Ionic diffusion in $K_x(KCl)_{1-x}$

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Abstract. The self-diffusion coefficients of the two ionic species in the $K_x(KCl)_{1-x}$ melt are evaluated using the Green–Kubo formulae. The evaluation is based on a simple model wherein the dynamics of a two-component system is made use of, which relates the self-diffusion coefficients to the pair potential and partial structure factor of the melt through frequency sum rules of the velocity auto-correlation function. Results thus obtained convincingly explain the increase in difference between the two diffusion coefficients with increasing x as observed in a molecular dynamics study. This difference is explicitly related to the different structural back-scattering of ions influenced by their screening due to the presence of valence electrons.

1. Introduction

The simplest and most widely studied system among the mixtures of metals and salts are the solutions of alkali metals in their halides, i.e. $M_x(MX)_{1-x}$, where M denotes the metal, X the halogen and x is the mole fraction of metal. As x varies from zero to one, the melt changes from a pure ionic liquid to pure liquid metal. In the limit $x \to 0$ (pure salt), no valence electrons are left, electrical conductivity, which is purely ionic in nature, drops rapidly and the electrons undergo a continuous metal–non-metal transition towards highly localized states. The gradual change in electronic structure with change in x gives rise to a number of remarkable thermodynamic, structural and dynamical properties of the metal–salt solutions. Recently, Meroni and Hansen [1] have presented molecular dynamics (MD) simulations of metal–salt solutions in which they have studied the static structure factor, self-diffusion coefficient and dynamical structure factor for different values of mole fraction in the $K_x(KCl)_{1-x}$ system. The MD simulations were performed using a model potential [2] at temperatures where K mixes with KCl at all concentrations. The model potential involves the interaction of ions via a screened Coulomb potential and the screening length λ varies with the density of valence electrons, i.e., with x. This model potential varies smoothly from the potential for pure salt to that of pure metal. In the MD simulations, it was found that for a small value of x the difference between the self-diffusion coefficient of the two species is small whereas for $x \geqslant 0.6$ this difference becomes about 60% which, in fact, makes the solution conducting. The conducting behaviour of molten salts has also been studied [3] for materials such as AgI and CuI, known as super-ionic conductor melts. In such systems, the difference between the diffusion coefficients of the two ionic species in the melt has been related [4] to the nature of the liquid structure through different back-scattering imposed on each ion species by the shell of second neighbours of like ions, but the reason for the increase in the difference of self-diffusion of the two ionic species in the

case of metal–salt solution with increasing concentration of metal has not been investigated so far. This, in fact, forms one of the motivations for studying the mole fraction dependence of the self-diffusion coefficients of the two species in the $M_x(MX)_{1-x}$ system.

In the present work, the mole fraction dependence of the self-diffusion coefficients of the two ionic species is studied by using the Green–Kubo relation. The Green–Kubo formula relates the self-diffusion coefficient to the time integral of the auto-correlation function of the single-particle velocity. For calculating the time evolution of the velocity auto-correlation function (VACF), we use a model proposed earlier by Tankeshwar *et al* [5], which is based on separating the configuration space of a many-body system into vibrational and stable packing parts. The extension of the model has been performed by Tankeshwar and Tosi [4, 6] for two- and three-component systems, which has provided an agreement between the ratio of self-diffusion coefficients of different species with the MD simulation data. This model has the advantage of relating the self-diffusion coefficient of two species to pair potential and to pair structure of the melt through sum rules of the VACF. Hence, the reason for the difference between two diffusion coefficients can be understood in terms of static properties. Therefore, firstly, we study the behaviour of the sum rules of the VACF of cations and anions separately for different values of x in the $K_x(KCl)_{1-x}$ system. Later these sum rules have been used to calculate the diffusion coefficients of K and Cl ions. It is found that the difference between the diffusion coefficients of K and Cl ions with increase in x arises due to screening of ions. This implies that ionic diffusion is strongly influenced by the charge ordering which, in turn, depends upon the number of valence electrons present in the system. The paper is organized as follows. Section 2 presents the theoretical formalism. Results and discussion are given in section 3. The work is summarized in the last section.

