# Densities of Ionic Liquid [BMIM][$BF_4$] + Ethanol, + Benzene, and + Acetonitrile at Different Temperature and Pressure

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Densities of three binary systems, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][$BF_4$]) + ethanol, [BMIM][$BF_4$] + benzene, and [BMIM][$BF_4$] + acetonitrile, over the miscible composition range at $T$ = (313.2 to 473.2) K were measured by means of a densimeter at elevated pressure up to 2.00 MPa. The total uncertainty of density was ± 0.0009 $g \cdot cm^{-3}$. The experimental densities were correlated by an empirical equation. The total average relative deviation (ARD) was 0.08 %, and then the excess molar volumes, $V^E$, were calculated using the experimental densities. The uncertainty of the excess molar volumes was estimated to be about ± 0.008 $cm^3 \cdot mol^{-1}$.

## Introduction

Room-temperature ionic liquids (RTILs) are a class of organic salts that are comprised entirely of ions at conditions around room temperature in their pure state. They are nonvolatile, thermally stable, and highly polar and are attracting growing interest as alternatives to conventional molecular liquids.[1−6] There are many studies on physical properties of the mixture system of ionic liquids with organic molecular compounds at atmospheric pressure and room temperature. However, studies at high temperature and elevated pressure are very limited. The density of pure [BMIM][$BF_4$] has been measured by Tomida et al.,[7] and the property of [BMIM][$BF_4$] has been researched in other studies.[8−10] In this paper, we determined the experimental density for the binary systems [BMIM][$BF_4$] + acetonitrile over the entire composition range and [BMIM][$BF_4$] + benzene and [BMIM][$BF_4$] + ethanol binary systems in the single-phase region at (313.2 to 473.2) K and pressure up to 2.00 MPa. In addition, the excess molar volumes, $V^E$, of these mixtures were calculated and discussed.

## Experimental Section

***Materials.*** [BMIM][$BF_4$] was purchased from Henan Lihua Pharmaceutical Co. Ltd. whose purity was more than 98 %, and the water mass fraction was less than 0.001. The other chemicals, acetonitrile, benzene, and ethanol, in the study were all supplied by Tianjin Reagent Co. with purity higher than 99.9 %, 99.5 %, and 99.7 %, respectively, and used without further purification. In this study, the mixtures of organic solvents with ionic liquid were gravimetrically prepared using an electronic balance (BS224 S, Beijing Sartorius Instrument System Co. Ltd.) with a standard uncertainty of 0.1 mg. The uncertainty in the mole fraction was less than 0.0001. The mixtures were then degassed in an ultrasonic cleaner (KQ3200DB, Kunshan Ultrasonic Instrument Co. Ltd.) at $T$ = 303 K for at least 30 min, then cooled to room temperature prior to use. During the experiments, the purity of the solvents was monitored by density measurements.

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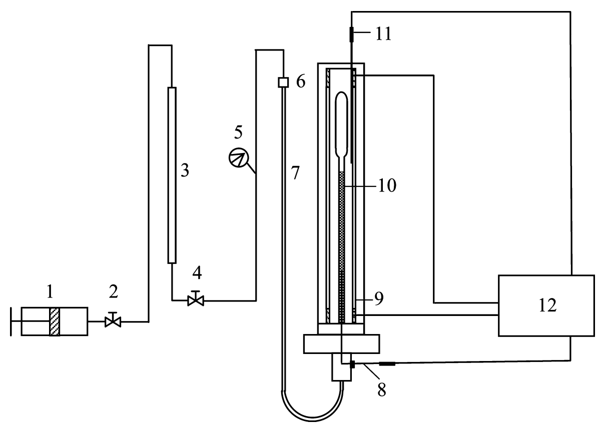


**Figure 1.** Schematic diagram of the experimental apparatus. 1, piston gauge; 2, stop valve; 3, oil−water separator; 4, pintle valve; 5, precision pressure gauge; 6, sample inlet; 7, U-shape stainless steel tube; 8, 11, thermocouple; 9, electric heater with red copper; 10, thick-walled glass capillary; 12, thermostat.

***Apparatus and Procedure.*** The experimental apparatus which was designed and manufactured to work at pressures ranging from (0.10 to 2.00) MPa and temperature ranging from (313.2 to 473.2) K was shown in Figure 1. A thick-walled glass capillary with dilation at one end in the core of the apparatus was used as the measuring tube with its advantages of resistance to pressure and ease of observation. The capillary which was about 40 cm in length with an inner diameter of (3.833 ± 0.001) mm was placed in the middle of a red copper tube with an electric heater. Considering the dilatability of glass, the coefficient of dilatation was $7.5 \cdot 10^{-6}$/K. The red copper tube has two narrow slots on both sides, through which the capillary can be seen. To maintain the temperature, a glass tube with insulation material was fixed on the outside of the red copper. The measuring system was kept vertical during the experiment. A thermocouple with a 1 mm diameter that passed through the bottom of the capillary was used to measure the temperature, and a thermocouple with a 2.5 mm diameter placed between the capillary and red copper was used to control the temperature. The temperature of the system was controlled by an XMTA-808 temperature controller (Yuyao Changjiang Merer Co. Ltd.,

