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Internal mobilities and diffusion in an ionic liquid mixture.

Céline Merlet ^{*} Paul A Madden^{*†} Mathieu Salanne [‡]

August 3, 2010

Abstract

The internal mobility gives the rate at which one ionic species moves relative to the other species present in an ionic mixture, it mirrors the differential strength of the interactions between different ionic species. In this work we examine the dependence of the internal mobilities of the Li^+ and K^+ ions on the composition in molten mixtures of LiF and KF. We compare them to the behaviour of the individual diffusion coefficients and the self-exchange velocities, which measure the rate at which an ion separates from its nearest-neighbour coordination shell. The examination is made using molecular dynamics simulations with polarizable, first-principles parameterised interaction potentials which are shown to reproduce the limited available experimental data on the transport properties of these mixtures extremely well. The results confirm that the composition-dependence of the internal mobilities in LiF/KF follows the unusual type-II behaviour, which is not reflected in that of the diffusion coefficients or the self-exchange velocities.

1 Introduction

The internal mobility measures the rate at which one ionic species in an ionic liquid mixture moves relative to the other ions present under the influence of an electrical potential gradient.¹ As such it is the quantity which determines the efficacy of separating the components of a mixture in a counter-current migration cell, a process which has been used to enrich rare chemicals^{2,3} or, under particular conditions, to separate isotopes.⁴ In a binary mixture containing (say) two different cations with a common anion the values of internal mobilities of the cations reflect the different strengths of their interactions with the anions and as such they contain information about microscopic processes which is not contained in other observables. The internal mobilities might be expected to be simply related to diffusion, however, in such a binary mixture the diffusion coefficients and the internal mobilities may have very different dependencies on composition. The diffusion coefficients of the two cations will, in general, change with composition in a way which represents the change of viscosity whereas the internal mobilities may change in quite different ways. In the system we study in the present paper one increases and one decreases (so-called “type II” behaviour¹), a phenomenon we seek to characterize more completely than has been possible to date and to link to other particular features of this system.

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Almost all systematic studies of internal mobilities to date have been made in binary mixtures of molten salts (see reference¹ for a review) and experimental data has been gathered using the Klemm method.⁵ In the latter an electrochemical cell is constructed such that anions are discharged from the melt at one electrode and introduced into it at the other, so that there is a flux of anions through the melt from one electrode to the other. Because of the difference between the internal mobilities of the two cationic species one species becomes concentrated close to each electrode. Recently, the results of such measurements have been published on the ionic mixture LiF/KF at 1023 K by Matsuura *et al.*⁶ This temperature is below the melting points of both LiF and KF so only a limited composition range could be studied, nevertheless the results suggest the unusual type II behaviour referred to above. Accurate measurements of the diffusion coefficients in molten salts are not readily obtained because of the high temperatures. Nevertheless, Rollet and co-workers⁷ have recently developed a high temperature, pulsed field gradient NMR cell and have used it to obtain values for the diffusion coefficients of Li⁺ and F⁻ in the LiF/KF mixtures across the whole composition range at 1123 K.

From an experimental perspective, then, the LiF/KF mixture has become uniquely well-characterised amongst molten fluorides. These melts are of interest because of their potential for use in a number of proposed nuclear technologies⁸ and it has become important to understand the behaviour of their physical properties over a wide range of conditions and to develop modelling techniques capable of accurate prediction. The fluorides are only molten at very high temperatures and are corrosive, so that experiments are difficult. Although transport data does exist on LiF/KF it has only been obtained at isolated temperatures and a limited range of compositions, so it is not sufficient to allow a complete picture. This has motivated our examination by computer simulation of the relationship between the internal mobility and other ion transport processes in this material. The strategy is to validate the simulations by comparison with the data that does exist and then to use the simulations to calculate a more complete set of observables at a wider range of temperatures so that this relationship is clarified.

