Molten Salt Ionic Mobilities in Terms of Group Velocity Correlation Functions

A. Klemm
Max-Planck-Institut für Chemie (Otto-Hahn-Intsitut), Mainz, Germany

(Z. Naturforsch. 32a, 927–929 [1977]; received August 1, 1977)

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, TICl, CuCl and AgCl are known whereas only one publication exists on an isotope effect of diffusion: ⁶Li and ⁷Li in mixtures of alkali nitrites.

For comparisons it would be desirable to calculate not only diffusion coefficients, as has been done, 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 its Hamiltonian we write

\[ H = H_0 (\{ r_i, p_i \}) + H_{\text{ext}} (\{ r_i, p_i \}, t); \]

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

If \( H_{\text{ext}} \) is small compared to the equilibrium Hamiltonian \( H_0 \) and can be separated and one-dimensionally specified as

\[ H_{\text{ext}} = -F(t) A(\{ r_i, p_i \}) \]

then, according to the theory of linear response, the deviation \( \Delta D(t) \) of the distribution function \( D(t) \) from its equilibrium value \( D_0 \) is

\[ \Delta D(t) = \frac{D_0}{kT} \int_{-\infty}^{0} F(t+t') \sum_i \left( \frac{\partial H_0}{\partial r_i} \frac{\partial A}{\partial r_i} - \frac{\partial H_0}{\partial p_i} \frac{\partial A}{\partial p_i} \right) A(\{ r_i(t'), p_i(t') \}_0) \, dt', \]

where \( \{ r_i(t'), p_i(t') \}_0 \) 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 \( B(\{ r_i, p_i \}) \) is zero in the absence of the perturbation, it's ensemble average in the presence of the perturbation is

\[ \langle B \rangle = \int \Delta D B \, d\tau', \]

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 \( E \), 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

\[ F(t) = E \]

and

\[ A = e z_\text{−} \bar{N} \left( a_1 \bar{r}_1 + a_2 \bar{r}_2 - \bar{r}_- \right) \]

where \( E \) is the absolute value of \( E \) and \( r \) the projection of \( r \) on \( E \). The bars symbolize means over the respective ions, \( N_- \) is the number of anions and \( e \) the elementary electric charge. The \( a \)'s are equivalent fractions:

\[ a_{1,2} = z_{1,2} \frac{x_{1,2}}{x_1 + x_2} \]

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

\[ (\bar{v}_a - \bar{v}_b) = b_{ab} E \]

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

\[ B = \bar{v}_a - \bar{v}_b. \]

Reprint requests to Prof. Dr. A. Klemm, Max-Planck-Institut für Chemie, Saarstraße 23, D-65300 Mainz.
Inserting these expressions for $AD$ and $B$ into (4) and considering (8), one obtains

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

with the correlation function

$$K_{ab}(t) = z_{-} N_{-} \langle [a_{1} v_{1}(t) + a_{2} v_{2}(t) - v_{-}(t)] \cdot [v_{a}(0) - v_{b}(0)] \rangle_0.$$  (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

$$C_{ab}(t) = z_{-} N_{-} \langle v_{a}(t) \cdot v_{b}(0) \rangle_0.$$  (12)

Due to the time reversal symmetry in our unmagnetic system,

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

One also has

$$C_{+b} = x_{1} C_{1b} + x_{2} C_{2b}.$$  (14)

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

$$K_{ab} = - C_{a-} + C_{b-} + a_{1} C_{a1} + a_{2} C_{a2} - a_{1} C_{b1} - a_{2} C_{b2}$$

and especially

$$K_{12} = - C_{1-} + C_{2-} + a_{1} C_{11} - a_{2} C_{22} + (a_{2} - a_{1}) C_{12}$$

and, also using (14),

$$K_{+b} = (x_{1} + a_{1}) C_{1b} - (x_{2} + a_{2}) C_{2b} + x_{1} a_{1} C_{11} + x_{2} a_{2} C_{22} + (x_{1} a_{2} + x_{2} a_{1}) C_{12} + C_{+ -}.$$  (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 $\kappa$ follow:

$$b_{1-} = b_{+ -} + x_{2} b_{12},$$  (18)

$$b_{2-} = b_{+ -} - x_{1} b_{12},$$  (19)

