Activity Coefficients at Infinite Dilution of Organic Compounds in Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide Using Inverse Gas Chromatography

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Activity coefficients at infinite dilution γ^∞ of organic compounds in the ionic liquid (IL) trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide were determined using inverse gas chromatography at three temperatures, $T = (302.45, 322.35, \text{ and } 342.45)$ K. Linear free energy relationship (LFER) correlations have been obtained for describing the gas-to-IL and water-to-IL partition coefficients.

Introduction

Ionic liquids (ILs) are commonly defined as substances composed only by ions which are liquid at or close to room temperature. ILs are emerging as alternative green solvents in diverse applications.[1−7] Despite that their properties are not yet deeply understood, publications usually highlight their negligible vapor pressure, thermal and chemical stability, and the possibility to design their physicochemical properties by suitable choice of the anion and the cation. Because of their negligible vapor pressure, ILs are claimed as "green" alternatives for volatile organic solvents (VOCs).

Knowledge of properties of ILs and their mixtures is important for design and process synthesis. Activity coefficients at infinite dilution γ_i^∞ are key pieces of information for the realization of many separation processes that employ ionic liquids. For example, the selectivity between components i and j in an ionic liquid $S_{i,j}^\infty$ ($S_{i,j}^\infty = (\gamma_i^\infty)/(\gamma_j^\infty)$) for the separation process can directly be derived from such data. The activity coefficient gives also information on the interactions between the solute and the ionic liquid. Recently, this thermodynamic property was predicted using the COSMO-RS method.[8−10] Eicke et al.[11] demonstrated that QSPR methods have a very good ability to predict values of ln γ_i^∞ and predict solute−solvent interactions for various solutes in IL solvents. To quantify intermolecular solute−IL interactions, Acree, Abraham, and co-workers reported mathematical correlations based on the general Abraham solvation parameter model for the gas-to-solvent, K, and water-to-solvent, P, partition coefficients.[12−14]

Recently, Sprunger et al.[15,16] modified the Abraham solvation parameter model

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

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

by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. The dependent variables in eqs 1 and 2 are solute descriptors as follows: E and S refer to the excess molar refraction in units of $(\text{cm}^3\cdot\text{mol}^{-1})/10$ and dipolarity/polarizability descriptors of the solute, respectively; A and B are measures of the solute hydrogen-bond acidity and basicity; V is the McGowan volume in units of $(\text{cm}^3\cdot\text{mol}^{-1})/100$; and L is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. Sprunger et al. calculated equation coefficients for 8 cations and 4 anions using a database that contained 584 experimental log K and 571 experimental log P values. No loss in predictive accuracy was observed by separating the equation coefficients into individual cation-specific and anion-specific values. The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more ILs.

In this work, activity coefficients at infinite dilution of 39 polar and nonpolar compounds (alkanes, alkenes, alkynes, cycloalkanes, aromatics, alcohols) have been determined in the ionic liquid trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide at T = (302.45, 322.35, and 342.45) K by gas−liquid chromatography. This ionic liquid has already been studied in the literature. However, it can be found two literature sources[17,18] for the thermodynamic properties of organic compounds in this phosphonium ionic liquid. These data show a large discrepancy. The modified LFER model proposed by Sprunger and co-workers was used to characterize the nature of solute interactions with this ionic liquid. The cation-specific coefficients were estimated using the partition coefficients of 45 organic compounds calculated at 298.15 K.

Experimental Procedures and Results

Materials or Chemicals. The ionic liquid trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, $[\text{P}_{14,666}{}^+]$-$[\text{NTf}_2{}^-]$, was prepared and dried following recently reported methods.[19] The ionic liquid was further dried under vacuum

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Table 1. Thermodynamic Properties of Pure Organic Compounds

