

Densities and Derived Volumetric Properties of Ionic Liquids with [Nf₂] and [NTf₂] Anions at High Pressures

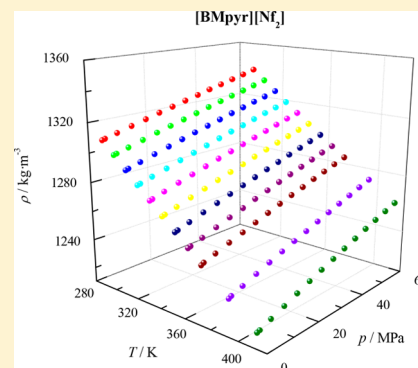
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Supporting Information

ABSTRACT: The densities of four ionic liquids: 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([E³Mim][Nf₂]), *n*-propyl-*n*-methylpyrrolidinium bis(fluorosulfonyl)imide ([PMpyr][Nf₂]), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ([BMpyr][Nf₂]), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMpyr][NTf₂]) were measured at temperatures (293.15 to 413.15) K and pressures (0.1 to 60) MPa. The experimental density data were modeled using the modified Tammann–Tait equation and the average absolute percentage deviations between measured and calculated values for all studied ionic liquids were less than 0.004%. The optimized parameters were used to calculate the isothermal compressibility, the isobaric thermal expansivity, the internal pressure, and the difference between specific heat capacities at constant pressure and at constant volume. The cation and anion influences on the properties of the ionic liquids were examined. The longer alkyl chains on cations are related to lower density of ionic liquids and ionic liquids with imidazole based cation are denser than those with pyrrolidinium cation. The presence of more stable [NTf₂][−] anion in ionic liquids leads to greater densities comparing to [Nf₂][−] anion.



1. INTRODUCTION

Ionic liquids (ILs) are formed by organic cations (such as imidazolium, pyrrolidinium, pyridinium, etc.) and organic or inorganic anions (such as bis(trifluoromethanesulfonyl)imide, bis(fluorosulfonyl)imide, dicyanamide, etc.). They are salts with unique properties such as melting points lower than 373.15 K, low vapor pressure, high thermal stability and miscibility with water and organic solvents, which make them very attractive compounds for industrial purposes. Ionic liquids show both polar and apolar behavior making them suitable solvents for various chemical reactions.^{1–4} Their physical and chemical properties, as well as the possibility of designing ionic liquids with desired characteristics, enable them to be used in a number of specific applications, for example, as good extraction solvents for metal ions and organic compounds, in the removal of pollutants such as phenolic compounds from water, or as a substitute for volatile more toxic solvents.^{1–13} Indeed, ILs have a great potential in absorption of CO₂ from natural gas,^{13–15} but an aggravating factor for their commercial use is the price of ionic liquids that is significantly higher than of other conventional solvents. This could be overcome by using supported ionic liquid membranes which consume a smaller amount of IL.^{13,16,17} The ionic liquids' mixtures with CO₂ are of particular interest because CO₂ dissolves very well in ionic liquid, while ILs are not miscible with CO₂ and, additionally, CO₂ has a great influence on solubility of organics in ILs depending on its concentration in mixtures.^{1,15,18–20} Besides that, the selected ionic liquids could also be used as active component in sensors

or electrolyte in batteries in electrochemical industries, as lubricant antistatic in engineering industries or stationary phase for gas chromatography in analytic applications.²¹

Although they were considered to be completely “green” for a long period, scientists started examining ILs toxicity in past few years and found out it was not negligible. Some studies show that the ILs with nonaromatic rings (such as pyrrolidinium) are less toxic than those with aromatic cations (such as imidazolium) and the toxicity increases with the rise in number of ring members.²² Their results also show that the toxicity of the ILs increases when the length of alkyl chain increases.²³ However, ionic liquids are definitely still less toxic than the volatile organic compounds, so the replacement of this solvents by ILs is a great solution to the environmental pollution.²⁴ In accordance with the aforementioned, three ionic liquids with nonaromatic pyrrolidinium cation and one with aromatic imidazolium cation, but with shorter alkyl chain, are chosen to be examined in this paper.

Density and the derived volumetric properties at various conditions of temperature and pressure are of highest importance for the numerous industrial processes as well as for theoretical calculations such as equations of state development. These data

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are also essential in the ionic liquids design in order to get the most suitable compound for a particular purpose.^{9,25–27}

There is some information about the ionic liquids properties at atmospheric pressure, but density data at high pressures are rather scarce. It is possible to find information about certain ILs based on bis(trifluoromethylsulfonyl)imide ([NTf₂][−]) or dimethylphosphate ([DMP][−]) anions with different cations, but information about ILs based on bis(fluorosulfonyl)imide ([Nf₂][−]) anion are very deficient and that is one of the reasons for their study in this work.^{28–31}

The densities of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([E³Mim][Nf₂]), *n*-propyl-*n*-methylpyrrolidinium bis(fluorosulfonyl)imide ([PMpyr][Nf₂]), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ([BMpyr][Nf₂]), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMpyr][NTf₂]) were measured at moderate temperatures (293.15–413.15) K and high pressures (0.1 to 60) MPa and presented in this paper. Further, the density data were modeled using the Tammann–Tait equation which enabled the calculation of the isothermal compressibility (κ_T), the isobaric thermal expansivity (α_p), the internal pressure (p_{int}), and the difference between specific heat capacities at constant pressure (c_p) and at constant volume (c_v). The influence of the corresponding cations and anions on the ILs behavior was also analyzed.

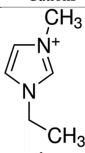
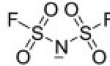
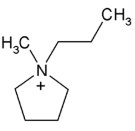
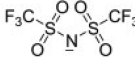
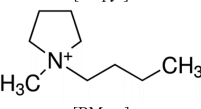
There are only three papers in the literature reporting high pressure densities for [BMpyr][NTf₂] which were compared to the experimental data in this work.^{9,32,33} As far as the authors know, the density and the derived volumetric properties data for the examined ionic liquids containing [Nf₂][−] anion have not been published before, and even their properties at atmospheric pressure were barely measured.^{34,35}

2. EXPERIMENTAL SECTION

2.1. Materials. The ionic liquids containing [Nf₂][−] anion were supplied by Solvionic, while [BMpyr][NTf₂] was provided by Iolitec. All used chemicals were of high purity, >0.99 mass fraction. Prior to use, all ionic liquids were dried by stirring under vacuum ($p = 0.2$ Pa) and heating at moderate temperatures (343.15 to 353.15) K for at least 48 h, in order to remove water and volatile compounds that could be present. The ILs were kept in bottles under argon gas, in a glovebox. To confirm their purity, densities measured at 293.15 K under atmospheric pressure were compared to corresponding literature data (Table 1), and structural formulas of cations and anions present in studied ionic liquids are given in Table 2.

2.2. Apparatus. The densities (ρ) at moderate temperatures and high pressures were measured using a DMA HP measuring cell produced by Anton Paar. This device does not have its own screen so it had to be coupled with a DMA 5000 densimeter, for temperature setting and results reading.²⁶ The measured data were automatically recorded on PC by means of APSofPrint software every 15 s. The temperature (T) at which

Table 2. Chemical Structures of Cations and Anions Present in the Examined Ionic Liquids

Chemical Structures	
Cations	Anions
 [E ³ Mim]	 [Nf ₂]
 [PMpyr]	 [NTf ₂]
 [BMpyr]	

density was determined was controlled by Peltier thermostat integrated in DMA HP, and the expanded uncertainty with a level of confidence of 95%, coverage factor $k = 2$, for the temperature was estimated to $U(T) = 0.01$ K. High pressures (p) were achieved with pressure generator from High Pressure Equipment Co., model no. 50-6-15, where acetone was selected as pressurizing fluid. The pressures were measured with pressure transducer WIKA S-10, and the estimated expanded uncertainty with confidence level of 95% ($k = 2$) for pressure was $U(p) = 0.05$ MPa. The detailed description of the used apparatus can be found in our previous paper.²⁶

The operating principle of the DMA HP densimeter is based on an oscillating U tube so it does not directly give the densities of the inserted compound but oscillation period of the measuring cell fulfilled with the sample. To determine densities from the measured periods it was necessary to calibrate the device so the classical calibration method proposed by Lagourette et al.³⁷ and improved by Comuñas et al.³⁸ was applied.²⁶

Since the viscosity of the sample can affect density measurements its influence was examined. The viscosity data presented in the literature for studied ionic liquids^{34,39–41} were included in an empirical equation proposed by Anton Paar for the DMA HP device, and it was estimated that density correction due to viscosity was lower than $0.4 \text{ kg}\cdot\text{m}^{-3}$.

