High-Pressure Densities of 1-Alkyl-3-methylimidazolium Hexafluorophosphates and 1-Alkyl-3-methylimidazolium Tetrafluoroborates at Temperatures from (313 to 473) K and at Pressures up to 200 MPa

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Pure component pressure−volume−temperature (*pVT*) data for five imidazolium-based ionic liquids, 1-ethyl-3-methylimidazolium hexafluorophosphate [emim][PF_6], 1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF_6], 1-octyl-3-methylimidazolium hexafluorophosphate [omim][PF_6], 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4], and 1-hexyl-3-methylimidazolium tetrafluoroborate [hmim][BF_4], were measured with a bellows type apparatus. High-pressure densities of ionic liquids showed smooth trends with temperature and pressure variations except for [emim][PF_6] which exhibited a solid phase transition at temperatures below 352.7 K and which solidified at 100 MPa at 352.7 K. Solid densities were measured and were about 6.3 % higher than those of the liquid. Isothermal compressibilities and thermal expansion coefficients were calculated from the Tait equation that was fit to the *pVT* data. Isothermal compressibilities increased with alkyl chain length which is probably related to the ionic liquid free volume.

Introduction

Room-temperature ionic liquids (ILs) are organic salts that are liquid at conditions around room temperature.[1] Many ILs have negligible vapor pressure and are being explored as possible environmentally benign solvents.[2] Since there are numerous ways of combining counterions to form ionic liquids, flexibility of function is one of the chief advantages in using ILs. Although accurate volumetric properties are very important in the use of any solvent in chemical processing, the number of available volumetric data of many ILs is limited.

Density data at ambient pressure have been reported by several researchers. High-pressure pressure−volume−temperature (*pVT*) data have been measured by Gu and Brennecke,[3] de Azevedo et al.,[4,5] Esperança et al.,[6,7] Tomida et al.,[8] and Gardas et al.[9] In our research, high-pressure density measurements of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and 1-butyl-3-methylimidazolium octylsulfate ([bmim][$OcSO_4$]) have been measured with a metal bellows apparatus at temperatures from (313 to 473) K and at pressures up to 200 MPa.[10]

In this research, high-pressure density data of five ionic liquids were measured at temperatures from (313 to 473) K and at pressures up to 200 MPa to study the effect of cation alkyl chain length. Isothermal compressibility and thermal expansion coefficient are discussed in terms of cation alkyl chain length.

Experimental

The ionic liquids (purity %), 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF_6]) (98 %), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) (98 %), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) (97 %), and 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) (99 %) were purchased from Tokyo Chemical Industries. The 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) (98 %) was purchased from Acros Organics. The ionic liquids were subjected to vacuum at 353 K for 6 h before measurement. The water mass fraction of each ionic liquid measured by Karl Fischer titration under a helium atmosphere after the vacuum treatment was $1 \cdot 10^{-4}$, $6 \cdot 10^{-5}$, $2.3 \cdot 10^{-4}$, $9 \cdot 10^{-4}$, and $2.3 \cdot 10^{-4}$ for [emim][PF_6], [hmim][PF_6], [omim][PF_6], [emim][BF_4], and [hmim][BF_4], respectively, and

Table 1. Experimental Densities for Ionic Liquids at 0.1 MPa

	ρ/kg·m^{-3}				
T/K	[emim][PF_6]	[emim][BF_4]	[hmim][PF_6]	[hmim][BF_4]	[omim][PF_6]
293.15		1284.4	1297.0	1148.5	1240.8
313.15		1269.1	1280.7	1134.7	1225.0
333.15		1254.0	1265.1	1121.0	1210.0
353.15	1421.8	1239.3	1249.8	1107.6	1195.2
373.15	1404.9				