T/K	P_1^0/Pa	ρ_1/kg·m^{-3}	ref	T/K	P_1^0/Pa	ρ_1/kg·m^{-3}	ref	T/K	P_1^0/Pa	ρ_1/kg·m^{-3}	ref	T/K	P_1^0/Pa	ρ_1/kg·m^{-3}	ref
	Hexane				Methanol				Cycloheptane				Tetrachloromethane		
302.45	24210.8	651.1	22,23	302.45	21131.5	782.7	41,42	302.45	4093.9	803.3	29,31	302.45	18332.6	1577.6	55,56
322.35	52499.3	632.6		322.35	53703.7	763.5		322.35	4499.8	786.1		322.35	40396.7	1554.3	
342.45	102946.7	613.0		342.45	121883.3	743.9		342.45	4916.8	768.4		342.45	80459.9	1530.5	
	3-Methylpentane				Ethanol				Benzene				Acetonitrile		
302.45	30193.3	657.7	24,25	302.45	10032.9	781.3	43,44	302.45	15412.3	869.1	24,32	302.45	14420.8	770.9	57,58
322.35	63600.9	637.8		322.35	28380.9	763.9		322.35	35082.5	847.7		322.35	32864.3	748.1	
342.45	121982.6	616.2		342.45	70240.0	745.8		342.45	71753.2	825.8		342.45	67951.5	724.3	
	Heptane				1-Propanol				Toluene				Nitromethane		
302.45	7526.3	675.6	26,27	302.45	3792.7	796.1	33,44	302.45	4785.1	858.2	33,34	302.45	5999.6	1117.2	55,59
322.35	18269.1	658.4		322.35	11683.1	779.7		322.35	12026.7	839.4		322.35	15131.0	1090.9	
342.45	39486.7	641.0		342.45	31874.0	762.7		342.45	26620.4	820.1		342.45	34112.5	1063.4	
	Octane				2-Propanol				Ethylbenzene				1-Nitropropane		
302.45	2362.3	695.2	22,28	302.45	7496.0	777.2	45,46	302.45	1720.7	864.7	35,36	302.45	1704.6	996.5	55,25
322.35	6456.9	678.7		322.35	22673.7	759.8		322.35	4626.3	855.2		322.35	4905.4	975.3	
342.45	15372.2	661.1		342.45	58865.7	741.6		342.45	11045.1	844.8		342.45	12166.7	953.2	
	Nonane				2-Methyl-1-Propanol				1-Hexene				Pyridine		
302.45	687.9	711.0	29,28	302.45	2019.6	795.1	47,48	302.45	29634.0	664.4	37,29	302.45	3509.4	973.0	60,61
322.35	2112.0	695.1		322.35	7039.7	778.2		322.35	62932.0	645.6		322.35	9258.1	953.6	
342.45	5635.2	678.6		342.45	20303.5	760.1		342.45	121361.8	626.6		342.45	21538.3	930.7	
	Decane				1-Butanol				1-Hexyne				Thiophene		
302.45	242.8	723.5	29,25	302.45	1181.3	802.5	49,44	302.45	20755.1	707.6	29,25	302.45	13012.0	1051.5	62,61
322.35	834.5	707.9		322.35	4347.4	786.8		322.35	46343.0	688.6		322.35	30183.6	1027.5	
342.45	2431.2	691.9		342.45	13125.3	770.8		342.45	94883.7	668.5		342.45	62828.5	1002.3	
	Undecane				Diethylether				1-Hexyne				Formaldehyde		
302.45	77.0	733.9	29,30	302.45	83734.1	702.8	50,51	303.15	7078.6	724.2	29,25	302.45	591761.3	724.3	25,25
322.35	301.9	719.1		322.35	165971.6	678.7		322.35	16555.3	706.7		322.35	1041122.7	682.7	
342.45	981.7	703.9		342.45	302135.9	652.5		342.45	36382.2	687.7		342.45	1726076.9	636.2	
	Methylcyclopentane				Diisopropylether				2-Butanone				Propionaldehyde		
302.45	22018.1	740.7	24,29	302.45	23957.6	716.3	52,25	302.45	15783.8	795.6	38,39	302.45	49551.4	786.2	29,25
322.35	47699.4	721.1		322.35	52506.6	695.1		322.35	38462.4	774.2		322.35	106243.6	762.5	
342.45	93728.8	700.6		342.45	103880.3	672.6		342.45	97682.6	752.1		342.45	209796.8	737.5	
	Cyclohexane				Chloroform				2-Pentanone				Butyraldehyde		
302.45	15724.8	769.9	24,28	302.45	31412.0	1469.0	41,39	302.45	5842.7	798.3	29,29	302.45	17645.4	794.7	29,63
322.35	35214.2	750.8		322.35	67338.7	1430.6		322.35	14476.2	778.5		322.35	40281.0	773.3	
342.45	70871.0	731.2		342.45	130924.9	1392.1		342.45	32521.1	758.2		342.45	84116.5	751.5	
	Methylcyclohexane				Dichloromethane				1,4-Dioxane						
302.45	7572.1	760.9	24,27	302.45	97206.8	1307.9	53,54	302.45	5928.3	1022.8	40,34				
322.35	17861.6	743.7		322.35	175130.4	1269.4		322.35	15203.4	999.8					
342.45	37725.8	726.2		342.45	300203.0	1229.7		342.45	34774.6	976.8					

for 4 days at 343 K to remove trace moisture. The water mass fraction of the ionic liquid, as determined by coulometric Karl Fischer titration, was $(57 \pm 5) \cdot 10^{-6}$. The solutes were purchased from Aldrich with a purity higher than 99.5 %. All support materials were purchased from Supelco.

Apparatus and Experimental Procedure. Inverse chromatography experiments were carried out using a Varian CP-3800 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. Helium flow rate was adjusted to obtain adequate retention times. Exit gas flow rates were determined using a soap bubble flow meter with an uncertainty of $\pm$ 0.1 $\text{cm}^3 \cdot \text{min}^{-1}$. Methane was used to determine the column hold-up time. 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 corresponding chromatograms were obtained using Galaxie software.

Column packing of 1 m length containing a mass fraction of (20 and 30) % of stationary phases (RTIL) on Chromosorb W-HP (60 to 80 mesh) was prepared using the rotary evaporator technique. After evaporation of the chloroform under vacuum, the support was equilibrated at 323 K during 6 h. 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 an uncertainty of $\pm$ 0.0003 g. A volume of the headspace vapor of samples of (1 to 5) μL was introduced to be in infinite dilution conditions. Each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible to within (0.01 to 0.03) min. To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the helium stream, the measurements of retention times were repeated systematically every day for three selected solutes.

