Densities and Derived Thermodynamic Properties of Ionic Liquids. 3. Phosphonium-Based Ionic Liquids over an Extended Pressure Range

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The current study focuses on several phosphonium-based ionic liquids, namely, trihexyltetradecylphosphonium chloride, trihexyltetradecylphosphonium acetate, and trihexyltetradecylphosphonium bis{(trifluoromethyl)sulfonyl}-amide. The objective was to study the influence of pressure as well as that of the anion on several properties of this type of ionic liquids. Densities in pure ionic liquids as a function of temperature and pressure have been determined. Other thermodynamic properties, such as the isothermal compressibility, the isobaric expansivity, and the thermal pressure coefficient, have been calculated. Density measurements have been performed at a broad range of temperature ($298 < T/\mathrm{K} < 333$) and pressure ($0.1 < p/\mathrm{MPa} < 65$) using a vibrating tube densimeter. A simple ideal-volume model was employed for the prediction of the molar volumes of the phosphonia at ambient conditions, which proved to compare favorably with the experimental results.

Introduction

Ionic liquids (ILs) have already proven to be clean alternatives and/or task-specific materials[1] in disparate applications[2] due to their multi-faced pure state and solution thermodynamic behavior[3], broad temperature range of liquid stability, and almost null vapor pressure.[4] Despite the fact that most of the published research studies are directed at two or three main classes of cations (namely, 1-alkyl-3-methylimidazolium, ammonium, and pyridinium), phosphonium-based ILs are mentioned as new options in this area in several review papers[5−7] and patents.[8−10]

The thermophysical characterization of benign ILs is by no means extensive. Examples of very recent reviews and systematic studies can be found, for instance, in refs 11 and 12 and references therein. We have recently published data for 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)amide [bmim][NTf_2], and 1-hexyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)amide [hmim] [NTf_2].[13]

In the case of phosphonium-based ionic liquids, the thermophysical property data are scarce.[14] We have thus focused on density measurements of several phosphonium-based ILs (namely, trihexyl(tetradecyl)phosphonium chloride, [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl], trihexyl(tetradecyl)phosphonium bis{(trifluoromethyl) sulfonyl}amide [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$], and trihexyl (tetradecyl)phosphonium acetate [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac].

Experimental Section

Densimeter. Densities were measured using an Anton Paar DMA 512P densimeter[15] in the temperature range 298 K to 333 K and pressure range 0.1 MPa to 65 MPa. Judging by the residuals of the overall fit in comparison with literature data for the calibrating liquids,[15] the overall density uncertainty is estimated to be better than 0.02 %. It should be noted that this figure may increase if one considers possible viscosity corrections.[16] This type of corrections, irrespective of their origin, rely on both the existence of pressure-dependent viscosity data and properly evaluated equations for the correlation between viscosity and signal damping. As for the first, to date there are no viscosity data of these ILs except for [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl] and [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$] at atmospheric pressure.[14] In the case of the latter, different corrections have been proposed,[16] which basically depend on the instrument model and viscosity range. These issues are still under debate, and in light of the above-mentioned caveats, we have not performed any viscosity corrections. Therefore, all the results of the subsequent derived properties and their discussions are based on raw density data. Nonetheless, at atmospheric pressure, one should expect a slight downward shift in density in the low-temperature range of about 0.15 % for [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl], decreasing to about 0.05 % in the high-temperature range. In the case of [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$], the shift is about 0.07 % at 298 K. Judging from the known shifts of viscosities presented by imidazolium-based ILs[12b,14c,17] upon anion substitution, one also expects that the other phosphonium (acetate) will present low viscosities and, thus, small density corrections.

Chemicals. [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl] was purchased from Cytec (sold under the brand name CYPHOS IL 101). The other ionic liquids were synthesized at the QUILL Centre, Belfast, by metathesis reaction of [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl] with [Li][$NTf_2$] and acetic acid to give [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$] and trihexyl(tetradecyl)phosphonium acetate [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac], respectively. The reaction was carried out according to procedures found elsewhere.[14a] All samples were washed thoroughly with water to remove the undesired salt formed in the reaction and any potential water-soluble impurity that might be present. To reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa) and moderate temperature (70 °C) were applied to the IL samples for several days always immediately prior to their use. Coulometric Karl-Fisher titrations revealed very low levels of water (expressed as parts per million

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Table 1. Experimental Density (ρ) Data for [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl] as a Function of Temperature (T) and Pressure (p)

	ρ/kg·m^{-3} at T/K							
p/MPa	298.13	303.15	308.13	313.15	318.15	323.14	328.16	333.14
0.19	891.62	888.51	885.65	882.72	879.82	876.69	873.88	870.88
1.00	892.02	888.97	886.07	883.19	880.27	877.16	874.33	871.36
3.00	893.07	890.03	887.18	884.30	881.41	878.29	875.50	872.51
5.01	894.09	891.06	888.26	885.40	882.52	879.43	876.64	873.64
7.50	895.36	892.35	889.57	886.75	883.89	880.82	878.05	875.05
10.00	896.59	893.60	890.87	888.06	885.24	882.18	879.42	876.42
15.01	899.02	896.10	893.38	890.63	887.86	884.84	882.11	879.11
19.99	901.33	898.48	895.82	893.11	890.37	887.38	884.69	881.72
25.01	903.60	900.78	898.17	895.49	892.81	889.86	887.20	884.25
29.99	905.77	903.01	900.42	897.81	895.15	892.24	889.62	886.71
35.01	907.93	905.17	902.63	900.04	897.43	894.57	891.98	889.11
39.99	910.01	907.28	904.75	902.21	899.63	896.82	894.24	891.46
45.01	912.05	909.34	906.82	904.32	901.78	899.01	896.49	893.73
50.00	914.03	911.34	908.83	906.35	903.87	901.13	898.62	895.96
55.00	915.93	913.27	910.78	908.34	905.90	903.19	900.74	898.14
59.99	917.83	915.17	912.67		907.87	905.21	902.79	900.26
65.00	919.63	916.99	914.51		909.78	907.16	904.80	902.35