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**Table 1. Comparison of the Measured Density of Doubly Distilled Water with the Literature Data**[a]

| $p$ | $T$ | $\rho_{exp}$ | $\rho_{lit}$ | $p$ | $T$ | $\rho_{exp}$ | $\rho_{lit}$ |
|---|---|---|---|---|---|---|---|
| MPa | K | $g\cdot cm^{-3}$ | $g\cdot cm^{-3}$ | MPa | K | $g\cdot cm^{-3}$ | $g\cdot cm^{-3}$ |
| 0.20 | 313.2 | 0.9930 | 0.99226 | 1.20 | 313.2 | 0.9935 | 0.99270 |
| | 353.2 | 0.9724 | 0.97166 | | 373.2 | 0.9597 | 0.95886 |
| | 393.2 | 0.9441 | 0.94341 | | 433.2 | 0.9085 | 0.90780 |
| 0.40 | 313.2 | 0.9931 | 0.99235 | 1.60 | 313.2 | 0.9936 | 0.99287 |
| | 353.2 | 0.9726 | 0.97173 | | 393.2 | 0.9446 | 0.94381 |
| | 393.2 | 0.9443 | 0.94353 | | 473.2 | 0.8654 | 0.86469 |
| 0.80 | 313.2 | 0.9933 | 0.99252 | 2.00 | 313.2 | 0.9938 | 0.99305 |
| | 373.2 | 0.9595 | 0.95868 | | 393.2 | 0.9448 | 0.94401 |
| | 433.2 | 0.9081 | 0.90756 | | 473.2 | 0.8657 | 0.86500 |

[a] Considering dilatability of glass, ultrapure water was used instead of distilled water, and the water densities were calibrated again.

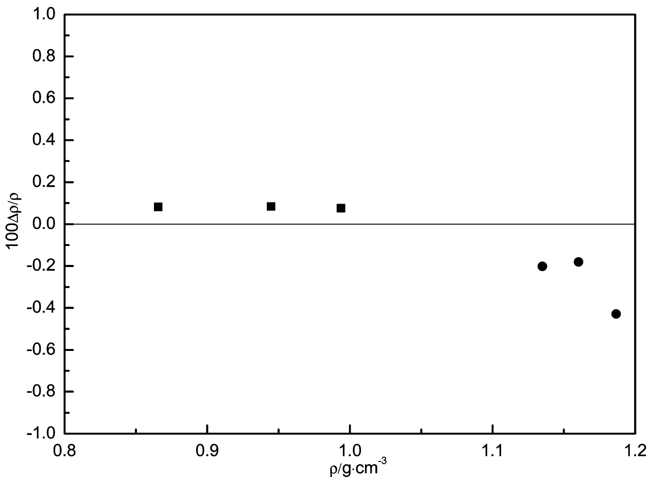


**Figure 2.** Deviation of experimental density with literature data at 2.00 MPa. ■, water; ●, [BMIM][$BF_4$].

China). The controller and its K thermocouple and the Pt-100 platinum resistance thermometer (Hufeng Electro Thermal Appliances Co. Ltd. Shanghai, China) were all calibrated by the Tianjin Measure Institution. The two thermocouples were connected to the thermostat. Mercury was used to transmit pressure and separate the sample and water. A YU-600A piston pressure gauge (the Forth Shanghai Automation Instrumentation Plant, China) was used to keep the pressure of the system, and a YB-150A precision pressure gauge (Tianlin Pressure Gauge Plant, Shanghai, China) was used to read the pressure. The uncertainty of the temperature control and measurement was ± 0.1 K, and the uncertainty of the pressure gauge was ± 0.01 MPa. The total uncertainty on density was estimated to be ± 0.0009 $g\cdot cm^{-3}$.

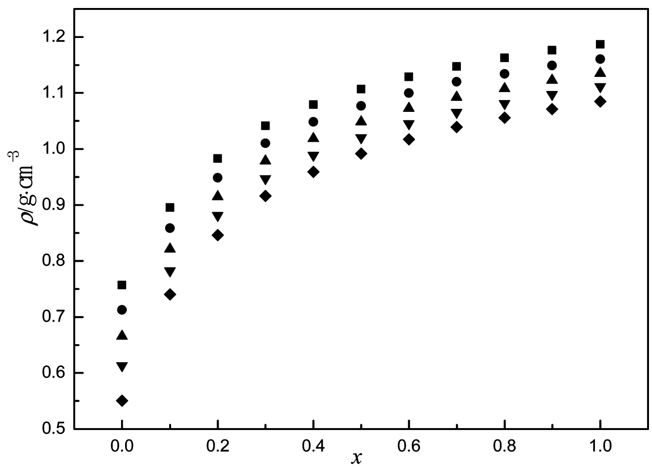


**Figure 3.** Density for [BMIM][$BF_4$]($x$) and acetonitrile($1-x$) at 2.00 MPa. $T$/K: ■, 313.2 K; ●, 353.2 K; ▲, 393.2 K; ▼, 433.2 K; ◆, 473.2 K.

