Partition Coefficients of Organic Compounds in New Imidazolium and Tetralkylammonium Based Ionic Liquids Using Inverse Gas Chromatography

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Partition coefficients of 51 organic compounds in two ionic liquids (IL), 1-ethyl-3-methylimidazolium dicyanamide and trimethylhexylammonium bis((trifluoromethyl)sulfonyl)amide, were measured using inverse gas chromatography from (322.5 to 352.5) K. These partition coefficients were converted into water-to-IL partition coefficients using the corresponding gas-to-water partition coefficients. Both sets of partition coefficients were analyzed using the Abraham solvation parameter model with cation-specific and anion-specific equation coefficients. The derived equations correlated the experimental gas-to-IL and water-to-IL partition coefficient data to within (0.12 and 0.14) log units, respectively.

Introduction

Ionic liquids (IL) have been widely promoted as “green solvents” and as interesting substitutes for traditional industrial solvents such as volatile organic compounds. Much of the interest in ILs is based on their chemical stability, thermal stability, low vapor pressure, and high ionic conductivity properties. ILs are comprised of an asymmetric, bulky organic cation and a weakly coordinating organic or inorganic anion. With the great variety of such combinations enabling the fine-tuning of their chemical properties, ILs have already become recognized by the chemical industry as new, target-oriented reaction media. Nowadays, ILs are emerging as alternative green solvents, in other words, as alternative reaction media for synthesis, catalysis, and biocatalysis, but also as electrolytes, lubricants, or modifiers of mobile and stationary phases in the separation sciences.[1−6]

ILs have been used in industrial processes for more than a decade, and their applications continue to expand. For instance, extractive distillation and liquid−liquid extraction with ILs as a separating agent is a novel method for the separation of an ethanol−water mixture,[7] of thiophene from aliphatic hydrocarbons,[8] and of methanol from aliphatic hydrocarbons.

The knowledge of the physicochemical properties of ILs is of great importance. Indeed, a large thermodynamic databank will give a better understanding of the behavior of ILs in mixtures depending on the ionic structures and the intermolecular interactions. Furthermore, measurement of physical properties for these substances is essential to evaluate the actual potential of an IL as a solvent for a particular application.

This study is a continuation of our investigations on thermodynamic properties of ILs.[9−15] In previous work, we have shown that the introduction of a polar chain in ILs also affects strongly the behavior of organic compounds in mixtures with the ILs. Short polar chains in imidazolium based ILs increased their selectivity toward mixtures containing (alcohol + aliphatic) or (aromatic + aliphatic). This work is focused on the behavior of an ammonium based IL, trimethylhexylammonium bis((trifluoromethyl)sulfonyl)amide [TMHA][Tf_2N], and on the influence of a dicyanamide anion grafted on an imidazolium based IL, 1-ethyl-3-methylimidazolium dicyanamide [EMIM][DCA].

In the literature, it can be found that the IL [TMHA][Tf_2N] has a wide electrochemical window (more than 5 V) and is considered to be hydrophobic because of two $-CF_3$ groups in its Tf_2N^- anion. Thus, it was found that [TMHA][Tf_2N] may be used as media in metal electrodeposition.[16] Recently, Yoshida et al.[17] have reported several highly conductive 1-ethyl-3-methylimidazolium [EMIM]-based ILs with polycyano anions such as dicyanamide [DCA]. The results observed in this study reveal that [DCA]-based ILs would be useful electrolytes for electrodeposition. The [DCA] anion based ILs exhibit low viscosity and are good solvents for metal ions resulting from the high complexing ability of [DCA].[18] The [DCA] ILs were also used to explore reactions of carbohydrates and other alcohols, which until now have been inaccessible in other ILs.[19]

Nevertheless, there is a lack of data characterizing the behavior of liquid mixtures containing these ILs. It is then impossible to quantify intermolecular solute−IL interaction or to predict their possible use for extraction and extractive distillation processes.

In this work, partition coefficients for a series of organic compounds dissolved in [EMIM][DCA] and [TMHA][TF_2N] are measured using the chromatography technique.

To quantify intermolecular solute−IL interactions, Acree, Abraham, and co-workers reported mathematical correlations based on the general Abraham solvation parameter model for the gas-to-solvent, K_L, and water-to-solvent, P, partition coefficients.[20−22]

Recently, Sprunger et al.[23,24] modified the Abraham solvation parameter model

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$$\log K_{\mathrm{L}} = c_{\mathrm{cation}} + c_{\mathrm{anion}} + (e_{\mathrm{cation}} + e_{\mathrm{anion}})\cdot\mathbf{E} + (s_{\mathrm{cation}} + s_{\mathrm{anion}})\cdot\mathbf{S} + (a_{\mathrm{cation}} + a_{\mathrm{anion}})\cdot\mathbf{A} + (b_{\mathrm{cation}} + b_{\mathrm{anion}})\cdot\mathbf{B} + (l_{\mathrm{cation}} + l_{\mathrm{anion}})\cdot\mathbf{L} \quad (1)$$

$$\log P = c_{\mathrm{cation}} + c_{\mathrm{anion}} + (e_{\mathrm{cation}} + e_{\mathrm{anion}})\cdot\mathbf{E} + (s_{\mathrm{cation}} + s_{\mathrm{anion}})\cdot\mathbf{S} + (a_{\mathrm{cation}} + a_{\mathrm{anion}})\cdot\mathbf{A} + (b_{\mathrm{cation}} + b_{\mathrm{anion}})\cdot\mathbf{B} + (v_{\mathrm{cation}} + v_{\mathrm{anion}})\cdot\mathbf{V} \quad (2)$$

by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. The dependent variables in eqs 1 and 2 are solute descriptors as follows: **E** and **S** refer to the excess molar refraction in units of $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})/10$ and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume in units of $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})/100$, and **L** is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. Sprunger et al. calculated equation coefficients for eight cations and four anions using a database that contained 584 experimental log K_{L} and 571 experimental log P values. No loss in predictive accuracy was observed by separating the equation coefficients into individual cation-specific and anion-specific values. The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more ILs.

Experimental Procedures and Results

Materials or Chemicals. For the ILs investigated here, [EMIM][DCA] (Alfa Aesar, 98 %) was purchased from commercial sources, and [TMHA][Tf$_2$N] was prepared at a purity of 99.8 % using methods reported earlier.[25,26] The synthesized sample of [TMHA][TF$_2$N] was characterized using ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 3.54$ (t, 2H, NCH_2(CH$_2$)$_4$CH$_3$), 3.34 (s, 9H, N(CH_3)$_3$), 1.93 (m, 2H, NCH$_2$CH_2(CH$_2$)$_3$CH$_3$), 1.39 to 1.32 (br m, 6H, N(CH$_2$)$_2$(CH_2)$_3$CH$_3$), and 0.89 (t, 3H, N(CH$_2$)$_5$CH_3).

Each IL was further purified by subjecting the liquid to a very low pressure of about 5 Pa at about 343 K for approximately 24 h. Next, packed columns were conditioned during 12 h. We assume that this procedure removed any volatile chemicals and water from the IL and Chromosorb. No other attempt was made to analyze impurities in the ILs.