Table 2. Experimental Density (ρ) Data for [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac] as a Function of Temperature (T) and Pressure (p)

	ρ/kg·m^{-3} at T/K							
p/MPa	298.15	303.15	307.97	313.07	317.74	323.96	329.14	334.11
0.21	890.60	887.54	884.70	881.57	878.87	875.25	872.15	869.21
0.54	890.77	887.71	884.86	881.77	879.06	875.43	872.35	869.41
1.00	891.01	887.96	885.13	882.02	879.32	875.70	872.61	869.67
3.00	892.04	889.03	886.22	883.14	880.46	876.87	873.78	870.81
5.01	893.09	890.08	887.29	884.26	881.60	878.00	874.92	871.98
7.50	894.35	891.38	888.60	885.61	882.99	879.40	876.33	873.42
9.99	895.56	892.64	889.90	886.96	884.32	880.77	877.71	874.78
15.01	897.96	895.15	892.45	889.57	886.95	883.42	880.41	877.50
19.99	900.29	897.52	894.88	892.06	889.47	885.99	883.00	880.11
25.01	902.57	899.86	897.23	894.49	891.91	888.48	885.53	882.67
29.99	904.74	902.08	899.51	896.77	894.26	890.86	887.95	885.12
35.01	906.90	904.28	901.72	899.05	896.54	893.19	890.32	887.57
40.02	908.99	906.41	903.88	901.21	898.76	895.47	892.64	889.93
45.01	911.02	908.45	905.95	903.32	900.88	897.65	894.88	892.22
49.99	912.98	910.44	907.95	905.38	902.96	899.78	897.06	894.45
55.00	914.91	912.40	909.92	907.36	904.98	901.85	899.19	896.66
59.99	916.81	914.31	911.84	909.27	906.93	903.86	901.27	898.81
65.01	918.66	916.16	913.69	911.16	908.84	905.84	903.30	900.91

in mass (ppm), below 60, 150, and 50 ppm for [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl], [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$], and [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac], respectively) to be compared with values in the range 1000 to 15 000 ppm of water for the untreated samples.

Results

Density measurements were carried out at a broad range of temperatures ($298 < T/K < 333$) and pressures ($0.1 < p/MPa < 65$). For [$(C_6H_{13})_3P(C_{14}H_{29})$][Cl], [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac], and [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$], the experimental data are reported in Tables 1 to 3, respectively, and in the case of [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac], a graphical illustration is given (Figure 1). For the sake of economy, data are presented at nominal temperatures that typically differ from the experimental ones by no more than 0.01 K. The only data available for comparison[14a] have been reported in a graphical form. Therefore, no accurate judgment of differences between experimental results is possible.

The absence of heat capacity and speed of sound data compelled the direct use of the derivatives of density in order to obtain other thermodynamic properties of this substance (namely, the isobaric thermal expansion coefficient, α_p; the isothermal compressibility, κ_T; and the thermal pressure coefficient, γ_v). The fitting of the isobaric density data was performed using a Tait equation[18] as presented by eq 1:

$$\rho = \rho^* + A \ln\left(\frac{B + 0.1/\text{MPa}}{B + p/\text{MPa}}\right) \quad (1)$$

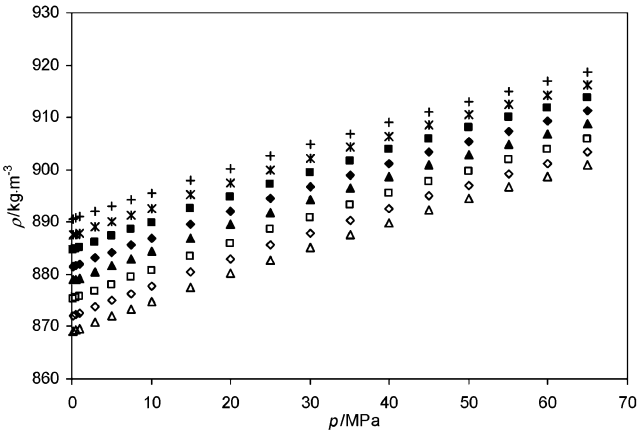

Figure 1. Isotherms of the experimental density of [$(C_6H_{13})_3P(C_{14}H_{29})$][Ac]: +, 298.15 K; ∗, 303.15 K; ■, 307.97 K; ◆, 313.07 K; ▲, 317.74 K; □, 323.96 K; ◇, 329.14 K; △, 334.11 K.

Table 3. Experimental Density (ρ) Data for [$(C_6H_{13})_3P(C_{14}H_{29})$][$NTf_2$] as a Function of temperature (T) and Pressure (p)