Internal mobilities have only been studied to a limited extent in computer simulations:^{9,10} the quantity to be calculated is a collective one (see below) and suffers from poor statistics so that very long runs are required to obtain reliable values. Since the internal mobility depends on the *relative* motion of the ions it might be expected to be related to the rate at which the first coordination shell of anions separate from a cation, and a measure of this is the Self-Exchange Velocity (SEV)¹ given by:

$$v = \frac{R_2 - \langle R(0) \rangle}{\tau}, \quad (1)$$

where R_2 is the distance at which $g(r)$, the radial distribution function between cation and anion, crosses unity after the first peak. $\langle R(0) \rangle$ is the average separation of the set of anions located within the coordination shell of each cation at the initial time (*i.e.* the particular anions found within R_2 of the cation), and τ is the time for this average distance to go from $\langle R(0) \rangle$ to R_2 . Since the physical process quantified by the SEV is easily envisaged, analyses of the way that different interactions might affect it have been used as the interpretative framework to explain the behaviour of the internal mobility in different systems.¹ The SEV is more easily calculated in a simulation than the internal mobility itself, since each ion contributes independently to the statistics, and has been more often calculated than the IM itself.¹

Ribeiro⁹ carried out a simulation study of the IMs in a 50:50 LiF/KF mixture (prior

to the publication of the experimental results) which, together with data on pure LiF and KF, indicated the type II behaviour in this system. He also calculated the SEVs of the ions in the same simulations and showed that the SEVs did not track the composition dependence of the IMs. This indicates that microscopic events which influence this behaviour are not reflected by the rates at which the first shell of coordinating ions separate (the so-called ‘Dynamic Dissociation Model’¹), as quantified by the SEV. This is somewhat surprising as a similar comparison of the IMs and SEVs in simulations of LiCl/KCl mixtures, which might be expected to be closely related to LiF/KF, had shown a good agreement between the two quantities.¹⁰ Ribeiro⁹ pointed to unusual intermediate-range order in the LiF/KF system, as evidenced by a significant ‘prepeak’ in the structure factor,¹¹ and suggested that the internal mobilities were affected by the relaxation of correlations beyond the first coordination shell.

This suggestion finds an interesting echo in a very different physical system. Voigtmann *et al*¹² have examined the relationship between the inter- and self-diffusion in the liquid metallic mixtures, such as $Zr_{64}Ni_{36}$ and $Al_{80}Cu_{20}$,¹³ which also appears to be anomalous in a similar way to the internal mobility and diffusion in the LiF/KF system. They have carried out an elaborate mode-coupling calculation to show how the collective and single particle dynamics are related and to show how the unusual behaviour in these systems can be related to the intermediate-range order. Our simulation studies can provide the information required to complete a similar analysis of the internal mobility in molten salts, though we will not pursue this here.

2 Simulation details

Polarizable interaction potentials for the LiF/KF system have been parameterized on the basis of condensed-phase *ab initio* electronic structure calculations using a force- and dipole-matching scheme which has been described extensively elsewhere.^{14,15} The parameters of the particular potentials used in the present work have appeared in a previous paper and have been shown¹⁶ to provide an excellent reproduction of a number of physical properties including the density of the mixtures and the diffusion coefficients of the Li^+ and F^- ions obtained by Sarou-Kanian *et al*. In a separate study¹¹ we examined the origin of the low- q features in the (simulated) static structure factors for several molten salt mixtures including LiF/KF, as previously reported by Ribeiro.⁹ Our results were very similar to Ribeiro’s despite the difference in interaction potentials.

Simulations were conducted for 11 different compositions at 1123 K, going from pure LiF to pure KF; this is the temperature at which Sarou-Kanian’s measurements of the diffusion coefficients were made.¹⁶ Experimental measurements of the internal mobility have only been made at 1023 K⁶ which is below the melting temperature of LiF and KF so that a direct comparison with experiment can only be made over a limited composition range at this temperature. The 5 compositions ($x_{LiF} = 0.3-0.7$) out of 11 that are melts at 1023 K were also simulated at this temperature.

The simulation cells for all the compositions contain 432 ions (216 anions and 216 cations). The mixtures were first equilibrated for 25 ps in the NPT ensemble, using an isotropic barostat, to optimize the size of the simulation cell and adjust the pressure to a value of 0 GPa. A second equilibration step of 25 ps was made in the NVT ensemble before running long NVT simulations with a weak Nosé-Hoover thermostat.¹⁷ Production runs of 2 ns were conducted for each composition and temperature.