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.

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. The 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 Pt100 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 (15 to 35) % of stationary phases (IL) on Chromosorb WHP (60 to 80 mesh) were prepared using the rotary evaporator technique. After evaporation of the chloroform under vacuum, the support was equilibrated at 333 K during 6 h. Before measurements, each packed column was conditioned during 12 h at 363 K with a flow rate of 20 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$. 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 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.

Table 1. Logarithm of Partition Coefficients, log K_{L}, of Organic Compounds in [EMIM][DCA]

T/K	322.65	332.85	343.15	R^2	298.15
Solute					
hexane	0.438	0.347	0.284	0.9878	0.616
3-methylpentane	0.430	0.327	0.277	0.9594	0.603
heptane	0.679	0.578	0.468	0.9995	0.933
2,2,4-trimethylpentane	0.623	0.516	0.401	0.9996	0.889
octane	0.931	0.794	0.678	0.9975	1.231
nonane	1.180	1.019	0.896	0.9938	1.514
decane	1.436	1.253	1.102	0.9967	1.830
undecane	1.707	1.499	1.323	0.9976	2.161
dodecane	1.993	1.758	1.554	0.9981	2.513
tridecane	2.298	2.034	1.808	0.9977	2.878
tetradecane	2.613	2.319	2.000	0.9996	3.349
methylcyclopentane	0.825	0.718	0.694	0.8818	0.967
cyclohexane	0.995	0.888	0.808	0.9923	1.214
methylcyclohexane	1.084	0.969	0.853	1.0000	1.360
cycloheptane	1.450	1.321	1.144	0.9925	1.824
benzene	2.250	2.101	1.962	0.9995	2.593
toluene	2.499	2.331	2.175	0.9995	2.884
ethylbenzene	2.667	2.486	2.318	0.9994	3.082
m-xylene	2.640	2.485	2.371	0.9921	2.954
p-xylene	2.742	2.545	2.381	0.9967	3.168
o-xylene	2.921	2.732	2.551	0.9997	3.361
1-hexene	0.766	0.650	0.558	0.9954	1.011
1-hexyne	1.599	1.462	1.323	1.0000	1.929
1-heptyne	1.823	1.665	1.516	0.9996	2.187
2-butanone	2.417	2.258	2.109	0.9995	2.784
2-pentanone	2.578	2.407	2.250	0.9993	2.967
3-pentanone	2.554	2.383	2.226	0.9993	2.943
1,4-dioxane	3.071	2.755	2.588	0.9679	3.623
methanol	2.835	2.676	2.522	0.9999	3.207
ethanol	2.856	2.688	2.500	0.9992	3.285
1-propanol	3.107	2.916	2.733	0.9998	3.552
2-propanol	2.768	2.586	2.416	0.9995	3.186
2-methyl-1-propanol	3.185	2.981	2.790	0.9994	3.655
1-butanol	3.362	3.155	2.955	0.9998	3.847
trifluoroethanol	3.644	3.442	3.231	0.9999	4.139
ether	0.991	0.875	0.774	0.9984	1.248
diisopropylether	0.978	0.834	0.721	0.9947	1.279
chloroform	2.498	2.330	2.174	0.9993	2.883
dichloromethane	2.135	1.991	1.857	0.9994	2.465
tetrachloromethane	1.946	1.791	1.648	0.9994	2.300
acetonitrile	2.787	2.637	2.495	0.9996	3.133
nitromethane	3.204	3.045	2.868	0.9992	3.607
1-nitropropane	3.333	3.142	2.964	0.9994	3.772
triethylamine	1.232	1.091	0.957	0.9998	1.560
pyridine	3.206	3.037	2.861	0.9999	3.619
thiophene	2.520	2.391	2.243	0.9987	2.855
formaldehyde	1.682	1.547	1.422	0.9994	1.992
propionaldehyde	2.031	1.894	1.767	0.9994	2.346
butyraldehyde	2.251	2.099	1.959	0.9993	2.596

Theoretical Basis. The retention data determined with inverse chromatography experiments were used to calculate

Table 2. Logarithm of Partition Coefficients, log K_L, of Organic Compounds in [TMHA][TF$_2$N]

T/K	322.65	343.85	352.65	R^2	298.15
solute					
hexane	1.114	0.880	0.776	0.9998	1.390
3-methylpentane	1.085	0.854	0.756	1.0000	1.354
heptane	1.432	1.160	1.044	1.0000	1.748
2,2,4-trimethylpentane	1.432	1.165	1.049	0.9999	1.744
octane	1.736	1.433	1.301	0.9999	2.090
nonane	2.038	1.701	1.553	0.9998	2.434
decane	2.335	1.965	1.801	0.9998	2.771
undecane	2.633	2.226	2.046	0.9998	3.112
dodecane	2.930	2.486	2.289	0.9998	3.453
tridecane	3.205	2.743	2.531	0.9995	3.756
tetradecane	3.430	3.001	2.820	1.0000	3.928
methylcyclopentane	1.327	1.101	0.997	0.9995	1.596
cyclohexane	1.459	1.225	1.122	0.9997	1.735
methylcyclohexane	1.635	1.379	1.267	0.9998	1.935
cycloheptane	2.020	1.641	1.521	0.9968	2.428
benzene	2.285	1.994	1.863	0.9996	2.629
toluene	2.628	2.297	2.148	0.9997	3.019
ethylbenzene	2.895	2.520	2.359	0.9999	3.333
m-xylene	2.965	2.592	2.425	0.9997	3.406
p-xylene	2.943	2.572	2.405	0.9997	3.382
o-xylene	3.090	2.710	2.539	0.9997	3.540
1-hexene	1.263	1.019	0.908	0.9995	1.553
1-hexyne	1.740	1.462	1.335	0.9996	2.071
1-heptyne	2.053	1.741	1.600	0.9996	2.423
2-butanone	2.614	2.291	2.144	0.9995	2.997
2-pentanone	2.877	2.528	2.372	0.9997	3.290
3-pentanone	2.873	2.521	2.363	0.9996	3.288
1,4-dioxane	2.826	2.484	2.330	0.9996	3.232
methanol	2.030	1.772	1.639	0.9972	2.348
ethanol	1.990	1.890	1.758	0.9036	2.177
1-propanol	2.494	2.161	2.014	0.9998	2.886
2-propanol	2.241	1.930	1.789	0.9996	2.611
2-methyl-1-propanol	2.654	2.301	2.143	0.9997	3.071
1-butanol	2.831	2.460	2.295	0.9998	3.269
trifluoroethanol	2.656	2.301	2.150	1.0000	3.069
ether	1.425	1.087	0.982	0.9964	1.787
diisopropyl ether	1.600	1.226	1.103	0.9976	2.007
chloroforme	2.048	1.762	1.635	0.9997	2.385
dichloromethane	1.752	1.510	1.401	0.9997	2.039
tetrachloromethane	1.834	1.564	1.443	0.9997	2.154
acetonitrile	2.622	2.352	2.224	0.9991	2.947
nitromethane	2.656	2.559	2.420	0.8900	2.846
1-nitropropane	3.289	2.926	2.763	0.9997	3.718
triethylamine	1.765	1.431	1.284	0.9998	2.157
pyridine	3.331	2.742	2.585	0.9921	3.942
thiophene	2.381	2.085	1.952	0.9997	2.731
formaldehyde	1.452	1.178	1.036	0.9973	1.791
propionaldehyde	2.093	1.824	1.707	0.9999	2.409
butyraldehyde	2.402	2.101	1.965	0.9996	2.760
ethyl acetate	2.402	2.079	1.936	0.9998	2.783
tetrahydrofuran	2.234	1.918	1.774	0.9995	2.610

