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Henry's Law Constant of Methanol in Pulping Spent Liquors

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A direct headspace gas chromatographic method was used to measure Henry's constants of methanol in pulping spent liquors. The liquors were from kraft pulp mills and laboratory pulping experiments using various wood species. All liquors studied had a total solids 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.

Introduction

Henry's law constant directly relates the partial vapor 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 constant 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 alkaline 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 an important source of biodegradable organic compounds that increase the biochemical oxygen demand (BOD). Furthermore, methanol is very volatile and can be released into the atmosphere through the vents and hoods of many kraft mill process facilities, e.g., a vent on a spent pulping liquor storage tank or an open hood of a vacuum brownstock pulp washer. Methanol air emission in kraft mills is now regulated by the U.S. Environmental Protection Agency through the Cluster Rule (4). The prediction of methanol air emission through process simulation (5, 6) can provide kraft mill engineers a tool for process optimization to reduce methanol emission. The emission prediction requires the methanol concentration in the flow of a vent or a hood that is proportional to the methanol concentration in the vapor phase inside a facility. For most kraft mill operation processes, it is a good approximation to use Henry's law to describe the methanol partitioning between the vapor and the process

stream liquid phases inside process facilities. Study of the Henry's constant of methanol in various kraft mill streams, therefore, can provide a database for air emission predictions.

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 as discussed by Christensen (7). 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 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. The direct headspace GC method measures the solute in the vapor and liquid phases directly and separately to determine Henry's constant. The indirect method makes two headspace measurements in two separate sample vials without measuring the liquid phase to derive the Henry's constant through material balance and VLE of the solute. The multiple extraction GC method was developed and experimentally demonstrated by Chai and Zhu (20) and is similar to dynamic gas extraction but is carried out in steps. It relies on VLE of the solute and the fact that the total solute mass can be integrated over infinite numbers of extractions to obtain a linear equation. The equation relates the n th measurements to the sum of the first $(n-1)$ measurements by the Henry's constant. Chai and Zhu (18) have compared methanol Henry's constants (or activity or partitioning coefficients) measured by several researchers using different static headspace GC methods and found that the data agree well. However, the headspace GC measured values are consistently higher than those predicted by UNIFAC and ASOG methods and are much higher than those measured by differential ebulliometry (21), which is known to be inaccurate in determining activity coefficients of very small values, such as methanol infinite dilution activity coefficient in water. Detailed comparisons of methanol Henry's constants can be found in a separate research that we conducted (22).

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 Section

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

$$H_i = \lim_{x \rightarrow 0} \frac{P_i}{x_i} = \lim_{x \rightarrow 0} \frac{y_i P}{x_i} \quad (1)$$

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where x_i and y_i are the mole fraction of the species i in the liquid and vapor phase, respectively. For a system at equilibrium in a static headspace, the vapor phase can be assumed to follow the ideal gas law

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

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, the mole fraction of solute i in the liquid phase can be approximated as

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

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. Equation 3 is still a good approximation even for pulping spent liquors with total solids content around 20%.

Combining eqs 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:

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

A direct headspace GC method (16) was used in the present study to determine the partition coefficient K_i . In this method, the initial methanol concentration C_0 in a sample black liquor was first measured using an indirect headspace GC method (23, 24) (a standard addition procedure). The methanol concentration C_G in the static headspace at VLE in terms of GC recorded peak area A was then measured. Therefore,

$$K_i = \frac{C_{Li}}{C_{Gi}} = \frac{C_0 - \beta C_{Gi}}{f A_i} \quad (5)$$

where f is the GC response factor and $\beta = V_G/V_L$ is the phase ratio. In the present study, the volume of the sample vial was 20 mL, and the liquor sample size was 10 mL for all the experiments conducted, which gave the headspace volume of 10 mL and the phase ratio $\beta = 1$. Therefore, if K_i is much greater than 1, i.e., $K_i > 10$, $C_{Gi} \ll C_{Li} (< C_0)$ can be ignored in eq 5, and, hence,

$$K_i \approx \frac{C_0}{f A_i} \quad (6)$$

We adopted an external calibration standard to obtain the GC response factor f by using a standard water-methanol solution with known methanol concentration of $C_{so} = 800$ mg/L and methanol VLE partition coefficient K_{si} (e.g., $K_{si} = 570$ at 70 °C (18)), and, hence,

