CHARACTERIZATION OF GAS-EXPANDED LIQUIDS

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CHARACTERIZATION OF GAS-EXPANDED LIQUIDS

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This thesis is dedicated in loving memory of my Grandmother,
Mrs. Helen Jones Lowe

TABLE OF CONTENTS

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I would first like to give honor to God who has made all of this possible. I have always known that with the Lord on my side, I would never be hindered.

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LIST OF TABLES

x

LIST OF FIGURES

SUMMARY

Solvatochromic shifts of seven probe indicators {4-nitroaniline, 4-nitroanisole, 4-nitrophenol, N,N-dimethyl-4-nitroaniline, N,N-dimethyl-4-nitrosoaniline, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate} have been measured in binary mixtures of carbon dioxide with acetone and methanol at 35°C and 40°C over the entire range of solvent composition. The indicators were used to specify the solvatochromic solubility parameters $E_T(30)$, α, β, and π^* which were calculated from the solvatochromic shifts of the maximum absorbance peak (v_{max}) observed by means of UV/Vis spectroscopy.

The UV-Vis data was then taken and applied to the theories of preferential solvation on the binary solvent mixtures. The data was analyzed to determine if the differences between the bulk and local compositions of the binary mixtures had an effect on the solvatochromic shifts and thus the trends observed for the solvatochromic parameters ($E_T(30)$, α, β, and π^*) as determined in part one of this project.

CHAPTER I

INTRODUCTION

The aim of this work has been to characterize solvents expanded with

carbon dioxide. Gas expanded liquids have recently become of interest as

chemical process solvents. These novel solvents have been successfully

incorporated into applications using anti-solvent crystallization ranging from

controlled particle formation[1] to selective separation[2-6]. The advantage of this

type of solvent lies in the ability to tune its solvation properties with the amount

of gas dissolved, and thus with pressure. Unlike a conventional organic anti-

solvent, a gas such a carbon dioxide may be easily removed from the primary

solvent simply by depressurizing, precluding downstream separation and

providing an environmentally benign alternative.

The idea of using supercritical fluids (SCFs) as the co-solvent is derived

from the fact that SCFs should be sensitive media for investigating solvation

phenomena since solvent-solute intermolecular interactions change gradually in

nature and intensity as the solvent density is varied without changing the

chemical nature of the solvent. Therefore, it is important to study the effects of

temperature and pressure on solvatochromic shifts. Taking advantage of the solvatochromic shifts of indicators, it is possible to study solute –solvent interactions. Solvatochromic shifts are a direct reflection of the transition energy of the indicator, providing detailed information about the solvation's sphere composition and solvent properties such as polarity and hydrogen bonding capabilities. Such a probe could also lend valuable information about the physicochemical properties (i.e. reaction rates, equilibrium constants, and solubilities) of solvents systems over a range of temperatures and pressures. Linear free energy relationships (LFER) or linear solvation energy relationships (LSER) have been proposed to relate such properties in solution [7-9]. Of the many expressions that have been proposed for the description of LSER's, the Kamlet-Taft expression was found to be very successful [10-12].

Using the Kamlet-Taft expression as a model, we were able to design experiments that would adequately probe the desired solvatochromic parameter. 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate and 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide are used to study the polarity of solvents. These indicators are sensitive to the dipolarity/polarizability (π^*) and the hydrogen-bond donor capability (α) of the solvent [11]. Likewise, 4-nitroanisole/4-nitrophenol and 4-nitroaniline/N,N-dimethyl-4-nitroaniline pairs were used to probe the hydrogen-bond acceptor ability (β) of the solvent [10]

2

while 4-nitroanisole and N,N-dimethyl-4-nitroaniline are sensitive to the dipolarity and polarizability (π^*) of the solvent [12].

In chapter 4, the effect of local composition about the solute molecule was taken into consideration. The local composition could significantly influence the solvatochromic shift of the indicator because of the differences in interaction energies and sizes between the molecules in the mixture[13,14]. Because of this, the average composition in the immediate vicinity of the molecule may be different from the bulk composition of the fluid. Chapter 4 aims to study how the local composition may change with temperature, density, composition, and molecular shape.

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CHAPTER II

BACKGROUND

CARBON DIOXIDE AS SOLVENT MEDIUM

Traditional organic solvents are major contributors to pollution and depletion of the ozone layer. Replacing them with a more environmentally benign solvent has been the goal of researchers for several years. One alternative is carbon dioxide because it is cheap, non-flammable and relatively non-toxic.

Carbon dioxide has several other advantages and a growing number of applications. It has been studied extensively as a replacement solvent for industrial processes [1-3]. Supercritical CO_2 is a very attractive solvent because it has the mass transport properties of a gas and the solvation power close to that of a liquid (Figure 2.1). The advantage of such properties could result in much higher reaction rates in supercritical fluids relative to a liquid solvent if the reaction is mass transfer limited. The solvent power of supercritical CO_2 can be tuned by adjusting the temperature and pressure to create a more suitable
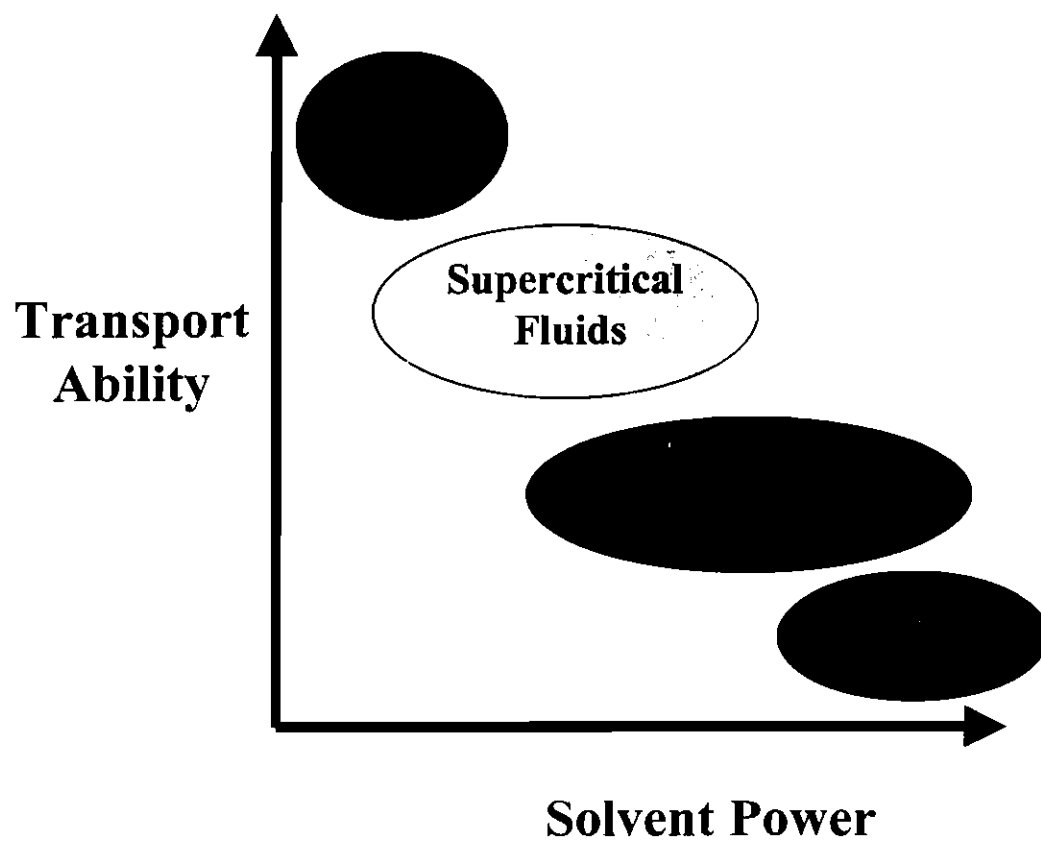
Figure 2.1. Solvent Power versus transcript ability of gasses, supercritical fluids, gas-expanded liquids, and liquids.

solvent for the desired application. The ability to tune solvent power is a powerful tool in separation technologies. It could allow not only selective separations of the solvent from the solute but it may also be possible to conveniently separate the product from the reactant. Other major advantages include (a.) the facile removal of the solvent, simply by depressurizing the system, which affords a product free of residual solvent and (b.) milder reaction conditions.

Supercritical CO_2 has demonstrated effective applicability in several areas. As a reaction solvent, it has been used in heterogeneous[4], homogeneous[5], and biocatalytic[6] systems. However, the most common use for $scCO_2$ is supercritical fluid extraction [7-9]. The ability of CO_2 to penetrate solids and dissolve solutes makes it a highly effective extraction solvent. It is used industrially to decaffeinate coffee and to extract flavors and essential oils from natural products. Supercritical CO_2 is also used in the processing of heat sensitive pharmaceutical compounds.

GAS-EXPANDED LIQUIDS

Carbon dioxide can also be used as reaction medium and in extraction processes in the form of a gas-expanded liquid. In gas expanded liquids, carbon dioxide is a co-solvent that is dissolved in an organic solvent such as alcohols, ketones, ethers and acetates. Chang *et al.* have elucidated the solubility of CO_2
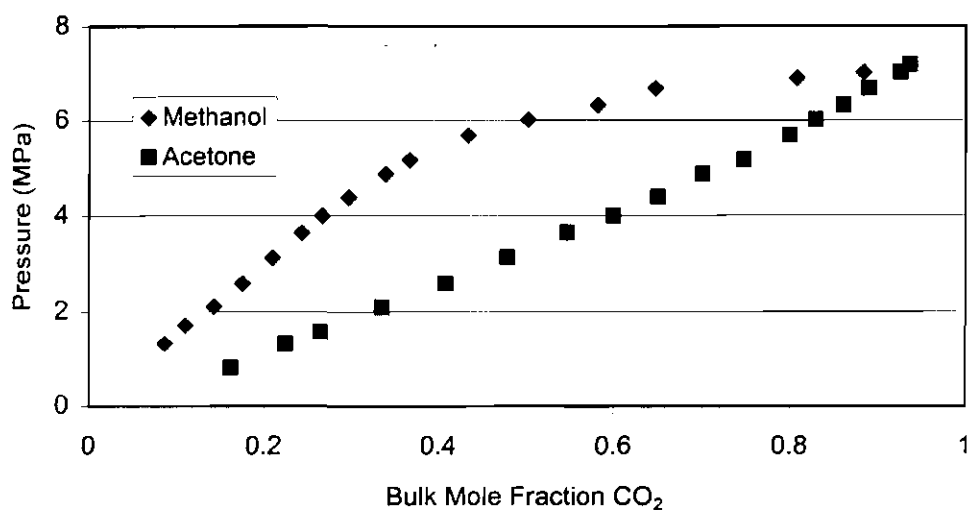
Figure 2.2. Solubility of CO_2 as a function of pressure.

as a function of pressure for several solvents (Figure 2.2)[10, 11]. The difference between using CO_2 as a supercritical fluid and a gas-expanded liquid is the experimental pressure. The supercritical point of CO_2 is 31.1°C and 7.38 MPa. Gas-expanded liquids are dissolved in solvents in relatively moderate pressures (< 8 MPa). Much like its supercritical counterpart, the solvent power of gas-expanded liquids can be tuned by varying the liquid phase concentration as the pressure is adjusted. As the pressure is increased, the CO_2 concentration in the liquid increases and the solvent power is lowered.

Gas expanded liquids have been used in gas anti-solvent (GAS) crystallization[12]. GAS recrystallization utilizes a gas or supercritical fluid as an anti-solvent for effecting precipitation of a solid dissolved in an organic liquid. The GAS system can nucleate the crystals homogeneously throughout the solution influencing uniform nucleation; whereas, in a traditional crystallization, cooling is employed to supersaturate the system to induce nucleation and growth of crystals. The disadvantage in the latter is that it relies on heat transfer from a surface, and therefore, nucleation often occurs at the cooler surface rather than uniformly. This process is useful in producing particles with little or no void space and of the desired size. Examples include producing biocompatible polymer microspheres for controlled for drug delivery[13], antibiotic micro-and nano-particles[14], and forming ultra-fine particles of difficult-to-comminute explosives[15].

Supercritical fluid extraction has been suggested as a viable alternative to other separation techniques for difficult separations. Such separation processes have been somewhat limited by the inherent reaction or nonselectivity of carbon dioxide to the compounds of interest. Gas antisolvent technology is has found greater success in this realm because unlike SFE, the CO_2 is not the extracting solvent but actually a highly soluble solute that forces other solutes out of solution. Examples include separating organic compounds such as acids[16] and β-carotene[17] from solution.

This technique has even been expanded to affect separations in reversed-phase HPLC and size exclusion chromatography. Another chromatographic technique that uses the advantages of gas-expanded liquids is liquid chromatography at the critical condition. The advantage of using a gas-expanded liquid is as a mobile phase cosolvent is that it enhances the fluidity of the solvent. This improves the ability to approach the critical condition through pressure control, increased efficiency, and a lower pressure drop across the column due to the low viscosity of the mobile-phase mixture.

Currently scientists are interested in using gas-expanded liquids as a reaction solvent to take advantage of the tunability[18]. The challenge has been the ability of the expanded liquid to effectively dissolve the catalyst. Overcoming that obstacle could better facilitate reactions that have reactants that are better dissolved in the expanded liquid as compared to the pure liquid solvent; thus, improving reaction rates.

SOLVATOCHROMIC COMPARISON METHOD

Dyes are highly colored compounds that usually contain polar functional groups, which serves to help them bind to fiber and determine its color. Most dyes are neutral, containing two charges of opposite sign that cancel. Dyes possess a large dipole moment and they are particularly interesting because their color is strongly dependent on the polarity and hydrogen bonding ability of the solvent. Depending on the solvent, the color can be purple, blue, green, orange, red or yellow. Such substances are called solvatochromic dyes. A proposed commercial use of these dyes is to detect adulteration of solvents.

In the ground state of solvatochromic dyes, the electron density is higher at the oxygen end of the molecule than at the nitrogen end. The resulting dipole points in the direction indicated by structure 2.3 and is quite large because of
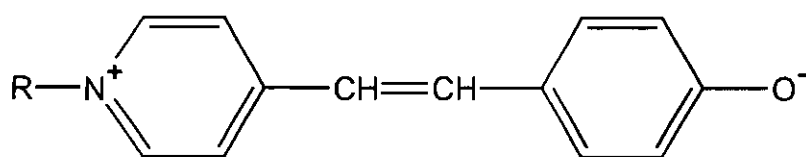
Figure 2.3. Structure of a solvatochromic dye.

the great distance between the charges. In a polar or hydrogen-bonding solvent, molecules interact strongly with the dipole of the dye and stabilize the ground state. Less polar solvents produce less stabilization. On electronic excitation of the molecule by absorption of visible light, electrons move from the negatively charged end to the positively charged end. This reduces the dipole moment and reduces the stabilization provided by the solvent. As a consequence, the energy gap between the ground and excited state is greater in a polar solvent such as methanol than in a nonpolar solvent such as acetone. From the Einstein relationship, $E=h\nu=hc/\lambda$, a larger excitation energy corresponds to a shorter wavelength for the absorbed light and longer wavelengths for the light that is not absorbed. Table 2.1 illustrates the relationship between energy of absorption and solution color. Note particularly that the color of the dye solution is the color of the light that was not absorbed. For example, in a nonpolar solvent, a merocyanin dye is purple (absorption of low-energy, long-wavelength yellow light), and in polar solvents it is yellow (absorbprion of high-energy, short-wavelength purple light).

Kamlet and Taft have outlined the solvatochromic comparison method. They have noted that to in order to study solute-solvent hydrogen-bonding, interactions, three important conditions need to be met[19]. (a) First, a plot of corresponding ν max values (or other appropriate spectroscopic of free-energy

12

Table 2.1. Relationship between energy of absorption and solution color.

Energy (kcal/mol)	Wavelength (nm)	Color of Absorbed Light	Color of Transmitted light
>75	<380	Ultraviolet	Colorless
75-66	380-435	Violet	Greenish Yellow
66-60	435-480	Blue	Yellow
60-58	480-490	Greenish Blue	Orange
58-57	490-500	Bluish Green	Red
57-51	500-560	Green	Purple
51-49	560-589	Greenish Yellow	Violet
49-48	589-595	Yellow	Blue
48-44	595-650	Orange	Greenish Blue
44-37	650-780	Red	Bluish Green
<37	>780	Infrared	Colorless

properties) for two solutes of differing hydrogen-bonding ability in a series of solvents of varying polarity, but wherein hydrogen-bonding is excluded, should show a linear relationship with a statistically acceptable correlation coefficient. This establishes how the spectra are influenced by changing solvent polarity. (b) Next, data points representing solvents in which hydrogen bonding occurs should be displaced from the regression line (all in the same direction) by statistically significant amounts. The deviations are presumed to reflect specific solute-solvent interaction effects. (c) Finally, the direction of the displacements should be consistent with the chemistry involved. The relative magnitudes

should reflect a reasonable order of solvent hydrogen-bond donor strengths in the case of solvent to solute (type A) bonding or solvent hydrogen-bond acceptor (HBA) strengths where the effects derive from solute to solvent (type B) hydrogen bonds[20].

Organic liquids are characterized by several properties that make them suitable for dissolving and for providing reaction media for various types of solutes. These properties include physical quantities, such as the liquid range (freezing to normal boiling temperatures), vapor pressure, density, refractive index, polarity, ability to form hydrogen bonds, and relative permittivity. Linear free energy relationships (LFER) or linear solvation energy relationships (LSER) have been proposed to relate such properties to diverse processes in solution: solubility, distribution between two liquids, retention in chromatography, rates of reaction, free energy and enthalpy of equilibria, wavelengths of light absorption and NMR chemical shifts[21-23]. In most cases, the quantity that describes the intensity or extent of such a process (called XYZ in the following for the sake of generality) depends on more than one solvent property. Of many expressions that have been proposed for the description of LSERs, the following Kamlet-Taft expression (equation 2.1) has been found to be very successful:

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi^* \qquad (2.1)$$

where XYZ, a, b, and s are solvent independent coefficients characteristic of the process and indicative of its sensitivity to the accompanying solvent properties, α is the hydrogen bond donation (HBD) ability of the solvent, β is its hydrogen bond acceptance (HBA) or electron pair donation ability to form a coordinative bond, and π^* is its polarity/polarizability parameter. Further terms (involving products of coefficients and solvent properties) may be added as required for specific processes.

