Molten Salt Ionic Mobilities in Terms of Group Velocity Correlation Functions

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The internal mobilities of additive binary molten salt systems are given in terms of correlation functions of mean ionic velocities. For isotopic systems the expressions obtained are expanded in terms of the relative difference of the masses of the two cationic or anionic species involved.

The existing experimental data on ionic mobilities in molten salts are richer and more precise than those on diffusion coefficients, mostly because conventional diffusion measurements are liable to be disturbed by convective mixing. For instance all the mobilities of the cationic isotopic species in natural LiCl, LiBr, LiJ, KCl, RbCl, RbBr, TlCl, CuCl and AgCl are known [1] whereas only one publication exists on an isotope effect of diffusion: ^{6}Li and ^{7}Li in mixtures of alkalinitrates [2].

For comparisons it would be desirable to calculate not only diffusion coefficients, as has been done [3–5], but also mobilities from velocity correlation functions extracted from computer simulations. In this paper relations between mobilities and the corresponding group velocity correlation functions are given.

We consider a system of N particles interacting classically by central forces. For it's Hamiltonian we write

$$H = H_0(\{\boldsymbol{r}_i, \boldsymbol{p}_i\}) + H_{\text{ext}}(\{\boldsymbol{r}_i, \boldsymbol{p}_i\}, t); \quad i = 1, \ldots, N, \tag{1}$$

where H_{ext} is the contribution to H of some external perturbation of the system.

If H_{ext} is small compared to the equilibrium Hamiltonian H_0 and can be separated and onedimensionally specified as

$$H_{\text{ext}} = -F(t)\, A(\{r_i, p_i\}) \tag{2}$$

then, according to the theory of linear response [6], the deviation $\Delta D(t)$ of the distribution function $D(t)$ from it's equilibrium value D_0 is

$$\Delta D(t) = \frac{D_0}{kT} \int_{-\infty}^{0} F(t+t') \sum_i^N \left(\frac{\partial H_0}{\partial p_i} \frac{\partial}{\partial r_i} - \frac{\partial H_0}{\partial r_i} \frac{\partial}{\partial p_i} \right) A(\{r_i(t'), p_i(t')\}_0)\, \mathrm{d}t', \tag{3}$$

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where $\{\boldsymbol{r}_i(t'), \boldsymbol{p}_i(t')\}_0$ is the unperturbed trajectory of the system ending at time $t' = 0$ at that point in phase space at which D_0 and $\Delta D(t)$ in (3) are taken.

If the ensemble average of a function $B(\{r_i, p_a\})$ is zero in the absence of the perturbation, it's ensemble average in the presence of the perturbation is

$$\langle B \rangle = \int \Delta D\, B\, \mathrm{d}\Gamma, \tag{4}$$

where the integration is over the phase space.

Let us now apply this formalism to the case where the perturbation is caused by a constant and homogeneous external electric field $\boldsymbol{E}$, and where the system is a homogeneous molten salt consisting of two kinds (1 and 2) of cations (+) and one kind of anions (−). In this case

$$F(t) = E \tag{5}$$

and

$$A = e\, z_-\, N_-\, (\alpha_1 \bar{r}_1 + \alpha_2 \bar{r}_2 - \bar{r}_-) \tag{6}$$

where E is the absolute value of $\boldsymbol{E}$ and r the projection of $\boldsymbol{r}$ on $\boldsymbol{E}$. The bars symbolize means over the respective ions. N_- is the number of anions and e the elementary electric charge. The α's are equivalent fractions:

$$\alpha_{1,2} = z_{1,2}\, x_{1,2} / (z_1 x_1 + z_2 x_2), \tag{7}$$

where the z's are the valencies of the ions and x_1 and $x_2 = 1 - x_1$ are the molar fractions of the cationic species 1 and 2. (6) implies the electrical neutrality of the salt.

