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Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Butyl-3-methylimidazolium Nitrate Using Gas–Liquid Chromatography

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Supporting Information

ABSTRACT: Activity coefficients at infinite dilution of 21 organic solutes in the ionic liquid 1-butyl-3-methylimidazolium nitrate ([BMIM][NO_3]) have been determined using gas–liquid chromatography over a temperature range of (303.15 to 363.15) K with the ionic liquid as the stationary phase. The partial molar excess enthalpies at infinite dilution and the solubility parameters of ionic liquid were determined for the solutes from the temperature dependence of the experimental activity coefficient at infinite dilution values.

INTRODUCTION

Ionic liquids (ILs) have been increasingly promoted as “green solvents”. Compared to conventional organic solvents such as volatile organic compounds, ILs have a number of unique properties: chemical stability, thermal stability, low vapor pressure, and high ionic conductivity properties. Ionic liquids can be used in separation processes as entrainers. The activity coefficients $\gamma_{i,3}^{\infty}$ at infinite dilution are determined to evaluate the interaction between ionic liquids and different solutes. From experimental values of $\gamma_{i,3}^{\infty}$, the selectivity at infinite dilution can be calculated for different separation problems.[1,2]

This work is a continuation of a study on the determination of activity coefficients at infinite dilution of various solutes (i) by the gas–liquid chromatographic method (GLC) for functional ionic liquids.[1–4] By the introduction of a functional group, ionic liquids can be widely used in organic synthesis, electrochemistry, and material science because of their unique properties. For the thermodynamic properties, most literature focuses on the ionic liquids with an alkyl carbon chain in the cations.[1,5] The functional ionic liquids may have the potential application in extraction and some industrial processes. The high selectivity for separation of aliphatic and aromatic hydrocarbons seems to be achieved. To the best of our knowledge, the activity coefficients at infinite dilution of organic solutes in [BMIM][NO_3] determined in this work are not yet available in the literature.

EXPERIMENTAL SECTION

The ionic liquid [BMIM][NO_3] was purchased from Shanghai Cheng Jie Chemical Co., Ltd. Its percent mass fraction purity was above 99 % according to the manufacturer's specifications with impurities: $w\ (Cl^-) < 6 \cdot 10^{-4}$. The water mass fraction analyzed by Karl Fischer analysis was less than $9 \cdot 10^{-4}$. The chemical shifts for the ^{1}H NMR spectrum (parts per million, C_3D_6O) appeared as follows: [BMIM][NO_3], δ: 8.929 (s, 1H, CH—N), 7.727–7.673 (d, 2H, CH═CH—N), 4.363–4.327 (t, 2H, CH_2Me), 4.038 (s, 3H, CH_3N), 1.944–1.906 (t, 2H, CH_2N), 1.413–1.357 (m, 2H, CH_2), 0.964–0.927 (t, 3H, CH_2CH_3). The characterization of [BMIM][NO_3] with ^{1}H NMR was almost the same as that of [BMIM][PF_6].[3] The solutes provided by Beijing Chemical Reagents Company were all analytical reagents, and the solutes were used without further purification because the GLC process separated the solutes from any impurities. Dry helium was used as the carrier gas, and the mass of the stationary phase was determined with a precision of ± 0.0001 g. According to the literature,[2] the mass fraction of the ionic liquid coating was about (27 to 60) % of the support material. In this work, the amount of ionic liquid was 60 % mass fraction of the support material to avoid possible residual adsorption effects of the solutes on chromosorb. Dichloromethane was used as a solvent to coat the ionic liquid onto the solid support; it was evaporated using a rotary evaporator under vacuum. The column was filled uniformly with the help of an ultrasound vibrator. Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GC column. The support was equilibrated at 323.15 K over 6 h.

The experimental process and the method of checking the stability of the experimental conditions in this work are the same as those described previously by Wang et al.[1,2,4] The $\gamma_{i,3}^{\infty}$ values were obtained by the equation proposed by Cruickshank et al.[6] and Everett.[7] The data for calculating the correction terms have been obtained in the following way. For all solutes, values of P_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.[8] The data needed for the equations have been reported in our previous paper.[9] The outlet pressure P_o was kept equal to the atmospheric pressure. Molar volumes of solutes V_i^0 were estimated using experimental values of their densities; partial molar volumes of the solute in the ionic liquid at infinite dilution 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 equations

