J. Chem. Eng. Data **2005,** *50,* 2045−2048

Henry's Law Constants and Infinite Dilution Activity Coefficients of Propane, Propene, Butane, 2-Methylpropane, 1-Butene, 2-Methylpropene, *trans*-2-Butene, *cis*-2-Butene, 1,3-Butadiene, Dimethyl Ether, Chloroethane, and 1,1-Difluoroethane in 2-Propen-1-ol

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Henry's law constants and infinite dilution activity coefficients of propane, propene, butane, 2-methylpropane, 1-butene, 2-methylpropene, *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, dimethyl ether, chloroethane, and 1,1-difluoroethane in 2-propen-1-ol in the temperature range of (250 to 330) K were measured by a gas stripping method. Partial molar excess enthalpies were calculated from the activity coefficients. A rigorous formula for evaluating the Henry's law constants from the gas stripping measurements was used for the data reduction of these highly volatile mixtures. The estimated uncertainties are about 2 % for the Henry's law constants and 3 % for the infinite dilution activity coefficients. In the evaluation of the infinite dilution activity coefficients, the nonideality (fugacity coefficient) of the solute cannot be neglected, especially at higher temperatures. The estimated uncertainty of the infinite dilution activity coefficients includes 1 % for the nonideality. In general, the Henry's law constants followed the order of increasing Henry's law constant with decreases in the normal boiling point temperature of the liquefied gas except for 1,3-butadiene, and the partial molar excess enthalpies of gases followed the order of increasing partial molar excess enthalpy with decreases of the polarity of the gases.

Introduction

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

Although a large number of alkane, alkene, + alkanol solubility data have been published, few are available for C_4 gases such as butane, 1-butene, and their isomers + alkanol mixtures. Solubility data will be useful for the development of predictive methods. Especially for group contribution methods, it may be necessary to take into account the differences between isomers.

To estimate the gas solubilities from a molecular theory or molecular simulation, however, an accurate intermolecular potential is necessary. The Henry's law 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 law constant is a suitable macroscopic property for correlating the intermolecular potential between different kinds of molecules.

Oxygenates have been used widely as fuel additives to increase the octane number. For these oxygenate processes, the solubility data for hydrocarbons + alcohols mixtures are needed both in the design of the production facilities and also in the determination of the properties of final products.

The gas stripping method originally proposed by Leroi et al.[1] has been used to measure the activity coefficients at infinite dilution of solutes in nonvolatile solvents, when the vapor pressures of solutes are negligibly small. In previous work,[2−8] the Henry's law constants for propane, propene, butane, 2-methylpropane, 1-butene, 2-methylpropene, *trans*-2-butene, and 1,3-butadiene in methanol, propanol (1-propanol, 2-propanol), butanol (1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol), and pentanol (1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol) were measured with this method. For these highly volatile solutes and solvents, a rigorous expression was derived for data reduction.

In this work, the Henry's law constants for propane, propene, butane, 2-methylpropane, 1-butene, 2-methylpropene, *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, dimethyl ether, chloroethane, and 1,1-difluoroethane in 2-propen-1-ol are measured by the gas stripping method. The infinite dilution activity coefficients of solutes and the partial molar excess enthalpies are evaluated. These data are not available in the literature.

Theory

The gas stripping method, originally proposed by Leroi et al.,[1] is based on the variation of the vapor-phase composition when the highly diluted solute in a liquid mixture in an equilibrium cell is stripped from the solution by the flow of inert gas (helium). The composition of the gas leaving the cell is periodically sampled and analyzed by means of gas chromatography. The peak area (S) of the solute decreases exponentially with the volume of inert

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10.1021/je0502647 CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/01/2005

gas flowing out of the cell by the following rigorous relation:[2]

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

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 law constant of the solute (g), Z is the compressibility factor of the saturated vapor in the cell, and φ_g^V represents the fugacity coefficient of the solute in the vapor phase. Superscripts V and L denote vapor and liquid phases, respectively. The $n_{s,0}^L$ is the number of moles of solvent in the liquid phase in the cell at $t = 0$. The V is the volume of the saturated gas flowing out of the cell, and $V_{GP,0}$ is the initial volume of the vapor phase in the cell. The volume of the vapor phase in the cell at time t (V_{GP}) slightly depends on the gas volume withdrawn from the cell. 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, R is the gas constant, and T is the absolute temperature.

