

# Partition Coefficients of Organic Compounds in Four New Tetraalkylammonium Bis(trifluoromethylsulfonyl)imide Ionic Liquids Using Inverse Gas Chromatography

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**ABSTRACT:** The activity coefficients at infinite dilution,  $\gamma_{i,2}^{\infty}$ , of 47 solutes including various (cyclo)alkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, ethers, aldehydes, and ketones, in the four ionic liquids (ILs) decyl-(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide, methyl(tributyl)ammonium bis(trifluoromethylsulfonyl)imide, octyl-(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide, and tetraoctylammonium bis(trifluoromethylsulfonyl)imide, were measured using inverse gas chromatography at temperatures from (323 to 343) K. The retention data were also 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. The derived equations correlated the experimental gas-to-IL and water-to-IL partition coefficient data to within average standard deviations of 0.100 and 0.133 log units, respectively.

## INTRODUCTION

Next generation ionic liquids (ILs) have spawned considerable interest over the past decade owing to their unique physical properties and designer solvent qualities. Indeed, each year witnesses a considerable rise in the number of applied and issued patents centered around employing ILs as advanced solvent media. ILs are popular solvent choices for manufacturing applications involving nanomaterials and organic synthesis, as chromatographic stationary phases for chemical separations, as extraction solvent systems for the removal of aromatic nitrogen and sulfur compounds from coal and petroleum feedstocks, and more recently, as solvents for lignocellulosic biomass processing used to produce liquid fuels from agricultural wastes and wood feedstocks. Select alkylimidazolium-based ILs have exhibited large selectivities for carbon dioxide over other gases, making them ideally suited for the removal and recovery of carbon dioxide from mixed gases. Saravananmyrigan et al.<sup>1</sup> have further demonstrated that ILs can be tuned by design to perform as selective, high-density absorbents for removal of sulfur dioxide, nitric oxide, and/or carbon dioxide from industrial flue gases. Such selectivity is typically achieved by functionalization of the cation and/or anion. Presently, more than  $10^3$  different ILs are commercially available, although the number of cation–anion combinations is of course staggeringly larger, in excess of  $10^{14,2,3}$ . Obviously, it is not feasible to experimentally study a large number of possible cation–anion combinations in any meaningful way. Consequently, the development of predictive methods is indispensable to navigate this vast chemical space and select the most appropriate IL for a given task.

This study is a continuation of our investigations regarding the thermodynamic properties of solutes dissolved in IL solvents. In

previous papers,<sup>4–10</sup> we have shown that the introduction of polar side chains within ions comprising the IL exerts pronounced influence over the interaction with solute species present in mixtures containing the IL. Short polar chains present in imidazolium-based ILs, for example, increased the selectivity toward mixtures containing {alcohol + aliphatic} or {aromatic + aliphatic} solutes. The present work is focused on the solvent character of four “unfunctionalized” (i.e., aliphatic) tetraalkylammonium-based ILs, methyl(tributyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{MB}_3\text{AM}]^+[\text{TF}_2\text{N}]^-$ , octyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{OM}_3\text{AM}]^+[\text{TF}_2\text{N}]^-$ , decyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{DM}_3\text{AM}]^+[\text{TF}_2\text{N}]^-$ , and tetraoctylammonium bis(trifluoromethylsulfonyl)imide,  $[\text{O}_4\text{AM}]^+[\text{TF}_2\text{N}]^-$  (molecular structures for these four ILs are presented in Figure 1), to determine what role (if any) the distribution of alkyl chain lengths play in the IL solvent's ability to dissolve select classes of organic compounds. These experimental data provide a benchmark for strategic future studies involving functionalized tetraalkylammonium-based ILs sporting polar alkyl chain substituents.

The Abraham solvation parameter model provides a convenient mathematical means to quantify and compare the solubilizing character of different solvent media using terms that represent the various types of solute–solvent interactions. The magnitude of the different solute–solvent interactions depends upon the hydrogen-bonding, electron-withdrawing, electron-donating, and aromatic functional groups contained in the molecules. Mathematical correlations based on the Abraham general solvation parameter model for the gas-to-solvent,

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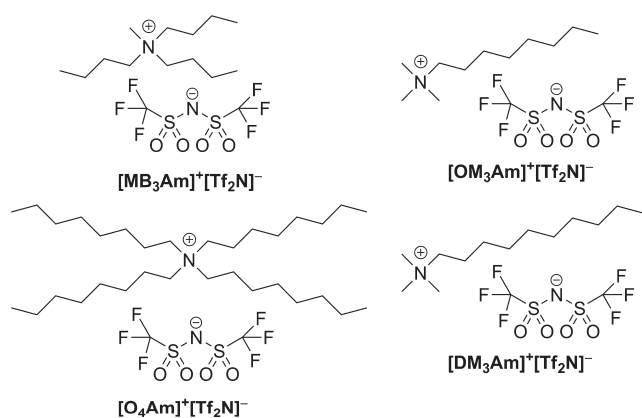


Figure 1. Chemical structures of the ILs scrutinized in this work.

$K_L$ , and water-to-solvent partition coefficients,  $P$ ,

$$\log P = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V \quad (1)$$

$$\log K_L = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + l \cdot L \quad (2)$$

have been reported for 26 different anhydrous ILs<sup>11–22</sup> and for two practical water-to-IL partition systems.<sup>23</sup> In eqs 1 and 2, the independent variables (descriptors) are properties of the neutral solute as follows:  $E$  is the solute excess molar refraction in  $\text{cm}^3 \cdot \text{mol}^{-1}/10$ ,  $S$  is the solute dipolarity/polarizability,  $A$  and  $B$  are the overall solute hydrogen bond acidity and basicity,  $V$  is McGowan's characteristic molecular 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. The regression coefficients and constants ( $c$ ,  $e$ ,  $s$ ,  $a$ ,  $b$ ,  $v$ , and  $l$ ) are obtained by regression analysis of experimental data for a specific process (i.e., a given partitioning process/system). In the case of processes involving two condensed solvent phases, the  $c$ ,  $e$ ,  $s$ ,  $a$ ,  $b$ ,  $v$ , and  $l$  coefficients represent differences in the solvent phase properties. For any fully characterized system/process (those with calculated values for the equation coefficients), further values of  $\log P$  and  $\log K$  can be estimated with known values for the solute descriptors.

