J. Chem. Eng. Data **2007,** *52,* 2306−2314

Density and Surface Tension Measurements of Imidazolium-, Quaternary Phosphonium-, and Ammonium-Based Room-Temperature Ionic Liquids: Data and Correlations

Prem Kilaru,[†] Gary A. Baker,[‡] and Paul Scovazzo*[,†]

Department of Chemical Engineering, University of Mississippi, 134 Anderson Hall, University, Mississippi 38677, and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110

Presented are experimental densities and surface tensions of imidazolium-, quaternary ammonium-, and phosphonium-based room-temperature ionic liquids (RTILs) in the temperature range of (298 to 350) K. Densities of the RTILs decrease slightly with temperature in the studied range (298 to 333) K. At 298 K, the densities of the phosphonium-based RTILs ranged from (0.88 to 1.05) g·cm^{-3}, while those of the ammonium-based RTILs ranged from (1.08 to 1.37) g·cm^{-3}. The volume expansivities of phosphonium and ammonium RTILs at 1 atm and 298 K are in the range of (5.5 to 6.5)·10^{-4} K^{-1}. Surface tension and temperature relationships were established using the van der Waals−Guggenheim equation, $\sigma = E^s(1 - T/T_c)^n$, where $n \approx 1$, for the RTILs studied. The Macleod−Sugden−Wright (MSW) equation was used to correlate surface tension with the respective molar volume of the various RTILs. The developed equation can accurately correlate surface tension for this grouping of RTILs with a maximum estimated error of 0.15 % within the temperature ranges considered.

Introduction

Room-temperature ionic liquids (RTILs) are three-dimensional networks of ions,[1] with hydrocarbon tails on the cationic structures, which remain in their molten state at or below 150 °C.[2] In contrast to their more mundane organic solvent counterparts, RTILs have a very low vapor pressures and are hence treated as green solvents for many organic reactions,[3] liquid−liquid extractions,[4] gas−liquid absorption,[5] membrane-based bioseparations,[6] gas separations,[7−9] and other areas. RTILs are generally thermally stable (> 250 °C),[10] nontoxic, nonflammable materials with tunable physiochemical properties such as density, viscosity, surface tension, thermal conductivity, and solubility of various liquid and gaseous solutes.[11−13] There has been a considerable growth of research on RTILs as possible replacements for conventional organic solvents. Some of this research focused on understanding the effects of structural variation on the physiochemical properties of RTILs,[12−19] in addition to contributing new experimental data to the RTIL property databank. In this direction, we focus in this report on density and surface tension measurements of linear alkyl quaternary phosphonium- and ammonium-based RTILs. Our interest in surface tension measurements lies in the application of RTILs as supported liquid membranes (SLMs)[6−9] of relevance in energy-efficient membrane-based gas separations.[7−9] While the negligible vapor pressure allows RTILs to be immobilized within the pores of a polymeric membrane support, the surface tension determines the hydrodynamic stability of the entrapped liquid. That is, the operating gas pressure on the membrane is directly related to the surface tension and inversely related to the pore size. To design a hydrodynamically stable membrane, the cross membrane pressure (ΔP_{cm}) should not exceed the equilibrium pressure (ΔP_{eq}) exerted on the surface of the liquid meniscus. Therefore, the design of efficient RTIL-based membrane systems requires an accurate database of surface tension data for the immobilized liquids.

In this work, we report on the density and surface tension measurements of five phosphonium and eight ammonium RTILs. Physical property data for the phosphonium and ammonium classes of RTILs are scarce because most of the literature results to date are focused on the 1-alkyl-3-methylimidazolium [Rmim] RTILs. For ease of comparison, we, therefore, also include surface tension results of four [Rmim] RTILs.

Materials and Procedures

In the following, the purity levels mentioned in the parentheses are specified by the supplier. Our analyses of halide content appear in Table 2. The basic structures of the cations and anions studied in this work are in Figure 1. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf_2N] (≈100 % purity) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C6mim][Tf_2N] (99 % pure) were obtained from Covalent Associates, Inc. 1-Ethyl-3-methylimidazolium trifluoromethane sulfonate [emim][TfO] (CAS # 145022-44-4) (≈100 % pure by mass fraction) was obtained from EMD chemicals, and 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] (CAS #174501-64-51) with > 96 % purity was purchased from Fluka Chemica, Sigma-Aldrich, Germany. The tetraalkylphosphonium RTILs used were sourced from Cytec Canada (Niagara Falls, ON) and include: trihexyl(tetradecyl)phosphonium chloride [P(14)666][Cl] (CAS # 258864-54-9) (96 % to 97 % purity with (0.1 to 0.4) % traces of tetradecene isomers, (0.1 to 0.5) % HCl, and (0.1 to 1.2) % [$PR_3H]^+Cl^-$); trihexyl(tetradecyl)phosphonium dicynamide [P(14)666][DCA] (residual chloride of 0.5 %); trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide [P(14)666][Tf_2N] (CAS# 460092-03-9) (> 97 % pure, < 0.1 % water, and < 0.1 % chloride content);[20] tributyl(ethyl)phosphonium diethylphosphate [P(2)444][DEP]; and tributyl(tetradecyl)phosphonium dodecylbenzenesulfonate [P(14)444][DBS]. The

---

* Corresponding author. E-mail: scovazzo@olemiss.edu. Phone: (662)-915-5354. Fax: (662)-915-7023.

[†] University of Mississippi.

[‡] Oak Ridge National Laboratory.

10.1021/je7003098 CCC: $37.00

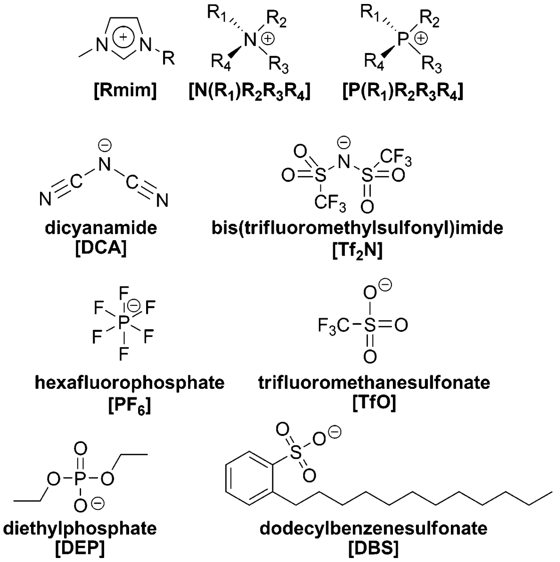

Figure 1. Chemical structures of cations and anions employed in this study.

alkylammonium RTILs dimethyl(butyl(*i*-propyl))ammonium bis((trifluoromethyl)sulfonyl)imide [N(4)113][Tf_2N], dimethyl(hexyl)(*i*-propyl) bis((trifluoromethyl)sulfonyl)imide [N(6)113][Tf_2N], dimethyl(decyl(*i*-propyl)) bis((trifluoromethyl)sulfonyl)imide [N(10)113][Tf_2N], and trioctyl(methyl)ammonium bis((trifluoromethyl)sulfonyl)imide [N(1)888][Tf_2N] were synthesized at Oak Ridge National Laboratory and stored in sealed septa-capped bottles. Trimethyl(butyl)ammonium bis(trifluoromethylsulfonyl)imide [N(4)111][Tf_2N] was purchased from Ionic Liquid Technologies, Germany. The other salts, trimethyl(hexyl)ammonium bis(trifluoromethylsulfonyl)imide [N(6)111][Tf_2N], trimethyl(decyl)ammonium bis(trifluoromethylsulfonyl)imide [N(10)111][Tf_2N], and triethyl(hexyl)ammonium bis(trifluoromethylsulfonyl)imide [N(6)222][Tf_2N] were synthesized at The University of Mississippi. The cation sources for the trimethyl(alkyl)ammonium RTILs were obtained from TCI America as bromides in 99+ % purity. Triethyl(hexyl)ammonium iodide was synthesized at the University of Mississippi. Lithium trifluoromethanesulfonimide (CAS #90076-65-6) with 99.95 % purity was obtained from Sigma-Aldrich. The numerals presented in the square brackets for phosphonium and ammonium RTILs indicate the number of carbons in each chain with the longest chain length usually provided in parentheses; this notation is used throughout this manuscript.