From eq 1, the Henry's law constant of the solute can be obtained from the slope of the line in a log−log plot as follows. The initial value of the Henry's law constant was set equal to zero, and the logarithm on the right-hand side in eq 1 was calculated. By a process of successive iterations, the value of the Henry's law constant was determined.

The infinite dilution activity coefficient of the solute (γ^∞) can be obtained from the following relationships:

$$H_g \equiv \lim_{x_g \to 0} \frac{f_g^V}{x_g} = f_g^{L,0}\,\gamma^\infty = f_g^{sat}\,\lambda\gamma^\infty = \varphi_g^{sat} P_g^{sat}\,\lambda\gamma^\infty \quad (3)$$

$$\gamma^\infty = \frac{H_g}{\varphi_g^{sat} P_g^{sat}\,\lambda} \quad (4)$$

where x_g is the mole fraction of the solute in the liquid phase, f_g^V is the fugacity of the solute in the vapor phase, $f_g^{L,0}$ is the fugacity of the pure solute in the reference state (pure liquid at system temperature and pressure), f_g^{sat} and φ_g^{sat} are respectively the fugacity and the fugacity coefficient of the solute at saturation, P_g^{sat} is the saturated vapor pressure of the pure solute. The λ is the Poynting correction factor and is well approximated as:

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

where P is the system pressure. The vapor pressures and the saturated liquid densities for pure substances were taken from ref 9. The thermodynamic properties appearing in the above equations (φ_g^V, φ_g^{sat}, Z, etc.) were calculated from 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 of the calculation methods were described in previous papers.[2,3]

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy of the solute at infinite dilution ($H^{E,\infty}$) can be obtained from the infinite dilution activity coefficients:[10]

$$\frac{\partial \ln \gamma^\infty}{\partial(1/T)} = \frac{H^{E,\infty}}{R} \quad (6)$$

Experimental Section

Details of the experimental apparatus were presented in our earlier papers.[2,5] About 36 cm^3 of the solvent was introduced into the equilibrium cell of volume about 40 cm^3, and the accurate quantity was determined by mass with the accuracy of 1 mg (0.003 %). Then the equilibrium cell was immersed in a constant-temperature bath filled with (ethylene glycol + water) and connected to a supply of helium. The temperature was controlled to within ±0.02 K and measured with a quartz thermometer (Hewlett-Packard Co., model 2804A) with an accuracy of 0.01 K (0.01 %). About 1 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. Then, helium began to flow into the equilibrium cell at a flow rate of about 2 cm^3·min^{-1}, which was measured with a mass flow meter (Kofloc Co., model 3300) with a maximum flow rate of 2 cm^3·min^{-1} and an accuracy of 1 %. The flow rate 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 condensation and was introduced into a gas chromatograph (Hitachi Ltd., model G-3000, with double FID detectors) to measure the solute peak area (S). Sampling for the gas chromatography (GC) was performed every 60 min and continued for about 20 h. The pressure in the cell, the temperatures of the bath, and the total number of 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 approximately equal to atmospheric pressure measured by a pressure transducer (Paroscientific, Inc., Digiquartz pressure transducer model 215A and Tsukasa Sokken Co. Ltd., Digiquartz Pressure Computer model 600S) to an uncertainty of 10 Pa (0.01 %).

The uncertainty of this measurement for the Henry's law constants may be considered to be within 2 %; it mostly depends on the uncertainty of the mass flow meter (1 %). The total uncertainty of the other measured variables such as the temperature, pressure, and mass of the solvent was estimated to be not larger than 1 %.