The uncertainties of the measured temperature and pressure, as well as of the oscillation period and reference fluids densities, were considered together with calibration equations,^{26,42} and the damping effect on the vibrating tube and the expanded combined uncertainty of measured density with confidence level of 95% ($k = 2$) was estimated to be $U(\rho) = 0.9 \text{ kg}\cdot\text{m}^{-3}$ at temperatures (293.15–363.15) K and $U(\rho) = 2.1 \text{ kg}\cdot\text{m}^{-3}$ at 373.15 K and higher temperatures.

Table 1. Comparison of Measured Pure Component Densities with Literature Values at $T = 293.15$ K under Atmospheric Pressure

compound	supplier	CAS	purity mass fraction	$\rho/\text{kg}\cdot\text{m}^{-3}$		purification method
				exp	lit.	
[E ³ Mim][Nf ₂]	Solvionic	235789-75-0	>0.999	1446.4	1446.2 ³⁴	dried
[PMpyr][Nf ₂]	Solvionic	852620-97-4	>0.999	1342.9	1342.1 ³⁴	dried
[BMpyr][Nf ₂]	Solvionic	1057745-51-3	>0.999	1310.6	1310.79 ³⁵	dried
[BMpyr][NTf ₂]	Iolitec	223437-11-4	>0.990	1399.6	1399.00 ³⁶	dried

Table 3. Densities of [E³Mim][Nf₂], [PMpyr][Nf₂], [BMpyr][Nf₂], and [BMpyr][NTf₂] at Moderate Temperatures and High Pressures

p^c/MPa	$\rho^a/\text{kg}\cdot\text{m}^{-3}$										
	T^b/K										
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	393.15	413.15
[E ³ Mim][Nf ₂]											
0.1	1446.4	1437.2	1428.0	1419.0	1410.0	1401.1	1392.3	1383.6	1374.5	1357.5	1341.1
1	1446.9	1437.7	1428.6	1419.6	1410.6	1401.7	1392.9	1384.3	1375.5	1358.5	1341.8
5	1449.3	1440.1	1431.0	1422.1	1413.2	1404.4	1395.7	1387.0	1378.3	1361.5	1345.0
10	1452.1	1443.0	1434.0	1425.2	1416.4	1407.6	1399.0	1390.5	1381.9	1365.3	1348.9
15	1454.9	1445.9	1437.0	1428.2	1419.5	1410.8	1402.3	1393.8	1385.3	1368.9	1352.8
20	1457.7	1448.8	1439.9	1431.2	1422.6	1414.0	1405.5	1397.1	1388.7	1372.5	1356.5
25	1460.4	1451.6	1442.8	1434.2	1425.6	1417.1	1408.7	1400.4	1392.0	1376.0	1360.2
30	1463.1	1454.3	1445.6	1437.1	1428.6	1420.1	1411.8	1403.6	1395.3	1379.4	1363.8
35	1465.8	1457.1	1448.4	1439.9	1431.5	1423.1	1414.9	1406.7	1398.5	1382.8	1367.3
40	1468.4	1459.8	1451.2	1442.7	1434.4	1426.1	1417.9	1409.8	1401.7	1386.1	1370.8
45	1471.0	1462.4	1453.9	1445.5	1437.2	1429.0	1420.9	1412.8	1404.8	1389.3	1374.2
50	1473.6	1465.0	1456.5	1448.2	1440.0	1431.8	1423.8	1415.8	1407.8	1392.5	1377.5
55	1476.1	1467.6	1459.2	1450.9	1442.7	1434.6	1426.6	1418.7	1410.8	1395.6	1380.7
60	1478.6	1470.1	1461.7	1453.5	1445.4	1437.3	1429.4	1421.6	1413.7	1398.7	1383.9
[PMpyr][Nf ₂]											
0.1	1342.9	1334.8	1326.8	1318.9	1311.0	1303.3	1295.6	1288.0	1279.9	1265.2	1250.9
1	1343.4	1335.3	1327.3	1319.4	1311.6	1303.8	1296.2	1288.6	1280.9	1266.1	1251.6
5	1345.5	1337.5	1329.5	1321.7	1313.9	1306.2	1298.6	1291.1	1283.5	1268.9	1254.5
10	1348.1	1340.2	1332.3	1324.5	1316.8	1309.2	1301.7	1294.2	1286.8	1272.3	1258.0
15	1350.7	1342.8	1335.0	1327.3	1319.7	1312.1	1304.7	1297.3	1289.9	1275.6	1261.5
20	1353.2	1345.4	1337.7	1330.0	1322.5	1315.0	1307.6	1300.3	1293.0	1278.9	1264.9
25	1355.7	1348.0	1340.3	1332.7	1325.2	1317.8	1310.5	1303.3	1296.1	1282.0	1268.3
30	1358.2	1350.5	1342.9	1335.4	1327.9	1320.6	1313.3	1306.2	1299.0	1285.1	1271.5
35	1360.6	1353.0	1345.4	1338.0	1330.6	1323.3	1316.1	1309.1	1301.9	1288.2	1274.7
40	1363.0	1355.4	1347.9	1340.5	1333.2	1326.0	1318.9	1311.8	1304.8	1291.2	1277.8
45	1365.4	1357.8	1350.4	1343.0	1335.8	1328.6	1321.6	1314.6	1307.5	1294.1	1280.8
50	1367.7	1360.2	1352.8	1345.5	1338.3	1331.2	1324.2	1317.3	1310.3	1296.9	1283.7
55	1370.0	1362.5	1355.2	1347.9	1340.8	1333.7	1326.8	1319.9	1312.9	1299.6	1286.6
60	1372.2	1364.8	1357.5	1350.3	1343.2	1336.2	1329.3	1322.5	1315.5	1302.3	1289.3
[BMpyr][Nf ₂]											
0.1	1310.6	1302.7	1294.8	1287.1	1279.4	1271.8	1264.2	1256.8	1248.9	1234.3	1220.3
1	1311.1	1303.2	1295.3	1287.6	1279.9	1272.3	1264.8	1257.3	1249.8	1235.2	1220.9
5	1313.2	1305.3	1297.6	1289.9	1282.3	1274.7	1267.3	1259.9	1252.5	1238.0	1223.9
10	1315.8	1308.0	1300.3	1292.7	1285.2	1277.7	1270.3	1263.0	1255.7	1241.4	1227.4
15	1318.4	1310.7	1303.0	1295.5	1288.0	1280.6	1273.3	1266.1	1258.8	1244.7	1230.9
20	1320.9	1313.3	1305.7	1298.2	1290.8	1283.5	1276.3	1269.1	1261.9	1248.0	1234.4
25	1323.4	1315.8	1308.3	1300.9	1293.6	1286.3	1279.2	1272.1	1265.0	1251.2	1237.7
30	1325.9	1318.3	1310.9	1303.6	1296.3	1289.1	1282.0	1275.0	1268.0	1254.3	1241.0
35	1328.3	1320.8	1313.4	1306.2	1298.9	1291.8	1284.8	1277.9	1270.9	1257.4	1244.2
40	1330.7	1323.3	1315.9	1308.7	1301.5	1294.5	1287.5	1280.6	1273.7	1260.4	1247.3
45	1333.0	1325.7	1318.4	1311.2	1304.1	1297.1	1290.2	1283.4	1276.5	1263.3	1250.4
50	1335.3	1328.0	1320.8	1313.7	1306.6	1299.7	1292.8	1286.1	1279.3	1266.2	1253.4
55	1337.6	1330.3	1323.1	1316.1	1309.1	1302.2	1295.4	1288.7	1282.0	1269.0	1256.3
60	1339.9	1332.6	1325.5	1318.4	1311.5	1304.7	1297.9	1291.2	1284.6	1271.7	1259.1
[BMpyr][NTf ₂]											
0.1	1399.6	1390.5	1381.6	1372.7	1363.9	1355.3	1346.6	1338.0	1329.0	1312.3	1295.9
1	1400.2	1391.2	1382.3	1373.4	1364.7	1356.0	1347.4	1338.8	1330.2	1313.5	1296.9
5	1403.0	1394.1	1385.3	1376.6	1367.9	1359.3	1350.8	1342.3	1333.8	1317.3	1300.9
10	1406.5	1397.7	1389.0	1380.4	1371.8	1363.3	1354.9	1346.6	1338.2	1321.9	1305.9
15	1410.0	1401.2	1392.6	1384.1	1375.6	1367.3	1359.0	1350.7	1342.5	1326.4	1310.7
20	1413.3	1404.7	1396.1	1387.7	1379.3	1371.1	1362.9	1354.8	1346.7	1330.8	1315.3
25	1416.6	1408.0	1399.6	1391.3	1383.0	1374.9	1366.8	1358.7	1350.7	1335.1	1319.8
30	1419.8	1411.3	1402.9	1394.7	1386.6	1378.5	1370.5	1362.6	1354.7	1339.3	1324.2
35	1423.0	1414.5	1406.3	1398.1	1390.0	1382.1	1374.2	1366.3	1358.5	1343.3	1328.5
40	1426.0	1417.7	1409.5	1401.4	1393.4	1385.5	1377.7	1370.0	1362.2	1347.3	1332.6
45	1429.1	1420.8	1412.6	1404.6	1396.7	1388.9	1381.2	1373.5	1365.9	1351.1	1336.6