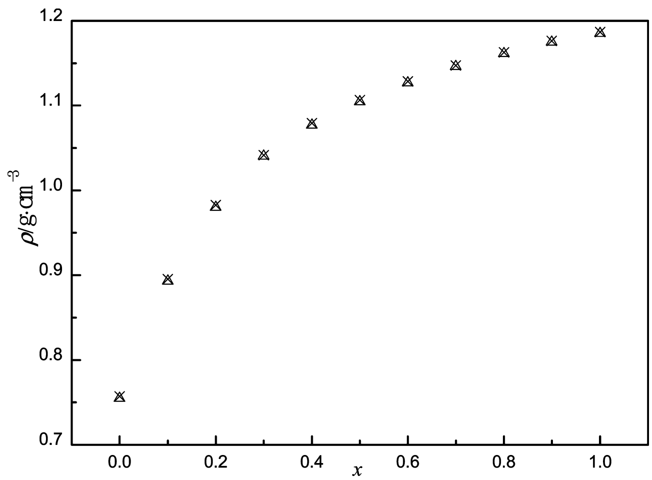


**Figure 4.** Density for [BMIM][$BF_4$]($x$) and acetonitrile($1-x$) at 313.2 K. $p$/MPa: Δ, 0.20 MPa; ×, 2.00 MPa.

During prepared and feed sample, water should be avoided in the air. The initial density was measured by a gravity cup (8.32 mL) at room temperature and atmospheric pressure. Then the sample was fed into the capillary and the temperature adjusted. The system pressure was changed by the piston pressure gauge when the temperature was stable. While the temperature and pressure were both stable, a cathetometer (Wuhan Optical Instrument Company, China) was used to measure the change of the interface with an uncertainty of ± 0.002 cm. Then the temperature or pressure was changed, and the steps were repeated to finish the measure of the samples.

**Table 2. Comparison of Experimental and Literature Values of Densities $\rho$ for Pure Compounds**[a]

| | | $p$ = 0.10 MPa | | | $p$ = 1.00 MPa | | $p$ = 2.00 MPa | |
|---|---|---|---|---|---|---|---|---|
| compound | $T$/K | $\rho_{exp}/g\cdot cm^{-3}$ | $\rho_{lit}/g\cdot cm^{-3}$ | $T$/K | $\rho_{exp}/g\cdot cm^{-3}$ | $\rho_{lit}/g\cdot cm^{-3}$ | $\rho_{exp}/g\cdot cm^{-3}$ | $\rho_{lit}/g\cdot cm^{-3}$ |
| $BMIMBF_4$ | 293.2 | 1.1983 | 1.2069[14] | 313.2 | 1.1860 | 1.1913[14] | 1.1867 | 1.1918[14] |
| | | | 1.191[13] | 353.2 | 1.1595 | 1.1618[14] | 1.1603 | 1.1624[14] |
| | 313.2 | 1.1832 | 1.196[7] | 393.2 | 1.1337 | 1.1367[14] | 1.1350 | 1.1373[14] |
| | | | 1.19459[12] | | | | | |
| | | | 1.1908[14] | | | | | |
| | | | 1.18143[18] | | | | | |
| ethanol | 298.2 | 0.7868 | 0.7851[15] | | | | | |
| benzene | 298.2 | 0.8755 | 0.87356[16] | | | | | |
| | | | 0.87311[18] | | | | | |
| acetonitrile | 298.2 | 0.7752 | 0.776[17] | | | | | |
| | | | 0.77693[18] | | | | | |

[a] References 7 and 12 to 14 reported that the water mass fraction of $BMIMBF_4$ was less than $330\cdot10^{-6}$, $70\cdot10^{-6}$, $250\cdot10^{-6}$, and $485\cdot10^{-6}$, respectively.

**Table 3. Experimental Densities $\rho$ for [BMIM][BF$_4$]($x$) + Ethanol(1 − $x$) Binary Mixtures**

| $T$/K | $x$ = 0.0000 | 0.2000 | 0.3000 | 0.3999 | 0.4998 | 0.6000 | 0.6996 | 0.8001 | 0.8998 | 1.0000 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\rho$/g·cm$^{-3}$ | | | | | |