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16

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CHAPTER III

CHARACTERIZATION OF METHANOL AND ACETONE EXPANDED

WITH CARBON DIOXIDE

When studying solvents via the solvatochromic comparison method, the most popular choices for studying the β parameter are 4-nitroaniline (Figure 3.1) and N, N-dimethyl-4-nitroaniline (Figure 3.2) or 4-nitroanisole (Figure 3.3) and 4-nitrophenol (Figure 3.4)[1]. The electronic transitions of the dyes are strongly dependent upon the degree of solute-solvent hydrogen bonding interaction. The solvents are of three types. (a) neither hydrogen bond accepting or hydrogen bond donating ($pK_{HB} < -0.5$), (b) hydrogen bond donating ($pK_{HB} > -0.2$), or (c) amphiprotic solvents. Both 4-nitroaniline and N, N-dimethyl-4-nitroaniline are capable of acting as HBD substrates (at the nitro oxygens) in hydrogen bond acceptor solvents, but only 4-nitroaniline can act as a hydrogen bond donor substrate in hydrogen bond donor solvents.

A similar comparison is made when studying the electronic transitions of 4-nitroanisole with 4-nitrophenol in corresponding solvents. Both 4-nitroanisole and 4-nitrophenol are capable of acting as HBD substrates (at the nitro oxygens)

18
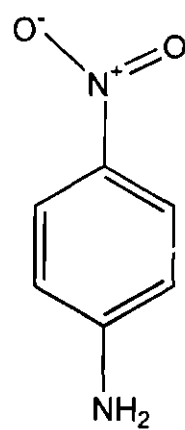
Figure 3.1. Structure of 4-nitroaniline.
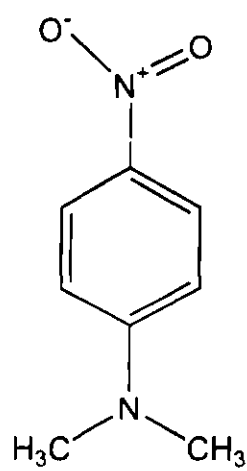
Figure 3.2. Structure of N,N-dimethyl-4-nitroaniline.
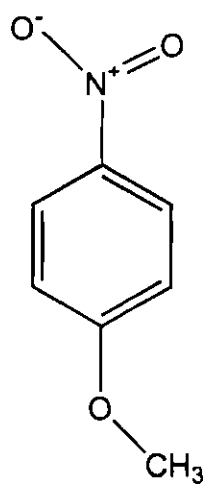
Figure 3.3. Structure of 4-nitroanisole.
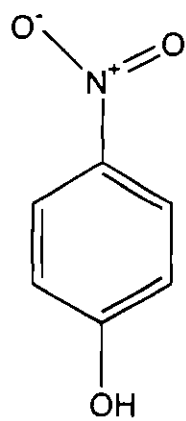
Figure 3.4. Structure of 4-nitrophenol.

in hydrogen bond acceptor solvents, but only 4-nitroanisole can act as a hydrogen bond donor substrate in hydrogen bond donor solvents.

Solvatochromic effects in amphiprotic solvents require separate treatment in the solvatochromic comparison method because multiple effects may result from simultaneous type-B bonding by 4-nitrophenol or 4-nitroaniline hydrogens to solvent oxygens and type –A bonding by solvent hydrogens to substrate nitro oxygens. Both types of hydrogen bonds lead to lower electronic transition energies.

Derivatives of 4-(N-pyridinio)-phenolate are known to undergo large solvent-induced absorbance shifts in going from polar to less polar solvents and are used to study the a parameter in the solvatochromic comparison method [2-4]. Dimroth and Reichardt investigated 32 derivatives of 4-(N-pyridinio)-phenolate (named $E_T(1)$ to $E_T(32)$) with regard to their capability of indicating polarity via the "energy of transition" (E_T). Probe $E_T(30)$ [or 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide, Figure 3.5] was found to be the most proper dye and since then has become the standard indicator for solvent polarity[5]. From the this dye, the $E_T(30)$ scale was devised. $E_T(30)$ values are defined as the molar electronic transition energies (E_T) of dissolved 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide, measured in kilocalories per mole (kcal/mol) at room temperature and normal pressure (1 bar) according to equation 3.1.
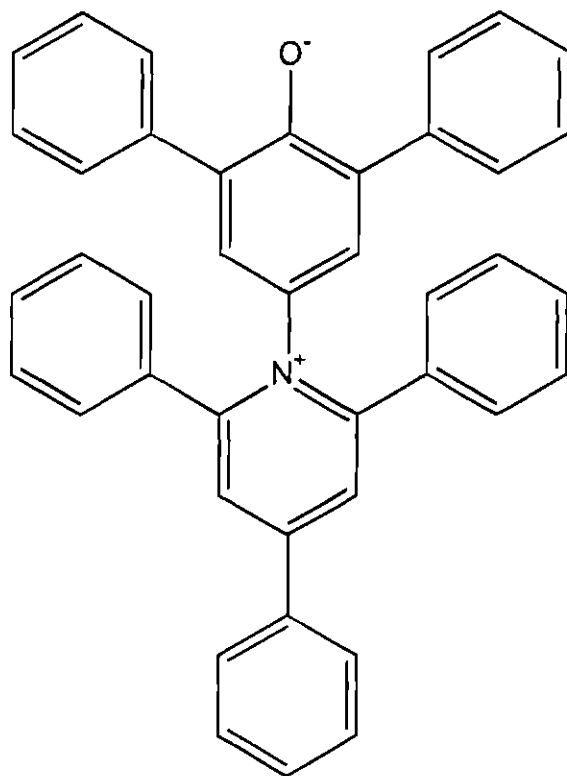
Figure 3.5. 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide
Reichardt's $E_T(30)$ indicator

$$E_T(30) \; (\text{kcal/mol})$$

$$= hc\,\nu_{max}N_A$$

$$= (2.8591 \times 10^{-3}) \; \nu_{max} \; (\text{cm}^{-1})$$

$$= 28591/\lambda_{max} \; (\text{nm}) \qquad\qquad (3.1)$$

A prerequisite to the measurement of the polarity of nonpolar solvents is that the dye has the appropriate solubility. Unfortunately, $E_T(30)$ dye is not sufficiently soluble in nonpolar solvents such as aliphatic hydrocarbons and TMS. Equation 3.2 allows the calculation of $E_T(30)$ values for non-polar solvents, in which the primary indicator dye ET(30) is not soluble enough[3].

$$E_T(30) \; (\text{kcal/mol}^{-1}) = \{[28591/\lambda'_{max} \; (\text{nm})] - 1.808\} \, / \, 0.9424 \qquad (3.2)$$

4-(2,4,6-Triphenylpyridinium)-2,6-diphenylphenoxide is a crystalline, stable compound. It is even stable in solution except in stronger acidic solutions in which it becomes protonated at the oxygen atom of the phenolate part. This causes the solvatochromic charge transfer absorption band to disappear (reversibly). Addition of trace amounts of an acid to the solution

immediately changes the color to pale yellow, the color of the protonated form.

The pKa of protonated 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide is

8.63 $\pm$ 0.03 in water. The dichloro-substituted betaine dye 2,6-dichloro-4-

(2,4,6-triphenyl-N-pyridinio)-phenolate (Figure 3.6) is called E_T (33) and (in the

form of the corresponding acid) has a pKa of 4.78 in water and is a more

suitable indicator molecule for more acidic solvents.

4-Nitroanisole and N,N-dimethyl-4-nitroaniline were chosen as

solvatochromic probes for assembling a π^* scale. Choosing solvents and

solutes for these studies are more complex than their a and B counterparts and

the following rules should be followed as closely as possible[6].

(a) Solvents which are neither hydrogen bond donating nor acceptors present

no problem since $\alpha = \beta = 0$ reduces equation 2.1 to

$$V_{max} = v_0 + s\pi^*$$ (3.2)

(b) For π^* values of solvents which are hydrogen bond accpetors ($\beta \neq 0$), but

not donors ($\alpha = 0$), only nonhydrogen bonding solutes (b = 0) should be

used. In this case, equation 2.1 again reduces to equation 3.2.
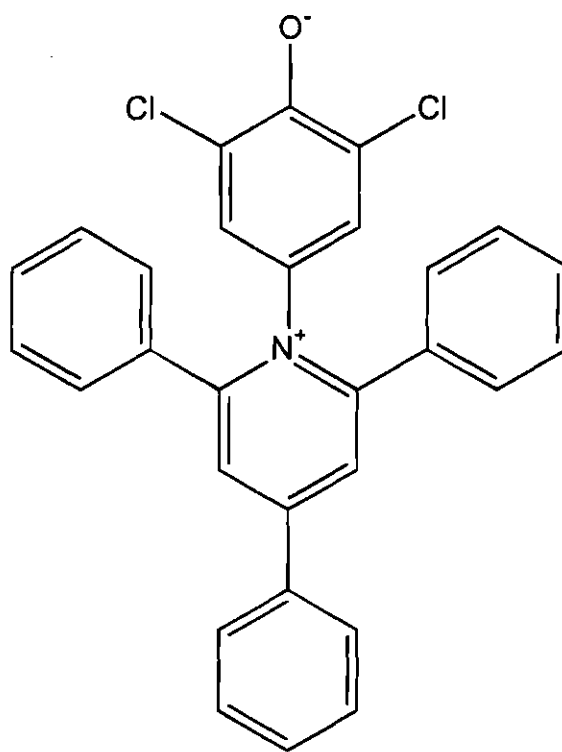
Figure 3.6.   2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate

(c) When using amphiprotic solvents, it is necessary to use indicator solutes that are neither hydrogen bond acceptors nor donors ($a = b = 0$, equation 2.1 again reduces to equation 3.2).

EXPERIMENTAL

Instrumentation. UV/Vis spectroscopy was performed with a Hewlett-Packard 8453 spectrophotometer. The measurements were performed using a high-pressure 10 ml barrel cell with quartz windows. The cell was equipped with a pressure gauge and thermocouple. The cell was also jacketed with a heating block that was warmed by heaters controlled by a variable autotransformer. The pathlengh was set to 1 cm. Carbon Dioxide was introduced into the system via an Isco Syringe Pump (Model 260). The jacketed syringe pump was cooled to $-5^{\circ}C$ with to better attain lower pressures within the cell.

Solvents. The solvents used were cyclohexane (Fisher Scientific, GR =99.7%), methyl alcohol (Aldrich, GR= 99.93%), acetone (Aldrich, GR> 99.9%), anhydrous 1-propanol (Aldrich, GR = 99.7 %), and methyl sulfoxide (Aldrich, 99.9%), carbon dioxide (Matheson).

Solvatochromic Indicators. The indicators used were 4-nitroaniline (Aldrich), 4-nitroanisole (Aldrich), 4-nitrophenol (Aldrich), N,N-dimethyl-4-nitroaniline (Acros), N,N-dimethyl-4-nitrosoaniline (Aldrich), 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide (Aldrich) and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Fluka).

Solvatochromic analysis of indicators in reference solvents. For the UV/Vis spectroscopic measurements, indicator dye solutions were made at 10^{-5} M for 4-nitroaniline, 4-nitroanisole, 4-nitrophenol, and N,N-dimethyl-4-nitroaniline, in either 1-propanol, cyclohexane, or methyl sulfoxide. Reference data was not needed for the determination of α so 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide or 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate indicators were not needed for these measurements. Solutions were prepared and transferred into the cell in a glove box filled with nitrogen. The cell was then capped, removed from the glove box, and placed on the UV-Vis spectrometer. Carbon dioxide was not added to the cell and spectra were taken at ambient temperature and pressure.

General Procedure for the Analysis of Solvatochromic Dyes in Carbon Dioxide Expanded With Methanol or Acetone at 35°C and 40°C. All solutions were prepared in a glove box purged with nitrogen. For the UV/Vis spectroscopic measurements, a stock solution was prepared by dissolving the indicator dye in 100 mL of methanol or acetone in a 100 mL volumetric flask. See Table 3.1 for the amount of indicator dye required for spectroscopic analysis. Sample solutions were prepared by transferring 1 mL of the stock solution into 100 ml of methanol or acetone in a 100 mL volumetric flask. The desired of amount (1 to 6 mL) of sample solution was then transferred into the barrel cell in accordance to the desired range of the mole fractions to be studied with respect to the volume capacity of the cell.

Table 3.1. Amount of Solvatochromic Dye Used to Make 100 mL Stock Solutions in Acetone and Methanol. (pathlengh = 1cm)

Solvatochromic Dye	Weight (mg)
4-Nitroanisole	65.5
4-nitroaniline	45.0
N,N-Dimethyl-4-nitroaniline	42.5
4-Nitrophenol	68.5
ET-30	100
ET-33	100

The cell was then removed from the glove box and connected to the Isco pump and pressure transducer. The desired amount of carbon dioxide was added to the cell and upon equilibrium of the solution, a UV-Vis spectrum was taken. Samples were taken at pressures of 0, 100, 200, 300, 400, 500, 600, 700, 800, 900, 975, 1000, and 1025 psi of carbon dioxide at 35°C. Samples were taken at pressures of 0, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1080, 1100, and 1125 psi at 40°C.

Analysis of the indicator dye at 100% CO_2 concentration was achieved by transferring 5 mL of the stock solution into 25 ml of methanol in a 25 mL volumetric flask. 1 mL of the diluted solution was transferred into the barrel cell. The methanol or acetone was evaporated off by direct connection to a vacuum pump for 3 hours. The cell was then loaded onto the UV-Vis spectrometer and connected to the Isco pump and pressure transducer. It was

then filled with carbon dioxide at 3000 psi while being heated to 35°C or 40°C. A UV-Vis spectrum was then taken.

Analysis of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide at 100% CO_2 concentration was achieved by transferring 5 mL of the stock solution into 25 mL of methanol in a 25 mL volumetric flask. 1 mL of the diluted solution was transferred into the barrel cell. The methanol was evaporated off by direct connection to a vacuum pump for 3 hours. The cell was then loaded onto the UV-Vis spectrometer and connected to the Isco pump and pressure transducer. It was then filled with carbon dioxide at 3000 psi while being heated to 35°C or 40°C. A UV-Vis spectrum was then taken.

Computation. Microsoft Origin 6.0 was used to obtain the maximum absorbance of the UV-Vis spectra of the solvatochromic dyes in each solvent mixture by performing a numerical smooth of the first order derivative of the absorbance data.

The solvatochromic parameters [$E_T(30)$, π^*, β, and α] were calculated from the maximum of absorbance of the indicators, expressed in wavenumber as kK (1kK=1000 cm-1).

The π^* parameter is calculated according to equation 3.3.

$$\Pi^* = \frac{v_a - v_0}{v_1 - v_0} \qquad (3.3)$$

where v_a is the wavenumber for the solvatochromic dye under investigation in the binary mixture at a specified temperature and pressure, while v_0 and v_1 are the wavenumbers for the same solvatochromic dye in reference solvents cyclohexane ($\pi^* = 0$) and methyl sulfoxide ($\pi^* = 1$), respectively, at ambient temperature and pressure[5].

Calculation of the β parameter was accomplished with equation 3.4,

$$\beta = 0.9\frac{\Delta v_c - \Delta v_i}{\Delta v_c - \Delta v_p} \qquad (3.4)$$

where Δv_c and Δv_p represent the difference in wavenumber for the solvatochromic dyes being compared in reference solvents cyclohexane ($\beta = 0$) and 1-propanol ($\beta = 0.9$) , respectively. The change in wavenumber for solvatochromic dyes in the binary solvent mixture of interest is represented by Δv_a.

Equation 3.5 is an alternative equation that can be used to calculate the β value for alcohols as outlined in detail by Kamlet and Taft[1]. Alcohols require a separate calculation to account for multiple effects arising from simultaneous type-B bonding by substrate hydrogens to solvent oxygens and type-A bonding by solvent hydrogens to substrate nitro oxygens[6,7]. These effects influence the solvatochromic shift, and therefore, the wavenumber of indicator (v_n).

30

$$\beta = \frac{-\Delta\Delta v_n}{(2.80)(0.825)} \qquad (3.5)$$

The $E_T(30)$ parameter is defined as the excitation energy of Reichardt's betaine dye in a particular solvent. This energy can be calculated as shown in equation 3.1 from the maximum of the long-wavelength absorption ban of the Reichardt's betaine. In these studies, the less basic betaine dye, 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate, was used in studies with methanol. It is therefore necessary to analyze the corresponding data according to the linear correlation between E_T values of Reichardt's betaine dye and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate. In this case, equation 3.6 is used.

$$E_T(30) = 0.17[E_T(30)] - 0.95\,[E_T(30)] + 45.88 \qquad (3.6)$$

The α parameter is then calculated according to equations 3.7 and 3.8.

$$\alpha = -1.47 - 0.53\,(\pi^*_x) + 0.05[E_T(30)_x\,] \qquad (3.7)$$

$$\alpha = -1.08 - 0.54\,(\pi^*_x) + 0.03[E_T(30)_x\,] \qquad (3.8)$$

These equations are derived from a linear regression of literature data for alcohols (equation 3.7) and ketones (equation 3.8)[8]. The solvatochromic parameters necessary to determine α are π^*_x and $E_T(30)_x$, where the subscript (x) represents the pressure of CO_2 added to the cell at a given temperature.

