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Thermophysical Properties of *N*-Octyl-3-methylpyridinium Tetrafluoroborate[†]

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Density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, and kinematic viscosity of the room-temperature ionic liquid *N*-octyl-3-methylpyridinium tetrafluoroborate have been measured over a temperature range. From the results, coefficients of thermal expansion, molar refractions, and dynamic viscosities have been derived. The properties are discussed further in terms of the effect of the variations of the alkyl chain length on the pyridinium cation.

Introduction

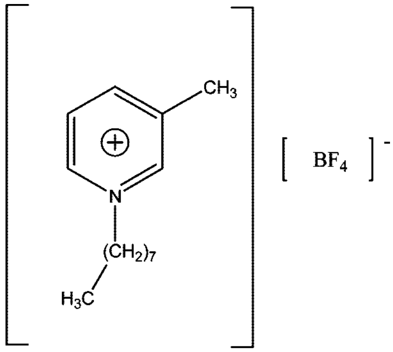
One of the alternatives to classical solvents that have acquired a growing interest[1–11] is room-temperature ionic liquids (RTILs). They have exceptional features since they can not only dissolve a wide range of polar and nonpolar organic and inorganic molecules but also in some cases act like a catalyst. RTILs also possess other desirable properties such as being nonflammable and nontoxic, and they present high thermal, chemical, and electrochemical stability.[1]

A thermophysical study of this type of compounds is necessary to enable an understanding of their properties depending on fundamental factors such as the ionic structures and intermolecular interactions. Such information give us the possibility of designed RTILs in the future with the desired properties.

We present here the thermophysical properties of a RTIL, *N*-octyl-3-methylpyridinium tetrafluoroborate ([o3mpy][BF_4]), which is shown in Figure 1. Density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, and kinematic viscosity of this RTIL have been measured from (278.15 to 328.15) K. From the experimental results, we have obtained coefficients of thermal expansion, molar refractions, and dynamic viscosities. To know the influence of the alkyl chain length in the thermophysical properties, results have been compared to those obtained for *N*-butyl-3-methylpyridinium tetrafluoroborate ([b3mpy][BF_4]), an ionic liquid with the same anion and dissimilar cation which we have investigated previously.[12] Thus, the differences have been analyzed paying special attention to the change in the alkyl chain length in the pyridinium cation and their consequences.

Experimental

The room-temperature ionic liquid *N*-octyl-3-methylpyridinium tetrafluoroborate, purity 98 %, was provided by Solvent Innovation. With the aim of decreasing the water content as much as possible, it was dried for 24 h under a vacuum of about 0.05 kPa under stirring and stored before use in a desiccator. Measurements were performed in a range of temperatures from (278.15 to 328.15) K with an interval of 2.5 K between each temperature, except in the case of refractive index, whose measurements were carried out from (283.15 to 328.15) K.



[o3mpy][BF_4]

Figure 1. Structure and abbreviation of the ionic liquid under study.

Densities, ρ, of the pure compound were determined with an Anton Paar DMA-58 vibrating tube densimeter automatically thermostatted within ± 0.01 K. The calibration was carried out with deionized doubly distilled water and dry air.

It is well-known that high viscosity values affect the experimental determination of density. With the aim of reducing the uncertainties in density values, we have used the following correction factor, recommended by Anton Paar for the DMA 512P densimeter:[13,14]

$$\frac{\Delta\rho}{\rho} = (-0.5 + 0.45\sqrt{\eta})\cdot 10^{-4} \tag{1}$$

where ρ is the raw density obtained from the experimental device; $\Delta\rho$ is the difference between the raw and corrected density; and η is the dynamic viscosity. The final uncertainty of density can be estimated in $\pm\ 10^{-4}\ \mathrm{g\cdot cm^{-3}}$.

Speeds of sound, u, were obtained with an Anton Paar DSA-48 vibrating tube densimeter and sound analyzer. The temperature was automatically kept constant within ± 0.01 K. The uncertainty of the speed of sound is $\pm\ 0.1\ \mathrm{m\cdot s^{-1}}$. Calibration of the apparatus was carried out with air and deionized double-distilled water.

Refractive indices, n_D, at 589.3 nm sodium D wavelength were measured using a high-precision automatic refractometer Abbemat-HP DR Kernchen, whose temperature was internally controlled within ± 0.01 K. The apparatus was calibrated with deionized double-distilled water. The corresponding uncertainty is $\pm\ 1\cdot 10^{-6}$.