	ρ/kg·m^{-3} at T/K						
p/MPa	298.15	303.25	308.15	318.27	323.33	328.39	333.43
0.21	1066.62	1062.61	1058.87	1051.54	1047.84	1044.49	1041.15
0.54	1066.84	1062.85	1059.07	1051.79	1048.07	1044.74	1041.43
1.00	1067.13	1063.14	1059.37	1052.10	1048.38	1045.08	1041.76
3.00	1068.44	1064.47	1060.76	1053.49	1049.81	1046.53	1043.19
5.01	1069.70	1065.77	1062.11	1054.88	1051.24	1047.96	1044.61
7.50	1071.30	1067.39	1063.74	1056.54	1052.94	1049.68	1046.40
9.99	1072.85	1068.97	1065.36	1058.20	1054.64	1051.40	1048.13
15.01	1075.88	1072.09	1068.53	1061.47	1057.95	1054.74	1051.51
19.99	1078.82	1075.07	1071.57	1064.60	1061.14	1057.90	1054.80
25.01	1081.69	1078.00	1074.54	1067.62	1064.22	1061.01	1057.94
29.99	1084.45	1080.84	1077.42	1070.51	1067.21	1064.03	1060.97
35.01	1087.15	1083.56	1080.23	1073.32	1070.14	1066.99	1063.96
40.00	1089.79	1086.26	1082.95	1076.09	1072.99	1069.88	1066.84
45.01	1092.36	1088.87	1085.64	1078.77	1075.75	1072.64	1069.67
50.00	1094.88	1091.44	1088.25	1081.37	1078.47	1075.39	1072.43
55.01	1097.34	1093.95	1090.80	1084.00	1081.14	1078.08	1075.17
59.99	1099.74	1096.39	1093.30	1086.50	1083.74	1080.67	1077.73
65.01	1102.11	1098.81	1095.75	1088.91	1086.30	1083.24	1080.29

where ρ^* is the density at a given temperature and at a reference pressure of 0.1 MPa. This equation is known to represent very well the density behavior of liquids overpressure at constant temperature.

The parameters for each isotherm are shown in Table 4. The isothermal compressibility is calculated using the isothermal pressure derivative of density according to eq 2:

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T = \left(\frac{\partial \ln \rho}{\partial p}\right)_T \quad (2)$$

Unfortunately, there is no equivalent of the Tait equation for the behavior of density with temperature at constant pressure. A detailed evaluation of the raw data reveals that deviations from linearity in density−temperature (or volume−temperature) plots are so mild that the determination of the thermal expansion coefficient (α_p) is extremely dependent on the choice of the type of function to screen the data. For those situations where the statistical scatter of the raw data is large as compared to an unambiguous determination of the curvature, the use of $\ln \rho = f(T)$ is preferred.[11,13] If this function proves to be linear, then $\ln V = f(T)$ is as well, and α_p is constant (temperature independent).

$$\alpha_p = -\left(\frac{\partial \ln \rho}{\partial T}\right)_p = \left(\frac{\partial \ln V}{\partial T}\right)_p \quad (3)$$

Table 4. Coefficients of the Tait Equation (eq 1) for the Density at Each Isotherm (0.1 < *p*/MPa < 65)

T/K	ρ^*/kg·m^{-3}	*A*/kg·m^{-3}	*B*/MPa
	$[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$		
298.13	891.57	−75.97	145.07
303.15	888.47	−72.48	134.47
308.13	885.59	−68.62	123.69
313.15	882.68	−69.36	122.54
318.15	879.76	−71.98	125.33
323.14	876.64	−74.84	128.79
328.16	873.83	−77.92	132.93
333.14	870.84	−90.25	155.31
	$[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$		
298.15	890.55	−77.69	148.90
303.15	887.48	−72.91	134.59
307.97	884.63	−70.47	127.01
313.07	881.51	−67.34	117.23
317.74	878.81	−69.16	119.29
323.96	875.19	−74.62	127.73
329.14	872.09	−81.08	138.23
334.11	869.16	−91.80	157.05
	$[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$		
298.15	1066.56	−102.95	157.40
303.25	1062.55	−103.31	154.42
308.15	1058.80	−105.08	154.07
318.27	1051.48	−97.55	138.74
323.33	1047.77	−106.88	149.71
328.39	1044.45	−106.23	147.35
333.43	1041.09	−103.54	140.99

Table 5. Parameters of the Linear Fit $\ln(\rho/\text{kg·m}^{-3}) = c + d(T/\text{K})$[a]

p/MPa	*c*	d/K^{-1}·10^4	*p*/MPa	*c*	d/K^{-1}·10^4
		$[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$			
0.19	6.993083	−6.709981	29.99	6.989075	−6.044042
1.00	6.992713	−6.682316	35.01	6.988516	−5.946346
3.00	6.992506	−6.635685	39.99	6.987972	−5.851881
5.01	6.992182	−6.586168	45.01	6.987427	−5.759328
7.50	6.991890	−6.528546	50.00	6.987008	−5.673339
10.00	6.991543	−6.470522	55.00	6.986118	−5.574437
15.01	6.991061	−6.362956	59.99	6.985596	−5.489385
19.99	6.990482	−6.256276	65.00	6.984427	−5.385921
25.01	6.989825	−6.149985			
		$[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$			
0.21	6.992997	−6.745849	25.01	6.989892	−6.188681
0.54	6.992735	−6.731317	29.99	6.989269	−6.086886
1.00	6.992842	−6.725562	35.01	6.988686	−5.987614
3.00	6.992638	−6.678801	40.02	6.988035	−5.888995
5.01	6.992373	−6.630674	45.01	6.987325	−5.791533
7.50	6.991853	−6.565559	49.99	6.986653	−5.697319
9.99	6.991472	−6.506218	55.00	6.985964	−5.604293
15.01	6.990979	−6.397984	59.99	6.985435	−5.518489
19.99	6.990425	−6.291792	65.01	6.984675	−5.427076

[a] $\alpha_p = -(\partial \ln \rho/\partial T)_p = -d$.

For $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$ and $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$, the behavior of ln ρ proved to be linear, with residuals within the expected accuracy of the density measurements. For $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$, this behavior is not linear, and the equation used was a second-order polynomial equation in ln *r*. The coefficients of the fittings are presented in Tables 5 and 6 for different ILs. In the case of $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$ and $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$, the α_p is directly given by the module of the slope of the linear equation. The other calculated properties (such as a_p, κ_T, and γ_v) are presented in Tables 7 to 13 , and some are plotted in Figures 2 to 5. As far as the authors are aware, no comparison data exist for these properties of these ionic liquids.

