J. Chem. Eng. Data **2004,** *49,* 368−371

Henry's Constants and Infinite Dilution Activity Coefficients of Propane, Propene, Butane, Isobutane, 1-Butene, Isobutene, *trans*-2-Butene, and 1,3-Butadiene in 2-Propanol at 250−330 K

Yoshimori Miyano*

Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts,
2640 Nishinoura, Tsurajimacho, Kurashiki 712-8505, Japan

The Henry's constants and the infinite dilution activity coefficients of propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in 2-propanol in the temperature range 250 K to 330 K are measured by a gas stripping method. The rigorous formula for evaluating the Henry's constants from the gas stripping measurements is used for these highly volatile mixtures. The accuracy of the measurements is about 2% for Henry's constants and 3% for the estimated infinite dilution activity coefficients. In the evaluations for the infinite dilution activity coefficients, the nonideality of the solute is not negligible, especially at higher temperatures, and the activity coefficients include the estimation uncertainty of about 1%.

Introduction

A systematic study of gas solubilities such as the Henry's constants is useful in providing design data for absorption processes as well as, indirectly, in aiding the analysis of molecular interactions in solutions.

Although a large number of alkane, alkene + alcohol solubility data were published, few data are available for C4-gases such as butane, 1-butene, and their isomers + alcohol mixtures. The solubility data will be useful to develop prediction methods. Especially for group contribution methods, it may be necessary to take into account the differences between isomers. For developing the molecular theory, on the other hand, the accurate intermolecular potential is necessary. The 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, the Henry's constant is a suitable macroscopic property for testing the intermolecular potential between different kinds of molecules.

The gas stripping method originally proposed by Leroi et al.[1] has been usually used for measuring the activity coefficients at infinite dilution of solutes in nonvolatile solvents, and the vapor pressures of solutes were negligibly small in most cases.[2,3] In previous work,[4,5] the Henry's constants of propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in methanol and 1-propanol were measured by this method. For these highly volatile solutes and solvents, careful data reduction was necessary and the rigorous expression was derived for this purpose.

In this work, the Henry's constants of propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in 2-propanol in the temperature range 250 K to 330 K are measured by the gas stripping method and evaluated by using the rigorous expression.

Theory

The gas stripping method originally proposed by Leroi et al.[1] is based on the variation of vapor phase composition when the highly diluted solute of the 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 from the cell, and this relationship was derived rigorously in the previous paper[4] as follows.

$$\ln \frac{S}{S_0} = \left(\frac{(H_g/\varphi_g^V)}{(1+\alpha)P_s^{sat} - \alpha(H_g/\varphi_g^V)} - 1 \right) \times \ln\left(1 - \frac{(1+\alpha)P_s^{sat} - \alpha(H_g/\varphi_g^V)}{ZRTn_{s,0}^L + V_{GP,0}(H_g/\varphi_g^V)} V \right) \quad (1)$$

where S_0 is the peak area of the solute at time $t = 0$, P_s^{sat} is the saturated vapor pressure of the pure solvent (s), H_g is the Henry's constant of the solute, Z is the compressibility factor of the saturated vapor in the cell, and φ_g^V is the fugacity coefficient of the solute (g) in the vapor phase. The superscripts V and L are vapor and liquid phase, respectively. The $n_{s,0}^L$ is the number of moles of solvent in the liquid phase in the cell at $t = 0$, R is the gas constant, and T is the absolute temperature. $V_{GP,0}$ is the initial volume of the vapor phase in the cell, and V is the volume of the saturated gas flowing out of the cell at the temperature T and the system pressure P. The volume of the vapor phase in the cell at time t, V_{GP}, slightly depends on the gas volume withdrawn from the cell, and it is expressed as

$$V_{GP} = V_{GP,0} + \alpha V, \quad \alpha = \frac{P_s^{sat} v_s^{L,sat}}{ZRT} \quad (2)$$

where $v_s^{L,sat}$ is the liquid molar volume of the solvent at saturation.

---

* Fax: +81-86-440-1062. E-mail: miyano@chem.kusa.ac.jp.

10.1021/je0342116 CCC: $27.50 © 2004 American Chemical Society
Published on Web 12/31/2003

From eq 1 the activity coefficient of the solute at infinite dilution can be obtained as the slope of the line in a log−log plot.