Synthesis of [N(6)111][Tf_2N] and [N(10)111][Tf_2N]. For [N(6)111][Tf_2N], equimolar aqueous solutions of trimethyl(hexyl)ammonium bromide and lithium bis(trifluoromethylsulfonyl)imide were mixed in a separation funnel and gently shaken for several minutes to assist the metathesis reaction. The immiscible RTIL phase was separated from the aqueous phase and washed three times with water to remove excess halide content and dried under vacuum ($<$ 0.013 atm) at 363 K for 48 h. The synthesis of [N(10)111][Tf_2N] followed the same procedure as [N(6)111][Tf_2N] with the substitution of trimethyl(*n*-decyl)ammonium bromide for trimethyl(*n*-hexyl)ammonium bromide.

Synthesis of [N(6)222]I and [N(6)222][Tf_2N]. Triethylamine (1.25 mol) was reacted with 1 mol of 1-iodohexane under reflux at 343 K with nitrogen bubbling into the reaction vessel. The reaction was carried out for (1 to 2) days with periodic addition of hexane. A white precipitate of triethyl(hexyl)ammonium iodide was separated using gravity filtration. Synthesis of [N(6)222][Tf_2N] was similar to that of [N(6)111][Tf_2N] and [N(10)111][Tf_2N] with the use of the [N(6)222]I in place of the quaternary ammonium bromide.

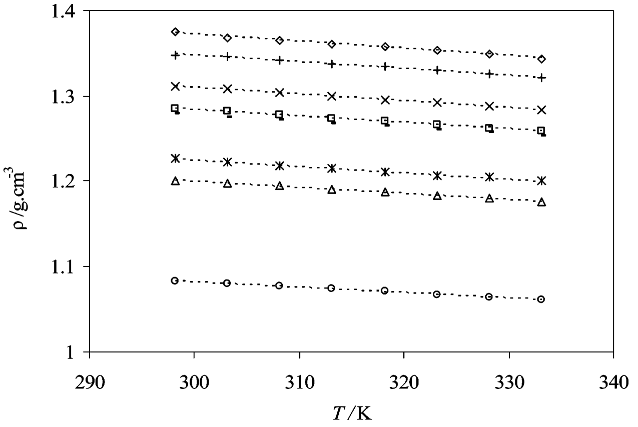

Figure 2. Temperature-dependent densities of quaternary ammonium RTILs. ◇, [N(4)111][Tf_2N]; +, [N(4)113][Tf_2N]; ×, [N(6)111][Tf_2N]; □, [N(6)113][Tf_2N]; -, [N(6)222][Tf_2N]; *, [N(10)111][Tf_2N]; Δ, [N(10)113][Tf_2N]; and ○, [N(1)888][Tf_2N]. Error bars are smaller than the data point symbols.

Synthesis of [N(n)113][Tf_2N] (n = 4, 6, 10) and [N(1)888][Tf_2N]. The ionic liquids, [N(*n*)113][Tf_2N] (for n = 4, 6, and 10), were prepared from dimethyl(isopropyl)amine by following recently reported synthetic methods.[21,22] In the case of [N(1)888][Tf_2N], the precursor salt [N(1)888]Br was first treated with aqueous decolorizing charcoal at 338 K for 48 h and then filtered to remove carbon.[23] This decolorizing step was repeated twice prior to metathesis.

Density Measurements. Densities of the phosphonium- and ammonium-based RTILs were measured in the temperature ranges from (298 to 333) K by weighing in a standard 5.0 cm^{-3} specific gravity bottle in a temperature-controlled nitrogen environment. At each temperature increment, the sample was allowed (20 to 30) min to attain thermal equilibrium and four to five readings were averaged. The standard deviation of all the measurements and the relative uncertainty in temperature do not exceed $\pm$ 0.0005 $g \cdot cm^{-3}$ and 0.1 °C, respectively.

Surface Tension Measurements. A PC-controlled KSV Sigma 70 Tensiometer (KSV Instruments Ltd., Finland) was used for surface tension measurements. Built-in auto-correction software is a major advantage of using this instrument to account for the correction factors as suggested in the literature.[24,25] The DúNoúy ring method was used for air−RTIL surface tension measurements of the phosphonium-based RTILs using a procedure found elsewhere.[26] Surface tension measurements for the quaternary ammonium RTILs were made under a dry nitrogen atmosphere to eliminate frequent drying of RTILs during the experiment. The tensiometer was calibrated by measuring the surface tension of deionized water at 293 K; measured values agreed to within 0.1 % of the literature value of 72.8 $mN \cdot m^{-1}$ at 293 K. The same instrumental settings were used for measuring surface tension for all the RTILs to avoid the use of scaling methods to account for discrepancies. Surface tensions were measured against temperature in the range between (295 and 350) K for phosphonium RTILs and between (295 and 333) K for ammonium RTILs. The temperature was maintained using an external water circulating bath (EX 7 Digital One; Thermo Neslab). The RTILs were thermally equilibrated for about (20 to 30) min at each temperature prior to recording a measurement. Four to five readings were taken at each temperature, and the results were averaged. We report the averages, all of which all had standard deviations $\leq$ 0.05 $mN \cdot m^{-1}$.

Table 1. Multitemperature Specific Gravity Data for Quaternary Phosphonium and Ammonium RTILs[a]

t (°C)	25	30	35	40	45	50	55	60
Phosphonium								
[P(14)666][Cl]	0.8826	0.8801	0.8779	0.8754	0.8731	0.8694	0.8669	0.8644
[P(14)666][DCA]	0.9209	0.9173	0.9163	0.9131	0.9101	0.9075	0.9050	0.9024
[P(14)666][Tf_2N]	1.0501	1.0483	1.0452	1.0420	1.0392	1.0356	1.0329	1.0296
[P(2)444][DEP]	0.9978	0.9957	0.9928	0.9897	0.9858	0.9826	0.9795	0.9758
[P(14)444][DBS]	0.9384	0.9371	0.9337	0.9311	0.9284	0.9254	0.9228	0.9201
Ammonium								
[N(4)113][Tf_2N]	1.3483	1.3457	1.3421	1.3378	1.3341	1.3297	1.3258	1.3215
[N(6)113][Tf_2N]	1.2846	1.2816	1.2775	1.2732	1.2699	1.2660	1.2660	1.2585
[N(10)113][Tf_2N]	1.2007	1.1977	1.1942	1.1908	1.1869	1.1869	1.1838	1.1760
[N(4)111][Tf_2N]	1.3747	1.3686	1.3656	1.3614	1.3573	1.3537	1.3497	1.3439
[N(6)111][Tf_2N]	1.3106	1.3078	1.3040	1.2995	1.2957	1.2921	1.2879	1.2839
[N(10)111][Tf_2N]	1.2263	1.2222	1.2186	1.2147	1.2106	1.2063	1.2047	1.2003
[N(6)222][Tf_2N]	1.2793	1.2754	1.2719	1.2676	1.2644	1.2608	1.2574	1.2530
[N(1)888][Tf_2N]	1.0823	1.0803	1.0773	1.0738	1.0738	1.0672	1.0639	1.0611

[a] Uncertainties in measurements do not exceed ± 0.0005.