Discussion

Although the current results cannot be compared with others, it is possible to use a simplified model to predict the observed molar volumes of the current phosphonia. We have recently developed such a model[11] that is briefly described below.

An "ideal" volumetric behavior has been observed[11] for 1-C$_n$-3-methylimidazolium-based ILs. Along with others,[17,19] we note an impressive degree of linearity in the plots of molar volume (V_m) versus the number of carbons in the alkyl chain (*n*). Moreover, a master slope ($\partial V_m/\partial(2n)$) for the variation of the molar volume per addition of two carbon atoms, ($\partial V_m/\partial(2n)$) = (34.4 ± 0.5) cm^3·mol^{-1}, is obtained irrespective of the anion

Table 6. Parameters of the Fit $\ln(\rho/\text{kg·m}^{-3}) = c + d(T/\text{K}) + e(T/\text{K})^2$ of $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$[a]

p/MPa	*c*	d/K^{-1}·10^3	e/K^{-2}·10^6
0.21	7.344237	−1.750823	1.687533
0.54	7.351172	−1.794973	1.759986
1.00	7.352072	−1.800316	1.770838
3.00	7.343841	−1.744170	1.688912
5.01	7.336134	−1.691937	1.613780
7.50	7.339679	−1.710236	1.652065
9.99	7.335781	−1.681868	1.616993
15.01	7.321877	−1.585370	1.481554
19.99	7.322457	−1.580665	1.490031
25.01	7.317829	−1.542338	1.443460
29.99	7.314496	−1.512687	1.410312
35.01	7.321268	−1.548119	1.481053
40.00	7.316786	−1.511697	1.436597
45.01	7.316609	−1.502222	1.433445
50.00	7.3206	−1.520069	1.474382
55.01	7.315902	−1.483507	1.429866
59.99	7.302904	−1.392209	1.294473
65.01	7.305186	−1.398713	1.314932

[a] $\alpha_p = -(\partial \ln \rho/\partial T)_p = -(d + 2e(T/\text{K}))$.

Table 7. Calculated Values of κ_T for $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$

	κ_T/GPa^{-1} at *T*/K							
p/MPa	298.13	303.15	308.13	313.15	318.15	323.14	328.16	333.14
0.19	0.586_5	0.605_7	0.623_2	0.640_3	0.651_8	0.661_9	0.669_7	0.666_4
1.00	0.583_0	0.601_9	0.610_5	0.635_7	0.647_3	0.657_4	0.665_4	0.662_6
3.00	0.574_4	0.592_4	0.600_2	0.624_8	0.636_3	0.646_5	0.654_7	0.653_4
5.01	0.566_1	0.583_2	0.588_0	0.614_2	0.625_8	0.636_0	0.644_3	0.644_4
7.50	0.556_1	0.572_1	0.576_1	0.601_5	0.613_1	0.623_4	0.631_9	0.633_5
10.00	0.546_4	0.561_5	0.553_8	0.589_3	0.600_9	0.611_3	0.619_9	0.622_9
15.01	0.527_8	0.541_1	0.533_1	0.566_2	0.577_7	0.588_2	0.597_0	0.602_7
19.99	0.510_6	0.522_3	0.513_8	0.544_9	0.556_3	0.566_8	0.575_9	0.583_9
25.01	0.494_3	0.504_5	0.495_9	0.524_9	0.536_3	0.546_8	0.556_0	0.566_0
29.99	0.479_1	0.488_0	0.479_0	0.506_5	0.517_7	0.528_3	0.537_6	0.549_3
35.01	0.464_6	0.472_5	0.463_4	0.489_1	0.500_2	0.510_8	0.520_1	0.533_3
39.99	0.451_1	0.457_9	0.448_6	0.473_0	0.484_0	0.494_4	0.503_9	0.518_4
45.01	0.438_2	0.444_1	0.434_7	0.457_8	0.468_6	0.479_0	0.488_4	0.504_1
50.00	0.426_0	0.431_1	0.421_6	0.443_5	0.454_2	0.464_5	0.474_0	0.490_6
55.00	0.414_5	0.418_9	0.409_3	0.430_1	0.440_6	0.450_8	0.460_3	0.477_8
59.99	0.403_6	0.407_3	0.397_6		0.427_8	0.437_9	0.447_3	0.465_6
65.00	0.393_2	0.396_2	0.397_7		0.415_7	0.425_7	0.435_1	0.454_0

Table 8. Calculated Valuesof γ_v for $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$