| | | | | | $p$ = 0.20 MPa | | | | | |
| 313.2 | 0.7695 | 0.9648 | 1.0223 | 1.0713 | 1.0976 | 1.1209 | 1.1418 | 1.1576 | 1.1731 | 1.1852 |
| 353.2 | 0.7335 | 0.9341 | 0.9922 | 1.0411 | 1.0693 | 1.0931 | 1.1248 | 1.1309 | 1.1460 | 1.1587 |
| | | | | | $p$ = 0.60 MPa | | | | | |
| 313.2 | 0.7697 | 0.9654 | 1.0225 | 1.0715 | 1.0979 | 1.1214 | 1.1422 | 1.1578 | 1.1735 | 1.1856 |
| 353.2 | 0.7342 | 0.9346 | 0.9926 | 1.0418 | 1.0700 | 1.0934 | 1.1252 | 1.1315 | 1.1463 | 1.1590 |
| 393.2 | 0.6906 | 0.9028 | 0.9633 | 1.0130 | 1.0416 | 1.0661 | 1.0970 | 1.1053 | 1.1207 | 1.1337 |
| | | | | | $p$ = 1.00 MPa | | | | | |
| 313.2 | 0.7703 | 0.9658 | 1.0229 | 1.0716 | 1.0980 | 1.1221 | 1.1429 | 1.1585 | 1.1736 | 1.1860 |
| 353.2 | 0.7348 | 0.9350 | 0.9929 | 1.0422 | 1.0704 | 1.0940 | 1.1258 | 1.1318 | 1.1465 | 1.1595 |
| 393.2 | 0.6915 | 0.9032 | 0.9639 | 1.0135 | 1.0420 | 1.0668 | 1.0977 | 1.1055 | 1.1210 | 1.1341 |
| | | | | | $p$ = 1.40 MPa | | | | | |
| 313.2 | 0.7709 | 0.9661 | 1.0235 | 1.0719 | 1.0984 | 1.1224 | 1.1434 | 1.1588 | 1.1737 | 1.1863 |
| 353.2 | 0.7354 | 0.9353 | 0.9934 | 1.0425 | 1.0706 | 1.0947 | 1.1265 | 1.1321 | 1.1468 | 1.1597 |
| 393.2 | 0.6921 | 0.9038 | 0.9642 | 1.0138 | 1.0423 | 1.0672 | 1.0981 | 1.1059 | 1.1213 | 1.1343 |
| 433.2 | 0.6367 | 0.8703 | 0.9336 | 0.9854 | 1.0151 | 1.0407 | 1.0643 | 1.0799 | 1.0958 | 1.1112 |
| | | | | | $p$ = 1.80 MPa | | | | | |
| 313.2 | 0.7713 | 0.9669 | 1.0238 | 1.0725 | 1.0991 | 1.1227 | 1.1438 | 1.1594 | 1.1742 | 1.1866 |
| 353.2 | 0.7362 | 0.9360 | 0.9938 | 1.0428 | 1.0709 | 1.0949 | 1.1267 | 1.1325 | 1.1472 | 1.1600 |
| 393.2 | 0.6931 | 0.9043 | 0.9645 | 1.0141 | 1.0429 | 1.0677 | 1.0986 | 1.1065 | 1.1217 | 1.1346 |
| 433.2 | 0.6381 | 0.8707 | 0.9339 | 0.9858 | 1.0159 | 1.0409 | 1.0644 | 1.0803 | 1.0961 | 1.1113 |
| | | | | | $p$ = 2.00 MPa | | | | | |
| 313.2 | 0.7717 | 0.9673 | 1.0241 | 1.0729 | 1.1016 | 1.1230 | 1.1443 | 1.1596 | 1.1746 | 1.1867 |
| 353.2 | 0.7380 | 0.9362 | 0.9940 | 1.0429 | 1.0710 | 1.0951 | 1.1269 | 1.1327 | 1.1475 | 1.1603 |
| 393.2 | 0.6934 | 0.9045 | 0.9649 | 1.0145 | 1.0431 | 1.0679 | 1.0988 | 1.1067 | 1.1218 | 1.1350 |
| 433.2 | 0.6384 | 0.8710 | 0.9342 | 0.9860 | 1.0161 | 1.0412 | 1.0646 | 1.0806 | 1.0963 | 1.1117 |

