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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 Benzene, Toluene, *o*-Xylene, *m*-Xylene, *p*-Xylene, and Styrene

Yoshimori Miyano,* Arisa Kimura, Mikiko Kuroda, Asami Matsushita, Ai Yamasaki, Yusuke Yamaguchi, Akihiro Yoshizawa, and Yoko Tateishi

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

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 benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene in the temperature range of (250 to 330) 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 uncertainties 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 polar gases. In general, the partial molar excess enthalpies and entropies of gases in the aromatics increase with decreases of the polarities of the gases and increasing molecular size 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. 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 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 (1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol) were measured with the gas stripping method originally proposed by Leroi et al.[9]

In this work, to develop the group contribution methods, the Henry’s law constants for the 12 gases in aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene) are measured by the gas stripping method. 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 (VLE) or the gas solubilities for the binary mixtures studied in this work are available, the Henry’s law constants determined from a direct measurement are not available in the literature.

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]

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

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. $n_{s,0}^L$ is the number of moles of solvent in the liquid phase in the cell at t

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

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$= 0$. 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 depends on the gas volume withdrawn from the cell, and it is expressed as

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

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. 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:

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

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

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

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

where P is the system pressure. The vapor pressures and the saturated liquid densities for pure substances were taken from ref 10. 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 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, 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 uncertainty 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 mass flowmeter (Kofloc Co., model 3300) with an uncertainty 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 uncertainty of 10 Pa (0.01 %).

Table 1. Henry's Law Constants and Infinite Dilution Activity Coefficients of Propane in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
	Benzene				1.11	0.27
279.99	1300	2.52	583	0.90		
289.99	1610	2.42	771	0.89	$\sigma = 0.45$ %	
309.99	2320	2.23	1274	0.85		
329.99	3190	2.11	1985	0.82		
	Toluene				0.62	−0.02
249.93	440	2.16	218	0.94		
270.00	800	2.05	432	0.92	$\sigma = 0.32$ %	
289.98	1300	1.95	771	0.89		
309.94	1940	1.86	1273	0.85		
329.99	2730	1.81	1985	0.82		
	o-Xylene				0.50	−0.16
249.97	440	2.15	218	0.94		
270.13	800	2.05	433	0.92	$\sigma = 0.40$ %	
289.99	1310	1.96	771	0.89		
309.84	1990	1.92	1270	0.85		
329.99	2790	1.85	1985	0.82		
	m-Xylene				0.44	−0.14
249.98	400	1.97	218	0.94		
270.10	730	1.86	433	0.92	$\sigma = 0.65$ %	
289.99	1220	1.83	771	0.89		
309.84	1840	1.77	1270	0.85		
329.99	2600	1.72	1985	0.82		
	p-Xylene				0.30	−0.23
289.99	1160	1.73	771	0.89		
299.99	1430	1.70	1000	0.87	$\sigma = 0.57$ %	
309.85	1730	1.67	1270	0.85		
319.99	2130	1.68	1601	0.84		
329.99	2500	1.66	1985	0.82		
	Styrene				0.91	−0.37
249.95	890	4.32	218	0.94		
270.07	1550	3.97	433	0.92	$\sigma = 0.26$ %	
309.84	3620	3.48	1270	0.85		
329.99	5020	3.32	1985	0.82		

[a] σ, average deviation defined by eq 7.

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 flowmeter (1 %). The total uncertainty 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. Benzene, *cis*-2-butene, *trans*-2-butene, chloroethane, 1,1-difluoroethane, and 1,3-butadiene were supplied by Aldrich Chemicals with specified minimum purities by GC of 99.9+ %, 99+ %, 99+ %, 99.7+ %, 98+ %, and 99+ %, respectively. Toluene, *o*-xylene, *m*-xylene, and *p*-xylene were supplied by Kishida Chemical Co. with specified minimum purities by GC of 99.5 %, 99 %, 99 %, and 99 %, respectively. Styrene was supplied by Wako Pure Chemicals Ind. 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.

