Transport and thermodynamic properties in low melting point ionic liquids related to *n*-alkyl chain length

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Letter

Transport and thermodynamic properties in low melting point ionic liquids related to *n*-alkyl chain length

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Room-temperature ionic liquids (RTIL) are offering 'green' alternatives to organic solvents in industrial processes. Therefore, we propose here, with *n*-alkyl chain length as the focus, some inter-relationships involving transport as well as thermodynamic properties. Experimental work is suggested to examine whether (a) extended defect models of melting are useful for RTIL and (b) the product of surface tension and isothermal compressibility, which has the dimensions of length, varies systematically with the choice of anions as well as with the number of carbon atoms in the *n*-alkyl chain.

The development of 'green' technologies has proliferated due to the promise of room-temperature ionic liquids (RTIL). While much of the recent work with RTIL as solvents has been directed toward the application of N-alkylpyridinium or 1,3-dialkylimidazolium salts, it is well recognized that variations in both cation and anion choices can be used to arrive at favorable solvent properties [1–8].

With the above motivation, we shall in this article make some proposals which could lead to the demonstration of useful relationships of physical and chemical properties, both for non-equilibrium properties, such as diffusion and viscosity, and for equilibrium thermodynamic quantities such as (a) critical constants T_c, V_c and p_c and (b) surface tension, to take but two examples. We shall find it useful to consider, in this approach, the length of the linear alkyl chain as an independent variable (the number n of carbon atoms in the *n*-alkyl group R) for choices of different anions (e.g., BF_4^- and PF_6^-) of 1-R-3-methylimidazolium salts.

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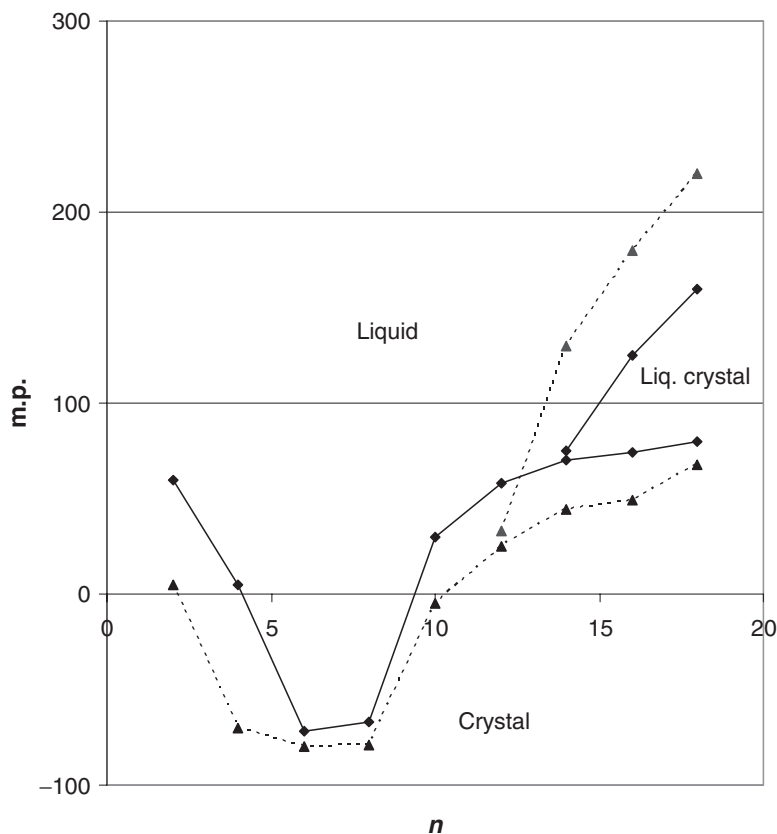
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Figure 1.   Melting points ($^{\circ}$C) *vs*. the linear-alkyl chain length (where *n* is the number of carbon atoms in the alkyl group R) of the 1-R-3-methylimidazolium cation (Rmim). Continuous lines refer to the hexafluorophosphate anion. Dashed lines denote data for the tetrafluoroborate anion.

   Thus, in figure 1, we have combined into one figure the results of Holbrey and Seddon [8] for the melting temperature T_m of the above salts with these two different anions. There is a similarity as the anion is changed, and in particular the low melting point, rather flat, regions are relatively insensitive to the change in anion. It would, of course, for the future, be interesting to see how further changes in anion choice affects the low-temperature region.

   In connection with this regime, it is relevant here to refer to recent work [9] on the *n*-alkanes in which melting temperatures were already studied phenomenologically as a function of chain length. This prompts the suggestion regarding figure 1 that here, in comparison with the *n*-alkanes, the rather constant low-temperature region is in fact approaching the 'saturation' or infinite chain length limit. However, it is tempting to propose that at both ends of the 'constant' T_m regimes in figure 1 there are 'crossovers' to other types of phase behavior.

