of binary parameters are given in this work. Comparisons between experimental and predicted critical properties for 61 multicomponent systems are shown. The new method is accurate, it is simple to use, and it requires considerably less computational effort than rigorous methods which solve the equations for the Gibbs criteria at the critical point.

A knowledge of the gas–liquid critical states of mixtures is of great practical importance, especially in hydrocarbon processing applications. Many hydrocarbon processing operations take place at high pressures and involve retrograde phenomena which are characteristic of the behavior of mixtures in the critical region. In addition, phase equilibrium calculations and fluid property predictions are difficult to make in the critical region. It is therefore often necessary to locate the critical point of a multicomponent system prior to carrying out other calculations in this region.

Attempts to predict critical properties have relied primarily on two approaches: (i) empirical methods involving the use of excess properties (Etter and Kay, 1961) or fitted correction factors (Chueh and Prausnitz, 1967); (ii) rigorous methods involving the solution of Gibbs criteria for the critical point in a mixture. These latter methods have used either equations of state (Peng and Robinson, 1977; Heidemann and Khalil, 1980; Michelsen, 1980) or the Corresponding States Principle (Teja and Rowlinson, 1973) to obtain the Gibbs energy and its derivatives required in the calculations.

Although the second approach is preferable to the first because of its basis in thermodynamics, the rigorous methods do not always lead to a solution and they may sometimes require a large amount of computing time. This is likely to prove disadvantageous in some simulation calculations. Moreover, methods which use simple equations of state do not predict all critical properties accurately, with the predicted critical volume showing the greatest deviations.

The method reported in this paper makes use of the concept of an excess critical property introduced by Etter and Kay in 1961. Etter and Kay demonstrated that this concept is useful in studying the effect of shape, size, and the chemical nature of the components on the critical properties of mixtures. They also obtained correlations for the excess critical properties for various classes of mixtures. We have chosen to fit a modified Wilson (1964) equation to sets of binary critical data obtained from the literature. The great attraction of the method is that it can very easily be extended to multicomponent mixtures using parameters obtained from the binary pairs only. No ternary or higher mixture data are required in the calculations. Moreover, once the binary parameters have been evaluated, the prediction of multicomponent critical properties requires no iterations. There is therefore a considerable saving in computation time. A possible further advantage is that the method may prove amenable to a group contribution approach (analogous to the use of ASOG or UNIFAC to obtain excess Gibbs energies). This would result in a powerful technique for the prediction of critical states from data on a limited number of binary mixtures.

The Modified Wilson Equation for Excess Critical Properties

Etter and Kay (1961) defined an excess critical property ϕ_c^E as

$$\phi_c^E = \phi_c - \phi_c^{IDEAL} \tag{1}$$

where ϕ is T, P, or V, ϕ_c is the critical property of the

Table I. Coefficients for the Prediction of Critical Temperatures (K)

component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1. methane[a]	-	1.521	1.517	1.108	1.735	0.1691	1.063	0.5385	-	-	-	0.3343 E-7	1.288	1.655	1.251	1.422	1.068	0.5311
2. ethane[a]	0.5691	-	0.8899	1.148	1.145	0.9895	1.505	0.6275	1.193	1.327	-	1.360	-	1.621	0.8666	-	-	1.248
3. propane	0.5401	1.104	-	1.040	1.225	1.325	1.500	-	-	1.868	-	-	0.4932	1.739	0.4405	-	-	1.677
4. n-butane	0.8048	0.8372	0.9541	-	1.165	1.264	1.330	-	-	-	-	-	-	1.450	0.4740	-	-	1.572
5. n-pentane	0.3653	0.8175	0.7836	0.8442	-	1.260	1.206	-	-	1.133	1.263	1.351	-	2.436	-	-	-	1.564
6. n-hexane	2.071	0.9353	0.6899	0.7547	0.7675	-	1.066	-	-	1.445	1.081	1.089	-	-	0.1012	-	-	-
7. n-heptane	0.7329	0.5173	0.5608	0.6971	0.8054	0.9336	-	0.5211	-	1.418	-	0.8599	-	-	0.1370	-	-	-
8. ethylene	1.600	1.459	-	-	-	-	1.493	-	1.335	0.5703	-	-	-	1.426	-	-	-	-
9. propene	-	0.8197	-	-	-	-	-	0.7008	-	-	-	-	-	-	-	-	-	-
10. benzene	-	0.7537	0.3856	-	0.8829	0.6456	0.6620	1.507	-	-	0.9107	1.118	-	-	-	-	-	-
11. toluene	-	-	-	-	0.7779	0.9225	-	-	-	1.089	-	1.309	-	-	-	-	-	-
12. cyclohexane	2.560	0.6331	-	-	0.6949	0.9161	1.151	-	-	0.8945	0.7342	-	-	0.7515	-	-	-	-
13. carbon monoxide	0.7451	-	1.529	-	-	-	-	-	-	-	-	-	-	0.9683	0.8088	0.7633	-	-
14. carbon dioxide	0.4980	0.5430	0.4643	0.6155	0.2436	-	-	0.6576	-	-	-	1.179	-	-	1.664	-	-	1.198
15. nitrogen	0.7736	1.093	1.638	1.492	-	2.293	2.040	-	-	-	-	-	1.033	-	0.8525	2.052	-	-
16. oxygen	0.6533	-	-	-	-	-	-	-	-	-	-	1.212	0.4903	1.159	-	0.9672	-	-
17. argon	0.9302	-	-	-	-	-	-	-	-	-	-	1.270	-	0.3135	1.034	-	-	-
18. hydrogen sulfide	1.600	0.8009	0.5113	0.5561	0.5303	-	-	-	-	-	-	-	-	0.8344	-	-	-	-

[a] Note that for the methane (1) + ethane (2) system $A_{12} = 0.5691$, $A_{21} = 1.521$.

Table II. Coefficients for the Prediction of Critical Pressures (bar)

component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1. methane	-	1.429	1.893	2.069	2.391	2.698	2.771	0.4858	-	-	-	2.635	1.312	1.130	1.189	-	-	1.325
2. ethane	0.6192	-	1.039	1.490	1.558	1.800	1.951	0.7836	1.291	0.4974	-	1.760	-	-	0.4685	-	-	1.144
3. propane	0.3438	0.9523	-	1.200	1.338	1.498	1.630	-	-	1.489	-	-	0.1002	1.564	0.09612	-	-	1.593
4. n-butane	0.2350	0.5909	0.8145	-	0.9129	1.263	1.387	-	-	-	-	-	-	0.6412	0.1663 E-4	-	-	1.694
5. n-pentane	0.1174	0.5370	0.7026	1.089	-	-	0.8161	-	-	-	-	-	-	0.5529	-	-	-	0.6770
6. n-hexane	0.03472	0.3978	0.5888	0.7629	-	-	1.150	-	-	1.239	0.8358	1.159	-	-	0.03451	-	-	-
7. n-heptane	0.5675 E-2	0.3228	0.5050	0.6682	1.199	0.8596	-	0.2766	-	1.295	-	1.199	-	-	0.1021 E-5	-	-	-
8. ethylene	1.632	1.239	-	-	-	-	2.034	-	1.345	1.601	-	-	-	1.091	-	-	-	-
9. propene	-	0.7415	-	-	-	-	-	0.6982	-	-	-	-	-	-	-	-	-	-
10. benzene	-	1.580	0.5889	-	-	0.7889	0.7465	0.4848	-	-	0.9602	1.042	-	-	-	-	-	-
11. toluene	-	-	-	-	-	1.175	-	-	-	1.040	-	-	-	-	-	-	-	-
12. cyclohexane	0.3166 E-5	0.4051	-	-	-	0.8531	0.8203	-	-	0.9601	-	-	-	0.2415	-	-	-	-
13. carbon monoxide	0.7203	-	2.406	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
14. carbon dioxide	0.8400	-	0.5505	1.402	1.507	-	-	0.9165	-	-	-	0.2068	-	-	-	-	-	0.5808
15. nitrogen	0.8146	1.596	2.343	2.688	-	2.315	2.233	-	-	-	-	-	-	-	-	1.172	-	-
16. oxygen	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8409	-	-	-
17. argon	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18. hydrogen sulfide	0.6330	0.8741	0.5523	0.4884	1.361	-	-	-	-	-	-	-	-	1.528	-	-	-	-

Table III. Predicted and Experimental Critical Temperatures and Pressures, Multicomponent Systems

mixture no.	source	C_1	C_2	C_3	nC_4	nC_5	nC_6	nC_7	CO_2	N_2	H_2S	T_c/K exptl	calcd	% dev	P_c/MPa exptl	calcd	% dev
1	j	0.690		0.075	0.235							310.93	308.24	−0.87	12.583	12.34	−1.94
2	j	0.666		0.115	0.219							310.93	310.76	−0.55	12.238	11.85	−3.16
3	j	0.630		0.185	0.185							310.93	313.44	0.81	11.307	11.05	−2.30
4	j	0.587		0.278	0.135							310.93	315.95	1.61	10.239	10.06	−1.78
5	e			0.3276	0.3398	0.3326						428.83	429.19	0.084	4.188	3.99	−4.69
6	e		0.3414	0.3421		0.3165						397.17	401.71	1.14	5.602	5.72	2.16
7	e		0.2542	0.2547	0.2554	0.2357						405.89	408.00	0.52	5.113	4.99	−2.34
8	e	0.2019	0.2029	0.2033	0.2038	0.1881						387.06	385.48	−0.41	7.220	6.81	−5.63
9	e				0.6449	0.2359	0.1192					450.22	449.69	−0.12	3.880	b	−
10	e				0.4858	0.3316	0.1213	0.0613				417.94	418.19	0.061	4.506	b	−
11	i		0.3977	0.2926	0.1997	0.0713	0.0369					385.44	387.79	0.61	5.624	b	−
12	i		0.726		0.171				0.103			385.92	385.01	−0.23	7.605	7.34	−3.46
13	i		0.514		0.412				0.074			400.37	400.85	0.12	6.40b	6.25	−2.44
14	i		0.801			0.064			0.135			391.48	390.31	−0.30	8.101	7.59	−6.36
15	i		0.612			0.271			0.117			421.48	421.13	−0.084	7.156	6.27	−12.33
16	i		0.615			0.296			0.089			415.92	415.82	−0.024	7.060	6.31	−10.56
17	i	0.415		0.542						0.043		322.03	323.68	0.51	8.674	7.96	−8.21
18	i	0.360		0.545						0.095		322.03	322.38	0.11	9.204	8.38	−8.92
19	i	0.4530		0.5005						0.0465		313.70	317.54	1.22	9.232	8.32	−9.85
20	i	0.4115		0.5030						0.0855		313.70	316.50	0.89	9.797	8.63	−11.91
21	i		0.6168		0.1376	0.0726			0.1730			423.15	420.53	−0.62	7.412	6.80	−8.32
22	i	0.4345	0.0835	0.4330						0.0490		313.70	310.54	−1.01	8.963	7.96	−11.17
23	i	0.9100	0.0560	0.0012						0.0330		199.26	200.46	0.60	5.341	5.33	−0.22
24	i	0.070							0.616		0.314	310.92	285.43	−8.20	8.274	7.91	−4.40
25	i	0.9590	0.0260	0.0001						0.0150		193.87	195.20	0.6863	4.932	4.94	0.1975
26	i	0.9500	0.0260	0.0078						0.0160		196.53	198.94	1.23	5.180	5.31	2.52
27	i	0.9450	0.0260	0.0081	0.0052					0.0160		199.54	200.35	0.41	5.456	5.63	3.19
28	i	0.7057	0.0669	0.0413	0.0508	0.1353						308.42	318.36	3.22	13.700	13.38	−2.34
29	d	0.193	0.470		0.337							354.26	345.96	−2.34	7.639	7.64	0.047
30	d	0.391	0.354		0.255							331.48	318.62	−3.82	9.721	9.47	−2.58
31	d	0.007	0.879		0.114							324.54	325.75	0.37	5.481	5.60	2.13
32	d	0.040	0.821		0.139							323.71	326.99	1.01	5.792	5.94	2.63
33	i		0.429		0.373				0.198			438.15	437.02	−0.26	6.61	6.39	−3.34
34	i		0.6626	0.1093	0.1057	0.0616	0.0608					310.53	278.51	−10.3	13.75	b	−
35	i	0.1015	0.3573	0.2629	0.1794	0.0657	0.0332					376.42	365.13	−3.0	6.54	b	−
36	h	0.4988							0.0987		0.4022	256.10	236.62	−7.61	11.03	11.13	0.90
37	e	0.652	0.0298	0.0113	0.300					0.0030	0.0035	320.00	319.14	−0.27	12.39	12.70	2.54
38	i	0.316	0.388	0.223	0.043	0.008				0.022		313.70	309.86	−1.22	7.85	7.27	−7.30
39	g		0.705		0.069				0.226			421.99	420.50	−0.35	8.62	8.24	−4.40
40	g		0.036		0.173				0.191			421.99	418.43	−0.84	8.06	7.62	−5.47
41	g		0.544		0.293				0.163			421.99	420.10	−0.45	7.42	6.94	−6.45
42	g		0.474		0.390				0.136			421.99	419.89	−0.50	6.86	6.43	−6.28
43	g		0.356		0.547				0.097			421.99	420.79	−0.28	6.05	5.66	−6.44
44	g		0.625		0.077				0.298			449.77	443.68	−1.35	8.24	7.93	−3.73
45	g		0.559		0.169				0.272			449.77	443.07	−1.49	7.89	7.40	−6.17
46	g		0.466		0.290				0.244			449.77	443.85	−1.32	7.35	6.72	−8.55
47	g		0.360		0.448				0.192			445.77	440.50	−1.18	6.65	5.97	−10.27
48	f		0.750		0.038	0.212						366.44	368.15	0.47	6.72	6.53	−2.85
49	f		0.739		0.070	0.191						368.44	367.69	0.34	6.62	6.44	−2.77
50	f		0.723		0.112	0.165						366.44	367.48	0.28	6.38	6.32	−0.86
51	f		0.692		0.188	0.120						366.44	367.66	0.33	6.12	6.15	0.37

mixture and ϕ_c^{IDEAL} is that of an ideal mixture of the same composition given by

$$\phi_c^{IDEAL} = \sum_i x_i \phi_{ci} \qquad (2)$$

ϕ_c^E is therefore a molecular interaction quantity equal to the difference between the actual and ideal values and is called an excess property by analogy with excess thermodynamic functions. However, it should be added that all quantities in eq 1 are not evaluated at the same temperature and pressure, unlike the properties in the definitions of excess thermodynamic functions.

We have used a modified form of the Wilson (1964) equation to fit binary excess critical temperature and excess critical pressure data obtained from the literature. No attempt was made to fit excess critical volume data, partly because of the scarcity of such data and partly because the assumption $V_c^E \approx 0$ appears to fit the available experimental data to sufficient accuracy for practical calculations.

The modified Wilson equation for an excess critical property ϕ_c^E may be written as

$$\phi_c^E = -C \sum_i x_i \ln \left(x_i + \sum_{j \neq i} x_j A_{ij} \right) \qquad (3)$$

For a binary system this reduces to

$$\phi_c^E = -C \left[x_1 \ln (x_1 + A_{12} x_2) + x_2 \ln (x_2 + A_{21} x_1) \right] \qquad (4)$$

The constant C was arbitrarily set equal to 2500 for both the excess critical temperature and the excess critical pressure correlation. This was to ensure that small positive values of A_{ij}'s would be obtained.

Results and Conclusions

Equation 4 was fitted to excess critical temperature and pressure data for 75 binary systems, using nonlinear least-squares techniques and minimizing the relative deviations between calculated and experimental data points. No attempt was made to weight the data.

The coefficients for the excess critical temperature are shown in Table I and for the excess critical pressure in Table II. Although both tables are far from complete, there are enough coefficients to provide an estimate of the critical states of multicomponent mixtures found in many hydrocarbon processing operations.

Data for the 75 binary systems correlated in this study were obtained from the compilation of Hicks and Young (1975). The overall average deviation between experimental and calculated critical temperatures was found to be 0.29% and between experimental and calculated pressures 1.01%. This compares with overall average deviations of 0.51% and 3.37% for the Chueh and Prausnitz (1967) method for those mixtures for which parameters have been tabulated by Chueh and Prausnitz. In general, the new method was found to be comparable for the prediction of critical temperatures with the methods of Chueh and Prausnitz and Grieves and Thodos (1962). However, the new method is significantly better for the prediction of critical pressures.

Table III shows comparisons between experimental and predicted critical pressures and temperatures for 61 multicomponent mixtures. Only the binary constants (A_{ij}'s) were required in the calculations using eq 3. The method gives good predictions of both the critical temperatures and pressures for the systems studied.

Conclusions

A modified Wilson equation has been used successfully to correlate and predict the excess critical temperature and pressure data of a large number of multicomponent systems. The method requires two parameters per binary pair

No.	x_1	x_2	x_3	T_c exp	T_c calc	dev	P_c exp	P_c calc	%
52	0.661	0.277	0.062	368.44	366.85	0.11	5.90	5.96	1.18
53	0.582	0.148	0.270	394.22	393.77	-0.11	6.41	6.21	-3.16
54	0.545	0.235	0.220	394.22	393.84	-0.096	6.10	5.98	-2.03
55	0.504	0.333	0.163	394.22	393.92	-0.076	5.70	5.75	0.84
56	0.460	0.438	0.102	394.22	394.13	-0.022	5.45	5.53	1.60
57	0.430	0.110	0.460	421.99	422.42	0.10	6.07	5.82	-4.15
58	0.366	0.240	0.394	421.99	422.94	0.23	5.74	5.41	-5.77
59	0.298	0.410	0.292	421.99	422.94	-0.077	5.19	5.03	-8.17
60	0.9430 0.027 0.0074	0.0049	0.0010 0.0140 0.0027	201.09	203.06^e	0.98	5.58	b	b
61	0.215	0.610	0.175	421.99	420.85	-0.27	4.65	4.64	-0.35

^{a} CO$_2$–N$_2$, N$_2$–CO$_2$ coefficients neglected due to lack of data. ^{b} Insufficient data for evaluation. ^{c} C$_1$–N$_2$, N$_2$–C$_2$ coefficients neglected due to lack of data. ^{d} Cota and Thodos (1962). ^{e} Etter and Kay (1961). ^{f} Mehra and Thodos (1963). ^{g} Mehra and Thodos (1968). ^{h} Ng et al. (1981). ^{i} Peng and Robinson (1977). ^{j} Riga et al. (1959).

and may prove amenable to a group contribution approach. It is accurate, simple to use, and, once the binary coefficients have been obtained, requires no iterations in the calculations.

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THE CALCULATION OF CRITICAL POINTS OF FLUID MIXTURES-EFFECT OF IMPROVED PURE COMPONENT CRITICAL POINT REPRESENTATION

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ABSTRACT

The poor representation of mixture critical volumes by cubic equations of state is well known and has been widely attributed to the fact that the pure component critical compressibility calculated from the equation of state (designated as ζ_{ci}) is, in general, not equal to the experimental critical compressibility (designated as Z_{ci}^{expt}) of most fluids. This work examines the behavior of two and three-constant cubic equations of state in the critical region and demonstrates that simply setting ζ_{ci} equal to Z_{ci}^{expt} does not necessarily lead to more accurate prediction of mixture critical points. The improvement in the pure component critical point representation creates the necessity for an additional mixing rule which is not inherent in the usual mixing rules for the equation of state constants.

The critical region behavior of two cubic equations of state was studied in this work. These equations, namely the Peng-Robinson and the Teja-Patel, were chosen as representative of two and three-constant equations of state.

SIMPLE EQUATIONS OF STATE

The Teja-Patel (1982) equation is a three-constant cubic equation that accurately accurately predicts the saturation density of a variety of fluids including paraffinic and aromatic hydrocarbons, water and alcohols. It offers more flexibility than the Peng-Robinson (1976) and Redlich-Kwong-Soave (1972) equations for thermodynamic property and phase equilibrium calculations and we have therefore examined the ability of this equation to correlate the behavior of binary systems in the critical region.

The Teja-Patel (TP) equation is given by:

$$P = \frac{RT}{V-b} - \frac{a[T]}{V(V-b) + c(V-b)} \tag{1}$$

where

$$a[T] = \alpha[T_R] \Omega_a R^2 T_c^2 / P_c \tag{2}$$

$$b = \Omega_b RT_c / P_c \tag{3}$$

$$c = \Omega_c RT_c / P_c \tag{4}$$

$$\alpha[T_R] = (1 + F(1 - T_R^{\frac{1}{2}}))^2 \tag{5}$$

and Ω_a, Ω_b, Ω_c are constants for a given substance and depend on the value of $P_c V_c / RT_c$ $(=\zeta_c)$ implied by the equation of state. F is a constant which is calculated from the vapor pressure curve of the substance. At the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \;\; ; \;\; \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \;\; ; \;\; \text{and} \;\; \frac{P_c V_c}{RT_c} = \zeta_c \tag{6}$$

The TP equation treats ζ_c as a parameter which is obtained by fitting the saturated liquid densities of each pure substance. We denote the equation with ζ_{ci} optimized in this manner as TP1. In general, the prediction of good liquid densities requires that ζ_{ci} be greater than Z_{ci}^{expt} by approximately 10%. This is due to the asymmetric nature of the phase envelope near the pure component critical points and requires a nonanalytic equation for accurate representation (Levelt Sengers, 1976). It should be noted here that when ζ_c is set equal to 0.3074 and c is set equal to b in the Teja-Patel equation, the Peng-Robinson (or PR) equation results.

Since the values of ζ_{ci} required to fit liquid densities are, in general, greater than the experimental values of ζ_{ci} at the critical point (Patel, 1982, Soave, 1972), an obvious modification of the TP1 equation for calculations in the critical region is to let:

$$\zeta_{ci} = Z_{ci}^{expt} \tag{7}$$

for each pure component considered. We denote this modification of the TP equation as TP2. The modification was suggested by Martin (1967) for improved critical region behavior. However, in this case, all the constraints of equation (6) are valid only if the equation of states has three or more constants. Such equations can be made to fit the critical points of the pure fluids exactly. Two-constant cubic equations such as that of Peng-Robinson (1976) imply a fixed value of the critical compressibility for all substances and cannot be made to fit the critical point exactly for substances whose experimental critical compressibilities do not equal that universal value.

The TP and PR equations may be extended to mixtures using the mixing rules (Patel 1982):

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \; ; \; b_m = \sum_i x_i b_i \; ; \; c_m = \sum_i x_i c_i \tag{8}$$

where the cross-interaction term is calculated using

$$a_{ij} = \xi_{ij}(a_{ii} a_{jj})^{\frac{1}{2}} \tag{9}$$

and ξ_{ij} is an adjustable parameter that is best evaluated from experimental data on the binary system.

Equations (8-9) are equivalent to those given by van der Waals for the parameters a and b in his equation of state. However, because of the temperature dependence of parameter a, these mixing rules are more complex than the original val der Waals one-fluid mixing rules. More importantly, the van der Waals a and b are functions of T_c and P_c only, whereas the TP constants are functions of T_c, P_c, ζ_c, and F. This point becomes obvious if the mixing rules given by equation (8) are rewritten in terms of the pseudocritical parameters T_{cm}, P_{cm}, ζ_{cm}, and F_m. The following mixture rules are then obtained:

$$\Omega_a[\zeta_{cm}] \frac{R^2 T_{cm}^2}{P_{cm}} \alpha[\frac{T}{T_{cm}} , F] = \sum_i \sum_j x_i x_j \Omega_a[\zeta_{ij}] \frac{R^2 T_{cij}^2}{P_{cij}} \alpha[\frac{T}{T_{cij}} , F] \tag{10}$$

$$\Omega_b[\zeta_{cm}] \frac{R T_{cm}}{P_{cm}} = \sum_i x_i \Omega_b[\zeta_{ci}] \frac{R T_{cii}}{P_{cii}} \tag{11}$$

$$\Omega_c[\zeta_{cm}] \frac{R T_{cm}}{P_{cm}} = \sum_i x_i \Omega_c[\zeta_{ci}] \frac{R T_{cii}}{P_{cii}} \tag{12}$$

where the square brackets indicate functional dependence. It is clear that the mixing rules are only sufficient for three out of the four pseudocritical properties T_{cm}, P_{cm}, ζ_{cm}, and F_m. Note that the Peng-Robinson mixing rules may also also be written in pseudocritical form:

$$\Omega_a[0.3074] \frac{R^2 T_{cm}^2}{P_{cm}} \alpha[\frac{T}{T_{cm}} , \omega_m] =$$

$$\sum_i \sum_j x_i x_j \Omega_a[0.3074] \frac{R^2 T_{cij}^2}{P_{cij}} \alpha[\frac{T}{T_{cij}} , \omega_{ij}] \tag{13}$$

$$\Omega_b[0.3074] \frac{R T_{cm}}{P_{cm}} = \sum_i x_i \Omega_b[0.3074] \frac{R T_{cm}}{P_{cm}} \tag{14}$$

$$\Omega_c[0.3074] \frac{R T_{cm}}{P_{cm}} = \sum_i x_i \Omega_c[0.3074] \frac{R T_{cm}}{P_{cm}} \tag{15}$$

Since $\zeta_{ci} = \zeta_{cm} = 0.3074$, this yields constant values of Ω_a, Ω_b, and Ω_c, leading to:

$$\frac{R^2 T_{cm}^2}{P_{cm}} \alpha[\frac{T}{T_{cm}}, \omega_m] = \sum_i \sum_j x_i x_j \frac{R^2 T_{cij}^2}{P_{cij}} \alpha[\frac{T}{T_{cij}}, \omega_{ij}]$$ (16)

$$\frac{RT_{cm}}{P_{cm}} = \sum_i x_i \frac{RT_{cii}}{P_{cii}}$$ (17)

Equations (14) and (15) are now the same since b=c and it therefore appears that we have two mixing rules (Eqns. 16 and 17) for three pseudocritical properties T_{cm}, P_{cm}, and ω_m. However, to obtain ζ_{cm} = 0.3074, we must have:

$$\zeta_{cm} = \sum_i x_i \zeta_{ci}$$ (18)

with all ζ_{ci} = 0.3074. Joffe (1971) has shown that eqn. (18) implies that

$$\omega_m = \sum_i x_i \omega_i$$ (19)

Hence, we actually have three mixing rules for the three pseudocritical properties T_{cm}, P_{cm}, and ω_m in the Peng-Robinson equation.