3 Transport Coefficients

The diffusion coefficients were calculated for all the compositions at 1123 K and 1023 K using the Einstein relation:

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\delta \mathbf{r}_i(t)|^2 \rangle, \quad (2)$$

where $\delta \mathbf{r}_i(t)$ is the displacement of a typical ion of species α in time t . The results are shown in figure Fig. 1, where the data for F^- and Li^+ are compared with the recent experimental results. Such a comparison has already been made in a previous paper,¹⁶ the comparison here is with the diffusion coefficients calculated in the present simulations, though the values are very similar to those reported previously. The comparison suggests a small but systematic underestimate of the diffusion coefficients in the simulations. The fluctuations in the experimental data are most probably associated with the difficulty of maintaining accurate temperature control in the NMR experiment. The agreement between simulation and experiment is very good for both species in pure LiF but appears to be worse in the mixtures: however, as we will see below the agreement between other calculated transport coefficients and experiment is good across the whole composition range. The trends shown by both sets of data suggest a slight increase in the Li^+ diffusion coefficient as the mixture becomes LiF-rich, whereas the F^- (and K^+) diffusion coefficient is almost constant.

A notable feature of the diffusion results is that the magnitudes of D_{Li} and D_{K} are quite similar, especially for the mixtures which are richer in KF. According to the Stokes-Einstein relationship,

$$D = \frac{k_{\text{B}}T}{4\pi\eta a}, \quad (3)$$

where k_{B} is Boltzmann's constant, T the temperature, η the shear viscosity and a a hydrodynamic radius, we might expect D_{Li} to be considerably larger than D_{K} because of its much smaller ionic radius (the crystal radii are $r_{\text{Li}} = 73$ pm and $r_{\text{K}} = 152$ pm¹⁸). The observations suggest that the hydrodynamic radii of Li^+ and K^+ are very similar. If we make use of the calculated values of the shear viscosity (see below) and calculate a hydrodynamic radius for K from equation 3 we obtain a value of $a=150$ pm for the KF-rich mixtures ($x_{\text{LiF}} < 0.6$) in close agreement with the crystal radius; for LiF-rich mixtures the value becomes slightly smaller. A natural way to interpret this is that, whilst the K^+ ion diffuses as an atomic species, the Li^+ ion carries at least some of its coordinating F^- ions with it in the diffusion process, giving the diffusing species a larger effective size than the bare ion. This type of explanation has been examined in detail in other molten salt mixtures,^{19,20} and it has been shown that the hydrodynamic radius exceeds crystal radius for those ions where the lifetime of the coordination shell exceeds the relaxation time of the stress tensor in the fluid. The similarity of the diffusion coefficients can thus be associated with the stronger associations between the Li^+ and F^- ions than between K^+ and F^- .

The viscosity of the simulated systems was calculated by integration of the correlation function of the stress tensor:

$$\eta = \frac{1}{k_{\text{B}}TV} \int_0^\infty \langle \sigma_{\alpha\beta}(0)\sigma_{\alpha\beta}(\tau) \rangle d\tau, \quad (4)$$

where $\sigma_{\alpha\beta}$ is one of the components of the stress tensor and V is the simulation cell volume. The correlation function was averaged over the five different anisotropic com-

ponents of the stress tensor and then averaged for two runs of two million steps each. The results shown in figure Fig. 2 suggest that the viscosity is roughly constant across the composition range, possibly increasing slightly as the LiF concentration increases. This is consistent with the near constancy of the F^- and K^+ diffusion coefficients and Stokes-Einstein behaviour. The results deviate from the broad trend close to the eutectic composition (at $x_{LiF} \sim 0.5$). Because the deviations are in the opposite sense for $T=1023$ K and 1123 K, we suspect that these deviations reflect a too short equilibration period. As the composition is changed close to the eutectic composition there are substantial changes in the local coordination around the ions which could mean that the time to fully equilibrate the cell volume becomes longer than we allowed for. On the other hand, it is notable that the deviations are not reflected in the diffusion coefficients.

