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Activity Coefficients at Infinite Dilution of Polar Solutes in 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate Using Gas–Liquid Chromatography

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Activity coefficients at infinite dilution γ_i^∞ of 17 polar solutes (linear and branched C_1 to C_5 alcohols, acetonitrile, acetone, 1,4-dioxane, tetrahydrofuran, ethyl acetate, and chloromethanes) in the ionic liquid 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4]) have been measured by the gas−liquid chromatographic 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 $H_i^{E,\infty}$ of the solutes in the ionic liquid were also derived from the temperature dependence of the γ_i^∞ values.

Introduction

This work continues our studies on the determination of activity coefficients at infinite dilution γ_i^∞ of various solutes (*i*) by the gas–liquid chromatographic method (GLC) for hydrophilic ionic liquids (ILs).[1–4] Heintz et al. and Letcher et al. measured γ_i^∞ of various solutes in a number of ILs. A complete list of literature containing their work has been given in our previous work.[4]

Experimental Section

The ionic liquid 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4]) was purchased from Hang Zhou Chemer Chemical Co., Ltd. Its mass fraction purity was greater than 99 % according to manufacturer's specifications, with the following certified mass fraction of impurities: w (Cl^-) < $5 \cdot 10^{-4}$, water > 10^{-3} . The solutes including linear and branched C_1 to C_5 alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-propanol, 2-methylpropanol, 2-butanol, 3-methylbutanol), acetonitrile, acetone, 1,4-dioxane, tetrahydrofuran, ethyl acetate, and chloromethanes (dichloromethane, trichloromethane, tetrachloromethane) were purchased from Beijing Chemical Reagents Company. Their mass fraction purities were greater than 99 %. The solutes were used without further purification.

Before use, the IL was subjected to vacuum evaporation at (323 to 333) K over 24 h to remove possible traces of solvents and moisture. The GLC apparatus, column preparation, packing method, experimental process, and the method of checking the stability of the experimental conditions in this work are the same as those described previously.[2–4] In this work, dry nitrogen was used as the carrier gas, and ethanol was used as solvent to coat the ionic liquid onto the solid support. The volume of the samples injected into the GC probes was about (0.1 to 3) μL. The experiments were carried out over a temperature range from (303.15 to 363.15) K.

Table 1. Relative Uncertainties in the Measured and Derived Quantities

parameters	relative 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_3	± 0.5 %
γ_i^∞	± 4 %

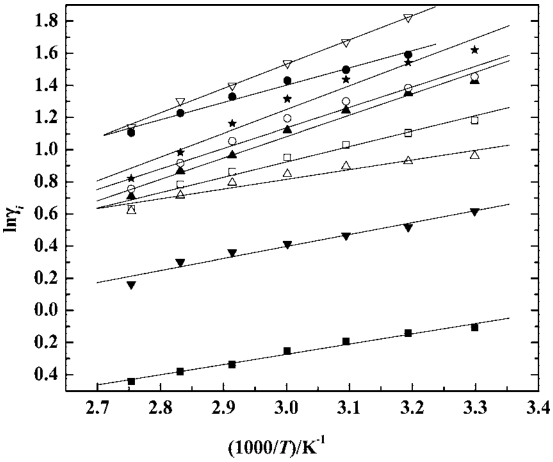

Figure 1. Plot of ln γ_i^∞ vs 1/T for the solutes together with a linear correlation of the data: ■, methanol; ▼, ethanol; Δ, 2-propanol; □, 1-propanol; ▲, 2-methylpropanol; ○, 2-butanol; ★, 1-butanol; ●, 3-methylbutanol; ▽, 1-pentanol; — linear correlation.

The γ_i^∞ values were obtained by the equation proposed by Cruickshank et al.[5] and Everett. [6] The way of deducing γ_i^∞ from the experiments was given in our previous work.[2–4] The data needed for the equations have been obtained in the following way. Molar volumes of solutes V_i^0 were estimated using their experimental densities; partial molar volumes of solute at infinite dilution V_i^∞ have been assumed to be equal to V_i^0. Values of P_i^0 for all solutes were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.[7] B_{11} is the second virial coefficient of the solute (1), and B_{12} is the cross second virial coefficient of the solute (1) with the carrier gas (2). B_{11}

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Table 2. Experimental Activity Coefficients at Infinite Dilution γ_i^∞ for Various Solutes in the Ionic Liquid 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate at Temperatures of (303.15 to 363.15) K

