Thermophysic Comparative Study of Two Isomeric Pyridinium-Based Ionic Liquids

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A comprehensive thermophysical study of isomeric room-temperature ionic liquids *n*-butyl-3-methyl-pyridinium tetrafluoroborate and *n*-butyl-4-methyl-pyridinium tetrafluoroborate has been performed. This paper reports various experimental data including density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, and kinematic viscosity. From the experimental results, coefficients of thermal expansion, dynamic viscosities and molar refractions of the studied ionic liquids have been determined. Results have been analyzed paying special attention to the different features of the isomers and their structural differences. Several theories and empirical relations have been applied in order to predict physical properties of ionic liquids. A good agreement between experimental and calculated data has been found. Furthermore, a study about the versatility and application of the different relationships has been carried out finding that in general density and coefficients of thermal expansion can be estimated with relatively good accuracy.

Introduction

Because of the growing social demand and a more severe environmental legislation, room-temperature ionic liquids (RTILs) are becoming a real alternative to the classical organic solvents. Their main characteristics are the nonvolatility, nonflammability, nontoxicity, and the thermal stability. In addition to these properties, RTILs are easily recyclable and can be used as catalysts in many reactions due to their high selectivity and capability to enhance reaction rates. Consequently, the determination of physicochemical properties of ionic liquids is a matter of considerably interest.[1]

One of the main problems involved in the use of ionic liquids is the presence of impurities, among which water is especially worth mentioning. Recent studies have shown that RTILs absorb water from the atmosphere at a fast rate until reaching a plateau after approximately 48 h, which corresponds approximately to 6−8% w/w of water.[2] It has also been suggested that water molecules are accommodated in the ionic liquid structure by forming hydrogen bonds with both the anion and the cation. It has been proven that the presence of water molecules in the RTIL structure reduces the electrostatic attractions between the ions, leading to a lower cohesive energy of the systems. In fact, even small quantities of water in the RTIL can cause large changes in the physicochemical properties.[3] It has also been shown that the presence of low concentrations of other impurities such as halides has been reported as well to significantly modify RTILs properties.[2] Therefore, the removal of water traces and other impurities is a crucial issue in the study and use of these fluids.

The most commonly used RTILs are formed by imidazolium, pyridinium, ammonium, and phosphonium cations combined with either organic or inorganic anions such as tetrafluoroborate, halide, ethanoate, or nitrate. In addition, the large variety of new possible combinations of anions and cations is rapidly increasing the number of RTILs under study. However, an important limitation to the use of RTILs is the lack of knowledge about how the structure of the ionic liquid may affect its physicochemical properties and solvent strength. In this context, thermophysical properties of pure ionic liquids could provide information not only about the structure of the fluid but also the intermolecular interactions, which are the basis for the improvement of thermodynamic models for the representation of the behavior of the RTILs in any of their applications.

Although many efforts have been made to gain understandings of the RTILs behavior,[1−11] there are few data available about the thermophysical properties of RTILs. A detailed literature search shows that the vast majority of the studies related to the physical and thermodynamic properties of ionic liquids are based on the distinct behavior of RTILs due to either the presence of different anions for the same cation or the dissimilarities in the size of the alkyl chain of the cation.[1,8−10] However, there are few works analyzing the influence of the shape and structure of the alkyl chain of the cation or the position of the substituents on the RTILs physical properties. Taken together, these facts highlight the need for determination of thermophysical properties of these fluids.

The foregoing reasons have motivated us to pursue a well-planned and systematic study of a series of RTILs-based compounds in view to analyze the behavior of their thermodynamic properties and the relationship with their molecular features. Specifically, in this paper, we report the thermophysical properties of two RTILs isomers, namely, *n*-butyl-3-methyl-pyridinium tetrafluoroborate ([b3mpy][BF₄]) and *n*-butyl-4-methyl-pyridinium tetrafluoroborate ([b4mpy][BF₄]), whose chemical structure is depicted in Figure 1. Density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, and kinematic viscosity of these isomeric ionic liquids have been experimentally determined. Measurements have been carried out in a range of temperatures from 278.15 to 328.15 K. Only dynamic viscosities and isobaric molar heat capacity at several temperatures for [b3mpy][BF4][11] and room-temperature density for [b4mpy][BF4][12] have been reported before. From our experimental results, coefficients of thermal expansion,

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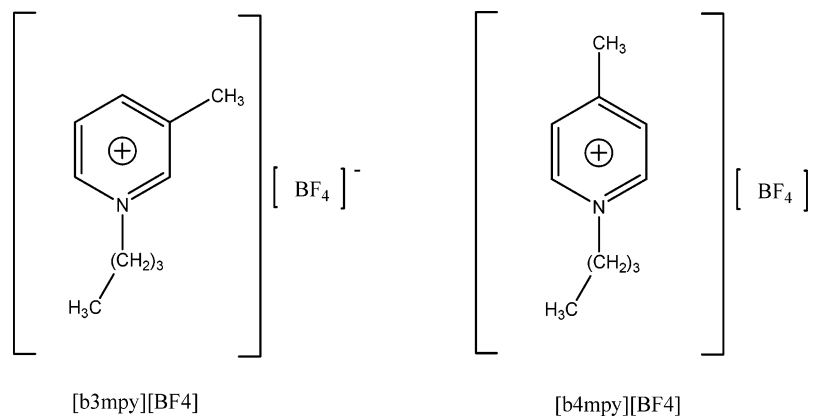
[b3mpy][BF4]   [b4mpy][BF4]

Figure 1. Structure and abbreviations of the ionic liquids under study.