partition coefficients of the solute in the IL. The net retention volume, V_N, was calculated with the following usual relationship:[27]

$$V_N = \frac{3}{2}\frac{\left[\left(\frac{P_i}{P_0}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]} \cdot U_0 \cdot t'_R \cdot \frac{T_{col}}{T_r}\left(1 - \frac{P_{0W}}{P_0}\right) \qquad (3)$$

where the adjusted retention time t'_R was taken as a 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, and P_{0W} is the vapor pressure of water at T_r. P_i and P_0 are respectively the inlet and outlet pressures.

Activity coefficient at infinite dilution of a solute 1 in the IL 2 $\gamma_{1,2}^{\infty}$ was calculated with the following expression:[27]

$$\ln \gamma_{1,2}^{\infty} = \ln\left(\frac{n_2 RT}{V_N P_1^0}\right) - P_1^0 \cdot \frac{B_{11} - V_1^0}{RT} + \frac{2B_{13} - V_1^{\infty}}{RT} \cdot J \cdot P_0 \qquad (4)$$

where 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, and P_1^0 is the probe vapor pressure at temperature T.

Partition coefficients K_L may be then calculated from the activity coefficients at infinite dilution, $\gamma_{1,2}^{\infty}$, using the following equation:

$$K_L = \frac{RT}{\gamma_{1,2}^{\infty} P_1^0 V_{solvent}} \qquad (5)$$

Thermodynamic properties of pure solutes needed for calculations are given in a previous work.[9]

Results and Discussion

Influence of Concurrent Retention Mechanisms. The errors in the K_L 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 cm$^3 \cdot$min^{-1}; the mass of the stationary phase, 2 %; the inlet and outlet pressures, 0.002 bar; and the temperature of the oven, 0.2 K. The main source of error in the calculation of the net retention volume is the determination of the weight of the

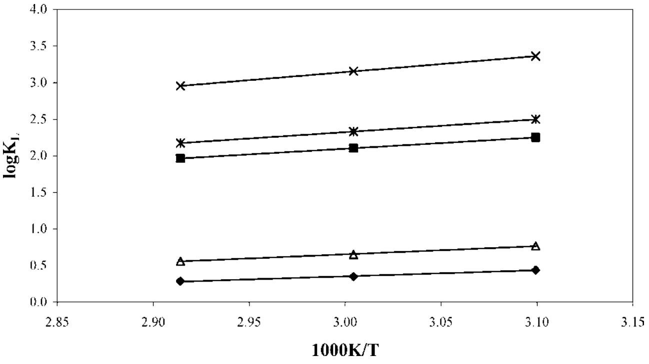

Figure 1. Logarithm of the partition coefficients of selected solutes in [EMIM][DCA] as a function of 1/*T*. ◆, hexane; Δ, hexene; ●, benzene; *, chloroform; ×, 1-butanol.

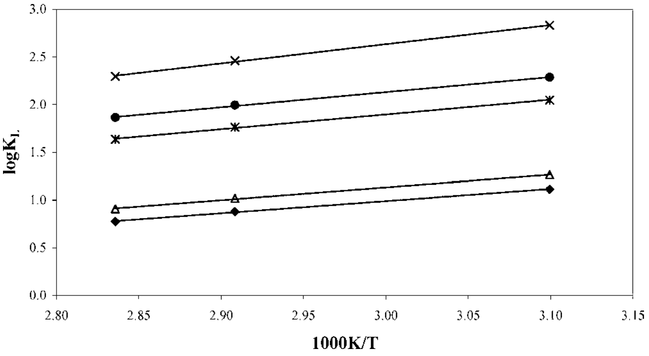

Figure 2. Logarithm of the partition coefficients of selected solutes in [TMHA][TF$_2$N] as a function of 1/*T*. ◆, hexane; Δ, hexene; ●, benzene; *, chloroform; ×, 1-butanol.

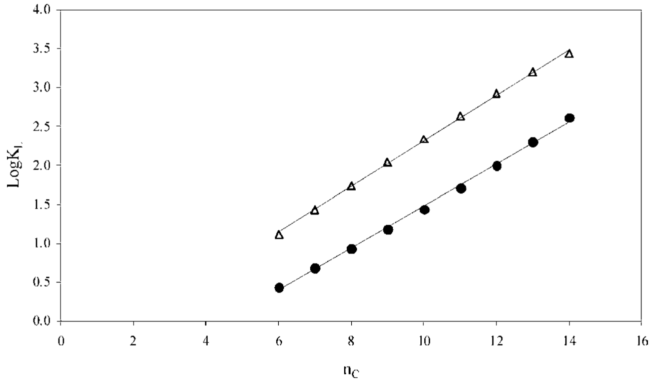

Figure 3. Logarithm of the partition coefficients of selected solutes as a function of carbon number of *n*-alkanes in: ◆, [EMIM][DCA; Δ, [TMHA][TF$_2$N].

Table 3. Partition Coefficients for Some Solutes in ILs Based on the [EMIM]$^+$ Cation at T = 323.15 K

	anion				
solute	[DCA]$^{-a}$	[SCN]$^{-b}$	[TFA]$^{-c}$	[Tf$_2$N]$^{-d}$	[C$_2$H$_5$SO$_4$]$^{-d}$
hexane	0.438	0.095	0.647	1.101	0.573
cyclohexane	0.995	0.708	1.139	1.528	0.994
1-hexene	0.766	0.462	0.923	1.334	0.797
benzene	2.250	2.489	2.218	2.577	2.212
methanol	2.835	2.793	3.137	2.393	

[a] This work. [b] Ref 31. [c] Ref 32. [d] Ref 29.

stationary phase. The estimated error in determining the net retention volume V_N is about 2 %. Taking into account that thermodynamic parameters are also subject to an error, the resulting error in the K_L values is about 3 %.

For [EMIM][DCA] and trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide ILs, no interfacial adsorption was observed, while the average relative standard deviation between two sets of data obtained with two different packed columns was about 2 %. In both ILs studied, 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 ILs, and gas−liquid interfacial adsorption is then predominant.

Partition Coefficients of Organic Compounds in ILs. The gas−liquid partition coefficients were calculated using eqs 3 to 5. Values for the gas−liquid partition coefficients are listed in Tables 1 and 2. The evolution of the logarithm of partition coefficient of solutes in both ILs studied in this work with respect to 1/T is presented in Figures 1 and 2. For some compounds of different families containing the same number of carbon atoms, we find that $K_{L,alcohol} > K_{L,aromatic} > K_{L,alkyne} > K_{L,alkene} > K_{L,alkane}$. This trend is in good agreement with the data obtained in all other ILs, whatever the cation or the anion.

