Journal of Molecular Liquids 188 (2013) 196–202

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermophysical properties of $[C_{N-1}C_1im][PF_6]$ ionic liquids

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ARTICLE INFO

Article history:
Received 25 June 2013
Received in revised form 30 August 2013
Accepted 9 September 2013
Available online 18 October 2013

Keywords:
Refractive indices
Viscosities
Densities
Hexafluorophosphate
Nanostructuration
Ionic liquids
Trend shift
Imidazolium
Alkyl chain effect

ABSTRACT

Densities, viscosities and refractive index, as a function of temperature, and isobaric thermal expansion coefficient, were determined for 1-alkyl-3-methylimidazolium hexafluorophosphate, $[C_{N-1}C_1im][PF_6]$ (where N = 5 to 10) series of ionic liquids. The density presents a regular decrease along the ionic liquid series, with no detectable alkyl chain length dependence of the thermal expansion coefficient. Both the refractive index and viscosity show a trend shift along the series around the $[C_6C_1im][PF_6]$ that could be associated to the impact of the change in the nanostructuration of the ionic liquids. The experimental results are compared with the analogous $[C_{N-1}C_1im][NTf_2]$ series and the effect of the anion is analyzed. The sphericity of the $[PF_6]^-$ anion is reflected in the lower pre-exponential VTF parameter, A_η, and the higher viscosity of the $[C_{N-1}C_1im][PF_6]$, when compared with the $[C_{N-1}C_1im][NTf_2]$ series, is ruled by the higher energy barriers, which are related with stronger electrostatic interaction due to the low charge dispersion of the $[PF_6]^-$.anion.

1. Introduction

The physicochemical properties of ionic liquids can vary considerably depending on the combination of cations and anions. Therefore, for the interpretation of their properties and a successful modeling of ionic liquids, highly accurate data regarding these physicochemical properties are needed, such as heat capacities, vapor pressures, viscosities, densities and refraction index. Recently, we reported several thermodynamic studies of the extended series of ILs $[C_{N-1}C_1im][NTf_2]$ (with N = 3–9, 11, and 13), and of the symmetric $[C_{N/2}C_{N/2}im][NTf_2]$ (with N = 4–24) [1–4]. Based on these works, it was possible to highlight the effect of the nanostructuration of $[C_{N-1}C_1im][NTf_2]$ and $[C_{N/2}C_{N/2}im][NTf_2]$ ionic liquid series and to evaluate the effect of the cation topological symmetry on the thermodynamic properties of vaporization, heat capacities and viscosity data. Understanding the impact of nanostructuration on the thermophysical properties of ionic liquids is highly relevant but previous works used only the even numbered ionic liquids, and consequently the complete characterization of important trends which are related with the nanostructuration is not possible, neither the identification of the outlier character of $[C_1C_1im][NTf_2]$ and $[C_2C_1im][NTf_2]$ [1–4].

In this work, the thermophysical properties of 1-alkyl-3-methylimidazolium hexafluorophosphate, $[C_{N-1}C_1im][PF_6]$ (with N = 5–10), specifically density, viscosity and refractive index, and their dependency with temperature were measured. Concerning this family of ionic liquids, most of the thermophysical studies have been focused on the following liquids: $[C_4C_1im][PF_6]$, $[C_6C_1im][PF_6]$ and $[C_8C_1im][PF_6]$, which prevent the identification of the nanostructuration on these ionic liquids [5–31]. The experimental results obtained will be used to evaluate the effect of the chemical nature of the anion, sphericity, and size, as well as the overall impact of the nanostructuration on the thermophysical properties of these ionic liquids.

2. Experimental section

2.1. Materials and purification

The 1-alkyl-3-methylimidazolium hexafluorophosphate, $[C_{N-1}C_1im][PF_6]$ (with N = 5–10), used in this work, was purchased from IOLITEC with a stated purity of better than 99%. All the ionic liquids were dried and purified under vacuum (<10 Pa) at moderate temperature (323 K) and constant stirring, in order to reduce the

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http://dx.doi.org/10.1016/j.molliq.2013.09.031

Table 1
Experimental results of density, ρ, at 0.1 MPa for the [$C_{N-1}C_1$im][PF_6] ionic liquid series as a function of temperature.