TABLE 1: Fitting Parameters and Standard Deviations for the Studied Properties

property	ionic liquid	A	B	C	s
$\rho/g\cdot cm^{-3}$	[b3mpy][BF$_4$]	-6.940×10^{-4}	1.3893		0.0002
	[b4mpy][BF$_4$]	-6.811×10^{-4}	1.3855		0.0002
$u/m\cdot s^{-1}$	[b3mpy][BF$_4$]	-2.4316	2309.4		0.4
	[b4mpy][BF$_4$]	-2.4591	2331.4		0.9
n_D	[b3mpy][BF$_4$]	-2.72593×10^{-4}	1.532393		0.000019
	[b4mpy][BF$_4$]	-2.71844×10^{-4}	1.533552		0.000015
$\sigma/mN\cdot m^{-1}$	[b3mpy][BF$_4$]	-0.06872	65.38		0.07
	[b4mpy][BF$_4$]	-0.07562	68.08		0.07
$C_p/J\cdot mol^{-1} K^{-1}$	[b3mpy][BF$_4$]	0.50433	261.88		0.20
	[b4mpy][BF$_4$]	0.52023	258.65		0.13
$\eta/mPa\cdot s$	[b3mpy][BF$_4$]	0.080300	936.810	176.5069	0.57
	[b4mpy][BF$_4$]	0.161446	758.922	191.6670	1.23

molar refractions, and dynamic viscosities have been determined for the several studied temperatures. In addition, entropies and enthalpies of surface formation per unit surface area have been calculated. Results have been analyzed and discussed in terms of the molecular characteristics of the ionic liquids.

The development of estimation methods and predicting models is important since it will permit the future rational design of RTILs with pre-selected features. With this aim, we have tested several models to estimate the properties of the two isomers studied in this paper at different temperatures. Some of these theories were not initially designed for RTILs and are normally applied to non-ionic compounds. In this group, we can include the parachor parameter,[13] the molar refraction related model,[13,14] and the Auerbach relation.[15] More specific models, recently designed for ionic liquids, have also been applied including the Glasser theory,[16] the intersticial model,[17] and the Kabo's method.[18] Densities, speeds of sound, and coefficients of thermal expansion are good examples of thermophysical properties that can be estimated using these methods. Theoretical results have been compared with experimental data to verify the predicting capability of these theories and models. Important conclusions about the potential use of the essayed models to predict RTILs properties have been obtained.

To the best of our knowledge, such a study of RTILs has not been performed before.

Experimental Section

The room-temperature ionic liquids *n*-butyl-4-methylpyridinium tetrafluoroborate 99% and *n*-butyl-3-methylpyridinium tetrafluoroborate 99% were provided by Solvent Innovation. With the aim of decreasing the water content as much as possible, RTILs were dried for 24 h under a vacuum of approximately 0.05 kPa under stirring and stored before use

in a desiccator. When in use, RTILs were under nitrogen atmosphere. 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.

Densities, ρ, of the pure compounds were determined with an Anton Paar DMA-58 vibrating tube densimeter automatically thermostated 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 the density values, we have used the following correction factor, recommended by Anton Paar for the DMA 512P densimeter:[19,20]

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

where ρ is the raw density obtained from the experimental device, Δr is the difference between the raw and the corrected density, and η is the dynamic viscosity obtained experimentally. The final uncertainty of density is estimated to be $\pm10^{-4}$ 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 measurements is ±0.1 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 $\pm1 \times 10^{-6}$.

Surface tensions, σ, were determined using a drop volume tensiometer Lauda TVT-2.[21] 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.[22] The uncertainty of the surface tension measurement is ± 0.01 mN·m^{-1} of the final value of surface tension.

Isobaric molar heat capacities were determined with a DSC Q1000 calorimeter from TA Instruments with samples sealed in aluminum pans and a scanning rate of 10 K/min under a nitrogen atmosphere. The temperature and energy were calibrated with indium, lead, and zinc and the absolute heat capacity was determined using a sapphire and an empty pan measurement. The uncertainty of the molar heat capacity measurement is ± 0.01 J·mol^{-1}·K^{-1}.

Kinematic viscosities, ν, were determined using an Ubbelohde viscosimeter with a Schoot-Geräte automatic measuring unit model AVS-440. The temperature was kept constant within ± 0.01 K by means of a Schoot-Geräte thermostat. The viscosimeter was calibrated with deionized doubly distilled water. The uncertainty of the time flow measurements is ± 0.01 s, and the corresponding uncertainty in the kinematic viscosity is $\pm 1 \times 10^{-4}$ mm^2·s^{-1}. From density and kinematic viscosity, the absolute viscosity, η, can be obtained: $\eta = \rho \cdot \nu$, the estimated uncertainty in the absolute viscosity is $\pm 1 \times 10^{-4}$ mPa·s.

Results and Discussion

A linear relationship between the thermodynamic properties and the temperature for the studied RTILs has been obtained. Therefore, the thermodynamic properties have been correlated using the following equation:

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

where Y is the studied property, and A and B are adjustable parameters. The best linear fitting parameters and the standard deviations of each property for both ionic liquids are gathered in Table 1.