Table 2. Volume Expansivities of Phosphonium and Ammonium RTILs Estimated at 1 atm and 298 K from Equation 2, along with Halide Content of Tested RTILs[a]

	volume expansivity,[b] $\alpha \cdot 10^4$ K^{-1}	halide content (chloride Wt %)[c]	stock sample water content (ppm, $mg \cdot kg^{-1}$)
Phosphonium			
[P(14)666][Cl]	5.96	N/A	5840
[P(14)666][DCA]	5.69	N/A	4230
[P(14)666][Tf_2N]	5.71	<0.05 (chloride)	526
[P(2)444][DEP]	6.43	<0.05 (chloride)	6620
[P(14)444][DBS]	5.77	<0.05 (chloride)	10900
Ammonium			
[N(4)113][Tf_2N]	5.79	<0.01 (bromide)	2200
[N(6)113][Tf_2N]	5.88	<0.05 (bromide)	2480
[N(10)113][Tf_2N]	5.82	<0.05 (bromide)	N/A
[N(4)111][Tf_2N]	6.05	0.27 (unknown)	1080
[N(6)111][Tf_2N]	5.92	0.15 (bromide)	909
[N(10)111][Tf_2N]	6.03	0.08 (bromide)	630
[N(6)222][Tf_2N]	5.79	0.10 (iodide)	1080
[N(1)888][Tf_2N]	5.93	0.44 (bromide)	1220

[a] The probable halide is indicated next to the reported value. [b] Uncertainties in measurements do not exceed ± $0.01 \cdot 10^4$ K^{-1}. [c] Halide content reported using the unit "Halide as mg-Cl/Kg" calculated from (moles of halide detected)·(MW of chloride)/(mass of RTIL tested)·100.

Residual Halide (Chloride) Tests. We measured the halide content to ensure repeatability of our reported data because its presence, as an impurity, may alter the physical properties of RTILs such as viscosity and density. We used a modified Volhard test to determine the residual halide content of the ammonium RTILs in this study. Acetonitrile was used as a solvent for the ammonium RTILs. We did only the back-titration step of the actual Volhard test with potassium thiocyanate solution because the halide precipitate was too small to collect and weigh.

The phosphonium RTILs halide content tests also used a modified Volhard technique but with water as the medium. Water was used as a medium because it was difficult to find a solvent that dissolved both the ionic liquid and the compounds required for the Volhard test. We confirmed our Volhard test procedure using samples spiked with known quantities of chloride, i.e., RTILs spiked with $[P_{(14)666}^{+}][Cl^{-}]$. However, the Volhard test is not applicable to $[P_{(14)666}^{+}][Cl^{-}]$ and $[P_{(14)666}^{+}][DCA^{-}]$ because Ag^{+} forms insoluble precipitants with their anions.

Water Content. The samples were prepared from the bulk ionic liquids stored in the glass containers. The sealed glass containers had septum ports to facilitate the use of syringes to transfer the sample into the sample vials under a nitrogen environment. Then the samples were placed in a vacuum desiccator to remove any moisture and other gaseous contaminants for (6 to 8) h. Then the samples were moved into a 50 mL capacity glass chamber which was then placed in the tensiometer vessel holder. The tensiometer was inside of a glovebox containing a desiccator with dry nitrogen flushing continuously. While measuring the surface tensions in the temperature ranges from (298 to 313) K, the samples were frequently taken out, dried, and placed in the vessel holder to remove any moisture dissolved during the measurements. We were unable to measure the RTILs after testing; however, we placed additional stock samples of the RTILs in a vacuum desiccator for 7 h and tested their water content. Table 2 reports this stock chemical water content for the phosphonium and ammonium RTILs. The following are the water content of the stock imidazolium RTILs: [emim][TfO], 9060 ppm; [bmim][PF_6], 1920 ppm; [emim][Tf_2N], 1090 ppm; and [C_6mim][Tf_2N], 1050 ppm.

Results

Table 1 summarizes RTIL densities (± 0.0005 $g \cdot cm^{-3}$) of phosphonium and ammonium RTILs in the temperature range from (298 to 333) K. The densities of the studied RTILs fall in the range from (0.883 to 1.35) $g \cdot cm^{-3}$ at 298 K. The densities of phosphonium-based RTILs lie at the lower end of this range (0.883 to 1.05) $g \cdot cm^{-3}$ due to the presence of higher alkyl chain lengths, and in every case except for [P(14)666][Tf_2N], the density is less than that for water. [P(2)444][DEP] represents a borderline case, being only marginally less dense than liquid water at these temperatures. Table 2 gives the volume expansivities for the RTILs calculated from the Table 1 density data at 298 K and the corresponding slopes obtained from Figures 1 and 2. Table 2 also lists the residual halide content of the tested RTILs.

Table 3 presents experimental multitemperature surface tension data, and Table 4 presents the surface tensions of phosphonium and ammonium RTILs at 298 K as well as the surface excess quantities calculated from eq 3, as discussed below. The surface tensions of phosphonium RTILs are in the range of (33.0 to 35.0) $mN \cdot m^{-1}$, whereas the values for ammonium salts are between (29.0 and 38.4) $mN \cdot m^{-1}$. The maximum standard deviation in surface tension measured at each temperature is 0.0023 $mN \cdot m^{-1}$.

Correlations

The temperature dependence of density for the RTILs can be generalized in the form of

$$\rho(g \cdot cm^{-3}) = A + B(T/K) \qquad (1)$$

Table 3. Multitemperature Surface Tension Data for Imidazolium, Phosphonium, and Ammonium RTILs[a]

