Study of Ether-, Alcohol-, or Cyano-Functionalized Ionic Liquids Using Inverse Gas Chromatography

Anne-Laure Revelli,[†] Fabrice Mutelet,*,[†] Jean-Noël Jaubert,[†] Marina Garcia-Martinez,[†] Laura M. Sprunger,[‡] William E. Acree, Jr.,[‡] and Gary A. Baker[§]

Laboratoire Réactions et Génie des Procédés CNRS UPR 3349, Nancy-Université, ENSIC, 1 rue Grandville, BP 20451 54001 Nancy, France, Department of Chemistry, 1155 Union Circle #305070, University of North Texas, Denton, Texas 76203-5017, and Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6201

Activity coefficients of 52 organic compounds in four ionic liquids (ILs), 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide, 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, 1-ethanol-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)imide, and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, were measured using inverse gas chromatography from (312 to 353) K. The retention data were also converted in gas-to-IL partition coefficients and water-to-IL partition coefficients using the corresponding gas-to-water partition coefficients. Both sets of partition coefficients were analyzed using the modified Abraham solvation parameter model. The derived equations correlated the experimental gas-to-IL and water-to-IL partition coefficient data to within (0.09 and 0.14) log units, respectively.

Introduction

The immediate need to reduce environmental pollution has brought great attention to the use of new classes of solvent. Ionic liquids (ILs) have been widely promoted 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 commonly comprised of an asymmetric, bulky organic cation and a weakly coordinating organic or inorganic anion.

Presently, there are more than 1000 different ILs commercially available, but it has been shown that there are > 10^{14} combinations possible.[1] The type of anion and the R groups in the different cations may be used to adjust the properties of the ILs. Therefore, the possibility arises to functionalize the IL for a specific application by stepwise tuning the relevant solvent properties.

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.[2–7] More precisely, extractive distillation and liquid−liquid extraction with ILs as a separating agent is a novel method for separation of ethanol−water mixture,[8] of thiophene from aliphatic hydrocarbons[9] and of methanol from aliphatic hydrocarbons.

Thermodynamic properties of alkyl imidazolium-based ILs are relatively well-described in the literature.[10–20] Nevertheless,

there is a lack of data concerning the polar alkyl chain grafted on the cation such as ether-, alcohol-, or cyano-functionalized ILs. A systematic study of interaction between organic compounds and such ILs is needed to have a better understanding of the behavior of ILs in mixtures. The ether-derivatized ILs were found capable of dissolving a large variety of substances such as triglycerides, sugars, cellulose, and amino acids.[21–23] These functionalized ILs increased water solubility compared to their alkyl-derivatized counterparts.[24] The potential of such ILs in gas separations has been recently reported with polymer gas separation membranes based on polymerizable ether-derivatized ILs.[25]

No thermodynamic property of cyanoalkyl-substituted ILs was found in the literature. Zhao and co-workers showed that these functionalized ILs should be used as electrolytes for lithium secondary batteries.[26] The dicyanamide [DCA] anion-based ILs exhibit low viscosity and are good solvents for metal ions resulting from the high complexing ability of [DCA].[27] The dicyanamide ILs were also used to explore reactions of carbohydrates and other alcohols, which until now have been inaccessible in other ILs.[28]

This study is a continuation of our investigations on thermodynamic properties of functionalized ILs.[29–36] 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. A short polar chain in imidazolium-based ILs increased their selectivity toward mixtures containing {alcohol + aliphatic} or {aromatic + aliphatic} groups. This work is focused on the behavior of four ether-, alcohol-, or cyano-functionalized imidazolium-based ILs: 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide ([(OC$_1$)$_2$im][Tf$_2$N]), 1-methylethyether-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([C$_2$OC$_1$mim][Tf$_2$N]), 1-ethanol-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([C$_2$OHmim][Tf$_2$N]), and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide ([C$_3$CNmim][DCA]). The molecular structures of the ILs are given in Figure 1. A gas−liquid chroma-

* To whom the correspondence should be addressed. E-mail: mutelet@ ensic.inpl-nancy.fr. Telephone number: +33 3 83 17 51 31. Fax number: +33 3 83 17 53 95.
[†] Nancy-Université.
[‡] University of North Texas.
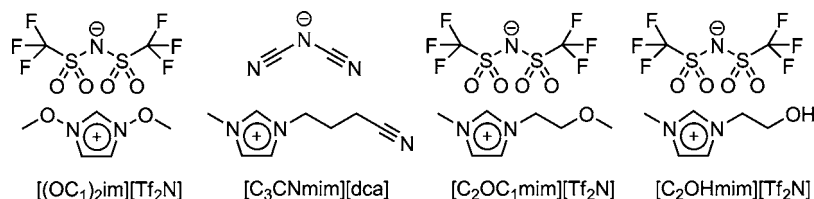[§] Oak Ridge National Laboratory.

Figure 1. Molecular structures of the ILs studied.

tography technique is used to quantify intermolecular solute−IL interaction and to predict their possible use for extraction and extractive distillation processes.

Using linear solvation energy relationship (LSER) and retention data, one can quantify intermolecular solute−IL interactions. Acree 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.[37–39] Sprunger et al.[40–42] modified the Abraham solvation parameter model as follows:

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

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

by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. In splitting the system constants into ion-specific contributions, the authors assumed that each solute−ion interaction was unaffected by the chemical nature of the counterion present in the IL.

