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Densities and Excess Volumes of the 1,3-Dimethylimidazolium Methylsulfate + Methanol System at Temperatures from (313.15 to 333.15) K and Pressures from (0.1 to 25) MPa

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Densities of pure 1,3-dimethylimidazolium methylsulfate ionic liquid [MMIM][CH_3SO_4] and its mixtures with methanol have been measured with an accuracy of ±0.2 $kg\cdot m^{-3}$ over a temperature range from (313.15 to 333.15) K and a pressure range from (0.1 to 25) MPa using a vibrating tube densimeter. The isothermal compressibilities, isobaric expansivities, and excess volumes have been calculated. The uncertainties of these properties have been estimated to be ±0.05 GPa^{-1}, $\pm 0.2\cdot 10^{-4}$ K^{-1}, and ±0.1 $cm^3\cdot mol^{-1}$. The exceptionally strong influence of pressure and temperature on the excess volumes has been observed.

Introduction

Recently, a considerable interest in the properties of ionic liquids has been observed. Ionic liquids compose a group of new compounds possessing some unique properties and presumably being able to resolve some important problems that modern chemical technology has faced. Research on the ionic liquids still is in its initial stage for at least two reasons: (i) pure ionic liquids and mixtures containing ionic liquids differ considerably from so-called "normal liquids", and their behavior is not fully understood; and (ii) new compounds with unknown properties are being synthesized. It is clear that availability of the experimental values of parameters has a crucial significance to find a quantitative description or even a prediction of some properties.

The volumetric data on pure ionic liquids and their mixtures providing the density dependence on both temperature and pressure are rare. Up to now we have noted only four papers reporting such measurements for pure ionic liquids[1−4] and none for the mixtures. Equally rare are measurements of the densities or excess volumes of such mixtures at normal pressure.[5−10]

The ionic liquids possess many unique properties if compared to "normal" fluids. These exceptional features can be observed also among volumetric properties. The densities of the ionic liquids are less influenced by pressure and temperature than typical organic liquids, and therefore the observed isobaric expansivities and isothermal compressibilities are considerably lower than usual.[1−4] We found it interesting to examine this aspect of volumetric properties of mixtures consisting of an ionic liquid and an ordinary organic solvent with special attention paid to excess functions (V^E, α^E, κ^E). It seems that this is the first time such properties of these mixtures have been measured and discussed.

Experimental Section

Materials. Methanol (Aldrich, puriss > 99.9 %) and 1,3-dimethylimidazolium methylsulfate (Fluka, puriss > 97 %) were dried and degassed under vacuum for 48 h at a temperature of about 80 °C. The water content determined by a Karl Fisher coulometer was about 0.3 % mass fraction. Methanol was dried over 0.4 nm molecular sieves for several days.

Water used in calibration was distilled twice. Methanol and water were degassed in the ELMA ultrasonic bath at about 50 °C for 60 min before a measurement. The liquid mixtures were prepared by mass using the WA 36 precision balance manufactured by MeraWag, with an accuracy of $5\cdot 10^{-5}$ g. The estimated uncertainty of the mole fraction was about 10^{-4}.

Apparatus. The Anton Paar density measuring cell for high pressures and high temperatures (DMA 512P) and the mPDS 2000 evaluation unit were used for measurements of the densities of pure components and their mixtures. This type of densimeter is applicable over the temperature and pressures ranges of (263 to 423) K and (0 to 70) MPa, respectively.

The density of a sample is determined by measuring of the oscillation period of the U-shaped tube made from Hastelloy C-256 stainless steel. The oscillation periods are determined with an accuracy of 1 ns, whereas repeatability of the measurements is about 10 ns, which assures six significant digits.

The temperature was controlled by the GR150 Grant thermostat filled with water. At temperatures of not less than 308 K it could operate without a forced cooling because of a spontaneous heat transfer into the surroundings. At lower temperatures, cooling water was provided by an additional thermostat with the C2G Grant refrigerated immersion cooler. The temperature of the cooling water was kept to be 3 K lower than that of the main thermostat. The temperature of the water was measured by the Grant Pt 1000 external temperature probe placed as close as possible to the inlet of the thermostatic circuit into a measuring cell. The temperature was kept constant within ±0.01 K. The HiP model 62-6-10 pressure generator with a Teflon packing manufactured by High Pressure Equipment Co. was used to compress the sample. Pressure was measured by the CL 362 unit with the CL 1L electric resistance wire strain gauge probe (manufactured by ZEPWN). The maximum uncertainty of the pressure measurements is claimed to be better than 0.2 %. A schematic diagram of the whole apparatus is shown in Figure 1.

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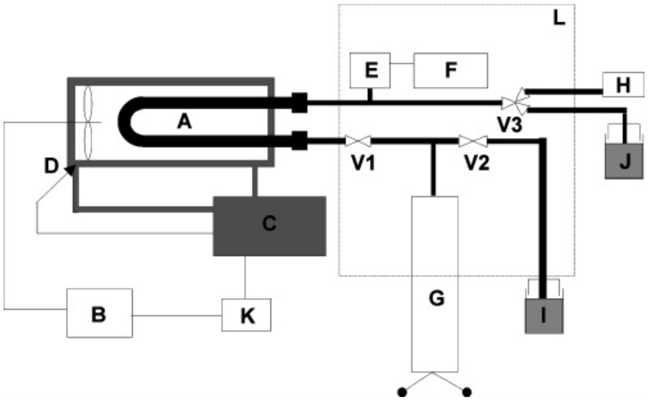

Figure 1. Schematic diagram of the densimeter: A, DMA 512P density measuring cell; B, mPDS 2000 evaluation unit; C, temperature control unit; D, temperature probe; E, electric resistance wire strain gauge probe; F, pressure measuring system; G, pressure generator; H, vacuum pump; I, sample vessel; J, waste vessel; K, computer; V1, V2, V3, valves; L, air thermostat.

