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Henry's Law Constants and Infinite Dilution Activity Coefficients of Propane, Propene, Butane, Isobutane, 1-Butene, Isobutene, *trans*-2-Butene, and 1,3-Butadiene in 2-Methyl-1-butanol, 3-Methyl-1-butanol, and 2-Methyl-2-butanol

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Henry's law constants and infinite dilution activity coefficients of propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in 2-methyl-1-butanol and 3-methyl-1-butanol in the temperature range of (250 to 330) K and 2-methyl-2-butanol in the temperature range of (270 to 330) K were measured by a gas stripping method. 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 estimated infinite dilution activity coefficients. In the evaluation of the infinite dilution activity coefficients, the nonideality of the solute cannot be neglected, especially at higher temperatures. The estimated uncertainty of the infinite dilution activity coefficients includes 1% for nonideality.

Introduction

A systematic study of gas solubilities including the Henry's law constant 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 + alkanol solubility data have been published, few data are available for C_4 gases such as butane, 1-butene, and their isomers + alkanol mixtures. The solubility data will be useful in developing prediction 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 testing 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,[2−6] the Henry's law constants for propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in methanol, propanol (1-propanol, 2-propanol), and butanol (1-butanol, 2-butanol, isobutanol, *tert*-butyl alcohol) 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, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol are measured by the gas stripping method using the rigorous expression. These experiments are performed in the temperature range of (250 to 330) K for the 2-methyl-1-butanol and 3-methyl-1-butanol systems. For the 2-methyl-2-butanol system, however, the experiments are performed in the temperature range of (270 to 330) K, which is higher than the freezing point (264.4 K) of the solvent. 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 dilute 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 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.[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,

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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. $n_{s,0}^L$ 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, and V is the volume of the saturated gas flowing out of 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, and it is expressed as

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

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. Then the new value of the Henry's law constant was obtained. These calculations were iterated until a fixed value of the Henry's law constant was obtained.

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

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

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

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} is the fugacity of the solute at saturation, P_g^{sat} is the saturated vapor pressure of the pure solute, and φ_g^{sat} represents the fugacity coefficient of the pure solute at saturation. λ is the Poynting correction factor and is well approximated as

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

where P is the system pressure. The vapor pressures and the saturated liquid densities for pure substances were 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 of the calculation methods were described in the previous papers.[2,3]

Experimental Section

Details of the experimental apparatus were presented in our earlier paper.[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. 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. 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 gas chromatography 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, and atmospheric pressure was measured by a pressure transducer (Paroscientific, Inc., Digiquartz pressure transducer model 215A and Tsukasa Sokken Co. Ltd., Digiquartz Pressure Computer model 600S) to an accuracy of 10 Pa.

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

Materials. Butane, isobutane, 1-butene, and isobutene 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. 2-Methyl-1-butanol, *trans*-2-butene, and 1,3-butadiene were supplied by Aldrich Chemicals at specific minimum purities by gas chromatography of 99%, 99%, and 99%, respectively. 3-Methyl-1-butanol was supplied by Kishida Chemical Co. with a specified minimum purity of 98+% by gas chromatography. 2-Methyl-2-butanol was supplied by Tokyo Kasei Kogyo Co. with a specified minimum purity of 98+% by gas chromatography.

Results and Discussion

The Henry's law constants and the infinite dilution activity coefficients measured in this work are numerically indicated in Tables 1 to 3 for the 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol systems, respectively. Because all experiments were conducted under atmospheric pressure, the estimated fugacity coefficients of the solute in the vapor phase and the compressibility factors of the vapor were around unity ($\varphi_g^V = 1$, $Z = 1$) 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 should be evaluated. The estimated uncertainty for the nonideality was about 1% as discussed in the previous paper.[2] Therefore, the uncertainty of the obtained infinite dilution activity coefficients may be considered to be no greater than 3%.

Figures 1 to 3 show the temperature dependence of the Henry's law constants of the eight gases in 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol, respectively.