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
				Alcohols			
methanol	0.898	0.869	0.823	0.777	0.713	0.684	0.642
ethanol	1.856	1.680	1.596	1.514	1.436	1.353	1.179
1-propanol	3.260	3.014	2.807	2.594	2.372	2.192	1.883
1-butanol	5.053	4.670	4.204	3.725	3.197	2.671	2.271
1-pentanol[a]		6.195	5.312	4.651	4.054	3.678	3.125
2-propanol	2.617	2.529	2.450	2.335	2.212	2.045	1.856
2-methylpropanol	4.170	3.866	3.473	3.067	2.623	2.382	2.032
2-butanol	4.281	3.988	3.670	3.302	2.868	2.503	2.129
3-methylbutanol[a]		4.908	4.463	4.176	3.777	3.415	3.021
				Solvents			
acetonitrile	1.401	1.386	1.376	1.367	1.361	1.350	1.344
acetone	2.472	2.528	2.551	2.612	2.663	2.711	2.736
1,4-dioxane	2.963	3.077	3.137	3.168	3.241	3.285	3.352
tetrahydrofuran	6.030	5.983	5.947	5.917	5.881	5.824	5.775
ethyl acetate	8.863	8.838	8.786	8.750	8.708	8.659	8.627
				Chloromethanes			
dichloromethane	1.668	1.743	1.840	1.927	2.010	2.087	2.174
trichloromethane	1.141	1.293	1.398	1.525	1.646	1.776	1.909
tetrachloromethane	8.108	8.630	9.131	9.581	9.997	10.370	10.669

[a] Values are measured over the temperature range (313.15 to 363.15) K.

and B_{12} have been estimated according to the equations suitable for polar liquids by Tsonopolous's method.[8] Critical parameters needed for the calculations were available from the literature.[8] The cross critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and acentric factor ω_{ij} were calculated using equations given in the literature.[8,9]

According to the error propagation law, γ_i^∞ is estimated to have an uncertainty within ± 4 %. The uncertainties in the measured and derived quantities are listed in Table 1.

Results and Discussion

Experimental results of γ_i^∞ for 17 solutes in [PDMIM][BF$_4$] at different temperatures are presented in Table 2. They were correlated with temperature by the following equation

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

The plots of measured ln γ_i^∞ vs $1/T$ values and the linear fit of their data are given in Figures 1 to 3, which show a fairly good fitting quality of eq 1. According to the Gibbs–Helmholtz equation, the values 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, which are listed in Table 3 as well as the coefficients a and b, the standard deviation σ of the fitted equations, and the values of γ_i^∞ at 298.15 K. The relative uncertainty of $H_i^{E,\infty}$ is about ± 10 %.

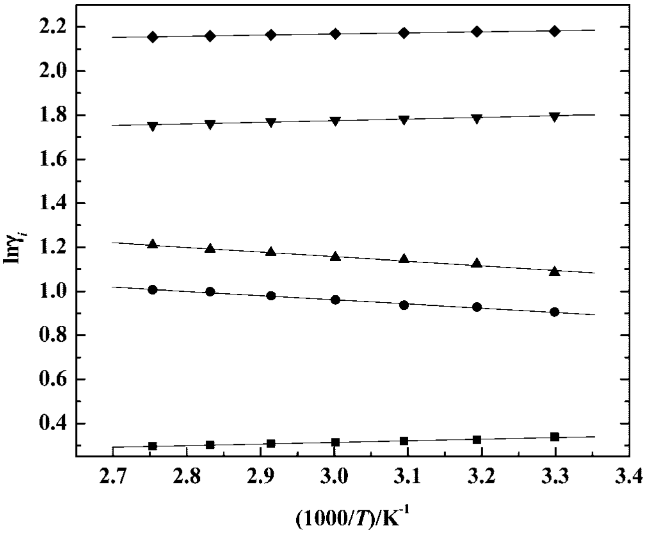

Figure 2. Plot of ln γ_i^∞ vs $1/T$ for the solutes together with a linear correlation of the data: ■, acetonitrile; ●, acetone; ▲, 1,4-dioxane; ▼, tetrahydrofuran; ♦, ethylacetate; — linear correlation.