Since a fourth mixing rule is required for the TP equation, we may assume that eqns. (10-12) may be used to obtain T_{cm}, P_{cm}, and F_m, whereas eqn. (18) may be used to obtain ζ_{cm}. We denote the Teja-Patel equation with these mixing rules as TP3.

The use of an overall pseudocritical value of ζ_{cm} in the calculations reduces the three-constant TP equation to a two-constant equation (since $b_m = c_m$ in this case). However, as ζ_{cm} varies with composition, each mixture is effectively replaced by a different hypothetical pure component, so that each mixture conforms to a different two-constant cubic equation of state.

RESULTS

We have calculated the critical locus curves of a number of binary mixtures using the various modifications of the TP and PR equations of state. In each case, Gibbs' criteria [1] for the critical point were solved using a technique that is similar in principle to those of Heidemann and Khalil (1980), Michelsen and Heidemann (1981), and Teja and Rowlinson (1973). Cubic lagrangian extrapolation was used to generate the guesses for the critical points required by the method. Since traces of the critical locus curves were made in small increments of mole fraction (typically 0.001) only one converged critical point anywhere on the curve was required to initialize the extrapolation procedure and to generate the complete critical locus. When binary interaction coefficients proved necessary for fitting the experimental data, these were determined by minimizing deviations between calculated and experimental mixture critical points. Only

binary systems have been studied in this work. The technique is, however, applicable to multicomponent mixtures, as shown by the authors cited above (Heidemann, 1980; Michelsen, 1981; Teja, 1973).

The TP1 equation and the PR equation gave very similar results and required similar values of the binary interaction coefficients to fit the critical curves. However, they gave poor predictions of the critical volumes, especially at large concentrations of fluids whose experimental critical compressibilities differ from the values of z_{ci} (TP1) or 0.3074 (PR). Figure 1 demonstrates this for the carbon dioxide + n-butane system.
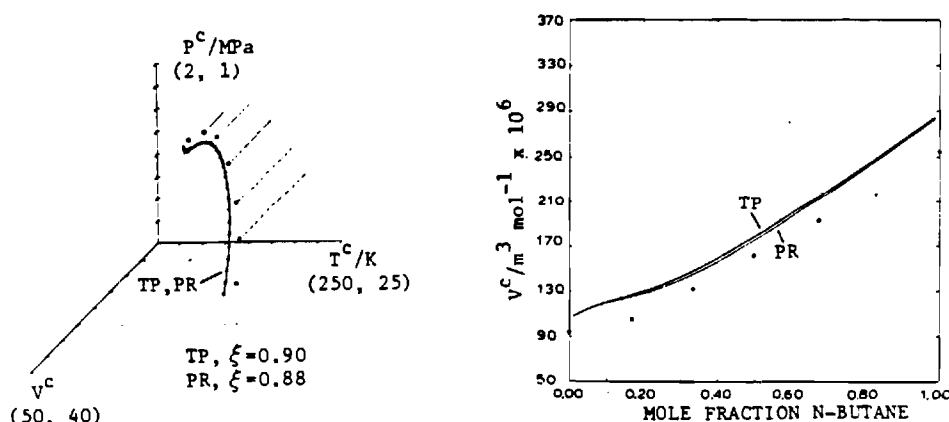
Fig. 1. The critical locus of a simple system using the TP1 and PR equations of state.

The displacement in volumes is readily apparent from the V_c vs x_c behavior of the system. Figure 2 shows how this displacement may be improved by essentially making the equation of state reproduce the pure component critical points (i.e., by setting $z_{ci} = Z_{ci}^{expt}$). Calculations with the TP2 and PR equations are shown in Fig. 2.

The PR equation cannot be made to fit the pure component critical points and simultaneously satisfy all the constraints of eqn. (6), because it only has two constants. The TP2 equation appears to give an excellent correlation of all critical properties (T_c, V_c, and P_c as functions of x_c). At first, this is surprising because no mixing rule has been used for z_{cm}. However, it should be noted that the experimental critical compressibilities of CO_2 and n-butane are identical being equal to 0.274 in both cases, so that the mixing rule for z_{cm} (eqn. (18)) would have made no difference to the calculated critical locus.

Figure 3 shows our calculations of the critical locus for an asymmetric system such as carbon dioxide + n-decane using the TP2, TP3, and PR equations.
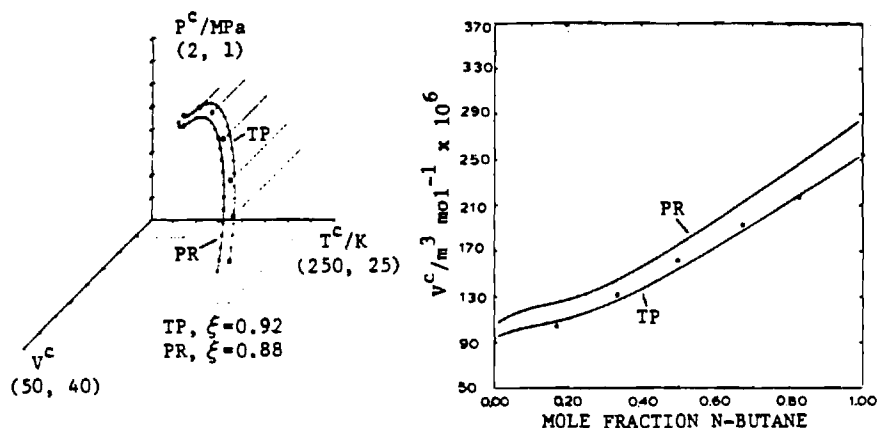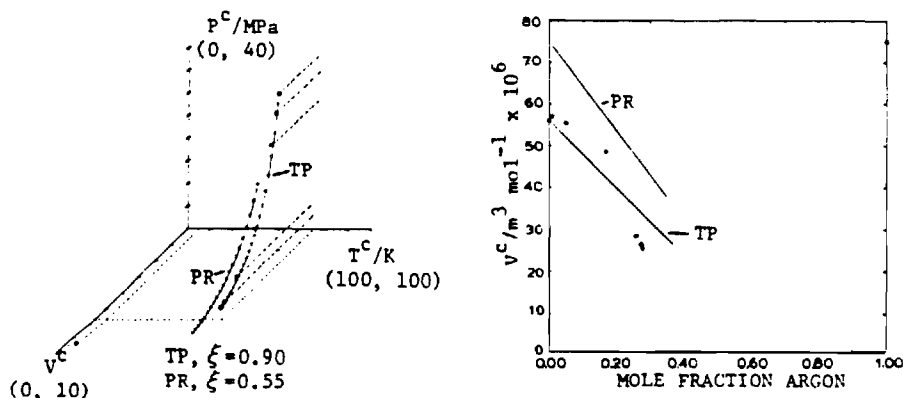
Fig. 2. The critical locus of a simple system using the TP2 and PR equations of state.
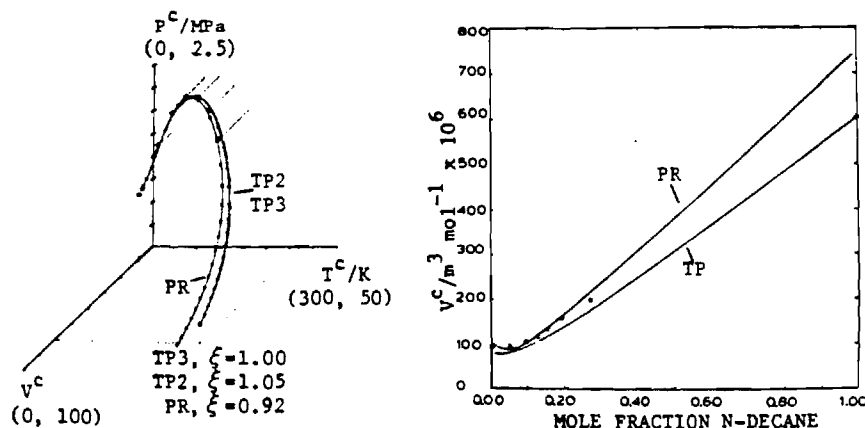
Fig. 3. The critical locus of an asymmetric system using the TP2, TP3, and PR equations of state.

The significant improvement over the PR equation is obvious. However, although the experimental critical compressibilities of the pure components are very different, the calculated values using the TP3 equation appear to be very similar to those using the TP2 equation. The value of the binary interaction coefficients (ξ_{ij}) is, however, 1.00 for the TP3 equation and 1.05 for the TP2 equation. We found that, in general, binary interaction coefficients were significantly closer to unity when the fourth mixing rule was introduced in the TP equation. Simply setting $\zeta_{ci} = Z_{ci}$ (as in the TP2 equation) caused large errors in the critical pressure predictions and required correspondingly large changes in the binary interaction coefficients to make calculations fit the experimental

data. Thus, although both the TP2 and TP3 equations worked equally well for the systems studied, the TP3 equation is recommended because of the closeness of the binary interaction coefficients to one. Finally, Figs. 4 and 5 show two complex systems--argon + water and isooctane + ammonia--where the advantages of the TP3 equation can readily be demonstrated.

Fig. 4. The critical locus of a complex system using the TP3 and PR equations of state.
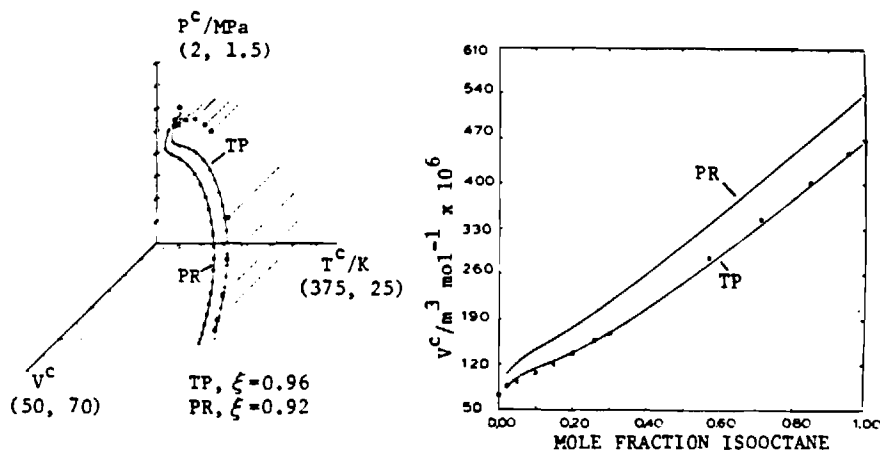
Fig. 5. The critical locus of another complex system using the TP3 and PR equations of state.

It would therefore appear that the use of the TP equation for the calculation of critical states of asymmetric and complex mixtures necessitates the use of mixing rules for each of the substance dependent equation of state parameters. This need is not obvious in simple mixtures because the critical compressibilities

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of the pure components are close to each other and this fact often masks the
distortion of the critical locus curve. This distortion can be seen when all
the critical properties are examined simultaneously. Critical point calculations
are particularly suited to such studies because their calculation requires three
differentiations of the mixing rules with respect to composition and therefore
they represent a most severe test of mixture models.

ACKNOWLEDGMENTS

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NOTES ON GRAPHS

Critical curves are given by solid or dashed curves while data are given by
circles. Each axis has a (ORIGIN, INCREMENT) coordinate. The origin number
begins at the coordinate axis ORIGIN and is incremented at each tic mark by the
INCREMENT. For added spatial effect, mixture data are projected into the P-T
plane using a fine dotted line and pure component data are projected into the
V-T plane by a heavier dotted line. Line of sight is adjusted to 45 by 45
degrees.

PHASE DIAGRAMS IN THE CRITICAL REGION USING AN EQUATION OF STATE

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The Teja-Patel cubic equation of state is used to predict critical curves in a variety of mixtures including mixtures of simple molecules, slightly asymmetric molecules, asymmetric molecules, and polar molecules. Density predictions are improved by introducing an additional mixing rule. Comparisons are shown with the Peng-Robinson equation of state and a corresponding states method.

INTRODUCTION:

Critical curves represent the boundary between the single phase and multiphase regions and are therefore of considerable importance in the phase diagram of fluids and fluid mixtures. In this work, we have employed two cubic equations of state as well as a Corresponding States method to calculate critical curves in a variety of binary systems. It is well known that cubic equations of state give poor representation of densities in the critical region. We show how the density predictions can be improved by introducing an additional mixing rule in one of the equations of state.

EQUATION OF STATE METHOD:

Teja and Patel [1] have recently proposed a cubic equation of state that accurately predicts the saturation density of a variety of fluids including paraffinic and aromatic hydrocarbon water and alcohols. They have also demonstrated the advantages of their equation of state over the Peng-Robinson and Soave equations for VLE calculations. In this work, therefore, we have examined the ability of the Teja-Patel equation to correlate the behavior of binary systems in the critical region.

The Teja-Patel (TP) equation is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+c(V-b)} \qquad (1)$$

where

$$a[T] = \alpha [T_R] \, \Omega_a \, R^2 T_c^2 / P_c \qquad (2)$$

$$b = \Omega_b \, RT_c / P_c \qquad (3)$$

$$c = \Omega_c \, RT_c / P_c \qquad (4)$$

$$\alpha[T_R] = \{1 + F(1-T_R^{0.5})\}^2 \qquad (5)$$

Ω_a, Ω_b, Ω_c are constants for a given substance which depend on the value of $(P_c V_c / RT_c)$ implied by the equation of state. F is a constant which is calculated from the vapor pressure curve of the substance. At the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \; ; \; \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \text{ and } \frac{P_c V_c}{RT_c} = \zeta_c \qquad (6)$$

The TP equation treats ζ_c as a parameter which is obtained by fitting the saturated liquid densities of each pure substance. We denote the value of ζ_c calculated in this manner as Z_m and the equation as TP1.

Since the values of Z_m required to fit liquid densities are, in general, greater than the experimental values of ζ_c at the critical point, an obvious modification of

the equation for calculations in the critical region is to let:

$$\zeta_c = Z_{c,expt} \qquad (7)$$

for each pure component considered. We denote this modification of the TP equation as TP2.

It should be noted here that when ζ_c is set equal to 0.3074 and c is set equal to b in the TP equation, the Peng-Robinson (or PR) equation results.

The TP equation may be extended to mixtures using the mixing rules

$$a_m = \sum_{ij} x_i x_j a_{ij} \ ; \ b_m = \sum_i x_i b_i \ ; \ c_m = \sum_i x_i c_i \qquad (8)$$

where the cross-interaction term is calculated using

$$a_{ij} = \xi_{ij} (a_{ii} a_{jj})^{1/2} \qquad (9)$$

and ξ_{ij} is an adjustable constant that is best evaluated from experimental data on the binary system.

Equations (8-9) are equivalent to those given by van der Waals for the parameters a and b in his equation of state. However, because of the temperature dependence of parameter a, these mixing rules are more complex than the original van der Waals one-fluid mixing rules. More importantly, the van der Waals a and b are functions of T_c and P_c only, whereas the TP constants are functions of T_c, P_c and ζ_c. Therefore, an additional mixing rule for ζ_c is required in our calculations. We have used the mixing rule:

$$\zeta_c = \sum_i x_i Z_{ci,expt} \qquad (10)$$

We denote this modification of the TP equation for mixtures as TP3.

CORRESPONDING STATES METHOD:

Only a brief description of this method is given here, since it has been described in detail elsewhere [2,3]. The equation of

state for a mixture is obtained via its configurational Helmholtz energy which, in turn, is obtained from the configurational Helmholtz energy of an equivalent substance (i.e. a one-fluid approximation) as follows:

$$A_m[V,T,x] = A_{eq}[V,T,x] + RT \sum_i x_i \ln x_i \qquad (11)$$

A_{eq} is obtained from the Helmholtz energy of the reference substance (methane in this study) whose properties are accurately known. Thus:

$$A_{eq}[V,T,x] = f A_0[V/h, T/f] - RT \ln h \qquad (12)$$

where the parameters f, h are obtained from the vdW one-fluid prescription as follows:

$$h = \sum_{ij} x_i x_j h_{ij} \ ; \ fh = \sum_{ij} x_i x_j f_{ij} h_{ij} \qquad (13)$$

The like-terms f_{ii}, h_{ii} are obtained from the ratios of the critical properties modified by shape factors [4] which depend on the size and shape of the molecules. The unlike terms are obtained from the Lorentz-Berthelot rules:

$$f_{ij} = \xi_{ij} (f_{ii} f_{jj})^{1/2} \qquad (14)$$

$$h_{ij} = \eta_{ij} (1/2 \ h_{ii}^{1/3} + 1/2 \ h_{jj}^{1/3})^3 \qquad (15)$$

Given an accurate equation of state for a reference fluid (and hence A_0), we can thus calculate the equation of state of the mixture using eqns. (11-15). The calculations can have up to two adjustable constants ξ_{ij} and η_{ij} per binary pair.

RESULTS

Given an equation of state for the binary mixture of interest, we can calculate its critical curve by solving Gibbs' equations for the critical point [5]. In this work, we have correlated the critical curves of various classes of systems, including simple systems, azeotropic systems, asymmetric systems and systems containing polar species. A summary of the single adjustable constant (ξ_{ij} or η_{ij}) required to obtain a best fit of the data is given in Table 1.

The TP1 equation and the PR equation yield very similar correlations and require similar values of the binary interaction coefficients to fit the critical curves. However, they give poor predictions of the critical volumes, especially at large concentrations of fluids whose experimental critical compressibilities differ from the values of Z_m (TP1) or 0.3074 (PR). This is shown in Fig. 1 for the methane + n-decane system. The experimental Z_c of n-decane of 0.247 is very different from 0.297 ($= Z_m$) or 0.3074, so that both the TP1 and PR equations are poor near the decane-rich end of the critical curve. When the TP2 equation ($\zeta_c = Z_{c,expt}$) was used for the same system, the volume predictions were improved but high binary interaction coefficients ($\xi_{ij} = 1.12$) were required to fit the pressure adequately. Obviously, a new mixing rule is required which allows the mixture ζ_c to vary continuously between the experimental critical compressibilities of the pure components, hence equation TP3.

Figures 2-5 show critical curves calculated using the TP3 and PR equations and using the Corresponding States Method (CSP). Figure 2 is an example of the continuous critical curve in a simple system (methane + n-pentane). The tilted nature of the curve predicted by the PR equation is typical of cubic equations with a fixed critical compressibility and is due to the inability of these equations to accurately predict volumes in the critical region. This error in volume increases as the pure component critical compressibilities deviate from the fixed values implied by these equations. When this limitation is overcome, either by using an additional mixing rule (as in the TP3 equation) or by using an accurate equation of state for the pure fluids (as in the CSP method), a marked improvement in the calculated curve results. This improvement is evident in the phase diagrams of CO_2 + ethane (azeotropic system), CO_2 + n-decane (asymmetric system) and H_2O + argon (system containing polar species) shown in Figs. 3-5. The H_2O + argon system is interesting because it exhibits gas-gas immiscibility. It is remarkable how well the TP3 equation is able to correlate this kind of behavior. This simple modification is also able to correlate data as well as the more complex CSP method and, indeed, is much better for mixtures containing components whose properties cannot be predicted from the properties of methane and the CSP method.

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APPENDIX.

Notes on diagrams: In Fig. 1-5, calculated critical curves are given by solid lines and experimental data (taken from the compilation of Hicks and Young [6]) are given by circles. Each P, V or T axis is labelled (ORIGIN, INCREMENT). This gives the co-ordinate of the origin and the increment per tic mark. For added spatial effect, mixture data are projected into the plane of the paper by a dotted line.

Table 1. Binary Interaction Coefficients ξ_{ij} and η_{ij}

System	TP1 ξ_{ij}	TP2 ξ_{ij}	TP3 ξ_{ij}	PR ξ_{ij}	CSP ξ_{ij}	η_{ij}
$CH_4 + C_3H_8$	0.98	1.08	1.05	1.00	1.00	1.04
$CH_4 + nC_4H_{10}$	1.00	-	1.04	0.97	1.00	1.02
$CH_4 + nC_5H_{12}$	1.02	-	1.14	1.02	1.00	1.02
$CH_4 + nC_6H_{14}$	1.03	-	1.04	1.00	1.00	0.96
$CH_4 + nC_7H_{16}$	1.02	-	1.06	0.98	1.00	0.94
$CH_4 + nC_{10}H_{22}$	1.00	1.12	1.04	0.98	1.00	0.81
$CO_2 + C_2H_6$	-	0.87	0.87	0.87	1.00	0.90
$CO_2 + C_3H_8$	0.88	0.89	0.89	0.89	1.00	0.88
$CO_2 + nC_4H_{10}$	0.90	-	0.92	0.88	1.00	0.88
$CO_2 + nC_5H_{12}$	0.93	-	0.92	0.90	1.00	0.85
$CO_2 + nC_{10}H_{22}$	0.93	-	1.00	0.92	1.00	0.81
$CO_2 + nC_{16}H_{34}$	1.00	-	1.09	1.00	-	-
$C_2H_4 + C_{10}H_8$	1.05	-	1.15	1.02	0.90	1.00
$NH_3 + iC_8H_{18}$	-	-	0.96	0.92	-	-
$C_2H_4 + C_2H_5OH$	0.96	1.15	1.35	1.10	-	-
$Ar + H_2O$	-	-	0.90	0.55	-	-

P* [MPa]
(0.0, 8.0)

T* [°K]
(150, 60)

V* [m³·mol⁻¹]×10⁶
(0, 100)

METHANE + N-DECANE
(ORIGIN, INCREMENT)
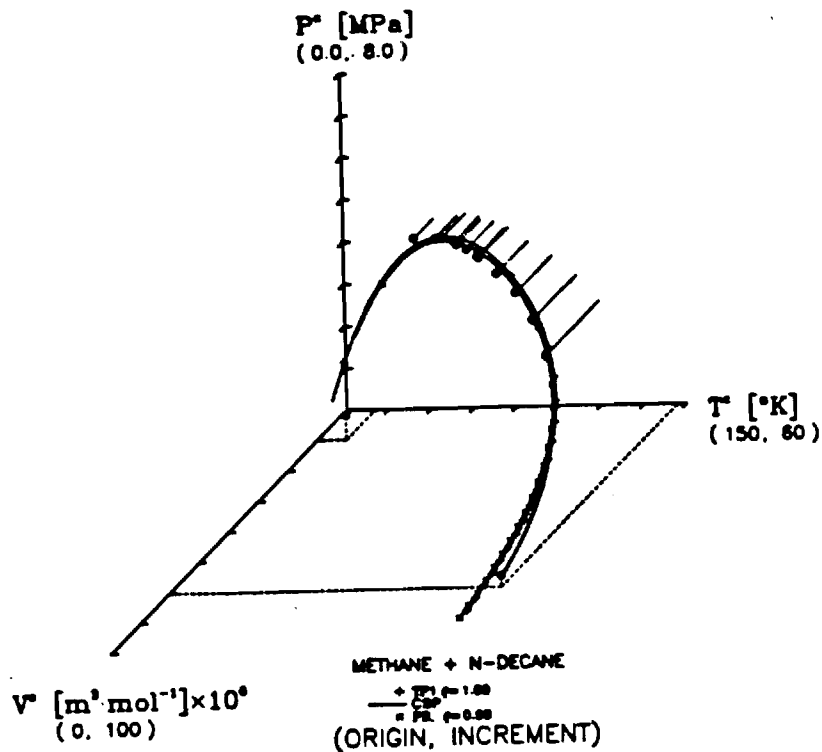
Figure 1. Methane + n-Decane System

P° [MPa]
(0.0, 3.0)

T° [°K]
(150, 50)

V° [m³·mol⁻¹]×10⁶
(50, 40)

METHANE + n-PENTANE

(ORIGIN, INCREMENT)
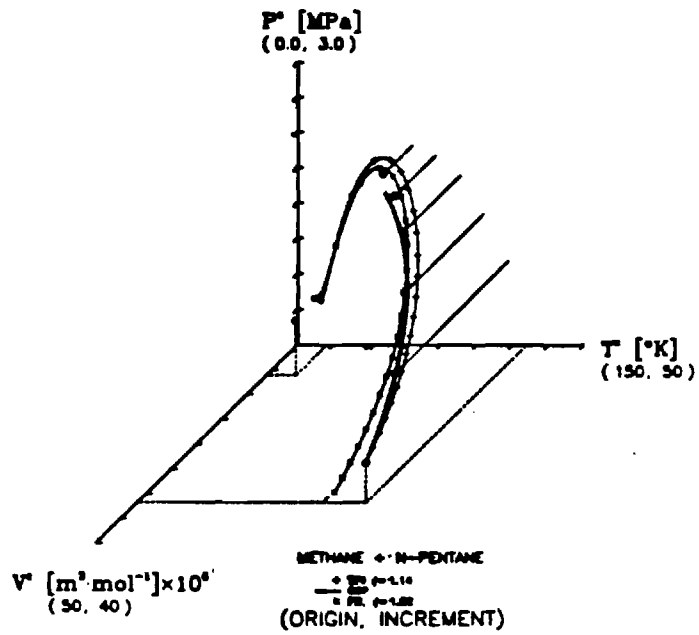
Figure 2. Methane + n-Pentane System

P° [MPa]
(4.0, 1.0)

T° [°K]
(290, 2)

