Thermodynamic Properties of Mixtures Containing Ionic Liquids: Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Propyl Boronic Acid-3-Alkylimidazolium Bromide and 1-Propenyl-3-alkylimidazolium Bromide Using Inverse Gas Chromatography

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Activity coefficients at infinite dilution γ^∞ of 28 organic compounds in eight room-temperature ionic liquids of the family of 1-propyl boronic acid-3-alkylimidazolium bromide and 1-propenyl-3-alkylimidazolium bromide (with alkyl = methyl, octyl, decyl, or dodecyl) were determined at 323.15 K using inverse gas chromatography. Using all the available γ^∞ data, the selectivities at infinite dilution S_{12}^∞ were determined. Indeed, such values are extremely useful for the design and the optimization of separation processes.

Introduction

Room-temperature ionic liquids (RTILs) are solvents that may have great potential in chemical analysis. RTILs have shown potential as unique solvents with wide range of solubility, miscibility, and other physicochemical properties accompanied by an extremely promising nonvolatile behavior. These liquid salts can be custom synthesized, be water-miscible or water-immiscible, and are capable of undergoing multiple solvation interactions with many types of molecules. All RTILs exhibit a high viscosity and, hence, a relatively low conductivity. The uses and properties of RTILs have been the focus of many recent scientific investigations.[1−13] The physical and physicochemical properties of RTILs depend on their large cation (alkylimidazolium, alkylpyridinium, alkylphosphonium, quaternary ammonium) and on their inorganic anion having a delocalized charge (PF_6^-, BF_4^-, and $(Tf_2)N$). It means that RTILs of various physical properties can be obtained by changing the cation or the anion. Because they are air and water stable and are able to solvate a variety of organic and inorganic species, ionic liquids are emerging as alternative green solvents, namely, as reaction media for synthesis, catalysis, and biocatalysis.[14−16] It has been observed that the solubility of an ionic liquid in water can strongly increase replacing the anion. The main factors that influence physical properties of RTILs are the charge distribution on the ions but also H-bonding ability, the polarity, and the dispersive interactions.

It is important to have reliable experimental phase equilibrium data for the development of thermodynamic models. Activity coefficients at infinite dilution (γ^∞) are very useful for process synthesis and design. Such thermodynamic data can be used to determine g^E model parameters and predict phase diagrams of mixtures containing ionic liquids. Activity coefficients at infinite dilution can be also used for the selection of solvents for azeotropic/extractive distillation and liquid extraction. Activity coefficients at infinite dilution γ^∞ give a direct measure of interactions between unlike molecules in the absence of solute−solute interactions.

Gas chromatography is widely used for determining thermodynamic properties of pure substances or solvent properties of binary mixtures. From retention data, the solute activity coefficient at infinite dilution, the gas−liquid partition coefficient, and other thermodynamic properties of mixing can be easily obtained. Using these parameters and appropriate models allow understanding of the intermolecular interactions responsible for solvation in the stationary phase.[17−18]

In other respects, numerous approaches were proposed to characterize the interactions between the solute and the stationary phase. Among others, Abraham and co-workers[19−22] developed the linear solvation energy relationship (LSER) to correlate many physicochemical properties. The LSER equation can be written as follows:

$$\log \mathrm{SP} = c + rR_2 + s\pi_2^{\mathrm{H}} + a\sum\alpha_2^{\mathrm{H}} + b\sum\beta_2^{\mathrm{H}} + l\log L^{16} \quad (1)$$

SP is some free energy related solute property such as gas−liquid partition coefficient, specific retention volume, or adjusted retention time at a given temperature. The independent variables in eq 1 are the solute excess molar refraction (R_2), the effective solute dipolarity/polarizability (π_2^{H}), the effective solute hydrogen bond acidity ($\sum\alpha_2^{\mathrm{H}}$), the effective solute hydrogen bond basicity ($\sum\beta_2^{\mathrm{H}}$), and the solute gas−liquid partition coefficient on hexadecane at 25 °C ($\log L^{16}$). The coefficients *c*, *r*, *s*, *a*, *b*, and *l* are not simply fitting coefficients, but they reflect complementary properties of the solvent phase. The *r* coefficient reflects the tendency of the phase to interact with gaseous solutes through dispersive-type interactions via electron pairs and π electrons. The coefficient *s* is a measure of the phase dipolarity/polarizability. The coefficient *a* represents the complementary property to solute hydrogen bond acidity and is a measure of the hydrogen bond basicity. Likewise, the coefficient *b* is a measure of the phase hydrogen bond acidity. Finally, the coefficient *l* is a combination of the work needed to create a

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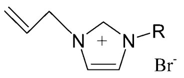
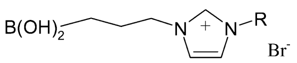
cavity in the phase and the general dispersion interaction energy between solute and solvent phase. The system constants are determined by multiple linear regression analysis of experimental log SP(log V_N in this work) values for a group of solutes of sufficient number and variety to establish the statistical and chemical validity of the model.