The valves (Swagelok), the pressure generator, the electric resistance wire strain gauge probe, and connecting tubes (Swagelok $^1/_4$ in.) were kept in an air thermostat at 313 K to prevent possible solidification of the ionic liquid, which has a normal melting point temperature of 308.90 K.[11]

Before the experiment, the densimeter and all tubes and valves were washed with methanol and acetone. Next the system was evacuated for several hours with a vacuum pump.

When the measured liquid was introduced and the equilibrium at the fixed temperature was reached, the oscillation periods were recorded. Recording was continued for about 1 min every 2 s. Hence, the resulting value of the period was taken as an average of about 30 counts.

All of the measurements were performed by changing the pressure along isotherms.

Procedure. The sample density ρ is related to the oscillation period τ by the following equation:

$$\rho(T, p) = a(T, p)\cdot\tau^2 + b(T, p) \tag{1}$$

The coefficients $a(T, p)$ and $b(T, p)$ are, in general, temperature- and pressure-dependent parameters, which are characteristic for the apparatus and have to be determined by measuring the periods for two substances of well-known densities at the T and p considered. However, it is difficult to find precisely known density values for two substances for all of the T, p sets of an experimental domain.

In this work we follow the calibration method developed by Lagourette et al.[12] and confirmed experimentally by others,[13,14] which assumes the a parameter to be independent of pressure. It enables one to select an empty evacuated U-tube as one reference. The second reference was water as usual. In this approach, the dependence between density ρ and the oscillation periods τ has the form

$$\rho(T, p) = \rho_w(T, p) + \rho_w(T, p_0)\cdot\frac{\tau^2(T, p) - \tau_w^{\,2}(T, p)}{\tau_w^{\,2}(T, p_0) - \tau_v^{\,2}(T)} \tag{2}$$

where subscripts w and v refer to water and the empty U-tube ("vacuum"), respectively, and p_0 designates a reference pressure equal to 0.1 MPa. The densities of water were calculated from the parameters recommended by the International Association for the Properties of Water and Steam.[15]

The overall accuracy of the density determination is a result of a few factors. Apart from the direct error of three different period measurements (for the sample, water, and the empty U-tube), which at least partly can be caused by a variation of temperature, it neglects the vacuum densities and uncertainties of the literature values of water densities. The higher the pressure, the lower the accuracies of the latter values. The errors of calibration have a systematic character because all densities calculated by eq 2 at the same temperature and pressure are influenced by them in the same manner. The other systematic errors, the extent of which is difficult to estimate, may result from an approximate character of eq 1 and the Lagourette et al. assumptions. For the pure ionic liquid and for its concentrated solutions this error may be greater due to the high viscosity of a sample.[16]

The maximum combined uncertainty for the densities should not exceed ± 0.1 kg·m^{-3} at normal pressure and about ± 0.2 kg·m^{-3} at higher pressures. The latter value is only twice greater than the estimated inaccuracy of the experimental densities of pure water, which values were used in the calculations. The average actual uncertainty for methanol and the mixtures with low concentration of the ionic liquid, although involving the random errors only, is probably 10 times better, as may be concluded from the standard deviations between the raw and correlated data.

For the calculated excess volumes the combined uncertainty, which includes also an error of mole fractions, is estimated to be about ± 0.1 cm^3·mol^{-1}.

The ranges of temperature and pressure used in the measurements, $313.15 \le T/\mathrm{K} \le 333.15$ and $0.1 \le p/\mathrm{MPa} \le 25$ MPa, resulted from the properties of both components. Particularly, lower temperatures and higher pressures could lead to the crystallization of pure 1,3-dimethylimidazolium methylsulfate.

Testing of the Apparatus. Because the apparatus has been used for the first time, the densities for pure methanol were measured over the wider ranges of temperature and pressure, that is, for temperatures $283.15 \le T/\mathrm{K} \le 333.15$ and pressures $0.1 \le p/\mathrm{MPa} \le 35$ MPa. The experimental densities, which are given in Table 1, were correlated by the Tait equation in the form

Table 1. Experimental Density ρ for Methanol as a Function of Temperature T and Pressure p

	ρ/kg·m^{-3} at								
p/MPa	T = 283.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K	T = 333.15 K
0.1	800.54	791.23	786.51	781.96	772.43	767.47	762.78	757.83	752.96
2.5	802.75	793.52	788.81	784.36	774.99	770.09	765.48	760.61	755.84
5.0	804.88	795.80	791.18	786.78	777.53	772.74	768.20	763.41	758.73
10.0	809.06	800.17	795.70	791.48	782.45	777.79	773.39	768.75	764.21
15.0	813.06	804.36	800.02	795.84	787.08	782.57	778.30	773.73	769.39
20.0	816.88	808.39	804.15	799.97	791.50	787.09	782.93	778.49	774.25
25.0	820.60	812.25	808.10	803.95	795.74	791.43	787.34	783.03	778.87
30.0	824.14	815.94	811.88	807.83	799.72		791.56		783.33
35.0	827.58	819.55	815.52	811.51	803.62		795.60		787.53

