# 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-Methylphenol, 3-Methylphenol, and 4-Methylphenol

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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-methylphenol, 3-methylphenol, and 4-methylphenol in the temperature range of (290 to 340) K were measured by a gas stripping method, and partial molar excess enthalpies and entropies were evaluated 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 accuracies are about 2 % for the Henry's law constants and 3 % for the infinite dilution activity coefficients. 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 polar gases. The activity coefficients of the solutes in 2-methylphenol were smaller than those in 3-methylphenol and 4-methylphenol, and the activity coefficients of solutes in 3-methylphenol had similar values to those in 4-methylphenol.

## 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. Solubility data are also useful for the development of predictive methods. Especially for group contribution methods, it may be necessary to take into account the differences between isomers. Dimethyl ether is being considered as a new alternative diesel fuel. In the design of these production facilities, the solubility data in liquids are needed.

Although a large number of solubility data for alkanes and alkenes in liquids have been published, few are available for $C_4$ gases such as butane, 1-butene, and their isomers. In a previous work,[1−8] the Henry's law constants for 12 gases (propane, propene, butane, 2-methylpropane, 1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 1,3-butadiene, dimethyl ether, chloroethane, and 1,1-difluoroethane) in alcohols were measured with the gas stripping method originally proposed by Leroi et al.[9] to investigate the effects of the hydroxyl group in alcohols.

In this work, to develop the group contribution methods, the Henry's law constants for the 12 gases in 2-methylphenol (*o*-cresol), 3-methylphenol (*m*-cresol), and 4-methylphenol (*p*-cresol), which contain the hydroxyl group, are measured by the gas stripping method, and the infinite dilution activity coefficients of solutes and the partial molar excess enthalpies and entropies are evaluated.

While some data for the vapor−liquid equilibria at high pressure for the binary mixtures[10] (propane + 3-methylphenol and propane + 4-methylphenol) are available, the Henry's law constants determined from a direct measurement are not available in the literature for the systems measured in this work.

## Theory

The gas stripping method, originally proposed by Leroi et al.,[9] 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 gas flowing out of the cell by the following rigorous relation.[1]

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

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 law constant of the solute (g), $Z$ is the compressibility factor of the saturated vapor in the cell, and $\varphi_g^V$ 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 $t = 0$. $V$ 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

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10.1021/je100529s

depends on the gas volume withdrawn from the cell, and it is expressed as:

$$V_{\mathrm{GP}} = V_{\mathrm{GP},0} + \alpha V \qquad \alpha = \frac{P_{\mathrm{s}}^{\mathrm{sat}} \upsilon_{\mathrm{s}}^{\mathrm{L,sat}}}{ZRT} \tag{2}$$

where $\upsilon_{\mathrm{s}}^{\mathrm{L,sat}}$ 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 as the slope of the linear relation in a log−log plot (the logarithm of the peak area versus the logarithm on the right-hand side in eq 1) 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 could be calculated. Then the new value of the Henry's law constant was obtained as the slope of the linear relation by using a least-squares method. These calculations were iterated until Henry's law constant became stable.

The infinite dilution activity coefficient of the solute ($\gamma_{\mathrm{g}}^{\infty}$) can be obtained from the following relationships:

$$H_{\mathrm{g}} \equiv \lim_{x_{\mathrm{g}} \to 0} \frac{f_{\mathrm{g}}^{\mathrm{V}}}{x_{\mathrm{g}}} = f_{\mathrm{g}}^{\mathrm{L},0} \gamma_{\mathrm{g}}^{\infty} = f_{\mathrm{g}}^{\mathrm{sat}} \lambda \gamma_{\mathrm{g}}^{\infty} = \varphi_{\mathrm{g}}^{\mathrm{sat}} P_{\mathrm{g}}^{\mathrm{sat}} \lambda \gamma_{\mathrm{g}}^{\infty} \tag{3}$$

