

Activity Coefficients at Infinite Dilution for Organic Compounds Dissolved in 1-Alkyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids Having Six-, Eight-, and Ten-Carbon Alkyl Chains

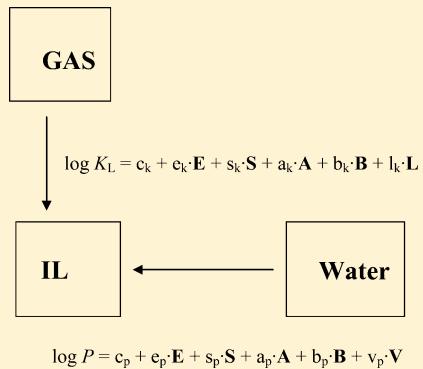
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ABSTRACT: Activity coefficients at infinite dilution ($\gamma_{1,2}^\infty$) for 40 diverse probe solutes, including various (cyclo)alkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, thiophene, ethers, nitroalkanes, and ketones, were measured by inverse gas chromatography at temperatures from 323 to 343 K in three homologous 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids (ILs), bearing hexyl, octyl, and decyl side chains. The retention data were further converted to gas-to-IL 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, with the derived equations tightly correlating the experimental gas-to-IL and water-to-IL partition coefficient data to within average standard deviations of 0.088 and 0.111 log units, respectively.



INTRODUCTION

Ionic liquids (ILs) have been increasingly utilized as solvent media in industrial manufacturing and chemical separation processes because of their low volatility and good thermal stability at high temperatures, recyclability, and thermal nonflammability. Representative applications include the use of ILs as potential green solvents in liquid–liquid extractions involving the removal of aromatic nitrogen and aromatic sulfur compounds from petroleum crude products and fuel oils,^{1–6} as entrainers and azeotrope breakers in extractive distillations,⁷ and as membrane coatings and absorbents for ethylene/acetylene,^{8,9} propyne/propylene,¹⁰ propylene/propane,^{11,12} 1-hexene/hexane,¹³ and CO₂/CH₄^{14,15} separations. Judicious selection of the cation–anion pair, combined with the introduction of functional groups to the IL, enables one to fine-tune the chemical selectivity and efficiency of the separation process. For example, ether- and hydroxyl-functionalized ILs are reported¹⁶ to show especially high capacity for solubilizing carbon dioxide and sulfur dioxide.

The present study continues our methodical investigation of the solubilizing ability of IL solvents using the solvation parameter model developed by Abraham and co-workers.^{17,18} The basic model is described by two linear free energy relationships (LFERs). The first relationship involves solute transfer between two condensed phases:

$$\log P = c_p + e_p \cdot E + s_p \cdot S + a_p \cdot A + b_p \cdot B + v_p \cdot V \quad (1)$$

and the second relationship governs solute transfer from the gas phase to a condensed phase

$$\log K_L = c_k + e_k \cdot E + s_k \cdot S + a_k \cdot A + b_k \cdot B + l_k \cdot L \quad (2)$$

where P and K_L refer to the solute's condensed phase-to-condensed phase partition coefficient (often the water-to-organic solvent partition coefficient) and the gas-to-condensed phase partition coefficient, respectively. The uppercase letters in eqs 1 and 2 represent the solute properties, whereas the lowercase letters represent the complementary properties of the ILs. The solute descriptors are the excess molar refraction (E), the combined dipolarity/polarizability (S), the hydrogen-bond acidity (A) and basicity (B), the logarithm of the solute's gas-to-n-hexadecane partition coefficient at 298 K (L), and the solute's McGowan volume in units of (cm³ mol⁻¹)/100 (V). Solute descriptors have been reported for about 5000 solutes based on experimental partition coefficient and chromatographic retention factor data or calculated by the group contribution method.^{17–24}

The advantage of characterizing ILs with the Abraham model is that once the equation coefficients are calculated, one can estimate $\log P$ and $\log K_L$ values of additional solutes provided that the solute coefficients are known. To date, we have

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characterized the solubilizing properties of more than 30 monocationic ILs^{25–36} and six trigeminal tricationic ILs³⁷ using eqs 1 and 2 of the solvation parameter model. We have also extended the solvation parameter model to include cation- and anion-specific equation coefficients by splitting each equation coefficient into distinct cation and anion contributions (i.e., $c_L = c_{k,cation} + c_{k,anion}$, and so forth),^{38–41} and to permit the estimation $\log K_L$ and $\log P$ values for solutes dissolved in anhydrous ILs based on calculated temperature-dependent IL functional group parameters for 21 groups: 12 groups characterizing the cations and 9 groups for the anions.⁴² Previous studies have shown that the best $\log K_L$ and $\log P$ predictions are obtained with IL-specific correlations (eqs 1 and 2), as one might expect. Studies have further shown that the predictive ability of the ion-specific equations is slightly better than expressions based on the group contribution version of the model. For many IL solvents, however, the group contribution model will be the only option available.