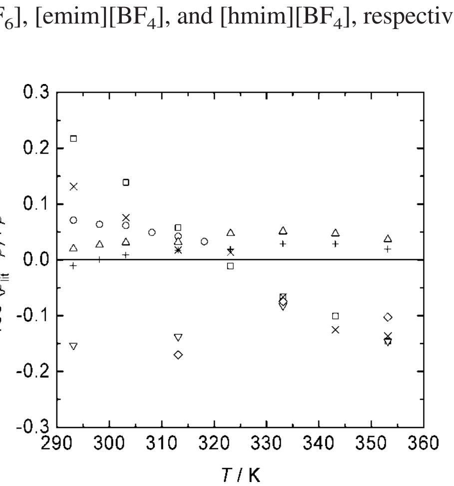

Figure 1. Deviations of the literature densities (ρ_{lit}) for ionic liquids with the PF_6^- anion from this work (ρ) at 0.1 MPa. Symbols, [hmim][PF_6]; □, Gardas et al.;[9] ○, Pereiro et al.;[19] Δ, Harris et al.;[18] ∇, Tomida et al.;[8] [omim][PF_6]; ×, Gardas et al.;[9] +, Harris et al.;[20] ◇, Tomida et al.[8]

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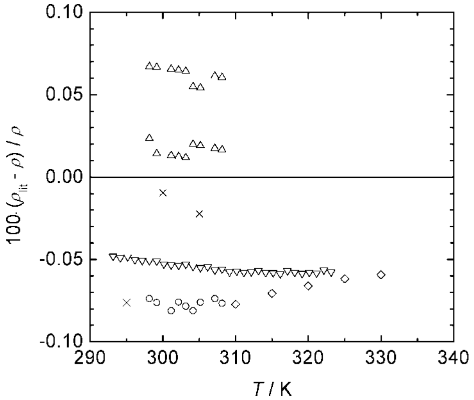

Figure 2. Deviations of the literature densities for ionic liquids with the BF_4^- anion from this work at 0.1 MPa. Symbols, [emim][BF4]; ×, Shiflett and Yokozeki;[14] ○, Navia et al.;[15] [hmim][BF4]; Δ, Navia et al.;[15] ∇, Sanmamed et al.;[16] ◇, Wagner et al.[17]

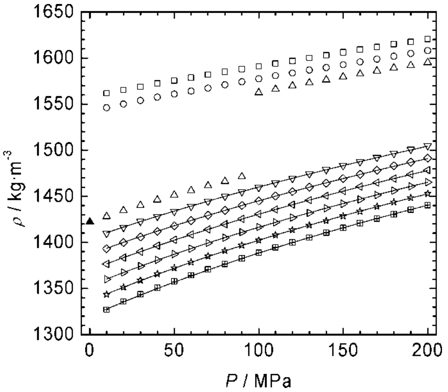

Figure 3. Density of [emim][PF_6] versus pressure at various temperatures. Symbols, □, 312.8 K; ○, 332.7 K; Δ, 352.7 K; ∇, 372.8 K; ◇, 392.9 K; triangle pointing left, 412.9 K;triangle pointing right, 432.6 K; ☆, 452.5 K; ⊞, 472.4 K; ▲, measured with a vibrating tube instrument. Line, Tait equation.

the ion content (Cl^-, Br^-) of each ionic liquid was measured with ion chromatography. From the ion chromatographic analyses, there were no detectable chloride ions for [emim][PF_6] and [hmim][PF_6], and for [omim][PF_6], [emim][BF_4], and [hmim][BF_4], the chloride mass fractions were determined to be $(172, 625, \text{and } 793) \cdot 10^{-6}$, respectively. The bromide ion was not detected in any of the samples.

High-pressure density data of the ionic liquids at elevated pressures were measured with a bellows apparatus.[10,11] The *PVT* apparatus consisted of a bellows dilatometer, a pressure vessel, multiple temperature control sections, a hand pump, pressure gauges, and a section for displacement measurement. The change of volume for the ionic liquid was determined from the change in length of the bellows, as measured by a linear variable differential transformer (LVDT). Measurements were replicated by measuring volume displacements upon increasing and decreasing pressure.

