Activity Coefficients at Infinite Dilution for Organic Solutes Dissolved in Three 1-Alkyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids Bearing Short Linear Alkyl Side Chains of Three to Five Carbons
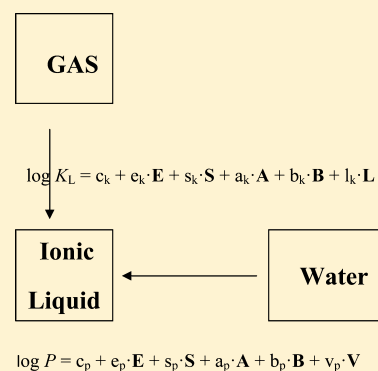
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ABSTRACT: In this work, we report the infinite dilution activity coefficients ($\gamma_{1,2}^{\infty}$) of 39 to 43 diverse organic solutes dissolved in three 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids (IL) homologues bearing propyl, butyl, and pentyl n-alkyl side chains, respectively, as determined by inverse gas chromatography at temperatures from 323 K to 343 K. The organic solutes include various (cyclo)alkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, thiophene, ethers, nitroalkanes, and ketones. The measured retention data were further transformed to gas-to-IL and water-to-IL partition coefficients using established thermodynamic approaches based upon the corresponding gas-to-water partition coefficients of the test solutes. Both sets of partition coefficients were interpreted with a modified form of the basic Abraham general solvation parameter model. The mathematical correlations obtained by regression analysis back-calculated the observed gas-to-IL and water-to-IL partition coefficient data to within average standard deviations of 0.104 and 0.136 log units, respectively.

GAS

$\log K_L = c_k + e_k \cdot \mathbf{E} + s_k \cdot \mathbf{S} + a_k \cdot \mathbf{A} + b_k \cdot \mathbf{B} + l_k \cdot \mathbf{L}$

Ionic Liquid

Water

$\log P = c_p + e_p \cdot \mathbf{E} + s_p \cdot \mathbf{S} + a_p \cdot \mathbf{A} + b_p \cdot \mathbf{B} + v_p \cdot \mathbf{V}$

■ INTRODUCTION

Ionic liquids (ILs) have been the subjects of enormous contemporary research efforts within academic and industrial circles as a result of the distinctive, wide-ranging, and tailorable solvent properties they bring. Effectively null vapor pressures, coupled with a very wide temperature range of liquid stability, account for the budding exploitation of ILs as solvents for diverse uses ranging from biofuels synthesis to actinide chemistry in the nuclear cycle. The industrial application of ILs is made particularly compelling by the fact that their properties can be deliberately altered by selection of a different cation−anion pairing or by the introduction of functionality to one of the ionic components. For instance, ether- and hydroxyl-functionalized ILs are reported to display especially high capacities for solubilizing CO_2 and SO_2.[1]

The present study continues our methodical examination of the solubilizing ability of IL solvents and the development of simple correlation equations allowing one to conveniently predict gas-to-liquid partition coefficients, K_L, infinite dilution activity coefficients, γ^{∞}, and mole fraction solubilities of volatile organic solutes and gases in ILs. To date, we have published predictive expressions for 18 different IL solvents, including trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)-imide,[2] 1-ethyl-3-methylimidazolium dicyanamide,[3] trimethyl-hexylammonium bis(trifluoromethylsulfonyl)amide,[3] 1,3-dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide,[4] 1-(methylethylether)-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide,[4] 1-ethanol-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide,[4] 1-(3-cyanopropyl)-3-methyl-imidazolium dicyanamide,[4] 1-hexyl-3-methylimidazolium tris-(pentafluoroethyl)trifluorophosphate,[5] 1-butyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide,[5] 1,3-didecyl-2-methylimidazolium bis(trifluoromethylsulfonyl)-imide,[5] 1-ethyl-3-methylimidazolium methanesulfonate,[5] decyl-(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide,[6] tributylmethylammonium bis(trifluoromethylsulfonyl)imide,[6] trimethyloctylammonium bis(trifluoromethylsulfonyl)imide,[6] and tetraoctylammonium bis(trifluoromethylsulfonyl)imide.[6] Finally, our most recent study involved three ILs based on the 1-alkyl-1-methylpyrrolidinium cation bearing six, eight, and ten-carbon n-alkyl side chains; namely, 1-hexyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide,[7] 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide,[7] and 1-decyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide.[7]

In the present study, we report infinite dilution activity coefficients and gas-to-IL partition coefficients for 39 to 43 assorted probe solutes dissolved in short chain members of the 1-alkyl-1-methylpyrrolidinium family: 1-propyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C3MPyrr]^+[Tf_2N]^-$), 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)imide ($[C4MPyrr]^+[Tf_2N]^-$), and 1-pentyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide ($[C5MPyrr]^+[Tf_2N]^-$). The outcomes of these measurements are used to derive IL-specific Abraham model correlations,[8] and to calculate ion-specific Abraham model equation coefficients for the $[C3MPyrr]^+$, $[C4MPyrr]^+$, and $[C5MPyrr]^+$ cations. The derived Abraham model correlations are valuable in that they allow one to predict gas-to-liquid partition coefficients and infinite dilution activity coefficients with a reasonable margin of error for additional solutes not directly studied herein.