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 12. All experiments were conducted under atmospheric pressure, and the estimated fugacity coefficients of the

Table 2. Henry's Law Constants and Infinite Dilution Activity Coefficients of Propene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
Benzene					0.42	−0.12
279.99	1100	1.77	712	0.89		
289.99	1380	1.74	935	0.87	$\sigma = 0.70$ %	
309.99	2040	1.67	1531	0.84		
329.99	2920	1.66	2367	0.80		
Toluene					0.13	−0.28
249.93	390	1.54	272	0.94		
270.00	720	1.51	530	0.91	$\sigma = 0.34$ %	
289.98	1200	1.51	935	0.87		
309.94	1820	1.49	1529	0.84		
329.99	2600	1.48	2367	0.80		
o-Xylene					0.13	−0.30
249.98	400	1.57	273	0.94		
270.13	740	1.56	533	0.91	$\sigma = 0.36$ %	
289.99	1230	1.55	935	0.87		
309.84	1860	1.53	1526	0.84		
329.99	2640	1.51	2367	0.80		
m-Xylene					0.04	−0.34
249.98	370	1.47	273	0.94		
270.10	690	1.46	532	0.91	$\sigma = 0.35$ %	
289.99	1170	1.47	935	0.87		
309.84	1780	1.46	1526	0.84		
329.99	2550	1.45	2367	0.80		
p-Xylene					0.00	−0.33
289.99	1100	1.39	935	0.87		
299.99	1380	1.39	1206	0.86	$\sigma = 0$ %	
309.85	1690	1.39	1526	0.84		
319.99	2060	1.39	1916	0.82		
329.99	2450	1.39	2367	0.80		
Styrene					0.34	−0.64
249.95	720	2.84	273	0.94		
270.07	1310	2.75	532	0.91	$\sigma = 0.31$ %	
309.84	3180	2.61	1526	0.84		
329.99	4530	2.58	2367	0.80		

[a] σ, average deviation defined by eq 7.

Table 3. Henry's Law Constants and Infinite Dilution Activity Coefficients of Butane in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
Benzene					1.44	0.62
279.99	320	2.51	133	0.95		
289.99	420	2.36	188	0.94	$\sigma = 1.45$ %	
309.99	700	2.22	347	0.92		
329.99	1010	1.96	592	0.89		
Toluene					0.71	0.11
249.93	81	2.11	39	0.98		
270.00	174	1.97	92	0.96	$\sigma = 0.28$ %	
289.98	331	1.88	188	0.94		
309.94	560	1.79	347	0.92		
329.99	880	1.71	592	0.89		
o-Xylene					0.59	−0.01
249.97	80	2.06	39	0.98		
270.13	174	1.95	92	0.96	$\sigma = 0.22$ %	
289.99	329	1.86	188	0.94		
309.84	570	1.80	346	0.92		
329.99	890	1.73	592	0.89		
m-Xylene					0.56	0.03
249.98	74	1.93	39	0.98		
270.10	157	1.77	92	0.96	$\sigma = 1.43$ %	
289.99	305	1.73	188	0.94		
309.84	540	1.70	346	0.92		
329.99	830	1.61	592	0.89		
p-Xylene					0.59	0.10
289.99	296	1.68	188	0.94		
299.99	391	1.64	258	0.93	$\sigma = 0.18$ %	
309.85	510	1.61	346	0.92		
319.99	650	1.58	457	0.90		
329.99	810	1.56	592	0.89		
Styrene					0.95	−0.29
249.95	159	4.14	39	0.98		
270.07	352	3.97	92	0.96	$\sigma = 1.64$ %	
309.84	1060	3.39	346	0.92		
329.99	1630	3.16	592	0.89		

[a] σ, average deviation defined by eq 7.