The dependent variables in eqs 1 and 2 are solutes descriptors as follows: **E** and **S** refer to the excess molar refraction in units of $(\text{cm}^3 \cdot \text{mol}^{-1})/10$ 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 $(\text{cm}^3 \cdot \text{mol}^{-1})/100$, 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. Two of the ILs investigated here, 1,3-dimethoxyimidazolium bis((trifluoro-methyl)sulfonyl)imide and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, were purchased from Sigma-Aldrich with a purity of 98.5 % in mass fraction. The synthesis of 1-ethylmethylether-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂OC₁mim][Tf₂N]) and 1-ethanol-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂OHmim][Tf₂N]) was performed similarly to that described by Baker and co-workers.[43–45] In both cases, the materials obtained were clear, colorless fluids with purities higher than 99.5 % in mass fraction based on thermogravimetric analysis[46] and NMR spectroscopy. NMR spectra of these ILs were measured using a Bruker Avance 400 MHz spectrometer, with the observed chemical shifts reported relative to the residual solvent peak from acetone as an internal reference {(¹H NMR; 400 MHz; acetone-d_6): [C₂OC₁mim][Tf₂N]: $\delta = 9.01$ (s, 1H), 7.74 (m, 1H), 7.70 (m, 1H), 4.54 (t, 2H), 4.08 (s, 3H), 3.81 (t, 2H), 3.35 (s, 3H); [C₂OHmim][Tf₂N]: $\delta = 9.03$ (s, 1H), 7.76 (m, 1H), 7.72 (m, 1H), 4.46 (t, 2H), 4.09 (s, 3H), 3.97 (t, 2H)}.

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 are conditioned during 12 h. We assume that this procedure removed any volatile chemicals and water from the IL and Chromosorb. Beyond this soft thermal treatment, no other attempt was made to analyze impurities within 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. 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 a soap bubble flow meter. 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 packings of 1 m in length containing from (20 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 is conditioned during 12 h at 363 K with a flow rate of 20 cm³·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.

Theoretical Basis. The retention data determined with inverse chromatography experiments were used to calculate partition coefficients of the solute in the IL. The net retention volume, V_N, was calculated with the following usual relationship:[47]

$$V_{N} = \frac{3}{2} \frac{\left[\left(\frac{P_i}{P_0}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]} \cdot U_0 \cdot t_R' \cdot \frac{T_{col}}{T_r}\left(1 - \frac{P_{ow}}{P_0}\right) \quad (3)$$

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_{ow} is the vapor pressure of water at T_r. P_i and P_0 are respectively the inlet and outlet pressures.

The activity coefficient at infinite dilution of solute 1 in the IL 2 $\gamma_{1,2}^{\infty}$ was calculated with the following expression:[47]

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

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. All thermodynamic properties of pure solutes needed for calculations are given in a previous work.[29]

Gas-to-IL partition coefficients K_L used in the LSER approach are calculated using the following equation:

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

Results and Discussion

Activity Coefficients at Infinite Dilution of Organic Compounds in ILs. The errors in the activity coefficient 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 corre-

Table 1. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P, of Organic Compounds in 1-Ethanol-3-methylimidazolium Bis((trifluoro-methyl)sulfonyl)imide

		T/K					T/K = 298.15	
solute	322.55	332.55	342.85	298.15	R^2		log P	log K_L
hexane	43.64	41.84	28.39	83.58	0.816		2.443	0.623
3-methylpentane	42.90	34.82	26.02	54.54	0.742		2.552	0.712
heptane	72.81	67.53	51.88	119.90	0.901		2.943	0.983
2,2,4-trimethylpentane	68.97	62.10	52.64	101.21	0.981		3.145	1.025
octane	119.15	104.43	89.72	177.01	0.998		3.433	1.323
nonane	212.44	181.74	150.66	343.57	0.996		3.739	1.589
decane	307.11	265.95	231.18	454.80	1.000		4.183	1.923
undecane	484.07	416.68	357.52	736.80	1.000		4.601	2.221
dodecane	710.18	618.42	538.67	1041.27	1.000		5.074	2.544
tridecane	1083.93	939.03	806.66	1633.96	0.999			2.862
tetradecane	1553.98	1355.70	1151.62	2362.93	0.996			3.185
methylcyclopentane	25.49	22.71	21.87	31.14	0.926		2.265	1.095
cyclohexane	25.10	22.89	21.24	31.56	0.998		2.135	1.235
methylcyclohexane	38.95	33.95	30.85	53.44	0.991		2.580	1.330
cycloheptane	39.01	34.36	30.47	54.88	1.000		2.235	1.645
benzene	2.12	2.08	2.05	2.21	1.000		1.771	2.401
toluene	3.36	3.28	3.25	3.50	0.933		2.063	2.713
ethylbenzene	5.62	5.48	5.37	5.98	0.997		2.361	2.941
m-xylene	5.61	5.44	5.34	5.98	0.986		2.409	3.019
p-xylene	5.57	5.44	5.29	6.00	0.995		2.414	3.004
o-xylene	4.83	4.78	4.72	4.98	0.990		2.450	3.190
1-hexene	21.43	19.61	18.95	25.19	0.943		2.215	1.055
1-hexyne	7.54	7.12	6.83	8.61	0.992		1.900	1.690
1-heptyne	12.18	11.66	10.96	14.15	0.988		2.404	1.964
2-butanone	0.57	0.54	0.51	0.68	0.988		0.287	3.007
2-pentanone	1.00	1.04	1.05	0.94	0.911		0.633	3.213
3-pentanone	0.99	1.03	1.06	0.91	0.955		0.677	3.177
1,4-dioxane	0.59	0.62	0.63	0.54	0.983		−0.264	3.446
methanol	0.89	0.85	0.80	1.04	0.997		−1.134	2.606
ethanol	1.23	1.21	1.13	1.38	0.900		−0.857	2.813
1-propanol	2.55	2.53	2.53	1.07	0.760		−0.193	3.367
2-propanol	1.46	1.40	1.33	1.67	0.996		−0.626	2.854
2-methyl-1-propanol	2.38	2.21	2.06	2.90	0.999		−0.114	3.186
1-butanol	2.49	2.36	2.16	3.05	0.973		−0.060	3.400
trifluoroethanol	0.54	0.54	0.56	0.52	0.653		−0.002	3.158
diethyl ether	2.86	2.81	2.91	2.78	0.228		0.387	1.557
diisopropyl ether	7.13	7.13	7.30	6.88	0.718		0.662	1.712
chloroform	1.89	1.88	1.86	1.95	0.384		1.352	2.142
dichloromethane	1.26	1.25	1.25	1.16	0.686		0.917	1.877
tetrachloromethane	6.61	6.41	5.82	7.96	0.918		1.957	1.767
acetonitrile	0.48	0.48	0.48	0.48	0.508		0.247	3.097
nitromethane	0.64	0.64	0.64	0.64	0.002		0.414	3.364
1-nitropropane	1.14	1.13	1.12	1.18	0.996		1.194	3.644
triethylamine	4.86	4.53	4.28	5.79	0.997		−0.215	2.145
pyridine	0.28	0.62	1.44	0.03	0.999			4.936
thiophene	1.77	1.77	1.71	1.86	0.804		1.512	2.552
formaldehyde	0.14	0.16	0.26	0.05	0.884			2.410
propionaldehyde	0.72	0.72	0.71	0.75	0.596		−0.151	2.369
butyraldehyde	1.11	1.11	1.11	1.11	0.093		0.322	2.652