Theoretical Basis. The retention data determined with inverse chromatography experiments were used to calculate activity coefficients at infinite dilution of the solute in the ionic liquid. The standardized retention volume V_N was calculated with the following usual relationship[20]

$$V_N = J \cdot U_0 \cdot t_R' \cdot \frac{T_{\text{col}}}{T_r} \cdot \left(1 - \frac{P_{\text{ow}}}{P_o}\right) \tag{3}$$

The adjusted retention time t_R' was taken as a difference between the retention time of a solute and that of the methane. T_{col} is the column temperature; U_0 is the flow rate of the carrier gas measured at room temperature T_r; P_{ow} is the vapor pressure of

Table 2. Experimental Activity Coefficients at Infinite Dilution γ_i^∞ of 39 Organic Compounds in Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide at Various Temperatures

	experimental γ_i^∞ at T/K						
solutes	302.45	322.35	342.45	A	B/K^{-1}	R^2	γ_i^∞ at 298.15 K
hexane	1.09	1.04	1.01	−0.55	191.53	0.989	1.09
3-methylpentane	1.04	0.98	0.94	−0.81	254.97	0.994	1.05
heptane	1.27	1.22	1.19	−0.29	159.70	0.995	1.28
octane	1.48	1.42	1.40	−0.12	155.81	0.980	1.49
nonane	1.87	1.80	1.74	−0.02	195.51	1.000	1.89
decane	1.97	1.89	1.84	0.11	170.25	0.995	1.98
undecane	2.32	2.18	2.10	0.00	253.51	0.993	2.34
methylcyclopentane	0.85	0.80	0.77	−0.97	244.03	0.997	0.86
cyclohexane	0.83	0.78	0.75	−1.10	275.53	0.994	0.84
methylcyclohexane	0.92	0.89	0.86	−0.68	182.22	0.994	0.93
cycloheptane	0.83	1.81	3.59	12.37	−3799.04	1.000	0.69
benzene	0.39	0.39	0.39	−0.88	−17.84	0.983	0.39
toluene	0.46	0.46	0.47	−0.54	−71.06	0.996	0.46
ethylbenzene	0.54	0.57	0.59	0.15	−233.60	0.988	0.53
1-hexene	0.91	0.87	0.85	−0.74	194.84	0.976	0.92
1-hexyne	0.70	0.69	0.67	−0.74	115.42	0.999	0.71
1-heptyne	0.77	0.78	0.80	0.03	−90.02	0.972	0.76
2-butanone	0.28	0.27	0.23	−2.99	526.29	0.862	0.29
2-pentanone	0.31	0.32	0.33	−0.42	−230.93	0.995	0.30
1,4-dioxane	0.51	0.49	0.48	−1.32	197.42	0.972	0.52
methanol	1.29	0.98	0.86	−3.27	1061.84	0.971	1.33
ethanol	1.56	1.23	1.01	−3.26	1119.29	0.999	1.64
1-propanol	1.53	1.21	1.00	−3.23	1105.39	1.000	1.61
2-propanol	1.55	1.22	0.99	−3.39	1158.34	1.000	1.64
2-methyl-1-propanol	1.49	1.15	0.95	−3.41	1149.05	0.997	1.56
1-butanol	1.62	1.26	1.04	−3.28	1136.18	0.997	1.70
diethyl ether	0.62	0.59	0.57	−1.13	195.94	0.987	0.62
diisopropyl ether	0.93	0.90	0.87	−0.61	162.61	0.992	0.94
chloroform	0.29	0.31	0.32	−0.50	−219.99	0.996	0.29
dichloromethane	0.23	0.25	0.27	−0.08	−417.91	0.991	0.23
tetrachloromethane	0.55	0.55	0.55	−0.58	−5.34	0.909	0.55
acetonitrile	0.56	0.50	0.46	−2.26	503.90	0.999	0.57
nitromethane	0.77	0.64	0.58	−2.82	771.67	0.986	0.80
1-nitropropane	2.19	1.62	1.35	−3.40	1259.49	0.991	2.29
pyridine	0.52	0.41	0.34	−4.43	1142.22	0.999	0.55
thiophene	0.42	0.40	0.38	−1.77	273.07	0.980	0.43
formaldehyde	0.06	0.06	0.07	−1.36	−449.74	0.999	0.06
propionaldehyde	0.35	0.33	0.31	−2.14	331.62	1.000	0.36
butyraldehyde	0.38	0.36	0.35	−1.55	172.04	0.975	0.38

Table 3. Experimental Activity Coefficients at Infinite Dilution at 302.45 K of Some Solutes with Two Columns Containing Different Amounts of Trihexyl(tetradecyl)phosphonium Bis(Trifluoromethylsulfonyl)imide

mass of IL	γ_i^∞							
(g)	hexane	cyclohexane	benzene	1-hexene	methanol	2-butanone	chloroform	acetonitrile
0.268	1.08	0.82	0.39	0.91	1.26	0.27	0.29	0.54
0.479	1.09	0.83	0.39	0.91	1.29	0.28	0.29	0.56

water at T_r; and P_o is the pressure at the column outlet. The factor J in eq 3 corrects for the influence of the pressure drop along the column and is given by eq 4[21]

$$J = \frac{3}{2} \cdot \frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \tag{4}$$

where P_i and P_o are, respectively, the inlet and outlet pressures.

The activity coefficient at infinite dilution of a solute 1 in the stationary phase 2 (RTIL) was calculated with the following expression[20]

$$\ln \gamma_{1,2}^\infty = \ln\left(\frac{n_2 \cdot R \cdot T}{V_N \cdot P_1^0}\right) - P_1^0 \cdot \frac{B_{11} - V_1^0}{RT} + \frac{2B_{13} - V_1^\infty}{RT} \cdot J \cdot P_0 \tag{5}$$

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. The values of P_1^0 result from correlated experimental data. The molar volume of the solute V_1^0 was determined from experimental densities, and the partial molar volumes of the solutes at infinite dilution V_1^∞ were assumed to be equal to V_1^0. Values of P_1^0 and densities ρ_1^0 are given in Table 1 with all references[22−63] used for the calculation of these parameters. Values of B_{11} and B_{13} have been estimated according to Tsonopolous's method.[64−66] Critical parameters and acentric factors used for the calculations were taken from the literature.[29,67]

Results and Discussion

Activity Coefficients and Selectivity at Infinite Dilution. The values of γ_i^∞ for 39 solutes in trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide obtained at different temperatures are listed in Table 2.