In this work, activity coefficients at infinite dilution have been determined for 29 polar and nonpolar compounds (alkanes, alkenes, alkynes, cycloalkanes, aromatics, alcohols) in eight ionic liquids: 1-propyl boronic acid-3-alkylimidazolium bromide (with alkyl = methyl, octyl, decyl, or dodecyl) and 1-propenyl-3-alkylimidazolium bromide (with alkyl = methyl, octyl, decyl, or dodecyl) at 323.15 K. The LSER model was then applied to characterize the nature of solute interactions with ionic liquids.



1-propenyl-3-R-imidazolium bromide
with R=methyl, octyl, decyl and dodecyl



1-propyl boronic acid-3-R-imidazolium bromide

Experimental Section

Materials and Chemicals. The ionic liquids were prepared according to the following procedure.

(a) Synthesis of 1-R-Imidazole. The 1-*R*-imidazole (with *R* = methyl, octyl, decyl, and dodecyl) was obtained by N-alkylation of 1-*H*-imidazole; 0.1 mol of 1-*H*-imidazole and 0.1 mol of 1-bromo-*R* (with *R* = methyl, octyl, decyl, and dodecyl) were mixed under alkaline medium (K_2CO_3/KOH) in the presence of 0.0075 mol of tetrabutylammonium bromide. The mixture was placed under microwave irradiation (300 W) for 2 min. Then the product was extracted from the mixture using CH_2Cl_2. After the removal of the solvent under reduced pressure, pure 1-*R*-imidazole was isolated with a yield higher than 92 % and characterized by ^{1}H NMR.

(b) Synthesis of 1-Propenyl-3-R-imidazolium Bromides. 1-Propenyl-3-*R*-imidazolium bromides were obtained by adding 0.05 mol of allylbromide to 0.01 mol of 1-*R*-imidazole under reflux for 2 h. The mixture was then solved in ethyl ether to remove alkylbromide in excess, and the residue was filtered and washed three times in 20 mL of ethyl ether to give in good yields (over 90 %) the excepted 1-propenyl-3-*R*-imidazolium bromides as yellow pastes (melting point < 30 °C). Each isolated compound was then characterized by ^{1}H NMR. These 1-propenyl-3-*R*-imidazolium bromides were used as starting materials in the synthesis of the corresponding 1- propylboronic acid−3-*R*-imidazolium bromides.

Synthesis of 1- Propylboronic Acid-3-R-Imidazolium Bromides. 1-Propylboronic acid-3-*R*-imidazolium bromides were synthesized in two steps by a hydroboration reaction conducted under argon in CCl_4 at 0 °C with a solution of borane methyl sulfide (11 mol·L^{-1}), followed by an acidic hydrolysis (1 mol·L^{-1} HCl) of the corresponding borane in methanol. Products were collected in the organic layer by three liquid/liquid ($CHCl_3$/water) biphasic extractions. Afterwards, chloroform was removed under reduced pressure, and 1-propylboronic acid-3-*R*-imidazolium bromides were isolated in pure form in good yield (85 %). The ^{1}H NMR spectrums had confirmed the propenyl group disappearance, indicating its total reduction. Each structure was confirmed by ^{1}H NMR and for *R* = octyl and decyl by ^{13}C NMR also. Only 1-propylboronic acid-3-dodecylimidazolium bromide was in solid state (melting point = 32 °C); the three others were pale yellow liquids.

The solutes were purchased from Aldrich with a purity higher than 99.5 %. The solutes were used without any purification because the gas−liquid chromatography technique separates any impurities in the column. All support materials were purchased from Supelco. The ionic liquid was further purified by subjecting the liquid to a very low vapor pressure for approximately 240 min. This procedure removed any volatile chemicals and water from the ionic liquid.