Table 4. Henry's Law Constants and Infinite Dilution Activity Coefficients of 2-Methylpropane in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
Benzene					1.50	0.57
279.99	520	2.81	198	0.94		
289.99	660	2.64	273	0.93	$\sigma = 0.68$ %	
309.99	1040	2.43	486	0.90		
329.99	1480	2.19	802	0.87		
Toluene					0.84	0.12
249.93	150	2.45	63	0.97		
270.00	298	2.25	139	0.95	$\sigma = 0.34$ %	
289.98	530	2.12	273	0.93		
309.94	860	2.01	485	0.90		
329.99	1300	1.91	802	0.87		
o-Xylene					0.70	−0.03
249.97	146	2.38	63	0.97		
270.13	299	2.25	140	0.95	$\sigma = 0.35$ %	
289.99	530	2.13	273	0.93		
309.84	870	2.04	484	0.90		
329.99	1310	1.94	802	0.87		
m-Xylene					0.62	−0.03
249.98	133	2.17	63	0.97		
270.10	271	2.04	140	0.95	$\sigma = 0.55$ %	
289.99	494	1.97	273	0.93		
309.84	810	1.89	484	0.90		
329.99	1220	1.80	802	0.87		
p-Xylene					0.72	0.09
289.99	479	1.91	273	0.93		
299.99	620	1.86	368	0.91	$\sigma = 0.28$ %	
309.85	780	1.83	484	0.90		
319.99	980	1.79	629	0.88		
329.99	1180	1.74	802	0.87		
Styrene					1.17	−0.22
249.95	310	5.06	63	0.97		
270.07	620	4.64	140	0.95	$\sigma = 0.80$ %	
309.84	1670	3.91	484	0.90		
329.99	2440	3.60	802	0.87		

[a] σ, average deviation defined by eq 7.

Table 5. Henry's Law Constants and Infinite Dilution Activity Coefficients of 1-Butene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
Benzene					0.63	0.11
279.99	275	1.76	165	0.95		
289.99	371	1.73	230	0.94	$\sigma = 0.12$ %	
309.99	620	1.65	420	0.91		
329.99	970	1.59	707	0.88		
Toluene					0.24	−0.13
249.93	74	1.52	50	0.98		
270.00	164	1.50	114	0.96	$\sigma = 0.31$ %	
289.98	316	1.47	230	0.94		
309.94	540	1.44	419	0.91		
329.99	870	1.42	707	0.88		
o-Xylene					0.20	−0.20
249.97	76	1.56	50	0.98		
270.13	171	1.55	115	0.96	$\sigma = 0.85$ %	
289.99	325	1.52	230	0.94		
309.84	570	1.51	418	0.91		
329.99	890	1.46	707	0.88		
m-Xylene					0.17	−0.18
249.98	71	1.46	50	0.98		
270.10	158	1.44	115	0.96	$\sigma = 0.64$ %	
289.99	307	1.43	230	0.94		
309.84	530	1.42	418	0.91		
329.99	840	1.38	707	0.88		
p-Xylene					0.14	−0.16
289.99	294	1.37	230	0.94		
299.99	390	1.35	314	0.93	$\sigma = 0.36$ %	
309.85	510	1.36	418	0.91		
319.99	650	1.35	550	0.90		
329.99	820	1.34	707	0.88		
Styrene					0.41	−0.55
249.95	138	2.83	50	0.98		
270.07	304	2.76	115	0.96	$\sigma = 0.43$ %	
309.84	970	2.58	418	0.91		
329.99	1540	2.52	707	0.88		

[a] σ, average deviation defined by eq 7.