■ EXPERIMENTAL PROCEDURES AND RESULTS

Materials or Chemicals. The preparation of the 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ILs followed methods reported by Jin et al.[9] with particular emphasis focused on precautions essential for accomplishing analytically pure spectroscopic-grade fluids bearing no discernible visual color.[10,11] Succinctly, this requires consideration of five frequently disregarded aspects of the synthesis: (i) single or double distillation of any and all bromoalkane and N-methylpyrrolidine starting materials; (ii) reaction for the better part of a week at sub-50 °C temperatures under flowing inert gas and adequate protection from room light; (iii) several (at least three or four) iterative recrystallizations of the resulting bromide salt; (iv) constant gentle (100−150 rpm) stirring of an aqueous solution of the multiply recrystallized 1-alkyl-1-methylpyrrolidinium bromide with activated carbon (∼1.0 wt % relative to the salt being cleaned; both type DARCO G60 and DARCO KB-G have worked well in our hands) for several days, after which centrifugation (5000 × g for 30 min suffices), cautious decantation, and supernatant syringe filtration (0.45 μm nylon is our filter of choice) are necessary to entirely remove the carbon. A slight penalty in overall yield during this step is unavoidable in exchange for optically superior materials; however, for purposes of achieving specialty fluids requisite to select studies, we keenly accept this quid pro quo. (v) Finally, following the metathesis step and copious rinsing of the hydrophobic IL with freshly drawn 18.2 MΩ cm water many times, a *graded drying*—first at 40 °C for two to three days using a trapped roughing pump and, to finish, at 70 °C to 80 °C for at least 24 h on a high-vacuum Schlenk line—must be implemented. As general instruction, although this may indeed be overkill, we tend to store our prized spectroscopic-grade, dried final materials in evacuated vacuum desiccators in a cold room held at 4 °C, our reasoning being that oxygen appears to be linked to the formation of color in certain instances and, by and large, the extreme viscosities present at this temperature should slow most decomposition pathways leading to degradation and any attendant discoloration. The water content of all three ionic liquid solvents was less that 150 ppm as determined by Karl Fisher titration. The purities and sources of the solutes used in the present investigation are listed in Table 1.

Density Measurement. Experimental densities of the ILs were measured using an Anton Paar DMA 60 digital vibrating-tube densimeter equipped with a DMA 512P measuring cell in

Table 1. Chemical Sources and Purities

	source	purity
Solvents		
1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	prepared in-house	99 % (mass); < 150 ppm water
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	prepared in-house	99 % (mass); < 150 ppm water
1-pentyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	prepared in-house	99 % (mass); < 150 ppm water
Solutes		
hexane	Aldrich	> 99.5 %
3-methylpentane	Aldrich	> 99.5 %
heptane	Aldrich	> 99.5 %
2,2,4-trimethylpentane	Aldrich	> 99.5 %
octane	Aldrich	> 99.5 %
nonane	Aldrich	> 99.5 %
decane	Aldrich	> 99.5 %
undecane	Aldrich	> 99.5 %
dodecane	Aldrich	> 99.5 %
tridecane	Aldrich	> 99.5 %
tetradecane	Aldrich	> 99.5 %
methylcyclopentane	Aldrich	> 99.5 %
cyclohexane	Aldrich	> 99.5 %
methylcyclohexane	Aldrich	> 99.5 %
cycloheptane	Aldrich	> 99.5 %
benzene	Aldrich	> 99.5 %
toluene	Aldrich	> 99.5 %
ethylbenzene	Aldrich	> 99.5 %
m-xylene	Aldrich	> 99.5 %
p-xylene	Aldrich	> 99.5 %
o-xylene	Aldrich	> 99.5 %
1-hexene	Aldrich	> 99.5 %
1-hexyne	Aldrich	> 99.5 %
1-heptyne	Aldrich	> 99.5 %
2-butanone	Aldrich	> 99.5 %
2-pentanone	Aldrich	> 99.5 %
3-pentanone	Aldrich	> 99.5 %
1,4-dioxane	Aldrich	> 99.5 %
methanol	Aldrich	> 99.5 %
ethanol	Aldrich	> 99.5 %
1-propanol	Aldrich	> 99.5 %
2-propanol	Aldrich	> 99.5 %
2-methyl-1-propanol	Aldrich	> 99.5 %
1-butanol	Aldrich	> 99.5 %
diethyl ether	Aldrich	> 99.5 %
diisopropyl ether	Aldrich	> 99.5 %
chloroform	Aldrich	> 99.5 %
dichloromethane	Aldrich	> 99.5 %
tetrachloromethane	Aldrich	> 99.5 %
acetonitrile	Aldrich	> 99.5 %
nitromethane	Aldrich	> 99.5 %
1-nitropropane	Aldrich	> 99.5 %
triethylamine	Aldrich	> 99.5 %
pyridine	Aldrich	> 99.5 %
thiophene	Aldrich	> 99.5 %

the temperature range from 298.15 K to 335.74 K at atmospheric pressure. The temperature in the vibrating-tube cell was determined by a platinum resistance thermometer PT-100 with an accuracy of ± 0.1 K. A thermostatic oil bath was used in the thermostat circuit of the measuring cell, which was maintained constant to within ± 0.1 K. n-Dodecane and tetrachloroethylene served as reference liquids in the calibration