Partition coefficient correlations based on eqs 1 and 2 are specific to a given IL. Sprunger et al.<sup>24–26</sup> modified the Abraham solvation parameter model

$$\begin{aligned} \log K_L = & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E \\ & + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A \\ & + (b_{\text{cation}} + b_{\text{anion}})B + (l_{\text{cation}} + l_{\text{anion}})L \end{aligned} \quad (3)$$

$$\begin{aligned} \log P = & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E \\ & + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A \\ & + (b_{\text{cation}} + b_{\text{anion}})B + (v_{\text{cation}} + v_{\text{anion}})V \end{aligned} \quad (4)$$

by expressing each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. In separating the equation coefficients, the authors make the assumption that a solute's interaction with a given cation is not influenced by the associated IL anion, and conversely that the solute's interaction with a given anion is not influenced by the surrounding IL cation. The major advantage derived from splitting the equation coefficients into individual cation- and anion-specific contributions is that it allows one to make predictions

for additional ILs for which the cation- and anion-specific coefficients are known. The 20 cation and 14 anion coefficients that have been calculated thus far were based on experimental data for 42 different ILs;<sup>20,22</sup> these coefficients can, however, be combined to yield predictive expressions for far more ILs (i.e.,  $20 \times 14 = 280$  ILs). Results from the present study will enable the calculation of four additional sets of cation-specific equation coefficients and enable one to generate partition coefficient predictions for solutes dissolved in an additional 56 ILs.

## EXPERIMENTAL PROCEDURES AND RESULTS

**Materials or Chemicals.** Decyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{DM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ , was prepared to a purity exceeding 99.8 % using methods reported previously.<sup>27,28</sup> The synthesis of the remaining ILs methyl-(tributyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{MB}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ , octyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide,  $[\text{OM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ , and tetraoctylammonium bis(trifluoromethylsulfonyl)imide,  $[\text{O}_4\text{AM}]^+[\text{Tf}_2\text{N}]^-$ , was performed similarly using twice-recrystallized bromide salts of the corresponding ammonium parents sourced from Sigma-Aldrich in  $\geq 98$  % purity. In all cases, the materials obtained were clear, nearly colorless fluids with purities better than 99.8 wt % based on thermogravimetric analysis<sup>29</sup> and verified by NMR spectroscopy.

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, which has been shown to attain low water content in the (10 to 60) ppm range for a series of conventional imidazolium-, ammonium-, and pyrrolidinium-type ILs,<sup>30</sup> no further attempt was made to analyze for impurities within the ILs. Densities and other physical properties of the ILs have been reported previously.<sup>27</sup> Test solutes were purchased from Aldrich at a purity  $\geq 99.5$  % and were used without further purification because our gas–liquid chromatography technique efficiently separates any impurities on 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 the corresponding chromatograms were obtained using Galaxie software.

Columns packed to 1 m lengths, containing from (15 to 35) % of stationary phases (IL) on Chromosorb WHP (60–80 mesh), were prepared using a rotary evaporation method. After evaporation of the chloroform in vacuo, the support was equilibrated at 333 K during 6 h. Before measurement, each packed column was conditioned for 12 h at 363 K at a flow rate of  $20 \text{ cm}^3 \cdot \text{min}^{-1}$ . 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  $\pm 0.0003$  g, which would correspond to less than a 0.1 % relative uncertainty in the mass of the IL in the packed column. A volume of the headspace vapor of samples of (1 to 5)  $\mu\text{L}$

**Table 1. Infinite Dilution Activity Coefficients and Partition Coefficients  $\log K_L$  and  $\log P$  of Organic Solutes in  $[\text{MB}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$** 

solutes	$\gamma^\infty$ at T/K			$\log K_L$	$\log P$
	322.85	332.65	343.15		
hexane	6.75	6.75	6.44	1.586	3.406
3-methylpentane	6.10	6.17	5.86	1.521	3.361
heptane	8.88	8.82	8.34	1.984	3.944
2,2,4-trimethylpentane	8.87	8.91	8.42	1.964	4.084
octane	11.57	11.49	10.80	2.363	4.473
nonane	16.54	16.13	14.97	2.742	4.892
decane	19.61	19.18	17.80	3.117	5.437
undecane	25.74	24.81	22.80	3.484	5.864
dodecane	32.35	31.31	28.79	3.782	6.312
methylcyclopentane	4.75	4.74	4.50	1.806	2.976
cyclohexane	4.74	4.71	4.44	1.959	2.859
methylcyclohexane	5.92	5.91	5.58	2.178	3.428
cycloheptane	12.40	17.74	23.93	2.502	3.092
benzene	0.90	0.93	0.92	2.796	2.166
toluene	1.13	1.19	1.19	3.196	2.546
ethylbenzene	1.56	1.64	1.63	3.494	2.914
<i>m</i> -xylene	1.49	1.56	1.56	3.573	2.963
<i>p</i> -xylene	1.51	1.62	1.56	3.557	2.967
<i>o</i> -xylene	1.38	1.46	1.46	3.724	2.984
1-hexene	4.31	4.40	4.25	1.704	2.864
1-hexyne	2.12	2.24	2.20	2.225	2.435
1-heptyne	2.79	2.89	2.85	2.619	3.059
2-butanone	0.40	0.38	0.35	3.025	0.305
2-pentanone	0.55	0.58	0.59	3.348	0.768
3-pentanone	0.50	0.54	0.56	3.354	0.854
1,4-dioxane	0.61	0.67	0.67	3.288	-0.422
methanol	0.96	0.75	0.88	2.357	-1.383
ethanol	1.53	1.40	1.27	2.565	-1.105
1-propanol	1.78	1.64	1.48	2.960	-0.600
2-propanol	1.67	1.54	1.40	2.660	-0.820
2-methyl-1-propanol	1.97	1.82	1.64	3.170	-0.130
1-butanol	2.10	1.89	1.73	3.364	-0.096
trifluoroethanol	0.50	0.48	0.45	3.124	-0.036
diethyl ether	1.65	1.67	1.65	1.681	0.511
diisopropyl ether	3.31	3.35	3.35	1.929	0.879
chloroform	0.84	0.87	0.88	2.577	1.787
dichloromethane	0.66	0.69	0.70	2.179	1.219
tetrachloromethane	2.11	2.11	2.07	2.367	2.557
acetonitrile	0.49	0.50	0.48	2.956	0.106
nitromethane	0.65	0.65	0.62	3.253	0.303
1-nitropropane	0.68	0.70	0.68	3.816	1.366
pyridine	0.55	0.56	0.56	3.622	0.182
thiophene	0.86	0.88	0.87	2.900	1.860
formaldehyde	0.11	0.12	0.13	2.114	
propionaldehyde	0.49	0.49	0.50	2.453	-0.067

was introduced to meet “infinite dilution” conditions. Each experiment was repeated at least twice to validate the reproducibility. Retention times were generally reproducible to within (0.01 to 0.03) min. To check stability under our experimental

conditions, such as the possible elution of the stationary phase by the helium stream, measurements of retention time were systematically repeated every day for three selected solutes. No changes in the retention times were observed during this stability study.