Although substantial progress has been made, the 24 different cation-specific and 14 different anion-specific equation coefficients and the 21 different IL functional group parameters that have been determined thus far do not allow us to estimate the solubilizing behavior of all ILs that are currently being tested or employed in industrial manufacturing or of interest in chemical separation processes. To expand the number of predictive correlations we have measured infinite dilution activity coefficients and gas-to-liquid partition coefficients for a series of organic compounds dissolved in the 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide IL homologues 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[HMPyrr]^+[Tf_2N]^-$), 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[OMPyrr]^+[Tf_2N]^-$), and 1-decyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[DMPyrr]^+[Tf_2N]^-$). These experimental data are used to derive IL-specific Abraham model $\log K_L$ and $\log P$ correlations and to calculate ion-specific equation coefficients for the $[HMPyrr]^+$, $[OMPyrr]^+$, and $[DMPyrr]^+$ cations.

EXPERIMENTAL PROCEDURES AND RESULTS

Materials or Chemicals. Synthesis and characterization of the 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ILs was performed as described earlier by Jin et al.⁴³ with special attention paid to procedures and precautions necessary for attaining highly pure “spec-grade” material.^{44,45}

Apparatus and Experimental Procedure. Inverse chromatography experiments were performed 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 maintained at 523 K during all experimental measurements. 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 determined using an Altech Digital Flow Check Mass Flowmeter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. A personal computer directly recorded detector signals and the corresponding chromatograms were constructed using Galaxie software.

Packed columns of 1-m length containing from 15 to 35 % IL stationary phase on Chromosorb WHP (60–80 mesh) were prepared using the rotary evaporator technique. After evaporation of the chloroform under vacuum, the support

was equilibrated at 333 K over the course of 6 h. Prior to chromatographic measurement, each packed column was conditioned for 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 columns and was checked throughout experiments. The masses of the stationary phase were determined with a precision of 0.0003 g. A 1–5 μL volume of the headspace vapor of samples was introduced and validated to be within infinite dilution conditions. Each experiment was repeated at least twice to check reproducibility. Retention times were generally reproducible to within 0.01 to 0.03 min. The retention time measurements were repeated systematically each day for three selected solutes in order to certify the day-to-day stability of the experimental setup and to rule out possible drift caused by elution of the stationary phase by the helium stream. No changes in the retention times were noted throughout the study.

Theoretical Basis. The retention data determined from inverse chromatography experiments were used to calculate partition coefficients of the solutes in the IL of interest. The net retention volume (V_N) was calculated by the following usual relationship²⁵

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

The adjusted retention time (t'_R) was computed as a difference between the retention time of a solute and that of methane, T_{col} is the column temperature, U_0 is the flow rate of the carrier gas measured at room temperature (T_r), and P_{0w} is the vapor pressure of water at T_r . P_i and P_o are respectively the inlet and outlet pressures.

The activity coefficient at infinite dilution of solute 1 in IL 2 ($\gamma_{1,2}^\infty$) is calculated from the following expression:⁴⁶

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

Here n_2 is the mole number of the stationary phase component inside the column, R is the ideal gas constant, T denotes the temperature of the oven, B_{11} refers to the second virial coefficient of the solute in the gaseous state at temperature T , B_{13} represents the mutual virial coefficient between the solute 1 and the carrier gas helium (denoted 3), and P_1^0 is the probe vapor pressure at temperature T .

Partition coefficient (K_L) may at this juncture be calculated from the activity coefficients at infinite dilution ($\gamma_{1,2}^\infty$) using the following expression:

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

Physical and thermodynamic properties of pure solutes needed for these calculations are given in a previous work.²⁸

RESULTS AND DISCUSSION

Activity Coefficients and Selectivity at Infinite Dilution. The error in the experimental determination of activity coefficients is evaluated at about 3 %. For all ILs studied in this work, no interfacial adsorption was observed, and the average relative standard deviation between data sets obtained

from two different packed columns was just 3–4 %. Experimental activity coefficients at infinite dilution and gas-to-IL partition coefficients calculated using eqs 3–7 are listed in Tables 1–6.

Table 1. Infinite Dilution Activity Coefficients and Partition Coefficients $\log K_L$ and $\log P$ of Organic Solutes in $[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	γ^∞ at T/K			$\log K_L$	$\log P$
	322.9	333.0	343.1	298.2	
hexane	7.74	7.38	7.11	1.52	3.34
3-methylpentane	6.52	6.46	6.37	1.53	3.37
heptane	10.58	9.43	9.58	1.90	3.86
octane	14.25	13.37	12.91	2.27	4.38
nonane	21.10	18.18	18.49	2.65	4.80
decane	25.99	18.97	22.74	3.03	5.35
undecane	34.39	30.96	30.11	3.39	5.77
methylcyclopentane	4.90	4.52	4.76	1.80	2.97
cyclohexane	5.16	4.64	4.67	1.88	2.78
methylcyclohexane	6.57	6.07	6.03	2.11	3.36
cycloheptane	14.01	19.01	25.09	2.39	2.98
benzene	0.76	0.77	0.78	2.80	2.17
toluene	1.00	1.01	1.04	3.20	2.55
ethylbenzene	1.38	1.43	1.46	3.53	2.95
m-xylene	1.28	1.39	1.42	3.66	3.05
p-xylene	1.35	1.40	1.42	3.60	3.01
o-xylene	1.17	1.28	1.31	3.79	3.05
1-hexene	4.56	4.63	4.44	1.69	2.85
1-hexyne	2.10	2.10	2.09	2.22	2.43
1-heptyne	2.24	2.79	2.78	2.80	3.24
2-butane	0.42	0.42	0.39	3.08	0.36
2-pantanone	0.59	0.65	0.66	3.39	0.81
3-pantanone	0.47	0.60	0.62	3.53	1.03
1,4-dioxane	0.58	0.42	0.44	3.18	-0.53
ethanol	1.41	1.40	1.31	2.67	-1.00
1-propanol	1.72	1.64	1.49	2.98	-0.58
2-propanol	1.55	1.53	1.40	2.73	-0.75
diethyl ether	1.56	1.76	1.76	1.79	0.62
diisopropyl ether	3.18	3.56	3.53	2.02	0.97
chloroform	0.68	0.72	0.74	2.57	1.78
dichloromethane	0.31	0.36	0.35	2.44	1.48
tetrachloromethane	1.78	1.85	1.86	2.35	2.54
acetonitrile	0.46	0.46	0.48	3.05	0.20
nitromethane	0.57	0.57	0.56	3.32	0.37
1-nitropropane	0.66	0.66	0.65	3.81	1.36
pyridine	0.52	0.52	0.53	3.62	0.18
thiophene	0.70	0.71	0.72	2.91	1.87

