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Henry's Law Constant of Methanol in Pulping Liquors

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Henry's Law Constant of Methanol in Pulping Spent Liquors

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Abstract

A direct headspace gas chromatographic method was used to study the Henry's constant

of methanol in pulping spent liquors collected from kraft pulp mills and from laboratory batch

pulping studies using various wood species. The total solids contents of the pulping spent

liquors was less than 25%. It was found that temperature and concentration of inorganic solids,

mainly sodium salts, are the two variables that significantly affect the Henry's constants of

methanol. A two-parameter (temperature and liquor total solids content) correlation was

developed based on the experimental data and is reported in this study.

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INTRODUCTION

Henry's law constant directly relates the partial pressure to the infinite dilution activity coefficient of a dissolved species in a given solution. In environmental science, the partial vapor pressure of a volatile pollutant species can be used to predict the air emission of the pollutant in many industrial sites. In the chemical industry, the partial vapor pressure dictates the design of strippers and other facilities to separate the volatile species. Therefore, the study of vapor-liquid equilibrium (VLE) of volatile solutes in infinitely dilute solutions has significant practical applications in chemical engineering and environmental science.

We report on Henry's law constants of methanol in pulping spent liquors in this study. It is well known that methanol can be formed through the reaction of methoxyl groups in hemicellulose and lignin with hydroxide during pulp manufacturing processes in kraft pulp mills [1-3]. The formation of methanol in these processes has created an environmental concern because methanol is soluble in water and becomes an important source of biodegradable organic compounds which increase the biochemical oxygen demand (BOD). Furthermore, methanol is very volatile and can be released into the atmosphere from various kraft mill processes. Methanol air emissions in kraft mills are now regulated by the U.S. Environmental Protection Agency through the Cluster Rule [4]. This study on the Henry's constant of methanol in various kraft mill streams, therefore, provides a database for emission predictions [5, 6].

The infinite dilution activity coefficient of methanol in water has been reported in several studies [7-13]. However, the data reported in these studies are not consistent. Furthermore, the extrapolation of these data to solutions that contain components in addition to methanol and water, such as those found in pulp and paper streams, is not reliable. There are many

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experimental methods available for the study of infinite dilution activity coefficient as reviewed by Kojima et al. [14] recently. Most of these methods can be used to determine the Henry's constants of solutes, but not without limitations in measurement accuracy and other related problems. Static headspace gas chromatography has been widely used to obtain partition coefficients (or Henry's constants) because of its accuracy, consistency, speed, and versatility. Direct [15, 16], indirect [17-19], and multiple extraction [20] headspace GC methods have been developed for this purpose.

In this study, a direct headspace gas chromatographic method described by Kolb et al. [16] was employed to directly determine the Henry's law constant of methanol in dilute solutions. Binary solution measurements were used to validate the experiments. Measurements in pulping spent liquors were used to derive an empirical correlation of Henry's law constant of methanol for air emission predictions in kraft mills.

EXPERIMENTAL

Measurement Facility and Method

All the measurements were conducted using a commercial headspace gas chromatograph. The instrument consists of a headspace sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) and a capillary gas chromatograph (HP-6890, Hewlett-Packard).

The Henry's law constant H_i of a species i is defined according to the following equation:

$$H_i = \lim_{x \to 0} \frac{y_i \cdot P}{x_i} \tag{1}$$

where x_i and y_i are the mole fraction of the species i in the vapor and liquid phase, respectively. For a system at equilibrium in a static headspace, we can assume that the vapor phase follows the ideal gas law,

$$y_i \cdot P = P_i^v = C_{Gi} \cdot RT \qquad (2)$$

where C_{Gi} is the solute mole concentration in the headspace (vapor phase) and R is the universal gas constant. In a system in which all solutes are at infinite dilution, we can approximate the mole fraction of solute i in the liquid phase as

$$x_i \approx \frac{n_i}{n_j} = \frac{C_{Li}}{\rho_j / M_j} = C_{Li} \cdot v_j \qquad (3)$$

where C_{Li} is the solute concentration in the liquid phase at equilibrium, and ρ_j, M_j, and v_j are the density, molecular weight, and the molar volume of the solvent, respectively.