The α value for pure carbon dioxide was calculated from an equation 3.9 proposed by Kamlet and Taft for the enhanced solvatochromic shift for 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate relative to 4-nitroanisole[4].

$$\alpha = \frac{\Delta\Delta\nu(2-1)}{6.24} \qquad ()$$

"2" represents the experimental wavenumber for 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate in the solvent of choice and "1" represents the calcuated wavenumber for the betaine dye relative 4-nitroanisole in the same solvent under the same experimental conditions.

RESULTS AND DISCUSSION

Bulk mole fractions have been calculated for carbon dioxide in methanol (Tables 3.2) and acetone (Tables 3.3) at 35°C and 40°C. Table 3.4 shows the agreement of experimental wavenumbers with literature values for pure reference solvents. The measured wavenumbers and corresponding values for the solvatochromic parameters ($E_T(30)$, α, β, and π^*) for the binary mixtures of methanol and acetone expanded with carbon dioxide are presented herein. The maximum of absorption for Reichardt's $E_T(30)$ dye in acetone-carbon dioxide have not been measured at mole fractions higher than 78.1% at 35°C and 72.7% at 40°C because of the low solubility of the indicator in non-polar solvents. Consequently, the corresponding $E_T(30)$ and α parameters for these mixtures cannot be calculated. The value given for 100% carbon dioxide is taken from the literature[9].

The π^* parameter. The experimental π^* values for 4-nitroanisole in pure methanol and pure carbon dioxide also agree with values found in the literature (Table 3.5a). Figure 3.7 and Table 3.5b show the experimental π^* values for binary mixtures of methanol and carbon dioxide as calculated by equation 3.3. The experimental wavenumbers for 4-nitroanisole agree with the literature values for the pure reference solvents, cyclohexane and dimethyl sulfoxide (Table 3.4).

33

Table 3.2. Correlation between pressure and bulk mole fraction in binary solvent mixtures of Methanol and CO_2 at 35°C and 40°C.

Pressure (psi)	Bulk Mole Fraction of CO_2 @ 35°C	Pressure (psi)	Bulk Mole Fraction of CO_2 @ 40°C
0	0.0%	0	0.00%
100	4.44%	100	3.54%
200	8.88%	200	7.07%
300	14.1%	300	11.97%
400	18.0%	400	14.94%
500	22.6%	500	19.18%
600	27.9%	600	24.76%
700	33.6%	700	30.45%
800	40.7%	800	35.37%
900	53.2%	900	40.77%
975	71.2%	1000	51.75%
1000	79.9%	1080	71.52%
1025	90.4%	1100	79.02%
3000	100%	1125	90.31%
		3000	100.0%

Table 3.3. Correlation between pressure and bulk mole fraction in binary solvent mixtures of acetone and CO_2 at 35°C.

Pressure (psi)	Bulk Mole Fraction of CO_2 @ 35°C	Pressure (psi)	Bulk Mole Fraction of CO_2 @ 40°C
0	0.0%	0	0.0%
100	10.7%	100	9.7%
200	21.6%	200	19.8%
300	32.2%	300	29.6%
400	42.3%	400	39.0%
500	51.9%	500	48.0%
600	61.1%	600	56.6%
700	69.9%	700	64.8%
800	78.1%	800	72.7%
900	86.0%	900	80.2%
1000	93.4%	1000	87.3%
3000	100%	1100	94.0%
		3000	100.0%

Table 3.4. Experimental and literature wavenumber values for indicator dyes in reference solvents.

Indicator		Solvent		
		Cyclohexane	DMSO	2-propanol
4-nitroanisole	Experimental	34.03	31.65	32.79
	Literature	34.13	31.70	32.89
4-nitroaniline	Experimental	30.98	25.71	26.70
	Literature	31.01	25.71	26.46
N,N-dimethyl-4-nitroaniline	Experimental	28.08	24.54	25.84
	Literature	28.18	24.67	25.90
4-nitrophenol	Experimental	34.98	30.96	31.92
	Literature	34.97	31.06	32.00

The experimental wavenumbers and π^* values for N,N-dimethyl-4-nitroaniline in pure methanol and pure carbon dioxide agree with values found in the literature (Table 3.6a). Figure 3.8 and Table 3.6b show the experimental π^* values for binary mixtures of acetone and carbon dioxide as calculated by equation 3.3. In this case, 4-nitroanisole was not used as the solvatochromic probe because the spectroscopic absorption band for acetone covers the entire range of where the solvatochromic peak for the indicator is located. N,N-dimethyl-4-nitroaniline is a suitable dye that has an absorption peak at a higher wavelength than 4-nitroanisole and acetone and is therefore not overlapped.
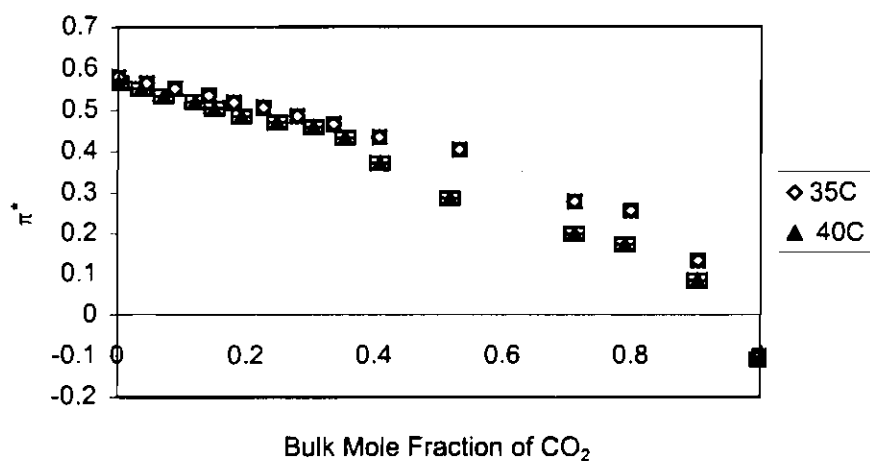
Figure 3.7. Experimental π^* values for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator probe.

Table 3.5a. Experimental and Literature π^* values for pure Methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator probe.

Solvent	Temperature	Experimental	Literature
Methanol	35°C	0.58	0.586
	40°C	0.57	
Carbon Dioxide	35°C	-0.10	-0.11
	40°C	-0.11	

Table 3.5b. Experimental wavenumbers and π^* values for 4-nitroanisole in binary solvent mixtures of methanol and CO_2 at 35°C and 40°C.

Bulk Mole Fraction of CO_2 @ 35C	v_{av} @ 35°C (± 0.05)	Average π^* @ 35°C (± 0.015)	Bulk Mole Fraction of CO_2 @ 40°C	v_{av} @ 40°C (± 0.05)	Average π^* @ 40°C (± 0.015)
0.0%	32.69	0.58	0.00%	32.73	0.57
4.44%	32.73	0.57	3.54%	32.76	0.55
8.88%	32.76	0.56	7.07%	32.81	0.53
14.1%	32.81	0.53	11.97%	32.84	0.52
18.0%	32.85	0.52	14.94%	32.88	0.50
22.6%	32.88	0.51	19.18%	32.93	0.49
27.9%	32.93	0.49	24.76%	32.97	0.47
33.6%	32.98	0.47	30.45%	33.00	0.46
40.7%	33.06	0.43	35.37%	33.06	0.43
53.2%	33.13	0.40	40.77%	33.21	0.37
71.2%	33.44	0.28	51.75%	33.42	0.30
79.9%	33.50	0.26	71.52%	33.64	0.20
90.4%	33.80	0.13	79.02%	33.70	0.17
100.0%	34.38	-0.099	90.31%	33.92	0.09
			100.0%	34.40	-0.11
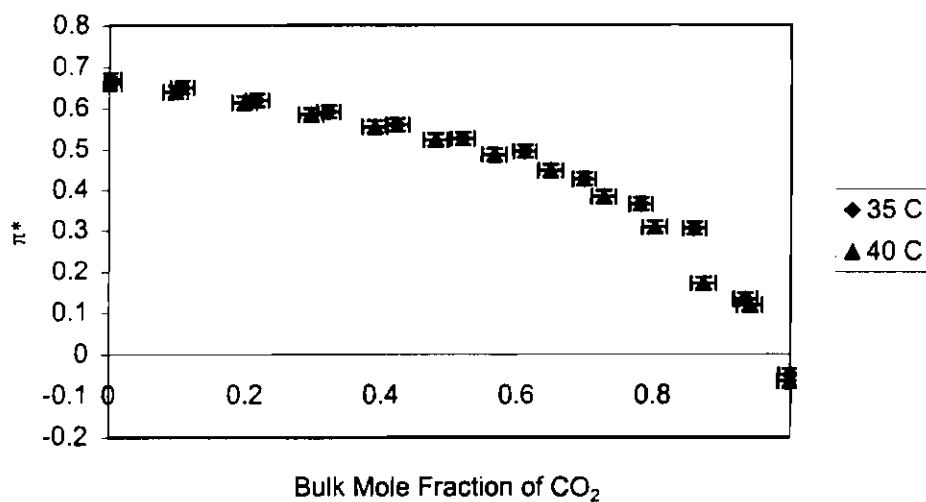
Figure 3.8. Experimental π^* values for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator.

Table 3.6a. Experimental and Literature π^* values for pure acetone and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator.

Solvent	Temperature	Experimental	Literature
Acetone	35°C	0.67	0.683
	40°C	0.66	
Carbon Dioxide	35°C	-0.05	-0.050
	40°C	-0.07	

Table 3.6b. Experimental $\pi*$ values for N,N-dimethyl-4-nitroaniline in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C.

Bulk Mole Fraction of CO_2 @ 35°C	Average v_{max} @ 35°C (±0.05)	Average $\pi*$ @ 35°C (±0.015)	Bulk Mole Fraction of CO_2 @ 40°C	Average v_{max} @ 40°C (±0.05)	Average $\pi*$ @ 40°C (±0.015)
0.0%	25.70	0.67	0.0%	25.73	0.66
10.7%	25.77	0.65	9.7%	25.81	0.64
21.6%	25.89	0.62	19.8%	25.91	0.61
32.2%	25.98	0.59	29.6%	26.01	0.58
42.3%	26.10	0.56	39.0%	26.11	0.55
51.9%	26.21	0.53	48.0%	26.22	0.52
61.1%	26.33	0.49	56.6%	26.35	0.49
69.9%	26.56	0.43	64.8%	26.49	0.45
78.1%	26.78	0.37	72.7%	26.72	0.38
86.0%	27.00	0.30	80.2%	26.99	0.31
93.4%	27.61	0.13	87.3%	27.47	0.17
100%	28.25	-0.05	94.0%	27.66	0.12
			100%	28.31	-0.07

As predicted, the π^* value decreases with increasing the amounts of carbon dioxide to solutions of methanol or acetone. This suggests that increasing amounts of carbon dioxide decrease the polarity of the methanol-carbon dioxide and acetone-carbon dioxide mixtures. In both instances, plotting the bulk mole fractions of carbon dioxide versus π^* is not linear but instead a curve that decreases by a small amount initially before giving a more drastic decrease as it approaches the π^* value of pure carbon dioxide. The π^* value for pure acetone is higher than that of methanol so the decrease is sharper for the acetone-carbon dioxide mixture as it approaches the π^* value of pure carbon dioxide.

The β parameter. The experimental β values for pure methanol and pure carbon dioxide also agree with values found in the literature (Tables 3.7a and 3.8a). Figures 3.9 and 3.10 and Tables 3.7b to 3.8c show the experimental β values for binary mixtures of methanol and carbon dioxide as calculated by equation 3.2. The experimental wavenumbers for 4-nitroanisole, 4-nitrophenol, N,N-dimethyl-4-nitroaniline, and 4-nitroaniline agree with the literature values for the pure reference solvents, cyclohexane and 1-propanol (Table 3.4).
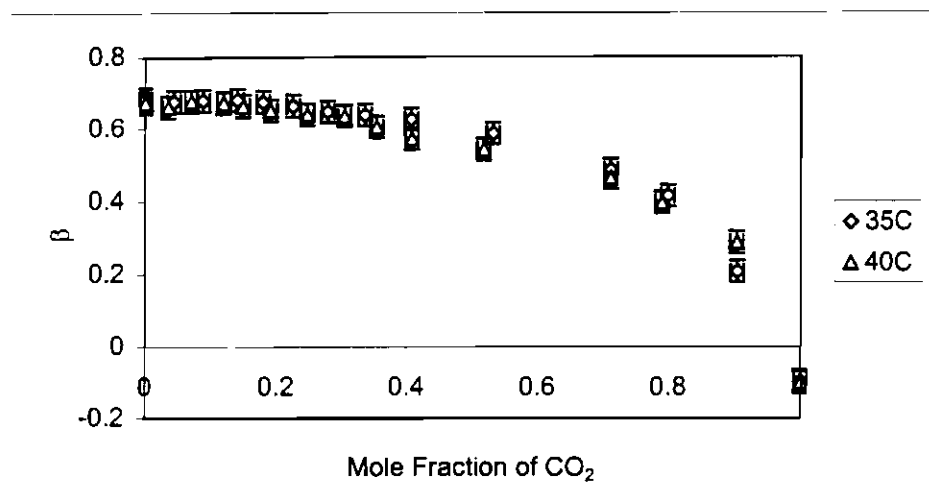
Figure 3.9. Experimental β values for binary mixtures of Methanol and CO_2 at 35°C and 40°C using 4-nitroaniline and N,N-dimethyl-4-nitroaniline as the indicator probes.

Table 3.7a. Experimental and Literature β values for pure Methanol and CO_2 at 35°C and 40°C using 4-nitroaniline and N,N-dimethyl-4-nitroaniline as the indicator probes.

Solvent	Temperature	Experimental	Literature
Methanol	35°C	0.69	0.660
	40°C	0.67	
Carbon Dioxide	35°C	-0.10	-0.080
	40°C	-0.10	

Table 3.7b. Experimental wavenumbers and β values for 4-nitroaniline and N,N-dimethyl-4-nitroaniline in binary solvent mixtures of methanol and CO_2 at 35°C.

Bulk Mole Fraction of CO_2	Average $(cm^{-1})_A$ (+0.05)	Average $(cm^{-1})_B$ (+0.05)	$\Delta\Delta\nu$	Average β @ 35°C (+0.03)
0.00%	26.96	25.61	1.35	0.68
4.44%	27.01	25.65	1.36	0.68
8.88%	27.02	25.66	1.36	0.68
14.1%	27.05	25.69	1.35	0.68
18.0%	27.12	25.73	1.39	0.67
22.6%	27.17	25.78	1.39	0.66
27.9%	27.25	25.82	1.43	0.65
33.6%	27.30	25.85	1.45	0.64
40.7%	27.35	25.87	1.48	0.63
53.2%	27.47	25.90	1.57	0.59
71.2%	28.17	26.37	1.80	0.49
79.9%	28.59	26.64	1.96	0.42
90.4%	29.57	27.14	2.43	0.21
100.0%	31.38	28.25	3.13	-0.10

Table 3.7c. Experimental wavenumbers and β values for 4-nitroaniline and N,N-dimethyl-4-nitroaniline in binary solvent mixtures of methanol and CO_2 at 40°C.

Bulk Mole Fraction of CO_2	Average $(cm^{-1})_A$ (+0.05)	Average $(cm^{-1})_B$ (+0.05)	$\Delta\Delta v$	Average β @ 40°C (+0.03)
0.0%	26.98	25.61	1.38	0.67
3.54%	27.04	25.64	1.40	0.66
7.07%	27.03	25.67	1.37	0.68
11.97%	27.07	25.69	1.38	0.67
14.94%	27.12	25.73	1.39	0.66
19.18%	27.18	25.76	1.42	0.65
24.76%	27.25	25.80	1.45	0.64
30.45%	27.29	25.61	1.68	0.64
35.37%	27.39	25.75	1.65	0.61
40.77%	27.49	25.89	1.61	0.57
51.75%	27.96	26.28	1.68	0.54
71.52%	28.20	26.35	1.85	0.47
79.02%	28.49	26.49	2.00	0.40
90.31%	29.44	27.19	2.25	0.29
100%	31.44	28.31	3.13	-0.10
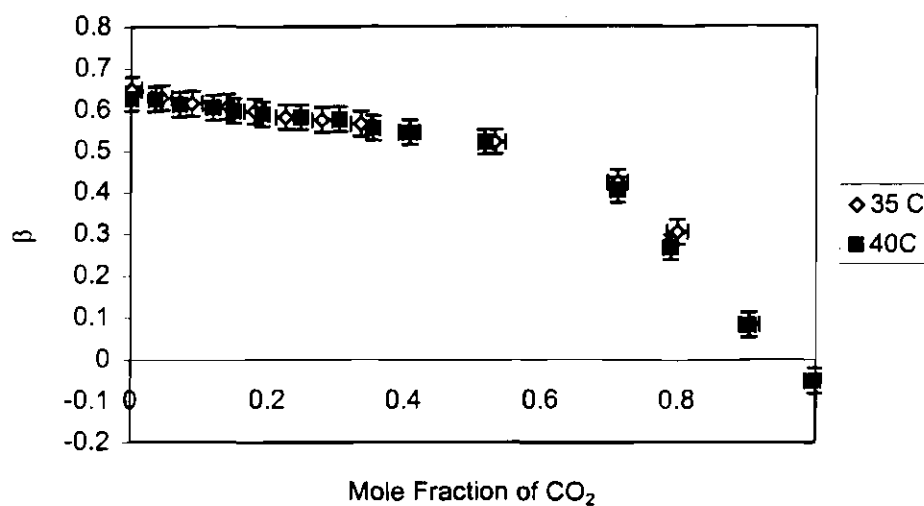
Figure 3.10. Experimental β values for pure Methanol and CO₂ at 35°C and 40°C using 4-nitrophenol and 4-nitroanisole as the indicator dye.

Table 3.8a. Experimental and Literature β values for pure Methanol and CO₂ at 35°C and 40°C using 4-nitrophenol and 4-nitroanisole as the indicator dye.