Table 3. continued

p^c/MPa	$\rho^a/\text{kg}\cdot\text{m}^{-3}$										
	T^b/K										
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	393.15	413.15
	[BMpyr][NTf ₂]										
50	1432.0	1423.8	1415.7	1407.8	1399.9	1392.2	1384.6	1377.0	1369.4	1354.7	1340.4
55	1434.9	1426.7	1418.7	1410.8	1403.1	1395.4	1387.9	1380.3	1372.8	1358.3	1344.1
60	1437.7	1429.6	1421.6	1413.8	1406.1	1398.5	1391.0	1383.6	1376.1	1361.7	1347.7

$^a U(\rho) = 0.9 \text{ kg}\cdot\text{m}^{-3}$ ($293.15 \text{ K} \leq T \leq 363.15 \text{ K}$) and $2.1 \text{ kg}\cdot\text{m}^{-3}$ ($373.15 \text{ K} \leq T \leq 413.15 \text{ K}$), (0.95 level of confidence). $^b U(T) = 0.01 \text{ K}$, (0.95 level of confidence). $^c U(p) = 0.05 \text{ MPa}$, (0.95 level of confidence).

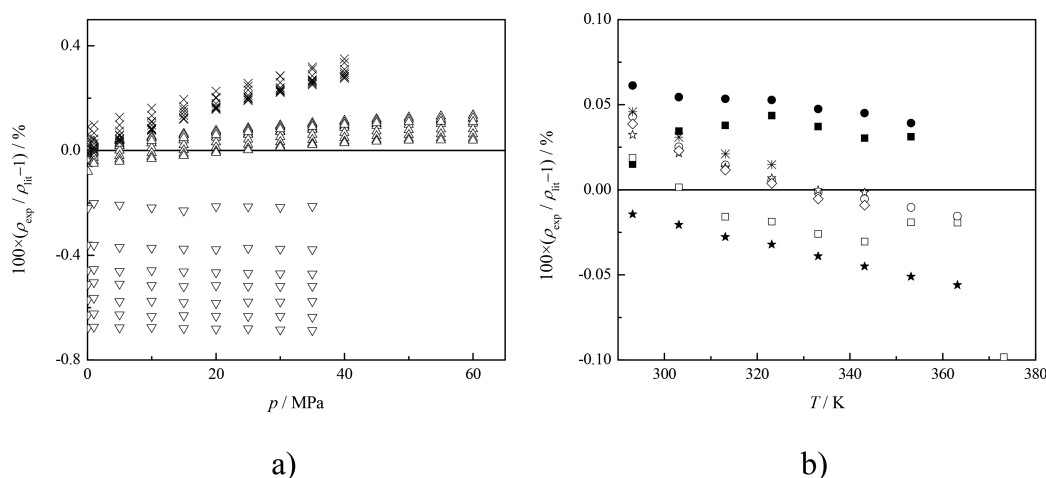


Figure 1. Comparison of the experimental densities (ρ_{exp}) with literature values (ρ_{lit}): (a) for [BMpyr][NTf₂] as a function of pressure (p) at various temperatures and (b) for all studied ILs as a function of temperature (T) at atmospheric pressure. The comparison was done for (a) [BMpyr][NTf₂] with (Δ) Regueira et al.³¹ at (293.15–393.15) K, (\times) Jacquemin et al.³³ at (293.15–413.15) K, and (∇) Gardas et al.⁹ at (293.15–393.15) K, and (b) [E³Mim][Nf₂] with (\blacksquare) Seki et al.³⁴ [PMpyr][Nf₂] with (\bullet) Seki et al.³⁴ [BMpyr][Nf₂] with (\star) Makino et al.³⁵ and for [BMpyr][NTf₂] with (\square) Gaciño et al.⁴³ (\circ) Harris and Woolf,⁴³ (\star) Seoane et al.,⁸ (\diamond) Pereiro et al.⁴¹ and ($*$) Geppert-Rybczyńska et al.⁴⁵

3. RESULTS AND DISCUSSION

3.1. Density Measurements. Densities of four ionic liquids (Table 2) were measured at temperatures (293.15–413.15) K and pressures (0.1–60) MPa and the obtained results are presented in Table 3 (Figure S1).

Literature data for high pressure densities were found only for [BMpyr][NTf₂] and they were compared with the experimental values showing good agreement (Figure 1a). Regueira et al.³² reported [BMpyr][NTf₂] density data as well as the parameters of the modified Tammann–Tait equation chosen for density modeling and the values calculated applying these parameters were compared to our measured densities in the temperature interval (293.15–393.15) K and at pressures up to 60 MPa. The agreement between these two data sets was excellent with an average absolute percentage deviation (AAD/% = $100/N \cdot \sum_{i=1}^N |\rho_i^{\text{exp}}/\rho_i^{\text{lit}} - 1|$) of 0.06% (about 0.8 kg·m^{−3}). The same procedure was used for the comparison of our results with those of Jacquemin et al.³³ at wide range of temperature (293.15–413.15) K and pressures up to 40 MPa and good agreement with AAD = 0.16% (about 2.2 kg·m^{−3}) was observed. On the other hand, data presented by Gardas et al.⁹ deviate a bit more from our densities at temperatures (293.15–393.15) K and pressures up to 35 MPa so AAD was 0.49% (about 6.8 kg·m^{−3}).

The density comparison with literature data for studied ionic liquids containing bis(fluorosulfonyl)imide anion was possible only at atmospheric pressure (Figure 1b). Seki et al.³⁴ reported densities of [E³Mim][Nf₂] and [PMpyr][Nf₂] to which our experimental results were compared at temperatures (293.15–353.15) K,

and they concurred with AADs of 0.03% (about 0.5 kg·m^{−3}) and 0.05% (about 0.7 kg·m^{−3}), respectively. Density data measured for [BMpyr][Nf₂] were compared with results of Makino et al.³⁵ and very good agreement with AAD = 0.04% (about 0.5 kg·m^{−3}) was achieved.

Papers reporting densities of [BMpyr][NTf₂] at atmospheric pressure are somewhat more numerous.^{8,36,39–41,43–45} Experimental results for [BMpyr][NTf₂] agreed very well with those of Gaciño et al.⁴³ at temperatures (293.15–373.15) K showing an AAD of 0.03% (about 0.4 kg·m^{−3}) (Figure 1b). The measured densities deviate poorly from the values presented by Harris and Woolf⁴⁴ at temperatures (293.15–363.15) K, the AAD was 0.02% (about 0.2 kg·m^{−3}) (Figure 1b). Seoane et al.⁸ and Pereiro et al.⁴¹ reported [BMpyr][NTf₂] densities which are very similar to our results in the temperature interval (293.15–343.15) K with AADs of 0.01% (about 0.2 kg·m^{−3}) and 0.02% (about 0.2 kg·m^{−3}), respectively (Figure 1b). The comparison of experimentally determined densities with those of Geppert-Rybczyńska et al.⁴⁵ was conducted at slightly narrower temperature range (293.15–323.15) K also giving good result, AAD = 0.03% (about 0.4 kg·m^{−3}) (Figure 1b).

The excellent agreement of measured densities with literature data^{8,34,35,41,43–45} for all four studied ionic liquids at atmospheric pressure (Figure 1b), with values of average absolute percentage deviation within reported uncertainty for density measurements, as well as good results obtained in the comparison of high pressure densities with literature^{9,32,33} for [BMpyr][NTf₂] (Figure 1a), confirm the accuracy of the measurement and

calibration procedures and the reliability of the obtained data (Table 3).