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 uncer-

Table 6. Henry's Law Constants and Infinite Dilution Activity Coefficients of 2-Methylpropene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			0.60	0.07
279.99	280	1.77	167	0.95		
289.99	379	1.74	234	0.94	$\sigma = 0.27$ %	
309.99	640	1.66	426	0.91		
329.99	1000	1.61	719	0.88		
		Toluene			0.26	−0.13
249.93	77	1.55	51	0.98		
270.00	168	1.52	116	0.96	$\sigma = 0.15$ %	
289.98	324	1.49	234	0.94		
309.94	560	1.46	426	0.91		
329.99	890	1.44	719	0.88		
		o-Xylene			0.18	−0.23
249.98	77	1.55	51	0.98		
270.13	172	1.54	117	0.96	$\sigma = 0.43$ %	
289.99	329	1.51	234	0.94		
309.84	570	1.50	425	0.91		
329.99	910	1.47	719	0.88		
		m-Xylene			0.13	−0.21
249.98	72	1.45	51	0.98		
270.10	160	1.43	116	0.96	$\sigma = 0.41$ %	
289.99	311	1.43	234	0.94		
309.84	540	1.41	425	0.91		
329.99	860	1.39	719	0.88		
		p-Xylene			0.07	−0.24
289.99	299	1.37	234	0.94		
299.99	399	1.37	319	0.92	$\sigma = 0.31$ %	
309.85	520	1.36	425	0.91		
319.99	670	1.36	559	0.90		
329.99	840	1.36	719	0.88		
		Styrene			0.50	−0.47
249.95	143	2.90	51	0.98		
270.07	311	2.79	116	0.96	$\sigma = 0.30$ %	
309.84	980	2.58	425	0.91		
329.99	1560	2.52	719	0.88		

[a] σ, average deviation defined by eq 7.

Table 7. Henry's Law Constants and Infinite Dilution Activity Coefficients of *trans*-2-Butene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			0.83	0.30
279.99	217	1.79	127	0.96		
289.99	294	1.74	179	0.95	$\sigma = 0.62$ %	
309.99	510	1.67	333	0.92		
329.99	780	1.56	568	0.90		
		Toluene			0.21	−0.15
249.93	54	1.49	37	0.98		
270.00	122	1.46	87	0.97	$\sigma = 0.09$ %	
289.98	244	1.44	179	0.95		
309.94	432	1.42	332	0.92		
329.99	700	1.40	568	0.90		
		o-Xylene			0.14	−0.23
249.98	53	1.48	37	0.98		
270.13	125	1.48	87	0.97	$\sigma = 0.58$ %	
289.99	246	1.46	179	0.95		
309.84	440	1.45	331	0.92		
329.99	710	1.42	568	0.90		
		m-Xylene			0.10	−0.22
249.98	50	1.39	37	0.98		
270.10	117	1.39	87	0.97	$\sigma = 0.44$ %	
289.99	233	1.38	179	0.95		
309.84	415	1.37	331	0.92		
329.99	670	1.35	568	0.90		
		p-Xylene			0.12	−0.16
289.99	223	1.32	179	0.95		
299.99	302	1.32	247	0.94	$\sigma = 0.30$ %	
309.85	399	1.32	331	0.92		
319.99	520	1.31	439	0.91		
329.99	650	1.30	568	0.90		
		Styrene			0.38	−0.55
249.95	97	2.71	37	0.98		
270.07	225	2.68	87	0.97	$\sigma = 0.96$ %	
309.84	760	2.52	331	0.92		
329.99	1220	2.43	568	0.90		

[a] σ, average deviation defined by eq 7.

Table 8. Henry's Law Constants and Infinite Dilution Activity Coefficients of *cis*-2-Butene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			0.46	0.01
279.99	176	1.61	114	0.96		
289.99	246	1.59	163	0.95	$\sigma = 0.31$ %	
309.99	434	1.53	307	0.93		
329.99	710	1.50	533	0.90		
		Toluene			0.23	−0.08
249.93	45	1.43	32	0.98		
270.00	105	1.40	77	0.97	$\sigma = 0.46$ %	
289.98	215	1.39	163	0.95		
309.94	382	1.35	307	0.93		
329.99	640	1.34	533	0.90		
		o-Xylene			0.19	−0.14
249.98	46	1.45	32	0.98		
270.13	109	1.44	78	0.97	$\sigma = 0.46$ %	
289.99	217	1.41	163	0.95		
309.84	395	1.40	306	0.93		
329.99	650	1.37	533	0.90		
		m-Xylene			0.04	−0.24
249.98	42	1.33	32	0.98		
270.10	100	1.33	78	0.97	$\sigma = 0.46$ %	
289.99	205	1.33	163	0.95		
309.84	373	1.33	306	0.93		
329.99	620	1.31	533	0.90		
		p-Xylene			0.05	−0.20
289.99	197	1.28	163	0.95		
299.99	270	1.28	226	0.94	$\sigma = 0.31$ %	
309.85	358	1.27	306	0.93		
319.99	472	1.28	409	0.92		
329.99	600	1.27	533	0.90		
		Styrene			0.42	−0.46
249.95	82	2.60	32	0.98		
270.07	190	2.52	78	0.97	$\sigma = 0.25$ %	
309.84	660	2.36	306	0.93		
329.99	1090	2.31	533	0.90		

