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Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Inverse Gas Chromatography

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Activity coefficients at infinite dilution (γ^∞) of organic compounds in the room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate were determined using inverse gas chromatography from (303.35 to 332.55) K. Retention data were used to estimate the influence of gas−liquid and gas−solid interfacial adsorption on the value of activity coefficients at infinite dilution of solutes in this ionic liquid. Most of the polar solutes were retained largely by partition, while *n*-alkanes were retained predominantly by interfacial adsorption on the ionic liquid studied. The solvation characteristics of the ionic liquid were evaluated using the Abraham solvation parameter model.

Introduction

Development of safer and environmentally friendly processes and products is needed to achieve sustainable production and consumption patterns. New chemical products, such as ionic liquids, which are of great interest to the chemical and related industries because of their attractive properties as solvents, should be considered. Ionic liquids (ILs) are low-melting organic salts built with an unsymmetrical organic cation and an anion that is mostly inorganic. Physical and chemical properties of ILs are influenced not only by the nature of the cation and the nature of cation substituents but also by the polarity and the size of the anion. Interactions between IL cations and anions are the consequence of energetic and geometric factors leading to a variety of strongly organized and oriented structures. These features infer to ILs numerous applications.[1−8] As environmentally benign "green" solvents, ionic liquids have been used in industrial processes for more than a decade, and their applications continue to expand. Recently, it was shown that imidazolium-based ionic liquids could be used in the liquid−liquid extraction of thiophene from aliphatic hydrocarbons[10−15] and of methanol from aliphatic hydrocarbons. It is then clear that ionic liquids may play an important role since regulations regarding liquid hydrocarbon fuels are continuously requiring sulfur content to be reduced to lower levels. The current specification in Europe and in the USA has defined the maximum sulfur mass fraction as less than $50 \cdot 10^{-6}$ in gasoline starting from 2005. This level will be reduced to $10 \cdot 10^{-6}$ by the year 2010.[9] Ionic liquids may also be used for the extraction of methanol from crude oil. Indeed, large amounts of methanol are used to prevent the hydrate plugs from forming in oil pipelines, but the presence of high concentrations of methanol in crude oils can lead to costly problems during refinery operations.

This study is a continuation of our investigations on thermodynamic properties of imidazolium-based ionic liquids.[16−20] Our aim is to focus on the influence of a polar moiety on the thermodynamic properties of the ionic liquid. More precisely, we try to define the best structure of the ionic liquids for a given industrial application. In previous works, we have shown that introduction of a polar chain in ionic liquids also strongly affects the behavior of organic compounds in mixtures with the ionic liquids. A short polar chain in imidazolium-based ionic liquids increased their selectivity toward mixtures containing {alcohol + aliphatic} or {aromatic + aliphatic}.[20]

Nevertheless, there is a lack of data for ionic liquids used as a reference in various studies. Moreover, it can be found that there are two literature sources for the thermodynamic properties of organic compounds in the extensively studied 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. These data present a large discrepancy (of about 30 %).

This work presents activity coefficients at infinite dilution for a series of organic compounds dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] measured using the inverse gas chromatography technique.

It must be pointed out that the retention in gas chromatography is a complex process involving partition between the gas and the liquid phase but also the adsorption at solid−liquid and gas−liquid interfaces. Therefore, the comprehensive retention model should consider not only the contribution resulting from the gas−liquid partitioning but also the adsorption occurring at the interface between the bulk liquid and the solid support and at the interface between the gas phase and the bulk liquid.[21−24] The classical equation taking into account partition and interfacial adsorption contributions in the GC mechanism can be written as follows[25−27]

$$V_N = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \tag{1}$$

where V_N, V_L, A_{GL}, and A_{LS} are the net retention volume per gram of packing, the volume of liquid phase per gram of packing, the liquid surface area per gram of column packing, and the liquid−solid interfacial surface area per gram of column

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packing, respectively. K_L, K_{GL}, and K_{GLS} represent the gas−liquid partition coefficient, the adsorption coefficient at the gas−liquid interface, and the coefficient for adsorption at the support surface, respectively. Performing a series of measurements with increasing loading of the liquid phase makes it possible to extrapolate the V_N/V_L ratio against $1/V_L$ toward $1/V_L = 0$ and to obtain the value of the gas−liquid partition coefficient, K_L, independent of adsorption contributions. This approach was successfully used to obtain gas−liquid partition coefficients of polar probes.[24,28] Several studies on the influence of concurrent retention mechanisms on the determination of stationary phase selectivity showed that the *n*-alkanes were retained predominantly by interfacial adsorption on RTILs.[17,19,23] This can be explained because of the immiscibility of *n*-alkanes with polar salts. Ionic liquids can easily adsorb on solid surfaces and may form a strongly structured interface at the surface of the support. Lynden-Bell et al.[29] used simulation to investigate the surface structure in models of 1-butyl-3-methylimidazolium ionic liquids with a number of inorganic anions. The authors found that the cations are preferentially aligned with their rings perpendicular to the phase surface and their NN axes parallel to the surface normal. The [BMIM] cation shows a strong preference for the butyl group to put away from the bulk of the liquid. Computer simulation predicted that pure ionic liquids of the 1-alkyl-3-methylimidazolium family show structuring of their liquid phases in a manner that is analogous to microphase separation between polar and nonpolar domains. Polar domain has the structure of a tridimensional network of ionic channels, whereas the structure of a nonpolar domain depends on the chain length of an alkyl chain.[30] This interface may induce the adsorption of polar solutes. For this reason, it was decided to use the above-described experimental procedure that allows the separation of the adsorption contribution.

To quantify intermolecular solute−IL interactions, we have used the linear solvation energy relationship (LSER) developed by Abraham et al.[31−34] This method allows us to correlate thermodynamic properties of phase transfer processes. The most recent representation of the LSER model is given by eq 2

$$\log \mathrm{SP} = c + eE + sS + aA + bB + lL \qquad (2)$$

where SP is a solute property related with the free energy change such as gas−liquid partition coefficient, specific retention volume, or adjusted retention time at a given temperature. The capital letters represent the solute properties and the lower case letters the complementary properties of the ionic liquids. The solute descriptors are the excess molar refraction *E*, dipolarity/polarizability *S*, hydrogen bond acidity basicity *A* and B, respectively, and the gas−liquid partition coefficient on *n*-hexadecane at 298 K, *L*. The coefficients *c*, *e*, *s*, *a*, *b*, and *l* are not simply fitting coefficients, but they reflect complementary properties of the solvent phase.

The system constants are identified as the opposing contributions of cavity formation and dispersion interactions, *l*, the contribution from interactions with lone pair electrons, *e*, the contribution from dipole-type interactions, *s*, the contribution from the hydrogen-bond basicity of the stationary phase (because a basic phase will interact with an acid solute), *a*, and *b* the contribution from the hydrogen-bond acidity of the stationary phase. The system constants are determined by multiple linear regression analysis of experimental log SP (log K_L in this work) values for a group of solutes of sufficient number and variety to establish the statistical and chemical validity of the model.

Recently, Sprunger et al.[35] proposed to separate the anion and cation contributions in the LSER model. The authors have modified the LSER equation, eq 3, by rewriting each of the five solvent coefficients (*e*, *s*, *a*, *b*, *l*) as a summation of their respective cation and anion

$$\log \mathrm{SP} = c + (e_{\mathrm{cation}} + e_{\mathrm{anion}})E + (s_{\mathrm{cation}} + s_{\mathrm{anion}})S + (a_{\mathrm{cation}} + a_{\mathrm{anion}})A + (b_{\mathrm{cation}} + b_{\mathrm{anion}})B + (l_{\mathrm{cation}} + l_{\mathrm{anion}})L \qquad (3)$$

Cation-specific and anion-specific equation coefficients of eight cations and four anions were established to estimate the logarithm of the gas-to-IL partition coefficients. The major advantage of this method is that we can make predictions for more ILs by combining the set of ion coefficients.

In this work, activity coefficients at infinite dilution of 44 polar and nonpolar compounds (alkanes, alkenes, alkynes, cycloalkanes, aromatics, alcohols) have been determined in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate at (303.35, 312.55, 322.55, and 332.55) K. Experimental results were analyzed using the LSER approach.