Temperature dependence of the corrected density for the studied RTILs is illustrated in Figure 2. Density values for both ionic liquids are quite similar and decrease linearly with temperature. Density values for [b4mpy][BF4] are, at medium and high temperatures, slightly higher than those for [b3mpy]-[BF4]. However, density values at low temperatures (from 278.15 to 285.65 K) are smaller than those for the ionic liquid [b3mpy][BF4]. As we mentioned before, we have found only one reference in literature related to the density at room temperature of the [b4mpy][BF4], which falls in the range of our measurements.[12]

Experimental values of density are used to calculate other thermodynamic properties such as the coefficient of thermal expansion, α, that can be determined using the following equation:

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

where V is the molar volume. Values of the coefficient of thermal expansion at 298.15 K are 5.91×10^{-4} K^{-1} for [b3mpy]-[BF4] and 5.80×10^{-4} K^{-1} for [b4mpy][BF4]. Since experimental densities and their temperature behavior of both RTILs are very similar, the differences in the coefficients of thermal expansion are small. These values are comparable to coefficients obtained for other ionic liquids such as 1-methyl-3-hexylimi-
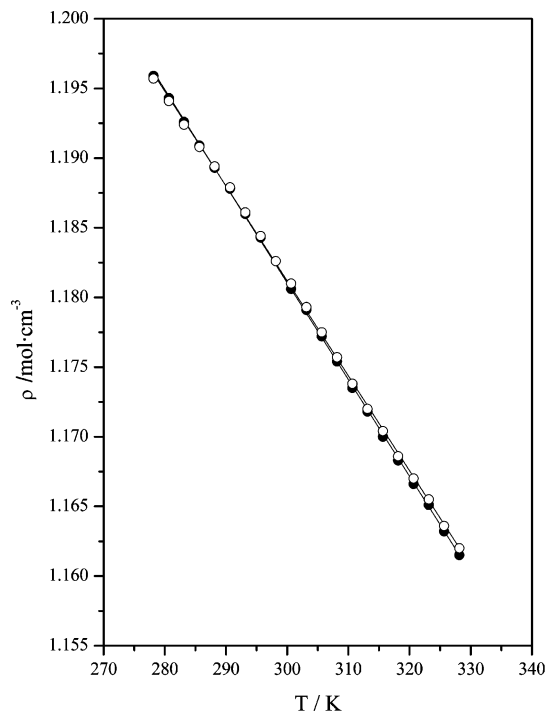

Figure 2. Densities as a function of temperature: ($\bullet$) [b3mpy][BF4], ($\bigcirc$) [b4mpy][BF4].

dazolium chlorogallate[6] (6.29×10^{-4} K^{-1}) or 1-ethyl-3-methylimidazolium aminoacetate[3] (5.20×10^{-4} K^{-1}).

Figure 3 shows the speeds of sound for [b3mpy][BF4] and [b4mpy][BF4], which decrease with temperature, with values for [b3mpy][BF4] being smaller than those for the ionic liquid [b4mpy][BF4] for the whole range of temperatures.

A similar behavior is found for the refractive index of the two ionic liquids, which is shown in Figure 4. Values of this property decrease linearly with temperature. Refractive index values are smaller for [b3mpy][BF4] than for [b4mpy][BF4].

A useful magnitude related both to density and to refractive index is molar refraction, R_m, that, in this case, has been calculated for the isomeric ionic liquids at all of the studied temperatures by means of the Lorentz−Lorenz relation:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2}V \qquad (4)$$

where V is the molar volume of the ionic liquid at each temperature. Values of molar refraction for the ionic liquid [b4mpy][BF4] are slightly higher than for [b3mpy][BF4]. As it is known, molar refraction is considered the hard core volume of one mole of molecules. Therefore, taking into account the similarities found for the density values of both ionic liquids and, consequently, the likenesses of the molar volume of these isomers, the differences in molar refraction indicate that isomer [b4mpy][BF4] shows a smaller free molar volume than [b3mpy]-[BF4].

In Figure 5, surface tension as a function of temperature of the [b4mpy][BF4] and [b3mpy][BF4] ionic liquids is shown. Surface tension values decrease with temperature, and they are higher for [b4mpy][BF4] than for the isomer [b3mpy][BF4]. The difference between the values increases when temperature decreases.
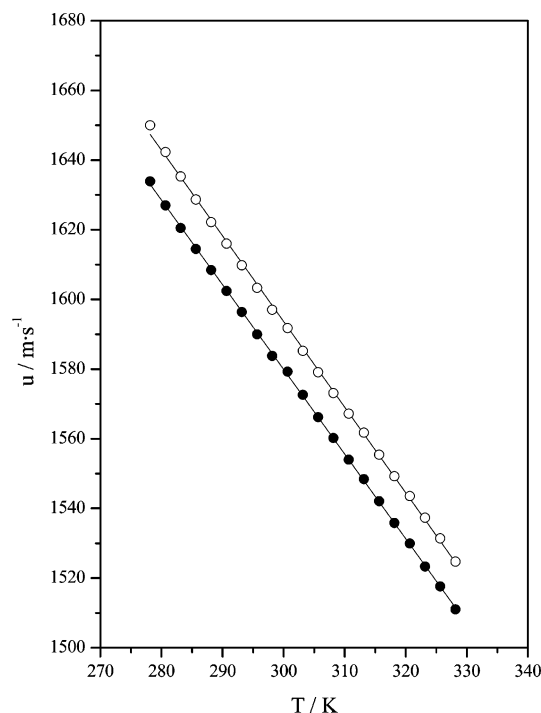
Figure 3. Speeds of sound as a function of temperature: (●) [b3mpy]-[BF$_4$], (○) [b4mpy][BF$_4$].
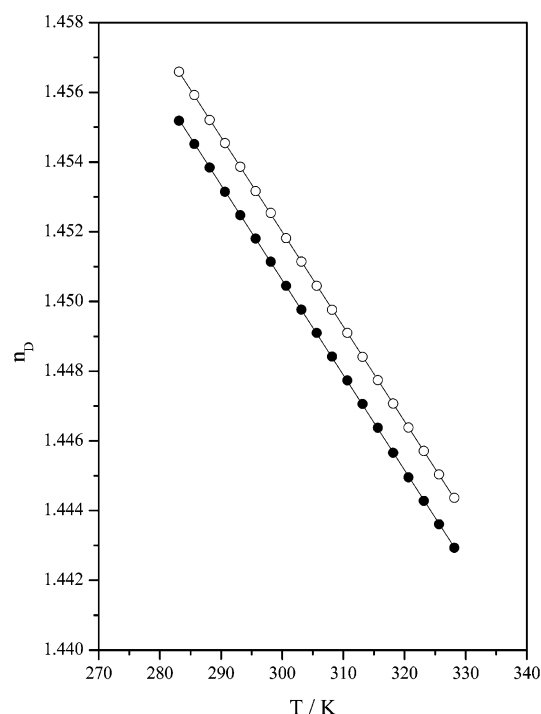