Table 2. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P, of Organic Compounds in 1-(Methylethylether)-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)imide

	T/K					T/K = 298.15	
solute	332.65	342.75	353.15	298.15	R^2	log P	log K_L
hexane	18.30	16.34	15.32	25.89	0.970	2.047	0.227
3-methylpentane	15.80	14.62	13.37	22.10	0.999	2.057	0.217
heptane	28.38	26.18	23.02	43.42	0.987	2.339	0.379
2,2,4-trimethylpentane	27.40	24.91	22.94	38.97	0.997	2.504	0.384
octane	43.63	38.91	34.67	69.07	0.999	2.646	0.536
nonane	72.21	62.69	54.95	124.36	0.997	2.834	0.684
decane	100.09	86.65	75.78	174.10	0.997	3.086	0.826
undecane	150.07	128.36	109.41	282.12	0.999	3.358	0.978
dodecane	218.00	186.21	157.15	419.70	1.000	3.653	1.123
tridecane		275.09	229.14	696.08			1.167
tetradecane		391.50	325.31	1003.06			1.285
methylcyclopentane	11.02	10.24	7.85	22.34	0.916	1.596	0.426
cyclohexane	11.00	10.06	9.36	15.16	0.995	1.458	0.558
methylcyclohexane	15.77	14.37	13.15	22.64	0.999	1.897	0.647
cycloheptane	15.62	14.24	13.07	22.26	0.999	1.428	0.838
benzene	1.18	1.19	1.16	1.23	0.510	0.673	1.303
toluene	1.76	1.78	1.77	1.74	0.515	0.804	1.454
ethylbenzene	2.74	2.74	2.69	2.83	0.688	1.002	1.582
m-xylene	2.75	2.75	2.73	2.80	0.731	1.000	1.610
p-xylene	2.74	2.72	2.65	2.93	0.878	1.006	1.596
o-xylene	2.44	2.45	2.45	2.41	0.463	0.982	1.722
1-hexene	9.76	9.17	8.75	12.12	0.992	1.511	0.351
1-hexyne	3.51	3.45	3.36	3.84	0.991	0.947	0.737
1-heptyne	5.33	5.10	5.03	5.95	0.917	1.359	0.919
2-butanone	0.49	0.45	0.42	0.66	1.000	−1.225	1.495
2-pentanone	0.86	0.86	0.87	0.84	0.998	−0.938	1.642
3-pentanone	0.83	0.85	0.86	0.77	1.000	−0.883	1.617
1,4-dioxane	0.60	0.61	0.62	0.57	0.997	−1.979	1.731
methanol	1.05	0.97	0.84	1.64	0.980	−2.462	1.278
ethanol	1.43	1.32	1.22	1.96	1.000	−2.452	1.218
1-propanol	1.79	1.62	1.46	2.66	1.000	−2.157	1.403
2-propanol	1.64	1.51	1.38	2.34	1.000	−2.267	1.213
2-methyl-1-propanol	2.18	1.99	1.79	3.25	1.000	−1.823	1.477
1-butanol	2.34	2.11	1.90	3.56	0.999	−1.855	1.605
trifluoroethanol	0.38	0.37	0.35	0.47	0.975	−1.566	1.594
diethyl ether	2.41	2.31	2.35	2.51	0.343	−0.658	0.512
diisopropyl ether	5.78	5.70	5.41	6.64	0.912	−0.497	0.553
chloroform	0.98	1.01	1.02	0.92	0.968	0.316	1.106
dichloromethane	0.72	0.75	0.76	0.64	0.974	0.010	0.970
tetrachloromethane	3.03	2.99	2.92	3.29	0.980	1.095	0.905
acetonitrile	0.44	0.44	0.44	0.45	0.598	−1.121	1.729
nitromethane	0.49	0.49	0.48	0.52	0.885	−1.039	1.911
1-nitropropane	0.75	0.75	0.74	0.76	0.700	−0.383	2.067
triethylamine	9.31	8.73	6.89	17.43	0.912	−1.514	0.846
pyridine	0.58	0.58	0.59	0.57	0.628	−1.474	1.966
thiophene	1.01	1.02	1.01	1.01	0.012	0.350	1.390
formaldehyde	0.07	0.08	0.09	0.05	0.994	−0.942	1.078
propionaldehyde	0.31	0.32	0.28	0.39	0.475		1.540
butyraldehyde	0.28	0.31	0.33	0.19	0.994	−0.761	1.569
ethyl acetate	0.91	0.92	0.93	0.87	0.925	−0.865	1.295
butyl acetate	1.78	1.79	1.78	1.78	0.009	−0.331	1.609
tetrahydrofuran	0.79	0.80	0.79	0.77	0.626	−1.281	1.279