$$\gamma_{\mathrm{g}}^{\infty} = \frac{H_{\mathrm{g}}}{\varphi_{\mathrm{g}}^{\mathrm{sat}} P_{\mathrm{g}}^{\mathrm{sat}} \lambda} \tag{4}$$

where $x_{\mathrm{g}}$ is the mole fraction of the solute in the liquid phase, $f_{\mathrm{g}}^{\mathrm{V}}$ is the fugacity of the solute in the vapor phase, $f_{\mathrm{g}}^{\mathrm{L},0}$ is the fugacity of the pure solute in the reference state (pure liquid at system temperature and pressure), $f_{\mathrm{g}}^{\mathrm{sat}}$ and $\varphi_{\mathrm{g}}^{\mathrm{sat}}$ are respectively the fugacity and the fugacity coefficient of the solute at saturation, and $P_{\mathrm{g}}^{\mathrm{sat}}$ is the saturated vapor pressure of the pure solute. $\lambda$ is the Poynting correction factor and is well-approximated as:

$$\lambda \approx \exp\left(\frac{(P - P_{\mathrm{g}}^{\mathrm{sat}}) \upsilon_{\mathrm{g}}^{\mathrm{L,sat}}}{RT}\right) \tag{5}$$

where $P$ is the system pressure. The vapor pressures and the saturated liquid densities for pure substances were taken from the ref 11. The thermodynamic properties appearing in the above equations ($\varphi_{\mathrm{g}}^{\mathrm{V}}$, $\varphi_{\mathrm{g}}^{\mathrm{sat}}$, $Z$, 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 the previous papers.[1,2]

## Experimental Section

Details of the experimental apparatus were presented in our earlier papers.[1,4] About 36 cm$^3$ of the solvent was introduced into the equilibrium cell, of volume about 40 cm$^3$, and the 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 2 cm$^3$ of the solute gas was introduced into the equilibrium cell by a syringe. 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 calibrated mass flow meter[1] (Kofloc Co., model 3300) with an accuracy of 1 %. 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 accuracy of 10 Pa (0.01 %).

The accuracy 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 (1 %). The total accuracy of the other measured variables such as the temperature, the pressure, and the mass of the solvent was estimated to be better 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 with 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 specified minimum purities by gas chromatography (GC) of 99 %, 99 %, 99.7 %, 98 %, and 99 %, respectively. 4-Methylphenol was supplied by Kishida Chemical Co. with specified minimum purities by GC of 99 %. Dimethyl ether, 2-methylphenol, and 3-methylphenol were supplied by Tokyo Kasei Kogyo Co. with a specified minimum purities of 99 %, 99 %, and 98 % by GC. All materials were used without further purification.

## 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. 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 ($\varphi_{\mathrm{g}}^{\mathrm{V}} = 1.00$, $Z = 1.00$) for all systems. However, for the evaluation of the infinite dilution activity coefficients, the nonideality of gases at saturation is not negligible and is evaluated by the virial equation of state truncated after the second or third virial coefficient. For highly volatile solutes such as propene, the vapor pressure at $T = 330$ K is about $P = 2400$ kPa; the estimated uncertainty for the vapor-phase fugacity coefficient at saturation was about 1 % as discussed in a previous paper[1] (the difference between the calculated values from the virial equation and the Soave equation of state[12] was less than 1 %). Therefore, the accuracy of the obtained infinite dilution activity coefficients may be considered to be no greater than 3 %.

Figure 1 shows the comparisons of the activity coefficients of the 12 solutes in 2-methylphenol with those in 3-methylphenol and 4-methylphenol at 310 K. As shown in this figure, the activity coefficients of the solutes in 3-methylphenol are larger than those in 2-methylphenol and have similar values with those in 4-methylphenol. The methyl group in 2-methylphenol exists near the hydroxyl group, and the methyl group in 4-methylphenol is in a place the most away from the hydroxyl group among these three methylphenols. The distance between the methyl group and the hydroxyl group in 3-methylphenol and 4-methylphenol may be enough length to place a part of a solute molecule between them. As a result, the probability of the existence of a solute molecule between the hydroxyl group and the methyl group in 2-methylphenol is the smallest among the

