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Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate Using Gas−Liquid Chromatography

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Activity coefficients at infinite dilution γ_i^∞ have been determined for 17 organic solutes, alkanes, alkenes, and alkyl benzenes, in the ionic liquid 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([HMIM][CF_3SO_3]) by the gas−liquid chromatographic (GLC) method with the ionic liquid as the stationary phase. The measurements were carried out in the temperature range of (303.15 to 363.15) K. The partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$ were also determined for the solutes from the temperature dependence of the γ_i^∞ values.

Introduction

This work is a continuation of our studies on the determination of activity coefficients at infinite dilution by the gas−liquid chromatographic (GLC) method for ionic liquids.[1–4]

Experimental section

The ionic liquid 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([HMIM][CF_3SO_3]) was purchased from Hang Zhou Chemer Chemical Co., Ltd. Its mass fraction purity was above 0.97 with the following certified amounts of impurities: $Cl^- < 10^{-2}$, water $< 10^{-2}$. The chemical shifts for the ^1H NMR spectrum (parts per million, DMSO) appeared as follows: δ9.130 [d, 1H, H(2)], 7.769 [s, 1H, H(4)], 7.694 [d, 1H, H(5)], 4.152 [t, 2H, NCH_2], 3.848 [d, 3H, NCH_3], 1.765 [s, 2H, NCH_2-CH_2], 1.243 [s, 6H, $NCH_2CH_2-(CH_2)_3$], and 0.835 [t, 3H, CH_3]. Impurity peaks were not observed, and there is a solvent (DMSO) peak at $\delta = 2.500$ in the ^1H NMR spectrum.

The hydrocarbons provided by Beijing Chemical Reagents Company were analytical reagents. The solutes were used without further purification.

The GLC apparatus, column preparation, packing method, and experimental process in this work are the same as described by Zhou.[1,2] In this work, the GC columns with length of 130 cm and inner diameter of 0.40 cm have been used. Dry nitrogen was used as the carrier gas, and isopropanol was used as solvent to coat the ionic liquid onto the solid support. The mass of the stationary phase (ionic liquid) was 4.5760 g with an uncertainty of ± 0.007 %. According to the literature,[4] the mass fraction of the ionic liquid coating was chosen as 60 % of the stationary phase. The column was filled uniformly with the help of an ultrasonic vibrator.

The values of γ_i^∞ were obtained by the equation proposed by Cruickshank et al.[5] and Everett.[6] For all solutes, values of the vapor pressure of the pure liquid solute (*i*) P_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.,[7] which are given in Table 1. The liquid molar volumes of pure solute V_i^0 were estimated using experimental values of their densities.[13] The partial molar volumes of the solute V_i^∞ have been assumed to be equal to V_i^0. Values of B_{11} and B_{12} have been estimated according to the Tsonopolous method[8] with an uncertainty of $< \pm 10$ $cm^3 \cdot mol^{-1}$. The critical parameters needed for the calculations were available from the literature,[6] which are given in Table 2. The mixed critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and the mixed acentric factor ω_{ij} were calculated by using equations given in

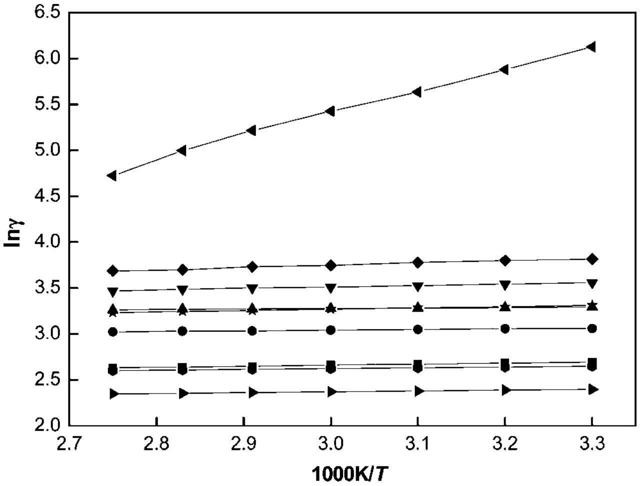

Figure 1. Plots of ln γ_i^∞ versus 1/*T* for the solutes: ■, pentane; ●, hexane; ★, heptane; ▼, octane; ◆, nonane; solid triangle pointing left, decane; solid triangle pointing right, cyclohexane; ◆, methylcyclohexane; ▲, 2,2,4-trimethylpentane.

