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Densities, Excess Volumes, Isobaric Expansivities, and Isothermal Compressibilities of the 1-Ethyl-3-methylimidazolium Ethylsulfate + Ethanol System at Temperatures (283.15 to 343.15) K and Pressures from (0.1 to 35) MPa

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Densities of pure 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid, [C_2mim][$EtSO_4$], and its mixtures with ethanol have been measured with an accuracy of $\pm$ 0.2 $kg \cdot m^{-3}$, over the temperature range of (283.15 to 343.15) K and pressure range of (0.1 to 35) MPa, using a vibrating tube densimeter. The experimental densities have been correlated by the Tait equation with the temperature-dependent parameters (for the pure ionic liquid) and by a van Laar type equation, involving parameters dependent on temperature and pressure (for the mixtures). Excess volumes have been derived directly from the experimental densities, and isobaric expansivities, isothermal compressibilities, and related excess properties have been calculated with the use of the correlation equation. The exceptionally strong influence of pressure and temperature on these properties has been confirmed.

Introduction

Ionic liquids are a class of novel solvents with very interesting properties, such as low melting points (< 100 °C), low viscosity, and in particular negligible vapor pressure. For this reason, a great number of applications are now being demonstrated for ionic liquids: as catalysts, reactions media, and electrolytes in electrochemistry; in fuel and solar cells; as lubricants; as a stationary phase for chromatography; as matrixes for mass spectrometry; as support for the immobilization of enzymes in separation technologies; as liquid crystals or templates for the synthesis of mesoporous nanomaterials and ordered films; as materials for embalming and tissue preservation, and so forth.[1]

This paper is the next part of our systematic study on the volumetric properties of ionic liquids and ionic liquids mixed with organic liquids.[2,3] This study has been undertaken because of the lack of the experimental $p\rho T$ data for these systems and difficulties in understanding their peculiar properties.

There are few volumetric data on pure ionic liquids and on mixtures of ionic liquids with organic liquids, involving the density dependence on both temperature and pressure. We presented their list in our previous publication,[3] which is the only paper published on this matter since then. The common conclusions from these measurements can be formulated as follows: relatively weak dependence of densities of pure ionic liquids on temperature and pressure and relatively strong analogous dependence of excess volumes have been observed. We have also noted exceptionally high absolute values of excess isobaric expansivities and excess isothermal compressibilities in the binary system of ionic liquids in alkanols.[2,3]

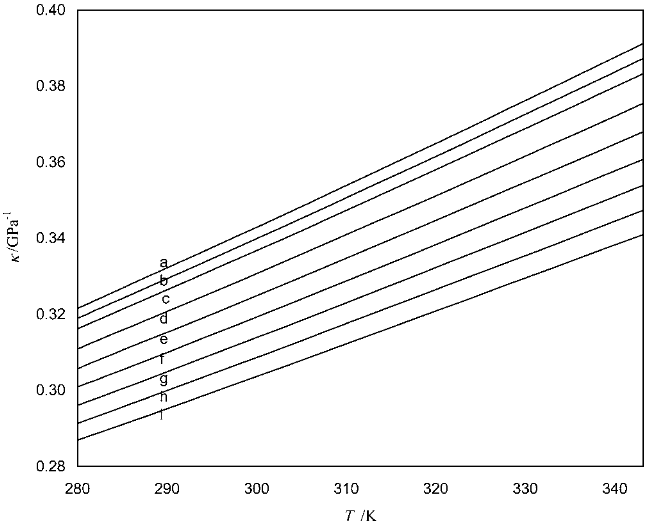

Figure 1. Isothermal compressibility κ of [C_2mim][$EtSO_4$] as a function of temperature T at constant pressure p. Solid lines are calculated from eqs 2 to 4 with the values of parameters given in Table 3. Each line is labeled by a letter corresponding to p/MPa: *a*, 0.1; *b*, 2.5; *c*, 5; *d*, 10; *e*, 15; *f*, 20; *g*, 25; *h*, 30; *i*, 35.

Densities of pure [C_2mim][$EtSO_4$] at different temperatures and under normal pressure have been determined experimentally in a number of laboratories covering the temperature range of (278.15 to 391.27) K.[1,4−14] The densities under different pressures are less numerous.[3,15] They were measured at (283.15 to 333.15) K under (0.1 to 35) MPa[3] and at (293 to 415) K under (0.1 to 40) MPa.[15] Recently we have measured densities for the binary system of [C_2mim][$EtSO_4$] with methanol as a function of temperature and pressure at (283.15 to 333.15) K and under (0.1 to 35) MPa. This paper is a continuation of our previous study.[3]

We have noted three publications reporting excess volumes of the 1-ethyl-3-methylimidazolium ethylsulfate + ethanol system. All concerns measurements under normal pressure and at temperatures 298.15 K,[1] (298.15, 313.15, 328.15) K[9] and (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K.[14]

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Table 1. Experimental Density ρ for $[C_2mim][EtSO_4]$ at Temperature T and Pressure p

T	$\rho/(\mathrm{kg \cdot m^{-3}})$ at p/MPa								
K	0.1	2.5	5	10	15	20	25	30	35
283.15	1247.60	1248.59	1249.58	1251.56	1253.65	1255.44	1257.31	1259.18	1261.04
288.15	1244.17	1245.15	1246.17	1248.17	1250.14	1252.10	1254.03	1255.90	1257.77
293.15	1240.67	1241.70	1242.72	1244.75	1246.75	1248.72	1250.66	1252.56	1254.46
298.15	1237.33	1238.32	1239.36	1241.41	1243.42	1245.42	1247.38	1249.31	1251.22
303.15	1233.95	1234.96	1236.02	1238.10	1240.14	1242.15	1244.14	1246.11	1248.06
308.15	1230.49	1231.54	1232.60	1234.71	1236.78	1238.83	1240.83	1242.81	1244.76
313.15	1227.14	1228.21	1229.29	1231.41	1233.51	1235.57	1237.60	1239.60	1241.57
318.15	1223.86	1224.94	1226.03	1228.17	1230.31	1232.40	1234.44	1236.49	1238.47
323.15	1220.46	1221.54	1222.66	1224.85	1226.99	1229.11	1231.18	1233.23	1235.25
328.15	1217.07	1218.15	1219.31	1221.50	1223.69	1225.81	1227.93	1229.99	1232.04
333.15	1213.67	1214.63	1215.87	1218.14	1220.35	1222.53	1224.65	1226.74	1228.80
338.15	1210.40	1211.52	1212.68	1214.94	1217.17	1219.36	1221.51	1223.61	1225.71
343.15	1207.08	1208.22	1209.36	1211.64	1213.88	1216.10	1218.28	1220.41	1222.51