V° [m³·mol⁻¹]×10⁶
(94, 9)

ETHANE + CARBON DIOXIDE

(ORIGIN, INCREMENT)
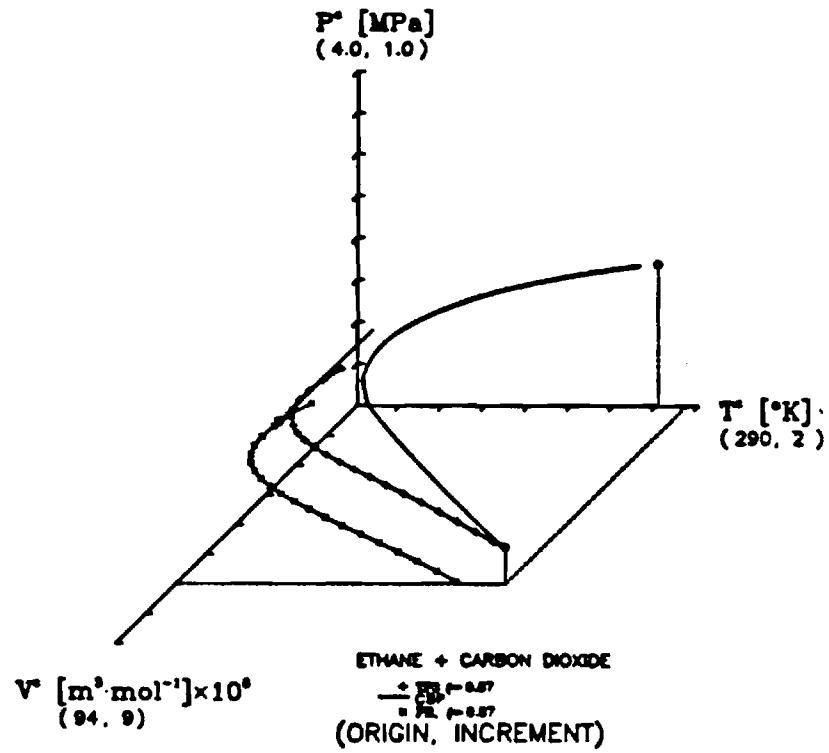
Figure 3. Ethane + Carbon Dioxide System

P° [MPa]
(0.0, 2.5)

T° [°K]
(300, 50)

V° [m³·mol⁻¹]×10⁶
(0, 100)

N—DECANE + CARBON DIOXIDE

(ORIGIN, INCREMENT)
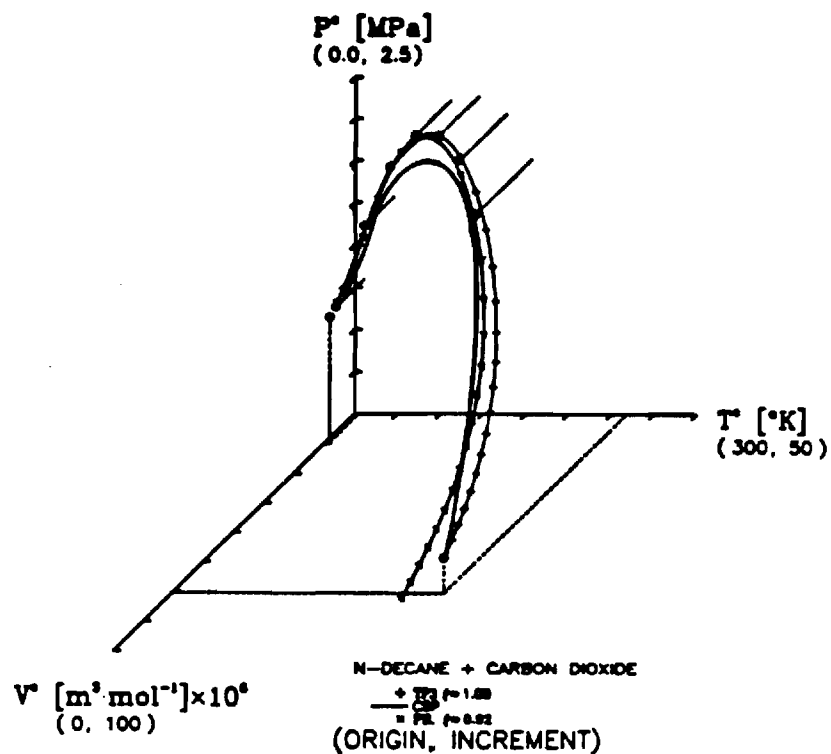
Figure 4.   n-Decane + Carbon Dioxide System

P° [MPa]
(0.0, 40.0)

T° [°K]
(100, 100)

V° [m³·mol⁻¹]×10⁶
(0, 10)

ARGON + WATER

(ORIGIN, INCREMENT)
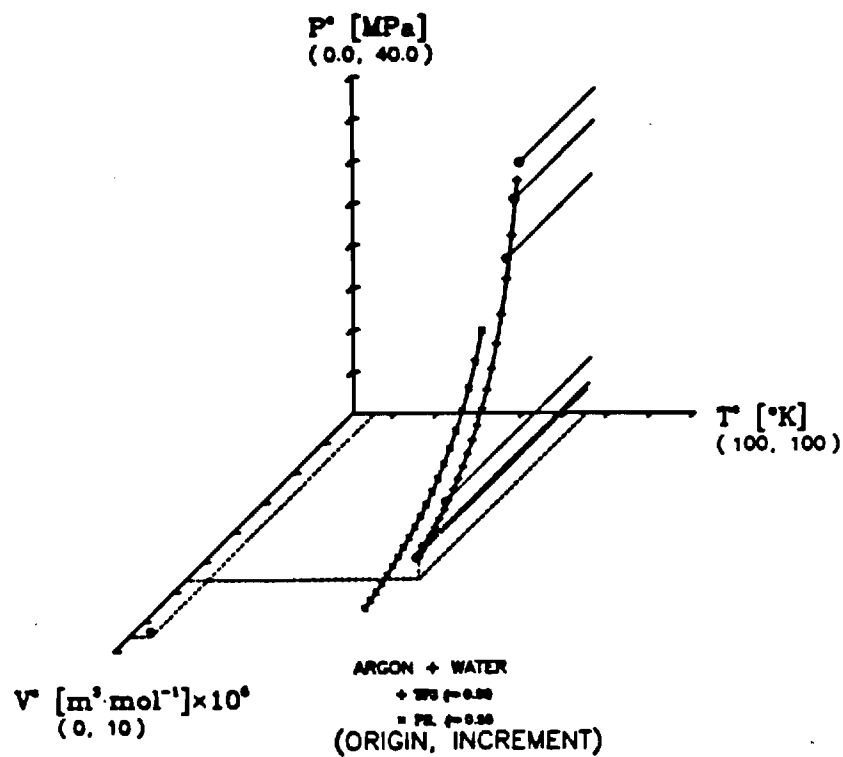
Figure 5.   Argon + Water System

THE CORRELATION AND PREDICTION
OF CRITICAL STATES OF MIXTURES
USING A CORRESPONDING STATES
PRINCIPLE

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Abstract

The calculation of critical states using a Corresponding States Principle is described. It is shown how a correlation of binary critical T^c - P^c behavior can lead to predictions of high pressure as well as low pressure phase equilibria and PVT properties. Critical states (including V^c - x^c behavior) of hydrocarbon systems as well as systems containing polar components have been successfully correlated using this method. The applicability of the method to asymmetric mixtures which are typical of supercritical extraction processes is examined.

Introduction

The PVT behavior of mixtures in the critical region is of practical importance in the petroleum and energy industries and also in processes involving supercritical gas extraction. Indeed, a knowledge of phase equilibria in the critical region is necessary for assessing the feasibility of supercritical gas extraction processes.

The calculation of critical lines of mixtures is also of theoretical interest, since the topology of these lines in the PVTx space is complex and it may be argued that their calculation provides a most severe test of any theory.

In this work, we outline an extended Corresponding States method which has been used with considerable success for the calculation of densities [1-3], vapor-liquid equilibria [3-5] and critical and azeotropic states [6,7] of

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$$h_{ii,o} = (V_{ii}^c/V_o^c) \, \phi_{ii,o} \tag{4}$$

where the shape factors $\theta_{ii,o}$ and $\phi_{ii,o}$ are unity for simple spherical fluids and are slowly varying functions of reduced temperature T_{Ri} and reduced volume V_{Ri} in the general case. They may be thought of as small perturbations of the reduced temperature and volume. Analytical expressions for the shape factors have been reported by Leland and Chappelear [10] and by Ely and Hanley [11]. They are of the form:

$$\theta_{ii,o} = 1 + (\omega_{ii} - \omega_o) \, F_1[T_{Ri}, V_{Ri}]$$

$$\phi_{ii,o} = (Z_o^c/Z_{ii}^c) \, \{1 + (\omega_{ii} - \omega_o) \, F_2[T_{Ri}, V_{Ri}]\}$$

where F_1 and F_2 are functions of the reduced temperature and volume. Although the Leland shape factor correlations were originally obtained for the n-alkanes (up to about n-decane) relative to methane, the utility of this method lies in the fact that they have been used successfully for other hydro-carbons and for polar and quantum fluids [3,7]. Deviations from experiment are small for the n-alkanes and somewhat larger for polar and quantum fluids, as expected [7]. It should be noted that the deviations of the shape factors from unity are proportional to the differences in the acen-tric factors as well as to the ratio of the critical com-pressibility factors of the two substances i and o. For normal fluids, the critical compressibility factor Z^c is a linear function of the acentric factor and a three-parameter form of the Corresponding States Principle results. For fluids for which Z^c is no longer a linear function of ω, a four-parameter Corresponding States Principle is obtained.

Given the properties of a reference substance (these may, for example, be obtained from an accurate equation of state or from tabulated PVT properties) and the shape factor correlations, then the calculation of the thermodynamic pro-perties of any substance i requires a knowledge only of its critical constants T_{ii}^c, V_{ii}^c, Z_{ii}^c and ω_{ii}.

Equation (2) may be extended to mixtures by assuming that the configurational Helmholtz energy of a mixture, after subtraction of a combinatorial term, is equal to that of a single hypothetical equivalent substance. This is the so-called one-fluid model for mixtures.

$$A_{mixture} [V,T,x] = A[V,T,x] + A_{comb} \tag{7}$$

The configurational Helmholtz energy of the equivalent sub-stance $A[V,T,x]$ may then be obtained from that of the refe-rence substance using eqn. (2):

mixtures when the components of the mixture do not differ too
greatly in size. The applicability of the method to asym-
metric mixtures (such as ethylene + naothalene, which are
typical of supercritical extraction processes) is examined.

The Extended Corresponding States Method

A large number of methods for the calculation of thermo-
dynamic properties make use of extensions of the (two para-
meter) Corresponding States Principle. These extended Corre-
sponding States methods may be divided into two broad cate-
gories. The first, and by far the largest, category involves
a perturbation of a thermodynamic (configurational) property
about that of a spherical reference fluid. The theoretical
justification for this perturbation was presented by Pitzer
[8] who showed that the compressibility Z_{11} of fluid i at
reduced temperature T_R and reduced pressure P_R is given by
the sum of the compressibility $Z^{(0)}$ of a spherical reference
fluid at the same reduced temperature and pressure and a de-
viation $\omega_{11} Z^{(1)}$ which is proportional to the acentric factor
ω_{11} of substance i. Thus

$$Z_{11}[T_R,P_R] = Z^{(0)}[T_R,P_R] + \omega_{11} Z^{(1)}[T_R,P_R] \qquad (1)$$

Teja et. al. [9] later showed that the perturbation may be
carried out about the property of a nonspherical reference
fluid.
The second category of extended Corresponding States
methods involves a perturbation of the variables T_R and V_R
(or P_R) and has been termed the shape factor approach by
Leland [10]. It is this approach that is described below.
For convenience, the shape factor approach will be described
in terms of the configurational Helmholtz energy rather than
compressibility, as the former is more suited to the calcu-
lations performed in this study.
Two pure substances i and o are defined to be in corre-
sponding states if the configurational Helmholtz energy of
substance i at temperature T and volume V may be obtained
from the configurational Helmholtz energy of substance 0 at
temperature $T/f_{11,o}$ and volume $V/h_{11,o}$ as follows:

$$A_{11}[T,V] = f_{11,o} A_o[T/f_{11,o}, V/h_{11,o}] - RT \ln h_{11,o} \qquad (2)$$

where the subscripts ii,o signify a property of i relative
to substance o. The parameters $f_{11,o}$ and $h_{11,o}$ are related
to the critical constants of substances i and o by

$$f_{11,o} = (T_{11}^c/T_o^c) \theta_{11,o} \qquad (3)$$

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$$A[V,T,x] = f \, A_o[T/f, \, V/h] - RT \ln h \qquad (8)$$

where the parameters f and h depend on the composition of the mixture. Various prescriptions may be written for these parameters. A convenient form of these prescriptions is as follows:

$$f \, h^\delta = \Sigma\Sigma \; x_i x_j f_{ij} h_{ij}^\delta \qquad (9)$$

$$h = \Sigma\Sigma \; x_i x_j h_{ij} \qquad (10)$$

When $\delta=0$, these equations reduce essentially to the modified Kay's model proposed by Prausnitz and Gunn [12]; setting $\delta=1$ leads to the van der Waals one fluid model [10], and setting $\delta=0.25$ leads to the model proposed by Plöcker et. al. [13] for mixtures in which the molecular sizes of the components differ by a factor of 3 or more. It should be added that the critical temperatures and volumes used in the original one-fluid models described above are "weighted" by the shape factors in equations (9) and (10). Moreover, to obtain the shape factors in a rigorous manner, an iterative solution of equations (9) and (10) is necessary.

In using eqns. (9) and (10), the like terms (i=j) may be obtained from pure component properties, but the unlike terms (i≠j) require mixture data for their evaluation. The usual procedure is to transfer the problem of evaluating f_{ij}, h_{ij} to the problem of evaluating the binary interaction coefficients ξ_{ij} and η_{ij}, where:

$$f_{ij} = \xi_{ij}(f_{ii}f_{jj})^{1/2} \qquad (11)$$

$$h_{ij} = \eta_{ij}\{(h_{ii}^{1/3} + h_{jj}^{1/3})/2\}^3 \qquad (12)$$

Values of ξ_{ij} and η_{ij} are generally close to unity and no further information is required to predict the properties of ternary and higher mixtures [7].

For nonpolar mixtures in which the molecular sizes of the components differ by a factor of 3 or less, it is usually sufficient to use one adjustable coefficient to characterize each binary system and it is common to assume $\eta_{ij}=1.0$, with ξ_{ij} being calculated from experimental data. Values of ξ_{ij} estimated from the correlation of various thermodynamic properties and phase equilibria agree very well with each other [7], but depend on the particular prescription (eqns. 9-10) chosen.

The combinatorial contribution to the Helmholtz energy for an ideal mixture is given by:

$$A_{comb} = RT \; \Sigma_i \; x_i \ln x_i \qquad (13)$$

When the molecules differ appreciably in size, this equation is known to be inadequate. The Flory-Huggins equation was derived for monmer-polymer mixtures (i.e. for molecules made up of like segments), but it has been applied to many different asymmetric mixtures. This equation is given by:

$$A_{comb} = RT\Sigma \ x_i \ln\psi_i \qquad (14)$$

where the volume fraction ψ_i is given by:

$$\psi_i = x_i \ V_{ii}/\Sigma_j \ x_j V_{jj} \qquad (15)$$

In the binary case, we may write the two volume fractions by:

$$\psi_1 = x_1/(x_1 + r \ x_2) \qquad (16)$$

$$\psi_2 = rx_2/(x_1 + rx_2) \qquad (17)$$

where

$$r = V_{11}/V_{22} \qquad (18)$$

is the ratio of molar volumes (or the ratio of semiarbitrarily defined segments). Since the systems considered in this study are not polymer solutions, we have treated r as an empricial parameter in this study. Previous studies have shown [7,14] that r = 1 when the components of a mixture do not differ appreciably in size.

Critical States of Binary Mixtures

Critical states of binary mixtures satisfy the following equations [6]:

$$A_{2x} \cdot A_{2v} - A_{xv}^2 = 0 \qquad (19)$$

$$A_{3x} \cdot A_{2v}^3 - 3 \ A_{2xv}A_{xv}A_{2v}^2 + 3 \ A_{x2v}A_{xv}^2 A_{2v} - A_{3v}A_{xv}^3 = 0 \qquad (20)$$

where the subscripts denote derivatives e.g.

$$A_{2xv} = \partial^3 A/\partial x^2 \ \partial V$$

It should be noted that these equations contain second and third derivatives of the Helmholtz energy (and, therefore, of the one-fluid model-eqns. 9, 10 and 14) with respect to composition. It may therefore be argued that the calculation of critical states represents a severe test of the mixture model chosen, since errors will tend to increase with successive differentiation of the function.

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Solution of the two equations at a given critical composition gives the critical temperature and volume (and hence the critical pressure) of the system. Details of the procedure are given elsewhere [6].

Results

Methane was chosen as the reference substance, since an accurate analytical equation of state is available for this substance and shape factor correlations relative to methane are also available. The critical properties and acentric factors of the pure components were taken from the compilation by Ambrose [15]. Results of the calculation of critical curves of binary mixtures are discussed below.

Figures 1-3 show typical results for a nonpolar hydrocarbon mixture (methane + propane) in which the components do not differ appreciably in size.
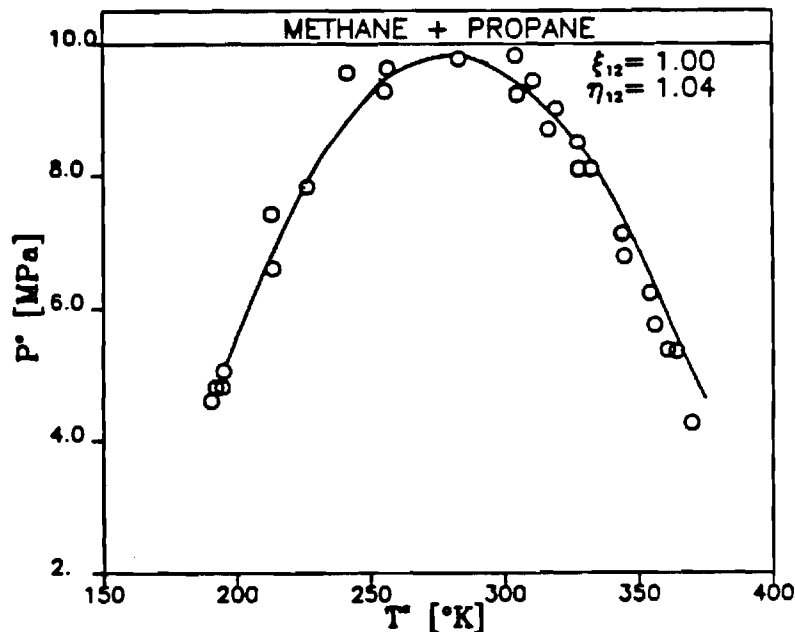
Figure 1. P^c vs T^c behavior of the methane + propane system. The predicted critical curve is shown by the full line whereas the experimental points are shown by circles.
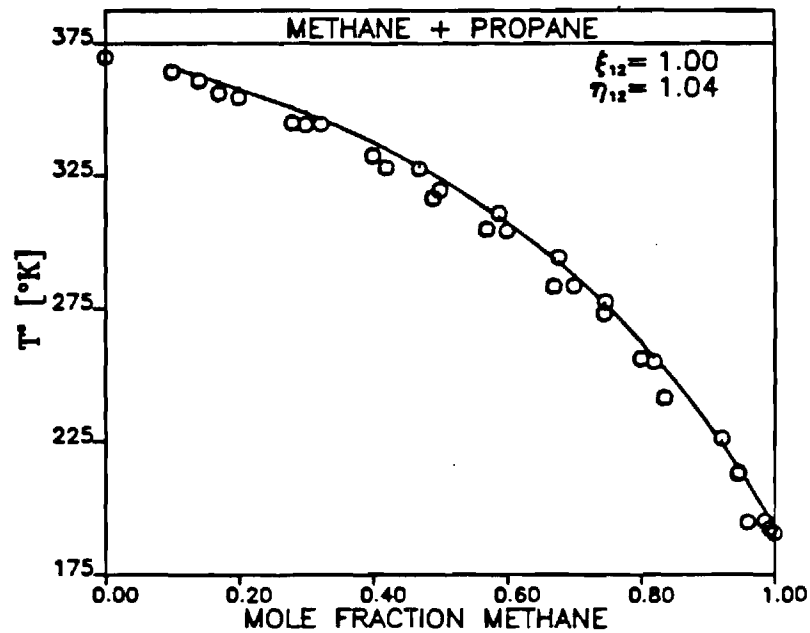
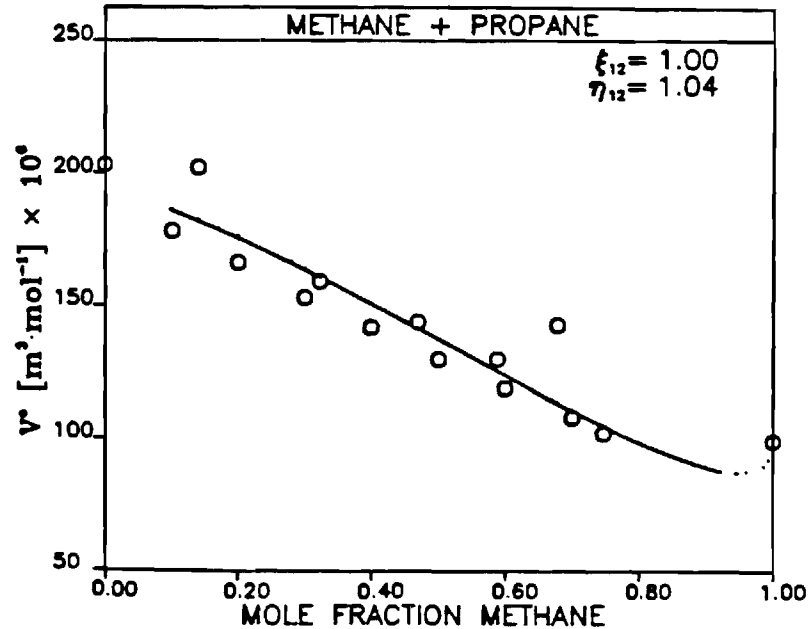Figure 2. The predicted and experimental T^c vs x^c behavior of the methane + propane system.

Figure 3. The predicted and experimental V^c vs x^c behavior of the methane + propane system with $\xi_{12} = 1.0$ and $\eta_{12} = 1.04$.