**Table 4. Experimental Densities $\rho$ for [BMIM][BF$_4$]($x$) + Benzene(1−$x$) Binary Mixtures**

| $T$/K | $x$ = 0.5000 | 0.5999 | 0.7001 | 0.8000 | 0.8999 | 1.0000 |
|---|---|---|---|---|---|---|
| | | | $\rho$/g·cm$^{-3}$ | | | |
| | | | $p$ = 0.20 MPa | | | |
| 313.2 | 1.1104 | 1.1289 | 1.1447 | 1.1576 | 1.1717 | 1.1852 |
| 353.2 | 1.0815 | 1.1017 | 1.1170 | 1.1302 | 1.1446 | 1.1587 |
| | | | $p$ = 0.60 MPa | | | |
| 313.2 | 1.1106 | 1.1298 | 1.1451 | 1.1578 | 1.1720 | 1.1856 |
| 353.2 | 1.0818 | 1.1021 | 1.1173 | 1.1308 | 1.1447 | 1.1590 |
| 393.2 | 1.0540 | 1.0754 | 1.0909 | 1.1046 | 1.1189 | 1.1337 |
| | | | $p$ = 1.00 MPa | | | |
| 313.2 | 1.1107 | 1.1303 | 1.1455 | 1.1581 | 1.1725 | 1.1860 |
| 353.2 | 1.0823 | 1.1022 | 1.1176 | 1.1309 | 1.1449 | 1.1595 |
| 393.2 | 1.0540 | 1.0756 | 1.0910 | 1.1047 | 1.1190 | 1.1341 |
| | | | $p$ = 1.40 MPa | | | |
| 313.2 | 1.1109 | 1.1305 | 1.1460 | 1.1583 | 1.1727 | 1.1863 |
| 353.2 | 1.0827 | 1.1029 | 1.1179 | 1.1311 | 1.1453 | 1.1597 |
| 393.2 | 1.0542 | 1.0762 | 1.0913 | 1.1049 | 1.1194 | 1.1343 |
| 433.2 | 1.0271 | 1.0488 | 1.0650 | 1.0790 | 1.0945 | 1.1112 |
| | | | $p$ = 1.80 MPa | | | |
| 313.2 | 1.1112 | 1.1312 | 1.1466 | 1.1586 | 1.1728 | 1.1866 |
| 353.2 | 1.0831 | 1.1032 | 1.1181 | 1.1315 | 1.1456 | 1.1600 |
| 393.2 | 1.0551 | 1.0766 | 1.0915 | 1.1050 | 1.1199 | 1.1346 |
| 433.2 | 1.0275 | 1.0492 | 1.0654 | 1.0793 | 1.0948 | 1.1113 |
| | | | $p$ = 2.00 MPa | | | |
| 313.2 | 1.1113 | 1.1315 | 1.1467 | 1.1590 | 1.1730 | 1.1867 |
| 353.2 | 1.0833 | 1.1035 | 1.1183 | 1.1316 | 1.1457 | 1.1603 |
| 393.2 | 1.0553 | 1.0768 | 1.0918 | 1.1052 | 1.1201 | 1.1350 |
| 433.2 | 1.0278 | 1.0496 | 1.0657 | 1.0797 | 1.0951 | 1.1117 |

The reliability of the apparatus was checked by measuring densities of ultrapure water. The results were shown in Table 1 compared with the values given in the literature.[11] The checking results verify the reliability of this apparatus.