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Table 1. Critical Constants P_c, V_c, T_c, and Z_c, Dipole Moment μ, and the Acentric Factor ω Used in the Calculation of the Virial Coefficients

solute	Z_c	T_c	P_c	V_c	ω	μ
		K	bar	$cm^3 \cdot mol^{-1}$		
hexane	0.264	508	30.3	368	0.3	0
heptane	0.261	540	27.4	428	0.35	0
octane	0.259	569	24.9	492	0.399	0
nonane	0.252	595	22.9	555	0.445	0
cyclohexane	0.273	554	40.7	308	0.211	0.3
methylcyclohexane	0.268	572	34.7	368	0.235	0
benzene	0.268	562	49	256	0.21	0
toluene	0.264	592	41.1	316	0.264	0.4
ethylbenzene	0.263	617	36.1	374	0.304	0.4
o-xylene	0.263	630	37.3	370	0.312	0.5
m-xylene	0.259	617	35.4	375	0.327	0.3
p-xylene	0.259	616	35.1	378	0.322	0.1
methanol	0.224	513	81	118	0.565	1.7
ethanol	0.24	514	61.5	167	0.649	1.7
1-propanol	0.254	537	51.8	219	0.629	1.7
acetonitrile	0.184	548	47.7	173	0.321	3.5
ethyl acetate	0.254	587	51.4	238	0.288	1.9
acetone	0.252	523	38.3	286	0.361	2.9
dichloromethane	0.277	510	60	193	0.193	1.8
trichloromethane	0.296	537	55	240	0.216	1.1
tetrachloromethane	0.271	556	45.6	276	0.194	0

Table 2. Uncertainties in the Measured and Derived Quantities

parameters	uncertainty/%
$t_r - t_G$	± 3.3
U_0	± 0.5
P_i	± 0.6
P_o	± 0.02
J	± 1
P_i^0	± 0.01 to 0.25
n_{IL}	± 0.5
γ_i^∞	± 4.5

suitable for nonpolar liquids by Tsonopolous's method.[10−13] The critical parameters needed for the calculations were available from the literature[13] and are listed in Table 1. The cross critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed acentric factor ω_{ij} were calculated by using equations given in the literature.[14,15] According to the error propagation law, $\gamma_{i,3}^\infty$ is estimated to have a relative uncertainty within ± 0.045. The uncertainties in the measured or derived quantities are listed in Table 2.

RESULTS AND DISCUSSION

The values of $\gamma_{i,3}^\infty$ of organic solutes in [BMIM][NO_3] obtained over a temperature range of (303.15 to 363.15) K were listed in Table 3. The results of $\gamma_{i,3}^\infty$ were correlated with temperature by the following equation.

$$\ln \gamma_{i,3}^\infty = a + \frac{b}{(T/K)} \qquad (1)$$

The plots of measured ln $\gamma_{i,3}^\infty$ versus $1/T$ values are given in Figures 1 to 3, which showed a fairly good fitting quality of eq 1.

A small activity coefficient of a solute in a solvent usually means that they have large mutual solubilities and strong molecular interaction. In comparison with those of the alkanes, the values of $\gamma_{i,3}^\infty$ are distinctly lower for the aromatic compounds, and the values of $\gamma_{i,3}^\infty$ increase with increasing size of the alkyl group. The $\gamma_{i,3}^\infty$ values of the linear n-alkanols increase with increasing their chain length. This indicates that the interaction between the solutes and the IL decreases with an increase of solute alkyl chain. For alkanes, cyclohydrocarbons, and alcohols, values of $\gamma_{i,3}^\infty$ decrease with an increasing temperature. This behavior indicates that the interactions of polar solute molecules with the IL liquid are stronger and the solutes have better solubilities in the IL. This dependency is converse for the rest of investigated solutes, aromatic compounds, acetone, acetonitrile, ethyl acetate, and chlorinated hydrocarbons. These properties are very common in most ionic liquids described by other literature.[16,17]

According to the Gibbs−Helmholtz equation (eq 2), 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.[5]

$$\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)} = \frac{H_i^{E,\infty}}{R} \qquad (2)$$

The coefficients a and b, the standard deviation σ of the fitted equation, $\gamma_{i,3}^\infty$ at the standard condition ($T = 298.15$ K) calculated using eq 1, and values of $H_i^{E,\infty}$ derived from eq 1 are listed in Table 4. Within each of the series, alkanes, cycloalkanes, and alcohols, the $H_i^{E,\infty}$ values are positive. For aromatic compounds, acetone, acetonitrile, ethyl acetate, and chlorinated hydrocarbons, the $H_i^{E,\infty}$ values are all negative which indicate stronger interaction between the solute and the ionic liquid. The same tendency was observed in the ionic liquid [EMIM][NO_3].[18] The activity coefficients at infinite dilution of heptanes, cyclohexane, benzene, *m*-xylene, methanol, acetonitrile, and acetone in these two ionic liquids [C_nMIM]NO_3 (n = 2, 4) at 323.15 K are compared in Figure 4. It can be observed that all of the $\gamma_{i,3}^\infty$ values decrease with the increasing carbon chain length on the cations. These results show that the experimental data obtained in this work are reasonable.