The logarithm of K_L of the *n*-alkanes increases linearly with an increase in carbon number (Figure 3). Most partition coefficients decrease with an increase in temperature. The low values of the gas−liquid partition coefficients of *n*-alkanes indicate their low solubility in ILs. The solubility of alcohols and chloroalkanes are better in [EMIM][DCA] than in [TMHA][TF$_2$N]. The magnitude of partition coefficients obtained with [EMIM][DCA] is significantly higher than the corresponding values for other ILs.[9−15,28−34] As an example, partition coefficients of a few solutes in ILs based on the [EMIM]$^+$ cation at T = 323.15 K are given in Table 3. Both ILs studied in this work have similar behaviors as all of the ILs that we previously characterized. In a few words, compounds with double or triple bonds interact more strongly than alkanes with the polar anion and cation of the ILs. In the series of chloromethanes, it was observed that K_L values strongly decrease from dichloromethane to tetrachloromethane. The K_L values for the alcohols are relatively high. The hydroxyl group could interact with the anion and/or the cation of the IL. Partition coefficients of alcohols increase with increasing chain length. Ketones and aldehydes have a lower solubility than alcohols. These families of compounds follow the same trend than hydrocarbons. Introducing a branched alkyl on these compounds decreases their solubility. The partition coefficient of nitroalkanes is also particularly high especially with both ILs. Pyridine has usually strong interactions with imidazolium ILs.

Table 4 presents selectivities at infinite dilution S_{12}^{∞} for four separation problems: hexane/benzene, hexane/methanol, hexane/thiophene, and cyclohexane/thiophene for ILs at T = 323.15 K:

Table 4. Selectivity Values S_{12}^{∞} for Different Separation Problems at 323.15 K

	S_{12}^{∞}				
solvent	hexane/benzene	hexane/methanol	hexane/thiophene	cyclohexane/thiophene	ref
[EMIM][DCA]	43.4	255	69.6	28.8	this work
[TMHA][Tf$_2$N]	9.9	8.5	10.7	7.2	this work
1-ethyl-3-methylimidazolium tetrafluoroborate	61.6	290.4			28
1-butyl-3-methylimidazolium tetrafluoroborate	60.1	106.9	85.8	31.8	10
1-hexyl-3-methylimidazolium tetrafluoroborate	22.3	29.2			28
1-octyl-3-methylimidazolium tetrafluoroborate	10.5	12.1			28
1-hexadecyl-3-methylimidazolium tetrafluoroborate	2.8	2.2	2.2	2.0	14
1-ethyl-3-methylimidazolium ethylsulfate	41.4				29
1-butyl-3-methylimidazolium octylsulfate	5.5	4.4	6.5	3.9	12
1-hexyl-3-methylimidazolium hexafluorophosphate	21.6	10.2			30
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	37.5	19.5			29
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	16.7				29
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	11.2	6.6			30
1-ethyl-3-methylimidazolium thiocyanate	74.6	538.5			31
1-ethyl-3-methylimidazolium trifluoroacetate	25.8				32
1-butyl-3-methylimidazolium trifluoromethanesulfonate	21.9	51.9	30.2	15.2	33
methacryloyloxyhexyl-N-methylimidazolium bromide	50.4	820	82	41.4	15
1-propenyl-3-methyl-imidazolium bromide	7	139.3	16.9	10.6	13
1-propenyl-3-octyl-imidazolium bromide	6.4	52.3	9.6	6.1	13
1-propyl boronic acid-3-octyl-imidazolium bromide	9.91	455.7	15.2	6.8	13
1-octyl-3-methylimidazolium chloride	8.7				34

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

Selectivities obtained with phosphonium or ammonium based ILs are generally of the same magnitude as with classical solvents used in industry. The selectivity for the [DCA] IL is relatively high. The S_{12}^{∞} values obtained with [EMIM][DCA] show the possibility of using this IL as an extractive medium for the four separation processes proposed in this study. The selectivity of [DCA] ILs for the (hexane + methanol) mixture is particularly large ($S_{12}^{\infty} = 255$) compared to the value for classical solvents.

Linear Solvation Energy Relationship (LSER) Characterization. The experimental data measured here can be used to calculate the Abraham model ion-specific equation coefficients for the [DCA] anion and the trimethyl-*n*-hexylammonium cation for both the gas-to-IL (see eq 1) and the water-to-IL (see eq 2) partitioning processes. The log K_L data needed to derive the Abraham gas-to-IL correlations are listed in the last column of Tables 1 and 2. The log P values for partition from water to the IL are calculated through eq 7,

$$\log P = \log K_L - \log K_W \tag{7}$$

and requires knowledge of the solute's gas phase partition coefficient into water, K_W, which is available for most of the solutes studied.[20] For solvents that are completely miscible with water, such as [EMIM][DCA],[35,36] the calculated log P refers to a hypothetical partition coefficient. Even though hypothetical, these log P correlations are still quite useful in that predicted log P values can be used to estimate the solute's infinite dilution activity coefficient or molar solubility in the anhydrous (dry) IL solvent for those solutes for which the solute descriptors are known. Approximately one-fifth of the solvent log P correlations that have been reported by Abraham and co-workers pertain to organic solvents (i.e., methanol, ethanol, acetonitrile) that are completely miscible with water at ambient room temperature. The hypothetical log P correlations have proved very useful in estimating the solubility of solutes in water-miscible solvent[37] and in solute descriptor computations.[38]

For convenience, we have tabulated in Tables 5 and 6 the log P and log K_L values at 298.15 K for [EMIM][DCA] and [TMHA][TF$_2$N], respectively. Also included in Table 5 are the experimental log K_L values and log P values derived from the infinite dilution activity coefficient measurements of Ma and co-workers.[39] The authors measured the $\gamma_{1,2}^{\infty}$ values for 27 solutes at (323.15, 333.15, 343.15, and 353.15) K using inverse gas chromatography with a [EMIM][DCA] stationary phase. We have extrapolated the published $\gamma_{1,2}^{\infty}$ data to 298.15 K and converted the extrapolated values to log K_L through eq 5. Examination of the numerical entries in Table 5 shows that 20 of the 48 solutes studied here were also studied by Ma and co-workers.[39] The average difference between our experimental log K_L data and the log K_L values calculated from the activity coefficient data of Ma and co-workers is 0.042 log units. The experimental values are sufficiently close and can be combined into a single Abraham model correlation. Our search of the chemical literature found experimental solubility and Henry's law constants for carbon dioxide[40] and ethene[41] which we have also converted into log K_L and log P values.

