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Activity Coefficients at Infinite Dilution in 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids

Gloria M. Foco,[†] Susana B. Bottini,*[,†] Nathalie Quezada,[‡] Juan C. de la Fuente,[‡] and Cor J. Peters[§]

PLAPIQUI, Universidad Nacional del Sur−CONICET, Bahía Blanca, Argentina, Departamento de Procesos Químicos, Biotecnológicos y Ambientales, Universidad Técnica Federico Santa María, Valparaíso, Chile, and Department of Chemical Technology, Faculty of Applied Science, Delft University of Technology, Delft, The Netherlands

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The paper reports the infinite dilution activity coefficients of a series of polar and nonpolar solutes (alkanes, alcohols, ketones, ethers, aromatic hydrocarbons, halogenated compounds) in 1-ethyl-, 1-butyl-, 1-hexyl-, and 1-octyl-3-methylimidazolium tetrafluoroborate ionic liquids. The data were measured by gas−liquid chromatography at (303, 323, and 343) K.

Introduction

Ionic liquids (ILs) are a class of novel solvents with very interesting properties. They are nonvolatile, nonflammable, and thermally stable and have good solvent power for both polar and nonpolar compounds. This makes ILs an attractive medium for separations and reactions.

Experimental data on the thermodynamics properties of mixtures containing ILs and organic solvents are of technological and theoretical interest. Heintz[1] presented a complete review on recent developments in thermodynamic and transport properties of non-aqueous mixtures containing ILs.

In particular, infinite dilution activity coefficients (γ_i^∞) are a good source of data to quantify the selectivity and solvent power of ILs and to gain information on the molecular interactions between ILs and organic solutes. This work reports the infinite dilution activity coefficients of a series of polar and nonpolar solutes in 1-alkyl-3-methylimidazolium tetrafluoroborate ($[\text{-MIM}]^+[BF_4]^-$) ILs.

Experimental Section

Chemicals. The solvents 1-ethyl-3-methylimidazolium tetrafluorborate $[EMIM^+][BF_4^-]$, 1-butyl-3-methylimidazolium tetrafluorborate $[BMIM^+][BF_4^-]$, 1-hexyl-3-methylimidazolium tetrafluorborate $[HMIM^+][BF_4^-]$, and 1-octyl-3-methylimidazolium tetrafluorborate $[OMIM^+][BF_4^-]$ were synthesized at the Laboratory of Biocatalysis and Organic Chemistry of Delft University of Technology and kindly provided to us to perform this research. The water content of these ILs was determined by Karl−Fisher titration, and the values are listed in Table 1. To reduce the amount of water, the ILs were subjected to vacuum (27 Pa) during (1 to 2) h. Table 1 also shows the final water contents obtained.

The solutes were chromatographic or reagent grade compounds. Since GLC is itself a separation technique, the experimental results are not influenced by small solute impurities[2].

Table 1. Mass Fraction Water Content *w* of the Ionic Liquids

	100 *w*	
solvents	original	after vacuum
$[EMIM^+][BF_4^-]$	1.34	0.01 (0.009−0.012)
$[BMIM^+][BF_4^-]$	0.17	0.02 (0.017−0.019)
$[HMIM^+][BF_4^-]$	0.09	0.02 (0.0224−0.0199)
$[OMIM^+][BF_4^-]$	0.37	0.07

Experimental Procedure. The infinite dilution activity coefficients were measured by inverse gas chromatography.[3] Details of the experimental technique are given in previous publications.[4,5]

A series of chromatographic columns were prepared using each BF_4 imidazolium−ionic liquid as stationary phase, and the retention times of different solutes in these chromatographic columns were measured. The specific retention volume (V_g^0) at 273.15 K (i.e., the normalized volume of carrier gas necessary to elute solute *i* out of a column with a mass M_s of solvent (IL)) is calculated from the measured retention time t_i of solute *i*:

$$V_g^0 = (t_i - t_a)\cdot F\cdot(273.15/T_f)\cdot((P_f - P_w^s)/P_o)\cdot J_3^2/M_s \qquad (1)$$

where t_a is the inert gas retention time; F is the carrier gas flow, measured at temperature T_f and pressure P_f in a soap-film meter; P_w^s is the saturated vapor pressure of water at T_f; P_o is the pressure at the column exit; and J_3^2 is the James−Martin correction factor for pressure gradient and gas compressibility inside the column.[6]