Solvent	Temperature	Experimental	Literature
Methanol	35°C	0.65	0.66
	40°C	0.63	
Carbon Dioxide	35°C	-0.05	-0.08
	40°C	-0.05	

Table 3.8b. Experimental wavenumbers for 4-nitrophenol and β values for 4-nitrophenol and 4-nitroanisole[a] in binary solvent mixtures of Methanol and CO_2 at 35°C.

Bulk Mole Fraction of CO_2	Average $(cm^{-1})_A$ (+0.05)	$\Delta\Delta\nu^a$	Average β (+0.03)
0.0%	32.12	0.58	0.65
4.44%	32.16	0.57	0.63
8.88%	32.20	0.57	0.62
14.1%	32.21	0.59	0.61
18.0%	32.24	0.61	0.60
22.6%	32.27	0.61	0.58
27.9%	32.29	0.64	0.58
33.6%	32.31	0.67	0.57
40.7%	32.36	0.70	0.55
53.2%	32.41	0.72	0.52
71.2%	32.64	0.81	0.42
79.9%	32.92	0.59	0.31
90.4%	33.43	0.38	0.08
100%	35.35	-0.97	-0.05

a. See Table 3.7 for 4-nitroanisole data.

Table 3.8c. Experimental wavenumbers for 4-nitrophenol and β values for 4-nitrophenol and 4-nitroanisole[a] in binary solvent mixtures of methanol and CO_2 at 40°C.

Bulk Mole Fraction of CO_2	Average (cm^{-1}) (± 0.05)	$\Delta\Delta v^a$	Average β (± 0.03)
0.0%	32.16	0.56	0.63
3.54%	32.17	0.59	0.63
7.07%	32.20	0.61	0.61
11.97%	32.22	0.62	0.61
14.94%	32.24	0.65	0.60
19.18%	32.26	0.67	0.59
24.76%	32.27	0.69	0.58
30.45%	32.28	0.71	0.58
35.37%	32.33	0.73	0.56
40.77%	32.36	0.74	0.54
51.75%	32.42	1.00	0.52
71.52%	32.68	0.96	0.41
79.02%	33.00	0.70	0.27
90.31%	33.43	0.49	0.08
100%	35.37	-0.97	-0.05

a. See Table 3.9 for 4-nitroanisole data.

The experimental β values for pure methanol and pure carbon dioxide also agree with values found in the literature (Tables 3.9a). Figure 3.11 and Tables 3.9b and 3.9c show the experimental β values for binary mixtures of acetone and carbon dioxide as calculated by equation 3.4. In this case, 4-nitroanisole and 4-nitrophenol could not be used as solvatochromic probes because the very broad spectroscopic absorption band for acetone covers the entire range where the solvatochromic peak for the indicators are located. Both N,N-dimethyl-4-nitroaniline and 4-nitroaniline have wavelengths higher than that of acetone and were deemed appropriate for these studies. However, the wavelength for 4-nitroaniline is initially totally unaffected by the nearby acetone peak but moves closer to the acetone absorption band with increasing amounts of carbon dioxide. This creates a slight peak distortion but peak analysis was not affected.

As predicted, the β value decreases with increasing the amounts of carbon dioxide to solutions of methanol or acetone. This suggests that increasing amounts of carbon dioxide decrease the basicity of the methanol-carbon dioxide and acetone-carbon dioxide mixtures. For methanol-carbon dioxide mixtures, plotting the bulk mole fractions of carbon dioxide versus β is not linear but instead a curve that decreases by a small amount initially before
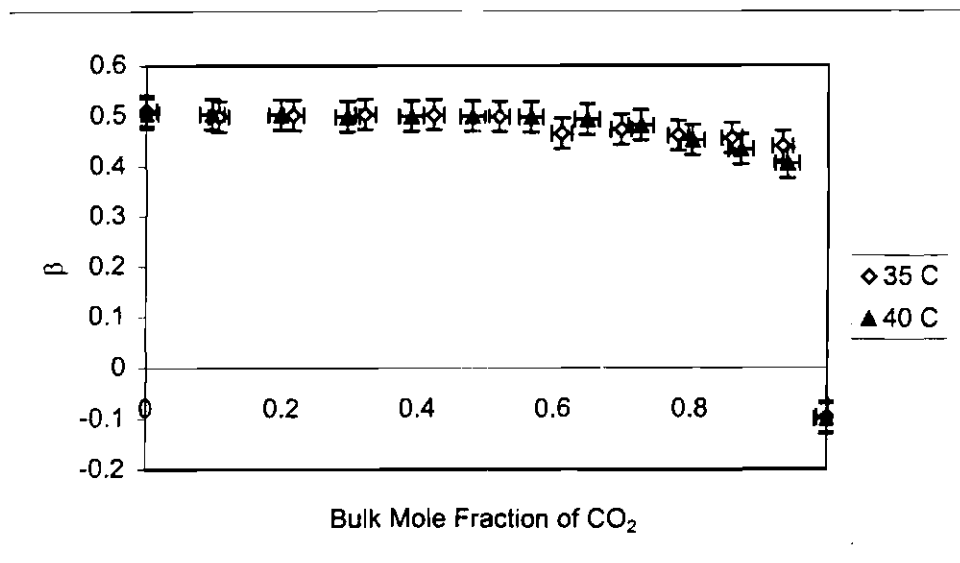
Figure 3.11.   Experimental β values for 4-nitroaniline and N,N-dimethyl-4-nitroaniline in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C.

Table 3.9a.   Experimental β values for 4-nitroaniline and N,N-dimethyl-4-nitroaniline in pure acetone and CO_2 at 35°C and 40°C.

Solvent	Temperature	Experimental	Literature
Acetone	35°C	0.51	0.507
	40°C	0.51	
Carbon Dioxide	35°C	-0.10	-0.080
	40°C	-0.10	

Table 3.9b. Experimental wavenumbers and β values for 4-nitroaniline(A) and N,N-dimethyl-4-nitroaniline (B) in binary solvent mixtures of acetone and CO_2 at 35°C.

Bulk Mole Fraction of CO_2	Average $(cm^{-1})_A$ (+0.05)	Average $(cm^{-1})_B$ (+0.05)	$\Delta\Delta v$	Average β (+0.03)
0.0%	27.44	25.73	1.71	0.51
10.7%	27.54	25.81	1.75	0.50
21.6%	27.65	25.91	1.74	0.50
32.2%	27.74	26.01	1.73	0.50
42.3%	27.86	26.11	1.75	0.50
51.9%	27.99	26.22	1.77	0.50
61.1%	28.17	26.35	1.82	0.47
69.9%	28.39	26.49	1.90	0.47
78.1%	28.64	26.72	1.92	0.46
86.0%	28.87	26.99	1.88	0.46
93.4%	29.52	27.47	2.05	0.44
100%	31.38	27.66	3.72	-0.10

Table 3.9c. Experimental wavenumbers and β values for 4-nitroaniline (A) and N,N-dimethyl-4-nitroaniline (B) in binary solvent mixtures of acetone and CO_2 at 40°C.

Bulk Mole Fraction of CO_2	Average $(cm^{-1})_A$ (+0.05)	Average $(cm^{-1})_B$ (+0.05)	$\Delta\Delta v$	Average β (±0.03)
0.0%	27.49	25.73	1.76	0.51
9.7%	27.57	25.81	1.76	0.50
19.8%	27.67	25.91	1.76	0.50
29.6%	27.78	26.01	1.77	0.50
39.0%	27.88	26.11	1.77	0.50
48.0%	28.00	26.22	1.78	0.50
56.6%	28.13	26.35	1.78	0.50
64.8%	28.27	26.49	1.78	0.49
72.7%	28.53	26.72	1.81	0.48
80.2%	28.86	26.99	1.87	0.45
87.3%	29.39	27.47	1.92	0.43
94.0%	29.64	27.66	1.98	0.41
100%	31.44	28.31	3.13	-0.10

giving a more drastic decrease as it approaches the β value of pure carbon dioxide. It is expected that the β for carbon dioxide should be small because the carbon has two electronegative substituents. A plot of the bulk mole fractions of carbon dioxide versus β for binary mixtures of acetone and carbon dioxide is not linear but unexpectedly remains almost constant throughout the entire range of mole fractions. It decreases by a small amount at approximately a 70% bulk mole fraction of carbon dioxide before catastrophically dropping to the β value of pure carbon dioxide. Upon evaluation of the experimental wavenumbers for N,N-dimethyl-4-nitroaniline and 4-nitroaniline, it is observed that increasing the bulk concentration of carbon dioxide has a relatively small effect on the solvatochromic shift of 4-nitroaniline in acetone when compared to the shift induced by increasing the concentration of carbon dioxide in methanol.

The α and $E_T(30)$ parameters. The experimental wavenumbers, $E_T(30)$ and α values for 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-phenolate in pure methanol and pure carbon dioxide agree with values found in the literature (Table 3.10a). Figure 3.12 and Tables 3.10b to 3.10c show the experimental $E_T(30)$ and α values for binary mixtures of methanol and carbon dioxide as calculated by equations 3.1 and 3.7, respectively. Equation 3.7 is derived from regressed data for several alcohols as reported by Marcus[8]. Reference solvents are not needed for the calculation of α or $E_T(30)$.

The $E_T(30)$ values show a steady but slow decline as expected from it's linear relationship with experimental wavenumbers. The α values show a more interesting trend. There is an initial increase in the α value which is likely due to an initial increase in density. The α value then begins to decline as expected with increasing amounts of carbon dioxide. However, the α value again changes direction and begins to increase. There are two theories for this observation. The solubility of 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-phenolate becomes smaller with increasing amounts of carbon dioxide which greatly affects to amount of carbon dioxide in the solvation sphere of the betaine dye. One the other hand, 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-phenolate is readily soluble in methanol. Therefore, the effect of increasing amounts of carbon dioxide is not apparent due to an unfair solvation advantage even the presence of very little methanol. The second theory involves the possible presence of carbonic acid at increased concentrations of carbon dioxide which would clearly increase the acidity of the solution and subsequently, the α value.

$E_T(30)$ and α values for 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide in pure acetone and pure carbon dioxide agree with values found in the literature (Table 3.11a). Figures 3.13 and Tables 3.11b to 3.11c show the experimental $E_T(30)$ and α values for binary mixtures of acetone and carbon dioxide as calculated by equations 3.1 and 3.8, respectively. Equation
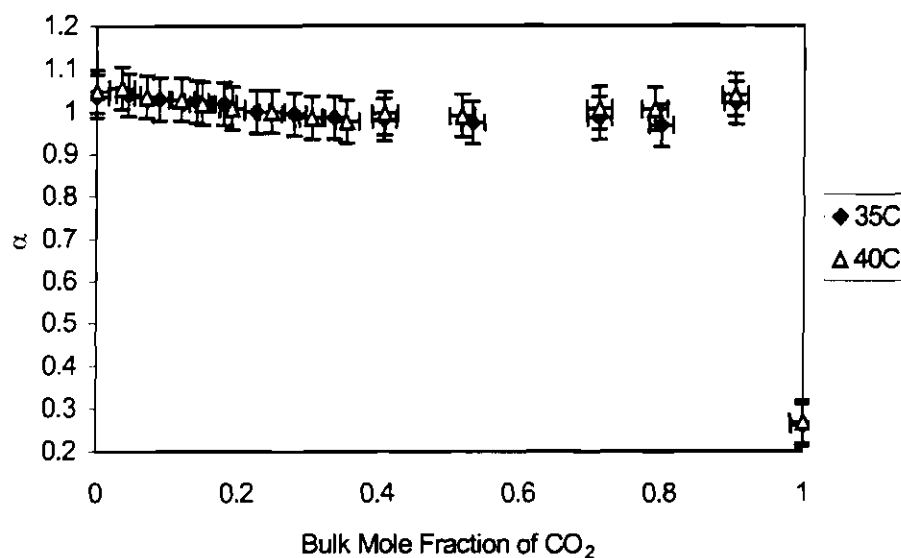
Figure 3.12. Experimental α values for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the indicator probe.

Table 3.10a. Experimental and Literature α values for pure methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the indicator probe.

Solvent	Temperature	Experimental	Literature
Methanol	35°C	1.04	0.99
	40°C	1.05	
Carbon Dioxide	35°C	0.26	0.00 - 0.19[a]
	40°C	0.27	0.252[b]

a. Values are calculated from estimated ET(30) values at various densities. No direct measurement was made.
b. Calculated from universal equation for the calculation of alpha using literature values for π^* and $E_T(30)$.

Table 3.10b. Experimental α and $E_T(30)$ values for 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate in binary solvent mixtures of methanol and CO_2 at 35°C.

Bulk Mole Fraction of CO_2	Wavenumber (cm^{-1}) $(+0.05)$	$E_T(33)$ $(+0.05)$	$E_T(30)$ $(+0.05)$	α $(+0.06)$
0.0%	22.44	64.16	55.41	1.04
4.44%	22.42	64.11	55.34	1.04
8.88%	22.32	63.80	54.97	1.03
14.1%	22.24	63.58	54.69	1.02
18.0%	22.16	63.35	54.41	1.02
22.6%	22.01	62.94	53.91	1.00
27.9%	21.92	62.66	53.59	0.99
33.6%	21.81	62.36	53.23	0.98
40.7%	21.69	62.00	52.80	0.98
53.2%	21.54	61.59	52.32	0.97
71.2%	21.21	60.63	51.23	0.98
79.9%	21.03	60.12	50.66	0.97
90.4%	20.94	59.88	50.38	1.02
100%	11.99	34.28	33.80	0.26

Table 3.10c. Experimental α and $E_T(30)$ values for 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate in binary solvent mixtures of methanol and CO_2 at 40°C.

Bulk Mole Fraction of CO_2	Wavenumber (cm^{-1}) $(+0.05)$	$E_T(33)$ (±0.05)	$E_T(30)$ (±0.05)	α (±0.06)
0.0%	22.46	64.23	55.50	1.05
3.54%	22.46	64.23	55.49	1.05
7.07%	22.30	63.76	54.92	1.03
11.97%	22.22	63.52	54.62	1.03
14.94%	22.12	63.24	54.28	1.02
19.18%	22.00	62.89	53.85	1.01
24.76%	21.91	62.64	53.56	1.00
30.45%	21.74	62.29	53.14	0.98
35.37%	21.66	61.92	52.70	0.98
40.77%	21.58	61.68	52.43	1.00
51.75%	21.27	60.79	51.41	0.99
71.52%	21.09	60.30	50.86	1.01
79.02%	21.00	60.03	50.56	1.00
90.31%	20.91	59.78	50.28	1.04
100%	11.99	34.28	33.80	0.27
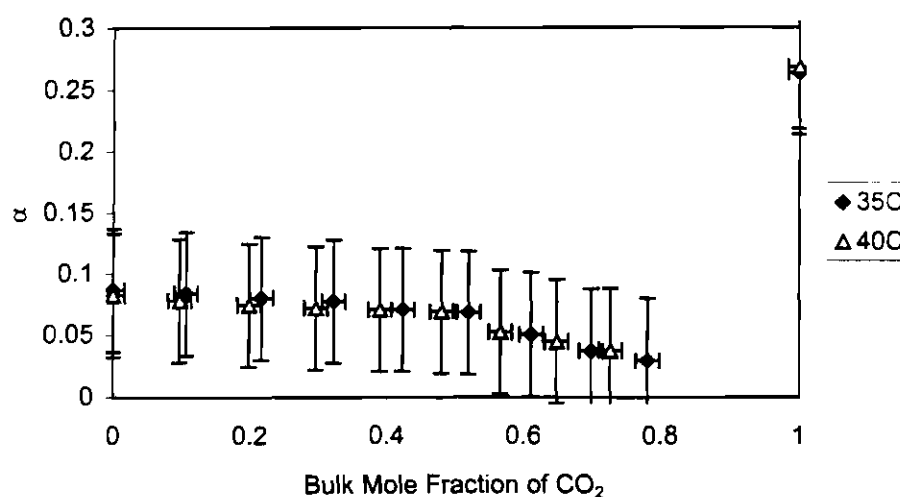
Figure 3.13. Experimental α values for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the probe indicator.

Table 3.11a. Experimental and Literature α values for pure acetone and CO_2 at 35°C and 40°C using 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the probe indicator.

Solvent	Temperature	Experimental	Literature
Acetone	35°C	0.09	0.080
	40°C	0.08	
Carbon Dioxide	35°C	0.26	0.00 - 0.19[a]
	40°C	0.27	0.252[b]

a. Values are calculated from estimated ET(30) values at various densities. No direct measurement was made.
b. Calculated from universal equation for the calculation of alpha using literature values for π* and $E_T(30)$.

Table 3.11b. Experimental α and $E_T(30)$ values for 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate in binary solvent mixtures of acetone and CO_2 at 35°C.

Bulk Mole Fraction of CO_2	Wavenumber (cm^{-1}) (± 0.05)	$E_T(30)$ (± 0.05)	α (± 0.06)
0.0%	14.83	42.40	0.09
10.7%	14.78	42.26	0.08
21.6%	14.72	42.07	0.08
32.2%	14.67	41.94	0.08
42.3%	14.56	41.63	0.07
51.9%	14.51	41.4ε	0.07
61.1%	14.27	40.8ℓ	0.05
69.9%	14.06	40.20	0.04
78.1%	13.93	39.83	0.03
100%	11.99	33.80	0.26

Table 3.11c. Experimental α and $E_T(30)$ values for 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate in binary solvent mixtures of acetone and CO_2 at 40°C.