Table 2. Experimental Density ρ for Ethanol at Temperature T and Pressure p

T	$\rho/(\mathrm{kg \cdot m^{-3}})$ at p/MPa								
K	0.1	2.5	5	10	15	20	25	30	35
283.15	0.79776	0.79974	0.80173	0.80558	0.80928	0.8128	0.8162	0.81947	0.82263
288.15	0.79365	0.79566	0.79773	0.80167	0.80543	0.80906	0.81252	0.81587	0.81904
293.15	0.78919	0.79125	0.79337	0.79742	0.8013	0.80499	0.80853	0.81194	0.81523
298.15	0.78492	0.78703	0.78921	0.79338	0.79734	0.80111	0.80475	0.80821	0.81158
303.15	0.78063	0.78281	0.78504	0.7893	0.79337	0.79725	0.80093	0.80449	0.80795
308.15	0.77626	0.77854	0.78082	0.78522	0.78937	0.79334	0.79714	0.80076	0.80427
313.15	0.77191	0.77426	0.77662	0.78113	0.7854	0.78945	0.79333	0.79704	0.80061
318.15	0.76758	0.76999	0.77241	0.77704	0.78143	0.78559	0.78955	0.79336	0.79698
323.15	0.76309	0.76556	0.76808	0.77284	0.77734	0.78159	0.78565	0.78953	0.79324
328.15	0.75854	0.76109	0.7637	0.76858	0.77322	0.77757	0.78173	0.7857	0.7895
333.15	0.75396	0.75661	0.75927	0.76432	0.76908	0.77356	0.77781	0.78187	0.78576
338.15	0.74942	0.75216	0.75489	0.76009	0.76499	0.76959	0.77396	0.77809	0.78206
343.15	0.74474	0.74757	0.75039	0.75574	0.76075	0.76547	0.76994	0.77417	0.77823

Table 3. Coefficients of the Tait Eqs 2 to 4 Fitted to the Experimental Densities of Pure $[C_2mim][EtSO_4]$ and Ethanol and the Root of Mean Squared Deviation σ of the Fit

T		B	ρ_0	σ^a
K	$A \cdot 10^2$	MPa	$\mathrm{kg \cdot m^{-3}}$	$\mathrm{kg \cdot m^{-3}}$
$[C_2mim]$ $[EtSO_4]$	8.42579	$B_0/\mathrm{MPa} = 632.764$ $B_1/\mathrm{MPa \cdot K^{-1}} = -1.80418$ $B_2/\mathrm{MPa \cdot K^{-2}} = 1.71261 \cdot 10^{-3}$	$\rho_{00}/\mathrm{kg \cdot m^{-3}} = 1553.21$ $\rho_{01}/\mathrm{kg \cdot m^{-3} \cdot K^{-1}} = -1.71706$ $\rho_{02}/\mathrm{kg \cdot m^{-3} \cdot K^{-2}} = 3.14227 \cdot 10^{-3}$ $\rho_{03}/\mathrm{kg \cdot m^{-3} \cdot K^{-3}} = -3.14234 \cdot 10^{-6}$	0.04
ethanol	8.57621	$B_0/\mathrm{MPa} = 304.887$ $B_1/\mathrm{MPa \cdot K^{-1}} = -1.03273$ $B_2/\mathrm{MPa \cdot K^{-2}} = 8.74371 \cdot 10^{-4}$	$\rho_{00}/\mathrm{kg \cdot m^{-3}} = 1242.87$ $\rho_{01}/\ \mathrm{kg \cdot m^{-3} \cdot K^{-1}} = -2.98340$ $\rho_{02}/\mathrm{kg \cdot m^{-3} \cdot K^{-2}} = 7.44651 \cdot 10^{-3}$ $\rho_{03}/\mathrm{kg \cdot m^{-3} \cdot K^{-3}} = -8.69231 \cdot 10^{-6}$	0.04

[a] $\sigma = [\sum_{i=1}^{n}(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}})^2/n]^{1/2}$.

Experimental Section

Materials. The 1-ethyl-3-methylimidazolium ethylsulfate (Solvent Innovation, mass fraction purity stated 99.7 %) was dried and degassed under vacuum for 48 h at a temperature of about 350 K. According to the producer note, the fluoride content was equal to 294.7 ppm, and no other halides were detected. The water content of 526 ppm was assessed by the Karl Fischer titration. Ethanol (Aldrich, puriss > 99.9 %) was dried over 0.4 nm molecular sieves for several days, and its water content was found to be 23 ppm. Alcohol was degassed in an ELMA (Germany) ultrasonic bath at about 320 K for 60 min before a measurement.

The water used in the calibration was purified, deionized (conductivity below 0.8 $\mu\mathrm{S \cdot cm^{-1}}$) by a reverse osmosis unit with an ion-exchange system (Cobrabid-Aqua, Poland), and next degassed in the same manner as ethanol. The liquid mixtures were prepared by mass using the WA 36 precision balance manufactured by MeraWag Poland, with an accuracy of $5 \cdot 10^{-5}$ g. The estimated uncertainty of the mole fraction was about 10^{-4}.

Apparatus and Procedure. The Anton Paar density measuring cell for high pressures and high temperatures (DMA 512P) and

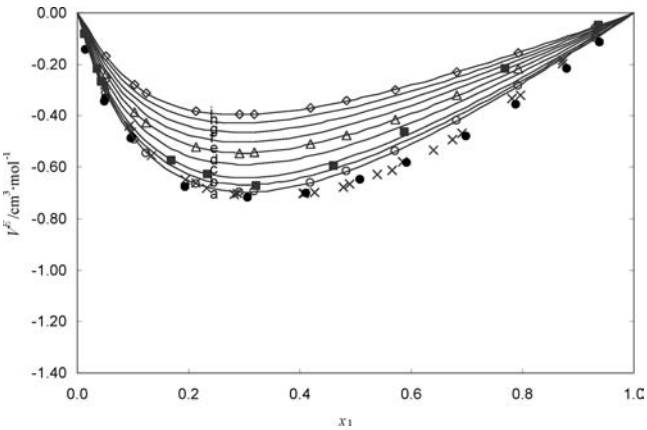

Figure 2. Excess volume V^E of the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)\mathrm{ethanol}\}$ system as a function of mole fraction x_1 at constant temperature $T/\mathrm{K} = 298.15$ and pressure p. Symbols denote experimental data: hollow, this work, measured under p/MPa equal: O, 0.1; Δ, 15.0; ◇, 35.0; filled, literature data under $p = 0.1$ MPa: ×, ref 1; ■, ref 9; ●, ref 14. Solid lines are calculated by eqs 8, 9, and 11 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to p/MPa: *a*, 0.1; *b*, 2.5; *c*, 5; *d*, 10; *e*, 15; *f*, 20; *g*, 25; *h*, 30; *i*, 35.

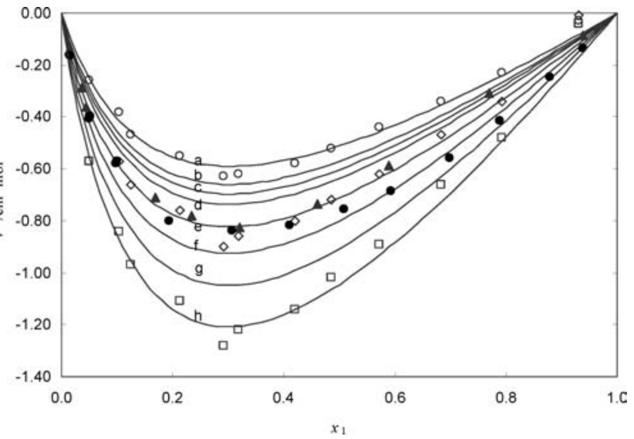

Figure 3. Excess volume V^E of the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)ethanol\}$ system as a function of mole fraction x_1 at constant temperature T and pressure p/MPa = 0.1. Symbols denote experimental data at T/K equal: ○, 283.15, this work; Δ, 313.15, this work; □, 343.15, this work; ▲, 313.15, ref 9; ●, 313.15, ref 14. Solid lines are calculated by eqs 8, 9, and 11 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to T/K: *a*, 283.15; *b*, 293.15; *c*, 298.15; *d*, 303.15; *e*, 313.15; *f*, 323.15; *g*, 333.15; *h*, 343.15.

