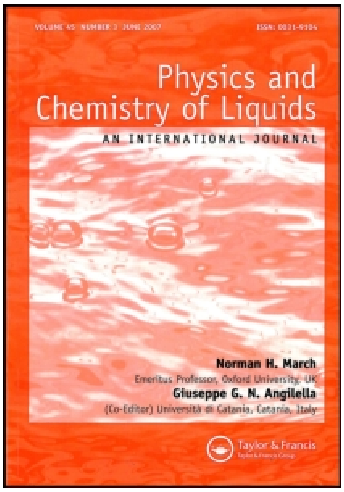

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Aqueous solutions of a "green" ionic liquid and of lithium chloride compared and contrasted

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Letter

Aqueous solutions of a "green" ionic liquid and of lithium chloride compared and contrasted

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Aqueous solutions of (a) a "green" ionic liquid and (b) lithium chloride are considered here. Proposals are made in respect to momentum transfer as characterized by shear viscosity, η. Arrhenius-type behavior as a function of temperature is contrasted with possible power-law form. More generally, η is written as a product of mass density, the velocity of sound squared, and a characteristic time. Experiments are proposed for testing present ideas also involving the Debye–Hückel screening length.

Keywords: Aqueous solution of ionic liquid and LiCl; Shear viscosity; Velocity of sound; Debye–Hückel screening length

In an earlier letter published in this journal [1], we have made some proposals concerning both experiment and theory on "green" ionic liquids [2–4]. Here, our interests are extended to focusing on a particular ionic liquid in aqueous solution. Besides noting some earlier thermodynamic studies on an aqueous solution of LiCl, summarized in figure 1 [5], our main focus is on transport properties as a function of absolute temperature, T, and in particular the shear viscosity η. We shall generalize here an earlier study [6] on transport properties of monatomic insulating liquids and liquid alkali metals. There it is stressed that one must first address the question, in the temperature range considered, whether η has an Arrhenius-type factor $\exp(E_b/k_BT)$, where E_b represents a barrier height to be compared with the thermal energy k_BT,

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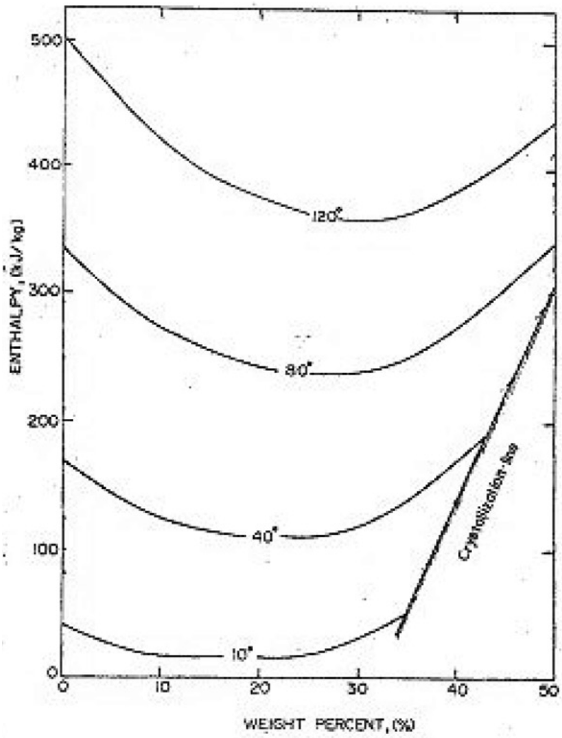

Figure1. Selected thermodynamic isotherms for LiCl in aqueous solution across the phase diagram (redrawn from Chaudhari and Patel [5]).

with k_B denoting Boltzmann's constant. If we have $E_b/k_BT \ll 1$, as in liquid alkali metals already mentioned above, then a temperature dependency of η like $T^{-1/2}$ can be anticipated.

Motivated at first by dimensional analysis, one can write for a neutral insulating liquid like argon:

$$\eta \sim \frac{d\xi^2}{t_c} \tag{1}$$

where d denotes a mass density, ξ is a correlation length expected to involve two-particle correlation functions, while t_c is a characteristic time entering the process of momentum transfer. Turning to an alternative form of equation (1) suitable for Coulomb liquids, one can rewrite it as

$$\eta \sim d v_s^2 t_c \tag{2}$$

where v_s (v_{sound}) is the sound velocity: a collective property of the aqueous solutions considered later. In turn, thermodynamics can be used to express v_s through the adiabatic bulk modulus B_{ad}, which is related to its isothermal counterpart B_T by

$$B_{\text{ad}}^{-1} = B_T^{-1} - \left(\frac{T\alpha^2}{C_p}\right) \tag{3}$$

α being the thermal expansion coefficient, while C_p is the heat capacity per unit volume at constant pressure.

We next note specifically that a characteristic length in a liquid metal is the Thomas–Fermi (TF) screening length L_{TF} [7]. It is therefore natural in electrolytes to note that this has the Debye–Hückel (DH) screening length L_{DH} as its counterpart.

By the way of illustration, in a liquid alkali metal

$$\eta \sim \frac{Mnv_{\text{sound}}^2 L_{TF}}{v_{\text{thermal}}} \tag{4}$$

where n is the number density of (monovalent) ions of mass M, while $v_{\text{thermal}} = (k_B T/M)^{1/2}$ measures the thermal velocity of these ions in equilibrium at temperature T.

It is tempting, but will, of course, need testing eventually by confrontation with experiment, to assume, by comparison, for the aqueous solutions under discussion here that the characteristic time t_c entering the result (2) will become

$$t_c \sim \frac{L_{DH}}{v_{\text{thermal}}} \tag{5}$$

where v_{thermal} will involve an appropriate average M of the various molecular/ionic masses involved. The introduction of the Debye–Hückel (DH) screening length L_{DH} into the formula (2) for the shear viscosity is the main proposal of this letter. Writing this length in the form

$$L_{DH} \sim \left(\frac{Kk_B T}{ne^2}\right)^{1/2} \tag{6}$$

with K the dielectric constant and e the ionic charge, this leads to the characteristic time t_c from equation (5) as

$$t_c \sim \left(\frac{Kk_B T}{ne^2}\right)^{1/2}. \tag{7}$$

To conclude, we wish to add some remarks about thermodynamics, for which literature studies already exist for LiCl in aqueous solution. In particular, figure 1 has been redrawn from the study of Chaudhari and Patel [5] for the enthalpy of LiCl in aqueous solution across the phase diagram, some isotherms being displayed there. The crystallization line is also shown. It should be of obvious interest for the future if such thermodynamic knowledge could also be obtained for green ionic liquids, to compare and contrast with the LiCl data.

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