The electrical conductivities of the LiF/KF mixtures were calculated from the mean squared displacement of the charge density according to the following formula:

$$\lambda = \frac{e^2}{k_B T V} \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\sum_i q_i \delta \mathbf{r}_i(t)|^2 \rangle, \quad (5)$$

where e is the elementary charge and q_i the magnitude of the charge on ion i . The expression is equivalent to, but computationally more convenient than, the usual Green-Kubo formula in terms of the time correlation function of the charge current.²¹ The results are shown in figure Fig. 3 where they are compared with a curve representing the experimental data.²² The agreement is excellent overall, though the simulation values at 1123 K do rise above the experimental line close to the eutectic composition as, to a lesser, extent do the 1023 K data.

It is of interest to compare the calculated conductivities with those predicted by the Nernst-Einstein formula,

$$\lambda^{NE} = \frac{e^2}{k_B T V} (N_F q_F^2 D_F + N_K q_K^2 D_K + N_{Li} q_{Li}^2 D_{Li}), \quad (6)$$

where N_{Li} is the number of Li^+ ions in the simulation cell. This formula could be derived from the expression for the conductivity if all correlations between the motion of different ions could be neglected. For the LiF/KF mixtures, the Nernst-Einstein conductivity, also shown in figure Fig. 3 is higher than the real one for all the compositions which indicates that there are associations between ions of opposite charge which reduces the collective conductivity of the mixture and shows that the deviations are most significant close to the eutectic composition. It is noteworthy that both the conductivity and its Nernst-Einstein approximant rise markedly and non-monotonically across the composition range, whilst the diffusion coefficients are of very similar size and do not change to anything like the same degree. The rise can be attributed, in large part, to a decrease in the molar volume which enters into the relationship between the conductivity and the diffusion coefficients in the Nernst-Einstein formula. The conductivities of mixtures are often approximated by combining the conductivities of the pure materials according to their mole fraction:²³

$$\lambda = x_1^2 \lambda_1 + x_2^2 \lambda_2 + 2x_1 x_2 \lambda_2, \quad (7)$$

if $\lambda_1 > \lambda_2$. The figure indicates that this would be a poor approximation for LiF/KF.

4 Internal mobilities

Klemm obtained an expression for the internal mobilities in a melt from group velocity correlation functions based on linear response theory.⁵ The internal mobility for a species a relative to a species b in a M_1X-M_2X mixture is:

$$u_{ab} = \frac{e}{3k_B T} \int_0^\infty K_{ab}(t) dt, \quad (8)$$

with $K_{ab}(t)$, a group velocity correlation function:

$$K_{ab}(t) = z_- N_- \langle [x_1 \overline{\mathbf{v}_1(t)} + x_2 \overline{\mathbf{v}_2(t)} - \overline{\mathbf{v}_-(t)}] \cdot [\overline{\mathbf{v}_a(0)} - \overline{\mathbf{v}_b(0)}] \rangle, \quad (9)$$

where $\overline{\mathbf{v}_\alpha} = N_\alpha^{-1} \sum_{i \in \alpha} \mathbf{v}_i$, \mathbf{v}_i is the velocity of ion i , x_α is the molar fraction of species α , z_- is the anion charge, N_- is the number of anions and a and b stand for 1, 2 or -. As we remarked above, for computational reasons it is more convenient to re-express this in terms of the mean-square displacement (MSD) of appropriate charge clouds. In these terms¹⁰ the internal mobility for K^+ relative to F^- is

$$u_{KF} = -\frac{eN_F}{6k_B T} \lim_{t \rightarrow \infty} \frac{1}{t} [x_K \langle \Delta_K^2 \rangle + x_{Li} \langle \Delta_K \Delta_{Li} \rangle - (1 + x_K) \langle \Delta_K \Delta_F \rangle - x_{Li} \langle \Delta_{Li} \Delta_F \rangle + \langle \Delta_F^2 \rangle] \quad (10)$$

where $\Delta_\alpha = N_\alpha^{-1} \sum_{i \in \alpha} (\mathbf{r}_i(t) - \mathbf{r}_i(0))$. The expression for Li^+ is easily obtained by the obvious substitutions.