Experimental Section

Materials or Chemicals. Sodium tetrafluoroborate (98 %), 1-methylimidazole (99 %), 1-bromobutane (99 %), and acetonitrile (99 %) were purchased from Acros Organics. Acetone (Normapur) was obtained from Prolabo, and ethyl acetate (purex for analysis) and dichloromethane were from Solvants Documentation Synthèses. All mixtures were prepared in ultrapure water (all water used was distilled and then filtered with an ELGA UHQ II system, $\kappa = 18$ MΩ). Imidazolium salt was synthesized according to standard methods.[36] An excess of 1-bromobutane was slowly added to a stirred solution of 1-methylimidazole in ethyl acetate. The mixture was then heated at reflux for 24 h. The reaction was stopped when two phases were formed. The bottom phase contained the 1-butyl-3-methylimidazolium bromide [BMIM][Br]. This was washed three times with ethyl acetate to remove any unreacted reagents. Residual ethyl acetate was removed by heating (70 °C) under vacuum (12 h). [BMIM][Br] was obtained as a colorless hygroscopic solid. A solution of $NaBF_4$ in acetone was added slowly to a rapidly stirring solution of [BMIM][Br]. The mixture was then stirred at room temperature for four days and filtered through celite, and the acetone was removed with a rotary evaporator. The resultant viscous liquid was dissolved in dichloromethane (CH_2Cl_2) and washed with small volumes of distilled water (3:1 v/v) until there was no precipitation of AgBr in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The CH_2Cl_2 was then evaporated. Traces of water and other volatile solvents were removed by freeze-drying immediately before the experiment. [BMIM][BF_4] was thereby obtained as colorless, very viscous, and hydrophilic liquids. The structure was confirmed by ^{1}H and ^{13}C NMR spectroscopies and mass spectrometry.[37,57] The residual water in the freshly prepared molten salt was titrated using a Karl Fisher apparatus (684KF Coulometer, Metrohm): [BMIM][BF_4] contained about $7.2 \cdot 10^{-4}$ g of water.

Apparatus and 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.

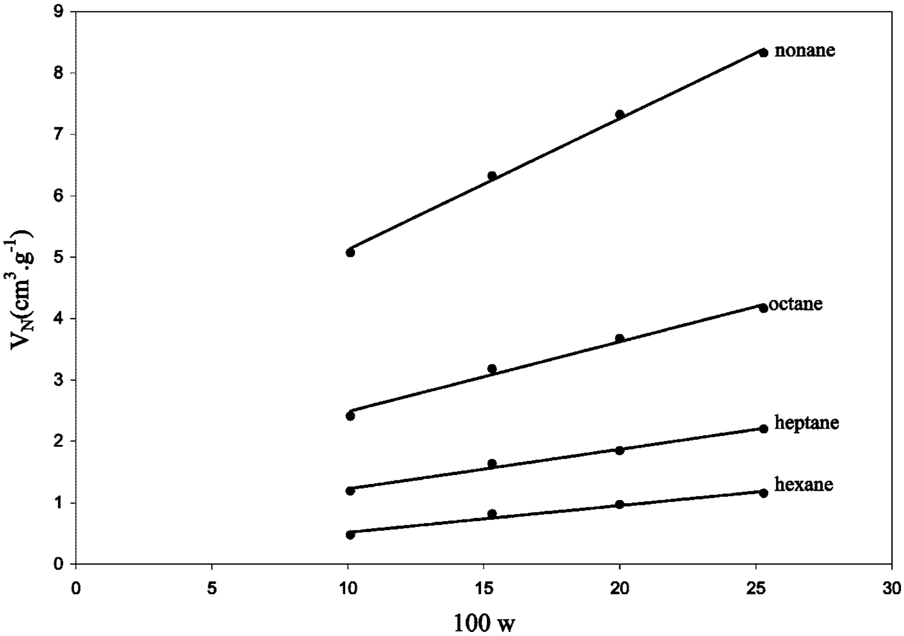

Figure 1. Plot of the net retention volume per gram of packing as a function of mass fraction loading *w* of 1-butyl-3-methylimidazolium tetrafluoroborate for *n*-alkanes.

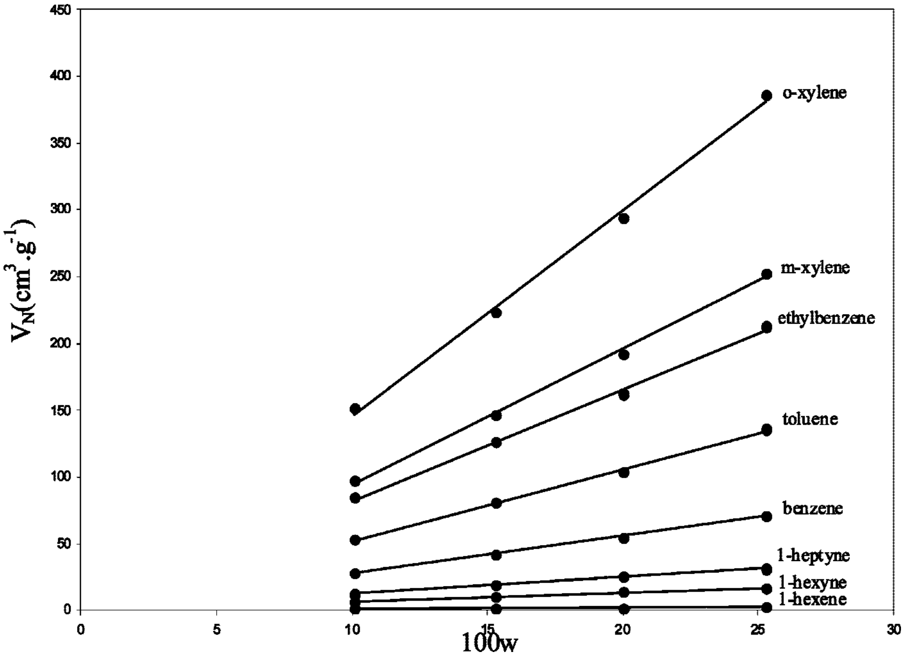

Figure 2. Plot of the net retention volume per gram of packing as a function of mass fraction loading *w* of 1-butyl-3-methylimidazolium tetrafluoroborate bromide for aromatics, alkenes, and alkynes.

Column packing of 1 m length containing a mass fraction of IL from (10 to 25) % on Chromosorb WHP (60 to 80 mesh) was prepared using the rotary evaporator technique. After evaporation of the chloroform 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 an uncertainty of ± 0.0003 g. A volume of the headspace vapor of samples of (1 to 5) μL were 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 elution 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 this study.

Theoretical Basis. The retention data determined with inverse chromatography experiments were used to calculate activity coefficients at infinite dilution of the solute in the ionic liquid with the following expression[38]

$$\ln \gamma_{1,2}^{\infty} = \ln\left(\frac{n_2RT}{V_N P_1^0}\right) - P_1^0\frac{B_{11}-V_1^0}{RT} + \frac{2B_{13}-V_1^{\infty}}{RT}JP_0 \qquad (4)$$

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

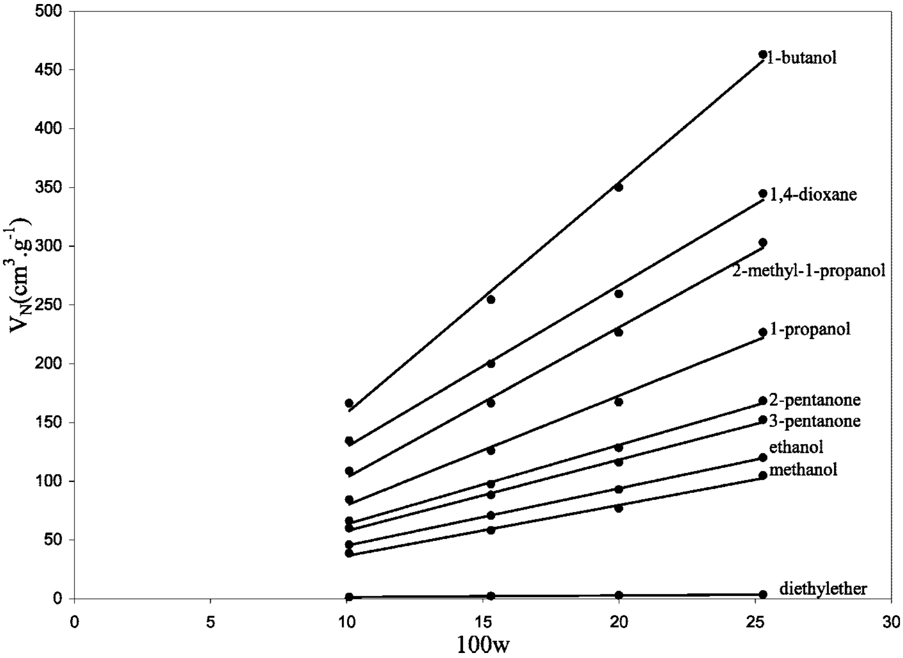

Figure 3. Plot of the net retention volume per gram of packing as a function of mass fraction loading *w* of 1-butyl-3-methylimidazolium tetrafluoroborate for some polar probes.