In the perturbed system any two ionic species (a and b) will move, in the ensemble average, with the relative velocity

$$\langle \bar{v}_a - \bar{v}_b \rangle = b_{ab}\, E \tag{8}$$

in the direction of $\boldsymbol{E}$. In our case a and b stand for 1, 2, + or −. In order to calculate the internal mobility b_{ab}, we specify ΔD by inserting (5) and (6) into (3) and write

$$B = \bar{v}_a - \bar{v}_b. \tag{9}$$

Inserting these expressions for ΔD and B into (4) and considering (8), one obtains

$$b_{ab} = (e/kT) \int_{-\infty}^{0} K_{ab}(t)\,dt \tag{10}$$

with the correlation function

$$K_{ab}(t) = z_- N_- \langle [\alpha_1 \overline{v_1(t)} + \alpha_2 \overline{v_2(t)} - \overline{v_-(t)}] \cdot [\overline{v_a(0)} - \overline{v_b(0)}] \rangle_0 . \tag{11}$$

The subscript 0 indicates that the ensemble average is to be taken in the absence of the perturbation. We further introduce the group velocity correlation functions

$$C_{ab}(t) = z_- N_- \langle \overline{v_a(t)} \; \overline{v_b(0)} \rangle_0 . \tag{12}$$

Due to the time reversal symmetry in our unmagnetic system,

$$C_{ab}(t) = C_{ba}(t) . \tag{13}$$

One also has

$$C_{+b} = x_1 C_{1b} + x_2 C_{2b} . \tag{14}$$

From (11), (12) and (13), it follows that

$$K_{ab} = -C_{a-} + C_{b-} + \alpha_1 C_{a1} + \alpha_2 C_{a2} - \alpha_1 C_{b1} - \alpha_2 C_{b2} \tag{15}$$

and especially

$$K_{12} = -C_{1-} + C_{2-} + \alpha_1 C_{11} - \alpha_2 C_{22} + (\alpha_2 - \alpha_1) C_{12} \tag{16}$$

and, also using (14),

$$K_{+-} = -(x_1 + \alpha_1) C_{1-} - (x_2 + \alpha_2) C_{2-} + x_1 \alpha_1 C_{11} + x_2 \alpha_2 C_{22} + (x_1 \alpha_2 + x_2 \alpha_1) C_{12} + C_{--} . \tag{17}$$

The internal mobilities b_{12} and b_{+-} are obtained by inserting (16) and (17), respectively, into (10). From these, the internal mobilities b_{1-} and b_{2-} and the specific conductance $\varkappa$ follow:

$$b_{1-} = b_{+-} + x_2 b_{12} , \tag{18}$$

$$b_{2-} = b_{+-} - x_1 b_{12} , \tag{19}$$

$$\varkappa = c_e F b_{+-} , \tag{20}$$

where c_e is the equivalent concentration of the salt and F Faraday's constant.

Let us now suppose that the two cationic species 1 and 2 have the same valency, which implies that $\alpha_{1,2} = x_{1,2}$, and that they differ in mass, i.e. that they are isotopes.

The dependence of the velocity autocorrelation functions on the mass of the ions has already been treated in [5]. We proceed in a somewhat different way and include the velocity crosscorrelation functions.

In classical mechanics the evolution of one component of the velocity of a particle i in an unperturbed system of N particles is given by

$$v_i(t) = v_i(0) + (L v_i) t + \tfrac{1}{2} (L^2 v_i) t^2 + \tfrac{1}{6} (L^3 v_i) t^3 + O(t^4) \tag{21}$$

with

$$L = \sum_j^N \left(v_j \frac{\partial}{\partial r_j} - \frac{1}{m_j} \frac{\partial \Phi}{\partial r_j} \frac{\partial}{\partial v_j} \right) , \tag{22}$$

where m_j is the mass of particle j and Φ the potential energy of the system due to the pair potentials. The derivatives in (21) have to be taken at the time $t = 0$.

From (22), the coefficients in (21) become

$$(L v_i) = -\frac{1}{m_i} \frac{\partial \Phi}{\partial r_i} , \tag{23}$$

$$(L^2 v_i) = -\frac{1}{m_i} \sum_j^N v_j \frac{\partial^2 \Phi}{\partial r_j \partial r_i} , \tag{24}$$

$$(L^3 v_i) = -\frac{1}{m_i} \sum_k^N \left(v_k \sum_j^N v_j \frac{\partial^3 \Phi}{\partial r_k \partial r_j \partial r_i} - \frac{1}{m_k} \frac{\partial \Phi}{\partial r_k} \frac{\partial^2 \Phi}{\partial r_k \partial r_i} \right) . \tag{25}$$