Experimental Procedure. Inverse chromatography experiments were carried out using a Varian CP-3800 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. Helium flow rate was adjusted to obtain adequate retention times. Methane was used to determine the column hold-up time. Exit gas flow rates were measured with an Alltech Digital Flow Check Mass Flowmeter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. A personal computer directly recorded detector signals, and corresponding chromatograms were obtained using Galaxie software.

Column packing of 1 m length containing from (4 to 14) % of stationary phases (RTIL) on Chromosorb W-AW (60−80 mesh) were prepared using the rotary evaporator technique. After evaporation of the dichloromethane under vacuum, the support was equilibrated at 323 K during 6 h. The mass of the packing material was calculated from the mass of the packed and empty column and was checked during experiments. The masses of the stationary phase were determined with a precision of 0.0003 g. A volume of the headspace vapor of samples of (1 to 5) μL was introduced to be in infinite dilution conditions. Each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible to within (0.01 to 0.03) min. To check the stability of the experimental conditions, such as the possible eluation of the stationary phase by the helium stream, the measurements of retention times were repeated systematically every day for three selected solutes. No changes in the retention times were observed during 3 months of continuous operation.

Calculation

Activity Coefficients at Infinite Dilution. The retention data determined with inverse chromatography experiments were used to calculate activity coefficients at infinite dilution of the solute in the ionic liquids.

The standardized retention volume, V_N, was calculated with the following usual relationship:[23]

$$V_N = JU_0 t_R{}' \frac{T_{col}}{T_r} \times \left(1 - \frac{P_{ow}}{P_o}\right) \tag{2}$$

The adjusted retention time $t_R{}'$ was taken as the difference between the retention time of a solute and that of the methane. T_{col} is the column temperature, U_0 is the flow rate of the carrier gas measured at the room temperature T_r, P_{ow} is the vapor pressure of water at T_r, and P_o is the pressure at the column outlet. The factor J in eq 2 corrects for the influence of the pressure drop along the column and is given by eq 3:[24]

$$J = \frac{3}{2} \frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \tag{3}$$

Table 1. Experimental Activity Coefficients at Infinite Dilution of 28 Organic Compounds in the 1-Propenyl-3-alkylimidazolium Bromide at 323.15 K

	γ^∞ values with alkyl =			
solutes	methyl	octyl	decyl	dodecyl
hexane	25.07	8.90	8.39	4.41
heptane	49.65	11.36	11.13	5.32
octane	63.02	14.94	14.35	6.37
nonane	65.61	17.42	16.91	6.93
cyclohexane	15.68	5.66	5.64	3.12
benzene	3.60	1.40	1.39	1.08
toluene	6.19	1.92	1.85	1.38
ethylbenzene	11.09	2.56	2.54	1.77
m-xylene	11.10	2.73	2.73	1.85
o-xylene	8.98	2.39	2.34	1.66
1-hexene	16.5	5.93	5.89	3.47
1-hexyne	8.27	2.04	2.02	1.56
1-heptyne	13.16	2.56	2.58	1.87
2-butanone	2.68	1.46	1.48	1.43
2-pentanone	4.32	1.93	1.78	1.62
1.4 dioxane	1.59	1.52	1.39	1.30
methanol	0.18	0.17	0.17	0.15
ethanol	0.27	0.27	0.26	0.23
1-propanol	0.54	0.28	0.28	0.23
2-propanol	0.69	0.36	0.35	0.29
2-methyl-1-propanol	0.33	0.29	0.29	0.23
ether	11.40	4.18	3.54	2.95
chloroforme	0.25	0.14	0.13	0.12
dichloromethane	0.33	0.28	0.27	0.25
tetrachloromethane	1.54	0.82	0.80	0.70
acetonitrile	1.04	0.98	0.89	0.86
1-nitropropane	1.83	1.23	1.14	1.12
thiophene	1.48	0.93	0.89	0.77

where P_i and P_o are respectively the inlet and outlet pressures of gas chromatography column.