Pressure (psi)	Wavenumber (cm^{-1}) (± 0.05)	$E_T(30)$ (± 0.05)	α (± 0.06)
0.0%	14.77	42.24	0.08
9.7%	14.71	42.04	0.08
19.8%	14.64	41.87	0.08
29.6%	14.59	41.72	0.07
39.0%	14.56	41.62	0.07
48.0%	14.52	41.50	0.07
56.6%	14.29	40.85	0.05
64.8%	14.17	40.50	0.05
72.7%	14.04	40.12	0.04
100.0%	11.99	33.80	0.27

3.8 which is derived from regressed data for several ketones as reported by Marcus[8]. The $E_T(30)$ values show a steady but slow decline as expected from it's linear relationship with experimental wavenumbers. The α values the same trend. Acetone is less polar than methanol which magnifies the solubility limitations of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide in non-polar solvents. Absorption peaks were not detected at higher concentration of carbon dioxide in the acetone-carbon dioxide binary mixture. The α value did not show the same trend as its methanol counterpart. A plausible explanation is the possibility of the presence of carbonic acid in binary mixtures of methanol and carbon dioxide. Such a species is less likely to be formed in an acetone-carbon dioxide binary mixture.

CONCLUSIONS

Solvatochromic parameters have been successfully calculated for binary mixtures of acetone and methanol with carbon dioxide. None of the results produced a linear relationship with solvatochromic property and bulk mole fraction. This is probably because the observed solvatochromic shifts are more of a reflection of the local composition than the bulk composition. Experimental results for the pure probe and reference solvents were in excellent agreement with the literature adding credibility to the calculations and techniques used to study the binary compositions.

The $\pi*$ values for the binary mixtures decreased as expected for both binary mixtures upon addition of carbon dioxide. It is clear that as the local density of the cybotactic region decreases with bulk mole fractions of carbon dioxide resulting in a lower π^*. β values showed a similar trend for methanol-carbon dioxide mixtures but 4-nitroaniline was less susceptible to increasing amounts of carbon dioxide than expected in acetone yielding little change in the β value in acetone-carbon dioxide solution. The α values showed the least amount of susceptibility to increased amounts of carbon dioxide in both acetone and methanol. It was observed that π^* and β values decreased in the direction

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that caused them to approach their respective values for pure carbon dioxide. A different trend was observed for α as both, the acetone-CO_2 and methanol-CO_2, plots progressed away from the α value for pure carbon dioxide. No literature could be found on direct measurements of an α value in carbon dioxide. In this work, α values that are presented from the literature are actually estimations based on calculations or calculations based on literature values for direct measurements for $E_T(30)$ and π^* values in pure CO_2. The lack of α values found in the literature is probably because α is a measurement of hydrogen bond acidity and carbon dioxide has no hydrogens. Yet, all calculations and estimations suggest that the α value for carbon dioxide is larger than that of acetone ($\alpha = 0.08$) and comparable to that of acetonitrile ($\alpha = 0.23$). Another reason for the lack of direct measurements is the poor solubility of the betaine dyes in non-polar solvents such as carbon dioxide. Neither of the betaine dyes used in these studies were soluble in pure carbon dioxide.

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CHAPTER IV

PREFERENTIAL SOLVATION OF SOLVATOCHROMIC INDICATORS IN MIXTURES OF METHANOL AND ACETONE WITH CARBON DIOXIDE

Solvatochromic indicators are used as a suitable analytes for spectroscopically studying solute-solvent interactions. The transition energy of these indicators depends on the solvation's sphere composition and the solvent properties. However the interpretation of the measurements is different in a single solvent than in a mixed solvent. A solvatochromic parameter measures the polarity of the solvent in its solvation sphere, which agrees with the polarity of the bulk only for single solvents. In a mixed solvent, the solvatochromic indicator can interact to different degrees with the solvents of the mixture causing the composition and polarity of the solvation sphere to be different from that of the bulk solvent. The term preferential or selective solvation is used to define this behavior. Preferential solvation leads to non-linear relationships between solvatochromic polarity and solvent composition. Solvent-solute interactions produced in solvent mixtures can also effect solvent-solvent interactions.

There are some instances when there is a linear relationship between solvatochromic parameters and the solvent composition. Such are called ideal binary systems. Ideal behavior is usually observed when two solvents with very similar properties are mixed. An example is a binary mixture of ethanol and methanol[1].

Other effects to be considered are solvent-solvent interactions (the general medium effect) and solute-solute interactions (the intersolute effect). Theoretically, it is safe to assume that solute-solute interactions are negligible and therefore the intersolute effect makes no significant contribution to the observed solvent effect because the concentration of the solute is always very low in these systems. Solvent-solvent interactions have been shown to have significant contributions and are typically manifested by the clustering or aggregation of the solvent molecules about the solute. Johnston and Kim studied the local compositions of supercritical fluid mixtures[2]; however, the literature is void of studies of local compositions in the pressure range of gas-expanded liquids. Eckert and coworkers observed that the partial molar volumes of non-volatile organics such as naphthalene and tetrabromoethane get very large negative in magnitude near the critical points of carbon dioxide and ethylene[3]. In the following years, a substantial number of experimental [2,4-6] and theoretical [7-9] studies have provided convincing evidence to suggest that the local density of the solvent about the solute is enhanced significantly, especially

in the near-critical region. As the supercritical fluid becomes more compressed, the solvent clusters about the solute due to attractive intermolecular forces. A clear understanding of clustering and its influence on local compositions is important in understanding how solvent-dependent processes such as reactions, extractions, and separations would be affected by activities of the solvent and solute molecules in SCF media.

In the previous chapter, solvatochromic properties were calculated for binary mixtures of methanol and acetone expanded with acetone. The results of those experiments should be a direct reflection of the cybotactic region of the solute molecule and provides information on the local composition for pure and binary solvent systems. It was apparent that increases in the bulk concentration of carbon dioxide caused significant solvatochromic shifts. This chapter seeks to provide additional information to assist in the elucidation of solvatochromism in gas expanded liquids by studying the cybotactic region for a solvatochromic probe molecule and determining the local composition as a function of temperature and increasing concentrations of carbon dioxide.

EXPERIMENTAL

The **instrumentation, solvents,** and **solvatochromic indicators** are the same as outlined in Chapter 3. The difference here lies within the data analysis to determine local compositions as described below.

Computation. The results of the data documented in Chapter 3 using Microsoft Origin 6.0 to obtain the maximum absorbance of the UV-Vis spectra of the solvatochromic dyes in each solvent mixture by performing a numerical smooth of the first order derivative of the absorbance data are used here. Herein we describe how any of the previously determined solvatochromic properties (ν_{max}, $E_T(30)$, π^*, B, and α) can be used to calculate the local composition of binary mixtures.

Bosch *et. al.* have studied the solute-solvent and solvent-solvent interactions of several solvatochromic indicators in liquid-liquid binary systems [1,10-11]. The simplest model used for such studies is shown in Scheme 1.

$$I(S1) \quad + \quad S2 \quad \Leftrightarrow \quad I(S2) \quad + \quad S1$$

Scheme 1

The model is based on solvent exchange equilibrium where I(S1) and I(S2) indicate the solvatochromic indicator (I) solvated by solvents 1 and 2,

respectively. S1 and S2 are the two single solvents that comprise the binary mixture. The constant of this equilibrium is defined by the preferential solvation parameter, $f_{2/1}$ as defined in equation 4.1.

$$f_{2/1} = \frac{\dfrac{x_2^s}{x_1^s}}{\dfrac{x_2^0}{x_1^0}} \qquad (4.1)$$

- where x_1^s and x_2^s are the mole fractions of solvents S1 and S2 in the microsphere of solvation of the indicator,

- x_1^0 and x_2^0 are the mole fractions of the two solvents in the bulk mixed solvent,

- and $f_{2/1}$ measures the tendency of the indicator to be solvate with the solvent S2 in reference to solvent S1.

The preferential solvation parameter is a variable parameter that can be fit to any appropriate solvatochromic property plotted against the bulk composition [10, 11]. The appropriate solvatochromic property is defined by Y as shown as equation 4.2.

$$Y = Y_1 + \frac{f_{2/1}(Y_2 - Y_1)x_2^0}{(1 - x_2^0) + f_{2/1}x_2^0} \qquad (4.2)$$

Y is calculated from the solvent composition (x^0_2), the preferential solvation parameter, $f_{2/1}$ and the Y values of the pure solvents S1 and S2 (Y_1 and Y_2).

Equation 4.2 does not consider the solvent-solvent interactions and because of this limitation, it does not apply to "synergetic" mixtures. The term "synergetic" was proposed to describe the behavior showed by some mixtures of dipolar hydrogen bond acceptors (dimethyl sulfoxide, acetonitrile, etc) with good hydrogen bond donors (i.e. alcohols)[12]. Two models have been proposed to take into account the solvent-solvent interactions. One is the Skwierczynski and Conners model and the other is the two-step solvent exchange model shown in Scheme 2. In some cases, the two models can be used interchangeably[13].

$$I(S1)m \quad + \quad mS2 \quad \Leftrightarrow \quad I((S2)m \quad + \quad mS1$$

$$I(S1)m \quad + \quad \frac{m}{2}S2 \quad \Leftrightarrow \quad I(S12)m \quad + \quad \frac{m}{2}S1$$
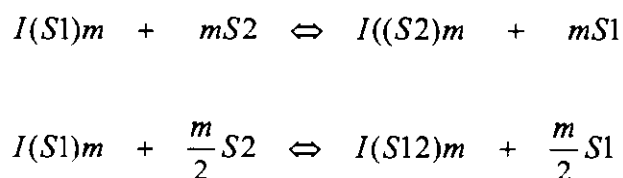
Scheme 2

In this model, S1 and S2 indicate the two pure solvents yielding the binary solvent mixture, and S12 represents a solvent formed by the intermolecular interaction of solvents 1 and 2. This new solvent can have properties that are quite different from those of solvents 1 and 2. The number of solvent

molecules solvating the solvatochromic indicator (I), is represented by m. The

constants of the two processes are defined by the preferential solvation

parameters $f_{2/1}$ defined in equation 4.1 and $f_{12/1}$ given in equation 4.3.

$$f_{12/1} = \frac{\dfrac{x_{12}^{s}}{x_{1}^{s}}}{\dfrac{x_{2}^{0}}{x_{1}^{0}}} \tag{4.3}$$

where x^{s}_{12} stands for the mole fraction of the solvent S12 and $f_{12/1}$ measures the

tendency of the indicator to be solvated by solvent S12 in reference to solvent

S1. The Y values for the binary mixture can then be calculated by equation 4.4.

$$Y = Y_1 + \frac{f_{2/1}(Y_2 - Y_1)x_2^0 + f_{12/1}(Y_{12} + Y_1)}{(1 - x_2^0) + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \tag{4.4}$$

Results and Discussion

Applicability of the equations to study solute-solvent interactions has been tested for the five indicators in methanol-carbon dioxide and acetone-carbon dioxide binary mixtures and pure solvents at 35°C and 40°C. Local compositions could not be determined for 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate in binary mixtures of acetone and carbon dioxide at carbon dioxide concentrations higher than 78.1% (35°C) and 72.7% (40°C). All of the indicators could be fit to equation 4.2 with the exception of $E_T(33)$ in binary mixtures of methanol and carbon dioxide which must be fitted to equation 4.4. None of the solvent systems studied were found to be ideal or show synergistic effects.

One-step solvent exchange model. Composite graphs plotting the bulk mole fractions of carbon dioxide against the corresponding local mole fractions are shown in Figures and Tables 4.1 to 4.4. Supporting data, including measured wavenumbers and local compositions for the binary mixtures and pure solvents, are presented herein. Evaluation of the composite graphs for methanol-carbon dioxide mixtures shows 4-nitroanisole (Figure 4.5, Table 4.5) to have the greatest degree of carbon dioxide present in its solvation sphere. It is followed by N,N-dimethyl-4-nitroaniline (Figure 4.6, Table 4.6), 4-nitroaniline (Figure 4.7, Table 4.7), 4-nitrophenol (Figure 4.8, Table 4.8),

71

Figure 4.1. Preferential Solvation ($f_{2/1}$) of Solvatochromic Dyes in Binary Mixtures of Methanol and Carbon Dioxide at 35°C. Calculated by equation 4.1.

Table 4.1. Preferential Solvation ($f_{2/1}$) of Solvatochromic Dyes in Binary
Mixtures of Methanol and Carbon Dioxide at 35°C.   Calculated by equation 4.1.

Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2				
	4-nitroanisole	4-nitroaniline	N,N-dimethyl-4-nitroaniline	4-nitrophenol	$E_T(33)$
0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
4.44%	1.91%	0.69%	0.92%	0.37%	0.12%
8.88%	3.93%	1.44%	1.91%	0.77%	0.24%
14.14%	6.47%	2.41%	3.19%	1.30%	0.41%
18.04%	8.46%	3.20%	4.22%	1.73%	0.55%
22.63%	10.93%	4.20%	5.53%	2.29%	0.73%
27.92%	13.98%	5.49%	7.19%	3.01%	0.96%
33.60%	17.52%	7.06%	9.19%	3.89%	1.25%
40.69%	22.35%	9.33%	12.07%	5.20%	1.69%
53.23%	32.30%	14.58%	18.54%	8.34%	2.77%
71.22%	50.90%	27.07%	33.11%	16.52%	5.83%
79.92%	62.49%	37.38%	44.32%	24.15%	9.05%
90.41%	79.77%	58.58%	65.35%	43.00%	19.07%
100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
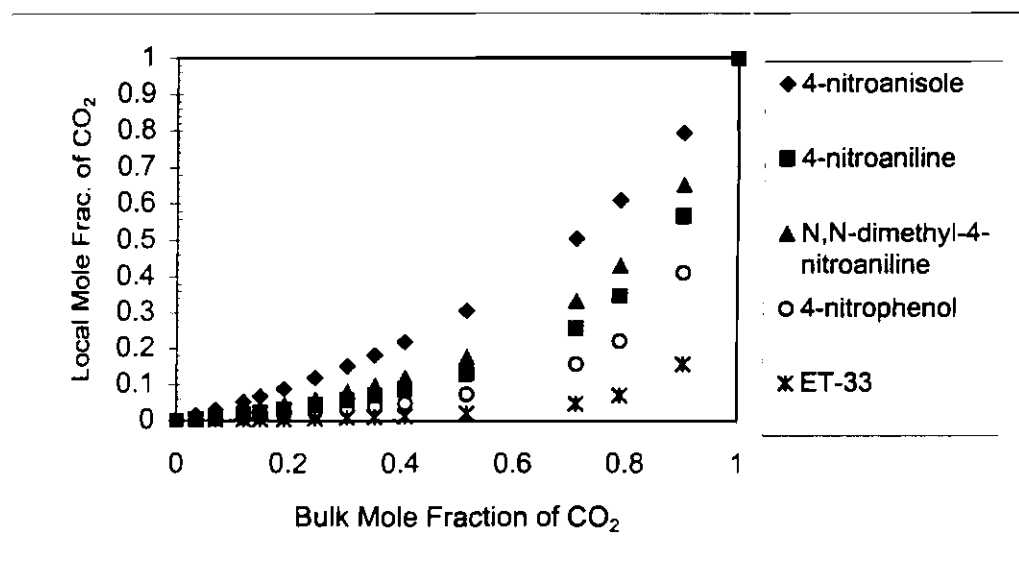
Figure 4.2. Preferential Solvation ($f_{2/1}$) of Solvatochromic Dyes in Binary Mixtures of Methanol and Carbon Dioxide at 40°C. Calculated by equation 4.1.

Table 4.2. Preferential Solvation $(f_{2/1})$ of Solvatochromic Dyes in Binary
Mixtures of Methanol and Carbon Dioxide at 40°C.   Calculated by equation 4.1.

Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2				
	4-nitroanisole	4-nitroaniline	N,N-dimethyl-4-nitroaniline	4-nitrophenol	$E_T(33)$
0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
3.54%	1.48%	0.51%	0.73%	0.27%	0.07%
7.07%	3.03%	1.05%	1.50%	0.57%	0.15%
11.97%	5.28%	1.87%	2.65%	1.01%	0.27%
14.94%	6.72%	2.40%	3.39%	1.30%	0.35%
19.18%	8.86%	3.21%	4.53%	1.75%	0.47%
24.76%	11.89%	4.40%	6.18%	2.41%	0.65%
30.45%	15.22%	5.77%	8.05%	3.18%	0.87%
35.37%	18.33%	7.11%	9.87%	3.94%	1.08%
40.77%	22.01%	8.79%	12.10%	4.91%	1.36%
51.75%	30.54%	13.05%	17.66%	7.44%	2.10%
71.52%	50.35%	25.71%	33.11%	15.65%	4.72%
79.02%	60.69%	34.49%	42.96%	22.01%	7.01%
90.31%	79.25%	56.54%	65.08%	41.10%	15.71%
100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
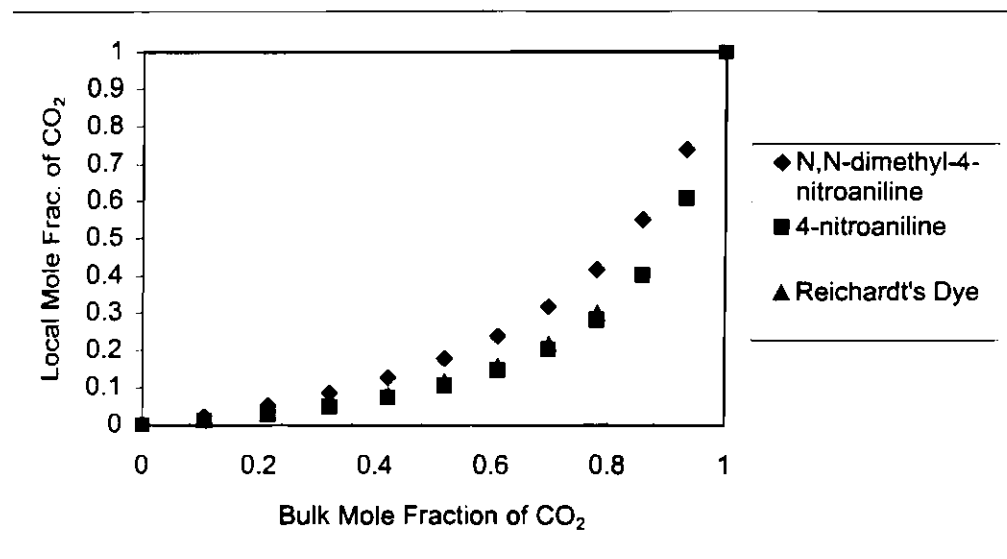
Figure 4.3. Preferential Solvation $(f_{2/1})$ of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at $35°C$. Calculated by equation 4.1.

