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

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Activity coefficients at infinite dilution γ_i^∞ of 17 alkanes, alkenes, and alkyl benzenes in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate were determined by gas chromatography using the ionic liquid as the stationary phase. The measurements were carried out at different temperatures between 303.15 K and 343.15 K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $H_i^{\mathrm{E},\infty}$ of the organic solutes in the ionic liquids have been derived.

Introduction

Ionic liquids (ILs) are low melting point salts that represent an exiting new class of reaction solvents. Being composed entirely of ions, they have a negligible vapor pressure and can be prepared from a wide range of cations and anions. Some of the ILs are miscible in water, alcohol, and so forth, depending on anions and cations. The key attraction of ILs is their possibility to be tuned by varying the nature of the cations and anions. Because of this combination of properties, ILs could find application in many fields, such as organic synthesis, catalytic reactions, and multiphase separations. An IL that did not hydrolyze was reported by Wilkes and Zaworotko in 1992.[1] Up to now, the applications of the ILs have been concentrated mostly in the synthesis. Physicochemical and thermophysical properties have not been studied systematically.

Activity coefficients at infinite dilution of a solute *i* (γ_i^∞) can be used to quantify the volatility of the solute as well as to provide information on the intermolecular energy between solvent and solute.[2,3] Values of γ_i^∞ are important for the selection of solvents for extraction and extractive distillation and the reliable design of thermal separation processes when the last traces of impurities have to be removed. The experimental data of γ_i^∞ are also important from a theoretical point of view to understand liquid theory. So, a study on thermophysical properties is important to predict the properties and characteristics of the ILs.[4]

Because ILs have a negligible vapor pressure, the most suitable method for measuring limiting activity coefficients of volatile solutes in ILs is the gas−liquid chromatographic (GLC) method using the ionic liquid as the stationary phase. Heintz et al.[5−11] and Letcher et al.[12−14] already measured γ_i^∞ of various solutes in [BMPy][BF_4] (4-methyl-*n*-butylpyridinium tetrafluoroborate),[5−6] [EMIM][$N(CF_3SO_2)_2$] (1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) amide),[7−9] [EMMIM] [$N(CF_3SO_2)_2$] (1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) amide),[7] [BMIM][$N(CF_3SO_2)_2$] (1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl) imide),[10] [OMIM][BF_4] (1-methyl-3-octylimidazolium tetrafluoroborate),[11] [HMIM][PF_6] (1-hexyl-3-methylimidazolium hexafluorophosphate),[12] [HMIM][BF_4] (1-hexyl-3-methylimidazolium tetrafluoroborate),[13] and [OMIM][Cl] (1-methyl-3-octylimidazolium chloride)[14] by the gas−liquid chromatographic method using the ionic liquid as the stationary phase. The major body of this work was concentrated on hydrophobic ILs, while the hydrophilic ILs were less investigated.

In this work, the γ_i^∞ values of 17 hydrocarbons including alkanes, alkenes, and alkyl benzenes in the hydrophilic ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate were measured over the temperature range (303.15 to 343.15) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $H_i^{\mathrm{E},\infty}$ of the organic solutes in the ILs have been derived.

Experimental Section

Materials. The hydrocarbons provided by Beijing Chemical Reagents Company were of analytical grade. Since the GLC process separated the solutes from any impurities, the solutes were used without further purification.

Preparation of [BMIM][BF_4]. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate was prepared by metathesis reactions from the corresponding bromide.

First, 1-butyl-3-methylimidazolium bromide was synthesized. Butyl bromide (1.1 mol) was added dropwise to 1-methylimidazole (1 mol) with agitation at 343 K. The reaction mixture was refluxed for 24 h, when cooled to room temperature, ethyl acetate was added to the mixture. The ethyl acetate was removed by a separating funnel followed by the addition of fresh ethyl acetate, and this step was repeated four times. The remaining ethyl acetate was removed by rotary evaporation, and the solution was dried under high vacuum at (343 to 353) K for at least 6 h to get 1-butyl-3-methylimidazolium bromide ([BMIM]-[Br]) at very high yield (99 %).

Second, the tetrafluoroborate salt was prepared by metathesis reactions from the corresponding bromide. [BMIM][Br] (0.1 mol) was dissolved in the acetonitrile (50 mL), and ammonium tertrafluorobarate (0.11 mol) was added. The mixture was refluxed for at least 24 h. When it was cooled to room temperature, the NH_4Br precipitate was removed by filtration. Any remaining precipitate was removed by further filtration at this step. The remaining acetonitrile was removed by rotary

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evaporation to obtain crude 1-butyl-3-methylimidazolium tetrafluorobarate. The crude [BMIM][BF_4] was dissolved in dichloromethane (50 mL) and cooled below 5 °C. Deionized water and a separation funnel were also cooled to below 5 °C. The dichloromethane solution was washed with cooled deionized water (30 mL) five times until the aqueous solution did not form any precipitate with 0.1 $mol \cdot L^{-1}$ $AgNO_3$ solution. The solvent dichloromethane was removed by rotary evaporation, and [BMIM][BF_4] was dried under high vacuum at (323 to 333) K for at least 6 h.