2. Theoretical formalism

We consider a metal–salt solution $K_x(KCl)_{1-x}$ containing N_1 cations of mass m_K and N_2 anions of mass m_{Cl}. $N_0 = N_1 - N_2$ is the number of valence electrons, ensuring overall neutrality, and $N = N_1 + N_2$ is the total number of ions. The number concentrations of cations and anions are $n_1 = N_1/N$ and $n_2 = N_2/N$, respectively. The ions are assumed to interact via the model pair potentials proposed by Hansen and Yoshida [2] given as

$$U_{\alpha\beta}(r) = \left(1 - \delta_{\alpha\beta}\right)B \, \exp(-Ar) + \left(Z_\alpha Z_\beta e^2/r\right) \exp(-r/\lambda) \tag{1}$$

where $1 \leqslant \alpha, \beta \leqslant 2$ are the indices of the species and $Z_\alpha = \pm 1$ is the valence of the ion species. In equation (1), the first term on the R.H.S is the Born–Mayer repulsion. The parameters A and B were considered to be the same as that of the pure molten salt. The second term is the screened Coulomb potential and λ is related to the concentration of metal in its halide. This model potential smoothly interpolates the variation in interaction potential between pure salt and pure metal, which, in turn, allows one to investigate the variation of various properties of the system with x.

The self-diffusion coefficient D_α of the species α is given by the Green–Kubo formula as

$$D_\alpha = \left(K_B T/m\right) \int_0^\infty C^\alpha(t) \, dt \qquad \alpha = K, \, Cl \tag{2}$$

where $C^\alpha(t)$ is the velocity auto-correlation function of the species denoted by α. This is defined as

$$C^\alpha(t) = \left(1/N_\alpha\right) \sum_{i=1}^{N_\alpha} \left\langle v_i^\alpha(t) v_i^\alpha(0) \right\rangle \Big/ \left\langle \left(v_i^\alpha\right)^2 \right\rangle \tag{3}$$

where $v_i^\alpha(t)$ is the velocity of the ith particle of species α at time t. The angular brackets in equation (3) represent the ensemble average. The exact calculation of $C(t)$ is not feasible for the system of present interest as it amounts to finding the solution to a many-body problem. There exists a microscopic way to evaluate $C(t)$ by using the Mori memory function formalism [7]. The microscopic method involves evaluation of the binary collision contribution [8] and a contribution to the memory function which is important at long times and can be calculated within the mode-coupling approximation [9]. However, such calculations have not yet been performed for a binary system. Therefore, in the present work we make use of a model [5, 10] based on the idea [11] of separating the configuration space of a many-body system into a vibrational and a stable packing part. The details of the model for a two-component system are given in the work of Tankeshwar and Tosi [4]. The expression obtained in this model for the VACF of species α is given as

$$C^\alpha(t) = \mathrm{sech}(t/\tau^\alpha) \cos(\omega^\alpha t). \tag{4}$$

In the above equation, $(\tau^\alpha)^{-1}$ and ω^α are jumping and vibrational frequencies, which are different for the two types of ion. Using equation (4) in equation (2), an expression for the diffusion coefficient is obtained as

$$D_\alpha = \frac{K_B T}{m_\alpha}(\pi/2)\tau^\alpha \, \mathrm{sech}(\pi\omega^\alpha \tau^\alpha/2). \tag{5}$$

On comparing the short-time expansion of equation (4) with the exact short-time expansion of VACF given by

$$C^\alpha(t) = 1 - C_2^\alpha \frac{t^2}{2!} + C_4^\alpha \frac{t^4}{4!} + \dots \tag{6}$$

we obtain

$$(\tau^\alpha)^{-2} = \frac{[C_4^\alpha - (C_2^\alpha)^2]}{4C_2^\alpha} \tag{7}$$

and

$$(\omega^\alpha)^2 = \frac{[5(C_2^\alpha)^2 - C_4^\alpha]}{4C_2^\alpha}. \tag{8}$$

From equations (5), (7) and (8) we find that if $C_4^\alpha = (C_2^\alpha)^2$, then $D = 0$, implying perfect solid-like behaviour, and for $C_4^\alpha \geqslant 5(C_2^\alpha)^2$ diffusion is gas-like and no back-scattering process is present. For the systems studied so far [4–6, 10, 12], it is found that C_4^α is always greater than $(C_2^\alpha)^2$.