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

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, also called black liquor from its color, is an aqueous solution containing dissolved organic and inorganic solids. It is a byproduct of the wood delignification process in pulp 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 dimethyl sulfide (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 kraft pulp mills and laboratory pulping processes were used in this study. Four softwoods of Douglas-fir, white spruce, western hemlock, and southern pine, and six hardwoods of aspen, basswood, birch, maple, oak, and sweetgum are used in laboratory pulping experiments. The total dissolved solids contents of all the liquors were less than 25%, and the black liquors were therefore treated as aqueous solutions. Analytical grade sulfonated lignin, mixed wood kraft lignin, sodium carbonate, sodium sulfate, sodium chloride, sodium hydroxide, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methyl ethyl ketone (MEK), and α -pinene were added to standard water-methanol solutions to study the effects of these minor constituents of black liquors on the Henry's constant of methanol.

Experimental Conditions. To achieve good signal-to-noise ratio in GC measurements, GC conditions were set as follows: 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 were as follows: gentle shaking for equilibration of the sample for 25 min, vial pressurization time of 0.2 min to create a pressure head in the headspace for sample transfer to the sample loop, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min. The sample loop is heated to avoid condensation. In instrument evaluation tests, we found that the GC signal peak area did not vary with the sample loop filling time and loop equilibrium time in certain operating ranges, respectively, indicating that the sample in the loop is a good representative of the sampled vapor phase.

Equilibrium Time. It was necessary to establish that vapor-liquid equilibrium had been achieved in these experiments. Sample size, temperature, and equilibration time are the three major factors that can affect equilibrium. To accelerate the vapor-liquid equilibrium process between the liquid and vapor phase in the headspace of a sample vial, the commercial HP-7694 headspace sampler applies gentle or strong shaking to the sample vial. In the experiments, we used a liquid sample volume $V_L = 10$ mL, or a phase ratio of $\beta = 1$, and applied gentle shaking. We found that an equilibrium time of 25 min is sufficient to achieve methanol vapor-liquid equilibrium in the static headspace of a sample vial (24). Similar equilibrium test was also conducted using black liquor at a temperature of 323 K in the present study and found that a 25-min equilibrium time is sufficient.

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 (repeatability test) using black liquor collected from a kraft mill to estimate the actual measurement uncertainty. We found that the maximum error of the 11 individual measurements relative to the average value of the 11 measurements was 15%. However, the relative standard deviation of the 11 measurements was 8.8%. We conducted

TABLE 1. List of Fitting Parameters of Eq 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 Pine73A	−5101	20.623	0.9999
Lab Pine74A	−4930	20.305	0.9991
Lab Pine75A	−4793	19.723	0.9991
Lab Pine76A	−5120	20.857	0.9996
Lab Aspen121	−5452	21.825	0.9997
Lab Bass122	−5767	22.733	0.9996
Lab Birch123	−4907	20.281	0.9976
Lab Oak125	−4305	18.366	0.9947
Lab Maple127	−5010	20.527	0.9996
Lab Douglas-fir102	−5175	20.903	0.9995
Lab Spruce103	−5128	20.787	0.9997
Lab Western Hemlock138	−4872	19.947	0.9998
Lab Sweetgum137	−4912	20.124	0.9996
mean	−5190	21.01	0.9989
RSTD	6.9%	5.0%	0.15%

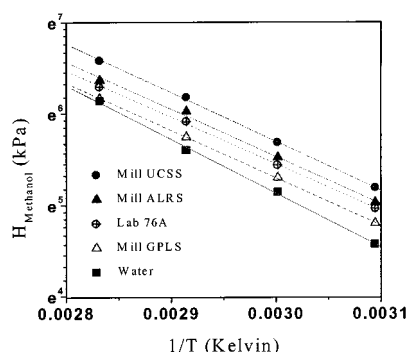


FIGURE 1. Effect of temperature on methanol Henry's constants in black liquors.

triplicate experiments and averaged the results; therefore, the actual measurement uncertainty of the data presented in this study is less than the relative standard deviation of the single measurement of 8.8%.