sponding 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}; mass of the stationary phase, 2 %; the inlet and outlet pressures, 0.2 kPa; 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 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 all ILs studied in this work, 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 %.

Experimental activity coefficients at infinite dilution calculated using eqs 3 to 5 are listed in Tables 1 to 4. Polar functionalized imidazolium ILs have similar behaviors to alkylimidazolium.

Activity coefficients at infinite dilution of most organic compounds decrease with an increase of the temperature. For compounds containing the same number of carbon atoms taken from different families, it was observed that $\gamma_{\text{alcohol}} < \gamma_{\text{aromatic}} < \gamma_{\text{alkyne}} < \gamma_{\text{alkene}} < \gamma_{\text{alkane}}$. This trend is in good agreement with the data obtained in all other ILs, whatever the cation or the anion.

The high γ^∞ values observed with n-alkanes indicate their low solubility in ILs. The solubility of alcohols and chloroalkanes are better in 1-(methoxyethyl)-3-methylimidazolium bis-((trifluoromethyl)sulfonyl)imide than in 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide. The gamma values for the alcohols are relatively small. The hydroxyl group could interact with the anion and/or the cation of the IL. These families of compounds follow the same trend than hydrocarbons. Introducing a branched alkyl on these compounds decreases their

Table 3. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P, of Organic Compounds in 1,3-Dimethoxyimidazolium Bis((trifluoro-methyl)sulfonyl)imide

	T/K				T/K = 298.15	
solute	312.45	323.15	332.70	R^2	log P	log K_L
hexane	44.89	44.58	36.03	0.924	2.631	0.811
3-methylpentane	36.05	35.2	28.73	0.928	2.647	0.807
heptane	76.55	72.38	27.48	0.959	2.983	1.023
2,2,4-trimethylpentane	71.22	69.04	52.53	0.888	3.184	1.064
octane	127.18	116.58	94.12	0.975	3.475	1.365
nonane	231.38	211.27	162.07	0.966	3.784	1.634
decane	339.55	305.42	238.18	0.98	4.250	1.930
undecane	551.18	482.89	392.25	0.994	4.618	2.238
dodecane	770.62	717.33	599	0.994	5.092	2.592
tridecane	1259	1216.13	935.58	0.982		2.875
tetradecane	1913	1646.5	1368.38	0.999		3.173
methylcyclopentane	25.42	22.49	18.88	0.983	2.251	1.081
cyclohexane	25.84	22.74	19.38	0.992	2.126	1.226
methylcyclohexane	39.76	34.25	30.31	1	2.581	1.371
cycloheptane	55.35	73.23	92.28	1	2.280	1.690
benzene	2.16	2.09	2.03	1	1.765	2.395
toluene	3.33	3.15	3.10	1	2.072	2.722
ethylbenzene	5.62	5.24	5.21	0.998	2.369	2.949
m-xylene	5.37	4.99	4.88	0.999	2.437	3.047
p-xylene	5.38	4.99	4.88	0.999	2.430	3.020
o-xylene	4.77	4.40	4.31	0.999	2.531	3.191
1-hexene	21.35	19.37	17.70	1	2.227	1.067
1-hexyne	6.71	6.34	6.12	1	1.977	1.767
1-heptyne	10.86	10.18	9.79	1	2.484	2.044
2-butanone	0.54	0.51	0.49	0.999	0.319	3.039
2-pentanone	0.85	0.90	0.94	1	0.712	3.292
3-pentanone	0.88	0.88	0.94	0.999	0.723	3.223
1,4-dioxane	0.45	0.51	0.54	0.999	−0.130	3.580
methanol	1.10	1.06	0.99	0.999	−1.193	2.547
ethanol	1.65	1.53	1.43	1	−0.979	2.691
1-propanol	2.47	2.15	2.02	0.998	−0.623	2.937
2-propanol	1.98	1.88	1.74	0.999	−0.735	2.745
2-methyl-1-propanol	3.41	2.86	2.66	0.998	−0.246	3.054
1-butanol	3.65	3.15	2.85	1	−0.200	3.260
2,2,2-trifluoroethanol	0.57	0.53	0.52	0.999	−0.077	3.083
diethyl ether	2.74	2.77	2.78	1	0.169	1.569
diisopropyl ether	7.45	7.28	7.31	1	0.629	1.679
chloroform	1.70	1.66	1.66	1	1.409	2.199
dichloromethane	1.01	1.04	1.06	1	0.984	1.944
tetrachloromehtane	6.03	5.67	4.94	0.987	1.879	1.819
acetonitrile	0.42	0.41	0.42	0.996	0.319	3.169
nitromethane	0.55	0.52	0.53	0.998	0.480	3.43
1-nitropropane	0.91	0.91	0.91	0.984	1.181	3.631
triethylamine	4.36	4.36	4.37	0.996	−0.089	2.271
pyridine	0.73	0.62	0.50	0.64	0.005	3.445
thiophene	1.83	1.80	1.76	0.999	1.523	2.553
formaldehyde	0.11	0.11	0.12	0.998		2.152
propionaldehyde	0.58	0.55	0.51	0.952	−0.098	2.422
butyraldehyde	0.94	0.87	0.82	0.993	0.347	2.677

solubility, and activity coefficients of alcohols increase with increasing chain length. Ketones and aldehydes have a lower solubility than alcohols.