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

| $T$/K | $H_g$/kPa | $\gamma_g^\infty$ | $P_g^{sat}$/kPa | $\varphi_g^{sat}$ | $H_g^{E,\infty}/RT_{300}$ | $S_g^{E,\infty}/R$ |
|---|---|---|---|---|---|---|
| | Propane | | | | 1.38 | −0.46 |
| 299.99 | 5330 | 6.34 | 999.5 | 0.87 | | |
| 309.99 | 6300 | 6.04 | 1274.4 | 0.85 | $\sigma = 0.24$ % | |
| 319.99 | 7370 | 5.83 | 1601.0 | 0.84 | | |
| 329.99 | 8430 | 5.58 | 1985.2 | 0.82 | | |
| | Propene | | | | 0.99 | −0.35 |
| 299.99 | 3790 | 3.81 | 1206.3 | 0.86 | | |
| 309.99 | 4530 | 3.71 | 1531.0 | 0.84 | $\sigma = 0.28$ % | |
| 319.99 | 5320 | 3.60 | 1915.5 | 0.82 | | |
| 329.99 | 6100 | 3.48 | 2366.7 | 0.80 | | |
| | Butane | | | | 1.72 | −0.22 |
| 299.99 | 1650 | 6.92 | 258.2 | 0.93 | | |
| 309.99 | 2080 | 6.61 | 347.1 | 0.92 | $\sigma = 0.42$ % | |
| 319.99 | 2550 | 6.26 | 457.4 | 0.90 | | |
| 329.99 | 3060 | 5.92 | 592.0 | 0.89 | | |
| | 2-Methylpropane | | | | 1.80 | −0.27 |
| 299.99 | 2630 | 7.92 | 367.8 | 0.91 | | |
| 309.99 | 3250 | 7.57 | 485.6 | 0.90 | $\sigma = 0.54$ % | |
| 319.99 | 3880 | 7.14 | 629.3 | 0.88 | | |
| 329.99 | 4560 | 6.73 | 802.3 | 0.87 | | |
| | 1-Butene | | | | 1.11 | −0.34 |
| 299.99 | 1240 | 4.29 | 314.3 | 0.93 | | |
| 309.99 | 1570 | 4.15 | 419.7 | 0.91 | $\sigma = 0.33$ % | |
| 319.99 | 1950 | 4.03 | 549.6 | 0.90 | | |
| 329.99 | 2360 | 3.87 | 707.2 | 0.88 | | |
| | 2-Methylpropene | | | | 1.16 | −0.26 |
| 299.99 | 1200 | 4.11 | 319.2 | 0.92 | | |
| 309.99 | 1530 | 3.98 | 426.4 | 0.91 | $\sigma = 0.24$ % | |
| 319.99 | 1890 | 3.84 | 558.5 | 0.90 | | |
| 329.99 | 2290 | 3.70 | 719.0 | 0.88 | | |
| | *trans*-2-Butene | | | | 1.17 | −0.28 |
| 299.99 | 970 | 4.25 | 246.8 | 0.94 | | |
| 309.99 | 1260 | 4.13 | 332.5 | 0.92 | $\sigma = 0.43$ % | |
| 319.99 | 1570 | 3.98 | 438.7 | 0.91 | | |
| 329.99 | 1910 | 3.82 | 568.3 | 0.90 | | |
| | *cis*-2-Butene | | | | 1.07 | −0.27 |
| 299.99 | 800 | 3.79 | 226.3 | 0.94 | | |
| 309.99 | 1040 | 3.69 | 307.4 | 0.93 | $\sigma = 0.36$ % | |
| 319.99 | 1320 | 3.57 | 408.7 | 0.92 | | |
| 329.99 | 1630 | 3.44 | 533.4 | 0.90 | | |
| | 1,3-Butadiene | | | | 0.97 | −0.09 |
| 299.99 | 790 | 2.87 | 298.2 | 0.93 | | |
| 309.99 | 1020 | 2.81 | 399.7 | 0.92 | $\sigma = 0.42$ % | |
| 319.99 | 1270 | 2.72 | 525.2 | 0.90 | | |
| 329.99 | 1560 | 2.63 | 678.1 | 0.89 | | |
| | Dimethyl Ether | | | | −6.02 | −3.72 |
| 299.99 | 56 | 0.10 | 618.0 | 0.91 | | |
| 309.98 | 84 | 0.12 | 811.8 | 0.89 | $\sigma = 2.24$ % | |
| 319.98 | 127 | 0.14 | 1047.5 | 0.87 | | |
| 329.99 | 195 | 0.18 | 1330.5 | 0.86 | | |
| | Chloroethane | | | | 0.75 | 0.15 |
| 299.99 | 298 | 1.83 | 170.3 | 0.96 | | |
| 309.98 | 392 | 1.77 | 235.3 | 0.95 | $\sigma = 0.64$ % | |
| 319.98 | 520 | 1.76 | 317.8 | 0.94 | | |
| 329.99 | 650 | 1.70 | 420.6 | 0.92 | | |
| | 1,1-Difluoroethane | | | | 1.55 | 0.15 |
| 299.99 | 2270 | 4.02 | 641.0 | 0.90 | | |
| 309.99 | 2790 | 3.84 | 846.0 | 0.88 | $\sigma = 0.27$ % | |
| 319.99 | 3370 | 3.67 | 1096.2 | 0.86 | | |
| 329.99 | 3960 | 3.49 | 1398.0 | 0.85 | | |

