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Activity Coefficients at Infinite Dilution of Polar Solutes in 1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate Using Gas−Liquid Chromatography

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Activity coefficients at infinite dilution of methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-propanol, 2-methyl-1-propanol, 2-butanol, 3-methyl-1-butanol, acetonitrile, ethyl acetate, acetone, tetrahydrofuran, 1,4-dioxane, dichloromethane, and trichloromethane in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate 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 were also determined for the solutes from the temperature dependence of the experimental activity values.

Introduction

This work continues our studies on the determination of activity coefficients γ_i^∞ at infinite dilution of various solutes (i) by the gas−liquid chromatographic method (GLC) for functional ionic liquids like 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([Hydemim][BF_4]).[1] By introducing a functional group, ionic liquids can be widely used in organic synthesis,[2] electrochemistry,[3] 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. The functional ionic liquids may have potential applications in extraction and such industrial processes according to our investigation on their thermodynamic properties.

Experimental Section

The ionic liquid [Hydemim][BF_4] was purchased from Lanzhou Institute of Chemical Physics of the Chinese Academy of Science. Its mass fraction purity was greater than 95 % according to manufacturer's specifications and impurities [$w(Cl^-) < 5\cdot10^{-4}$]. Water mass fractions analyzed by Karl Fischer analysis were less than $4\cdot10^{-4}$. The solutes provided by Beijing Chemical Reagents Company were analytical reagents and were used without further purification. Dry helium was used as the carrier gas, and ethanol was used as solvent to coat the ionic liquid onto the solid support.

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 Zhang et al.[1,4–6] The γ_i^∞ values were obtained by the equation proposed by Cruickshank et al.[7] and Everett.[8] For all solutes, values of P_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.[9] The calculated results of vapor pressure of these solutes from T = (303.15 to 363.15) K have been reported in our previous paper.[10] The data needed for the equations have been obtained in the following way. Molar volumes of solutes V_i^0 were estimated using experimental values of their densities; partial molar volumes of solute at infinite dilution V_i^∞ have been assumed to be equal to V_i^0. Values of the second virial coefficient of the solute (B_{11}) and the cross second virial coefficient (B_{12}) of the solute (1) with the carrier gas (2) have been estimated according to the equations suitable for polar liquids by Tsonopolous's method.[11–13] Critical parameters needed for the calculations were available from the literature.[14] 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.[15,16] The uncertainty of the mass of the stationary phase measurement was within ± 0.0001 and the flow rate of the carrier gas within ± 0.1 $cm^3\cdot min^{-1}$. Volumes of the samples injected into the GC probes were from (0.1 to 2) μL. The temperature of the GC column was maintained constant to within ± 0.05 K. According to the error propagation law, γ_i^∞ is estimated to have a relative uncertainty within ± 0.06. The uncertainties in the measured or derived quantities are listed in Table 1.

Results and Discussion

The values of γ_i^∞ of different polar solutes in [Hydemim][BF_4] obtained over a temperature range of (303.15 to 363.15) K are listed in Table 2. 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, the standard deviation σ of the fitted equation, γ_i^∞, 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 3. The plots of measured ln γ_i^∞ versus 1/T values are given in Figures 1 and 2, which showed a fairly good fitting quality of eq 1. The γ_i^∞ values for 1-pentanol and 3-methylbutanol at 303.15 K were not determined since the retention times were far beyond the scope allowed by GC.

A small activity coefficient of a solute in a solvent usually means that they have large mutual solubilities and strong molecular interactions. The γ_i^∞ values of the linear n-alkanols increase with increasing chain length. Branching in the alkanol skeleton slightly reduces the γ_i^∞ values in comparison with the corresponding linear alcohol and also increases with the

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Table 1. Uncertainties in the Measured and Derived Quantities

parameters	$t_r - t_G$	U_0	P_i	P_0	J	P_i^0	n_{IL}	γ_i^∞
uncertainty	± 3 %	± 0.5 %	± 0.6 %	± 0.02 %	± 1 %	0.25 %	± 0.5 %	± 7.1 %

Table 2. Experimental Activity Coefficients at Infinite Dilution for Various Polar Solutes in the Ionic Liquid [Hydemim][BF$_4$] as the Stationary Phase at Temperatures of (303.15 to 363.15) K