Most organic compounds have a better solubility in 1-(methoxyethyl)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide than in 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide. The magnitude of activity coefficients obtained with 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide is significantly higher than the corresponding values for ether derivatized-imidazolium ILs.[29–36,49–52]

Selectivities at infinite dilution S_{12}^∞ are listed in Table 5 for four separation problems: hexane/benzene, hexane/methanol, hexane/thiophene, and cyclohexane/thiophene for ILs at $T =$ 323.15 K:

$$S_{12}^\infty = \frac{\gamma_{1/RTIL}^\infty}{\gamma_{2/RTIL}^\infty} \qquad (6)$$

Selectivities obtained with [Tf₂N] based ILs and classical solvent used in industry are of the same order of magnitude. The selectivity of such ILs does not increase by replacing the alkyl

chain by an ether chain. Concerning dicyanamide ILs, 1-cyanopropyl-3-methylimidaolium dicyanamide has a relatively high selectivity. The S_{12}^∞ values obtained with DCA ILs show the possibility of using these ILs 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 compared to the value for classical solvents. Then, the [C₂OHmim] cation coupled to the [TF₂N] anion has a small selectivity.

Linear Solvation Energy Relationship (LSER) Characterization. The experimental data measured here can be used to calculate the Abraham model ion-specific equation coefficients for ILs studied 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 4. The log P values for partition from water to the IL are calculated through eq 7

$$\log P = \log K_L - \log K_W \qquad (7)$$

and require knowledge of the solute's gas-phase partition coefficient into water, K_W, which is available for most of the

Table 4. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P, of Organic Compounds in 1-(3-Cyanopropyl)-3-methylimidazolium Dicyanamide

	T/K				T/K = 298	
solute	312.75	322.55	332.55	R^2	log P	log K_L
hexane	255.25	240.87	144.86	0.998	1.956	0.136
3-methylpentane	204.65	181.9	133.13	0.731	2.041	0.201
heptane	590.88	429.27	286.94	0.945	2.219	0.259
2,2,4-trimethylpentane	529.55	443.97	294.38	0.997	2.433	0.313
octane	736.63	639.12	501.59	0.98	2.906	0.796
nonane	1220.93	1088.08	938.87	0.999	3.325	1.175
decane	1634.74	1444.55	1376.77	0.998	3.809	1.549
undecane	2289.91	2038.96	1919.43	0.999	4.289	1.909
dodecane	2847.35	2571.19	2518.27	0.999		2.308
tridecane	3601.89	3275.51	3241.91	0.999		2.729
methylcyclopentane	110.72	94.77	83.97	0.999	1.848	0.678
cyclohexane	100.70	86.40	73.46	0.999	1.750	0.850
methylcyclohexane	177.87	151.09	133.57	0.999	2.190	0.940
cycloheptane	146.05	128.03	113.7	1	1.955	1.365
benzene	4.56	4.48	4.42	1	1.678	2.308
toluene	8.12	8.00	7.87	1	1.923	2.573
ethylbenzene	15.84	15.61	15.37	1	2.158	2.738
m-xylene	15.63	15.27	14.86	1	2.212	2.822
p-xylene	14.5	14.31	14.05	1	2.246	2.836
o-xylene	11.85	11.69	11.57	1	2.306	3.046
1-hexene	91.46	80.09	75.32	0.993	1.822	0.662
1-hexyne	18.31	17.45	16.77	1	1.768	1.558
1-heptyne	33.99	32.55	31.52	1	2.224	1.784
2-butanone	2.56	2.43	2.21	1	−0.153	2.567
2-pentanone	5.02	5.06	5.02	1	0.132	2.712
3-pentanone	4.77	4.83	4.82	1	0.193	2.693
1,4 dioxane	1.56	1.59	1.62	1	−0.483	3.227
methanol	0.59	0.59	0.58	1	−0.669	3.071
ethanol	1.18	1.23	1.11	0.99	−0.589	3.081
1-propanol	1.67	1.92	1.53	0.946	−0.217	3.343
2-propanol	2.27	2.13	2.02	1	−0.560	2.920
2-methyl-1-propanol	3.23	2.99	2.82	1	0.036	3.336
1-butanol	2.89	3.19	2.46	0.952	0.127	3.587
trifluoroethanol	0.19	0.21	0.2	0.994	0.671	3.831
diethyl ether	16.94	15.93	15.16	1	−0.207	0.963
diisopropyl ether	68.77	62.51	58.26	1	−0.162	0.888
chloroform	1.41	1.48	1.57	1	1.764	2.554
dichloromethane	0.94	1.02	1.11	1	1.286	2.246
tetrachloromethane	10.16	10.15	10.12	1	2.082	1.892
acetonitrile	0.94	0.94	0.96	1	0.190	3.040
nitromethane	0.78	0.78	0.8	1	0.572	3.522
1-nitropropane	2.37	2.3	2.3	1	1.119	3.569
pyridine	1.53	1.55	1.58	1	0.019	3.459
thiophene	2.44	2.43	2.48	1	1.634	2.674
formaldehyde	0.20	0.43	0.52	0.955	0.353	2.373
propionaldehyde	1.40	1.94	1.89	0.958		2.406
butyraldehyde	3.52	3.51	3.49	1	0.045	2.375