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

| $T$/K | $H_g$/kPa | $\gamma_g^\infty$ | $P_g^{sat}$/kPa | $\varphi_g^{sat}$ | $H_g^{E,\infty}/RT_{300}$ | $S_g^{E,\infty}/R$ |
|---|---|---|---|---|---|---|
| | Propane | | | | 0.59 | −1.24 |
| 289.98 | 4200 | 6.31 | 770.5 | 0.89 | | |
| 299.98 | 5350 | 6.36 | 999.3 | 0.87 | $\sigma = 1.23$ % | |
| 309.99 | 6500 | 6.24 | 1274.4 | 0.85 | | |
| 319.99 | 7670 | 6.06 | 1601.0 | 0.84 | | |
| 329.99 | 8880 | 5.88 | 1985.2 | 0.82 | | |
| | Propene | | | | 0.47 | −0.94 |
| 289.98 | 3260 | 4.10 | 934.9 | 0.87 | | |
| 299.98 | 4100 | 4.13 | 1206.0 | 0.86 | $\sigma = 0.89$ % | |
| 309.99 | 4950 | 4.05 | 1531.0 | 0.84 | | |
| 319.99 | 5860 | 3.97 | 1915.5 | 0.82 | | |
| 329.99 | 6800 | 3.88 | 2366.7 | 0.80 | | |
| | Butane | | | | 1.05 | −0.90 |
| 289.98 | 1270 | 7.22 | 187.7 | 0.94 | | |
| 299.98 | 1690 | 7.06 | 258.1 | 0.93 | $\sigma = 0.84$ % | |
| 309.99 | 2170 | 6.88 | 347.1 | 0.92 | | |
| 319.99 | 2690 | 6.60 | 457.4 | 0.90 | | |
| 329.99 | 3270 | 6.33 | 592.0 | 0.89 | | |
| | 2-Methylpropane | | | | 1.16 | −0.93 |
| 289.98 | 2100 | 8.35 | 272.7 | 0.93 | | |
| 299.98 | 2690 | 8.11 | 367.7 | 0.91 | $\sigma = 0.73$ % | |
| 309.99 | 3380 | 7.87 | 485.6 | 0.90 | | |
| 319.99 | 4100 | 7.54 | 629.3 | 0.88 | | |
| 329.99 | 4880 | 7.21 | 802.3 | 0.87 | | |
| | 1-Butene | | | | 0.87 | −0.68 |
| 289.98 | 1040 | 4.86 | 230.1 | 0.94 | | |
| 299.98 | 1370 | 4.75 | 314.2 | 0.93 | $\sigma = 0.32$ % | |
| 309.99 | 1750 | 4.62 | 419.7 | 0.91 | | |
| 319.99 | 2170 | 4.48 | 549.6 | 0.90 | | |
| 329.99 | 2660 | 4.36 | 707.2 | 0.88 | | |
| | 2-Methylpropene | | | | 0.91 | −0.60 |
| 289.98 | 1020 | 4.66 | 233.6 | 0.94 | | |
| 299.98 | 1330 | 4.56 | 319.1 | 0.92 | $\sigma = 0.41$ % | |
| 309.99 | 1690 | 4.42 | 426.4 | 0.91 | | |