Combining Eqns. (2), (3), and (1) leads to a relationship between the Henry's constant of species i and its partition coefficient $K_i = C_{Li}/C_{Gi}$ in a static headspace:

$$H_i = \frac{RT}{v_j K_i} = \frac{\rho_j RT}{M_j \cdot K_i} \qquad (4)$$

A direct headspace GC method [16] was used in the present study to determine the partition coefficient K_i. In this method, we first measured the initial methanol concentration C_0 in a sample black liquor using an indirect headspace GC method [21, 22] (a standard addition

procedure). We then measured the methanol concentration C_G in the static headspace in terms of GC recorded peak area A. Therefore, we obtain

$$K_i = \frac{C_{Li}}{C_{Gi}} = \frac{C_0 - \beta C_{Gi}}{f \cdot A_i} \tag{5}$$

where f is the GC response factor and $\beta = V_G/V_L$ is the phase ratio. $\beta = 1$ (or V_L=10 mL) was used in this study. Therefore, if K_i is much greater than 1, i.e., $K_i > 10$, $C_{Gi} << C_{Li}$ ($< C_0$) can be ignored in Eqn. (5), and, hence,

$$K_i \approx \frac{C_0}{f \cdot A_i} \tag{6}$$

We used a standard water-methanol solution with known methanol concentration of $C_{s0} =$ 800 mg/L and methanol VLE partition coefficient K_{si}, (e.g., $K_{si} = 570$ at 70°C [18]), to obtain f, and, hence,

$$K_i = \frac{A_{si}}{A_i} \cdot \frac{C_o}{C_{so}} \cdot K_{si} \tag{7}$$

where A_{si} is the GC peak area recorded in measuring the headspace vapor of the standard solution at the temperature corresponding to K_{si}.

Pulping Spent Liquor and Chemicals

Pulping spent liquor or black liquor is an aqueous water solution containing dissolved organic and inorganic solids. It is a byproduct of the wood deligninfication process in pulp and

paper manufacturing. The dissolved organic materials are complex substances derived from cellulose, hemicellulose, lignin, and other extractives in the wood. The soluble inorganic solids are mainly sodium salts with minimal quantities of potassium salts. The total solids content of pulping spent liquor or weak (unconcentrated) black liquor is around 5-20% with the organic to inorganic ratio around 0.45. Black liquor is caustic with a pH value of about 13. It also contains many volatile organic compounds (VOCs), such as methanol, methyl ethyl ketone (MEK), and dimethylsulfide (DMS), formed during pulping. The concentrations of these VOCs are very low and can be assumed to be at infinite dilution from a thermodynamic point of view.

Weak black liquors derived from various wood species and collected from both several kraft pulp mills and laboratory pulping processes were used in this study. The total dissolved solids contents of the liquors was less than 25%, therefore, the black liquors were treated as aqueous solutions. Analytical grade sulfonated lignin, sodium carbonate, sodium sulfate, sodium chrolide, sodium hydroxide, dimethylsulfide (DMS), dimethyldisulfide (DMDS), methyl ethyl ketone (MEK), and α-pinene, were also added to standard water-methanol solutions to study the effects of these minor species contained in black liquors on the Henry's constant of methanol.

Experimental Conditions

GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow: 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: gentle shaking for equilibration of the sample for 25 minutes, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min.

RESULTS AND DISCUSSIONS

Equilibrium Time

One key factor in this VLE study is to achieve vapor-liquid equilibrium. The commercial HP-7694 headspace sampler can apply gentle and strong shaking to the sample vial to accelerate the equilibrium process between the liquid and vapor phases. Sample volume used in the vial is one factor that affects the time required to achieve equilibrium. In the experiments, we used a phase ratio of $\beta = 1$, or a liquid sample volume $V_L = 10$ mL, and gentle shaking. We found that an equilibrium time of 25 minutes is sufficient to achieve methanol vapor-liquid equilibrium in the sample vial static headspace [22].

Measurement Uncertainty

Although black liquor can be treated as an aqueous solution, the distribution of various dissolved solids in the liquor can be inhomogeneous, which makes it difficult to obtain uniform and representative samples during experiments. Therefore, liquor sampling can contribute to measurement uncertainty. Sampling of the liquid phase and the vapor phase can also contribute to measurement uncertainty. We conducted 11 replicate measurements of methanol Henry's law constant in black liquor collected from a kraft mill to estimate the actual measurement uncertainty. We found the maximum error in a single measurement to be 15%. However, the relative standard deviation was 8.8%. We conducted triplicate experiments and averaged the measurements; therefore, the actual measurement uncertainty of the data presented in this study is less than 8.8%.