Density dependence on temperature and pressure for all studied ionic liquids is presented in Figure S1 in the Supporting Information to the paper, and densities obtained at boundary values of the examined temperature interval are shown in Figure 2. The measured densities decrease when temperature

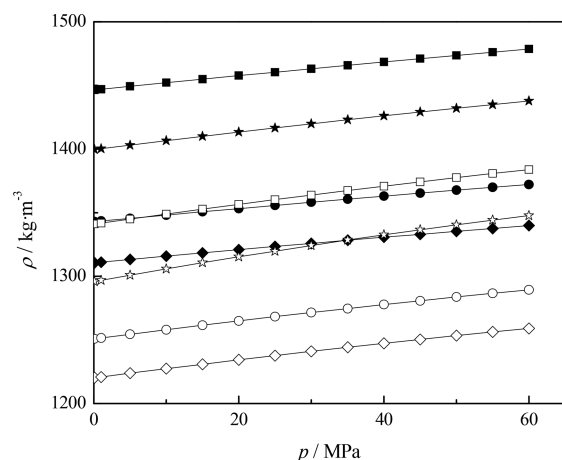


Figure 2. Densities (ρ) as a function of pressure (p) of (■,□) [E³Mim][Nf₂], (●,○) [PMpyr][Nf₂], (◆,◇) [BMpyr][Nf₂] and (★,☆) [BMpyr][NTf₂] at 293.15 K (full symbols) and 413.15 K (empty symbols). Lines are guides for eyes.

increases at constant pressure and rise with increase in pressure along isotherms, as expected (Figure 2 and Figure S1). The small slope of the isotherms on Figure 2 implies that temperature affects density to a greater extent than pressure.³³

The densities of the ionic liquids with the same anion, but different cations, show that [E³Mim][Nf₂] is significantly denser than [PMpyr][Nf₂] and [BMpyr][Nf₂] (Figure 2). This fact can be explained by the presence of stronger bonds between cation and anion within [E³Mim][Nf₂] due to the higher polarity and stability of [E³Mim]⁺ compared to [PMpyr]⁺ and [BMpyr]⁺ cations as a result of the resonance structures of the aromatic ring of imidazole as well as of its planar configuration which allows denser packaging (Table 2).^{32,46,47} In the case of the [E³Mim]⁺ cation, two short alkyl chains, methyl and ethyl, are bonded to an imidazole ring at different places, while in [PMpyr]⁺ and [BMpyr]⁺ cations methyl group and a bit longer propyl and butyl chains, respectively, are linked to the same nitrogen atom of pyrrolidine (Table 2). The alkyl chains can obstruct the access of anion to cation, especially when they are on the same atom, which could weaken ionic bonds leading to poorer packaging of [PMpyr][Nf₂] and [BMpyr][Nf₂] and, therefore, lower densities in comparison to [E³Mim][Nf₂]. In support of that, [PMpyr][Nf₂] is denser than [BMpyr][Nf₂] confirming that the density decreases as the length of the alkyl chain rises, due to dispersive interactions, as well as higher steric hindrance.^{9,32,33,46–49} Further, the influence of the different anion on the properties of ionic liquids can be observed for [BMpyr][Nf₂] and [BMpyr][NTf₂]. It is evident that the ionic liquid containing the [NTf₂][−] cation is denser than that one with the same cation but [Nf₂][−] anion (Figure 2) due to the greater stability of the [NTf₂][−] anion which provides stronger ionic bonding.^{43,47,50,51}

As compared to other common organic solvents, such as alkanes, alcohols, aromatic hydrocarbons, etc. studied in our

previous papers^{26,52,53} ionic liquids have significantly higher densities thanks to their strong Coulombic interionic interactions.^{9,54}

3.2. Density Modeling. The measured high pressure densities of examined ionic liquids at temperatures (293.15–413.15) K and pressures up to 60 MPa were fitted to the modified Tammann–Tait equation:⁵⁵

$$\rho(T, p) = \frac{\rho^{\text{ref}}(T)}{1 - C \ln \left(\frac{B(T) + p}{B(T) + p^{\text{ref}}} \right)} \quad (1)$$

where ρ^{ref} denotes density of the sample at reference pressure (p^{ref}) and it depends on temperature as follows:

$$\rho^{\text{ref}}(T) = \sum_{i=0}^2 a_i T^i \quad (2)$$

parameter $B(T)$ also depends on temperature:

$$B(T) = \sum_{i=0}^2 b_i T^i \quad (3)$$

while C is the temperature independent parameter. a_i , b_i , and C in eqs 1–3 are adjustable parameters.

The first step of density modeling was the optimization of a_i parameters from eq 2 using densities measured at atmospheric pressure which was chosen as p^{ref} . After that, parameters b_i and C were determined from the rest of the density data, at pressures higher than 0.1 MPa, using eq 1 with incorporated optimized parameters a_i . The quality criteria for optimization procedure were the absolute average percentage deviation (AAD), the percentage maximum deviation (MD), the average percentage deviation (Bias), and the standard deviation (σ).^{27,38}

$$\text{AAD} = \frac{100}{N} \sum_{i=1}^N \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \quad (4)$$

$$\text{MD} = \max \left(100 \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \right), \quad i = 1, N \quad (5)$$

$$\text{Bias} = \frac{100}{N} \sum_{i=1}^N \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \quad (6)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2}{N - m}} \quad (7)$$

where, ρ^{exp} and ρ^{cal} refer to the experimentally determined density and the calculated value using the eq 1, respectively, N is the number of experimental data while m represents the number of the optimized parameters of the modified Tammann–Tait equation. Standard deviation, eq 7, was chosen for the objective function that had to be minimized during the parameters optimization.

The results of the high pressure modeling are presented in Table 4.

The average absolute percentage deviations between the experimentally determined densities and values calculated from eq 1 using parameters presented in Table 4 were 0.003% (about 0.04 kg·m^{−3}) for [E³Mim][Nf₂] and [BMpyr][Nf₂] while for [PMpyr][Nf₂] and [BMpyr][NTf₂] AADs were 0.004% (about 0.05 kg·m^{−3}). The excellent agreement of the calculated densities

Table 4. Parameters of the Modified Tammann–Tait Equation

	[E ³ min][Nf ₂]	[PMpyr][Nf ₂]	[BMPyr][Nf ₂]	[BMPyr][NTf ₂]
$a_0/\text{kg}\cdot\text{m}^{-3}$	1753.72	1613.76	1573.58	1692.53
$a_1/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	−1.1677	−1.0339	−0.9982	−1.0948
$a_2/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-2}$	4.0802×10^{-4}	3.7561×10^{-4}	3.4522×10^{-4}	3.2554×10^{-4}
b_0/MPa	572.051	527.343	508.851	409.806
$b_1/\text{MPa}\cdot\text{K}^{-1}$	−1.4765	−1.3550	−1.2503	−1.0856
$b_2/\text{MPa}\cdot\text{K}^{-2}$	1.1458×10^{-3}	1.0627×10^{-3}	0.9020×10^{-3}	0.8353×10^{-3}
C	9.6523×10^{-2}	8.9031×10^{-2}	9.0566×10^{-2}	8.4834×10^{-2}
AAD/%	0.003	0.004	0.003	0.004
MD/%	0.024	0.025	0.025	0.026
Bias/%	0.0003	0.001	0.0001	0.0004
$\sigma/\text{kg}\cdot\text{m}^{-3}$	0.063	0.073	0.060	0.070

with measured ones verifies the suitability of the modeling procedure and the accuracy of the obtained parameters.

3.3. Derived Properties. One of the advantages of knowing the density of a substance is the possibility of determining several derived volumetric properties from density data. The isothermal compressibility (κ_T), the isobaric thermal expansivity (α_p), the internal pressure (p_{int}), and the difference between specific heat capacities at constant pressure and at constant volume ($c_p - c_v$) were calculated for the studied ionic liquids at temperatures (293.15–413.15) K and pressures (0.1–60) MPa using the following equations.

The isothermal compressibility shows how the change of pressure affects density at constant temperature:^{27,56}

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (8)$$

Density data fitting to the modified Tammann–Tait equation enables its differentiation with respect to pressure which leads to calculation of κ_T :²⁷

$$\kappa_T = \frac{C}{(B(T) + p) \left(1 - C \ln \frac{B(T) + p}{B(T) + p^{\text{ref}}} \right)} \quad (9)$$

The isobaric thermal expansivity demonstrates the influence of temperature change on density at constant pressure:^{27,56}

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (10)$$

Integrating the eq 1 into eq 10 gives²⁷

$$\alpha_p = \frac{-\rho^{\text{ref}}(T)}{\rho^{\text{ref}}(T)} - \frac{C \frac{B'(T)(p^{\text{ref}} - p)}{(B(T) + p)(B(T) + p^{\text{ref}})}}{\left(1 - C \ln \frac{B(T) + p}{B(T) + p^{\text{ref}}} \right)} \quad (11)$$

where $\rho^{\text{ref}}(T)$ and $B'(T)$ stand for the derivatives with respect to T of the ρ^{ref} and $B(T)$ of eqs 2 and 3, respectively.²⁷

The thermal pressure coefficient (γ) is calculated as the ratio of the isobaric thermal expansivity and the isothermal compressibility:^{27,56}

$$\gamma = \frac{\alpha_p}{\kappa_T} \quad (12)$$

The internal pressure is very important property in terms of the study of the intermolecular interactions and it represents the change of the internal energy under isothermal change of the volume of the sample:^{27,56}

$$p_{\text{int}} = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_p - p = T\gamma - p = \frac{T\alpha_p}{\kappa_T} - p \quad (13)$$

where U is an internal energy and V denotes volume of the sample.