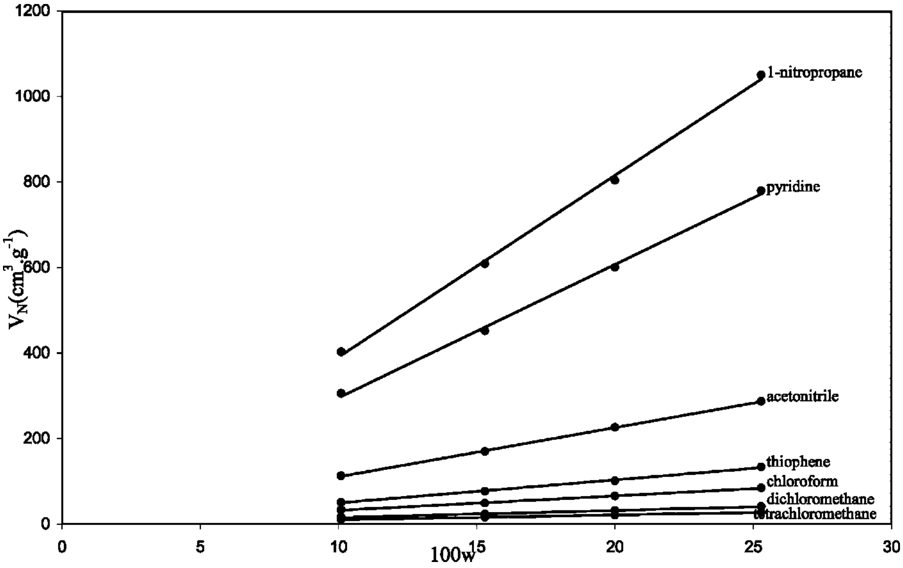

Figure 4. Plot of the net retention volume per gram of packing as a function of mass fraction loading *w* of 1-butyl-3-methylimidazolium tetrafluoroborate for some polar probes.

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 gelium 3; $P_1{}^0$ is the probe vapor pressure at temperature T; P_0 is the pressure at the column outlet. V_N denotes the standardized retention volume calculated using the classical equation described in the literature.[38] The factor J corrects for the influence of the pressure drop along the column.[39] The values of $P_1{}^0$ and B_{11} have been taken from the literature.[40] 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} were estimated using Tsonopolous's method.[41−43] Critical parameters and acentric factors used for the calculations were taken from the literature.[40,44]

However, in the case where gas−liquid adsorption takes place in the column, eq 4 when the last two terms are neglected can be rewritten as follows

$$\gamma_{1,2}^{\infty} = \frac{RT\rho_2}{P_1^0 M_2 K_L} \tag{5}$$

where ρ_2 is the density of the solvent; M_2 is the molecular weight of the stationary phase; and K_L is the bulk solution partition coefficient. The best method of determining K_L in the presence of interfering adsorption effects is to plot V_N/V_L against $1/V_L$. Then according to eq 1, K_L is obtained from the intercept.

Results and Discussion

Influence of Concurrent Retention Mechanisms. To correct for gas−liquid adsorption, the net retention volume V_N was

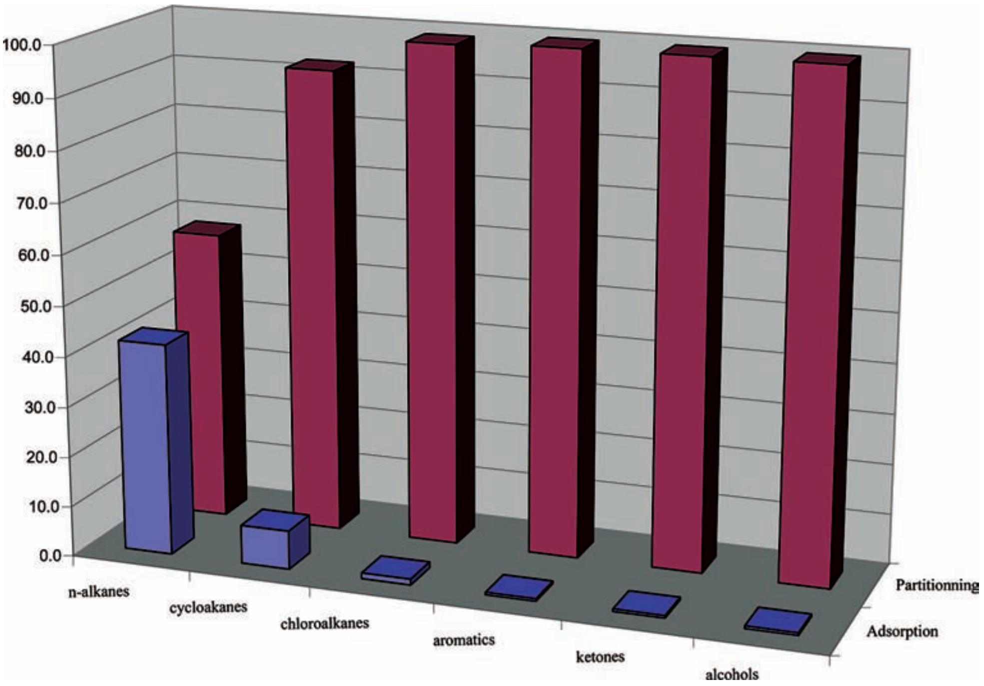

Figure 5. Relative percent contribution of gas−liquid partitioning and gas−liquid interfacial adsorption to retention on 1-butyl-3-methylimidazolium tetrafluoroborate (15.30 % w/w) at 322.55 K.

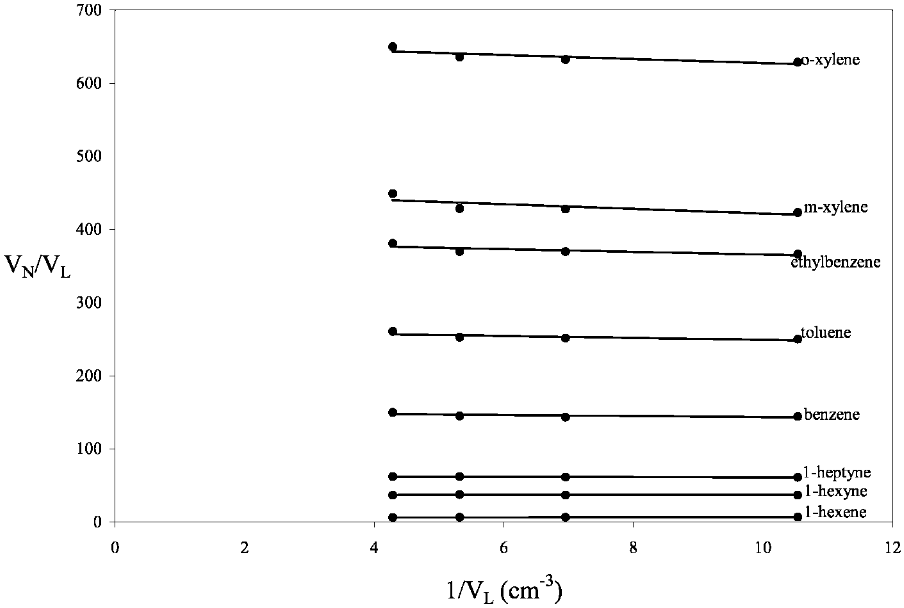

Figure 6. Plot of V_N/V_L against $1/V_L$ for aromatics, alkenes, and alkynes on 1-butyl-3-methylimidazolium tetrafluoroborate.

calculated for all the solutes at different solvent liquid loading V_L. Then, the graphs of V_N/V_L versus $1/V_L$ were drawn for each solute, and the partition bulk coefficient K_L was obtained from the intercept. A horizontal line is expected for a pure partitioning system and a line with a slope and positive intercept on the V_N/V_L axis for a mixed retention mechanism. The K_L value is then used in eq 5 to calculate the activity coefficient at infinite dilution for bulk solvent loading, i.e., assuming that no adsorption of the solute at the gas−liquid interface occurs. Nevertheless, special attention has to be paid when a retention model is used. From our experience, we observed that reduced retention times have to be higher than 1 min. Indeed, short retention times induce high uncertainties on the infinite dilution activity coefficient. In this case, values of corrected γ^∞ values may be ten times higher than uncorrected values.

The activity coefficients at infinite dilution not corrected from interfacial adsorption are calculated using eq 4. The errors in the γ^∞ values may be obtained from the law of propagation of errors. The following measured parameters exhibit errors which must be taken into account in the error calculations with their corresponding standard deviations: the adjusted retention time t_R', ± 0.01 min; the flow rate of the carrier gas, ± 0.1 $\text{cm}^3 \cdot \text{min}^{-1}$; mass of the stationary phase, 2 %; the inlet and outlet pressures, ± 0.002 bar; the temperature of the oven, ± 0.1 K. The main source of uncertainty in the calculation of the net retention volume is the determination of the mass of the stationary phase. The estimated uncertainty in determining the net retention volume V_N is about 2 %. Taking into account that thermodynamic parameters are also subject to an uncertainty, the resulting uncertainty in the γ^∞ values is about 3 %.