The activity coefficients at infinite dilution of solutes in a given solvent can be used to estimate the solvent solubility parameter. The activity coefficients at infinite dilution can be represented by a two-term equation which the combinatorial term can be represented by the Kikik et al.[19] modification to Flory's equation; the residual term is given by the regular solution theory:

$$\ln \gamma_i^\infty = \ln \gamma_i^{\infty comb} + \ln \gamma_i^{\infty res} \qquad (3)$$

$$\ln \gamma_i^{\infty comb} = \ln(r_i/r_s)^{2/3} + 1 - (r_i/r_s)^{2/3} \qquad (4)$$

$$\ln \gamma_i^{\infty res} = (\nu_i/RT)(\delta_i - \delta_s)^2 \qquad (5)$$

where r_i is the van der Waals volumes of solute; r^s is the van der Waals volumes of solvent; ν_i is the solute molar volume; δ_i and δ_s are the solubility parameters of solute and solvent, respectively. A residual function Y can be rearranged from eq 5 according to

Table 3. Experimental Activity Coefficients at Infinite Dilution of Organic Solutes in the Ionic Liquid 1-Butyl-3-Methylimidazolium Nitrate ([BMIM][NO_3]) as the Stationary Phase from (303.15 to 363.15) K

solute	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
hexane	63.87	58.09	53.07	48.78	45.09	41.82	38.97
heptane	105.41	97.11	89.90	83.62	78.12	73.24	68.90
octane	168.31	153.86	141.43	130.60	121.28	113.04	105.77
nonane	262.80	238.46	217.69	199.81	184.32	170.81	158.96
cyclohexane	29.84	27.59	25.63	23.92	22.42	21.09	19.89
methylcyclohexane	45.27	42.14	39.39	37.00	34.86	32.96	31.20
benzene	1.85	1.88	1.91	1.95	2.01	1.99	2.02
toluene	3.09	3.15	3.19	3.24	3.29	3.33	3.37
ethylbenzene	5.53	5.55	5.56	5.56	5.60	5.59	5.61
o-xylene	4.31	4.38	4.44	4.49	4.54	4.58	4.63
m-xylene	5.42	5.47	5.50	5.55	5.57	5.62	5.61
p-xylene	5.06	5.17	5.16	5.22	5.22	5.24	5.26
methanol	0.32	0.32	0.32	0.31	0.31	0.30	0.30
ethanol	0.56	0.54	0.53	0.52	0.51	0.51	0.51
1-propanol	0.77	0.73	0.71	0.69	0.67	0.66	0.65
acetonitrile	0.60	0.61	0.62	0.62	0.63	0.63	0.64
ethyl acetate	2.93	2.98	3.01	3.04	3.07	3.18	3.25
acetone	1.11	1.12	1.13	1.16	1.17	1.23	1.25
dichloromethane	0.46	0.49	0.53	0.55	0.58	0.60	0.64
trichloromethane	0.28	0.32	0.33	0.39	0.42	0.45	0.50
tetrachloromethane	2.09	2.18	2.40	2.52	2.65	2.81	2.83

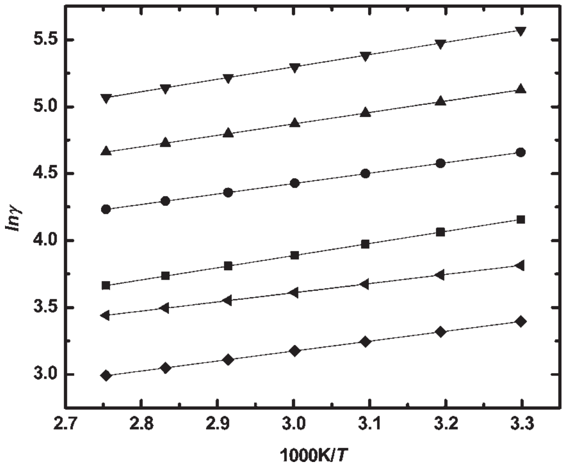

Figure 1. Plot of ln γ_i^∞ of [BMIM][NO_3] vs $1/T$ for the solutes: ■, hexane; ●, heptane; ▲, octane; ▼, nonane; ◆, cyclohexane; left-pointing triangle, methylcyclohexane; —, linear correlation.