Activity coefficients at infinite dilution for most organic compounds were found to decrease with increased temperature. As observed with imidazolium and ammonium cations, the solubility of apolar compounds increases with an increase in the alkyl chain length grafted onto the pyrrolidinium cation. For compounds containing the same number of carbon atoms but originating from different solute families, the trend $\gamma_{\text{aromatic}} < \gamma_{\text{alkyne}} < \gamma_{\text{alkene}} < \gamma_{\text{alkane}}$ was observed. This overall trend is followed for all ILs, regardless of the cation or anion identity. That is to say, the presence of double or triple bonds in a solute tends to increase the solute/IL interactions.

For the alcohols, the low $\gamma_{1,2}^\infty$ values can be ascribed to the lone pair of electrons on the oxygen atom of the alcohol interacting with the positively charged cation and to the acidic

Table 2. Logarithm of Partition Coefficients $\log K_L$ of Organic Solutes in $[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	T/K				
	322.9	333.0	343.1	R^2	298.2
hexane	1.20	1.08	0.97	1.000	1.52
3-methylpentane	1.19	1.06	0.95	0.999	1.53
heptane	1.52	1.41	1.26	0.991	1.90
octane	1.84	1.69	1.54	1.000	2.27
nonane	2.16	2.01	1.81	0.991	2.65
decane	2.47	2.38	2.09	0.918	3.03
undecane	2.79	2.58	2.36	1.000	3.39
methylcyclopentane	1.44	1.34	1.19	0.988	1.80
cyclohexane	1.55	1.45	1.31	0.991	1.88
methylcyclohexane	1.74	1.62	1.48	0.998	2.11
cycloheptane	2.02	1.88	1.75	0.999	2.39
benzene	2.38	2.23	2.09	0.999	2.80
toluene	2.73	2.55	2.39	1.000	3.20
ethylbenzene	3.00	2.80	2.63	0.999	3.53
m-xylene	3.09	2.87	2.69	0.996	3.66
p-xylene	3.06	2.85	2.67	0.999	3.60
o-xylene	3.22	2.99	2.81	0.996	3.79
1-hexene	1.35	1.21	1.10	0.993	1.69
1-hexyne	1.82	1.67	1.54	0.999	2.22
1-heptyne	2.24	1.98	1.83	0.977	2.80
2-butanone	2.60	2.41	2.25	0.995	3.08
2-pantanone	2.88	2.67	2.50	0.995	3.39
3-pantanone	2.94	2.66	2.49	0.980	3.53
1,4-dioxane	2.86	2.83	2.65	0.874	3.18
ethanol	2.20	2.02	1.87	0.995	2.67
1-propanol	2.50	2.31	2.15	0.997	2.98
2-propanol	2.26	2.06	1.92	0.993	2.73
diethyl ether	1.40	1.22	1.11	0.984	1.79
diisopropyl ether	1.59	1.40	1.27	0.987	2.02
chloroform	2.15	1.99	1.85	0.998	2.57
dichloromethane	2.08	1.90	1.82	0.960	2.44
tetrachloromethane	1.95	1.79	1.66	0.997	2.35
acetonitrile	2.62	2.48	2.32	0.999	3.05
nitromethane	2.87	2.70	2.55	0.999	3.32
1-nitropropane	3.30	3.11	2.93	0.999	3.81
pyridine	3.13	2.95	2.78	1.000	3.62
thiophene	2.49	2.33	2.18	0.999	2.91

proton of the alcohol hydrogen bonding with oxygen atoms of the anion. Branched-chain alcohols have a lower solubility compared to linear alcohols, and their solubility decreases with increasing chain length. Notably, ketones strongly interact with these ILs, showing even higher solubility. Pyridine and nitroalkanes have strong interactions with all three ILs.

Table 7 compares values of γ^∞ in $[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$ and $[\text{OMPyrr}]^+[\text{Tf}_2\text{N}]^-$ obtained in this work with γ^∞ measured by Nebig et al.⁴⁷ at $T = 323.15$ K. In some cases, the differences are outstandingly small (for example, 0.2 % for 1-hexene in $[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$), but the overall standard deviation for these solutes is around 5 %, which is within expectations when comparing dilutor technique results to inverse gas chromatography measurements.