In order to calculate the self-diffusion coefficient from equation (5) we need to know expressions for the sum rules, C_2^α and C_4^α. Expressions obtained for the sum rules of the system K$_x$(KCl)$_{1-x}$ are given as

$$C_2^K = \frac{n_K}{2m_K} \int \mathrm{d}\mathbf{r}\, g_{KK}(r)U_{xx}^{KK} + \frac{n_{Cl}}{2m_K} \int \mathrm{d}\mathbf{r}\, g_{KCl}(r)U_{xx}^{KCl} \tag{9}$$

and

$$C_4^K = \frac{n_K}{m_{Cl}^2} \int \mathrm{d}\mathbf{r}\, g_{KK}(r)(U_{xi}^{KK})^2 + \frac{n_{Cl}}{2m_K}\left(\frac{1}{m_K} + \frac{1}{m_{Cl}}\right) \int \mathrm{d}\mathbf{r}\, g_{KCl}(r)(U_{xi}^{KCl})^2 + \frac{(C_2^K)^2}{2} \tag{10}$$

where $n_K = n(1+x)/2$ and $n_{Cl} = n(1-x)/2$ with n as the number density of the ions. The last term in equation (10) represents the approximate three-body contribution [4] to the fourth sum rule. In equations (9) and (10), $g_{KK}(r)$ and $g_{KCl}(r)$ are the partial cation–cation

and cation–anion radial distribution functions. $U^{KK}(r)$ and $U^{KCl}(r)$ are the corresponding pair potentials and the notation

$$U^{KK}_{ij} = \frac{\mathrm{d}^2 U^{KK}(r)}{\mathrm{d}r_i\,\mathrm{d}r_j} \tag{11}$$

has been used with the convention of summation over the repeated Cartesian index i. Here r_i represents the ith component of r. The second and fourth sum rules for the anion follow by interchanging indices K and Cl in equations (9) and (10). Clearly, each sum rule contains a contribution from like ions and a contribution from unlike ions. We shall separately consider these two contributions below, representing them by the notation $C_2^K = C_2^{KK} + C_2^{KCl}$ etc. Obviously, $C_2^{ClK} = n_K m_K C_2^{KCl}/(m_{Cl} n_{Cl})$.

3. Results and discussion

In order to calculate the self-diffusion coefficient we need to know the values of the sum rules for the two species separately. The numerical calculations of sum rules C_2^α and C_4^α require the interaction potential and partial pair correlation function as input. For the pair potential, we use the expression given by equation (1). The variation of screening parameter λ and of some other relevant quantities with mole fraction x of metal in $K_x(KCl)_{1-x}$ taken from the work of Meroni and Hansen [1] are given in table 1. For the partial pair correlation function we use the results due to MD simulations of Meroni and Hansen [1] corresponding to the interaction potential used in the present work. The numerical integration involved in the expressions of the sum rules is carried out using the Gauss quadrature method. The accuracy of our numerical work is better than 5%. The various contributions to the sum rules for the VACFs of cation and anion are given in tables 2 and 3, respectively. It can be seen from table 2 that various contributions to the sum rules decrease with increasing x. The contributions to the second and fourth sum rules of the cation due to cations i.e. V_{2KK} and V_{4KK}, decrease with increasing x; this is because of decreasing height of the first peak of $g_{KK}(r)$ with increasing x. This implies that the cation–cation contribution to the sum rules is influenced by screening of the ions due to the presence of valence electrons. It is noted that the decrease in V_{2KCl} for $x = 0.1$ to 0.9 is about 25-fold, which can be attributed mainly to the decrease of n_{Cl} with increasing x. The effect of interaction on V_{2KCl} for different x can be seen explicitly from the fourth column of table 2 where we have given V_{2KCl}/n_{Cl}. The decrease in V_{2KCl}/n_{Cl} with increasing x can be understood from the fall of the first peak height of $g_{KCl}(r)$, which represents the effect of charge ordering in the system.