Analysis of the experimental log K_L and log P data in Table 5 gave

Table 5. Logarithm of the Gas-to-IL and Water-to-IL Partition Coefficients for Organic Vapors and Gases Dissolved in [EMIM][DCA] at 298.15 K

solute	log K_L	log P	ref
hexane	0.616	2.436	this work
3-methylpentane	0.603	2.443	this work
heptane	0.933	2.893	this work
2,2,4-trimethylpentane	0.889	3.009	this work
octane	1.231	3.341	this work
nonane	1.514	3.664	this work
decane	1.830	4.090	this work
undecane	2.161	4.541	this work
dodecane	2.513	5.043	this work
tridecane	2.878		this work
tetradecane	3.349		this work
methylcyclopentane	0.967	2.137	this work
cyclohexane	1.214	2.114	this work
methylcyclohexane	1.360	2.610	this work
cycloheptane	1.824	2.404	this work
benzene	2.593	1.963	this work
toluene	2.884	2.234	this work
ethylbenzene	3.082	2.502	this work
m-xylene	2.954	2.344	this work
p-xylene	3.168	2.578	this work
o-xylene	3.361	2.701	this work
1-hexene	1.011	2.171	this work
1-hexyne	1.929	2.139	this work
1-heptyne	2.187	2.627	this work
2-butanone	2.784	0.064	this work
2-pentanone	2.967	0.387	this work
3-pentanone	2.943	0.443	this work
1,4-dioxane	3.623	−0.087	this work
methanol	3.207	−0.533	this work
ethanol	3.285	−0.385	this work
1-propanol	3.552	−0.008	this work
2-propanol	3.186	−0.294	this work
2-methyl-1-propanol	3.655	0.355	this work
1-butanol	3.847	0.387	this work
2,2,2-trifluoroethanol	4.139	0.979	this work
ether	1.248	0.078	this work
diisopropyl ether	1.279	0.229	this work
chloroform	2.883	2.093	this work
dichloromethane	2.465	1.505	this work
tetrachloromethane	2.300	2.490	this work
acetonitrile	3.133	0.283	this work
nitromethane	3.607	0.657	this work
1-nitropropane	3.772	1.322	this work
triethylamine	1.560	−0.800	this work
pyridine	3.619	0.179	this work
thiophene	2.855	1.815	this work
propionaldehyde	2.346	−0.174	this work
butyraldehyde	2.596	0.266	this work
benzene	2.507	1.877	Ma et al.
toluene	2.812	2.162	Ma et al.
o-xylene	3.307	2.647	Ma et al.
p-xylene	3.115	2.525	Ma et al.
m-xylene	3.099	2.489	Ma et al.
dichloromethane	2.358	1.398	Ma et al.
trichloromethane	2.796	2.006	Ma et al.
tetrachloromethane	2.194	2.384	Ma et al.
methanol	3.153	−0.588	Ma et al.
ethanol	3.21	−0.460	Ma et al.
1-propanol	3.501	−0.059	Ma et al.
2-propanol	3.151	−0.329	Ma et al.
1-butanol	3.826	0.366	Ma et al.
2-methyl-1-propanol	3.633	0.333	Ma et al.
acetone	2.487	−0.303	Ma et al.
cyclohexanone	4.019	0.419	Ma et al.
cyclohexane	1.201	2.101	Ma et al.
heptane	1.057	3.017	Ma et al.
ethyl ether	1.236	0.066	Ma et al.
triethylamine	1.437	−0.923	Ma et al.
tetrahydrofuran	2.371	−0.179	Ma et al.
ethyl acetate	2.390	0.230	Ma et al.
acetonitrile	3.041	0.191	Ma et al.
pyridine	3.569	0.129	Ma et al.
carbon dioxide	0.300	0.380	Scovazzo et al.
ethene	−0.299	0.641	Camper et al.

$$\log K_{\mathrm{L}} = -0.888(0.055) + 0.361(0.082)\mathbf{E} + 2.833(0.075)\mathbf{S} + 4.690(0.104)\mathbf{A} + 0.364(0.074)\mathbf{B} + 0.596(0.014)\mathbf{L}$$
$$(N = 74, \mathrm{SD} = 0.109, R^2 = 0.989, F = 1178) \tag{11}$$

and

$$\log P = -0.404(0.105) + 0.344(0.095)\mathbf{E} + 0.945(0.100)\mathbf{S} + 0.987(0.133)\mathbf{A} - 4.526(0.088)\mathbf{B} + 2.957(0.087)\mathbf{V}$$
$$(N = 70, \mathrm{SD} = 0.126, R^2 = 0.992, F = 1585) \tag{12}$$

where N denotes the number of experimental values used in the regression analysis, SD refers to the standard deviation, R^2 is the squared correlation coefficient, and F corresponds to the Fisher F-statistic. Very similar results were obtained when the two log K_{L} and log P data sets were analyzed separately. Solute descriptors used in the analysis are listed in Table 7. Equations 11 and 12 provide a very accurate mathematical description of the log K_{L} and log P values as shown in Figures 4 and 5, respectively.

Table 6. Logarithm of the Gas-to-IL and Water-to-IL Partition Coefficients for Organic Vapors and Gases Dissolved in [TMHA][TF$_2$N] at 298.15 K

solute	log *K*	log *P*
hexane	1.390	3.210
3-methylpentane	1.354	3.194
heptane	1.748	3.708
2,2,4-trimethylpentane	1.744	3.864
octane	2.090	4.200
nonane	2.434	4.584
decane	2.771	5.031
undecane	3.112	5.492
dodecane	3.453	5.983
tridecane	3.756	
tetradecane	3.928	
methylcyclopentane	1.596	2.766
cyclohexane	1.735	2.635
methylcyclohexane	1.935	3.185
cycloheptane	2.428	3.008
benzene	2.629	1.999
toluene	3.019	2.369
ethylbenzene	3.333	2.753
m-xylene	3.406	2.796
p-xylene	3.382	2.792
o-xylene	3.540	2.880
1-hexene	1.553	2.713
1-hexyne	2.071	2.281
1-heptyne	2.423	2.863
2-butanone	2.997	0.277
2-pentanone	3.290	0.710
3-pentanone	3.288	0.788
1,4 dioxane	3.232	−0.478
methanol	2.348	−1.392
ethanol	2.177	−1.493
1-propanol	2.886	−0.674
2-propanol	2.611	−0.869
2-methyl-1-propanol	3.071	−0.229
1-butanol	3.269	−0.191
trifluoroethanol	3.069	−0.091
ether	1.787	0.617
diisopropyl ether	2.007	0.957
chloroform	2.385	1.595
dichloromethane	2.039	1.079
tetrachloromethane	2.154	2.344
acetonitrile	2.947	0.097
nitromethane	2.846	−0.104
1-nitropropane	3.718	1.268
triethylamine	2.157	−0.203
pyridine	3.942	0.502
thiophene	2.731	1.641
propionaldehyde	2.409	−0.111
butyraldehyde	2.760	0.430
ethyl acetate	2.783	0.623
tetrahydrofuran	2.610	0.060