We now introduce m_-, m_+ and ε_i by writing

$$m_{i \in -} = m_- , \qquad m_{i \in +} = m_+ (1 + \varepsilon_i) , \tag{26}$$

where m_+ is some reference mass for the cations. From (21), (23), (24) and (25) it is seen that an expansion of $v_i(t)$ in powers of the ε's has the form

$$v_{i \in +}(t) = v_i(t)_0 + (-\varepsilon_i + \varepsilon_i^2 + O(\varepsilon^3)) a_i + (1 - \varepsilon_i + O(\varepsilon^2)) \sum_{k \in +} a_{ik} (-\varepsilon_k + \varepsilon_k^2 + O(\varepsilon^3)) , \tag{27}$$

$$v_{i \in -}(t) = v_i(t)_0 + \sum_{k \in +} b_{ik} (-\varepsilon_k + \varepsilon_k^2 + O(\varepsilon^3)) . \tag{28}$$

The functions a and b depend on the velocities and positions of all particles at $t = 0$. The ensemble averages $\langle v_i(t') v_j(t' + t) \rangle$ are, however, independent of the velocities and positions of the particles at $t = 0$, and also independent of t'. One therefore obtains from (27) and (28) to second order

$$\langle v_{i \in +}(0) v_{j \in -}(t) \rangle = E_0 + E_1 \bar{\varepsilon} + E_2 \bar{\varepsilon}^2 + E_3 \overline{\varepsilon^2} + E_4 \varepsilon_i + E_5 \varepsilon_i^2 + E_6 \bar{\varepsilon} \varepsilon_i , \tag{29}$$

$$\langle v_{i \in +}(0) v_{i \in +}(t) \rangle = F_0 + F_1 \bar{\varepsilon} + F_2 \bar{\varepsilon}^2 + F_3 \overline{\varepsilon^2} + F_4 \varepsilon_i + F_5 \varepsilon_i^2 + F_6 \bar{\varepsilon} \varepsilon_i , \tag{30}$$

$$\langle v_{i\in+}(0)\,v_{j\in+}(t)\rangle = G_0 + G_1\,\bar\varepsilon + G_2\,\bar\varepsilon^2 + G_3\,\overline{\varepsilon^2} \quad (31)$$
$$+ G_4(\varepsilon_i+\varepsilon_j) + G_5(\varepsilon_i^2+\varepsilon_j^2) + G_6\,\bar\varepsilon(\varepsilon_i+\varepsilon_j) + G_7\,\varepsilon_i\,\varepsilon_j\,,$$

$$\langle v_{i\in-}(0)\,v_{j\in-}(t)\rangle = H_0 + H_1\,\bar\varepsilon + H_2\,\bar\varepsilon^2 + H_3\,\overline{\varepsilon^2}\,, \quad (32)$$

where the functions E, F, G and H depend on t and, with the exception of E_0, F_0, G_0 and H_0, on the choice of m_+. They are independent of the molar fractions of the cationic isotopes.

The r. h. sides of (29) – (32) have the same form if on the l. h. sides the v-values of single particles are replaced by mean v-values of all particles of the same kind and mass, e. g. $v_{i\in-}$ by $\overline{v_{i\in-}}$.

We now return to the case of two cationic species (isotopes) and write

$$\bar\varepsilon = x_1\,\varepsilon_1 + x_2\,\varepsilon_2\,, \quad \overline{\varepsilon^2} = x_1\,\varepsilon_1{}^2 + x_2\,\varepsilon_2{}^2, \quad \varepsilon_{12} = \varepsilon_1 - \varepsilon_2\,. \quad (33)$$