Results and Discussions

Effect of Temperature. Twenty-two black liquor samples were collected from both kraft mills and our laboratory pulping processes of various wood species. Because the operating process temperature of weak black liquor in kraft mills varies significantly, we measured the Henry's constants of the 22 black liquors in a temperature range of 50–80 °C. Our measurements indicate that the Henry's constant of methanol in all the black liquors follows the van't Hoff relationship with temperature. Table 1 lists the linear regression results along with the correlation coefficients for the liquors tested. Only the results from four black liquor samples are shown in Figure 1 for clarity. The van't Hoff eq 25 is given by

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

where a is directly related to the partial molar excess enthalpy of a solute in a solvent and b is an empirical constant.

For comparison, we have also plotted Henry's constants of methanol in water in Figure 1. The results as listed in

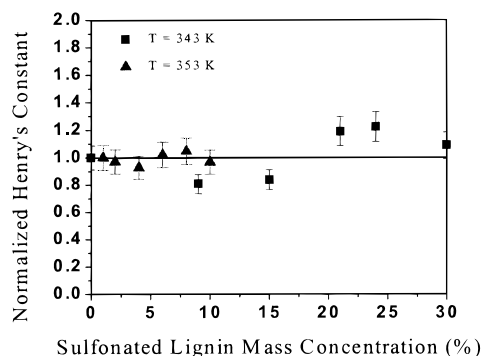


FIGURE 2. Effect of spiked sulfonated lignin concentration on methanol Henry's constants in methanol–water mixtures.

Table 1 show that the slopes for the 22 black liquor samples were very close to the slope of the methanol–water mixture. The relative standard deviations of the slopes for black liquors (22 data sets) and all the samples (23 data sets including water–methanol mixture) were 6.4 and 6.9%, respectively. Also, the slopes of all the black liquor samples were slightly smaller than that of the water–methanol mixture, indicating that the partial molar excess enthalpy of methanol in black liquor (a multicomponent 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 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, 343 and 353 K, and various sulfonated lignin concentrations. Similar experiments were also conducted using mixed wood lignin (MWL) in a slightly caustic solution (MWL can only be dissolved in caustic solutions) yielded from kraft pulping of softwood to liner board grade pulps (Westvaco Corp., SC). It was found that Henry's constant of methanol is only a weak function (increases with the increase) of mixed wood lignin mass concentration ranging from 0 to 13%.

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. Henry's constants in these solutions were measured. As shown in Figure 3, our results indicate that the Henry's constant of methanol is proportional to the hydroxide concentration 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 Figure 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. Black liquor contains significant amounts of inorganic solids. These inorganic solids are mainly sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) plus minimal amounts of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium chloride (NaCl), and potassium salts. To understand the effect of inorganic solids on methanol Henry's constant, we

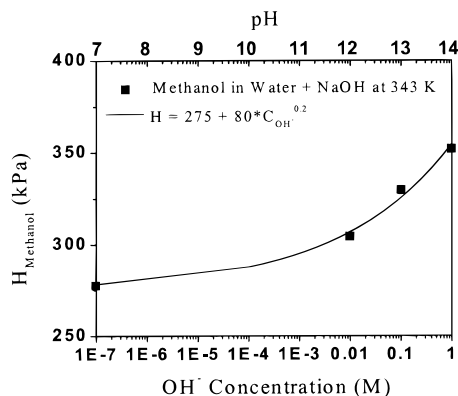


FIGURE 3. Effect of spiked OH^- concentration (pH) on methanol Henry's constants in methanol–water mixtures.