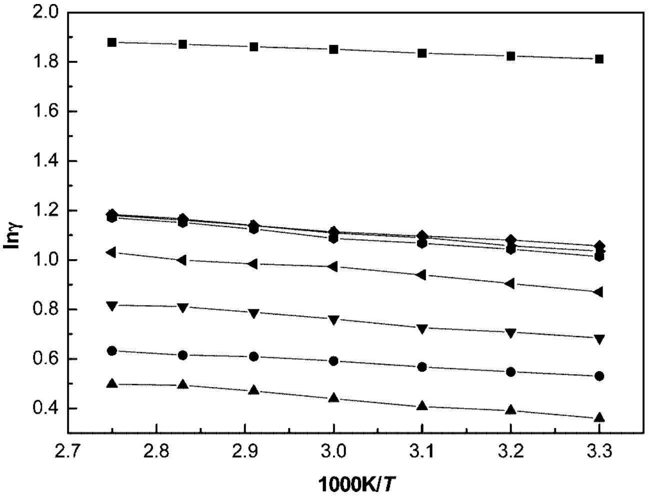

Figure 2. Plot of of ln γ_i^∞ versus 1/*T* for the solutes: ▲, benzene; ▼, toluene; ▲, ethyl benzene; ♦, *m*-xylene; ⬢, *p*-xylene; solid triangle pointing left, *o*-xylene; ■, cyclohexene; ●, styrene.

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Table 1. Vapor Pressure P_i^0 of the Solutes (i) from T = (303.15 to 363.15) K

	P_i^0/kPa						
solutes (i)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 363.15
			Alkanes				
pentane	82.0	116	159	214	283	367	480
hexane	24.9	37.3	54.1	76.4	105	143	189
heptane	7.79	12.3	18.9	28.1	40.5	57.1	78.6
octane	2.46	4.14	6.69	10.5	15.9	23.1	33.4
nonane	0.782	1.41	2.41	4.03	6.31	9.81	14.5
decane	0.245	0.473	0.865	1.51	2.52	4.06	6.33
2,2,4-trimethylpentane	8.33	13.0	19.5	28.6	43.5	56.8	77.4
cyclohexane	16.2	24.6	36.3	51.9	72.5	99.0	132
methylcyclohexane	7.83	12.2	18.4	27.0	38.6	53.9	73.6
			Alkenes				
cyclohexene	16.0	22.6	35.4	48.1	70.4	92.7	129
styrene	1.08	1.89	3.18	5.14	8.02	12.1	17.8
			Alkyl Benzenes				
benzene	15.9	24.3	36.2	52.2	73.5	101	136
toluene	4.89	7.89	12.3	18.6	27.2	38.9	54.3
ethylbenzene	1.68	2.87	4.69	7.40	11.3	16.8	24.3
o-xylene	1.78	2.04	3.40	5.44	8.43	12.7	18.6
m-xylene	1.49	2.55	4.18	6.63	10.2	15.2	22.0
p-xylene	1.55	2.27	4.34	6.94	10.5	15.6	22.7

Table 2. Critical Constants Z_c, T_c, P_c, and V_c and Acentric Factors ω of the Solutes and the Carrier Gas Used in Calculation of the Virial Coefficients