It is seen that P^c vs T^c vs. x^c curves can be correlated with ξ_{12} = 1.0 and η_{12} = 1.04 when the van der Waals one-fluid prescription (δ=1) and the ideal combinatorial term (r=1) are used for this system. In general, only one binary interaction coefficient - close to unity - is required for such systems [6,7]. Moreover, Barber et. al. [16] have shown that the single binary interaction coefficient calculated from the critical states of mixtures can be used to predict vapor-liquid equilibria and second virial coefficients of the system. This is shown in Figs. 4 and 5 which show the azeotropic locus and second virial coefficients of propane + perfluorocyclobutane mixtures calculated with ξ_{12} = 0.89 which was obtained from the correlation of the critical states of the system [16]. A number of authors [1,3,5] have used two binary interaction coefficients to characterize each binary mixture. Our studies have shown that the use of two adjustable coefficients leads to values which are not unique and which do not necessarily show a regular trend for a series of binary mixtures with a common component. The latter is usually true when only one adjustable coefficient is used in the calculations.
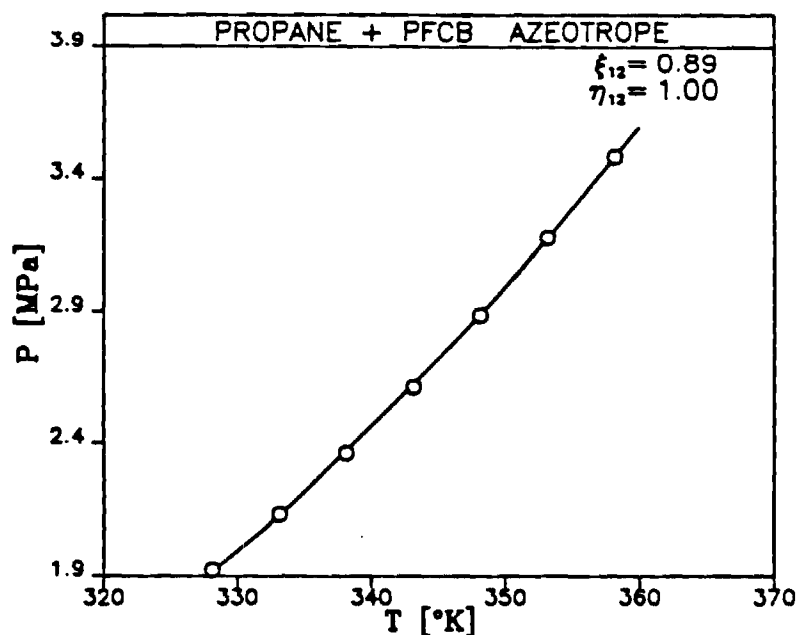

Figure 4. The azeotropic locus of propane + perfluorocyclobutane mixtures predicted with ξ_{12} = 0.89, η_{12} = 1.0.
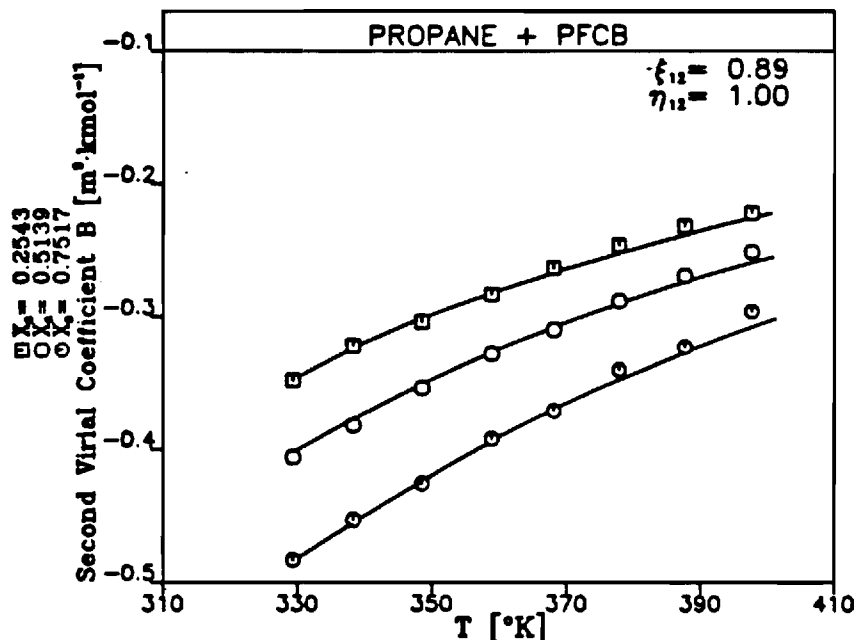
Figure 5. Second virial coefficients of propane + perfluoro-
cyclobutane mixtures predicted with ξ_{12} = 0.89,
η_{12} = 1.0

Figures 6-12 show the results of our calculations for
three asymmetric mixtures (methane + n-decane, CO_2 + n-decane
and ethylene + napthalene) in which the components differ in
size (as measured by the ratio of their critical volumes) by
a factor of 3 or more. These systems are typical of those
found in supercritical extraction. In general, there is a
great deal of uncertainty in the available values of the cri-
tical volumes of large molecules (indeed, the critical vol-
umes of many single and multi-ring aromatic compounds are not
known). For asymmetric mixtures, we have therefore replaced
eqn. (4) with

$$h_{ii,o} = \{ (T^c_{ii}/P^c_{ii})/(T^c_o/P^c_o) \} \, \phi_{ii,o} \qquad (21)$$

This equation has the advantage that critical volumes are not
required and is equivalent to a slight modification of the
mixture model (i.e. of multiplying $h_{ii,o}$ in eqns. (9) and
(10) by z^c_{ii}/z^c_o). We have found that this modification leads
to better predictions than the original model (there is of
course little change for mixtures of small molecules since
$z^c_{ii} \approx z^c_o$). Figs. 6-12 show that one adjustable binary inter-
action coefficient is no longer adequate for the correlation
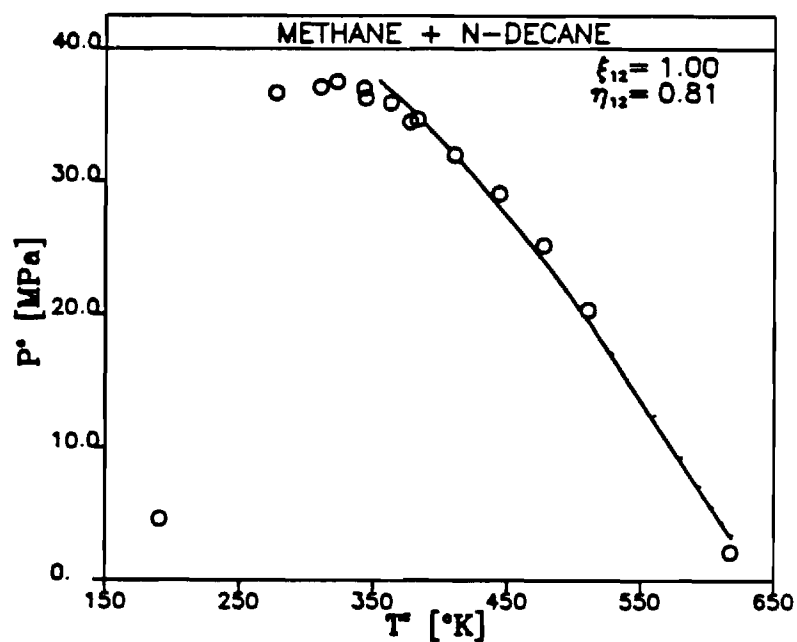of the critical properties of asymmetric mixtures.

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Figure 6. P^c vs T^c behavior of the methane + n-decane system
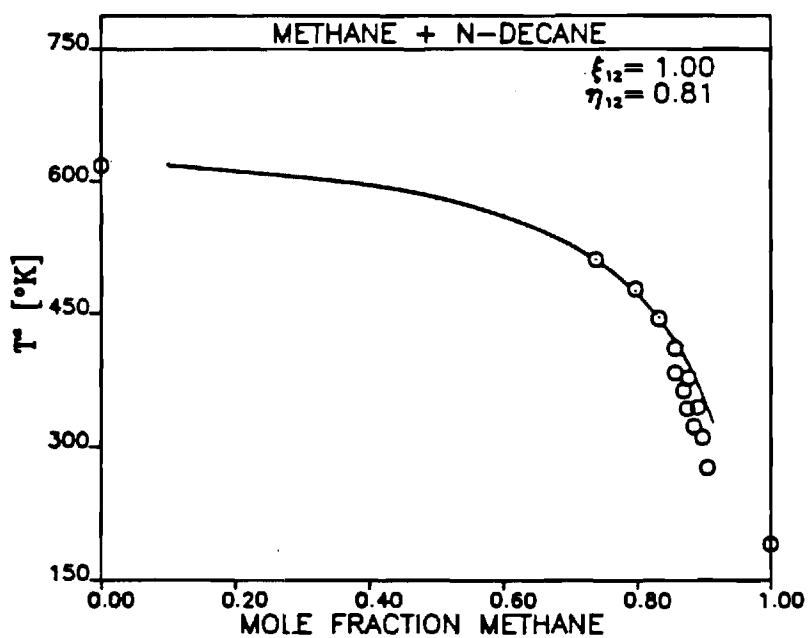

Figure 7.   The predicted and experimental T^c vs x^c behavior
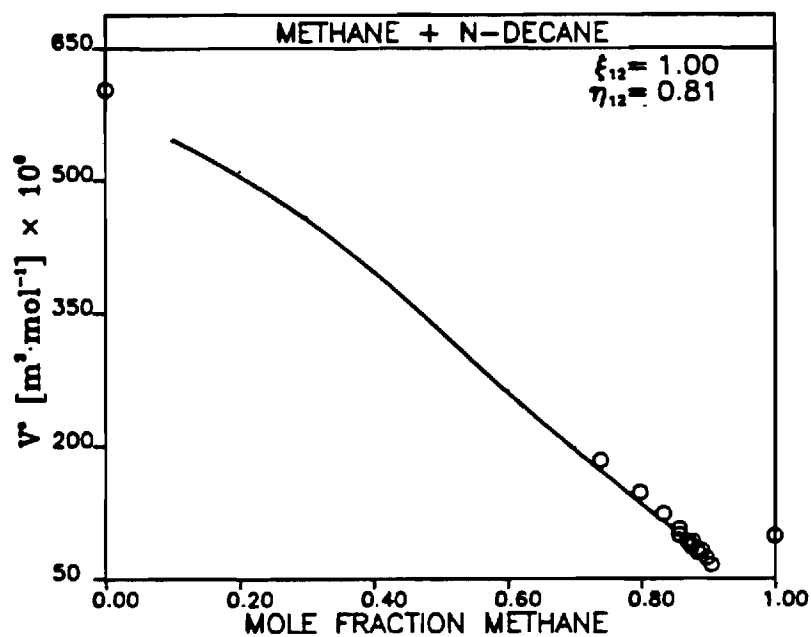of the methane + n-decane system

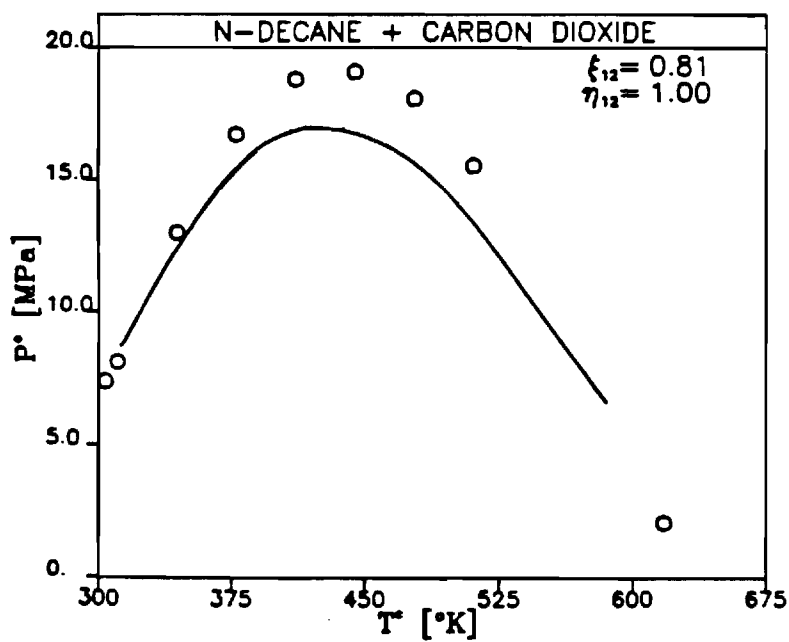Figure 8. V^c vs x^c behavior of the methane + n-decane system

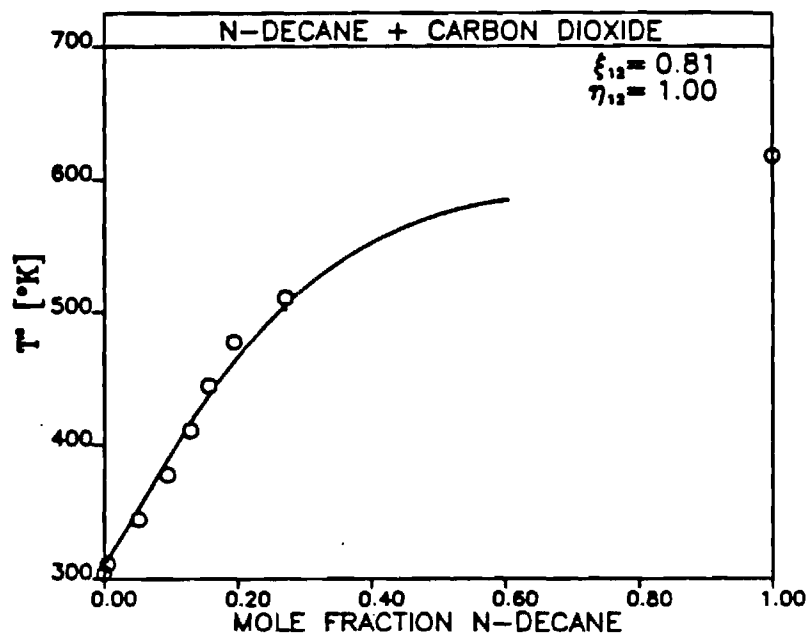Figure 9. The predicted T^c vs x^c behavior of the n-decane + CO_2 system

Figure 10. The predicted and experimental T^c vs x^c behavior
of the n-decane + CO_2 system

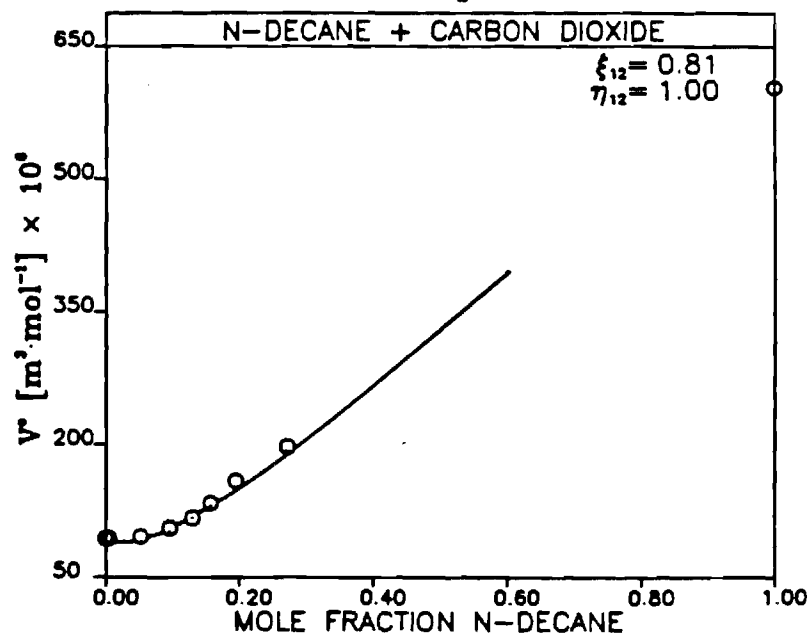Figure 11. The predicted and experimental V^c vs x^c behavior
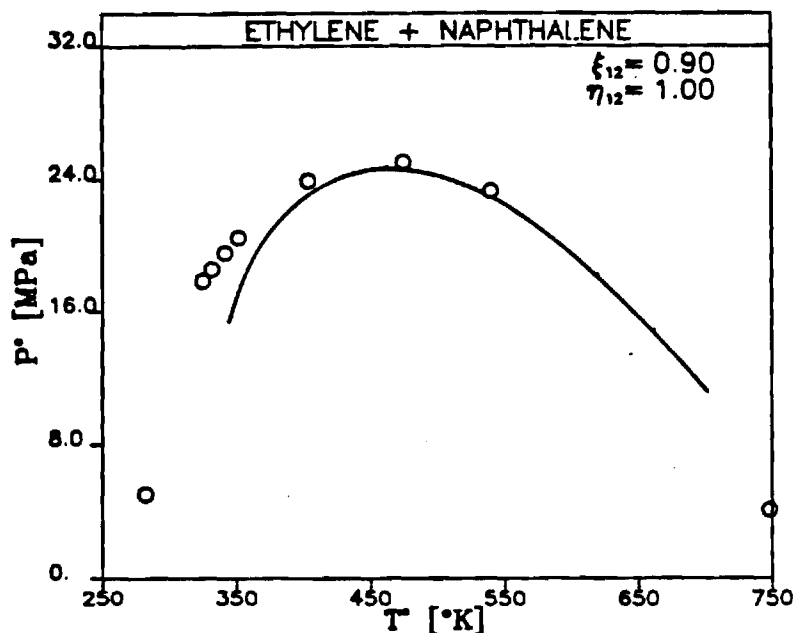of the n-decane + CO_2 system

Figure 12. The predicted and experimental P^c vs T^c behavior
of the ethylene + napthalene system

The use of the Flory-Huggins combinational term did not
lead to a reduction in the number of adjustable coefficients
required. It would therefore appear that only a small con-
tribution to the Helmholtz energy can be attributed to the
combinatorial term. The major effect of varying r appears to
be on the critical pressure of the system, with critical
temperature remaining practically unchanged. However, the
accuracy of critical data in practice does not warrant the
use of three adjustable constants in any method and r was set
to unity in all other systems reported here. Use of the
Plocker et. al. [13] one-fluid model ($\delta=0.25$) did not also
lead to a reduction in the number of adjustable constants re-
quired. Hence the van der Waals one-fluid model ($\delta=1$) was
used in all calculations presented in this work. Our calcu-
lations lead us to believe that only slight modifications of
the van der Waals one-fluid model are required for the treat-
ment of asymmetric mixtures.

It may be argued that part of the errors that arise in
the treatment of asymmetric mixtures may result from the fact
that the properties of large molecules (such as n-decane or
n-hexadecane) cannot be obtained from the properties of
methane using the shape factor correlations. That this is
not so is demonstrated conclusively in Figures 13 and 14,
which shown T^c vs x^c curves for n-hexane + n-tridecane and
n-hexane + cis-decalin mixtures. These systems can be

adequately correlated with the extended corresponding states
method, although the components of the mixture are large.
The relative size differences in these systems are, of
course, less than 3.
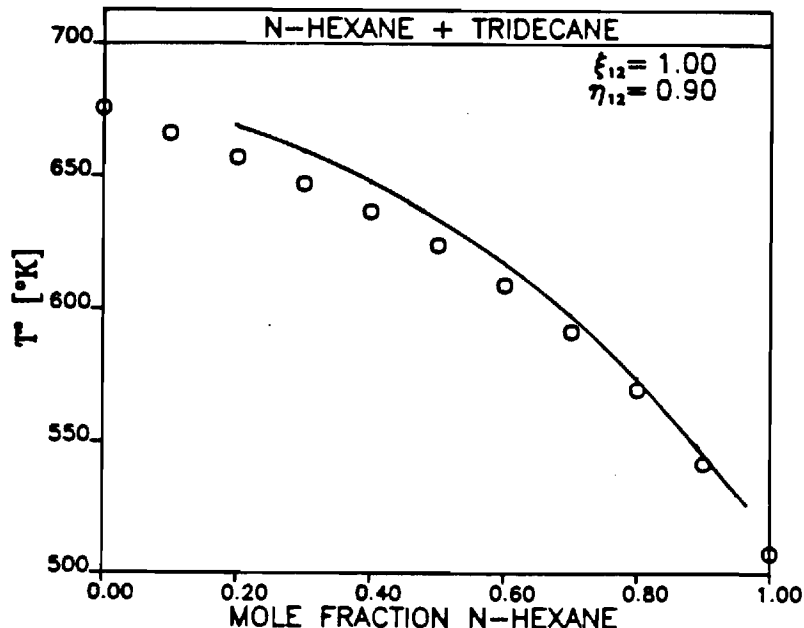
Figure 13. Experimental and calculated T^c vs x^c behavior of
the n-hexane + n-tridecane system

A final observation that should be mentioned is that T^c
vs x^c behavior of many systems (including asymmetric mix-
tures) can often be correlated equally well by various mix-
ture models (e.g. van der Waals, Plöcker et. al. etc.). It is
obvious that T^c vs x^c behavior alone is not sufficient to
distinguish between the various models and we therefore sug-
gest that a simultaneous fit of P^c-T^c-V^c-x^c data be used to
obtain any adjustable constants. In general, we have found
the van der Waals one-fluid model to be the best among the
mixture models tested - although there is room for improve-
ment for asymmetric mixtures.

Conclusions

We have examined the applicability of an extended Cor-
responding States Method using shape factors to the calcula-
tion of critical states of asymmetric mixtures which are
typical of systems used in supercritical extraction. Various
modifications of the method have been evaluated. In general,
the van der Waals one-fluid model appears to yield results
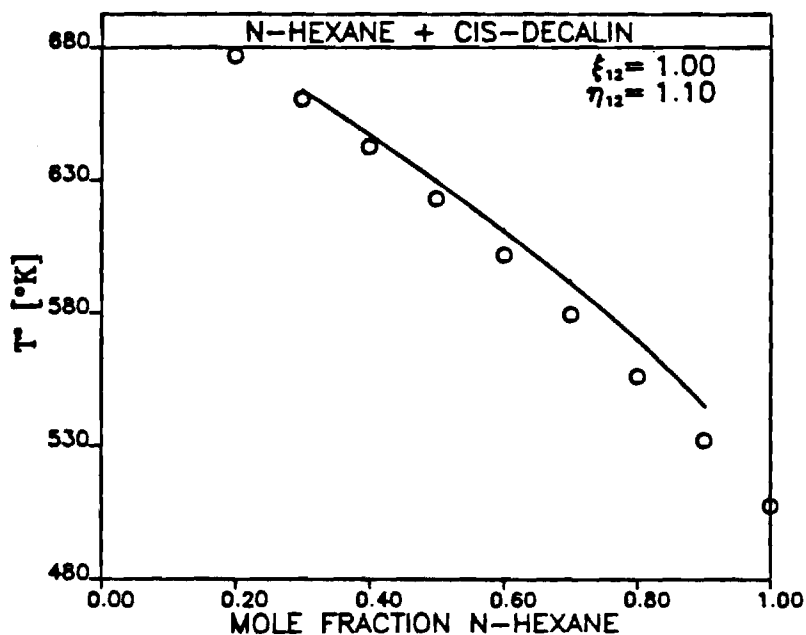
Figure 14. Experimental and calculated T^c vs x^c behavior of
the n-hexane + cis-decalin system

which compare well with experiment, although there remains
room for improvement. The method provides a means for the
quantitative prediction of the behavior of interest in super-
critical extraction.

Acknowledgment

Nomenclature

A   Helmholtz energy
F   functions in eqns. (5) and (6)
f   Corresponding States energy parameter
h   Corresponding States size parameter
P   pressure
R   gas constant
r   adjustable constant
T   temperature
V   volume
x   mol fraction
Z   compressibility factor

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Greek Symbols

δ	exponent in mixture model (eqn. 9)
ξ	binary interaction coefficient
η	binary interaction coefficient
ω	acentric factor
θ	shape factor for energy (temperature)
ϕ	shape factor for size (volume)
ψ	volume (or segment) fraction

Subscripts

comb	combinatorial
i,j	components i.j
o	reference fluid
1,2	components 1,2

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HIGH PRESSURE DENSITIES OF MIXTURES OF COAL CHEMICALS

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ABSTRACT

Densities of seven coal chemicals (benzene, toluene, tetralin, quinoline, m-cresol, bicyclohexyl and 1-methylnapthalene) and their binary mixtures at temperatures between 298K and 338K and pressures between 0.1 MPa and 34.5 MPa were measured using a high-pressure vibrating tube densitometer and are reported in this paper. The pure component densities were correlated using a modified Tait equation. The pure components were then used as reference fluids in a corresponding states method for the prediction of the densities of the mixtures.

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INTRODUCTION:

The thermodynamic and transport properties of the components of coal fluids, especially at elevated pressures and temperatures, are of great importance in the design and development of processes for coal liquefaction and gasification. Coal liquids typically consist of a variety of components including polycyclic aromatic hydrocarbons with substituted functional groups of nitrogen, sulfur and oxygen. These fluids have a wide range of properties, making the task of physical property prediction very difficult. Moreover, measurements on actual coal liquids are extremely difficult to make because of the reactive nature of the components, devolatilization, aging and so on. It is also not certain that physical property data obtained using fluids from one coal sample can be used for fluids from other coal samples. A strong case can therefore be made for the study of model coal compounds and their mixtures, as these studies are much more likely to yield fundamental information for the development of predictive methods.

Until recently, most available physical property correlations for coal liquids were based on petroleum data. The application of these petroleum-based correlations, however, often leads to unacceptable errors because of the extreme conditions and much higher aromatic content of the coal liquids. This has led to several attempts to develop specific correlations for coal liquids [1 - 3]. These studies have revealed a need for more experimental data on model coal compounds and their mixtures.

This work is therefore concerned with the measurement of high pressure densities of seven model coal compounds (benzene, toluene, tetralin,

quinoline, m-cresol, bicyclohexyl and 1-methylnapthalene) and their binary mixtures. An attempt has also been made to develop a generalized corresponding states method [4 - 5] for the prediction of the densities of mixtures.

EXPERIMENTAL

Densities of pure liquids and binary liquid mixtures were measured using a vibrating tube densitometer (model DMA 60, Mettler Co.) with an external thermostatted high-pressure cell (model DMA 512, Mettler Co.). The measuring principle of the instrument is based on the change in the natural frequency of a hollow oscillator when filled with different fluids. The mass of the liquid, and thus its density, changes this natural frequency. A simple relationship exists between the density of the sample and the natural frequency of the filled sample and it is possible to employ this relationship to obtain accurate densities of fluids.

The temperature in the external high pressure cell was maintained constant within ± 0.005K by means of an ultrahigh precision water bath (model Excal UHP 100, Neslab Instrument Co.) and a flow through cooler (model EN-350, Neslab). A flow-rate of 13 1 min^{-1} of water was used to maintain the constant temperature. The temperature was measured at the exit of the high pressure cell with a platinum resistance thermometer and a digital readout (model DT-4, Fischer, W. Germany). The estimated accuracy of the temperature measurement was ± 0.1K.

The sample in the high pressure cell was pressurized using triple distilled mercury. The use of mercury reduces the amount of sample required to about 7 cm^3. Moreover, mercury did not interact with any of the fluids

studied. The mercury was compressed by means of a pressure generator (model 50615, Superpressure, Inc.) with a capacity of 20 cm^3. A schematic diagram of the apparatus showing details of the various connections is shown in Fig. 1.

Two pressure gages were used for the measurement of pressure -- a Heise gage for pressures up to 10.2 MPa and an Ashcroft gage for pressures beyond 10.2 MPa. Above 10.2 MPa, the Heise gage (P_2) was isolated from the system by a valve (Fig. 1). The Heise gage had an estimated accuracy of 0.06 MPa and the Ashcroft (P_1) gage had an estimated accuracy of 0.3 MPa.

The purest commercially available grades of pure compounds were used in the experiments, with minimum purities of > 99 mol%. No further purification was attempted. Mixtures were prepared by weighing.

The density apparatus was calibrated using two reference fluids chosen on the basis of the availability of their high pressure densities as well as the closeness of their densities to those being measured. Triple-distilled water and n-octane (purity > 99 mol%, Alfa Chemicals) were used as the reference fluids for calibration. The densities of water were taken from Kell and Whalley [6, 7] and those of n-octane from Chappelow et al [8] and Benson and Winnick [9].

The samples were introduced into the high pressure cell by means of a custom-made syringe which ensured an air-tight fit at the sample port. Care was taken to ensure that no air remained in the experimental tube. Further details of the experimental procedure are given elsewhere [10]. We estimate

that the densities measured in this apparatus are accurate to ±0.00002 g cm^{-3}.