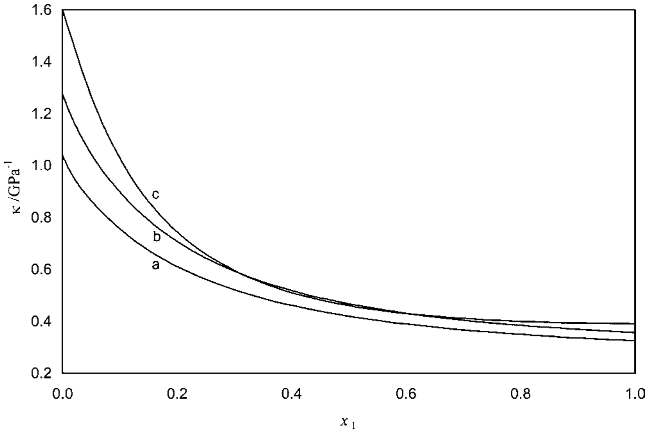

Figure 4. Isothermal compressibility κ of the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)ethanol\}$ system as a function of mole fraction x_1 at constant temperature T and pressure p/MPa = 0.1. Solid lines are calculated on the basis of eqs 7 to 9 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to T/K: *a*, 283.15; *b*, 313.15; *c*, 343.15.

the mPDS 2000 evaluation unit were used for measurements of the densities. The density of a sample was determined by measurement of the oscillation period of the U-shaped tube. The maximum uncertainty of the pressure measurements is claimed to be ± 0.01 MPa, and temperature was kept constant within ± 0.01 K. A detailed description of the apparatus and a procedure can be found elsewhere.[2]

The densimeter was calibrated with water and an empty evacuated U-tube following the procedure of Lagourette et al.[16] In this approach, the dependence between density and the oscillation periods has the form

$$\rho(T,p) = \rho_w(T,p) + \rho_w(T,p_0) \cdot \frac{\tau^2(T,p) - \tau_w^2(T,p)}{\tau_w^2(T,p) - \tau_v^2(T)} \tag{1}$$

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.[17]

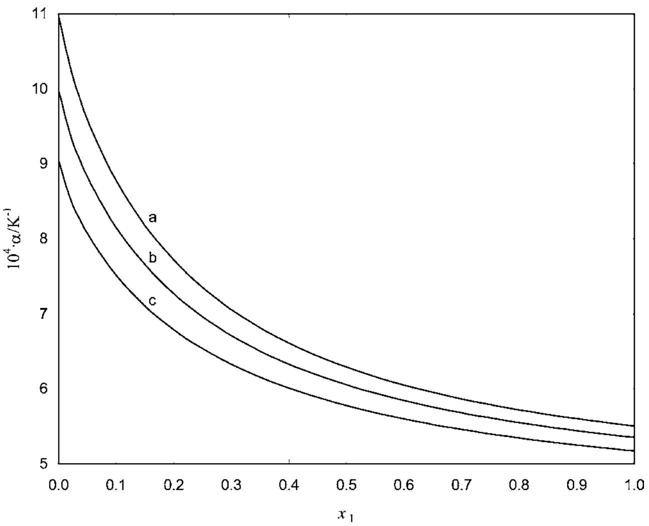

Figure 5. Isobaric expansivity α of the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)ethanol\}$ system as a function of mole fraction x_1 at constant temperature T/K = 298.15 and pressure p. Solid lines are calculated on the basis of eqs 7 to 9 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to p/MPa: *a*, 0.1; *b*, 15; *c*, 35.

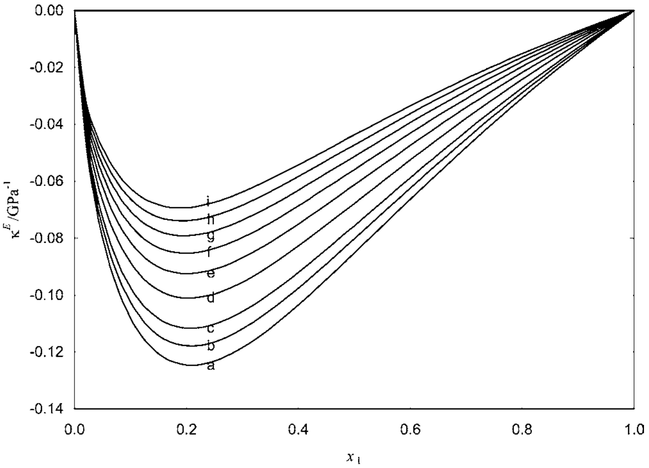

Figure 6. Excess isothermal compressibility κ^E of the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)ethanol\}$ system against mole fraction x_1 at constant temperature T/K = 298.15 and pressure p. Solid lines are calculated on the basis of eqs 7 to 9 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to p/MPa: *a*, 0.1; *b*, 2.5; *c*, 5; *d*, 10; *e*, 15; *f*, 20; *g*, 25; *h*, 30; *i*, 35.

The maximum combined uncertainty for the densities of pure compounds 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 two times greater than the estimated accuracy of the experimental densities of pure water used in the calibration. The actual combined standard uncertainties for pure components and probably for the mixtures at low concentration of the ionic liquid (involving only random errors) are about ± 0.04 kg·m^{-3} as may be concluded from the standard deviations between the raw and the correlated data. The combined standard uncertainty for the mixture density must be higher than that of a pure component due to errors in concentration. This is estimated to be ± 0.2 kg·m^{-3}.

Results and Discussion

Densities of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Pure Ethanol. The densities of pure $[C_2mim][EtSO_4]$ were measured at temperatures T/K = (283.15, 288.15, 293.15,

Table 4. Experimental Densities ρ for the $\{x_1[C_2mim][EtSO_4] + (1 - x_1)Ethanol\}$ Solutions as a Function of Mole Fraction x_1, Temperature T, and Pressure p

