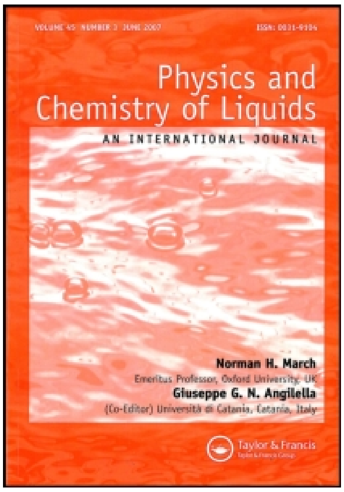

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Melting points and other properties of ionic liquids, with emphasis on the pressure dependence

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LETTER

Melting points and other properties of ionic liquids, with emphasis on the pressure dependence

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The focus of this letter is on melting points (T_m) of 'green' ionic liquids, which have values of T_m around room temperature. To aid in their chemical interpretation, we place some emphasis on T_m as a function of pressure p, in cases where such experimental information is available. Finally, some comments are made on the effects of pressure *via* isothermal compressibility κ_T and the velocity v_s of sound. Some measurements of κ_T and v_s as a function of p are invoked.

Keywords: 'green' ionic liquids; pressure-dependence of melting; topological defects and melting; wetting index

1. Introduction

In an earlier study, we were concerned with phase-transition regularities in critical constants, fusion temperatures and enthalpies of chemically similar chainlike structures [1]. Because the development of 'green' technologies has proliferated, due at least in part to the promise of room-temperature ionic liquids (RTILs), we have also considered how both thermodynamic properties and transport are affected by *n*-alkyl chain length in appropriate RTILs [2].

Here the work on melting temperatures (T_m) of RTILs is first generalised to embrace experimental information on the pressure dependence of T_m. Then a brief discussion will follow on the wetting index (WI) of such liquids, with proposals as to the way this index may be expected to vary with pressure.

To introduce the study of the melting temperature T_m for RTILs, we first stress that inorganic ionic compounds typically display high-melting points due to strong electrostatic interactions (see Table 1 for the alkali halides). We have also included the ionic radii involved in Table 1.

Returning to RTILs, let us first consider T_m at atmospheric pressure. As discussed by Trohalaki *et al.* [3], in conjunction with their Table 1, the melting points are known for 'energetic ionic liquids' based on 1-substituted 4-amino-1,2,4-triazolium bromides and nitrates. As noted in [3], the nitrate salts generally have lower melting points than those for the bromide counterparts. For the *n*-alkyl-substituted compounds, the melting points increase, in general, as the length of the alkyl group increases (compare also Figure 1 of [1]).

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Table 1. Melting temperatures (T_m in K) for alkali halides. Values in parentheses are ionic radii (in pm) for coordination numbers CN = 6, but for Cs the CN may be 8.

	F (133)	Cl (181)	Br (196)	I (220)
Li (76)	1121	883	825	742
Na (102)	1269	1074	1020	933
K (138)	1131	1044	1007	954
Rb (162)	1106	988	955	915
Cs (167)	976	918	909	894

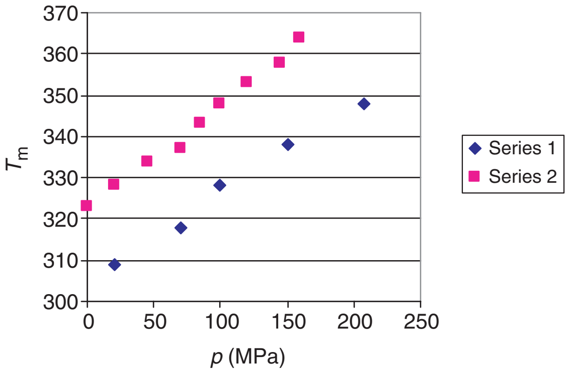

Figure 1. Melting temperature (T_m in K) *vs.* p (MPa). Series 1 is for [mmim][H_3CSO_4], and Series 2 for [emim][Tos].

Let us turn to this point to consider the effect of pressure p on the thermodynamic properties of RTILs, and in particular first of all consider the form of the melting curve T_m *versus* p. Following that, we shall refer briefly to some other properties, including compressibility and velocity of sound, which have also been measured as a function of pressure. We have redrawn in Figure 1 the plot of the melting temperature under pressure for the RTILs investigated experimentally in [4]. The important point which these research workers revealed was the substantial increase in the melting temperature with increasing pressure for ionic liquids such as dimethylimidazolium methanesulfonate [mmim][H_3CSO_4] and ethyl-methylimidazolium *para*-toluenesulfonate [emim][Tos].

In the last section of the present Letter, we offer a plausible explanation of this behaviour based on a ‘topological defects model’ applied to the melting point of RTILs. Following this brief survey of $T_m(p)$, we turn to discuss some experimental factors on two further thermodynamic quantities.

2. Velocity of sound $v_s(p)$ and other properties of ionic liquids as a function of pressure p

Next, we summarise some of the important measurements of de Azevedo *et al.* [5] for some thermodynamic properties of 1-butyl-3-methylimidazolium tetrafluoroborate [$bmim^+$][BF_4^-] and hexafluorophosphate [$bmim^+$][PF_6^-] over an extended pressure range.