Densities of pure ionic liquid [BMIM][$BF_4$] and organic solvents were listed in Table 2 together with the corresponding literature values.[7,12−18] The deviation of experimental density with literature data was shown in Figure 2. The results verified the reliability of the apparatus. There was an appreciable difference for the density data among the various literature for [BMIM][$BF_4$] because of the different water content.

## Results and Discussion

The experimental densities for [BMIM][$BF_4$] (1) + ethanol (2), [BMIM][$BF_4$] (1) + benzene (2), and [BMIM][$BF_4$] (1) + acetonitrile (2) binary mixtures are presented in Tables 3 to 5. The values show that for all the systems when the mole fraction is constant the densities of the mixtures decrease with the increase of system temperature. This result is obvious for other mixtures.[18−20] At constant pressure or temperature, the densities increased obviously with the increase in [BMIM][$BF_4$] mole fraction. The $\rho-x$ curves were shown in Figure 3 and Figure 4.

The experimental densities were fitted using the following empirical eq 1

$$\rho/\mathrm{g{\cdot}cm^{-3}} = A + B(T/\mathrm{K}) + C(p/\mathrm{MPa}) \qquad (1)$$

In the formulas, $\rho$, $T$, and $p$ are experimental density, temperature, and pressure, respectively; $A$, $B$, and $C$ are the function of $x$. The correlation results and the average relative deviations are show in Table 6.

The values of average relative deviations ARD between the calculated and experimental datum points are obtained using the equation as follows

$$\mathrm{ARD} = \frac{1}{n}\sum\frac{\rho_{\mathrm{cal}} - \rho}{\rho} \qquad (2)$$

where $\rho_{\mathrm{cal}}$ is the calculated value; $\rho$ is the experimental value; and $n$ is the number of data points.

In the literature,[21−23] the experimental density was fitted by one parameter $T$, and the results show that $\rho-T$ curves are almost linear. In this paper, pressure was also fitted as a parameter. The average relative deviations for ([BMIM][$BF_4$]) + ethanol, [BMIM][$BF_4$] + benzene, and [BMIM][$BF_4$] + acetonitrile were 0.12 %, 0.04 %, 0.09 %, respectively. The

**Table 5. Experimental Densities $\rho$ for [BMIM][$BF_4$]($x$) + Acetonitrile($1-x$) Binary Mixtures**

| | $x$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$/K | 0.0000 | 0.1000 | 0.2000 | 0.3000 | 0.4000 | 0.5000 | 0.6000 | 0.6999 | 0.7998 | 0.8993 | 1.0000 |
| | $\rho$/g·cm$^{-3}$ | | | | | | | | | | |
| | $p$ = 0.20 MPa | | | | | | | | | | |
| 313.2 | 0.7548 | 0.8931 | 0.9800 | 1.0403 | 1.0770 | 1.1046 | 1.1268 | 1.1462 | 1.1612 | 1.1747 | 1.1852 |
| 353.2 | 0.7097 | 0.8567 | 0.9464 | 1.0078 | 1.0466 | 1.0756 | 1.0978 | 1.1177 | 1.1330 | 1.1475 | 1.1587 |
| | $p$ = 0.60 MPa | | | | | | | | | | |
| 313.2 | 0.7553 | 0.8939 | 0.9809 | 1.0408 | 1.0774 | 1.1054 | 1.1270 | 1.1464 | 1.1616 | 1.1748 | 1.1856 |
| 353.2 | 0.7103 | 0.8572 | 0.9471 | 1.0083 | 1.0469 | 1.0759 | 1.0981 | 1.1181 | 1.1332 | 1.1475 | 1.1590 |
| 393.2 | 0.6629 | 0.8197 | 0.9135 | 0.9773 | 1.0170 | 1.0467 | 1.0710 | 1.0907 | 1.1067 | 1.1216 | 1.1337 |
| | $p$ = 1.00 MPa | | | | | | | | | | |
| 313.2 | 0.7560 | 0.8945 | 0.9814 | 1.0410 | 1.0780 | 1.1056 | 1.1275 | 1.1467 | 1.1618 | 1.1751 | 1.1860 |
| 353.2 | 0.7105 | 0.8575 | 0.9476 | 1.0089 | 1.0473 | 1.0763 | 1.0987 | 1.1184 | 1.1334 | 1.1479 | 1.1595 |
| 393.2 | 0.6636 | 0.8203 | 0.9138 | 0.9775 | 1.0174 | 1.0470 | 1.0714 | 1.0912 | 1.1070 | 1.1217 | 1.1341 |
| 433.2 | 0.6102 | 0.7804 | 0.8802 | 0.9461 | 0.9879 | 1.0194 | 1.0441 | 1.0646 | 1.0805 | 1.0965 | 1.1111 |
| | $p$ = 1.40 MPa | | | | | | | | | | |
| 313.2 | 0.7562 | 0.8949 | 0.9819 | 1.0412 | 1.0784 | 1.1060 | 1.1279 | 1.1469 | 1.1620 | 1.1753 | 1.1863 |
| 353.2 | 0.7111 | 0.8579 | 0.9479 | 1.0093 | 1.0477 | 1.0765 | 1.0993 | 1.1187 | 1.1336 | 1.1483 | 1.1597 |
| 393.2 | 0.6646 | 0.8207 | 0.9142 | 0.9781 | 1.0178 | 1.0476 | 1.0717 | 1.0915 | 1.1071 | 1.1219 | 1.1343 |
| 433.2 | 0.6112 | 0.7814 | 0.8806 | 0.9466 | 0.9884 | 1.0196 | 1.0442 | 1.0649 | 1.0807 | 1.0967 | 1.1112 |
| | $p$ = 1.80 MPa | | | | | | | | | | |
| 313.2 | 0.7568 | 0.8953 | 0.9824 | 1.0413 | 1.0790 | 1.1063 | 1.1283 | 1.1471 | 1.1625 | 1.1754 | 1.1866 |
| 353.2 | 0.7119 | 0.8583 | 0.9485 | 1.0097 | 1.0481 | 1.0768 | 1.0997 | 1.1195 | 1.1339 | 1.1486 | 1.1600 |
| 393.2 | 0.6653 | 0.8209 | 0.9145 | 0.9783 | 1.0182 | 1.0478 | 1.0721 | 1.0918 | 1.1073 | 1.1221 | 1.1346 |
| 433.2 | 0.6128 | 0.7822 | 0.8810 | 0.9470 | 0.9888 | 1.0198 | 1.0448 | 1.0653 | 1.0813 | 1.0970 | 1.1113 |
| 473.2 | 0.5492 | 0.7402 | 0.8456 | 0.9157 | 0.9587 | 0.9911 | 1.0167 | 1.0388 | 1.0556 | 1.0708 | 1.0847 |
| | $p$ = 2.00 MPa | | | | | | | | | | |
| 313.2 | 0.7570 | 0.8955 | 0.9828 | 1.0415 | 1.0792 | 1.1066 | 1.1286 | 1.1474 | 1.1627 | 1.1762 | 1.1867 |
| 353.2 | 0.7125 | 0.8585 | 0.9487 | 1.0099 | 1.0483 | 1.0770 | 1.0999 | 1.1198 | 1.1342 | 1.1488 | 1.1603 |
| 393.2 | 0.6658 | 0.8210 | 0.9149 | 0.9785 | 1.0184 | 1.0482 | 1.0723 | 1.0922 | 1.1076 | 1.1228 | 1.1350 |
| 433.2 | 0.6135 | 0.7825 | 0.8812 | 0.9474 | 0.9890 | 1.0200 | 1.0452 | 1.0655 | 1.0815 | 1.0974 | 1.1117 |
| 473.2 | 0.5507 | 0.7405 | 0.8462 | 0.9160 | 0.9590 | 0.9916 | 1.0170 | 1.0391 | 1.0558 | 1.0710 | 1.0849 |