	$\rho/(kg\cdot m^{-3})$ at p/MPa								
x_1	0.1	2.5	5	10	15	20	25	30	35
				$T = 283.15$ K					
0.05056	868.10	870.00	871.83	875.33	878.74	882.02	885.17	888.22	891.19
0.10296	925.77	927.45	929.13	932.41	935.57	938.63	941.59	944.47	947.26
0.12466	946.96	948.54	950.16	953.34	956.40	959.38	962.25	965.06	967.80
0.21262	1015.49	1016.98	1018.48	1021.37	1024.17	1026.89	1029.52	1032.11	1034.62
0.29186	1063.41	1064.67	1066.03	1068.69	1071.27	1073.82	1076.29	1078.72	1081.08
0.31855	1076.89	1078.19	1079.51	1082.11	1084.66	1087.15	1089.57	1091.95	1094.27
0.41984	1120.15	1121.36	1122.61	1125.05	1127.44	1129.77	1132.05	1134.29	1136.48
0.48466	1142.52	1143.68	1144.88	1147.23	1149.51	1151.78	1153.99	1156.16	1158.29
0.57131	1167.90	1169.02	1170.16	1172.41	1174.61	1176.78	1178.91	1181.01	1183.08
0.68271	1194.68	1195.76	1196.85	1199.00	1201.12	1203.21	1205.24	1207.27	1209.25
0.79194	1216.13	1217.15	1218.19	1220.26	1222.32	1224.34	1226.31	1228.28	1230.19
0.93175	1237.97	1238.92	1239.94	1241.93	1243.92	1245.88	1247.81	1249.69	1251.56
				$T = 293.15$ K					
0.05056	860.03	861.91	863.83	867.52	871.06	874.47	877.74	880.91	883.98
0.10296	917.84	919.60	921.37	924.78	928.08	931.25	934.32	937.28	940.18
0.12466	939.10	940.76	942.46	945.77	948.96	952.04	955.03	957.93	960.74
0.21262	1007.62	1009.27	1010.81	1013.80	1016.71	1019.53	1022.26	1024.93	1027.53
0.29186	1055.30	1056.61	1058.04	1060.80	1063.50	1066.12	1068.67	1071.18	1073.62
0.31855	1069.32	1070.62	1071.98	1074.68	1077.32	1079.89	1082.37	1084.82	1087.22
0.41984	1112.70	1113.96	1115.24	1117.75	1120.22	1122.63	1124.97	1127.27	1129.54
0.48466	1135.13	1136.31	1137.55	1139.97	1142.34	1144.68	1146.94	1149.19	1151.37
0.57131	1160.59	1161.75	1162.92	1165.25	1167.52	1169.75	1171.93	1174.07	1176.19
0.68271	1187.41	1188.51	1189.64	1191.86	1194.04	1196.18	1198.27	1200.33	1202.37
0.79194	1208.95	1210.00	1211.08	1213.21	1215.31	1217.38	1219.40	1221.40	1223.38
0.93175	1230.93	1231.90	1232.97	1235.05	1237.08	1239.09	1241.05	1242.97	1244.90
				$T = 298.15$ K					
0.05056	855.98	857.88	859.83	863.62	867.22	870.7	874.05	877.28	880.40
0.10296	913.93	915.61	917.40	920.89	924.24	927.48	930.60	933.63	936.57
0.12466	935.16	936.81	938.54	941.91	945.16	948.30	951.34	954.29	957.15
0.21262	1003.90	1005.45	1007.01	1010.07	1013.02	1015.88	1018.67	1021.38	1024.03
0.29186	1052.00	1052.97	1054.41	1057.22	1059.95	1062.62	1065.22	1067.75	1070.23
0.31855	1065.62	1066.90	1068.30	1071.05	1073.73	1076.33	1078.88	1081.37	1083.79
0.41984	1109.11	1110.35	1111.65	1114.21	1116.72	1119.15	1121.54	1123.89	1126.17
0.48466	1131.56	1132.76	1133.99	1136.46	1138.86	1141.21	1143.53	1145.80	1148.02
0.57131	1157.07	1158.20	1159.39	1161.74	1164.05	1166.31	1168.52	1170.70	1172.85
0.68271	1183.93	1185.01	1186.16	1188.41	1190.60	1192.77	1194.89	1197.00	1199.05
0.79194	1205.61	1206.51	1207.59	1209.76	1211.88	1213.98	1216.03	1218.05	1220.04
0.93175	1227.50	1228.53	1229.57	1231.66	1233.72	1235.74	1237.73	1239.69	1241.63
				$T = 303.15$ K					
0.05056	851.90	853.85	855.87	859.72	863.43	866.98	870.39	873.69	876.89
0.10296	910.06	911.70	913.54	917.10	920.52	923.82	927.00	930.09	933.10
0.12466	931.25	932.93	934.69	938.12	941.44	944.64	947.74	950.74	953.67
0.21262	1000.10	1001.68	1003.26	1006.36	1009.37	1012.29	1015.12	1017.88	1020.58
0.29186	1048.63	1049.46	1050.92	1053.74	1056.51	1059.18	1061.79	1064.33	1066.82
0.31855	1061.99	1063.29	1064.70	1067.49	1070.22	1072.86	1075.44	1077.96	1080.42
0.41984	1105.54	1106.82	1108.14	1110.73	1113.28	1115.76	1118.18	1120.55	1122.89
0.48466	1128.01	1129.22	1130.50	1132.99	1135.43	1137.83	1140.16	1142.46	1144.71
0.57132	1153.59	1154.71	1155.92	1158.31	1160.66	1162.94	1165.19	1167.40	1169.59
0.68271	1180.46	1181.59	1182.73	1185.00	1187.24	1189.45	1191.60	1193.74	1195.84
0.79194	1202.24	1203.10	1204.19	1206.38	1208.54	1210.64	1212.73	1214.77	1216.82
0.93175	1224.05	1225.06	1226.12	1228.23	1230.32	1232.36	1234.37	1236.36	1238.34
				$T = 313.15$ K					
0.05056	843.63	845.70	847.81	851.86	855.73	859.44	862.99	866.42	869.72
0.10296	902.00	903.78	905.71	909.43	912.99	916.40	919.72	922.91	926.01
0.12466	923.22	925.01	926.88	930.46	933.91	937.23	940.45	943.56	946.56
0.21262	992.44	994.08	995.74	998.97	1002.07	1005.09	1008.03	1010.88	1013.65
0.29186	1041.30	1042.32	1043.83	1046.78	1049.64	1052.42	1055.15	1057.79	1060.38
0.31855	1054.58	1055.91	1057.39	1060.28	1063.09	1065.82	1068.49	1071.08	1073.63
0.41984	1098.28	1099.64	1101.01	1103.69	1106.30	1108.84	1111.34	1113.78	1116.18
0.48466	1120.82	1122.08	1123.39	1125.96	1128.48	1130.94	1133.35	1135.70	1138.01
0.57132	1146.49	1147.66	1148.92	1151.37	1153.79	1156.13	1158.44	1160.72	1162.93
0.68271	1173.47	1174.61	1175.83	1178.16	1180.44	1182.70	1184.92	1187.08	1189.22
0.79194	1195.34	1196.17	1197.31	1199.56	1201.76	1203.92	1206.06	1208.15	1210.22
0.93175	1217.11	1218.16	1219.26	1221.43	1223.56	1225.65	1227.71	1229.75	1231.75
				$T = 323.15$ K					
0.05056	835.32	837.47	839.71	843.97	848.02	851.88	855.60	859.16	862.58
0.10296	893.98	895.85	897.87	901.75	905.47	909.03	912.49	915.79	919.01
0.12466	915.32	917.14	919.07	922.82	926.40	929.85	933.19	936.42	939.53
0.21262	984.81	986.48	988.21	991.57	994.80	997.91	1000.95	1003.91	1006.77
0.29186	1034.05	1035.04	1036.64	1039.70	1042.66	1045.53	1048.35	1051.07	1053.73

