Henry’s Constants of Gases in Methanol at High Temperatures up to the Critical Point of Methanol

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ABSTRACT

Henry’s constants of propane, isobutane, 1-butene and trans-2-butene in methanol in the temperature range of 350 K to 500 K are experimentally obtained. The Henry’s constants at low temperatures were measured by a gas stripping method, and a similar method is applied to measure the Henry’s constants at high temperatures up to the critical point of methanol. The rigorous formula for evaluating the Henry’s constants from these measurements is applied to the data reduction for these highly volatile mixtures. The plot of Henry’s constants versus temperature goes through a maximum and approaches a unique point at the critical temperature of methanol.

KEYWORDS
experimental data, Henry’s constant, solubility, methanol, isobutane, 1-butene, propane, trans-2-butene

1. INTRODUCTION

The study of gas solubilities is useful in providing design data for absorption processes, as well as, indirectly, in aiding the analysis of molecular interactions in solutions. For practical use, much attention has been given to the thermodynamic properties near the critical point of mixtures. High temperature data are rarely available and are difficult to measure. Hayduk and Buckley (1971) observed that all gas solubilities in a solvent tend towards a common value as the solvent critical temperature is approached. Beutier and Renon (1978) and Schotte (1985) showed that this is due to the thermodynamic relationship for the solute (g) at the solvent (s) critical point.

\[ \left( \frac{H_g}{\phi_g^V} \right)_{T_{c,s}} = P_{c,s} \]

\[ \left( \frac{d \ln H_g}{dT} \right)_{T_{c,s}} = -\infty \]

where \( H_g \) is the Henry’s constant of the solute, \( \phi_g^V \) the fugacity coefficients of the solute in the vapor phase, \( P_{c,s} \) the critical pressure of the solvent and \( T_{c,s} \) is the critical temperature of the solvent, \( T \) is the absolute temperature.

To develop a molecular theory, on the other hand, an accurate intermolecular potential is necessary. Henry’s constant is directly related to the residual chemical potential of the solute at infinite dilution which is evaluated from the intermolecular potential between a solute molecule and a solvent.
molecule. Therefore Henry’s constant is a suitable macroscopic property for testing the intermolecular potential between different kinds of molecules.

The gas stripping method which was originally proposed by Leroi et al. (1977) is usually used to measure the activity coefficients at infinite dilution of solutes in nonvolatile solvents, when the total pressures are negligibly small.

In previous work (Miyano et al., 2003, Miyano & Fukuchi, 2004), Henry’s constants of gases in methanol at temperatures lower than the boiling point temperature of methanol were measured by the gas stripping method. At higher temperatures and high pressures, the similar method to the gas stripping method is applied to measure the Henry’s constants in this work.

2. EXPERIMENTAL SECTION

The gas stripping method originally proposed by Leroi et al. (1977) is based on the variation of vapor phase composition when the highly diluted solute in a liquid mixture in an equilibrium cell is stripped from the solution by a flow of inert gas (helium). The composition of the gas leaving the cell is periodically sampled and analyzed by gas chromatography. The peak area, S, of the solute decreases exponentially with the volume of inert gas flowing out of the cell by the following rigorous relation (Miyano et al., 2003)

\[
\frac{\ln S}{S_0} = \left( \frac{H_g \phi_g^V}{(1+\alpha)P_{sat}^* - \alpha(H_g \phi_g^V)} \right) \ln \left( 1 - \frac{(1+\alpha)P_{sat}^* - \alpha(H_g \phi_g^V)}{\frac{ZRTn_{v,sat}^L}{V_{GP,0}} + \frac{V_{sat}^L}{V_{GP,0}}(H_g \phi_g^V)} \right)
\]

where \( S_0 \) is the peak area of solute at time \( t = 0 \), \( P_{sat}^* \) the saturated vapor pressure of the pure solvent, \( Z \) the compressibility factor of the saturated vapor in the cell. The superscripts V and L denote vapor and liquid phase, respectively. \( n_{v,sat}^L \) is the number of moles of solvent in the liquid phase in the cell at \( t = 0 \). \( V_{GP,0} \) is the initial volume of the vapor phase in the cell, \( V \) the volume of the saturated gas flowing out of the cell. The volume of vapor phase in the cell at time \( t \), \( V_{GP} \), slightly depends on the gas volume withdrawn from the cell and is given by:

\[
V_{GP} = V_{GP,0} + \alpha V, \quad \alpha = \frac{P_{sat}^* n_{v,sat}^L}{ZRT}
\]

where \( n_{v,sat}^L \) is the liquid molar volume of solvent at saturation and \( R \) is the gas constant.

At higher temperatures where the vapor pressure of solvent becomes higher than atmospheric pressure, the inert gas for withdrawal of the vapor from the equilibrium cell is not necessary, and the vapor in the cell can flow out simply by opening an outlet valve. In this case, we can get the same relationship expressed by the eq. (3) between the solute peak area and the vapor volume flowing out of the cell at the system temperature and pressure.