$$\rho = \frac{\rho_0(p_0)}{1 - A \ln \dfrac{B + p}{B + p_0}} \tag{3}$$

with the reference pressure p_0 equal to 0.1 MPa. Alternatively, an equation with the ρ_0 and B parameters dependent on temperature was used to correlate the overall data. The following temperature dependencies were assumed:

$$\rho_0(T, p_0) = \rho_{00} + \rho_{01}T + \rho_{02}T^2 + \rho_{03}T^3 \tag{4}$$

$$B(T) = B_0 + B_1T + B_2T^2 \tag{5}$$

The number of terms was found to be statistically significant. Simultaneously, it was found that the temperature dependence of the A parameter can be neglected. The fitted parameters of equations and the standard deviations are shown in Table 2.

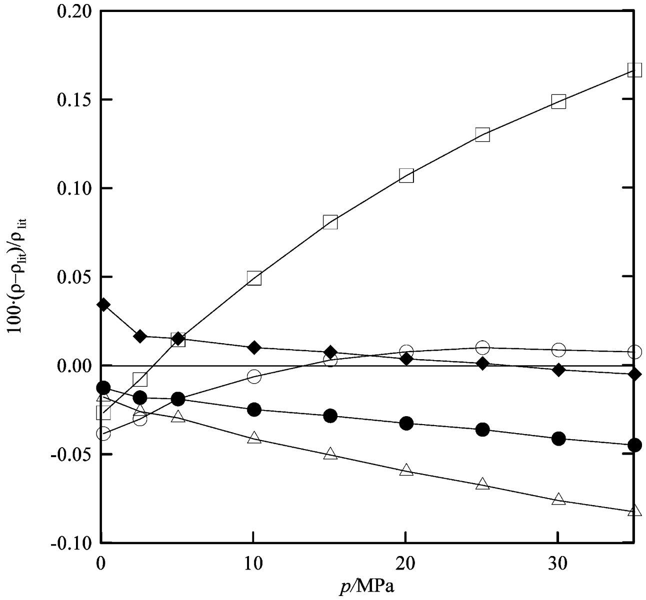

Figure 2. Fractional deviations $100\cdot(\rho - \rho_{\text{lit.}})/\rho_{\text{lit.}}$ between the measured and literature density values of methanol at 298.15 K as a function of pressure. The literature data are taken from O, ref 18; ●, ref 19; △, ref 20; □, ref 17; ◆, ref 21. Dotted interpolation lines visualize the observed trends.

Experimental densities agree well with the previously reported literature data.[17−20] They are usually slightly higher than the data of Machado and Streett[18] and slightly lower than those of Sun et al.[19] In both cases the maximum relative deviations do not exceed 0.04 %. The data of Hrubý et al.[20] are higher, with the maximum deviations equal to 0.07 %. Only the data of Ledwig and Würflinger[17] are outstanding, also with respect to all of the data reported in the literature. At 283.15 K they deviate from the presented data over −0.20 % to +0.10 %. As expected, the highest residuals between densities are observed at the highest pressures. A good agreement with the densities calculated by the NIST correlation[21] can be noted. Comparison between measured densities at 298.15 K and those reported previously is shown in Figure 2.

On the basis of the Tait equation with the temperature-dependent parameters, the isothermal expansivities and isobaric

Table 2. Coefficients of the Tait Equation Fitted to Experimental Densities of Methanol and Root Mean Squared Deviations σ

T/K	$A\cdot10^2$	B/MPa	ρ_0/kg·m^{-3}	σ/kg·m^{-3}
283.15	9.2266	82.195	800.58	0.02
293.15	9.3907	78.505	791.26	0.02
298.15	9.1883	73.680	786.50	0.01
303.15	8.7548	67.677	781.98	0.03
313.15	9.0900	65.490	772.22	0.02
318.15	9.0769	62.833	767.47	0.01
323.15	9.1023	60.802	762.79	0.01
328.15	9.1298	58.879	757.84	0.01
333.15	9.2287	57.239	752.98	0.02
(283.15 to 333.15)	9.2203	B_0/MPa = 307.86 B_1/MPa·K^{-1} = −1.0481 B_2/MPa·K^{-2} = 8.8657·10^{-4}	ρ_{00}/kg·m^{-3} = 1200.5 ρ_{01}/kg·m^{-3}·K^{-1} = −2.4218 ρ_{02}/kg·m^{-3}·K^{-2} = 5.4228·10^{-3} ρ_{03}/kg·m^{-3}·K^{-3} = −6.5608·10^{-6}	0.06

Table 3. Calculated Isobaric Expansivities κ and Isothermal Compressibilities α of Methanol Compared with the Literature Data