Table 4. Comparison of γ^{∞} Values Obtained in This Work with γ^{∞} Values Measured by Letcher et al.[18] and Banerjee et al.[17] at T = 303.15 K

solutes	Banerjee et al.	Letcher et al.	this work
		γ_i^{∞}	
hexane	0.77	1.09	1.09
heptane	0.78	1.25	1.27
octane	0.84	1.31	1.48
cyclohexane	0.61	0.77	0.83
1-hexene	0.50	0.88	0.91
1-hexyne	0.45	0.66	0.70
1-heptyne	0.49	0.59	0.77
methanol	0.94	1.25	1.29
ethanol	0.88	1.34	1.56
benzene	0.41	0.38	0.39

The uncertainty of γ_i^{∞} values may be obtained from the law of propagation of errors. The following measured parameters exhibit uncertainties which must be taken into account in the error calculations with their corresponding standard deviations: the adjusted retention time t_R', ± 0.01 min; the flow rate of the carrier gas, ± 0.1 $\text{cm}^3 \cdot \text{min}^{-1}$; mass of the stationary phase, ± 2 %; the inlet and outlet pressures, ± 0.002 bar; the temperature of the oven, ± 0.1 K. The main source of uncertainty in the calculation of the net retention volume is the determination of the mass of the stationary phase. The estimated uncertainty in determining the net retention volume V_N is about ± 2 %. Taking into account that thermodynamic parameters are also subject to an error, the resulting uncertainty in the γ_i^{∞} values is about ± 3 %.

The values of γ_i^{∞} have been approximated by the linear regression

$$\ln \gamma_i^{\infty} = A + \frac{B}{T} \tag{6}$$

The coefficients A and B, the correlation coefficients R^2, and the values of γ_i^{∞} (298.15 K) calculated with these coefficients are also given in Table 2. The quality of the linear regression is very good because the correlation coefficients lie between 0.96 and 0.99.

Two columns were prepared containing various amounts of ionic liquids to investigate the effects of adsorption on the retention mechanisms. Table 3 reports infinite dilution activity coefficients of some selected solutes at 302.45 K measured with two columns. The difference between both sets of γ_i^{∞} values is of the order of the experimental uncertainty. Most of the solutes are retained mainly by partition, and the experimental results are not affected by solute adsorption onto the solid support. As

Table 6. Experimental log K and log P Values for Solutes Dissolved in Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide at 298.15 K

solute	log K_{obs}	log P_{obs}
hexane	2.184	4.004
3-methylpentane	2.105	3.945
heptane	2.639	4.599
octane	3.084	5.194
nonane	3.492	5.642
decane	3.976	6.236
undecane	4.413	6.793
methylcyclopentane	2.330	3.500
cyclohexane	2.493	3.393
methylcyclohexane	2.776	4.026
benzene	2.839	2.209
toluene	3.290	2.640
ethylbenzene	3.701	3.121
1-hexene	2.177	3.337
1-hexyne	2.429	2.639
1-heptyne	3.005	3.445
2-butanone	3.003	0.283
2-pentanone	3.365	0.785
1,4-dioxane	3.118	−0.592
methanol	2.184	−1.556
ethanol	2.419	−1.251
1-propanol	2.879	−0.681
2-propanol	2.538	−0.942
2-methyl-1-propanol	3.191	−0.109
1-butanol	3.346	−0.114
diethyl ether	1.887	0.717
diisopropyl ether	2.265	1.215
chloroform	2.652	1.862
dichloromethane	2.405	1.445
tetrachloromethane	2.609	2.799
acetonitrile	2.693	−0.157
nitromethane	2.958	0.008
pyriline	3.349	−0.091
thiophene	2.887	1.847
propanal	2.360	−0.160
butanal	2.778	0.448
carbon dioxide	−0.024	0.056
ethene	0.094	1.034
propene	0.542	1.512
1,3-butadiene	0.940	1.390
butene	0.858	1.868

Table 5. Selectivity Values S_{12}^{∞} for Different Separation Problems: (a) Hexane−Benzene, (b) Hexane−Methanol, (c) Hexane−Thiophene

		S_{12}^{∞}			
solvent	T/K	(a)	(b)	(c)	ref
trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide	298.15	2.8	0.8	2.6	this work
trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate	308.15	1.5	-	-	68
trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl) trifluorophosphate	308.15	3.3	0.5	-	69
tributylmethylphosphonium methylsulfate	308.15	10.2	-	-	70
sulfolane	298.15	20.5	-	-	71
1-ethyl-3-methylimidazolium tetrafluoroborate	298.15	61.6	290.4	-	72
1-hexyl-3-methylimidazolium tetrafluoroborate	298.15	22.3	29.2	-	72
1-octyl-3-methylimidazolium tetrafluoroborate	298.15	10.5	12.1	-	72
1-hexadecyl-3-methylimidazolium tetrafluoroborate	298.15	2.8	2.2	2.2	73
1-ethyl-3-methylimidazolium ethylsulfate	298.15	41.4	-	-	74
1-butyl-3-methylimidazolium octylsulfate	298.15	5.5	4.4	6.5	75
1-hexyl-3-methylimidazolium hexafluorophosphate	298.15	21.6	10.2	-	76
n-acryloyloxypropyl-*N*-methylimidazolium bromide	313.15	27.6	551.6	69.2	77
n-methacryloyloxyhexyl-*N*-methylimidazolium bromide	313.15	50.4	820	82	77
1-propenyl-3-methyl-imidazolium bromide	323.15	7	139.3	16.9	78
1-propenyl-3-octyl-imidazolium bromide	323.15	6.4	52.3	9.6	78
1-propyl boronic acid-3-octyl-imidazolium bromide	323.15	9.91	455.7	15.2	78
1-propyl boronic acid-3-decyl-imidazolium bromide	323.15	4.1	109	6.9	78
1-propyl boronic acid-3-dodecyl-imidazolium bromide	323.15	3.8	116.3	5.2	78