The measurements conducted during this research offer an important means to evaluate the performance of pyrrolidinium-based ILs as solvents in various separation problems. This is achieved through the calculation of selectivity (S_{12}^∞) and capacity (k_1^∞) values at infinite dilution

Table 3. Infinite Dilution Activity Coefficients and Partition Coefficients $\log K_L$ and $\log P$ of Organic Solutes in $[\text{OMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	γ^∞ at T/K			$\log K_L$	$\log P$
	323.0	333.0	343.1	298.2	
hexane	5.01	4.80	4.05	1.63	3.45
3-methylpentane	4.61	4.52	4.08	1.63	3.47
heptane	6.40	6.06	5.13	2.03	3.99
octane	8.10	7.80	6.54	2.44	4.55
nonane	11.27	10.72	9.14	2.86	5.01
decane	14.77	12.51	10.98	3.15	5.47
undecane	16.82	15.64	14.64	3.70	6.08
methylcyclopentane	3.13	3.36	2.84	1.94	3.11
cyclohexane	3.45	3.31	3.06	2.04	2.94
methylcyclohexane	4.22	4.04	3.90	2.31	3.56
cycloheptane	8.62	12.10	15.39	2.60	3.19
benzene	0.60	0.62	0.61	2.89	2.26
toluene	0.76	0.78	0.74	3.27	2.62
ethylbenzene	1.03	0.98	1.04	3.64	3.06
m-xylene	1.00	0.84	1.05	3.77	3.16
p-xylene	1.01	0.99	1.05	3.72	3.13
o-xylene	0.92	0.87	0.97	3.88	3.14
1-hexene	3.17	3.02	2.58	1.74	2.90
1-hexyne	1.57	1.58	1.34	2.25	2.46
1-heptyne	1.94	1.89	1.90	2.74	3.18
2-butanone	0.36	0.34	0.31	3.11	0.39
2-pentanone	0.49	0.51	0.48	3.40	0.82
3-pentanone	0.45	0.47	0.44	3.38	0.88
1,4-dioxane	0.32	0.60	0.31	3.47	-0.24
methanol	0.97	1.09	0.71	2.33	-1.41
ethanol	1.33	1.26	0.98	2.55	-1.12
1-propanol	1.49	1.29	1.14	2.99	-0.57
2-propanol	1.40	1.27	1.06	2.67	-0.81
2-methyl-1-propanol	1.59	1.44	1.22	3.20	-0.10
diethyl ether	1.34	1.34	1.14	1.69	0.52
diisopropyl ether	2.57	2.58	2.26	1.98	0.93
chloroform	0.56	0.58	0.53	2.56	1.77
dichloromethane	0.26	0.27	0.28	2.51	1.55
tetrachloromethane	1.39	1.30	1.15	2.33	2.52
acetonitrile	0.43	0.39	0.37	2.98	0.13
nitromethane	0.54	0.51	0.48	3.29	0.34
1-nitropropane	0.55	0.52	0.51	3.85	1.40
pyridine	0.42	0.39	0.41	3.68	0.24
thiophene	0.57	0.55	0.53	2.97	1.93

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

$$k_1^\infty = \frac{1}{\gamma_{1/\text{RTIL}}^\infty} \quad (7)$$

In eq 6, $\gamma_{1/\text{RTIL}}^\infty$ and $\gamma_{2/\text{RTIL}}^\infty$ denote the infinite dilution coefficients of solutes 1 and 2, respectively, in the IL solvent. Selectivities and capacities at infinite dilution are collected in Table 8 for four separation problems at 323.15 K; these include hexane/benzene, hexane/methanol, hexane/thiophene, and cyclohexane/thiophene separations. With regard to aliphatic/aromatic separations, these results indicate that pyrrolidinium-based ILs generally exhibit poorer performances compared to imidazolium-based ILs. The selectivities obtained using pyrrolidinium-based ILs (between 6 and 10) are lower than that for classical solvents used industrially such as sulfolane