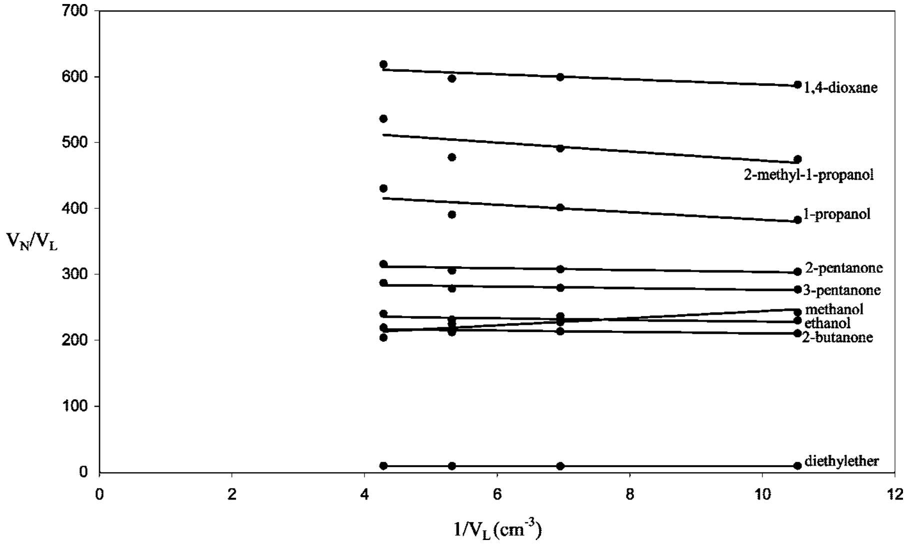

Figure 7. Plot of V_N/V_L against $1/V_L$ for alcohols, ketones, 1,4-dioxane, and ether on 1-butyl-3-methylimidazolium tetrafluoroborate.

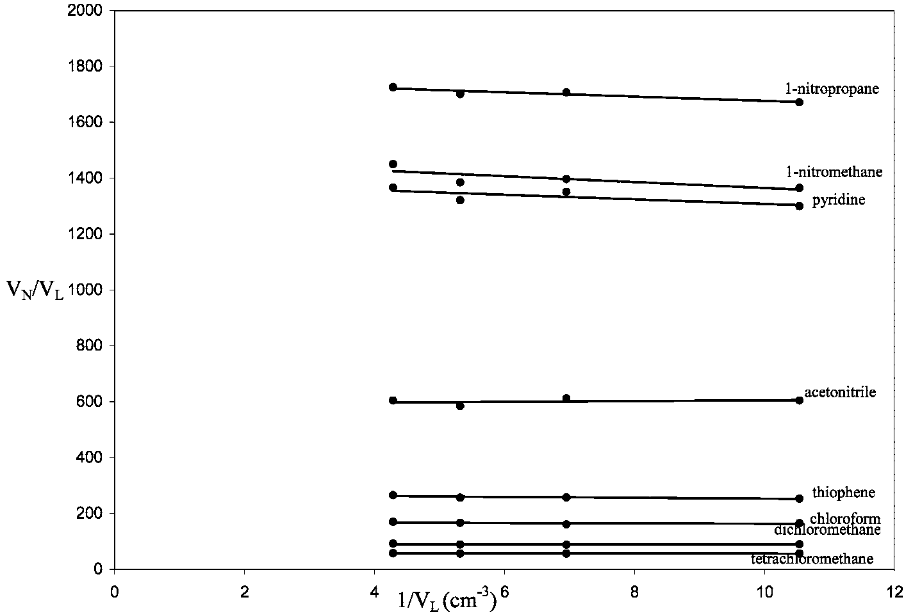

Figure 8. Plot of V_N/V_L against $1/V_L$ for some test probes on 1-butyl-3-methylimidazolium tetrafluoroborate.

In Figures 1 to 4, the net retention volume per gram of packing V_N as a function of the percent phase loading is plotted for nonpolar and polar solutes. In [BMIM][BF_4], the polar solutes are retained by partitioning with a small contribution from adsorption while the *n*-alkanes are retained predominantly by adsorption. Indeed, *n*-alkanes are almost immiscible in ionic liquids, and gas−liquid interfacial adsorption is then predominant. Figure 1 indicates that the retention of the *n*-alkanes with the ionic liquid stationary phase does not follow the pattern observed with polar solutes. Probably, at low loading of the stationary, the support is not completely coated, and results do not follow the initial straight line. Relative percent contribution of gas−liquid partitioning and gas−liquid interfacial adsorption to retention on 1-butyl-3-methylimidazolium tetrafluoroborate with w = 15.30 % at 322.55 K is represented in Figure 5. The average contribution of gas−liquid partitioning and gas−liquid interfacial adsorption for polar solutes to retention is 95 % and 5 %, respectively.

The gas−liquid partition coefficients were calculated from Figures 6 to 8, and activity coefficients at infinite dilution were determined from values of K_L constants. Values for the gas−liquid partition coefficients with their uncertainty and activity coefficients at infinite dilution uncorrected and corrected from interfacial adsorption are listed in Tables 1 and 2. Activity coefficients at infinite dilution of *n*-alkanes are multiplied by two when corrected from interfacial adsorption. As expected, adsorption effects decrease with temperature.

The magnitude of the activity coefficient values obtained in this study is significantly higher than the corresponding values for other ionic liquids.[16−20,45−53] As an example, the γ^∞ value for hexane in 1-butyl-3-methylimidazolium tetrafluoroborate is 132.86 (this work), while in 1-butyl-3-methylimidazolium octyl sulfate,[17] it is 4.75; in 1-hexyl-3-methylimidazolium tetrafluoroborate[45] it is 22.1; and in 1-ethyl-3-methylimidazolium thiocyanate[52] it is about 300 (the highest value found in the literature). The high values of activity coefficients at infinite dilution of *n*-alkanes indicate their low solubility in ionic liquids. This trend is in good agreement with the data obtained in the imidazolium[16−20,45−49] and pyridinium[50,51] ionic liquids. 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.

Table 1. Experimental Activity Coefficients at Infinite Dilution of 44 Organic Compounds in the 1-Butyl-3-methylimidazolium Tetrafluoroborate at (303.35 and 312.55) K as a Function of Loading w