The activity coefficient at infinite dilution of a solute *1* in the stationary phase *2* (RTIL) was calculated with the following expression:

$$\ln \gamma_{1,2}^{\infty} = \ln\left(\frac{n_2 RT}{V_\mathrm{N} P_1{}^0}\right) - P_1{}^0 \frac{B_{11} - V_1{}^0}{RT} + \frac{2B_{13} - V_1^{\infty}}{RT} J P_\mathrm{o} \qquad (4)$$

n_2 is the mole number of the stationary phase component inside the column, R is the ideal gas constant, T is the temperature of the oven, B_{11} is the second virial coefficient of the solute in the gaseous state at temperature T, B_{13} is the mutual virial coefficient between the solute (1) and the carrier gas helium (3), $P_1{}^0$ is the probe vapor pressure at temperature T. The values of $P_1{}^0$ and B_{11} have been taken from the literature.[25] The molar volume of the solute $V_1{}^0$ was determined from experimental densities, and the partial molar volumes of the solutes at infinite dilution V_1^∞ were assumed to be equal to $V_1{}^0$. Values of B_{13} have been estimated using Tsonopolous's method.[26−28] Critical parameters and acentric factors used for the calculations were taken from the literature.[25,29]

Results and Discussion

Activity coefficients at infinite dilution of organic compounds in ionic liquids are calculated using eqs 2 to 4. The accuracy of γ^∞ values reported in Tables 1 and 2 may be obtained from the law of propagation of errors. The following measured parameters exhibit errors and must be taken into account in the errors calculations with their corresponding standard deviations. Exit gas flow rates were measured with an uncertainty of ± 0.1 $\mathrm{cm^3/min}$. At a given temperature, each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible within (0.01 to 0.03) min. The pressure drop and the inlet and outlet pressures were measured with an uncertainty of ± 0.002 bar. The masses of the stationary phase were determined with a precision of ± 0.0003 g. The temperature of the oven was measured with a Pt 100 probe and controlled to within ± 0.1 K. Taking into account that thermodynamic parameters are also subject to an error, γ^∞values are estimated to be accurate within ± 3 %. However, the peak shape of pyridine, 1-nitropropane, and triethylamine on ionic liquids is asymmetric, resulting in inaccurate activity coefficients. In this case, γ^∞ values are estimated to be accurate within ± 9 %.

Table 2. Experimental Activity Coefficients at Infinite Dilution of 23 Organic Compounds in the 1-Propyl Boronic Acid-3-Alkylimidazolium Bromide at 323.15 K

	γ^∞ values with alkyl =			
solutes	methyl	octyl	decyl	dodecyl
hexane		18.23	5.45	4.65
heptane	77.64	20.25	7.04	5.36
octane	80.97	23.65	8.81	6.34
nonane	83.18	26.17	9.92	6.99
cyclohexane		8.15	3.89	3.25
benzene	18.07	1.84	1.33	1.21
toluene	38.76	2.41	1.80	3.36
ethylbenzene	45.06	3.28	2.37	3.83
m-xylene	48.15	3.57	2.11	1.98
o-xylene	44.02	3.11	1.89	1.78
1-hexene		8.32	3.76	3.60
1-hexyne		2.77	1.77	1.86
1-heptyne	42.90	3.70	2.22	2.20
2-butanone	21.80	1.88	1.59	1.33
2-pentanone	24.23	2.32	1.67	1.63
1.4 dioxane	11.21	1.78	1.38	1.32
methanol	0.05	0.04	0.05	0.04
chloroforme	3.01	0.23	0.12	0.19
dichloromethane	3.20	0.41	0.25	0.34
tetrachloromethane	21.21	1.23	0.79	0.90
acetonitrile	3.30	1.28	0.95	1.16
1-nitropropane	15.84	1.58	1.19	1.51
thiophene	19.37	1.20	0.79	0.90

1-Propenyl-3-Alkylimidazolium Bromide. Experimental activity coefficients at infinite dilution of 28 organic compounds are listed in Table 1. The γ^∞ values for the *n*-alkanes increase with an increase in carbon number. The γ^∞ values of *n*-alkanes are higher than the values obtained with cyclohexane, alkenes, alkynes, and aromatics. Introduction of a double or triple bond in the *n*-alkanes causes a decreasing of the γ^∞ values. Cyclization of the alkane skeleton (e.g., cyclohexane) also reduces the value of γ^∞ in comparison to that of the corresponding linear alkanes (e.g., hexane). The more polar the solute, the greater the interaction with the ionic liquid. Aromatics (with its π-delocalized electrons) have smaller γ^∞ values than *n*-alkanes, presumably because of the interaction with the cation species. In the serie of chloromethanes, it was observed that γ^∞ values strongly increase from dichloromethane to tetrachloromethane. This behavior already observed with different ionic liquids[1,2] indicates that polar compounds have better solubility in the RTILs when attractive interaction between polar molecules and the charged ions of the solvent is possible. In the case of alcohols, the lone pair of electrons on the oxygen atom could interact with the ionic liquid cation, and the acidic proton is attracted to oxygen atoms in the anion. γ^∞ values of *n*-alkanols increase with increasing chain length. γ^∞ values of branched alkanol skeleton are smaller than γ^∞ values of the corresponding linear alcohol. γ^∞ values of ketones, pyridine, thiophene, acetonitrile, and acetone are lower in comparison with those of the alcohols. In all cases, γ^∞ values of solutes decrease with increasing alkyl chain length of the ionic liquid. In Figure 1, γ^∞ values of some solutes as a function of the logarithm of the carbon number of the alkyl chain is plotted. It was found that