One more property that can be derived from density data is the difference between the specific heat capacity at constant pressure (c_p) and the specific heat capacity at constant volume (c_v):^{27,56}

$$c_p = c_v + T \frac{\left(\frac{\partial p}{\partial T} \right)_p^2}{\rho^2 \left(\frac{\partial \rho}{\partial p} \right)_T} \quad (14)$$

The measurement of isobaric heat capacity is significantly easier to perform than for isochoric one so the knowledge of the presented difference enables calculation of the heat capacity at constant volume from the isobaric heat capacity data.

The combining of eqs 8 and 10 with eq 14 leads to the term:^{27,56}

$$c_p - c_v = \frac{\alpha_p^2 T}{\rho \kappa_T} \quad (15)$$

The calculated values for the isothermal compressibility, the isobaric thermal expansivity, the internal pressure, and the difference between specific heat capacities at constant pressure and at constant volume for the examined ionic liquids in the temperature interval (293.15–413.15) K and at pressures (0.1–60) MPa are given in the Supporting Information to this paper (Tables S1–S4).

Literature data of the isothermal compressibility and the isobaric thermal expansivity at high pressures were found only for [BMPyr][NTf₂].^{9,32,33} The κ_T and α_p values obtained in this work (Table S4) agree very well with those calculated using the modified Tammann–Tait equation with its parameters determined by Regueira et al.³² at temperatures (293.15–413.15) K and pressures up to 60 MPa, AAD for κ_T was 3.5% (about 0.02 GPa^{-1}) and that for α_p was 3.5% (about $0.02 \times 10^{-3} \text{ K}^{-1}$). The values presented here deviate somewhat more from the κ_T calculated using the parameters given by Jacquemin et al.³³ at (293.15–413.15) K and pressures (0.1–40) MPa with AAD = 14.9% (about 0.07 GPa^{-1}) while the deviations of the isobaric thermal expansivities are quite low, the AAD was 2.5% (about $0.02 \times 10^{-3} \text{ K}^{-1}$). The comparison of the presented results with data of Gardas et al.⁹ gave opposite results to the one with the data of Jacquemin et al.³³ The agreement of our isothermal

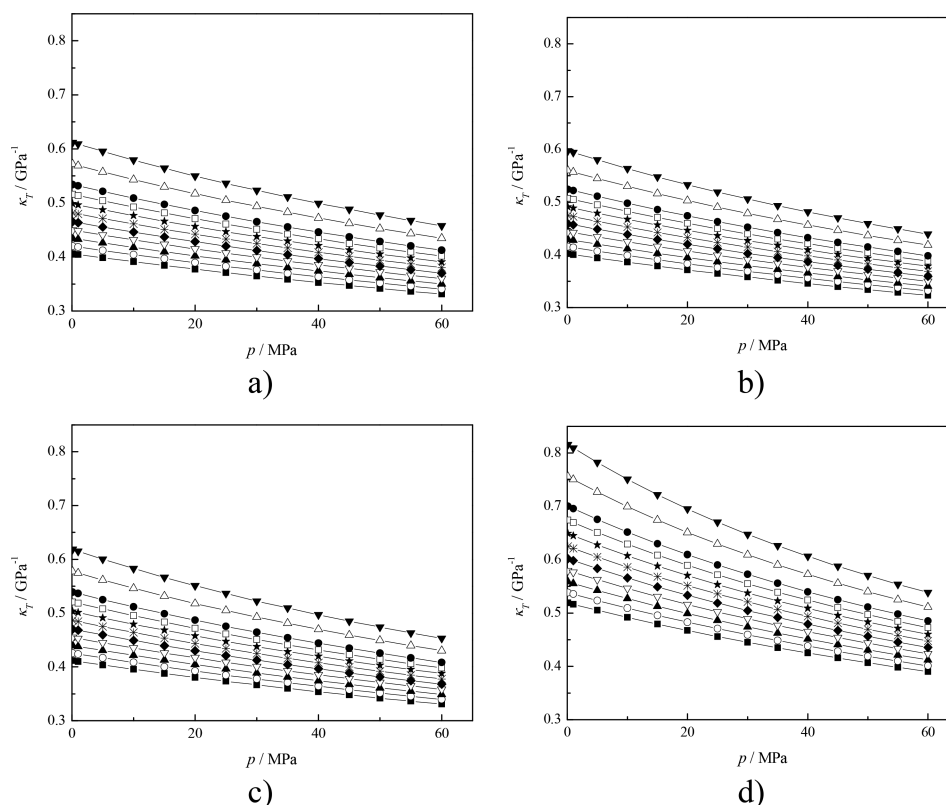


Figure 3. Isothermal compressibilities (κ_T) as a function of pressure (p) of: a) $[\text{E}^3\text{Mim}][\text{Nf}_2]$, b) $[\text{PMpyr}][\text{Nf}_2]$, c) $[\text{BMpyr}][\text{Nf}_2]$ and d) $[\text{BMpyr}][\text{NTf}_2]$ at \blacksquare 293.15 K, \circ 303.15 K, \blacktriangle 313.15 K, ∇ 323.15 K, \blacklozenge 333.15 K, $*$ 343.15 K, \star 353.15 K, \square 363.15 K, \bullet 373.15 K, \triangle 393.15 K and \blacktriangledown 413.15 K. Lines are guides for eyes.

compressibilities with those of Gardas et al.⁹ at (293.15–393.15) K and pressures up to 35 MPa was perfect, AAD = 0.95% (about 0.006 GPa^{-1}), and for α_p it was a little poorer with AAD of 7.1% (about $0.05 \times 10^{-3} \text{ K}^{-1}$). Good agreement of the obtained isothermal compressibilities and isobaric thermal expansivities with literature data, as well as low comparison criteria obtained in density modeling (Table 4), approve the modified Tammann–Tait equation use and the accuracy of the calculated derived properties.

The isothermal compressibility of all examined ionic liquids decreases with temperature drop at constant pressure, and that is more noticeable at atmospheric than at higher pressures (Tables S1–S4, Figure 3). When pressure increases κ_T decreases along isotherms, especially at higher ones, and the declines are the biggest for $[\text{BMpyr}][\text{NTf}_2]$, while for the other studied ionic liquids they are quite similar (Figure 3).

The observation of κ_T of the ionic liquids with the same anion and similar cations, $[\text{PMpyr}][\text{Nf}_2]$ and $[\text{BMpyr}][\text{Nf}_2]$, results in a conclusion that ionic liquids with longer alkyl chains, $[\text{BMpyr}][\text{Nf}_2]$, are more compressible due to a bigger cation and more unoccupied space in a molecule.^{32,49,51,56} Considering the length of alkyl chain it could be expected that $[\text{E}^3\text{Mim}][\text{Nf}_2]$ has lower compressibility than $[\text{PMpyr}][\text{Nf}_2]$ and $[\text{BMpyr}][\text{Nf}_2]$, but actually its compressibility is higher than that of $[\text{PMpyr}][\text{Nf}_2]$ and very similar to that of $[\text{BMpyr}][\text{Nf}_2]$. The reason for this could be explained by the cation base of $[\text{E}^3\text{Mim}][\text{Nf}_2]$. The imidazole ring, due to its double bonds, is shorter than the single bonds of pyrrolidine; it has smaller diameter leaving more room for compression (Table 2).^{32,47,49,57} $[\text{BMpyr}][\text{NTf}_2]$ has the largest isothermal compressibilities among measured samples possibly because of the bigger anion.

The $[\text{NTf}_2]^-$ anion has a more branched structure than $[\text{Nf}_2]^-$ and conformational flexibility and, hence, occupies more space which gives it greater potential for compression.^{32,49,58,59}

The isobaric thermal expansivity rises with temperature drop along isobars and decreases when pressure increases at constant temperature (Tables S1–S4, Figure 4). This is not characteristic behavior of this property noticed for molecular liquids but it is common for ionic liquids.⁵⁴ Gardas et al.⁹ also reported $\frac{\partial \alpha_p}{\partial T} < 0$. In the paper of Jacquemin et al.³³ that ratio is positive while α_p of Regueira et al.³² decreases when temperature rises up to 343.15 K at constant pressure, and at higher temperatures it is directly proportional to temperature. The isobaric thermal expansivity calculation is highly sensitive to density modeling and parameters optimization, much more than the isothermal compressibility, so that could be the reason for the mentioned differences in its dependence on temperature.