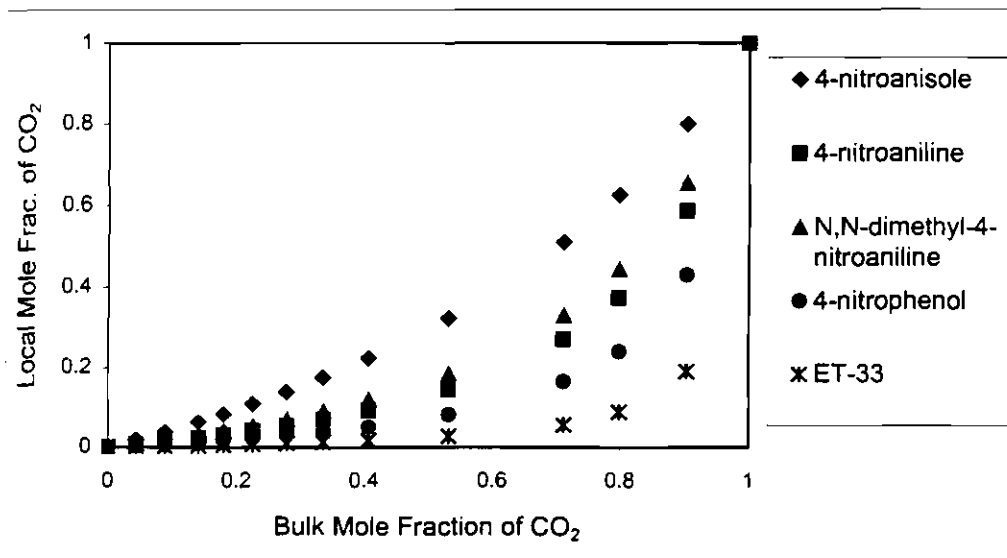Table 4.3. Preferential Solvation ($f_{2/1}$) of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 35°C. Calculated by equation 4.1.

| Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2		
	4-nitroaniline	N,N-dimethyl-4-nitroaniline	$E_T(30)$
0.00%	0.00%	0.00%	0.00%
10.66%	1.30%	2.33%	1.41%
21.65%	2.95%	5.24%	3.21%
32.19%	4.96%	8.67%	5.39%
42.28%	7.45%	12.78%	8.08%
51.92%	10.61%	17.76%	11.47%
61.11%	14.72%	23.92%	15.87%
69.86%	20.29%	31.67%	21.76%
78.15%	28.18%	41.70%	30.03%
85.99%	40.22%	55.11%	N/A
93.38%	60.69%	73.83%	N/A
100.0%	100.0%	100.0%	100.0%
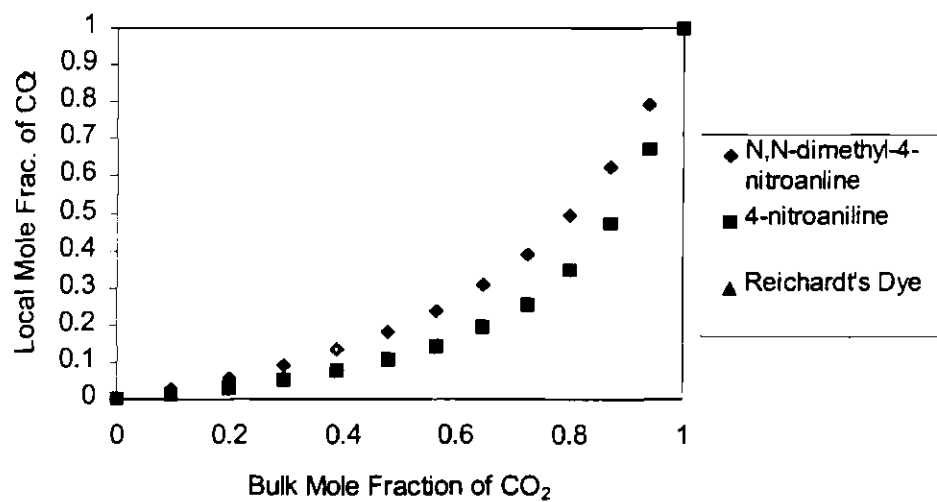
Figure 4.4. Preferential Solvation $(f_{2/1})$ of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 40°C. Calculated by equation 4.1.

Table 4.4. Preferential Solvation ($f_{12/2}$) of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 40°C. Calculated by equation 4.1.

Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2		
	4-nitroaniline	N,N-dimethyl-4-nitroaniline	$E_T(30)$
0.00%	0.00%	0.00%	0.00%
9.67%	1.37%	2.51%	1.37%
19.81%	3.11%	5.60%	3.11%
29.58%	5.18%	9.16%	5.18%
38.96%	7.66%	13.28%	7.66%
47.96%	10.70%	18.11%	10.70%
56.59%	14.49%	23.82%	14.49%
64.84%	19.34%	30.67%	19.34%
72.70%	25.72%	38.98%	25.72%
80.19%	34.48%	49.26%	N/A
87.30%	47.20%	62.24%	N/A
94.04%	67.21%	79.07%	N/A
100.0%	100.0%	100.0%	100.0%

Figure 4.5. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator. See Table 3.5b for experimental data.

Table 4.5. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator.

Temperature	Average $f_{2/1}$ (+0.02)
35°C	0.42
40°C	0.41

Figure 4.6. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator. See Tables 3.7b and 3.7c for experimental data.

Table 4.6. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator.

Temperature	Average $f_{2/1}$ ($\pm$0.02)
35°C	0.20
40°C	0.20

Figure 4.7. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroaniline as the probe indicator. See Tables 3.7b and 3.7c for experimental data.

Table 4.7. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroaniline as the probe indicator.

Temperature	Average $f_{2/1}$ (+0.02)
35°C	0.15
40°C	0.14

Figure 4.8. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitrophenol as the indicator. See Tables 3.8b and 3.8c for experimental data.
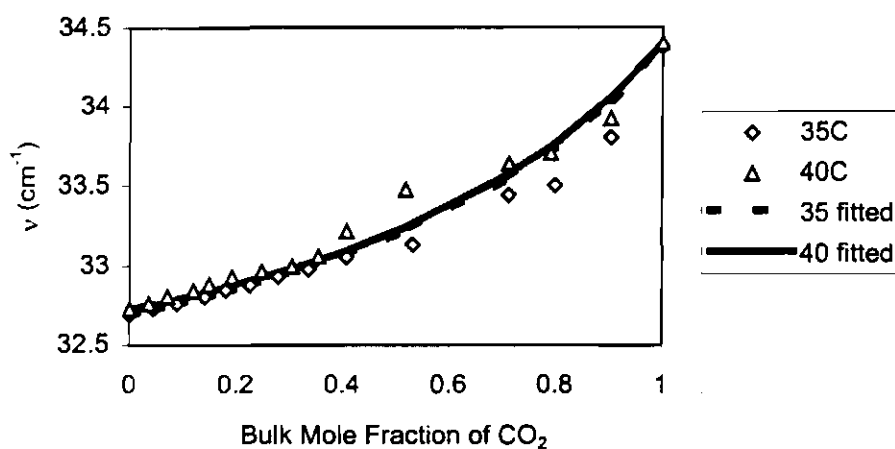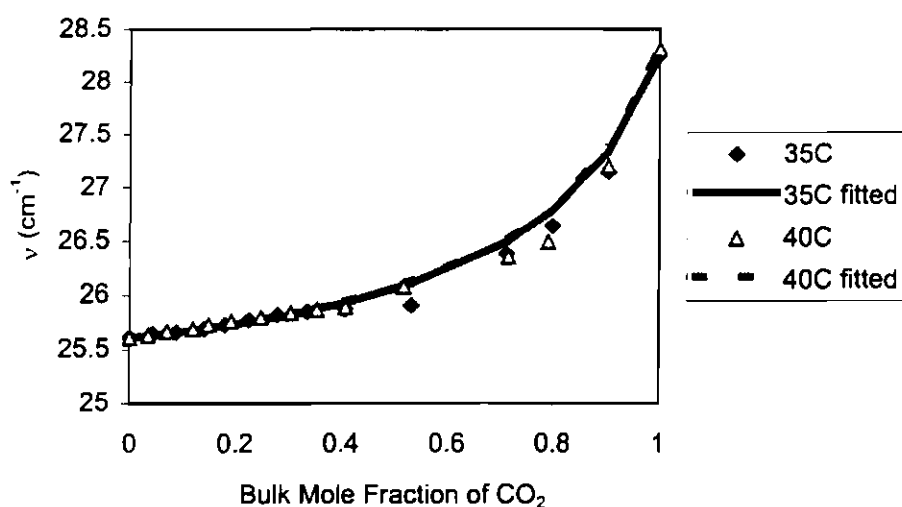
Table 4.8. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitrophenol as the indicator.

Temperature	Average $f_{2/1}$ (± 0.02)
35°C	0.08
40°C	0.08

and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Figure 4.9, Table 4.9). The trends were the same at 35°C and 40°C. The exact trend was observed by Rafols et. al. in a similar system of 2-propanol and benzene[1]. 2-propanol and methanol are understandably similar while benzene and carbon dioxide are both apolar, polarizable solvents without hydrogen bonding properties. They found 4-nitroanilsole ($f_{2/1}$ = 2.13) to have the greatest degree of solubility in carbon dioxide followed very closely by N.N-diethyl-4-nitroaniline ($f_{2/1}$ = 1.46). Results from the two systems suggest that hydrogen bonding has a significant effect on the amount of carbon dioxide present in the solvation sphere. Neither 4-nitroanisole or N,N-dimethyl-4-nitroaniline can significantly hydrogen bond and is less susceptible to solvation by the methanol as indicated by the results. Also in the work by Rafols et. al., 4-nitroaniline ($f_{2/1}$ = 0.36) had a higher preferential solvation value than 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate ($f_{2/1}$ = 0.022) according to their calculations using equation 4.2. 4-nitrophenol was not a probe indicator in their studies.

In acetone-carbon dioxide mixtures, N,N-dimethyl-4-nitroaniline (Figure 4.10, Table 4.10) was found to have the greatest degree of carbon dioxide present in its solvation sphere, followed by 4-nitroaniline (Figure 4.11, Table 4.11), and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Figure 4.12, Table 4.12) which were approximately equal. The $f_{2/1}$ value for the
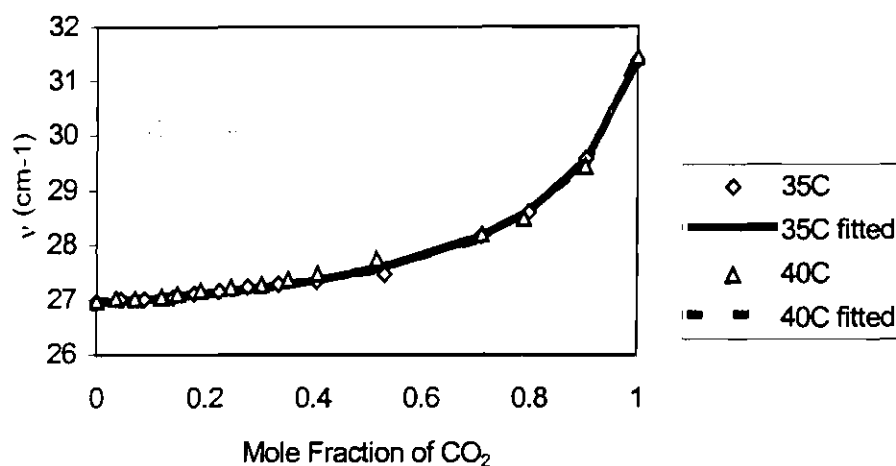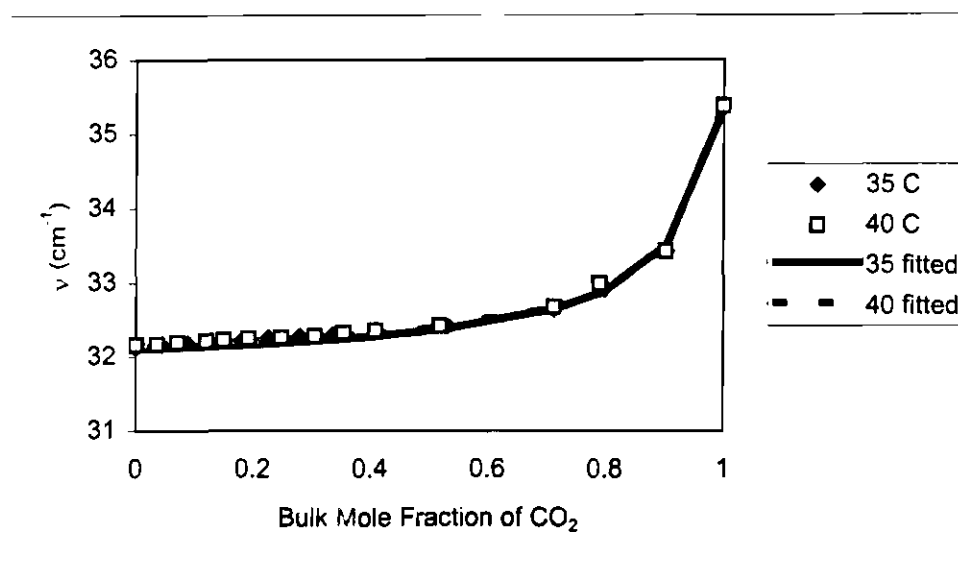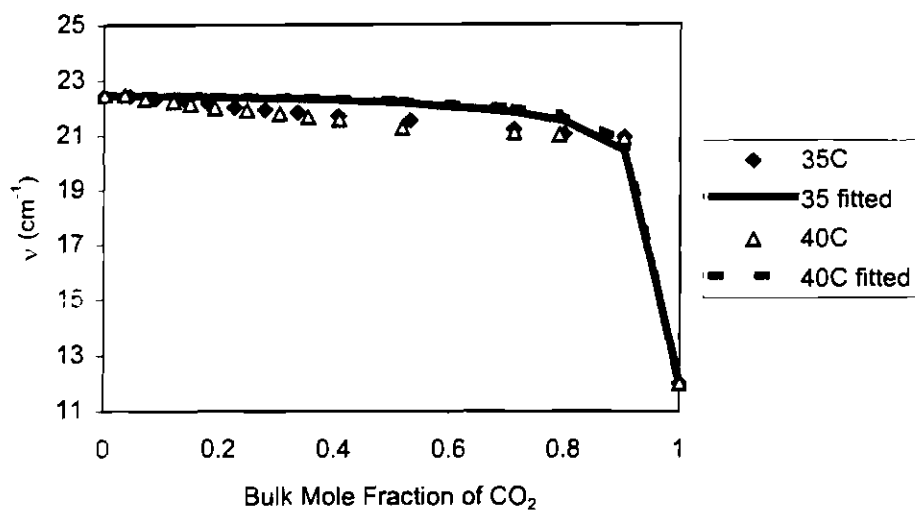
Figure 4.9. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the indicator. See Tables 3.10b and 3.10c for experimental data.

Table 4.9. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-phenolate as the indicator.

Temperature	Average $f_{2/1}$ (+0.02)
35°C	0.03
40°C	0.02

28.5
28
27.5
27
26.5
26
25.5

ν (cm^{-1})

0   0.2   0.4   0.6   0.8   1

Bulk Mole Fraction of CO_2

♦ 35C
—— 35C fitted
△ 40C
—— 40C fitted
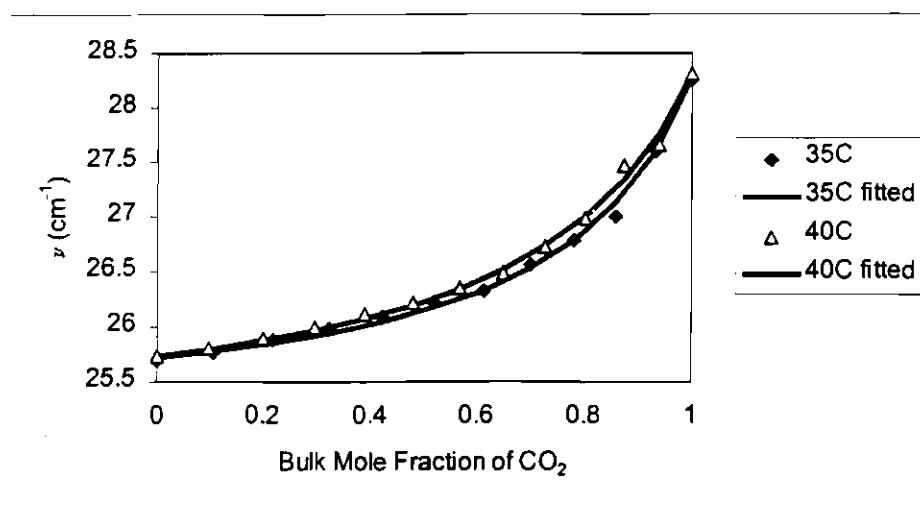
Figure 4.10. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator. See Tables 3.9b and 3.9c for experimental data.

Table 4.10. Preferential solvation parameters ($f_{2/1}$) for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator.