Figure 4. Refractive index as a function of temperature: (●) [b3mpy]-[BF$_4$], (○) [b4mpy][BF$_4$].

From the experimental surface tension measurements, the entropy and enthalpy of surface formation per unit surface area can be evaluated by applying:

$$\Delta S = -(\partial \sigma / \partial T)_p \tag{5}$$

$$\Delta H = \sigma - T(\partial \sigma / \partial T)_p \tag{6}$$

Given that the experimental values vary linearly with temperature, the entropy of surface formation per unit surface area
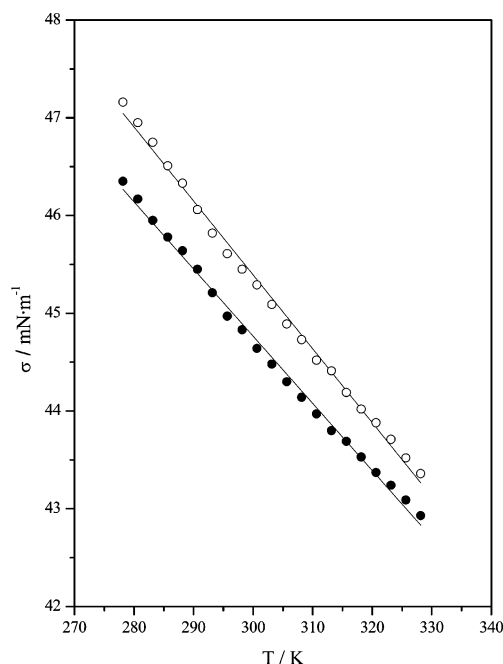

Figure 5. Surface tension as a function of temperature: (●) [b3mpy]-[BF$_4$], (○) [b4mpy][BF$_4$].

is, in this range, independent of temperature. Entropy values are 0.07 mN·m^{-1} K^{-1} for the ionic liquid [b3mpy][BF$_4$] and 0.08 mN·m^{-1} K^{-1} for [b4mpy][BF4]. The enthalpy of surface formation per unit area changes slightly with temperature, with values of 65.32 mN·m^{-1} and 67.99 mN·m^{-1} for [b3mpy][BF$_4$] and [b4mpy][BF4] at 298.15 K, respectively. Results show that both entropy and enthalpy of surface formation per unit area of the ionic liquid [b3mpy][BF$_4$] are somewhat smaller than for [b4mpy][BF$_4$]. The principle of independent surface action[23] can be used to describe the microscopic structure of a liquid surface. According to this theory, the surface tension of a substance should correspond to the part of the molecule that is actually present at the interface which also has its own local surface free energy. The requirement of maintaining electro-neutrality makes it impossible that the surface could completely consist of one type of ion, and this can be considered as a general statement for all of the room-temperature ionic liquids. In this case, the orientation of both anions and cations in the surface seems to be a determinant factor of the actual value of surface tension. Furthermore, a decrease of the entropy of surface formation could indicate an enhancement of the degree of surface orientation.[23] Therefore, the position of the methyl group in the [b3mpy][BF$_4$] could induce a better orientation of the ions into the surface than in the case of [b4mpy][BF$_4$].

As shown in Figure 6, isobaric molar heat capacity of the two isomeric ionic liquids studied increases when temperature does. Results indicate that isomer [b3mpy][BF$_4$] presents smaller values of isobaric molar heat capacity than ionic liquid [b4mpy]-[BF$_4$]. Values of isobaric molar heat capacity obtained for [b3mpy][BF$_4$] at several temperatures are comparable to those obtained earlier by Crosthwaite et al.[11] since the differences between both data series are less than 1.5%. The heat capacity of a substance is defined as the amount of energy per mole that the compound can store before the temperature of the substance increases. In general, the energy can be stored in vibrational, translational, and rotational modes. Previous studies have pointed out that the differences in the values of heat capacities of RTILs of the same family are related to an enhancement of the energy storage modes due to a higher number of atoms in the molecule.[4] This is not the case of the compounds that we
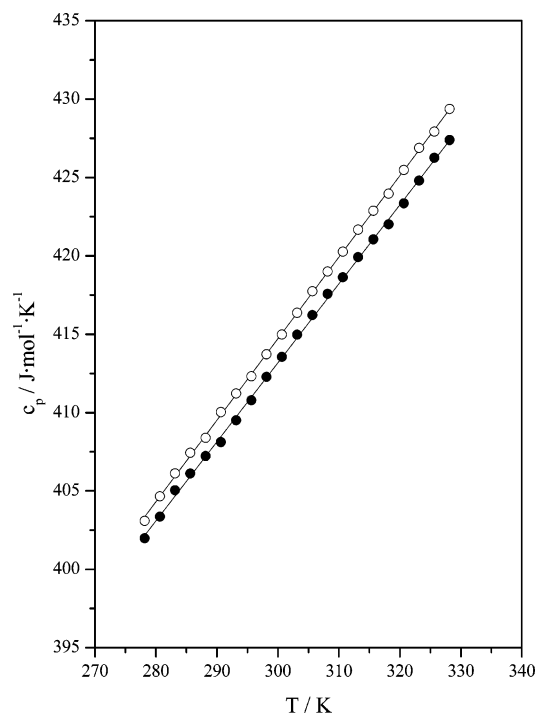
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Figure 6. Isobaric heat capacity as a function of temperature: (●) [b3mpy][BF$_4$], (○) [b4mpy][BF$_4$].

