Activity Coefficients at Infinite Dilution of Polar Solutes in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Gas−Liquid Chromatography

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Activity coefficients at infinite dilution γ_1^∞ of 17 polar solutes included linear and branched C_1 to C_5 alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4-dioxane, and cyclohexanone 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 temperatures between (303.15 and 343.15) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $H_1^{E,\infty}$ of the organic solutes in the ionic liquid have been derived.

Introduction

An ionic liquid (IL) that did not hydrolyze was reported by Wilkes and Zaworotko in 1992.[1] ILs have been considered as new and promising solvents for green industrial chemistry. Being composed entirely of ions, they have a negligible vapor pressure and can be prepared from a wide range of cations and anions. 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. With this increased application, physicochemical and thermophysical properties of ILs are required.

Activity coefficients at infinite dilution of a solute i (γ_1^∞) 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_1^∞ 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. Heintz and coworkers[4−12] and Letcher et al.[13−15] already measured γ_1^∞ of various solutes in 4-methyl-*n*-butylpyridinium tetrafluoroborate ([BMPy][BF_4]),[4,5] 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) amide ([EMIM][$N(CF_3SO_2)_2$]),[6−8] 1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) amide ([EMMIM] [$N(CF_3SO_2)_2$]),[6] 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl) imide ([BMIM][$N(CF_3SO_2)_2$]),[9] 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF_4]),[10] 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([HMIM]-[$N(CF_3SO_2)_2$]),[11] trimethylbutylammonium bis(trifluoromethylsulfonyl) imide ([Me_3BuN][$N(CF_3SO_2)_2$]),[12] 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF_6]),[13] 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF_4]),[14] and 1-methyl-3-octylimidazolium chloride ([OMIM][Cl])[15] by the gas−liquid chromatographic using the IL as the stationary phase.

Several properties such as density,[16−23] viscosity,[16−23] conductivity,[16−22] heat capacities,[18−19] vapor pressure,[20] solubilities,[24] and γ_1^∞ [25] of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and its mixtures were reported.

This work continues our study,[25] and we report γ_1^∞ of 17 polar solutes including linear and branched C_1 to C_5 alcohols, chlorinated methane, acetone, acetonitrile, ethyl acetate, 1,4-dioxane, and cyclohexanone in the hydrophilic IL [BMIM][BF_4] over temperature range (303.15 to 343.15) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $H_1^{E,\infty}$ of the organic solutes in the ILs have been derived.

Experimental Section

Materials. All compounds provided by Beijing Chemical Reagents Company were of analytical grade (mass fraction was about 99 %). Since the GLC process separated the solutes from any impurities, the solutes were used without further purification. 1-Butyl-3-methylimidazolium tetrafluoroborate synthesized as described previously.[25] The water content of the [BMIM][BF_4] was determined to be about 200 ppm by the Karl Fischer titration. Chromosorb PAW-DMDCS 100/120 mesh was used as solid support for the IL 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 IL was performed by dispersing a certain portion of Chromosorb in a solution of the IL 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 with a Varian chrompack CP-3800 gas chromatograph equipped with a thermal conductivity detector. Dry helium was used as the carrier gas. The GC columns had a length of 100 cm and inside diameter of 0.40 cm. 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 g. To avoid possible residual adsorption effects of the solvent on Chromosorb, the mass fraction of the IL was about 30 % of the support material. The column was filled with the help of an ultrasound vibrator in order to provide uniform packing of the material in the column.

Volumes of the samples injected into the GC probes were from (0.1 to 3) μL. No differences in retention times t_r were

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10.1021/je060305e CCC: $37.00

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 1	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
			Alcohols		
methanol	0.813	0.716	0.646	0.596	0.529
ethanol	1.588	1.391	1.272	1.165	1.067
1-propanol	2.802	2.480	2.227	1.958	1.638
1-butanol	4.141	3.675	3.296	2.984	2.720
1-pentanol	6.957	5.906	5.153	4.561	4.004
2-propanol	2.628	2.222	1.861	1.661	1.532
2-butanol	3.848	3.439	3.116	2.792	2.562
2-methylpropanol	4.135	3.558	3.209	2.865	2.617
3-methylbutanol	6.628	5.736	5.079	4.532	4.075
			Chloromethanes		
dichloromethane	1.099	1.148	1.197	1.236	1.281
trichloromethane	1.114	1.207	1.285	1.360	1.432
tetrachloromethane	5.728	6.090	6.271	6.419	6.522
			Other Polar Solutes		
acetone	1.157	1.186	1.209	1.232	1.254
acetonitrile	0.734	0.742	0.752	0.757	0.768
ethyl acetate	3.301	3.338	3.357	3.386	3.408
1,4-dioxane	1.528	1.536	1.549	1.559	1.572
cyclohexanone[a]	2.638(323.15K)	2.625(333.15K)	2.607(343.15K)	2.583(353.15K)	2.568(363.15K)

[a] Values are measured over the temperature range (323.15 to 363.15) K.

found by injecting individual pure components or their mixtures. Experiments were carried out over 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 difference of the retention times of the three measurements were generally reproducible within (0.01 to 0.05) min. Absolute values of retention times varied between (20 and ≈500) 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[26] 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.