	κ/GPa^{-1} and α/10^{-4} K^{-1} at						
	p = 0.1 MPa	p = 2.5 MPa	p = 5.0 MPa	p = 10.0 MPa	p = 20.0 MPa	p = 30.0 MPa	reference
T = 283.15 K							
κ/GPa^{-1}	1.13				0.879		Sun et al.[18]
	1.12				0.921		this work
α/10^{-4} K^{-1}	11.7				10.4		Sun et al.[18]
	11.6				10.4		this work
T = 313.15 K							
κ/GPa^{-1}	1.40				1.10		Sun et al.[18]
	1.40	1.31	1.27	1.21	1.09	1.00	Machado and Streett[17]
	1.40	1.34	1.30	1.22	1.09	0.988	this work
α/10^{-4} K^{-1}	12.4				10.8		Sun et al.[18]
	12.5	12.3	12.1	11.6	10.9	10.3	Machado and Streett[17]
	12.4	12.1	11.9	11.5	10.8	10.2	this work
T = 333.15 K							
κ/GPa^{-1}	1.62				1.24		Sun et al.[18]
	1.58	1.53	1.48	1.39	1.23	1.11	Machado and Streett[17]
	1.61	1.55	1.50	1.39	1.23	1.10	this work
α/10^{-4} K^{-1}	12.9				11.2		Sun et al.[18]
	13.3	13.0	12.7	12.2	11.3	10.7	Machado and Streett[17]
	13.2	12.9	12.6	12.1	11.2	10.6	this work

Table 4. Experimental Density ρ for [MMIM][CH_3SO_4] as a Function of Temperature T and Pressure p

	ρ/kg·m^{-3} at				
p/MPa	$T = 313.15$ K	$T = 318.15$ K	$T = 323.15$ K	$T = 328.15$ K	$T = 333.15$ K
0.1		1318.59	1314.45	1311.21	1308.09
2.5	1322.36	1318.99	1315.38	1311.78	1308.74
5.0	1323.15	1320.26	1316.90	1313.33	1309.91
10.0	1325.84	1322.52	1319.03	1315.53	1312.06
15.0	1327.82	1324.34	1321.09	1317.58	1314.05
20.0	1329.86	1326.38	1322.91	1319.52	1316.06
25.0	1331.73	1328.18	1324.79	1321.46	1318.04

Table 5. Experimental Densities ρ for the [MMIM][CH_3SO_4] (1) + Methanol (2) Solutions as a Function of Mole Fraction x_1, Temperature T, and Pressure p

		ρ/kg·m^{-3} at								
T/K	p/MPa	$x_1 = 0.0595$	$x_1 = 0.1256$	$x_1 = 0.2255$	$x_1 = 0.3487$	$x_1 = 0.4358$	$x_1 = 0.5999$	$x_1 = 0.6780$	$x_1 = 0.7985$	$x_1 = 0.8788$
313.15	0.1	897.40	995.68	1099.73	1178.03	1214.89	1259.56	1272.43	1293.34	1306.67
	2.5	899.34	997.08	1103.45	1178.78	1215.88	1260.50	1273.27	1293.66	1307.60
	5.0	901.48	998.93	1105.04	1180.09	1217.10	1261.63	1274.40	1294.78	1308.84
	10.0	905.53	1002.32	1107.82	1182.55	1219.41	1263.81	1276.57	1296.86	1310.84
	15.0	909.28	1005.47	1110.58	1184.88	1221.54	1265.86	1278.54	1298.79	1312.82
	20.0	912.87	1008.72	1112.94	1187.36	1223.84	1267.94	1280.59	1300.72	1314.73
	25.0	916.36	1011.65	1115.61	1189.55	1225.91	1269.90	1282.63	1302.59	1316.65
318.15	0.1	892.75	991.27	1098.10	1173.63	1211.01	1256.25	1268.88	1289.56	1302.95
	2.5	894.76	992.74	1099.36	1175.27	1212.06	1256.87	1269.52	1289.80	1303.55
	5.0	896.93	994.61	1101.05	1176.67	1213.30	1258.23	1270.74	1290.94	1304.76
	10.0	901.12	997.98	1103.84	1179.19	1215.63	1260.12	1272.88	1293.07	1306.85
	15.0	905.02	1001.35	1106.40	1181.55	1217.87	1262.34	1274.94	1295.12	1308.87
	20.0	908.73	1004.57	1109.09	1183.86	1220.12	1264.21	1276.82	1296.98	1310.76
	25.0	912.33	1007.78	1111.62	1186.11	1222.20	1266.38	1278.86	1298.82	1312.67
323.15	0.1	888.46	987.09	1094.44	1170.54	1207.30	1253.26	1265.81	1286.17	1298.59
	2.5	890.23	989.02	1095.16	1171.75	1208.50	1253.51	1266.27	1286.42	1298.95
	5.0	892.75	990.75	1097.24	1173.09	1209.85	1254.68	1267.47	1287.58	1301.07
	10.0	896.85	994.31	1100.14	1175.63	1211.92	1256.64	1269.70	1289.70	1302.92
	15.0	900.92	997.64	1102.68	1177.98	1214.35	1258.78	1271.77	1291.70	1305.22
	20.0	904.77	1000.97	1105.59	1180.36	1216.74	1260.99	1273.77	1293.67	1307.19
	25.0	908.35	1004.08	1107.96	1182.75	1218.87	1262.92	1275.80	1295.54	1309.14
328.15	0.1	883.92	982.93	1090.95	1166.83	1203.70	1249.89	1261.59	1282.63	1295.17
	2.5	886.03	984.76	1091.73	1167.85	1204.86	1250.01	1262.64	1282.83	1295.60
	5.0	888.29	986.63	1093.17	1169.21	1206.08	1251.05	1263.86	1284.04	1297.04
	10.0	892.59	990.09	1096.09	1171.74	1208.51	1253.24	1266.15	1286.21	1299.34
	15.0	896.65	993.64	1098.86	1174.17	1210.72	1255.37	1268.18	1288.18	1301.53
	20.0	900.42	996.92	1101.57	1176.56	1212.91	1257.49	1270.32	1290.28	1303.85
	25.0	904.13	1000.12	1104.13	1178.72	1215.10	1259.44	1272.25	1292.24	1305.86
333.15	0.1	879.42	978.71	1087.29	1163.08	1200.14	1244.84	1258.96	1279.02	1291.97
	2.5	881.45	980.35	1087.93	1163.89	1201.18	1245.50	1259.28	1279.21	1292.00
	5.0	883.90	982.47	1089.62	1165.49	1202.46	1246.55	1260.49	1280.50	1293.62
	10.0	888.26	986.20	1092.34	1168.15	1204.81	1248.07	1262.75	1282.63	1295.87
	15.0	892.46	989.32	1095.34	1170.47	1207.22	1250.67	1264.91	1284.64	1297.80
	20.0	896.41	992.83	1098.06	1173.01	1209.38	1252.91	1267.00	1286.71	1300.22
	25.0	900.18	996.24	1100.60	1175.34	1211.69	1255.04	1269.05	1288.75	1302.69