## THEORETICAL BASIS

The retention data determined using inverse chromatography experiments were used to calculate partition coefficients for each solute in the IL. The net retention volume,  $V_N$ , was calculated from the following relationship:<sup>31</sup>

$$V_N = \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} U_o \cdot t'_R \cdot \frac{T_{col}}{T_r} \cdot \left(1 - \frac{P_w^0}{P_o}\right) \quad (5)$$

The adjusted retention time  $t'_R$  was taken as a difference between the retention time of a solute and that of methane,  $T_{col}$  is the column temperature,  $U_o$  is the flow rate of the carrier gas measured at the room temperature ( $T_r$ ), and  $P_w^0$  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 the IL “2”,  $\gamma_{1,2}^\infty$ , was calculated with the following expression:<sup>31</sup>

$$\ln \gamma_{1,2}^\infty = \ln \left( \frac{n_2 RT}{V_N P_1^0} \right) - P_1^0 \cdot \frac{B_{11} - V_1^0}{RT} + \frac{2B_{13} - V_1^\infty}{RT} \cdot J P_o \quad (6)$$

Here,  $n_2$  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:

$$K_L = \frac{RT}{\gamma_{1,2}^\infty P_1^0 V_{solvent}} \quad (7)$$

Thermodynamic properties of pure solutes needed for these calculations can be found in a previous work.<sup>4</sup>

## RESULTS AND DISCUSSION

The errors in the experimental determination of activity coefficient are evaluated to be about 3 %. For all ILs studied in this work, no interfacial adsorption was observed while the average relative standard deviation between data sets obtained from different packed columns was (3 to 4) %. Experimental activity coefficients at infinite dilution and gas-to-IL partition coefficients calculated using eqs 3 to 7 are listed in Tables 1 to 8. Most solutes were found to be more soluble in the tetraalkylammonium ILs than in dialkylimidazolium ILs. Activity coefficients at infinite dilution for most organic compounds decreased with an increase in temperature. Naturally, the solubility of apolar compounds increases with an increase in the alkyl chain length grafted onto the ammonium cation. For compounds containing the same number of carbon atoms but originating from different

**Table 2. Logarithm of the Gas-to-IL Partition Coefficients for Solutes Dissolved in  $[\text{MB}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$** 

T/K	322.85	332.65	343.15	$R^2$	298.15
Solutes					
hexane	1.284	1.177	1.080	0.999	1.586
3-methylpentane	1.244	1.146	1.049	1.000	1.521
heptane	1.617	1.486	1.368	0.999	1.984
2,2,4-trimethylpentane	1.611	1.486	1.368	1.000	1.964
octane	1.943	1.794	1.656	0.999	2.363
nonane	2.266	2.097	1.941	0.999	2.742
decane	2.585	2.396	2.221	0.999	3.117
undecane	2.899	2.692	2.499	0.999	3.484
dodecane	3.213	2.984	2.774	0.999	3.782
methylcyclopentane	1.497	1.388	1.286	0.999	1.806
cyclohexane	1.640	1.526	1.418	1.000	1.959
methylcyclohexane	1.826	1.701	1.582	1.000	2.178
cycloheptane	2.116	1.979	1.850	1.000	2.502
benzene	2.386	2.240	2.103	1.000	2.796
toluene	2.728	2.561	2.405	1.000	3.196
ethylbenzene	2.987	2.807	2.636	1.000	3.494
<i>m</i> -xylene	3.051	2.865	2.689	1.000	3.573
<i>p</i> -xylene	3.034	2.848	2.672	1.000	3.557
<i>o</i> -xylene	3.185	2.993	2.815	1.000	3.724
1-hexene	1.397	1.288	1.182	1.000	1.704
1-hexyne	1.847	1.712	1.584	1.000	2.225
1-heptyne	2.183	2.028	1.881	1.000	2.619
2-butanone	2.596	2.443	2.295	1.000	3.025
2-pentanone	2.879	2.712	2.551	1.000	3.348
3-pentanone	2.878	2.709	2.546	1.000	3.354
1,4-dioxane	2.818	2.651	2.493	1.000	3.288
methanol	2.101	2.010	1.827	0.965	2.357
ethanol	2.174	2.035	1.896	1.000	2.565
1-propanol	2.496	2.331	2.178	0.999	2.960
2-propanol	2.226	2.072	1.928	1.000	2.660
2-methyl-1-propanol	2.672	2.495	2.331	0.999	3.170
1-butanol	2.850	2.668	2.496	1.000	3.364
trifluoroethanol	2.653	2.486	2.329	1.000	3.124
diethyl ether	1.374	1.265	1.157	1.000	1.681
diisopropyl ether	1.570	1.442	1.317	1.000	1.929
chloroform	2.170	2.025	1.889	1.000	2.577
dichloromethane	1.845	1.727	1.613	1.000	2.179
tetrachloromethane	1.980	1.842	1.712	1.000	2.367
acetonitrile	2.601	2.475	2.346	1.000	2.956
nitromethane	2.836	2.688	2.546	1.000	3.253
1-nitropropane	3.309	3.129	2.959	1.000	3.816
pyridine	3.171	3.011	2.858	1.000	3.622
thiophene	2.478	2.328	2.187	1.000	2.900
formaldehyde	1.764	1.640	1.512	1.000	2.114
propionaldehyde	2.090	1.961	1.834	1.000	2.453
butyraldehyde	2.408	2.257	2.117	0.999	2.832

solute families, it was observed that  $\gamma_{\text{aromatic}} < \gamma_{\text{alkyne}} < \gamma_{\text{alkene}} < \gamma_{\text{alkane}}$ . This overall trend is followed for all ILs, regardless of the cation or anion identity. The presence of double or triple bonds in a solute increases the solute–IL interactions. Generally, activity coefficients at infinite dilution of the alcohols are