RESULTS

As these were our first experiments with this apparatus, we measured high pressure densities of n-decane for comparison with the measurements of Snyder et al [11] who used a different technique. The average absolute deviations between our data and that of Snyder et al were 0.024% at 298.2K, 0.005% at 318.2K and 0.036% at 338.16K for pressures up to 34.5 MPa. This was considered satisfactory.

Experimental densities of the seven coal chemicals studied by us are given in Tables 1 - 6, as are the densities of the six binary systems containing benzene.

CORRELATION OF PURE COMPONENT DENSITIES

High pressure densities of pure liquids have been correlated with a number of equations of state in the past [12 -14]. Several authors have shown [15, 16] that the Tait [12] equation is probably the best two-parameter equation for accurately representing density data of organic liquids at pressures up to 100 MPa. We have chosen the form of the Tait equation which was used successfully by Winnick and co-workers [9, 11] and rewritten in terms of reduced pressure P_r and reduced temperature T_r as follows:

$$V_R = V_{Ro} - V_{Ro} \left(\frac{1}{K'_o + 1} \right) \ln \left\{ \frac{1 + (K'_o + 1)(P_R - P_{Ro})}{K_o} \right\} \qquad (1)$$

Where V_R is the reduced volume, V_{RO} the reduced volume at ambient pressure (or some reference pressure P_0) P_{RO} is the ambient reduced pressure, K_0 is the bulk modulus at ambient pressure and $K'_0 = (\partial K / \partial P)_t \big|_{P=P_0}$, also evaluated at ambient pressure. The two physical constants K_0 and K'_0 depend on reduced temperature as follows:

$$K_0 = K_{01} + K_{02} \, T_r \qquad (2)$$

$$K'_0 = K'_{01} + K'_{02} \, T_r \qquad (3)$$

The four constants K_{01}, K_{02}, K'_{01} and K'_{02} were evaluated by nonlinear regression techniques and are given in Table 7. The overall average absolute deviation for the densities of the seven liquids was 0.014%.

PREDICTION OF MIXTURE DENSITIES

A generalized corresponding states method for the correlation and prediction of saturated liquid densities has been presented by Teja [4, 5]. The method is extended here to the correlation and prediction of the densities of mixtures of coal chemicals at high pressure. The generalized corresponding states equation for the density of mixture may be written as [4]:

$$V = \frac{RT_{cm}}{P_{cm}} \left\{ Z_c^{(r_1)} V_R^{(r_1)} + \Omega \left(Z_c^{(r_2)} V_R^{(r_2)} - Z_c^{(r_1)} V_R^{(r_1)} \right) \right\} \qquad (4)$$

$$\Omega = \left(\omega_m - \omega^{(r_1)} \right) \Big/ \left(\omega^{(r_2)} - \omega^{(r_1)} \right) \qquad (5)$$

Where the superscripts $r1$ and $r2$ refer to the properties of two reference substances evaluated at the same reduced temperature and pressure and ω is the acentric factor.

In our work, the densities of the binary mixtures were correlated using eqn. (4) with the pure components being chosen as the reference fluids. The reduced volumes $V_R^{(r1)}$ and $V_R^{(r2)}$ of the reference fluids were determined from the modified Tait equation (eqns. 1 - 3). The critical properties and acentric factors of the pure components were either taken from the literature [17] or, in the case of quinoline, bicyclohexyl and tetralin, estimated using Lyderson's method. The pseudocritical properties T_{cm}, P_{cm} and ω_m required in the calculations were calculated using the mixing rules proposed by Wong et al. [18]:

$$(T_{cm}/P_{cm}) = \sum_i \sum_j x_i x_j (T_{cij}/P_{cij}) \tag{6}$$

$$(T_{cm}^2/P_{cm}) = \sum_i \sum_j x_i x_j (T_{cij}^2/P_{cij}) \tag{7}$$

$$(T_{cm}/P_{cm})^{2/3}\omega_m = \sum_i \sum_j x_i x_j (T_{cij}/P_{cij})^{2/3}\omega_{ij} \tag{8}$$

together with the combining rules:

$$T_{cij} = (T_{cii}T_{cjj})^{\frac{1}{2}} \tag{9}$$

$$(T_{cij}/P_{cij}) = n_{ij} \left\{ (T_{cii}/P_{cii})^{1/3} + (T_{cjj}/P_{cjj})^{1/3} \right\}^3 / 8 \tag{10}$$

where n_{ij} is a binary interaction coefficient which is obtained from a best fit of the data. The advantage of this approach is that n_{ij} is close to 1.0 and is independent of temperature, pressure and composition -- at least in the range of conditions studied in this work. In addition, no ternary or higher coefficients are required in the calculation of the properties of multicomponent systems.

The average absolute deviations between calculated and experimental densities for the six binary systems are given in Table 8. The smallest deviations were obtained for the benzene + toluene system with $n_{12} = 1.0$. This system shows the least deviations from ideal behavior. In addition, the critical points of benzene and toluene are close, so that the reduced conditions for the mixtures are close to those of the pure components -- thus requiring very little extrapolation of the reference fluid properties. This results in excellent predictions for the binary system. The largest deviations between calculated and experimental densities were obtained for the quinoline mixtures. This is in part due to the extrapolation required in the reference fluid densities, but mostly due to the fact that the critical properties of quinoline had to be estimated. This could give rise to considerable error in the GCSP treatment. Moreover, the pure-component (Tait) equation fit for quinoline also showed the largest deviations from experiment.

Overall, however, the agreement between calculated and experimental mixture densities is satisfactory. The agreement can be improved if reference fluid data over wide ranges of reduced temperature and pressure are available and if the critical properties and acentric factors of the pure fluids are known.

ACKNOWLEDGEMENT

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TABLE 1:
DENSITY OF BENZENE + BICYCLOHEXYL
AT 298.2K, 318.2K & 338.2K

Pres(MPa)	T (K)	X1 0.00	0.25	0.5	0.75	1.00
0.1	298.2	.87286	.87012	.86685	.86400	.86374
	318.2	.86361	.85987	.85560	.85098	.84776
	338.2	.85469	.85062	.84603	.83891	.83062
0.689	298.2	.87312	.87038	.86719	.86440	.86414
	318.2	.86372	.86003	.85583	.85121	.84797
	338.2	.85495	.85094	.84635	.83932	.83112
3.447	298.2	.87480	.87218	.86913	.86645	.86642
	318.2	.86556	.86199	.85783	.85349	.85042
	338.2	.85701	.85312	.84870	.84191	.83428
6.895	298.2	.87673	.87405	.87132	.86884	.86917
	318.2	.86762	.86416	.86025	.85610	.85346
	338.2	.85931	.85553	.85119	.84485	.83763
13.79	298.2	.88043	.87789	.87543	.87349	.87456
	318.2	.87170	.86870	.86510	.86133	.85944
	338.2	.86403	.86044	.85655	.85073	.84442
20.685	298.2	.88423	.88188	.87949	.87799	.87946
	318.2	.87575	.87280	.86945	.86634	.86508
	338.2	.86826	.86503	.86153	.85630	.85085
27.58	298.2	.88790	.88567	.88369	.88237	.88454
	318.2	.87964	.87698	.87404	.87124	.87063
	338.2	.87227	.86935	.86612	.86137	.85678
34.475	298.2	.89136	.88939	.88741	.88648	.88922
	318.2	.88334	.88076	.87812	.87582	.87562
	338.2	.87620	.87347	.87049	.86640	.86246

TABLE 2:
DENSITY OF BENZENE + QUINOLINE
AT 298.2K, 318.2K & 338.2K

Pres(MPa)	T (K)	X1 0.00	0.25	0.5	0.75	1.00
0.1	298.2	1.07847	1.03824	.99094	.93336	.86374
	318.2	1.06417	1.02550	.98235	.91784	.84776
	338.2	1.05692	1.01921	.97348	.90493	.83062
0.689	298.2	1.07875	1.03857	.99125	.93377	.86414
	318.2	1.06403	1.02541	.98231	.91798	.84797
	338.2	1.05699	1.01936	.97371	.90530	.83112
3.447	298.2	1.08009	1.04012	.99291	.93573	.86642
	318.2	1.06555	1.02710	.98416	.92016	.85042
	338.2	1.05868	1.02115	.97578	.90782	.83428
6.895	298.2	1.08171	1.04201	.99491	.93799	.86917
	318.2	1.06732	1.02908	.98638	.92273	.85346
	338.2	1.06052	1.02326	.97802	.91068	.83763
13.79	298.2	1.08490	1.04535	.99877	.94248	.87456
	318.2	1.07089	1.03297	.99072	.92766	.85944
	338.2	1.06463	1.02754	.98297	.91643	.84442
20.685	298.2	1.08816	1.04896	1.00271	.94689	.87946
	318.2	1.07439	1.03677	.99479	.93249	.86508
	338.2	1.06854	1.03172	.98773	.92176	.85085
27.58	298.2	1.09127	1.05237	1.00653	.95115	.88454
	318.2	1.07768	1.04039	.99881	.93728	.87063
	338.2	1.07234	1.03564	.99198	.92681	.85678
34.475	298.2	1.09455	1.05580	1.01025	.95529	.88922
	318.2	1.08104	1.04408	1.00280	.94162	.87562
	338.2	1.07606	1.03965	.99627	.93177	.86246

TABLE 3:
DENSITY OF BENZENE + M-CRESOL
AT 298.2, 318.2 & 338.2K

Pres(MPa)	T (K)	X1 0.00	0.25	0.5	0.75	1.00
0.1	298.2	1.02021	.98689	.94917	.90839	.86374
	318.2	1.00646	.97250	.93778	.89318	.84776
	338.2	.99789	.96268	.92584	.87913	.83062
0.689	298.2	1.02045	.98720	.94954	.90877	.86414
	318.2	1.00638	.97252	.93790	.89338	.84797
	338.2	.99811	.96291	.92615	.87953	.83112
3.447	298.2	1.02195	.98871	.95137	.91090	.86642
	318.2	1.00807	.97432	.93992	.89564	.85042
	338.2	.99996	.96487	.92838	.88194	.83428
6.895	298.2	1.02370	.99072	.95352	.91339	.86917
	318.2	1.00994	.97649	.94236	.89834	.85346
	338.2	1.00195	.96708	.93099	.88488	.83763
13.79	298.2	1.02726	.99452	.95774	.91792	.87456
	318.2	1.01389	.98060	.94681	.90357	.85944
	338.2	1.00623	.97194	.93630	.89106	.84442
20.685	298.2	1.03048	.99824	.96191	.92262	.87946
	318.2	1.01749	.98456	.95129	.90851	.86508
	338.2	1.01016	.97634	.94122	.89656	.85085
27.58	298.2	1.03384	1.00172	.96588	.92693	.88454
	318.2	1.02103	.98848	.95558	.91341	.87063
	338.2	1.01406	.98051	.94571	.90178	.85678
34.475	298.2	1.03721	1.00532	.96974	.93127	.88922
	318.2	1.02452	.99239	.95974	.91792	.87562
	338.2	1.01792	.98463	.95042	.90688	.86246

TABLE 4:
DENSITY OF BENZENE + TETRALIN
AT 298.2K, 318.2K & 338.2K

Pres(MPa)	T (K)	X1 0.00	0.25	0.5	0.75	1.00
0.1	298.2	.95472	.93869	.91884	.89489	.86374
	318.2	.94269	.92620	.91106	.88012	.84776
	338.2	.93339	.91724	.89751	.86681	.83062
0.689	298.2	.95505	.93900	.91919	.89504	.86414
	318.2	.94272	.92628	.91105	.88037	.84797
	338.2	.93367	.91750	.89781	.86715	.83112
3.447	298.2	.95671	.94075	.92106	.89709	.86642
	318.2	.94460	.92821	.91298	.88266	.85042
	338.2	.93558	.91970	.90008	.86984	.83428
6.895	298.2	.95858	.94279	.92319	.89941	.86917
	318.2	.94657	.93034	.91541	.88535	.85346
	338.2	.93782	.92206	.90277	.87278	.83763
13.79	298.2	.96226	.94648	.92745	.90411	.87456
	318.2	.95066	.93471	.91997	.89045	.85944
	338.2	.94244	.92703	.90807	.87885	.84442
20.685	298.2	.96586	.95041	.93151	.90858	.87946
	318.2	.95448	.93883	.92431	.89538	.86508
	338.2	.94675	.93167	.91295	.88434	.85085
27.58	298.2	.96937	.95419	.93571	.91293	.88454
	318.2	.95835	.94291	.92869	.90027	.87063
	338.2	.95089	.93599	.91770	.88962	.85678
34.475	298.2	.97283	.95790	.93962	.91727	.88922
	318.2	.96214	.94687	.93292	.90494	.87562
	338.2	.95487	.94025	.92224	.89466	.86246

TABLE 5:
DENSITY OF BENZENE + TOLUENE
AT 298.2K, 318.2K & 338.2K

Pres(MPa)	T (K)	X1 0.00	0.25	0.5	0.75	1.00
0.1	298.2	.85191	.85388	.85636	.85943	.86374
	318.2	.83875	.84009	.84196	.84430	.84752
	338.2	.82415	.82543	.82676	.82860	.83062
0.689	298.2	.85233	.85430	.85678	.85989	.86414
	318.2	.83905	.84042	.84223	.84459	.84767
	338.2	.82463	.82590	.82724	.82910	.83098
3.447	298.2	.85450	.85653	.85901	.86214	.86642
	318.2	.84144	.84289	.84468	.84712	.85014
	338.2	.82751	.82889	.83028	.83206	.83408
6.895	298.2	.85700	.85903	.86156	.86481	.86917
	318.2	.84437	.84577	.84769	.85011	.85319
	338.2	.83069	.83203	.83355	.83547	.83749
13.79	298.2	.86176	.86398	.86661	.86976	.87456
	318.2	.84985	.85136	.85339	.85597	.85908
	338.2	.83706	.83865	.83851	.84229	.84445
20.685	298.2	.86654	.86883	.87150	.87489	.87946
	318.2	.85499	.85653	.85887	.86142	.86469
	338.2	.84301	.84451	.84629	.84840	.85093
27.58	298.2	.87113	.87352	.87628	.87972	.88454
	318.2	.86018	.86171	.86402	.86679	.87017
	338.2	.84845	.85003	.85289	.85422	.85692
34.475	298.2	.87561	.87800	.88082	.88428	.88922
	318.2	.86492	.86662	.86898	.87178	.87530
	338.2	.85359	.85551	.85748	.85973	.86290

TABLE 6:
DENSITY OF BENZENE + METHYLNAPTHALENE
AT 298.2K, 318.2K & 338.2K

Pres(MPa)	T (K)	0.00	0.25	X1 0.5	0.75	1.00
0.1	298.2	1.00566	.98136	.95196	.91292	.86374
	318.2	.99360	.97461	.93828	.90757	.84776
	338.2	.98650	.96628	.92918	.89084	.83062
0.689	298.2	1.00596	.98164	.95229	.91324	.86414
	318.2	.99352	.97458	.93838	.90773	.84797
	338.2	.98655	.96646	.92943	.89122	.83112
3.447	298.2	1.00735	.98321	.95407	.91526	.86642
	318.2	.99512	.97635	.94034	.90988	.85042
	338.2	.98822	.96839	.93157	.89385	.83428
6.895	298.2	1.00909	.98508	.95605	.91755	.86917
	318.2	.99693	.97824	.94261	.91240	.85346
	338.2	.99029	.97051	.93402	.89632	.83763
13.79	298.2	1.01242	.98868	.96001	.92200	.87456
	318.2	1.00074	.98221	.94706	.91721	.85944
	338.2	.99479	.97492	.93905	.90223	.84442
20.685	298.2	1.01582	.99231	.96396	.92656	.87946
	318.2	1.00437	.98606	.95127	.92196	.86508
	338.2	.99871	.97918	.94383	.90764	.85085
27.58	298.2	1.01905	.99574	.96787	.93067	.88454
	318.2	1.00787	.98981	.95550	.92651	.87063
	338.2	1.00253	.98318	.94848	.91264	.85678
34.475	298.2	1.02222	.99917	.97150	.93475	.88922
	318.2	1.01125	.99344	.95940	.93094	.87562
	338.2	1.00609	.98707	.95269	.91738	.86246

TABLE 7:
CONSTANTS OF EQUATION (1)

PURE COMPONENT REFERENCE	K_o'		K_o		AAD%
	K_{o1}'	K_{o2}'	K_{o1}	K_{o2}	
Toluene	-11.08677	36.75960	853.3514	-1144.5598	.009
Benzene	-12.73497	35.31400	692.01231	-866.2329	.017
M-Cresol	7.791875	-4.53251	1024.4754	-1388.1166	.011
1-Methylnapthalene	-6.03599	28.28938	1528.391	-2339.657	.017
Bicyclohexyl	-31.21234	88.59727	1579.561	-2351.007	.011
Quinoline	-22.53084	45.95379	1574.177	-2447.529	.023
Tetralin	13.242625	-12.37027	1173.597	-1657.2045	.013

TABLE 8:

RESULTS OF CORRESPONDING STATES CALCULATIONS

Binary System Benzene +	# of Data Points	n_{12}	AADEV %
1-Methylnapthalene	252	0.886	1.63
Tetralin	252	0.923	1.33
Toluene	252	1.003	0.039
Quinoline	252	0.804	3.146
M-Cresol	252	0.987	0.152
Bicyclohexyl	252	1.038	0.358

MERCURY RESERVOIR

WATER BATH

COOLER

DMA-60

HIGH-PRESSURE CELL (DMA-512)

DIGITAL THERMOMETER (PRT)
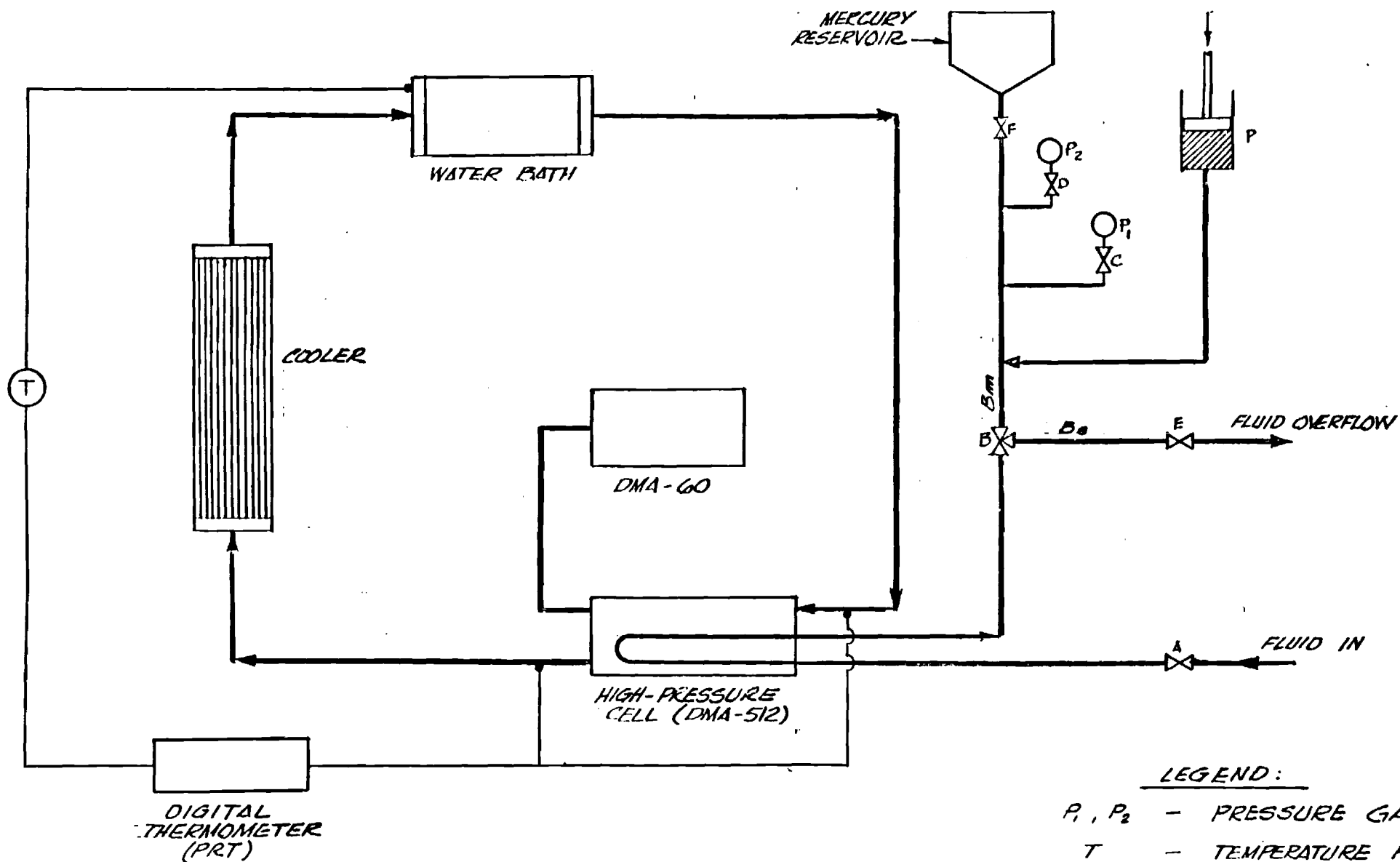
P_2

P_1

P

FLUID OVERFLOW

FLUID IN

FIG. 1

SCHEMATIC OF EXPERIMENTAL APPARATUS

LEGEND:

P_1, P_2 — PRESSURE GAGE.

T — TEMPERATURE PROBE.

PRT — PLATINUM RESISTANCE THERMOMETER.

P — PRESSURE GENERATOR.

NWH

Calculation of Transport Properties of Mixtures for Synfuels Process Design

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A generalized corresponding states principle based on two nonspherical reference fluids has been used to correlate and predict the viscosities and thermal conductivities of mixtures of interest in synfuels process design. It is shown that an appropriate choice of reference fluids leads to good predictions of the transport properties over a range of pressures and temperatures for both defined and undefined mixtures. The need for reference fluid transport property data is discussed.

Introduction

Methods for the calculation of thermodynamic and transport properties are required in the design of processes for coal gasification and liquefaction. However, since coal fluids and synfuels typically consist of a variety of components including polycyclic and polynuclear aromatic hydrocarbons, traditional methods for estimating transport properties are often inapplicable to synfuels. Moreover, the range of temperatures and pressures encountered in synfuels plants and the analytical problems of indentifying the components compounds the difficulties associated with the task of physical properties estimation.

Some progress toward obtaining transport properties correlations has been made recently by Brulé and Starling (1982), Hwang et al. (1982), and Baltatu et al. (1983). All these correlations are based on some form of the Corresponding States Principle. An alternative formulation of this principle, termed the Generalized Corresponding States Principle (GCSP), is presented in this work. When combined with a new set of mixing rules, the GCSP method is shown to lead to accurate calculations of viscosities and thermal conductivities of defined mixtures of interest in synfuels processing. The new method is also shown to work well for coal liquids.

The Generalized Corresponding States Method

A pure fluid (with critical properties T_c, P_c, V_c, and molecular weight M) is defined to be in corresponding states with a reference fluid o, if the reduced property X (where X may be the compressibility, reduced viscosity, reduced thermal conductivity, or reduced diffusivity) of the two substances at the same reduced temperature T_R and reduced pressure P_R is given by

$$X[T_R, P_R] = X^o[T_R, P_R] \tag{1}$$

It should be noted here that correspondence defined in terms of the same reduced temperature and pressure is not necessarily equivalent to correspondence defined in terms of reduced temperature and density (the exception being the case when the critical compressibilities of the two fluids are equal). This formulation of the Corresponding States Principle therefore differs from the formulation adopted by Brule et al. (1982a,b), Ely and Hanley (1981,1983), and others (Murad and Gubbins, 1977; Rowlinson and Watson, 1969).

Equation 1 is strictly valid only for pairs of substances (such as argon and krypton) in which the molecules interact with spherically symmetric two-parameter potentials. The resulting statement then describes the two-parameter corresponding states principle and the superscript o denotes the properties of a spherical reference substance.

In the more general case of nonspherical molecules, Pitzer et al. (1955) have shown that eq 1 for the compressibility Z may be written as

$$Z[T_R, P_R] = Z^o[T_R, P_R] + \omega Z^1[T_R, P_R] \tag{2}$$

where ω is the acentric factor and Z^1 is a departure function. Equation 2 may be viewed as a first-order Taylor

$$Z[T_R, P_R, \omega] = Z[T_R, P_R, \omega = 0] + \omega \frac{\delta Z[T_R, P_R]}{\delta \omega}\bigg|_{=0} \quad (3)$$

Analogous expansions for transport properties have been proposed by Joasi et al. (1962), Letsou and Stiel (1972), Roy and Thodos (1970), and Stiel and Thodos (1964). To adopt the Pitzer et al. corresponding states principle for easy use on digital computers, Lee and Kesler (1975) replaced the derivative in eq 3 by its finite difference approximation

$$\frac{\delta Z[T_R, P_R]}{\delta \omega}\bigg|_{=0} = \frac{Z[T_R, P_R, \omega_1] - Z[T_R, P_R, \omega = 0]}{\omega_1} \quad (4)$$

where ω_1 represents the acentric factor for some appropriately chosen reference fluid. Thus, eq 3 becomes

$$Z[T_R, P_R, \omega] =$$
$$Z^0[T_R, P_R] + \frac{\omega}{\omega_1}[Z^1[T_R, P_R, \omega_1] - Z^0[T_R, P_R]] \quad (5)$$

They then used an eleven-constant modified Benedict–Webb–Rubin equation for essentially argon to represent Z^0, and for essentially n-octane to represent Z^1. The result was an accurate, analytic CSP for nonpolar fluids.

While eq 5 leads to good predictions for hydrocarbons, it is much less accurate for molecules with permanent dipoles and/or quadrupoles. This is because the method is an expansion in acentricity only and, more importantly, because both reference fluids (argon and n-octane) are nonpolar.