Table 4. Logarithm of Partition Coefficients $\log K_L$ of Organic Solutes in $[\text{OMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	T/K				
	323.0	333.0	343.1	R^2	298.2
hexane	1.40	1.28	1.23	0.956	1.63
3-methylpentane	1.35	1.23	1.15	0.984	1.63
heptane	1.75	1.61	1.54	0.974	2.03
octane	2.10	1.93	1.84	0.973	2.44
nonane	2.44	2.25	2.13	0.987	2.86
decane	2.72	2.57	2.42	1.000	3.15
undecane	3.11	2.89	2.68	1.000	3.70
methylcyclopentane	1.65	1.48	1.42	0.921	1.94
cyclohexane	1.73	1.61	1.51	0.996	2.04
methylcyclohexane	1.94	1.81	1.68	1.000	2.31
cycloheptane	2.24	2.09	1.97	0.991	2.60
benzene	2.49	2.34	2.20	0.998	2.89
toluene	2.86	2.68	2.55	0.992	3.27
ethylbenzene	3.14	2.98	2.78	0.996	3.64
m-xylene	3.21	3.10	2.83	0.949	3.77
p-xylene	3.19	3.01	2.81	0.999	3.72
o-xylene	3.34	3.17	2.95	0.993	3.88
1-hexene	1.52	1.41	1.35	0.965	1.74
1-hexyne	1.96	1.81	1.74	0.950	2.25
1-heptyne	2.31	2.16	2.00	1.000	2.74
2-butanone	2.67	2.51	2.36	0.999	3.11
2-pentanone	2.96	2.78	2.65	0.993	3.40
3-pentanone	2.96	2.78	2.65	0.992	3.38
1,4-dioxane	3.12	2.69	2.81	0.489	3.47
methanol	2.10	1.88	1.91	0.640	2.33
ethanol	2.24	2.08	2.01	0.947	2.55
1-propanol	2.57	2.43	2.28	1.000	2.99
2-propanol	2.31	2.15	2.05	0.986	2.67
2-methyl-1-propanol	2.76	2.58	2.45	0.994	3.20
diethyl ether	1.47	1.35	1.31	0.932	1.69
diisopropyl ether	1.69	1.55	1.48	0.968	1.98
chloroform	2.24	2.09	2.01	0.974	2.56
dichloromethane	2.17	2.03	1.92	0.998	2.51
tetrachloromethane	2.07	1.96	1.88	0.989	2.33
acetonitrile	2.67	2.56	2.44	0.998	2.98
nitromethane	2.91	2.76	2.63	0.997	3.29
1-nitropropane	3.38	3.22	3.05	1.000	3.85
pyridine	3.22	3.08	2.90	0.995	3.68
thiophene	2.59	2.49	2.32	0.973	2.97

($S_{\text{hexane/benzene}} = 30.5$), dimethylsulfoxide ($S_{\text{hexane/benzene}} = 22.7$), and *N*-methyl-2-pyrrolidinone ($S_{\text{hexane/benzene}} = 12.5$).³⁸ All the same, a better capacity and selectivity may be obtained for relatively short alkyl chains grafted to the pyrrolidinium cation, as observed with 1-butyl-1-methylpyrrolidinium.⁴⁸ Indeed, long alkyl chains grafted onto the cation are known to increase capacity, while being a detriment to selectivity. For desulfurization applications, pyrrolidinium-based ILs show a large capacity for thiophene and selectivity is relatively high as well.

Linear Solvation Energy Relationship (LSER) Characterization. The Abraham solvation parameter model provides a very convenient method to mathematically describe the solubilizing properties of IL solvents. Mathematical correlations of the type of eqs 1 and 2 can be developed for each individual IL, or alternatively, one may use the ion-specific version of the model suggested by Sprunger et al.^{38–41}

Table 5. Infinite Dilution Activity Coefficients and Partition Coefficients $\log K_L$ and $\log P$ of Organic Solutes in $[\text{DMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	γ^∞ at T/K			$\log K_L$	$\log P$
	322.6	332.5	342.8	298.2	
hexane	3.97	3.78	3.68	1.81	3.63
3-methylpentane	3.65	3.36	3.40	1.76	3.60
heptane	4.91	4.75	4.62	2.24	4.20
octane	6.13	5.92	5.76	2.66	4.77
nonane	8.32	8.01	7.65	3.06	5.21
decane	9.42	9.05	8.70	3.47	5.79
undecane	11.68	11.18	10.66	3.88	6.26
methylcyclopentane	2.90	2.76	2.66	1.98	3.15
cyclohexane	2.81	2.71	2.62	2.15	3.05
methylcyclohexane	3.38	3.28	3.15	2.40	3.65
cycloheptane	7.00	9.72	13.35	2.71	3.30
benzene	0.62	0.63	0.64	2.88	2.25
toluene	0.77	0.78	0.80	3.31	2.66
ethylbenzene	1.01	1.04	1.06	3.65	3.07
m-xylene	0.99	1.00	1.03	3.74	3.13
p-xylene	1.00	1.01	1.03	3.71	3.12
o-xylene	0.92	0.94	0.96	3.86	3.12
1-hexene	2.68	2.62	2.57	1.91	3.07
1-hexyne	1.50	1.48	1.47	2.35	2.56
1-heptyne	1.81	1.83	1.83	2.77	3.21
2-butanone	0.39	0.37	0.34	3.06	0.34
2-pentanone	0.52	0.53	0.54	3.40	0.82
3-pentanone	0.47	0.48	0.50	3.41	0.91
1,4-dioxane	0.38	0.35	0.38	3.50	-0.21
methanol	1.61	1.32	1.36	2.24	-1.50
ethanol	1.46	1.34	1.22	2.59	-1.08
1-propanol	1.62	1.47	1.32	2.98	-0.58
2-propanol	1.52	1.38	1.25	2.69	-0.79
2-methyl-1-propanol	1.70	1.53	1.39	3.21	-0.09
1-butanol	2.20	1.85	1.64	3.28	-0.18
diethyl ether	1.27	1.25	1.25	1.80	0.63
diisopropyl ether	2.29	2.28	2.26	2.09	1.04
chloroform	0.39	0.39	0.41	2.79	2.00
dichloromethane	0.27	0.30	0.30	2.49	1.53
tetrachloromethane	1.32	1.12	1.31	2.48	2.67
acetonitrile	0.49	0.50	0.49	2.99	0.14
nitromethane	0.63	0.62	0.60	3.24	0.29
1-nitropropane	0.62	0.61	0.60	3.81	1.36
pyridine	0.47	0.47	0.47	3.64	0.20
thiophene	0.60	0.60	0.61	2.96	1.92