Table 7. Solute Descriptors of Compounds Studied

solute	E	S	A	B	L	V
acetone	0.179	0.700	0.040	0.490	1.696	0.5470
cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8611
tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223
ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466
pyridine	0.631	0.840	0.000	0.520	3.022	0.6753
hexane	0.000	0.000	0.000	0.000	2.668	0.9540
3-methylpentane	0.000	0.000	0.000	0.000	2.581	0.9540
heptane	0.000	0.000	0.000	0.000	3.173	1.0949
2,2,4-trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358
octane	0.000	0.000	0.000	0.000	3.677	1.2358
nonane	0.000	0.000	0.000	0.000	4.182	1.3767
decane	0.000	0.000	0.000	0.000	4.686	1.5176
undecane	0.000	0.000	0.000	0.000	5.191	1.6590
dodecane	0.000	0.000	0.000	0.000	5.696	1.7994
tridecane	0.000	0.000	0.000	0.000	6.200	
tetradecane	0.000	0.000	0.000	0.000	6.705	
methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454
cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454
methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863
cycloheptane	0.350	0.100	0.000	0.000	3.704	0.9863
benzene	0.610	0.520	0.000	0.140	2.786	0.7164
toluene	0.601	0.520	0.000	0.140	3.325	0.8573
ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982
m-xylene	0.623	0.520	0.000	0.160	3.839	0.9982
p-xylene	0.613	0.520	0.000	0.160	3.839	0.9982
o-xylene	0.663	0.560	0.000	0.160	3.939	0.9982
1-hexene	0.078	0.080	0.000	0.070	2.572	0.9110
1-hexyne	0.166	0.220	0.100	0.120	2.510	0.8680
1-heptyne	0.160	0.230	0.120	0.100	3.000	1.0090
2-butanone	0.166	0.700	0.000	0.510	2.287	0.6879
2-pentanone	0.143	0.680	0.000	0.510	2.755	0.8288
3-pentanone	0.154	0.660	0.000	0.510	2.811	0.8288
1,4-dioxane	0.329	0.750	0.000	0.640	2.892	0.6810
methanol	0.278	0.440	0.430	0.470	0.970	0.3082
ethanol	0.246	0.420	0.370	0.480	1.485	0.4491
1-propanol	0.236	0.420	0.370	0.480	2.031	0.5900
2-propanol	0.212	0.360	0.330	0.560	1.764	0.5900
2-methyl-1-propanol	0.217	0.390	0.370	0.480	2.413	0.7309
1-butanol	0.224	0.420	0.370	0.480	2.601	0.7309
2,2,2-trifluoroethanol	0.015	0.600	0.570	0.250	1.224	0.5022
ether	0.041	0.250	0.000	0.450	2.015	0.7309
diisopropyl ether	−0.060	0.160	0.000	0.580	2.530	1.0127
chloroform	0.425	0.490	0.150	0.020	2.480	0.6167
dichloromethane	0.387	0.570	0.100	0.050	2.019	0.4943
tetrachloromehtane	0.458	0.380	0.000	0.000	2.823	0.7391
acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042
nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237
1-nitropropane	0.242	0.950	0.000	0.310	2.894	0.7055
triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538
pyridine	0.631	0.840	0.000	0.520	3.022	0.6753
thiophene	0.687	0.570	0.000	0.150	2.819	0.6411
propionaldehyde	0.196	0.650	0.000	0.450	1.815	0.5470
butyraldehyde	0.187	0.650	0.000	0.450	2.270	0.6879
carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2810
ethene	0.107	0.100	0.000	0.070	0.289	0.3470

As noted above, each of the calculated equation coefficients corresponds to the sum of the respective cation-specific and anion-specific contribution. We have recently reported[42] updated log K_{L} equation coefficients of $c_{\mathrm{cation}} = -0.526$, $e_{\mathrm{cation}} = 0.248$, $s_{\mathrm{cation}} = 2.286$, $a_{\mathrm{cation}} = 2.319$, $b_{\mathrm{cation}} = 1.047$, and $l_{\mathrm{cation}} = 0.641$ for the 1-ethyl-3-methylimidazolium cation. Equation coefficients of $c_{\mathrm{anion}} = -0.362$, $e_{\mathrm{anion}} = 0.113$, $s_{\mathrm{anion}} = 0.547$, $a_{\mathrm{anion}} = 2.371$, $b_{\mathrm{anion}} = -0.683$, and $l_{\mathrm{anion}} = -0.045$ are calculated for the [DCA] anion by subtracting the updated [EMIM] equation coefficients from those in eq 11. Anion-specific equation coefficients of $c_{\mathrm{anion}} = -0.379$, $e_{\mathrm{anion}} = -0.055$, s_{anion}

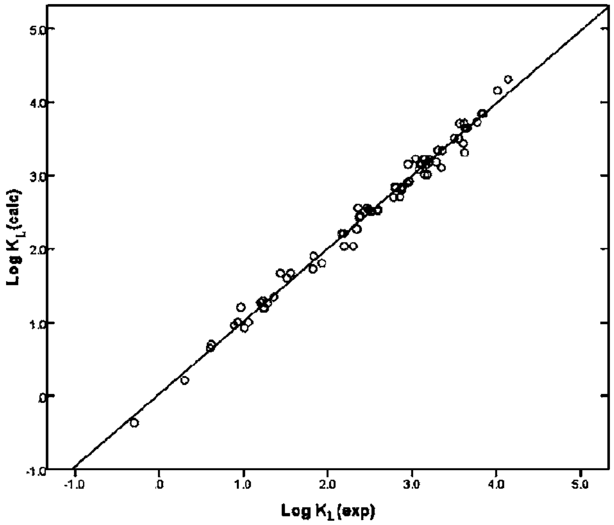

Figure 4. Plot of the logarithm of the experimental gas-to-[EMIM][DCA] partition coefficients versus calculated values based on eq 11.

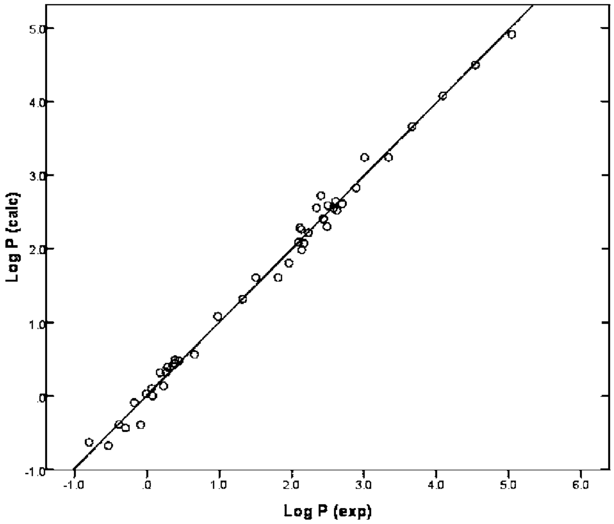

Figure 5. Plot of the logarithm of the experimental water-to-[EMIM][DCA] partition coefficients versus calculated values based on eq 12.

$= 0.701$, $a_{\text{anion}} = 2.434$, $b_{\text{anion}} = -0.828$, and $v_{\text{anion}} = -0.148$ for [DCA] for the log P correlation were calculated in a similar fashion.