From table 3, the variation of V_{2ClK} can be understood in a similar manner as the relation $V_{2ClK} = (1 + x)/(1 - x)(m_K/m_{Cl})V_{2KCl}$ is always true. The decrease in V_{2ClCl} with increasing x is due to the combined effects of decreasing n_{Cl} and the correlation among anions with increasing x. The effect of correlations among anions can clearly be seen from V_{2ClCl}/n_{Cl}, given in the fourth column of table 3. The decrease in V_{2ClCl}/n_{Cl} with increasing x is due to a fall in peak height of $g_{ClCl}(r)$ and shifting of the first peak position towards a large r value as found in MD simulations [1]. Thus, we see that our results for the sum rules, which are short-time properties of the VACF, are influenced by the structural changes in the system with changing mole fraction.

The self-diffusion coefficients of cations and anions are calculated from equation (5) by using the numerical values of sum rules given in tables 2 and 3, respectively. The results obtained for D_K and D_{Cl} are given in table 4 along with the MD results of Meroni and Hansen [1] for comparison. We are unable to produce diffusion coefficients at $x = 0.8$

Table 1. Characteristics of a metal–salt solution. x is metal concentration, n is ionic number density, T is the mean temperature, n_{Cl} is the ionic number density of the anion, n_K is the ionic number density of the cation and λ is the screening length.

x	n 10^2 (ions Å^{-3})	T (K)	n_{Cl} 10^2 (ions Å^{-3})	n_K 10^2 (ions Å^{-3})	λ (Å)
0.0	2.41	1121	1.205	1.205	$+\infty$
0.1	2.24	1112	1.008	1.232	1.787
0.2	2.07	1123	0.828	1.242	1.614
0.3	1.88	1102	0.658	1.222	1.519
0.4	1.72	1135	0.516	1.204	1.454
0.6	1.48	1141	0.296	1.184	1.365
0.9	1.11	1169	0.055	1.0545	1.285

Table 2. The values of frequency sum rules of VACF of the cation for different values of mole fraction x. The subscripts KK and KCl on V_2 and V_4 represent the contributions to the second and fourth sum rules of the cation due to cations and anions, respectively.

x	V_{2KK} $(10^{26}$ s$^{-2})$	V_{2KCl} $(10^{26}$ s$^{-2})$	$\frac{V_{2KCl}}{n_{Cl}}$ $(10^{24}$ s^{-2} ion^{-1} Å$^3)$	V_{4KK} $(10^{52}$ s$^{-4})$	V_{4KCl} $(10^{52}$ s$^{-4})$
0.0	0.0	4.1868	3.747	6.3007	32.7030
0.1	0.8261	1.7416	1.727	1.6979	16.4185
0.2	0.7349	1.3030	1.573	1.2685	12.1302
0.3	0.6523	1.1337	1.722	0.97751	11.8282
0.4	0.6072	0.7954	1.541	0.97755	7.9515
0.6	0.5623	0.4468	1.509	0.8959	4.5158
0.9	0.4289	0.07658	1.379	0.5864	0.6887

Table 3. The values of frequency sum rules of VACF of the anion for different values of mole fraction x. The subscripts ClK and $ClCl$ on V_2 and V_4 represent the contributions to the second and fourth sum rules of the anion due to cations and anions, respectively.

x	V_{2ClK} $(10^{26}$ s$^{-2})$	V_{2ClCl} $(10^{26}$ s$^{-2})$	$\frac{V_{2ClCl}}{n_{Cl}}$ $(10^{24}$ s^{-2} ion^{-1} Å$^3)$	V_{4ClK} $(10^{52}$ s$^{-4})$	V_{4ClCl} $(10^{52}$ s$^{-4})$
0.0	4.6177	0.0	0.0	36.0690	7.6612
0.1	2.3478	0.704 5	0.6989	22.1325	1.3764
0.2	2.1557	0.480 75	0.5806	20.0681	0.7206
0.3	2.3222	0.322 6	0.490	24.2277	0.3937
0.4	2.0470	0.226 0	0.438	20.4631	0.2401
0.6	1.9714	0.106 1	0.358	19.9224	0.0972
0.9	1.6048	0.012 5	0.225	14.4326	0.0065