	$T = 303.35$ K						$T = 312.55$ K					
	uncorrected values of γ^∞						uncorrected values of γ^∞					
	100 w				corrected data		100 w				corrected data	
solutes	10.10	15.30	20.00	25.29	K_L	γ^∞	10.10	15.30	20.00	25.29	K_L	γ^∞
hexane	94.31	91.43	94.92	97.27	3.6 ± 0.1	132.86	53.98	81.01	81.63	88.05	2.6 ± 0.1	130.45
3-methylpentane	63.86	75.22	79.77	83.22	3.1 ± 0.2	126.11	50.49	58.14	66.88	72.27	2.9 ± 0.2	94.30
heptane	120.31	153.58	158.75	163.29	6.0 ± 0.7	259.08	104.58	109.00	140.75	145.15	4.1 ± 1.0	250.01
2,2,4-trimethylpentane	131.90	157.46	164.29	173.75	4.5 ± 0.3	321.18	106.39	119.42	146.13	154.18	4.2 ± 0.3	231.46
octane	188.44	244.70	256.17	273.12	11.5 ± 0.3	424.91	159.46	180.85	219.51	237.48	8.4 ± 0.1	368.37
nonane	305.91	419.55	450.19	484.31	17.5 ± 0.6	955.62	262.08	297.41	366.37	417.22	12.6 ± 1.2	792.80
methylcyclopentane	43.92	50.33	51.84	52.73	8.5 ± 0.1	62.19	40.53	41.03	46.62	47.20	7.0 ± 0.3	53.50
cyclohexane	44.97	49.18	46.28	51.62	11.9 ± 0.1	62.53	40.89	39.86	45.00	44.88	10.6 ± 0.3	48.41
methylcyclohexane	66.93	75.49	77.65	79.54	15.7 ± 0.1	98.30	60.39	60.76	68.33	71.27	12.6 ± 0.3	82.69
cycloheptane	63.26	67.67	68.04	70.26	37.6 ± 0.8	78.71	82.31	80.45	89.34	93.24	29.3 ± 0.2	98.21
benzene	2.51	2.56	2.53	2.46	344.2 ± 4.2	2.20	2.50	2.32	2.44	2.35	240.6 ± 7.5	2.17
toluene	4.23	4.31	4.24	4.16	555.7 ± 15.9	4.37	4.20	3.89	4.09	4.03	402.2 ± 7.2	3.96
ethylbenzene	7.41	7.62	7.49	7.35	928.5 ± 59.1	7.25	7.44	6.95	7.39	7.15	636.2 ± 21.1	6.73
m-xylene	7.77	7.78	7.82	7.48	1041.4 ± 10.1	7.81	7.23	6.98	7.48	7.18	683.0 ± 29.8	7.40
p-xylene	7.05	7.18	7.20	6.93	1037.0 ± 14.6	7.36	7.06	6.49	6.95	6.76	720.5 ± 12.8	6.68
o-xylene	6.21	6.34	6.37	6.11	1553.3 ± 27.5	6.53	5.53	5.74	6.09	5.90	1122.9 ± 68.9	5.55
1-hexene	36.41	37.40	38.11	40.34	8.2 ± 0.7	48.02	30.82	32.96	35.26	37.23	7.1 ± 0.4	39.33
1-hexyne	7.77	7.45	7.47	7.65	68.0 ± 0.9	8.29	7.17	6.90	7.32	7.51	52.1 ± 1.1	7.53
1-heptyne	12.74	12.43	12.57	12.73	128.6 ± 3.8	13.22	12.35	11.55	12.28	12.53	90.9 ± 1.4	12.54
2-butanone	1.61	1.64	1.65	1.58	493.4 ± 17.2	1.50	1.63	1.50	1.61	1.56	342.4 ± 7.1	1.48
2-pentanone	2.80	2.85	2.87	2.75	764.5 ± 32.5	2.60	2.82	2.64	2.78	2.71	507.5 ± 10.0	2.60
3-pentanone	2.81	2.89	2.90	2.77	691.1 ± 33.0	2.63	2.84	2.62	2.80	2.71	466.0 ± 10.3	2.57
1,4-dioxane	1.35	1.39	1.38	1.29	1556.3 ± 59.4	1.26	1.38	1.27	1.36	1.31	1023.2 ± 23.4	1.24
methanol	1.32	1.32	1.33	1.22	452.2 ± 25.8	1.22	1.19	1.06	1.21	1.22	293.9 ± 16.3	1.22
ethanol	2.33	2.28	2.29	2.23	535.5 ± 6.4	2.15	2.12	1.75	2.00	1.98	374.0 ± 4.1	1.91
1-propanol	3.34	3.33	3.39	3.11	974.4 ± 53.0	3.12	3.06	2.79	2.98	2.75	672.1 ± 34.6	2.70
2-propanol	3.23	3.24	3.30	3.18	479.9 ± 12.0	3.20	2.93	2.72	2.87	2.79	333.9 ± 7.8	2.76
2-methyl-1-propanol	4.83	4.80	4.78	4.20	1356.5 ± 119.5	4.17	4.22	3.79	4.14	4.07	792.0 ± 13.7	3.99
1-butanol	5.38	5.21	5.33	4.73	2035.8 ± 103.9	4.74	4.63	4.09	4.37	3.99	1375.4 ± 71.9	3.82
2,2,2-trifluoroethanol	0.37	0.37	0.33	0.36	2579.2 ± 84.9	0.36	0.37	0.32	0.34	0.35	1786.3 ± 39.2	0.33
diethylether	8.46	8.99	8.93	9.44	13.8 ± 0.1	10.15	8.38	8.26	8.72	9.05	11.0 ± 0.3	9.39
diisopropylether	26.90	27.69	26.58	30.17	15.9 ± 1.3	30.70	23.86	24.19	26.60	28.77	10.2 ± 1.2	33.47
chloroform	1.03	1.05	1.07	1.02	359.8 ± 13.3	1.04	1.09	1.03	1.07	1.06	253.3 ± 6.7	1.04
dichloromethane	0.70	0.71	0.71	0.69	175.0 ± 5.3	0.69	0.76	0.69	0.75	0.73	130.7 ± 3.0	0.72
tetrachloromethane	5.37	5.51	5.54	5.40	115.5 ± 2.9	5.53	5.38	5.11	5.52	5.33	81.9 ± 2.7	5.44
acetonitrile	0.66	0.66	0.67	0.66	1241.7 ± 18.2	0.65	0.65	0.61	0.64	0.63	887.2 ± 14.2	0.63
nitromethane	0.58	0.59	0.56	-	3274.4 ± 41.2	0.59	0.60	0.55	0.58	0.57	2268.6 ± 49.5	0.56
1-nitropropane	1.56	1.55	1.56	-	4385.4 ± 58.5	1.54	1.53	1.40	1.50	-	2845.7 ± 3.9	1.46
triethylamine	14.91	25.62	25.24	14.00	112.5 ± 46.3	9.44	16.43	25.42	22.14	14.66	81.8 ± 18.8	8.90
pyridine	1.00	1.01	0.95	0.97	3318.2 ± 102.4	1.00	1.01	0.94	1.00	0.99	2141.8 ± 32.2	0.99
thiophene	1.62	1.62	1.64	1.53	573.9 ± 19.2	1.56	1.63	1.52	1.60	1.54	402.7 ± 14.1	1.52
formaldehyde	0.22	0.22	0.23	0.22	91.8 ± 2.7	0.22	0.23	0.45	0.24	0.23	66.6 ± 3.6	0.23
propionaldehyde	1.36	1.37	1.41	1.36	171.4 ± 5.6	1.38	1.33	1.29	1.35	1.31	125.7 ± 5.8	1.33
butyraldehyde	2.22	2.21	2.27	2.19	301.9 ± 7.3	2.19	2.21	2.09	2.19	2.14	214.1 ± 6.7	2.13

Introduction of a double or triple bond in the *n*-alkanes decreases the γ^∞ values. Cyclization of the alkane skeleton reduces the value of γ^∞ in comparison to that of the corresponding linear alkanes (e.g., hexane). Aromatics with their π-delocalized electrons have smaller γ^∞ values, presumably because of the interaction with the cation species. Using computer simulation, Lynden and co-workers[29] showed that the cations are found to interact predominantly with the ring of the benzene, while the anions interact with the ring hydrogens to a first approximation.

In the series of chloromethanes, it was observed that γ^∞ values strongly increase from dichloromethane to tetrachloromethane. This behavior already observed with different ionic liquids[17,19] 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. The γ^∞ values for the alcohols are relatively small (ranging between 1.2 and 4.6). The lone pair of electrons on the oxygen atom could interact with the ionic liquid cation, and the acidic proton is attracted by oxygen atoms in the cation. γ^∞ values of the branched alkanol skeleton are smaller than γ^∞ values of the corresponding linear alcohol. γ^∞ values of *n*-alkanols increase with increasing chain length. γ^∞ values of ethers and amine are higher in comparison with those of the alcohols.

In Table 3, our results are compared with other activity coefficients measured by Foco et al.[45] and Zhou et al.[53] The deviations between our uncorrected data and the results by Foco et al.[45] at 303.15 K amount on average to 7.5 %. γ^∞ values obtained follow the same trend as those measured in this work. As can be seen from Table 3, the γ^∞ data by Zhou et al.[53] are about 32 % lower than our uncorrected values and those obtained by Foco et al.[45] If we plot γ values obtained in this study as a function of the data set of Zhou et al.,[53] there is a linear relationship. This observation indicates that the differences are not due to the thermodynamic properties of pure compounds used in the γ calculation but to the determination of the mass of the stationary phase or to the measurement of the flow rate or to the purity of the ionic liquid.

The selectivity value S_{12}^∞ gives the suitability of a solvent as an entrainer in extractive distillation. It is defined as

$$S_{12}^\infty = \frac{\gamma_{1/\mathrm{RTIL}}^\infty}{\gamma_{2/\mathrm{RTIL}}^\infty} \tag{6}$$

Table 4 shows selectivities S_{12}^∞ for four separation problems: hexane/benzene, hexane/methanol, hexane/thiophene, cyclohexane/thiophene for ionic liquids based on the 1-alkyl-3-meth-

Table 2. Experimental Activity Coefficients at Infinite Dilution of 44 Organic Compounds in the 1-Butyl-3-methylimidazolium Tetrafluoroborate at (322.55 and 332.55) K as a Function of Loading w