The displacement of the dilatometer was calibrated with mercury and mercury−water mixtures to determine volume as a function of the temperature, pressure, area, and bellows displacement as described in the Supporting Information. Deviation in the calibration was less than 0.04 % for most parts of mercury and mercury + water mixtures. Measurement of pure water *PVT* over the range (313 to 473) K from (10 to 200) MPa gave an average deviation of 0.05 % with the literature (Supporting Information).

High-pressure density measurements made by a dilatometer require a low-pressure density datum, because the dilatometer measures volumetric changes from a reference value. The reference condition for the IL densities was 313 K and 0.1 MPa except [emim][PF_6] in which the reference condition was 353 K and 0.1 MPa since this compound has a relatively high melting point ($T_m = 334.05$ K).[12] Densities of ILs at 0.1 MPa were measured with a vibrating tube instrument (Anton Paar SVM 3000, Graz). The measurement temperature was (293 to 353) K for [hmim][PF_6], [omim][PF_6], [emim][BF_4], and [hmim][BF_4] and (353 to 373) K for [emim][PF_6]. Samples were measured in duplicate.

In the measurement procedure, the dilatometer ($v = 4.87$ cm^3) was filled with the ionic liquid under vacuum and loaded into the pressure vessel. For [emim][PF_6], which is a solid at room

Table 2. Experimental Densities (ρ) for [emim][PF_6]

	T/K								
P/MPa	312.8	332.7	352.7	372.8	392.9	412.9	432.6	452.5	472.4
	ρ/kg·m^{-3}								
0.1			1422[a]						
10	1562	1546	1428	1410	1393	1377	1360	1344	1327
20	1565	1550	1434	1416	1400	1384	1367	1351	1336
30	1569	1554	1440	1423	1406	1390	1374	1359	1344
40	1572	1557	1446	1428	1412	1397	1381	1366	1351
50	1576	1561	1451	1434	1418	1403	1387	1372	1358
60	1579	1564	1456	1439	1424	1408	1393	1379	1364
70	1582	1567	1461	1445	1429	1414	1399	1385	1371
80	1585	1571	1466	1450	1435	1420	1405	1391	1377
90	1588	1574	1471	1455	1440	1425	1411	1397	1383
100	1591	1577	1562	1460	1445	1431	1417	1402	1389
110	1594	1581	1566	1465	1450	1436	1422	1408	1395
120	1597	1584	1570	1470	1455	1441	1427	1414	1400
130	1600	1587	1573	1474	1460	1446	1432	1419	1405
140	1603	1590	1576	1479	1464	1451	1437	1423	1411
150	1606	1593	1580	1483	1469	1456	1442	1429	1416
160	1609	1596	1583	1488	1474	1460	1447	1434	1421
170	1612	1599	1586	1492	1478	1465	1451	1439	1426
180	1615	1602	1589	1497	1483	1469	1456	1444	1431
190	1617	1605	1592	1501	1487	1474	1461	1448	1436
200	1620	1608	1595	1505	1491	1478	1465	1453	1440

[a] Measured with a vibrating tube instrument.

Table 3. Experimental Densities (ρ) for [emim][BF_4]