because at this concentration MD data of $g(r)$ are not available to us. From table 4, it can be seen that for $x = 0$ (pure salt) the two diffusion constants of different ions are close to each other. With increasing mole fraction of K in the KCl salt, the self-diffusion coefficients of both the species increase. It can be seen from table 4 that the increase in D_K with increasing x is faster than that in D_{Cl}. The absolute values of D_K and D_{Cl} obtained in the present work differ from the MD value at most by 25%. This may be due to the model employed for the calculation of diffusion coefficients and/or due to the numerical accuracy in obtaining the sum rules. At $x = 0.9$ the ratio D_K/D_{Cl} is around 1.5, which

is in close agreement with the MD result. However, D_K/D_{Cl} increases smoothly with increasing x in the present case, whereas this increase is not smooth in the MD work. Since our work relates the single-particle diffusion to the static structure factor, the smooth change in D_K/D_{Cl} with changing x is followed from a continuous change of the static structure factor with mole fraction x.

Table 4. Diffusion coefficients of the two ionic species (in units of 10^{-5} C m^2 s^{-1}). D_K and D_{Cl} are the results obtained from equation (5), and D_K^{MD} and D_{Cl}^{MD} are MD results of Meroni and Hansen.

x	D_K	D_{Cl}	D_K^{MD}	D_{Cl}^{MD}
0.0	8.93	8.41	6.5	5.9
0.1	14.54	13.35	13.4	12.20
0.2	19.47	17.49	18.10	14.60
0.3	24.99	20.11	19.90	18.50
0.4	32.23	25.12	28.20	27.90
0.6	43.29	29.89	37.10	35.70
0.8	—	—	55.2	39.1
0.9	59.69	39.79	61.40	38.00

The reason for the increase in D_K and D_{Cl} with increasing x can be understood in terms of the variation of two contributions to the second sum rule on which the diffusion depends strongly and inversely. From tables 2 and 3 it can be seen that the decrease in V_{2K} with increasing x is much faster than the decrease in V_{2Cl}. This difference in contributions to the second sum rule can be understood as being influenced mainly by a fall in n_{Cl} and screening length λ with increasing x. In order to see the effect of screening of ions by the presence of valence electrons on diffusion coefficients, we calculate these coefficients, say at $x = 0.9$, by using the same value of λ and hence of $g(r)$ as that for, say, $x = 0.2$. We find that for $x = 0.9$, $D_K = 37.87 \times 10^{-5}$ cm^2 s^{-1} and $D_{Cl} = 32.60 \times 10^{-5}$ cm^2 s^{-1}. On comparing these values of diffusion coefficients with those given in table 4 at $x = 0.9$ we find that the effect of λ is to increase the difference in diffusion coefficients of D_K and D_{Cl}. This analysis implies that the increase in diffusion coefficients with increasing x is mainly due to the decrease in n_{Cl}. On the other hand, the difference between two diffusion coefficients increases due to screening of ions by electrons. The effect of screening is greater on D_K than on D_{Cl} as demonstrated by their values given in table 4. Thus, we see that the metal–non-metal transition influences the diffusive motion of ions in the solution.

4. Summary and conclusion

In this paper, we have studied the self-diffusion coefficients of two ionic species in the mixture of potassium in its chloride as a function of mole fraction of K. We have used the Green–Kubo formulae, which relate the self-diffusion to the time integral of the VACF. The VACF is calculated using a simple model relating the dynamics of the system to its static properties through the frequency sum rules. Expressions for the sum rules are calculated numerically using the interaction potential proposed by Yoshida and Hansen and the corresponding pair correlation function. The numerical results of the sum rules have been used to calculate the self-diffusion of K and Cl ions in $K_x(KCl)_{1-x}$ as a function of x. The results obtained are compared with MD data of Meroni and Hansen and a reasonably good agreement is achieved. It is found that the difference between D_K and D_{Cl} increases

with increasing x. The increase in $D_K - D_{Cl}$ is due to screening of ions by the presence of valence electrons.

Acknowledgments

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