In order 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 to 8) h for hexane and benzene. No changes of the retention times were observed during 80 h of continuous operation.

Cruickshank et al.[27] and Everett[28] developed the following equation for obtaining the $\gamma_{1,3}^{\infty}$ for a volatile solutes (1) in an involatile solvent (3) from GC:

$$\ln \gamma_{1,3}^{\infty} = \ln\left(\frac{n_3RT}{V_N p_1^0}\right) - \frac{B_{11} - V_1^0}{RT} p_1^0 + \frac{2B_{12} - V_1^{\infty}}{RT} J p_0 \qquad (1)$$

In eq 1, $\gamma_{1,3}^{\infty}$ is the activity coefficient of solute 1 at infinite solution in the stationary phase, p_1^0 is the vapor pressure of the pure liquid solute 1, n_3 is the number of moles of the stationary phase component on the column, 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 flowmeter, T_{col} is the column temperature, T_f is the flowmeter temperature, p_{0w} is saturation pressure of water at T_f, and p_0 is the pressure at the column outlet.

Table 2. Coefficients of Equation 4, Standard Deviation σ, γ_1^{∞} at 298.15 K Calculated Using Equation 4, and Values of $H_1^{E,\infty}$ Derived from Equation 4

solute 1	a	b / K	σ	$\gamma^{\infty}_{1\,298K}$[a]	$H_1^{E,\infty}$ / J·mol^{-1} [b]
		Alcohols			
methanol	−3.7900	1014.7	0.0118	0.86	8436
ethanol	−2.8960	1084.8	0.0111	1.66	9019
1-propanol	−3.4274	1357.3	0.0235	3.08	11285
1-butanol	−2.1844	1420.2	0.0028	4.39	11808
1-pentanol	−2.7512	1432.4	0.0071	7.48	11909
2-propanol	−3.7772	1064.0	0.0296	2.79	8846
2-butanol	−2.1616	1092.2	0.0046	4.08	9081
2-methylpropanol	−2.4848	1180.0	0.0119	4.36	9811
3-methylbutanol	−2.2679	1259.1	0.0056	7.06	10468
		Chloromethanes			
dichloromethane	1.3969	−394.31	0.0022	1.08	−3278
trichloromethane	2.2514	−647.90	0.0060	1.08	−5387
tetrachloromethane	2.8412	−327.93	0.0137	5.70	−2726
		Other Polar Solutes			
acetone	0.8309	−207.21	0.0012	1.15	−1723
acetonitrile	0.0693	−114.95	0.0021	0.73	−955.7
ethyl acetate	1.4636	−81.376	0.0012	3.29	−676.6
1,4-dioxane	0.6696	−74.896	0.0013	1.52	−622.7
cyclohexanone	0.7163	82.473	0.0014	2.70	685.7

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

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_1^0 is the liquid molar volume of pure solute, and V_1^{∞} 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_1^0 were taken from the Antoine equation, with Antoine coefficients given by Boublik et al.[29] Molar volumes of solutes V_1^0 were calculated from their literature densities;[30] partial molar volumes of sulute at infinite dilution V_1^{∞} have been assumed to be equal toV_1^0. Values of B_{11} have been estimated according to the equations suitable for polar liquids by Tsonopolous's method[31] with an uncertainty of < ± 10 cm^3·mol^{-1}. Critical parameters

Table 3. Selectivity at Infinite Dilution S_{12}^{∞} (Hexane (1)[a] + Solutes (2)) for the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate at 303.15 K

hexane (1) + alcohol (2)	S_{12}^{∞}	hexane (1) + chloromethane (2)	S_{12}^{∞}
hexane (1) + methanol (2)	74.78	hexane (1) + dichloromethane (2)	55.32
hexane (1) + ethanol (2)	38.29	hexane (1) + trichloromethane (2)	54.58
hexane (1) + propanol (2)	21.70	hexane (1) + tetrachloromethane (2)	10.61
hexane (1) + 2-propanol (2)	23.14	hexane (1) + acetone (2)	52.55

[a] The value of γ_1^{∞} of hexane was from ref 25.

needed for the calculations were available from the literature.[31] Values of B_{12} have also been estimated according to Tsonopoulos's method.[31] 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 literature.[31,32]

The factor J appearing in eqs 1 and 2 corrects for the influence of the pressure drop along the column given by[33]

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

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. The error estimation procedure has been described in a previous work.[25] The values of γ_1^{∞} are estimated to have an uncertainty within ± 4 %.