The chemical shifts for the ^{1}H NMR spectrum (parts per million, D_2O) appear as follows: δ 8.575 [s, 1H, H(2)], 7.390 [s, 1H, H(4)], 7.350 [s, 1H, H(5)], 4.133 [t, 2H, NCH_2], 3.817 [s, 3H, NCH_3], 1.809 [m, 2H, $NCH_2{-}CH_2$], 1.295 [m, 2H, $NCH_2CH_2{-}CH_2$], and 0.853 [t, 3H, CH_3]. The ^{13} C NMR spectrum (parts per million, D_2O) contains peaks: 138.625 [C(2)], 126.155 [C(4)], 124.861 [C(5)], 51.931 [$N{-}CH_2$], 38.233 [NCH_3], 33.980 [$NCH_2{-}CH_2$], 21.445 [$NCH_2CH_2{-}CH_2$], and 15.288 [CH_3]. Impurity peaks were not observed in the ^{1}H NMR and ^{13} C NMR spectra, and there is a solvent (D_2O) peak at $\delta = 4.653$ in the ^{1}H NMR spectrum. The chemical shift of other peaks corresponded to the structure of [BMIM][BF_4]. The water content of the product [BMIM][BF_4] was determined to be about 200 ppm by the Karl Fischer titration. The purity of the ionic liquid was >99 %.

Chromosorb PAW-DMDCS 100/120 mesh was used as a solid support for the ionic liquid in the GC column. Before use, Chromosorb was subjected to vacuum treatment with heating to remove traces of adsorbed moisture. Chromosorb and the GC column were purchased from Varian.

Apparatus and Procedure. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb in a solution of the ionic liquid in dichloromethane followed by evaporation of the solvent using a rotating evaporator. The Chromosorb was weighed before and after the coating process. The experiments were performed by a Varian chrompack CP-3800 gas chromatograph equipped with a thermionic conductivity detector. Dry helium was used as the carrier gas. The GC columns with length of 100 cm and inside diameter of 0.40 cm have been used. The mass of the stationary phase (1-butyl-3-methylimidazolium tetrafluoroborate) was 1.8250 g. The uncertainty of the mass of the stationary phase measurement was within ±0.0001. To avoid possible residual adsorption effects of the solvent on Chromosorb, the mass fraction of ionic liquid was ≈30 % of the support material. The column was equably filled with the help of an ultrasound vibrator to provide uniform packing of the material in the column.

Volumes of the samples injected into the GC probes were from (0.1 to 2) μL. No differences in retention times t_r were found by injecting individual pure components or their mixtures. Experiments were carried out over the temperature range (303.15 to 343.15) K. The temperature of the GC column was maintained constant to within ±0.05 K. At a given temperature, each experiment was repeated at least three times to check the reproducibility. The differences in the retention times of the three measurements were generally reproducible within (0.01 to 0.05) min. Absolute values of retention times varied between 1.0 and ≈400 min depending on the individual solute. At each temperature, values of the dead time t_G identical to the retention time of the nonretainable component were measured. Methane[15] was used as the nonretainable component under the assumption that the effect of the solubility of methane in 1-butyl-3-methylimidazolium tetrafluoroborate was negligible.

To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the carrier gas stream, the measurements of retention times were repeated systematically every 6−8 h for hexane and benzene. No changes of the retention times were observed during 80 h of continuous operation.

Cruickshank et al.[16] and Everett[17] developed the following equation for obtaining the $\gamma_{i,3}^{\infty}$ value for a volatile solute (i) in an involatile solvent (3) from GC

$$\ln \gamma_{i,3}^{\infty} = \ln\left(\frac{n_3RT}{V_N p_i^0}\right) - \frac{B_{11} - V_i^0}{RT} p_i^0 + \frac{2B_{12} - V_i^{\infty}}{RT} J p_0 \qquad (1)$$

In eq 1, $\gamma_{i,3}^{\infty}$ is the activity coefficient of solute i at infinite solution in the stationary phase, p_i^0 is the vapor pressure of the pure liquid solute i, n_3 is the number of moles of the stationary phase component on the column, and V_N is the standardized retention volume obtained by

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{p_{0w}}{p_0}\right] \qquad (2)$$

where t_r is the retention time, t_G is the dead time, U_0 is the flow rate, measured by a soap bubble flow meter, T_{col} is the column temperature, T_f is the flow meter temperature, p_{0w} is the saturation pressure of water at T_f, and p_0 is the pressure at the column outlet.