Table 4.. Continued

x_1	$\rho/(\mathrm{kg \cdot m^{-3}})$ at p/MPa 0.1	2.5	5	10	15	20	25	30	35
0.31855	1047.28	1048.63	1050.16	1053.16	1056.05	1058.87	1061.63	1064.29	1066.91
0.41984	1091.13	1092.5	1093.93	1096.70	1099.39	1102.02	1104.58	1107.10	1109.55
0.48466	1113.75	1115.00	1116.36	1119.02	1121.59	1124.12	1126.59	1129.01	1131.39
0.57132	1139.53	1140.71	1142.02	1144.55	1147.01	1149.42	1151.81	1154.14	1156.41
0.68271	1166.57	1167.74	1168.97	1171.37	1173.72	1176.03	1178.31	1180.52	1182.71
0.79194	1188.51	1189.35	1190.5	1192.81	1195.06	1197.29	1199.48	1201.62	1203.73
0.93175	1210.34	1211.42	1212.55	1214.78	1216.96	1219.11	1221.21	1223.29	1225.34
				$T = 333.15$ K					
0.05056	826.91	829.15	831.49	835.97	840.22	844.27	848.14	851.85	855.41
0.10296	885.77	887.83	889.93	893.99	897.89	901.61	905.17	908.61	911.93
0.12466	907.28	909.17	911.19	915.10	918.84	922.44	925.91	929.24	932.47
0.21262	977.10	978.86	980.64	984.14	987.50	990.73	993.88	996.92	999.88
0.29186	1026.55	1027.68	1029.31	1032.48	1035.56	1038.53	1041.42	1044.25	1046.98
0.31855	1039.85	1041.25	1042.83	1045.92	1048.93	1051.83	1054.66	1057.43	1060.13
0.41984	1083.92	1085.39	1086.84	1089.70	1092.49	1095.20	1097.84	1100.42	1102.94
0.48466	1106.62	1107.91	1109.29	1112.04	1114.72	1117.29	1119.85	1122.34	1124.77
0.57132	1132.56	1133.80	1135.10	1137.70	1140.25	1142.73	1145.17	1147.56	1149.90
0.68271	1159.67	1160.86	1162.12	1164.60	1167.03	1169.40	1171.73	1174.00	1176.25
0.79194	1181.63	1182.51	1183.7	1186.07	1188.40	1190.67	1192.91	1195.12	1197.28
0.93175	1203.54	1204.68	1205.83	1208.10	1210.35	1212.54	1214.70	1216.82	1218.92
				$T = 343.15$ K					
0.05056	818.25	820.66	823.11	827.83	832.27	836.51	840.54	844.41	848.12
0.10296	877.67	879.77	881.99	886.23	890.27	894.14	897.85	901.43	904.85
0.12466	899.50	901.47	903.69	907.82	911.68	915.39	918.99	922.46	925.77
0.21262	969.67	971.48	973.32	976.91	980.38	983.71	986.96	990.09	993.12
0.29186	1019.38	1020.57	1022.23	1025.50	1028.64	1031.72	1034.69	1036.01	1040.41
0.31855	1032.60	1034.03	1035.67	1038.87	1041.94	1044.93	1047.86	1050.69	1053.46
0.41984	1076.98	1078.52	1080.00	1082.95	1085.80	1088.59	1091.31	1093.96	1096.54
0.48466	1099.67	1100.97	1102.41	1105.21	1107.95	1110.61	1113.23	1115.78	1118.28
0.57132	1125.70	1126.98	1128.32	1131.01	1133.60	1136.16	1138.67	1141.10	1143.48
0.68271	1152.86	1154.10	1155.37	1157.89	1160.38	1162.80	1165.19	1167.53	1169.82
0.79194	1175.00	1175.81	1177.05	1179.48	1181.84	1184.18	1186.47	1188.72	1190.93
0.93175	1196.87	1198.02	1199.21	1201.52	1203.82	1206.06	1208.26	1210.44	1212.58

Table 5. Coefficients of the Equation Fitted to the Experimental Densities of the ([C_2mim][$EtSO_4$] + Ethanol) System as a Function of Mole Fraction, Temperature, and Pressure: Eqs 7 to 9 and the Root of Mean Squared Deviation σ of the Fit

i	k	a_{ik} / $\mathrm{cm^3 \cdot mol^{-1}}$	b_{ik}	σ^a / $\mathrm{kg \cdot m^{-3}}$
0	0	–0.157654	37.2499	0.31
0	1	0.161119	0.766519	
0	2	–0.120687	–0.386087	
1	0	–6.35519	5.24187	
1	1	$3.27008 \cdot 10^{-2}$	$5.24187 \cdot 10^{-2}$	
1	2	$-3.30101 \cdot 10^{-2}$	$-1.71900 \cdot 10^{-2}$	

[a] $\sigma = [\sum_{i=1}^{n}(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{calc}})^2/n]^{1/2}$.

298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15, 333.15, 338.15, and 343.15) and under pressures p/MPa = (0.1, 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 35.0) at each temperature; altogether 117 experimental data points were obtained. They are given in Table 1. The difference between densities measured in this work and densities reported by Jacquemin et al.[15] fluctuates from 0.1 % for pressures equal 5 MPa to 1.6 % for pressures equal to 30 MPa. The densities measured in this work are very close to our previous measurements.[3] The densities of ethanol were measured under the same conditions as for the ionic liquid and are given in Table 2. Those measured under normal pressure are very close to the literature data[18−23] being usually slightly lower by about 0.03 %. The deviations with the values measured by Hales and Ellender[23] do not exceed 0.005 %.

Experimental densities were correlated by the Tait equation

$$\rho(T, p) = \frac{\rho_0(T, p_0)}{1 - A \ln \dfrac{B(T) + p}{B(T) + p_0}} \qquad (2)$$

with the reference pressure p_0 equal to 0.1 MPa. The ρ_0 and B parameters were assumed to be dependent on temperature according to the following equations:

$$\rho_0(T, p_0) = \rho_{00} + \rho_{01}(T/\mathrm{K}) + \rho_{02}(T/\mathrm{K})^2 + \rho_{03}(T/\mathrm{K})^3 \qquad (3)$$

$$B(T) = B_0 + B_1(T/\mathrm{K}) + B_2(T/\mathrm{K})^2 \qquad (4)$$

The number of terms in these equations and the constancy of the A parameter resulted from the statistical analysis. The fitted parameters of equations and the standard deviations are shown in Table 3.

Isobaric Expansivities and Isothermal Compressibilities of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate. The temperature and pressure influence on the expansivity is weak when compared to the "typical" organic liquids. Depending on the equation applied to correlate the density−temperature dependence, the expansivities of ionic liquids reported in literature are both dependent[3,6,10,24] and independent[25,26] of temperature. In the former case a small decrease in expansivity with an increase in temperature has been observed. This is a striking feature which was only reported for a few low alcohols at low temperatures.[27] The expansivities, calculated by eqs 2 to 4 with the values of parameters given in Table 3, exhibit minima as a

Table 6. Experimental Excess Volumes V^E for the {x_1[C$_2$mim][EtSO$_4$] + (1 − x_1)Ethanol} Solutions as a Function of Mole Fraction x_1, Temperature *T*, and Pressure *p*