Table 5. Selectivity Values S_{12}^∞ for Different Separation Problems at 323.15 K

solvent		S_{12}^∞				
anion	cation	hexane/benzene	hexane/methanol	hexane/thiophene	cyclohexane/thiophene	ref
[Tf$_2$N]	1,3-dimethoxyimidazolium	21.3	42.05	24.8	12.6	this work
	1-(methylethylether)-3-methylimidazolium	15.5	17.4	18.1	10.9	this work
	1-ethanol-3-methylimidazolium	20.6	49.1	24.7	14.2	this work
	1-ethyl-3-methylimidazolium	37.5	19.5			48
	1-(hexylmethylether)-3-methylimidazolium	9.1	6.8	10.0	6.4	49
	1,3-di(hexylmethylether)imidazolium	4.9	3.2	5.3	3.7	49
	1-butyl-3-methylimidazolium	16.7				50
	1-hexyl-3-methylimidazolium	9.5	6.1			51
	trimethylhexylammonium	9.9	8.5	10.7	7.2	36
	4-methyl-*N*-butyl-pyridinium	18.8	21.2	10.6	6.1	52
	triethylsulphonium	21.6	17.8	25.5	14.3	53
	trihexyl(tetradecyl)phosphonium	2.7	1.1	2.6	1.95	29
[DCA]	1-cyanopropyl-3-methylimidaolium	56.0	432	105	41.3	this work
	1-ethyl-3-methylimidazolium	43.4	255	69.6	28.8	36
[Tf$_2$N]	1-ethanol-3-methylimidazolium	20.6	49.1	24.7	14.2	this work
[BF$_4$]	1-ethanol-3-methylimidazolium				136.1	54
[PF$_6$]	1-ethanol-3-methylimidazolium				59.7	54

solutes studied. For solvents that are completely miscible with water, 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

Table 6. 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
diethyl 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

Figure 2. Plot of the logarithm of the experimental gas-to-IL partition coefficients for 1-ethanol-3-methyl-imidazolium bis((trifluoromethyl)sulfonyl)imide versus calculated values based on eq 8. ○, experimental log *K* at 298.15 K.

Analysis of the experimental log K_L and log *P* data in Table 1 for 1-ethanol-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide gave:

$$\log K_L = 0.917(0.069) + 0.140(0.086)\mathbf{E} + 2.504(0.079)\mathbf{S} + 2.867(0.115)\mathbf{A} + 1.295(0.085)\mathbf{B} + 0.608(0.016)\mathbf{L} \quad (8)$$

$$(N = 47, \ SD = 0.091, \ R^2 = 0.988, \ F = 694.5)$$

$$\log P = -0.443(0.159) + 0.592(0.146)\mathbf{S} - 0.901(0.203)\mathbf{A} - 3.474(0.142)\mathbf{B} + 3.049(0.126)\mathbf{V} \quad (9)$$

$$(N = 47, \ SD = 0.131, \ R^2 = 0.989, \ F = 932.3)$$

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. All regression analyses were performed using SPSS statistical software. The standard errors in the calculated coefficients are given in parentheses. Solute descriptors used in the analysis are tabulated in Table 6. Equations 8 and 9 provide a very accurate mathematical description of the log K_L and log *P* values as shown in Figures 2 and 3, respectively.

As noted above each of the calculated equation coefficient corresponds to the sum of the respective cation-specific and anion-specific contribution. In establishing the computation methodology, the six 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.[39–41] A reference point is needed because the cation-specific and anion-specific equation coefficients come as a paired set. The equation coefficients in eqs 8 and 9 thus correspond to the ion-specific coefficients for the 1-ethanol-3-methyl-imidazolium cation.

The experimental partition coefficient data for 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (see Table 2) and 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide (see Table 3) were analyzed in a similar fashion. The Abraham model correlations for 1-(methylethylether)-3-methylimidazolium bis((trifluoro-methyl)sulfonyl)imide are given by eqs 10 and 11:

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[48] and in solute descriptor computations.[49] For convenience, we have tabulated in the last two rows of Tables 1 to 4 the log *P* and log K_L values at 298.15 K for 1-ethanol-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, 1,3-dimethoxyimidazolium bis((trifluoromethyl)-sulfonyl)imide, and 1-(3cyanopropyl)-3-methylimidazolium dicyanamide, respectively.
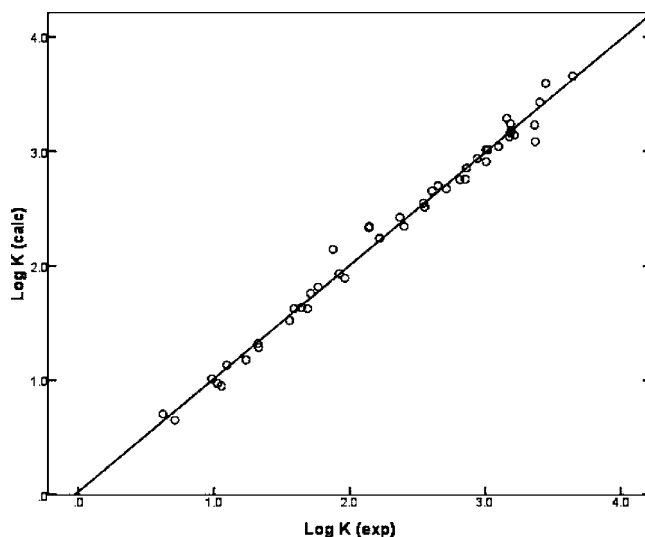
$$\log K_{\mathrm{L}} = -0.487(0.055) + 0.118(0.070)\mathbf{E} + 1.720(0.066)\mathbf{S} + 1.132(0.095)\mathbf{A} + 0.332(0.070)\mathbf{B} + 0.273(0.013)\mathbf{L} \quad (10)$$