Table 3. Coefficients a and b of Equation 1, 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	$\gamma_{i298.15\mathrm{K}}^\infty$	$H_i^{E,\infty}$/kJ·mol^{-1}	σ
		Alcohols			
methanol	−2.1862	637.76	0.95	5.30	0.018
ethanol	−1.8351	744.19	1.94	6.19	0.031
1-propanol	−1.9509	958.27	3.54	7.97	0.035
1-butanol	−3.1865	1478.71	5.89	12.29	0.059
1-pentanol	−3.0117	1514.55	7.91	12.59	0.016
2-propanol	−1.0007	605.38	2.80	5.03	0.035
2-methylpropanol	−2.9174	1332.93	4.73	11.08	0.039
2-butanol	−2.6951	1276.81	4.89	10.62	0.053
3-methylbutanol	−1.8319	1077.65	5.94	8.96	0.025
		Solvents			
acetonitrile	0.0903	74.33	1.40	0.62	0.0011
acetone	1.5354	−191.35	2.44	−1.59	0.0040
1,4-dioxane	1.7889	−210.58	2.95	−1.75	0.0061
tetrahydrofuran	1.5472	76.03	6.06	0.63	0.0023
ethylacetate	2.0142	51.28	8.90	0.43	0.0011
		Chloromethanes			
dichloromethane	2.1240	−489.57	1.62	−4.07	0.0027
trichloromethane	3.1908	−923.26	1.10	−7.68	0.0091
tetrachloromethane	3.7735	−506.77	7.96	−4.21	0.0080

The γ_i^∞ values of the linear n-alkanols increase with increasing chain length. Branching in the alkane skeleton slightly reduces the γ_i^∞ values in comparison with the corresponding linear alcohol. The γ_i^∞ values of other polar solutes was in the order of ethylacetate > tetrahydrofuran > 1,4-dioxane > acetone > acetonitrile. The γ_i^∞ values of dichloromethane and trichloromethane are similar and clearly lower than that for tetrachloromethane. This behavior indicates that more polar solutes have better solubilities in the ionic liquid because of the preferred attractive interaction of polar molecules with the charged ions of the IL, and they were prone to strongly retain in the IL stationary phase. Furthermore, the γ_i^∞ values for 1-pentanol and

Table 4. Selectivity S_{ij}^{∞} at Infinite Dilution for Different Ionic Liquids at 323.15 K

ionic liquids	hexane (i)/ methanol (j)	hexane (i)/ chloroform (j)
1-propenyl-3-methylimidazolium bromide[a]	139.28	100.28
1-propenyl-3-octylimidazolium bromide[a]	52.35	63.57
1-propenyl-3-decylimidazolium bromide[a]	49.35	64.54
1-propenyl-3-dodecylimidazolium bromide[a]	29.4	36.75
1-propyl boronic acid-3-octylimidazolium bromide[a]	455.75	79.26
1-propyl boronic acid-3-decylimidazolium bromide[a]	109	45.42
1-propyl boronic acid-3-dodecylimidazolium bromide[a]	116.25	24.47
1-butyl-3-methylimidazolium tetrafluoroborate[b]	83.93	42.19
1-butyl-3-methylimidazolium trifluoromethanesulfonate[c]	51.02	36.72
this work[d]	227.10	133.77

[a] Ref 11. [b] Refs 2 and 3. [c] Ref 4. [d] The γ_i^{∞} value of hexane at 323.15 K was from ref 1.

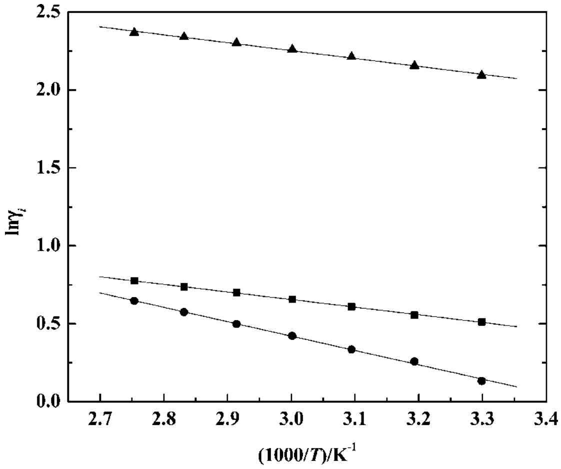

Figure 3. Plot of ln γ_i^{∞} vs 1/T for the solutes together with a linear correlation of the data: ■, dichloromethane; ●, trichloromethane; ▲, tetrachloromethane; — linear correlation.

3-methylbutanol at 303.15 K were not determined since the retention times were so far beyond the scope allowed by GC.

The selectivity S_{ij}^{∞} is defined as $S_{ij}^{\infty} = \gamma_{i,\mathrm{IL}}^{\infty}/\gamma_{j,\mathrm{IL}}^{\infty}$[10] (where i, j refers to the solutes to be separated). The values of S_{ij}^{∞} for hexane (i)/methanol (j) and hexane (i)/chloroform (j) were calculated at T = 323.15 K and are presented in Table 4. The results indicated that [PDMIM][BF$_4$] can play an important role for the separation of chloroform and methanol from alkanes.

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