Materials. Butane, 2-methylpropane, 1-butene, and 2-methylpropene were supplied by Takachiho Kagaku Kogyo with specified minimum mass fraction purities of 0.998, 0.99, 0.99, and 0.99, respectively. Propane and propene were supplied by Japan Fine Products at specified minimum mass fraction purities of 0.995 and 0.995, respectively. *cis*-2-Butene, *trans*-2-butene, chloroethane, 1,1-difluoroethane, and 1,3-butadiene were supplied by Aldrich Chemicals with specific minimum purities by GC of 99+ %, 99+ %, 99.7+ %, 98+ %, and 99+ %, respectively. 2-Propen-1-ol was supplied by Kishida Chemical Co. with a specified minimum purity of 99 % by GC. Dimethyl ether was supplied by Tokyo Kasei Kogyo Co. with a specified minimum purity of 99+ % by GC. All materials were used without further purification.

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

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}$/kJ·mol^{-1}	T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}$/kJ·mol^{-1}
Propane						Propene					
249.94	1620	7.92	218.0	0.94	1.49	249.94	1230	4.87	272.4	0.94	0.33
270.01	2910	7.44	431.7	0.92	1.89	270.01	2250	4.76	530.5	0.91	0.77
289.99	4660	6.99	770.8	0.89	2.24	289.99	3690	4.65	935.1	0.87	1.14
310.00	6860	6.58	1274.6	0.85	2.54	310.00	5460	4.47	1531.2	0.84	1.46
329.99	9300	6.16	1985.2	0.82	2.81	329.99	7560	4.31	2366.7	0.80	1.75
Butane						2-Methylpropane					
249.98	374	9.71	39.3	0.98	1.86	249.94	640	10.5	62.9	0.97	1.61
270.01	780	8.84	91.8	0.96	2.54	270.01	1260	9.51	139.5	0.95	2.55
289.99	1450	8.20	187.8	0.94	3.12	289.99	2220	8.83	272.8	0.93	3.35
310.00	2390	7.58	347.2	0.92	3.62	310.00	3480	8.11	485.7	0.90	4.05
329.99	3510	6.79	592.0	0.89	4.07	329.99	4830	7.14	802.3	0.87	4.67
1-Butene						2-Methylpropene					
249.94	296	6.08	49.7	0.98	0.66	249.94	293	5.94	50.5	0.98	0.93
270.01	640	5.85	114.3	0.96	1.22	270.01	630	5.68	116.0	0.96	1.32
289.99	1210	5.62	230.2	0.94	1.70	289.99	1190	5.46	233.7	0.94	1.66
310.00	2020	5.35	419.8	0.91	2.12	310.00	1990	5.19	426.5	0.91	1.95
329.99	3080	5.04	707.2	0.88	2.49	329.99	3060	4.94	719.0	0.88	2.20
trans−2-Butene						*cis*−2-Butene					
250.00	225	6.23	36.7	0.98	0.69	249.94	174	5.53	31.8	0.98	0.92
270.00	490	5.85	86.7	0.97	1.43	270.06	397	5.28	77.5	0.97	1.33
289.99	960	5.67	179.0	0.95	2.07	289.99	780	5.06	162.7	0.95	1.68
310.00	1640	5.38	332.6	0.92	2.63	309.98	1370	4.85	307.3	0.93	1.99
329.99	2450	4.91	568.3	0.90	3.12	329.99	2160	4.57	533.4	0.90	2.26
1,3-Butadiene						Dimethyl Ether					
250.00	186	4.12	46.1	0.98	−0.65	249.94	129	1.23	108.6	0.97	0.02
270.01	418	4.06	107.0	0.96	0.40	270.06	273	1.22	238.6	0.95	0.29
289.99	820	4.02	217.6	0.94	1.31	289.99	500	1.20	460.7	0.92	0.51
310.00	1410	3.89	399.8	0.92	2.10	309.98	850	1.20	811.8	0.89	0.71
329.99	2120	3.59	678.1	0.89	2.79	329.99	1280	1.16	1330.5	0.86	0.88
Chloroethane						1,1-Difluoroethane					
249.94	65	3.09	21.3	0.99	−0.44	249.94	540	5.09	109.5	0.96	0.21
270.06	165	3.07	54.7	0.98	0.54	270.06	1130	4.94	243.8	0.94	1.30
289.99	347	2.99	120.1	0.97	1.37	289.99	2000	4.68	475.7	0.91	2.24
309.98	640	2.87	235.3	0.95	2.10	309.98	3190	4.39	845.8	0.88	3.06
329.99	1040	2.69	420.6	0.92	2.74	329.99	4560	4.02	1398.0	0.85	3.78