Typical results for the relevant MSDs are shown in figure Fig. 4. A surprising feature of these results is the change of slope at a time of order 20 ps. The MSDs of the ion positions, used to calculate the diffusion coefficients, and of the total charge density, involved in the calculation of the conductivity, are perfectly linear on this timescale. Furthermore, all the relaxation times involving the coordination shells of the ions, are sub-picosecond, so that it is difficult to imagine the type of process which might be affecting the relative motion of the charge densities of different species on this timescale. Although the behaviour is common for all compositions, the change of slope is most pronounced close to the eutectic composition. The internal mobility is obtained from the slope of the MSDs at $t \rightarrow \infty$, so it is the long-time slope that we examine below.

The results at 1023 K may be compared with Matsuura's experimental data.⁶ Our calculated IMs are close to these results, with the exception of the points at $x_{LiF} = 0.5$ which appear to be anomalous. We may also compare our results at this temperature with Ribeiro's simulation results (obtained with an empirically parameterised potential).⁹ Ribeiro studied only the single mixture at $x_{LiF} = 0.5$ and the two pure melts (the real materials would be supercooled at this temperature) and suggested that the LiF/KF system was a type-II system and would be likely to show a Chemla crossing point on the LiF-rich side at a composition below the liquidus. Matsuura extrapolated internal mobilities derived from conductivities for pure LiF and KF into the supercooled region and came to the same conclusion.

We have results for the full composition range at 1123 K which gives clear evidence of type-II behaviour and a Chemla crossing point at $x_{LiF} = 0.7$. The results clearly show that, despite the close similarities of their diffusion coefficients, the K^+ ions move three times faster *relative to the* F^- ions than do the Li^+ ones for $x_{LiF} \sim 0.15$ whereas the Li^+ ions move twice as quickly compared to K^+ at $x_{LiF} = 0.9$. We recall that the diffusion

coefficients of the two ions are similar at all compositions. The existence of Chemla crossing point means that this mixture could be used to separate lithium isotopes by the counter-current migration method.⁴

5 Dynamic Dissociation Model

For most systems which have been studied to date, there has been good agreement between the composition dependence of the Self-Exchange Velocities (SEVs) and the internal mobilities (IMs). As described in the introduction, the SEV is a measure of the rate at which an ion separates from its first coordination shell and, by proposing mechanisms for this process (the Dynamic Dissociation Model), Okada has been able to rationalise the ways in which the IMs are affected by the composition of a mixture and the chemical identities of the cations involved for many different systems.¹

The SEV can be obtained from relatively short simulations because each cation contributes to the statistics. For all the compositions, the time evolution of the average distance between initially neighbouring unlike ions was calculated from 500 different initial times. The SEV obtained for the mixtures at two different temperatures are given in figure Fig. 6. The SEV for K^+ is larger than that for Li^+ which is consistent with the idea that Li^+ holds its coordination shell more tightly than K^+ . However, the SEVs clearly do not reproduce the behaviour of the internal mobilities as they *increase* for both cations going from pure KF to pure LiF, whereas it was shown that u_{KF} *decreases* for the same change in composition.

A particular prediction of the Dynamic Dissociation Model is that the internal mobilities should be inversely proportional to the molar volume.¹ The internal mobility may be expressed as

$$u = \frac{A}{V_m - V_0} \exp\left(-\frac{E}{RT}\right), \quad (11)$$

where V_m is the molar volume of the mixture and A , V_0 and E are constants independent of the second cation. The quantity $V_m - V_0$ could be thought of as the free volume available to an ion and the Arrhenius-like factor expresses the energy cost of a cation separating from a coordinating anion. This prediction of the dependence of the internal mobility on composition and temperature has been found to work well for the systems studied to date (largely of Type-I character). Plots of the inverses of the internal mobilities and SEVs obtained in our simulations of the LiF/KF mixtures *versus* molar volume are given in figure Fig. 6. It can be seen that the SEVs obey equation 11 very well but the internal mobilities do not.