T/K	ρ/(kg·m^{-3})					
	[C_4C_1im] [PF_6]	[C_5C_1im] [PF_6]	[C_6C_1im] [PF_6]	[C_7C_1im] [PF_6]	[C_8C_1im] [PF_6]	[C_9C_1im] [PF_6]
293.15	1371.8	1332.2	1298.5	1266.7	1240.9	1217.0
298.15	1367.4	1327.8	1294.2	1262.6	1236.9	1213.1
303.15	1363.2	1323.7	1290.1	1258.5	1232.9	1209.2
308.15	1359.0	1319.6	1286.1	1254.5	1229.0	1205.3
313.15	1354.9	1315.5	1282.1	1250.6	1225.1	1201.5
318.15	1350.8	1311.6	1278.2	1246.8	1221.3	1197.8
323.15	1346.8	1307.6	1274.3	1243.0	1217.6	1194.1
328.15	1342.7	1303.7	1270.5	1239.3	1213.9	1190.4
333.15	1338.7	1299.8	1266.7	1235.5	1210.2	1186.8
338.15	1334.7	1295.9	1262.9	1231.8	1206.6	1183.2
343.15	1330.6	1292.0	1259.1	1228.1	1202.9	1179.6
348.15	1326.6	1288.1	1255.3	1224.4	1199.3	1176.0
353.15	1322.7	1284.3	1251.5	1220.7	1195.6	1172.4
358.15	1318.7	1280.4	1247.7	1217.0	1192.0	1168.8
363.15	1314.8	1276.6	1244.0	1213.3	1188.4	1165.3

Note: the magnitude of the experimental differentiation between the two independent set of density data: ± 0.2 kg·m^{-3}.

presence of water or other volatile contents. This process was performed systematically before and during the thermophysical property measurements.

2.2. Density and viscosity

The density, ρ, and dynamic viscosity, η, measurements were performed with an automated SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter. The description concerning the operation of this equipment is available in the literature [32]. The measurements were carried out at atmospheric pressure in the temperature range from 293.15 to 363.15 K for the pure ionic liquids. The apparatus was calibrated using the three standard calibration samples, APN7.5, APN26 and APN415 in the same experimental conditions of the ionic liquid measurements. The reproducibility of the dynamic viscosity and density measurements is, according to the manufacturer, 0.35% and $\pm$ 0.5 kg·m^{-3}, respectively from 288.15 K to 378.15 K and the uncertainty of temperature is within $\pm$0.02 K. For each ionic liquid, at least two independent measurements of the density and viscosity were performed, using the same experimental conditions and different samples.

2.3. Refractive index

The refractive indices were measured at the sodium D-line using a Bellingham model RFM340 refractometer ($\pm 3 \times 10^{-5}$ stated precision), as a function of temperature (288.15 to 318.15) K. The apparatus was calibrated with degassed water (Millipore quality) and toluene (Spectranal, 99.9%). The temperature in the refractometer cell is controlled using an external thermostatic bath within a temperature fluctuation of ($\pm 5 \times 10^{-3}$) K, measured with a resolution better than 1×10^{-3} K and an uncertainty within $\pm$0.02 K. Samples were directly introduced into the flow cell (prism assembly) using a syringe; the flow cell was kept closed after sample injection. For each ionic liquid at least two independent experiment were performed and in each experiment at least three measurements were taken at each temperature. The refractive indices were measured with respect to air and no corrections were applied.

3. Results and discussion

3.1. Density

The experimental density data for the studied ionic liquids are presented in Table 1. Fig. 1 displays the logarithm of density as a function of temperature and the respective relative deviations between the experimental density measured in this work and those reported in the literature.