compressibilities of methanol have been calculated. Their accuracies are difficult to estimate precisely as they depend significantly on the form of an equation chosen to represent density as a function of pressure and temperature. The errors of derived values of parameters calculated through the statistical analysis are lower than differences resulting from the various equations. Nevertheless, the latter ones do not exceed ±0.05 GPa^{-1} for compressibilities and $\pm 0.2 \cdot 10^{-4}$ K^{-1} for expansivities, which may be considered as maximum errors of the derived parameters. The calculated expansivities and compressibilities are very close to those reported by Machado and Streett[18] and Sun et al.[19] (see Table 3).

Results

Densities of Pure 1,3-Dimethylimidazolium Methylsulfate. The measured densities for 1,3-dimethylimidazolium methylsulfate are given in Table 4. At normal pressures the measured data are about 0.4 % higher than those reported previously in the literature.[22,23] This difference is not meaningless; however, such a discrepancy is rather typical for ionic liquids. For example, maximum residuals between densities reported for the [C_8MIM][PF_6] ionic liquid at 298 K are about 5 %.[1,24−27] This may be due to some experimental difficulties or the existence of some contaminants present in an ionic liquid.

Various equations were used to correlate the data. The density dependencies as a function of pressure were correlated by the Tait equation as well as simple polynomials. In both cases the root mean squared deviations were about 10 times higher than those observed for the correlation of the pure methanol densities, which suggests higher experimental errors when the ionic liquid has been measured. The isobaric expansivities and isothermal compressibilities were estimated by the linear regression of ln $\rho = f(T, p = \text{const})$ and ln $\rho = f(T = \text{const}, p)$, which turned out to be statistically sufficient. The expansivities vary between $(5.08 \text{ and } 5.46) \cdot 10^{-4}$ K^{-1} and seem to slightly decrease with increasing pressure, although this tendency is not obvious because of the scattering of the calculated values. The expansivity of [MMIM][CH_3SO_4] averaged over (0.1 to 25) MPa is

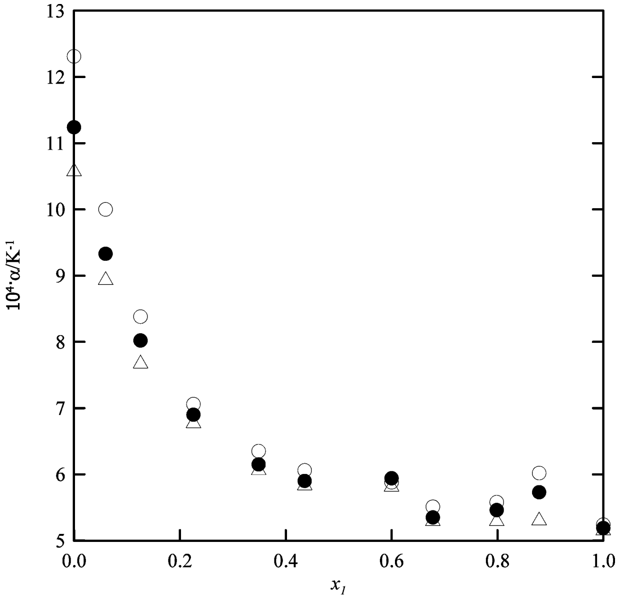

Figure 3. Isobaric expansivities α of the x_1[MMIM][CH_3SO_4] + (1 − x_1)methanol solutions calculated from the experimental densities, as a function of concentration x_1 at T = 318.15 K and at p = ○, 2.5 MPa; ●, 15 MPa; and △, 25 MPa.

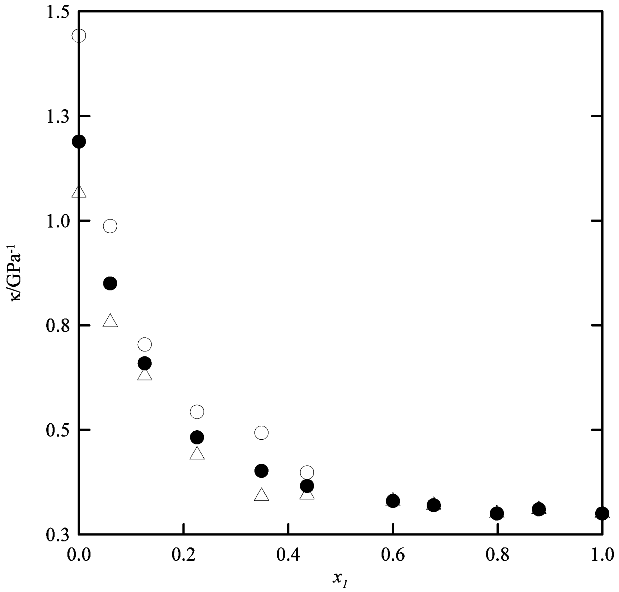

Figure 4. Isothermal compressibilities κ of the x_1[MMIM][CH_3SO_4] + (1 − x_1)methanol solutions calculated from the experimental densities, as a function of concentration x_1 at T = 318.15 K and at p = ○, 0.1 MPa; ●, 15 MPa; and △, 25 MPa.