$$\begin{aligned} \log K_L = & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E \\ & + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A \\ & + (b_{\text{cation}} + b_{\text{anion}})B + (l_{\text{cation}} + l_{\text{anion}})L \end{aligned} \quad (8)$$

$$\begin{aligned} \log P = & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E \\ & + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A \\ & + (b_{\text{cation}} + b_{\text{anion}})B + (v_{\text{cation}} + v_{\text{anion}})V \end{aligned} \quad (9)$$

wherein each equation coefficient is split into a cation- and an anion-specific contribution. The experimental data measured here can be used to calculate the Abraham model ion-specific equation coefficients for the $[\text{HMPyrr}]^+$, $[\text{OPPyrr}]^+$, and $[\text{DMPyrr}]^+$ cations for both the gas-to-IL (eq 8) and water-to-

Table 6. Logarithm of Partition Coefficients $\log K_L$ of Organic Solutes in $[\text{DMPyrr}]^+[\text{Tf}_2\text{N}]^-$

solutes	T/K				
	322.6	332.5	342.8	R^2	298.2
hexane	1.48	1.37	1.25	1.000	1.81
3-methylpentane	1.43	1.34	1.21	0.992	1.76
heptane	1.85	1.70	1.56	1.000	2.24
octane	2.20	2.04	1.88	1.000	2.66
nonane	2.55	2.37	2.19	1.000	3.06
decane	2.90	2.70	2.50	1.000	3.47
undecane	3.25	3.02	2.80	1.000	3.88
methylcyclopentane	1.66	1.54	1.43	1.000	1.98
cyclohexane	1.80	1.68	1.56	1.000	2.15
methylcyclohexane	2.02	1.88	1.75	1.000	2.40
cycloheptane	2.30	2.16	2.01	1.000	2.71
benzene	2.46	2.31	2.16	1.000	2.88
toluene	2.83	2.66	2.50	1.000	3.31
ethylbenzene	3.13	2.94	2.76	1.000	3.65
m-xylene	3.20	3.01	2.82	1.000	3.74
p-xylene	3.18	2.99	2.80	1.000	3.71
o-xylene	3.32	3.12	2.93	1.000	3.86
1-hexene	1.57	1.45	1.33	1.000	1.91
1-hexyne	1.96	1.82	1.68	1.000	2.35
1-heptyne	2.32	2.16	2.00	1.000	2.77
2-butanone	2.62	2.46	2.31	1.000	3.06
2-pentanone	2.92	2.75	2.58	1.000	3.40
3-pentanone	2.92	2.75	2.58	1.000	3.41
1,4-dioxane	3.04	2.90	2.71	0.989	3.50
methanol	1.86	1.78	1.61	0.961	2.24
ethanol	2.18	2.03	1.89	1.000	2.59
1-propanol	2.52	2.36	2.20	1.000	2.98
2-propanol	2.26	2.11	1.96	1.000	2.69
2-methyl-1-propanol	2.72	2.54	2.37	1.000	3.21
1-butanol	2.82	2.66	2.49	1.000	3.28
diethyl ether	1.48	1.37	1.25	1.000	1.80
diisopropyl ether	1.72	1.58	1.46	1.000	2.09
chloroform	2.38	2.24	2.09	1.000	2.79
dichloromethane	2.13	1.97	1.87	0.986	2.49
tetrachloromethane	2.07	2.00	1.80	0.928	2.48
acetonitrile	2.59	2.44	2.30	0.999	2.99
nitromethane	2.82	2.66	2.52	1.000	3.24
1-nitropropane	3.32	3.14	2.96	1.000	3.81
pyridine	3.16	2.99	2.81	1.000	3.64
thiophene	2.54	2.39	2.24	1.000	2.96

Table 7. Comparison of Values of γ^∞ in $[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$ and in $[\text{OPPyrr}]^+[\text{Tf}_2\text{N}]^-$ Obtained in This Work with γ^∞ Measured by Nebig et al. (ref 47) at T = 323.15 K

solutes	$[\text{HMPyrr}]^+[\text{Tf}_2\text{N}]^-$		$[\text{OPPyrr}]^+[\text{Tf}_2\text{N}]^-$	
	γ^∞ (this work)	γ^∞ (ref 47)	γ^∞ (this work)	γ^∞ (ref 47)
hexane	7.21	7.74	4.90	5.01
heptane	10.26	10.58	6.54	6.40
octane	13.93	14.25	8.39	8.10
1-hexene	4.55	4.56	3.22	3.17

IL (eq 9) partitioning processes. The log P values for partition from water to the IL are calculated through eq 10

$$\log P = \log K_L - \log K_W \quad (10)$$

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

Table 8. Selectivities ($S_{1,2}^{\infty}$) and Capacities (k_1^{∞}) at Infinite Dilution for Different Separation Problems at 323.15 K