Temperature	Average $f_{2/1}$ (± 0.02)
35°C	0.20
40°C	0.24
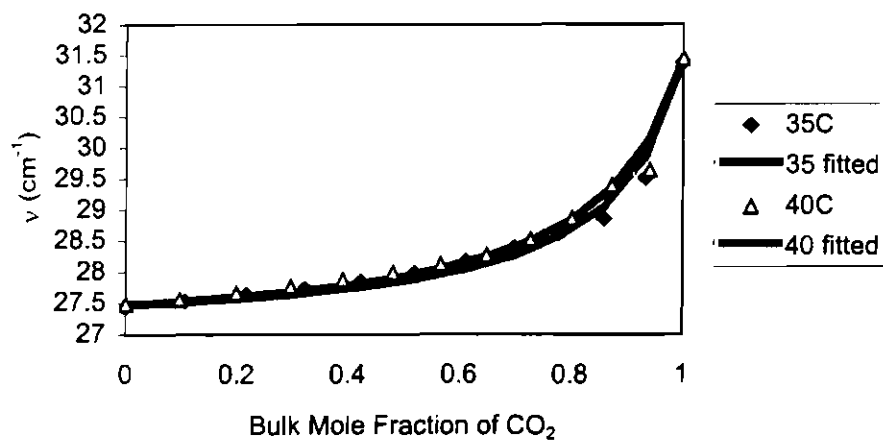
Figure 4.11. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 4-nitroaniline as the indicator probe. See Tables 3.9b and 3.9c for experimental data.

Table 4.11. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 4-nitroaniline as the indicator probe.

Temperature	Average $f_{2/1}$ (±0.02)
35°C	0.11
40°C	0.13
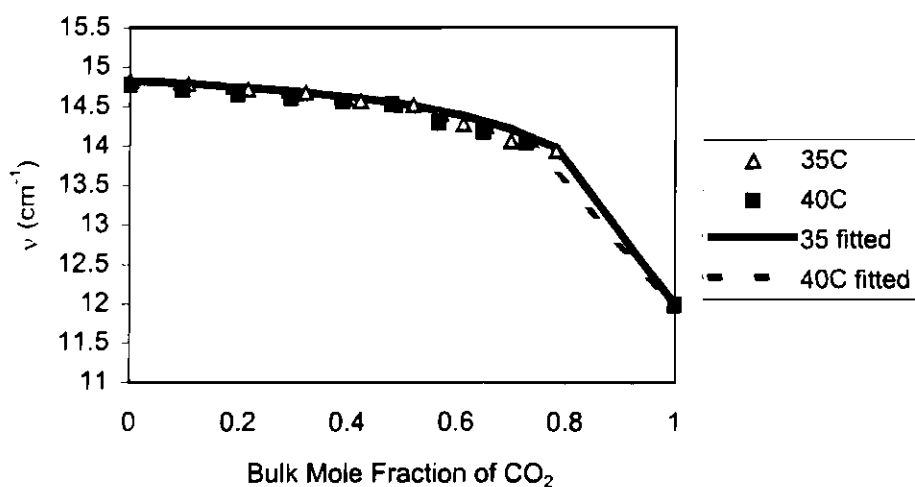
Figure 4.12. Preferential solvation parameters ($f_{2/1}$) for 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C. See Tables 3.11b and 3.11c for experimental data.

Table 4.12. Preferential solvation parameters ($f_{2/1}$) for 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C.

Temperature	Average $f_{2/1}$ (± 0.02)
35°C	0.12
40°C	0.13

betaine dye could possibly be misleading due to the inability to effectively dissolve the dye at high carbon dioxide concentration. The curve fit is directly affected by this and is very likely to cause an increase in the $f_{2/1}$ value. The trends were the same at 35°C and 40°C.

This trend was not observed by Bosch et. al. in a similar system of 2methylpropan-2-ol and benzene but all of the values were very close[11]. Bosch et. al. found 4-nitroaniline ($f_{2/1}$ = 0.66) to have the greatest degree of solubility in carbon dioxide followed by 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate ($f_{2/1}$ = 0.51). N,N-diethyl-4-nitroaniline ($f_{2/1}$ = 0.35) had the lowest preferential solvation value according to their calculations using equation 4.2. 2-methylpropan-2-ol and acetone are not as similar to each other as 2-propanol and methanol but in comparison to methanol, the two have similarities. Acetone and 2-methylpropan-2-ol are both less polar than methanol. Acetone is an aprotic solvent while 2-methylpropan-2-ol is protic. However, by default a less protic solvent also has a lower pKa. 2-methylpropanal (18.00) and acetone (19.3) both have higher pKa's than methanol (15.54) giving them a lower hydrogen bonding effect.

Two-step solvent exchange model. Equation 4.4 was applied to fit the data under the assumption that a secondary solvent is formed by intermolecular interaction of carbon dioxide with methanol or acetone at 35°C and 40°C. This equation has three variable parameters: $f_{2/1}$, $f_{12/1}$, and Y12. For methanol–carbon

dioxide mixtures, all of the Y12 values (based on experimental wavenumber as the solvatochromic property of choice) were slightly to moderately higher than the average for the pure components. This indicates that for all systems studied, the properties of the secondary solvent are closer to methanol than carbon dioxide. The exception is 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate which has a Y12 value considerably lower than the average of the Y values for the pure solvents. The secondary solvent still has properties closer to methanol because carbon dioxide red shifts the absorption peaks upfield rather than downfield as observed for the other dyes.

Composite graphs plotting the bulk mole fractions of carbon dioxide against the corresponding local mole fractions are shown in Figures and Tables 4.13 to 4.16. Supporting data, including measured wavenumbers and local compositions for the binary mixtures and pure solvents, are presented herein. The $f_{12/1}$ values for methanol-carbon dioxide mixtures show that 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Figure and Table 4.17) has the greatest degree of solvation in the secondary solvent. However as mentioned previously, the Y12 value is much closer to methanol in comparison to what is observed for other dyes. This could explain why additional volumes of carbon dioxide have little effect on the solvatochromic shift of the betaine dye.

0.2

0.16

0.12

0.08

0.04

0

Local Mole Fraction of CO_2

0   0.2   0.4   0.6   0.8   1

Bulk Mole Fraction of CO_2

♦ 4-nitroanisole

■ 4-nitroaniline

▲ N,N-dimethyl-4-nitroaniline

◊ 4-nitrophenol

✗ ET-33

Figure 4.13. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Methanol and Carbon Dioxide at 35°C. Calculated by equation 4.3.

Table 4.13. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Methanol and Carbon Dioxide at 35°C. Calculated by equation 4.3.

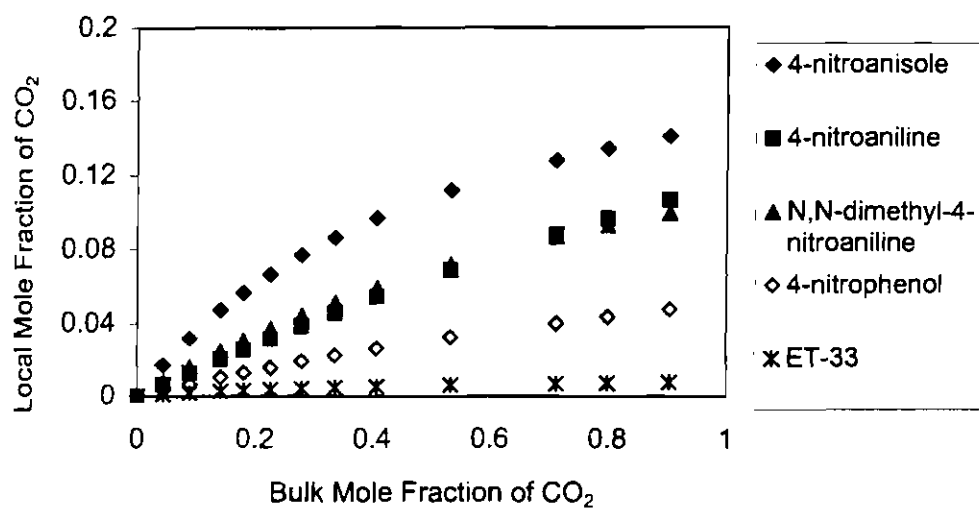| Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2				
	4-nitroanisole	4-nitroaniline	N,N-dimethyl-4-nitroaniline	4-nitrophenol	ET(33)
0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
4.44%	1.72%	0.66%	0.85%	0.35%	0.10%
8.88%	3.20%	1.30%	1.64%	0.68%	0.19%
14.14%	4.69%	2.03%	2.51%	1.05%	0.27%
18.04%	5.66%	2.57%	3.10%	1.31%	0.33%
22.63%	6.67%	3.18%	3.76%	1.60%	0.38%
27.92%	7.70%	3.86%	4.46%	1.92%	0.44%
33.60%	8.66%	4.58%	5.16%	2.25%	0.49%
40.69%	9.70%	5.44%	5.96%	2.63%	0.55%
53.23%	11.19%	6.88%	7.20%	3.25%	0.62%
71.22%	12.81%	8.80%	8.68%	4.03%	0.71%
79.92%	13.44%	9.67%	9.30%	4.37%	0.74%
90.41%	14.10%	10.67%	9.97%	4.74%	0.77%
100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Figure 4.14. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary
Mixtures of Methanol and Carbon Dioxide at 40°C. Calculated by equation 4.3.

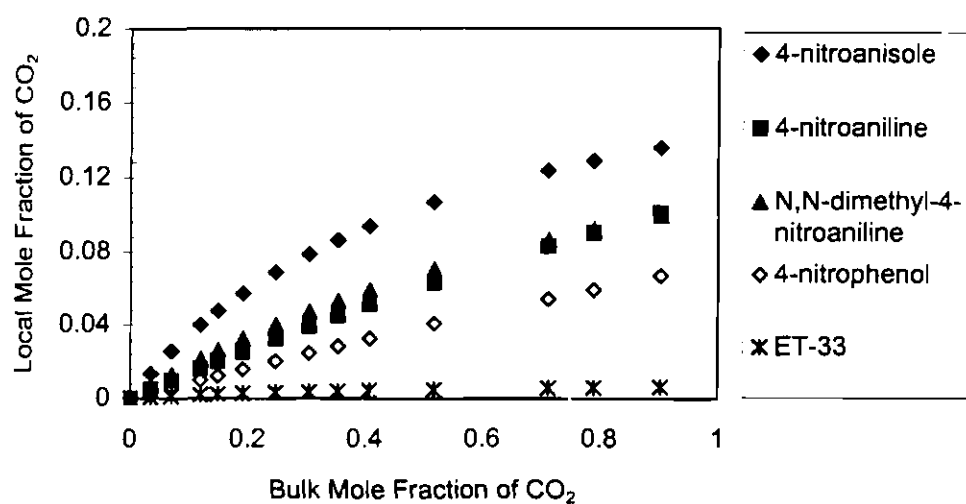Table 4.14. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Methanol and Carbon Dioxide at 40°C. Calculated by equation 4.3.

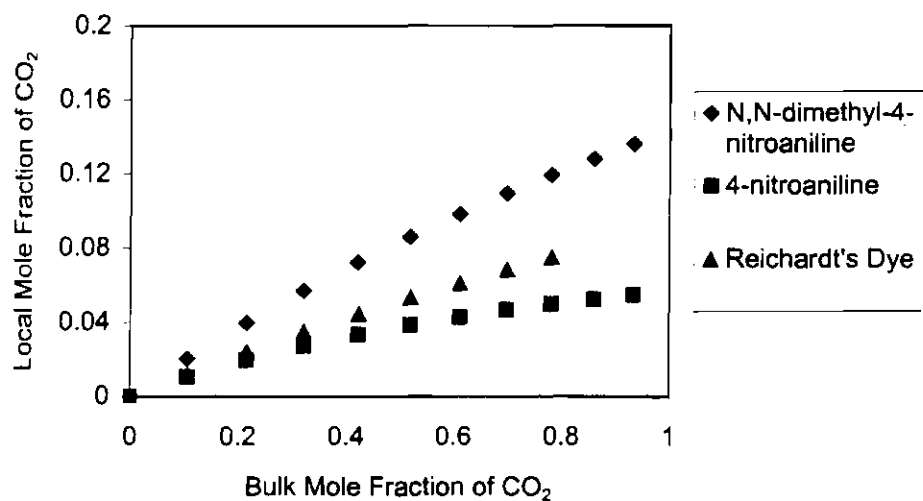| Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2				
	4-nitroanisole	4-nitroaniline	N,N-dimethyl-4-nitroaniline	4-nitrophenol	ET(33)
0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
3.54%	1.36%	0.49%	0.69%	0.30%	0.07%
7.07%	2.55%	0.97%	1.33%	0.59%	0.12%
11.97%	3.99%	1.62%	2.16%	1.00%	0.19%
14.94%	4.77%	2.01%	2.63%	1.24%	0.23%
19.18%	5.75%	2.55%	3.27%	1.58%	0.27%
24.76%	6.89%	3.24%	4.05%	2.02%	0.32%
30.45%	7.89%	3.93%	4.78%	2.47%	0.37%
35.37%	8.65%	4.50%	5.37%	2.85%	0.40%
40.77%	9.40%	5.12%	5.97%	3.25%	0.44%
51.75%	10.67%	6.32%	7.06%	4.06%	0.49%
71.52%	12.37%	8.31%	8.68%	5.43%	0.57%
79.02%	12.91%	9.05%	9.24%	5.96%	0.59%
90.31%	13.59%	10.08%	9.96%	6.71%	0.62%
100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Figure 4.15. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 35°C. Calculated by equation 4.3.

Table 4.15. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 35°C. Calculated by equation 4.3.

Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2		
	4-nitroaniline	N,N-dimethyl-4-nitroaniline	$E_T(30)$
0.00%	0.00%	0.00%	0.00%
10.66%	1.07%	2.04%	1.24%
21.65%	1.98%	3.98%	2.43%
32.19%	2.73%	5.70%	3.50%
42.28%	3.34%	7.23%	4.47%
51.92%	3.85%	8.60%	5.34%
61.11%	4.29%	9.82%	6.13%
69.86%	4.66%	10.92%	6.85%
78.15%	4.98%	11.91%	7.50%
85.99%	5.26%	12.80%	N/A
93.38%	5.51%	13.60%	N/A
100.0%	100.0%	100.0%	100.0%

Figure 4.16. Preferential Solvation $(f_{12/1})$ of Solvatochromic Dyes in Binary
Mixtures of Acetone and Carbon Dioxide at $40°C$. Calculated by equation 4.3.

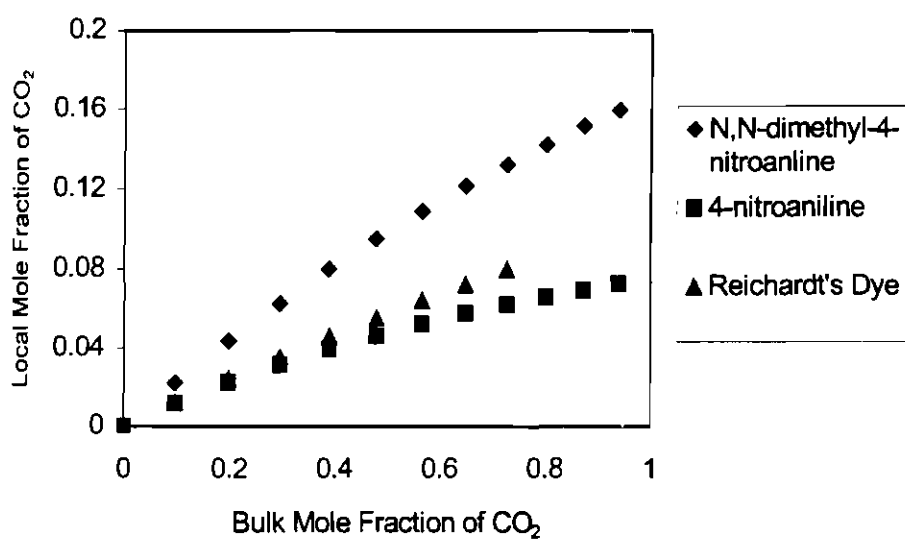Table 4.16. Preferential Solvation ($f_{12/1}$) of Solvatochromic Dyes in Binary Mixtures of Acetone and Carbon Dioxide at 40°C. Calculated by equation 4.3.

Bulk Mole Fraction of CO_2	Local Mole Fraction of CO_2		
	4-nitroaniline	N,N-dimethyl-4-nitroaniline	$E_T(30)$
0.00%	0.00%	0.00%	0.00%
9.67%	1.17%	2.23%	1.23%
19.81%	2.25%	4.37%	2.45%
29.58%	3.16%	6.28%	3.57%
38.96%	3.94%	7.98%	4.60%
47.96%	4.62%	9.50%	5.54%
56.59%	5.21%	10.87%	6.41%
64.84%	5.72%	12.10%	7.21%
72.70%	6.17%	13.22%	7.95%
80.19%	6.58%	14.22%	N/A
87.30%	6.93%	15.13%	N/A
94.04%	7.25%	15.96%	N/A
100.0%	100.0%	100.0%	100.0%

Figure 4.17. Preferential solvation parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate as the indicator probe. See Tables 3.10b and 3.10c for experimental data.
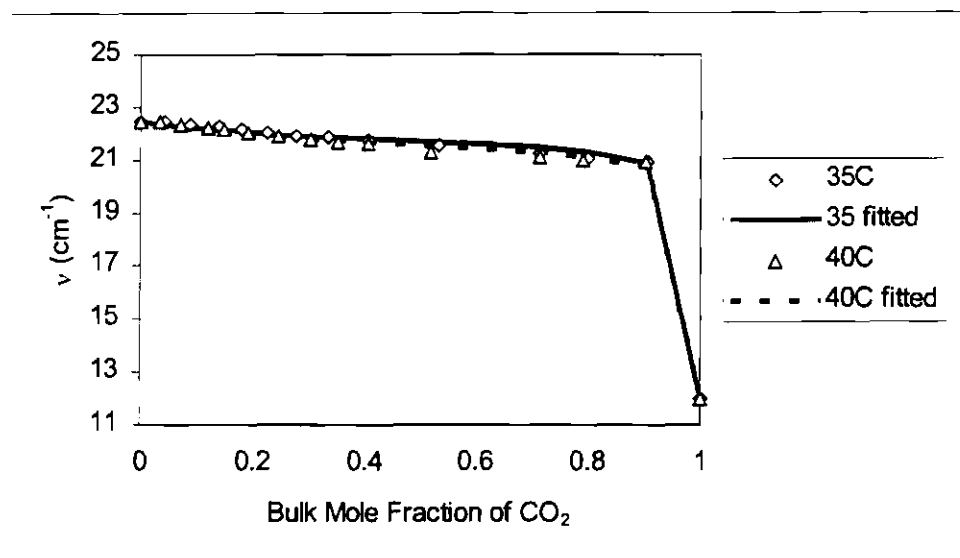
Table 4.17. Preferential solvation parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate as the indicator probe.