| 319.99 | 2110 | 4.30 | 558.5 | 0.90 | | |
| 329.99 | 2580 | 4.16 | 719.0 | 0.88 | | |
| | *trans*-2-Butene | | | | 0.80 | −0.72 |
| 289.98 | 790 | 4.68 | 178.9 | 0.95 | | |
| 299.98 | 1050 | 4.57 | 246.7 | 0.94 | $\sigma = 0.45$ % | |
| 309.99 | 1360 | 4.49 | 332.5 | 0.92 | | |
| 319.99 | 1710 | 4.35 | 438.7 | 0.91 | | |
| 329.99 | 2120 | 4.23 | 568.3 | 0.90 | | |
| | *cis*-2-Butene | | | | 0.80 | −0.63 |
| 289.98 | 660 | 4.29 | 162.6 | 0.95 | | |
| 299.98 | 890 | 4.20 | 226.2 | 0.94 | $\sigma = 0.29$ % | |
| 309.99 | 1160 | 4.09 | 307.4 | 0.93 | | |
| 319.99 | 1480 | 3.99 | 408.7 | 0.92 | | |
| 329.99 | 1840 | 3.88 | 533.4 | 0.90 | | |
| | 1,3-Butadiene | | | | 0.67 | −0.51 |
| 289.98 | 680 | 3.32 | 217.5 | 0.94 | | |
| 299.98 | 900 | 3.26 | 298.1 | 0.93 | $\sigma .= 0.53$ % | |
| 309.99 | 1170 | 3.22 | 399.7 | 0.92 | | |
| 319.99 | 1460 | 3.13 | 525.2 | 0.90 | | |
| 329.99 | 1800 | 3.05 | 678.1 | 0.89 | | |
| | Dimethyl Ether | | | | −4.85 | −2.81 |
| 289.97 | 46 | 0.11 | 460.4 | 0.92 | | |
| 299.98 | 73 | 0.13 | 617.8 | 0.91 | $\sigma = 1.24$ % | |
| 309.98 | 108 | 0.15 | 811.8 | 0.89 | | |
| 319.99 | 156 | 0.18 | 1047.8 | 0.87 | | |
| 329.99 | 220 | 0.20 | 1330.5 | 0.86 | | |
| | Chloroethane | | | | 0.78 | 0.04 |
| 289.97 | 246 | 2.13 | 120.0 | 0.97 | | |
| 299.98 | 341 | 2.10 | 170.2 | 0.96 | $\sigma = 0.67$ % | |
| 309.98 | 454 | 2.05 | 235.3 | 0.95 | | |
| 319.99 | 590 | 1.99 | 317.9 | 0.94 | | |
| 329.99 | 750 | 1.93 | 420.6 | 0.92 | | |
| | 1,1-Difluoroethane | | | | 1.49 | −0.02 |
| 289.98 | 2050 | 4.79 | 475.6 | 0.91 | | |
| 299.98 | 2590 | 4.59 | 640.9 | 0.90 | $\sigma = 0.37$ % | |
| 309.99 | 3180 | 4.37 | 846.0 | 0.88 | | |
| 319.99 | 3820 | 4.16 | 1096.2 | 0.86 | | |
| 329.99 | 4520 | 3.98 | 1398.0 | 0.85 | | |