ILs		hexane/benzene	hexane/methanol	hexane/thiophene	cyclohexane/thiophene	ref
anion	cation					
[Tf ₂ N] ⁻	1-hexyl-1-methylpyrrolidinium	10.2/1.32	8.2/1.06	11.1/1.43	7.4/1.43	this work
	1-octyl-1-methylpyrrolidinium	8.4/1.67	5.2/1.03	8.8/1.75	6.1/1.75	this work
	1-decyl-1-methylpyrrolidinium	6.4/1.61	2.5/0.62	6.6/1.67	4.7/1.67	this work
	1-butyl-1-methylpyrrolidinium	13.8/1.14				48
	methyltributylammonium	7.5/1.11	7.3/1.08	7.8/1.17	5.5/1.17	49
	octyltrimethylammonium	8.5/1.37	6.75/1.08	9/1.45	5.9/1.45	49
	decyltrimethylammonium	5.9/1.41	5.3/1.09	6.46/1.54	4.46/1.54	49
	tetraoctylammonium	3.2/2.5	2.0/1.08	3.25/2.5	2.35/2.5	49
	1,3-dimethoxyimidazolium	21.3/0.47	42.05/0.94	24.8/0.94	12.6/0.94	27
	1-(methylmethylether)-3-methylimidazolium	15.5/0.85	17.4/0.93	18.1/1.0	10.9/1.0	27
	1-ethanol-3-methylimidazolium	20.6/0.47	49.1/1.12	24.7/0.56	14.2/0.56	27
	1-ethyl-3-methylimidazolium	37.5/1.43	19.5/1.20			50
	1-(hexylmethylether)-3-methylimidazolium	9.1/1.23	6.8/0.91	10.0/1.35	6.4/1.35	51
	1,3-bis(hexylmethylether)imidazolium	4.9/1.67	3.2/1.06	5.3/1.75	3.7/1.75	51
	1-butyl-3-methylimidazolium	16.7/1.11				52
	1-hexyl-3-methylimidazolium	9.5/1.29	6.1/0.82			53
	trimethylhexylammonium	9.9/1.01	8.5/0.86	10.7/1.09	7.2/1.09	26
	4-methyl-N-butylpyridinium	18.8/1.43	21.2/0.83	10.6/1.56	6.1/1.56	54
	triethylsulfonium	21.6/0.91	17.8/0.77	25.5/1.05	14.3/1.05	55
	trihexyl(tetradecyl)phosphonium	2.7/2.56	1.1/1.02	2.6/2.5	1.95/2.5	28
	1-(2-methoxyethyl)-1-methylpiperidinium	17.9/1.09	12.5/0.76	20.7/1.26	12.0/1.26	56
	4-(2-methoxyethyl)-4-methylmorpholinium	25.8/0.75	27.9/0.81	31.7/0.92	16.5/0.92	57
	1-propyl-1-methylpiperidinium	19.8/1.07	12.8/0.69	22.6/1.22	13.1/1.22	58
	1-butyl-1-methylpiperidinium	15.4/1.27	8.2/0.68	16.8/1.39	10.4/1.39	59

solutes studied.³⁰ Water-to-IL partition coefficients calculated through eq 8 pertain to a hypothetical partitioning process involving solute transfer from water to the anhydrous IL. $\log P$ values calculated in this manner are still quite useful in that predicted $\log P$ values can be used to estimate the solute's infinite dilution activity coefficient in the IL. For convenience, we have captured in Tables 1, 3, and 5 the $\log P$ and $\log K_L$ values at 298.15 K for anhydrous [HMPyrr]⁺[Tf₂N]⁻, [OMPyrr]^{+[Tf₂N]⁻, and [DMPyrr]^{+[Tf₂N]⁻, respectively.}}

Analysis of the 36 experimental $\log K_L$ and $\log P$ data in Table 1 for [HMPyrr]^{+[Tf₂N]⁻ gave}

$$\begin{aligned} \log K_L = & -0.533(0.093) - 0.110(0.099)\mathbf{E} \\ & + 2.146(0.095)\mathbf{S} + 2.278(0.196)\mathbf{A} \\ & + 0.650(0.114)\mathbf{B} + 0.767(0.026)\mathbf{L} \end{aligned} \quad (11)$$

($N = 36$, SD = 0.088, $R^2 = 0.984$, $F = 367.3$)

and

$$\begin{aligned} \log P = & -0.226(0.152) - 0.083(0.132)\mathbf{E} + 0.560(0.144)\mathbf{S} \\ & - 1.301(0.275)\mathbf{A} - 4.501(0.159)\mathbf{B} \\ & + 3.673(0.128)\mathbf{V} \end{aligned} \quad (12)$$

($N = 36$, SD = 0.123, $R^2 = 0.994$, $F = 1098$)

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. The standard errors in the calculated coefficients are given in parentheses immediately following the respective values. The solute descriptors used in the analysis are listed in Table 9. As an informational note 1,4-dioxane was

excluded from the regression analyses because of uncertainties associated in extrapolating the measured $\log K_L$ data back to 298.15 K. The squared correlation coefficients for the $\log K_L$ versus T^{-1} curves for this one solute was much smaller than unity, as shown in fifth column of Table 2.