Equation 2 below gives the thermodynamic relationship between the retention volume (V_g^0) and the infinite dilution activity coefficient (γ_i^∞) of solute *i* in solvent *s*:

$$\ln \gamma_i^\infty = \ln(R\cdot 273.15/(M_s\cdot P_i^s\cdot V_g^0))\cdot(B_{ii} - \upsilon_i)\cdot P_i^s/(R\cdot T) \qquad (2)$$

In this expression, the virial equation of state is used to correct for the non-ideality of the gas phase. B_{ii}, υ_i, and P_i^s represent, respectively, the second virial coefficient, the liquid molar volume, and the vapor pressure of solute *i* at column temperature T; R is the universal gas constant; and M_s is the molecular weight of the solvent. For all the solutes studied in this work, second virial coefficients were calculated with the Hayden−O'Connell

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* Corresponding author. Fax: +54 91 883 764. E-mail: sbottini@plapiqui.edu.ar.
[†] Universidad Nacional del Sur−CONICET.
[‡] Universidad Técnica Federico Santa María.
[§] Delft University of Technology.

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Table 2. Infinite Dilution Activity Coefficients of a Series of Solutes in Different Columns Containing Variable Amounts of Untreated and Vacuumed Ionic Liquids[a]

		γ^{∞} at 323 K				
ionic liquid	g of solvent	hexane	cyclohexane	benzene	1-hexene	methanol
EMIM BF_4	1.415	113.21	46.17	2.42	43.23	0.43
	0.938	110.37	44.43	2.44		0.42
	0.628 AV		46.38	2.51	43.21	0.42
BMIM BF_4	0.868	76.51	38.38	2.43	32.22	1.21
	0.881AV	78.43	40.01	2.60	34.50	1.29
HMIM BF_4	0.645	28.78	15.88	1.69	16.50	1.12
	0.998 AV	29.62	16.51	1.65	14.78	1.08
OMIM BF_4	0.447	12.74	7.96	1.32	7.70	0.97
	0.902 AV	12.82	7.99	1.29	7.51	0.94

[a] AV, after vacuum.

model,[7] saturation pressures with Antoine equation, and liquid molar volumes with the correlation of Yen−Woods.[8]

A Varian (model Star 3400 Cx) gas chromatograph with a TCD detector and a Hewlett-Packard (model 3392) integrator were used in the measurements. The carrier gas was hydrogen, flowing at (20 to 30) $cm^3 \cdot min^{-1}$. A soap-film meter was used to measure the gas flow rates. Pressure drop inside the column, (400 to 500) mbar, was read with a cathetometer from a U tube mercury manometer; the value of the atmospheric pressure was determined with a quartz transducer (Paroscientific). Temperatures were measured with a platinum resistance thermometer (Systemtechnik AB S1220). Hamilton 25 μL syringes were used to inject the solutes into the carrier gas.

The stationary phase for each chromatographic column was prepared by dissolving weighed amounts of solvent (ionic liquid) and inert support (Chromosorb W, 60/80 mesh) in methanol, at different chromosorb/ionic liquid mass ratios. Methanol was then evaporated from the solution in an inert atmosphere, using a rotoevaporator. Stainless steel tubing, 1/8 in. o.d. by (2 and 3) m long, were packed with each stationary phase.

The retention times of the solutes injected in a 2 m chromatographic column having a support material with 25 % by mass of ionic liquid varied between 0.5 min (hexane) and 40 min (ethyl benzene). Both short and long retention times introduce uncertainties in the calculated γ^{∞} values. For this reason, it was necessary to prepare different chromatographic columns in order to get reasonable values of the retention times for the different solutes. The length of the columns varied between 1.5 m and 3 m, and the amount of ionic liquids in the solid support ranged from (20 to 35) % by mass.

The retention time of a selected solute (hexane) was measured systematically every 2 h to check for the stability of the experimental conditions. Also the γ^{∞} values of benzene (solute with an intermediate retention time) were measured in different columns of the same ionic liquid to verify the reproducibility of the results.

From a propagation of error analysis, the γ^{∞} values reported in Tables 2 to 5 are estimated to be accurate within ± 5 %. This error was calculated on the basis of the following absolute deviations in the measured variables: ± 0.13 mbar for column pressure drop, ± 0.7 $cm^3 \cdot min^{-1}$ for the carrier gas flow, ± 0.1 K for temperatures, ± 0.002 g for the solvent mass in the column, and ± 0.12 s for the retention times.