literature:[20]

$$Y_i = -\frac{\ln \gamma_i^{\infty\mathrm{res}}}{\nu_i} + \frac{{\delta_i}^2}{RT} = \frac{2\delta_s}{RT}\delta_i - \frac{{\delta_s}^2}{RT} \qquad (6)$$

This equation shows that there is a linear relation between Y_i and the solute solubility parameter δ_i for a given solvent and temperature T. The value of the solvent solubility parameter δ_s can be obtained from the slope of this line. The values of experimental ln γ^∞ were obtained from this work, the values of ln $\gamma^{\infty\mathrm{comb}}$ were calculated by eq 4, and the values of ln $\gamma^{\infty\mathrm{res}}$ can be calculated from eq 3. The values of Y_i for each solvent were then calculated by eq 6 based on these results. Information on ν_i, δ_i, and r_i were obtained from the literature.[21] The van der Waals volume of the IL was calculated by the group contribution method.[22]

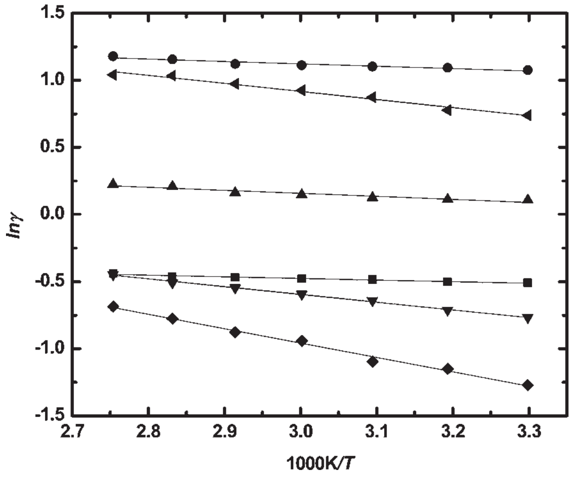

Figure 2. Plot of ln γ_i^∞ of [BMIM][NO_3] vs $1/T$ for the solutes: ■, acetonitrile; ●, ethyl acetate; ▲, acetone; ▼, dichloromethane; ◆, trichloromethane; left-pointing triangle, tetrachloromethane; —, linear correlation.

The linear dependence between Y_i and δ_i at 303.15 K obtained from the γ^∞ data on [BMIM][NO_3] was displayed in Figure 5. Values of solubility parameters of [BMIM][NO_3] from (303.15 to 363.15) K given in Table 5 indicate that δ approaches a constant in the range of temperature studied. The average value of the solubility parameter is 25.73 $(\mathrm{J \cdot cm^{-3}})^{1/2}$. This observation is in good agreement with results obtained from the Kamlet−Taft equation[23,24] or by Mutelet et al.[25−27] which indicate that the solubility parameters show a slight dependence on the temperature.

The selectivities, S_{ij}^{∞}, can be calculated according to the equation: $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$. In this work, the selectivities of [BMIM][NO_3] for the alkane/aromatic hydrocarbon, and aromatic (1)/aromatic (2) hydrocarbon are calculated from the $\gamma_{i,3}^{\infty}$ data. They are listed in Table 6 together. From Table 6 it can be seen that the ionic liquid is suitable for the benzene or toluene/alkane separations. This ionic liquid shows good separation ability as compared with the experimental selectivities of sulfolane.[28]

The values of selectivity S_{ij}^{∞} for the separation of a hexane/benzene mixture at T = 298.15 K using ILs with the cation $[BMIM]^+$ and different anions are summarized in the literature.[2] The value S_{ij}^{∞} of the current work is 36.62, and for a given cation $[BMIM]^+$, S_{ij}^{∞} values for the anions [$MDEGSO_4$] and [BF_4]

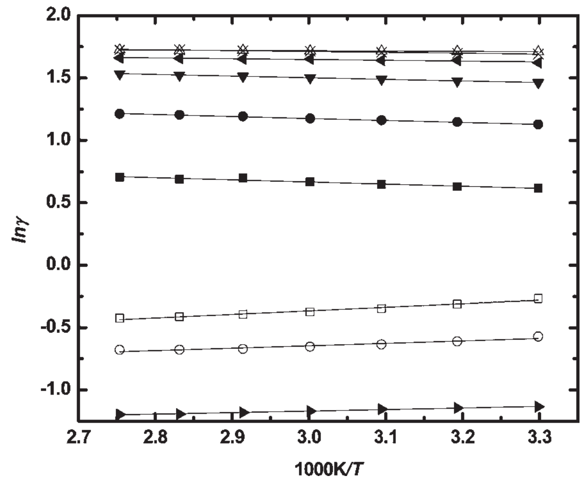

Figure 3. Plot of ln γ_i^{∞} of [BMIM][NO_3] vs $1/T$ for the solutes: ■, benzene; ●, toluene; ◆, ethylbenzene ▼, *o*-xylene; ×, *m*-xylene; left-pointing triangle, *p*-xylene; right-pointing triangle, methanol; ○, ethanol; □, 1-propanol; —, linear correlation.