	V^E/cm^3·mol^{-1} at p/MPa								
x_1	0.1	2.5	5	10	15	20	25	30	35
T = 283.15 K									
0.05056	−0.26	−0.25	−0.24	−0.22	−0.21	−0.19	−0.18	−0.17	−0.16
0.10296	−0.38	−0.37	−0.35	−0.32	−0.29	−0.28	−0.25	−0.24	−0.22
0.12466	−0.47	−0.45	−0.43	−0.40	−0.36	−0.34	−0.32	−0.29	−0.28
0.21262	−0.55	−0.53	−0.51	−0.47	−0.42	−0.40	−0.37	−0.34	−0.32
0.29186	−0.63	−0.59	−0.57	−0.53	−0.48	−0.45	−0.42	−0.39	−0.36
0.31855	−0.62	−0.59	−0.57	−0.53	−0.48	−0.45	−0.42	−0.39	−0.36
0.41984	−0.58	−0.55	−0.53	−0.49	−0.44	−0.42	−0.39	−0.36	−0.33
0.48466	−0.52	−0.5	−0.48	−0.44	−0.39	−0.37	−0.34	−0.32	−0.29
0.57131	−0.44	−0.42	−0.40	−0.37	−0.32	−0.31	−0.29	−0.26	−0.24
0.68271	−0.34	−0.32	−0.31	−0.28	−0.24	−0.24	−0.22	−0.20	−0.18
0.79194	−0.23	−0.22	−0.2	−0.18	−0.15	−0.16	−0.14	−0.13	−0.12
0.93175	−0.03	−0.02	−0.02	−0.01	0.02	0.00	0.00	0.01	0.01
T = 293.15 K									
0.05056	−0.30	−0.29	−0.28	−0.26	−0.24	−0.22	−0.21	−0.19	−0.18
0.10296	−0.44	−0.43	−0.41	−0.38	−0.34	−0.32	−0.29	−0.27	−0.25
0.12466	−0.53	−0.51	−0.49	−0.45	−0.42	−0.39	−0.36	−0.34	−0.31
0.21262	−0.60	−0.58	−0.56	−0.51	−0.47	−0.44	−0.41	−0.38	−0.35
0.29186	−0.66	−0.63	−0.60	−0.55	−0.51	−0.47	−0.43	−0.40	−0.37
0.31855	−0.70	−0.67	−0.64	−0.59	−0.54	−0.50	−0.47	−0.43	−0.41
0.41984	−0.65	−0.62	−0.60	−0.55	−0.51	−0.47	−0.44	−0.41	−0.38
0.48466	−0.58	−0.56	−0.53	−0.49	−0.45	−0.42	−0.38	−0.36	−0.33
0.57131	−0.50	−0.48	−0.46	−0.42	−0.38	−0.35	−0.32	−0.3	−0.27
0.68271	−0.38	−0.36	−0.34	−0.32	−0.29	−0.26	−0.24	−0.22	−0.20
0.79194	−0.26	−0.25	−0.23	−0.21	−0.19	−0.18	−0.16	−0.15	−0.13
0.93175	−0.03	−0.01	−0.01	−0.01	0.00	0.00	0.01	0.01	0.02
T = 298.15 K									
0.05056	−0.32	−0.31	−0.30	−0.27	−0.25	−0.24	−0.22	−0.20	−0.19
0.10296	−0.47	−0.45	−0.43	−0.39	−0.36	−0.33	−0.31	−0.28	−0.26
0.12466	−0.56	−0.54	−0.51	−0.47	−0.44	−0.40	−0.37	−0.35	−0.32
0.21262	−0.64	−0.61	−0.59	−0.54	−0.50	−0.46	−0.42	−0.39	−0.36
0.29186	−0.73	−0.67	−0.64	−0.58	−0.54	−0.50	−0.46	−0.42	−0.39
0.31855	−0.73	−0.70	−0.67	−0.61	−0.57	−0.53	−0.49	−0.46	−0.42
0.41984	−0.69	−0.66	−0.63	−0.58	−0.54	−0.49	−0.46	−0.43	−0.40
0.48466	−0.61	−0.59	−0.56	−0.51	−0.47	−0.44	−0.40	−0.37	−0.35
0.57131	−0.53	−0.50	−0.48	−0.44	−0.4	−0.37	−0.34	−0.31	−0.29
0.68271	−0.40	−0.38	−0.36	−0.33	−0.30	−0.27	−0.25	−0.23	−0.21
0.79194	−0.28	−0.25	−0.23	−0.21	−0.20	−0.18	−0.16	−0.15	−0.13
0.93175	−0.02	−0.02	−0.01	−0.01	0.00	0.01	0.01	0.01	0.02
T = 303.15 K									
0.05056	−0.35	−0.33	−0.32	−0.29	−0.27	−0.25	−0.23	−0.22	−0.20
0.10296	−0.51	−0.48	−0.46	−0.42	−0.38	−0.35	−0.33	−0.30	−0.28
0.12466	−0.60	−0.57	−0.54	−0.50	−0.46	−0.42	−0.40	−0.37	−0.34
0.21262	−0.68	−0.65	−0.62	−0.57	−0.52	−0.48	−0.45	−0.41	−0.38
0.29186	−0.80	−0.72	−0.69	−0.63	−0.58	−0.53	−0.49	−0.45	−0.41
0.31855	−0.78	−0.74	−0.70	−0.65	−0.60	−0.55	−0.51	−0.48	−0.44
0.41984	−0.72	−0.69	−0.67	−0.61	−0.56	−0.52	−0.48	−0.45	−0.42
0.48466	−0.65	−0.62	−0.59	−0.54	−0.50	−0.46	−0.42	−0.39	−0.36
0.57131	−0.56	−0.53	−0.50	−0.46	−0.42	−0.39	−0.36	−0.33	−0.30
0.68271	−0.42	−0.40	−0.38	−0.35	−0.32	−0.29	−0.27	−0.25	−0.22
0.79194	−0.31	−0.26	−0.25	−0.22	−0.20	−0.18	−0.17	−0.15	−0.14
0.93175	−0.02	−0.01	0.00	0.01	0.01	0.02	0.02	0.03	0.03
T = 313.15 K									
0.05056	−0.39	−0.37	−0.36	−0.33	−0.30	−0.28	−0.26	−0.24	−0.23
0.10296	−0.57	−0.54	−0.51	−0.47	−0.43	−0.39	−0.36	−0.34	−0.31
0.12466	−0.66	−0.63	−0.60	−0.55	−0.5,	−0.47	−0.43	−0.40	−0.37
0.21262	−0.76	−0.73	−0.69	−0.63	−0.58	−0.53	−0.49	−0.46	−0.42
0.29186	−0.90	−0.82	−0.79	−0.72	−0.66	−0.61	−0.57	−0.53	−0.49
0.31855	−0.86	−0.81	−0.78	−0.71	−0.66	−0.61	−0.56	−0.52	−0.49
0.41984	−0.80	−0.77	−0.74	−0.68	−0.62	−0.58	−0.53	−0.50	−0.46
0.48466	−0.72	−0.69	−0.65	−0.60	−0.55	−0.51	−0.47	−0.43	−0.40
0.57131	−0.62	−0.58	−0.56	−0.51	−0.47	−0.43	−0.39	−0.36	−0.33
0.68271	−0.47	−0.44	−0.42	−0.39	−0.35	−0.32	−0.29	−0.27	−0.25
0.79194	−0.34	−0.29	−0.27	−0.25	−0.22	−0.20	−0.18	−0.16	−0.15
0.93175	−0.01	0.00	0.00	0.01	0.02	0.02	0.03	0.04	0.04
T = 323.15 K									
0.05056	−0.44	−0.42	−0.40	−0.37	−0.34	−0.31	−0.29	−0.27	−0.25
0.10296	−0.65	−0.61	−0.58	−0.53	−0.48	−0.44	−0.41	−0.38	−0.35
0.12466	−0.74	−0.70	−0.67	−0.61	−0.56	−0.51	−0.47	−0.44	−0.41
0.21262	−0.85	−0.81	−0.77	−0.70	−0.64	−0.59	−0.55	−0.51	−0.47
0.29186	−1.02	−0.92	−0.88	−0.81	−0.74	−0.69	−0.64	−0.59	−0.55