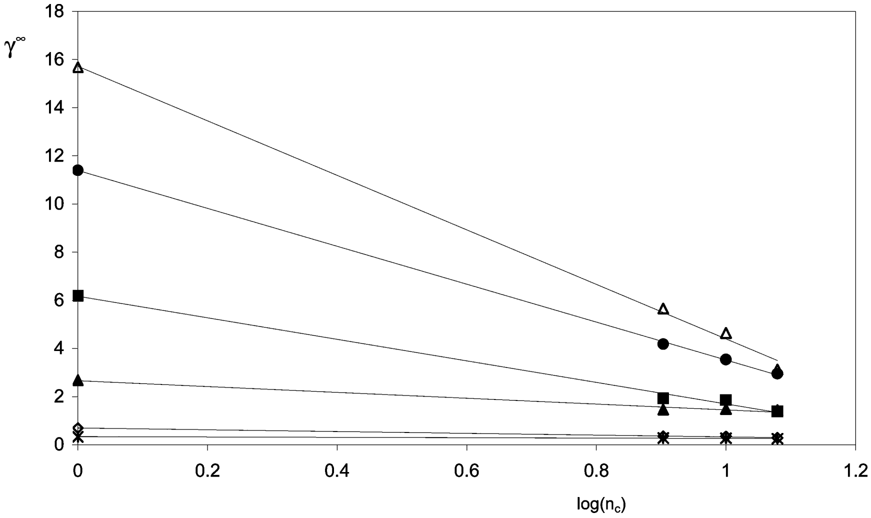


Figure 1. Plot of activity coefficient at infinite dilution of various solutes as a function of the logarithm of the carbon number of 1-propenyl-3-*R*-imidazolium bromide: △, cyclohexane; ■, toluene; ▲, 2-butanone; ◇, 2-propanol; ×, dichloromethane; ●, ether.

Table 3. LSER Descriptors of Solutes Used to Characterize Ionic Liquids

solutes	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	log L^{16}
hexane	0	0	0	0	2.668
heptane	0	0	0	0	3.173
octane	0	0	0	0	3.677
nonane	0	0	0	0	4.182
cyclohexane	0.305	0.10	0	0	2.964
benzene	0.610	0.52	0	0.14	2.768
toluene	0.601	0.52	0	0.14	3.325
ethylbenzene	0.613	0.51	0	0.15	3.778
m-xylene	0.623	0.52	0	0.16	3.839
o-xylene	0.663	0.56	0	0.16	3.939
1-hexene	0.078	0.08	0	0.07	2.572
1-hexyne	0.166	0.23	0.12	0.1	2.510
1-heptyne	0.160	0.23	0.12	0.1	3.000
2-butanone	0.166	0.70	0	0.51	2.287
2-pentanone	0.143	0.68	0	0.51	2.755
1.4 dioxane	0.329	0.75	0	0.64	2.892
methanol	0.278	0.44	0.43	0.47	0.970
ethanol	0.246	0.42	0.37	0.48	1.485
1-propanol	0.236	0.42	0.37	0.48	2.031
2-propanol	0.212	0.36	0.33	0.56	1.764
2-methyl-1-propanol	0.217	0.39	0.37	0.48	2.413
1-butanol	0.224	0.42	0.37	0.48	2.601
ether	0.041	0.25	0	0.45	2.015
chloroforme	0.425	0.49	0.15	0.02	2.48
dichloromethane	0.387	0.57	0.10	0.05	2.019
tetrachloromethane	0.458	0.38	0	0	2.833
acetonitrile	0.237	0.9	0.07	0.32	1.739
1-nitropropane	0.242	0.95	0	0.31	2.894
thiophene	0.687	0.57	0	0.15	2.819

there is a linear relationship between γ^∞ values and the logarithm of the carbon number of the alkyl chain.