Table 2. Density^a as a Function of Temperature at p = 101.33 kPa for 1-Alkyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imides

	ρ (g/·cm^3)		
T/K	$[C3MPyrr]^+[Tf_2N]^-$	$[C4MPyrr]^+[Tf_2N]^-$	$[C5MPyrr]^+[Tf_2N]^-$
293.15	1.4301	1.3974	1.3660
303.15	1.4218	1.3892	1.3581
313.15	1.4128	1.3811	1.3501
323.15	1.4038	1.3727	1.3420
333.15	1.3944	1.3641	1.3346

^{a}Standard uncertainties are $u(\rho)$ = 0.0001 g·cm^{-3} and $u(T)$ = 0.1 K.

of the instrument. The experimental mass densities of ($[C3MPyrr]^+[Tf_2N]^-$), ($[C4MPyrr]^+[Tf_2N]^-$), and ($[C5MPyrr]^+[Tf_2N]^-$) at 293.15 K, 303.15 K, 313.15 K, 323.15 K, and 333.15 K are listed in Table 2.

Apparatus and Experimental Procedures. The chromatographic instrumentation and experimental procedure have been described in detail in earlier publications[6,7] and will be only briefly described here. Inverse chromatography measurements were performed on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a heated on-column injector. The injector and detector temperatures were set at 523 K for the duration of all experimental measurements. The column hold-up time was determined using methane gas as the unretained solute.

Packed columns of 1 m length containing between 15 % to 35 % IL stationary phase coated onto a 60−80 mesh Chromosorb WHP support material were prepared by a rotary evaporation method. The mass of the packing material was computed from the mass of the empty and packed columns and was checked periodically during the course of the experiment measurements. The masses of the individual stationary phases were determined with a precision of 0.0003 g. A 1 μL to 5 μL volume of the headspace vapor of probe samples was introduced and validated to represent "infinite dilution" conditions. Each experiment was performed a minimum of three times to ensure that the measured values were reproducible. Measured retention times were usually reproducible to within 0.01 min to 0.03 min. No drift in the retention time was observed throughout the course of our study.

■ RESULTS AND DISCUSSION

Activity Coefficients and Selectivity at Infinite Dilution. The infinite dilution activity coefficients ($\gamma_{1,2}^\infty$) and gas-to-liquid partition coefficients (K_L) of the various solutes for the given IL were calculated from the measured retention data as described in a previous publication.[7] The uncertainties in $\gamma_{1,2}^\infty$ and K_L were estimated by a error propagation to be less than 3 %, taking into account uncertainties in the following measured quantities and their standard deviations (given in parentheses): mass of the stationary phase (2 %); inlet and outlet pressures (0.2 kPa); adjusted retention time of the solute, t_R' (0.01 min); flow rate of the carrier gas (0.1 cm^3 min^{-1}); and oven temperature (0.2 K). No interfacial adsorption was observed in the case of the three ILs considered in the present study. The average relative standard deviation between the two sets of data obtained with packed columns at two different IL loadings was about 2 %. The infinite dilution activity coefficients and the gas-to-IL partition coefficients are listed in Tables 3 through 5.

Table 3. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P,^{a} of Organic Compounds in 1-Propyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide

	γ^∞ at T/K			298.15	
solutes	323.15	333.15	343.15	log K_L	log P
hexane	16.52	14.98	14.05	1.334	3.154
3-methylpentane	14.31	13.54	11.70	1.268	3.108
heptane	24.04	23.11	22.29	1.764	3.724
2,2,4-trimethylpentane	22.53	22.01	21.56	1.757	3.877
octane	35.75	31.11	30.64	2.036	4.146
nonane	55.52	48.66	47.46	2.396	4.546
decane	74.71	65.68	60.00	2.679	4.999
undecane	108.16	92.78	85.13	3.015	5.395
methylcyclopentane	10.33	10.31	9.16	1.598	2.768
cyclohexane	10.21	9.53	8.53	1.716	2.616
methylcyclohexane	14.07	12.80	12.22	1.931	3.141
cycloheptane	29.14	42.98	54.69	2.289	2.879
benzene	0.99	1.01	1.03	2.885	2.255
toluene	1.37	1.38	1.45	3.267	2.617
m-xylene	1.97	1.99	2.05	3.639	3.029
p-xylene	1.96	2.00	2.03	3.626	3.036
o-xylene	1.78	1.83	1.87	3.777	3.037
1-hexene	7.96	7.75	7.65	1.628	2.788
1-hexyne	3.35	3.18	3.01	2.139	2.349
1-heptyne	4.52	4.52	4.51	2.564	3.004
2-butanone	0.57	0.58	0.64	3.277	0.557
2-pentanone	0.88	0.88	0.91	3.372	0.792
3-pentanone	0.81	0.82	0.86	3.373	0.873
1,4-dioxane	0.74	0.74	0.76	3.430	−0.270
methanol	1.38	1.28	1.15	2.474	−1.266
ethanol	1.75	1.57	1.49	2.718	−0.952
1-propanol	2.17	1.95	1.79	3.046	−0.514
2-propanol	1.92	1.79	1.62	2.792	−0.688
2-methyl-1-propanol	2.51	2.29	2.10	3.242	−0.058
1-butanol	2.79	2.35	2.27	3.427	−0.033
diethyl ether	2.62	2.70	2.75	1.735	0.455
diisopropyl ether	5.88	5.75	5.53	1.842	0.752
chloroform	0.85	0.91	0.96	2.678	1.888
dichloromethane	0.66	0.72	0.78	2.341	1.381
tetrachloromethane	2.55	2.62	2.64	2.389	2.579
1-nitropropane	0.77	0.77	0.77	3.936	1.486
triethylamine	8.98	8.10	7.19	1.954	−0.406
pyridine	0.63	0.63	0.64	3.721	0.281
thiophene	0.86	0.88	0.89	3.012	1.978

^{a}Standard uncertainties are $u(\gamma^\infty)$ = 3 %, $u(K_L)$ = 3 %, $u(P)$ = 3 %, and $u(T)$ = 0.05 K.

Activity coefficients at infinite dilution for most of the organic compounds considered were found to decrease with

Table 4. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P,[a] of Organic Compounds in 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide

	γ^∞ at T/K			298.15	
solutes	323.15	333.15	343.15	log K_L	log P
hexane	13.95	13.55	12.63	1.393	3.213
3-methylpentane	12.28	11.86	10.99	1.344	3.184
heptane	19.69	18.42	17.50	1.753	3.713
2,2,4-trimethylpentane	19.20	17.91	17.15	1.736	3.856
octane	28.17	25.33	23.49	2.069	4.180
nonane	42.72	38.32	34.71	2.427	4.577
decane	54.31	49.02	44.23	2.780	5.100
undecane	76.92	68.22	61.06	3.122	5.502
dodecane	104.77	93.75	83.01	3.459	5.989
methylcyclopentane	8.68	8.24	7.85	1.643	2.813
cyclohexane	8.74	7.96	7.59	1.764	2.664
methylcyclohexane	11.51	10.74	10.08	1.973	3.183
cycloheptane	23.88	32.01	41.68	2.280	2.870
benzene	0.92	0.93	0.94	2.849	2.219
toluene	1.25	1.27	1.29	3.239	2.589
ethylbenzene	1.83	1.85	1.87	3.530	2.950
m-xylene	1.78	1.80	1.83	3.619	3.009
p-xylene	1.78	1.80	1.81	3.600	3.010
o-xylene	1.61	1.64	1.66	3.762	3.022
1-hexene	7.51	7.21	7.12	1.606	2.766
1-hexyne	2.89	2.87	2.83	2.209	2.419
1-heptyne	3.98	3.98	3.94	2.567	3.007
2-butanone	0.54	0.50	0.46	3.069	0.349
2-pentanone	0.80	0.81	0.82	3.357	0.777
3-pentanone	0.73	0.75	0.77	3.361	0.861
1,4-dioxane	0.71	0.72	0.72	3.388	−0.312
methanol	1.40	1.28	1.18	2.430	−1.310
ethanol	1.73	1.57	1.43	2.656	−1.014
1-propanol	2.07	1.87	1.68	3.012	−0.548
2-propanol	1.90	1.72	1.57	2.740	−0.740
2-methyl-1-propanol	2.37	2.12	1.92	3.205	−0.095
1-butanol	2.59	2.32	2.08	3.396	−0.064
diethyl ether	2.53	2.54	2.60	1.671	0.391
diisopropyl ether	5.19	5.28	5.40	1.917	0.827
chloroform	0.83	0.86	0.88	2.612	1.821
dichloromethane	0.66	0.70	0.73	2.236	1.276
tetrachloromethane	2.44	2.45	2.47	2.347	2.366
acetonitrile	0.52	0.51	0.50	3.103	0.253
nitromethane	0.65	0.58	0.57	3.340	0.390
1-nitropropane	0.74	0.73	0.73	3.893	1.443
triethylamine	7.07	7.07	7.09	2.120	−0.241
pyridine	0.59	0.59	0.59	3.693	0.253
thiophene	0.82	0.83	0.84	2.979	1.939

[a]Standard uncertainties are $u(\gamma^\infty)$ = 3 %, $u(K_L)$ = 3 %, $u(P)$ = 3 %, and $u(T)$ = 0.05 K.