Table 7. Solute Descriptors of Compounds Studied

solute	*E*	*S*	*A*	*B*	*V*	*L*
hexane	0.000	0.000	0.000	0.000	0.9540	2.668
3-methylpentane	0.000	0.000	0.000	0.000	0.9540	2.581
heptane	0.000	0.000	0.000	0.000	1.0949	3.130
octane	0.000	0.000	0.000	0.000	1.2358	3.677
nonane	0.000	0.000	0.000	0.000	1.3767	4.182
decane	0.000	0.000	0.000	0.000	1.5176	4.686
undecane	0.000	0.000	0.000	0.000	1.6585	5.191
methylcyclopentane	0.225	0.100	0.000	0.000	0.8454	2.907
cyclopentane	0.263	0.100	0.000	0.000	0.7045	2.477
cyclohexane	0.305	0.100	0.000	0.000	0.8454	2.964
cycloheptane	0.350	0.100	0.000	0.000	0.9863	3.704
methylcyclohexane	0.244	0.060	0.000	0.000	0.9863	3.319
benzene	0.610	0.520	0.000	0.140	0.7176	2.786
toluene	0.601	0.520	0.000	0.140	0.8573	3.325
ethylbenzene	0.613	0.510	0.000	0.150	0.9982	3.788
1-hexene	0.078	0.080	0.000	0.070	0.9110	2.572
1-heptene	0.092	0.080	0.000	0.070	1.0519	3.063
1-octene	0.094	0.080	0.000	0.070	1.1928	3.568
1-hexyne	0.166	0.220	0.100	0.120	0.8680	2.510
1-heptyne	0.160	0.230	0.090	0.100	1.0089	3.000
1-octyne	0.155	0.220	0.090	0.100	1.1498	3.521
2-butanone	0.166	0.700	0.000	0.510	0.6879	2.287
2-pentanone	0.143	0.680	0.000	0.510	0.8288	2.755
1,4-dioxane	0.329	0.750	0.000	0.640	0.6810	2.892
methanol	0.278	0.440	0.430	0.470	0.3082	0.970
ethanol	0.246	0.420	0.370	0.480	0.4491	1.485
1-propanol	0.236	0.420	0.370	0.480	0.5900	2.031
2-propanol	0.212	0.360	0.330	0.560	0.5900	1.764
2-methyl-1-propanol	0.217	0.390	0.370	0.480	0.7309	2.413
1-butanol	0.224	0.420	0.370	0.480	0.7309	2.601
diethyl ether	0.041	0.250	0.000	0.450	0.7309	2.015
diisopropyl ether	−0.060	0.160	0.000	0.580	1.0127	2.530
chloroform	0.425	0.490	0.150	0.020	0.6167	2.480
dichloromethane	0.387	0.570	0.100	0.050	0.4943	2.019
tetrachloromethane	0.458	0.380	0.000	0.000	0.7391	2.823
acetonitrile	0.237	0.900	0.070	0.320	0.4042	1.739
nitromethane	0.313	0.950	0.060	0.310	0.4237	1.892
pyridine	0.631	0.840	0.000	0.520	0.6753	3.022
thiophene	0.687	0.560	0.000	0.150	0.6411	2.943
propanal	0.196	0.650	0.000	0.450	0.5470	1.815
butanal	0.187	0.650	0.000	0.450	0.6879	2.270
carbon dioxide	0.000	0.280	0.050	0.100	0.2809	0.058
ethene	0.107	0.100	0.000	0.070	0.3474	0.289
propene	0.103	0.080	0.000	0.070	0.4883	0.946
1,3-butadiene	0.320	0.230	0.000	0.100	0.5862	1.543
butene	0.100	0.080	0.000	0.070	0.6292	1.529

observed with imidazolium-based ionic liquids, cations with a long alkyl chain length tend to increase the solubility of most organic compounds in IL and to limit the adsorption contribution in the retention mechanism. The results of γ_i^∞ suggest that the intermolecular interactions between the ionic liquid and the solute become stronger with an increasing number of polarizable electrons present in double bonds and aromatic rings, probably due to the increasing strength of ion-induced dipole interactions. The following trend was observed in the ionic liquid studied: γ_i^∞ *n*-hexane > γ_i^∞ *n*-hexene > γ_i^∞ *n*-hexyne > γ_i^∞ benzene. The activity coefficients of the linear *n*-alkanes, *n*-alkynes, alkylbenzenes, ketones, and aldehydes increase with increasing chain length.

The activity coefficients are below unity apart from the alkanes and alcohols indicating a strong affinity of the solutes for the ionic liquid. The γ_i^∞ values of *n*-alkanes are higher than the values obtained with cyclohexane, alkenes, alkynes and aromatics. Introduction of a double or triple bond in the n-alkanes decreases the γ_i^∞ values. Cyclization of the alkane skeleton reduces the value of γ_i^∞ in comparison to that of the corresponding linear alkanes (e.g., hexane). Aromatics have smaller γ_i^∞ values, this is probably due to the interaction of their delocalized π electrons with the positive charge on the cation of the ionic liquid.