	T/K								
P/MPa	313.2	332.6	352.7	372.8	392.9	413.0	432.9	452.6	472.4
					ρ/kg·m^{-3}				
0.1	1269[a]								
10	1274	1259	1244	1230	1216	1202	1189	1176	1163
20	1278	1264	1249	1235	1221	1208	1195	1182	1169
30	1282	1268	1254	1240	1227	1213	1200	1188	1175
40	1287	1273	1259	1245	1232	1219	1206	1193	1181
50	1291	1277	1263	1250	1237	1224	1211	1199	1187
60	1295	1281	1267	1254	1241	1229	1216	1204	1192
70	1299	1285	1272	1258	1246	1233	1221	1209	1197
80	1302	1289	1276	1263	1250	1238	1226	1214	1202
90	1306	1293	1280	1267	1254	1242	1230	1219	1207
100	1310	1297	1284	1271	1259	1247	1235	1223	1212
110	1313	1300	1287	1275	1263	1251	1239	1228	1217
120	1317	1304	1291	1279	1267	1255	1243	1232	1221
130	1320	1307	1295	1282	1270	1259	1247	1236	1226
140	1323	1311	1298	1286	1274	1263	1252	1240	1230
150	1327	1314	1302	1290	1278	1267	1255	1245	1234
160	1330	1317	1305	1293	1282	1270	1259	1248	1238
170	1333	1321	1309	1297	1285	1274	1263	1252	1242
180	1336	1324	1312	1300	1289	1278	1267	1256	1246
190	1339	1327	1315	1303	1292	1281	1270	1260	1250
200	1342	1330	1318	1307	1295	1285	1274	1264	1253

[a] Measured with a vibrating tube instrument.

Table 4. Experimental Densities (ρ) for [hmim][PF_6]

	T/K								
P/MPa	312.9	332.6	352.7	372.9	393.0	412.9	432.8	452.5	472.3
					ρ/kg·m^{-3}				
0.1	1281[a]								
10	1287	1271	1256	1241	1226	1211	1197	1183	1169
20	1292	1277	1262	1248	1233	1219	1205	1191	1177
30	1298	1283	1268	1254	1240	1226	1212	1199	1185
40	1303	1289	1274	1260	1246	1232	1219	1206	1193
50	1308	1294	1280	1266	1252	1239	1226	1213	1200
60	1313	1299	1285	1271	1258	1245	1232	1219	1207
70	1318	1304	1290	1277	1264	1251	1238	1226	1213
80	1322	1309	1295	1282	1269	1256	1244	1232	1220
90	1327	1313	1300	1287	1274	1262	1250	1237	1226
100	1331	1318	1305	1292	1279	1267	1255	1243	1231
110	1335	1322	1309	1296	1284	1272	1260	1248	1237
120	1339	1326	1314	1301	1289	1277	1265	1254	1242
130	1343	1330	1318	1306	1293	1282	1270	1259	1247
140	1347	1334	1322	1310	1298	1286	1275	1263	1253
150	1351	1338	1326	1314	1302	1291	1279	1268	1257
160	1355	1342	1330	1318	1306	1295	1284	1273	1262
170	1358	1346	1334	1322	1310	1299	1288	1277	1267
180	1362	1350	1338	1326	1314	1303	1292	1282	1271
190	1366	1353	1342	1330	1318	1307	1297	1286	1276
200	1369	1357	1345	1334	1322	1311	1301	1290	1280

[a] Measured with a vibrating tube instrument.

temperature, samples were loaded into a stainless cup ($v = 0.83$ cm^3) in the molten state ($T = 353$ K), and mercury was used to fill the dilatometer. The compressibility of the mercury of Grindlay and Linde[13] was used in the data reduction (Supporting Information). For a given condition, the displacement of a rod connected to the bellows was measured by LVDT at equilibrium. The uncertainty of pressure measurement was ± 0.1 MPa below 100 MPa and ± 0.25 MPa from 100 MPa up to 200 MPa. Temperature uncertainty is estimated to be ± 0.1 K. The uncertainty in the density measurements was estimated to be ± 0.1 % for [hmim][PF_6], [omim][PF_6], [emim][BF_4], and [hmim][BF_4] and ± 0.3 % for [emim][PF_6] due to the amount of possible sample that could be loaded (Supporting Information).

To confirm that there was minimal decomposition of the ILs, all samples were heat treated at 473 K for 6 h, and the density was measured before and after the treatment. The deviation was less than 0.04 %, which was less than the experimental uncertainty indicating the absence of reaction (Supporting Information).