Real molecules can be both nonspherical and polar. To develop a corresponding states principle for such fluids, it is useful to consider the insights obtained from statistical mechanical perturbation theory. One statistical mechanical approach (Flytzani-Stephanopoulis et al., 1975) has been to use a multidimensional Taylor series expansion in nonsphericity, dimensionless dipole moment, and other appropriately chosen parameters. Unfortunately, it has proved difficult to obtain the contributions of the various terms in the expansion. Moreover, synergistic effects between nonsphericity and dipole moment do not appear in the first-order terms which are normally used in corresponding states methods.

Perturbation theory calculations do, however, demonstrate that accuracy is greater and convergence is more rapid if the reference fluid for the expansion is very similar to the fluid under study. This suggests that the reference fluids for a corresponding states theory should not be restricted to argon and n-octane, as in the Lee–Kesler method. Moreover, these reference fluids need not be the same for all fluids but should be chosen such that they are similar to the fluids of interest.

Therefore, we have proposed (Teja, 1980; Teja et al., 1981a,b,c) the following generalized corresponding states principle (GCSP)

$$X[T_R, P_R, \theta] = X^{r1}[T_R, P_R, \theta^{r1}] + \frac{\theta - \theta^{r1}}{\theta^{r2} - \theta^{r1}}\{X^{r2}[T_R, P_R, \theta^{r2}] - X^{r1}[T_R, P_R, \theta^{r1}]\} \quad (6)$$

Here X is any dimensionless configurational property such as the compressibility or enthalpy departure or it can also be the reduced viscosity, thermal conductivity, or diffusivity. r1 and r2 refer to appropriately chosen reference fluids, and θ is some characterizing property. Although θ was taken to be the acentric factor in the work discussed below, other characterizing parameters could equally have been chosen.

The use of eq 6 in calculating high-accuracy liquid densities (Teja, 1980), vapor pressures (Teja et al., 1981a), vapor–liquid equilibria (Wong et al., 1983), and other ... (Teja and Rice, 1981b,c) has been described

thermal conductivity calculations for synfuel process design.

When applying corresponding states theory to mixtures, an appropriate choice of mixture pseudocritical properties must first be made. For defined mixtures, we have shown (Wong et al., 1983) that the mixing rules given below are especially useful for a large range of mixtures including asymmetric mixtures and mixtures containing polar components. The mixing rules are

$$\omega(T_c/P_c)^{2/3} = \sum_i \sum_j z_i z_j \omega_{ij}(T_{cij}/P_{cij})^{2/3} \quad (7)$$

$$T_c/P_c = \sum_i \sum_j z_i z_j(T_{cij}/P_{cij}) \quad (8)$$

$$T_c^2/P_c = \sum_i \sum_j z_i z_j(T_{cij}^2/P_{cij}) \quad (9)$$

with

$$T_{cij} = \xi_{ij}(T_{cii}T_{cjj})^{1/2} \quad (10)$$

$$P_{cij} = 8T_{cij}/[(T_{cii}/P_{cii})^{1/3} + (T_{cjj}/P_{cjj})^{1/3}]^3 \quad (11)$$

$$\omega_{ij} = 1/2(\omega_{ii} + \omega_{jj}) \quad (12)$$

Equations 8–11 are somewhat different from the commonly used van der Waals one-fluid mixing rules, but they become identical with the van der Waals rules when the critical compressibilities of the components are equal. In addition, eq 7 and 12 reduce to the more common linear mixing rule for the acentric factor when the components are of equal size. In the more general case, however, a nonlinear mixing rule for the acentric factor is required (Starling et al., 1979).

The mixing rules given above, based on semitheoretical and semiempirical arguments, have been shown to work well for thermodynamic properties and phase equilibria. They offer the advantage that they do not contain the critical volume, which is subject to greater experimental errors than the critical temperature and pressure. These mixing rules have been retained for the calculation of transport properties in this work.

The components of undefined mixtures such as distillable coal-fluid fractions cannot, of course, be identified. Such a mixture may, however, be treated either as a mixture of pseudocomponents or as a single pseudocomponent. In general, the second approach is adopted when the bulk properties (e.g., viscosity) of a single-phase system are to be calculated and the first approach is adopted when the properties (e.g., VLE) of multiphase systems are to be calculated.

The undefined coal liquid fractions studied in this work were treated as single pseudocomponents. The characterization parameters (T_c, P_c, and ω) required in the GCSP calculations were calculated using two methods. The method of Wilson et al. (1981) for coal liquids gives

$$\log T_c = 1.0719 + 0.38882 \log SG + 0.66709 \log T_b \quad (13)$$

$$\log P_c = 1.05918 - 0.05445K_w + 3.12579(1 - T_b/T_c) \quad (14)$$

$$K_w = (1.8T_b)^{1/3}/SG \quad (15)$$

$$\omega = [\ln (1.01325/P_c) - f^{(0)}]/f^{(1)} \quad (16)$$

$$f^{(0)} = 5.92714 - 6.09648/(T_b/T_c) - 1.28862 \ln (T_b/T_c) + 0.169347(T_b/T_c)^6 \quad (17)$$

$$f^{(1)} = 15.2518 - 15.6875/(T_b/T_c) - 13.4721 \ln (T_b/T_c) + 0.43577(T_b/T_c)^6 \quad (18)$$

where T_b is the average boiling point in K and SG is the specific gravity at 60 °F/60 °F. The units of T_c and P_c are K and bar, respectively.

The correlations of Brule et al. (1982b) are given by

$$T_c =$$
$$429.138 + 0.886861 T_b - 4.596433 \times 10^{-4} T_b^2 -$$
$$2.410089 \times 10^{-3} API \times T_b + 1.630489 \times 10^{-7} T_b^3 -$$
$$9.323778 \times 10^{-7} API \times T_b^2 - 1.430628 \times 10^{-8} API^2 \times$$
$$T_b^2; \quad (T_b \text{ in } °F \text{ and } T_c \text{ in } K) \quad (19)$$

$$API = 141.5/SG - 131.5 \quad (20)$$

$$V_c =$$
$$3.01514 M^{1.02247} \times (SG)^{-0.06447}; \quad (V_c \text{ in } cm^3 \text{ g-mol}^{-1}) \quad (21)$$

$$\gamma = 333.333 + 151.244(T_c/T_b) - 519.841(T_b/T_c) +$$
$$38.9063(T_b/T_c)^4 + 1255.01 \log (T_b/T_c) \quad (22)$$

$$\gamma = \omega[1 + 0.106683 \sin (4\pi\omega) + 0.0139024 \cos (4\pi\omega) -$$
$$0.00992134 \sin (8\pi\omega) + 0.01993780 \cos (8\pi\omega) -$$
$$0.03202890 \sin (12\pi\omega) - 0.0115012 \cos (12\pi\omega)] \quad (23)$$

$$Z_c = 1/(1.28\omega + 3.41) \quad (24)$$

$$P_c = Z_c R T_c / V_c \quad (25)$$

Here, the acentric factor is found by trial and error using eq 22 and 23 and SG is the specific gravity at 68 °F/68 °F. M is the average molecular weight which can be calculated from T_b and SG if it is not known (see, for example eq 30 of Brule et al., 1982b).

The Wilson and Starling correlations allow the calculation of the characterizing parameters (T_c, P_c, and ω) required in the GCSP calculations. It should be added here that the GCSP is formulated in terms of the readily available conditions of temperature and pressure. No density calculations are required, unlike the currently available methods (Brule and Starling, 1981a).

Viscosity Calculations

For the calculation of viscosity η of a pure fluid or mixture, eq 6 is written in terms of $\ln \eta_R$

$$(\ln \eta_R) = (\ln \eta_R)^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}\{(\ln \eta_R)^{r2} - (\ln \eta_R)^{r1}\} \quad (26)$$

where

$$\eta_R = \eta T_c^{1/6} M^{-1/2} P_c^{-2/3} \quad (27)$$

Use of eq 26 requires knowledge of the viscosity of two reference fluids as a function of reduced temperature and pressure. A compilation by Stephan and Lucas (1979) was used to obtain these data. Stephan and Lucas have tabulated the viscosities of a number of pure fluids over considerable ranges of temperature and pressure. In this work, the viscosity tables were first converted to tables of $\ln \eta_R$ vs. T_R and P_R. Two-variable linear interpolation was then used between appropriate values of P_R and $1/T_R$ to obtain a particular reduced reference viscosity, $\ln \eta_R$. The reference fluid viscosities were then combined in eq 26 to obtain the viscosity of interest.

Defined Mixtures. Before applying the GCSP method to undefined coal liquids, it was necessary to test the technique on defined mixtures over a range of pressures and temperatures.

Table I gives the results of our calculations for a binary mixture of methane + n-butane ($x_1 = 0.394$). In these calculations, the two pure components were used as the reference fluids and the data for the pure components were taken from the compilation by Stephan and Lucas. The mixing rules given in eq 7–12 were used in the calculation

of 278–411 K and a pressure range of 80–350 bar, the percent deviation between predicted and experimental viscosities ranged from −5.0% to +0.8% with the average absolute deviation being 2.78%. For temperatures between 444 and 511 K (with pressures up to 350 bar), the reference fluid data for n-butane had to be extrapolated to the mixture reduced conditions. Percent deviations were now greater and ranged from −0.5% to −27% with average absolute deviations of 13.02%. However, no binary coefficients were used in the calculations (i.e., ξ_{12} was set equal to 1.0). With a binary interaction coefficient $\xi_{12} = 1.03$, the overall average deviations could be reduced to 2.34%, with the exception of the data at 511 K. It is obvious that less confidence can be given to the predictions when reference fluid data have to be extrapolated over an extended range of conditions.

Table II summarizes our results for the methane + n-decane system. In this case, an average absolute deviation of 20.2% was obtained if the binary interaction coefficient was set equal to 1.0. The deviation could be reduced to 1.76% if a single binary interaction coefficient, independent of temperature, pressure, and composition, is used in the calculations. Very few data on aromatic mixtures could be found in the literature and, indeed, high-pressure data for such mixtures are nonexistent. Our results for the benzene + n-hexane system at 1 atm are also given in Table II. Good predictions for this system could be obtained at all temperatures and compositions without the use of binary interaction coefficients. More experimental data for aromatic mixtures at high pressures, however, are needed to aid in the development of the method.

Undefined Coal Liquid Mixtures. Coal liquids are complex and essentially unknown mixtures, having some characteristics of petroleum fluids but a high degree of aromaticity. A petroleum type reference fluid, n-decane, and an aromatic reference fluid, benzene, were therefore chosen for the GCSP calculations. The viscosities of benzene and n-decane were obtained in tabular form from the compilation by Stephan and Lucas. Values of the viscosity at particular values of reduced temperature and pressure were obtained by numerical interpolation from the tables.

Four Exxon coal liquids (IHS, IA-3, IA-6, and IA-10) were examined in this work. The coal liquids were treated as single pseudocomponents, and their characterization parameters (T_c, P_c, and ω) were calculated using the Wilson et al. (eq 13–18) and the Starling et al. (eq 19–25) correlations. It should be noted that neither critical volumes nor densities were required in the GCSP calculations. The Wilson and Starling correlations for T_c, P_c, ω require the average boiling point T_b and the specific gravity SG of the coal liquids. The Starling correlation also uses the molecular weight M, but this can be estimated from T_b if necessary. For the Exxon coal liquids, T_b and M were given, but the specific gravity was not. The specific gravity was therefore extrapolated from the reported density data. The Starling correlation uses the SG at 68 °F/68 °F, whereas the Wilson correlation follows the petroleum standards of SG at 60 °F/60 °F. The difference between the two specific gravities, however, ranged from 0.3% to 0.4% and could be neglected. The calculated characterization parameters from the two correlations are given in Table III.

The results for the viscosity predictions for the four coal liquids are presented in Table IV. The average absolute deviation for all 209 data points was 13.6% when T_c, P_c, ω were calculated from the Starling correlation and 17.8% when the characterization parameters were calculated from the Wilson correlation. Since the coal liquids were treated as single pseudocomponents, no binary interaction parameters were used in the calculations (i.e., the viscosities of coal liquids were calculated solely from the properties of the reference fluids—n-decane and benzene). Although

the results are satisfactory, it is likely that even lower deviations would have been obtained if a characterization parameter based on viscosity rather than one based on vapor pressures (i.e., the acentric factor ω) had been used in the calculations.

When each coal liquid is examined separately, the Wilson and Starling characterization parameters lead to similar predictions for the IHS liquid (average absolute deviations of 14.0 and 14.6%, respectively) and for the IA-3 liquid (10.0 and 11.3%, respectively). However, for the IA-6 and IA-10 liquids, better results are obtained when parameters from the Starling correlations are used.

When the data for all coal liquids were grouped according to temperature, greater deviations (24%) were observed at the higher temperatures (>700 K) as shown in Table V. Because of the scarcity of experimental data for the reference fluids at high temperatures, some extrapolation of the data proved necessary. Hence it was not surprising that greater deviations were observed at these temperatures. In addition, the viscosity at high temperatures is an order of magnitude smaller than the viscosity at ambient temperatures and is thus much more sensitive to extrapolation in reference fluid properties. No trends were observed in deviations with pressure, similar deviations between experimental and calculated viscosities being obtained at both low and high pressures.

Thermal Conductivity Calculations

Equation 6 for the thermal conductivity λ of a pure fluid or fluid mixture may be written as

$$\lambda_R = \lambda_R^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}\{\lambda_R^{r2} - \lambda_R^{r1}\} \qquad (28)$$

where

$$\lambda_R = \lambda M^{1/2} T_c^{1/6} P_c^{-2/3} \qquad (29)$$

and the superscripts r1 and r2 again refer to the properties of two reference fluids.

The absolute thermal conductivity λ of any fluid is made up of two contributions (Ely and Hanley, 1983)

$$\lambda = \lambda_{int} + \lambda_{trans} \qquad (30)$$

For polyatomic fluids at low densities, the internal degrees of freedom make important contributions to the thermal conductivity. The internal contributions are given by (Reid et al., 1977)

$$\lambda_{int} = 1.32 \, \eta_g \left(C_p - \frac{5}{2}R\right)\Big/ M \qquad (31)$$

where η_g is the dilute gas viscosity and C_p is the heat capacity. The dilute gas viscosity η_g may be obtained from the relationship

$$\eta_g = 26.69(MT)^{1/2}/\sigma^2\Omega_v^2 \qquad (32)$$

Here, η_g is in cP, T in K, the molecular diameter σ in Å, and Ω_v is the collision integral given by (Neufeld et al., 1972)

$$\Omega_v = \frac{A}{T^{*B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} \qquad (33)$$

where $T^* = KT/\epsilon$, $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, $F = 2.43787$, and ϵ is the potential energy parameter.

Because C_p in eq 31 differs from gas to gas at the same reduced temperature, any corresponding states treatment cannot adequately take into account the contribution of the internal degrees of freedom to the thermal conductivity, unless the contribution is small. Hence eq 28 must be written as

$$\lambda_R = \lambda_R^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}\{\lambda_R^{r2} - \lambda_R^{r1}\} + \lambda_{R'} \qquad (34)$$

where

$$\lambda_{R'} = \lambda_{int} M^{1/2} T_c^{1/6} P_c^{-2/3} \qquad (35)$$

and

$$\lambda_{R''} = \lambda_{int} M^{1/2} T_c^{1/6} P_c^{-2/3} \qquad (36)$$

Thermal conductivities of a number of pure fluids were calculated using both eq 28 and 34. The results are summarized in Table VI. Only the dense fluid region was considered ($P > 10$ bar), as this region is likely to be of greatest interest in synfuel processes. The reference fluids used in each case are also given in Table VI. Reference fluid data were obtained from the NBS TRAPP data bank (Ely and Hanley, 1981a). Numerical linear interpolation was used to obtain the thermal conductivity of a particular reference fluid at a given reduced temperature and pressure. As can be seen from our results, the average absolute deviations between experimental and calculated values were very similar for eq 28 and 34. It appears that the small contribution from the internal degrees of freedom can be obtained from the properties of the reference fluids, provided appropriate reference fluids are chosen. Equation 28 was therefore used in all subsequent calculations.

Defined Mixtures. The results for three defined mixtures using the GCSP method with the mixing rules given by eq 7-12 are presented in Table VII. All experimental data were obtained from the NBS TRAPP data bank. The pure components were used as the reference fluids. The average absolute deviation for the 620 mixture data points covering a temperature range of 293–573 K and a pressure range of 50–500 bar was found to be 4.59% with the binary interaction coefficient set equal to 1.0. When a single binary interaction coefficient (ξ_{12}^{cp}) independent of temperature, pressure, and composition, was determined for each system, the average absolute deviation could be reduced to 2.68% over the whole temperature and pressure range considered.

Undefined Coal Liquid Mixtures. Experimental data on the thermal conductivity of two coal liquid fractions have recently become available (Perkins et al., 1983). These data cover the temperature and pressure range from ambient conditions to 49 K and 136 bar, respectively, for an SRC-I fraction and a Utah COED fraction. Characterization data for these fractions are given in Table VIII. Included in this table are the parameters calculated from the Starling and Wilson correlations. The highly aromatic nature of these mixtures is obvious.

A summary of the results for the thermal conductivity predictions for the two coal liquid fractions is presented in Table IX. The two reference fluids used in the calculations are the same as those used in the viscosity calculations, i.e., n-decane and benzene. Data for the reference fluids were obtained from the TRAPP data bank. The average absolute deviation for all 42 data points was 16.98% when T_c, P_c, and ω were calculated from the Starling correlation and 12.37% when the characterization parameters were calculated from the Wilson correlation. The Starling correlation resulted in better predictions for the SRC-I fraction, however. It should be added that no binary interaction parameters were used in the calculations, the thermal conductivities of the coal liquid fractions being predicted solely from the thermal conductivities of n-decane and benzene. The deviations between predictions and experiment are therefore satisfactory. Moreover, no noticeable increase in deviation could be detected with either pressure or temperature.

In conclusion, the GCSP has been demonstrated to be a powerful technique for the correlation and prediction of the transport properties of mixtures of interest in synfuels

and pressures of interest. In this respect, it should be mentioned that data for polycyclic aromatic hydrocarbons and for defined mixtures containing these substances over extended ranges of pressure and temperature are virtually nonexistent in the literature. These data are necessary both for developing reference fluid equations and for testing corresponding states correlations. The limited data on real coal liquids available in the literature leads to the conclusion that, for transport property prediction, coal liquids can be treated as single pseudocomponents and the characterizing parameters (T_c, P_c, ω) can be calculated from readily available properties (T_b, SG, M) via correlations such as those of Starling and Wilson. It is probable that a third (pseudocomponent) parameter based on viscosity and/or thermal conductivity would lead to further improvement in the transport property predictions, rather than the use of the acentric factor which is based on the vapor pressure. However, the use of the acentric factor does offer the advantage that the same values of all characterization parameters are used for both thermodynamic and transport property predictions.

Acknowledgment

Nomenclature

C_p = heat capacity

f = function defined in eq 17 and 18

K_w = Watson characterization factor

M = molecular weight

P = pressure

R = gas constant

SG = specific gravity

T = temperature

V = volume

X = any thermodynamic or transport property

x = mole fraction

Z = compressibility

Greek Letters

ϵ = potential energy parameter

γ = orientation parameter equation   delete

ξ = binary interaction coefficient

η = viscosity

λ = thermal conductivity

σ = molecular diameter

θ = characterization parameter

Ω = collision integral

ω = acentric factor

Subscripts

b = boiling point value

c = critical point value

i, j = component i, j

R = reduced

Superscripts

r1, r2 = reference fluid r1 and r2

o = spherical reference fluid

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Table I. Viscosity Predictions for Methane + n-Butane (x₁ = 0.396) (T_c, P_c, ω from Reid et al., 1977)

no. of data	temp, K	press. range, bar	AAD%,[a] $\xi_{12} = 1.0$	AAD %, $\xi_{12} = 1.03$
12	276	80–350	2.42	0.55
12	311	80–350	2.64	1.39
11	344	80–350	2.57	1.48
11	378	80–350	1.89	1.93
11	411	80–350	4.66	2.77
12	444	80–350	7.79	5.83
12	511	80–350	18.24	16.90
overall AAD %			5.82	4.49[b]

[a] AAD% = $(100/n)\sum_{i=1}^{n} |1 - \eta/\eta_{expt}|$. [b] 2.76% if data at 511 K are excluded.

η / η (Greek eta)

INITIAL TABLE WIDTH IS SINGLE COLUMN

Table II. Viscosity Predictions of Binary Systems

x_1	no. of data	temp range, K	press. range, bar	AAD %, $\xi_{12} = 1.0$	AAD %, $\xi_{12} = \xi_{12}^{opt}$	ξ_{12}^{opt}
		Methane + n-Decane				
0.1	20	311–444	80–350	7.38	1.96	1.45
0.3	21	311–444	100–350	21.1	2.35	1.45
0.5	18	311–444	170–350	33.5	2.65	1.45
		Benzene + n-Hexane				
0.93	3	298–323	1	1.59		1.00
0.818	3	298–323	1	1.48		1.00
0.735	3	298–323	1	4.92		1.00
0.595	3	298–323	1	4.78		1.00
0.437	3	298–323	1	7.42		1.00

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Table III. Characterization Parameters of Coal Liquids

type	T_b, K	M	SG, 60/60	SG, 68/68	Starling correl T_c, K	P_c, bar	ω	Wilson correl T_c, K	P_c, bar	ω
IHS	544	179	0.9572	0.9541	762.5	26.1	0.4828	775.2	26.71	0.4333
IA-10	517	164	0.9634	0.9591	739.6	28.2	0.4325	751.2	30.33	0.3929
IA-6	533	172	0.9675	0.9641	755.2	27.2	0.4560	767.9	28.86	0.4126
IA-3	519	167	1.0124	1.0086	752.0	28.45	0.4029	768.1	35.14	0.3703

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Table IV. Viscosities of Coal Liquids Predicted by GSCP with Benzene and Decane as Reference Fluids

type	no. of points	temp range, K	press. range, bar	GCSP + Wilson AAD %	GCSP + Starling AAD %
IHS	28	311–728	6.9–138	13.96	14.56
IA-3	27	450–700	13.8–138	9.97	11.28
IA-6	81	366.5–700	13.8–138	20.52	14.96
IA-10	73	366.5–700	13.8–138	19.14	12.61
All data	209	311–728	6.9–138	17.79	13.61

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Table V. Temperature Breakdown of Viscosity Data for all Coal Liquids

temp, K	GCSP + no. of points	GCSP + Wilson AAD %	Starling AAD %
<366	43	10.44	5.92
450	66	19.66	13.91
533	60	19.74	14.32
>700	24	21.04	24.06

Table VI. Thermal Conductivity Predictions for Pure Fluids (T_c, P_c, ω from Reid et al., 1977)

fluid	ref fluids	temp range, K	press. range, bar	no. of data	AAD %, eq 18	AAD %, eq 34
C_3H_8	C_1, n-C_4	212-412	100-500	55	11.19	9.58
n-C_5H_{12}	C_1, n-C_4	298-425	48-1200	36	7.86	7.71
n-C_6H_{14}	C_1, n-C_5	273-573	48-484	112	6.39	4.33
n-C_7H_{16}	C_1, n-C_4	293-453	1-484	99	4.59	5.42
n-$C_{12}H_{26}$	n-C_9, n-C_{10}	307-501	48-484	108	14.35	13.77
n-$C_{16}H_{34}$	n-C_9, n-C_{10}	313-533	96-484	60	12.03	10.65
n-$C_{17}H_{36}$	n-C_9, n-C_{10}	313-553	48-484	78	8.04	7.47
n-$C_{18}H_{38}$	n-C_9, n-C_{10}	313-573	96-484	60	1.35	1.42
$C_6H_5C_2H_5$	C_1, C_6H_6	293-453	192-1450	63	5.07	
$C_6H_5CH_3$	C_6H_6, $C_6H_5C_2H_5$	303-428	48-484	140	5.77	
$C_6H_5C_3H_7$	C_6H_6, $C_6H_5C_4H_9$	293-453	192-1450	63	2.87	

INITIAL TABLE WIDTH IS DOUBLE COLUMN

Table VII. Thermal Conductivity Predictions for Binary Mixtures

system	no. of points	temp range, K	press. range, bar	$\xi_{12} = 1.0$ AAD%	$\xi_{12} = \xi_{12}^{opt}$ ξ_{12}^{opt}	AAD %
n-hexane + n-heptane	270	293-573	49-494	6.83	1.1484	2.75
n-hexane + n-octane	270	293-573	49-494	1.31	0.9839	1.03
$CH_4 + CO_2$	80	335-436	70-413	8.13	1.1372	8.03
overall	620			4.59		2.68

INITIAL TABLE WIDTH IS DOUBLE COLUMN

Table VIII. Characterization Parameters for Coal Liquids

	COED	SRC-I
°API	29.4	49.7
K_w	10.8	11.2
M	135	132
saturates, %	71.6	61.2
olefins, %	4.0	1.0
aromatics, %	26.4	37.2
Starling Correlation		
T_c, K	681.9	565.2
P_c bar	30.8	27.2
ω	0.4383	0.3035
Wilson Correlation		
T_c, K	686.0	555.3
P_c, bar	27.2	30.9
ω	0.3789	0.2739

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Table IX. Thermal Conductivities of Coal Liquids Predicted by GCSP with Benzene and Decane as the Reference Fluids

type	no. of data	temp range, K	press. range, bar	GCSP + Wilson AAD %	GCSP + Starling AAD %
SRC-I	24	302-494	34-136	18.15	15.36
COED	18	297-494	34-136	5.51	19.16
all data	42			12.73	16.98

The correlation and prediction of the viscosities of mixtures
over a wide range of pressure and temperature

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Abstract

A generalized corresponding states principle (GCSP) based on
the known properties of two reference fluids has been used to
correlate the viscosities of fluid mixtures over a wide range of
pressure and temperature. It is shown that good predictions of
the viscosities for a variety of mixtures can be obtained with
this method. Asymmetric mixtures, however, require the use of
one adjustable constant. Comparisons with the TRAPP method are
shown and the advantages and limitations of the two methods are
discussed.