Each calculated equation coefficient corresponds to the sum of the respective cation-specific and anion-specific contributions. In establishing this computation methodology, the equation coefficients for the [Tf₂N]⁻ anion were set equal to zero to provide a reference point from which all equation coefficients would be calculated.^{38–41} A common reference point is needed because the cation-specific and anion-specific equation coefficients are generated as a paired set. The equation coefficients in eqs 11 and 12 thus correspond to the ion-specific coefficients for the [HMPyrr]⁺ cation.

The experimental $\log K_L$ and $\log P$ data in Tables 3 and 5 for [OMPyrr]^{+[Tf₂N]⁻ and [DMPyrr]^{+[Tf₂N]⁻ were analyzed in a similar manner, to give the following Abraham model correlations:}}

$$\begin{aligned} \log K_L = & -0.587(0.082) - 0.064(0.090)\mathbf{E} \\ & + 2.080(0.086)\mathbf{S} + 2.176(0.160)\mathbf{A} \\ & + 0.486(0.103)\mathbf{B} + 0.822(0.023)\mathbf{L} \end{aligned} \quad (13)$$

($N = 37$, SD = 0.080, $R^2 = 0.986$, $F = 449.1$)

$$\begin{aligned} \log P = & -0.253(0.121) + 0.520(0.096)\mathbf{S} \\ & - 1.460(0.203)\mathbf{A} - 4.696(0.116)\mathbf{B} \\ & + 3.815(0.103)\mathbf{V} \end{aligned} \quad (14)$$

($N = 37$, SD = 0.102, $R^2 = 0.997$, $F = 2372$)

and

Table 9. Solute Descriptors of Organic Compounds Considered in this Study

solute	E	S	A	B	L	V
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
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
methylcyclopentane	0.225	0.100	0.000	0.000	2.907	0.8454
cyclohexane	0.310	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
<i>m</i> -xylene	0.623	0.520	0.000	0.160	3.839	0.9982
<i>p</i> -xylene	0.613	0.520	0.000	0.160	3.839	0.9982
<i>o</i> -xylene	0.663	0.560	0.000	0.160	3.939	0.9982
1-hexene	0.080	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	0.090	0.100	3.000	1.0089
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
diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309
diisopropyl ether	-0.063	0.170	0.000	0.570	2.501	1.0127
chloroform	0.425	0.490	0.150	0.020	2.480	0.6167
dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943
tetrachloromethane	0.460	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
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

$$\log K_L = -0.395(0.062)E - 0.241(0.070)E + 1.991(0.067)S + 2.112(0.110)A + 0.268(0.076)B + 0.822(0.018)L \quad (15)$$

(N = 40, SD = 0.063, R² = 0.990, F = 682)

$$\log P = -0.083(0.128) - 0.142(0.114)E + 0.419(0.124)S - 1.467(0.197)A - 4.859(0.129)B + 3.824(0.108)V \quad (16)$$

(N = 40, SD = 0.108, R² = 0.997, F = 2167)

Equations 13 and 14 pertain to solute transfer to anhydrous [OMPyrr]⁺[Tf₂N]⁻, and eqs 15 and 16 in turn describe the partition coefficient data for solutes dissolved in [DMPyrr]⁺[Tf₂N]⁻. The eE term was found to be negligible in the log P correlation (e = 0.023) for [OMPyrr]⁺[Tf₂N]⁻, so

it was eliminated from the final correlation. Methanol and 1,4-dioxane were removed from the [OMPyrr]⁺[Tf₂N]⁻ data sets because of low squared correlation coefficients in the log K_L versus T⁻¹ plots used to extrapolate the measured partition coefficient data back to 298.15 K. The derived Abraham model correlations provide a good mathematical description of the experimental gas-to-anhydrous IL partition coefficient data (eqs 13 and 15) and water-to-anhydrous IL partition coefficient data (eqs 14 and 16) for both [OMPyrr]⁺[Tf₂N]⁻ and [DMPyrr]⁺[Tf₂N]⁻. Since both ILs contain the [Tf₂N]⁻ anion, the calculated coefficients in eqs 13–16 thus correspond to the cation-specific coefficients for [OMPyrr]⁺ and [DMPyrr]⁺.

CONCLUSION

The Abraham model correlations that have been derived for [HMPyrr]⁺[Tf₂N]⁻, [OMPyrr]⁺[Tf₂N]⁻, and [DMPyrr]⁺[Tf₂N]⁻ would be expected to provide very reasonable predictions for the log K_L values for additional

solutes having descriptor values that fall within the range of chemical space defined by $E = -0.063$ to $+0.687$, $S = 0.000$ to 0.950 , $A = 0.000$ to 0.570 , $B = 0.000$ to 0.640 , $L = 0.970$ to 5.191 , and $V = 0.308$ to 1.659 . The cation-specific and anion-specific equation coefficients can be combined to yield predictive equations for numerous ILs not yet studied. Specifically, the present study expands our library of calculated cation-specific equation coefficients to 27 which, when combined with our hitherto reported equation coefficients for 14 unique anions, yield predictive equations for 378 different ILs. Once a substantial inventory of ion-specific coefficients has been established, it is easy to see how adding a handful of cation- and/or anion-specific equation coefficients can quickly enlarge the databank of IL permutations which can be predicted within such an Abraham solvation parameter framework. Indeed, expanding this chemical space forms a significant portion of our current research efforts.

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Notes

The authors declare no competing financial interest.

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