Results

The density data of five ionic liquids at ambient pressure are shown in Table 1, and comparisons of the densities measured in this work and literature values are shown in Figures 1 to 2. Density data for [emim][PF_6] do not seem to have been previously reported. The [emim][BF_4] densities of this work corresponded well with the measurement of Shiflett and Yokozeki[14] and Navia et al.[15] to within 0.1 %. The [hmim][BF_4] densities of this work corresponded well with the measurement of Sanmamed et al.[16] and Navia et al.[15] and Wagner et al.[17] to within 0.1 %. The [hmim][PF_6] densities of this work cor-

Table 5. Experimental Densities (ρ) for [hmim][BF$_4$]

	T/K								
P/MPa	313.3	332.5	352.6	372.7	393.0	413.0	432.9	452.6	472.5
	ρ/kg·m^{-3}								
0.1	1135[a]								
10	1139	1126	1113	1099	1087	1074	1062	1049	1037
20	1144	1131	1118	1105	1093	1080	1068	1056	1045
30	1149	1136	1123	1111	1098	1086	1075	1063	1052
40	1154	1141	1128	1116	1104	1092	1081	1069	1058
50	1158	1146	1133	1121	1109	1098	1086	1075	1064
60	1162	1150	1138	1126	1114	1103	1092	1081	1070
70	1167	1154	1142	1131	1119	1108	1097	1086	1076
80	1171	1159	1147	1135	1124	1113	1102	1092	1081
90	1174	1163	1151	1139	1128	1118	1107	1097	1087
100	1178	1167	1155	1144	1133	1122	1112	1101	1092
110	1182	1170	1159	1148	1137	1126	1116	1106	1096
120	1186	1174	1163	1152	1141	1131	1121	1111	1101
130	1189	1178	1167	1156	1145	1135	1125	1115	1105
140	1193	1181	1170	1160	1149	1139	1129	1119	1110
150	1196	1185	1174	1163	1153	1143	1133	1123	1114
160	1199	1188	1177	1167	1157	1147	1137	1128	1118
170	1202	1192	1181	1170	1160	1150	1141	1131	1122
180	1206	1195	1184	1174	1164	1154	1145	1135	1126
190	1209	1198	1187	1177	1167	1158	1148	1139	1130
200	1212	1201	1191	1180	1171	1161	1152	1143	1134

[a] Measured with a vibrating tube instrument.

Table 6. Experimental Densities (ρ) for [omim][PF$_6$]

	T/K								
P/MPa	312.8	332.6	352.6	372.8	392.8	413.0	432.7	452.5	472.3
	ρ/kg·m^{-3}								
0.1	1225[a]								
10	1230	1215	1200	1186	1171	1157	1144	1130	1116
20	1236	1221	1207	1193	1179	1165	1152	1138	1125
30	1241	1227	1213	1199	1186	1172	1159	1146	1133
40	1247	1233	1219	1205	1192	1179	1166	1153	1141
50	1252	1238	1224	1211	1198	1185	1173	1160	1148
60	1257	1243	1230	1217	1204	1191	1179	1167	1155
70	1261	1248	1235	1222	1209	1197	1185	1173	1162
80	1266	1253	1240	1227	1215	1203	1191	1179	1168
90	1270	1257	1245	1232	1220	1208	1197	1185	1174
100	1275	1262	1249	1237	1225	1213	1202	1191	1180
110	1279	1266	1254	1242	1230	1218	1207	1196	1185
120	1283	1270	1258	1246	1235	1223	1212	1201	1191
130	1287	1274	1262	1250	1239	1228	1217	1206	1196
140	1291	1278	1266	1255	1243	1232	1222	1211	1201
150	1294	1282	1270	1259	1248	1237	1226	1216	1205
160	1298	1286	1274	1263	1252	1241	1231	1220	1210
170	1302	1290	1278	1267	1256	1245	1235	1225	1215
180	1305	1293	1282	1271	1260	1249	1239	1229	1219
190	1309	1297	1286	1274	1264	1253	1243	1233	1223
200	1312	1300	1289	1278	1268	1257	1247	1237	1228