Effect of Temperature

Since the operating process temperature of weak black liquor in kraft mills varies significantly, we measured the Henry's constants of 13 black liquors from both kraft mills and our laboratory pulping processes using birch and southern pine in a temperature range of 50-80°C. Our measurements indicate that the Henry's constant of methanol in all the black liquors examined follows the van't Hoff relationship with temperature. Table I lists the linear regression results along with the correlation coefficients for all the liquors tested. Only the results from 4 black liquor samples are shown in Fig. 1 for clarity. The van't Hoff equation [23] is given by:

$$\ln(H) = \frac{a}{T} + b \qquad\qquad (8)$$

For comparison, we have also plotted Henry's constants of methanol in water in Fig. 1. The results as listed in Table I show that the slopes for all 13 black liquor samples were very close to the slope of the methanol-water data. The relative standard deviations of the with (14 data sets) and without water (13 data sets) were 5.8 and 5.0%, respectively. Also, the slopes obtained from the black liquor data were slightly smaller than those of the water-methanol mixture, indicating that the partial molar excess enthalpy of methanol in black liquor (a multi-component system) is only slightly smaller than that in water (a two-component system).

Figure 1 indicates that there are significant variations in measured methanol Henry's constants among various black liquors. The variations in the compositions of the black liquors due to inorganic and organic solids content, pH, and the presence of other species are a possible cause of these differences.

Effect of Lignin

Black liquor contains significant amounts of dissolved organic materials, such as lignin. To understand the effect of lignin on Henry's constants of methanol, we have measured methanol Henry's constants in several model solutions containing water, methanol, and sulfonated lignin. We found that the methanol Henry's constant is not affected by the presence of sulfonated lignin. Figure 2 shows the normalized Henry's constants of methanol measured in such solutions at two temperatures, 70 and 80°C, and various sulfonated lignin concentrations.

Effect of pH

We took a similar approach to study the effect of pH on the Henry's constant of methanol in black liquors. Black liquor is a caustic solution with a nominal pH value of about 13. Different amounts of sodium hydroxide were added to methanol-water solutions and the Henry's constant was measured. As shown in Fig. 3, our results indicate that the Henry's constant of methanol is proportional to the hydroxide concentration raised to the power of 0.2, which means that the effect of pH is not significant. It should be noted that the sodium ion concentration also contributes to the variations shown in Fig. 3. The effect of ionic strength, or more specifically, sodium salt concentration on methanol Henry's constant is discussed in the next section.

Effect of Inorganic Salt

Significant amounts of inorganic solids are present in black liquors. These inorganic solids are mainly sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) plus minimal amounts of sodium thiosulfate ($Na_2S_2O_3$), sodium chloride (NaCl), and potassium salts. To

understand the effect of inorganic solids on methanol Henry's constant, we measured the Henry's constant in water-methanol solutions containing Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, and NaCl, respectively. We found that the logarithm of Henry's constant of methanol increases linearly with the sodium salt mass concentration at a given temperature, but with the type of salt as shown in Fig. 4. The measured Henry's constants of methanol in actual black liquors are also shown Fig. 4. The total mass concentrations of the inorganic materials (more than 95% are sodium salts) in the 13 black liquor samples studied were obtained by subtracting the lignin (organic solids) content from the measured total solids content. We used the following equation to express this relation [24]:

$$\ln(H) = c \cdot S_{Salt} + d \qquad (9)$$

where S_{salt} is the total sodium salt mass concentration of the liquor.

Effects of dimethylsulfide, dimethyldisulfide, methyl ethyl ketone, α-pinene, β-pinene, fatty acids, resin acids

Many other chemical species, such as dimethylsulfide (DMS), dimethyldisulfide (DMDS), α-pinene, β-pinene, fatty acids, resin acids (MEK), presented in weak black liquors can affect the methanol Henry's constant. To determine the effect of these compounds, we prepared methanol-water solutions containing one of these compounds to study their individual effects on Henry's constant of methanol. The results indicate that the effect of these compounds at the concentration levels present in weak black liquor on methanol Henry's constant is insignificant. Figures 5-8 show the effects of α-pinene, DMS, MEK, and DMDS.