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

T/K	H_g/kPa	γ^∞	T/K	H_g/kPa	γ^∞
	Propane			1-Butene	
250.05	630	3.09	250.05	148	3.02
270.06	1220	3.12	270.06	331	3.02
290.01	2070	3.10	290.01	640	2.99
310.00	3170	3.04	310.00	1100	2.91
329.97	4470	2.96	329.97	1690	2.78
	Propene			Isobutene	
250.05	690	2.72	250.05	151	3.04
270.06	1290	2.73	270.06	337	3.02
290.01	2160	2.73	290.01	650	2.96
310.00	3230	2.64	310.00	1100	2.87
329.97	4510	2.57	329.97	1680	2.72
	Butane			*trans*-2-Butene	
250.05	129	3.33	250.05	107	2.96
270.06	296	3.34	270.06	244	2.91
290.01	580	3.31	290.01	490	2.90
310.00	1020	3.23	310.00	860	2.84
329.97	1600	3.10	329.97	1370	2.73
	Isobutane			1,3-Butadiene	
250.05	221	3.60	250.05	128	2.83
270.06	473	3.57	270.06	288	2.79
290.01	890	3.54	290.01	560	2.73
310.00	1490	3.46	310.00	950	2.60
329.97	2250	3.33	329.97	1450	2.46

Table 2. Henry's Law Constants and Infinite Dilution Activity Coefficients of Solutes in 3-Methyl-1-butanol

T/K	H_g/kPa	γ^∞	H_g/kPa	H_g/kPa	γ^∞
	Propane			1-Butene	
249.92	610	2.96	249.92	140	2.88
270.01	1160	2.97	270.01	315	2.88
289.98	2010	3.01	289.98	620	2.89
310.00	3090	2.97	310.00	1070	2.83
330.00	4400	2.92	330.00	1680	2.75
	Propene			Isobutene	
249.92	650	2.56	249.92	141	2.85
270.01	1230	2.59	270.01	318	2.86
289.98	2070	2.61	289.98	620	2.85
310.00	3120	2.56	310.00	1070	2.78
330.00	4390	2.50	330.00	1670	2.70
	Butane			*trans*-2-Butene	
249.92	126	3.27	249.92	99	2.76
270.01	288	3.25	270.01	234	2.79
289.98	570	3.25	289.98	473	2.80
310.00	1090	3.20	310.00	850	2.78
330.00	1610	3.12	330.00	1360	2.73
	Isobutane			1,3-Butadiene	
249.92	211	3.46	249.92	117	2.60
270.01	462	3.49	270.01	269	2.61
289.98	870	3.47	289.98	530	2.60
310.00	1460	3.40	310.00	920	2.53
330.00	2260	3.35	330.00	1440	2.44

The order of the Henry's law constants of the eight gases in 2-methyl-1-butanol at $T = 290$ K is as follows: propene ($T_b = 225.5$ K) > propane (231.1 K) > isobutane (261.4 K) > isobutene (266.2 K) $\approx$ 1-butene (266.9 K) > butane (272.7 K) $\approx$ 1,3-butadiene (268.7 K) > *trans*-2-butene (274.0 K). The same order is observed for the 2-methyl-2-butanol and 3-methyl-1-butanol systems. The Henry's law constants of nonpolar gases in nonpolar 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. This means that 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol can be approximately treated as nonpolar solvents.

The molecular size of 1,3-butadiene, which is nonpolar, 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, the Henry's law constant of the smaller molecule becomes smaller in general. This may be the reason that 1,3-butadiene does not follow the simple relationship described above.

Figures 4 to 6 show the temperature dependence of the infinite dilution activity coefficients for the same systems. The temperature dependence of the infinite dilution activity coefficients is negligibly small for the 3-methyl-1-butanol and also the 2-methyl-1-butanol systems, but it becomes larger for the 2-methyl-2-butanol system as shown in these Figures.

