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Volumetric behavior of two pyridinium-based ionic liquids

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ABSTRACT

In this work the volumetric behavior in a broad range of temperatures (283.15 K–333.15 K) and pressures (0.1 MPa–65 MPa) of two pyridinium-based ionic liquids, namely: 1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide and 1-propyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide, is presented. The density–pressure–temperature data have been correlated successfully with two empirical equations: Tait and TRIDEN equations. Using these equations, relevant derived properties such as isobaric expansibility and isothermal compressibility have been obtained. Finally, the Paduszynski–Domanska group contribution method has been used to predict the volumetric behavior of our ionic liquids; a reasonable agreement between experiment and predicted data is found.

1. Introduction

In the last decade, ionic liquids have been paid more attention due to their unusual properties which can be used as an attractive alternative to common organic solvents. There are an enormous number of ionic liquids; it can be made by different cations and anions. The most studied are those compounds containing imidazolium rings [1], the reason is found in their great stability chemical and electrochemical. In the second place are ionic liquids derivate of pyridinium rings which show high thermal stability, lower cost and toxicity. Among the anions, tetrafluoroborate and hexafluorophosphate are the most common, although, bis(trifluoromethylsulfonyl)imide is one of the most robust anions and it presents lower viscosity and higher thermal and electrochemical stability [2–6].

The limitation of using ionic liquids is lack of knowledge about how the structure of the ionic liquid may affect its physicochemical properties. In this context, thermophysical properties are an useful tool for providing information about not only the structure but also the intermolecular interactions which are the basis for thermodynamic models that represent the behavior of the ionic liquids. The foregoing reasons have motivated us to study two pyridinium-based ionic liquids containing the bis(trifluoromethylsulfonyl)imide anion.

In a previous work [7] we have reported thermophysical properties at ambient pressure of 1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide ([e2mpy][Tf_2N]) and 1-propyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide([p2mpy][Tf_2N]), now we present densities of these ionic liquid measured in a temperature range from (283.15 to 333.15) K and in a pressure range from (0.1 to 65.0) MPa. Temperature and pressure dependence of density data have been properly correlated with the Tait [8] and TRIDEN [9] equations using their parameters and thermodynamic relations, the isobaric expansibility, and the isothermal compressibility have been calculated.

Due to the importance of the knowledge of density of ionic liquids, a great variety of models for the prediction of this fundamental property have been developed in the last years. Among these methods, those based on the group contribution procedure [10–17] present the main advantage of its simplicity. In this paper, we have checked the predictions of the method proposed by Paduszynski and Domanska [18].

2. Experimental

The ionic liquids, n-ethylpyridinium bis(trifluoromethylsulfonyl)imide, 1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide and 1-propyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide with purities better than 99% in mass fraction were obtained from IoLiTec. To reduce the water content as much as possible, the IL was dried under a vacuum of about 0.05 kPa during 24 h under stirring and stored before use in desiccator. The water content of sample was less than 300 ppm as determined

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Table 1
Sample table.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
1-Ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	IoLiTec	0.99	None	0.99	–
1-Propyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	IoLiTec	0.99	None	0.99	–

by Karl-Fischer titration. On the other hand, the halide content was checked by ^{19}F NMR, being the content less than 100 ppm. This information is summarized in Table 1. Measurements were performed in the temperature range of 283.15 K–333.15 K and in the pressure range of 0.1 MPa–65 MPa.

Densities, ρ, were measured using a high pressure, high temperature Anton Paar DMA HP cell connected to an evaluation unit Anton Paar DMA 5000. The cell temperature is controlled to $\pm 1{\cdot}10^{-3}$ K by means of an integrated Peltier thermostat. The required pressure was created by a hand pump 750.1100 from Sitec, Switzerland and measured by a pressure transducer US181 from Measuring Specialities, USA. The uncertainty in the pressure measurement is 5 kPa. A vacuum pump was employed for evacuating the whole apparatus. Hexane, water and dichloromethane were used to calibrate the densimeter in order to cover a wide range of densities. Besides, toluene was employed to check the calibration over a wide range of temperature and pressure. Details of the calibration procedure can be found in a previous paper [19]; additionally a curve of the correction of density, $\triangle\rho$, as a function of viscosity, η, was also obtained [20,21]:

$$\Delta\rho(\eta) = \frac{\eta^2}{q_1 + q_2\eta + q_3\eta^2} \quad (1)$$

the parameters q_i have been previously reported [21].

In order to obtain accurate density values of high-viscosity samples using vibrating tube densimeters it is necessary taking into account the corresponding viscosity-induced errors. The modern densimeters operating at atmospheric pressure correct the density values automatically however at high pressures this correction is not calculated. So, to determine densities with reliability at high pressure, two sets of high-pressure data are required: density and viscosity. The high-pressure viscosity data are very scarce, therefore to obtain good values of density as a function of pressure an alternative tool, suggested by Sanmamed et al. [22], has been used in this work. This procedure exploits the fact that the ln η of ionic liquids behaves linearly as a function of pressure up to 60 MPa. Therefore a relation between the slope of ln η versus p curve and ln η_0 can be established:

$$\left(\frac{\partial \ln\ \eta}{\partial p}\right)_T = R + R' \ln\ \eta_0 \quad (2)$$

That is, estimating the viscosity at a given pressure is only necessary to know the viscosity at atmospheric pressure, η_0. For our liquids these viscosity data can be found in a previous paper [7]. On the other hand, the values of $R = 0.00289141$ and $R' = 0.0016472$ used here have been obtained fitting high-pressure viscosity data of some pyridinium-based ionic liquids [23] with a modified Litovitz equation [24]. Once the viscosity at a given temperature and pressure is estimated, the corresponding viscosity correction can be calculated through Eq. (1) and applied to the density measurements. The estimated uncertainty of our density measurements ± 0.1 kg m^{-3}.