The experimental density data, in the temperature range, was described using a second order polynomial equation correlation, according to Eq. (1):

$$\ln(\rho/\text{kg}\cdot\text{m}^{-3}) = a + b \cdot T + c \cdot T^2 \tag{1}$$

The comparison with the literature data was limited due to the lack of data for the odd number of the studied ionic liquids series ([C_5C_1im][PF_6], [C_7C_1im][PF_6] [C_9C_1im][PF_6]). Only densities of three ionic liquids, [C_4C_1im][PF_6], [C_6C_1im][PF_6] and [C_8C_1im][PF_6], were found in the literature. The densities obtained in this work are in good agreement with the literature results, with deviations under 0.1% [12,33]. Higher

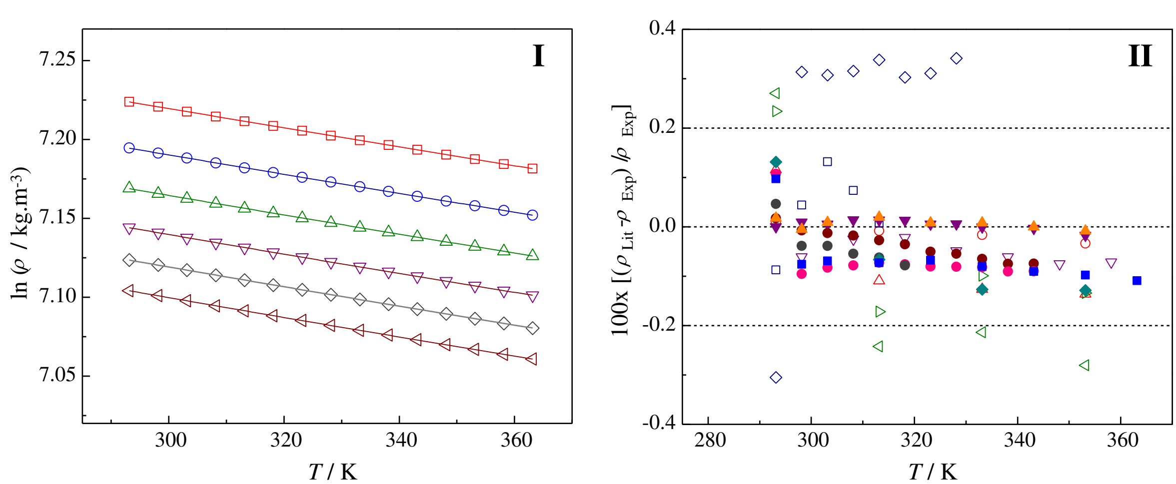

Fig. 1. (I) Logarithm of density as a function of temperature for [$C_{N-1}C_1$im][PF_6] ionic liquid family. The thin lines results from the linear fitting of the experimental results. □ – [C_4C_1im][PF_6]; ○ – [C_5C_1im][PF_6]; △ – [C_6C_1im][PF_6]; ▽ – [C_7C_1im][PF_6]; ◇ – [C_8C_1im][PF_6]; ◁ – [C_9C_1im][PF_6].(II) Relative deviations between the experimental density measured in this work (ρ_{exp}) and those reported in the literature (ρ_{exp}) as a function of temperature for [$C_{N-1}C_1$im][PF_6] ionic liquid series. Tomida et al. [13] ◆ – [C_4C_1im][PF_6]; Y. Geng et al. [14] ◇ – [C_4C_1im][PF_6]; D. Tomida et al. [15] ◁ – [C_6C_1im][PF_6], ▷ – [C_8C_1im][PF_6]; Taguchi et al. [16] △ – [C_6C_1im][PF_6], ○ – [C_8C_1im][PF_6]; A.B. Pereiro et al. [20] ● – [C_4C_1im][PF_6], ● – [C_8C_1im][PF_6]; W. Fan et al. [21] ▼ – [C_4C_1im][PF_6]; K. R. Harris et al. [22] ▲ – [C_8C_1im][PF_6]; K. R. Harris et al. [23] ■ – [C_6C_1im][PF_6]; Tokuda et al. [25] □ – [C_4C_1im][PF_6]; A. Muhammad et al. [26] ▽ – [C_6C_1im][PF_6]; A.B. Pereiro et al. [31] ● – [C_6C_1im][PF_6].