The expansivity variation due to the change in pressure is the largest for $[\text{BMpyr}][\text{NTf}_2]$, and also it has the greatest values of α_p among examined ionic liquids. Comparison of the isobaric thermal expansivities between studied samples shows similar relations to those between isothermal compressibilities. Ionic liquids containing $[\text{NTf}_2]^-$ anion are more expansible than those with $[\text{Nf}_2]^-$ and a longer alkyl chain in cation leads to higher isobaric thermal expansivity probably because of greater molecule volume.^{49,51} In line with that, $[\text{BMpyr}][\text{Nf}_2]$ are more expansible than $[\text{PMpyr}][\text{Nf}_2]$ but $[\text{E}^3\text{Mim}][\text{Nf}_2]$ has α_p higher than both of them, very similar to that of $[\text{BMpyr}][\text{NTf}_2]$.

It can be concluded that the density change with temperature or pressure is rather small and the anion type has a greater influence on κ_T and α_p than the cation.⁵⁴ The length of alkyl

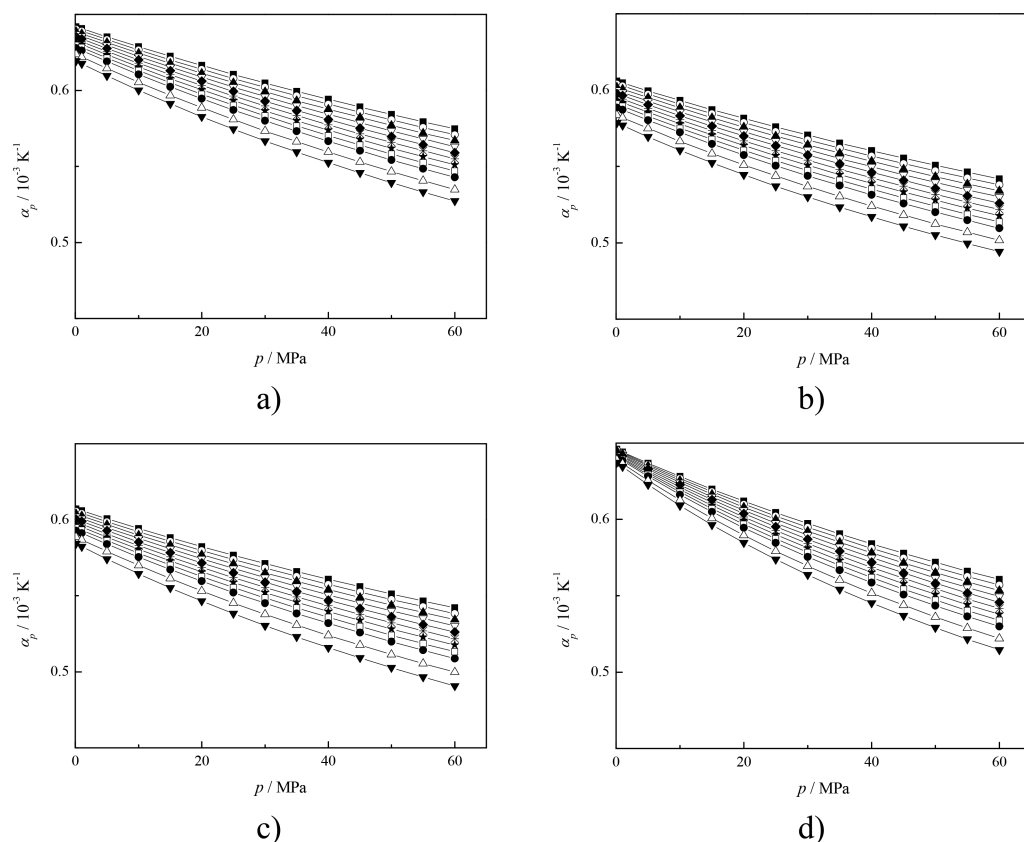


Figure 4. Isobaric thermal expansivities (α_p) as a function of pressure (p) of (a) $[\text{E}^3\text{Mim}][\text{Nf}_2]$, (b) $[\text{PMpyr}][\text{Nf}_2]$, (c) $[\text{BMpyr}][\text{Nf}_2]$, and (d) $[\text{BMpyr}][\text{NTf}_2]$ at \blacksquare 293.15 K, \circ 303.15 K, \blacktriangle 313.15 K, ∇ 323.15 K, \blacklozenge 333.15 K, $*$ 343.15 K, \star 353.15 K, \square 363.15 K, \bullet 373.15 K, \triangle 393.15 K and \blacktriangledown 413.15 K. Lines are guides for eyes.

chain in the cation is directly proportional to molecule volume and accordingly to expansivity and compressibility. Ionic liquids with the imidazole based cation are more compressible and expansible in comparison to those with pyrrolidinium cation. ILs containing $[\text{NTf}_2]^-$ have higher values of the isothermal compressibility and the isobaric thermal expansivity as compared to those with $[\text{Nf}_2]^-$ anion.^{32,47,49,51,57–59}

With regard to mechanical coefficients of conventional solvents, such as *n*-hexane, *n*-heptane, *n*-octane, ethanol, or toluene,^{27,52,53} the densities of ionic liquids are not so sensitive to changes in temperature and pressure, that is, ILs are less compressible and expansible due to the strong Coulombic interaction between their anion and cation.^{9,33,51,54,57}

One of the important volumetric properties calculated from density data is the internal pressure that could clarify the intermolecular interactions in the studied ionic liquids (Tables S1–S4).^{60,61} Obtained values of p_{int} show that the expansion of samples leads to increase in its internal energy possibly as a result of strong attractive forces between its particles. The internal pressure of the ionic liquids examined here decreases when temperature rises at constant pressure, and it also decreases with pressure increase along all studied isotherms for $[\text{E}^3\text{Mim}][\text{Nf}_2]$ and $[\text{BMpyr}][\text{Nf}_2]$ (Figure S2). p_{int} of $[\text{PMpyr}][\text{Nf}_2]$ shows the mentioned dependence on pressure change at temperatures up to 373.15 K and at higher isotherms it increases with pressure rise, while for $[\text{BMpyr}][\text{NTf}_2]$ the temperature of such behavior change is 413.15 K (Figure S2). $[\text{E}^3\text{Mim}][\text{Nf}_2]$ has the highest values of internal pressure among observed ionic liquids which could be the indicator of the strongest attractions between its molecules possibly because of the imidazole ring

planarity and small size that provides the closest packing of molecules.^{47,49} The comparison of ionic liquids with the same anion and cation base, $[\text{PMpyr}][\text{Nf}_2]$ and $[\text{BMpyr}][\text{Nf}_2]$, shows that ionic liquids with longer alkyl chain have lower p_{int} which could be the consequence of larger molecules and their poorer packing, as well as of steric hindrance.⁴⁹ Unlike previous properties, $[\text{BMpyr}][\text{NTf}_2]$ has the lowest values of p_{int} of all studied samples leading to the conclusion that the larger and more branched $[\text{NTf}_2]^-$ anion obstructs molecular contact which weakens intermolecular attractive forces.⁴⁹

The differences between the specific heat capacity at constant pressure (c_p) and the specific heat capacity at constant volume (c_v) for all measured ionic liquids decrease as temperature goes up at constant pressure and when pressure rises along isotherms (Tables S1–S4). The $c_p - c_v$ differences are the greatest for $[\text{E}^3\text{Mim}][\text{Nf}_2]$, and for $[\text{BMpyr}][\text{Nf}_2]$ they are higher than for $[\text{PMpyr}][\text{Nf}_2]$ at lower temperatures and pressures while the relation is opposite at higher pressures and higher temperatures. The differences between the isobaric and the isochoric specific heat capacities are by far the lowest for the studied ionic liquid containing the $[\text{NTf}_2]^-$ anion. The calculation of this property is of great importance in determination of the specific heat capacity at constant volume.

4. CONCLUSIONS

The densities of four ionic liquids, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide, *n*-propyl-*n*-methylpyrrolidinium bis(fluorosulfonyl)imide, 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide, and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide were determined at temperatures (293.15–413.15) K

and pressures up to 60 MPa. The measured densities were fitted to the modified Tammann–Tait equation which enabled calculation of the derived volumetric properties at the mentioned ranges of temperature and pressure.

As expected, densities decrease when temperature rises along isobars and increase with rise in pressure at constant temperature. The obtained density data lead to the conclusion that the longer is alkyl chain on the cation, the lower is the ionic liquid density due to dispersive interactions and steric hindrance. Ionic liquids with an imidazole based cation are denser than those with the pyrrolidinium cation. Additionally, ILs containing more stable $[\text{NTf}_2]^-$ anion have greater densities than those with $[\text{Nf}_2]^-$ anion.