3. Results

Corrected densities, from now on called densities, for the studied ionic liquids are collected in Table 2 and graphically represented in Figs. 1 and 2 together with correlated values using the Tait equation.

Table 2
Densities, ρ, of [e2mpy][Tf$_2$N] and [p2mpy][Tf$_2$N] as a function of pressure and temperature[a].

T (K)	ρ (kg m^{-3}) at p (MPa)												
	0.1	2.5	5.0	7.5	10.0	15.0	20.0	25.0	30.0	35.0	45.0	55.0	65.0
[e2mpy][Tf$_2$N]													
283.15	1520.3	1522.2	1523.8	1525.4	1527.0	1530.1	1533.1	1536.0	1538.8	1541.6	1546.9	1551.8	1556.4
288.15	1515.4	1517.2	1518.9	1520.6	1522.2	1525.3	1528.3	1531.3	1534.2	1536.9	1542.2	1547.3	1552.0
293.15	1510.5	1512.4	1514.1	1515.7	1517.4	1520.6	1523.6	1526.6	1529.5	1532.4	1537.8	1542.9	1547.7
298.15	1505.6	1507.5	1509.2	1510.9	1512.5	1515.8	1519.0	1522.0	1525.0	1527.8	1533.3	1538.5	1543.4
303.15	1500.8	1502.7	1504.5	1506.2	1507.9	1511.2	1514.3	1517.5	1520.5	1523.4	1528.9	1534.2	1539.2
308.15	1495.9	1497.9	1499.7	1501.4	1503.1	1506.5	1509.7	1512.9	1515.9	1518.9	1524.5	1529.9	1534.9
313.15	1491.1	1493.2	1495.0	1496.8	1498.5	1502.0	1505.2	1508.4	1511.5	1514.5	1520.3	1525.7	1530.8
318.15	1486.3	1488.4	1490.3	1492.1	1493.8	1497.3	1500.6	1503.9	1507.0	1510.1	1515.9	1521.4	1526.6
323.15	1481.5	1483.7	1485.6	1487.4	1489.2	1492.7	1496.2	1499.5	1502.6	1505.7	1511.7	1517.3	1522.5
328.15	1476.8	1478.9	1480.8	1482.7	1484.5	1488.1	1491.6	1494.9	1498.2	1501.4	1507.4	1513.0	1518.4
333.15	1472.0	1474.3	1476.2	1478.1	1480.0	1483.6	1487.2	1490.5	1493.9	1497.0	1503.2	1509.0	1514.3
[p2mpy][Tf$_2$N]													
283.15	1478.5	1480.5	1482.1	1483.7	1485.4	1488.6	1491.5	1494.5	1497.3	1500.1	1505.5	1510.5	1515.3
288.15	1473.7	1475.7	1477.3	1479.0	1480.6	1483.7	1486.8	1489.9	1492.7	1495.6	1500.9	1506.0	1510.9
293.15	1469.0	1470.9	1472.6	1474.3	1475.9	1479.2	1482.3	1485.3	1488.3	1491.1	1496.6	1501.8	1506.7
298.15	1464.2	1466.1	1467.8	1469.6	1471.2	1474.5	1477.7	1480.8	1483.8	1486.6	1492.2	1497.4	1502.5
303.15	1459.5	1461.5	1463.2	1465.0	1466.6	1470.0	1473.2	1476.4	1479.5	1482.4	1488.0	1493.3	1498.4
308.15	1454.8	1456.8	1458.5	1460.3	1462.0	1465.4	1468.7	1471.9	1475.0	1478.0	1483.7	1489.1	1494.2
313.15	1450.0	1452.1	1453.9	1455.8	1457.5	1461.0	1464.3	1467.5	1470.7	1473.7	1479.5	1485.0	1490.2
318.15	1445.4	1447.4	1449.3	1451.1	1452.9	1456.4	1459.9	1463.1	1466.4	1469.4	1475.3	1480.8	1486.1
323.15	1440.7	1442.8	1444.7	1446.7	1448.5	1452.0	1455.5	1458.7	1462.0	1465.2	1471.2	1476.9	1482.1
328.15	1436.1	1438.3	1440.2	1442.1	1443.9	1447.5	1451.0	1454.5	1457.8	1460.9	1467.1	1472.7	1478.1
333.15	1431.4	1433.6	1435.5	1437.5	1439.4	1443.1	1446.6	1450.1	1453.4	1456.7	1462.8	1468.6	1474.2

[a] $\sigma(\rho) = \pm 0.1$ kg m^{-3}, $\sigma(T) = \pm 1{\cdot}10^{-3}$ K, $\sigma(p) = \pm 5{\cdot}10^{-3}$ MPa.