solute (i)	Z_c	$\frac{T_c}{\mathrm{K}}$	$\frac{P_c}{\mathrm{bar}}$	$\frac{V_c}{\mathrm{cm^3 \cdot mol^{-1}}}$	ω
		Alkanes			
pentane	0.268	470	33.7	311	0.252
hexane	0.264	508	30.3	368	0.30
heptane	0.261	540	27.4	428	0.350
octane	0.259	569	24.9	492	0.399
nonane	0.252	595	22.9	555	0.445
decane	0.256	618	21.1	624	0.49
cyclohexane	0.273	554	40.7	308	0.211
methylcyclohexane	0.268	572	34.7	368	0.235
2,2,4-trimethylpentane	0.266	544	25.7	470	0.304
		Alkenes			
cyclohexene	0.27	560	42.9	292	0.210
styrene	0.274	647	39.4	374	0.257
		Alkyl Benzenes			
benzene	0.268	562	49.0	256	0.210
toluene	0.264	592	41.1	316	0.264
ethyl benzene	0.263	617	36.1	374	0.304
o-xylene	0.263	630	37.3	370	0.312
m-xylene	0.259	617	35.4	375	0.327
p-xylene	0.259	616	35.1	378	0.322
nitrogen	0.290	126	33.5	89.5	0.0400

Table 3. Relative Uncertainties in the Measured and Derived Quantities

parameters	uncertainty
$t_r - t_G$	± 2.6 %
U_0	± 0.4 %
P_i	± 0.7 %
P_o	± 0.02 %
J	± 1 %
P_i^0	± 0.01 % to ± 0.25 %
n_3	± 0.6 %
$\gamma_{i,3}^\infty$	± 5 %

the literature.[8,9] The pressure drop was recorded by GC automatically with an uncertainty of ± 0.2 kPa. The errors in the γ_i^∞ were obtained from the law of propagation of errors. The relative uncertainties in the measured and derived quantities are listed in Table 3.

Results and Discussion

The values of γ_i^∞ of different solutes in [HMIM][CF_3SO_3] obtained over a temperature range of (303.15 to 363.15) K were listed in Table 4. The results of γ_i^∞ were correlated with temperature by the following equation

$$\ln \gamma_i^\infty = a + \frac{b}{(T/\mathrm{K})} \tag{1}$$

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_i^{E,\infty}$ can be obtained from the slope of a straight line derived from eq 1.

The coefficients a and b and the standard deviation σ of the fitted equation, γ_i^∞, at 298.15 K calculated using eq 1 and values of $H_i^{E,\infty}$ derived from eq 1 are listed in Table 5. The plots of measured ln γ_i^∞ vs $1/T$ are given in Figures 1 and 2, which showed fairly good fitting quality of eq 1.

The γ_i^∞ values of the linear n-alkanes increase with increasing chain length. The branching of the alkane skeleton (e.g., cyclohexane, methylcyclohexane, or 2,2,4-trimethylpentane) decreases the value of γ_i^∞ in comparison with the corresponding linear alkanes: hexane, heptane, and octane. The introduction of a double bond in the six-membered ring (cyclohexene) also causes a decrease of γ_i^∞.

The values of γ_i^∞ for benzene and the alkyl benzenes were distinctly lower in comparison with those of the alkanes and alkenes. However, similarly as with the alkanes, the γ_i^∞ values increase with increasing size of the alkyl group (see Table 4).

The selectivity S_{ij}^∞ is defined as below[10]

$$S_{ij}^\infty = \frac{\gamma_{i3}^\infty}{\gamma_{j3}^\infty} \tag{2}$$

It indicates suitability of a solvent for separating mixtures of components i and j by extraction. The values of selectivity for the separation of the hexane (i)/benzene (j) mixture at T = 298.15 K using different ILs with cation [HMIM]$^+$ and three anions are taken from the literature.[4,11,12] The results of this work are presented in Table 6, which indicates that for a given cation [HMIM]$^+$ γ_i^∞ values for the anions [PF_6]$^-$ and [BF_4]$^-$ are higher than those for the anions [Tf_2N]$^-$ and [CF_3SO_3]$^-$, and in the case of a given anion [CF_3SO_3]$^-$, γ_i^∞ values for the cation [BMIM]$^+$ are higher than those for [HMIM]$^+$. It means that the activity coefficients and intermolecular interactions of different solutes in ILs are very much dependent on the chemical structure of the anion, and it would appear that increasing the

Table 4. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Various Solutes in the Ionic Liquid 1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate as the Stationary Phase at Temperatures of (303.15 to 363.15) K