RTIL	temp T/K	surface tension, σ/mN·m^{-1}	temp T/K	surface tension, σ/mN·m^{-1}	RTIL	temp T/K	surface tension, σ/mN·m^{-1}	temp T/K	surface tension, σ/mN·m^{-1}
[emim][TfO]					[emim][Tf_2N]				
	296.28	44.46	328.68	43.37		298.70	41.62	316.20	40.67
	300.79	44.36	333.64	43.15		302.05	41.38	319.33	40.50
	304.95	44.20	337.82	42.99		305.74	41.19	322.63	40.39
	308.14	44.07	343.49	42.82		309.16	41.02	326.13	40.19
	312.41	43.90	347.91	42.62		312.60	40.87	331.02	39.94
	317.15	43.81	353.56	42.49					
	321.93	43.64							
[bmim][PF_6]					[C_6mim][Tf_2N]				
	298.15	47.92	319.95	46.55		297.22	35.98	323.57	34.63
	301.32	47.71	325.06	46.15		301.22	35.79	327.48	34.45
	305.79	47.48	328.68	46.04		305.48	35.54	331.24	34.26
	309.60	47.29	332.22	45.81		309.14	35.35	334.91	34.07
	315.44	46.92	335.61	45.41		312.48	35.15	340.92	33.76
						316.28	35.03	346.42	33.44
						319.87	34.84		
[P(14)666][Cl]					[P(14)666][DCA]				
	297.99	33.62	323.95	31.43		295.06	35.22	322.47	33.24
	302.94	33.15	327.96	31.15		299.35	34.85	326.14	32.94
	307.40	32.72	332.81	30.76		302.95	34.58	327.42	32.61
	312.09	32.30	337.27	30.42		305.04	34.45	333.02	32.20
	315.84	32.01	342.09	30.00		310.40	34.06	338.60	31.66
	319.49	31.74	347.68	29.55		314.39	33.80	343.13	31.33
						318.38	33.50	348.47	31.09
[P(14)666][Tf_2N]					[P(2)444][DEP]				
	298.2	33.08	327.9	30.65		296.66	33.60	329.67	31.14
	303.0	32.57	332.9	30.28		302.18	33.29	336.36	30.66
	308.0	32.15	338.9	29.68		307.24	33.14	343.40	30.15
	313.0	31.77	344.2	29.45		312.34	32.82	347.75	29.82
	318.0	31.40	349.8	28.93		318.36	32.24	350.86	29.59
	323.3	31.09				323.59	31.62		
[N(4)113][Tf_2N]					[N(10)113][Tf_2N]				
	299.10	38.38	313.40	37.54		300.00	36.13	313.00	34.92
	300.10	38.33	315.40	37.41		300.60	36.06	315.20	34.74
	301.40	38.25	317.00	37.32		301.80	35.94	317.00	34.59
	303.00	38.17	319.00	37.21		303.00	35.81	318.20	34.48
	305.20	38.03	321.10	37.10		305.10	35.61	320.30	34.32
	307.80	37.86	323.10	37.03		306.50	35.48	323.10	34.10
	310.60	37.70	324.90	36.93		308.10	35.35	325.30	33.96
						310.20	35.14	328.10	33.79
[N(6)113][Tf_2N]					[N(1)888][Tf_2N]				
	300.10	36.74	312.30	35.78		299.46	29.06	321.00	27.63
	302.00	36.58	315.20	35.55		303.25	28.93	326.30	27.18
	303.10	36.49	318.00	35.33		310.18	28.53	329.60	27.01
	304.00	36.42	320.60	35.14		313.77	28.23	336.79	26.69
	306.00	36.25	322.60	35.01		318.67	27.85		
	308.10	36.11							
[N(4)111][Tf_2N]					[N(10)111][Tf_2N]				
	298.35	38.05	320.39	37.28		300.96	35.42	324.03	33.71
	302.33	37.90	326.40	37.09		302.95	35.12	330.53	33.36
	306.15	37.80	330.16	36.91		307.75	34.81	337.12	32.82
	309.93	37.69	335.64	36.68		312.28	34.55	342.53	32.51
	314.79	37.48	340.58	36.50		318.08	34.20	347.26	32.23
[N(6)111][Tf_2N]					[N(6)222][Tf_2N]				
	300.35	35.88	318.15	34.64		299.54	35.17	324.94	32.98
	302.35	35.71	322.55	34.36		302.65	34.90	329.34	32.72
	304.25	35.57	326.25	34.14		307.05	34.45	335.04	32.47
	307.65	35.32	331.35	33.86		313.73	33.88	341.93	31.98
	311.05	35.09	333.35	33.77		319.84	33.49	347.11	31.45
	314.75	34.86							

[a] The standard deviation of the experimental surface tensions does not exceed 0.05 mN·m^{-1}.

where ρ is the density, and A and B are the y-intercept and slope of the $\rho - T$ curve. The volume expansivities of ammonium- and phosphonium-based RTILs at atmospheric pressure and 298 K are estimated using the equation

$$\alpha = \frac{1}{\rho} \cdot \frac{d\rho}{dT} \tag{2}$$

In eq 2, α is the volume expansivity in K^{-1} and $d\rho/dT = B$.

The surface tension is a measure of the free energy of a minimum surface area at a boundary layer that separates liquid and vapor phases. The basic thermodynamic relationship applied to the surface of a homogeneous liquid is

$$G^s = H^s - T \cdot S^s \tag{3}$$

where G^s is the Gibbs energy as related to the surface tension of the homogeneous liquid; H^s is surface excess enthalpy; and

Table 4. Surface Tension (Surface Free Energy), Surface Excess Energy, and Surface Excess Entropy of Quaternary Phosphonium and Ammonium RTILs

	σ / $\text{mN}\cdot\text{m}^{-1}$ [a]	E^{s} / $\text{mN}\cdot\text{m}^{-1}$	S^{s} / $\text{mN}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	r^2	T_{c} / K	n
Imidazolium						
[emim][TfO]	44.4	55.06 ± 0.17	0.0356 ± 0.0005	0.9976	1545	0.998
[emim][Tf_2N]	41.6	56.63 ± 0.26	0.0504 ± 0.0008	0.9979	1123	1.000
[bmim][PF_6]	47.9	67.41 ± 0.57	0.0652 ± 0.0018	0.9938	1034	1.001
[C6mim][Tf_2N]	35.9	51.08 ± 0.14	0.0508 ± 0.0004	0.9991	1005	1.001
Phosphonium						
[P(14)666][Cl]	33.4	57.18 ± 0.36	0.0797 ± 0.0110	0.9980	717	0.997
[P(14)666][DCA]	35.0	58.73 ± 0.52	0.0795 ± 0.0016	0.9950	739	0.995
[P(14)666][Tf_2N]	33.0	56.42 ± 0.42	0.0786 ± 0.0013	0.9976	718	0.999
[P(2)444][DEP]	33.7	56.96 ± 0.79	0.0780 ± 0.0024	0.9923	730	1.002
[P(14)444][DBS] [b]						
Ammonium						
[N(4)113][Tf_2N]	38.4	55.58 ± 0.21	0.0575 ± 0.0007	0.9970	967	1.000
[N(6)113][Tf_2N]	36.9	59.86 ± 0.25	0.0771 ± 0.0008	0.9976	776	0.999
[N(10)113][Tf_2N]	36.2	61.39 ± 0.43	0.0844 ± 0.0014	0.9957	727	0.999
[N(4)111][Tf_2N]	38.1	49.06 ± 0.22	0.0368 ± 0.0007	0.9936	1333	1.000
[N(6)111][Tf_2N]	36.0	55.10 ± 0.25	0.0642 ± 0.0008	0.9964	858	0.999
[N(10)111][Tf_2N]	35.5	55.67 ± 0.38	0.0676 ± 0.0012	0.9986	824	0.999
[N(6)222][Tf_2N]	35.2	57.72 ± 0.70	0.0757 ± 0.0022	0.9934	762	1.000
[N(1)888][Tf_2N]	29.3	49.76 ± 0.85	0.0688 ± 0.0027	0.9895	723	1.000

[a] At 298 K. [b] Viscosity too high to reliably determine surface tension by the DúNoúy ring method.

S^{s} is surface excess entropy, which is measured by the slope of the surface tension−temperature profiles, $-d\sigma/dT$. The equation can be written in terms of surface tension, σ. The van der Waals−Guggenheim equation[27] models the temperature dependence of surface tension for traditional organic liquids

$$\sigma = E^{\text{s}}\left(1 - \frac{T}{T_{\text{c}}}\right)^{n} \qquad (4)$$

where $n = 11/9$ for many organic liquids (and approximately unity for molten metals)[27] and E^{s} is the total surface energy of the liquid, which equals the surface enthalpy as long as there is negligible volume change due to thermal expansion at the temperatures well removed from the critical temperature (T_{c}). Use of eq 4 assumes that there is no interfacial tension between the liquid and the vapor phases when the temperature of the liquid reaches the critical point.[28] This assumption follows from the view that, at T_{c}, there exists no clear distinction between the liquid and vapor phases. Therefore, the boundary layer separating liquid−vapor coexisting phases disappears. The parameters of eqs 3 and 4 for imidazolium, phosphonium, and ammonium RTILs with the associated r^2 values are in Table 4.