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Table 1. Experimental Thermophysical Properties of [o3mpy][BF_4] at Atmospheric Pressure as a Function of Temperature

T K	ρ $g\cdot cm^{-3}$	ν $mm\cdot s^{-1}$	η $mPa\cdot s$	n_D	R_m $cm^3\cdot mol^{-1}$	σ $mN\cdot m^{-1}$	u $m\cdot s^{-1}$	$C_{P,m}$ $J\cdot mol^{-1}\cdot K^{-1}$
278.15	1.1064	2481	2745			39.82	1571.9	433.8
280.65	1.1050	1926	2128			39.28	1564.9	435.7
283.15	1.1036	1540	1699	1.459783	72.725	38.70	1557.7	437.4
285.65	1.1021	1229	1355	1.459069	72.727	38.30	1549.2	439.4
288.15	1.1007	1016	1118	1.458354	72.721	37.91	1541.2	441.4
290.65	1.0994	817.5	898.8	1.457635	72.709	37.52	1533.5	443.7
293.15	1.0977	680.9	747.4	1.456913	72.722	37.19	1526.3	446.1
295.65	1.0963	558.5	612.2	1.456202	72.717	36.81	1518.7	448.4
298.15	1.0945	461.9	505.5	1.455474	72.737	36.51	1511.4	450.5
300.65	1.0933	388.3	424.5	1.454765	72.718	36.23	1505.4	452.8
303.15	1.0915	327.0	357.0	1.454053	72.74	35.94	1498.1	455.0
305.65	1.0897	279.8	304.9	1.453326	72.759	35.67	1491.2	457.2
308.15	1.0881	238.4	259.4	1.452613	72.767	35.46	1484.6	459.2
310.65	1.0863	204.7	222.4	1.451903	72.789	35.22	1478.1	461.3
313.15	1.0847	177.0	192.0	1.451207	72.799	35.02	1472.3	463.3
315.65	1.0831	155.6	168.5	1.450469	72.803	34.81	1465.7	465.1
318.15	1.0814	136.4	147.5	1.449763	72.819	34.63	1459.3	467.0
320.65	1.0798	119.2	128.7	1.449030	72.824	34.46	1453.2	468.7
323.15	1.0783	104.7	112.9	1.448307	72.824	34.28	1446.5	470.3
325.65	1.0765	92.72	99.81	1.447604	72.846	34.13	1440.4	472.0
328.15	1.0749	82.15	88.30	1.446898	72.855	33.98	1433.6	473.7

Surface tensions, σ, were determined using a drop volume tensiometer Lauda TVT-2.[15] The temperature was kept constant within ± 0.01 K by means of an external Lauda E-200 thermostat. Details of the experimental procedure can be found in a previous paper.[16] The uncertainty of the surface tension measurement was ± 0.01 $mN\cdot m^{-1}$ of the final value of surface tension.

Isobaric molar heat capacities were determined using a differential scanning calorimeter (Q1000 from TA Instruments). The measurements were carried out using (3.00 ± 0.01) mg of sample sealed at room temperature in aluminum pans with a mechanical crimp. The heating scan was performed at a scan rate of 10 $K\cdot min^{-1}$. Temperature calibration was made with standard samples of indium, using its melting transition (429.76 K), and with a sample of Mn_3GaC, using its ferro- to antiferromagnetic transition (171.83 K). Additionally, to determine the heat capacity, the zero-heat flow procedure described by TA Instruments has been followed using as a standard compound a synthetic sapphire sample measured in the same conditions. These calibration measurements allow us to estimate an overall uncertainty of ± 0.5 K in temperature and ± 3 % in the heat capacities, the reproducibility of the molar heat capacity measurements being ± 0.1 $J\cdot mol^{-1}\cdot K^{-1}$.

Kinematic viscosities, ν, were determined using an Ubbelohde viscosimeter with a Schoot-Geräte automatic measuring unit (model AVS-440). $CaCl_2$ drying tubes were used to protect the samples from moisture in the air. The temperature was kept constant within ± 0.01 K by means of a Schoot-Geräte thermostat. The viscosimeter constant was provided by the supplier and was $K = 0.9822\ mm^2\cdot s^{-2}$. From density and kinematic viscosity, the absolute viscosity, η, can be obtained, $\eta = \rho\cdot\nu$, and the estimated uncertainty in the absolute viscosity was 0.6 % in the final value.

Results and Discussion

With the aim of finding a relationship between the characteristics of the RTILs and the ionic structures, we have compared the experimental values measured for [o3mpy][BF_4] with those obtained previously for [b3mpy][BF_4][12] for each property. The differences between these liquids have been analyzed to determine the effect of the variations in the alkyl chain length of the pyridinium cations.