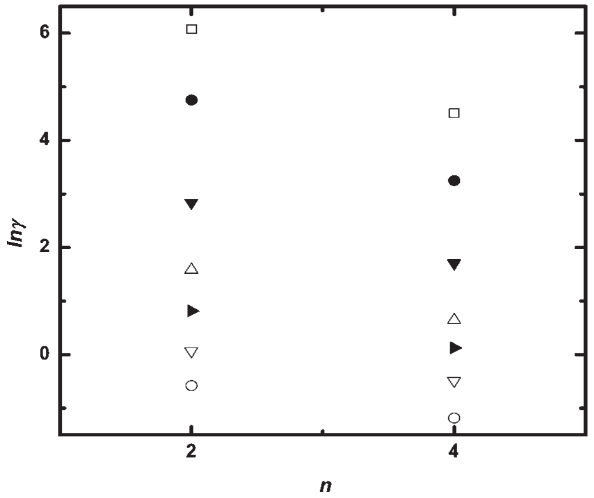

Figure 4. ln γ_i^{∞} of solutes in 1-alkyl-3-methylimidazolium nitrate ([EMIM][NO_3] and [BMIM][NO_3]) as a function of carbon chain n: □, heptanes; ●, cyclohexane; △, benzene; ▼, *m*-xylene; ○, methanol; ▽, acetonitrile; right-pointing triangle, acetone.

Table 4. Coefficients of eq 1, a and b, Calculated (at 298.15 K) Activity Coefficients at Infinite Dilution ($\gamma_{i,298.15K}^{\infty}$) of Solutes in [BMIM][$NO_3$] Using eq 1, Values of $H_i^{E,\infty}$ Derived from eq 1, and Standard Deviation σ

solute *i*	r_i^a $cm^3 \cdot mol^{-1}$	δ_i^a $(J \cdot cm^{-3})^{0.5}$	a	b K	$\gamma_{i,298.15K}^{\infty}$	$H_i^{E,\infty}$ $kJ \cdot mol^{-1}$	σ
hexane	68.260	14.988	1.166	0.907	67.167	7.541	0.016
heptane	78.490	15.208	2.085	0.780	110.069	6.485	0.009
octane	88.720	15.360	2.314	0.852	176.426	7.084	0.026
nonane	98.950	15.527	2.529	0.922	276.557	7.666	0.004
cyclohexane	61.400	16.700	0.943	0.744	31.091	6.186	0.002
methylcyclohexane	70.46	16.27	1.565	0.681	47.017	5.662	0.020
benzene	48.400	18.706	1.181	−0.171	1.834	−1.422	0.015
toluene	59.510	18.346	1.654	−0.159	3.065	−1.322	0.004
ethylbenzene	69.74	18.043	1.793	−0.025	5.523	−0.208	0.009
o-xylene	70.66	18.453	1.894	−0.131	4.284	−1.089	0.004
m-xylene	70.66	18.09	1.917	−0.068	5.407	−0.565	0.013
p-xylene	70.66	17.838	1.838	−0.064	5.078	−0.532	0.023
methanol	21.710	29.523	−1.538	0.123	0.324	1.021	0.004
ethanol	31.940	26.421	−1.230	0.195	0.562	1.620	0.006
1-propanol	42.17	24.557	−1.219	0.285	0.767	2.366	0.010
acetonitrile	28.37	24.094	−0.113	−0.121	0.595	−1.006	0.003
ethyl acetate	52.77	18.346	1.653	−0.177	2.885	−1.472	0.032
acetone	39.040	19.774	0.835	−0.226	1.080	−1.879	0.015
dichloromethane	34.71	20.378	1.136	−0.577	0.450	−4.797	0.004
trichloromethane	43.5	19.028	2.264	−1.074	0.262	−8.930	0.005
tetrachloromethane	52.3	17.577	2.721	−0.602	2.021	−5.005	0.043

[a] Obtained from ref 21.

are 39.7 and 37.3, respectively, which are much higher than those for the anions [$OcOSO_3$], [CF_3SO_3], and [NO_3]. It means that the activity coefficients and intermolecular interactions of different solutes in IL are very much dependent on the chemical structure of the anion.