In Table 4, our results are compared with activity coefficients measured by Banerjee et al.[17] and Letcher et al.[18] Our measured activity coefficients at 302.45 K are in good agreement with literature values of Letcher et al. at 303.15 K except for the *n*-alkyne solutes. Indeed, the γ_i^∞ values measured by Letcher decrease with increasing chain length while our values increase. The only explanation we found is the difference between the vapor pressure value of the pure compound used to estimate activity coefficients. For example, the vapor pressure of 1-heptyne used by Letcher is 8580 Pa, while the experimental value used in this work is 7080 Pa at 303.15 K. To check the quality of our thermodynamic data, we also used Design Institute for Physical Properties Data (DIPPR)[25] for 1-heptyne, and we found 7146 Pa. This illustrates the importance of thermodynamic data of the pure component used for the calculation of the activity coefficient. This observation may also explain the difference trend with temperature for some solutes. Indeed, γ_i^∞ values of *n*-alkanes measured by Letcher slightly increase with an increase of the temperature, while our data slightly decrease. The values obtained by Banerjee are systematically lower than the data presented in this work. These differences are not due to the thermodynamic properties of pure compounds used in the activity coefficient calculation but to the determination of the mass of the stationary phase, the flow rate, or the purity of the ionic liquids.

Table 5 shows selectivities S_{12}^∞ for different separation problems: hexane/benzene, hexane/methanol, hexane/thiophene, cyclohexane/thiophene for other ionic liquids based on 1-alkyl-3-methylimidazolium cation and for few solvents at different temperatures. The selectivities for the investigated IL are very low compared to the value obtained with imidazolium-based ionic liquids, indicating the limited potential of this phosphonium IL for separation. For instance, the selectivity for hexane/benzene is 2.2, while it is 60.1 with 1-butyl-3-methylimidazolium tetrafluoroborate or 30.5 with sulfolane used commercially for separating aliphatic/ aromatic hydrocarbons. As observed with imidazolium-based ionic liquids, phosphonium ILs with a long alkyl chain on the cation have a low selectivity. It is obvious that the chemical nature of the cation and the anion plays an important role in separation of mixtures containing polar and aliphatic compounds.

LSER Characterization. The experimental activity coefficient data measured here can be used to calculate the Abraham model ion-specific equation coefficients for the trihexyl(tetradecyl)phosphonium cation for both the gas-to-IL (see eq 1) and water-to-IL (see eq 2) partitioning processes. To calculate the equation coefficients for the trihexyl(tetradecyl)phosphonium cation, one first extrapolates the measured infinite dilution activity coefficients, $\gamma_{\text{solute}}{}^\infty$, to 298 K and then coverts the resulting numerical values to log *K* values through eq 7

$$\log K = \log\left(\frac{RT}{\gamma_{\text{solute}}{}^\infty P_{\text{solute}}{}^{\text{o}} V_{\text{solvent}}}\right) \tag{7}$$

or log *P* values for partition from water to the ionic liquid through eq 8

$$\log P = \log K - \log K_{\text{w}} \tag{8}$$

The calculation of log *P* requires knowledge of the solute's gas phase partition coefficient into water, K_{w}, which is available for most of the solutes being studied. We have tabulated in Table 1 the log *P* and log *K* values at 298 K calculated from activity coefficient data in Table 2. Also included in the table are the log *P* and log *K* values for carbon dioxide, ethane, propene, 1,3-butadiene, and butane. These later values were calculated from measured Henry's law constants and experimental solubility data taken from the published literature.[79]

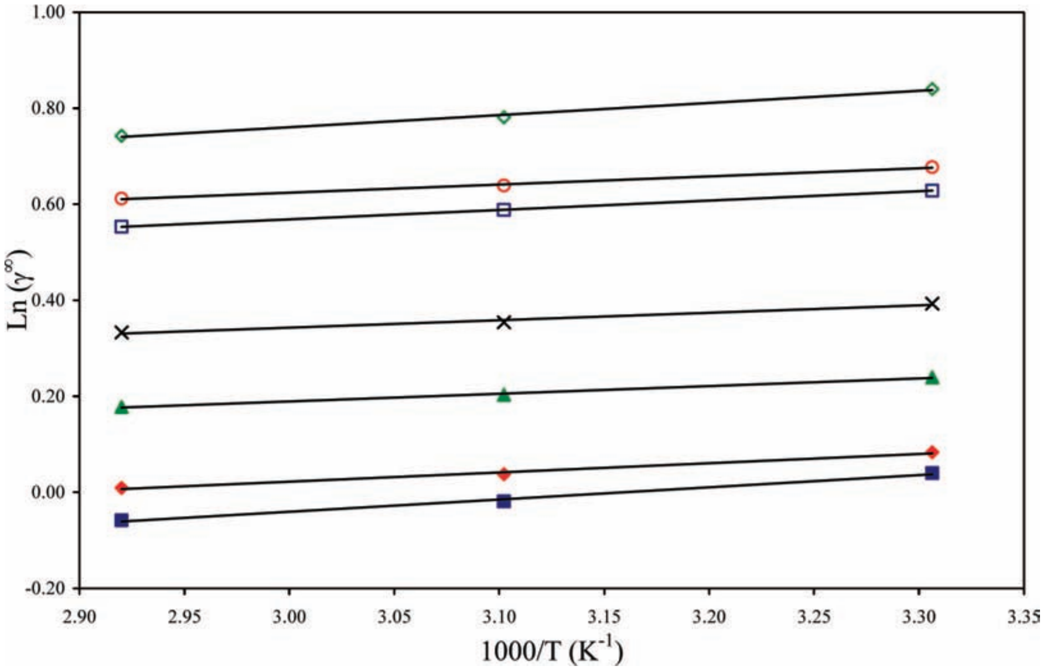

Figure 1. Plot of ln(γ^∞) versus 1/T for the alkanes. ■, Hexane; ◆, 3-Methylpentane; ▲, Heptane; ×, Octane; □, Nonane; ○, Decane; ◇, Undecane.