Table 2. Fitting Parameters and Standard Deviations for the Studied Properties

property	A	B	C	s
$\rho/g\cdot cm^{-3}$	$-6.367\cdot 10^{-4}$	1.2841		0.0003
n_D	$-2.86520\cdot 10^{-4}$	1.540910		0.000008
$u/m\cdot s^{-1}$	−2.7538	2335.0		1.9
$\sigma/mN\cdot m^{-1}$	0.0014981	−1.02066	207.68	0.06
$C_p/J\cdot mol^{-1}K^{-1}$	0.82310	204.85		0.60
$\eta/mPa\cdot s^{a}$	0.039216	1255.83	165.541	7.08

[a] $\eta_0 = A$; $T_0 = C$.

Values of density, speed of sound, refractive index, molar refraction, surface tension, isobaric molar heat capacity, kinematic viscosity, and dynamic viscosity of the ionic liquid *N*-octyl-3-methylpyridinium tetrafluoroborate are gathered in Table 1.

A linear dependence of the thermodynamics properties density, refractive index, speed of sound, and heat capacity with temperature has been found in the range of the measurements for the liquid under study. Therefore, experimental data have been correlated with the following equation

$$Y = A\cdot(T/K) + B \qquad (2)$$

where Y is the studied property; A and B are adjustable parameters; and T is the absolute temperature. The best linear fitting parameters and the standard deviations of each property are collected in Table 2.

As shown in Figure 2, density decreases slightly with temperature, being more dense than water and other common organic compounds. From the comparison of the results for both ionic liquids [o3mpy][BF_4] and [b3mpy][BF_4], we have found that density decreases with an increase in the alkyl substituent as expected.

Experimental values of density have been used to calculate the coefficient of thermal expansion, α, applying the following equation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad (3)$$

where V is the molar volume. The coefficient of thermal expansion in the [o3mpy][BF_4] liquid decreases very slightly when temperature increases, showing a value of $\alpha = 5.86\cdot 10^{-4}\ K^{-1}$ at 298.15 K. It is noticeable that several RTILs investigated

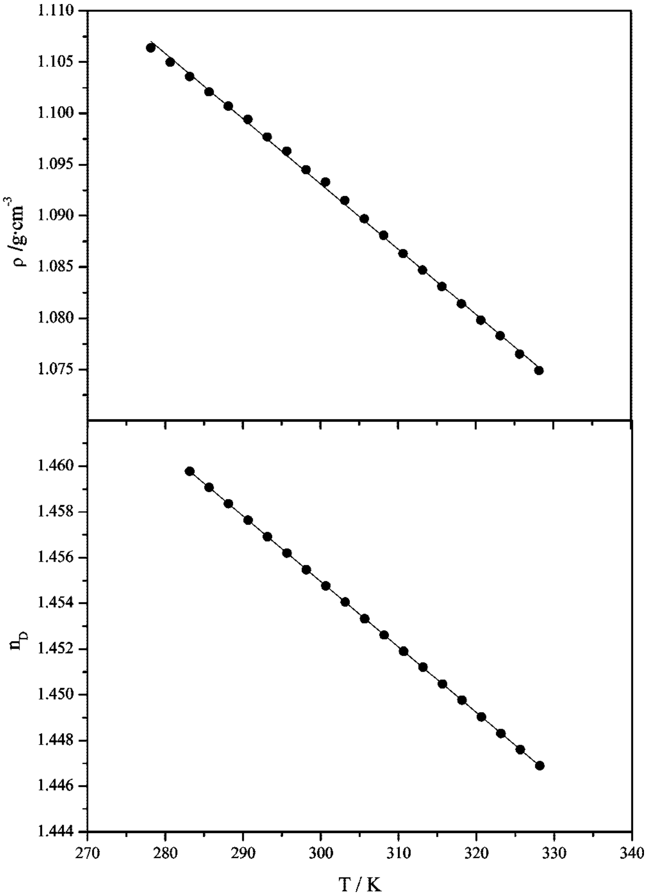

Figure 2. Density and refractive index as a function of temperature for [o3mpy][BF_4].