three methylphenols, and the effect of the hydroxyl group on the activity coefficients in the 2-methylphenol is the smallest. In general, the activity coefficients of hydrocarbons like alkanes, alkenes, and so forth, have a small value in nonpolar solvents and have a large value in polar solvents like alcohols or phenols. As a result, the activity coefficients of solutes in 2-methylphenol are smaller than those in 3-methylphenol and 4-methylphenol, and the activity coefficients of solutes in 4-methylphenol have similar values to those in 3-methylphenol. This means that the

**Table 3. Henry's Law Constants and Infinite Dilution Activity Coefficients of Solutes in 4-Methylphenol**

| $T$/K | $H_g$/kPa | $\gamma_g^\infty$ | $P_g^{sat}$/kPa | $\varphi_g^{sat}$ | $H_g^{E,\infty}/RT_{300}$ | $S_g^{E,\infty}/R$ |
|---|---|---|---|---|---|---|
| | Propane | | | | 1.07 | −0.80 |
| 309.99 | 6560 | 6.29 | 1274.4 | 0.85 | | |
| 319.99 | 7740 | 6.12 | 1601.0 | 0.84 | $\sigma = 0.22$ % | |
| 329.99 | 8950 | 5.93 | 1985.2 | 0.82 | | |
| 340.02 | 10200 | 5.74 | 2435.3 | 0.80 | | |
| | Propene | | | | 0.70 | −0.73 |
| 309.99 | 4970 | 4.07 | 1531.0 | 0.84 | | |
| 319.99 | 5940 | 4.02 | 1915.5 | 0.82 | $\sigma = 0.33$ % | |
| 329.99 | 6890 | 3.92 | 2366.7 | 0.80 | | |
| 340.02 | 7900 | 3.84 | 2894.1 | 0.79 | | |
| | Butane | | | | 1.45 | −0.53 |
| 309.99 | 2170 | 6.88 | 347.1 | 0.92 | | |
| 319.99 | 2700 | 6.62 | 457.4 | 0.90 | $\sigma = 0.21$ % | |
| 329.99 | 3270 | 6.32 | 592.0 | 0.89 | | |
| 340.02 | 3920 | 6.09 | 754.6 | 0.88 | | |
| | 2-Methylpropane | | | | 1.42 | −0.70 |
| 309.99 | 3400 | 7.93 | 485.6 | 0.90 | | |
| 319.99 | 4140 | 7.62 | 629.3 | 0.88 | $\sigma = 0.12$ % | |
| 329.99 | 4940 | 7.30 | 802.3 | 0.87 | | |
| 340.02 | 5830 | 7.03 | 1008.8 | 0.85 | | |
| | 1-Butene | | | | 1.06 | −0.52 |
| 309.99 | 1760 | 4.66 | 419.7 | 0.91 | | |
| 319.99 | 2210 | 4.55 | 549.6 | 0.90 | $\sigma = 0.33$ % | |
| 329.99 | 2690 | 4.40 | 707.2 | 0.88 | | |
| 340.02 | 3220 | 4.26 | 896.6 | 0.87 | | |
| | 2-Methylpropene | | | | 1.03 | −0.50 |
| 309.99 | 1700 | 4.44 | 426.4 | 0.91 | | |
| 319.99 | 2140 | 4.34 | 558.5 | 0.90 | $\sigma = 0.33$ % | |
| 329.99 | 2600 | 4.20 | 719.0 | 0.88 | | |
| 340.02 | 3120 | 4.07 | 911.9 | 0.87 | | |
| | *trans*-2-Butene | | | | 0.91 | −0.62 |
| 309.99 | 1360 | 4.48 | 332.5 | 0.92 | | |
| 319.99 | 1710 | 4.35 | 438.7 | 0.91 | $\sigma = 0.10$ % | |
| 329.99 | 2130 | 4.25 | 568.3 | 0.90 | | |
| 340.02 | 2590 | 4.14 | 724.7 | 0.88 | | |
| | *cis*-2-Butene | | | | 0.96 | −0.49 |
| 309.99 | 1170 | 4.12 | 307.4 | 0.93 | | |
| 319.99 | 1490 | 4.03 | 408.7 | 0.92 | $\sigma = 0.27$ % | |
| 329.99 | 1850 | 3.91 | 533.4 | 0.90 | | |
| 340.02 | 2260 | 3.80 | 685.0 | 0.89 | | |
| | 1,3-Butadiene | | | | 1.01 | −0.20 |
| 309.99 | 1180 | 3.26 | 399.7 | 0.92 | | |
| 319.99 | 1480 | 3.16 | 525.2 | 0.90 | $\sigma = 0.03$ % | |
| 329.99 | 1820 | 3.07 | 678.1 | 0.89 | | |
| 340.02 | 2200 | 2.99 | 862.3 | 0.88 | | |
| | Dimethyl Ether | | | | −4.63 | −2.66 |
| 309.98 | 114 | 0.16 | 811.8 | 0.89 | | |
| 319.98 | 168 | 0.19 | 1047.5 | 0.87 | $\sigma = 1.29$ % | |
| 329.99 | 236 | 0.21 | 1330.5 | 0.86 | | |
| 340.01 | 325 | 0.24 | 1666.8 | 0.84 | | |
| | Chloroethane | | | | 0.97 | 0.20 |
| 309.98 | 464 | 2.09 | 235.3 | 0.95 | | |
| 319.98 | 610 | 2.06 | 317.8 | 0.94 | $\sigma = 0.57$ % | |
| 329.99 | 760 | 1.98 | 420.6 | 0.92 | | |
| 340.01 | 950 | 1.93 | 546.7 | 0.91 | | |
| | 1,1-Difluoroethane | | | | 1.63 | 0.08 |
| 309.99 | 3250 | 4.46 | 846.0 | 0.88 | | |
| 319.99 | 3910 | 4.26 | 1096.2 | 0.86 | $\sigma = 0.19$ % | |
| 329.99 | 4630 | 4.07 | 1398.0 | 0.85 | | |
| 340.02 | 5380 | 3.88 | 1759.1 | 0.83 | | |