The compressibility factors of the vapor in the cell were approximated with that of the saturated vapor of pure methanol. The pressures in the cell were also approximated with the vapor pressures of pure methanol. In all experiments performed in this work, the estimated mole fractions of methanol were greater than 0.999 in the vapor phase and 0.9999 in the liquid phase, respectively, and therefore these approximations may be valid within this experimental error. The compressibility factors of the saturated vapor and the vapor pressures of pure methanol were interpolated from literature data Reuck et al.
Eq. (3) shows that $H_g / \varphi_g$ can be obtained from this experiment directly. To calculate the values of the Henry’s constants, however, we need the values of the fugacity coefficients of solute gas in the vapor phase, $\varphi_g$, which were estimated using the Soave equation of state Soave (1972) with a mixing rule.

\[
an_{\text{mix}} = \sum_i \sum_j z_i z_j (1 - k_{ij}) \sqrt{a_i a_j} \quad (k_{ij} = 0 \text{ when } i = j)
\]

\[
b_{\text{mix}} = \sum_i z_i b_i
\]

where $z_i$ is the mole fraction of component $i$. $a_i$ and $b_i$ are the parameters in the Soave equation of state for a pure component $i$, $a_{\text{mix}}$ and $b_{\text{mix}}$ are the parameters for the mixtures. $k_{ij}$ is the binary interaction parameter which value was determined from fitting to the obtained Henry’s constants by using an iteration method described later.

The volume of the saturated vapor flowing out of the equilibrium cell, $V$, can be evaluated from

\[
V = \frac{m}{M} \frac{ZRT}{P_{\text{sat}}^s}
\]

where $m$ is the mass of methanol flowing out of the cell and which was measured by an electronic balance, and $M$ is the molar mass of methanol.

### 2.1 Experimental apparatus and procedure

The experimental apparatus used for measuring the Henry’s constants at temperature higher than 350 K is shown in Figure 1. About 120 cm$^3$ of the degassed methanol was introduced into the equilibrium cell, which had a volume of about 126 cm$^3$. The accurate quantity was determined by mass. Then the equilibrium cell was connected to a supply of solute gas. The temperature in the cell was controlled within ±0.1 K, and measured by a Pt100 resistance thermometer with an accuracy of 0.1 K. After evacuating the connecting lines, about 5 cm$^3$ of the solute gas was introduced into the equilibrium cell by a syringe. The amount of the solute gas introduced into the cell was adjusted to keep the mole fraction lower than $10^{-4}$ in solution. After achieving equilibrium, the vapor in the cell began to flow out the cell with a flow rate of about 8 cm$^3 \cdot \text{min}^{-1}$ at standard state conditions (101 kPa and 273 K). The flow rate was controlled by a fine metering valve (SS-BMW, Swagelok Co.) kept at 500 - 600 K to avoid any condensation of the flashed vapor. The vapor flowing out from the metering valve was kept at 373 K and atmospheric pressure, and is introduced in the
gas chromatograph (GC) (Hitachi Ltd., Model G-3000, with TCD detector) to measure the solute peak area, $S$. The vapor flowing out from the gas chromatograph was cooled down in a glass condenser, and the mass of the condensed vapor (liquefied methanol) was measured by an electronic balance with an accuracy of 1 mg.

GC sampling, was performed every 40 min and continued for about 10 hours. The masses of methanol flowing out of the cell and the atmospheric pressure, which was measured by a pressure transducer (Paroscientific, Inc., Digiquartz Pressure Transducer Model 215A and Tsukasa Sokken Co. Ltd., Digiquartz Pressure Computer Model 600S) with an accuracy of 10 Pa, were also measured every 40 min.

The accuracy of this measurement of the Henry’s constants may be considered within 5 % at temperatures higher than 350 K. It is determined mostly by the uncertainties of the mass flow measurement and the estimation of the fugacity coefficient of the solute gas in the vapor phase at high pressures.

3. MATERIALS

The isobutene and 1-butene were supplied by Takachiho Kagaku Kougyo at specified minimum mass fraction purities of 0.99 and 0.99, respectively. The propane was supplied by Japan Fine Products at specified minimum mass fraction purity of 0.995. The trans-2-butene was supplied by Adlich chemicals at specific minimum mass fraction purity of 0.99. The methanol was of HPLC grade and supplied by Aldrich Chemicals, with a specified minimum purity of 99.9 %.

Figure 2. $H_g / \phi_g^V$ of propane, isobutane, 1-butene and trans-2-butene in methanol. (▲: propane, Miyano & Fukuchi (2004), △: propane, Leu et al. (1992), ■: propane, Kretschmer & Wiebe (1952), ； isobutene, Miyano et al. (2003), ○: 1-butene, Miyano et al. (2003), ◇: trans-2-butene, ◇: trans-2-butene, Miyano & Fukuchi (2004)), □; critical point of methanol
4. RESULTS AND DISCUSSION

As indicated in eq. (3), \( \frac{H_g}{\varphi_g^V} \) can be obtained directly from this experiment. **Figure 2** shows the temperature dependency of \( \frac{H_g}{\varphi_g^V} \) of propane, isobutene, 1-butene, trans-2-butene in methanol in the temperature range of 250 K to 500 K. As shown in this figure, the literature values of \( \frac{H_g}{\varphi_g^V} \) at low temperatures (Miyano et al., 2003, Miyano and Fukuchi 2004) can be smoothly combined with those at higher temperatures obtained in this work. The smoothed line goes through a maximum around at 490 K and approaches the critical point of methanol.