Macleod, Sugden, and Wright[29] formulated an empirical relationship to estimate the surface tension of a pure liquid from the density difference between liquid and vapor phases with two specific constants, p and $[P]'$

$$\sigma^{1/p} = [P]'(\rho_{\text{L}} - \rho_{\text{V}}) \qquad (5)$$

In this expression, σ is the surface tension in $\text{mN}\cdot\text{m}^{-1}$; ρ_{L} and ρ_{V} are the densities of liquid and vapor states in $\text{mol}\cdot\text{cm}^{-3}$, respectively; and p and $[P]'$ are constants that depend only on the liquid. The parachor $[P]$ (which has a different value than $[P]'$) is defined at $p = 4$ as the relative volume between two liquids having equal surface tensions when the condition $\rho_{\text{L}} \gg \rho_{\text{V}}$ is met. The density of the RTIL vapor is neglected in eq 5 because the RTILs have negligible low vapor pressure under the conditions studied. Therefore, eq 5 can be written in terms of the RTIL molar volume, V_{RTIL}.

$$\sigma_{\text{RTIL}}^{1/p} = \frac{[P]'}{V_{\text{RTIL}}} \qquad (6)$$

The regression analysis of the values of surface tension at different temperatures with the corresponding molar volumes provides the constants p and $[P]'$ for each RTIL. These constants are in Table 5.

Discussion

Figures 2 and 3 present the temperature dependencies of density for ammonium- and phosphonium-based RTILs, respectively. The density slightly decreases with temperature in the range studied, (298 to 333) K. Table 2 contains estimated volume expansivities of RTILs at 298 K and 1 atm pressure. The volume expansivities of ammonium and phosphonium salts are in the range of $(5.5 \text{ to } 6.5)\cdot 10^{-4}\ \text{K}^{-1}$. These are similar to the literature values for imidazolium- and pyridinium-based RTILs, i.e., $(5 \text{ to } 6)\cdot 10^{-4}\ \text{K}^{-1}$.[30]

Figures 4 to 6 show how the measured surface tensions vary with temperature for the imidazolium, quaternary phosphonium, and ammonium classes of RTILs investigated. Note that the RTILs [N(4)113][Tf_2N] and [N(10)113][Tf_2N] in Figure 6 have overlapping $\sigma-T$ profiles with [N(4)111][Tf_2N] and [N(6)111][Tf_2N], respectfully. The temperature dependence of surface tension for the different phosphonium-based RTILs studied is similar, as shown by the similarity in the slopes of the $\sigma-T$ profiles. This indicates that the anion does not exert a significant effect on the variation of surface excess entropy for the range of phosphonium RTILs we looked at. The surface tensions of the four phosphonium RTILs decrease in the order: [P(14)666][DCA] > [P(2)444][DEP] > [P(14)666][Cl] > [P(14)666][Tf_2N]. On the other hand, the significant variation in the surface excess entropy determined for the imidazolium and ammonium types of RTILs can clearly be attributed to variation in the cationic structure and alkyl chain length.

Figure 7 plots the variation in the surface tension along the [N(n)111][Tf_2N] and [N(n)113][Tf_2N] RTIL series as the highest alkyl chain length is elongated. The solid line indicates a decrease in the surface tension for the [N(n)111][Tf_2N] series as n increases from 4 to 6, followed by a reduction in the rate

Table 5. Results of Regression Analysis between Temperature-Dependent Surface Tension and RTIL Molar Volume Using Equation 6, Yielding Constants *p* and [*P*]′

RTIL	[*P*]′	*P*
	Phosphonium	
[P(14)666][Cl]	1897.47	3.059
[P(14)666][DCA]	1414.86	4.116
[P(14)666][Tf_2N]	1635.87	4.311
[P(2)444][DEP]	992.90	3.708
	Ammonium	
[N(4)113][Tf_2N]	1221.40	2.624
[N(6)113][Tf_2N]	915.70	3.653
[N(10)113][Tf_2N]	981.76	4.129
[N(4)111][Tf_2N]	946.82	3.012
[N(6)111][Tf_2N]	1034.52	3.083
[N(10)111][Tf_2N]	1182.38	3.230
[N(6)222][Tf_2N]	1101.29	3.153
[N(1)888][Tf_2N]	1311.62	4.186

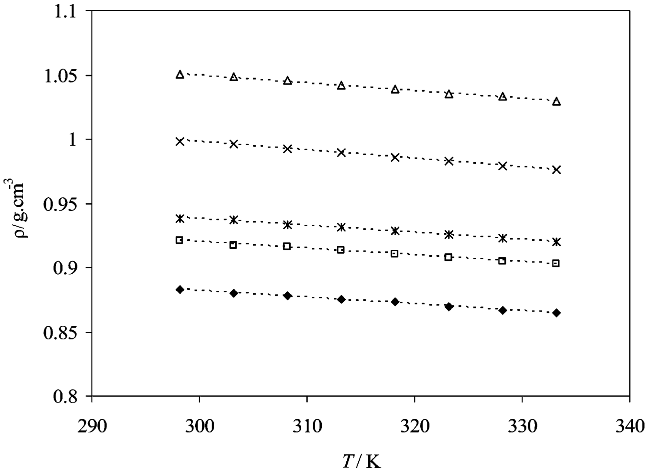

Figure 3. Temperature-dependent densities of quaternary phosphonium RTILs. Δ, [P(14)666][Tf_2N]; ×, [P(2)444][DEP]; *, [N(14)444][DBS]; □, [N(14)666][DCA; and ◊, [N(14)666][Cl]. Error bars are smaller than the data point symbols.

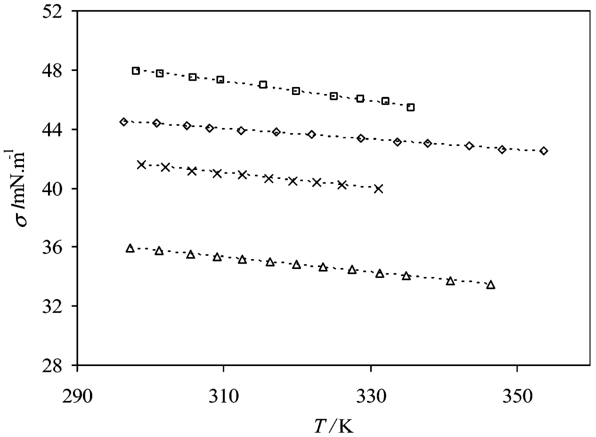

Figure 4. Temperature dependence of surface tension for [Rmim] RTILs. □, [bmim][PF_6]; ◊, [emim][TfO]; ×, [emim][Tf_2N]; and Δ, [C6mim][Tf_2N]. Error bars are smaller than the data point symbols.

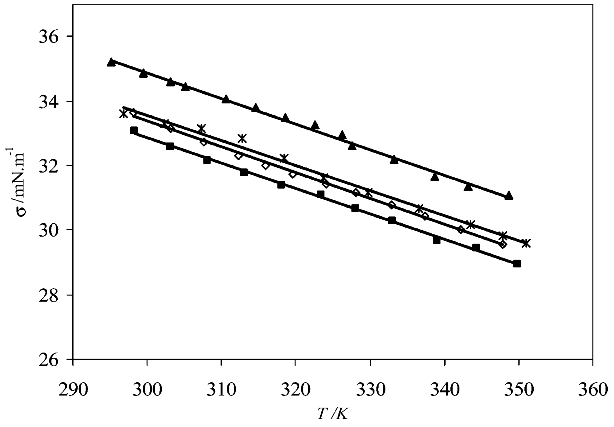

Figure 5. Plots of the temperature dependence of surface tension for phosphonium RTILs, demonstrating that the anion does not affect the surface excess entropy. ▲, [P(14)666][DCA]; *, [P(2)444][DEP]; ■, [P(14)666]-[Tf_2N]; and ◊, [P(14)666][Cl]. Error bars are smaller than the data point symbols.