1-Propyl Boronic Acid-3-Alkylimidazolium Bromide. Experimental γ^∞ values of 23 organic compounds are listed in Table 2. The high values of activity coefficient at infinite dilution of *n*-alkanes indicate their low solubility in 1-propyl boronic acid-3-alkylimidazolium bromide. Activity coefficient at infinite dilution of *n*-alkanes increase with an increase in carbon number. The γ^∞ values of *n*-alkanes are higher than the values obtained with cyclohexane, alkenes, alkynes, and aromatics. Alkene and aromatic hydrocarbons with polarizable electrons showed stronger interactions with the ionic liquids than alkanes, probably due to the increasing strength of ion-induced dipole interactions. Solutes with polar functional groups had higher solubility due to attractive interactions with ions of the ionic liquids. In the serie of chloromethanes, the same behavior is observed as in many ionic liquids. The γ^∞ values strongly increase from dichloromethane to tetrachloromethane. In the case of methanol, the lone pair of electrons on the oxygen atom could interact with the ionic liquid cation, and the acidic proton is attracted to oxygen atoms in the anion. In the serie of 1-propyl boronic acid-3-alkylimidazolium bromide, alcohols have a high solubility (γ^∞ values close to zero) and no peak was observed for ethanol and 2-propanol. No linear relationship between γ^∞ values and of the logarithm of the carbon number of the alkyl chain was found for 1-propyl boronic acid-3-alkylimidazolium bromide.

LSER Characterization. Equation 1 was used to characterize ionic liquids studied. System constants *c*, *r*, *s*, *a*, *b*, and *l* of ionic liquids were obtained by multiple linear regression of the logarithm of the standardized retention volume log V_N of 28 solutes. LSER parameters of probes are given in Table 3. The system constants for 1-propenyl-3-alkylimidazolium bromide at 323.15 K are summarized in Table 4. LSER model was not applied on 1-propyl boronic acid-3-alkylimidazolium bromide because of lack of information on alcohols. Indeed, our data contain 23 solutes, which is not a sufficient amount to obtain meaningful values of the system constant.

1-Propenyl-3-Alkylimidazolium Bromide. LSER parameters of 1-propenyl-3-alkylimidazolium bromide are very similar to those obtained for the 1-butyl-3-methylimidazolium octyl sulfate[2] and 2-hydroxy-4-morpholinepropanesulfonate.[14] The ($c + l \log L^{16}$) term gives information on the effect of cohesion of the ionic liquids on solute transfer from the gas phase. In general, the ionic liquids are cohesive solvents.[14] The *l* term decreases with increasing alkyl chain length of the ionic liquid. The ionic liquid interacts weakly via nonbonding and π-electrons (*r* system constant is zero) and is not much different to other polar nonionic liquids. The dipolarity/polarizability (*s* system constants) of this family of ionic liquids is similar as the most dipolar/polarizable nonionic stationary phases. The hydrogen-bond basicity of the ionic liquid (*a* system constants) is considerably larger than values obtained for nonionic phases (0 to 2.1),[14] and RTILs are not hydrogen-bond acid ($b = 0$). The increase of the alkyl chain length of the ionic liquid causes a decrease of the hydrogen bond basicity and of the polarity.

Selectivity at Infinite Dilution for the Ionic Liquids. Activity coefficients at infinite dilution are important properties used for the selection of solvents and for the reliable design of thermal separation processes.[30] As an example, the knowledge of the

Table 4. LSER Descriptors of Ionic Liquids Determined at 323.15 K[a]

	system constants						statistics		
ionic liquids	*r*	*s*	*a*	*b*	*l*	*c*	*ρ*	SD	*n*
1-propenyl-3-methylimidazolium bromide	0	2.16 (0.09)	5.19 (0.18)	0	0.53 (0.05)	−1.86	0.990	0.089	28
1-propenyl-3-octylimidazolium bromide	0	1.72 (0.08)	4.96 (0.16)	0	0.57 (0.05)	−1.60	0.989	0.088	28
1-propenyl-3-decylimidazolium bromide	0	1.73 (0.07)	4.89 (0.17)	0	0.66 (0.04)	−1.58	0.990	0.089	28
1-propenyl-3-dodecylimidazolium bromide	0	1.44 (0.07)	4.87 (0.16)	0	0.72 (0.03)	−1.51	0.991	0.088	28

[a] *ρ*, multiple correlation coefficient; SD, standard deviation in the estimation; and *n*, number of solutes.