Figure 7. Viscosity as a function of temperature: (●) [b3mpy][BF$_4$], (○) [b4mpy][BF$_4$].

are studying here, and we cannot use this argument. However, the position of the methyl group affects this property, making slightly larger the ability of energy storage of the isomer [b4mpy][BF$_4$] than for its homologous [b3mpy][BF$_4$], and the position 4 of the methyl in the pyridine ring seems to be quite more capable of storing energy than that in position 3. A more exhaustive study involving some room-temperature ionic liquids of the same family might confirm this statement.

Dynamic viscosity of the ionic liquids as a function of temperature is graphically represented in Figure 7. The temperature dependency of the dynamic viscosity values presents convex curved profiles, and consequently, the data were fitted to a Vogel–Fulcher–Tamman equation[24–26] as follows:

$$\eta = \eta_0 \exp[B/(T - T_0)] \tag{7}$$

where η_0, B, and T_0 are the adjustable parameters collected in Table 1.

Results show that dynamic viscosity of the studied ionic liquids decreases dramatically with temperature, being considerably greater for the isomer [b4mpy][BF$_4$] than for [b3mpy][BF$_4$] at low temperatures whereas the differences are reduced when the temperature increases. As we have mentioned before, viscosity data for [b3mpy][BF$_4$] at several temperatures have been reported before.[11] Both value series are in good agreement, with the difference between them being of the order of approximately 2%.

Values of density, speed of sound, refractive index, molar refraction, surface tension, isobaric molar heat capacity, kinematic viscosity and dynamic viscosity of the ionic liquids *n*-butyl-3-methyl-pyridinium tetrafluoroborate and *n*-butyl-4-methyl-pyridinium tetrafluoroborate at the studied temperatures can be found in Supporting Information.

Thermodynamic Properties Predictions

The rational design of these kinds of compounds with pre-selected features is of great importance. Therefore, the develop-
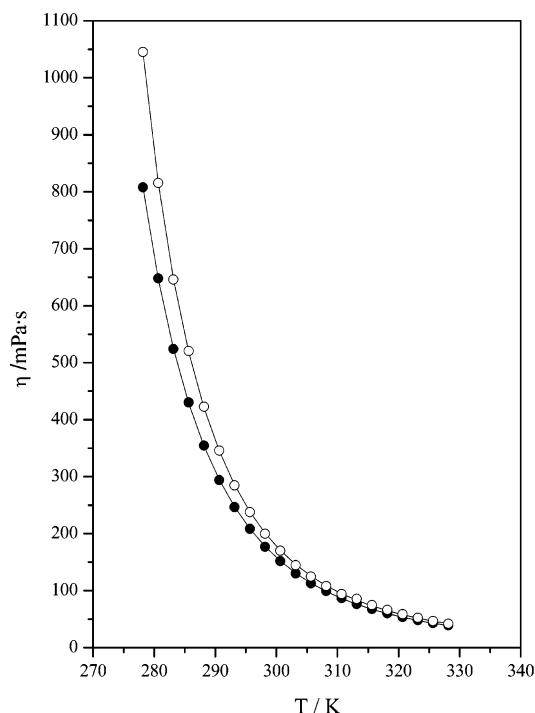
ment of estimation methods and predicting models of physical properties of unknown salts from their structure is needed as a previous step. The getting of accurate and new prediction methods of thermodynamic properties of the room-temperature ionic liquids is limited to the knowledge we have of them. For instance, previous works have proven that the use of estimation methods such as parachor parameter model,[13] though in principle for noncharged compounds, can also be used as a first approach in the prediction of physical properties of ionic liquids. In this paper, we have applied the parachor parameter model to obtain properties such as density and surface tension of the studied ionic liquids. Following the suggestions of Seddon et al.,[13] who claimed that not many experimental data of physicochemical properties of ionic liquids are available, the parachor contribution data for neutral compounds could be used to estimate the density of these kinds of chemicals from their surface tension and vice versa. These authors applied the parameter to imidazolium-based RTILs and obtained good accuracy. However, in the future, better results could be obtained following the same scheme when the experimental thermodynamic database of room-temperature ionic liquids is wide enough to get the parachor contribution data.

The parachor, *P*, is a relationship between density and surface tension, and it is defined by the following equation:

$$P = \frac{(Fw)\cdot\sigma^{1/4}}{\rho} \tag{8}$$

where *Fw* is the formula weight. It has been proven that, over moderate temperatures ranges, *P* is essentially constant.