From the viewpoint of a molecular simulation of the Henry's law constant, it is considered that the volume change of the solvent may cause a drastic change in the

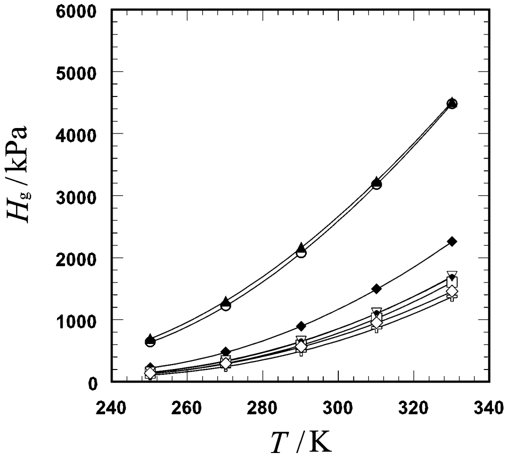

Figure 1. Henry's law constants of eight gases in 2-methyl-1-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

Table 3. Henry's Law Constants and Infinite Dilution Activity Coefficients of Solutes in 2-Methyl-2-butanol

T/K	H_g/kPa	γ^∞	T/K	H_g/kPa	γ^∞
	Propane			1-Butene	
270.02	1050	2.68	270.02	289	2.63
280.00	1350	2.62	280.00	396	2.54
290.00	1710	2.57	290.00	530	2.47
300.00	2130	2.53	300.00	690	2.40
310.00	2600	2.49	310.00	890	2.35
320.00	3080	2.44	320.00	1100	2.28
330.00	3600	2.39	330.00	1340	2.19
	Propene			Isobutene	
270.02	1160	2.44	270.02	290	2.60
280.00	1470	2.37	280.00	399	2.52
290.00	1840	2.31	290.00	530	2.45
300.00	2240	2.25	300.00	700	2.38
310.00	2680	2.20	310.00	890	2.31
320.00	3150	2.14	320.00	1100	2.24
330.00	3650	2.08	330.00	1360	2.19
	Butane			*trans*-2-Butene	
270.02	247	2.79	270.02	214	2.55
280.00	347	2.73	280.00	298	2.47
290.00	476	2.70	290.00	409	2.42
300.00	630	2.64	300.00	540	2.35
310.00	810	2.56	310.00	700	2.29
320.00	1020	2.50	320.00	880	2.24
330.00	1250	2.42	330.00	1090	2.18
	Isobutane			1,3-Butadiene	
270.02	389	2.94	270.02	267	2.59
280.00	530	2.88	280.00	365	2.48
290.00	710	2.84	290.00	484	2.37
300.00	920	2.79	300.00	620	2.26
310.00	1160	2.70	310.00	790	2.16
320.00	1450	2.67	320.00	970	2.07
330.00	1750	2.59	330.00	1170	1.98

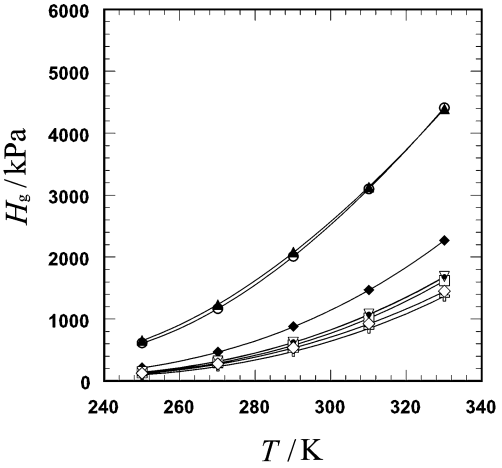

Figure 2. Henry's law constants of eight gases in 3-methyl-1-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

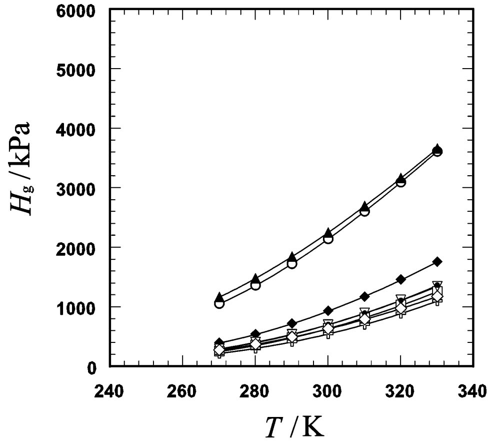

Figure 3. Henry's law constants of eight gases in 2-methyl-2-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