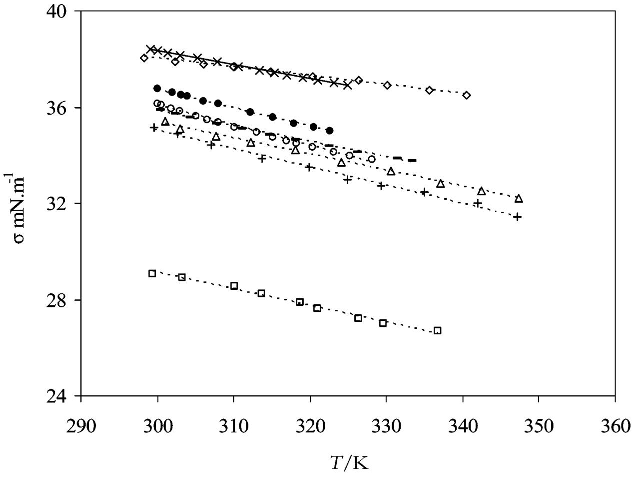

Figure 6. Temperature dependence of surface tension of ammonium-based RTILs. ×, [N(4)113][Tf_2N]; ◊, [N(4)111][Tf_2N]; ●, [N(6)113][Tf_2N]; -, [N(6)111][Tf_2N]; ○, [N(10)113][Tf_2N]; Δ, [N(10)111][Tf_2N]; +, [N(6)-222][Tf_2N]; □, [N(1)888][Tf_2N]. Error bars are smaller than the data point symbols.

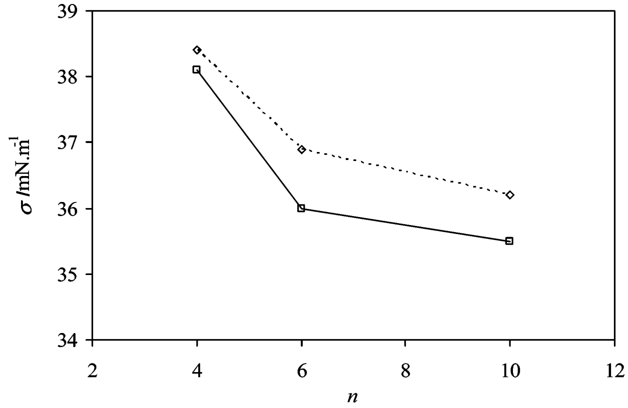

Figure 7. Effect of alkyl chain length on the measured surface tension of quaternary ammonium RTILs. Solid line, −, [N(*n*)111][Tf_2N] and dashed line, ---, [N(*n*)113][Tf_2N]. As can be seen, an increase in the primary alkyl group length decreases the surface tension; however, due to cation surface orientation changes, the addition of a propyl group in place of a methyl group increases the surface tension. Error bars are smaller than the data point symbols.

of decrease as *n* increases further to 10 carbons. The decrease in surface tension with the length of the longest alkyl chain in this homologous series indicates the influence of chain length on the free energy available on the surface, because the surface tension is a measure of the local free energy of each molecule exposed to the surface (Langmuir's principle of independent surface action). Similar trends are observed for [Rmim] RTILs with PF_6^-, BF_4^-, Cl^-, and Br^- anions.[26] If we assume that the $[R_4N]^+$ ion orients normal to the surface, similar to the imidazolium ring with lower alkyl chain lengths,[31] the increase of alkyl chain length should change the angle of orientation of the $[R_4N]^+$ cation due to the appearance of hydrocarbon tails

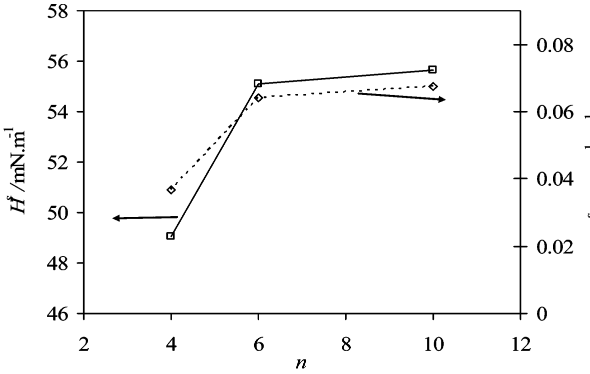

Figure 8. Effect of alkyl chain length on surface excess properties of [N(*n*)-111][Tf_2N] RTILs. The increase in S^s with alkyl chain length can be attributed to the presence of van der Waals forces on the surface.[13] Error bars are smaller than the data point symbols.

on the surface with a subsequent lowering in observed surface tension. The replacement of a methyl group with an isopropyl moiety in the [N(*n*)113] series might likely alter the angle of orientation for the cation but in the opposite direction, approximately normal to the surface. An increase in the surface tension of the analogous members of the [N(*n*)113] series, shown by the dotted profile in Figure 7, supports this assumption. If we assume that an isopropyl group in place of a methyl group would only change the angle of orientation of the cation but not appear on the surface, then the observed increase in surface tension should be due to Coulombic interactions alone. However, a synergistic affect of the appearance of both van der Waals and Coulombic forces on the surface can be inferred from an increase in the gap between the surface tensions of the two series as n increases from $n = 4$ to $n = 6$. Therefore, it can be concluded that surface tension is a measure of both Coulombic and van der Waals interactions at the surface; however, we cannot draw more specific conclusions regarding the relative contributions at this point.

Four imidazolium RTILs are included to compare our surface tension results with those in the open literature. Our surface tension value for [bmim][PF_6] measured at 298 K, as reported in Table 2 (47.9 mN·m^{-1}), agrees fairly well with published values: our value is 4.4 % higher than the reported value of Law and Watson,[26] 1.9 % higher than that of Dzyuba et al.,[12] and 1.8 % lower than the value published by Huddleston et al.[2] The surface tension values for [emim][Tf_2N] and [C6mim]-[Tf_2N] are 6.7 % and 2.6 % higher, respectively, than values reported by Dzyuba et al.[12] Likewise, our measured value for [P(14)666][Tf_2N] is only 4.1 % higher than a recently reported value.[22] Table 6 compares our surface tension results with available RTIL results alongside those for a range of common organic solvents. The surface tensions of our ammonium and phosphonium RTILs fall in the range of imidazolium RTILs with Tf_2N^- anions, imidazolium RTILs with longer alkyl chain lengths ($n > 6$) coupled to PF_6^- and BF_4^- anions, and polar organic solvents such as acetic anhydride, carbon disulfide, and acetophenone. Surface tensions of ammonium and phosphonium RTILs are (30 to 50) % lower than those of lower alkyl chain length ($n \leq 4$) imidazolium RTILs with PF_6^- and BF_4^- anions or polar organics like aniline and ethylene glycol. Similarly, the magnitude of these values is two to three times lower than that of high-temperature inorganic molten salts. On the whole, as can be concluded from Table 6, the surface tensions of high-temperature molten salts are bound in the (66 to 157) mN·m^{-1} range. Conversely, RTILs lie in a much more narrow range from (28 to 55) mN·m^{-1}, with phosphonium RTILs occupying the low end (32 to 35) mN·m^{-1}, ammonium RTILs falling in the range of (35 to 38) mN·m^{-1} (with the exception of [N(1)888]-[Tf_2N]), and imidazolium RTILs spanning a broad regime of (30 to 50) mN·m^{-1}. In comparison, lower alcohols and hydrocarbon liquids exhibit surface tensions of (18 to 30) mN·m^{-1}.