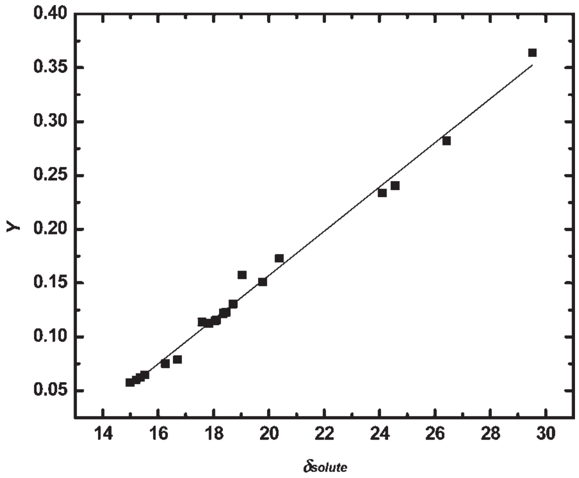

Figure 5. Residual function Y for [BMIM][NO_3] versus solute solubility parameters δ_{solute}. Regression line: $Y = 0.02055\delta_{\text{solute}} - 0.25382$ ($R^2 = 0.9916$).

Table 5. Solubility Parameters δ $(J\cdot cm^{-3})^{1/2}$ of the Ionic Liquid[a]

T/K	intercept	slope	δ from intercept	δ from slope	R^2
303.15	−0.2538	0.0206	25.29	25.88	0.992
313.15	−0.2466	0.0199	25.33	25.92	0.992
323.15	−0.2405	0.0194	25.41	26.02	0.993
333.15	−0.2340	0.0189	25.45	26.07	0.993
343.15	−0.2279	0.0183	25.49	26.09	0.993
353.15	−0.2220	0.0178	25.52	26.13	0.994
363.15	−0.2158	0.0173	25.52	26.11	0.994

[a] R^2: correlation coefficient.

The experimental retention time t_r and the input pressure P_i obtained in the measurement of activity coefficient at infinite dilution of organic solutes in ionic liquid [BMIM][NO_3] are listed in the Supporting Information. Based on these data, the influences of saturation vapor pressure P_i^o and B_{11} and B_{12}, taken from different data source, on the activity coefficients at infinite dilution in the ionic liquid at 323.15 K, respectively, are calculated and listed in Tables 7 and 8. From the results of $|\gamma_{i,\text{exp}}^\infty - \gamma_{i,\text{cal}}^\infty|/\gamma_{i,\text{exp}}^\infty$, where $\gamma_{i,\text{exp}}^\infty$ is the value calculated in this work based on ref 8 as listed in Table 3 and $\gamma_{i,\text{ref}}^\infty$ is the value calculated based on a different data source of P_i^o and B_{11} and B_{12}.

Table 7. Influence of Saturation Vapor Pressure (P_i^0) on Activity Coefficients at Infinite Dilution of Heptane, Benzene, Toluene, and *o*-Xylene in the Ionic Liquid 1-Butyl-3-methylimidazolium Nitrate at 323.15 K

solute	P_i^0	γ_i^∞	$|\gamma_{i,\text{exp}}^\infty - \gamma_{i,\text{cal}}^\infty|/\gamma_{i,\text{exp}}^\infty\cdot 10^4$
heptane	18.897[a]	89.9564	
	18.89717[b]	89.9556	0.089
	18.89907[c]	89.9467	1.078
benzene	36.1712[a]	1.9153	
	36.25399[b]	1.9110	22.45
	36.2689[c]	1.9102	26.63
toluene	12.294[a]	3.1957	
	12.2937[b]	3.1958	0.313
	12.29816[c]	3.1946	3.442
o-xylene	3.3977[a]	4.4428	
	3.397668[b]	4.4428	0
	3.401092[c]	4.4384	9.904

[a] Obtained from ref 8. [b] Obtained from ref.13. [c] Obtained from ref 29.