Isothermal compressibilities of the studied ILs increase with temperature at constant pressure and decrease when pressure rises along isotherms. Opposite to density, when the alkyl chain of the cation enlarges the κ_T also increases possibly due to an increase in a molecule volume. Ionic liquids with an imidazolium cation are more compressible than those containing a pyrrolidine based cation. $[\text{BMpyr}][\text{NTf}_2]$ has the largest isothermal compressibilities among the examined compounds indicating that densities of the ILs with $[\text{NTf}_2]^-$ anion will change more than those with the $[\text{Nf}_2]^-$ anion as response to change in pressure, due to various conformations of $[\text{NTf}_2]^-$.

The isobaric thermal expansivity decreases with increase both in temperature and pressure. The relationship between a sample's expansivities is similar to the one between its compressibilities.

$[\text{E}^3\text{Mim}][\text{Nf}_2]$ has the highest of the calculated internal pressure values which could be the indicator of the strongest intermolecular attraction forces possibly because of the imidazole ring planarity that enables a closer approach of its molecules, while $[\text{BMpyr}][\text{NTf}_2]$ has the lowest values of p_{int} . The ILs with longer alkyl chain on the cation have lower p_{int} probably as result of the steric hindrance.

As compared to conventional organic solvents, ionic liquids have higher densities and lower mechanical coefficients. The fact that the densities of the ILs will not change significantly because of changes in temperature and pressure is very useful for their application and could be the result of the strong Columbic interactions within ionic liquids.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00771.

Diagrams of density (ρ) and internal pressures (p_{int}) as a function of temperature (T) and pressure (p) for all studied ionic liquids, as well as four tables with their derived properties (PDF)

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Notes

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■ REFERENCES

- (1) Kazemi, S.; Peters, C. J.; Kroon, M. C. Effect of Carbon Dioxide Addition on the Phase Behavior of Epoxidation Reaction Mixtures in Ionic Liquids. *J. Chem. Eng. Data* **2013**, *58*, 1597–1601.
- (2) Wasserscheid, P.; Keim, W. Ionic Liquids-New 'Solutions' for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.
- (3) Sowmiah, S.; Cheng, C. I.; Chu, Y. H. Ionic Liquids for Green Organic Synthesis. *Curr. Org. Synth.* **2012**, *9*, 74–95.
- (4) Florusse, L. J.; Raeissi, S.; Peters, C. J. High-Pressure Phase Behavior of Ethane with 1-Hexyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2008**, *53*, 1283–1285.
- (5) Han, D.; Row, K. H. Recent Applications of Ionic Liquids in Separation Technology. *Molecules* **2010**, *15*, 2405–2426.
- (6) Werner, S.; Haumann, M.; Wasserscheid, P. Ionic Liquids in Chemical Engineering. *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 203–230.
- (7) Višak, Z. P.; Calado, M. S.; Vuksanović, J. M.; Ivaniš, G. R.; Branco, A. S. H.; Grozdanić, N. D.; Kijevčanin, M. Lj.; Šerbanović, S. P. Solutions of Ionic Liquids with Diverse Aliphatic and Aromatic Solutes – Phase Behavior and Potentials for Applications: A Review Article. *Arabian J. Chem.* **2014**, No. jarabc.2014.10.003, DOI: 10.1016/j.arabc.2014.10.003.
- (8) Seoane, R.; Corderi, S.; Gomez, E.; Calvar, N.; González, E. J.; Macedo, E. A.; Domínguez, A. Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 2492–2504.
- (9) Gardas, R. L.; Costa, H. F.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, I. M. Densities and Derived Thermodynamic Properties of Imidazolium-, Pyridinium-, Pyrrolidinium-, and Piperidinium-Based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 805–811.
- (10) Leouifoudi, I.; Ziad, A.; Amechrouq, A.; Oukerrou, M. A.; Mouse, H. A.; Mbarki, M. Identification and Characterisation of Phenolic Compounds Extracted from Moroccan Olive Mill Wastewater. *Food Sci. Technol.* **2014**, *34*, 249–257.
- (11) Hou, Y.; Ren, Y.; Peng, W.; Ren, S.; Wu, W. Separation of Phenols from Oil Using Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.* **2013**, *52*, 18071–18075.
- (12) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley: Weinheim, Germany, 2007.
- (13) Althuluth, M.; Overbeek, J. P.; vanWees, H. J.; Zubeir, L. F.; Haije, W. G.; Berrouk, A.; Peters, C. J.; Kroon, M. C. Natural Gas Purification Using Supported Ionic Liquid Membrane. *J. Membr. Sci.* **2015**, *484*, 80–86.
- (14) Althuluth, M.; Mota-Martinez, M. T.; Berrouk, A.; Kroon, M. C.; Peters, C. J. Removal of Small Hydrocarbons (Ethane, Propane, Butane) from Natural Gas Streams Using the Ionic Liquid 1-Ethyl-3-Methylimidazolium tris(pentafluoroethyl)trifluorophosphate. *J. Supercrit. Fluids* **2014**, *90*, 65–72.
- (15) Pereda, S.; Raeissi, S.; Andreatta, A. E.; Bottini, S. B.; Kroon, M.; Peters, C. J. Modeling Gas Solubilities in Imidazolium Based Ionic

Liquids with the [Tf₂N]⁻ Anion Using the GC-EoS. *Fluid Phase Equilib.* **2016**, *409*, 408–416.

(16) Shahkaramipour, N.; Adibi, M.; Seifkordi, A. A.; Fazli, Y. Separation of CO₂/CH₄ through Alumina-Supported Geminal Ionic Liquid Membranes. *J. Membr. Sci.* **2014**, *455*, 229–235.

(17) Kreiter, R.; Overbeek, J. P.; Correia, L. A.; Vente, J. F. Pressure Resistance of Thin Ionic Liquid Membranes Using Tailored Ceramic Supports. *J. Membr. Sci.* **2011**, *370*, 175–178.

(18) Raeissi, S.; Peters, C. J. Carbon Dioxide Solubility in the Homologous 1-Alkyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)imide Family. *J. Chem. Eng. Data* **2009**, *54*, 382–386.

(19) Blanchard, L. A.; Brennecke, J. F. Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292.

(20) Kroon, M. C.; Peters, C. J. Supercritical Fluids in Ionic Liquids. In *Ionic Liquids Further UnCOILed*; Wiley: NJ, 2014.

(21) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley – VCH Verlag GmbH & Co: Germany, 2003.

(22) Ventura, S. P. V.; Gonçalves, A. M. M.; Sintra, T.; Pereira, J. L.; Gonçalves, F.; Coutinho, J. A. P. Designing Ionic Liquids: the Chemical Structure Role in the Toxicity. *Ecotoxicology* **2013**, *22*, 1–12.

(23) Grzonkowska, M.; Sosnowska, A.; Barycki, M.; Rybinska, A.; Puzyn, T. How the structure of ionic liquid affects its toxicity to *Vibrio fischeri*. *Chemosphere* **2016**, *159*, 199–207.

(24) Ventura, S. P. V.; Gonçalves, A. M. M.; Gonçalves, F.; Coutinho, J. A. P. Assessing the Toxicity on [C₃mim][Tf₂N]⁻ to Aquatic Organisms of Different Trophic Levels. *Aquat. Toxicol.* **2010**, *96*, 290–297.

(25) Hiraga, Y.; Goto, M.; Sato, Y.; Smith, J. R. L. Measurement of High Pressure Densities and Atmospheric Pressure Viscosities of Alkyl Phosphate Anion Ionic Liquids and Correlation with the ϵ^* -Modified Sanchez-Lacombe Equation of State. *J. Chem. Thermodyn.* **2017**, *104*, 73–81.

(26) Ivaniš, G. R.; Tasić, A. Ž.; Radović, I. R.; Djordjević, B. D.; Šerbanović, S. P.; Kijevčanin, M. Lj. An Apparatus Proposed for Density Measurements in Compressed Liquid Regions at Pressures of 0.1–60 MPa and Temperatures of 288.15–413.15 K. *J. Serb. Chem. Soc.* **2015**, *80*, 1073–1085.

(27) Ivaniš, G. R.; Tasić, A. Ž.; Radović, I. R.; Djordjević, B. D.; Šerbanović, S. P.; Kijevčanin, M. Lj. Modeling of Density and Calculations of Derived Volumetric Properties for n-Hexane, Toluene and Dichloromethane at Pressures 0.1–60 MPa and Temperatures 288.15–413.15 K. *J. Serb. Chem. Soc.* **2015**, *80*, 1423–1433.

(28) Mutelet, F.; Hassan, E. S. R. E.; Stephens, T. W.; Acree, W. E. J.; Baker, G. A. Activity Coefficients at Infinite Dilution for Organic Solutes Dissolved in Three 1-Alkyl-1-methylpyrrolidinium Bis-(trifluoromethylsulfonyl)imide Ionic Liquids Bearing Short Linear Alkyl Side Chains of Three to Five Carbons. *J. Chem. Eng. Data* **2013**, *58*, 2210–2218.