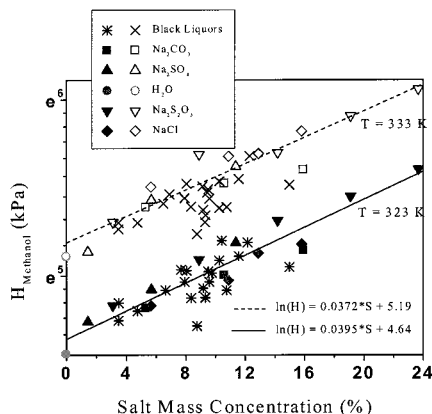


FIGURE 4. Effect of sodium salt mass concentration on methanol Henry's constants in methanol–water mixtures and black liquors.

measured the Henry's constant in water–methanol solutions containing Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, 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 not dependent on the type of salt as shown in Figure 4. The measured Henry's constants of methanol in actual black liquors are also shown in Figure 4. The total mass concentrations of the inorganic materials (more than 95% are sodium salts) in the 22 black liquor samples studied were obtained by subtracting the lignin (organic solids measured by UV absorption) content from the measured total solids content. We used the following equation to express this relation (26):

$$\ln(H) = c S_{\text{Salt}} + d \quad (9)$$

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

Effects of Dimethyl Sulfide, Dimethyl Disulfide, Methyl Ethyl Ketone, α -Pinene, β -Pinene, Fatty Acids, and Resin Acids. Many other chemical species, such as dimethyl sulfide (DMS), dimethyl disulfide (DMS), methyl ethyl ketone (MEK), α -pinene, β -pinene, fatty acids, and resin acids, present 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 on methanol Henry's constant is insignificant at the concentration levels present in weak black liquor. Figures 5–8 show the effects of α -pinene, DMS, MEK, and DMS.

Empirical Correlation. The results presented in this work show that temperature and inorganic solids (salts) content

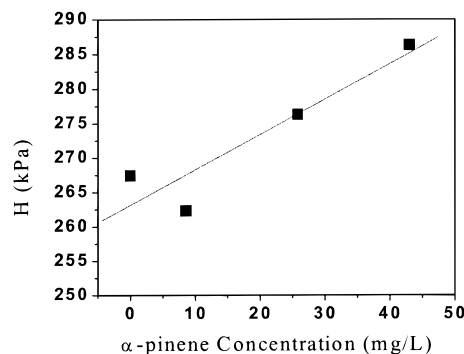


FIGURE 5. Effect of spiked α -pinene concentration on methanol Henry's constants in methanol–water mixtures.

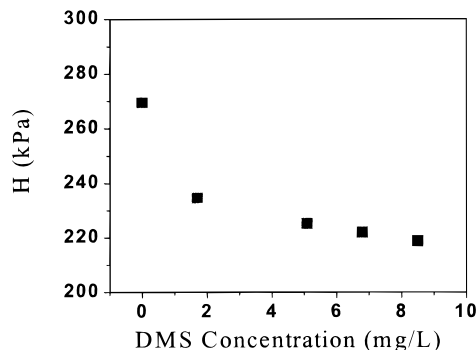


FIGURE 6. Effect of spiked dimethyl sulfide concentration (DMS) on methanol Henry's constants in methanol–water mixtures.

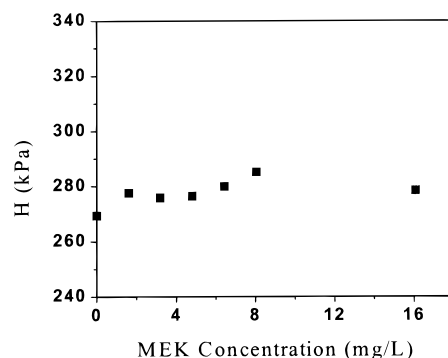


FIGURE 7. Effect of spiked methyl ethyl ketone (MEK) concentration on methanol Henry's constants in methanol–water mixtures and black liquors.