equal to $5.2 \cdot 10^{-4}$ K^{-1}, which agrees with the value reported by Pereiro et al.[23] The isothermal compressibility is practically independent of temperature and is equal to (0.31 ± 0.01) GPa^{-1}.

Densities and Related Properties of the [MMIM][CH_3SO_4] + Methanol Mixtures. The experimental densities for the mixtures at nine different mole fractions are given in Table 5. The data were correlated in a similar manner as those for the pure ionic liquid, and the isobaric expansivities and isothermal compressibilities were calculated. The dependencies ln $\rho = f(T, p = \text{const}, x_1 = \text{const})$ could be correlated by a linear expression that leads to the expansivities independent of temperature. Analogous dependence on pressure for the mixtures at higher concentrations of methanol had to be correlated by a second-order polynomial. Exemplary calculated isobaric expansivities and isothermal compressibilities at 318.15 K as a function of concentration are shown in Figures 3 and 4.

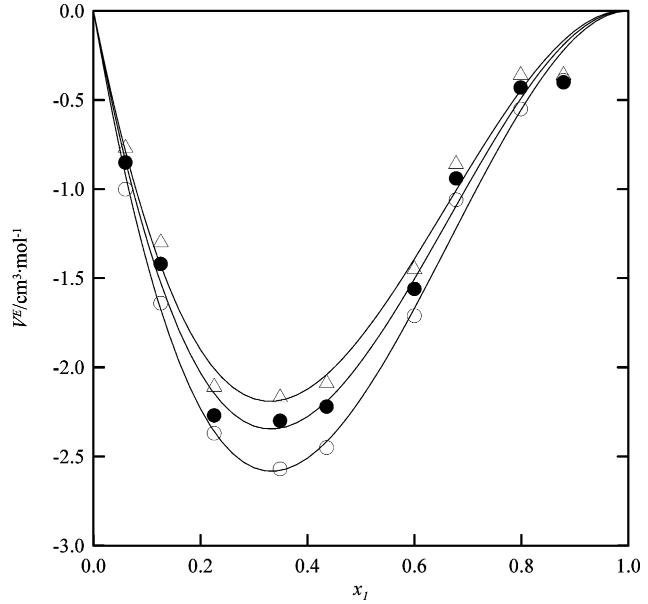

Figure 5. Excess volumes V^E of the x_1[MMIM][CH_3SO_4] + (1 − x_1)-methanol solutions calculated from the experimental densities, as a function of concentration x_1 at T = 318.15 K and at p = ○, 0.1 MPa; ●, 15 MPa; and △, 25 MPa. The solid lines are calculated by using the Redlich−Kister equation.

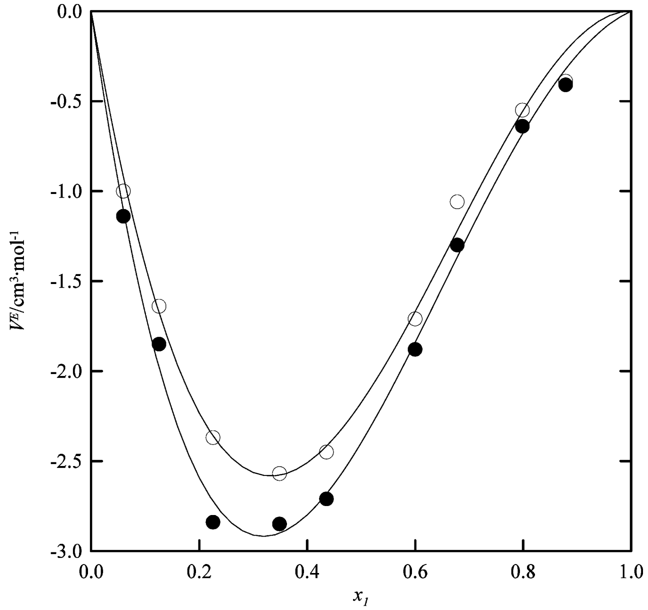

Figure 6. Excess volumes V^E of the x_1[MMIM][CH_3SO_4] + (1 − x_1)-methanol solutions calculated from the experimental densities, as a function of concentration x_1 at p = 0.1 MPa and at T = ○, 313.15 K; and ●, 333.15 K. The solid lines are calculated by using the Redlich−Kister equation.

Excess volumes were calculated according to the formula

$$V^E = M_1 x_1 (1/\rho - 1/\rho_1) + M_2 x_2 (1/\rho - 1/\rho_2) \qquad (6)$$

where M_1 and M_2 are molecular weights of the pure components and ρ, ρ_1, and ρ_2 designate densities of solution and both pure components, respectively. The calculated values are given in Table 6, and some of them are shown in Figures 5 and 6. To correlate the data, usually the Redlich−Kister equation with two parameters was sufficient. For a few systems one additional parameter was necessary. The resulting standard deviations were between (0.08 and 0.10) cm^3·mol^{-1}.