	γ_v/MPa·K^{-1} at *T*/K							
p/MPa	298.13	303.15	308.13	313.15	318.15	323.14	328.16	333.14
0.19	1.144_0	1.107_7	1.074_5	1.048_0	1.029_5	1.013_8	1.001_9	1.006_9
1.00	1.146_2	1.110_3	1.087_0	1.051_2	1.032_4	1.016_5	1.004_3	1.008_5
3.00	1.155_2	1.120_2	1.097_2	1.062_1	1.042_8	1.026_3	1.013_6	1.015_6
5.01	1.163_3	1.129_3	1.110_3	1.072_4	1.052_5	1.035_5	1.022_2	1.022_1
7.50	1.174_0	1.141_1	1.123_1	1.085_4	1.064_9	1.047_2	1.033_2	1.030_6
10.00	1.184_3	1.152_4	1.149_0	1.098_0	1.076_9	1.058_5	1.043_8	1.038_7
15.01	1.205_5	1.175_9	1.173_5	1.123_8	1.101_5	1.081_8	1.065_8	1.055_7
19.99	1.225_3	1.197_9	1.197_0	1.148_2	1.124_6	1.103_7	1.086_4	1.071_5
25.01	1.244_2	1.218_9	1.218_9	1.171_5	1.146_8	1.124_6	1.106_0	1.086_5
29.99	1.261_6	1.238_4	1.241_3	1.193_4	1.167_5	1.144_1	1.124_3	1.100_4
35.01	1.279_8	1.258_5	1.262_9	1.215_7	1.188_7	1.164_2	1.143_2	1.114_9
39.99	1.297_4	1.278_0	1.283_9	1.237_2	1.209_2	1.183_6	1.161_4	1.128_9
45.01	1.314_3	1.296_8	1.305_1	1.258_1	1.229_1	1.202_4	1.179_1	1.142_5
50.00	1.331_6	1.315_9	1.322_1	1.279_2	1.249_1	1.221_3	1.197_0	1.156_4
55.00	1.344_8	1.330_9	1.341_1	1.296_1	1.265_2	1.236_5	1.211_1	1.166_7
59.99	1.360_1	1.347_8	1.354_4		1.283_1	1.253_4	1.227_1	1.179_0
65.00	1.369_7	1.359_2	1.354_4		1.295_7	1.265_2	1.238_0	1.186_4

Table 9. Calculated Values of κ_T for $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$

	κ_T/GPa^{-1} at T/K							
p/MPa	298.15	303.15	307.97	313.07	317.74	323.96	329.14	334.11
0.21	0.585_1	0.609_4	0.626_1	0.650_5	0.658_5	0.666_4	0.671_5	0.671_6
0.54	0.583_6	0.607_8	0.624_3	0.648_5	0.656_5	0.664_5	0.669_8	0.670_0
1.00	0.581_7	0.605_6	0.621_9	0.645_8	0.653_8	0.662_0	0.667_4	0.667_8
3.00	0.573_4	0.596_0	0.611_6	0.634_2	0.642_3	0.651_0	0.657_0	0.658_6
5.01	0.565_2	0.586_7	0.601_5	0.623_0	0.631_1	0.640_3	0.647_0	0.649_6
7.50	0.555_4	0.575_6	0.589_5	0.609_6	0.617_7	0.627_5	0.634_9	0.638_7
9.99	0.546_0	0.564_9	0.578_0	0.596_8	0.604_9	0.615_2	0.623_2	0.628_2
15.01	0.527_9	0.544_4	0.556_0	0.572_5	0.580_6	0.591_8	0.601_0	0.608_0
19.99	0.511_0	0.525_5	0.535_7	0.550_1	0.558_2	0.570_2	0.580_3	0.589_1
25.01	0.495_0	0.507_6	0.516_6	0.529_3	0.537_3	0.549_9	0.560_9	0.571_2
29.99	0.480_0	0.491_1	0.499_0	0.510_1	0.518_0	0.531_1	0.542_8	0.554_5
35.01	0.465_8	0.475_4	0.482_3	0.492_0	0.499_9	0.513_4	0.525_7	0.538_5
40.02	0.452_4	0.460_6	0.466_7	0.475_2	0.483_0	0.496_8	0.509_6	0.523_4
45.01	0.439_8	0.446_9	0.452_2	0.459_5	0.467_2	0.481_3	0.494_5	0.509_2
49.99	0.427_9	0.433_8	0.438_5	0.444_8	0.452_4	0.466_7	0.480_2	0.495_7
55.00	0.416_5	0.421_5	0.425_5	0.430_9	0.438_4	0.452_8	0.466_6	0.482_8
59.99	0.405_7	0.409_8	0.413_2	0.417_9	0.425_3	0.439_8	0.453_8	0.470_6
65.01	0.395_4	0.398_7	0.401_6	0.405_6	0.412_9	0.427_4	0.441_7	0.458_9

Table 10. Calculated Values of γ_v for $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$

	γ_v/MPa·K^{-1} at T/K							
p/MPa	298.15	303.15	307.97	313.07	317.74	323.96	329.14	334.11
0.21	1.153_0	1.107_0	1.077_5	1.037_1	1.024_4	1.012_3	1.004_5	1.004_5
0.54	1.153_3	1.107_6	1.078_2	1.038_0	1.025_3	1.012_9	1.005_0	1.004_7
1.00	1.156_2	1.110_7	1.081_4	1.041_4	1.028_6	1.016_0	1.007_8	1.007_0
3.00	1.164_9	1.120_6	1.092_1	1.053_1	1.039_9	1.026_0	1.016_5	1.014_1
5.01	1.173_1	1.130_1	1.102_3	1.064_3	1.050_7	1.035_6	1.024_9	1.020_8
7.50	1.182_1	1.140_6	1.113_7	1.077_0	1.062_9	1.046_3	1.034_2	1.028_0
9.99	1.191_6	1.151_8	1.125_7	1.090_2	1.075_6	1.057_6	1.044_0	1.035_7
15.01	1.212_1	1.175_2	1.150_8	1.117_6	1.102_0	1.081_1	1.064_6	1.052_3
19.99	1.231_4	1.197_3	1.174_6	1.143_7	1.127_1	1.103_5	1.084_2	1.068_0
25.01	1.250_3	1.219_1	1.197_9	1.169_2	1.151_7	1.125_4	1.103_3	1.083_4
29.99	1.268_0	1.239_5	1.219_9	1.193_3	1.175_0	1.146_1	1.121_4	1.097_8
35.01	1.285_4	1.259_5	1.241_4	1.216_9	1.197_7	1.166_3	1.139_0	1.111_9
40.02	1.301_7	1.278_4	1.261_8	1.239_3	1.219_3	1.185_5	1.155_7	1.125_1
45.01	1.316_8	1.296_1	1.280_8	1.260_3	1.239_5	1.203_4	1.171_3	1.137_4
49.99	1.331_6	1.313_2	1.299_4	1.280_9	1.259_2	1.220_9	1.186_4	1.149_4
55.00	1.345_7	1.329_7	1.317_2	1.300_6	1.278_2	1.237_7	1.201_0	1.160_8
59.99	1.360_4	1.346_6	1.335_4	1.320_5	1.297_5	1.254_8	1.215_9	1.172_7
65.01	1.372_7	1.361_2	1.351_2	1.338_2	1.314_4	1.269_7	1.228_8	1.182_7