[a] σ, average deviation defined by eq 7.

Table 9. Henry's Law Constants and Infinite Dilution Activity Coefficients of 1,3-Butadiene in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			0.33	0.04
279.99	200	1.36	155	0.95		
289.99	276	1.35	218	0.94	$\sigma = 0.21$ %	
309.99	481	1.32	400	0.92		
329.99	760	1.29	678	0.89		
		Toluene			−0.12	−0.30
249.93	52	1.16	46	0.98		
270.00	122	1.18	107	0.96	$\sigma = 0.54$ %	
289.98	245	1.20	218	0.94		
309.94	436	1.20	399	0.92		
329.99	710	1.20	678	0.89		
		o-Xylene			0.00	−0.20
249.97	55	1.22	46	0.98		
270.13	127	1.23	108	0.96	$\sigma = 0.40$ %	
289.99	250	1.22	218	0.94		
309.84	446	1.23	398	0.92		
329.99	720	1.22	678	0.89		
		m-Xylene			−0.16	−0.32
249.98	51	1.13	46	0.98		
270.10	119	1.15	107	0.96	$\sigma = 0.69$ %	
289.99	242	1.18	218	0.94		
309.84	427	1.18	398	0.92		
329.99	700	1.18	678	0.89		
		p-Xylene			0.06	−0.09
289.99	236	1.16	218	0.94		
299.99	318	1.15	298	0.93	$\sigma = 0.24$ %	
309.85	418	1.16	398	0.92		
319.99	540	1.15	525	0.90		
329.99	680	1.15	678	0.89		
		Styrene			0.15	−0.57
249.95	95	2.11	46	0.98		
270.07	216	2.09	107	0.96	$\sigma = 0.25$ %	
309.84	740	2.05	398	0.92		
329.99	1200	2.02	678	0.89		

[a] σ, average deviation defined by eq 7.

tainty 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[11] was less than 1 %). Therefore, the uncertainty of the obtained infinite dilution activity coefficients may be considered to be no greater than 3 %.

Table 10. Henry's Law Constants and Infinite Dilution Activity Coefficients of Dimethyl Ether in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			−0.64	−0.80
279.95	352	1.13	335	0.93		
289.97	480	1.15	460	0.92	$\sigma = 1.06$ %	
309.98	830	1.18	812	0.89		
329.99	1380	1.26	1331	0.86		
		Toluene			−0.32	−0.45
250.04	113	1.07	109	0.97		
270.20	249	1.10	240	0.95	$\sigma = 0.34$ %	
289.98	475	1.13	461	0.92		
309.84	820	1.16	809	0.89		
329.99	1290	1.17	1331	0.86		
		o-Xylene			−0.12	−0.35
250.05	130	1.23	109	0.97		
269.91	278	1.24	237	0.95	$\sigma = 0.28$ %	
289.97	520	1.25	460	0.92		
309.98	900	1.27	812	0.89		
329.99	1410	1.27	1331	0.86		
		m-Xylene			−0.07	−0.26
249.97	123	1.17	109	0.97		
270.05	274	1.22	239	0.95	$\sigma = 1.19$ %	
289.98	510	1.21	461	0.92		
309.89	850	1.21	810	0.89		
329.99	1330	1.21	1331	0.86		
		p-Xylene			−0.21	−0.38
289.97	491	1.17	460	0.92		
299.98	650	1.18	618	0.91	$\sigma = 0.34$ %	
309.98	840	1.18	812	0.89		
319.99	1070	1.20	1048	0.87		
329.99	1320	1.20	1331	0.86		
		Styrene			−0.55	−0.63
250.04	102	0.97	109	0.97		
270.20	234	1.03	240	0.95	$\sigma = 0.48$ %	
289.98	443	1.06	461	0.92		
309.84	780	1.11	809	0.89		
329.99	1260	1.14	1331	0.86		

[a] σ, average deviation defined by eq 7.