The infinite dilution activity coefficient of the solute, γ^∞, can be obtained from the following relationship:

$$H_g = f_g^{L,o}\gamma^\infty = f_g^{sat}\lambda\gamma^\infty = \varphi_g^{sat}P_g^{sat}\lambda\gamma^\infty \tag{3}$$

$$\gamma^\infty = \frac{H_g}{\varphi_g^{sat}P_g^{sat}\lambda} \tag{4}$$

where $f_g^{L,o}$ is the fugacity of the pure solute at a reference state (pure liquid at the system temperature and pressure), f_g^{sat} is the fugacity of the solute at saturation, φ_g^{sat} is the fugacity coefficient of the solute at saturation, and P_g^{sat} is the saturated vapor pressure of the solute. λ is the Poynting correction factor and is well approximated as

$$\lambda \approx \exp\left(\frac{(P - P_g^{sat})v_g^{L,sat}}{RT}\right) \tag{5}$$

The vapor pressures for pure substances were evaluated from the data bank in the literature.[6] The saturated liquid densities for pure substances were also evaluated from the data book.[7] The thermodynamic properties appearing in the above equations, φ_g^V, φ_g^{sat}, Z, and so forth, were calculated by the virial equation of state truncated after the second virial coefficient. For propane and propene, however, the virial equation of state truncated after the third virial coefficient was used for this purpose because of its high volatility. The details for the calculation methods were described in the previous papers.[4]

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

$$(P - P_s^{sat})V + \frac{S_0}{KC_2(C_1 + 1)}[(1 - C_2V)^{C_1+1} - 1] = ZRTn_{He} \tag{6}$$

$$C_1 = \frac{H_g/\varphi_g^V}{(1+\alpha)P_s^{sat} - \alpha H_g/\varphi_g^V}, \quad C_2 = \frac{(1+\alpha)P_s^{sat} - \alpha H_g/\varphi_g^V}{ZRTn_{s,0}^L + V_{GP,0}H_g/\varphi_g^V} \tag{7}$$

where n_{He} is the number of moles of helium flowing out of the cell and it was measured by a mass flow meter. K is the proportionality constant between the peak area of the solute detected by gas chromatography and its partial pressure. The values of K for all solutes were determined by using pure solutes.

Experimental Apparatus and Materials

An experimental apparatus described previously[4] was used for measuring the Henry's constants. About 43 cm^3 of the solvent (2-propanol) was introduced into the equilibrium cell, whose volume is about 44 cm^3, and the accurate quantity was determined by mass. Then the equilibrium cell was immersed in a constant-temperature bath (filled with ethylene glycol + water) and connected to a supply of solute gas and helium. The temperature was controlled within ±0.02 K and measured with a quartz thermometer (Hewlett-Packard Co., model 2804A) with an accuracy of 0.01 K. After the connecting lines were evacuated, the lines were pressurized with a solute gas at an arbitrary pressure, and then the solute gas was introduced into the equilibrium cell. The amount of the solute gas introduced into the cell was adjusted to keep the mole fraction lower than 3 × 10^{-4} in the solution. After the connecting lines were evacuated again, helium was added to the equilibrium cell with a flow rate of about 2 cm^3·min^{-1}, which was measured with a mass flow meter (Koflok Co., model 3300, maximum flow rate = 2 cm^3·min $^{-1}$, accuracy = 1%) and was controlled with a fine metering valve (double needles, Swagelok Co., SS2-D). The gas flowing out of the equilibrium cell was kept at a higher temperature than that of the bath to avoid any condensations, and it was introduced into a gas chromatograph (Hitachi Ltd., model G-3000, with double FID detectors) for measuring the solute peak area, S. The sampling for the gas chromatography was done every 60 min and continued for about 20 h. The pressure in the cell, the temperatures of the bath, and the total moles of helium, n_{He}, which could be obtained from the integration of the flow rate, were also measured every 60 min. The pressure in the cell was approximated equal to the atmospheric pressure and measured by a pressure transducer (Paroscientific, Inc., Digiquartz pressure transducer model 215A and Tsukasa Sokken Co. Ltd., Digiquartz pressure computer model 600S, accuracy = 10 Pa). The Henry's constant was evaluated from eq 1 using these sequential data.