**Table 3. Infinite Dilution Activity Coefficients and Partition Coefficients  $\log K_L$  and  $\log P$  of Organic Solutes in  $[\text{OM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$** 

solutes	$\gamma^\infty$ at T/K			$\log K_L$	$\log P$
	322.85	332.65	343.15		
hexane	6.21	5.83	5.36	1.672	3.492
3-methylpentane	5.62	5.24	4.87	1.633	3.473
heptane	8.27	7.81	7.18	2.060	4.020
2,2,4-trimethylpentane	8.10	7.66	7.14	2.046	4.166
octane	11.00	10.32	9.47	2.458	4.568
nonane	15.95	14.81	13.36	2.835	4.985
decane	19.33	17.95	16.20	3.222	5.542
undecane	25.83	23.68	21.10	3.592	5.972
dodecane	33.12	30.51	27.15	3.973	6.503
methylcyclopentane	4.18	3.95	3.67	1.870	3.040
cyclohexane	4.08	3.84	3.57	2.010	2.910
methylcyclohexane	5.23	4.93	4.60	2.238	3.488
cycloheptane	10.83	14.65	19.42	2.561	3.141
benzene	0.73	0.74	0.73	2.792	2.162
toluene	0.97	0.98	0.98	3.226	2.576
ethylbenzene	1.39	1.40	1.38	3.541	2.961
<i>m</i> -xylene	1.39	1.39	1.38	3.646	3.036
<i>p</i> -xylene	1.38	1.39	1.37	3.638	3.048
<i>o</i> -xylene	1.24	1.26	1.25	3.779	3.119
1-hexene	3.99	3.80	3.60	1.808	2.968
1-hexyne	1.92	1.89	1.82	2.321	2.531
1-heptyne	2.48	2.46	2.39	2.668	3.118
2-butanone	0.41	0.38	0.34	3.151	0.431
2-pentanone	0.57	0.57	0.57	3.481	0.901
3-pentanone	0.52	0.53	0.54	3.495	0.995
1,4-dioxane	0.62	0.62	0.61	3.484	−0.226
methanol	0.92	0.78	0.81	2.289	−1.451
ethanol	1.47	1.32	1.19	2.620	−1.050
1-propanol	1.70	1.55	1.37	3.008	−0.552
2-propanol	1.63	1.48	1.32	2.720	−0.760
2-methyl-1-propanol	1.87	1.70	1.51	3.218	−0.082
1-butanol	2.01	1.80	1.59	3.399	−0.061
trifluoroethanol	0.40	0.38	0.35	3.086	−0.074
diethyl ether	1.60	1.57	1.53	1.757	0.587
diisopropyl ether	3.22	3.15	3.08	2.000	0.950
chloroform	0.63	0.65	0.66	2.508	1.718
dichloromethane	0.51	0.53	0.54	2.129 <sup>a</sup>	1.169 <sup>a</sup>
tetrachloromethane	1.63	1.63	1.60	2.302	2.492
acetonitrile	0.48	0.46	0.44	3.079	0.229
nitromethane	0.60	0.58	0.55	3.320	0.370
1-nitropropane	0.62	0.61	0.60	3.873	1.423
pyridine	0.45	0.44	0.43	3.629	0.189
thiophene	0.69	0.69	0.69	2.860	1.820
formaldehyde	0.10	0.11	0.12	2.191	
propionaldehyde	0.48	0.47	0.46	2.498	−0.022

<sup>a</sup> Not included in the LSER analysis.

relatively small, with the solubility of alcohols and chloroalkanes being higher in  $[\text{O}_4\text{Am}]^+[\text{Tf}_2\text{N}]^-$  than in the other tetraalkylammonium studied in this work. The hydroxyl group



**Table 4. Logarithm of the Gas-to-IL Partition Coefficients for Solutes Dissolved in  $[\text{OM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$** 

T/K	322.85	332.65	343.15	$R^2$	298.15
Solutes					
hexane	1.295	1.161	1.048	0.997	1.672
3-methylpentane	1.256	1.122	1.016	0.995	1.633
heptane	1.633	1.481	1.351	0.998	2.060
2,2,4-trimethylpentane	1.619	1.467	1.343	0.996	2.046
octane	1.969	1.795	1.646	0.998	2.458
nonane	2.298	2.107	1.939	0.999	2.835
decane	2.626	2.414	2.228	0.999	3.222
undecane	2.948	2.719	2.512	0.999	3.592
dodecane	3.270	3.020	2.795	0.999	3.973
methylcyclopentane	1.490	1.355	1.244	0.997	1.870
cyclohexane	1.622	1.484	1.371	0.997	2.010
methylcyclohexane	1.819	1.670	1.545	0.997	2.238
cycloheptane	2.105	1.943	1.807	0.997	2.561
benzene	2.345	2.186	2.047	0.998	2.792
toluene	2.711	2.528	2.368	0.998	3.226
ethylbenzene	2.984	2.786	2.611	0.999	3.541
<i>m</i> -xylene	3.067	2.861	2.682	0.998	3.646
<i>p</i> -xylene	3.042	2.830	2.663	0.995	3.638
<i>o</i> -xylene	3.188	2.978	2.795	0.998	3.779
1-hexene	1.412	1.271	1.158	0.996	1.808
1-hexyne	1.851	1.684	1.550	0.996	2.321
1-heptyne	2.179	2.005	1.852	0.998	2.668
2-butanone	2.659	2.484	2.327	0.999	3.151
2-pentanone	2.944	2.753	2.585	0.999	3.481
3-pentanone	2.944	2.748	2.578	0.998	3.495
1,4-dioxane	2.879	2.664	2.500	0.994	3.484
methanol	2.129	2.072	1.836	0.890	2.289
ethanol	2.204	2.056	1.917	1.000	2.620
1-propanol	2.524	2.352	2.190	1.000	3.008
2-propanol	2.264	2.102	1.951	0.999	2.720
2-methyl-1-propanol	2.698	2.513	2.343	0.999	3.218
1-butanol	2.879	2.694	2.507	1.000	3.399
trifluoroethanol	2.602	2.430	2.272	0.999	3.086
diethyl ether	1.408	1.284	1.172	0.999	1.757
diisopropyl ether	1.604	1.463	1.328	1.000	2.000
chloroform	2.092	1.944	1.808	0.999	2.508
dichloromethane	1.786	1.664	1.547	1.000	2.129
tetrachloromethane	1.914	1.776	1.648	0.999	2.302
acetonitrile	2.640	2.484	2.352	0.998	3.079
nitromethane	2.853	2.687	2.544	0.998	3.320
1-nitropropane	3.319	3.122	2.948	0.999	3.873
triethylamine	1.923	1.799	1.569	0.972	2.272
pyridine	3.134	2.958	2.783	1.000	3.629
thiophene	2.427	2.273	2.131	0.999	2.860
formaldehyde	1.797	1.657	1.524	1.000	2.191
propionaldehyde	2.124	1.991	1.852	1.000	2.498

can potentially interact with either the anion and/or the cation of the IL. Interestingly, these classes of compound follow similar trends as the hydrocarbons. Branched-chain alcohols have a lower solubility compared to linear alcohols, and their solubility decreases with increasing chain length. The presence