Table 5. Selectivity S_{12}^{∞} at Infinite Dilution for Different Ionic Liquids at 323.15 K

ionic liquids	hexane (1) + benzene (2)	hexane (1) + hexene (2)	hexane (1) + methanol (2)	2-pentanone (1) + benzene (2)	hexane (1) + chloroform (2)
1-propenyl-3-methylimidazolium bromide	6.96	1.52	139.28	1.20	100.28
1-propenyl-3-octylimidazolium bromide	6.36	1.50	52.35	1.27	63.57
1-propenyl-3-decylimidazolium bromide	6.03	1.43	49.35	1.38	64.54
1-propenyl-3-dodecylimidazolium bromide	4.08	1.27	29.4	1.50	36.75
1-propyl boronic acid-3-octylimidazolium bromide	9.91	2.19	455.75	1.26	79.26
1-propyl boronic acid-3-decylimidazolium bromide	4.09	1.45	109	1.26	45.42
1-propyl boronic acid-3-dodecylimidazolium bromide	3.84	1.29	116.25	1.35	24.47

separation factor at infinite dilution is needed to avoid the oversizing of a distillation column. Aliphatic hydrocarbons show an important deviation from Raoult's law, in contrast to aromatic compounds, chloroalkane, and alcohols, in both ionic liquids investigated in this work. This information may be a useful tool for extractive distillation or extraction. The selectivity that indicates the suitability of a solvent for separating mixtures of components 1 and 2 by extractive distillation is given by[31]

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

The selectivity value S_{12}^{∞} relative to the RTILs studied in this work at 323.15 K are presented in Table 5. The S_{12}^{∞} values were calculated from the γ^{∞} values listed in Tables 1 and 2. The large S_{12}^{∞} values show that RTILs can play an important role in separating aromatics, alcohols, and chloroalkanes from alkanes. A further analysis of Table 5 shows that selectivity increases with decreasing length of the alkyl chain for the different separation problems for imidazolium compounds with bromide as anion. This behavior was already observed for ionic liquids with bis(trifluoromethylsulfonyl)imide.[32] The S_{12}^{∞} values obtained for different binary mixtures indicate that 1-propenyl-3-alkylimidazolium bromide and 1-propyl boronic acid−3-alkylimidazolium bromide can play an important role for the separation of aromatics, chloroalkanes, and alcohols from alkanes.

From LSER treatment, we can study the tendencies of ionic liquids to be selective toward any pair of organic compounds. Thus eq 1 shows large values for the *s*, *a*, and *l* descriptors, which demonstrate the selectivity of 1-propenyl-3-alkylimidazolium bromide. As shown in Table 5, in a given pair of organic compounds of similar log L^{16} coefficients, the organic compound with a large dipolarity/polarizability is preferentially retained (see, for example, hexane (1) + benzene (2) and hexane (1) + hexene (2) in Table 5). Ionic liquids have structural features that would facilitate hydrogen-bond acceptor basicity interactions (electron-rich oxygen, nitrogen, and fluorine atoms). The selectivity value, S_{12}^{∞}, for (2-pentanone (1) + benzene (2)) agrees well with the LSER observation. 2-Pentanone is preferentially retained, as expected, because the ketone has a large hydrogen-bond basicity parameter (0.51) and benzene has a low value (0.14), the other LSER parameters being similar for the two organic compounds. Finally, the LSER treatment and the analysis of selectivity lead to the same conclusions about the interactions that are governing partitioning on the two ionic liquids.

Conclusions

Activity coefficients at infinite dilution of various solutes in eight ionic liquids have been measured at 323.15 K using inverse gas chromatography. It has been observed that γ^{∞} values of polar and nonpolar solutes decrease with increasing alkyl chain length of the ionic liquid. It was also found that there is a linear relationship between γ^{∞} values and the logarithm of the carbon number of the alkyl chain of ionic liquids. The S_{12}^{∞} values obtained for different binary mixtures indicate that 1-propenyl-3-alkylimidazolium bromide and 1-propyl boronic acid−3-alkylimidazolium bromide can play an important role for the separation of aromatics, chloroalkanes, and alcohols from alkanes. LSER treatment and the analysis of selectivity or activity coefficient at infinite dilution lead to the same conclusions about the interactions that are governing partitioning on the two ionic liquids.

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