Results and Discussion

The values of γ_1^{∞} of polar solutes in 1-butyl-3-methylimidazolium tetrafluoroborate measured at temperature of (303.15 to 343.15) K were listed in Table 1. The values of γ_1^{∞} for cyclohexanone were measured at temperatures of (323.15 to 363.15) K because the retention times of cyclohexanone were so far beyond the scope allowed by the GC detector on the same experimental condition at 303.15 K. They have been approximated by the linear regression

$$\ln \gamma_{1,3}^{\infty} = a + \frac{b}{(T/\mathrm{K})} \tag{4}$$

The coefficients a and b and the standard deviation σ as well as the values of γ_1^{∞} at 298 K calculated based on eq 4 with these coefficients are given in Table 2.

The activity coefficients of the linear *n*-alkanols increase with increasing chain length. The branching of the alkane skeleton (2-propanol, 2-butanol, 2-methylpropanol, or 3-methylbutanol) reduces the value of γ_1^{∞} in comparison with the corresponding linear alcohols 1-propanol, 1-butanol, and 1-pentanol. The values of $\gamma_1^{\infty}$of dichloromethane and trichloromethane at 298.15 K were within the experimental uncertainty, but introducing the fourth chlorine atom increases the γ_1^{∞} substantially. This result for dichloromethane, trichloromethane, and tetrachloromethane was similar to those reported in ref 5. IL stationary phases seem to have a dual nature. They appear to act as a low-polarity stationary phase with nonpolar compounds. However, molecules with strong proton donor groups were strongly retained.[34] Dichloromethane and trichloromethane are polar solutes; tetrachloromethane is a nonpolar solute. Since the interactions of polar solute molecules with the IL liquid are stronger than for nonpolar molecules, the retention time of dichloromethane and trichloromethane should be greater than tetrachloromethane. The values of γ_1^{∞} for dichloromethane and trichloromethane were clearly smaller than that for tetrachloromethane. This behavior indicated that more polar solutes have better solubilities in the IL because of the preferred attractive interaction of polar molecules with the charged ions of the IL. The values of γ_1^{∞} for other polar solutes was in the order ethyl acetate > cyclohexanone >1,4-dioxane > acetone > acetonitrile. An increase in temperature results in γ_1^{∞} for alkanols and chlorinated methanes and cyclohexanone decreases; however, for acetone, acetonitrile, ethyl acetate, and 1,4-dioxane increases result.

The selectivity at infinite dilution for the IL, which indicated suitability of a solvent for separating mixtures of components 1 and 2 by extraction is given by[35]

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

The values of the S_{12}^{∞} for alkanes (values of γ_1^{∞} from ref 25) + alkanols, chlorinated methanes, and other polar solutes were estimated to be larger than 1 from Table 1. For example, the values of the S_{12}^{∞} for hexane (1) + alkanol (2) and hexane (1) + chlorinated methane (2) are presented in Table 3. Therefore, the IL 1-butyl-3-methylimidazolium tetrafluoroborate can play an important role for the separation of alkanols, chlorinated methanes, acetone, acetonitrile, ethyl acetate, 1,4-dioxane, and cyclohexanone from alkanes.

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_1^{\mathrm{E},\infty}$ can be directly obtained from straight line derived from

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

where R is the gas constant. The values of $H_i^{\mathrm{E},\infty}$ for the compounds studied are listed in Table 2.

$H_1^{\mathrm{E},\infty}$ is positive and increases with chain length of the linear alkanols. Branching of the alkyl chain in alkanols decreases slightly the positive values of $H_1^{\mathrm{E},\infty}$ as compared to the linear isomers. For chlorinated methanes, acetone, acetonitrine, ethyl acetate, and 1, 4-dioxane, $H_1^{\mathrm{E},\infty}$ is negative. This is most probably due to the high polarizibility of the chlorine atoms and the special strength of ion-induced dipole interactions.

As suggested by Heintz and co-workers,[4−10] a quantitative interpretation of the results of γ_1^{∞} and $H_1^{\mathrm{E},\infty}$ 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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Received for review July 5, 2006. Accepted November 3, 2006.

JE060305E