Empirical Correlation

The results presented in this work show that temperature and inorganic solids content are the two main variables that affect Henry's constants of methanol in black liquors. The effects of pH, lignin concentration, and other organic compounds are not significant and can be neglected. Because the ratio of the inorganic to organic solids in black liquors does not vary significantly and the total solids content can be easily determined with very good accuracy, the total solids content S can be used to account for the effect of inorganic sodium salts on Henry's constant of methanol. To demonstrate the validity of this assumption, we plotted the measured methanol Henry's constants in the 13 black liquors against the total solids content. As shown in Fig. 9, we found the logarithm of Henry's constant of methanol is linearly related to total solids content at four different temperatures tested. The scatter in data can be attributed to experimental errors, the effects of minor variables, such as pH, the presence of other components, and the small variations of inorganic/organic ratio from liquor to liquor. This is demonstrated by the fact that the measured Henry's constants of methanol in a given black liquor sample at the 4 temperatures (50, 60, 70, and 80°C) are very consistent, i.e., all the measured data points either lower or higher than the expected (regression predicted) value.

The experimental data can be correlated using the following expression based on the theoretical work of Stumm and Morgan [23] and Schwarzenbach et al. [24]:

$$\ln(H) = -\frac{A}{T} + B \cdot S + C \qquad\qquad (10a)$$

or
$$H = m\left[\exp(-\frac{A}{T} + B \cdot S)\right]. \qquad\qquad (10b)$$

with $m = 1.1902 \times 10^{13}$, $A = 6000$, $B = 1.5$, and H in Pa. Figure 10 plots the direct comparison of the methanol Henry's constants of 13 black liquors measured at 4 temperatures with those predicted using Eqn. (10). We found that the model-predicted methanol Henry's constants agree very well with those measured experimentally.

CONCLUSIONS

A headspace gas chromatographic technique was used to study Henry's constants of methanol in various kraft pulping spent liquors collected from kraft mills and laboratory pulping processes. We found that temperature and inorganic solids content are the two major variables that affect methanol Henry's constants. The effects of other parameters, such as pH, lignin content, and the presence of other organic compounds are insignificant. We developed a two-parameter (temperature and total solids content) empirical model for the prediction of methanol Henry's constant based on the experimental data obtained in this study.