Table 3. Infinite Dilution Activity Coefficients in $[EMIM^+][BF_4^-]$

	γ_i^{∞}		
solutes	T = 303 K	T = 323 K	T = 343 K
hexane	124.88	113.21	64.75
heptane	201.52	172.56	138.52
isooctane	221.60	167.85	162.38
cyclohexane	53.72	46.17	38.89
benzene	2.42	2.51	2.47
toluene			4.03
ethyl benzene		7.05	6.87
1-hexene	46.24	43.21	36.64
methanol	0.43	0.43	0.42
ethanol		0.76	
1-propanol		0.95	0.87
2-propanol		1.05	1.01
chloroform		0.73	0.84
1,2-dichloroethane		1.32	1.37
trichloroethylene		3.66	3.79
ethyl acetate		3.08	3.32
methyl ethyl ketone		1.66	1.77
acetone		1.11	1.14

Table 4. Infinite Dilution Activity Coefficients in $[BMIM^+][BF_4^-]$

	γ_i^{∞}		
solutes	T = 303 K	T = 323 K	T = 343 K
hexane	93.41	76.51	67.54
heptane	134.05	115.28	99.01
isooctane	144.82	127.16	125.07
cyclohexane	44.94	38.38	32.79
benzene	2.39	2.43	2.48
toluene		4.14	4.13
ethyl benzene		6.65	7.20
1-hexene	35.37	32.22	30.47
methanol	1.32	1.21	1.07
ethanol		1.91	1.63
1-propanol		2.64	2.28
2-propanol		2.47	2.17
chloroform		1.13	1.29
carbon tetrachloride		5.50	5.73
1,2-dichloroethane		1.51	1.63
trichloroethylene		3.98	4.32
ethyl ether			8.05
ethyl acetate		2.86	2.99
methyl ethyl ketone		1.64	1.72
acetone		1.05	1.11

Results

For every IL studied in this work, different columns were prepared containing various amounts of untreated and vacuumed ionic liquids. Table 2 reports infinite dilution activity coefficients at 323 K measured with these columns. Good reproducibility was obtained. The variations between the different sets of γ^{∞} values lie within the experimental uncertainty. Therefore, it can be concluded that the experimental results are not affected by solute adsorption onto the solid support or by the amount of water contained in the IL.

Tables 3 to 6 report the infinite dilution activity coefficients of several solutes in $[EMIM^+][BF_4^-]$, $[BMIM^+][BF_4^-]$, $[HMIM^+][BF_4^-]$, and $[OMIM^+][BF_4^-]$ at (303, 323, and 343) K. The values given in these tables correspond to results obtained with the most appropriate column for each particular solute (i.e., columns with the highest amount of IL for solutes

Table 5. Infinite Dilution Activity Coefficients in [HMIM$^+$][BF$_4$$^-$]

	γ_i^∞			
		T = 323 K		
solutes	T = 303 K	this work	lit[10]	T = 343 K
hexane	34.79	29.62	18.2	26.06
heptane	47.69	39.87	25.6	33.64
isooctane	54.10			44.51
cyclohexane	18.65	16.51	10.3	15.20
benzene	1.63	1.65	0.95	1.68
toluene				2.61
ethyl benzene		3.63		4.05
1-hexene	15.92	14.78		14.84
methanol	1.19	1.08	0.61	0.99
ethanol		1.47		1.31
1-propanol		1.86		1.63
2-propanol		1.61		1.57
chloroform				
carbon tetrachloride		3.30		3.61
1,2-dichloroethane		0.81		0.92
trichloroethylene		1.06		1.19
ethyl ether				2.53
ethyl acetate		5.58		5.48
methyl ethyl ketone		1.14		1.21
acetone		0.85		0.91

Table 6. Infinite Dilution Activity Coefficients in [OMIM$^+$][BF$_4$$^-$]