**Table 6. Parameters of the Equation 1 and Average Relative Deviations**

| $A$ | $10^4B$ | $10^4C$ | 100ARD |
|---|---|---|---|
| | [BMIM][$BF_4$]($x$) + Ethanol($1-x$) | | |
| $0.184x^3 - 0.550x^2 + 0.637x + 1.111$ | $11.24x^3 - 23.54x^2 + 16.74x - 10.71$ | $66.14x^3 - 109.6x^2 + 49.69x + 4.563$ | 0.12 |
| | [BMIM][$BF_4$]($x$) + Benzene($1-x$) | | |
| $0.080x^3 - 0.260x^2 + 0.356x + 1.205$ | $9.903x^3 - 21.90x^2 + 16.89x - 11.21$ | $17.60x^3 - 21.04x^2 + 0.046x + 13.51$ | 0.04 |
| | [BMIM][$BF_4$]($x$) + Acetonitrile($1-x$) | | |
| $0.309x^3 - 0.761x^2 + 0.706x + 1.131$ | $15.53x^3 - 30.88x^2 + 20.86x - 11.70$ | $3.466x^3 - 11.52x^2 + 7.090x + 9.487$ | 0.09 |

**Table 7. Excess Molar Volume $V^E$ for [BMIM][$BF_4$]($x$) + Ethanol($1-x$) Binary Mixtures**

| | $x$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $T$/K | 0.2000 | 0.3000 | 0.3999 | 0.4998 | 0.6000 | 0.6996 | 0.8001 | 0.8998 |
| | | | | $V^E$/cm$^3$·mol$^{-1}$ | | | | |
| | | | | $p$ = 0.20 MPa | | | | |
| 313.2 | −0.982 | −1.248 | −2.013 | −1.345 | −0.949 | −0.800 | −0.386 | −0.306 |
| 353.2 | −1.409 | −1.647 | −2.327 | −1.718 | −1.245 | −2.456 | −0.569 | −0.313 |
| | | | | $p$ = 0.60 MPa | | | | |
| 313.2 | −1.010 | −1.235 | −1.994 | −1.335 | −0.960 | −0.799 | −0.351 | −0.291 |
| 353.2 | −1.398 | −1.627 | −2.337 | −1.742 | −1.227 | −2.442 | −0.602 | −0.309 |
| 393.2 | −2.347 | −2.642 | −3.238 | −2.438 | −1.814 | −2.752 | −0.895 | −0.478 |
| | | | | $p$ = 1.00 MPa | | | | |
| 313.2 | −0.999 | −1.223 | −1.958 | −1.300 | −0.990 | −0.835 | −0.387 | −0.251 |
| 353.2 | −1.378 | −1.596 | −2.321 | −1.724 | −1.234 | −2.453 | −0.583 | −0.261 |
| 393.2 | −2.300 | −2.623 | −3.216 | −2.404 | −1.827 | −2.776 | −0.861 | −0.464 |
| | | | | $p$ = 1.40 MPa | | | | |
| 313.2 | −0.975 | −1.230 | −1.943 | −1.297 | −0.980 | −0.852 | −0.375 | −0.211 |
| 353.2 | −1.356 | −1.602 | −2.313 | −1.701 | −1.286 | −2.515 | −0.588 | −0.294 |
| 393.2 | −2.307 | −2.608 | −3.202 | −2.397 | −1.844 | −2.800 | −0.880 | −0.466 |
| 433.2 | −4.272 | −4.495 | −4.983 | −3.869 | −2.968 | −2.462 | −1.224 | −0.475 |
| | | | | $p$ = 1.80 MPa | | | | |
| 313.2 | −1.011 | −1.221 | −1.958 | −1.333 | −0.975 | −0.848 | −0.414 | −0.239 |
| 353.2 | −1.359 | −1.582 | −2.285 | −1.679 | −1.250 | −2.483 | −0.593 | −0.289 |
| 393.2 | −2.272 | −2.560 | −3.168 | −2.393 | −1.841 | −2.808 | −0.919 | −0.480 |
| 433.2 | −4.183 | −4.417 | −4.929 | −3.887 | −2.924 | −2.422 | −1.242 | −0.489 |
| | | | | $p$ = 2.00 MPa | | | | |
| 313.2 | −1.022 | −1.226 | −1.979 | −1.584 | −0.987 | −0.896 | −0.429 | −0.273 |
| 353.2 | −1.251 | −1.480 | −2.187 | −1.593 | −1.189 | −2.434 | −0.551 | −0.282 |
| 393.2 | −2.255 | −2.558 | −3.158 | −2.373 | −1.815 | −2.780 | −0.883 | −0.435 |
| 433.2 | −4.180 | −4.407 | −4.901 | −3.857 | −2.916 | −2.394 | −1.227 | −0.458 |

**Table 8. Excess Molar Volume $V^E$ for [BMIM][$BF_4$]($x$) + Benzene($1-x$) Binary Mixtures**

| | $x$ | | | | |
|---|---|---|---|---|---|
| $T$/K | 0.5000 | 0.5999 | 0.7001 | 0.8000 | 0.8999 |
| | | | $V^E$/cm$^3$·mol$^{-1}$ | | |
| | | | $p$ = 0.20 MPa | | |
| 313.2 | −4.220 | −3.269 | −2.294 | −1.199 | −0.531 |
| 353.2 | −5.130 | −4.150 | −2.843 | −1.530 | −0.662 |
| | | | $p$ = 0.60 MPa | | |
| 313.2 | −4.159 | −3.310 | −2.278 | −1.146 | −0.503 |
| 353.2 | −5.127 | −4.155 | −2.838 | −1.568 | −0.615 |
| 393.2 | −6.420 | −5.279 | −3.648 | −2.059 | −0.847 |
| | | | $p$ = 1.00 MPa | | |
| 313.2 | −4.120 | −3.326 | −2.278 | −1.148 | −0.515 |
| 353.2 | −5.074 | −4.061 | −2.779 | −1.486 | −0.564 |
| 393.2 | −6.328 | −5.208 | −3.574 | −1.993 | −0.790 |
| | | | $p$ = 1.40 MPa | | |
| 313.2 | −4.075 | −3.283 | −2.281 | −1.111 | −0.485 |
| 353.2 | −5.098 | −4.133 | −2.799 | −1.489 | −0.606 |
| 393.2 | −6.274 | −5.235 | −3.568 | −1.969 | −0.811 |
| 433.2 | −8.011 | −6.448 | −4.434 | −2.415 | −0.951 |
| | | | $p$ = 1.80 MPa | | |
| 313.2 | −4.068 | −3.325 | −2.313 | −1.103 | −0.462 |
| 353.2 | −5.078 | −4.107 | −2.754 | −1.490 | −0.585 |
| 393.2 | −6.305 | −5.201 | −3.522 | −1.928 | −0.842 |
| 433.2 | −8.000 | −6.439 | −4.446 | −2.420 | −0.980 |
| | | | $p$ = 2.00 MPa | | |
| 313.2 | −4.049 | −3.339 | −2.304 | −1.133 | −0.466 |
| 353.2 | −5.050 | −4.099 | −2.734 | −1.457 | −0.560 |
| 393.2 | −6.267 | −5.168 | −3.499 | −1.891 | −0.804 |
| 433.2 | −7.971 | −6.430 | −4.432 | −2.422 | −0.959 |

total average relative deviations were 0.08 %, which was not reported at in previous literature.

The excess molar volume, $V^E$, is calculated from the density measurement according to eq 3

$$V^E = \frac{xM_1 + (1-x)M_2}{\rho} - \frac{xM_1}{\rho_1} - \frac{(1-x)M_2}{\rho_2} \tag{3}$$