[a] Measured with a vibrating tube instrument.

responded well with the measurement of Harris et al.,[18] Pereiro et al.,[19] and Tomida et al.[8] to within 0.2 %, but there were deviations between this work and the data of Gardas et al.[9] The [omim][PF$_6$] densities of this work corresponded well with the measurement of Harris et al.[20] and Tomida et al.[8] to within 0.2 %, but there were deviations between this work and the data of Gardas et al.,[9] Gu and Brennecke,[3] and Blanchard et al.[21]

Experimental density data of five ionic liquids for nine isotherms (312 to 473) K are shown in Tables 2 to 6, and the density of [emim][PF$_6$] as a function of pressure is shown in Figure 3. Correlation and analysis of the data are discussed in a later section. All experimental data showed smooth trends with temperature and pressure variations except for [emim][PF$_6$], which exhibited a liquid−solid phase transition (Figure 3). The density increase upon solidification was roughly 6.3 % at 352.7 K for a pressure increase from (90 to 100) MPa.

Comparison of densities for ILs between this work and the literature[3,9,22,24] are shown in Figures 4 to 5. Average relative deviations were 0.084 % for pressures up to 20 MPa for [hmim][PF$_6$] (Figure 4) and 0.069 % for pressures up to 60 MPa for [omim][PF$_6$] (Figure 5). Data of Gu and Brennecke for [omim][PF$_6$] deviated from this work by more than 1 %. The reason for these deviations, which did not seem to be related to the pressure ranges studied, can probably be attributed to impurities and water.

Trends of the densities according to the IL are discussed next. The densities changed regularly with alkyl chain length and became larger according to [emim][PF$_6$] > [bmim][PF$_6$][10] > [hmim][PF$_6$] > [omim][PF$_6$]. In other words, the IL with the longer alkyl chain had the highest molar volume among the ILs. This trend was also observed for measured ILs with the BF$_4^-$ anion. Comparing the anions PF$_6^-$ and BF$_4^-$, the

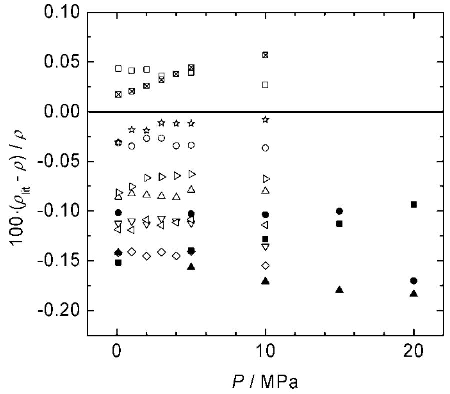

Figure 4. Deviations of the literature densities ($\rho_{\rm lit.}$) for [hmim][PF$_6$] from this work (ρ). Symbols, Gardas et al.:[9] □, 313.15 K; ○, 323.15 K; Δ, 333.15 K; ∇, 343.15 K; ◇, 353.15 K; triangle pointing left, 363.15 K; triangle pointing right, 373.15 K; ☆, 383.15 K; square with an X, 393.15 K; Tomida et al.:[22] ■, 313.15 K; ●, 333.15 K; ▲, 353.15 K.

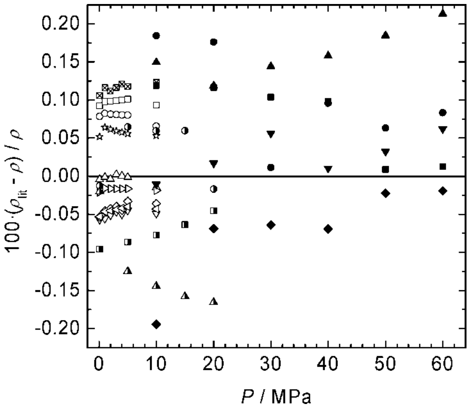

Figure 5. Deviations of the literature densities ($\rho_{\rm lit}$) for [omim][PF$_6$] from this work (ρ). Symbols, Gardas et al.:[9] □, 313.15 K; ○, 323.15 K; Δ, 333.15 K; ∇, 343.15 K; ◇, 353.15 K; triangle pointing left, 363.15 K; triangle pointing right, 373.15 K; ☆, 383.15 K; square with an X, 393.15 K; Tomida et al.:[22] ◨, 313.15 K; ◑, 333.15 K; ▴, 353.15 K; Marsh:[24] ■, 323.15 K; ●, 348.15 K; ▲, 373.15 K; ▼, 398.15 K; ◆, 423.15 K.