	γ_i^∞		
solutes	T = 303 K	T = 323 K	T = 343 K
hexane	13.24	12.82	12.20
heptane	16.69	16.31	15.24
isooctane		17.73	17.04
cyclohexane	8.52	7.99	7.36
benzene	1.28	1.29	1.29
toluene		1.75	1.82
ethyl benzene		2.35	2.66
1-hexene	7.92	7.51	7.42
methanol	1.09	0.94	0.85
ethanol		1.24	1.10
1-propanol		1.44	1.27
2-propanol		1.41	1.27
chloroform		0.62	0.70
carbon tetrachloride		2.39	2.62
1,2-dichloroethane		0.93	0.95
trichloroethylene		1.67	1.76
ethyl ether		3.20	3.39
ethyl acetate		1.55	1.62
methyl ethyl ketone		1.01	1.04
acetone		0.78	0.83

with low retention time and columns with the lowest amount of solvent for solutes with high retention time).

The high values of the activity coefficients of alkanes in ILs is typical of polar/nonpolar behavior. For polar solutes or solutes with high polarizability, the γ values are much lower, indicating the presence of attractive forces between solute and solvent. Similar results have been reported in the literature for other ILs.[9−12]

Letcher et al.[11] have measured infinite dilution activity coefficients in [HMIM$^+$][BF$_4$$^-$]. The values reported by these authors at 323 K have also been included in Table 5. There is a difference of the order of (60 to 70) % between both sets of data. The γ^∞ obtained in this work are all in excess with respect to the Letcher et al. values.[11] According to the results shown in Table 2, these differences cannot be attributed to adsorption problems or water content in the IL. The cause of the discrepancy in the results is not known. Only the water content was checked in both laboratories, and no further analyses were carried out to detect the presence of other impurities and/or decomposition of the ILs that could affect the results.

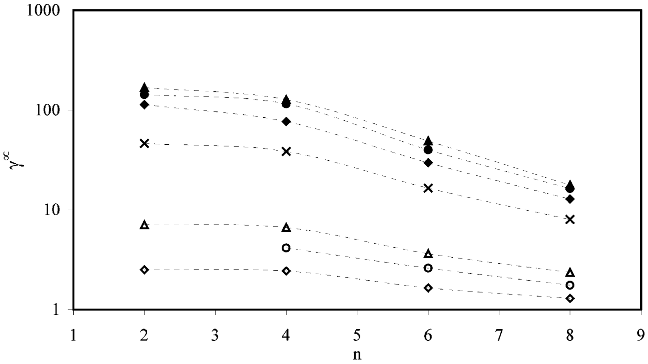

Figure 1. Infinite dilution activity coefficients γ^∞ of hydrocarbons in 1-alkyl-3-methylimidazolium tetrafluoroborate as a function of carbon chain n. ▲, ●, ◆, alkanes; ×, cyclohexane; △, ○, ◇, aromatics.

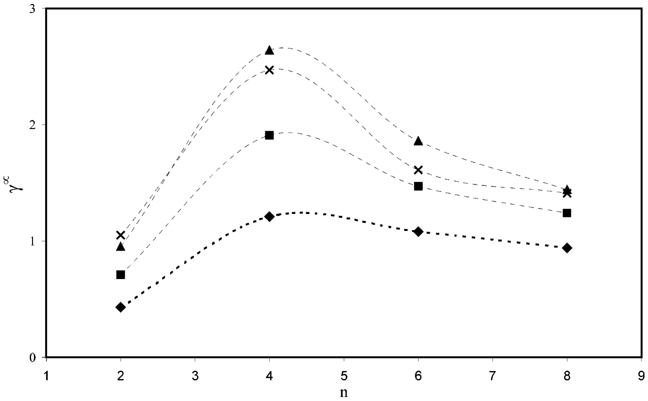

Figure 2. Infinite dilution activity coefficients γ^∞ of alcohols in 1-alkyl-3-methylimidazolium tetrafluoroborate as a function of carbon chain n. ▲, 1-propanol; ×, 2-propanol; ■, ethanol; ◆, methanol.

Figures 1 and 2 show the change of the infinite dilution activity coefficients of hydrocarbons and alcohols, with the number of carbon atoms contained in the cation aliphatic chain. For a given solute, the value of the activity coefficient in general decreases with the increased number of carbon atoms in the IL aliphatic chain. An exception is found for alcohols. For this family of solutes, the activity coefficient increases from [EMIM$^+$][BF$_4$$^-$] to [BMIM$^+$][BF$_4$$^-$]; this could be attributed to a stronger attraction between the polar solutes and the IL core [-MIM$^+$][BF$_4$$^-$] in the solvent with the shortest aliphatic chain. Similar behavior is observed for the chlorinated solutes, though in this case the increase from [EMIM$^+$][BF$_4$$^-$] to [BMIM$^+$][BF$_4$$^-$] is less pronounced.