Table 11. Henry's Law Constants and Infinite Dilution Activity Coefficients of Chloroethane in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			−0.37	−0.44
279.95	84	1.05	82	0.97		
289.97	123	1.06	120	0.97	$\sigma = 0.91$ %	
309.98	237	1.07	235	0.95		
329.99	431	1.12	421	0.92		
		Toluene			−0.46	−0.47
250.04	20	0.92	22	0.99		
270.20	51	0.95	55	0.98	$\sigma = 0.53$ %	
289.98	115	1.00	120	0.97		
309.84	226	1.02	234	0.95		
329.99	406	1.05	421	0.92		
		o-Xylene			−0.22	−0.29
250.05	22	1.02	22	0.99		
269.91	55	1.04	54	0.98	$\sigma = 0.20$ %	
289.97	123	1.06	120	0.97		
309.98	237	1.07	235	0.95		
329.99	419	1.09	421	0.92		
		m-Xylene			−0.10	−0.14
249.97	22	1.03	21	0.99		
270.05	54	1.02	55	0.98	$\sigma = 0.64$ %	
289.98	119	1.03	120	0.97		
309.89	230	1.04	235	0.95		
329.99	407	1.05	421	0.92		
		p-Xylene			−0.34	−0.36
289.97	116	1.00	120	0.97		
299.98	167	1.03	170	0.96	$\sigma = 0.58$ %	
309.98	229	1.03	235	0.95		
319.99	306	1.04	318	0.94		
329.99	405	1.05	421	0.92		
		Styrene			−0.33	−0.34
250.04	20	0.95	22	0.99		
270.20	52	0.97	55	0.98	$\sigma = 0.96$ %	
289.98	113	0.98	120	0.97		
309.84	228	1.03	234	0.95		
329.99	400	1.04	421	0.92		

[a] σ, average deviation defined by eq 7.

Table 12. Henry's Law Constants and Infinite Dilution Activity Coefficients of 1,1-Difluoroethane in Pure Solvents[a]

T/K	H_g/kPa	γ^∞	P_g^{sat}/kPa	φ_g^{sat}	$H^{E,\infty}/RT_{300}$	$S^{E,\infty}/R$
		Benzene			0.59	−0.25
279.99	770	2.42	345	0.93		
289.99	1020	2.37	476	0.91	$\sigma = 0.24$ %	
309.99	1650	2.27	846	0.88		
329.99	2500	2.20	1398	0.85		
		Toluene			0.37	−0.43
249.93	251	2.38	110	0.96		
270.00	530	2.33	243	0.94	$\sigma = 0.68$ %	
289.98	980	2.28	476	0.91		
309.94	1600	2.20	845	0.88		
329.99	2430	2.14	1398	0.85		
		o-Xylene			0.52	−0.38
249.97	286	2.70	110	0.96		
270.13	600	2.61	244	0.94	$\sigma = 0.95$ %	
289.99	1080	2.52	476	0.91		
309.84	1770	2.44	843	0.88		
329.99	2630	2.31	1398	0.85		
		m-Xylene			0.50	−0.36
249.98	275	2.60	110	0.96		
270.10	560	2.46	244	0.94	$\sigma = 0.82$ %	
289.99	1040	2.42	476	0.91		
309.84	1690	2.33	843	0.88		
329.99	2530	2.23	1398	0.85		
		p-Xylene			0.59	−0.24
289.99	1010	2.36	476	0.91		
299.99	1290	2.29	641	0.90	$\sigma = 0.38$ %	
309.85	1640	2.27	843	0.88		
319.99	2040	2.23	1096	0.86		
329.99	2480	2.18	1398	0.85		
		Styrene			0.31	−0.95
249.95	393	3.72	110	0.96		
270.07	840	3.67	244	0.94	$\sigma = 0.63$ %	
309.84	2530	3.50	843	0.88		
329.99	3870	3.40	1398	0.85		

[a] σ, average deviation defined by eq 7.