In (29) – (32) ε_1, ε_2 and $\overline{\varepsilon^2}$ can be replaced by $\bar\varepsilon$ and ε_{12} and one arrives, using the notation of (12), at

$$C_{1-} = e_0 + e_1\,\bar\varepsilon + e_2\,\bar\varepsilon^2 + e^3\,x_2\,\varepsilon_{12} + e_4\,x_2\,\bar\varepsilon\,\varepsilon_{12}$$
$$+ (e_5\,x_1\,x_2 + e_6\,x_2{}^2)\,\varepsilon_{12}^2\,, \quad (34)$$

$$C_{11} = f_0 + f_1\,\bar\varepsilon + f_2\,\bar\varepsilon^2 + f_3\,x_2\,\varepsilon_{12} + f_4\,x_2\,\bar\varepsilon\,\varepsilon_{12}$$
$$+ (f_5\,x_1\,x_2 + f_6\,x_2{}^2)\,\varepsilon_{12}^2\,, \quad (35)$$

$$C_{12} = g_0 + g_1\,\bar\varepsilon + g_2\,\bar\varepsilon^2 + g_3(x_1-x_2)\,\varepsilon_{12} \quad (36)$$
$$+ g_4(x_1-x_2)\,\bar\varepsilon\,\varepsilon_{12} + [g_5\,x_1\,x_2 + g_6(x_1{}^2+x_2{}^2)]\,\varepsilon_{12}^2\,,$$

$$C_{--} = h_0 + h_1\,\bar\varepsilon + h_2\,\bar\varepsilon^2 + h_3\,x_1\,x_2\,\varepsilon_{12}^2\,. \quad (37)$$

C_{2-} and C_{22} are obtained from (34) and (35), respectively, by exchanging the subscripts 1 and 2. Since $C_{11} = C_{12}$ if $\varepsilon_{12} = 0$, it follows that

$$f_0 = g_0\,, \quad f_1 = g_1\,, \quad f_2 = g_2\,. \quad (38)$$

The expansions to second order (34) – (37) are of the same form if the ε's are replaced by μ's, where

$$m_{i\in+}^{-1/2} = m_+{}^{-1/2}(1+\mu_i)\,. \quad (39)$$

Our Eqs. (35) and (37) correspond to the Eqs. (19) in [5].

By introducing (34) – (37) into (16) and (17), and using (10), one gets

$$b_{12} = (A_1 + x_1\,x_2\,A_2)\,\varepsilon_{12} + (A_3 + x_1\,x_2\,A_4)\,\bar\varepsilon\,\varepsilon_{12}$$
$$+ (x_1-x_2)\,(A_5 + x_1\,x_2\,A_6)\,\varepsilon_{12}^2\,, \quad (40)$$

$$b_{+-} = B_0 + B_1\,\bar\varepsilon + B_2\,\bar\varepsilon^2 + (x_1-x_2)\,x_1\,x_2\,(B_3 + B_4\,\bar\varepsilon)\,\varepsilon_{12}$$
$$+ x_1\,x_2\,(B_5 + x_1\,x_2\,B_6)\,\varepsilon_{12}^2\,, \quad (41)$$

where the coefficients A and B are time integrals of linear combinations of the functions e, f, g and h. They are independent of the molar fractions x_1 and x_2 and depend, with the exception of B_0, on the choice of m_+.

In many papers on the mobility of isotopes in molten salts the quotient $(b_{12}/b_{+-})/\varepsilon_{12}$ with $\varepsilon_{12} = 2(m_1-m_2)/(m_1+m_2)$ has been called the mass effect μ. According to (40) and (41) to first order

$$\mu = [A_1 + x_1(1-x_1)\,A_2]/B_0\,. \quad (42)$$

This dependence of μ on x_1 could be checked by experiments on lithium salts with different concentrations of ^{6}Li and ^{7}Li.

The evaluation of the group velocity correlation functions dealt with in this paper requires very extensive computor simulations and is correspondingly expensive at present, but hopefully the situation will change in future.

[1] A. Klemm and K. Heinzinger, Advances in Chemistry Series, Washington **28**, 248 [1969].
[2] J. P. Apercé, F. Lantelme, and M. Chemla, C. R. Hebd. Séanc. Acad. Sci. Paris C **264**, 461 [1967].
[3] J. W. E. Lewis and K. Singer, JCS Faraday II, **71**, 41 [1975].
[4] J. P. Hansen and J. R. McDonald, Phys. Rev. **A 11**, 2111 [1975].
[5] F. Lantelme, P. Turq, and P. Schofield, Mol. Physics **31**, 1085 [1976].
[6] cf. e. g. W. A. Steele, "Time-Correlation Functions" in "Transport Phenomena in Fluids", ed. by H. J. M. Hanley, New York 1969.