Table 6. Selectivities S_{12}^∞ of Solute (1)/Solute (2) at Infinite Dilution for Ionic Liquid [BMIM][NO_3] and Sulfolane at T = 323.15 K

		(2)					
	(1)	benzene	toluene	ethylbenzene	*o*-xylene	*m*-xylene	*p*-xylene
[BMIM][NO_3]	hexane	27.74	16.62	9.55	11.96	9.65	10.28
	heptane	47.00	28.16	16.18	20.26	16.35	17.42
	octane	73.93	44.29	25.45	31.87	25.71	27.40
	nonane	113.79	68.18	39.17	49.05	39.58	42.17
	cyclohexane	13.40	8.03	4.61	5.78	4.66	4.97
	methylcyclohexane	20.59	12.34	7.09	8.88	7.16	7.63
	benzene		0.599	0.344	0.431	0.348	0.371
	toluene	1.67		0.575	0.719	0.581	0.619
	ethylbenzene	2.90	1.740		1.252	1.010	1.077
	o-xylene	2.320	1.390	0.799		0.807	0.860
	m-xylene	2.875	1.723	0.990	1.239		1.065
	p-xylene	2.698	1.617	0.929	1.163	0.939	
sulfolane[a]	*n*-pentane	14.97	9.79	6.50	na	na	na
	n-hexane	20.52	13.41	8.90	na	na	na
	n-heptane	26.94	17.61	11.69	na	na	na
	cyclohexane	12.52	8.18	5.43	na	na	na
	methylcyclo-hexane	17.36	11.35	7.53	na	na	na

[a] Ref 28.

Table 8. Influence of B_{11} and B_{12} on Activity Coefficients at Infinite Dilution of Methylcyclohexane and *o*-Xylene in the Ionic Liquid 1-Butyl-3-methylimidazolium Nitrate from (303.15 to 323.15) K

T/K	B_{11}	B_{12}	γ_i^∞	$\lvert\gamma_{i,\mathrm{exp}}^\infty - \gamma_{i,\mathrm{cal}}^\infty\rvert/\gamma_{i,\mathrm{exp}}^\infty \cdot 10^3$
		o-Xylene		
303.15	−4286.46[a]	−172.012[a]	4.312	3.01
	−4228[b]	−128.6[b]	4.325	
313.15	−3725.6[a]	−159.218[a]	4.377	2.74
	−3796[b]	−119[b]	4.389	
323.15	−3275.11[a]	−147.52[a]	4.440	2.70
	−3419[b]	−110[b]	4.452	
		Methylcyclohexane		
303.15	−2508.28[a]	−152.999[a]	45.287	3.40
	−2827[b]	−119[b]	45.441	
313.15	−2241.49[a]	−141.614[a]	42.160	3.58
	−2537[b]	−109.2[b]	42.311	
323.15	−2020.92[a]	−131.171[a]	39.408	3.96
	−2309[b]	−100.9[b]	39.564	

[a] Ref 13. [b] Ref 30.

It can be seen that different literature and calculation equations have a little influence on the activity coefficients.

CONCLUSIONS

Infinite dilution activity coefficients have been measured for a series of polar and nonpolar organic solutes at the temperature range of (303.15 to 363.15) K. The results in comparison with another ionic liquid demonstrate a significant influence of chain length of the alkyl on cation of the ILs on the $\gamma_{i,3}^\infty$ values. The partial molar excess enthalpies at infinite dilution of the ionic liquids were calculated for the solutes from the temperature dependence of the experimental activity coefficients at infinite dilution. The solubility parameters of the ionic liquid were also determined by the regular solution theory. These data are very important in understanding the nature of ILs.

ASSOCIATED CONTENT

S **Supporting Information.** Experimental retention time t_r and the input pressure P_i obtained in the measurement of activity coefficient at infinite dilution of organic solutes in ionic liquid 1-butyl-3-methylimidazolium nitrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Zhou, Q.; Wang, L.-S.; Wu, J.-S.; Li, M.-Y. Activity coefficients at infinite dilution of polar solutes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2007**, *52*, 131–134.

(2) Ge, M.-L.; Wang, L.-S.; Li, M.-Y.; Wu, J.-S. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-butyl-3-methylimidazolium trifluoromethanesulfonate using gas-liquid chromatography. *J. Chem. Eng. Data* **2007**, *52*, 2257–2260.

(3) Li, Y.; Wang, L.-S.; Cai, S.-F. Mutual solubility of alkyl imidazolium hexafluorophosphate ionic liquids and water. *J. Chem. Eng. Data* **2010**, *55*, 5289–5293.

(4) Zhang, Y.; Wang, L.-S.; Li, Y. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2009**, *54*, 2887–2890.

(5) Domańska, U.; Marciniak, A. Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate. *J. Phys. Chem. B* **2008**, *112*, 11100–11105.

(6) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. The use of gas-liquid chromatography to determine activity coefficients and second virial coefficients of mixtures. *Proc. R. Soc. London* **1966**, *A295*, 259–270.