	γ_i^∞						
solutes (i)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 363.15
			Alkanes				
pentane	14.79	14.63	14.46	14.32	14.11	14.01	13.90
hexane	21.33	21.24	21.08	20.89	20.76	20.69	20.53
heptane	26.91	26.73	26.61	26.47	26.37	26.27	26.10
octane	35.02	34.48	33.94	33.42	33.15	32.73	32.03
nonane	45.43	44.61	43.71	42.29	41.75	40.32	39.89
decane	456.8	356.7	279.2	227.3	183.9	147.9	112.5
cyclohexane	10.98	10.90	10.77	10.71	10.60	10.53	10.48
methylcyclohexane	14.12	14.00	13.88	13.77	13.67	13.56	13.48
2,2,4-trimethylpentane	27.47	26.91	26.71	26.28	25.90	25.70	25.35
			Alkenes				
cyclohexene	6.124	6.197	6.264	6.365	6.432	6.498	6.552
styrene	1.700	1.728	1.763	1.807	1.839	1.849	1.883
			Alkyl Benzenes				
benzene	1.433	1.478	1.501	1.550	1.600	1.637	1.645
toluene	1.981	2.029	2.065	2.141	2.198	2.249	2.266
ethylbenzene	2.875	2.945	2.994	3.043	3.121	3.207	3.266
o-xylene	2.387	2.469	2.558	2.644	2.674	2.716	2.799
m-xylene	2.816	2.879	2.974	3.028	3.120	3.190	3.252
p-xylene	2.757	2.837	2.907	2.966	3.078	3.160	3.223

Table 5. Coefficients of Equation 1, *a* and *b*, γ_i^∞ at 298.15 K Calculated Using Equation 1, Values of $H_i^{E,\infty}$ Derived from Equation 1, and Standard Deviation σ

solute i	a	b/K	$\gamma_{i,298.15\text{K}}{}^{a}$	$H_i^{E,\infty b}$ kJ·mol^{-1}	σ
		Alkane			
pentane	2.309	116.9	14.90	0.9718	0.00179
hexane	2.825	71.93	21.45	0.5980	0.00155
heptane	3.112	53.31	26.85	0.4432	0.00082
octane	3.044	155.4	35.35	1.292	0.00368
nonane	2.995	250.6	46.32	2.084	0.00629
decane	−2.127	2507	535.6	20.85	0.03433
cyclohexane	2.106	88.13	11.04	0.7327	0.00137
methylcyclohexane	2.363	86.41	14.19	0.7184	0.00053
2,2,4-trimethylpentane	2.839	143.3	27.64	1.192	0.00263
		Alkene			
cyclohexene	2.233	−127.7	6.075	−1.062	0.00155
styrene	1.162	−191.7	1.681	−1.593	0.00421
		Alkyl Benzenes			
benzene	1.247	−269.2	1.412	−2.238	0.00724
toluene	1.553	−264.5	1.946	−2.199	0.00664
ethylbenzene	1.821	−233.1	2.828	−1.938	0.00572
o-xylene	1.806	−282.0	2.365	−2.344	0.00783
m-xylene	1.993	−269.8	2.967	−2.243	0.00332
p-xylene	1.972	−291.3	2.703	−2.422	0.00529

[a] Range of uncertainties is within ± 4 %. [b] Range of uncertainties is within ± 6 %.

Table 6. Selectivities, S_{ij}^∞, at Infinite Dilution of Various Solvents for the Hexane (*i*)/Benzene (*j*) Separation at T = 298.15 K

solvents	S_{ij}^∞
[HMIM][PF_6][a]	21.6
[HMIM][BF_4][a]	23.1
[HMIM][Tf_2N][b]	12.4
[BMIM][CF_3SO_3][c]	21.8
[HMIM][CF_3SO_3] (this work)	15.2

[a] Ref 9. [b] Ref 11. [c] Ref 4.

length of the alkyl chain on the cation reduces the magnitude of the γ_i^∞. The results indicate that [HMIM][CF_3SO_3] is not an ideal extraction solvent for separation of hexane and benzene binary systems.

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