Table 1. Henry's Constants and Infinite Dilution Activity Coefficients of Solutes in 2-propanol

T/K	H_g/kPa	γ^∞	T/K	H_g/kPa	γ^∞
Propane			1-Butene		
249.96	930	4.5	249.97	216	4.4
270.04	1750	4.5	270.03	477	4.4
290.00	2950	4.4	290.00	910	4.3
310.00	4470	4.3	310.00	1560	4.1
330.00	6260	4.2	330.00	2390	3.9
Propene			Isobutene		
249.96	950	3.8	249.97	215	4.4
270.04	1770	3.7	270.03	474	4.3
290.00	2930	3.7	290.00	920	4.2
310.00	4380	3.6	310.00	1530	4.0
330.00	6020	3.4	330.00	2320	3.8
Butane			*trans*−2-Butene		
249.97	202	5.2	249.96	155	4.3
270.03	454	5.1	270.04	358	4.3
290.00	900	5.1	290.00	720	4.2
310.00	1540	4.9	310.00	1250	4.1
330.00	2400	4.6	330.00	1950	3.9
Isobutane			1,3-Butadiene		
249.96	331	5.4	249.97	174	3.9
270.04	700	5.3	270.03	390	3.8
290.00	1310	5.2	290.00	760	3.7
310.00	2160	5.0	310.00	1280	3.5
330.00	3300	4.7	330.00	1960	3.3

The accuracy of this measurement for the Henry's constants may be considered to be within 2%; it mostly depends on the accuracy of the mass flow meter.

The butane, isobutane, 1-butene, and isobutene were supplied by Takachiho Kagaku Kogyo at specified minimum mass fraction purities of 0.998, 0.99, 0.99, and 0.99, respectively. The propane and propene were supplied by Japan Fine Products at specified minimum mass fraction purities of 0.995 and 0.995, respectively. The *trans*-2-butene and 1,3-butadiene were supplied by Aldrich Chemicals at specific minimum mass fraction purities of 0.99 and 0.99, respectively. The 2-propanol was supplied by Kishida Chemical Co. with a specified minimum mass fraction purity of 0.998.

Results and Discussion

The Henry's constants and the infinite dilution activity coefficients measured in this work are numerically indi-

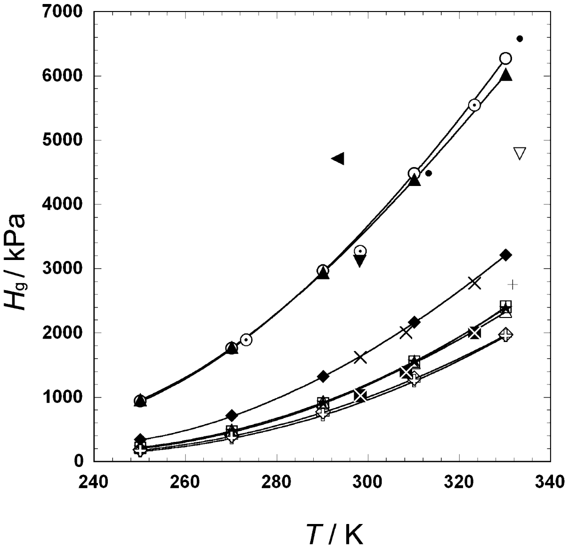

Figure 1. Henry's constants of eight gases in 2-propanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ★, 1-butene; △, isobutene; ✙, *trans*-2-butene; ◇, 1,3-butadiene; ⊙, propane;[9] ●, propane;[11] solid triangle pointing left, propene;[10] ▽ propene;[11] ▼, propene;[12] white × in a black box, butane;[9] ×, isobutane;[9] +, isobutane.[13]

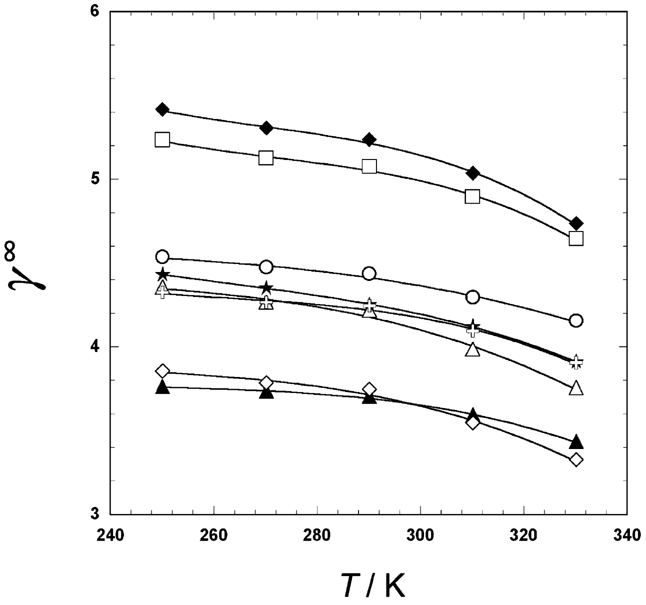

Figure 2. Infinite dilution activity coefficients of eight gases in 2-propanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ★, 1-butene; △, isobutene; ✙, *trans*-2-butene; ◇, 1,3-butadiene.