information of the distribution of the methyl group and the hydroxyl group in the methylphenols must be included in the estimation method based on a group contribution method.

The activity coefficients of dimethyl ether in methylphenol were very small, and some chemical reaction or association of dimethyl ether and methylphenol may have occurred, but any reactants were not detected by the GC.

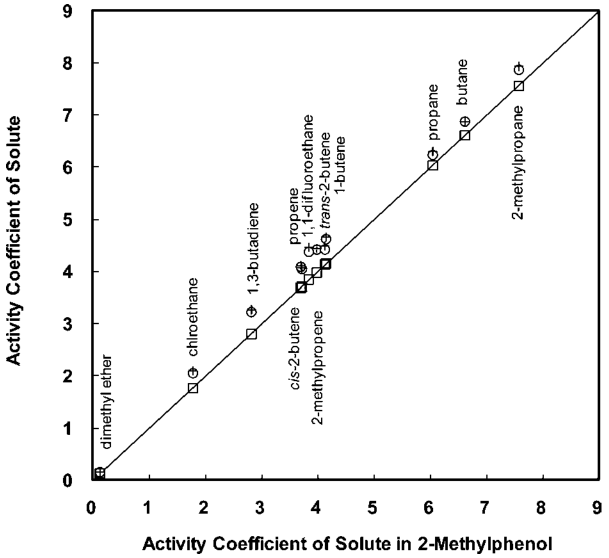

**Figure 1.** Comparison of the activity coefficient of solutes in 3-methylphenol and 4-methylphenol with those in 2-methylphenol at 310 K: ○, 3-methylphenol; +, 4-methylphenol; □, 2-methylphenol.