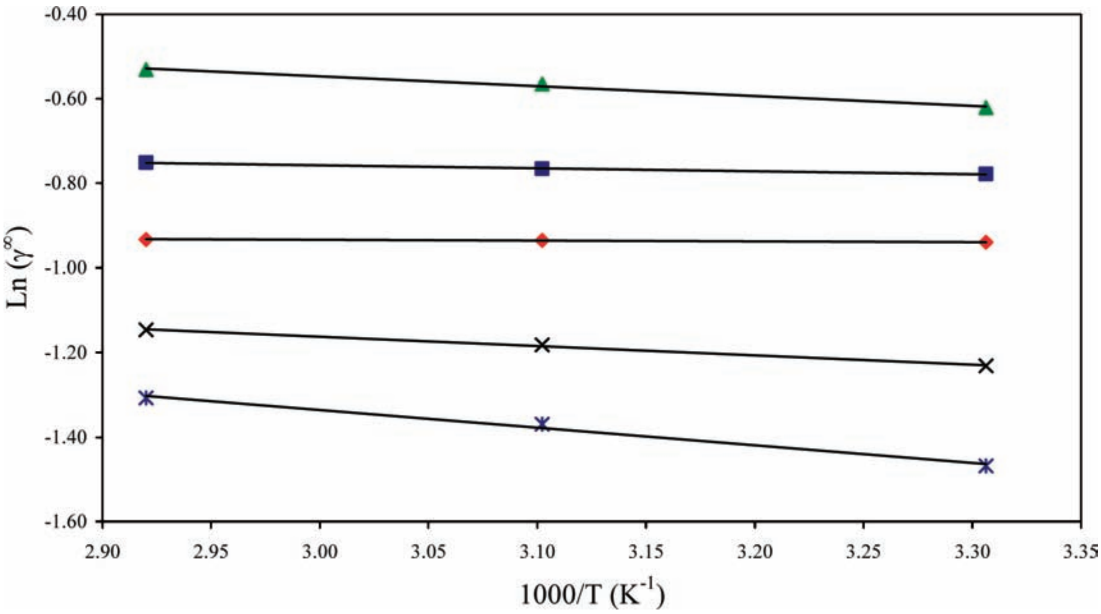

Figure 2. Plot of ln (γ^∞) versus 1/T for the aromatics and chloroalkanes. *, Dichloromethane; ×, Chloroform; ◆, Benzene; ■, Toluene; ▲, Ethylbenzene.

Analysis of the experimental log K and log P data in Table 1 gave

$$\log K = -0.447(0.066) - 0.619(0.144)E + 1.666(0.137)S + 2.262(0.182)A + 0.031(0.157)B + 0.957(0.021)L \quad (N = 41,\ \mathrm{SD} = 0.115,\ R^2 = 0.985,\ F = 466.5) \tag{9}$$

$$\log P = -0.261(0.101) - 0.124(0.163)E + 0.020(0.167)S - 1.334(0.215)A - 4.986(0.183)B + 4.304(0.093)V \quad (N = 41,\ \mathrm{SD} = 0.133,\ R^2 = 0.996,\ F = 1767.7) \tag{10}$$

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. Solute descriptors used in the analysis are given in Table 7. Equations 9 and 10 provide a very accurate mathematical description of the experimental log K and log P values as shown in Figures 3 and 4, respectively.

As noted above, our experimental activity coefficients at 302.45 K are in reasonably good agreement with the published values measured by Letcher et al. at 303.15 K. Both sets of data were measured at temperatures only slightly above 298.15 K, and extrapolation of the measured values back to the common temperature of 298.15 K involves only a small numerical correction. It is possible to combine the partition coefficient data in Table 1 and partition coefficients calculated from the Letcher et al. data into the same regression analysis

$$\log K = -0.406(0.058) - 0.576(0.123)E + 1.602(0.125)S + 2.338(0.156)A - 0.009(0.147)B + 0.959(0.018)L \quad (N = 59,\ \mathrm{SD} = 0.112,\ R^2 = 0.982,\ F = 587.6) \tag{11}$$

and

$$\log P = -0.155(0.092) - 0.163(0.146)E - 0.029(0.157)S - 1.271(0.192)A - 5.042(0.179)B + 4.246(0.085)V$$
$$(N = 59, \mathrm{SD} = 0.136, R^2 = 0.996, F = 2544.8) \quad (12)$$

The correlations obtained from such analyses are essentially identical to those derived from our data alone. Combination of the data sets does lead to slightly improved statistics resulting from the larger number of experimental data used in deriving eqs 11 and 12. The combined database does contain four additional solutes (cyclopentane, 1-heptene, 1-heptyne, and 1-octyne). From a predictive standpoint eqs 11 and 12 are preferred as the derived correlations are based on a slightly larger number of compounds and data points.