	T = 322.55 K						T = 332.55 K					
	uncorrected values of γ^∞						uncorrected values of γ^∞					
	100 w				corrected data		100 w				corrected data	
solutes	10.10	15.30	20.00	25.29	K_L	γ^∞	10.10	15.30	20.00	25.29	K_L	γ^∞
hexane	75.62	65.91	73.76	79.93	2.5 ± 0.2	97.36	56.43	49.08	66.68	68.58	2.4 ± 0.1	74.19
3-methylpentane	72.80	51.28	62.44	67.25	2.4 ± 0.1	82.92	44.60	43.06	56.13	66.47	-	152.01
heptane	91.44	96.72	116.67	130.64	3.2 ± 0.3	216.04	109.80	88.48	109.94	113.65	3.3 ± 0.4	142.31
2,2,4-trimethylpentane	92.42	106.06	116.92	139.91	3.4 ± 1.2	197.53	89.22	80.85	124.64	122.71	-	271.78
octane	140.45	170.35	198.02	211.10	5.8 ± 0.4	333.47	144.03	128.62	164.43	182.29	4.2 ± 0.5	297.93
nonane	232.94	270.08	334.94	370.58	9.7 ± 0.3	612.49	218.55	201.34	295.55	312.07	7.8 ± 0.7	463.75
methylcyclopentane	37.09	40.33	40.71	44.00	6.1 ± 1.1	42.76	36.55	32.07	37.32	42.25	3.4 ± 0.5	55.40
cyclohexane	35.98	37.17	39.02	41.51	8.3 ± 1.0	42.66	36.05	34.29	35.08	37.79	7.2 ± 1.6	35.28
methylcyclohexane	54.35	56.08	61.47	61.76	10.9 ± 0.1	64.23	53.95	51.12	52.69	58.22	8.5 ± 2.2	57.10
cycloheptane	111.60	108.82	120.74	122.27	21.4 ± 0.4	131.04	154.93	139.01	147.95	161.56	16.4 ± 0.1	166.53
benzene	2.48	2.32	2.36	2.39	158.9 ± 5.9	2.25	2.50	2.16	2.31	2.35	116.5 ± 11.8	2.16
toluene	4.17	3.85	3.95	4.00	262.3 ± 5.6	3.97	4.21	3.63	3.85	3.96	183.3 ± 5.1	3.84
ethylbenzene	7.39	6.80	7.00	7.10	394.6 ± 7.3	6.85	7.40	6.41	6.81	7.01	270.3 ± 12.7	6.51
m-xylene	7.39	6.78	6.98	6.96	453.6 ± 14.0	6.89	7.35	6.36	6.75	6.95	304.8 ± 15.0	6.56
p-xylene	7.01	6.44	6.64	6.77	447.0 ± 6.6	6.71	6.99	6.08	6.39	6.64	307.7 ± 17.4	6.26
o-xylene	6.08	5.62	5.76	5.89	655.2 ± 9.9	5.83	6.14	5.30	5.62	5.08	511.9 ± 39.8	4.77
1-hexene	29.67	29.20	30.95	33.64	5.5 ± 0.3	36.27	28.11	26.18	30.08	32.92	3.7 ± 0.2	38.84
1-hexyne	7.35	6.84	7.22	7.46	36.2 ± 0.9	7.47	7.53	6.58	6.89	7.27	28.0 ± 1.8	6.82
1-heptyne	12.41	11.45	12.20	12.19	63.3 ± 0.3	11.94	12.75	10.91	11.62	12.22	43.8 ± 2.5	11.74
2-butanone	1.55	1.42	1.47	1.49	225.2 ± 4.6	1.44	1.42	1.23	1.30	1.35	164.9 ± 8.2	1.25
2-pentanone	2.85	2.61	2.71	2.74	324.6 ± 6.4	2.66	2.86	2.48	2.64	2.71	229.9 ± 4.6	2.53
3-pentanone	2.85	2.62	2.71	2.74	296.0 ± 5.8	2.66	2.87	2.49	2.65	2.72	211.2 ± 10.0	2.52
1,4-dioxane	1.40	1.28	1.32	1.33	640.7 ± 13.6	1.28	1.42	1.22	1.29	1.33	448.1 ± 22.7	1.22
methanol	0.96	0.92	0.99	1.14	190.5 ± 15.7	1.22	1.04	0.86	0.93	1.05	132.1 ± 16.8	1.18
ethanol	1.92	1.80	1.82	1.83	258.8 ± 9.2	1.70	1.78	1.03	1.61	1.28	183.6 ± 60.2	1.53
1-propanol	2.80	2.48	2.62	2.49	439.6 ± 25.9	2.43	2.57	2.18	2.30	2.31	304.3 ± 13.1	2.14
2-propanol	2.65	2.36	2.50	2.54	220.3 ± 6.4	2.50	2.42	2.09	2.20	2.29	159.8 ± 9.2	2.15
2-methyl-1-propanol	3.74	3.36	3.56	3.31	541.0 ± 39.6	3.28	3.44	2.92	3.10	3.06	367.3 ± 14.7	2.84
1-butanol	4.12	3.67	3.87	3.39	861.8 ± 92.5	3.33	3.73	3.15	3.31	2.93	613.4 ± 51.0	2.69
2,2,2-trifluoroethanol	0.36	0.32	0.34	0.33	1130.6 ± 52.0	0.32	0.36	0.30	0.31	0.33	767.8 ± 41.4	0.30
diethylether	8.11	8.05	8.45	7.92	9.2 ± 0.7	8.18	8.69	7.75	8.57	8.28	7.6 ± 0.3	7.42
diisopropylether	21.55	24.96	25.70	27.28	8.9 ± 1.2	26.92	22.28	22.23	24.30	25.04	7.1 ± 0.4	24.26
chloroform	1.13	1.07	1.07	1.10	170.2 ± 5.9	1.09	1.20	1.05	1.11	1.15	123.8 ± 6.2	1.09
dichloromethane	0.80	0.76	0.77	0.78	91.1 ± 3.0	0.79	0.88	0.76	0.80	0.84	70.6 ± 3.7	0.79
tetrachloromethane	5.33	5.06	5.27	5.37	57.6 ± 1.0	5.38	5.52	4.88	5.18	5.42	42.6 ± 2.3	5.20
acetonitrile	0.63	0.58	0.62	0.63	591.7 ± 20.5	0.64	0.66	0.55	0.60	0.61	435.0 ± 16.9	0.61
nitromethane	0.61	0.55	0.57	0.57	1470.7 ± 42.0	0.56	0.62	0.52	0.56	0.57	992.0 ± 52.6	0.56
1-nitropropane	1.53	1.39	1.43	-	1741.8 ± 26.3	1.46	1.54	1.30	1.36	-	1081.7 ± 4.9	1.50
triethylamine	11.45	23.36	24.68	28.67	14.0 ± 2.4	35.28	13.13	17.92	25.93	27.21	5.8 ±	59.39
pyridine	1.04	0.93	0.98	0.99	1390.2 ± 35.6	0.97	1.06	0.90	0.96	1.01	948.9 ± 46.1	0.94
thiophene	1.65	1.50	1.55	1.57	268.8 ± 5.6	1.54	1.66	1.42	1.52	1.59	194.6 ± 9.8	1.49
formaldehyde	0.25	0.24	0.25	0.25	47.1 ± 1.4	0.26	0.27	0.24	0.26	0.27	37.3 ± 1.8	0.25
propionaldehyde	1.30	1.23	1.26	1.29	91.2 ± 1.8	1.29	1.31	1.15	1.23	1.26	70.2 ± 3.3	1.21
butyraldehyde	2.11	2.03	2.07	2.10	144.8 ± 4.8	2.15	2.19	1.90	2.01	2.09	105.5 ± 2.7	2.06

Table 3. Comparison of γ^∞ Values Obtained in This Work with γ^∞ Values Measured by Foco et al.[45] and Zhou et al.[53] at T = 303.15 K

	γ^∞			
	ref 45	ref 53	this work	
solutes			uncorrected data	corrected data
hexane	93.41	60.80	91.43	132.86
heptane	134.05	92.45	153.58	259.08
2,2,4-trimethylpentane	144.82	92.69	157.46	321.18
cyclohexane	44.94	32.41	49.18	62.53
benzene	2.39	1.74	2.56	2.2
toluene		2.91	4.31	4.09
ethylbenzene		5.61	7.62	7.25
1-hexene	35.37		37.40	48.02
methanol	1.32	0.83	1.32	1.10
ethanol		1.59	2.28	2.15
1-propanol		2.80	3.33	2.82
2-propanol		2.63	3.24	3.03
chloroform		1.11	1.05	0.95
tetrachloromethane		5.73	5.51	5.21

ylimidazolium cation at T = 313.15 K. The selectivity for investigated ILs is high. The value of 85.8 shows the possibility of using [BMIM][BF$_4$] as an extractive medium for the separation of thiophene from alkanes. This value is eight times higher than for most ionic liquids. The selectivity of [BMIM][BF$_4$] for the {hexane + benzene} mixture at 313.15 K is very large compared to the value for classical solvents such as dimethylsulfoxide ($S_{12}^\infty = 22.7$) or sulfolane ($S_{12}^\infty = 30.5$). The selectivity decreases with increasing length of the alkyl chain. It is obvious that the chemical nature of the cation and the anion plays an important role in separation of mixtures containing polar and aliphatic compounds. Table 4 shows that selectivity decreases when [BF$_4$] is changed by [OcSO$_4$] or [Tf$_2$N].

From these results and our previous works, some observation can be made. It is clear that decreasing alkyl chain length of imidazolium-based ionic liquids tends to increase solubility of most organic compounds in ionic liquids. Introduction of a polar chain in ionic liquids also strongly affects the behavior of organic compounds in mixtures with the ionic liquids.