INTRODUCTION

Methods for the calculation of thermodynamic and transport properties are required in the design of process equipment and in simulation studies. In particular, viscosity is an important property in the determination of pressure drops in pipe flow and in the calculation of power requirements for mixing and flow. Since it is unlikely that experimental viscosities of all fluids and fluid mixtures at all conditions of interest can be found in the literature, methods for the estimation of this property are of considerable importance.

For design calculations, a method for the estimation of any physical property should be applicable over a wide range of composition, temperature and pressure. Many of the currently available methods for viscosity [1] are limited to specific regions of the phase diagram and are not therefore useful when wide ranges of conditions are encountered.

Some progress towards developing methods for the calculation of viscosity of dense fluid mixtures has been made recently by Brule and Starling [2], Ely and Hanley [3-4], Mo and Gubbins [5], and Christensen and Fredenslund [6]. All of these methods are based on some form of the corresponding states principle which requires the properties of one reference fluid. An alternative formulation of this principle, based on the properties of two reference fluids, is presented in this work. The one reference fluid and two reference fluid methods are compared and the limitations of each method are outlined.

1

THE CORRESPONDING STATES PRINCIPLE:

A pure fluid (with critical properties T_c, V_c, P_c and molecular weight M) is defined to be in corresponding states with a reference fluid o if at the same reduced temperature T_R $(=T/T_c)$ and volume V_R $(=V/V_c)$ the following equations are valid:

$$Z = Z^{(o)} [T_R, V_R] \tag{1}$$

$$\eta_R = \eta_R^{(o)} [T_R, V_R] \tag{2}$$

where

$$\eta_R = \eta\xi = \eta M^{-1/2} V_c^{2/3} T_c^{-1/2} \tag{3}$$

Z is the compressibility and η the viscosity. For practical convenience, since the two parameter corresponding states principle predicts a universal value for the critical compressibility, equations [1-3] are often expressed in terms of the reduced pressure P_R $(= P/P_c)$ instead of the reduced volume V_R as one of the independent variables. Thus, equivalently:

$$Z = Z^{(o)} [T_R, P_R] \tag{1a}$$

$$\eta_R = \eta_R^{(o)} [T_R, P_R] \tag{2a}$$

$$\eta_R = \eta\xi = \eta M^{-1/2} P_c^{-2/3} T_c^{1/6} \tag{3a}$$

The two parameter corresponding states principle is, however, valid only for simple spherically symmetric molecules, such as Ar, Kr, Xe, and perhaps, CH_4.

Two different approaches have been adopted for extending the principle to non-spherical fluids. In the first approach,

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scaling factors (termed shape factors by Leland and co-workers [7]) are introduced in the reduced temperature and volume as follows:

$$Z = Z[T_R/\theta, V_R/\phi] \qquad (4)$$

and

$$N\xi' = N_R^{(0)}[T_R/\theta, V_R/\phi] \qquad (5)$$

The shape factors θ, ϕ vary with the temperature and volume and their function is to define the state of the reference fluid that corresponds to the state of the fluid of interest. Analyltical expressions for the shape factors of the n-alkanes relative to methane have been obtained by Leland and Chappelear [7] and can be expressed as:

$$\theta = 1 + (\omega - \omega_{ref}) f_1[T_R, V_R] \qquad (6)$$

$$\phi = (Z_{cref}/Z_c) \{1 + (\omega - \omega_{ref}) f_2[T_R, V_R]\} \qquad (7)$$

where the ω's are Pitzer's acentric factors and f_1, f_2 are slowly varying functions of reduced temperature and volume. Although the shape factors were originally obtained from the PVT and vapor pressure behavior of the n-alkanes, they have been used successfully for the prediction of other thermodynamic properties [7-9] and for other fluids [10]. Recently, Ely and Hanley [3,4] and Baltatu [11] have used these shape factors for the calculation of transport properties with some success.

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The second approach for extending the corresponding states princple to non-spherical fluids involves a first-order perturbation of the compressibility about its value for a spherical reference fluid, that is:

$$Z = Z [T_R, P_R, \omega = 0] + \omega \frac{\partial Z}{\partial \omega} \Big|_{\omega=0} \qquad (8)$$

Here, the first term represents the compressibility of a spherical reference fluid such as argon and the second term represents a (complex) deviation function whose magnitude increases with the acentric factor. This was the approach adopted by Pitzer et al [12] for thermodynamic properties. Similar expansions for transport properties have been proposed by Thodos, Stiel and co-workers [13-15]. For ease of computation, Lee and Kesler [16] replaced the derivative in eqn. (8) by its finite difference approximation. Thus, eqn. (8) becomes:

$$Z = Z^o (T_R, P_R] + \frac{\omega}{\omega^r} \{Z^r[T_R, P_R] - Z^o[T_R, P_R]\} \qquad (9)$$

They then used a modified Benedict-Webb-Rubin equation for argon to represent Z^o and for n-octane to represent Z^r. The result was an accurate, analytical CSP for nonpolar fluids.

While eqn. (9) leads to good predictions for nonpolar fluids, it is much less accurate for polar fluids. This is because the method is a perturbation in the acentric factor only and, more importantly, because both reference fluids (argon and n-octane) are nonpolar. To develop a corresponding states

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principle for such fluids, it is useful to consider the insights obtained from statistical mechanical perturbation theory. Perturbation theory calculations demonstrate that accuracy is greater and convergence is more rapid if the reference fluid for the expansion is very similar to the fluid under study. This suggests that the reference fluids for a corresponding states theory should not be restricted to argon and n-octane, as in the Lee-Kesler method. Moreover, these reference fluids need not be the same for all fluids but should be chosen such that they are similar to the fluid of interest. Therefore, we have proposed [17-20] the following generalized corresponding states principle (GCSP):

$$Z = Z^{r1}[T_R, \ P_R, \ \omega^{r1}] + (\frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}) \ \{Z^{r2}[T_R, \ P_R, \ \omega^{r2}]$$

$$- \ Z^{r1}[T_R, \ P_R, \ \omega^{r1}]) \tag{10}$$

and for the viscosity [19]:

$$X = X^{r1}[T_R, \ P_R, \ \omega^{r1}] + (\frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}) \ \{X^{r2}[T_R, \ P_R, \ \omega^{r2}]$$

$$-X^{r1}[T_R, \ P_R, \ \omega^{r1}]\} \tag{11}$$

where

$$X = \ln \ (\eta \xi) \tag{12}$$

In these equations, r1 and r2 represent two (non-spherical)

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reference fluids which are chosen such that they are similar to the fluid(s) of interest. It should be noted that when $\omega^{rl} = 0$ (ie. one of the reference fluids is spherical), eqn. (10) reduces to the Lee-Kesler corresponding states principle (eqn. 9).

When applying corresponding states theory to mixtures, an appropriate choice of mixture pseudocritical properties must first be made. For viscosity calculations with the shape factor approach, Ely and co-workers [3, 21] have used the mixing model given by:

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j (T_{cij}\theta_{ij}) (V_{cij}\phi_{ij}) \tag{13}$$

$$V_{cm} = \sum_i \sum_j x_i x_i (V_{cij}\phi_{ij}) \tag{14}$$

$$T_{cm}^{1/2} V_{cm}^{4/3} M_m^{1/2'} = \sum_i \sum_j x_i x_j (T_{cij}\theta_{ij})^{1/2} (V_{cij}\phi_{ij})^{4/3} M_{ij}^{1/2} \tag{15}$$

When $i \neq j$, the cross-terms are obtained using:

$$T_{cij}\theta_{ij} = (T_{cii}\theta_{ii}T_{cjj}\theta_{jj})^{1/2} \tag{16}$$

and

$$V_{cij}\phi_{ij} = \frac{1}{8} \{(V_{cii}\phi_{ii})^{1/3} + (V_{cjj}\phi_{jj})^{1/3}\}^3 \tag{17}$$

$$M_{ij} = 2 M_i M_j/(M_i + M_j) \tag{18}$$

Equations (13) and (14) represent the "van der Waals one-fluid"

mixing rules for the calculation of the pseudocriticals. Although they are not exact, the van der Waals mixing rules are satisfactory if the components of a mixture are not too dissimilar. In practice, the rules break down when the ratio of the critical volumes of the components of a mixture exceeds about 3.0 [22]. In their most recent work, Ely and Baker [21] have modified eqn. (5) by adding a term to account for differences in size as follows:

$$\eta \xi' = \eta_R^{(0)} \ [T_R/\theta, \ V_R/\phi] + \Delta\eta_{mix}^{ENS} \tag{5a}$$

where $\Delta\eta_{mix}^{ENS}$, the correction for size differences, is given by Ely [23]. The mass mixing rule (eqn. 15) was obtained by Ely and Hanley [3] by scaling the equations for the radial distribution function for a fluid in nonequilibrium due to the presence of shear. It differs from the mass mixing rule of Mo and Gubbins [5] who considered the generalized Enskog theory.

Given the properties of a reference fluid (such as methane) and the shape factors (obtained from PVT and saturation data) for the fluids of interest, viscosities may be predicted using eqns. (5a) and (13-18).

For viscosity calculations using the Pitzer approach, we have used the mixing model proposed by Wong et al [20] and given by:

$$(T_{cm}^2/P_{cm}) = \sum_i \sum_j x_i x_j \ (T_{cij}^2/P_{cij}) \tag{19}$$

$$(T_{cm}/P_{cm}) = \sum_i \sum_j x_i x_j \ (T_{cij}/P_{cij}) \tag{20}$$

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$$\omega_m (T_{cm}/P_{cm})^{2/3} = \sum_i \sum_j x_i x_j (T_{cij}/P_{cij})^{2/3} \omega_{ij} \qquad (21)$$

Equations (19) and (20) are somewhat different from the commonly used van der Waals one-fluid mixing rules, but become identical to the van der Waals rules when the critical compressibilities of the components are equal (since we have assumed that V_c is replaceable by T_c/P_c in the van der Waals one-fluid model). Equation (21) may be justified by noting that the acentric factor characterizes the nonsphericity or size/shape of the molecule and $(T_c/P_c)^{2/3}$, being essentially proportional to the surface area, characterizes the interaction between molecules. It was used successfully by Wong et al [20] in their phase equilibrium calculations using the GCSP.

To complete the model, a mixing rule for mass is needed. For simplicity, we have chosen the mass balance given by:

$$M_m = \sum_i x_i M_i \qquad (22)$$

Although this differs from the more complex mass mixing rules proposed by Mo and Gubbins [5] and Ely and Hanley [3], we have found that the simple rule works well in transport property calculations using the GCSP. Moreover, as shown below, a binary interaction coefficient can be incorporated in the calculations to allow for the deficiencies of the complete model represented by eqns. (19-22).

When $i \neq j$

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$$T_{cij} = \xi_{ij} (T_{cii}T_{cjj})^{1/2} \tag{23}$$

$$(T_{cij}/P_{cij})^{1/3} = \frac{1}{2} \{(T_{cii}/P_{cii})^{1/3} + (T_{cjj}/P_{cjj})^{1/3}\} \tag{24}$$

$$\omega_{ij} = \frac{1}{2} (\omega_{ii} + \omega_{jj}) \tag{25}$$

In eqn. (23), ξ_{ij} is a binary interaction coefficient which is usually set equal to unity. It differs from unity in systems in which there are significant differences in size and in which the van der Waals one fluid model is known to be a poor approximation. An alternative approach to having an experimentally-determined binary interaction coefficient would be to add a size correction term as was done by Ely (eqn. 5a). We have chosen to follow the former approach as the binary interaction coefficient allows us to account for limitations of the mixing model represented by eqns. (19-25).

The mixing rules given above offer the advantage that they do not contain the critical volume, which is subject to greater experimental errors than the critical pressure and temperature. Moreover, it should be added that the two extended corresponding states approaches (the shape factor approach and the acentric factor expansion approach) are not equivalent for nonspherical molecules since correspondence at the same T_R and P_R is not the same as correspondence at the same T_R and V_R. Finally, when calculating the viscosity at a given temperature and pressure, the shape factor approach requires a density calculation whereas the GCSP method does not. It should also be noted that the shape

factor method requires accurate viscosities and PVT data for one (spherical) reference fluid whereas the GCSP method requires viscosities (but no PVT data) for two reference fluids.

In this work, it is shown that with an appropriate choice of reference fluids, the GCSP approach may be used to correlate and predict the viscosities of a variety of mixtures over a wide range of temperatures, pressures and compositions. The approach is also compared with the shape factor approach of Ely and co-workers.

RESULTS AND CONCLUSIONS

We have compared the viscosity predictions of the two corresponding states methods for a number of binary mixtures. The first method uses shape factors and is available in a computer package (TRAPP) from GPA and the National Bureau of Standards. It has been described most recently by Ely and Baker [21] and requires accurate properties (both PVT and viscosities) of methane as well as the size difference correction of Ely [23]. No binary interaction coefficients are used, so that no viscosity data (other than those of the single reference fluid) are required.

In the second method, the Generalized Corresponding States Principle (GCSP) described above has been used. Use of the GCSP requires a knowledge of the viscosity of two reference fluids as a function of reduced temperature and pressure. A compilation by Stephan and Lucas [24] was used to obtain these data. Stephan and Lucas have tabulated the viscosities of a number of pure fluids over the dense fluid region. These data were used,

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together with linear interpolation and, in some cases, extrapolation to obtain the reference fluid viscosities at the conditions of interest. This method has the advantage that the data can easily be changed when better data become available without having to refit the reference equation of state or the shape factor correlations. However, because of the present lack of "wide-range" data for many fluids, only a limited choice of reference fluids is available. Moreover, for the fluids studied in this work, reference fluid data often needed to be extrapolated leading to larger than average errors. Moreover, in this work, the pure components were used as the reference fluids. This was a matter of accuracy and convenience, rather than a requirement of the method. In another paper [25] we have shown that the viscosity and thermal conductivity of several coal liquids can be calculated using benzene and n-decane as the reference fluids. Thus, if the pure component reference fluid data were not available, other (similar) reference fluids could equally have been used. Given the properties of the reference fluids, the GCSP method (like the TRAPP method) requires only the critical properties, acentric factors and molecular weights of the fluids of interest. If a binary interaction coefficient is included in the calculations, however, then viscosity data for the particular system must be used for its evaluation. In this case, the method becomes one of correlation rather than prediction.

Comparison of experimental and calculated values of the viscosity of several binary mixtures using both the GCSP and the

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TRAPP methods are shown below.

(a)   Methane + n-butane (x_1 = 0.396)

For a mixture of methane and n-butane over a temperature range 278-411 K and a pressure range 1-350 bar, the percent deviation between predicted and experimental viscosities using the GCSP method ranged from -5.0% to +0.8% with an average absolute deviation (AAD) of 2.78%. The AAD for the TRAPP method was 6.49%. No binary interaction coefficients were used in either method. For temperatures between 444 K and 511 K, however, the AAD for the GCSP method was 13.02% whereas the TRAPP method gave an AAD of 6.20%. The reason for the increase in the AAD for the GCSP method becomes obvious when the data required by the method are analyzed. The mixing rules (eqns. 19-25) give a pseudo-critical temperature of the methane + n-butane mixture of 348.2 K. A mixture temperature of 511 K therefore corresponds to a reduced temperature of 1.47. Since the critical temperatures of methane and butane (the two reference fluids) are 190.7 K and 425.2 K respectively, the viscosities of methane at 280.2 K and of n-butane at 625.0 K are required in the calculations. Data for n-butane were only available in intervals of 20 K up to 520 K. The viscosity of n-butane at 625 K was therefore obtained by an extrapolation of the data at 500 K and 520 K. It is obvious that less confidence can be given to the predictions when reference fluid data have to be extrapolated over an extended range of conditions. The TRAPP method does not require such extrapolations and average errors were in the region of six

percent over the range of temperatures and pressures studied, as can be seen in Table 1. However, when reference fluid data did not have to be extrapolated, then better predictions were obtained with the GCSP method.

(b)   Ethane + ethylene

Results for the ethane + ethylene system for three different compositions over a temperature range 323 K - 473 K and a pressure range 1-600 bar are shown in Table 2. For this system, no extrapolation of the reference fluid data was required. For all 176 data points, the GCSP method gave an AAD of 6.93% and the TRAPP method gave an AAD of 7.34%. No binary interaction coefficients were used in either method.

(c)   Benzene + n-hexane and benzene + n-decane

Results for these two systems containing an aromatic compound are presented in Table 3. Experimental data were available at atmospheric pressure and over a limted temperature range. The GCSP method gave an AAD of 4.0% for the benzene + n-hexane system and 8.8% for the more asymmetric benzene + n-decane system. The TRAPP method, on the other hand, gave very large errors for the benzene + n-hexane system ranging from 20% at the lowest temperatures to 100% at 323 K. This was due to the methane reference with shape factors predicting the wrong phase at 323 K. It is obvious that the ability of the GCSP method to use different reference fluids offers a tremendous advantage in the prediction of viscosities of components for which the shape

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factors are not valid. No binary interaction coefficients were used.

(d) Methane + n-decane

Results for the methane + n-decane system are presented in Table 4. This sytem is highly asymmetric (with the ratio of the critical volumes of the two components being greater than 6) and it is obvious that the modified van der Waals mixing rule combined with the linear mass mixing rule (eqns. 19-25) does not work well for this type of mixture. The GCSP method gives an AAD of 20.2% when no binary interaction coefficient is used in the calculations. The AAD can be reduced to 2.31% when a value of $\xi_{12} = 1.45$ is used in the calculations. In contrast, the viscosity of methane + n-decane mixtures can be predicted to within ten percent by the TRAPP method. It appears that the Enskog correction to the mixing rules for asymmetric mixtures introducted by Ely [23] in the TRAPP method works well for this system.

(e) Hydrogen + nitrogen

Results for hydrogen + nitrogen mixtures are summarized in Table 5. Mixture data were available at two different mole fractions of hydrogen (0.46 and 0.75) over a temperature range of 288 K - 523 K and a pressure range of 1 - 800 bar. Although reference fluid data for hydrogen had to be extrapolated beyond 200 bar, the GCSP method gave an AAD of 8.24% without any binary interaction coefficients. The TRAPP method was less successful

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in predicting the viscosities of this system, giving an AAD of 19.05%.

In an effort to reduce errors even further, effective critical temperatures and pressures for the quantum fluid (hydrogen) were used in the calculations [26]. The results are also shown in Table 5. In general, use of the effective critical constants resulted in decreased errors. However, the decrease in AAD from 8.24% to 6.64% was not sufficient to warrant the use of effective critical constants. It appears that with the use of appropriate reference fluids, no special treatment is required for quantum fluids such as hydrogen.

CONCLUSIONS

This work has demonstrated that the GCSP method can be applied for the calculation of the viscosities of a variety of mixtures over a wide range of temperatures and pressures. In general, the predictions are better than those of the TRAPP method; the exception being highly asymmetric systems, where the GCSP method requires the use of a binary interaction coefficient because of the inadequacy of the mixing rules used. The GCSP method is simple to use and involves no iterations. Further, no density calculations are required unlike the TRAPP method. The ability to change reference fluids allows the treatment of non-traditional mixtures such as those containing quantum fluids. The method is capable of systematic improvement and extension as "wide range" viscosity data for the reference fluids become available.

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Table 1. Viscosity predictions for methane + n-butane
($x_1 = 0.396$)

# of Points	Temp. (K)	Press. Range (bar)	GCSP AAD% $\xi_{12} = 1.0$	TRAPP AAD%
12	278	80-350	2.42	5.46
12	311	80-350	2.64	4.07
11	344	80-350	2.57	6.22
11	378	80-350	1.69	8.96
11	411	80-350	4.66	8.08
12	444	80-350	7.79	6.84
12	478	80-350	13.01	5.91
12	511	80-350	18.24	5.84
93			6.75	6.38

Table 2. Viscosity predictions for the ethane + ethylene system

x_1	# of points	Temp. range (K)	Pressure range (bar)	GCSP AAD% $\xi_{12} = 1.0$	TRAPP AAD%
0.354	60	323-473	1-600	5.97	5.96
0.699	56	323-473	1-500	8.25	8.97
0.813	60	323-473	1-600	6.67	7.21
			Overall	6.93	7.34

Table 3. Viscosity prediction for aromatic systems

x_1	# of points	Temp. range (K)	Pressure (bar)	GCSP AAD% $\xi_{12} = 1.0$	TRAPP AAD%	TRAPP AAD% (323K Data omitted)
benzene + n-hexane						
0.930	3	298-323	1.0	1.59	18.2	19.8
0.818	3	298-323	1.0	1.48	43.3	16.0
0.735	3	298-323	1.0	4.92	46.1	20.1
0.595	3	298-323	1.0	4.78	42.3	14.5
0.437	3	298-323	1.0	7.42	40.3	11.5
		Overall		4.04	38.0	16.4
benzene + n-decane						
0.5	3	298-323	1.0	8.79	6.00	

Table 4. Viscosities of methane + n-decane mixtures

x_1	# of points	Temp. range (K)	Pressure range (bar)	GCSP AAD% $\xi_{12} = 1.0$	GCSP AAD% $\xi_{12} = 1.45$	TRAPP AAD%
0.1	20	311–444	80–350	7.38	1.96	14.49
0.3	21	311–444	100–350	21.10	2.35	3.50
0.5	18	311–444	170–350	<u>33.50</u>	<u>2.65</u>	<u>10.11</u>
				20.23	2.31	9.24

Table 5. Viscosity predictions for hydrogen + nitrogen mixtures

x_1	# of points	Temp range (K)	Press. range (bar)	GCSP AAD% $\xi_{12} = 1.0$	GCSP* AAD% $\xi_{12} = 1.0$	TRAPP AAD%
0.46	18	288-373	1-400	4.49	4.85	16.36
0.75	54	288-373	1-800	<u>9.49</u>	<u>7.24</u>	<u>19.95</u>
			Overall	8.24	6.64	19.05

GCSP* = Generalized Corresponding States Principle with effective criticals for hydrogen.

Correlation and Prediction of Diffusion Coefficients by Use of a Generalized Corresponding States Principle

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A generalized corresponding states prinicple (GCSP) based on the properties of two (nonspherical) reference fluids is extended here to diffusion coefficients. The prediction of self-diffusion coefficients requires a knowledge of the self-diffusion coefficients of two (similar) fluids, whereas the prediction of infinite dilution diffusion coefficients in a given solvent requires a knowledge of the infinite dilution diffusion coefficients of two fluids in the same solvent. The composition dependence of binary diffusion coefficients can be correlated by using the measured (or predicted) infinite dilution diffusion coefficients. Good agreement between experiment and calculation has been obtained by using, at most, one adjustable constant to characterize each binary system. The new method is as good as, and often better than, the commonly available predictive equations.

Introduction

The importance of diffusion in mass transfer and other chemical engineering calculations is well recognized. The availability of experimental data on diffusion coefficients is, however, limited, and the desired values must usually be estimated. Diffusion coefficients for dilute gases can be estimated with a fair degree of accuracy from a knowledge of intermolecular forces via the kinetic theory (see, for example, Reid et al. (1977)). On the other hand, no completely satisfactory theory exists for diffusion in liquids and dense gases. Perhaps the most productive theory for liquids in terms of practical applications is the hydrodynamic theory as discussed by Umesi and Danner (1981). Methods based on this theory, however, require a knowledge of the viscosity of the fluid (or fluid mixture) at the conditions of interest. These data may not always be available, and it is useful to develop correlations which relate the diffusion coefficient to other easily available or measurable physicochemical quantities.

The corresponding states principle has proved to be a powerful tool for the prediction of the thermodynamic properties of fluids using readily available data on the critical properties and vapor pressures of the fluids of interest. Many attempts have therefore been made to apply the principle to the calculation of transport prop-

erties including those by Mathur and Thodos (1965), Slattery and Bird (1958), Fair and Lerner (1956), Hanley (1976), Murad and Gubbins (1977), and Murad (1981). Recently, a generalized corresponding states principle (GCSP) based on the properties of two reference fluids has been applied successfully to the calculation of the viscosity (Teja and Rice, 1981a) and thermal conductivity (Teja and Rice, 1981b). In this work, the GCSP method is extended to the correlation and prediction of diffusion coefficients in liquids. The new method offers the advantage that no viscosity data are required in the calculations.

Generalized Corresponding States Principle for Diffusion Coefficients

A pure fluid i (with critical parameters T_{cii}, P_{cii}, V_{cii} and molecular weight M_{ii}) is defined to be in corresponding states with a reference fluid 0 if the reduced self-diffusion coefficient $\xi_{ii}D_{ii}$ of the two substances at the same reduced temperature T_R and reduced pressure P_R is given by

$$\xi_{ii}D_{ii} = \xi_{00}D_{00} \tag{1}$$

where

$$\xi = M^{1/2}T_c^{-1/2}V_c^{-1/3} \tag{2}$$

Equation 1 is strictly valid only for pairs of substances

(such as the noble gases) in which the molecules interact with spherically symmetric two-parameter potentials (i.e., for conformal substances). It is a statement of the two-parameter corresponding states principle.

In the more general case of nonconformal fluids, one can generalize the corresponding states principle either by changing the reduction parameters T_c and V_c (or P_c)—as was done by means of shape factors by Leland and Chappelear (1968) and by Murad (1981)—or one can rewrite eq 1 as a Taylor series expansion in the acentric factor ω. The latter approach was used successfully by Pitzer et al. (1955) for thermodynamic properties and is adopted here for diffusion coefficients. Thus, for nonconformal fluids, eq 1 is rewritten as

$$\xi_{ii}D_{ii} = \xi_{00}D_{00} + \omega_i\Delta(\xi D) \tag{3}$$

Here, $\xi_{00}D_{00}$ is the reduced self-diffusion coefficient of a simple fluid with zero acentric factor and $\Delta(\xi D)$ is a (complicated) deviation function.