The activity coefficient relates to the partial molar excess properties as follows:

$$\ln \gamma_g^\infty = \frac{H_g^{E,\infty}}{RT} - \frac{S_g^{E,\infty}}{R} \tag{6}$$

where $H_g^{E,\infty}$ and $S_g^{E,\infty}$ are the partial molar excess enthalpy and the partial molar excess entropy of the solute at infinite dilution, respectively. In the temperature range of (290 to 340) K, the partial molar excess properties were assumed to be constants, and the infinite dilution activity coefficients were correlated by eq 6. From the correlations the partial molar excess properties can be obtained as the slopes and the intercepts of the linear relations. The reduced partial molar excess properties ($H_g^{E,\infty}/RT_{300}$ and $S_g^{E,\infty}/R$) are also indicated in Tables 1 to 3, where $T_{300}$ = 300 K. The average relative deviation for the infinite dilution activity coefficients in these correlations is defined as follows:

$$\sigma = \sqrt{\frac{1}{N}\sum_{j=1}^{N}\left[\frac{\gamma_{j,\mathrm{cal}}^\infty - \gamma_j^\infty}{\gamma_j^\infty}\right]^2} \tag{7}$$

where $N$ is the number of data points, $\gamma_j^\infty$ is the experimentally obtained infinite dilution activity coefficients of solutes, and $\gamma_{j,\mathrm{cal}}^\infty$ is the infinite dilution activity coefficient calculated from eq 6. The average relative deviations for all systems are within the accuracy of the experimental value (3 %), and the maximum deviation is 2.24 % for the dimethyl ether + 2-methylphenol system.

The $H_g^{E,\infty}$ and $S_g^{E,\infty}$ of hydrocarbons in phenols increase with increasing molecular size of the solutes; the $H_g^{E,\infty}$ are positive, and the $S_g^{E,\infty}$ are negative. The negative values of the $S_g^{E,\infty}$ mean that some structures are formed in the solution. The $H_g^{E,\infty}$ and $S_g^{E,\infty}$ of the solutes in 3-methylphenol are smaller than those in other methylphenols. It is considered that a strong solution structure in the 3-methylphenol solution may occur, which may depend on the suitable distance between the hydroxyl group and the methyl group. The distance in 2-methylphenol is too short, and that in 4-methylphenol is too long to place a part of a solute molecule between them. The strong solution structure causes the decrease of both $S_g^{E,\infty}$ and $H_g^{E,\infty}$ to decrease the partial molar excess Gibbs energy.

## Conclusions

Henry's law constants, the infinite dilution activity coefficients, and the partial molar excess properties of the 12 gases in 2-methylphenol, 3-methylphenol, and 4-methylphenol at $T$ = (290 to 340) K have been obtained from gas stripping measurements.

The Henry's law constant could be directly obtained from this experimental method. However, the nonideality of the solute at the reference state should be estimated to obtain infinite dilution activity coefficients precisely.

The activity coefficients of the solutes in 2-methylphenol have been smaller than those in 3-methylphenol and 4-methylphenol. This may depend on the distance between the methyl group and the hydroxyl group in the methylphenols. The hydroxyl group in 2-methylphenol is partially protected by the methyl group, and the effect of the hydroxyl group on the activity coefficients decreases.

As the partial molar excess enthalpies and entropies of the solutes in 3-methylphenol have been smaller than those in other methylphenols, a strong solution structure in the 3-methylphenol solution may occur, which depends on the suitable distance between the hydroxyl group and the methyl group. The distance in 2-methylphenol is too short, and that in 4-methylphenol is too long to place a part of a solute molecule between them. To develop the estimation method based on a group contribution method, the information of the distribution of the methyl group and the hydroxyl group in the methylphenols must be included in the estimation method.

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Received for review May 21, 2010. Accepted September 22, 2010. 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 (21560785), which is gratefully acknowledged.

JE100529S