cated in Table 1. As all experiments were obtained under atmospheric pressure, the estimated fugacity coefficients of the solute in the vapor phase and the compressibility factors of the vapor were approximately unity ($\varphi_g^V = 1$, $Z = 1$) for all systems. On the other hand, for evaluation of the infinite dilution activity coefficients, the nonideality of gases at saturation is not negligible. For highly volatile solutes such as propene, the vapor pressure at $T = 330$ K is about $P = 2400$ kPa and the nonideality should be evaluated. As described in the previous section, the nonideality of the solute was calculated by the virial equation of state. To examine the viability of the virial equation of state at these high pressures, the Soave equation of state[8] was used for comparative purposes for calculating the fugacity coefficients of the solute at saturation. The calculated results from the virial equation of state truncated after the third virial coefficient agree with those calculated from the Soave equation of state within 1%. This means that the evaluated activity coefficients slightly depend on the estimation method for the nonideality, and it is difficult to judge which estimation method is better. Therefore, it is considered that the accuracies of the obtained infinite dilution activity coefficients in Table 1 may be within 3%.

Figure 1 shows the temperature dependencies of the Henry's constants of the eight gases in 2-propanol in the temperature range 250 K to 330 K. The gas solubilities in 2-propanol were measured for propane, butane, and isobutane by Kretschmer and Wiebe[9] and for propene at 200−400 kPa by Goozechak et al.[10] The vapor−liquid equilibrium (VLE) data were measured for propane and propene in 2-propanol by Zabaloy et al.,[11] for propene + 2-propanol by Horstmann et al.,[12] and for isobutane + 2-propanol by Zabaloy et al.[13] In general, it is difficult to estimate the Henry's constants from gas solubility data at atmospheric pressure or VLE data. The VLE and gas solubility data are usually measured at an intermediate concentration, and the smoothed data are obtained from the correlation by using an activity coefficient equation. Then the Henry's constants can be obtained from the extrapolation of the equation to the infinite dilution condition. Therefore, the Henry's constants obtained from such an extrapolation will strongly depend on the equation. For comparative purposes, however, this figure contains the extrapolated values which had been estimated by using the Margules equation.[6] The Henry's constants obtained in this work agree well with the estimated values from the gas solubility data[9] and give slightly large deviations from the estimated values from the VLE data.[10−12]

The order of Henry's constants at 290 K is as follows: propane ($T_b = 231.1$ K) > propene (225.5 K) > isobutane (261.4 K) > isobutene (266.2 K) > 1-butene (266.9 K) > butane (272.7 K) > 1,3-butadiene (268.7 K) > *trans*-2-butene (274.0 K). It is expected that the Henry's constants of nonpolar gases in nonpolar solvents generally follow an order of increasing Henry's constant with decreases in the normal boiling point temperature (T_b) of the liquefied gas. In polar solvents such as 2-propanol, however, the Henry's constants of polar gases such as propene decrease in general because of the dipole-pair intermolecular interaction. As a result, the Henry's constants of propene are smaller than those of propane at higher temperatures. On the other hand, both butane and 1,3-butadiene are nonpolar gases and the Henry's constant of butane at 290 K is larger than that of 1,3-butadiene. This may be due to an entropic effect that 1,3-butadiene can be inserted more easily into a liquid than butane because the molecular size of 1,3-butadiene, which has two double bonds, is smaller than that of butane.

The order of Henry's constants at 290 K in methanol[4] and 1-propanol[5] was as follows: propane > propene > isobutane > butane >1-butene > isobutene > *trans*-2-butene > 1,3-butadiene. The isobutene is the strongest polar gas in these eight gases, and its Henry's constants decrease in strong polar solvents. It is expected, therefore, that the polarity of 2-propanol is weaker than those of methanol and 1-propanol. The Henry's constants of 1,3-butadiene are much smaller than those of *trans*-2-butadiene in methanol and are approximately equal to those of *trans*-2-butene in 1-propanol. This may be due to the polarity of solvents.