The Henry's law constants of nonpolar gases in liquids generally follow the order of increasing Henry's law constant with decreases in the normal boiling point temperature of the liquefied gas. The order of the Henry's law constants of the twelve gases in benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene at $T = 290$ K generally follows the above relationship except some polar gases (propene, 2-methylpropene, 1-butene, *cis*-2-butene, dimethyl ether, 1,1-difluoroethane, and chloroethane). The Henry's law constants of polar gases in nonpolar or polar solvents generally become smaller than the expected values from the simple relationship because of the dipole-induced−dipole or dipole−dipole interactions.

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

$$\ln \gamma^\infty = \frac{H^{E,\infty}}{RT} - \frac{S^{E,\infty}}{R} \tag{6}$$

where $H^{E,\infty}$and $S^{E,\infty}$are the partial molar excess enthalpy and the partial molar excess entropy of the solute at infinite dilution, respectively. In the temperature range of (250 to 330) 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 ($H^{E,\infty}/RT_{300}$ and $S^{E,\infty}/R$) are also indicated in Tables 1 to 12, where $T_{300} = 300$ K. The average deviation for the infinite dilution activity coefficients in these correlations is defined as follows:

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

where N is the number of data point, γ_j^∞ is the experimentally obtained infinite dilution activity coefficients, and $\gamma_{j,\text{cal}}^\infty$ is the

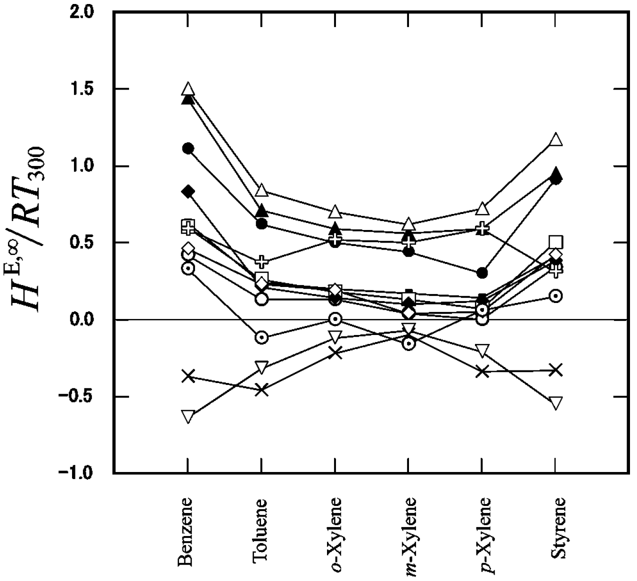

Figure 1. Partial molar excess enthalpies of solutes in aromatics: ●, propane; ○, propene; ▲, butane; △, 2-methylpropane; ■, 1-butene; □, 2-methylpropene; ◆, *trans*-2-butene; ◇, *cis*-2-butene; ⊙, 1,3-butadiene; ▽, dimethyl ether; ×, chloroethane; open plus sign, 1,1-difluoroethane.