Solubility Parameters of 1-Alkyl-3-methylimidazolium Tetraflouorborate Ionic Liquids

Data on infinite dilution activity coefficients of different solutes in a given solvent can be used to estimate the value of the solvent solubility parameter. For this purpose a two-term (combinatorial + residual) equation is used to represent infinite dilution activity coefficients:

$$\ln \gamma_i^\infty = \ln \gamma_i^{\infty\text{comb}} + \ln \gamma_i^{\infty\text{res}} \tag{3}$$

where the combinatorial term can be represented by the Kikik et al.[13] modification to Flory's equation, and the residual term is given by the regular solution theory:

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

$$\ln \gamma_i^{\infty\text{res}} = (\upsilon_i/RT)(\delta_i - \delta_s)^2 \tag{5}$$

In these equations, r_i/r_s represents the ratio between the van

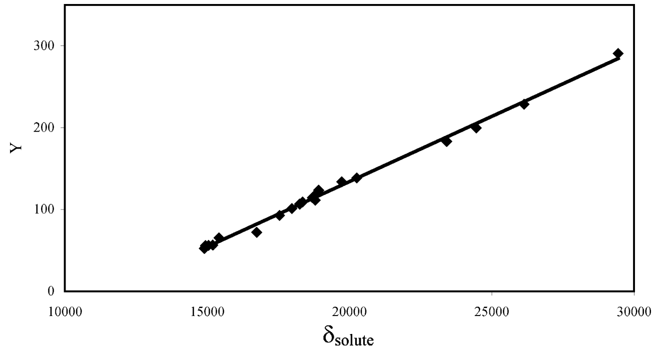

Figure 3. Residual function Y for $[HMIM^+][BF_4^-]$ vs solute solubility parameters δ_{solute}. Regression line: $Y = 0.0159\ \delta_{solute} - 184.36$ ($R^2 = 0.9955$).

Table 7. Solubility Parameters of the Ionic Liquids

	$\delta \times 10^4/(J\cdot m^{-3})^{1/2}$
EMIM	2.44
BMIM	2.43
HMIM	2.33
OMIM	2.25

der Waals volumes of solute and solvent; v_i is the solute molar volume; and δ_i and δ_s are the solubility parameters of solute and solvent, respectively. Equation 5 can be rearranged in terms of a residual function Y:

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

This equation shows that, for a given solvent and temperature T, there is a linear relation between Y_i and the solute solubility parameter δ_i. From the slope of this line, the value of the solvent solubility parameter δ_s can be obtained.

The values of Y_i for each solvent were calculated as the difference between the experimental γ_i^∞ from Tables 3 to 6 and the corresponding $\gamma_i^{\infty comb}$ calculated by eq 4. Information on v_i, δ_i, and r_i were obtained from the literature.[14] The following values were calculated for the standardized van der Waals volumes of ionic liquids: r(EMIM) = 6.7538; r(BMIM) = 8.1026; r(HMIM) = 9.4514, and r(OMIM) = 10.5002

Figure 3 shows, as an example, the linear dependence between Y_i and δ_i obtained from the γ_i^∞ data on $[HMIM^+][BF_4^-]$. Table 7 reports the solubility parameters calculated by this procedure for the 1-alkyl-3-methylimidazolium tetrafluoroborate ILs studied in this work. A comparison between the values of the solubility parameters of ILs and water gives an energy of vaporization of the ILs about three times that of water. If Trouton's law is applied, this represents a normal boiling temperature of the ILs above 1100 K, a value compatible with the negligible vapor pressure of these compounds.

Conclusions

Infinite dilution activity coefficients have been measured for a series of polar and nonpolar organic solutes in four different 1-alkyl-3-methylimidazolium tetrafluoroborate ILs. The solutes studied include polar and nonpolar compounds. The high γ^∞ values of alkanes denote a very low solubility of these compounds in ILs. On the other hand, associating, polar and polarizable compounds present great affinity, as indicated by the rather low γ^∞ values. In general, the γ^∞ values decrease as the length of the IL alkyl chain increases.

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