Results and Discussion

The Henry's law constants, the infinite dilution activity coefficients, and the partial molar excess enthalpies measured in this work are numerically indicated in Table 1. All experiments were conducted under atmospheric pressure, and the estimated fugacity coefficients of the solute in the vapor phase and the compressibility factors of the vapor were around unity ($\varphi_g^V = 1.00$, $Z = 1.00$) for all systems. However, for the 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 (φ_g^{sat}) should be evaluated. The estimated uncertainty for the vapor phase fugacity coefficient at saturation was about 1 % as discussed in the previous paper[2] (the difference between the calculated values from the virial equation and the Soave equation of state[11] was less than 1 %). Therefore, the uncertainty of the obtained infinite dilution activity coefficients may be considered to be no greater than 3 %.

Figure 1 shows the temperature dependence of the Henry's law constants of 12 gases in 2-propen-1-ol. The Henry's law constants of nonpolar gases in any solvents generally follow the order of increasing Henry's law constant with decreases in the normal boiling point temperature (T_b) of the liquefied gas. The order of the Henry's law constants of the 12 gases in 2-propen-1-ol at $T = 290$ K is as follows:

Propane ($T_b = 231.1$ K, $\mu = 0$ D) > propene (225.5K, 0.4 D) > 2-methylpropane (261.4 K, 0.1 D) > 1,1-difluoroethane (248.2 K, 2.3 D) > butane (272.7 K, 0 D) >1-butene (266.9 K, 0.3 D) > 2-methylpropene (266.2 K, 0.5 D) > *trans*-2-butene (274.0 K, 0 D) > 1,3-butadiene (268.7 K, 0 D) > *cis*-2-butene (276.9 K, 0.3 D) > dimethyl ether (248.3 K, 1.3 D) > chloroethane (285.5 K, 2.0 D), where μ is the dipole moment (1 D = 3.162×10^{-25}·J$^{1/2}$·m$^{3/2}$), and the values were cited from ref 12. For nonpolar gases ($\mu = 0$ D), the Henry's law constants in 2-propen-1-ol follow the above simple relationship except for 1,3-butadiene. The molecular

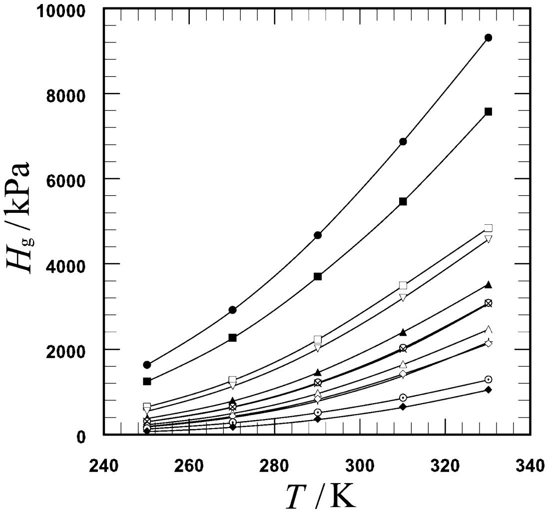

Figure 1. Henry's law constants of 12 gases in 2-propen-1-ol: ●, propane; ■, propene; ▲, butane; □, 2-methylpropane; ○, 1-butene; ×, 2-methylpropene; △, *trans*-2-butene; +, *cis*-2-butene; ◇, 1,3-butadiene; ⊙, dimethyl ether; ◆, chloroethane; ▽, 1,1-difluoroethane.

