Pressure and Temperature Dependence of Isobaric Heat Capacity for [Emim][BF_4], [Bmim][BF_4], [Hmim][BF_4], and [Omim][BF_4][†]

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The isobaric molar heat capacities as a function of temperature and pressure are, for the first time, reported for a set of imidazolium-based ionic liquids. The selected compounds belong to the 1-alkyl-3-methylimidazolium series, concretely, [Emim][BF_4], [Bmim][BF_4], [Hmim][BF_4], and [Omim][BF_4]. Isobaric heat capacity were determined in the temperature and pressure intervals of (283.15 to 323.15) K and (0.1 to 60) MPa using a micro DSCII calorimeter recently adapted to work at high pressure. The data at atmospheric pressure were compared with literature data; as a rule, good results were obtained for all liquids. Isobaric molar heat capacities for the studied ionic liquids show quite a different behavior than that obtained for usual organic solvents, which could be understood as these compounds behave like highly compressed molecular fluids. This is consistent with the behavior of other previously reported thermodynamic properties.

Introduction

Room temperature ionic liquids (RTILs) have a very small vapor pressure[1] and other unique properties which make them potential substitutes to conventional volatile organic solvents in industrial applications.[2−10] They have been used especially as green solvents and catalysts, in many areas of organic synthesis, and in separation chemistry.[11] During the past decade, an expanding interest has been grown not only in the use of RTILs in industrial applications but also in the knowledge of their thermophysical behavior. In spite of the great number of papers in the last few years (examples of recent reviews and systematic studies can be found in refs 12 and 13), most of these works report only experimental measurements of a reduced set of thermophysical properties at atmospheric pressure. However, other properties of RTILs such as the second-order thermodynamic derivatives are still lacking, especially at high pressures. Previous works have shown that RTILs show not only qualitatively different values for these second-order magnitudes, as compared to usual organic solvents, but also quite different behavior against temperature and pressure.[14−22]

It is the aim of this work to analyze the isobaric molar heat capacity, $C_{p,\mathrm{m}}$, for a set of imidazolium-based RTILs as well as its dependencies against temperature and pressure. To this end, a recently adapted micro DSCII calorimeter to work at high pressure[23] was used for measuring $C_{p,\mathrm{m}}$. The RTILs were selected with a view on finding the influence of the alkyl chain of the imidazolium cation over $C_{p,\mathrm{m}}$: this quantity was determined for 1-ethyl-3-methylimidazolyum tetrafluoroborate, [Emim][BF_4], 1-butyl-3-methylimidazolyum tetrafluoroborate, [Bmim][BF_4], 1-hexyl-3-methylimidazolyum tetrafluoroborate, [Hmim][BF_4], and 1-octyl-3-methylimidazolyum tetrafluoroborate, [Omim][BF_4]. The uncertainty of these measurements was estimated to be 0.2 %, which is an excellent value in the considered temperature and pressure interval. The obtained values were critically compared with data from other authors at atmospheric pressure, since they are the only available $C_{p,\mathrm{m}}$ literature data. The dependence of $C_{p,\mathrm{m}}$ against temperature and pressure is analyzed, and the results are related to the length of the alkyl chain of the imidazolium.

Materials and Equipment

Chemicals. For calibrating the apparatus, 1-butanol from Aldrich with a purity higher than 99.8 % was used, and it was dried and degassed prior to use. [Emim][BF_4] and [Bmim][BF_4] samples were obtained from Merck with purities higher than 98 % and 99 %, respectively. [Hmim][BF_4] and [Omim][BF_4] were purchased from Solvent Innovation with a purity greater than 99 %. To reduce the water content and volatile compounds to negligible values, vacuum at a moderate temperature (333.15 K) was applied to the RTIL samples for at least three days prior to use. The water contents of the studied samples were determined by Karl Fischer titration, and in mass fraction, they were $8 \cdot 10^{-3}$, $1 \cdot 10^{-3}$, $6 \cdot 10^{-4}$, and $2 \cdot 10^{-3}$ for [Emim][BF_4], [Bmim][BF_4], [Hmim][BF_4], and [Omim][BF_4], respectively.