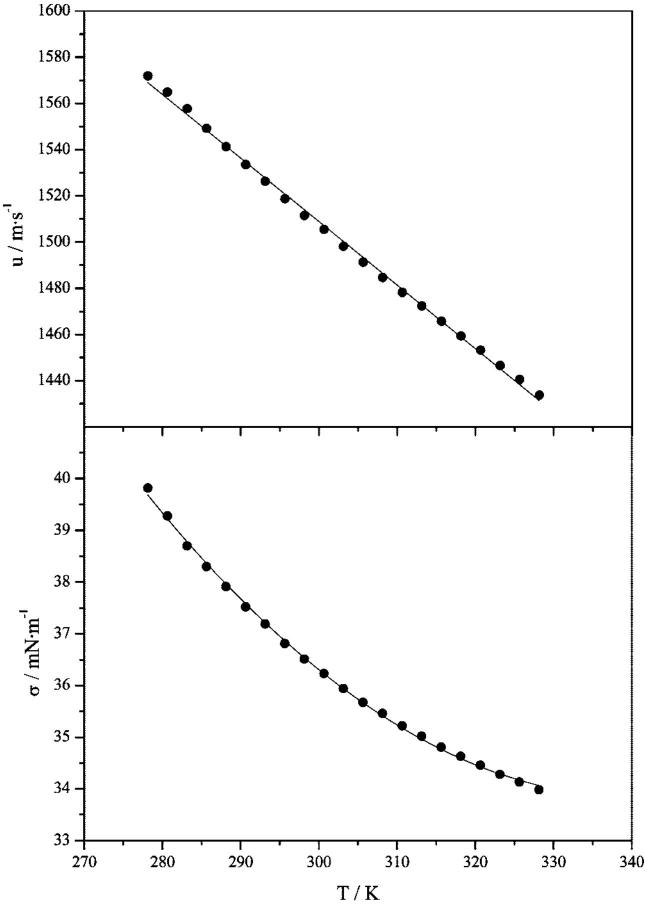

Figure 3. Speed of sound and surface tension as a function of temperature for [o3mpy][BF_4].

previously exhibit a similar degree of volume expansion being $\alpha = 5.91 \cdot 10^{-4}$ K^{-1} for [b3mpy][BF_4], $\alpha = 5.80 \cdot 10^{-4}$ K^{-1} for [b4mpy][BF_4] at 298.15 K,[12] and $\alpha = 5.20 \cdot 10^{-4}$ K^{-1} for *N*-ethyl-3-methylimidazolium aminoacetate.[6] However, their values of density are quite different which seem to indicate that all these compounds show a similar behavior with temperature.

In Figure 2, refractive indices as a function of temperature are presented. Although experimental values are somewhat smaller for [o3mpy][BF_4] than for [b3mpy][BF_4], in both cases, the property decreases linearly with temperature with a very similar slope.

The molar refraction, R_m, of the liquid has been calculated from experimental data of both density and refractive index at all the studied temperatures using the Lorentz–Lorenz relation

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V \tag{4}$$

where *V* is the molar volume of the RTIL at each temperature. The values are gathered in Table 1. As is known, molar refraction is considered the hard core volume of one mole of molecules. Results show that not only the molar refraction but also the free molar volume for [o3mpy][BF_4] are larger than values found for the analogous [b3mpy][BF_4].

The dependence of speeds of sound with temperature is shown in Figure 3. The property decreases when the temperature increases, being considerably smaller than experimental data for [b3mpy][BF_4].

As shown in Figure 3, surface tension and temperature are related by means of a polynomial equation of second order, in contrast to obtained results for [b3mpy][BF_4]. Therefore, experimental data have been correlated with the following equation

$$\sigma = A \cdot (T/K)^2 + B \cdot (T/K) + C \tag{5}$$

where *A*, *B*, and *C* are adjustable parameters and *T* is the absolute temperature. The best fitting parameters and the standard deviation are collected in Table 2.

Several works[10,11] have studied how molecular parameters such as surface orientation and intermolecular interactions which are established in both the bulk and the surface influence this property, trying to find which factors are reflected with intensity in the experimental values. As is known, according to the Langmuir's principle of independent surface action, the measured property is a sign of the part of the molecule that is actually present in the surface, which is essentially constitute for both kinds of ions in order to maintain the electroneutrality. Therefore, the compounds tend to expose to the vapor phase their parts with lower surface energy to minimize the surface tension. From the comparison of experimental data, we can say that [o3mpy][BF_4] presents a lower surface tension in all the ranges of temperatures than the corresponding butyl homologue. These results are in agreement with conclusions derived from earlier studies.[10,11]

Isobaric molar heat capacities for [o3mpy][BF_4], which are represented in Figure 4, increase when temperature does. As known,[4] in general the molecule which contains more atoms would have more energy storage modes and thus a higher heat capacity. Therefore, comparing two liquids which contain the same anion, it is expected that the larger the cation, the higher the heat capacity. From experimental values, we found that our