Table 6. Comparison between the Ranges of Surface Tension Measured for Our RTILs and Values for RTILs and More Conventional Solvents Reported in the Literature

	σ/(mN·m^{-1})	t/(°C)	ref
Hydrocarbons			
benzene	28.90	20	33
toluene	28.40	20	33
hexane	18.40	20	33
heptane	22.30	20	33
octane	23.80	20	33
m-xylene	28.60	20	33
Polar Organics			
methanol	22.50	20	27
ethanol	22.40	20	27
diethylene Glycol	30.90	20	27
acetic anhydride	31.20	30	33
carbon disulfide	32.40	20	33
Start of Imidazolium RTILs Range			
[C8mim][Tf_2N]	30.63	25	34
[C6mim][Tf_2N]	35.00	25	12
[C8mim][BF_4]	31.50	25	26
Phosphonium-Based RTILs: (32 to 35) mN·m^{-1}		25	this work
[C8mim][PF_6]	35.60		26
[bmim][Tf_2N]	37.00	25	12
	31.76	30	34
[emim][Tf_2N]	39.00		12
Ammonium-Based RTILs: (29 to 38.4) mN·m^{-1}		25	this work
Ringed Polar organics			
acetophenone	39.20	30	33
aniline	42.90	20	33
nitrobenzene	43.90	20	33
Continuation of Imidazolium RTILs Range			
[C6mim][PF_6]	43.40	25	12
	37.45	25	34
[bmim][BF_4]	40.60	25	26
	46.60	25	2
[bmim][PF_6]	48.80	25	2
	45.90	25	26
	47.00	25	12
[emim][BF_4]	54.40		35
High-Temperature Molten Salts			
NaCl	98.00	1000	28
KI	69.00	800	28
CsCl	78.00	830	28
$BaCl_2$	157.00	1000	28
$BiCl_3$	66.00	271	28

Figures 8 and 9 illustrate the effect of chain length ($n = 4$, 6, and 10) on the surface excess enthalpies (H^s) and entropies (S^s) of the respective [N(*n*)111] and [N(*n*)113] series. Both H^s and S^s increase as n varies from 4 to 10 in each series, but again the rate falls off as n increases. This result lies in contrast to the findings of Law and Watson[26] for [Rmim] RTILs with PF_6^-, BF_4^-, Cl^-, and Br^- anions with variation in chain lengths from 4 to 12. We should point out that no general correlations exist in the literature[32] between H^s, S^s, and alkyl chain length in molecular liquids. However, the increase in S^s with alkyl chain length in both [N(*n*)111] and [N(*n*)113] RTIL series can be attributed to the presence of van der Waals forces on the surface.[26] If the decrease in surface tension upon external heating represents breaking of bonds, then lower energy is required to break the short-range van der Waals forces than the long-range Coulombic forces. Therefore, an increase of surface excess entropy was expected with variation of alkyl chain length on the surface, as it represents a change in the ratio of van der

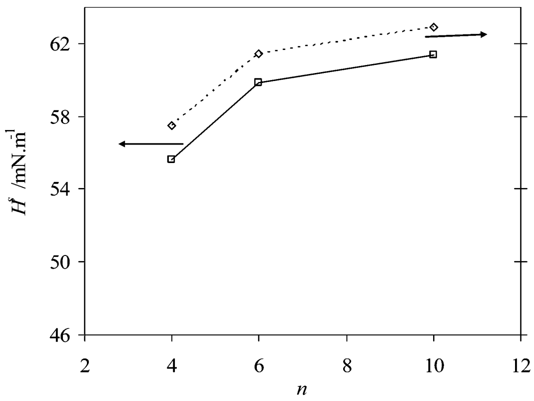

Figure 9. Effect of alkyl chain length on surface excess properties of [N(*n*)-113][Tf$_2$N]. The increase in S^s with alkyl chain length can be attributed to the presence of van der Waals forces on the surface.[13] Error bars are smaller than the data point symbols.

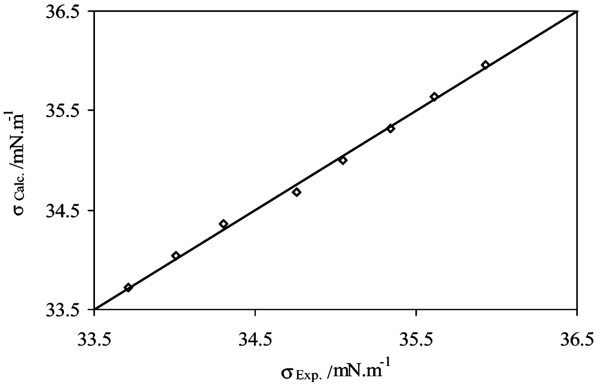

Figure 10. Representative phosphonium RTIL result showing that eq 6, combined with appropriate constants in Table 4, can accurately estimate surface tension of [P(14)666][X] in the range T = (295 to 333) K. Error bars are smaller than the data point symbols.

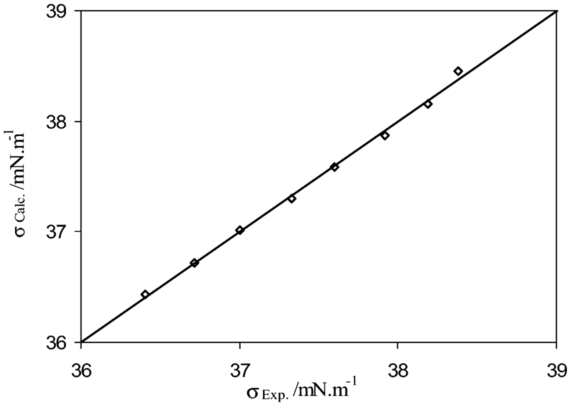

Figure 11. Representative ammonium RTIL result illustrating that eq 6, using constants found in Table 4, reliably estimates the surface tension of [N(*n*)113][Tf$_2$N] in the temperature range from (295 to 333) K. Error bars are smaller than the data point symbols.

Waals to Coulombic forces acting at the surface. A maximum 129 % increase of surface excess entropy was observed which is estimated from the lowest surface excess entropy minus the highest surface excess entropy divided by the lowest surface excess entropy found in Table 4. In addition, the surface excess entropy S^s is temperature-dependent; therefore, the increase of surface excess entropy (slope) with chain length increases the value of the surface excess enthalpy (*y*-intercept) of $\sigma-T$ profiles, but surface excess enthalpy is nearly temperature-independent if the measured temperatures are far removed from the T_c of the liquid.[27]

Figures 10 and 11 offer representative figures for the phosphonium and ammonium RTILs, calculated versus experimentally determined surface tensions of the RTILs [P(14)666]-[Cl] and [N(4)113][Tf$_2$N]. These results clearly show that employing eq 6 with the parameters summarized in Table 5 can be used to accurately estimate surface tension for the ten RTILs considered in our study. A maximum error of 0.1 % was observed for these determinations within 95 % confidence intervals. Thus, this model can be used to reliably estimate surface tension from the molar volumes of these RTILs, using the constants p and $[P]'$ for a particular RTIL. The constant p varies from 2.624 to 4.311 for the studied RTILs (Table 5). The constant $[P]'$ is a function of structure of the liquid's surface and may be divided into the individual group contribution parameters of the surface tension.[29] However, the RTIL surface cohesive energies also include Coulombic interactions, and we cannot explicitly partition $[P]'$ into individual group contributions with the limited data currently available, although this may be a possibility in the future.

Conclusions

The surface tensions of phosphonium and ammonium RTILs range alongside those of the imidazolium RTILs where phosphonium RTILs conspicuously occupy the lower end, (33 to 35) mN·m^{-1}. Surface tensions of the studied RTILs decrease with temperature. The van der Waals−Guggenheim equation describes the temperature dependence of surface tension with the slope (n) of a log−log plot similar to that of molten metals. Changing anions has a negligible effect on the surface tension of higher alkyl chain phosphonium RTILs. Increasing the size of the alkyl chains in ammonium RTILs lowers the surface tension due to the increase in the ratio of van der Waals to Coulombic forces, whereas the addition of alkyl chains to the cation increases the surface tensions of the RTILs due to orientation of hydrocarbon tails on the surface. Equation 6 can estimate surface tensions of the RTIL with molar volumes at a specified temperature with a maximum error of ± 0.25 %. The eq 6 parameters p and $[P]'$ are constants and depend on the liquid. In the future, extensive data on surface tensions may divide $[P]'$ of eq 6 into individual contributions of the groups in the RTILs.