Table 5. Infinite Dilution Activity Coefficients and Logarithm of Partition Coefficients, log K_L and log P,[a] of Organic Compounds in 1-Pentyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide

	γ^∞ at T/K			298.15	
solutes	323.15	333.15	343.15	log K_L	log P
hexane	11.73	10.58	9.92	1.407	3.227
3-methylpentane	10.48	9.82	9.41	1.396	3.236
heptane	15.09	14.26	13.56	1.852	3.812
2,2,4-trimethylpentane	14.78	13.90	13.48	1.840	3.960
octane	20.16	18.87	17.90	2.230	4.340
nonane	29.77	27.48	25.86	2.603	4.753
decane	36.91	34.00	31.63	2.957	5.277
undecane	51.15	45.64	41.17	3.285	5.665
dodecane	67.28	60.58	54.93	3.649	6.179
methylcyclopentane	6.87	6.69	6.56	1.756	2.926
cyclohexane	6.81	6.57	6.25	1.881	2.781
methylcyclohexane	8.97	8.54	8.14	2.079	3.289
cycloheptane	18.33	25.07	33.32	2.397	2.987
benzene	0.82	0.83	0.85	2.889	2.259
toluene	1.09	1.11	1.14	3.281	2.632
ethylbenzene	1.57	1.58	1.61	3.577	2.997
m-xylene	1.53	1.54	1.58	3.671	3.061
p-xylene	1.53	1.55	1.56	3.652	3.062
o-xylene	1.39	1.40	1.43	3.805	3.065
1-hexene	6.04	5.95	5.88	1.691	2.851
1-hexyne	2.49	2.45	2.40	2.269	2.479
2-butanone	0.48	0.44	0.41	3.103	0.383
2-pentanone	0.69	0.70	0.71	3.401	0.821
3-pentanone	0.64	0.65	0.67	3.400	0.899
1,4-dioxane	0.66	0.67	0.67	3.404	−0.296
methanol	1.36	1.24	1.15	2.424	−1.216
ethanol	1.65	1.50	1.35	2.642	−1.028
1-propanol	1.89	1.72	1.55	3.031	−0.529
2-propanol	1.76	1.62	1.45	2.750	−0.730
2-methyl-1-propanol	2.13	1.92	1.74	3.230	−0.070
1-butanol	2.30	2.06	1.86	3.430	−0.030
diethyl ether	2.05	2.01	1.95	1.690	0.410
diisopropyl ether	4.43	4.09	3.94	1.867	0.777
chloroform	0.76	0.79	0.80	2.617	1.827
dichloromethane	0.61	0.65	0.65	2.230	1.270
tetrachloromethane	2.13	2.13	2.14	2.377	2.396
acetonitrile	0.50	0.50	0.49	3.087	0.237
nitromethane	0.58	0.56	0.55	3.414	0.464
1-nitropropane	0.68	0.67	0.67	3.902	1.452
triethylamine	5.25	5.20	5.03	2.248	−0.112
pyridine	0.53	0.53	0.54	3.719	0.279
thiophene	0.74	0.76	0.76	3.000	1.960

[a]Standard uncertainties are $u(\gamma^\infty)$ = 3 %, $u(K_L)$ = 3 %, $u(P)$ = 3 %, $u(T)$ = 0.05 K.

increased temperature with the exceptions being the aromatics, chloroalkanes, pyridine, and thiophene. As noted previously with the imidazolium and ammonium cations, the solubility of apolar solutes generally increases with increasing alkyl chain length grafted onto the pyrrolidinium cation. For compounds having identical numbers of carbon atoms but belonging to different solute families, the trend $\gamma_{aromatic} < \gamma_{alkyne} < \gamma_{alkene} < \gamma_{alkane}$ was observed. This overall trend is followed for all ILs, irrespective of the anion or cation identity. The presence of double or triple bonds within a solute molecule tended to

enhance interactions between the dissolved solute and surrounding IL solvent molecules. For the alcohol solutes, the low $\gamma_{1,2}^\infty$ values can be attributed to the two lone pairs of electrons on the oxygen atom of the alcohol interacting with the positively charged cation and to the acidic proton of the alcohol forming hydrogen bonds with oxygen atoms of the [Tf$_2$N]$^-$ anion. Branched-chain alcohols displayed a lower solubility than linear alcohols, and their solubility was found to decrease with increasing alkyl chain length. Pyridine, ketones, and nitroalkanes exhibited strong interactions with all three ILs. Table 6 compares values of γ^∞ in [C4MPyrr]$^+$[Tf$_2$N]$^-$

Table 6. Comparison of Values of γ^∞ in 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide Obtained in this Work with γ^∞ Measured by Kato et al.[12] at $T = 323.15$ K

	$[C4MPyrr]^+[Tf_2N]^-$	
solutes	γ^∞ (this work)	γ^∞ (ref 12)
n-hexane	13.95	12.1
n-heptane	19.69	18.2
n-octane	28.17	25.2
cyclohexane	8.74	7.91
benzene	0.92	0.88
1-hexene	7.51	6.82
2-butanone	0.54	0.55
2-pentanone	0.80	0.68
ethanol	1.73	1.63
2-propanol	1.90	1.77

obtained in this work with γ^∞ measured by Kato et al.[12] at $T = 323.15$ K. In some cases, the overall standard deviation for these solutes is around 6 %, which is within expectations when comparing dilutor technique results to inverse gas chromatography measurements.