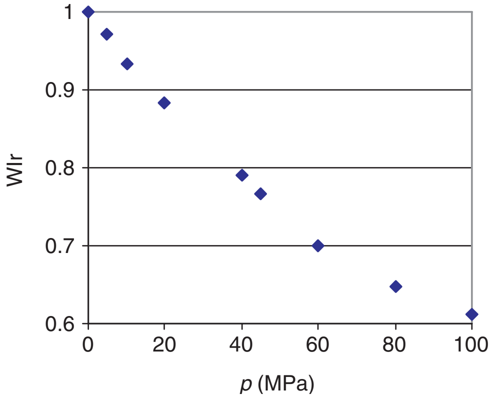

Figure 2. Plot of the relative wetting index WIr *vs*. pressure (in MPa) for [bmim][PF_6].

Starting with the velocity of sound $v_s(p)$, de Azevedo *et al*. fit their measured data to a 2-variable [3,3/3,3] Padé approximant:

$$v_s(p) = \frac{\sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} T^i p^j}{\sum_{k=0}^{2} \sum_{l=0}^{2} b_{kl} T^k p^l} \tag{1}$$

The coefficients a_{ij} and b_{kl} are tabulated in [5] have fit over an interval (283 K < T < 383 K; 0.1 MPa < p < 100 MPa) for [bmim^+][PF_6^-]. The velocity of sound v_s along isotherms was found experimentally to increase with increasing pressure p from values $\sim$1400 ms^{-1} at atmospheric pressure to $\sim$1600 ms^{-1} at $p = 100$ MPa (see Figure 1 of [5]). Similarly, the isotherms of the compressibility κ_T, which decreases considerably with increasing pressure p up to 100 MPa are given in Figure 6 of [5].

Using this data for $v_s(p)$ and $\kappa_T(p)$, as well as the density ρ (in kg m^{-3}) for butyl-methyl-imidazolium hexafluorophosphate [bmim][PF_6], we have utilised our recent analysis [6] to calculate the wetting index (WI) given by

$$\text{WI} = 1000 \rho v_{\text{char}} \kappa_T^2 / \ell^2 \tag{2}$$

This result is based on the assumptions: (i) that the length ℓ in Equation (2), defined as the product of surface tension and κ_T, is insensitive to pressure variation, at least over the range $0 < p < 100$ MPa; and (ii) that the characteristic velocity v_{char} introduced in [6] in the formula proposed for the wetting index WI is replaced by the velocity of sound $v_s(p)$ over the above pressure range. To avoid multiplicative constants, and the length ℓ, we work with a relative wetting index WIr which is WI(p) divided by WI(0). Then we plot this relative wetting index WIr at $T = 314$ K ± 1 K in Figure 2, over the pressure range up to 100 MPa.

One can see that the relative wetting index decreases appreciably but not linearly with increasing pressure, due to the combined effect of moderate increase of the density and velocity of sound and to the pronounced decrease of the compressibility κ_T. Therefore, ionic liquids such as [bmim][PF_6] are expected to have lower penetrabilities into pores at higher pressures.

3. Conclusions

In summary, we have focused attention here on fairly recent experimental studies on melting points $T_m(p)$ of ionic liquids under pressure and on the velocity of sound $v_s(p)$. For the cases examined, $T_m(p)$ increases with increasing pressure. Using the results of de Azevedo *et al.* [5], we have then estimated what effects might be anticipated for the wetting index WI(p).

A fundamental characterisation of RTILs might be that the melting transition is mediated by topological defects, and in particular dislocations, such as are characterised by a Burgers vector, each corresponding to a lattice vector of the undefected lattice. Then it is plausible that a single type of dislocation contributes with a Burgers vector of magnitude b to the melting, with the average $\bar{b} \cong b$ then decreasing but very slowly with pressure. Then with the identification $k_B T_m \sim G\bar{b}^3$, where G is the shear modulus just below T_m for the frozen RTIL and k_B is Boltzmann's constant, one anticipates that the pressure dependence for T_m would follow G, which in turn should notably increase with increasing pressure p, at least for pressures up to 100 MPa. That is, the behaviour of $T_m(p)$, not only for [mmim][H_3CSO_4] and [emim][Tos] of Figure 1, but also for [$bmim^+$][PF_6^-] as in [5], is rationalised. Another type of topological defect, a disclination, is also possible. The presence of topological defects should be manifested in other ways also – perhaps including the readiness with which glass phases are formed. Thus, the experimental study of the behaviour of T_m with changing pressure of the frozen RTIL seems of interest for the future.

In a related context, we conclude by referring to a certain class of 'green' ionic liquids for which it is known that when the alkyl chain length exceeds a certain minimum value, the glass transition is replaced by crystallisation. Then we suggest that two possibilities are obtained in a simple picture of interpenetrating sublattices, with anions on one sublattice and cations on the other: either (i) both cations and anions will freeze simultaneously on their own sublattices, or (ii) only one of the sublattices will be ordered, while the other remains of liquid-like character, with mobile ions moving in a periodic field provided by the frozen sublattice. This situation would then lead to a superionic material. Then, this makes clear the potential interest of further experimental studies such as those reported very recently by Leys *et al.* [7] on the temperature dependence of the electrical conductivity of imidazolium ionic liquids.

We wish to draw attention to the fact that the NIST database for various properties of ionic liquids (Ionic Liquids Database *ILThermo*) provides free access to a large variety of compounds indicating the values for properties and the corresponding literature sources.

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