6 Conclusion

Computer simulations have been used to obtain a more complete set of information on the relationship between the internal mobility and the other transport properties in LiF/KF mixtures than had been available to date. Previous studies^{6,9} had suggested that the behaviour of the internal mobilities in this system was unusual and could not readily be accounted for with Okada's Dynamic Dissociation Model. Our far more extensive set of results have confirmed this suggestion, the internal mobilities of Li^+ and K^+ respectively increase and decrease with increasing LiF concentrations in the mixtures, and exhibit a Chemla crossing point at about $x_{LiF}=0.7$. This behaviour is not accounted for by considering the rate at which the two cations separate from their first

neighbour coordination shells, as measured by the Self-Exchange Velocity. Ribeiro⁹ pointed to the existence of an appreciable extent of intermediate range order in this mixture, as witnessed by an appreciable prepeak in the Li-Li partial structure factor which becomes most pronounced for $x_{\text{LiF}} \sim 0.5$ ¹¹ and suggested that the unusual behaviour of the internal mobilities was related to dynamical events involving these longer range correlations. We have seen that relatively long-lived correlations influence the internal mobility, which seems to be consistent with this suggestion. It would be interesting to pursue this idea through the type of mode-coupling analysis which has recently been used to explain unusual behaviour of the interdiffusion in binary metallic mixtures.¹²

In closing we note that the interaction potentials, which were parameterized on a purely first-principles basis,^{14,15} have successfully reproduced the known transport coefficients in these mixtures without any empirical information. This further underpins the use of these simulation methods to predict difficult-to-measure properties in the molten fluorides.²⁴

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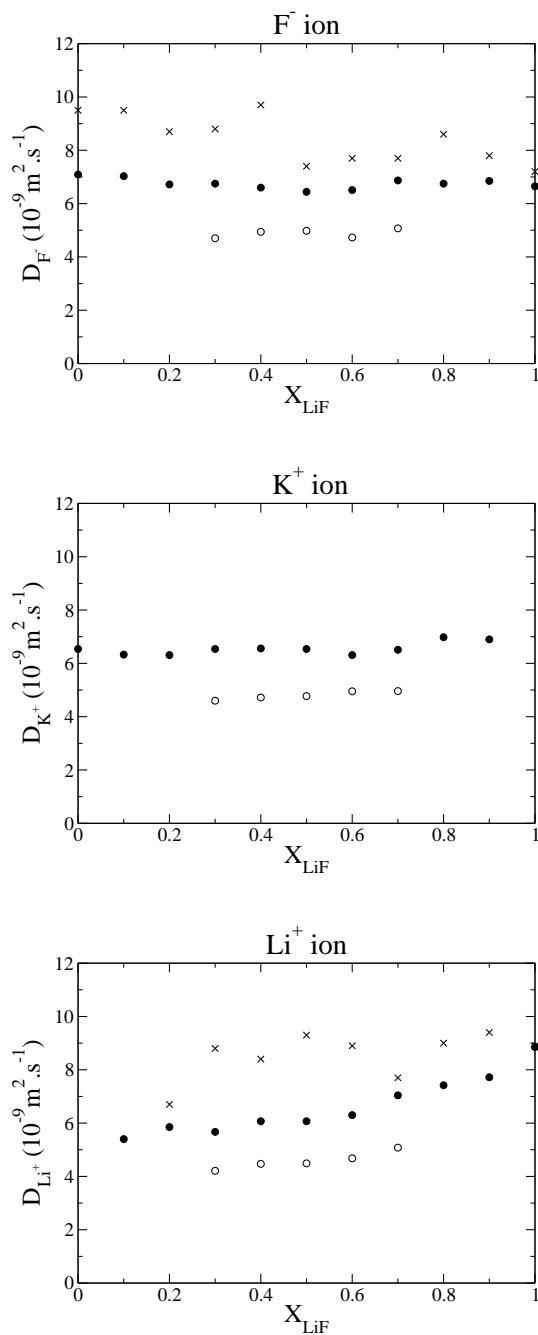


Fig. 1 Self-diffusion coefficients of F^- , Li^+ and K^+ as a function of x_{LiF} at 1023 K (open symbol) and at 1123 K (full symbol), data from simulations (circle) show good agreement with the experimental data obtained for Li^+ and F^- at 1123 K (cross).¹⁶