The γ^∞ measurements may be used to evaluate the prospective performance of pyrrolidinium-based ILs as solvents for various practical chemical separation problems. This may be achieved by predictive calculations of the infinite dilution activity coefficient ratio of the two solutes in the ionic liquid solvent

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

and the reciprocal of the smaller of the two infinite dilution activity coefficients:

$$k_1^\infty = \frac{1}{\gamma_{1/\mathrm{IL}}^\infty} \qquad (2)$$

Selectivity values (S_{12}^∞) and capacity values (k_1^∞) at infinite dilution are collected in Table 7 for four trial separation problems involving hexane/benzene, hexane/pyridine, cyclohexane/thiophene, and hexane/thiophene separations at 323.15 K. Numerical values for 15 of the 18 IL solvents were taken from the published chemical and engineering literature.[2,6,7,13−19]

In regard to aliphatic/aromatic separations, the calculated selectivity and capacity results reveal that pyrrolidinium-based ILs generally exhibit poorer performance compared to imidazolium-based ILs. The best selectivity was observed for such separations with and 1-ethyl-3-methylimidazolium nitrate ($[EMIM]^+[NO_3]^-$)[20] and 1-ethyl-3-methylimidazolium thiocyanate ($[EMIM]^+[SCN]^-$).[21] The selectivities obtained with pyrrolidinium-based ILs are smaller than those of sulfolane ($S_{\text{hexane/benzene}} = 30.5$), dimethyl sulfoxide ($S_{\text{hexane/benzene}} = 22.7$), and *N*-methyl-2-pyrrolidinone ($S_{\text{hexane/benzene}} = 12.5$).[22] Sulfolane, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone are three of the classical industrial solvents used in such separations. A better capacity value and selectivity may be obtained for relatively short alkyl chains grafted to the pyrrolidinium cation, as observed with 1-propyl-1-methylpyrrolidinium. In fact, long alkyl chains grafted onto the IL cation are known to increase capacity value, while being a detriment to selectivity. Interactions of pyrrolidinium-based ILs with alkanes, thiophene, and pyridine produce interesting selectivities for the potential isolation of sulfur and nitrogen compounds from aliphatic hydrocarbons. The selectivity and the capacity values obtained with 1-propyl-1-methylpyrrolidinium in the removal of nitrogen and sulfur compounds from aliphatic hydrocarbon mixtures, as exemplified by the hexane/pyridine and hexane/thiophene separation problems, appear quite large.

Linear Solvation Energy Relationship (LSER) Correlations. It is fairly straightforward to select a solvent exhibiting a suitable chemical selectivity whenever one has measured infinite dilution activity coefficients for all solutes in need of separation. It is, of course, impractical (and not entirely *possible*) to measure $\gamma_{1,2}^\infty$ values for every possible solute−solvent combination. As an alternative, researchers have come to rely

Table 7. Selectivities (S_{12}^∞) and Capacities (k_1^∞) at Infinite Dilution for Different Separation Problems at 323.15 K

ILs						
anion	cation	hexane/benzene	hexane/pyridine	hexane/thiophene	cyclohexane/thiophene	reference
$[Tf_2N]^-$	1-propyl-1-methylpyrrolidinium	16.69/1.01	26.2/1.59	19.23/1.16	11.88/1.16	this work
	1-butyl-1-methylpyrrolidinium	15.2/1.10	23.64/1.69	17/1.22	10.67/1.22	this work
	1-pentyl-1-methylpyrrolidinium	14.3/1.22	22.13/1.89	15.8/1.35	9.20/1.35	this work
	1-hexyl-1-methylpyrrolidinium	10.2/1.32	14.88/1.92	11.1/1.43	7.4/1.43	7
	1-octyl-1-methylpyrrolidinium	8.4/1.67	11.92/2.38	8.8/1.75	6.1/1.75	7
	1-decyl-1-methylpyrrolidinium	6.4/1.61	8.44/2.20	6.6/1.67	4.7/1.67	7
	methyltributylammonium	7.5/1.11	12.27/1.82	7.8/1.17	5.5/1.17	6
	octyltrimethylammonium	8.5/1.37	13.8/2.22	9/1.45	5.9/1.45	6
	decyltrimethylammonium	5.9/1.41	9.13/2.17	6.46/1.54	4.46/1.54	6
	1-(hexylmethylether)-3-methylimidazolium	9.1/1.23		10.0/1.35	6.4/1.35	13
	1,3-bis(hexylmethylether)imidazolium	4.9/1.67		5.3/1.75	3.7/1.75	13
	4-methyl-*N*-butylpyridinium	18.8/1.43		10.6/1.56	6.1/1.56	14
	triethylsulfonium	21.6/0.91		25.5/1.05	14.3/1.05	15
	trihexyl(tetradecyl)phosphonium	2.7/2.56		2.6/2.5	1.95/2.5	2
	1-(2-methoxyethyl)-1-methylpiperidinium	17.9/1.09	51.56/1.56	20.7/1.26	12.0/1.26	16
	4-(2-methoxyethyl)-4-methylmorpholinium	25.8/0.75	29/1.82	31.7/0.92	16.5/0.92	17
	1-propyl-1-methylpiperidinium	19.8/1.07		22.6/1.22	13.1/1.22	18
	1-butyl-1-methylpiperidinium	15.4/1.27		16.8/1.39	10.4/1.39	19