In Table 6 there are 50 experimental log K_L and 48 experimental log P values for solutes dissolved in trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide. Analysis of the experimental data yielded the following Abraham correlation models

$$\log K_L = -0.462(0.090) + 2.073(0.081)\mathbf{S} + 2.022(0.150)\mathbf{A} + 0.637(0.103)\mathbf{B} + 0.684(0.021)\mathbf{L}$$
$$(N = 50,\ \text{SD} = 0.123,\ R^2 = 0.968,\ F = 1337.2) \tag{13}$$

and

$$\log P = -0.275(0.136) + 0.407(0.115)\mathbf{S} - 1.478(0.176)\mathbf{A} - 4.320(0.114)\mathbf{B} + 3.510(0.111)\mathbf{V}$$
$$(N = 48,\ \text{SD} = 0.140,\ R^2 = 0.994,\ F = 1858) \tag{14}$$

for the transfer of organic solutes to ILs from both the gas phase and from water. The e **E** term was negligible (calculated values of e < 0.01) and has been eliminated from both correlations. The statistics of both correlations are quite good as evidenced near unity squared correlation coefficients and small standard deviations of SD = (0.123 and 0.140) log units. Figures 6 and 7 graphically compare the experimental partition coefficients to predict values based on eqs 13 and 14. In establishing the computation methodology, the equation coefficients for the bis((trifluoromethyl)sulfonyl)imide anion were set equal to zero to provide a reference point from which all equation coefficients would be calculated.[22,23] A reference point is needed because the cation-specific and anion-specific equation coefficients come as a paired set. The equation coefficients in eqs 13 and 14 thus correspond to the ion-specific coefficients for the trimethyl-*n*-hexylammonium cation. As noted in previous papers, the cation-specific and anion-specific equation coefficients can be combined to yield predictive equations for the different ILs. The study increases our calculated cation-specific and anion-specific equation coefficients each by one. We have now reported equation coefficients for 11 cations (counting trimethyl-*n*-hexylammonium cation) and for 9 anions (counting the

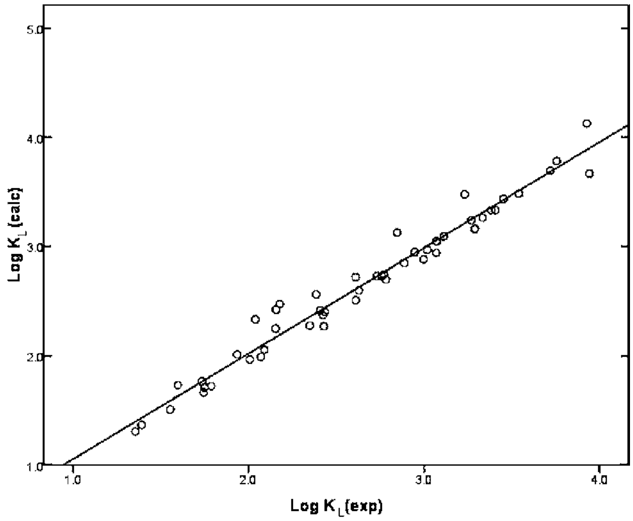

Figure 6. Plot of the logarithm of the experimental gas-to-[TMHA][Tf$_2$N] partition coefficients versus calculated values based on eq 13.

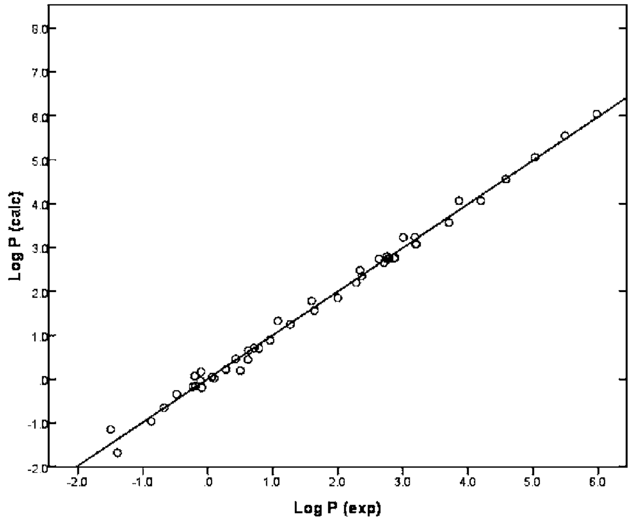

Figure 7. Plot of the logarithm of the experimental water-to-[TMHA][Tf$_2$N] partition coefficients versus calculated values based on eq 14.

[DCA] anion). The 11 sets of cation-specific equation coefficients and 9 sets of anion-specific equation coefficients can be combined to yield predictive equations for 99 different ILs.

Concluding Remarks. Partition coefficients of organic compounds in two new ILs [EMIM][DCA] and [TMHA][Tf_2N] were measured using inverse gas chromatography from (322.5 to 352.5) K. Selectivities obtained with ammonium based ILs are generally of the same magnitude as with classical solvents used in industry. The S_{12}^{∞} selectivity values obtained with [EMIM]-[DCA] show the possibility of using this IL as an extractive medium for the four separation processes proposed in this study. The selectivity of [DCA] ILs for the (hexane + methanol) mixture is particularly large ($S_{12}^{\infty} = 255$) compared to the value for classical solvents. The partition coefficients were also converted into water-to-IL partition coefficients using the corresponding gas-to-water partition coefficients. Both sets of partition coefficients were analyzed using the Abraham solvation parameter model with cation-specific and anion-specific equation coefficients. The derived equations correlated the experimental gas-to-IL and water-to-IL partition coefficient data to within (0.12 and 0.14) log units, respectively.

Supporting Information Available:

This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356.

(2) Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398.

(3) Wasserscheid, P.; Welton T. *Ionic liquids in synthesis*; Wiley-VCH: New York, **2003**.

(4) MacFarlane, D. R.; Seddon, K. R. Ionic liquids-progress on the fundamental issues. *Aust. J. Chem.* **2007**, *60*, 3–5.

(5) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.

(6) Brennecke, J. F.; Maginn, E. J. Ionic liquids: Innovative fluids for chemical processing. *AIChE J.* **2001**, *47*, 2384–2389.

(7) Arlt, M.; Seiler, M.; Jork, C.; Schneider, T. DE Patent 10114734, 2001.

(8) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Solvent extraction of thiophene from n-alkanes (C_7, C_{12}, and C_{16}) using the ionic liquid [C_8mim][BF_4]. *J. Chem. Thermodyn.* **2008**, *40*, 966–972.

(9) Revelli, A.-L.; Sprunger, L. M.; Gibbs, J.; Acree, W. E.; Baker, G. A.; Mutelet, F. Activity Coefficients at Infinite Dilution of Organic Compounds in Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide Using Inverse Gas Chromatography. *J. Chem. Eng. Data* **2009**, *54*, 977–985.

(10) Revelli, A.-L.; Mutelet, F.; Turmine, M.; Solimando, R.; Jaubert, J.-N. Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Inverse Gas Chromatography. *J. Chem. Eng. Data* **2008**, *54*, 90–101.

(11) Mutelet, F.; Butet, V.; Jaubert, J.-N. Application of Inverse Gas Chromatography and Regular Solution Theory for Characterization of Ionic Liquids. *Ind. Eng. Chem. Res.* **2005**, *44*, 4120–4127.

(12) Mutelet, F.; Jaubert, J.-N. Accurate measurements of thermodynamic properties of solutes in ionic liquids using inverse gas chromatography. *J. Chromatogr., A* **2006**, *1102*, 256–267.