Each calculated coefficient corresponds to the sum of the respective cation-specific and anion-specific contribution. In

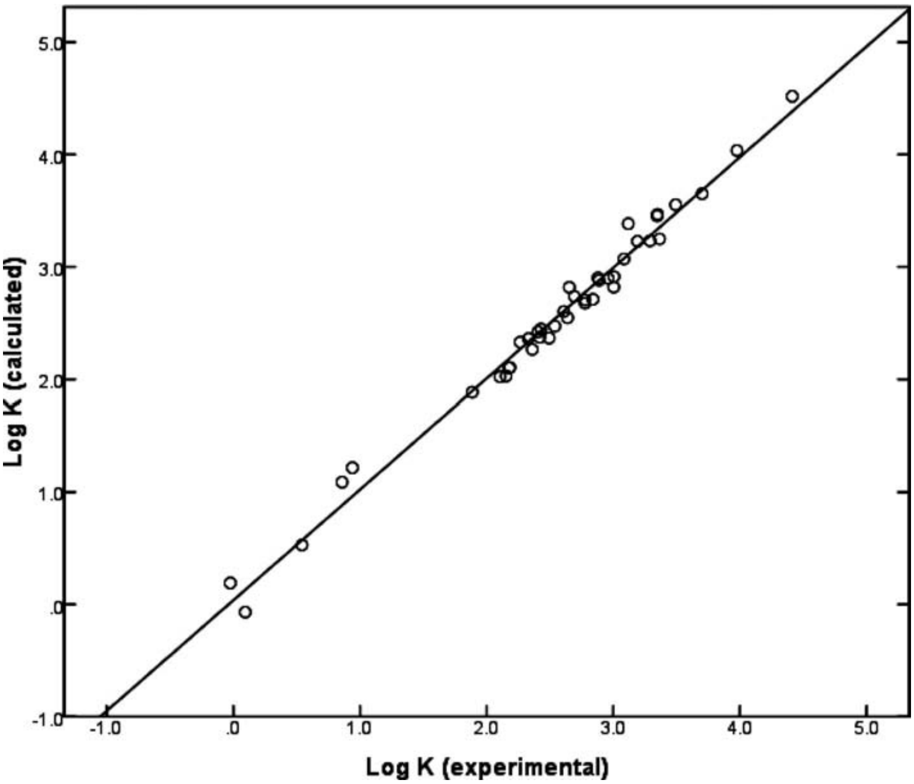

Figure 3. Comparison of observed log K data versus calculated values based on eq 9.

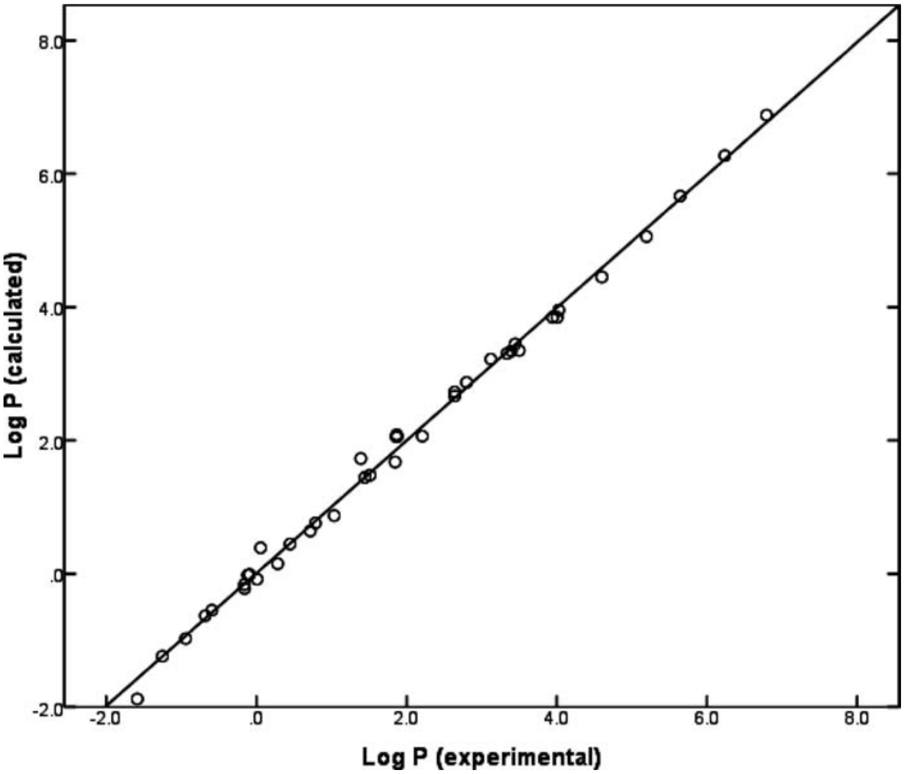

Figure 4. Comparison of observed log P data versus calculated values based on eq 10.

establishing the computation methodology, the equation coefficients for the bis(trifluoromethylsulfonyl)imide were set equal to zero to provide a reference point from which all other equation coefficients would be calculated. The equation coefficients in eqs 11 and 12 thus correspond to the ion-specific coefficients for the trihexyl(tetradecyl)phosphonium cation. As noted in previous papers, the cation-specific and anion-specific equation coefficients can be combined to yield predictive equations for the different ionic liquids. To date, we have reported equation coefficients for nine cations (counting trihexyl(tetradecyl)phosphonium) and four anions (bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, and ethylsulfate).[16] The four sets of reported anion-specific equation coefficients can be combined with the values reported here for trihexyl(tetradecyl)phosphonium to give correlations for predicting both log K and log P values for solutes dissolved in trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, trihexyl(tetradecyl)phosphonium hexafluorophosphate, trihexyl(tetradecyl)phosphonium tetrafluoroborate, and trihexyl(tetradecyl)phosophonium ethylsulfate.

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