densities of the IL having the BF_4^- anion were smaller than the ILs having the PF_6^- anion.

Tait Equation Correlation

The experimental specific volume data (V_S) were correlated with the Tait equation that had the following form:

$$V_s(P,T) = \frac{1}{\rho(P,T)} = \frac{1}{\rho(P_0,T)}(1 - C\ln(1 + P/B(T))) \quad (1)$$

$$\frac{1}{\rho(P_0,T)} = a_0 + a_1\cdot T + a_2\cdot T^2 \quad (2)$$

$$B(T) = b_0\cdot\exp(-b_1\cdot T) \quad (3)$$

where T is the absolute temperature in Kelvin and $\rho(P_0, T)$ is the density at ambient pressure P_0 and system temperature with units of kg·m^{-3}. The $B(T)$ is dependent on temperature; C is a constant; and a_0, a_1, a_2, b_0, and b_1 are fitting parameters. The parameters of the Tait equation were determined by minimizing the following objective function:

$$\mathrm{ARD} = \frac{1}{N}\sum_i^N\left|\frac{\rho_{i,\rm calc} - \rho_i}{\rho_i}\right| \quad (4)$$

where ARD is the average relative deviation of all data for a given IL.

Figure 3 shows correlation results, and Table 7 shows parameter values determined in this work. For [emim][PF$_6$], liquid state density data (≥ 373 K) were used to determine Tait equation parameters. The data could be fit to within an ARD of 0.014 % for all ILs.

The thermal expansion coefficients can be calculated from eq 5 as:

$$\alpha_P = (\partial \ln V_s(P,T)/\partial T)_P = \frac{(a_1 + 2a_2T)}{(a_0 + a_1T + a_2T^2)} - \frac{b_1\cdot C\cdot P}{(B(T) + P)\cdot(1 - C\ln(1 + P/B(T)))} \quad (5)$$

where the constants shown are those used in eqs 1 to 3. The uncertainty of thermal expansion coefficients was estimated to be ± 2.2 % for all ILs based on the uncertainty in density and its effect on the calculated α_P.

Figure 6shows the thermal expansion coefficients for the PF_6^- ILs. The thermal expansion coefficients of ionic liquid varied from about ($4.2\cdot10^{-4}$ to $6.2\cdot10^{-4}$) K^{-1} over the range of conditions and showed smaller temperature dependence compared with water or methanol (Figure S5, Supporting Information).[23] Equation 5 was also fit to data in the literature, and the results were plotted. From the calculations shown in Figure 6, it can be seen that there is great variation between the values of various researchers that may be related to the number of data and the variation of density with temperature (Figure 1).

The isothermal compressibilities were calculated from the following equation that was derived from eq 6:

$$\beta_T = -(1/V_s)(\partial V/\partial P)_T = \{(P + B(T))[1/C - \ln(1 + P/B(T))]\}^{-1} \quad (6)$$

The uncertainty of isothermal compressibilities was estimated to be about ± 3.3 % for all ILs based on the uncertainty in density and its effect on the calculated β_T.

Figure 7 shows the isothermal compressibilities of the PF_6^- ILs. The isothermal compressibilities varied from ($0.22\cdot10^{-3}$ to $0.49\cdot10^{-3}$) MPa^{-1} over the range of conditions studied and showed smaller pressure dependence compared with methanol but similar to that of water (Figure S6, Supporting Information).