The parachor of a compound is calculated as the sum of its parachor contributions which are obtained from quantitative structure property relationship (QSPR) methods. Therefore, the larger the database is, the better the parachor contribution values are. Rowley et al.[27] improved original contribution data using the Design Institute for Physical Properties (DIPPR) database for neutral organics in the development of the QSPR correlation.

TABLE 2: Errors in the Estimation of Physical Properties with Parachor Parameter, Molar Refraction, and Auerbach Relation

	property	[b3mpy][BF$_4$]	[b4mpy][BF$_4$]
parachor parameter	ρ/g·cm^{-3}	1.27	0.94
	σ/mN·m^{-1}	5.27	3.86
molar refraction	ρ/g·cm^{-3}	7.92	7.70
	n_D	3.13	3.04
Auerbach relation	ρ/g·cm^{-3}	3.74	3.72
	σ/mN·m^{-1}	3.93	3.90
	u/m·s^{-1}	2.52	2.50

In this case, the parachor has been determined for [b4mpy]-[BF$_4$] and [b3mpy][BF$_4$] from available parachor contribution data,[27] which were calculated using the experimental superficial tension with uncertainties of less than 1%. This method is not able to differ isomeric compounds, and consequently, the parachor for RTILs studied in this work is the same for both liquids and has a temperature-independent value of 526.19.

The experimental parachor can be obtained using eq 7 and experimental properties at each temperature. The calculated parameter changes with temperature for both liquids: in the case of [b4mpy][BF$_4$], it is from 519.53 to 523.48, whereas for [b3mpy][BF$_4$], it varies from 517.20 to 522.41. Since *P* is proportional to molar volume, the values obtained experimentally, which are smaller than the ones obtained from the theory, imply that ions in the liquid are more closely packed than parachor theory estimates. This could be explained taking into account that the parachor parameter model does not consider Coulombic interactions between ions, which are characteristic of RTILs.

The differences between experimental and calculated values are evaluated by means of error, *E*, defined by:

$$E/\% = \frac{100}{n} \sum \left| \frac{Y_{exp} - Y_{calc}}{Y_{exp}} \right| \tag{9}$$

where *n* is the number of experimental data points for each property and Y_{exp} and Y_{cal} are the experimental and calculated value of the studied property respectively. Errors in the estimations are shown in Table 2.

Density predictions are in good agreement with experimental values for both liquids, since the errors are smaller than 1.5%. The lower differences are obtained at high temperatures, although in all cases the estimated value is very similar to the experimental data. The errors in the surface tension predictions are much larger than in the density, with the differences being approximately 7% at low temperatures and less when temperature increases. From these results, we can conclude that estimations for density are good for both compounds, being the obtained values for [b4mpy][BF$_4$] are better than for [b3mpy]-[BF$_4$].

Taking into account the small differences found between experimental and theoretical data, whose values are comparable to results obtained for uncharged compounds, with typical errors in the order of 5%,[28,29] parachor parameter can be used for the estimation of the density and surface tension of these kinds of RTILs.

Likewise to parachor parameter, the molar refraction of a compound defined by the Lorentz–Lorentz relation can be determined as the sum of the contributions of each of the atoms in the molecule. Using this relationship, we find the density of a compound can be estimated from its refractive index and vice versa. In the same way, molar refraction contributions for neutral compounds can be used to calculate this property, to obtain a first approximation of the physical properties.

The R_m was determined for [b3mpy][BF$_4$] and [b4mpy][BF$_4$] from available contribution data,[14] obtaining a value of 58.67 for both compounds since again the method makes no differences between isomeric compounds. This value is higher than the experimental molar refraction for both liquids for the whole range of temperatures indicating that this method overestimates the actual hard core volume of the studied ionic liquids. The differences between experimental and calculated data are gathered in Table 2. The errors in the density predictions using this theory are much larger than those obtained with parachor parameter, being that the differences are close to 8%. In contrast, refractive index predictions are better, getting errors smaller than 3.5%. Estimations are quite similar for both liquids.

Another expression designed in principle for noncharged chemicals is the Auerbach relation.[15] It is a well-known empirical relation between different physical properties such as surface tension, density, and speed of sound of liquids:

$$u = \left(\frac{\sigma}{0.00063 \cdot \rho} \right)^{2/3} \tag{10}$$

From this equation, each one of these properties has been determined at several temperatures using experimental values of the two other properties implied in the Auerbach relation. For example, speeds of sound have been calculated using experimental values of density and surface tension, and in a similar way, density and surface tension can be obtained. With the purpose of checking the validity of this equation for ionic liquids, we have compared experimental and predicted values of these properties, finding that estimated values for [b3mpy]-[BF$_4$] and [b4mpy][BF$_4$] are better at high temperatures, increasing the differences at low temperatures. The errors in the estimations are gathered in Table 2. Taking into account the differences obtained in each property, we notice that the prediction of speeds of sound is in good agreement with experimental values whereas the results worsen in density and surface tension predictions. From the results, density estimations from parachor parameter model are better than values obtained from the Auerbach relation. Moreover, the parachor seems to be more useful since only experimental surface tension values are required to perform the estimations, and therefore, less experimental data from the IL under study are necessary to calculate the desired physical property. Although discrepancies between data are quite similar, in general, we have obtained better results for [b4mpy][BF$_4$].