Table 6. Experimental Excess Volumes V^E for the [MMIM][CH_3SO_4] (1) + Methanol (2) Solutions as a Function of Mole Fraction x_1, Temperature T, and Pressure p

		$V^E/cm^3 \cdot mol^{-1}$								
T/K	p/MPa	$x_1 = 0.0595$	$x_1 = 0.1256$	$x_1 = 0.2255$	$x_1 = 0.3487$	$x_1 = 0.4358$	$x_1 = 0.5999$	$x_1 = 0.6780$	$x_1 = 0.7985$	$x_1 = 0.8788$
313.15	0.1	−1.00	−1.64	−2.37	−2.57	−2.45	−1.71	−1.06	−0.55	−0.39
	2.5	−0.97	−1.60	−2.49	−2.54	−2.45	−1.74	−1.09	−0.55	−0.48
	5.0	−0.95	−1.57	−2.45	−2.50	−2.42	−1.72	−1.09	−0.56	−0.52
	10.0	−0.90	−1.49	−2.34	−2.39	−2.30	−1.62	−0.99	−0.47	−0.42
	15.0	−0.85	−1.42	−2.27	−2.30	−2.22	−1.56	−0.94	−0.43	−0.40
	20.0	−0.81	−1.36	−2.17	−2.24	−2.16	−1.50	−0.89	−0.39	−0.37
	25.0	−0.77	−1.30	−2.11	−2.17	−2.09	−1.45	−0.86	−0.36	−0.36
318.15	0.1	−1.03	−1.69	−2.58	−2.61	−2.51	−1.80	−1.12	−0.57	−0.41
	2.5	−1.00	−1.64	−2.54	−2.61	−2.49	−1.77	−1.10	−0.52	−0.42
	5.0	−0.97	−1.60	−2.49	−2.56	−2.43	−1.74	−1.07	−0.49	−0.40
	10.0	−0.92	−1.52	−2.39	−2.46	−2.34	−1.63	−1.00	−0.44	−0.36
	15.0	−0.88	−1.45	−2.30	−2.38	−2.27	−1.59	−0.96	−0.43	−0.36
	20.0	−0.83	−1.39	−2.22	−2.30	−2.19	−1.51	−0.90	−0.38	−0.33
	25.0	−0.79	−1.34	−2.14	−2.23	−2.13	−1.49	−0.87	−0.36	−0.32
323.15	0.1	−1.07	−1.75	−2.68	−2.74	−2.60	−1.94	−1.25	−0.66	−0.40
	2.5	−1.02	−1.71	−2.58	−2.69	−2.56	−1.83	−1.17	−0.57	−0.32
	5.0	−1.00	−1.65	−2.55	−2.62	−2.49	−1.77	−1.11	−0.51	−0.38
	10.0	−0.94	−1.57	−2.45	−2.52	−2.38	−1.67	−1.06	−0.48	−0.33
	15.0	−0.90	−1.50	−2.34	−2.42	−2.30	−1.61	−1.00	−0.43	−0.33
	20.0	−0.85	−1.44	−2.27	−2.35	−2.25	−1.57	−0.96	−0.42	−0.33
	25.0	−0.81	−1.38	−2.18	−2.28	−2.18	−1.51	−0.93	−0.38	−0.32
328.15	0.1	−1.10	−1.80	−2.77	−2.80	−2.65	−1.99	−1.20	−0.66	−0.40
	2.5	−1.07	−1.76	−2.68	−2.75	−2.62	−1.89	−1.20	−0.59	−0.37
	5.0	−1.03	−1.71	−2.61	−2.67	−2.55	−1.81	−1.14	−0.54	−0.34
	10.0	−0.98	−1.61	−2.49	−2.56	−2.45	−1.73	−1.09	−0.50	−0.33
	15.0	−0.92	−1.54	−2.40	−2.47	−2.35	−1.66	−1.02	−0.45	−0.32
	20.0	−0.87	−1.47	−2.31	−2.38	−2.27	−1.60	−0.99	−0.43	−0.34
	25.0	−0.83	−1.41	−2.22	−2.29	−2.20	−1.54	−0.93	−0.40	−0.33
333.15	0.1	−1.14	−1.85	−2.84	−2.85	−2.71	−1.88	−1.30	−0.64	−0.41
	2.5	−1.09	−1.79	−2.74	−2.77	−2.66	−1.82	−1.22	−0.56	−0.32
	5.0	−1.07	−1.75	−2.69	−2.73	−2.60	−1.76	−1.19	−0.55	−0.36
	10.0	−1.00	−1.67	−2.56	−2.62	−2.49	−1.62	−1.13	−0.51	−0.34
	15.0	−0.95	−1.56	−2.46	−2.52	−2.41	−1.60	−1.08	−0.47	−0.31
	20.0	−0.90	−1.50	−2.37	−2.43	−2.32	−1.54	−1.03	−0.44	−0.33
	25.0	−0.85	−1.44	−2.28	−2.35	−2.25	−1.49	−0.98	−0.41	−0.37

The isobaric expansivities and isothermal compressibilities, which were determined through the fit to the experimental density data, enable one to determine appropriate excess functions. The excess expansivities α^E and excess compressibilities κ^E were calculated by using the equations

$$\alpha^E = \alpha - \varphi_1^{id}\alpha_1 - \varphi_2^{id}\alpha_2 \tag{7}$$

$$\kappa^E = \kappa - \varphi_1^{id}\kappa_1 - \varphi_2^{id}\kappa_2 \tag{8}$$

where the subscripts refer to the pure components and φ_i^{id} is an ideal volume fraction given by the relationship

$$\varphi_i^{id} = \frac{x_i V_i}{x_1 V_1 + x_2 V_2} \tag{9}$$

where V_i stands for a molar volume for a pure component.