where $x$ stands for the mole fraction of [BMIM][$BF_4$]; $M_1$ and

**Table 9. Excess Molar Volume $V^E$ for [BMIM][BF$_4$]($x$) + Acetonitrile(1−$x$) Binary Mixtures**

| | $x$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$/K | 0.1000 | 0.2000 | 0.3000 | 0.4000 | 0.5000 | 0.6000 | 0.6999 | 0.7998 | 0.8993 |
| | | | | $V^E$/cm$^3$·mol$^{-1}$ | | | | | |
| | | | | $p$ = 0.20 MPa | | | | | |
| 313.2 | −1.344 | −2.008 | −2.482 | −2.097 | −1.658 | −1.251 | −1.033 | −0.661 | −0.431 |
| 353.2 | −2.052 | −2.825 | −3.210 | −2.815 | −2.307 | −1.691 | −1.327 | −0.788 | −0.510 |
| | | | | $p$ = 0.60 MPa | | | | | |
| 313.2 | −1.364 | −2.049 | −2.481 | −2.094 | −1.687 | −1.229 | −1.005 | −0.652 | −0.385 |
| 353.2 | −2.050 | −2.828 | −3.213 | −2.799 | −2.280 | −1.677 | −1.335 | −0.761 | −0.462 |
| 393.2 | −3.024 | −3.971 | −4.367 | −3.776 | −3.057 | −2.429 | −1.780 | −1.069 | −0.616 |
| | | | | $p$ = 1.00 MPa | | | | | |
| 313.2 | −1.357 | −2.031 | −2.448 | −2.099 | −1.664 | −1.226 | −0.981 | −0.631 | −0.374 |
| 353.2 | −2.048 | −2.843 | −3.229 | −2.793 | −2.278 | −1.696 | −1.312 | −0.728 | −0.440 |
| 393.2 | −3.008 | −3.944 | −4.326 | −3.759 | −3.041 | −2.423 | −1.786 | −1.054 | −0.567 |
| 433.2 | −4.592 | −5.843 | −6.078 | −5.283 | −4.357 | −3.349 | −2.400 | −1.253 | −0.570 |
| | | | | $p$ = 1.40 MPa | | | | | |
| 313.2 | −1.369 | −2.048 | −2.435 | −2.110 | −1.672 | −1.236 | −0.968 | −0.610 | −0.344 |
| 353.2 | −2.030 | −2.831 | −3.225 | −2.793 | −2.266 | −1.728 | −1.323 | −0.726 | −0.473 |
| 393.2 | −2.962 | −3.897 | −4.308 | −3.734 | −3.041 | −2.396 | −1.780 | −1.024 | −0.544 |
| 433.2 | −4.587 | −5.783 | −6.050 | −5.278 | −4.320 | −3.320 | −2.402 | −1.262 | −0.586 |
| | | | | $p$ = 1.80 MPa | | | | | |
| 313.2 | −1.352 | −2.045 | −2.395 | −2.115 | −1.648 | −1.235 | −0.940 | −0.624 | −0.311 |
| 353.2 | −2.005 | −2.820 | −3.204 | −2.774 | −2.247 | −1.726 | −1.371 | −0.709 | −0.468 |
| 393.2 | −2.907 | −3.864 | −4.264 | −3.716 | −3.012 | −2.390 | −1.769 | −1.005 | −0.538 |
| 433.2 | −4.498 | −5.684 | −5.958 | −5.211 | −4.250 | −3.308 | −2.394 | −1.296 | −0.598 |
| 473.2 | −7.664 | −9.180 | −9.404 | −8.201 | −6.830 | −5.386 | −4.135 | −2.586 | −1.228 |
| | | | | $p$ = 2.00 MPa | | | | | |
| 313.2 | −1.350 | −2.060 | −2.402 | −2.121 | −1.662 | −1.253 | −0.962 | −0.635 | −0.413 |
| 353.2 | −1.978 | −2.794 | −3.176 | −2.753 | −2.220 | −1.707 | −1.367 | −0.702 | −0.457 |
| 393.2 | −2.870 | −3.840 | −4.235 | −3.681 | −2.992 | −2.355 | −1.753 | −0.978 | −0.579 |
| 433.2 | −4.453 | −5.631 | −5.936 | −5.161 | −4.203 | −3.292 | −2.346 | −1.257 | −0.585 |
| 473.2 | −7.506 | −9.076 | −9.285 | −8.096 | −6.777 | −5.318 | −4.081 | −2.546 | −1.223 |

$M_2$ are the molar masses of the [BMIM][BF$_4$] and the other organic liquids; and $\rho$, $\rho_1$, and $\rho_2$ are the densities of the mixture, [BMIM][BF$_4$], and the other organic liquids, respectively. The results of $V^E$ are given in Tables 7 to 9. The uncertainty of the excess molar volumes is estimated to be about ± 0.008 cm$^3$·mol$^{-1}$.

The excess molar volumes included in Tables 7 to 9 show that the $V^E$ values are negative over the entire composition range for the [BMIM][BF$_4$] (1) + acetonitrile (2) binary mixtures. The negative $V^E$ indicates that a more efficient packing and/or attractive interaction occurred when the ionic liquid and organic compounds were mixed. A minimum in $V^E$ occurs at a mole fraction of this ionic liquid near 0.4 for [BMIM][BF$_4$] (1) + ethanol (2) and 0.3 for [BMIM][BF$_4$] (1) + acetonitrile (2). It is immiscible for the [BMIM][BF$_4$] (1) + benzene (2) system with mole fraction of benzene ranging from 0.5 to 0.9. A mole fraction reaches 0.1 for [BMIM][BF$_4$] (1) + ethanol (2) when upper critical points (UCST) appear.[24] It is immiscible for [BMIM][BF$_4$] (1) + ethanol (2). The experimental $V^E$ values are shown in their miscible range.

## Conclusion

Densities of the binary systems of ionic liquid ([BMIM][BF$_4$]) and organic solvents (ethanol, benzene, or acetonitrile) were measured at temperature from (313.2 to 473.2) K and pressures up to 2.00 MPa. The equation for the fitting experimental densities was developed, and the excess molar volumes have been calculated. The values of correlation were all negative. The total ARD of the fitting was 0.08 %.

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