Methodology. Measurements were made using an adaptation at high pressures[23] of the commercially available differential scanning calorimeter micro DSC II from Setaram. In this adaptation, conventional vessels at atmospheric pressure were replaced by two identical stainless steel vessels (reference and measurement) able to withstand pressure up to 70 MPa, each of them containing 0.5 mL of liquid. They are connected to a high pressure line, which contains a pressure generator that consists of a manually operated piston screw pump, a digital pressure sensor, and a large buffer volume, to allow the pressure control in the equipment. Calibration consisted of two thermal scanning experiences: in the first one, the reference and the measurement vessel are empty, and in the second one, the measurement vessel is filled with the standard fluid (1-butanol in this work). In the last experience, pressure in the measurement vessel is kept at 0.1 MPa. The measurement experiences were also thermal scanning runs in which the measurement vessel is

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[†] Part of the “2009 Iberian Conference on Ionic Liquids”.

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10.1021/je9004992 CCC: \$40.75

Table 1. Isobaric Molar Heat Capacity $C_{p,\mathrm{m}}$ of [Emim][BF$_4$] at the Temperature T and Pressure p

p/MPa	T/K = 283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
	$C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}								
0.1	300.19	301.67	303.23	304.87	306.58	308.36	310.23	312.17	314.18
2	300.22	301.70	303.26	304.90	306.61	308.40	310.26	312.20	314.21
4	300.24	301.73	303.29	304.93	306.64	308.43	310.29	312.23	314.24
6	300.27	301.76	303.32	304.96	306.67	308.46	310.32	312.26	314.27
8	300.30	301.79	303.35	304.99	306.70	308.49	310.35	312.29	314.30
10	300.33	301.82	303.38	305.02	306.73	308.52	310.38	312.32	314.33
12	300.35	301.85	303.41	305.05	306.77	308.55	310.42	312.35	314.36
14	300.38	301.87	303.44	305.08	306.80	308.59	310.45	312.38	314.39
20	300.46	301.96	303.53	305.18	306.89	308.68	310.54	312.47	314.48
30	300.60	302.10	303.68	305.33	307.05	308.84	310.70	312.63	314.63
40	300.73	302.25	303.83	305.49	307.21	309.00	310.86	312.79	314.78
50	300.87	302.39	303.98	305.64	307.37	309.16	311.02	312.94	314.93
60	301.00	302.54	304.13	305.80	307.52	309.32	311.17	313.10	315.08

Table 2. Isobaric Molar Heat Capacity $C_{p,\mathrm{m}}$ of [Bmim][BF$_4$] at the Temperature T and Pressure p

p/MPa	T/K = 283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
	$C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}								
0.1	360.25	362.17	364.16	366.20	368.30	370.45	372.67	374.95	377.29
2	360.28	362.20	364.17	366.21	368.31	370.47	372.69	374.97	377.31
4	360.31	362.22	364.19	366.23	368.33	370.49	372.71	374.99	377.34
6	360.34	362.24	364.21	366.25	368.34	370.50	372.73	375.01	377.36
8	360.37	362.27	364.23	366.26	368.36	370.52	372.74	375.03	377.39
10	360.39	362.29	364.25	366.28	368.37	370.53	372.76	375.05	377.41
12	360.42	362.31	364.27	366.30	368.39	370.55	372.78	375.08	377.44
14	360.45	362.34	364.29	366.31	368.40	370.57	372.80	375.10	377.47
20	360.54	362.40	364.35	366.36	368.45	370.61	372.85	375.16	377.54
30	360.68	362.52	364.44	366.45	368.53	370.69	372.94	375.26	377.67
40	360.82	362.64	364.54	366.53	368.61	370.77	373.03	375.37	377.80
50	360.96	362.75	364.64	366.61	368.69	370.85	373.12	375.47	377.93
60	361.11	362.87	364.73	366.70	368.77	370.93	373.21	375.58	378.05