**Table 5. Infinite Dilution Activity Coefficients and Partition Coefficients  $\log K_L$  and  $\log P$  of Organic Solutes at in  $[\text{DM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$** 

solutes	$\gamma^\infty$ at T/K			$\log K_L$	$\log P$
	322.85	332.65	343.15	298.15 K	
hexane	4.20	4.10	3.93	1.783	3.603
3-methylpentane	3.88	3.78	3.62	1.721	3.561
heptane	5.26	5.14	4.92	2.207	4.167
2,2,4-trimethylpentane	5.41	5.29	4.92	2.164	4.284
octane	6.53	6.41	6.10	2.629	4.739
nonane	8.87	8.63	7.61	3.035	5.185
decane	10.07	9.82	9.32	3.445	5.765
undecane	12.45	12.19	11.41	3.866	6.246
dodecane	15.13	14.77	13.77	4.247	6.777
methylcyclopentane	2.99	2.99	2.83	2.009	3.179
cyclohexane	2.90	2.96	2.80	2.191	3.091
methylcyclohexane	3.57	3.57	3.39	2.397	3.647
cycloheptane	7.70	10.76	14.62	2.675	3.255
benzene	0.71	0.73	0.72	2.803	2.173
toluene	0.84	0.89	0.89	3.307	2.657
ethylbenzene	1.16	1.20	1.19	3.590	3.010
<i>m</i> -xylene	1.11	1.14	1.11	3.685	3.075
<i>p</i> -xylene	1.12	1.15	1.13	3.664	3.074
<i>o</i> -xylene	1.03	1.07	1.07	3.817	3.157
1-hexene	2.70	2.86	2.76	1.986	3.146
1-hexyne	1.61	1.63	1.57	2.324	2.534
1-heptyne	1.95	2.02	1.97	2.756	3.196
2-butanone	0.33	0.32	0.29	3.136	0.416
2-pentanone	0.44	0.47	0.47	3.490	0.910
3-pentanone	0.41	0.43	0.44	3.480	0.980
1,4-dioxane	0.56	0.57	0.57	3.346	-0.364
methanol	0.79	0.91	0.66	2.509	-1.231
ethanol	1.29	1.19	1.07	2.638	-1.032
1-propanol	1.48	1.37	1.21	3.029	-0.531
2-propanol	1.38	1.28	1.15	2.743	-0.737
2-methyl-1-propanol	1.59	1.47	1.31	3.247	-0.053
1-butanol	1.70	1.55	1.38	3.448	-0.012
trifluoroethanol	0.46	0.44	0.41	3.059	-0.101
diethyl ether	1.23	1.24	1.21	1.809	0.639
diisopropyl ether	2.19	2.32	2.30	2.176	1.126
chloroform	0.65	0.68	0.68	2.573	1.783
dichloromethane	0.51	0.55	0.56	2.210	1.250
tetrachloromethane	1.46	1.50	1.47	2.438	2.628
acetonitrile	0.44	0.44	0.42	3.017	0.167
nitromethane	0.56	0.58	0.55	3.356	0.406
1-nitropropane	0.59	0.59	0.57	3.843	1.393
triethylamine	2.17	2.40	2.31	2.585	0.225
pyridine	0.46	0.47	0.47	3.660	0.220
thiophene	0.65	0.70	0.68	2.973	1.933
formaldehyde	0.09	0.10	0.11	2.393	
propionaldehyde	0.40	0.42	0.41	2.584	0.064
butyraldehyde	0.47	0.53	0.51	3.051	0.721

of a carboxyl group in a solute substantially increases its solubility in these ILs.

**Table 6. Logarithm of the Gas-to-IL Partition Coefficients for Solutes Dissolved in [DM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup>**

T/K	322.85	332.65	343.15	R <sup>2</sup>	298.15
Solutes					
hexane	1.437	1.314	1.199	0.999	1.783
3-methylpentane	1.389	1.271	1.161	1.000	1.721
heptane	1.797	1.651	1.516	0.999	2.207
2,2,4-trimethylpentane	1.770	1.630	1.513	0.997	2.164
octane	2.154	1.985	1.831	0.999	2.629
nonane	2.504	2.315	2.169	0.994	3.035
decane	2.852	2.641	2.445	0.999	3.445
undecane	3.200	2.963	2.749	0.999	3.866
dodecane	3.536	3.283	3.052	0.999	4.247
methylcyclopentane	1.627	1.491	1.382	0.996	2.009
cyclohexane	1.772	1.623	1.507	0.994	2.191
methylcyclohexane	1.975	1.825	1.698	0.997	2.397
cycloheptane	2.248	2.096	1.957	0.999	2.675
benzene	2.381	2.231	2.095	0.999	2.803
toluene	2.776	2.587	2.429	0.997	3.307
ethylbenzene	3.050	2.858	2.685	0.999	3.590
<i>m</i> -xylene	3.131	2.934	2.765	0.998	3.685
<i>p</i> -xylene	3.110	2.913	2.737	0.999	3.664
<i>o</i> -xylene	3.249	3.047	2.864	0.999	3.817
1-hexene	1.550	1.395	1.281	0.992	1.986
1-hexyne	1.908	1.760	1.632	0.998	2.324
1-heptyne	2.270	2.097	1.949	0.998	2.756
2-butanone	2.669	2.503	2.350	0.999	3.136
2-pentanone	2.970	2.785	2.618	0.999	3.490
3-pentanone	2.965	2.782	2.613	0.999	3.480
1,4-dioxane	2.848	2.671	2.510	0.999	3.346
methanol	2.152	1.923	1.897	0.824	2.509
ethanol	2.213	2.062	1.925	0.999	2.638
1-propanol	2.540	2.366	2.214	0.998	3.029
2-propanol	2.282	2.118	1.972	0.999	2.743
2-methyl-1-propanol	2.727	2.542	2.374	0.999	3.247
1-butanol	2.908	2.716	2.541	0.999	3.448
trifluoroethanol	2.578	2.407	2.253	0.999	3.059
diethyl ether	1.472	1.352	1.242	0.999	1.809
diisopropyl ether	1.720	1.558	1.428	0.996	2.176
chloroform	2.140	1.986	1.854	0.998	2.573
dichloromethane	1.830	1.695	1.582	0.997	2.210
tetrachloromethane	2.011	1.859	1.732	0.997	2.438
acetonitrile	2.618	2.476	2.350	0.999	3.017
nitromethane	2.853	2.674	2.529	0.996	3.356
1-nitropropane	3.317	3.130	2.961	0.999	3.843
triethylamine	2.039	1.845	1.711	0.989	2.585
pyridine	3.148	2.966	2.802	0.999	3.660
thiophene	2.484	2.310	2.173	0.995	2.973
formaldehyde	1.828	1.677	1.548	0.998	2.393
propionaldehyde	2.151	1.997	1.873	0.996	2.584
butyraldehyde	2.500	2.304	2.170	0.988	3.051