Table 8. Solute Descriptors of the 43 Organic Compounds Included 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
decane	0.000	0.000	0.000	0.000	5.696	1.7990
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
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
triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538

on predictive models to estimate $\gamma_{1,2}^{\infty}$ values in order to aid in solvent selection.

The Abraham solvation parameter model[23,24] affords a convenient mathematical means to compare and to quantify the solubilizing ability of different ionic liquids using numerical quantities that describe the various types of solute−IL interactions. The magnitude of the different types of solute−IL interactions depends upon the polarity, polarizability, and hydrogen-bonding functional groups contained in both the solute and IL solvent molecules. For ionic liquid solvents, Sprunger et al.[25,26] suggested a modified form of the Abraham model to describe solute transfer from the gas phase to the ionic liquid solvent:

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

and to describe solute transfer from water to the ionic liquid solvent:

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

where P and K_L refer to the solute's condensed phase-to-condensed phase partition coefficient (often the hypothetical water-to-dry IL partition coefficient) and the gas-to-IL partition coefficient, respectively. The term "dry" is used to distinguish

this type of solute transfer process from a direct partitioning process where the IL phase would be in physical contact with the aqueous phase. Each uppercase alphabetic letter in eqs 3 and 4 represents a property of the transferred solute, whereas each lowercase letter corresponds to the complementary property of the IL solvent. The solvent coefficients are given as a paired cation–anion sum, and to allow calculation of the individual cation and anion values the Sprunger et al. set of all of the equation coefficients for the bis(trifluoromethylsulfonyl)-imide anion, $[Tf_2N]^-$, equal to zero. The six Abraham model 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 measured at 298 K (L); and the solute's McGowan volume given in units of (cm^3 mol^{-1})/100 (V). Currently we have published Abraham model expressions that accurately describe the partitioning behavior of neutral solutes in more than 33 monocationic ILs[1−7,27−34] and in six trigeminal (tricationic) ILs[35] using eqs 3 and 4 of the solvation parameter model.

The log P values for partition into the IL from water are computed through eq 5.

$$\log P = \log K_L - \log K_W \qquad (5)$$

The solutes' gas phase partition coefficients into water (K_W) needed for these calculations are given elsewhere.[28] Water-to-IL partition coefficients calculated through eq 5 pertain to thermodynamic transfer processes whereby the solute is transferred to the dry IL from aqueous solution. Log P values defined in this fashion are very useful because predicted log P values permit one to estimate the solute's infinite dilution activity coefficient in the IL, which can in turn be used to compute numerical values of (S_{12}^∞) and (k_1^∞) needed to solve a particular chemical separation problem. Included within the last two columns of Tables 3 to 5 are the log K_L and log P values at 298.15 K for dry $[C3MPyrr]^+[Tf_2N]^-$, $[C4MPyrr]^+[Tf_2N]^-$, and $[C5MPyrr]^+[Tf_2N]^-$, respectively.

Analysis of the 39 experimental log K_L and log P data listed in Table 3 for $[C3MPyrr]^+[Tf_2N]^-$ gave the following two mathematical correlations:

$$\log K_L = -0.466(0.115) + 2.562(0.087)S$$
$$+ 2.505(0.184)A + 0.271(0.107)B + 0.682(0.032)L \qquad (6)$$

$$(N = 39, \quad SD = 0.116, \quad R^2 = 0.976, \quad F = 352.7)$$

and

$$\log P = -0.236(0.170) + 0.908(0.172)S - 1.015(0.239)A$$
$$- 4.691(0.149)B + 3.446(0.143)V \qquad (7)$$

$$(N = 39, \quad SD = 0.143, \quad R^2 = 0.993, \quad F = 985.0)$$

The equation coefficients in eqs 6 and 7 correspond to the ion-specific coefficients for the $[C3MPyrr]^+$ cation because the anion is $[Tf_2N]^-$ and its coefficients are all defined to be zero. This is in accordance with the established computation methodology for calculating ion-specific equation coefficients for ion-specific version of the Abraham model.[25,26] In the corresponding statistical information associated with eqs 6 and 7 the number of experimental values used in the respective regression analysis is denoted by N, the squared correlation