Table 3. Isobaric Molar Heat Capacity $C_{p,\mathrm{m}}$ of [Hmim][BF$_4$] at the Temperature T and Pressure p

p/MPa	T/K = 283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
	$C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}								
0.1	422.77	425.00	427.34	429.80	432.36	435.03	437.81	440.70	443.69
2	422.81	425.04	427.38	429.83	432.39	435.06	437.84	440.72	443.72
4	422.85	425.08	427.42	429.87	432.43	435.10	437.87	440.75	443.74
6	422.89	425.12	427.46	429.91	432.47	435.13	437.90	440.78	443.77
8	422.94	425.17	427.50	429.95	432.50	435.17	437.93	440.81	443.80
10	422.98	425.21	427.54	429.99	432.54	435.20	437.97	440.84	443.82
12	423.02	425.25	427.59	430.03	432.58	435.23	438.00	440.87	443.85
14	423.07	425.29	427.63	430.07	432.61	435.27	438.03	440.90	443.88
20	423.20	425.42	427.75	430.18	432.72	435.37	438.13	440.99	443.96
30	423.41	425.63	427.95	430.38	432.91	435.55	438.29	441.14	444.09
40	423.63	425.84	428.15	430.57	433.09	435.72	438.45	441.28	444.22
50	423.85	426.05	428.36	430.77	433.28	435.89	438.61	441.43	444.35
60	424.07	426.26	428.56	430.96	433.46	436.07	438.77	441.58	444.49

filled with the sample keeping it at the measurement pressure p. All experiences were made in the working temperature interval and at the rate of 0.25 K·min^{-1}. The heat capacity per unit volume c_p was easily calculated from the experiences by correcting them for the volume variation with pressure in the measurement vessel. Heat capacity data for the standard fluid were taken from the Zabransky et al. compilation.[24] More details about the experimental methodology and calibration procedures can be found elsewhere.[23]

Results and Discussion

The isobaric molar heat capacity $C_{p,\mathrm{m}}$ for [Emim][BF$_4$], [Bmim][BF$_4$], [Hmim][BF$_4$], and [Omim][BF$_4$] in the temperature and pressure intervals of (283.15 to 323.15) K and (0.1 to 60) MPa was calculated from the directly determined isobaric heat capacity per unit volume c_p together with their densities ρ, obtained from ref 19, by means of the next relation

$$C_{p,\mathrm{m}} = c_p \frac{P_\mathrm{m}}{\rho} \tag{1}$$

where P_m is the molecular weight of the ionic liquid. The following polynomial in temperature but with pressure-dependent coefficients was used to correlate these values:

$$\frac{C_{p,\mathrm{m}}}{R} = \sum_{\mathrm{i}=1}^{3} A_\mathrm{i}(p) \cdot \left(\frac{T/\mathrm{K}}{100}\right)^{\mathrm{i}-1} \tag{2}$$

where R is the universal gas constant. $A(p)$ is given by:

$$A_\mathrm{i}(p) = A_{\mathrm{i}1} + A_{\mathrm{i}2} \cdot p/\mathrm{MPa} \tag{3}$$

where $A_{\mathrm{i}1}$ and $A_{\mathrm{i}2}$ are the fitting parameters. The experimental

Table 4. Isobaric Molar Heat Capacity $C_{p,\mathrm{m}}$ of [Omim][BF$_4$] at the Temperature *T* and Pressure *p*

	T/K = 283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
p/MPa	$C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}								
0.1	489.23	493.12	496.79	500.26	503.51	506.55	509.38	512.00	514.41
2	489.23	493.12	496.79	500.25	503.50	506.55	509.38	512.00	514.41
4	489.23	493.12	496.79	500.25	503.50	506.54	509.37	512.00	514.41
6	489.24	493.11	496.78	500.24	503.50	506.54	509.37	512.00	514.41
8	489.24	493.11	496.78	500.24	503.49	506.53	509.37	512.00	514.41
10	489.24	493.11	496.78	500.24	503.49	506.53	509.37	511.99	514.41
12	489.24	493.11	496.78	500.23	503.48	506.53	509.36	511.99	514.42
14	489.24	493.11	496.77	500.23	503.48	506.52	509.36	511.99	514.42
20	489.24	493.11	496.76	500.22	503.47	506.51	509.35	511.99	514.42
30	489.25	493.10	496.75	500.20	503.45	506.49	509.34	511.98	514.43
40	489.26	493.09	496.73	500.18	503.42	506.47	509.32	511.98	514.44
50	489.26	493.09	496.72	500.16	503.40	506.45	509.31	511.97	514.44
60	489.27	493.08	496.70	500.14	503.38	506.43	509.30	511.97	514.45