solutes	T = 303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K
methanol	1.03	0.961	0.913	0.886	0.851	0.824	0.800
ethanol	2.45	2.25	2.09	1.97	1.88	1.79	1.71
1-propanol	4.76	4.35	4.04	3.70	3.49	3.27	3.09
1-butanol	8.54	7.66	6.91	6.19	5.72	5.30	4.83
1-pentanol[a]		12.4	10.9	10.1	9.14	8.35	7.61
2-propanol	4.02	3.83	3.67	3.55	3.41	3.29	3.18
2-methylpropanol	7.86	7.18	6.55	6.10	5.69	5.27	4.94
2-butanol	6.88	6.48	6.11	5.78	5.49	5.30	4.94
3-methylbutanol[a]		11.5	10.2	9.19	8.23	7.51	6.86
acetonitrile	0.850	0.864	0.878	0.892	0.906	0.917	0.932
ethyl acetate	7.16	7.23	7.33	7.45	7.67	7.87	7.99
acetone	1.53	1.58	1.66	1.71	1.77	1.83	1.88
tetrahydrofuran	4.36	4.51	4.65	4.79	4.92	5.06	5.19
1,4-dioxane	1.57	1.81	1.76	1.94	1.94	2.14	2.12
dichloromethane	2.73	2.83	2.95	3.06	3.18	3.29	3.38
trichloromethane	4.24	4.38	4.47	4.55	4.67	4.78	4.86

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

Table 3. Coefficients of Equation 1, *a* and *b*, Calculated (at 298.15 K) Activity Coefficients at Infinite Dilution ($\gamma_{i,298.15\mathrm{K}}^\infty$) Using Equation 1, Values of $H_i^{\mathrm{E},\infty}$ Derived from Equation 1, Standard Deviation *σ*, Calculated (at 313.15 K) Henry's Coefficient $K_{i,313.15}$ from Equation 2, and $\rho_{298.15\mathrm{K}}$ of Solutes

solute i	a	b / K	$\gamma_{i,298.15\mathrm{K}}^\infty$	$H_i^{\mathrm{E},\infty}$ / kJ·mol^{-1}	σ	$K_{i,313.15}$ / kPa	$\rho_{298.15\mathrm{K}}$[a]
methanol	−1.466	448.6	1.04	3.73	0.0100	34.0	0.7866
ethanol	−1.231	639.4	2.49	5.32	0.0097	40.2	0.7851
1-propanol	−1.0612	793.3	4.95	6.6	0.0061	30.5	0.7998
1-butanol	−1.280	1037.9	9.03	8.63	0.0069	18.1	0.8060
1-pentanol	−0.9836	1095.6	14.7	9.11	0.0067	10.4	0.8112
2-propanol	−0.0138	425.5	4.11	3.54	0.0022	54.4	0.7813
2-methyl-1-propanol	−0.7412	849.3	8.22	7.06	0.0040	27.7	0.7978
2-butanol	−0.0173	590.3	7.12	4.91	0.0072	40.6	0.8026
3-methyl-1-butanol	−1.335	1183.3	13.9	9.84	0.0030	15.2	0.8070
acetonitrile	0.3936	169.0	0.841	1.41	0.0011	20.6	0.7766
ethyl acetate	2.658	−212.5	6.99	−1.77	0.0089	75.2	0.8940
acetone	1.660	−374.1	1.50	−3.11	0.0033	40.1	0.7844
tetrahydrofuran	2.524	−318.7	4.28	−2.65	0.0002	181	0.8820
1,4-dioxane	2.236	−531.1	1.58	−4.42	0.0037	103	1.0280
dichloromethane	2.326	−402.1	2.66	−3.34	0.0033	288	1.3162
trichloromethane	2.257	−245.6	4.19	−2.04	0.0033	211	1.4797

[a] Densities of solutes are obtained from ref 21.

Table 4. Selectivity Values S_{12}^∞ for Hexane (1)/Methanol (2) at Infinite Dilution for Different Ionic Liquids

solvents	T/K	S_{12}^∞	ref
trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide	298.15	0.8	8
n-acryloyloxypropyl-*N*-methylimidazolium bromide	313.15	820	9
n-methacryloyloxyhexyl-*N*-methylimidazolium bromide	313.15	552	9
triethylsulphonium bis(trifluoromethylsulfonyl)imide	298.15	13.3	10
4-methyl-*N*-butyl-pyridinium bis(trifluoromethylsulfonyl)imide	298.15	8.4	11
1,3-dimethylimidazolium dimethylphosphate	313.15	1865	12
1-ethyl-3-methylimidazolium diethylphosphate	313.15	544.1	12
[Hydemim][BF$_4$]	298.15	471	this work[a]

[a] The γ_i^∞ of hexane is obtained from ref 1.

increasing carbon number, and the effect decreases with temperature. This indicates that the molecular interaction increases with the increasing polarity of the solutes, and more polar solutes have better solubilities in the ionic liquid for the attractive interaction of polar molecules with the charged ions of the IL. These properties are very common in ionic liquids described by other literature.[17,18] The same effect can be encountered by changing the position of the hydroxyl group in the alkanols (1-alkanol to 2-alkanol), such as 1-propanol to 2-propanol and 1-butanol to 2-butanol. For the linear alkanol and acetonitrile, $H_i^{\mathrm{E},\infty}$ was positive. The value of $H_i^{\mathrm{E},\infty}$ for ethyl acetate, acetone, 1,4-dioxane, tetrahydrofuran, and chloromethanes became negative. This is probably due to the high polarizibility of the oxygen and chlorine atoms and the special strength of ion-induced dipole interactions as well.