Table 6.. Continued

x_1	V^E/cm^3·mol^{-1} at p/MPa 0.1	2.5	5	10	15	20	25	30	35
0.31855	−0.96	−0.91	−0.87	−0.79	−0.73	−0.67	−0.62	−0.58	−0.54
0.41984	−0.90	−0.85	−0.82	−0.75	−0.69	−0.64	−0.59	−0.55	−0.51
0.48466	−0.81	−0.76	−0.72	−0.66	−0.60	−0.55	−0.51	−0.47	−0.44
0.57131	−0.69	−0.65	−0.62	−0.57	−0.52	−0.47	−0.44	−0.4,	−0.37
0.68271	−0.52	−0.49	−0.47	−0.42	−0.38	−0.35	−0.32	−0.29	−0.27
0.79194	−0.37	−0.31	−0.29	−0.26	−0.24	−0.21	−0.19	−0.17	−0.15
0.93175	−0.01	−0.01	0.00	0.01	0.02	0.03	0.03	0.04	0.04
$T = 333.15$ K									
0.05056	−0.51	−0.48	−0.46	−0.42	−0.39	−0.36	−0.33	−0.31	−0.29
0.10296	−0.74	−0.70	−0.66	−0.60	−0.55	−0.50	−0.46	−0.43	−0.40
0.12466	−0.84	−0.80	−0.76	−0.69	−0.63	−0.58	−0.53	−0.49	−0.46
0.21262	−0.96	−0.92	−0.87	−0.79	−0.72	−0.66	−0.61	−0.57	−0.53
0.29186	−1.13	−1.04	−0.99	−0.91	−0.83	−0.77	−0.71	−0.66	−0.61
0.31855	−1.08	−1.02	−0.97	−0.89	−0.81	−0.75	−0.69	−0.64	−0.59
0.41984	−1.01	−0.98	−0.92	−0.84	−0.77	−0.71	−0.66	−0.61	−0.57
0.48466	−0.91	−0.87	−0.82	−0.74	−0.68	−0.62	−0.57	−0.53	−0.49
0.57131	−0.79	−0.76	−0.71	−0.65	−0.59	−0.54	−0.50	−0.46	−0.42
0.68271	−0.59	−0.58	−0.54	−0.48	−0.44	−0.40	−0.37	−0.34	−0.31
0.79194	−0.42	−0.38	−0.34	−0.31	−0.28	−0.25	−0.22	−0.20	−0.18
0.93175	−0.03	−0.05	−0.03	−0.01	0.00	0.01	0.02	0.03	0.03
$T = 343.15$ K									
0.05056	−0.57	−0.54	−0.51	−0.47	−0.43	−0.40	−0.36	−0.34	−0.32
0.10296	−0.84	−0.79	−0.75	−0.68	−0.62	−0.56	−0.52	−0.48	−0.45
0.12466	−0.97	−0.91	−0.88	−0.80	−0.73	−0.67	−0.62	−0.58	−0.54
0.21262	−1.11	−1.05	−1.00	−0.90	−0.82	−0.75	−0.69	−0.64	−0.59
0.29186	−1.28	−1.18	−1.12	−1.02	−0.94	−0.86	−0.80	−0.59	−0.69
0.31855	−1.22	−1.14	−1.08	−0.99	−0.90	−0.83	−0.77	−0.71	−0.66
0.41984	−1.14	−1.10	−1.04	−0.96	−0.88	−0.81	−0.75	−0.70	−0.65
0.48466	−1.02	−0.96	−0.92	−0.83	−0.76	−0.69	−0.64	−0.59	−0.55
0.57131	−0.89	−0.84	−0.80	−0.73	−0.66	−0.61	−0.56	−0.52	−0.47
0.68271	−0.66	−0.63	−0.59	−0.54	−0.49	−0.45	−0.41	−0.37	−0.34
0.79194	−0.48	−0.40	−0.38	−0.35	−0.31	−0.28	−0.25	−0.23	−0.21
0.93175	−0.04	−0.03	−0.03	−0.01	0.00	0.01	0.02	0.02	0.03

function of temperature. Further studies are necessary to confirm or to disregard this observation as this feature may result from the mathematical form of the equation used to correlate the data.[3]

Equations 2 to 4 enable us to calculate the related properties of isothermal compressibilities κ and isobaric expansivities α from the equations

$$\kappa = (\partial \ln \rho/\partial p)_T \tag{5}$$

and

$$\alpha = -(\partial \ln \rho/\partial T)_p \tag{6}$$

The accuracies of these parameters 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 the derived values of parameters calculated through the statistical analysis are lower than differences resulting from the various equations. Nevertheless, the latter values do not exceed $\pm$ 0.01 GPa^{-1} for compressibilities and $\pm$ 0.1·10^{-4} K^{-1} for expansitivities, which may be considered as the maximum error of these derived parameters.

The calculated values of isobaric expansivities for [C$_2$mim][EtSO$_4$] are situated between (5.15 to 5.58)·10^{-4} K^{-1}. Compared to our previous measurements, they are 5 % lower, and the minima with respect to temperature is more flat although observed at the same temperature of about 315 K.[3] The values for ionic liquids usually vary between (4 to 7)·10^{-4} K^{-1} and are significantly lower than those of typical organic liquids. For example, the isobaric expansivities of ethanol calculated on the base of parameters from Table 3 equal to (9.04 to 12.67)·10^{-4} K^{-1} in the range of pressure at (0.1 to 35) MPa and temperature (283.15 to 343.15) K. The expansivities of ionic liquids partly resemble this property of water, although they are considerably less dependent on temperature.

Typically, as for ionic liquids, isothermal compressibilities are comparatively low. Again, their values are closer to the compressibilities of water than those of ordinary organic liquids. The particularly weak temperature dependence is noticeable. The calculated values are similar to values previously measured.[3] For example, the compressibilities of ethanol at the same ranges of temperature and pressure are between (0.75 to 1.60) GPa^{-1}. In comparison with other ionic liquids, the expansivities reported for [C$_2$mim][EtSO$_4$] are slightly lower than average values.[1−3,24−26,28−32] This may be explained by relatively small ions included in the [C$_2$mim][EtSO$_4$] molecule.

The results reveal a dependence of temperature and pressure which is typical for ionic liquids. The calculated isothermal compressibilities as function of temperature under constant pressures are shown in Figure 1.

Densities and Excess Volumes of the 1-Ethyl-3-methylimidazolium Ethylsulfate + Ethanol Mixtures. The densities for the mixtures [C$_2$mim][EtSO$_4$] + ethanol were measured at twelve different mole fractions, at temperatures T/K = (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, 333.15, and 343.15) and under pressures p/MPa = (0.1, 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 35.0). We obtained 864 data points excluding densities of pure components. These data are given in Table 4.

The experimental densities ρ of a binary system can be expressed as a function of temperature, pressure, and composition, having a following form[3]

$$\rho(T,p,x_1) = \frac{M_1x_1 + M_2x_2}{M_1x_1/\rho_1^0(T,p) + M_2x_2/\rho_2^0(T,p) + x_1x_2\left(\dfrac{a_0(T,p)}{b_0(T,p)x_1 + x_2} + \dfrac{a_1(T,p)}{b_1(T,p)x_1 + x_2}\right)} \tag{7}$$

where M_1 and M_2 are molecular weights, ρ_1^0 and ρ_2^0 stand for the density for a pure component. The third term in the denominator represents the excess volume which is expressed by the van Laar type equation. The $a_i(T, p)$ and $b_i(T, p)$ parameters were assumed to depend linearly on T and p according to formulas

$$[a_i(T,p)/\mathrm{cm^3{\cdot}mol^{-1}}] = a_{i0} + a_{i1}[(p/\mathrm{MPa}) - 0.1] + a_{i2}[(T/\mathrm{K}) - 283] \tag{8}$$

$$b_i(T,p) = b_{i0} + b_{i1}[(p/\mathrm{MPa}) - 0.1] + b_{i2}[(T/\mathrm{K}) - 283] \tag{9}$$

It was confirmed statistically so that the higher-order terms in the above expansions could be neglected.