   Turning to other physical and chemical properties of 1-alkyl-3-methylimidazolium salts, we next draw attention to the important experimental study of bis(trifluoro-methane sulfonyl)imides presented by Tokuda *et al*. [10, figure 8] which has been converted by us by redrawing their data for transport coefficients for mass
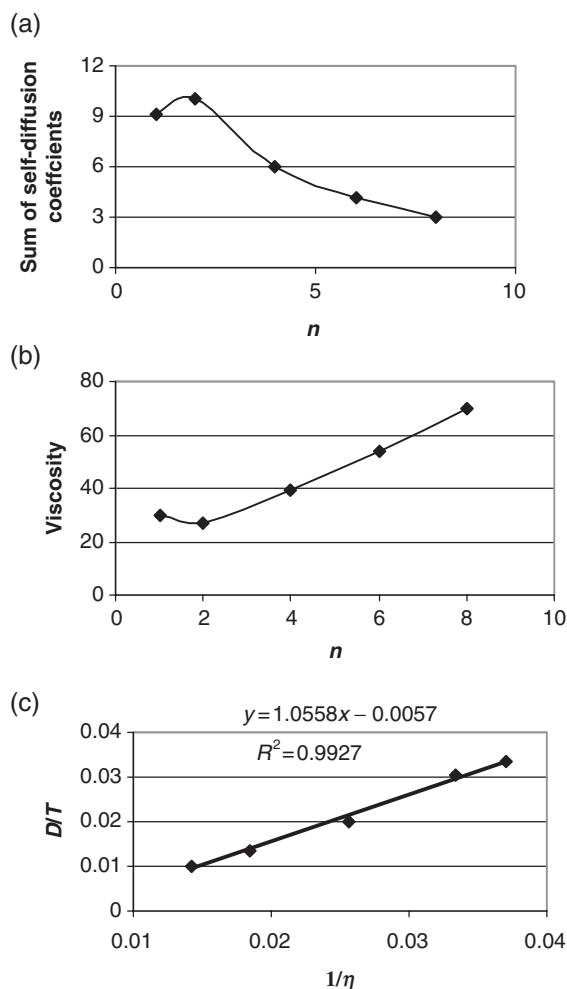
(a)

(b)

(c)

Figure 2. Transport coefficients for some RTILs. (a): diffusion coefficient D as a function of chain length (n). (b): viscosity (η) as it varies with chain length (n). (c): D/T *vs.* η^{-1} showing approximate validity of Stokes–Einstein relation (equation (1)) with the variation of the Stokes radius.

(D in figure 2a) and momentum (viscosity η in figure 2b): we have also plotted D/T *versus* η^{-1} in figure 2(c), as is motivated by the Stokes–Einstein relation, which reads:

$$D = k_B T / c\pi\eta r_S \qquad (1)$$

where $k_B T$ is the thermal energy corresponding to the absolute temperature (assumed to be 300 K), c is a constant, while r_S denotes the effective hydrodynamic Stokes radius. Measurements of transport properties as a function of the nature of the anion (in addition to the length of the alkyl chain) have been reported by Every *et al.* [11].

We next consider some models which result in predictions of inter-relationships between thermodynamic quantities. Let us start with surface tension σ on which some measurements exist for low melting point ionic liquids [12,13].

Going back to Frenkel, but especially emphasized by Egelstaff and Widom [14] for simple liquids and by Freeman and March [15] for organic species, the product (ℓ) of σ and isothermal compressibility K_T is readily shown to have dimensions of length. Then,

$$\sigma K_T \equiv \ell, \tag{2}$$

and ℓ is a fraction of an Å (Angström) for both simple liquids [15] and a whole variety of organic liquids. If measurements of K_T become available, either in the crystalline phase just below T_m, or in the liquid phase just above T_m, we believe it is of interest to find: (i) how ℓ depends on the *n*-alkyl chain length and (ii) how anionic species affect this 'characteristic length'.

The second 'model' we appeal to is a dislocation-mediated mechanism of melting. Interest in such a model, which goes back to work associated with the names of Kuhlmann-Wilsdorf and Cotterill, has been reopened recently by Burakovsky *et al*. [16,17] and by Kleinert and Jiang [18]. Both groups of authors, when their treatments are applied to transition metals such as tungsten and nickel, are led to a result, as stressed by Matthai and March [19] having the general shape

$$k_B T_m = \Omega F S, \tag{3}$$

where F is a function of the elastic constants. In the monatomic d-electron metals considered in refs. [16–19], S is a structure-dependent factor, which is therefore different for body-centered-cubic (bcc) W and face-centered-cubic (fcc) Ni, while Ω denotes the atomic volume. Matthai and March [19] appeal to the simplest form of the function F given in [16–19] to reach the result

$$k_B T_m = \Omega G S, \tag{4}$$

where G is the shear modulus of the solid at T_m. In the transition metals, one has $S_{fcc}/S_{bcc} \approx 5/7$, so that S appears to be not very sensitive to structure.

Though some workers (see, for example [20]) have given attention to the crystal structure into which certain liquids freeze, we have not, to date, found experimental values for the shear modulus G. We believe it would be valuable to test whether equation (4) is useful in the case of low-melting point ionic liquids, when the atomic volume Ω appropriate to the transition metals is replaced by a molecular volume. Comparison then, using measured data for the latter volume plus shear modulus data, could be made with figure 1 to test, and if necessary to refine, equation (4).

In conclusion, self-diffusion and viscosity coefficients in some selected RTILs shown in figures 2(a) and 2(b), respectively, at around room temperature, show features depending on the *n*-alkyl chain length which, however, approximately compensate to allow the approximate validity of the Stokes–Einstein relation (1), when any variation of the hydrodynamic radius with chain length is neglected. Finally, two further relations, which are useful in monatomic liquids, are proposed as worthy of experimental test in RTIL. These are (i) the microscopic length ℓ defined in equation (2), and its possible dependence on (a) the chosen anion and (b) the alkyl chain length; and (ii) the proposed relation of the melting temperature data depicted in figure 1

to the shear modulus of the associated crystals near their melting temperature. Regularities in the latent heat in relation to molecular volume and/or shear modulus seem also worthy of experimental study.

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