The measurements conducted during this research offer an important means to assess the suitability of these tetraalkylammonium ILs as solvents in various separations. This is achieved through

the calculation of the selectivity,  $S_{12}^{\infty}$ , and capacity,  $k_1^{\infty}$ , values at infinite dilution:

$$S_{12}^{\infty} = \frac{\gamma_{1/RTIL}^{\infty}}{\gamma_{2/RTIL}^{\infty}} \quad (8)$$

$$k_1^{\infty} = \frac{1}{\gamma_{1/RTIL}^{\infty}} \quad (9)$$

In eq 8  $\gamma_{1/RTIL}^{\infty}$  and  $\gamma_{2/RTIL}^{\infty}$  denote the infinite dilution coefficients of the solutes 1 and 2 in the IL solvent. Selectivities and capacities at infinite dilution are reported in Table 9 for four separation problems at 323.15 K: hexane/benzene, hexane/methanol, hexane/thiophene, and cyclohexane/thiophene. With regard to aliphatic/aromatic separations, these results indicate that tetraalkylammonium are poor choices compared to imidazolium ILs. The selectivities obtained using ammonium-based ILs (between 3 and 9) are lower than classical solvents used industrially such as sulfolane ( $S_{\text{hexane/benzene}} = 30.5$ ), dimethylsulfoxide ( $S_{\text{hexane/benzene}} = 22.7$ ), and *N*-methyl-2-pyrrolidinone ( $S_{\text{hexane/benzene}} = 12.5$ ).<sup>38</sup> Nevertheless, a better capacity and selectivity may be obtained by a moderate lengthening in the alkyl chain grafted to the ammonium cation. Indeed, long alkyl chains grafted on the cation are known to increase the capacity, while being detrimental to selectivity. Although the results presented for these specific tetraalkylammonium ILs do not suggest that they will not attract particular interest for these separation problems, that it not to say that they will not be ideal for others.

**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 methyl(tributyl)ammonium, octyl(trimethyl)ammonium, decyl(trimethyl)ammonium, and tetraoctylammonium cations for both the gas-to-IL (see eq 1) and water-to-IL (see eq 2) 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 solutes studied.<sup>11,12</sup> 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 tabulated in the last two columns of Tables 1, 3, 5, and 7 the log  $K_L$  and log *P* values at 298.15 K for anhydrous [MB<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> and [OM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> and [DM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> and [O<sub>4</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup>, respectively. The numerical values of log  $K_L$  at 298 were obtained by extrapolating the measured values at higher temperatures assuming a log  $K_L$  versus 1/*T* linear relationship.

The 44 experimental log  $K_L$  and log *P* data in Table 1 for [MB<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> were analyzed in accordance with eqs 1 and 2 of the Abraham model. The calculated equation coefficients and associated statistical information are given in Table 10, 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 below the respective value. The  $e \cdot E$  term

**Table 7. Infinite Dilution Activity Coefficients and Partition Coefficients  $\log K_L$  and  $\log P$  of Organic Solutes in  $[\text{O}_4\text{AM}]^+[\text{Tf}_2\text{N}]^-$**

solutes	$\gamma^\infty$ at T/K			$\log K_L$	$\log P$
	323.15	333.15	343.15	298.15 K	
hexane	1.30	1.29	1.28	2.165	3.985
3-methylpentane	1.22	1.22	1.21	2.098	3.938
heptane	1.50	1.48	1.47	2.620	4.580
2,2,4-trimethylpentane	1.52	1.51	1.50	2.587	4.707
octane	1.73	1.71	1.69	3.066	5.176
nonane	2.19	2.14	2.09	3.503	5.653
decane	2.30	2.32	2.21	3.937	6.257
undecane			2.54		
dodecane			2.72		
methylcyclopentane	0.98	0.97	0.97	2.331	3.501
cyclohexane	0.95	0.94	0.92	2.483	3.383
methylcyclohexane	1.07	1.06	1.05	2.761	4.011
cycloheptane	2.21	3.16	4.37	3.088	3.678
benzene	0.40	0.41	0.41	2.914	2.284
toluene	0.47	0.48	0.49	3.370	2.720
ethylbenzene	0.59	0.60	0.61	3.715	3.135
<i>m</i> -xylene		0.60	0.62	3.802	3.192
<i>p</i> -xylene		0.60	0.62	3.779	3.189
<i>o</i> -xylene		0.57	0.58	3.906	3.166
1-hexene	1.05	1.05	1.04	2.178	3.338
1-hexyne	0.75	0.76	0.76	2.506	2.716
1-heptyne	0.84	0.86	0.87	2.963	3.403
2-butanone	0.29	0.28	0.26	3.032	0.312
2-pentanone	0.35	0.36	0.37	3.432	0.852
3-pentanone	0.32	0.33	0.35	3.423	0.923
1,4-dioxane	0.47	0.47	0.47	3.263	-0.447
methanol	0.65	0.76	0.82	2.692	-1.048
ethanol	1.18	1.12	1.05	2.553	-1.117
1-propanol	1.22	1.14	1.04	2.959	-0.601
2-propanol	1.21	1.13	1.05	2.651	-0.829
2-methyl-1-propanol	1.17	1.09	1.00	3.226	-0.074
trifluoroethanol	0.48	0.37	0.36	2.761	-0.399
diethyl ether	0.71	0.71	0.71	1.898	0.728
diisopropyl ether	1.08	1.08	1.08	2.268	1.218
chloroform	0.34	0.35	0.36	2.685	1.895
dichloromethane	0.29	0.30	0.31	2.281	1.321
tetrachloromethane	0.63	0.64	0.64	2.625	2.815
acetonitrile	0.50	0.49	0.49	2.818	-0.032
nitromethane	0.63	0.61	0.59	3.073	0.123
1-nitropropane	0.48	0.48	0.47	3.769	1.319
triethylamine	1.03	1.05	1.02	2.631	0.270
pyridine	0.33	0.33	0.34	3.644	0.204
thiophene	0.40	0.40	0.41	2.985	1.945
formaldehyde	0.07	0.08	0.09	2.118	
propionaldehyde	0.25	0.35	0.35	2.783	0.260
butyraldehyde			0.31		