ACKNOWLEDGEMENT

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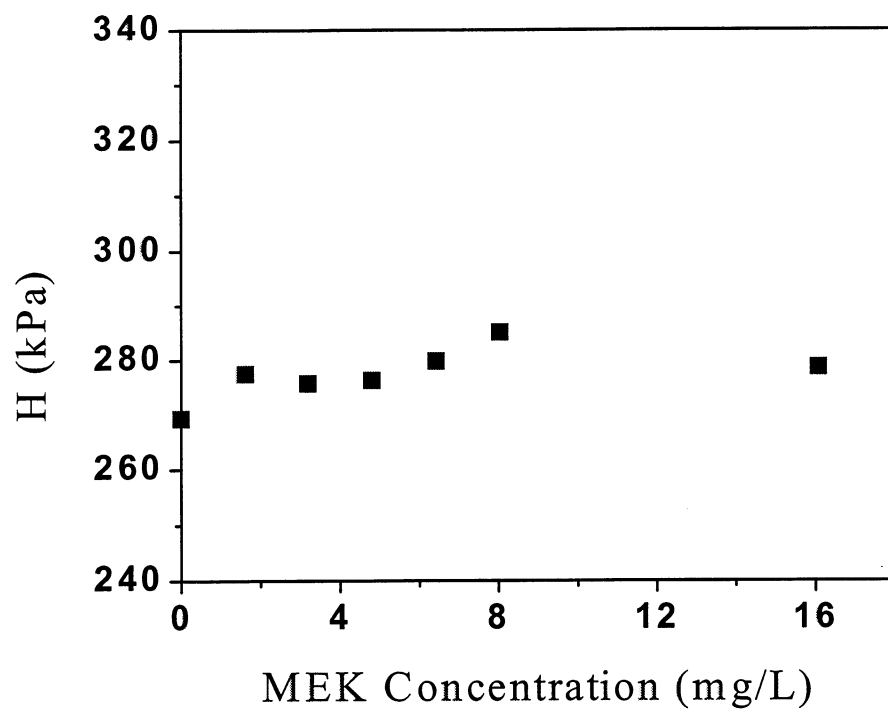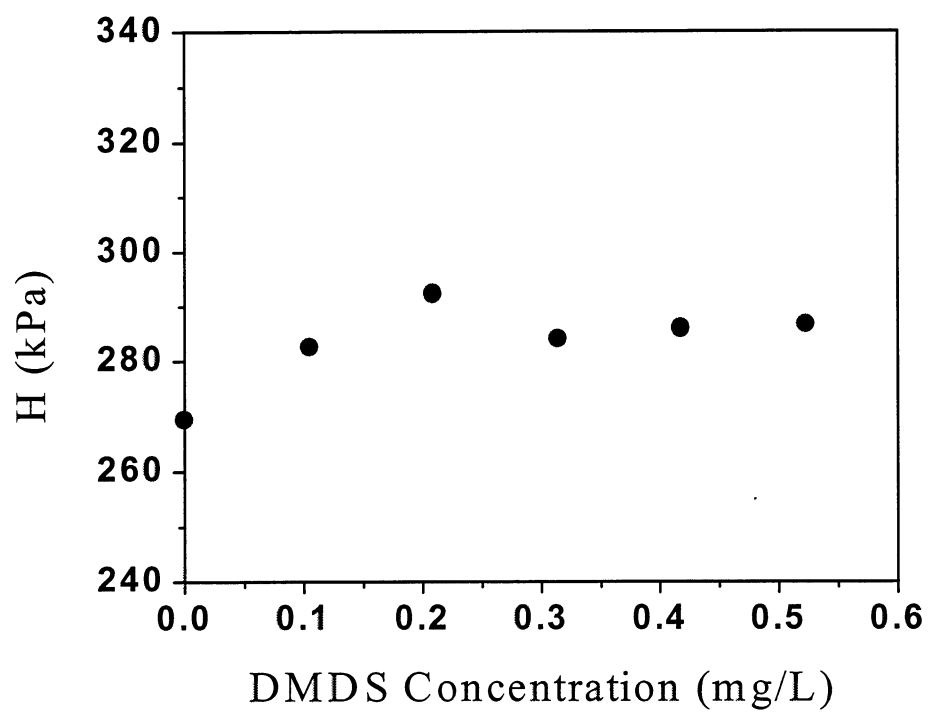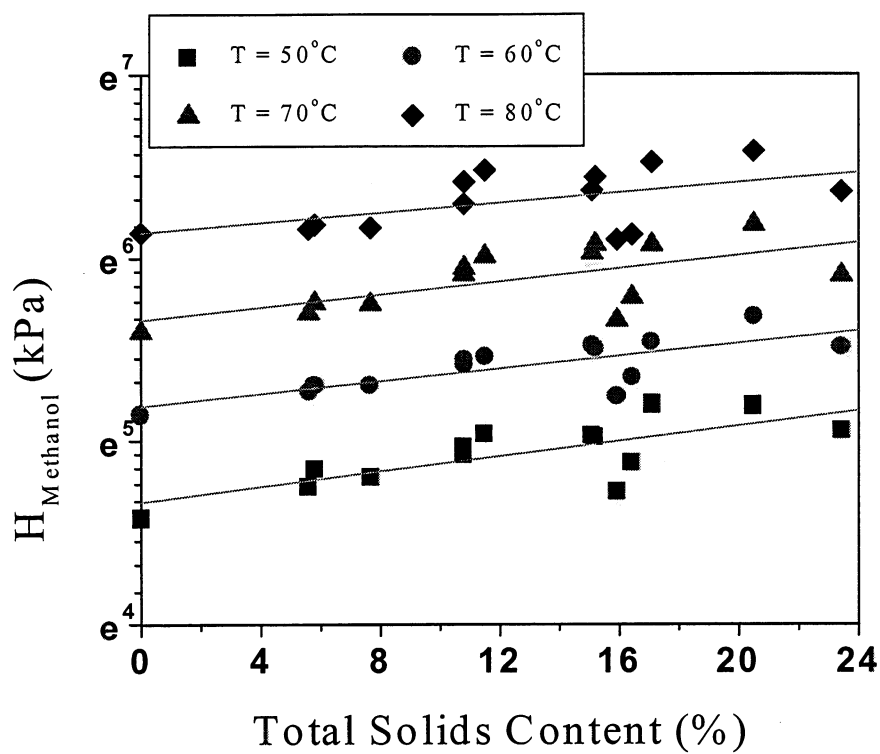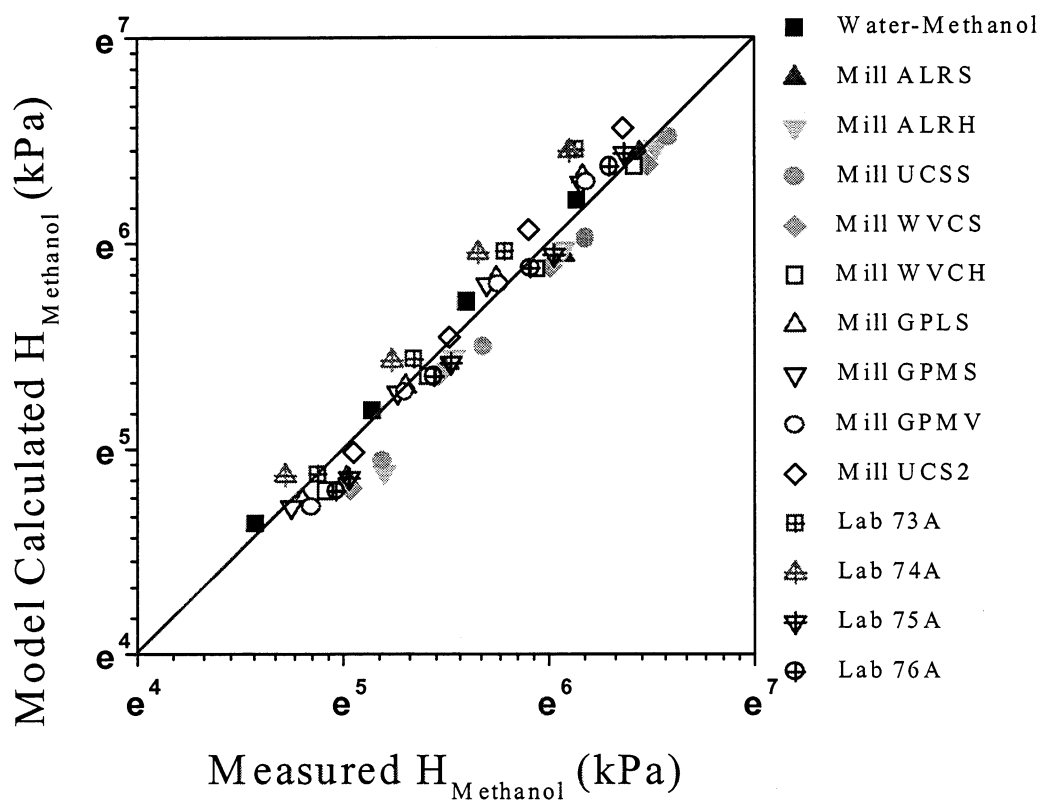Table I: A list of fitting parameters of Eqn. (8) for a water-methanol mixture and black liquors.

Sample	a	b	Correlation Coefficient
Water-Methanol	-5878	22.766	0.9992
Mill ALRS	-5337	21.708	0.9996
Mill ALRH	-5164	21.024	0.9981
Mill UCSS	-5092	20.729	0.9996
Mill WVCS	-5179	20.835	0.9999
Mill WVCH	-5525	22.118	0.9980
Mill GPLS	-5119	20.988	0.9947
Mill GPMS	-5553	22.187	0.9983
Mill GPMV	-5734	22.648	0.9996
Mill UCS2	-5325	21.233	0.9997
Lab 73A	-5101	20.623	0.9999
Lab 74A	-4930	20.305	0.9991
Lab 75A	-4793	19.723	0.9991
Lab 76A	-5120	20.857	0.9996
Mean	**-5275**	**N/A**	**0.9989**
RSTD	**5.8%**	**N/A**	**0.14%**