coefficient is R^2, the standard deviation is given by SD, and the Fisher F-statistic is expressed simply as F. Given within parentheses immediately following each calculated equation coefficient is its respective standard error. The $e_p \cdot E$ and $e_k \cdot E$ terms were removed from the respective correlation because the calculated e-coefficients were very small and the standard errors exceeded the numerical values of e. It is important to note that removal of these terms did not adversely affect the predictive ability of either correlation. The derived Abraham model correlations back-calculated the observed log K_L and log P data to within standard deviations of SD = 0.116 (eq 6) and SD = 0.143 (eq 7). Numerical values of the solute descriptors used in the analysis are gathered in Table 8.

The experimental log K_L and log P data in Tables 4 and 5 for $[C4MPyrr]^+[Tf_2N]^-$ and $[C5MPyrr]^+[Tf_2N]^-$ were analyzed in similar fashion, to yield the following respective Abraham model expressions:

$$\log K_L = -0.522(0.087) + 2.388(0.067)S$$
$$+ 2.446(0.154)A + 0.381(0.089)B + 0.711(0.023)L \qquad (8)$$

$$(N = 43, \quad SD = 0.099, \quad R^2 = 0.982, \quad F = 505.0)$$

$$\log P = -0.269(0.135) + 0.747(0.114)S - 1.094(0.213)A$$
$$- 4.594(0.117)B + 3.512(0.110)V \qquad (9)$$

$$(N = 43, \quad SD = 0.133, \quad R^2 = 0.995, \quad F = 1783)$$

and

$$\log K_L = -0.549(0.087) + 2.317(0.092)S$$
$$+ 2.425(0.155)A + 0.385(0.096)B + 0.747(0.023)L \qquad (10)$$

$$(N = 42, \quad SD = 0.097, \quad R^2 = 0.982, \quad F = 400.4)$$

$$\log P = -0.303(0.134) + 0.727(0.113)S - 1.107(0.212)A$$
$$- 4.622(0.116)B + 3.630(0.109)V \qquad (11)$$

$$(N = 42, \quad SD = 0.132, \quad R^2 = 0.995, \quad F = 1888.9)$$

As before, the $e_p \cdot E$ and $e_k \cdot E$ terms were removed because the calculated e-coefficients were small and their standard errors exceeded their numerical values. Equations 8 and 9 pertain to solute transfer to dry $[C4MPyrr]^+[Tf_2N]^-$, and eqs 10 and 11 in turn describe the partition coefficient data for solutes dissolved in $[C5MPyrr]^+[Tf_2N]^-$. Both sets of mathematical correlations back-calculate the observed partition coefficient data to within a standard deviation of less than 0.14 log units. Since both ILs contain the $[Tf_2N]^-$ anion, the calculated coefficients in eqs 8−11 thus correspond to the cation-specific coefficients for $[C4MPyrr]^+$ and $[C5MPyrr]^+$.

■ CONCLUDING REMARKS

The Abraham model correlations that were obtained in the present investigation for $[C3MPyrr]^+[Tf_2N]^-$, $[C4MPyrr]^+[Tf_2N]^-$, and $[C5MPyrr]^+[Tf_2N]^-$ would be expected to provide very reasonable gas-to-dry IL and water-to-dry IL partition coefficient predictions for additional solutes having descriptor values that fall within the range of values given in Table 8. The predicted partition coefficients can be used to estimate infinite dilution activity coefficients of solutes

dissolved in dry $[C3MPyrr]^+[Tf_2N]^-$, $[C4MPyrr]^+[Tf_2N]^-$, and $[C5MPyrr]^+[Tf_2N]^-$. On particular consequence, the present study also expands our library of calculated cation-specific equation coefficients by three, which when pooled with our previously reported equation coefficients for 14 unique anions, allows us to make log K_L, log P, $\gamma_{1,2}^\infty$, S_{12}^∞, and k_1^∞ predictions for an additional 42 ionic liquids containing any one of the three 1-alkyl-1-methylpyrrolidinium cations studied here ($[C3MPyrr]^+$, $[C4MPyrr]^+$, or $[C5MPyrr]^+$) paired with one of the following anions: tetrafluoroborate, hexafluorophosphate, thiocyanate, ethylsulfate, octylsulfate, trifluoromethanesulfonate, dicyanamide, tris(pentafluoroethyl)trifluorophosphate, tetracyanoborate, trifluoroacetate, nitrate, bis(pentafluoroethylsulfonyl)imide, methanesulfonate, and diethylphosphate. 1-Propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, and 1-pentyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide are not included in the count because their Abraham model correlations were determined in the present study and thus would not be additional correlations. A significant portion of our research efforts is now directed toward determining ion-specific equation coefficients for cations and anions that have not been previously studied.

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Notes
The authors declare no competing financial interest.

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