Figure 2 shows the temperature dependency of the infinite dilution activity coefficients for the same systems. From this figure, it seems that the infinite dilution activity coefficients for C4 gases can be separated into three groups.

The first group is the alkane butane and its isomers. The second group is the alkene 1-butene and its isomers, and the last group is the dialkene 1,3-butadiene. Each group shows very close values of the infinite dilution activity coefficients. The order of the infinite dilution activity coefficients is alkane > alkene > dialkene for C4 gases. The infinite dilution activity coefficients of C4 gases in methanol and 1- propanol were also classified into the three groups as shown in the previous papers.[4,5]

Conclusion

The Henry's constants and the infinite dilution activity coefficients of eight gases in 2-propanol have been obtained from gas stripping measurements at temperatures from 250 K to 330 K. In evaluating the Henry's constants from the gas stripping measurements, the Henry's constant did not depend on the nonideality of the solute and the solvent so much. The activity coefficients, on the other hand, strongly depended on the nonideality of the solute at the reference state.

The accuracy of the Henry's constants measured by this work has been within 2% in the entire temperature range. The accuracy of the infinite dilution activity coefficients, on the other hand, has been within 3%, which is worse than that for the Henry's constants because of the inaccuracy of the estimated nonideality of gases, especially highly volatile gases such as propane and propene.

Literature Cited

(1) Leroi, J.-C.; Masson, J.-C.; Renon, H.; Fabries, J.-F.; Sannier, H. Accurate Measurement of Activity Coefficients at Infinite Dilution by Inert Gas Stripping and Gas Chromatography. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 139−144.

(2) Fukuchi, K.; Miyoshi, K.; Watanabe, T.; Yonezawa, S.; Arai, Y. Measurement and correlation of infinite dilution activity coefficients of bis (2,2,2-trifluoroetyl) ether in dodecane or alkanol. *Fluid Phase Equilib.* **2001**, *182*, 257−263.

(3) Fukuchi, K.; Miyoshi, K.; Watanabe, T.; Yonezawa, S.; Arai, Y. Measurement and correlation of infinite dilution activity coefficients of alkanol or either in aqueous solution. *Fluid Phase Equilib.* **2002**, *194−197*, 937−945.

(4) Miyano, Y.; Nakanishi, K.; Fukuchi, K. Henry's constants of butane, isobutane, 1-butene, and isobutene in methanol at 255−320 K. *Fluid Phase Equilib.* **2003**, *208*, 223−238.

(5) Miyano, Y. Henry's constants and infinite dilution activity coefficients of propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene and 1,3-butadiene in 1-propanol at $T = 260$ K to 340 K, *J. Chem. Thermodyn.*, in press.

(6) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

(7) Smith, B. D.; Srivastava, R. *Thermodnamic Data for Pure Compounds*, Part A and Part B.; Elsevier: Amsterdam, 1986.

(8) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(9) Kretschmer, C. B.; Wiebe, R. Solubility of Gaseous Paraffins in Methanol and isopropyl alcohol. *J. Am. Chem. Soc.* **1952**, *74*, 1276−1277.

(10) Goozechak, O. Ya.; Sarancha, B. H.; Romanyuk, I. M.; Yavorskaya, O. M.; Choorik, G. P. The solubility of propylene in organic solvents. *Zh. Prikl. Khim.* **1984**, *57*, 1798−1801.

(11) Zabaloy, M. S.; Mabe, B. G.; Bottini, S. B.; Brignole, E. A. Isothermal Vapor-Liquid Equilibrium Data for the Binaries Propane-2-Propanol and Propylene-2-propanol. *J. Chem. Eng. Data* **1993**, *38*, 40−43.

(12) Horstmann, S.; Gardeler, H.; Bolts, R.; Rarey, J.; Gmehling, J. Isothermal Vapor-Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Diethyl Ether + Ethyl *tert*-Butyl Ether, 1-Pentene + Methyl Acetate, and Propene + 2-Propanol. *J. Chem. Eng. Data* **1999**, *44*, 383−387.

(13) Zabaloy, M. S.; Mabe, G. B.; Bottini, S. B.; Brignole E. A. Vapor Liquid Equilibria in Ternary Mixtures of Water-Alcohol- Non Polar Gases. *Fluid Phase Equilib.* **1993**, *83*, 159−166.

Received for review October 27, 2003. Accepted December 1, 2003. This paper reports part of the work supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (13650820), which is gratefully acknowledged.

JE0342116