Table 7. Tait Equation (Equations 1 to 3) Parameter Value for the Ionic Liquids Studied and the Deviation from a Least-Squares Fit[a]

	V_s (0.1 MPa, T)/m^3·kg^{-1}			$B(T)$/MPa			
	$a_0\cdot10^4$	$a_1\cdot10^7$	$a_2\cdot10^{10}$	b_0	$b_1\cdot10^3$		
	m^3·kg^{-1}	m^3·kg^{-1}·K^{-1}	m^3·kg^{-1}·K^{-2}	MPa	K^{-1}	C	ARD·10^2
[emim][PF$_6$]	5.772	2.855	2.048	806.7	3.163	0.1125	0.014
[emim][BF$_4$]	6.496	4.153	0.849	706.0	2.994	0.1002	0.010
[hmim][PF$_6$]	6.491	3.615	1.883	610.8	3.449	0.0952	0.009
[hmim][BF$_4$]	7.241	4.641	1.226	597.1	3.310	0.0957	0.011
[omim][PF$_6$]	6.794	3.729	2.116	591.4	3.607	0.0930	0.013

[a] ARD: average relative deviation, eq 4.

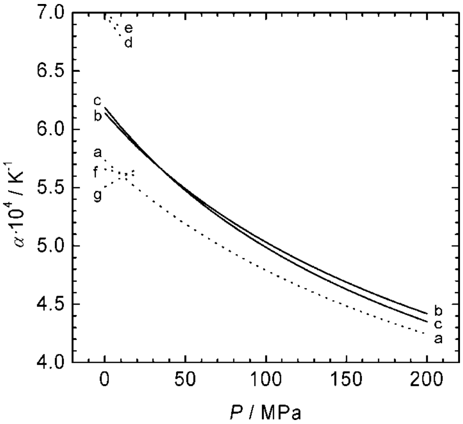

Figure 6. Thermal expansion coefficients of ionic liquids with the PF_6^- anion at 313 K. Solid lines, this work; dashed line, literature. [bmim][PF_6]: a (ref 10). [hmim][PF_6]: b (eq 5), d (ref 9), f (ref 22). [omim][PF_6]: c (eq 5), e (ref 9), g (ref 22).

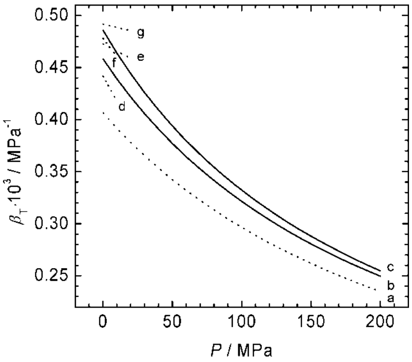

Figure 7. Isothermal compressibilities of ILs with the PF_6^- anion at 313 K. Solid lines, this work; dashed line, literature. [bmim][PF_6]: a (ref 10). [hmim][PF_6]: b (eq 5), d (ref 9), f (ref 22). [omim][PF_6]: c (eq 5), e (ref 9), g (ref 22).

Equation 6 was fit to the data in the literature, and the results were plotted in Figure 7. The values and slopes showed fair agreement for derived values for all of the data sets. The isothermal compressibilities increased as the alkyl chain length increased for both BF_4^- and PF_6^-. It is likely that the alkyl chain makes the IL sterically bulky and increases the free volume, so that the IL becomes compressible.

Conclusions

Pressure−volume−temperature data of five ionic liquids are reported. For [emim][PF_6], a solid−liquid transition was found. The coefficients of thermal expansion of ionic liquid increased as temperature increased. The specific volumes and isothermal compressibilities of ILs became larger as the alkyl chain length increased.

Supporting Information Available:

Additional information on the bellows dilatometer calibration, thermal expansion, isothermal compressibility, extrapolation of *PVT* data to 0.1 MPa, and decomposition check of the IL. This material is available free of charge via the Internet at http://pubs.acs.org.

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