Table 5. Fitting Coefficients A_{ij} of Equation 2 and the Standard Deviation σ

	[Emim][BF$_4$]	[Bmim][BF$_4$]	[Hmim][BF$_4$]	[Omim][BF$_4$]
A_{11}	40.899	41.884	56.999	−9.052
A_{12}	−0.040	0.158	−0.016	0.076
A_{21}	−6.863	−3.531	−9.591	38.355
A_{22}	0.027	−0.104	0.015	−0.050
A_{31}	1.826	1.427	2.620	−5.078
A_{32}	−0.004	0.017	−0.003	0.008
σ/J·mol^{-1}·K^{-1}	0.3	0.4	0.5	1.6

$C_{p,\mathrm{m}}$ results as well as the fitting parameters are given in Tables 1, 2, 3, 4, and 5.

Literature data[25−29] were compared with results of this work with the aid of the absolute average relative deviation, ARD, defined as follows:

$$\mathrm{ARD} = \frac{1}{N}\sum_{\mathrm{i}=1}^{N}\left|\frac{C_{p,\mathrm{m,i}}^{\mathrm{lit}} - C_{p,\mathrm{m,i}}^{\mathrm{tw}}}{C_{p,\mathrm{m,i}}^{\mathrm{tw}}}\right| \qquad (8)$$

where *N* is the total number of considered data and the superscripts lit and tw denote literature and this work, respectively. Comparisons were made only at atmospheric pressure, since there are not available $C_{p,\mathrm{m}}$ literature data at higher pressures. The obtained ARD values are given in Table 6. Good results were obtained for the studied RTILs, if the uncertainty of the different data sources are considered. It is worth noting that the worst results were obtained for the data of refs 28 and 29, obtained using a calorimetric methodology significantly less accurate (about 5 %) than the other measurements, which present uncertainties similar to that of this work.

Table 6. ARD between Literature Data and Results of This Work: Isobaric Molar Heat Capacity

ARD			
[Emim][BF$_4$]	[Bmim][BF$_4$]	[Hmim][BF$_4$]	[Omim][BF$_4$]
0.01,[25] 0.007[26]	0.004,[27] 0.003,[25] 0.05[28]	0.03[29]	0.02[29]

Figures 1, 2, 3, and 4 show $C_{p,\mathrm{m}}$ plotted against pressure for several temperatures and for the four ionic liquids of this work. As it can be seen, the used experimental methodology allows accurate characterization of the variation of this property with the length of the alkyl chain of the imidazolium ring, temperature, and pressure. $C_{p,\mathrm{m}}$ increases against the number of carbons of the alkyl chain, as expected because of the increase of degrees of freedom as the cation becomes bigger. $C_{p,\mathrm{m}}$ increases as temperature is increased over the whole *T* and *p* range for the four liquids, as usually found for common organic solvents. As for pressure dependence, $C_{p,\mathrm{m}}$ increases as pressure is raised over the whole *p* range for most isotherms of the four liquids; only some isotherms of [Omim][BF$_4$] show positive pressure