The correlation equation requires twelve adjustable parameters (a_{00}, a_{01}, a_{02}, a_{10}, a_{11}, a_{12}, b_{00}, b_{01}, b_{02}, b_{10}, b_{11}, and b_{12}) which were adjusted to the experimental densities with the standard deviation of 0.31 $\mathrm{kg{\cdot}m^{-3}}$. The values of parameters are given in Table 5.

Experimental excess volumes were calculated from the measured densities of solutions and pure components using a formula

$$V^{\mathrm{E}} = M_1x_1(1/\rho - 1/\rho_1^0) + M_2x_2(1/\rho - 1/\rho_2^0) \tag{10}$$

where M_1 and M_2 are molecular weights of the pure components and ρ, ρ_1^0, and ρ_2^0 designate densities of solution and pure components, respectively. The calculated values are collected in Table 6. They can be reproduced giving an overall standard deviation equal to 0.036 $\mathrm{cm^3{\cdot}mol^{-1}}$ by the equation

$$V^{\mathrm{E}}(T,p,x_1) = x_1x_2\left(\frac{a_0(T,p)}{b_0(T,p)x_1 + x_2} + \frac{a_1(T,p)}{b_1(T,p)x_1 + x_2}\right) \tag{11}$$

with the values of parameters taken from Table 5.

Figures 2 and 3 show excess volumes, experimental and calculated, using eq 11. Figure 2 displays excess volumes at T/K = 298.15 under nine pressures, and in Figure 3 the dependencies under normal pressure and at eight temperatures are shown. The presented excess volumes are negative and highly asymmetric, with the minimum value at the ionic liquid mole fraction about 0.3. This minimum moves slightly toward a higher ionic liquid concentration with increasing pressure or temperature. A similar behavior was observed for the [C_2mim][$EtSO_4$] + methanol system.[3] Figures 2 and 3 show also the data under normal pressure reported already in the literature.[1,9,14] They are very close to our data, although a systematic discrepancy at higher concentration of the ionic liquid should be noted.

Similarly, as it was noted previously for the system of methanol with [mmim][$MeSO_4$][2] or [C_2mim][$EtSO_4$][3], a relatively strong pressure and temperature influence on the values of excess volumes is observed. The values of the derivative $(\partial V^{\mathrm{E}}/\partial T)_p$, which are negative, decrease with increasing temperature and decreasing pressure, while the positive values of the $(\partial V^{\mathrm{E}}/\partial p)_T$ increase under the same conditions. The extremum values of the derivative $(\partial V^{\mathrm{E}}/\partial T)_p$ are in the range from $-4{\cdot}10^{-3}$ $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$ (T = 283.15 K, p = 35 MPa) to $-21{\cdot}10^{-3}$ $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$ (T = 343.15 K, p = 0.1 MPa). The extremum values of the derivative $(\partial V^{\mathrm{E}}/\partial p)_T$ are in the range from 6 $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}GPa^{-1}}$ (T = 283.15 K, p = 35 MPa) to $30{\cdot}10^{-3}$ $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}GPa^{-1}}$ (T = 343.15 K, p = 0.1 MPa). They are close to values observed for the 1-ethyl-3-methylimidazolium ethylsulfate + methanol system.[3]

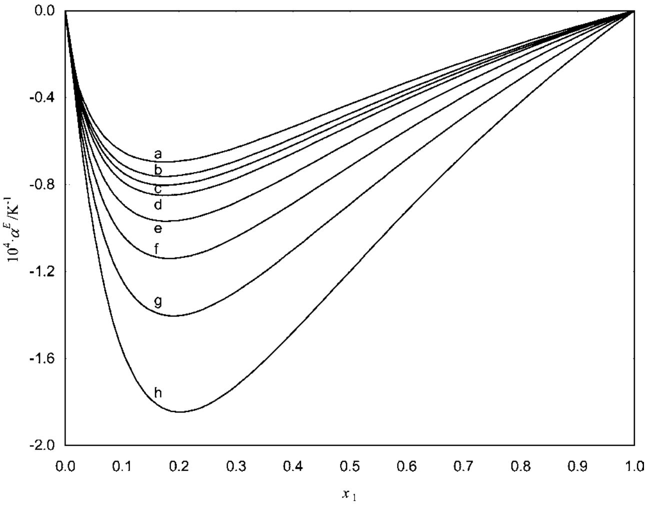

Figure 7. Excess isobaric expansivity α^{E} of the {x_1[C_2mim][$EtSO_4$] + (1 − x_1)ethanol} system as a function of mole fraction x_1 at constant temperature T and pressure p/MPa = 0.1. Solid lines are calculated on the basis of eqs 7 to 9 with the values of parameters given in Tables 3 and 5. Each line is labeled by a letter corresponding to T/K: *a*, 283.15; *b*, 293.15; *c*, 298.15; *d*, 303.15; *e*, 313.15; *f*, 323.15; *g*, 333.15; h, 343.15.

Isothermal Compressibilities, Isobaric Expansivities, and the Corresponding Excess Properties of the 1-Ethyl-3-methylimidazolium Ethylsulfate + Ethanol Mixtures. We are able to calculate isothermal compressibilities and isobaric expansivities of the mixture using eqs 7 to 9. Figures 4 and 5 show dependencies of both properties with respect to mole fractions. Moving along the concentration scale, the compressibility and the expansivity fall nonlinearly from a high value for pure ethanol to the considerably lower one for pure ionic liquid. Generally, the compressibilities increase with increasing temperature with a striking exception at temperatures higher than 333.15 K and for the ionic liquid mole fraction greater than about 0.3. As the observed effect is weak, it is not clear, however, if this is a real phenomenon or a result of experimental uncertainties.

We calculated excess compressibilities κ^{E} and excess expansivities α^{E} by the equations

$$\kappa^{\mathrm{E}} = \kappa - \varphi_1^{\mathrm{id}}\kappa_1^0 - \varphi_2^{\mathrm{id}}\kappa_2^0 \tag{12}$$

$$\alpha^{\mathrm{E}} = \alpha - \varphi_1^{\mathrm{id}}\alpha_1^0 - \varphi_2^{\mathrm{id}}\alpha_2^0 \tag{13}$$

where the superscript ^{0} refers to the pure component and φ_i^{id} is an ideal volume fraction given by the following relation

$$\varphi_i^{\mathrm{id}} = \frac{x_iV_i^0}{x_1V_1^0 + x_2V_2^0} \tag{14}$$

in which V_i^0 stands for a molar volume of a pure component.

Typical dependencies of excess compressibilities and excess expansivities are given in Figures 6 and 7. The shape of the calculated curves is rather unusual. First of all, the absolute maximum values of both functions are very large. They are at least one order of magnitude larger than that which was observed in "normal" organic mixtures.[33] The curves are unsymmetrical with the minimum located at an ionic liquid mole fraction of about 0.2 which is slightly higher if compared to the 1-ethyl-3-methylimidazolium ethylsulfate + methanol system.[3] Finally, pressure and temperature considerably influence both properties which is also rather unexpected when compared to typical organic liquids.

Conclusions

The measured $p\rho T$ properties of the pure 1-ethyl-3-methylimidazolium ethylsulfate and its mixtures with ethanol show some striking features, which should be attributed to the presence of the ionic liquid in the studied system. Atypical behavior of isothermal compressibilities was noted. A relatively strong temperature and pressure influence on the volumetric excess functions—excess volumes, isothermal compressibilities, and isobaric expansivities—has been observed. These two latter properties show very high absolute values as was previously observed.[3]

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