The second and third terms in eq 1 are correction terms that arise from the nonideality of the mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} is the mixed virial coefficient of the solute (1) with the carrier gas helium (2), V_i^0 is the liquid molar volume of pure solute, and V_i^{∞} is the partial molar volume of solute in the ionic liquid at infinite dilution.

The data for calculating the correction terms have been obtained in the following way. For all solutes, values of p_i^0 were taken from the Antoine equation, with Antoine coefficients given by Boublik et al.[18] 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 B_{11} have been estimated according to the equations suitable for nonpolar liquids by Tsonopolous's method[19] with an uncertainty of $< \pm 10$ $cm^3 \cdot mol^{-1}$. Critical parameters needed for the calculations were available from the literature.[19] Values of B_{12} have also been estimated according to Tsonopolous's method.[19] The mixed critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed factor ω_{ij} were calculated by using equations given in the literatures.[19,20]

The factor J appearing in eqs 1 and 2 corrects for the influence of the pressure drop along the column given by[21]

$$J = \frac{3}{2}\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \qquad (3)$$

where p_i and p_0 are the inlet and outlet pressures of the GC column, respectively.

The outlet pressure p_0 was kept equal to the atmospheric pressure. The pressure drop ($p_i - p_0$) was varied between (20.3 and 101.3) kPa, providing suitable retention times with sharp peaks. The pressure drop and outlet pressure were measured using a membrane manometer with an uncertainty of ±0.2 kPa.

Retention time, dead time, column temperature, flow rate, input and output pressure, and the mass of stationary phase all have experimental errors.

Table 1. Experimental Activity Coefficients at Infinite Dilution for Various Solutes in the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate as the Stationary Phase at Temperatures of (303.15 to 343.15) K

solute *i*	$T = 303.15$ K	$T = 313.15$ K	$T = 323.15$ K	$T = 333.15$ K	$T = 343.15$ K
			Alkanes		
pentane	40.66	39.72	38.07	36.29	35.83
hexane	60.80	57.47	54.22	50.55	47.03
heptane	92.45	86.71	81.65	78.90	71.52
octane	139.1	136.0	127.0	118.7	111.1
nonane	224.3	193.3	187.0	178.8	169.8
decane	413.5	335.4	319.9	296.4	278.7
cyclohexane	32.41	30.21	28.30	26.88	24.55
methylcyclohexane	48.71	45.59	42.42	39.84	37.33
2,2,4-trimethylpentane	92.69	88.61	83.82	79.48	75.49
			Alkenes		
cyclohexene	14.13	13.54	12.89	12.42	11.89
styrene	2.287	2.293	2.339	2.411	2.475
			Alkyl Benzenes		
benzene	1.739	1.758	1.770	1.798	1.830
toluene	2.913	2.935	2.949	2.990	3.030
ethylbenzene	5.612	5.537	5.485	5.416	5.366
o-xylene	4.198	4.180	4.161	4.160	4.141
m-xylene	5.248	5.241	5.232	5.227	5.217
p-xylene	4.968	5.150	5.277	5.326	5.474

Table 2. Coefficients of eq 4, Standard Deviation σ, γ_i^∞ at 298.15 K Calculated Using eq 4, $H_i^{E,\infty}$, and Values of Derived from eq 4

solute *i*	*a*	*b*/K	s	$\gamma^\infty_{i\ 298\mathrm{K}}$ [a]	$H_i^{E,\infty}$/J·mol^{-1} [b]
			Alkanes		
pentane	2.5330	356.28	0.0102	41.6	2962
hexane	2.9853	597.00	0.0109	64.1	4964
heptane	2.4640	625.38	0.0179	95.7	5200
octane	1.8808	679.54	0.0198	146.6	5650
nonane	2.5021	889.91	0.0050	241.5	7399
decane	2.8163	957.81	0.0047	415.2	7963
cyclohexane	1.1893	696.44	0.0125	33.9	5790
methylcyclohexane	1.6134	689.17	0.0035	50.6	5730
2,2,4-trimethylpentane	2.7617	538.24	0.0055	96.2	4475
			Alkenes		
cyclohexene	1.1645	450.41	0.0030	14.5	3745
styrene	1.7457	−301.59	0.0129	2.08	−2507
			Alkyl Benzenes		
benzene	0.9752	−128.80	0.0047	1.72	−1071
toluene	1.3989	−100.84	0.0040	2.89	−838.4
ethylbenzene	1.3411	116.25	0.0009	5.65	966.5
o-xylene	1.3228	33.750	0.0012	4.20	280.6
m-xylene	1.6074	15.356	0.0002	5.25	127.7
p-xylene	2.3924	−237.65	0.0069	4.93	−1796