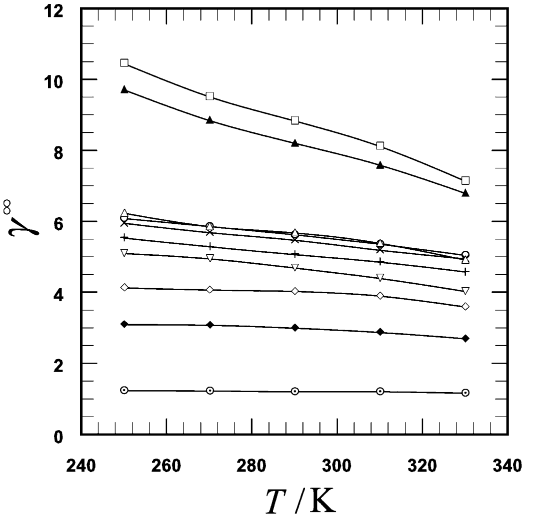

Figure 2. Infinite dilution activity coefficients of gases in 2-propen-1-ol: ▲, butane; □, 2-methylpropane; ○, 1-butene; ×, 2-methylpropene; △, *trans*-2-butene; +, *cis*-2-butene; ◇, 1,3-butadiene; ⊙, dimethyl ether; ◆, chloroethane; ▽, 1,1-difluoroethane.

size of 1,3-butadiene is smaller than others because it has two double bonds, which will make it easier to insert the molecule into a liquid. As the result, under the condition that the solutes have almost the same boiling point temperatures the Henry's law constant of the smaller molecule becomes smaller than that of larger molecules. This may be the reason that 1,3-butadiene does not follow the simple relationship.

In a strong polar solvent like 2-propen-1-ol, on the other hand, the Henry's law constants of polar gases decreases in general because of the dipole−pair intermolecular interaction. As the result, the Henry's law constant of propene becomes smaller than that of propane, the Henry's law constant of 2-methylpropene becomes smaller than thats of butane and 1-butene, and so on.

The infinite dilution activity coefficients for C_4 gases in methanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol could be classified 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 showed very similar values of the infinite dilution activity coefficients, and the order of the infinite dilution activity coefficients was alkane > alkene > dialkene for C_4 gases. Similar phenomena can be observed for the 2-propen-1-ol systems as show in Figure 2.

As observed in a previous paper,[13] the infinite dilution activity coefficients for asymmetric mixtures (mixture of nonpolar + strong polar substances) strongly depend on the temperature, and the partial molar excess enthalpies for these asymmetric mixtures have large values in general. On the other hand, for symmetric mixtures such as (nonpolar + nonpolar) or (strong polar + strong polar), the partial molar excess enthalpies have small values in general, and the activity coefficients of symmetric mixtures have values near to unity. As 2-propen-1-ol is a strong polar solvent, the values of the partial molar excess enthalpies of nonpolar gases such as propane or butane are large, but the values of dimethyl ether, which is a strong polar solute, are small as expected. The activity coefficients of dimethyl ether weakly depend on the temperature.

Conclusions

Henry's law constants, the infinite dilution activity coefficients, and the partial molar excess enthalpies of 12 gases in 2-propen-1-ol at $T = (250 \text{ to } 330)$ K have been obtained from gas stripping measurements.

The Henry's law constant did not depend on the nonideality (the fugacity coefficient) of the solute and the solvent for the systems studied in this work. However, the nonideality of the solute at the reference state should be considered in order to obtain infinite dilution activity coefficients precisely.

The Henry's law constants of the nonpolar gases in the 2-propen-1-ol have followed the order of increasing Henry's law constant with decreases in the normal boiling point temperature of the liquefied gas except for 1,3-butadiene. The Henry's low constants of polar gases in 2-propen-1-ol, however, have become smaller than that expected from the simple relationship.

The partial molar excess enthalpies of gases in the strong polar solvent like 2-propen-1-ol generally follow the order of increasing partial molar excess enthalpy with decreases of the polarity of the gases.

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Received for review July 7, 2005. Accepted August 23, 2005. 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 (16560663), which is gratefully acknowledged.

JE0502647