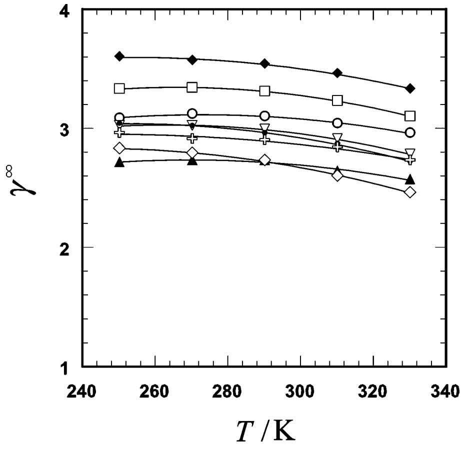

Figure 4. Infinite dilution activity coefficients of eight gases in 2-methyl-1-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

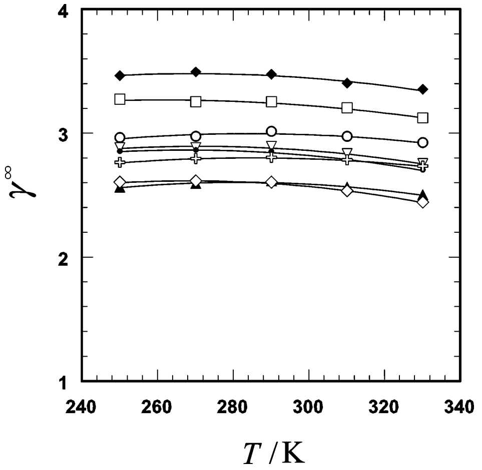

Figure 5. Infinite dilution activity coefficients of eight gases in 3-methyl-1-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

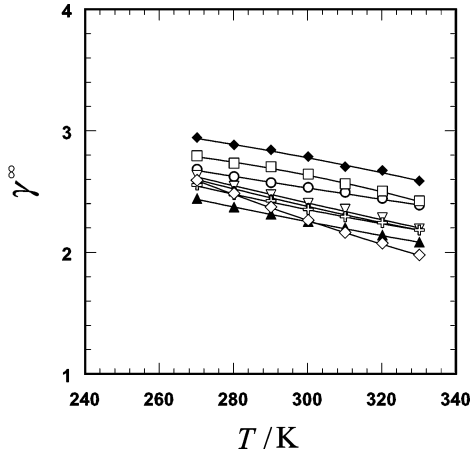

Figure 6. Infinite dilution activity coefficients of eight gases in 2-methyl-2-butanol: ○, propane; ▲, propene; □, butane; ◆, isobutane; ▽, 1-butene; ●, isobutene; open +, *trans*-2-butene; and ◇, 1,3-butadiene.

probability of the insertion of a solute molecule into the solvent and, therefore, the volume change of the solvent may cause a larger temperature dependence of the Henry's law constant and the infinite dilution activity coefficient. The molar volumes of 2-methyl-2-butanol are 106.2 $cm^3 \cdot mol^{-1}$ at 270 K and 113.9 $cm^3 \cdot mol^{-1}$ at 330 K. This causes a change in the molar volume of 7.7 $cm^3 \cdot mol^{-1}$. The changes in the molar volume of 2-methyl-1-butanol and 3-methyl-1-butanol in the same temperature range are 6.8 and 6.3 $cm^3 \cdot mol^{-1}$, respectively. The volume change of 2-methyl-2-butanol is about 13−22% larger than those of 2-methyl-1-butanol and 3-methyl-1-butanol. This may be the reason that the temperature dependence of the infinite dilution activity coefficients of gases in 2-methyl-2-butanol is larger than those in the other two solvents.

The temperature dependence of the infinite dilution activity coefficients of 1,3-butadiene is larger than that of other gases. As described previously, 1,3-butadiene has the smallest molecular size among these gases. This may be the reason that 1,3-butadiene shows such phenomena.

The infinite dilution activity coefficients for C_4 gases in methanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol can 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-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol systems.

Conclusions

Henry's law constants and infinite dilution activity coefficients of eight gases in 2-methyl-1-butanol and 3-methyl-1-butanol at $T = (250 \text{ to } 330)$ K and 2-methyl-2-butanol at $T = (270 \text{ to } 330)$ K have been obtained from gas stripping measurements. The Henry's law constant did not depend on the nonideality 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 eight gases in the three alkanols studied here 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 temperature dependence of the infinite dilution activity coefficients of gases in 2-methyl-2-butanol is larger than those in the other two alkanols.

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