Discussion

Densities of Pure [MMIM][CH_3SO_4]. The observed density values are typical for the ionic liquids. The temperature and pressure dependencies are weak when compared to the majority of organic liquids, and hence the isobaric expansivities and isothermal compressibilities are relatively low.

Densities of Mixtures and Excess Volumes. The excess volume data for the same system at 298.15 K and under normal pressure have been reported in the literature.[9] At these conditions the [MMIM][CH_3SO_4] exists as a supercooled liquid. The data mentioned exhibit a similar concentration dependence, but the minimum is higher, being equal to -1.24 $cm^3 \cdot mol^{-1}$. The presented excess volumes are negative and highly asymmetric, with the minimum value at the ionic liquid mole fraction about 0.35. At the highest concentrations of the ionic liquid the excess volume as a function of mole fraction becomes flatter, and its curvature changes its sign. This characteristic feature may result from the experimental errors; however, it has also been observed for the same system at 298.15 K.[9] Similar flatness, although of lower extent, has been reorted for the [MMIM][CH_3SO_4] + 2-propanol mixtures at (293.15 to 303.15) K.[10]

The excess volumes are relatively strongly influenced by temperature or pressure (see Figures 5 and 6). The higher the temperature, the lower the minimum value of the excess volume. Over the temperature range of 20 K this effect is about 0.3 $cm^3 \cdot mol^{-1}$ at 0.1 MPa and about 0.2 $cm^3 \cdot mol^{-1}$ at 25 MPa. The pressure exhibits also a strong influence on the excess volumes. Generally, the higher the pressure, the closer-to-zero the excess volumes. For this system the minimum value of the excess volume increases by about 0.5 $cm^3 \cdot mol^{-1}$ if the pressure increases from (0.1 to 25) MPa.

It is worth noting that the pressure and temperature influence on the excess volume is about 1 order greater than in "normal" organic mixtures. For the system measured at $T = 318.15$ K and $p = 0.1$ MPa, and the mole fraction of [MMIM][CH_3SO_4] $x_1 = 0.2255$, which roughly corresponds to the minimum, the derivatives of the V^E with respect to T or p are equal: $(\partial V^E/\partial T)_p = -2.2 \cdot 10^{-2}$ $cm^3 \cdot K^{-1} \cdot mol^{-1}$ and $(\partial V^E/\partial p)_T = 20$ $cm^3 \cdot GPa^{-1} \cdot mol^{-1}$. The former value roughly agrees with a derivative calculated from the temperature dependence of the

[MMIM][CH_3SO_4] + 2-propanol excess volumes, which is equal to $-1.3\cdot10^{-2}$ $cm^3\cdot K^{-1}\cdot mol^{-1}$.[10] The typical absolute values for the temperature derivative are more than 10 times lower, whereas for the pressure the absolute values are about 3 to 4 times lower[28−32] than those observed for the ionic liquid. This characteristic behavior of the ionic liquids is visible also for excess isobaric expansivities and excess isothermal compressibilities.

Isobaric Expansivities and Isothermal Compressibilities. Both properties for mixtures change with concentration from the relatively low and almost independent of pressure and temperature values in the pure ionic liquid, which are equal to about $5.2\cdot10^{-4}$ K^{-1} for expansivity and about 0.30 GPa^{-1} for compressibility, into values for pure methanol that are about twice greater for the former and about four times greater for the latter property. The expansivities and compressibilities of pure methanol are also more significantly dependent on pressure and temperature. It is interesting to note that the [MMIM][CH_3SO_4] + methanol solutions still possess the above-mentioned volumetric properties typical for ionic liquids at the mole fractions of 1,3-dimethylimidazolium methylsulfate down to about 0.35 (see Figures 3 and 4). Probably the structure typical for an ionic liquid is still present in such solutions.

This unusual dependence on composition can be observed also for the excess isobaric expansivities and excess isothermal compressibilities. They are negative and exhibit a highly asymmetric composition dependence with a minimum located approximately at $x_1 = 0.2$. Its value varies between $(-3\cdot10^{-4}$ and $-1\cdot10^{-4})$ K^{-1} for the excess isobaric expansivities (α^E) and from (−0.35 to −0.20) GPa^{-1} for excess isothermal compressibilities (κ^E). Note that estimated uncertainties of the derived expansivities and compressibilities are about $\pm0.2\cdot10^{-4}$ K^{-1} and ±0.05 GPa^{-1}, respectively. Again, the extent of both properties is considerably greater than in mixtures not containing ionic liquids.[32]

Conclusions

The measured $p\rho T$ properties of the pure 1,3-dimethylimidazolium methylsulfate and its mixtures with methanol show some striking features, which should be attributed to the presence of an ionic liquid in the system studied. Apart from those already reported, that is, low values of the isobaric expansivities and isothermal compressibilities, it was observed that the excess volumes are significantly more dependent on pressure and temperature than in so-called "normal" organic mixtures. This leads also to the unusually high absolute values of the excess isobaric expansivities and excess isothermal compressibilities. Such an observation is for the first time formulated in the literature.

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