Recently, new theoretical models for ionic liquids have been developed. This is the case of the interstice model,[17] which is similar to hole model of molten salts. The model is based on several assumptions related to the interstices of the structure of the RTILs. Because of the different structures of the ions which form part of the RTILs, there are a significantly amount of interstices. Their number is considered to be 2*N* for 1 mol of 1−1 ionic liquid, with *N* as the Avogadro constant. Furthermore, these interstices are supposed to be bubbles which change their volume when they are in movement. Nevertheless, they cannot disappear.

The expression to calculate the interstice volume, *v*, according to classical statistical mechanics, is:

$$v = 0.6791 \cdot \left(\frac{k_b \cdot T}{\sigma} \right)^{3/2} \tag{11}$$

where k_b is the Boltzmann constant. From this equation, the average volume of the interstices for both RTILs at each temperature can be obtained from the experimental superficial

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TABLE 3: Values of Parameters of ILs for the Interstice Model at Several Temperatures

ionic liquid	T/K	Σv/V	α_{cal}/K^{-1}	α_{exp}/K^{-1}
[b3mpy][BF$_4$]	283.15	0.10	5.41×10^{-4}	5.96×10^{-4}
	298.15	0.11	5.71×10^{-4}	5.91×10^{-4}
	313.15	0.13	6.01×10^{-4}	5.85×10^{-4}
[b4mpy][BF$_4$]	283.15	0.10	5.27×10^{-4}	5.84×10^{-4}
	298.15	0.11	5.59×10^{-4}	5.80×10^{-4}
	313.15	0.12	5.88×10^{-4}	5.74×10^{-4}

tension. Afterward, the molar volume of the interstice is determined as $\Sigma v = 2 \cdot N \cdot v$. The volume fraction of interstices is calculated as $\Sigma v/V$, where V is the molar volume. In all cases, volume fraction lies between 0.09 and 0.14, which is in good agreement with most of the materials that present a $10-15\%$ volume expansion in transition from the solid to the liquid state.

The model considers that the volume of an ionic liquid is the sum of two components; the inherent volume, V_i, and the total volume of all interstices:

$$V = V_i + 2 \cdot N \cdot v \tag{12}$$

The thermal expansion coefficient, α, is derived from the model taking into account that the expansion of an ionic liquid only results from the extension of the interstices when temperature increases:

$$\alpha = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_p = \frac{3 \cdot N \cdot v}{V \cdot T} \tag{13}$$

From this equation, the coefficients of thermal expansion at each temperature have been calculated. The obtained results are collected in Table 3. With the aim of evaluating the validity of this model, we have compared empirical and theoretical data of α. A good agreement between both values has been found for intermediate temperatures in the studied range. From these results, it can be concluded that the interstice model can be used to estimate coefficients of thermal expansion of RTILs with relatively good accuracy.

The theory of Glasser[16] proposes a method for estimating lattice potential energies of ionic liquids to predict their relative stabilities. Lattice energy is the energy required to remove the ions from their position in the crystal structure to infinite separation. Therefore, the larger the lattice energy, the more stable the compound. With this aim, Glasser developed a procedure based on the chemical formula, the ionic charges, and the molecular volume of the ionic substance, without dependence of structural information for the evaluation of the energy. When Coulombic interactions are the main contribution to lattice potential energy, the application of this theory is more reliable.

The lattice energy for a 1:1 salt type (expressed in kJ·mol^{-1}) is calculated with the following equation:

$$U_{POT} = 1981.2 \cdot \left(\frac{\rho}{Fw}\right)^{1/3} + 103.8 \tag{14}$$

When this equation is applied to the RTILs studied in this paper, using the experimental density at 298.15 K, $U_{POT} = 442.3$ kJ·mol^{-1} for both liquids, [b3mpy][BF$_4$] and [b4mpy][BF$_4$]. This value is similar to the lattice energy obtained in other ionic liquids such as 1-methyl-3-hexylimidazolium chlorogallate (406.1 kJ·mol^{-1})[6] or 1-ethyl-3-methylimidazolium aminoacetate (469 kJ·mol^{-1})[3] and lower than that of other inorganic fused salts such as CsI (602.5 kJ·mol^{-1}). Therefore, the energy required to remove ions from their position in the structure is

less than that for inorganic salts, which explains why ionic liquids are liquids at room temperature.

The vaporization enthalpies of ionic liquids can be estimated at 298.15 K from experimental values of surface tension with the following equation:[18]

$$\Delta_l^g H_m^o = A \cdot (\sigma \cdot V^{2/3} \cdot N_A^{1/3}) + B \tag{15}$$

where A and B are empirical parameters obtained by Kabo et al.[18] Their values are $A = 0.01121$ and $B = 2.4$ kJ·mol^{-1}.

The estimated enthalpies of vaporization were found to be quite similar for both liquids: $\Delta_l^g H_m^o = 206.2$ kJ·mol^{-1} for [b3mpy][BF$_4$] and $\Delta_l^g H_m^o = 209.0$ kJ·mol^{-1} for [b4mpy][BF$_4$]. Results show that vaporization enthalpies of RTILs are much larger than enthalpies for most organic liquids including hexane (31.52 ± 0.13 kJ·mol^{-1}), 1-propanol (47.45 ± 0.1 kJ·mol^{-1}), or water (43.99 ± 0.07 kJ·mol^{-1}).[30] This is a sign of the importance of Coulomb forces in ionic liquids.