LSER Characterization. The ionic liquid studied in this work was analyzed using the LSER approach. Coefficients c, e, s, a, b, and l of [BMIM][BF$_4$] were obtained by multiple linear

Table 4. Selectivity Values S_{12}^{∞} for Different Separation Problems at 313.15 K

	S_{12}^{∞}				
solvent	hexane/benzene	hexane/methanol	hexane/thiophene	cyclohexane/thiophene	ref
1-ethyl-3-methylimidazolium tetrafluoroborate	61.6	290.4	-	-	45
1-butyl-3-methylimidazolium tetrafluoroborate	60.1	106.9	85.8	31.8	this work
1-hexyl-3-methylimidazolium tetrafluoroborate	22.3	29.2	-	-	45
1-octyl-3-methylimidazolium tetrafluoroborate	10.5	12.1	-	-	45
1-hexadecyl-3-methylimidazolium tetrafluoroborate	2.8	2.2	2.2	2.0	19
1-ethyl-3-methylimidazolium ethylsulfate	41.4	-	-	-	56
1-butyl-3-methylimidazolium octylsulfate	5.5	4.4	6.5	3.9	17
1-hexyl-3-methylimidazolium hexafluorophosphate	21.6	10.2	-	-	46
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	37.5	19.5	-	-	56
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	16.7	-	-	-	56
n-acryloyloxypropyl-*N*-methylimidazolium bromide	27.6	551.6	69.2	62.0	20
n-methacryloyloxyhexyl-*N*-methylimidazolium bromide	50.4	820	82	41.4	20
1-propenyl-3-methyl-imidazolium bromide	7	139.3	16.9	10.6	18
1-propenyl-3-octyl-imidazolium bromide	6.4	52.3	9.6	6.1	18
1-propyl boronic acid-3-octyl-imidazolium bromide	9.91	455.7	15.2	6.8	18
1-propyl boronic acid-3-decyl-imidazolium bromide	4.1	109	6.9	4.9	18
1-propyl boronic acid-3-dodecyl-imidazolium bromide	3.8	116.3	5.2	3.6	18
1-octyl-3-methylimidazolium chloride	8.7	-	-	-	55

Table 5. LSER Descriptors of Solutes Used to Characterize Ionic Liquids[31−34]

solutes	*E*	*S*	*A*	*B*	*L*
hexane	0	0	0	0	2.668
3-methylpentane	0	0	0	0	2.581
heptane	0	0	0	0	3.173
2,2,4-trimethylpentane	0	0	0	0	3.106
octane	0	0	0	0	3.677
nonane	0	0	0	0	4.182
methylcyclopentane	0.225	0.1	0	0	2.816
cyclohexane	0.305	0.1	0	0	2.964
methylcyclohexane	0.244	0.1	0	0	3.323
cycloheptane	0.35	0.1	0	0	3.704
benzene	0.61	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
p-xylene	0.613	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	2.51
1-heptyne	0.16	0.23	0.12	0.1	3
2-butanone	0.166	0.7	0	0.51	2.287
2-pentanone	0.143	0.68	0	0.51	2.755
3-pentanone	0.154	0.66	0	0.51	2.811
1,4-dioxane	0.329	0.75	0	0.64	2.892
methanol	0.278	0.44	0.43	0.47	0.97
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
2,2,2-trifluoroethanol	0.015	0.6	0.57	0.25	1.224
diethylether	0.041	0.25	0	0.45	2.015
diisopropylether	0	0.19	0	0.41	2.482
chloroform	0.425	0.49	0.15	0.02	2.48
dichloromethane	0.387	0.57	0.1	0.05	2.019
tetrachloromethane	0.458	0.38	0	0	2.833
acetonitrile	0.237	0.90	0.07	0.32	1.739
nitromethane	0.313	0.95	0.06	0.31	1.892
1-nitropropane	0.242	0.95	0	0.31	2.894
triethylamine	0.101	0.15	0	0.79	3.04
pyridine	0.631	0.84	0	0.52	3.022
thiophene	0.687	0.57	0	0.15	2.819
formaldehyde	0.22	0.73	0	0.33	0.73
propionaldehyde	0.196	0.65	0	0.45	1.815
butyraldehyde	0.187	0.65	0	0.45	2.27

regression of the logarithm of the gas−liquid partition coefficients log K_L of 44 solutes. LSER parameters of organic compounds used for the determination of LSER coefficients are given in Table 5.

System constants determined at different phase loadings from $\log(V_N/V_L)$ but also from the extrapolated values of the gas−liquid partition coefficients are summarized in Table 6. We can notice that there is a statistical difference between the system constants calculated from the sorption coefficients $\log(V_N/V_L)$ and from the gas−liquid partition coefficient log K_L. There is some dependence of the system constants on the phase loading. The LSER coefficients vary with phase loading. This result confirms that interfacial adsorption has an important influence on the determination of physicochemical properties of ionic liquids using inverse gas chromatography.

The system constants for [BMIM][BF_4] studied in this work at 313.15 K but also for other ionic liquid stationary phases are summarized in Table 7. The system constants for ionic liquids not studied in this work are taken from the literature.[16−20,48]

LSER coefficients of [BMIM][BF_4] are slightly different from those obtained with other ionic liquids of the imidazolium bromide type. The $(c + lL)$ 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.[48] The ionic liquid interacts via nonbonding and π-electrons (*e* system constant) and is not much different from other polar nonionic liquids. Dipolarity/polarizality of [BMIM][BF_4] is slightly higher than the most dipolar/polarizable ionic and nonionic stationary phases. The polarizability decreases slightly when the alkyl chain length is increased on the imidazolium ring. As expected, the hydrogen-bond basicity of the ionic liquid (*a* system constants) is considerably larger than values obtained for nonionic phases ($0.11 < a < 2.3$), but this value is the lowest found with imidazolium-based ionic liquids. [BMIM][BF_4] is sligthly hydrogen-bond acidic. Ionic liquids have structural features that would facilitate hydrogen-bond acceptor basicity interactions (electron-rich oxygen, nitrogen, and fluorine atoms). Imidazolium bromide based ionic liquids containing a (meth)acryloyloxyalkyl chain have the highest hydrogen-bond basicity with an *a* constant of about 5.4. This is great support for the idea that the interactions between the −OH group and ionic liquids are very strong. The evolution of the LSER coefficients of [BMIM][BF_4] with respect to temperature is presented in Figure 9. All LSER coefficients decrease with an increase of temperature. This indicates that the selectivity of the ionic liquids toward mixtures containing sulfur organic compounds (or polar compounds) and hydrocarbons is higher at low temperature. Finally, the LSER treatment indicates that the largest selectivity is found when two components have different polarity and different hydrogen bond acidity.

Sprunger and co-workers[35,54] proposed LSER correlations for the prediction of the partition coefficients of solutes in ionic liquids. The calculated cation-specific and anion-specific coefficients needed in eq 4 are taken from the literature. Figure 10

Table 6. System Constants for 1-Butyl-3-methylimidazolium Tetrafluoroborate[a]