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

The retention time t_r and the dead time t_G have absolute deviations of ±0.05 min and 0.01 min, respectively, and values of $(t_r - t_G)$ lie between 1 min and 400 min. Hence, the maximal experimental errors can be 3.6 %. In a similar way, the error limits of the flow rate U_0 are estimated to be ±0.5 % at column temperature and ±0.01 % at the flow meter temperature. Because the input and output pressures may, in principle, be measured as frequently as necessary, it was more important to eliminate short-term fluctuations in pressure and to facilitate achievement of the long-term stability of the experimental conditions. Taking into account this fact, the error limits of the input pressure p_i and the output pressure p_0 are estimated to be ±0.6 % and ±0.02 %, respectively. Then, the error of J in eq 3 was estimated to be not larger than ±1 %. The experimental error of the saturation pressures is estimated to be (0.01 to 0.25) %. Reliable estimation of the experimental error of the mole number n_3 of ionic liquid is rather difficult because of the uncertainty in estimating the amount of ionic liquid that the adsorption of air moisture during weighing of the stationary phase and the filling process of the column.

Taking into account the possible influence of these factors, the uncertainty of determining n_3 was estimated to be ±0.5 %. Furthermore, the good reproducibility of γ_i^∞ obtained with different amounts of stationary phases justifies the error limits adopted for n_3.

According to the error propagation law, γ_i^∞ is estimated to have an uncertainty within ±4 %.

Results and Discussion

The values of γ_i^∞ of different solutes (alkanes, alkenes, and alkyl benzenes) in 1-butyl-3-methylimidazolium tetrafluoroborate obtained at several temperatures were listed in Table 1. They have been approximated by the linear regression

$$\ln \gamma_{i,3}^\infty = a + \frac{b}{(T/K)} \tag{4}$$

The coefficients a and b and standard deviation σ as well as the values of γ_i^∞ at 298 K calculated based on eq 4 with these coefficients are given in Table 2. The quality of the linear regression was very good because the standard deviation σ lies at about 0.01.

The activity coefficients 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) reduces 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 reduction 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 increased with increasing size of the alkyl group (see Table 2).

The selectivity at infinite dilution for the ionic liquid, which indicated suitability of a solvent for separating mixtures of components 1 and 2 by extraction was given by[22]

$$S_{12}^\infty = \frac{\gamma_{1/\mathrm{IL}}^\infty}{\gamma_{2/\mathrm{IL}}^\infty} \tag{5}$$

The values of S_{12}^∞ for three isomeric xylenes at 303.15 K were 1.25 (*m*-xylene/*o*-xylene), 1.06 (*m*-xylene/*p*-xylene), and 1.18 (*p*-xylene/*o*-xylene), respectively. This result indicated that 1-butyl-3-methylimidazolium tetrafluoroborate never was an ideal extraction solvent for the separation of xylenes. The values of S_{12}^∞ for alkanes and alkyl benzenes were estimated to be larger than 1 from Table 1, therefore, ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate can play an important role for the separation of alkyl benzenes from alkanes.

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_i^{\mathrm{E},\infty}$ can be directly obtained from the slope of a straight line derived from eq 4

$$\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)} = \frac{H_i^{\mathrm{E},\infty}}{R} \tag{6}$$

where R was the gas constant. The values of $H_i^{\mathrm{E},\infty}$ for the compounds studied were listed in Table 2. $H_i^{\mathrm{E},\infty}$ was positive and increases with chain length of the linear alkanes. The introduction of double bonds decreases the positive values of $H_i^{\mathrm{E},\infty}$. For molecules containing the aromatic ring, $H_i^{\mathrm{E},\infty}$ became negative; however, increasing the size of the alkyl group in the aromatic ring compensated for this effect, and in the case of ethylbenzene, $H_i^{\mathrm{E},\infty}$ was again positive.

The results of γ_i^∞ and $H_i^{\mathrm{E},\infty}$ suggest that the intermolecular interactions between the ionic liquid and the solute become stronger with an increasing number of polarizable electrons present in double bonds and aromatic rings, probably due to the increasing strength of ion-induced dipole interactions. As suggested by Heintz,[5−11] a quantitative interpretation of the results of γ_i^∞ and $H_i^{\mathrm{E},\infty}$ has to be given in terms of an extended theory of electrolyte solutions which accounts for ionic as well as for polar and nonpolar interactions. In this respect, the results obtained in this work as well as in the previous ones provide a basis for such theoretical investigations.

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