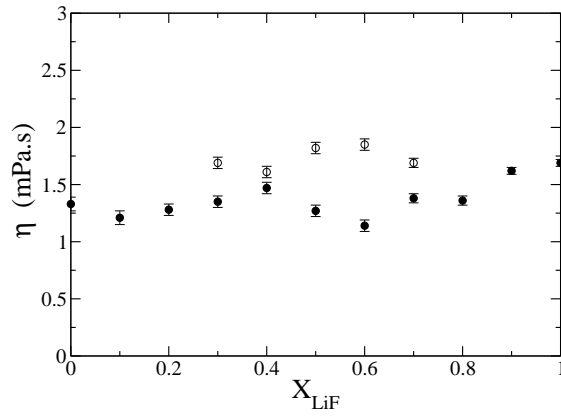


Fig. 2 Calculated viscosities for the LiF/KF mixtures at 1023 K (open symbol) and at 1123 K (full symbol). The error bars are calculated from the fluctuations in the plateau value of the stress tensor integral.

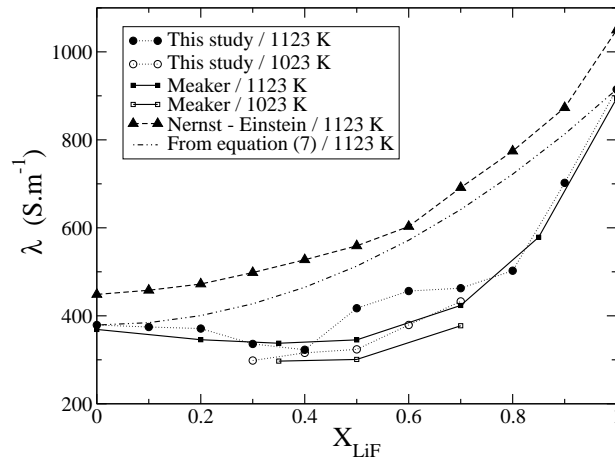


Fig. 3 Calculated and experimental²² electrical conductivities for the LiF/KF mixtures at 1123 K and 1023 K. The circles give the simulation values and the full-lines the experimental values. The Nernst-Einstein conductivity values obtained from the self-diffusion coefficients are shown as triangles and the dashed-dot line shows the conductivity predicted by the empirical formula (7).

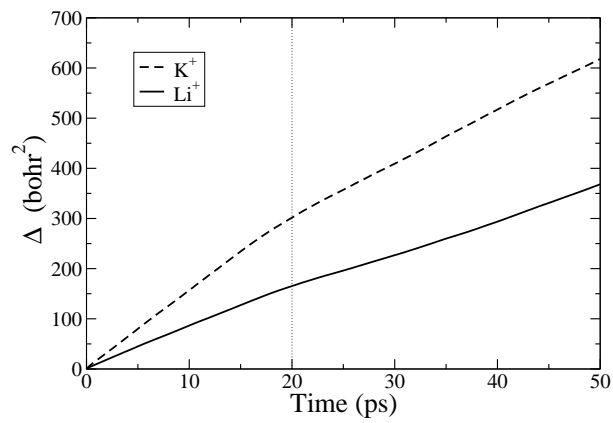


Fig. 4 The MSDs (see equation (11)) for the calculation of the internal mobilities for $x_{\text{LiF}}=0.5$. Note the change of slope at ~ 20 ps.