		system constants						statistics		
T/K	100 *w*	*e*	*s*	*a*	*b*	*l*	*c*	*F*	*ρ*	*n*
303.35	25.29	0.46 (0.09)	2.59 (0.08)	3.21 (0.10)	0.53 (0.07)	0.53 (0.02)	−0.70 (0.07)	1042	0.993	42
	20.00	0.34 (0.07)	2.69 (0.07)	3.19 (0.09)	0.35 (0.07)	0.53 (0.02)	−0.67 (0.07)	1216	0.994	43
	15.30	0.29 (0.07)	2.67 (0.06)	3.19 (0.09)	0.32 (0.06)	0.54 (0.02)	−0.66 (0.06)	1235	0.994	43
	10.10	0.29 (0.08)	2.60 (0.07)	3.12 (0.09)	0.43 (0.07)	0.55 (0.02)	−0.67 (0.07)	1088	0.993	43
	log K_L	0.56 (0.09)	2.82 (0.08)	3.27 (0.11)	0.48 (0.09)	0.50 (0.02)	−0.77 (0.08)	977	0.992	43
312.55	25.29	0.45 (0.02)	2.53 (0.07)	3.06 (0.09)	0.47 (0.08)	0.49 (0.08)	−0.72 (0.07)	1105	0.994	42
	20.00	0.32 (0.08)	2.66 (0.06)	3.07 (0.09)	0.32 (0.06)	0.50 (0.02)	−0.71 (0.07)	1151	0.993	44
	15.30	0.29 (0.07)	2.61 (0.06)	3.25 (0.09)	0.31 (0.06)	0.55 (0.02)	−0.83 (0.06)	1208	0.994	43
	10.10	0.26 (0.07)	2.50 (0.06)	2.97 (0.09)	0.35 (0.06)	0.51 (0.02)	−0.64 (0.06)	1054	0.993	43
	log K_L	0.56 (0.09)	2.75 (0.08)	3.16 (0.11)	0.40 (0.09)	0.47 (0.02)	−0.79 (0.08)	947	0.992	43
322.55	25.29	0.40 (0.07)	2.56 (0.07)	3.01 (0.08)	0.31 (0.06)	0.46 (0.02)	−0.76 (0.06)	1330	0.995	42
	20.00	0.33 (0.07)	2.57 (0.06)	2.92 (0.09)	0.26 (0.06)	0.46 (0.02)	−0.70 (0.06)	1245	0.993	44
	15.30	0.32 (0.07)	2.52 (0.07)	2.96 (0.08)	0.28 (0.06)	0.47 (0.02)	−0.72 (0.06)	1226	0.994	43
	10.10	0.28 (0.07)	2.46 (0.07)	2.89 (0.09)	0.32 (0.08)	0.48 (0.02)	−0.70 (0.06)	1123	0.994	42
	log K_L	0.52 (0.08)	2.66 (0.07)	3.03 (0.10)	0.32 (0.07)	0.44 (0.02)	−0.78 (0.07)	1000	0.992	44
332.55	25.29	0.41 (0.07)	2.47 (0.07)	2.92 (0.08)	0.30 (0.06)	0.44 (0.02)	−0.79 (0.06)	1173	0.994	42
	20.00	0.35 (0.07)	2.53 (0.06)	2.85 (0.08)	0.23 (0.06)	0.43 (0.02)	−0.75 (0.06)	1323	0.994	44
	15.30	0.31 (0.07)	2.40 (0.07)	2.84 (0.09)	0.29 (0.06)	0.44 (0.02)	−0.73 (0.07)	963	0.992	43
	10.10	0.31 (0.07)	2.32 (0.06)	2.70 (0.08)	0.38 (0.06)	0.44 (0.02)	−0.72 (0.06)	1084	0.993	43
	log K_L	0.52 (0.08)	2.50 (0.07)	2.85 (0.10)	0.38 (0.08)	0.42 (0.02)	−0.79 (0.07)	866	0.992	43

[a] *w*: phase loading; *F*: Fischer statistic; *ρ*: multiple correlation coefficient; and *n*: number of solutes.

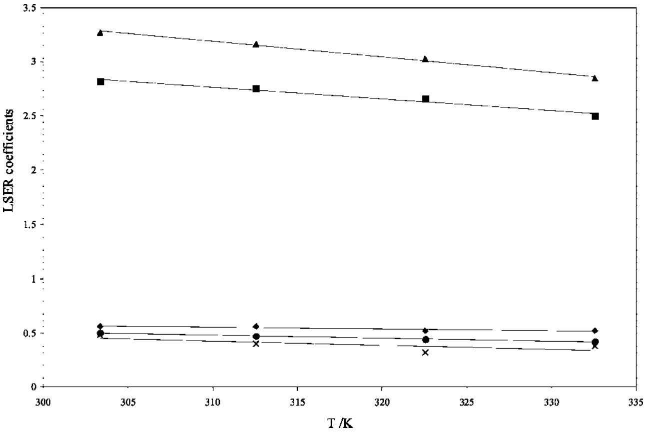

Figure 9. Evolution of LSER coefficients as function of temperature. ◆, contribution from interactions with lone pair electrons "*e*"; ■, contribution from dipole-type interactions "*s*"; ▲, hydrogen bond basicity "*a*"; ×, hydrogen bond acidity "*b*"; ●, cavity formation and dispersion interactions "*l*".

compares the calculated value of log *K* against the experimental values. Calculated log *K* are in good agreement with experimental data except for the low value and more precisely data of apolar solutes. This important deviation may be explained by the fact that Sprunger et al.[35,54] used Foco et al.[45] and Zhou et al.[53] data sets to estimate the coefficients of eq 4. Moreover, these log *K* are not corrected from interfacial adsorption. Nevertheless, this application shows that the predictive model proposed by Sprunger et al. may be a powerful tool to estimate the behavior of solutes in ionic liquids.

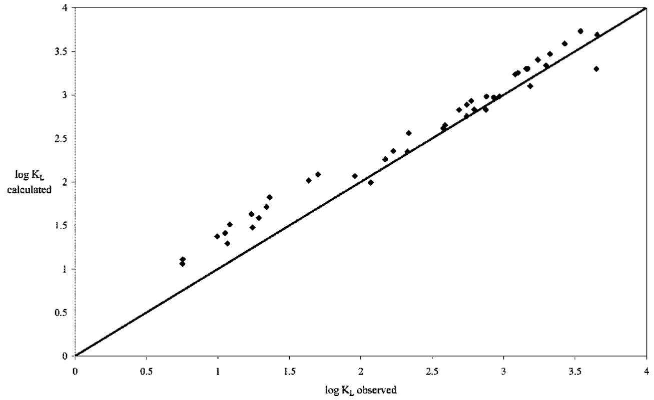

Figure 10. Comparison of experimental log K_L data and predicted values based on the Abraham model with the cation-specific and anion-specific equation.

Concluding Remarks

Activity coefficients at infinite dilution of organic compounds in [BMIM][BF_4] have been measured from (303.35 to 332.55) K. Through this work, we have shown that interfacial adsorption plays a significant role in the retention mechanism of apolar

Table 7. LSER Descriptors of Ionic Liquids Determined at 313.15 K[a]

	system constants						statistics		
ionic liquids	*e*	*s*	*a*	*b*	*l*	*c*	*ρ*	SE	*n*
1-butyl-3-methylimidazolium tetrafluoroborate	0.56 (0.09)	2.82 (0.08)	3.27 (0.11)	0.48 (0.09)	0.50 (0.02)	−0.77 (0.08)	0.992	0.065	43
n-acryloyloxypropyl-*N*-methylimidazolium bromide	0	2.88 (0.14)	5.50 (0.19)	0	0.48 (0.06)	−1.03 (0.119)	0.99	0.080	30
n-methacryloyloxyhexyl-*N*-methylimidazolium bromide	0	2.46 (0.10)	5.36 (0.18)	0	0.57 (0.05)	−0.87 (0.11)	0.99	0.088	28
1-propenyl-3-methyl-imidazolium 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-octyl-imidazolium 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-decyl-imidazolium 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-dodecyl-imidazolium bromide	0	1.44 (0.07)	4.87 (0.16)	0	0.72 (0.03)	−1.51	0.991	0.088	28
1-butyl-3-methylimidazolium octyl sulfate	0	1.47 (0.06)	4.05 (0.14)	0	0.68 (0.03)	−0.237 (0.09)	0.990	0.082	29
1-ethyl-3-methylimidazolium tosylate	0.54 (0.12)	2.40 (0.12)	4.81 (0.19)	0.17 (0.14)	0.48 (0.03)	−0.84 (0.12)	0.99	0.080	29
n-butylammonium thiocyanate	0.14 (0.09)	1.65 (0.09)	2.76 (0.16)	1.32 (0.11)	0.45 (0.02)	−0.75 (0.10)	0.995	0.058	23
di-*n*-propylammonium thiocyanate	0.30 (0.05)	1.73 (0.06)	2.66 (0.10)	0.68 (0.07)	0.47 (0.01)	−0.6 (0.06)	0.998	0.032	23
ethylammonium nitrate	0.27 (0.16)	2.21 (0.16)	3.38 (0.28)	1.03 (0.17)	0.21 (0.04)	−0.87 (0.20)	0.994	0.089	17
n-propylammonium nitrate	0.25 (0.06)	2.02 (0.06)	3.50 (0.10)	0.9 (0.07)	0.36 (0.01)	−0.97 (0.07)	0.998	0.037	23
2-bis(2-hydroxyethyl)amino)ethanesulfonate	0.27	1.96	3.06	0	0.32	−0.80	0.996	0.048	27
2-(cyclohexylamino)ethanesulfonate	0.07	1.57	3.67	0	0.51	−0.83	0.996	0.060	18
2-hydroxy-4-morpholinepropanesulfonate	0	1.76	3.20	0	0.49	−0.91	0.994	0.053	18
4-morpholinepropanesulfonate	0	1.60	3.41	0	0.44	−0.94	0.990	0.097	34

[a] *ρ*: Multiple correlation coefficient; SE: standard error in the estimation; and *n*: number of solutes.

compounds. When corrected, important increases of activity coefficients at infinite dilution of nonpolar compounds were observed. Interfacial adsorption contribution of polar solutes in [BMIM][BF_4] is lower than in imidazolium-based ionic liquids with a bromide anion.

In the separation of aliphatic hydrocarbons from thiophene or methanol, [BMIM][BF_4] shows a higher selectivity than that found by previous workers using classical organic solvents.

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