$$(N = 52, \ \mathrm{SD} = 0.079, \ R^2 = 0.974, \ F = 346.2)$$

$$\log P = 0.079(0.093) - 0.369(0.147)\mathbf{E} - 0.337(0.151)\mathbf{S} - 2.378(0.207)\mathbf{A} - 4.566(0.144)\mathbf{B} + 1.977(0.135)\mathbf{V} \quad (11)$$

$$(N = 48, \ \mathrm{SD} = 0.134, \ R^2 = 0.999, \ F = 1056)$$

and for 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide are given by eqs 12 and 13:

$$\log K_{\mathrm{L}} = -0.762(0.063) - 0.013(0.046)\mathbf{E} + 2.557(0.072)\mathbf{S} + 2.427(0.106)\mathbf{A} + 1.157(0.077)\mathbf{B} + 0.584(0.015)\mathbf{L} \quad (12)$$

$$(N = 48, \ \mathrm{SD} = 0.084, \ R^2 = 0.989, \ F = 791.1)$$

$$\log P = -0.412(0.133) - 0.104(0.123)\mathbf{E} + 0.761(0.124)\mathbf{S} - 1.124(0.171)\mathbf{A} - 3.776(0.118)\mathbf{B} + 3.055(0.106)\mathbf{V} \quad (13)$$

$$(N = 46, \ \mathrm{SD} = 0.130, \ R^2 = 0.993, \ F = 1110.2)$$

The statistics of both sets of correlations are quite good as evidenced by the near unity values of the squared correlation coefficients and by the small standard deviations of SD = 0.079 and SD = 0.134 log units for the log K_{L} and log P correlations for 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide and of SD = 0.084 and SD = 0.130 log units for the log K_{L} and log P correlations for 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide. The anion for both ILs is NTF$_2$; hence the calculated equation coefficients in eqs 10 to 13 correspond to the ion-specific values for the 1-(methoxyethyl)-3-methylimidazolium cation (eqs 10 and 11) and the 1,3-dimethoxyimidazolium cation (eqs 12 and 13).

The last IL studied, 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, contains the dicyanamide anion, [DCA], for which we recently reported[36] log K_{L} 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 $l_{\mathrm{anion}} = -0.045$ and log P equation coefficients of $c_{\mathrm{anion}} = -0.379$, $e_{\mathrm{anion}} = -0.055$, $s_{\mathrm{anion}} = 0.701$, $a_{\mathrm{anion}} = 2.434$,
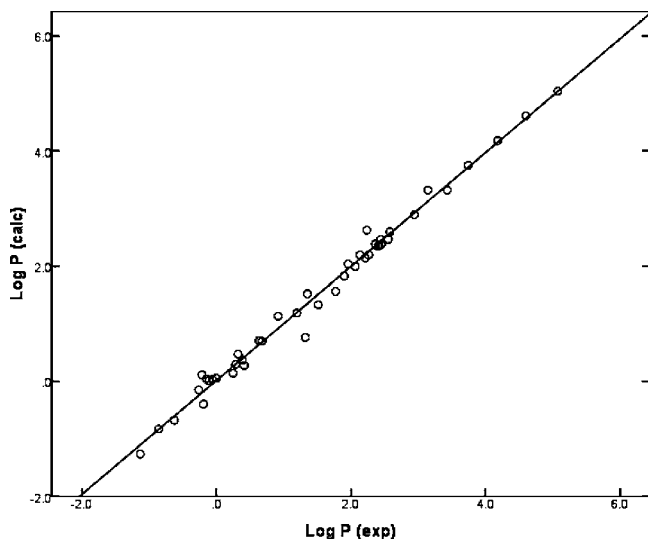
Figure 3. Plot of the logarithm of the experimental water-to-IL partition coefficients for 1-ethanol-3-methyl-imidazolium bis((trifluoromethyl)sulfonyl)imide versus calculated values based on eq 9. ○, experimental log P at 298.15 K.
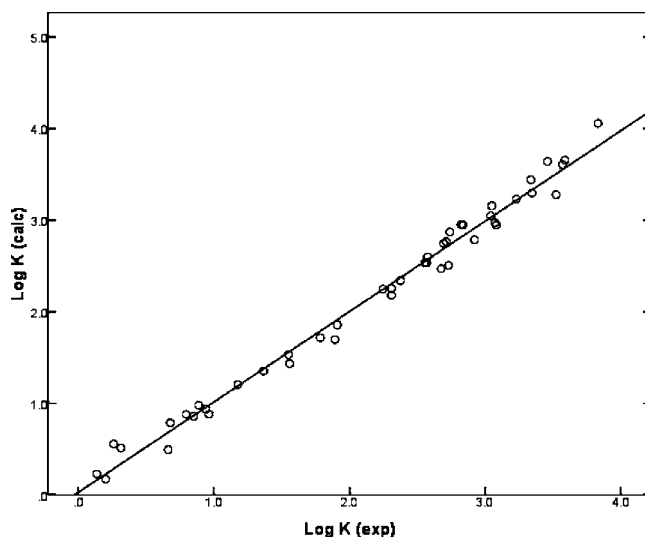
Figure 4. Plot of the logarithm of the experimental gas-to-IL partition coefficients for 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide versus calculated values based on eq 14. ○, experimental log K at 298.15 K.
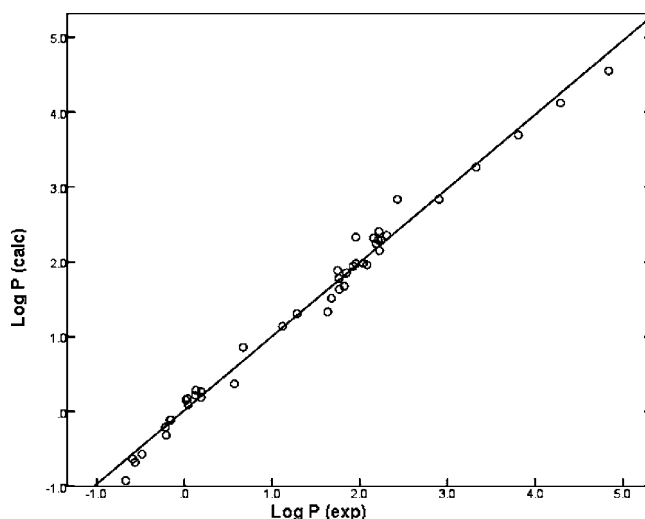
Figure 5. Plot of the logarithm of the experimental water-to-IL partition coefficients for 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide versus calculated values based on eq 15. ○, experimental log P at 298.15 K.