Temperature	Average $f_{2/1}$ (+0.02)	Average $f_{12/1}$ (+0.02)	Y12 (+0.01)
35°C	0.03	3.1	21.5
40°C	0.02	3.1	21.3

2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate is followed by 4-nitroanisole (Figure and Table 4.18), N,N-dimethyl-nitroaniline (Figure and Table 4.19), 4-nitroaniline (Figure and Table 4.20), and 4-nitrophenol (Figure and Table 4.21) , respectively, at 35°C and 40°C. The exact same trend is observed by Rafols et. al. in binary mixtures of 2-propanol and benzene[1].

The $f_{12/2}$ values for acetone-carbon dioxide binary mixtures show 4-nitroaniline (Figure and Table 4.22) to have the greatest degree of solubility in solvent S12. It is followed by N,N-dimethyl-4-nitroaniline (Figure and Table 4.23) and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Figure and Table 4.24), which are very close to being equal. Bosch et. al., observed the same trend for the the binary mixtures of 2-methyl-2-propanol and benzene[11].
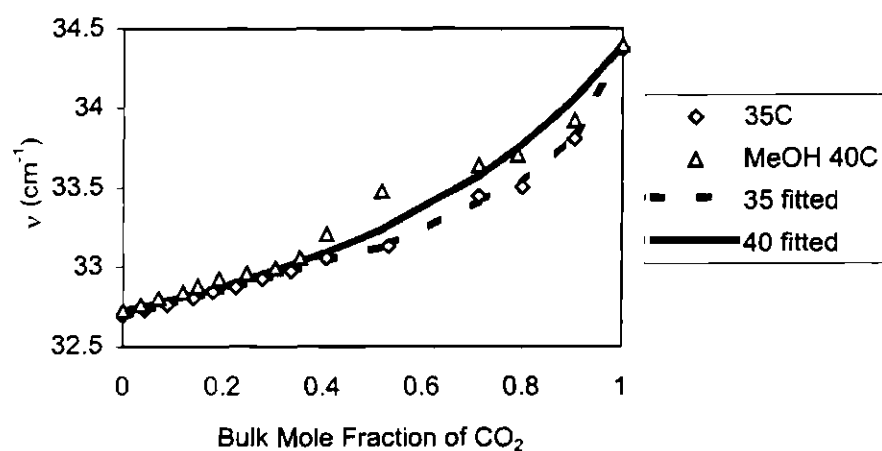
Figure 4.18. Preferential solvation parameters ($f_{12/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator probe. See Table 3.5b for experimental data.

Table 4.18. Preferential solvation parameters for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroanisole as the indicator probe.

Temperature	Average $f_{2/1}$ (±0.02)	Average $f_{12/1}$ (±0.02)	Y12 (±0.01)
35°C	0.42	2.45	33.05
40°C	0.41	2.50	33.13

Figure 4.19. Preferential Solvation Parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator. See Table 3.7b and 3.7c for experimental data.
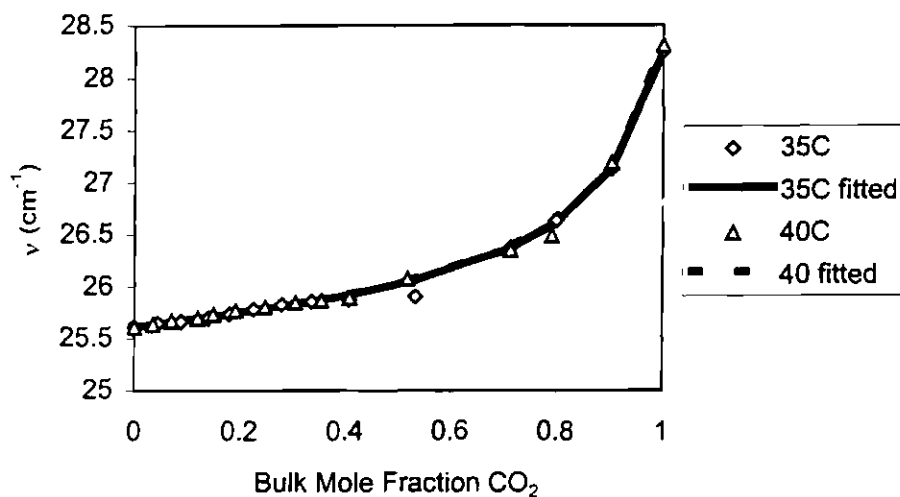
Table 4.19. Preferential Solvation Parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using N,N-dimethyl-4-nitroaniline as the indicator.

Temperature	Average $f_{2/1}$ (± 0.02)	Average $f_{12/1}$ (± 0.02)	Y12 (± 0.01)
35°C	0.2	1.7	26.0
40°C	0.2	1.7	26.0

Figure 4.20. Preferential solvation parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroaniline as the indicator. See Table 3.7b and 3.7c for experimental data.

Table 4.20. Preferential solvation parameters $(f_{12/1})$ for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitroaniline as the indicator.

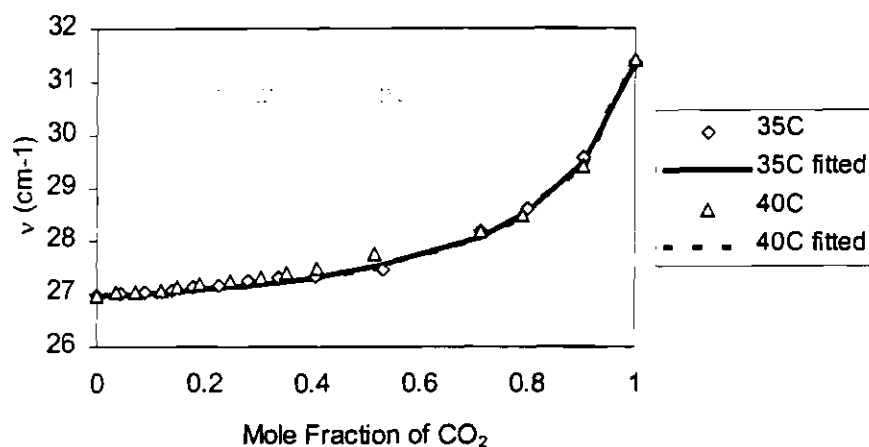| Temperature	Average $f_{2/1}$ (±0.02)	Average $f_{12/1}$ (±0.02)	Y12 (±0.01)
35°C	0.15	1.15	27.4
40°C	0.14	1.14	27.4

Figure 4.21. Preferential solvation parameters ($f_{12/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitrophenol as the indicator. See Table 3.8b and 3.8c for experimental data.
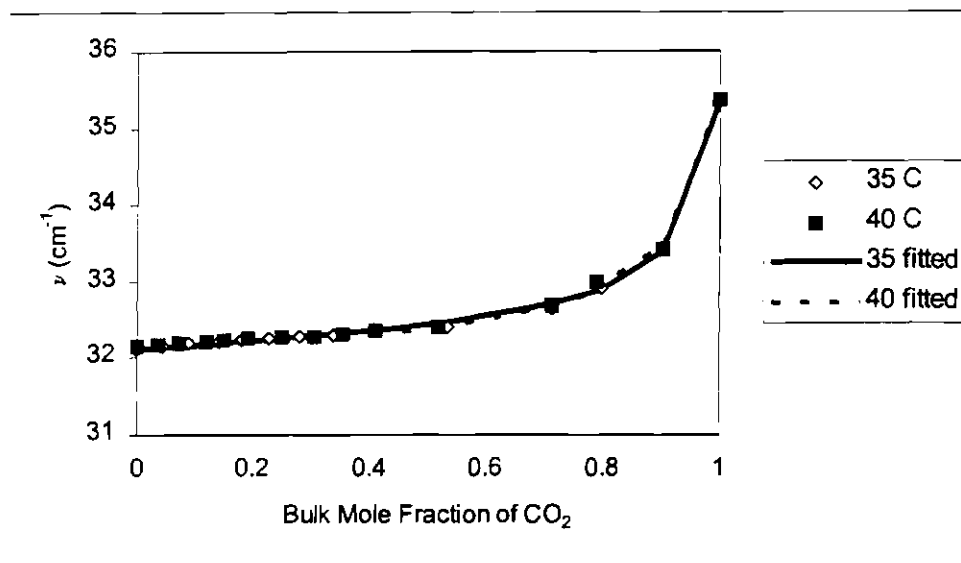
Table 4.21. Preferential solvation parameters ($f_{12/1}$) for binary solvent mixtures of methanol and CO_2 at 35°C and 40°C using 4-nitrophenol as the indicator.

Temperature	Average $f_{2/1}$ (+0.02)	Average $f_{12/1}$ (+0.02)	Y12 (+0.01)
35°C	0.08	1.08	32.5
40°C	0.08	1.08	32.4

Figure 4.22. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 4-nitroaniline as the probe indicator. See Table 3.9b and 3.9c for experimental data.
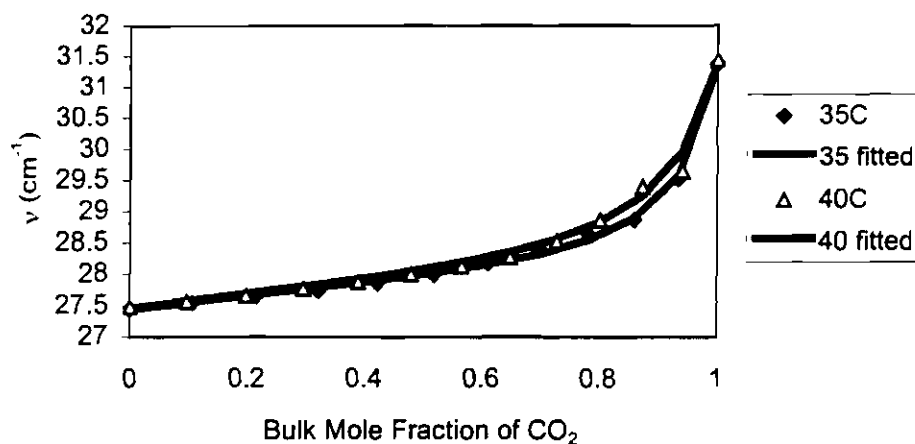
Table 4.22. Preferential solvation parameters $(f_{2/1})$ for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 4-nitroaniline as the probe indicator.

Temperature	Average $f_{2/1}$ (+0.02)	Average $f_{12/1}$ (+0.02)	Y12 ($\pm$0.01)
35°C	0.11	1.83	28.1
40°C	0.13	1.60	28.2

Figure 4.23. Preferential solvation parameters ($f_{12/1}$) N,N-dimethyl-4-nitroaniline in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C. See Table 3.9b and 3.9c for experimental data.
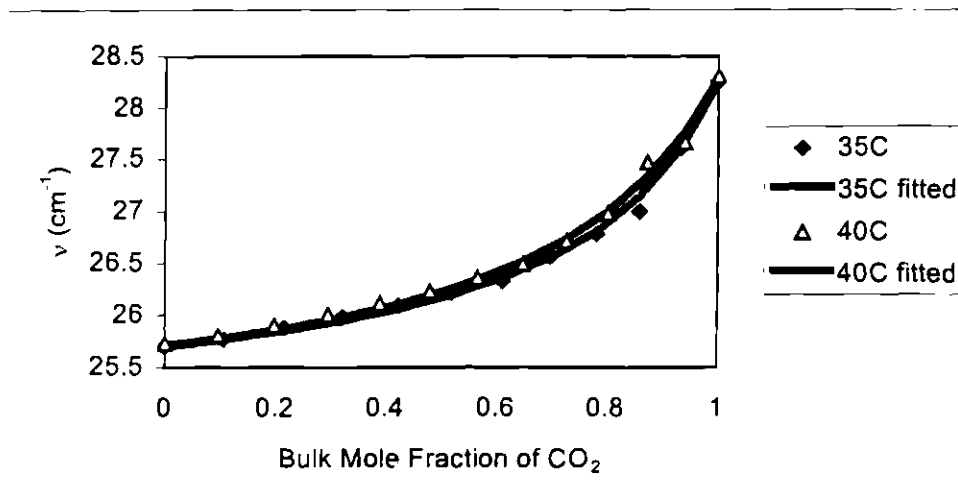
Table 4.23. Preferential solvation parameters ($f_{12/1}$) N,N-dimethyl-4-nitroaniline in binary solvent mixtures of acetone and CO_2 at 35°C and 40°C.

Temperature	Average $f_{2/1}$ (+0.02)	Average $f_{12/1}$ (+0.02)	Y12 (+0.01)
35°C	0.20	1.20	26.20
40°C	0.24	1.20	26.23

Figure 4.24. Preferential solvation parameters ($f_{12/1}$) for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate as the probe indicator. See Table 3.11b and 3.11c for experimental data.
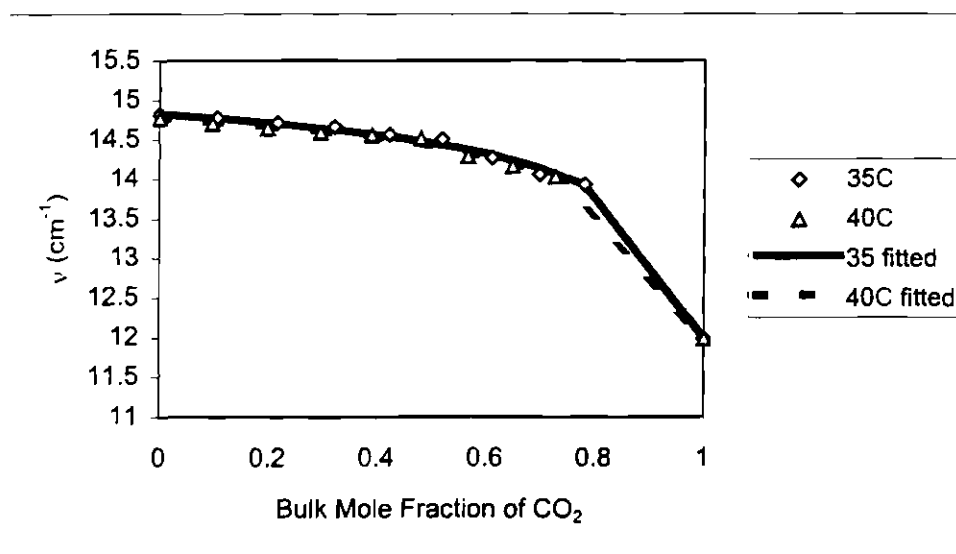
Table 4.24. Preferential solvation parameters ($f_{12/1}$) for binary solvent mixtures of acetone and CO_2 at 35°C and 40°C using 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-1-phenolate as the probe indicator.

Temperature	Average $f_{2/1}$ (+0.02)	Average $f_{12/1}$ (+0.02)	Y12 (±0.01)
35°C	0.12	1.20	14.4
40°C	0.13	1.13	14.4

Conclusions

The local compositions have been determined by studying the solvatochromic behavior of the cybotactic region of solute molecules in binary mixtures and pure solvents. Preferential solvation trends were very similar to those reported for the same indicator dyes in comparable systems. Results for binary mixtures of methanol-carbon dioxide and acetone-carbon dioxide all showed enrichment of carbon dioxide in the cybotactic region with increasing bulk mole fractions of carbon dioxide. The local compositions in the cybotactic region were dependent on pressure and temperature.

Local compositions did not show a linear correlation to bulk composition. Invariably, the bulk mole fraction of carbon dioxide was greater than the local mole fraction of carbon dioxide. These calculations could explain observations detailed in Chapter 3 where plots of bulk mole fractions of carbon dioxide versus solvatochromic parameters were not linear. It is also clear that the local composition enrichment is strongly dependent upon the solute probe as none of the indicators gave the same local compositions in either of the binary mixtures. This is very important when calculating α and β values because they are dependent upon more than one indicator. Solvatochromic parameters, π^* and $E_T(30)$, are dependent on only the direct measurement of a single indicator.

Comparisons of the two equations based on one-step (equation 4.2) and two-step (equation 4.4) models, used to calculate the preferential solvation parameters, show the same trends. It is generally understood that the division between the two theories is artificial because the one-step systems are particular cases of the two-step model. Nevertheless, the fit to the one-step model is useful to avoid overparameterization of the equation and obtain good estimates of the parameters. 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate in the methanol-carbon dioxide binary mixture was best fit by equation 4.4. This again shows that the two-step model gives a better fit to binary systems that have a large variation in wavenumber.

These studies could lead to improvements in separation processes by providing information about cluster formation in low-density binary fluids. It also adds promise to the ability to determine the effect of local organic co-solvent and supercritical fluid composition on chromatographic retention or extraction selectivity.

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VITA

Victor Terrell Wyatt was born to Hazel and Eli Wyatt on August 8, 1973 in Fayette, MS. He grew up in Union Church, MS as the younger of two children with one older sister, Cynthia. He graduated as the Valedictorian of Jefferson County High School in May of 1991. He then enrolled at Jackson State University and received a B.S. in Chemistry in May 1995. During this time, he worked as a summer intern at Ithaca College, University of Wisconsin-Madison, Florida State University, and Dow Chemical. He entered the Georgia Institute of Technology in 1996 earning a M.S. in Chemistry in June of 1998. In the summer of 1997, he worked as a summer intern with Celanese in Corpus Christi, TX.

He is a member of Kappa Alpha Psi Fraternity, Inc where he proudly serves as the liason to Aid to Children of Imprisoned Mothers, Inc. Upon completing his doctoral degree in December of 2001, he will join the research group of Dr. John Pojman at the University of Southern Mississippi in Hattiesburg, MS.