Table 11. Calculated Values of κ_T for $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$

	κ_T/GPa^{-1} at T/K						
p/MPa	298.15	303.25	308.15	318.27	323.33	328.39	333.43
0.21	0.612_4	0.628_8	0.643_2	0.667_6	0.680_4	0.689_3	0.704_3
0.54	0.611_0	0.627_3	0.641_7	0.665_8	0.678_7	0.687_6	0.702_5
1.00	0.609_0	0.625_3	0.639_6	0.663_5	0.676_5	0.685_2	0.700_0
3.00	0.600_7	0.616_5	0.630_6	0.653_2	0.666_7	0.675_1	0.689_3
5.01	0.592_6	0.608_0	0.621_9	0.643_3	0.657_2	0.665_3	0.678_9
7.50	0.582_7	0.597_8	0.611_4	0.631_3	0.645_7	0.653_6	0.666_4
9.99	0.573_2	0.587_8	0.601_2	0.619_8	0.634_6	0.642_2	0.654_3
15.01	0.555_0	0.568_8	0.581_6	0.597_7	0.613_3	0.620_4	0.631_2
19.99	0.537_9	0.551_0	0.563_4	0.577_2	0.593_5	0.600_1	0.609_8
25.01	0.521_7	0.534_1	0.546_1	0.558_0	0.574_8	0.580_9	0.589_6
29.99	0.506_6	0.518_3	0.529_9	0.540_0	0.557_3	0.563_0	0.570_8
35.01	0.492_1	0.503_3	0.514_5	0.523_1	0.540_7	0.546_0	0.552_9
40.00	0.478_5	0.489_2	0.499_9	0.507_1	0.525_1	0.530_0	0.536_2
45.01	0.465_6	0.475_8	0.486_2	0.492_1	0.510_3	0.514_9	0.520_4
50.00	0.453_3	0.463_0	0.473_2	0.477_9	0.496_2	0.500_5	0.505_5
55.01	0.441_7	0.450_9	0.460_7	0.464_5	0.482_9	0.487_0	0.491_3
59.99	0.430_6	0.439_5	0.449_0	0.451_8	0.470_3	0.474_1	0.478_0
65.01	0.420_0	0.428_5	0.437_7	0.439_7	0.458_3	0.461_8	0.465_3

considered (Cl^-, Br^-, $[NO_3]^-$, $[BF_4]^-$, $[PF_6]^-$, and $[NTf_2]^-$). That linearity prompted us to anchor the effective volume occupied by one type of anion in 1 mol of IL (1 mol of anion and 1 mol of cation) from which point one can establish the effective volume ("molar size") occupied by all the other anions and cations. This can be used as a predictive tool for the estimation of molar volumes of ILs.

We anchored the "size" of the $[PF_6]^-$ anion by using 1.73 Å for the P−F bond length and 1.35 Å for the van der Waals radius of the fluorine ion.[20] In other words, we set the size of this anion as an equivalent hard sphere of radius equal to 3.08 Å. This value leads to an effective volume of 73.71 cm^3·mol^{-1}. The molar volume (V_m) of a given ionic liquid, [C][A], is considered as the sum of the effective molar volumes (V^*) occupied by the cation ($[C]^+$) and the anion ($[A]^-$):

$$V_m = V^*_c + V^*_a \quad (4)$$

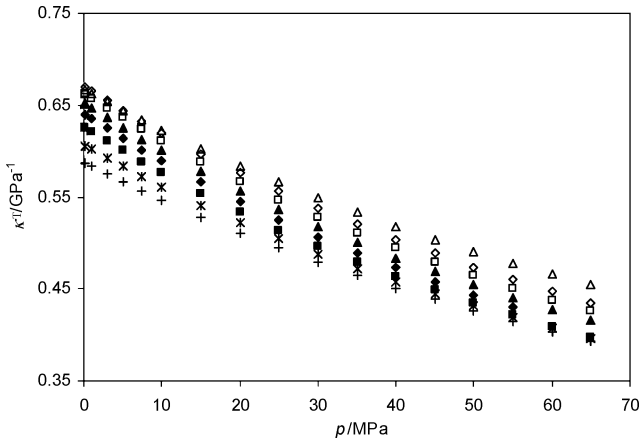

Figure 2. Isotherms for the isothermal compressibility of $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$: +, 298.13 K; ∗, 303.15 K; ■, 308.13 K; ◆, 313.15 K; ▲, 318.15 K; □, 323.14 K; ◇, 328.16 K; △, 333.14 K.