$$\kappa = c_{e} F b_{+ -},$$  (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 $a_{1,2} = x_{1,2}$, 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. 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

$$v_{i}(t) = v_{i}(0) + (L_{vi}) t + \frac{1}{2} (L^{2}_{vi}) t^{2} + \frac{1}{6} (L^{3}_{vi}) t^{3} + O(t^{4})$$

with

$$L = \sum_{j} \left( v_{j} \frac{\partial}{\partial r_{j}} - \frac{1}{m_{j}} \frac{\partial}{\partial r_{j}} \frac{\partial}{\partial r_{j}} \frac{\partial}{\partial \Phi} \right),$$  (22)

where $m_{j}$ is the mass of particle $j$ and $\Phi$ 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

$$(L_{vi}) = - \frac{1}{m_{i}} \frac{\partial}{\partial r_{i}},$$  (23)

$$(L^{2}_{vi}) = - \frac{1}{m_{i}} \sum_{j} v_{j} \left( \frac{\partial}{\partial r_{j}} \frac{\partial}{\partial r_{i}} \right),$$  (24)

$$(L^{3}_{vi}) = - \frac{1}{m_{i}} \sum_{j} \sum_{k} \left( \frac{\partial}{\partial r_{k}} \frac{\partial}{\partial r_{j}} \frac{\partial}{\partial r_{i}} \right),$$  (25)

We now introduce $m_{-}$, $m_{+}$ and $\epsilon_{i}$ by writing

$$m_{i} = m_{-}, \quad m_{i} = m_{+} (1 + \epsilon_{i}),$$  (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 $\epsilon$’s has the form

$$v_{i}(t) = v_{i}(0) + (L_{vi}) t + \frac{1}{2} (L^{2}_{vi}) t^{2} + \frac{1}{6} (L^{3}_{vi}) t^{3} + O(t^{4})$$

with

$$(L_{vi}) = - \frac{1}{m_{-}} \frac{\partial}{\partial r_{i}},$$  (27)

$$(L^{2}_{vi}) = - \frac{1}{m_{-}} \sum_{j} v_{j} \left( \frac{\partial}{\partial r_{j}} \frac{\partial}{\partial r_{i}} \right),$$  (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

$$\langle v_{i}(0) v_{ie-}(t) \rangle = E_{0} + E_{1} \tilde{\epsilon} + E_{2} \tilde{\epsilon}^{2} + E_{3} \tilde{\epsilon}^{3} + E_{4} \epsilon_{i} + E_{5} \epsilon_{i}^{2} + E_{6} \epsilon_{i}^{3},$$  (29)

$$\langle v_{i}(0) v_{ie+}(t) \rangle = F_{0} + F_{1} \tilde{\epsilon} + F_{2} \tilde{\epsilon}^{2} + F_{3} \tilde{\epsilon}^{3} + F_{4} \epsilon_{i} + F_{5} \epsilon_{i}^{2} + F_{6} \epsilon_{i}^{3},$$  (30)
The expansions to second order \((34) - (37)\) are of the same form if the \(\varepsilon\)'s are replaced by \(\mu\)'s, where
\[
m_{\varepsilon+}^{-\frac{1}{2}} = m_{\varepsilon-}^{-\frac{1}{2}} (1 + \mu_i) .
\]
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
\[
b_{12} = (A_1 + x_1 x_2 A_2) \varepsilon_{12} + (A_3 + x_1 x_2 A_4) \varepsilon_{12} + (x_1 - x_2) (A_5 + x_1 x_2 A_6) \varepsilon_{12} + x_1 x_2 (B_5 + x_1 x_2 B_6) \varepsilon_{12} ,
\]
\[
b_{\varepsilon-} = B_0 + B_1 \varepsilon + B_2 \varepsilon^2 + (x_1 - x_2) x_1 x_2 (B_3 + B_4) \varepsilon_{12} + x_1 x_2 (B_5 + x_1 x_2 B_6) \varepsilon_{12} ,
\]
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 \((b_{12}/b_{\varepsilon-})/\varepsilon_{12}\) has been called the mass effect \(\mu\). According to \((40)\) and \((41)\) to first order
\[
\mu = [A_1 + x_1 (1 - x_1) A_2]/B_0 .
\]
This dependence of \(\mu\) 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 computer simulations and is correspondingly expensive at present, but hopefully the situation will change in future.