Conclusions

In this paper, we have investigated the thermophysical properties of two isomeric room-temperature ionic liquids, *n*-butyl-3-methyl-pyridinium tetrafluoroborate and *n*-butyl-4-methyl-pyridinium tetrafluoroborate. The study is based on experimental measurements in a wide interval of temperatures, of properties such as density, speed of sound, refractive index, surface tension, isobaric molar heat capacities, and kinematic viscosity. From the experimental results, coefficients of thermal expansion, molar refractions, and dynamic viscosities at the studied temperatures have been obtained. Furthermore, we have calculated entropies and enthalpies of surface formation per unit surface area. Results have been analyzed and discussed paying special attention to the molecular characteristics of the ionic liquids.

We have also studied several theories proposed earlier to estimate the properties of the studied ionic liquids at different temperatures. Although some of them are not specifically designed for ionic liquids, a good agreement between experimental and predicted data has been found. Furthermore, theoretical results have been comprehensively analyzed with the aim of evaluating the validity of these theories and models, obtaining relevant information about the potential use of these theories when they are applied to room-temperature ionic liquids. Despite limitations of the parachor contributions of the parachor parameter model, they can be used providing relatively good results especially in density estimations, with differences between experimental and predicted data comparable to those obtained for noncharged compounds. In the same way, determination of the molar refraction as the sum of molar refraction contribution data for uncharged compounds permits to predict refractive index from experimental density values. Furthermore, taking into account the small errors, we find that speeds of sound can be calculated using the Auerbach relation whereas surface tension and density estimations found with this equation are quite different from experimental data. More specific theories for RTILs have been applied including the interstice model, which can be used with good accuracy to get volumetric properties such as the thermal expansion coefficient. Finally, using the Kabo's method and the theory of Glasser, the enthalpy of vaporization at 298.15 K and the lattice energy of the ionic liquids can be estimated.

More work is in progress to complete the thermophysical study of this family of RTILs.

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Supporting Information Available: Values of density, speed of sound, refractive index, molar refraction, surface tension, isobaric molar heat capacity, and kinematic viscosity and dynamic viscosity of the ionic liquids *n*-butyl-3-methyl-pyridinium tetrafluoroborate and *n*-butyl-4-methyl-pyridinium tetrafluoroborate. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tokuda, H.; Hayamizu, K.; Ishii, K.; Hasan Susan, M. A. B.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.

(2) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, *72*, 2275.

(3) Yang, J.-Z.; Zhang, Q.-G.; Wang, B.; Tong, J. *J. Phys. Chem. B* **2006**, *110*, 22521.

(4) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954.

(5) Zhang, Q.; Li, Z.; Zhang, J.; Zhang, S.; Zhu, L.; Yang, J.; Zhang, X.; Deng, Y. *J. Phys. Chem. B* **2007**, *111*, 2864.

(6) Tong, J.; Liu, Q.-S.; Guan, W.; Yang, J.-Z. *J. Phys. Chem. B* **2007**, *111*, 3197.

(7) Zhang, Q.-G.; Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Huang, M. *Fluid Phase Equilibr.* **2004**, *226*, 207.

(8) Tokuda, H.; Hayamizu, K.; Ishii, K.; Hasan Susan, M. A. B.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.

(9) Davila, M. J.; Aparicio, S.; Alcalde, R.; Garcia, B.; Leal, J. M. *Green Chem.* **2007**, *9*, 221.

(10) Tokuda, H.; Ishii, K.; Hasan Susan, M. A. B.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833.

(11) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. *J. Chem. Thermodyn.* **2005**, *37*, 559.

(12) Ye, C.; Shreeve, J. M. *J. Phys. Chem. A* **2007**, *111*, 1456.

(13) Deetlefs, M.; Seddon, K. R.; Shara, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 642.

(14) Wildman, S. A.; Crippen, G. M. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 868.

(15) Auerbach, R. *Experientia* **1948**, *4*, 473.

(16) Glasser, L. *Thermochim. Acta* **2004**, *421*, 87.

(17) Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Xu, W.-G. *Green Chem.* **2004**, *6*, 541.

(18) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. *J. Phys. Chem. A* **2006**, *110*, 7303.

(19) Fandiño, O.; Pensado, A. S.; Lugo, L.; Lopez, E. R.; Fernandez, J. *Green Chem.* **2005**, *7*, 775.

(20) Lundstrum, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M. F.; Caudwell, D. R.; Trusler, J. P. M. *J. Chem. Eng. Data* **2005**, *50*, 1377.

(21) Miller, R.; Hofmann, A.; Hartmann, R.; Schano, K.-H.; Halbig, A. *Adv. Mater.* **1992**, *5*, 370.

(22) Giner, B.; Cea, P.; Lopez, M. C.; Royo, F. M.; Lafuente, C. *J. Colloid Interface Sci.* **2004**, *275*, 284.

(23) Law, G.; Watson, P. R. *Langmuir* **2001**, *17*, 6138.

(24) Vogel, H. *Phys. Z.* **1921**, *22*, 645.

(25) Fulcher, G. S. *J. Am. Ceram. Soc.* **1923**, *8*, 339.

(26) Tamman, G.; Hesse, W. Z. *Anorg. Allg. Chem.* **1926**, *156*, 245.

(27) Knotts, T. A.; Wilding, W. V.; Oscarson, J. L.; Rowley, R. L. *J. Chem. Eng. Data* **2001**, *46*, 1007.

(28) Dominguez-Perez, M.; Segade, L.; Franjo, C.; Cabeza, O.; Jimenez, E. *Fluid Phase Equilibr.* **2005**, *232*, 9.

(29) Cumber, P. *J. Hazard Mater.* **2002**, *A89*, 127.

(30) Chickos, J. S.; Acree, W. E., Jr. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519.