(7) Everett, D. H. Effect of gas imperfection of G. L. C. measurements: A refined method for determining activity coefficients and second virial coefficients. *Trans. Faraday Soc.* **1965**, *61*, 1637–1645.

(8) Boublik, T.; Fried, V.; Hala, E. *The Vapor Pressure of Pure Substances*, Physical Science Data 17; Elsevier: Amsterdam, The Netherlands, 1984.

(9) Yang, X.-J.; Wu, J.-S.; Ge, M.-L.; Wang, L.-S.; Li, M.-Y. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-hexyl-3-methyl-imidazolium trifluoromethanesulfonate using gas-liquid chromatography. *J. Chem. Eng. Data* **2008**, *53*, 1220–1222.

(10) Tsonopoulos, C. An empirical correlation of second virial coefficients. *AIChE J.* **1974**, *20*, 263–272.

(11) Tsonopoulos, C. Second virial coefficients of polar haloalkanes. *AIChE J.* **1975**, *21*, 827–829.

(12) Tsonopoulos, C. Second virial coefficients of water pollutants. *AIChE J.* **1978**, *24*, 1112–1115.

(13) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, McGraw-Hill Book Co.: New York, 2001.

(14) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Eqilibria*, 2nd ed.; Prentice Hall: New York, 1986.

(15) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. *DECHEMA Chemistry Data Series IX*, Part 1; DECHEMA: Frankfurt/Main, 1986.

(16) Domańska, U.; Paduszyński, K. Gas—liquid chromatography measurements of activity coefficients at infinite dilution of various organic solutes and water in tri-iso-butylmethylphosphonium tosylate ionic liquid. *J. Chem. Thermodyn.* **2010**, *42*, 707–711.

(17) Li, Y.; Wang, L. S.; Zhang, Y. Activity coefficients at infinite dilution of polar solutes in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate using gas liquid chromatography. *J. Chem. Eng. Data* **2010**, *55*, 1732–1734.

(18) Sobota, M.; Dohnal, V.; Vrbka, P. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methyl-imidazolium nitrate. *J. Phys. Chem. B* **2009**, *113*, 4323–4332.

(19) Kikic, I.; Alessi, P.; Rasmussen, P.; Fredenslund, A. On the combinatorial part of the UNIFAC and UNIQUAC models. *Can. J. Chem. Eng.* **1980**, *58*, 253–258.

(20) Foco, G. M.; Bottini, S. B.; Quezada, N.; de la Fuente, J. C.; Peters, C. J. Activity coefficients at infinite dilution in 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids. *J. Chem. Eng. Data* **2006**, *51*, 1088–1091.

(21) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill Book Co.: New York, 1999.

(22) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.

(23) Lee, S. H.; Lee, S. B. The hildebrand solubility parameters, cohesive energy densities and internal energies of 1-alkyl-3-methylimidazolium-based room temperature ionic liquids. *Chem. Commun.* **2005**, 3469–3471.

(24) Swiderski, K.; McLean, A.; Gordon, C. M.; Vaughan, D. H. Estimates of internal energies of vaporisation of some room temperature ionic liquids. *Chem. Commun.* **2004**, 2178–2179.

(25) Revelli, A.-L.; Mutelet, F.; Jaubert, J.-N. Partition coefficients of organic compounds in new imidazolium based ionic liquids using inverse gas chromatography. *J. Chromatogr., A* **2009**, *1216*, 4775–4786.

(26) Mutelet, F.; Jaubert, J.-N. Measurement of activity coefficients at infinite dilution in 1-hexadecyl-3-methylimidazolium tetrafluoroborate ionic liquid. *J. Chem. Thermodyn.* **2007**, *39*, 1144–1150.

(27) Mutelet, F.; Butet, V.; Jaubert, J.-N. Application of inverse gas chromatography and regular solution theory for characterization of ionic liquids. *Ind. Eng. Chem. Res.* **2005**, *44*, 4120–4127.

(28) Möllmann, C.; Gmehling, J. Measurement of activity coefficients at infinite dilution using gas-liquid chromatography. 5. results for *N*-methylacetamide, *N*,*N*-dimethylacetamide, *N*,*N*-dibutylformamide, and sulfolane as stationary phases. *J. Chem. Eng. Data* **1997**, *42*, 35–40.

(29) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill Book Co: Boston, 2005.

(30) Yan, P.-F.; Yang, M.; Liu, X.-M.; Wang, C.; Tan, Z.-C.; Urs, W.-B. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate [EMIM][TCB] using gas—liquid chromatography. *J. Chem. Thermodyn.* **2010**, *42*, 817–822.