We have recently proposed a generalized corresponding states principle (GCSP) for thermodynamic and transport properties which no longer retains the simple fluid as a reference fluid and obtains the deviation function in eq 3 from a difference in the properties of two reference fluids. We may write the GCSP for self-diffusion coefficients as

$$\xi_{ii}D_{ii} = \xi_{11}D_{11} + \frac{\omega_i - \omega_1}{\omega_2 - \omega_1}\{\xi_{22}D_{22} - \xi_{11}D_{11}\} \tag{4}$$

where the subscripts 1 and 2 refer to two (nonspherical) reference fluids chosen so that they are similar to the fluid or fluids of interest. Equation 4 provides a simple method for the calculation of the self-diffusion coefficient of any fluid if the self-diffusion coefficients of two similar fluids *at the same reduced conditions* are available. A knowledge of only T_c, V_c (or P_c), and ω of the fluid of interest is required. In contrast, methods based on the hydrodynamic theory—such as that of Tyn and Calus (1975)—require the viscosity and the density at the conditions of interest. The Tyn–Calus equation is given by

$$D_{ii} = 0.0229V_{bi}^{0.636}\rho_i T/(\mu_i M_i) \tag{5}$$

where V_{bi} (cm^3 mol^{-1}) is the molar volume of i at its normal boiling point, ρ_i (g cm^{-3}) is the density, and μ_i (cP) is the viscosity of i at temperature T.

Equation 4 implies that the self-diffusion coefficients of similar fluids are proportional to their acentric factors. Hildebrand (1971) has suggested that diffusion coefficients may be proportional to the surface area of the diffusing species. If the surface area is assumed to be proportional to $V_c^{2/3}$, we may then write eq 4 as

$$\xi_{ii}D_{ii} = \xi_{11}D_{11} + \frac{V_{cii}^{2/3} - V_{c11}^{2/3}}{V_{c22}^{2/3} - V_{c11}^{2/3}}\{\xi_{22}D_{22} - \xi_{11}D_{11}\} \tag{6}$$

Calculations based on eq 6 are also shown below. In this case only T_c and V_c need to be known for the fluid of interest, so that a two-parameter generalized corresponding states principle results.

More useful in mass trasnfer calculations is the diffusion coefficient of species i at infinite dilution. Unlike the properties considered so far (compressibility, viscosity, thermal conductivity, and self-diffusion coefficient), this is a property solely of the interactions between two different species (viz., the solute and the solvent). It cannot therefore be predicted from the self-diffusion coefficients of two reference fluids. However if the infinite dilution coefficients of two reference fluids in a common solvent are known, then we may write for the infinite dilution coefficient D^0_{is} of i in the same solvent s

$$\xi_{ii}D^0_{is} = \xi_{11}D^0_{1s} + \frac{\omega_i - \omega_1}{\omega_2 - \omega_1}\{\xi_{22}D^0_{2s} - \xi_{11}D^0_{1s}\} \tag{7}$$

where all quantities are evaluated at the same reduced temperature and pressure. Equation 7 simply states that in a given solvent, the infinite dilution diffusion coefficients of three similar substances (i, 1, and 2) are proportional to the acentric factors of the three species. This is expected to work well for nonpolar fluids in nonpolar solvents and to a lesser extent for mixtures containing polar fluids. If the infinite dilution diffusion coefficients are assumed to be proportional to $V_c^{2/3}$, we may write

$$\xi_{ii}D^0_{is} = \xi_{11}D^0_{1s} + \left\{\frac{V_{cii}^{2/3} - V_{c11}^{2/3}}{V_{c22}^{2/3} - V_{c11}^{2/3}}\right\}\{\xi_{22}D^0_{2s} - \xi_{11}D^0_{1s}\} \tag{8}$$

This is analogous to eq 6. Both eq 7 and 8 compare favorably in terms of the amount of data required with the Wilke–Chang (1955) equation which is prominent among the methods recommended for infinite dilution diffusion coefficients in the literature. The Wilke–Chang equation is given by

$$D^0_{is} = 7.4 \times 10^{-8}\frac{(\phi_s M_s)^{1/2}T}{\mu_s V_{bi}^{0.6}} \tag{9}$$

where the subscript s refers to the solvent and subscript i to the diffusing species. ϕ_s is an association factor for the solvent. Equation 9 requires a knowledge of the viscosity of the solvent μ_s at the temperature of the solution. In contrast, the GCSP equations require only the critical properties of the diffusing species.

In studies concerned with the rate at which concentration gradients approach their equilibrium values, mutual diffusion coefficients and their concentration dependence are of interest. In general, it can be shown that a single mutual diffusion coefficient D_{ij} is sufficient in binary systems to describe this rate. Several liquid models indicate how D_{ij} might be expected to vary with concentration; e.g., the Darken (1948) equation gives

$$D_{ij} = (D^*_{ii}x_i + D^*_{jj}x_j)\left(\frac{\partial \ln a_i}{\partial \ln x_i}\right)_{T,P} \tag{10}$$

where a_i is the activity of species i and the asterisks denote tracer diffusion coefficients at x_i, x_j. Although in some cases the Darken equation does provide a reasonable prediction of how D_{ij} varies with composition, there are many instances where large deviations have been noted. Reid et al. (1977) recommend the Vignes (1966) equation

$$D_{ij} = (D^0_{ij})^{x_j}(D^0_{ji})^{x_i}\left(\frac{\partial \ln a_i}{\partial \ln x_i}\right)_{TP} \tag{11}$$

This offers the advantage that in the limit $x_j \to 0$, it correctly predicts $D_{ij} \equiv D_{ji} = D^0_{ji}$. Similarly, as $x_i \to 0$, $D_{ij} = D^0_{ij}$. However, large deviations have been noted when the Vignes equation is applied to some systems, e.g., benzene + cyclohexane (Loflin and McLaughlin, 1969). This is usually because the thermodynamic factor ($\partial \ln a/\partial \ln x$) overcorrects for the concentration dependence. It should be added that the quantity ($\partial \ln a/\partial \ln x$) must be known or estimated from other sources before the Vignes equation can be used to predict D_{ij}.

Other methods which do not require a thermodynamic factor have also been proposed. These latter methods include the method of Wilke (1949), which may be written as

$$D_{ij}\mu_m = D^0{}_{ij}\mu_i x_i + D^0{}_{ji}\mu_j x_j \qquad (12)$$

and that of Leffler and Cullinan (1970), which may be written as

$$D_{ij}\mu_m = (D^0{}_{ij}\mu_i)^{x_i}(D^0{}_{ji}\mu_j)^{x_j} \qquad (13)$$

In eq 12 and 13, μ_i, μ_j, and μ_m are the viscosities of component i, component j, and the mixture m, respectively. These viscosities must be known at the temperature of interest and this limits the application of the two equations because the viscosity data may not always be available.

The simplest equation proposed for the concentration dependence of mutual diffusion coefficients is that of Caldwell and Babb (1956), who write

$$D_{ij} = x_i D^0{}_{ij} + x_j D^0{}_{ji} \qquad (14)$$

Surprisingly, Umesi and Danner (1981) recently found that for nonpolar mixtures eq 14 gave absolute average deviations between prediction and experiment of 13.9% compared with 13.7% for the Wilke equation and 11.4% for the Leffler and Cullinan equation. None of these equations is, however, expected to work well for polar and associated mixtures.

By analogy with eq 4 and 7, we may write

$$\xi_m D_{ij} = \xi_{ii} D^0{}_{ji} + \frac{\omega_m - \omega_i}{\omega_j - \omega_i}\{\xi_{jj} D^0{}_{ij} - \xi_{ii} D^0{}_{ji}\} \qquad (15)$$

Here the subscript m denotes a mixture quantity. (Note that $\xi_m D_{ij} \rightarrow \xi_{ii} D^0{}_{ji}$ as $x_j \rightarrow 0$ and $\xi_m D_{ij} \rightarrow \xi_{jj} D^0{}_{ij}$ as $x_i \rightarrow 0$ as shown below, so that the "reference fluids" are, in effect, the two infinitely dilute solutions).

The mixture (pseudo-critical)quantities are obtained as follows

$$T_{cm}V_{cm} = \sum_i\sum_j x_i x_j T_{cij}V_{cij} \qquad (16)$$

$$V_{cm} = \sum_i\sum_j x_i x_j V_{cij} \qquad (17)$$

$$M_m = \sum_i x_i M_i \qquad (18)$$

$$\omega_m = \sum_i x_i \omega_i \qquad (19)$$

There is some theoretical justification (Leland and Chappelear, 1968) for the use of eq 16 and 17 for nonpolar mixtures, although their use for other types of mixtures is questionable. Equation 18 represents a mass balance, and although it differs from the more complicated relationships suggested by Mo and Gubbins (1976) and by Ely and Hanley (1981), we have preferred to retain the simple mass balance because it has worked well in our previous transport property calculations. Equation 19, on the other hand, is completely arbitrary. Its only justification is that it has been used successfully in our earlier calculations and that it leads to a simple form of eq 15 as shown below.

The cross terms in eq 16 and 17 are obtained as follows

$$T_{cij}V_{cij} = \psi_{ij}(T_{cii}V_{cii}T_{cjj}V_{cjj})^{1/2}; \quad i \neq j \qquad (20)$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \qquad (21)$$

where ψ_{ij} is a binary interaction coefficient which serves as an adjustable constant in the calculations—in part because of our inability to represent intermolecular forces correctly by means of eq 16–19.

In the case of binary mixtures in which the two pure components are used as the reference fluids, use of eq 19 in eq 15 leads to the simple relationship

$$\xi_m D_{ij} = x_i\xi_{ii}D^0{}_{ji} + x_j\xi_{jj}D^0{}_{ij} \qquad (22)$$

This is not unlike the Caldwell and Babb (1956) relationship, except that all quantities are evaluated at the same reduced temperature and pressure. Moreover, as x_i
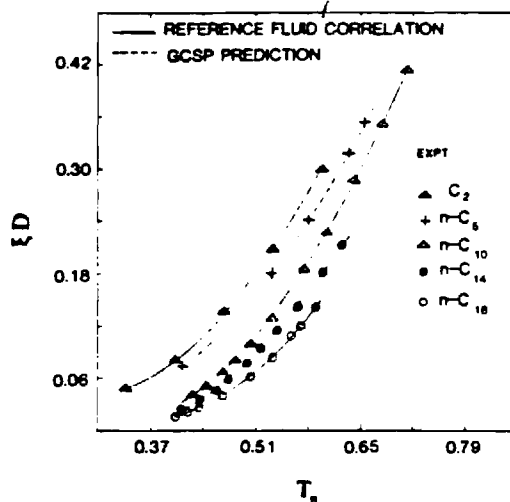

Figure 1. Self-diffusion coefficients of the n-alkanes over the normal liquid range. The experimental data are those of Ertl (1973). The dashed lines represent calculated values using the GCSP. Only the calculated lines for n-pentane and n-tetradecane are shown for clarity.

$\rightarrow 0$, $\xi_m \rightarrow \xi_{jj}$, $D_{ij} \rightarrow D^0{}_{ij}$, and as $x_j \rightarrow 0$, $\xi_m \rightarrow \xi_{ii}$, $D_{ij} \equiv D_{ji} = D^0{}_{ji}$. The expression therefore leads to the correct infinite dilution diffusion coefficients at the two ends of the concentration range. It should also be noted that the acentric factor does not appear in eq 22. Thus, although eq 15 is indeterminate for mixtures of spherical fluids (all $\omega_i = 0$) eq 22 may be used when all $\omega_i = 0$.

Calculations using eq 4 and 5 for self-diffusion coefficients, eq 7 and 8 for infinite dilution diffusion coefficients, and eq 22 for the concentration dependence of mutual diffusion coefficients are shown below. Whenever possible, the calculated values have been compared with predictions using the most prominent methods found in the literature. In all cases, the GCSP calculations require fewer data, assuming the reference fluid data are available.

Data Used for Evaluation

Accurate measurments of diffusion coefficients are difficult to make, and consequently, there is a considerable amount of uncertainty in the reported experimental values. Observations of the same system reported in the literature often differ considerably. In addition, for evaluation purposes, the GCSP method requires a knowledge of diffusion coefficients over extended ranges of reduced temperature and pressure or a large number of substances. Most data in the literature have been measured at temperatures between 273 and 333 K and 1 atm pressure. As a result, only limited comparisons can be shown below. In particular, the calculations shown below are restricted to low pressures, where pressure effects can be neglected. In principle, of course, the method can be used at any reduced temperature and pressure where reference fluid data are available.

The most extensive sets of self-diffusion data in the literature are those of Ertl (1973) and Ertl and Dullien (1973). They measured the self-diffusion coefficients of five halogenated benzenes (C_6H_5X where $X = H$, F, Cl, Br, and I) and seven n-alkanes (C_nH_{n+2n} where $n = 7, 9, 10, 12, 14, 16$, and 18) over a range of temperatures between the boiling and melting points of the substances. Their data are shown in Figures 1 and 2 as plots of the reduced self-diffusion coefficient ξD vs. the reduced temperature T_R. Not surprisingly, the data exhibit a regular trend with size. Etrl and Dullien (1973) were able to fit their data to the Arrhenius equation with average errors between 1.0 and 4.0% over the normal liquid range of the pure sub-

Table I. Comparisons of Experimental and Predicted Self-Diffusion Coefficients for the n-Alkanes

| substance	temp range, K	no. of points	AAD%			data ref	ref fluids
			eq 4	eq 6	eq 5		
CH_4	90–111	6	8.75	8.94	11.74	Dullien (1972)	C_2, n-C_{10}
n-C_5H_{12}	194–308	5	6.20	6.32	3.57	Dullien (1972)	C_2, n-C_{10}
n-C_7H_{16}	194–369	8	7.61	6.29	4.15	Dullien (1972)	C_2, n-C_{10}
n-C_9H_{20}	235–422	11	6.19	5.18	5.90	Ertl (1973)	C_2, n-C_{10}
n-$C_{12}H_{26}$	264–435	10	5.17	5.18	5.81	Ertl (1973)	n-C_{10}, n-C_{18}
n-$C_{14}H_{30}$	279–434	11	4.66	2.47	11.49	Ertl (1973)	n-C_{10}, n-C_{18}
overall AAD%			7.08	6.41	7.27		
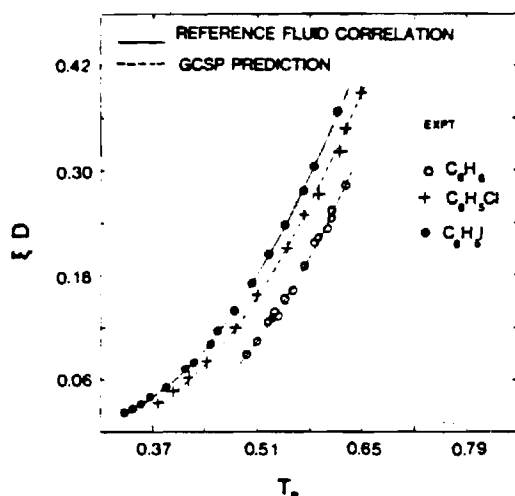
Figure 2. Self-diffusion coefficients of the halogenated benzenes over the normal liquid range. The experimental data are those of Ertl (1973). The dashed line represents calculated values for chlorobenzene using the GCSP.

stances. We have retained Ertl and Dullien's equations in the form

$$\ln (\xi D) = A + B/T_R \qquad (23)$$

as our equations for the reference substances in this work. Use of eq 23 is a matter of accuracy and convenience. It does not imply that diffusive motion proceeds via an activation process, nor does it necessarily preclude any anomalous behavior of the diffusion coefficient near the melting point of the substance (Kruger and Weiss, 1970). It was found that eq 23 fitted the data for the reference fluids within the accuracy of the experimental measurements for the range of temperatures $(0.3 < T_R < 0.7)$ studied.

The choice of reference substances is also arbitrary. In this work, this choice was primarily based on the availability of data. Thus, for example, it would have been interesting to predict the self-diffusion coefficients of n-butane at various temperatures given the self-diffusion coefficients of methane and eicosane. However, it proved impossible to find data for methane and eicosane over the same range of reduced temperatures. As extrapolation of the reference equations over large ranges of reduced temperatures is not recommended, the self-diffusion coefficients of n-butane had to be predicted by use of the known self-diffusion coefficients of ethane and n-decane. Data for infinite dilution diffusion coefficients proved even more difficult to find in the literature, especially over a range of reduced temperatures. As a result, only very limited comparisons can be shown between theory and experiment. In the few cases shown below, data for the reference fluids were again fit to eq 23 within the accuracy of the experimental measurements.

Mutual diffusion coefficient data are relatively abundant in the literature, although there is a considerable amount

Table II. Comparisons of Experimental and Calculated Self-Diffusion Coefficients for the Halogenated Benzenes[a]

substance	temp range, K	no. of points	AAD%, eq 6	data ref
C_6H_5Cl	229–410	15	6.50	Ertl (1973)
C_6H_5Br	241–430	16	4.18	Ertl (1973)
C_6H_5F	237–356	17	11.05	Ertl (1973)
overall AAD%			7.33	

[a] Equation 6 with benzene and iodobenzene as the reference fluids.

Table III. Infinite Dilution Diffusion Coefficients of Toluene in Water Predicted from the Properties of Benzene and Ethylbenzene in Water

T, K	$D_{exptl} \times 10^5$, cm^2/s[a]	$D_{calcd} \times 10^5$, cm^2/s	
		GCSP/eq 7	GCSP/eq 8
275	0.45	0.52	0.52
283	0.62	0.66	0.66
293	0.85	0.87	0.87
313	1.34	1.43	1.43
333	2.15	2.22	2.22

[a] Data of Vadovic and Colver (1973).

Table IV. Experimental and Predicted Infinite Dilution Coefficients of n-Butane in Water[a]

T_R	$D_{exptl} \times 10^5$, cm^2/s	$D_{calcd} \times 10^5$,[b] cm^2/s
0.652	0.50	0.56
0.690	0.89	0.92
0.737	1.59	1.58
0.784	2.51	2.54

[a] Using propane and n-pentane as the reference fluids. [b] From eq 7. Experimental data of Witherspoon and Bonoli (1969).

of uncertainty in the reported experimental values because of experimental difficulties. In addition, the GCSP method requires a knowledge of the infinite dilution diffusion coefficients over a range of temperatures, so that values of this property at the same reduced temperature (and pressue) as the mixture can be used in the calculations. We have therefore chosen to study 13 binary systems where mutal diffusion and infinite dilution diffusion data were available at three or more temperatures. These systems include nonpolar, polar, as well as aqueous mixtures and cover the broad range of mixtures that are likely to be of practical interest. Since all experimental data were reported at 1 atm pressure, pressure effects are ignored in the folowing calculations. For analytical representation and for interpolation/extrapolation, the reference fluid infinite dilution diffusion coefficients were fitted to eq 23.

Results and Discussion

Self-Diffusion Coefficients. Tables I and II summarize the results of our calculations of the self-diffusion coefficients of the n-alkanes and the halogenated benzenes using the generalized corresponding states principle (eq 4 and 6) and the Tyn–Calus method (eq 5). Equation 4 requires a knowledge of the critical temperature, critical

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Table V. Comparisons between Experimental and Calculated Mutual Diffusion Coefficients

system	temp range of data	no. of data	AAD%,[a] $\psi = 1$	AAD%,[a] $\psi = \psi_{opt}$	ψ_{opt}	AAD%,[a] Vignes	data ref
c-C_6H_{12} + C_6H_6	298–333	33	5.75	0.86	1.04	3.64	Sanni (1971)
CCl_4 + c-C_6H_{12}	298–328	33	1.44	0.24	0.99	0.96	Sanni (1973)
C_6H_6 + CCl_4	283–313	19	1.57	1.44	0.99	4.24	Johnson (1956)
$C_6H_5CH_3$ + c-C_6H_{12}	298–328	33	6.42	1.50	1.04	7.46	Sanni (1971)
C_6H_6 + $C_6H_5CH_3$	298–313	22	3.08	0.61	1.02	2.06	Sanni (1971)
$C_6H_5CH_3$ + c-$C_6H_{11}CH_3$	298–333	12	9.58	1.03	1.09		Haluska (1971)
C_6H_5Br + C_6H_5Cl	283–313	15	0.87	0.87	1.00		Johnson (1956)
$C_6H_5CH_3$ + C_6H_5Cl	283–313	15	1.84	1.47	1.01		Johnson (1956)
C_6H_6 + $CHCl_3$	298–328	33	1.11	1.11	1.00		Sanni (1971)
$(CH_3)_2CO$ + $CHCl_3$	298–328	33	10.83	2.11	0.89	3.23	Tyn (1975)
$C_6H_5CH_3$ + $C_6H_5NH_2$	298–333	21	91.10	11.26	1.38		Haluska (1971)
C_2H_5OH + H_2O	298–346	33	102.1	5.43	1.43	29.03	Tyn (1975)
$(CH_3)_2CO$ + H_2O	298–328	44	171.5	11.08	2.06	25.21	Tyn (1975)

[a] AAD% $= (100/n)\sum_1^n |1 - (D_{calcd}/D_{exptl})|$.

volume, and the acentric factor of the diffusing species, whereas eq 6 assumes that diffusion is proportional to the surface area (or $V_c^{2/3}$) and requires a knowledge only of the critical temperature and critical volume of the diffusing species. The reference fluids used were ethane and n-decane for the lower n-alkanes, n-decane and n-octadecane for the higher n-alkanes, and benzene and iodobenzene for the halogenated benzenes. The Tyn–Calus equation, although not requiring any reference fluid data, does require a knowledge of the viscosity and density of the fluid at the temperature of interest, as well as a knowledge of the normal boiling point of the fluid. The temperature range of the experimental data covered the normal liquid range from the melting point to the boiling point.

As can be seen in Table I, the average absolute deviation between experimental self-diffusion coefficients and those calculated using eq 4, 5, and 6 are approximately the same, with eq 6 being marginally better in its predictions for the n-alkanes. Surprisingly, this equation requires the least amount of data for the diffusing species (only T_c and V_c). The Tyn–Calus equation requires the most data.

Table II shows the average absolute deviations between experimental and calculated self-diffusion coefficients for three halogenated benzenes using eq 6. Once again, the agreement between theory and experiment is within the accuracy of the experimental measurements ($\pm 10\%$). Equation 4 could not be used here because the acentric factors of the three halogenated benzenes considered are approximately equal, so that a different third parameter is required. The Tyn–Calus equation could not be used because of a lack of viscosity and density data.

It would appear that the generalized corresponding states prinicple with diffusion being assumed proportinal to surface area of the diffusing species as measured by $V_c^{2/3}$ (eq 6) provides a reliable and accurate method for the prediction of self-diffusion coefficients over the normal liquid range (see Figures 1 and 2). In principle, the method can be extended to other temperatures and pressures provided that data for two reference fluids are available at the same reduced conditions. The method is simple to use and requires a minimum of information (T_c and V_c) for the fluid of interest.

Infinite Dilution Diffusion Coefficients. Tables III and IV show the experimental and calulated infinite dilution diffusion coefficients of toluene in water and of butane in water. Because of a lack of data of many substances over the same range of reduced temeratures, very similar reference fluids had to be used in the calculations. It is perhaps not surprinsing that the diffusion coefficients of toluene can be predicted by using data on the diffusion coefficients of benzene and ethyl benzene. Nevertheless, it is encouraging to note that the average error was found

to be only 6.6% using either eq 7 or 8 when the solvent is water. Similar conclusions apply in the case of butane in water. In contrast, the average error for the Wilke–Chang equation was ~8%. It is difficult to reach any general conclusions based on these limited comparisons. However, it does appear that, as in the case of self-diffusion coefficients, the generalized corresponding states principle can be used to predict infinite dilution diffusion coefficients with quantitative agreement between prediction and experiment.

Mutual Diffusion Coefficients. Table V shows the average absolute deviations between calculated and experimental mutal diffusion coefficients for the 13 binary mixtures studied in this work. As expected, the average deviations are least for nonpolar mixtures and greatest for aqueous mixtures. Deviations between experiment and calculation can be reduced considerably if one adjustable parameter is used to characterize each binary mixture. Over the range of temperatures studied, the binary interaction coefficient appears to be independent of temperature, so that data at one temperature can be used to accurately predict mutual diffusion coefficients at a different temperature. The GCSP calculations appear to be closer to experiment than those using the Vignes equation and require less input information. The deviations also appear to be considerably smaller than those reported by Umesi and Danner (1981) for nonpolar mixtures using the Wilke (AAD = 13.7%), Leffler and Cullinan (AAD = 11.4%), and Caldwell and Babb (AAD = 13.9%) equations.

In summary, the generalized corresponding states principle appears to be a powerful tool for the prediction of diffusion coefficients. It is easy to use and requires a minimum amount of readily available data. A thorough evaluation using extensive reference fluid data is, however, required before its application to polar fluids can be recommended, although even for such fluids, the method may be used to extrapolate data over a temperature range.

Nomenclature

A, B = constants in eq 23
D = diffusion coefficient
M = molecular weight
P = pressure
T = temperature
V = molar volume
x = mole fraction
Greek Letters
$\xi = M^{1/2}T_c^{-1/2}V_c^{-1/3}$
μ = viscosity
ϕ = association factor
ω = acentric factor
Subscripts
b = normal boiling point

c = critical
i, j = component i, j
m = mixture (pseudocritical) value
R = reduced value
s = solvent
1,2 = (reference) 1,2

Superscripts

0 = infinite dilution value
* = tracer value

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