Table 12. Calculated Values of α_p for $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$

	α_p/K^{-1} at T/K						
p/MPa	298.15	303.25	308.15	318.27	323.33	328.39	333.43
0.21	0.743_7	0.727_0	0.710_9	0.676_8	0.659_7	0.642_2	0.624_6
0.54	0.744_6	0.727_2	0.710_4	0.674_9	0.657_0	0.638_8	0.620_5
1.00	0.743_4	0.726_0	0.709_0	0.673_3	0.655_3	0.636_9	0.618_6
3.00	0.736_2	0.719_5	0.703_4	0.669_3	0.652_2	0.634_6	0.617_1
5.01	0.728_8	0.712_9	0.697_4	0.664_9	0.648_5	0.631_8	0.615_1
7.50	0.724_3	0.708_0	0.692_1	0.658_9	0.642_1	0.624_9	0.607_8
9.99	0.716_8	0.700_9	0.685_4	0.652_8	0.636_4	0.619_6	0.602_8
15.01	0.701_2	0.686_5	0.672_3	0.642_5	0.627_4	0.612_1	0.596_7
19.99	0.691_4	0.676_7	0.662_4	0.632_4	0.617_3	0.601_9	0.586_4
25.01	0.680_9	0.666_6	0.652_7	0.623_7	0.609_0	0.594_1	0.579_2
29.99	0.671_0	0.657_0	0.643_5	0.615_2	0.600_8	0.586_3	0.571_6
35.01	0.664_2	0.649_6	0.635_3	0.605_6	0.590_5	0.575_2	0.559_9
40.00	0.654_4	0.640_1	0.626_3	0.597_5	0.582_8	0.568_0	0.553_1
45.01	0.646_8	0.632_6	0.618_7	0.590_0	0.575_4	0.560_6	0.545_8
50.00	0.640_2	0.625_6	0.611_3	0.581_9	0.566_7	0.551_6	0.536_3
55.01	0.630_2	0.616_0	0.602_2	0.573_6	0.558_9	0.544_3	0.529_5
59.99	0.619_7	0.606_9	0.594_4	0.568_5	0.555_2	0.541_9	0.528_5
65.01	0.614_0	0.600_9	0.588_2	0.562_0	0.548_4	0.534_9	0.521_4

Table 13. Calculated Values of γ_v for$[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$

	γ_v/MPa·K^{-1} at T/K						
p/MPa	298.15	303.25	308.15	318.27	323.33	328.39	333.43
0.21	1.214_4	1.156_3	1.105_1	1.013_8	0.969_6	0.931_7	0.886_9
0.54	1.218_7	1.159_3	1.107_0	1.013_6	0.968_0	0.929_0	0.883_3
1.00	1.220_7	1.161_0	1.108_4	1.014_8	0.968_7	0.929_5	0.883_7
3.00	1.225_6	1.167_1	1.115_3	1.024_6	0.978_2	0.940_0	0.895_3
5.01	1.229_9	1.172_4	1.121_4	1.033_6	0.986_9	0.949_6	0.906_0
7.50	1.242_9	1.184_4	1.132_1	1.043_6	0.994_4	0.956_2	0.912_1
9.99	1.250_5	1.192_3	1.140_0	1.053_3	1.002_8	0.964_9	0.921_4
15.01	1.263_4	1.207_0	1.156_0	1.075_0	1.023_0	0.986_7	0.945_4
19.99	1.285_3	1.228_2	1.175_8	1.095_6	1.039_9	1.003_0	0.961_7
25.01	1.305_0	1.248_0	1.195_4	1.117_9	1.059_5	1.022_8	0.982_3
29.99	1.324_6	1.267_6	1.214_5	1.139_2	1.078_0	1.041_3	1.001_5
35.01	1.349_7	1.290_5	1.234_9	1.157_8	1.092_0	1.053_5	1.012_6
40.00	1.367_5	1.308_5	1.252_7	1.178_2	1.109_9	1.071_7	1.031_5
45.01	1.389_1	1.329_5	1.272_6	1.199_0	1.127_6	1.088_8	1.048_8
50.00	1.412_2	1.351_0	1.292_0	1.217_5	1.142_0	1.101_9	1.061_0
55.01	1.426_9	1.366_0	1.307_0	1.235_1	1.157_4	1.117_7	1.077_7
59.99	1.439_3	1.380_8	1.323_8	1.258_5	1.180_4	1.143_0	1.105_7
65.01	1.462_0	1.402_5	1.343_8	1.278_4	1.196_8	1.158_3	1.120_6

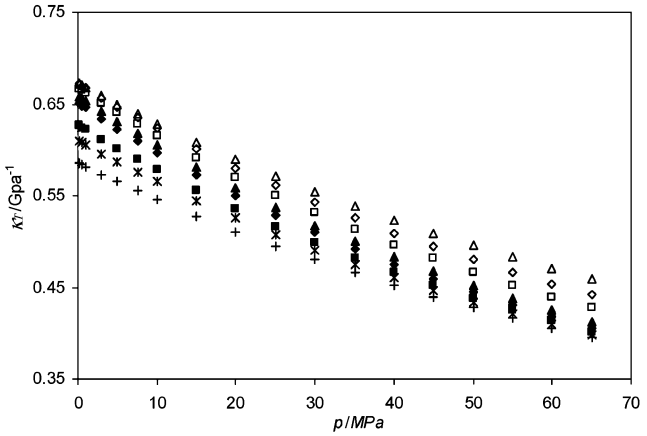

Figure 3. Isotherms for the isothermal compressibility of $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$: +, 298.15 K; ∗, 303.15 K; ■, 307.97 K; ◆, 313.07 K; ▲, 317.74 K; □, 323.96 K; ◇, 329.14 K; △, 334.11 K.

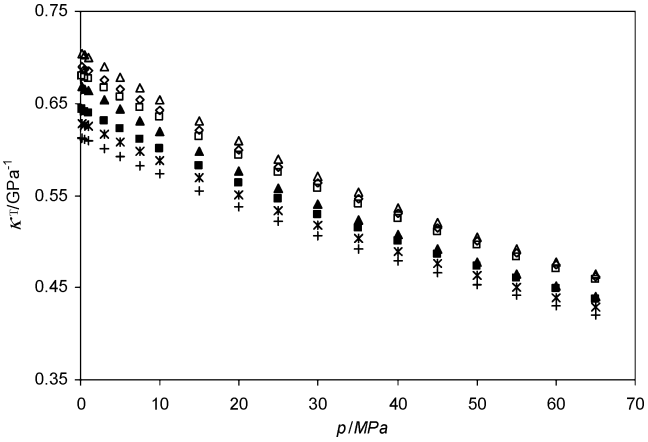

Figure 4. Isotherms for the isothermal compressibility of $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$: +, 298.15 K; ∗, 303.25 K; ■, 308.15 K; ▲, 318.27 K; □, 323.33 K; ◇, 328.29 K; △, 333.43 K.