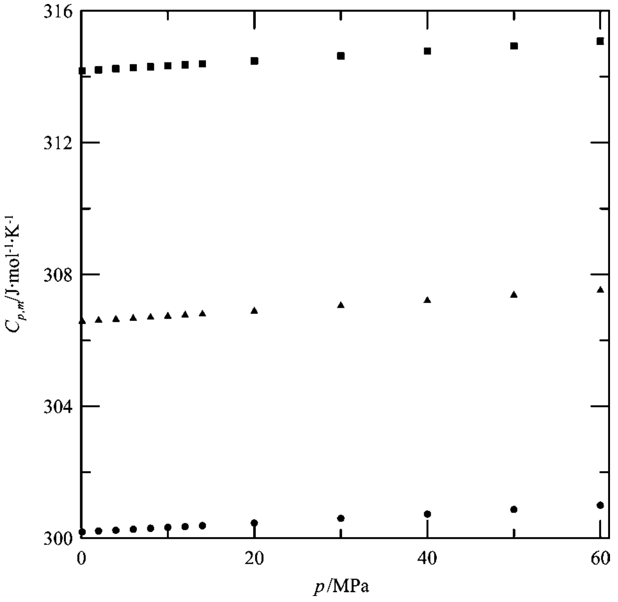

Figure 1. Isobaric molar heat capacity $C_{p,\mathrm{m}}$, of [Emim][BF$_4$] plotted against pressure *p* at: ●, 283.15 K; ▲, 303.15 K; ■, 323.15 K.

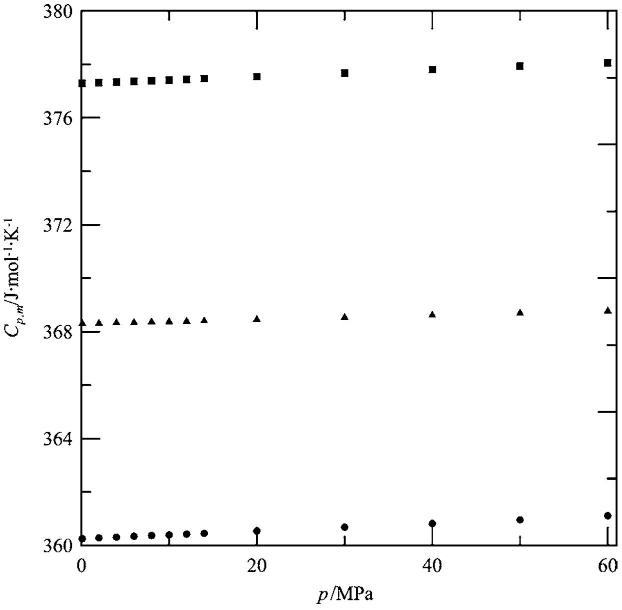

Figure 2. Isobaric molar heat capacity $C_{p,\mathrm{m}}$, of [Bmim][BF$_4$] plotted against pressure *p* at: ●, 283.15 K; ▲, 303.15 K; ■, 323.15 K.

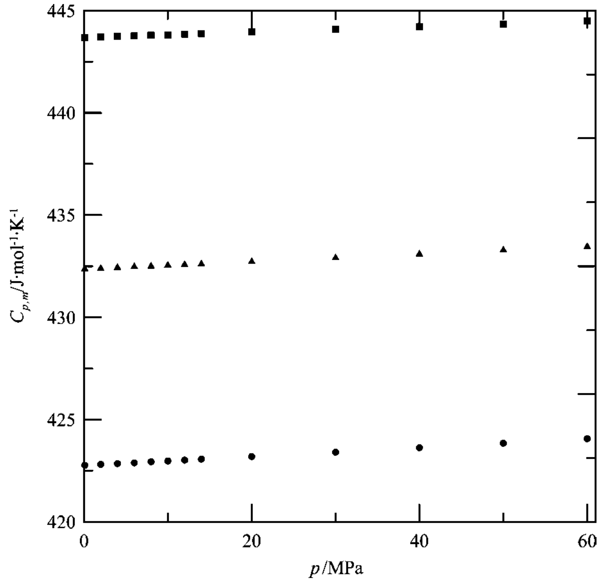

Figure 3. Isobaric molar heat capacity $C_{p,\mathrm{m}}$, of [Hmim][BF_4] plotted against pressure p at: ●, 283.15 K; ▲, 303.15 K; ■, 323.15 K.