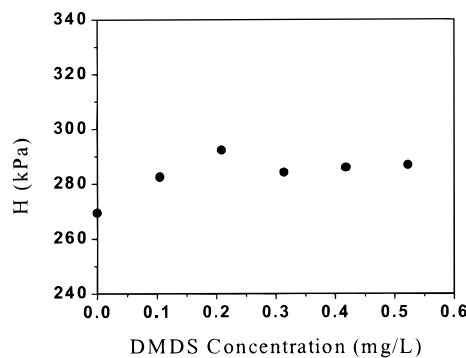


FIGURE 8. Effect of spiked dimethyl disulfide concentration (DMS) on methanol Henry's constants in methanol–water mixtures.

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

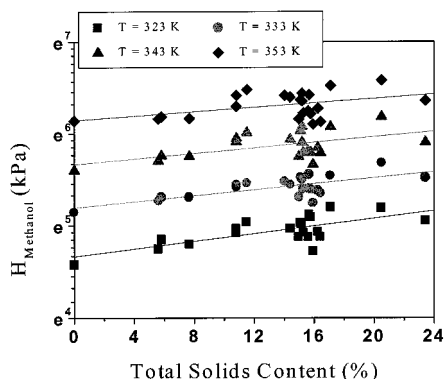


FIGURE 9. Correlation of measured methanol Henry's constants with total solids contents in black liquors.

organic solids (wood lignin) 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 salts on Henry's constant of methanol. Furthermore, the slight effect of wood lignin on methanol Henry's constant can be accounted for by using the total solids content. To demonstrate the validity of this assumption, we plotted the measured methanol Henry's constants in the 22 black liquors against the total solids content. As shown in Figure 9, we found that the logarithm of Henry's constant of methanol is linearly related to total solids content at four different temperatures tested, indicating that the minor effect of wood lignin on methanol Henry's constant is well accounted for by using the total solids content. The scatter in the 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 four temperatures (50, 60, 70, and 80 °C) are very consistent, i.e., all the measured data points are either lower or higher than the expected (regression) value.

The experimental data can be correlated using the following expression, based on the work of Stumm and Morgan (25) and Schwarzenbach et al. (26)

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

or

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

with $m = 3.77 \times 10^{12}$, $A = 5620$, $B = 1.63$, and H in Pa. Figure 10 plots the direct comparison of the methanol Henry's constants of 22 black liquors measured at four temperatures with those predicted using eq 10. We found that the model-predicted methanol Henry's constants agree very well with those measured experimentally.

Conclusions

We studied Henry's constants of methanol in various kraft pulping spent liquors collected from kraft mills and laboratory pulping processes by a headspace gas chromatographic technique. 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

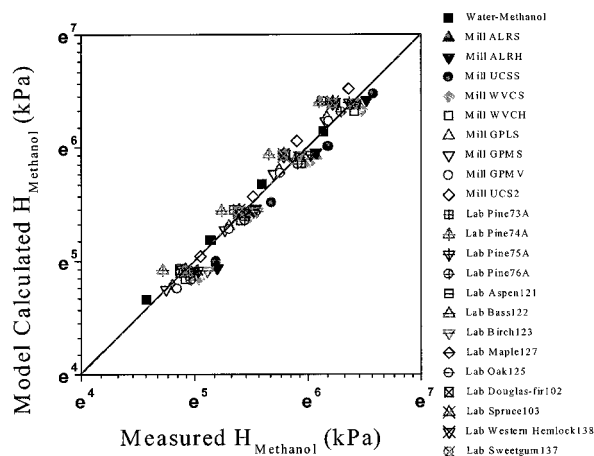


FIGURE 10. A comparison of measured methanol Henry's constants in black liquors with those predicted by the semiempirical correlation.

the prediction of methanol Henry's constant based on the experimental data obtained in this study.

Acknowledgments

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