(29) Regueira, T.; Lugo, L.; Fernández, J. High Pressure Volumetric Properties of 1-ethyl-3-methylimidazolium ethylsulfate and 1-(2-methoxyethyl)-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)-imide. *J. Chem. Thermodyn.* **2012**, *48*, 213–320.

(30) Widowati, E.; Lee, M. PVT Properties for Binary Ionic Liquids of 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide with Anisole or Acetophenone at Pressures up to 50 MPa. *J. Chem. Thermodyn.* **2012**, *49*, 54–61.

(31) Tomé, L. I. N.; Carvalho, P. J.; Freire, M. G.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P.; Gardas, R. L. Measurements and Correlation of High-Pressure Densities of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 1914–1921.

(32) Regueira, T.; Lugo, L.; Fernández, J. Influence of the Pressure, Temperature, Cation and Anion on the Volumetric Properties of Ionic Liquids: New Experimental Values for Two Salts. *J. Chem. Thermodyn.* **2013**, *58*, 440–448.

(33) Jacquemin, J.; Nancarrow, P.; Rooney, D. W.; Costa Gomes, M. F.; Husson, P.; Majer, V.; Pádua, A. A. H.; Hardacre, C. Prediction of

Ionic Liquid Properties. II. Volumetric Properties as a Function of Temperature and Pressure. *J. Chem. Eng. Data* **2008**, *53*, 2133–2143.

(34) Seki, S.; Tsuzuki, S.; Hayamizu, K.; Umebayashi, Y.; Serizawa, N.; Takei, K.; Miyashiro, H. Comprehensive Refractive Index Property for Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2211–2216.

(35) Makino, T.; Kanakubo, M.; Umecky, T.; Suzuki, A.; Nishida, T.; Takano, J. Electrical Conductivities, Viscosities and Densities of N-methoxymethyl and N-butyl-N-methylpyrrolidinium Ionic Liquids with the bis(fluorosulfonyl)amide Anion. *J. Chem. Eng. Data* **2012**, *57*, 751–755.

(36) Vraneš, M.; Dožić, S.; Djerić, V.; Gađurić, S. Physicochemical Characterization of 1-butyl-3-methylimidazolium and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide. *J. Chem. Eng. Data* **2012**, *57*, 1072–1077.

(37) Lagourette, B.; Boned, C.; Saint-Guirons, H.; Xans, P.; Zhou, H. Densimeter Calibration Method versus Temperature and Pressure. *Meas. Sci. Technol.* **1992**, *3*, 699–703.

(38) Comuñas, M. J. P.; Bazile, J. P.; Baylaucq, A.; Boned, C. Density of Diethyl Adipate using a New Vibrating Tube Densimeter from (293.15 to 403.15) K and up to 140 MPa. Calibration and Measurements. *J. Chem. Eng. Data* **2008**, *53*, 986–994.

(39) Shamsipur, M.; Beigi, A. A. M.; Teymouri, M.; Pourmortazavi, S. M.; Irandoust, M. Physical and Electrochemical Properties of Ionic Liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. *J. Mol. Liq.* **2010**, *157*, 43–50.

(40) Vraneš, M.; Tot, A.; Papović, S.; Zec, N.; Dožić, S.; Gađurić, S. Ideal and Non-ideal Behaviour of {1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide + *c*-butyrolactone} Binary Mixtures. *J. Chem. Thermodyn.* **2015**, *81*, 66–76.

(41) Pereiro, A. B.; Veiga, H. I. M.; Esperança, J. M. S. S.; Rodríguez, A. Effect of Temperature on the Physical Properties of Two Ionic Liquids. *J. Chem. Thermodyn.* **2009**, *41*, 1419–1423.

(42) Segovia, J.; Fandiño, O.; López, E.; Lugo, L.; Martín, M. C.; Fernández, J. Automated Densimetric System: Measurements and Uncertainties for Compressed Fluids. *J. Chem. Thermodyn.* **2009**, *41*, 632–638.

(43) Gaciño, F. M.; Regueira, T.; Lugo, L.; Comuñas, M. J. P.; Fernández, J. Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 4984–4999.

(44) Harris, K. R.; Woolf, L. A.; Kanakubo, M.; Ruther, T. Transport Properties of N-Butyl-N-methylpyrrolidinium Bis-(trifluoromethylsulfonyl)amide. *J. Chem. Eng. Data* **2011**, *56*, 4672–4685.

(45) Geppert-Rybczyńska, M.; Lehmann, J. K.; Heintz, A. Physicochemical Properties of Two 1-alkyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide Ionic Liquids and of Binary Mixtures of 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide with Methanol or Acetonitrile. *J. Chem. Thermodyn.* **2014**, *71*, 171–181.

(46) Kolbeck, C.; Lehmann, J.; Lovelock, K. R. J.; Cremer, T.; Paape, N.; Wasserscheid, P.; Froba, A. P.; Maier, F.; Steinruck, H. P. Density and Surface Tension of Ionic Liquids. *J. Phys. Chem. B* **2010**, *114*, 17025–17036.

(47) Seki, S.; Kobayashi, T.; Kobayashi, Y.; Takei, K.; Miyashiro, H.; Hayamizu, K.; Tsuzuki, S.; Mitsugi, T.; Umebayashi, Y. Effects of Cation and Anion on Physical Properties of Room-Temperature Ionic Liquids. *J. Mol. Liq.* **2010**, *152*, 9–13.

(48) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.

(49) Fakhræe, M.; Gholami, M. R. Biodegradable Ionic Liquids: Effects of Temperature, Alkyl Side-Chain Length, and Anion on the Thermodynamic Properties and Interaction Energies As Determined

by Molecular Dynamics Simulations Coupled with ab Initio Calculations. *Ind. Eng. Chem. Res.* **2015**, *54*, 11678–11700.

(50) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.

(51) Jacquemin, J.; Husson, P.; Mayer, V.; Cibulka, I. High-Pressure Volumetric Properties of Imidazolium-Based Ionic Liquids: Effect of the Anion. *J. Chem. Eng. Data* **2007**, *52*, 2204–2211.

(52) Abdussalam, A. A.; Ivaniš, G. R.; Radović, I. R.; Kijevčanin, M. Lj. Densities and Derived Thermodynamic Properties for the (n-heptane + n-octane), (n-heptane + ethanol) and (n-octane + ethanol) Systems at High Pressures. *J. Chem. Thermodyn.* **2016**, *100*, 89–99.

(53) Abdussalam, A. A.; Radović, I. R.; Ivaniš, G. R.; Kijevčanin, M. Lj. High Pressure Densities and Derived Thermodynamic Properties for the (n-heptane + n-octane + ethanol) Ternary System. *J. Chem. Thermodyn.* **2017**, *109*, 91–99.

(54) Troncoso, J.; Cerdeiría, C. A.; Navia, P.; Sanmamed, Y. A.; González-Salgado, D.; Romani, L. Unusual Behavior of the Thermodynamic Response Functions of Ionic Liquids. *J. Phys. Chem. Lett.* **2010**, *1*, 211–214.

(55) Dymond, J. H.; Malhotra, R. The Tait Equation: 100 Years On. *Int. J. Thermophys.* **1988**, *9*, 941–951.

(56) Safarov, J.; Millero, F.; Feistel, R.; Heintz, A.; Hassel, E. Thermodynamic Properties of Standard Seawater: Extensions to High Temperatures and Pressures. *Ocean Sci.* **2009**, *5*, 235–246.

(57) Królikowska, M.; Hofman, T. Densities, Isobaric Expansivities and Isothermal Compressibilities of the Thiocyanate-based Ionic Liquids at Temperatures (298.15–338.15 K) and Pressures up to 10 MPa. *Thermochim. Acta* **2012**, *530*, 1–6.

(58) Pensado, A. S.; Comuñas, M. J. P.; Fernández, J. The Pressure–Viscosity Coefficient of Several Ionic Liquids. *Tribol. Lett.* **2008**, *31*, 107–118.

(59) Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Pádua, A. A. H.; Sheppard, O.; Soper, A. K. Liquid Structure of the Ionic Liquid 1,3-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}amide. *J. Phys. Chem. B* **2006**, *110*, 12055–12061.

(60) Marcus, Y. Internal Pressure of Liquids and Solutions. *Chem. Rev.* **2013**, *113*, 6536–6551.

(61) Veldhorst, A. A.; Faria, L. F. O.; Ribeiro, M. C. C. Local Solvent Properties of Imidazolium-based Ionic Liquids. *J. Mol. Liq.* **2016**, *223*, 283–288.