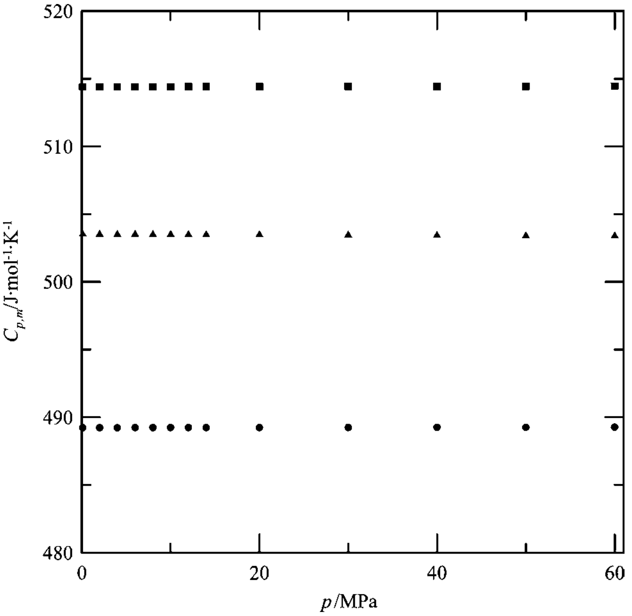

Figure 4. Isobaric molar heat capacity $C_{p,\mathrm{m}}$, of [Omim][BF_4] plotted against pressure p at: ●, 283.15 K; ▲, 303.15 K; ■, 323.15 K.

dependence. Because of the very small variation against p, $C_{p,\mathrm{m}}$ could be considered as pressure-independent for this liquid. Usual organic solvents present negative $C_{p,\mathrm{m}}$ pressure dependency at low pressure, and as pressure is raised, $C_{p,\mathrm{m}}$ starts to increase against p. From this point of view, the behavior of these RTILs is that of a common solvent at high pressure, a fact also supported by other thermodynamic properties: isothermal compressibility κ_T and isobaric thermal expansivity α_p are small for RTILs,[14,16−18,20−22] as it happens for a highly compressed usual organic solvent.[30] Moreover, α_p for RTILs presents also an unusual temperature dependence: it decreases against T over the whole T and p range,[20−22] and common organic solvents present this T dependency only at high pressure. This behavior is, in fact, linked with that of $C_{p,\mathrm{m}}$ against p, since these two magnitudes are connected through the well-known thermodynamic relation

$$\left(\frac{\partial C_{p,\mathrm{m}}}{\partial p}\right) = -TV_{\mathrm{m}}\left(\alpha_p^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)\right) \qquad (9)$$

Thus, $C_{p,\mathrm{m}}$ increases against p only if α_p decreases enough against T, because of the quadratic term in the equation, which always is positive. Therefore, the obtained results for $C_{p,\mathrm{m}}$ correspond to those of a molecular liquid at high pressure, as it was obtained for other thermodynamic quantities of RTILs.

Conclusions

Isobaric heat capacities as a function of temperature and pressure were reported for four ionic liquids which differ in the length of the alkyl chain of the imidazolium ring. $C_{p,\mathrm{m}}$ increases with temperature and the alkyl chain, as it would expected for a common organic solvent, but it was found that this quantity increases with pressure for most of the studied ionic liquids over the whole temperature and pressure range, which constitutes an anomalous behavior. This, together with previous results for other thermodynamic quantities, suggests that ionic liquids behave like organic solvents at high pressure.

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Received for review June 12, 2009. Accepted October 23, 2009. The authors are grateful to the Dirección Xeral de I + D da Xunta de Galicia (Projects PGIDIT-06-PXIB-3832828-PR and INCITE08E1R383012ES) and Universidad de Vigo (Project 08 VI-A12) for financial support. Assistance to P.N. by Xunta de Galicia (Project PGIDIT-06-PXIB-3832828-PR) is greatly appreciated. They are also indebted to Prof. José Tojo, alas since deceased, and his research group for their kind help in the determination of the water content for the studied samples.

JE9004992