Table 4 shows selectivities S_{12}^∞ for a separation problem: hexane (1)/methanol (2) for different functionalized ionic liquids. The highest literature value of selectivity $S_{12}^\infty = 1865$ was obtained for 1,3-dimethylimidazolium dimethylphosphate.[20] The S_{12}^∞ of hexane (1)/methanol (2) ($S_{12}^\infty = 471$) obtained with [Hydemim][BF$_4$] are similar to those, obtained with *n*-methacryloyloxyhexyl-*N*-methylimidazolium bromide,[19] indicated that the [Hydemim][BF$_4$] is also good for separation.

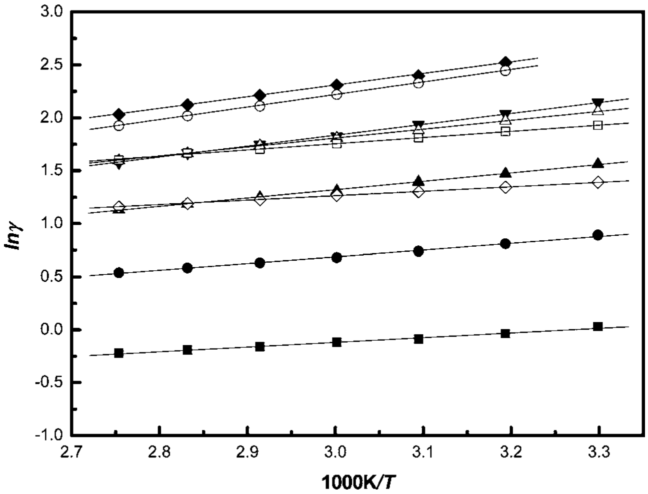

Figure 1. Plot of ln γ_i^∞ vs 1/T for the solutes: ■, methanol; ●, ethanol; ▲, 1-propanol; ▼, 1-butanol; ◆, 1-pentanol; ◇, 2-propanol; △, 2-methylpropanol; □, 2-butanol; ○, 3-methylbutanol; solid line indicates a linear correlation.

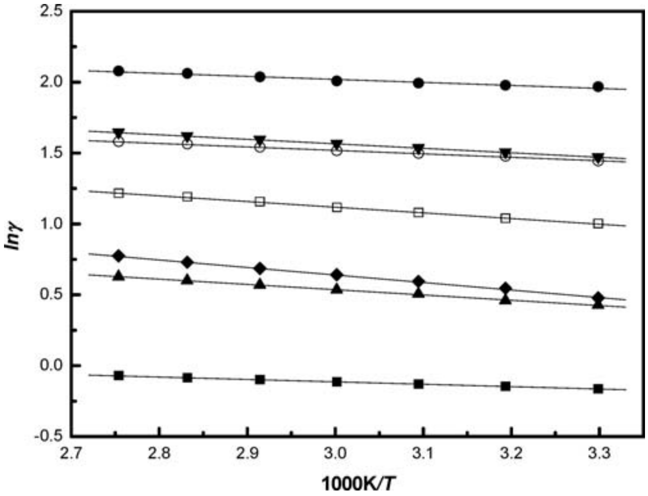

Figure 2. Plot of ln γ_i^∞ vs 1/T for the solutes: ■, acetonitrile; ●, ethyl acetate; ▲, acetone; ▼, tetrahydrofuran; ◆, 1,4-dioxane; □, dichloromethane; ○, trichloromethane; solid line indicates a linear correlation.

Values of γ_i^∞ can be used to calculate Henry's coefficient K_i defined by

$$K_i = \lim_{x_i \to 0} \frac{P_i}{x_i} = P_{i0}\gamma_i^\infty \qquad (2)$$

where P_i is the partial pressure of the solute, P_{i0} is the vapor pressure of the pure liquid solute, and x_i is mole fraction in the liquid mixture. Equation 2 allows the approximate calculation of the partition of the solute between the liquid and the vapor phase at low values of x_i. The Henry's coefficient K_i of polar solutes in the ionic liquid [Hydemim][BF$_4$] have been calculated at T = 313.15 K (listed in Table 3). It has been found that methanol and tetrahydrofuran have almost the same boiling points, but their partition in this ionic liquid is different: K_i(tetrahydrofuran)/K_i(methanol) = 5.3. It indicates that this ionic liquid can be used for removing trail tetrahydrofuran from methanol by an absorbent process.

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