$b_{\mathrm{anion}} = -0.828$, and $v_{\mathrm{anion}} = -0.148$ for the [DCA] anion. Analysis of the log K_{L} and log P partition coefficient data in Table 4 yielded the following two Abraham model correlations:[55,56]

$$\log K_{\mathrm{L}} = -1.489(0.098) - 0.418(0.117)\mathbf{E} + 3.089(0.115)\mathbf{S} + 4.807(0.163)\mathbf{A} + 0.626(0.135)\mathbf{B} + 0.644(0.025)\mathbf{L} \quad (14)$$

$$(N = 45, \ \mathrm{SD} = 0.121, \ R^2 = 0.987, \ F = 607.3)$$

$$\log P = -0.928(0.156) + 0.373(0.146)\mathbf{E} + 1.224(0.154)\mathbf{S} + 1.042(0.207)\mathbf{A} - 4.307(0.166)\mathbf{B} + 3.046(0.125)\mathbf{V} \quad (15)$$

$$(N = 44, \ \mathrm{SD} = 0.150, \ R^2 = 0.988, \ F = 613.1)$$

The derived correlations provide a reasonably accurate mathematical description of the observed partition coefficient data, as evidenced by standard deviations of SD = 0.121 and SD = 0.150. Figures 4 and 5 compare the experimental log K_{L} and log P data to predicted values based on eqs 14 and 15.

The calculated coefficients in eqs 14 and 15 correspond to the sum of the respective cation-specific and anion-specific

contribution. The cation-specific values are obtained by simply subtracting the reported[36] anion-specific values for [DCA] from the calculated IL-specific equation coefficients in eqs 14 and 15, that is, $c_{cation} = c_{IL} - c_{cation}$, and so forth. Performing the subtraction we obtain log K_L coefficients of $c_{cation} = -1.127$, $e_{cation} = 0.303$, $s_{cation} = 2.542$, $a_{cation} = 2.436$, $b_{cation} = -0.057$, and $l_{cation} = 0.689$, and log P coefficients of $c_{cation} = -0.549$, $e_{cation} = 0.428$, $s_{cation} = 0.523$, $a_{cation} = -1.392$, $b_{cation} = -3.479$, and $v_{cation} = 3.184$ for the 1-(3-cyanopropyl)-3-methylimidazolium cation.

Concluding Remarks

Activity coefficients at infinite dilution of organic compounds in four functionalized ILs were measured using inverse gas chromatography. High selectivities obtained with dicyanamide-based ILs indicate that such ILs should be used for the liquid−liquid extraction of numerous volatile organic compounds from aliphatic mixtures. Grafting a polar chain on the cation of dicyanamide-based ILs increases their potential spectacularly. [Tf₂N] ILs do not present a particular interest since the selectivity values obtained are equivalent to the classical solvent used in the industry.

Gas-to-IL partition coefficients and water-to-IL 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 0.09 and 0.14 log units, respectively. 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 provided ion-specific coefficients for 3-dimethoxyimidazolium, 1-(methylethylether)-3-methylimidazolium, 1-ethanol-3-methyl-imidazolium, and 1-(3-cyanopropyl)-3-methylimidazolium cations. We have now reported equation coefficients for 15 cations (counting the four cations studied here) and for nine anions. The calculated ion-specific equation coefficients can be combined to yield Abraham model correlations for a total of 135 different ILs. The descriptor space for several of the calculated ion-specific equation coefficients was quite narrow, and additional experimental measurements are needed to expand the approach to more ILs and to a more diverse set of chemical solutes.

Correlations based on the calculated ion-specific equation coefficients do pertain to 298.15 K. ILs are commonly used as stationary phases in gas chromatographic separations, and there is a growing need to prediction log K_L values at higher temperatures. In this regard, Sprunger et al.[50] showed that the Abraham model, with ion-specific equation coefficients, can be used to predict the enthalpy of solvation of organic gases and gaseous solutes, ΔH_{solv}, into several ILs. The authors reported equation coefficients for nine different cations and eight different anions. The published ΔH_{solv} correlations will allow one to extrapolate the predicted 298 K log K_L values to other temperatures not too far removed from 298 K.

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