was found to negligible in the  $\log P$  correlation ( $e = -0.023$ ) so it was removed from the final derived correlation. Solute descriptors used in the analysis are listed in Table 11. Both equations provide a very

**Table 8. Logarithm of the Gas-to-IL Partition Coefficients for Solutes Dissolved in  $[\text{O}_4\text{AM}]^+[\text{Tf}_2\text{N}]^-$**

T/K	323.15	333.15	343.15	$R^2$	298.15 K
Solutes					
hexane	1.798	1.667	1.543	1.000	2.165
3-methylpentane	1.742	1.613	1.495	1.000	2.098
heptane	2.194	2.040	1.898	1.000	2.620
2,2,4-trimethylpentane	2.173	2.025	1.886	1.000	2.587
octane	2.582	2.407	2.245	1.000	3.066
nonane	2.963	2.768	2.587	1.000	3.503
decane	3.342	3.114	2.926	0.998	3.937
undecane			3.259		
dodecane			3.613		
methylcyclopentane	1.962	1.831	1.706	1.000	2.331
cyclohexane	2.108	1.972	1.847	1.000	2.483
methylcyclohexane	2.350	2.202	2.064	1.000	2.761
cycloheptane	2.646	2.485	2.338	1.000	3.088
benzene	2.486	2.334	2.190	1.000	2.914
toluene	2.883	2.708	2.544	1.000	3.370
ethylbenzene	3.191	3.006	2.828	1.000	3.715
<i>m</i> -xylene		3.061	2.877	1.000	3.802
<i>p</i> -xylene		3.042	2.859	1.000	3.779
<i>o</i> -xylene		3.169	2.986	1.000	3.906
1-hexene	1.813	1.682	1.560	1.000	2.178
1-hexyne	2.091	1.941	1.802	1.000	2.506
1-heptyne	2.490	2.319	2.160	1.000	2.963
2-butanone	2.578	2.413	2.261	1.000	3.032
2-pentanone	2.932	2.750	2.584	1.000	3.432
3-pentanone	2.924	2.743	2.577	1.000	3.423
1,4-dioxane	2.781	2.607	2.446	1.000	3.263
methanol	2.085	1.849	1.659	0.998	2.692
ethanol	2.104	1.939	1.791	1.000	2.553
1-propanol	2.475	2.293	2.136	0.999	2.959
2-propanol	2.189	2.021	1.868	1.000	2.651
2-methyl-1-propanol	2.708	2.518	2.348	1.000	3.226
trifluoroethanol	2.405	2.328	2.167	0.953	2.761
diethyl ether	1.564	1.441	1.331	1.000	1.898
diisopropyl ether	1.881	1.741	1.612	1.000	2.268
chloroform	2.272	2.122	1.985	1.000	2.685
dichloromethane	1.933	1.806	1.690	1.000	2.281
tetrachloromethane	2.226	2.081	1.948	1.000	2.625
acetonitrile	2.418	2.278	2.141	1.000	2.818
nitromethane	2.650	2.497	2.356	1.000	3.073
1-nitropropane	3.258	3.065	2.901	0.999	3.769
triethylamine	2.214	2.056	1.922	0.999	2.631
pyridine	3.144	2.965	2.796	1.000	3.644
thiophene	2.553	2.397	2.253	1.000	2.985
formaldehyde	1.752	1.616	1.496	1.000	2.118
propionaldehyde	2.210	1.929	1.798	0.965	2.783
butyraldehyde			2.243		

accurate mathematical description of the  $\log K_L$  and  $\log P$  values for organic solutes dissolved in  $[\text{MB}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$  as evidenced by standard deviations of  $\text{SD} = 0.083$  and  $\text{SD} = 0.113$  log units. Standard deviations for the  $\log P$  correlations are generally slightly larger because the values used in the regression analysis also include the

Table 9. Selectivities ( $S_{12}^{\infty}$ ) and Capacities ( $k_1^{\infty}$ ) at Infinite Dilution for Different Separation Problems at 323.15 K

ILs		$S_{12}^{\infty}/k_1^{\infty}$				reference
Anion	Cation	Hexane/Benzene	Hexane/Methanol	Hexane/Thiophene	Cyclohexane/Thiophene	
[Tf <sub>2</sub> N] <sup>−</sup>	methyltributylammonium	7.5/1.11	7.3/1.08	7.8/1.17	5.5/1.17	this work
	octyltrimethylammonium	8.5/1.37	6.75/1.08	9/1.45	5.9/1.45	this work
	decyltrimethylammonium	5.9/1.41	5.3/1.09	6.46/1.54	4.46/1.54	this work
	tetraoctylammonium	3.2/2.5	2.0/1.08	3.25/2.5	2.35/2.5	this work
	1,3-dimethoxyimidazolium	21.3/0.47	42.05/0.94	24.8/0.94	12.6/0.94	18
	1-(methylethylether)-3-methylimidazolium	15.5/0.85	17.4/0.93	18.1/1.0	10.9/1.0	18
	1-ethanol-3-methylimidazolium	20.6/0.47	49.1/1.12	24.7/0.56	14.2/0.56	18
	1-ethyl-3-methylimidazolium	37.5/1.43	19.5/1.20			32
	1-(hexylmethylether)-3-methylimidazolium	9.1/1.23	6.8/0.91	10.0/1.35	6.4/1.35	33
	1,3-bis(hexylmethylether)imidazolium	4.9/1.67	3.2/1.06	5.3/1.75	3.7/1.75	33
	1-butyl-3-methylimidazolium	16.7/1.11				34
	1-hexyl-3-methylimidazolium	9.5/1.29	6.1/0.82			35
	trimethylhexylammonium	9.9/1.01	8.5/0.86	10.7/1.09	7.2/1.09	15
	4-methyl-N-butylpyridinium	18.8/1.43	21.2/0.83	10.6/1.56	6.1/1.56	36
	triethylsulfonium	21.6/0.91	17.8/0.77	25.5/1.05	14.3/1.05	37
	triethyl(tetradecyl) phosphonium	2.7/2.56	1.1/1.02	2.6/2.5	1.95/2.5	4