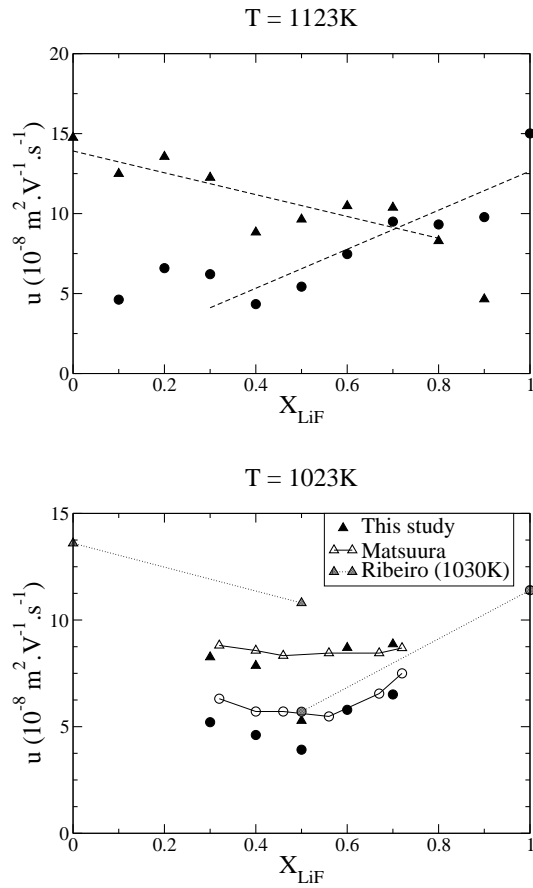


Fig. 5 Internal mobilities for lithium (circle) and potassium (triangle) at 1123 K (top) and at 1023 K (bottom). The internal mobilities were calculated from the long-time slopes of the MSD, as shown in Fig. 4. Experimental values at 1023 K⁶ and simulated values at 1030K from reference⁹ are added for comparison. Dashed lines are added in the figure at 1123 K to facilitate the identification of the type II trend.

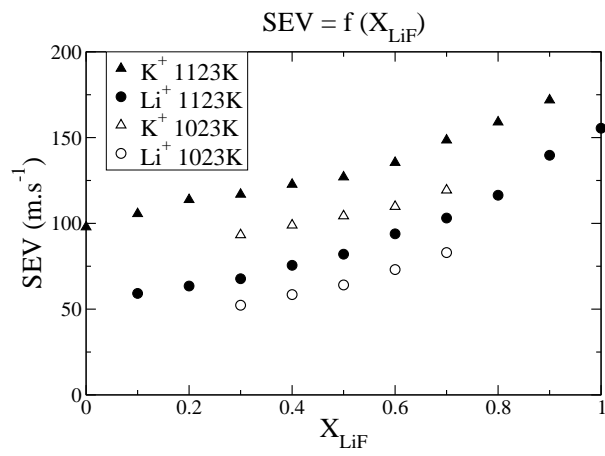


Fig. 6 Values of the Self-Exchange Velocities of the cations in the LiF-KF mixtures at 1123 K and 1023 K, obtained from equation (1).

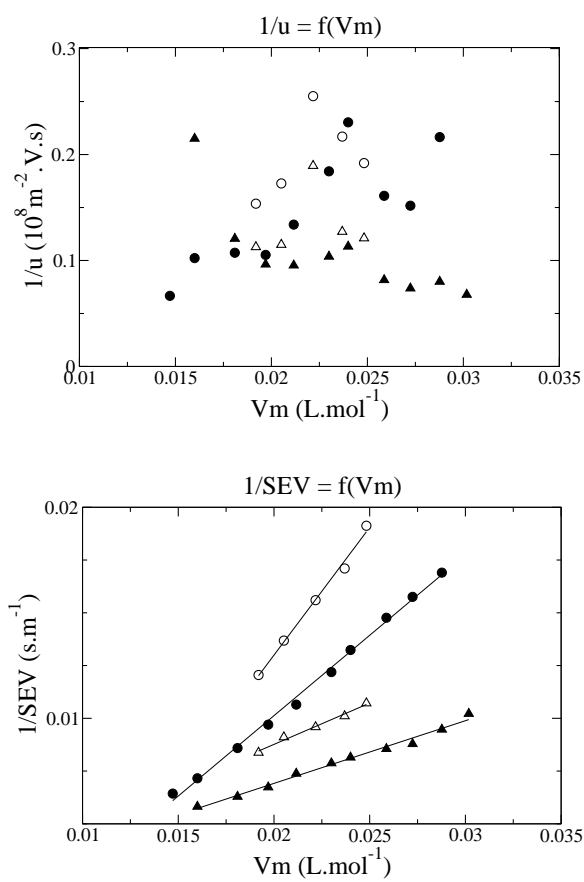


Fig. 7 Plots of the inverses of the internal mobilities (upper panel) and Self-Exchange Velocities (lower panel) *versus* the molar volume in order to test the predictions of the Dynamic Dissociation model (equation (11)).