Differences between the effective volumes occupied by different anions are merely taken from the differences between corresponding straight lines (each straight line corresponds to a fixed anion). The obtained effective molar volumes of several anions and 1-C_n-3-methylimidazolium and phosphonium cations at 298.15 K and atmospheric pressure are reported in Table 14. The molar volume of a given IL is obtained by the mere sum of the volumes of the anion and cation. For the 1-C_n-3-methylimidazolium-based ILs, the agreement between experimental and predicted values is excellent (better than 1 % and often much better).

The observed common master slope constitutes a fingerprint of ideal behavior in regard to volumetric properties of ILs. The volume of ILs increases by almost exactly the same amount as the addition of units in the alkyl chain in the methylimidazolium cation proceeds (irrespective of the interactions with totally

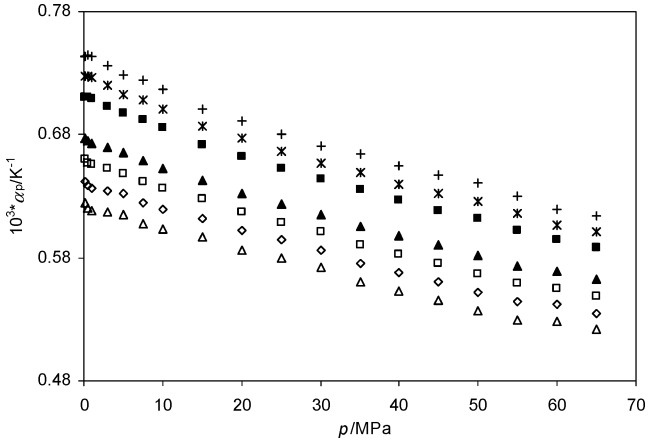

Figure 5. Isotherms for the isobaric expansivity of $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$: +, 298.15 K; ∗, 303.25 K; ■, 308.15 K; ◆, 318.27 K; ▲, 323.33 K; □, 328.29 K; △, 333.43 K.

different anions differing in size, shape, and chemical structure). This suggests that binary mixtures constituted by pairs of ILs will be formed with almost null variation of volume (almost null excess molar volume). This is, in fact, what was recently experimentally observed.[21]

As a consequence of the above-mentioned volumetric ideal behavior generally presented by ionic liquids it is possible, for example, to take the effective volume (molar size) occupied by the chloride anion (25.86 $cm^3 \cdot mol^{-1}$) in imidazolium-based ionic liquids and then establish an effective volume occupied by the $[(C_6H_{13})_3P(C_{14}H_{29})]^+$ cation. For instance, at atmospheric pressure and 298.15 K, $V^*_{[(C_6H_{13})_3P(C_{14}H_{29})]^+} = 556.6$ $cm^3 \cdot mol^{-1}$. This volume can then be used as a predictive tool for the estimation of molar volumes of other ILs and anions. Using the effective volume of $[NTf_2]^-$ (158.7 $cm^3 \cdot mol^{-1}$), it is possible to establish the volume of $[(C_6H_{13})_3P(C_{14}H_{29})][NTf_2]$ as 715.3 $cm^3 \cdot mol^{-1}$, which can be compared with the volume, 716.3 $cm^3 \cdot mol^{-1}$, obtained experimentally, showing a deviation of about 0.15 %. The effective volume occupied by the acetate anion is 53.0 $cm^3 \cdot mol^{-1}$ and later can be used for the calculation of molar volumes of new compounds.

Conclusions

The work performed maps the density behavior of three important phosphonium-based ionic liquids over wide pressure and temperature ranges. The density of this class of ionic liquids is significantly lower than that of the commonly used imidazolium-based ILs. Both $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$ and $[(C_6H_{13})_3P(C_{14}H_{29})][Ac]$ show mass densities lower than unity.

At atmospheric pressure, isothermal compressibilities of the ionic liquids studied in this work are higher (≈ 20 %) than those of the imidazolium-based ILs. This result is the expected one because the long alkyl chains connected to the phosphorus atom allow for an open structure with enhanced free-volume. At

Table 14. Effective Size (expressed as molar volume) of Several Anions (V^*_a) and Cations (V^*_c) at 298.15 K and 1 Bar Nominal Pressure[a]

$V^*_a/cm^3 \cdot mol^{-1}$						
$[Cl]^-$	$[Br]^-$	$[NO_3]^-$	$[CH_3CO_2]^-$	$[BF_4]^-$	$[PF_6]^-$	$[NTf_2]^-$
25.9	27.8	39.1	53.0[b]	53.4	73.7	158.7

$V^*_c/cm^3 \cdot mol^{-1}$							
$[C_0mim]^+$	$[C_2mim]^+$	$[C_4mim]^+$	$[C_6mim]^+$	$[C_8mim]^+$	$[C_{10}mim]^+$	$[C_{12}mim]^+$	$[(C_6)_3(C_{14})P]^+$
64.82	99.20	133.58	167.96	202.34	236.72	271.10	556.6[b]

[a] See text. [b] Calculated in this work.

higher pressures this effect diminishes and phosphonia compressibilities become more similar to those of the imidazolia. A very simple ideal-volume model was successfully employed for the estimation of densities of phosphonium-based ionic liquids.

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