Table 10. Equation Coefficients for the Abraham Model  $\log K_L$  and  $\log P$  Correlations for [MB<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup>, [OM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup>, [DM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup>, and [O<sub>4</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup>

IL	property	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v/l</i>	<i>N</i>	SD	R <sup>2</sup>	<i>F</i>
[MB <sub>3</sub> Am] <sup>+</sup> [Tf <sub>2</sub> N] <sup>−</sup>	log <i>K<sub>L</sub></i>	−0.506 (0.079)	−0.169 (0.083)	2.103 (0.080)	2.298 (0.115)	0.412 (0.092)	0.777 (0.022)	44	0.083	0.983	452.1
	log <i>P</i>	−0.233 (0.123)	0.000 (0.101)	0.404 (0.154)	−1.313 (0.113)	−4.542 (0.104)	3.687 (0.104)	44	0.113	0.996	2551
[OM <sub>3</sub> AM] <sup>+</sup> [Tf <sub>2</sub> N] <sup>−</sup>	log <i>K<sub>L</sub></i>	−0.426 (0.082)	−0.338 (0.089)	2.242 (0.082)	2.195 (0.123)	0.684 (0.021)	0.779 (0.022)	44	0.092	0.981	396.5
	log <i>P</i>	−0.165 (0.129)	−0.181 (0.118)	0.569 (0.118)	−1.419 (0.164)	−4.677 (0.115)	3.711 (0.103)	44	0.123	0.996	1976
[DM <sub>3</sub> AM] <sup>+</sup> [Tf <sub>2</sub> N] <sup>−</sup>	log <i>K<sub>L</sub></i>	−0.363 (0.089)	−0.339 (0.098)	1.986 (0.090)	2.144 (0.135)	0.422 (0.094)	0.809 (0.024)	46	0.102	0.974	303.2
	log <i>P</i>	−0.128 (0.135)	−0.131 (0.125)	0.329 (0.126)	−1.458 (0.175)	−4.550 (0.120)	3.816 (0.108)	46	0.132	0.996	1832
[O <sub>4</sub> AM] <sup>+</sup> [Tf <sub>2</sub> N] <sup>−</sup>	log <i>K<sub>L</sub></i>	0.000 (0.134)	−0.287 (0.110)	1.478 (0.110)	1.845 (0.158)	0.189 (0.121)	0.816 (0.013)	42	0.124	0.998	3749
	log <i>P</i>	0.226 (0.198)	0.000 (0.144)	−0.212 (0.144)	−1.756 (0.240)	−4.739 (0.139)	3.825 (0.174)	42	0.164	0.993	1332

experimental uncertainty in the log *K<sub>w</sub>* values used to convert the measured log *K<sub>L</sub>* data to log *P*.

As noted above, each of the calculated equation coefficients corresponds to the sum of the respective cation-specific and anion-specific contributions. In establishing the computational methodology, the equation coefficients for the [Tf<sub>2</sub>N]<sup>−</sup> anion were set equal to zero to provide a reference point from which all equation coefficients would be calculated.<sup>28–30</sup> A reference point is needed because the cation- and anion-specific equation coefficients are generated as a paired set. The log *K<sub>L</sub>* and log *P* equation coefficients for [MB<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup> thus correspond to the ion-specific coefficients for the [MB<sub>3</sub>AM]<sup>+</sup> cation.

Tabulated in Table 3 are 44 experimental log *K<sub>L</sub>* and log *P* values for solutes dissolved in [OM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup>. The calculated Abraham model equation coefficients for transfer of organic solutes to the

IL both from the gas phase and from water are given in Table 10. The statistics of both correlations are quite good as evidenced by squared correlation coefficients near unity and small standard deviations of 0.092 and 0.123 log units. The log *K<sub>L</sub>* and log *P* equation coefficients correspond to the ion-specific coefficients for the [OM<sub>3</sub>AM]<sup>+</sup> cation because the anion-specific values for the [Tf<sub>2</sub>N]<sup>−</sup> anion were defined to be zero, as discussed above.

The experimental log *K<sub>L</sub>* and log *P* data in Tables 5 and 7 for [DM<sub>3</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup> and [O<sub>4</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup> were analyzed in a similar fashion to give the equation coefficients listed in Table 10. Preliminary regression analysis showed the *c* term in the log *K<sub>L</sub>* correlation for [O<sub>4</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup> and the *e*·*E* term in the log *P* correlation for [O<sub>4</sub>AM]<sup>+</sup>[Tf<sub>2</sub>N]<sup>−</sup> to be negligible; both terms were thus removed from the final set of equations. The derived Abraham model correlations provide a good mathematical description of the



**Table 11. 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
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	1.9400
tetradecane	0.000	0.000	0.000	0.000	6.705	2.0810
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
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	0.080	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
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	-0.063	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
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

experimental gas-to-anhydrous IL partition coefficient data and water-to-anhydrous IL partition coefficient.

The Abraham model correlations that have been derived for  $[\text{MB}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ ,  $[\text{OM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ ,  $[\text{DM}_3\text{AM}]^+[\text{Tf}_2\text{N}]^-$ ,

and  $[\text{O}_4\text{AM}]^+[\text{Tf}_2\text{N}]^-$  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  $0.790$ ,  $L = 0.970$  to  $6.705$ , and  $V = 0.308$  to  $2.081$ . The cation- and anion-specific equation coefficients can be combined to yield predictive equations for many different ILs. The present study increases our calculated cation-specific equation coefficients by 4. We have now reported equation coefficients for 24 unique cations, counting the 4 tetraalkylammonium cations introduced here, and for 14 different anions. The 24 sets of cation-specific equation coefficients and 14 sets of anion-specific equation coefficients can be combined to yield predictive equations for 336 different ILs.

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