(13) Mutelet, F.; Jaubert, J.-N.; Rogalski, M.; Boukherissa, M.; Dicko, A. 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. *J. Chem. Eng. Data* **2006**, *51*, 1274–1279.

(14) Mutelet, F.; Jaubert, J.-N. Measurement of activity coefficients at infinite dilution in 1-hexadecyl-3-methylimidazolium tetrafluoroborate ionic liquid. *J. Chem. Thermodyn.* **2007**, *39*, 1144–1150.

(15) Mutelet, F.; Jaubert, J.-N.; Rogalski, M.; Harmand, J.; Sindt, M.; Mieloszynski, J.-L. Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Methacryloyloxyalkyl-3-methylimidazolium Bromide Using Inverse Gas Chromatography. *J. Phys. Chem. B.* **2008**, *112*, 3773–3785.

(16) Matsumoto, H.; Miyazaki, Y.; Ishikawa, H. Japanese Patent Applications 11-297355 A, 1997.

(17) Yoshida, Y.; Kondo, M.; Saito, G. Ionic liquids formed with polycyano 1,1,3,3-tetracyanoallyl anions: Substituent effects of anions on liquid properties. *J. Phys. Chem. B* **2009**, *113*, 8960–8966.

(18) Deng, M.-J.; Chen, P.-Y.; Leong, T.-I.; Sun, I.-W.; Chang, K.; Tsai, W.-T. Dicyanamide anion based ionic liquids for electrodeposition of metals. *Electrochem. Commun.* **2008**, *10*, 213–216.

(19) Forsyth, S. A.; MacFarlane, D. R.; Thomson, R. J.; Von Itzstein, M. Rapid, clean, and mild O-acetylation of alcohols and carbohydrates in an ionic liquid. *Chem. Commun.* **2002**, 714–715.

(20) Acree, W. E., Jr.; Abraham, M. H. The analysis of solvation in ionic liquids and organic solvents using the Abraham model linear free energy relationship. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1441–1446.

(21) Abraham, M. H.; Acree, W. E., Jr. Comparative analysis of solvation and selectivity in room temperature ionic liquids using the Abraham linear free energy relationship. *Green. Chem.* **2006**, *8*, 906–915.

(22) Abraham, M. H.; Zissimos, A. M.; Huddleston, J. G.; Willauer, H. D.; Rogers, R. D.; Acree, W. E., Jr. Some novel liquid partitioning systems: Water-ionic liquids and aqueous biphasic systems. *Ind. Eng. Chem. Res.* **2003**, *42*, 413–418.

(23) Sprunger, L.; Clark, M.; Acree, W. E., Jr.; Abraham, M. H. Characterization of room-temperature ionic liquids by the Abraham model with cation-specific and anion-specific equation coefficients. *J. Chem. Inf. Model.* **2007**, *47*, 1123–1129.

(24) Sprunger, L. M.; Proctor, A.; Acree, W. E., Jr.; Abraham, M. H. LFER correlations for room temperature ionic liquids: Separation of equation coefficients into individual cation-specific and anion-specific contributions. *Fluid Phase Equilib.* **2008**, *265*, 104–111.

(25) Kilaru, P.; Baker, G. A.; Scovazzo, P. Density and Surface Tension Measurements of Imidazolium-, Quaternary Phosphonium-, and Ammonium-Based Room-Temperature Ionic Liquids: Data and Correlations. *J. Chem. Eng. Data* **2007**, *52*, 2306–2314.

(26) Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. The Large Scale Synthesis of Pure Imidazolium and Pyrrolidinium Ionic Liquids. *Green Chem.* **2007**, *9*, 449–454.

(27) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. The use of gas-liquid chromatography to determine activity coefficients and second virial coefficients of mixtures. *Proc. R. Soc. London* **1966**, *A295*, 259–270.

(28) Foco, G. M.; Bottini, S. B.; Quezada, N.; de la Fuente, J. C.; Peters, C. J. *J. Chem. Eng. Data* **2006**, *51*, 1088–1091.

(29) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique. *J. Chem. Eng. Data* **2002**, *7*, 1411–1417.

(30) Letcher, T. M.; Soko, B.; Ramjugernath, D.; Deenadayalu, N.; Nevines, A.; Naicker, P. K. Activity Coefficients at Infinite Dilution of Organic Solutes in 1- Hexyl-3-Methylimidazolium Hexafluorophosphate from Gas-Liquid Chromatography. *J. Chem. Eng. Data* **2003**, *48*, 708–711.

(31) Domańska, U.; Marciniak, A. Measurements of activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons, alcohols, and water in the new ionic liquid [EMIM][SCN] using GLC. *J. Chem. Thermodyn.* **2008**, *40*, 860–866.

(32) Domańska, U.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Ethyl-3-methylimidazolium Trifluoroacetate. *J. Phys. Chem. B* **2007**, *111*, 11984–11988.

(33) Domańska, U.; Marciniak, A. Activity Coefficients at Infinite Dilution, Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate. *J. Phys. Chem. B* **2008**, *112*, 11100–11105.

(34) David, W.; Letcher, T. M.; Ramjugernath, D.; Raal, J. D. Activity coefficients of hydrocarbon solutes at infinite dilution in the ionic liquid, 1-methyl-3-octyl-imidazolium chloride from gas-liquid chromatography. *J. Chem. Thermodyn.* **2003**, *35*, 1335–1341.

(35) MacFarlane, D. R.; Forsyth, S. A.; Golding, J.; Deacon, G. B. Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion. *Green Chem.* **2002**, *4*, 444–448.

(36) MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. Low viscosity ionic liquids based on organic salts of the dicyanamide anion. *Chem. Commun.* **2001**, *16*, 1430–1431.

(37) Acree, W. E.; Abraham, M. H. Solubility predictions for crystalline polycyclic aromatic hydrocarbons (PAHs) dissolved in organic solvents based upon the Abraham general solvation model. *Fluid Phase Equilib.* **2002**, *201*, 245–258.

(38) Acree, W. E.; Abraham, M. H. Solubility of Crystalline Nonelectrolyte Solutes in Organic Solvents: Mathematical Correlation of Benzil Solubilities with the Abraham General Solvation Model. *J. Solution Chem.* **2002**, *31*, 293–303.

(39) Ma, L.-N.; Ji, W.-R.; Ji, J.-B. Measurement of Infinite Diluted Activity Coefficient of Solutes in 1-Ethyl-3-methylimidazolium Dicyanamide. *J. Chem. Eng. Chin. Univ.* **2008**, *22*, 547–552.

(40) Scovazzo, P.; Camper, D.; Kieft, J.; Koval, C.; Noble, R. Regular Solution Theory and CO_2 Gas Solubility in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855–5850.

(41) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. Gas Solubilities in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049–3054.

(42) Sprunger, L. M.; Gibbs, J.; Proctor, A.; Acree, W. E., Jr.; Abraham, M. H.; Meng, Y.; Yao, C.; Anderson, J. L. Linear Free Energy Relationship Correlations for Room Temperature Ionic Liquids: Revised Cation-Specific and Anion-Specific Equation Coefficients for Predictive Applications Covering a Much Larger Area of Chemical Space. *Ind. Eng. Chem. Res.* **2009**, *48*, 4145–4154.

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