The vapor-liquid equilibria for propane + methanol mixtures have been measured by some researchers (Kretschmer and Wiebe, 1952, Leu et al., 1992). From high-pressure vapor-liquid equilibrium data, \( \frac{H_g}{\varphi_g^V} \) can be obtained by using the definition of the Henry’s constant as follows:

\[
f_g^V = H_g \, x_g \quad \text{at infinite dilution} \quad (x_g \to 0)
\]

Using a fugacity coefficient, this equation can be rewritten as:

\[
P y_g = p_g = (H_g / \varphi_g^V) x_g \quad \text{at infinite dilution} \quad (x_g, y_g \to 0)
\]

where \( y_g \) is the mole fraction of the solute in the vapor phase, \( P \) the total pressure, \( p_g \) the partial pressure of the solute in the vapor phase, and \( x_g \) the mole fraction of the solute in the liquid phase. From eq. (9), the value of \( \frac{H_g}{\varphi_g^V} \) can be obtained as the slope of the plot of the solute partial pressure versus the solute mole fraction in liquid phase at infinite dilution without any estimated values, such as fugacities. For comparative purposes, Figure 2 contains some of the literature values.

To evaluate Henry’s constant, it is necessary to estimate the fugacity coefficient of solute gas in the vapor mixture of the solute and methanol at the system temperature and pressure and at infinite dilution. For these estimations, the Soave equation of state Soave (1972) was used in this work. As is well known, the calculated properties such as Henry’s constants or fugacity coefficients from an equation of state are sensitive to a binary interaction parameter, and it is important to determine its optimal value. In the equation of state calculations performed in this work, therefore, the optimal value of the binary interaction parameter defined by eq.(5) was determined by fitting to the experimentally obtained \( \frac{H_g}{\varphi_g^V} \) as follows:

First of all the initial value of the binary interaction parameter was settled to zero. Then the Henry’s constant and the fugacity coefficient were calculated by the Soave equation of state with the mixing rule and the binary interaction parameter. The obtained value of \( \frac{H_g}{\varphi_g^V} \) from this calculation was compared with that obtained from the experiment. If there was a difference between the calculated and experimental values, the value of the binary interaction parameter was adjusted to reduce the difference. Above calculation were iterated until the complete agreement between the calculated and experimental values of \( \frac{H_g}{\varphi_g^V} \) was obtained.

Furthermore, for methanol, a parameter in the equation of state was determined at each temperature by fitting to the vapor pressure obtained from the literature Reuck et al. (1993).
4.1 Volume Effect of Vapor Phase

In general, the existence of vapor phase in the cell affects the evaluation of the Henry’s constants measured by the gas stripping method. When a solution contacts to fresh inert gas, some amounts of solute and solvent in the solution will move into the inert gas bubbles to keep the equilibrium. If there is a space to keep the vapor at the upper part in the cell, the vapor can stay there for its residence time, and some amounts of solute in the vapor will redissolve into the solution. This will lower the rate of gas stripping. Therefore the evaluated value of the Henry’s constant without the correction of the volume effect of the vapor phase will become smaller than the true value. A similar phenomenon is observed for the similar method used at higher temperatures. The saturated vapor at the vapor-liquid interface can stay in the cell during its residence time and this will result in a smaller value for the Henry’s constant.

For example, the Henry’s constant of 1-butene at 471 K was 18500 kPa and the composition ratio, \( y_g/x_g \), was about 5.2. The initial volume of the vapor phase in the equilibrium cell was about 8.1 cm\(^3\), which is 6.4 % of the cell volume. If the volume effect of vapor phase is neglected (\( V_{GP}=0 \) and \( \alpha=0 \)), a smaller value of 18100 kPa was obtained. The difference is 2.2 %. This difference is directly proportional to the volume of the vapor phase in the cell.

On the other hand, the Henry’s constant of propane was 31600 kPa at 471 K and the composition ratio was about 7.9. The initial volume of the vapor phase in the cell was the same, about 8.1 cm\(^3\). When the volume effect was neglected, a smaller value of 30100 kPa was obtained. The difference is 4.7 %.

As mentioned above, the volume effect of the vapor phase will depend on the volume ratio of the vapor phase in the cell, the composition ratio, and also the flow rate of vapor withdrawn from the cell. As the volume of the vapor phase in the cell was very small in this work, the volume effect was negligibly small and within the experimental error in most cases.

5. CONCLUSION

Henry’s constants for propane, isobutane, 1-butene, trans-2-butene in the methanol divided by the fugacity coefficient, \( H_g/\phi_V \), have been directly measured in a very wide temperature range of 350 K to 500 K. The value of \( H_g/\phi_V \) increases with the temperature, and goes through a maximum around at 490 K and approaches the critical point of the solvent, with a slope of \(-\infty\).
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REFERENCES