Acknowledgment

The authors thank Cytec Canada, Inc, Niagara Falls, ON, for supplying phosphonium RTILs. Thanks to Mr. Lee Ferguson for making the [N(6)222][Tf$_2$N] ionic liquid used in this work. Special thanks go to Dr. John O'Haver, Associate Professor, Chemical Engineering, University of Mississippi, for letting us use the KSV Sigma 70 Tensiometer.

Literature Cited

(1) Camper, D.; Becker, C.; Koval, C.; Noble, R. Low Pressure Hydrocarbon Solubility in Room Temperature Ionic Liquids Containing Imidazolium Rings Interpreted Using Regular Solution Theory. *Ind. Eng. Chem. Res.* **2005**, *44*, 1928−1933.

(2) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem.* **2001**, *3*, 156−164.

(3) Seddon, K. R. Ionic Liquids for Clean Technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(4) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for Clean Liquid-Liquid Extraction *Chem. Commun.* **1998**, 1765−1766.

(5) Anthony, J. L.; Aki, S. N. V. K; Maginn, E. J; Brennecke, J. F. Feasibility of using ionic liquids for carbon dioxide capture. *Int. J. Environ. Technol. Manage.* **2004**, *4*, 105.

(6) Branco, L. C.; Crespo, J. G.; Afonso, C. A. M. Studies on the Selective Transport of Organic Compounds by Using Ionic Liquids as Novel Supported Liquid Membranes. *Chem.−Eur. J.* **2002**, *8* (17), 3865−3871.

(7) Gan, Q.; Rooney, D.; Xue, M.; Thompson, G.; Zou, Y. An experimental study of gas transport and separation properties of ionic liquids supported on nanofiltration membranes. *J. Membr. Sci* **2006**, *280*, 948−956.

(8) Scovazzo, P.; Visser, A. E.; Davis, J. H., Jr.; Rogers, R. D.; Koval, C. A.; DuBois, D. L.; Noble, R. D. Supported Ionic Liquid Membranes (SILMs) and Facilitated Ionic Liquid Membranes (FILMs). *ACS Symp. Ser.* **2002**, *818 (Ionic Liquids*), 69−87.

(9) Scovazzo, P.; Kieft, J.; Finan, D. A.; Koval, C.; DuBois, D.; Noble, R. Gas Separations Using Non-Hexafluorophosphate [PF6]- Anion Supported Ionic Liquid Membranes. *J. Membr. Sci.* **2004**, *238*, 57−63.

(10) Bradaric, C. J.; Downard, A.; Kennedy, C.; Robertson, A. J.; Zhou, Y. Industrial Preparation of Phosphonium Ionic Liquids. *Green Chem.* **2003**, *5*, 143−152.

(11) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. CO_2 Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124* (6), 926−927.

(12) Dzyuba, S. V.; Bartsch, R. A. Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis-(trifluoromethylsulfonyl) imides on physical properties of the ionic liquids. *Chem. Phys. Chem.* **2002**, *3*, 161−166

(13) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, Md. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation *J. Phys Chem. B* **2005**, *109* (13), 6103−10.

(14) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, Md. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. Variation of Anionic Species. *J. Phys. Chem. B* **2004**, *108* (42), 16593−16600.

(15) Tokuda, H.; Ishii, K.; Susan, Md. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. Physicochemical Properties and Structures of Room-Temperature Ionic Liquids. 3. Variation of Cationic Structures. *J. Phys. Chem. B* **2006**, *110* (6), 2833−2839.

(16) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental vapor pressures of 1-alkylimidazolium bis(trifluoromethylsulfonyl)imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *J. Phys. Chem. A* **2006**, *110*, 7303−7306.

(17) Martin, J. D. Structure-property relationships in ionic liquids. *ACS Symp. Ser.* **2002**, *818 (Ionic Liquids)*, 413−427.

(18) Wassell, D. F.; Seddon, K. R. Structure - property relationships for ionic liquids. *Abstracts of Papers*, 223rd ACS National Meeting, Orlando, FL, April 7−11, 2002; American Chemical Society, Washington, DC, 2002.

(19) Baltus, R. E.; Culbertson, B. H.; Dai, S.; Luo, H.; DePaoli, D. W. Low-Pressure Solubility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance. *J. Phys. Chem. B* **2004**, *108* (2), 721−727.

(20) *Cyphos 101 IL, Cyphos 105 IL, Cyphos 109 IL*; Cytec Industries: Canada, Niagara Falls, ON.

(21) Baker, S. N.; McCleskey, T. M.; Pandey, S.; Baker, G. A. Fluorescence studies of protein thermostability in ionic liquids. *Chem. Commun.* **2004**, *940*.

(22) Page, P. M.; McCarty, T. A.; Baker, G. A.; Baker, S. N.; Bright, F. V. Comparison of Dansylated Aminopropyl Controlled Pore Glass Solvated by Molecular and Ionic Liquids. *Langmuir* **2007**, *23*, 843.

(23) Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449.

(24) Harkins, W. D.; Jordan, H. F. A method for the determination of surface tension from the maximum pull on a ring. *J. Am. Chem. Soc.* **1930**, *52*, 1751−1772.

(25) Huh, C.; Mason, S. G. Rigorous theory of ring tensiometry. *Colloid Polym. Sci.* **1975**, *253* (7), 566−580.

(26) Law, G.; Watson, P. R. Surface Tension Measurements of N-alkylimidazolium Ionic Liquids. *Langmuir* **2001**, *17*, 6138−6141.

(27) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; 6th ed.; Wiley-Interscience: New York, 1997.

(28) Reiss, H.; Mayer, S. W. Theory of surface tension of molten salts. *J. Chem. Phys.* **1961**, *34* (6), 2001−2003.

(29) Reid, R. C.; Sherwood, T. K. *The properties of gases and liquids: Their estimation and correlation*, 2nd ed.; McGraw-Hill: New York, 1966.

(30) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of Imidazolium and Pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(31) Law, G.; Watson, P. R. Surface Orientation in Ionic Liquids. *Chem. Phys. Lett.* **2001**, *345*, 1−4.

(32) Korosi, G.; Kovats, E. S. Density and surface tension of 83 organic liquids. *J. Chem. Eng. Data* **1981**, *26* (3), 323−332.

(33) Mayer, S. W. A molecular parameter relationship between surface tension and liquid compressibility. *J. Phys. Chem.* **1963**, *67*, 2160.

(34) Rebelo, L. P. N.; Lopes, J. N. C.; Esperanca, J. MS. S.; Filipe, E. On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040−6043.

(35) Zhou, Z. B.; Matsumoto, H.; Tatsumi, K. Structure and properties of new ionic liquids based on alkyl- and alkenyl trifluoroborates *Chem. Phys. Chem.* **2005**, *6*, 1324−1332.

Received for review May 31, 2007. Accepted August 26, 2007. The bulk of funding for this work came from the Defense Advanced Projects Agency (DARPA Award DAAD 19-03-0053) and the Mississippi Space Grant Consortium. The authors thank the Graduate Student Council, The University of Mississippi, for providing funding for the purchase of [N(4)111][Tf_2N] ionic liquid and standard specific gravity bottles.

JE7003098