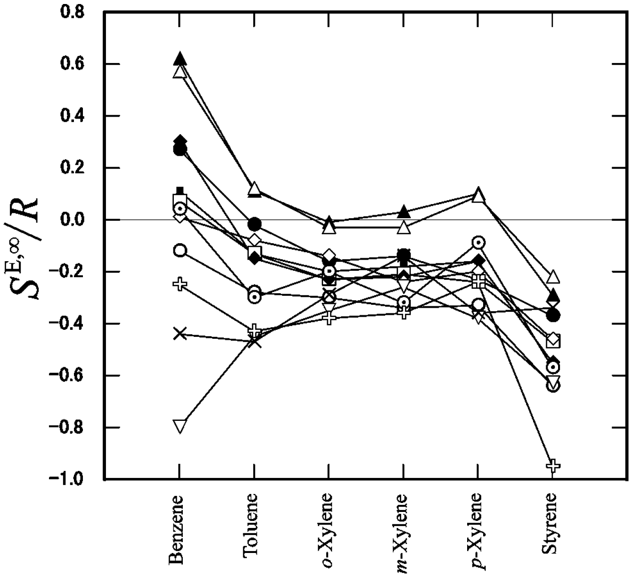

Figure 2. Partial molar excess entropies of solutes in aromatics: ●, propane; ○, propene; ▲, butane; △, 2-methylpropane; ■, 1-butene; □, 2-methylpropene; ◆, *trans*-2-butene; ◇, *cis*-2-butene; ⊙, 1,3-butadiene; ▽, dimethyl ether; ×, chloroethane; open plus sign, 1,1-difluoroethane.

infinite dilution activity coefficient calculated from eq 6. The average deviations for all systems are within the uncertainty of the experimental value (3 %), and the maximum deviation is 1.64 % for the butane + styrene system. The partial molar excess properties for the systems studied in this work do not so deviate from zero, and almost of the systems will be not so far from an ideal solution.

Figures 1 and 2 show the $H^{E,\infty}/RT_{300}$ and $S^{E,\infty}/R$ for each solute in the six aromatics. In general, the partial molar excess enthalpies and entropies of the 12 solutes in the aromatics will increase with decreases of the polarities of the solutes and increasing molecular size of the solutes.

For alkanes and alkenes in benzene, $H^{E,\infty}$ are positive, and $H^{E,\infty}$ for a large molecule like butane or 2-methyl-propane is a large positive value as shown in Figure 1. The similar phenomena can be observed for $S^{E,\infty}$ as shown in Figure 2. $S^{E,\infty}$ values increase with increasing size of the solute. Benzene is a symmetrical and planar molecule, and the solution structure of the pure benzene will be a parallel planar structure to keep a minimum Gibbs energy. The large molecule like butane will disturb the structure, and $H^{E,\infty}$ and $S^{E,\infty}$ become positive and increase with increasing the molecular size of the solute.

On the other hand, $H^{E,\infty}$ and $S^{E,\infty}$ for dimethyl ether and chloroethane are negative. These gases have dipole moments and the dipole-induced−dipole interaction between the solute and benzene will reduce the value of $H^{E,\infty}$ and probably make some structures around the solute molecule, and $S^{E,\infty}$ becomes negative. $H^{E,\infty}$ for alkanes and alkenes in toluene and xylenes are smaller than those in benzene. The results suggest that $H^{E,\infty}$ and $S^{E,\infty}$ for alkanes and alkenes decrease with increasing size of the alkyl groups in the aromatic ring.

$H^{E,\infty}$ in styrene are similar to those in benzene, but $S^{E,\infty}$ in styrene for all solutes are negative. Styrene has a long branch (ethylene), and the solution structure of the pure styrene will be more random than that in benzene. The negative values of $S^{E,\infty}$ suggest that a kind of solution structure may be constructed around the solute molecule, which is more regular structure than the pure styrene structure.

Conclusions

Henry's law constants, the infinite dilution activity coefficients, and the partial molar excess properties of the 12 gases in the aromatics (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene) at T = (250 to 330) 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 in order to obtain infinite dilution activity coefficients precisely.

Generally the Henry's law constants of the nonpolar gases in the aromatics have followed the order of increasing Henry's law constant with decreases in the normal boiling point temperature of the liquefied gas. The Henry's low constants of polar gases, however, have become smaller than the expected values from the simple relationship. The partial molar excess enthalpies and the partial molar excess entropies of the 12 gases in the aromatics will increase with decreases of the polarities of the gases and increasing molecular size of the gases, and $H^{E,\infty}$ and $S^{E,\infty}$ for alkanes and alkenes in aromatics will decrease with increasing size of the alkyl groups in the aromatic ring.

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