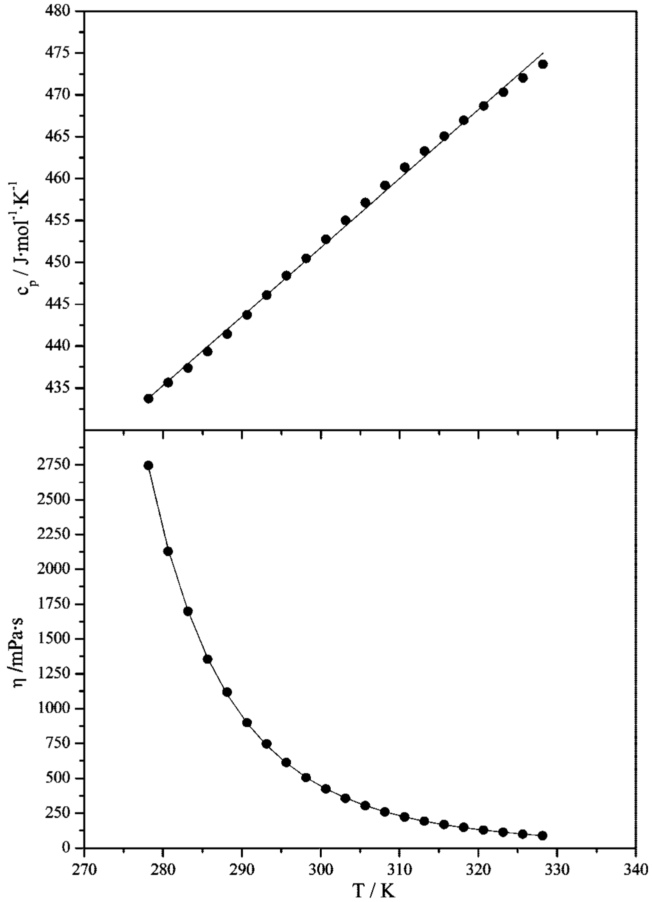

Figure 4. Isobaric heat capacity and viscosity as a function of temperature for [o3mpy][BF_4].

liquids follow this general trend since the heat capacities measured for [o3mpy][BF_4] are larger than those for [b3mpy][BF_4].

As shown in Figure 4, the temperature dependency of the dynamic viscosity values has been fitted to a Vogel−Fulcher−Tamman equation[17–19] since it presents convex curved profiles

$$\eta = \eta_0 \exp[B/(T/\mathrm{K} - T_0/\mathrm{K})] \qquad (6)$$

where η_0, B, and T_0 are the adjustable parameters gathered in Table 2 and T is the absolute temperature. The viscosity values experiment a pronounced decrease when the temperature begins to increase until they achieve a gentle descent at high temperatures. It is noticeable not only that [o3mpy][BF_4] is more viscous than conventional solvents but also viscosity values are much larger than those for [b3mpy][BF_4], especially at low temperatures. Similar results have been obtained when the effect of the variations of the alkyl chain length in viscosity data has been analyzed.[3,5,9] This transport property seems to be determined by several factors such as the size and shape of the ionic structures and intermolecular interactions.[2,7] The presence of a longer alkyl chain produces an increase of the cation size and lengthens their shape. Both effects hinder the fluency of the ions, resulting in a greater property. Interactions also play a key role in the viscosity data, the van der Waals and Coulombic interactions being the most important in pyridinium-based ionic liquids. It should be noted that the fact that these interactions are more strongly affected by the variation in the length of the alkyl chain permits us to suggest which factor determines the sign of the property for the liquid under study. Thus, the greater experimental data for [o3mpy][BF_4] than for [b3mpy][BF_4], which in part are due to an increase of the interactions, seem to indicate that van der Waals attractions have a greater influence on the values of the system.

Conclusions

We have made measurements of the thermophysical properties of pyridinium-based ionic liquid, to amplify the knowledge of the relationship between ionic structures and properties. This work is fundamental for introducing this kind of liquids in industrial applications, and in this way, we can take advantage of their interesting properties.

Here, we have presented a thermophysical study of the ionic liquid *N*-octyl-3-methylpyridinium tetrafluoroborate over a broad range of temperatures. Results have been compared with those of *N*-butyl-3-methylpyridinium tetrafluoroborate to identify the effect of the length of the alkyl chain in the features. Thus, we have obtained a decrease of density, refractive index, speed of sound, and surface tension when the alkyl substituent chain length on the cation increases. In contrast, isobaric molar heat capacity and dynamic viscosity values are greater for [o3mpy][BF_4]. Volumetric properties and molar refraction could indicate a worse arrangement of ions when the alkyl chain increases, which agree with obtained information from speeds of sound. From surface tension, we can suggest that intermolecular interactions decrease for [o3mpy][BF_4]. Finally, from viscosity experimental data, we can suggest that van der Waals interactions between the chains are important among the intermolecular interactions of the liquid under study.

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