

Improved Representation of Velocity Correlations in Aqueous Electrolyte Solutions

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A general definition of the salt molecule for any asymmetric polyvalent electrolyte in solution is given which fulfils the requirement that the solute mass flux in the presence of an electric field strength vanishes when referred to the proper representative point of the molecule. Effectively this is the definition of the mass flux in the microscopic representation of an electrolyte solution. The electric current density arising from a gradient in the chemical potential also vanishes when referred to the same representative point. Time integrals over the velocity cross-correlation functions have been calculated for aqueous NaCl, LiCl, CaCl₂ and BaCl₂ solutions using conductivity data, transport numbers and mutual diffusion coefficients fulfilling the above requirements. A first approximation is also given for the calculation of velocity correlation coefficients in the case where transport numbers are not available.

In a number of previous papers¹⁻³ we have reported time integrals over velocity cross-correlation functions

$$f_{ii} = \frac{v_i c_s N V}{3} \int_0^\infty \langle v_1^{(i)}(0) \cdot v_2^{(i)}(t) \rangle dt \quad i = a, c \quad (1)$$

$$f_{ij} = \frac{v_j c_s N V}{3} \int_0^\infty \langle v_1^{(i)}(0) \cdot v_1^{(j)}(t) \rangle dt \quad i, j = c, a \quad i \neq j \quad (2)$$

for aqueous electrolyte solutions in the concentration range $0 < \tilde{c}_s / \text{mol dm}^{-3} \leq 4$. The salt may be any electrolyte which ionizes in a solvent *w* (water), to give *v_a* anions (a) of valence *z_a* and *v_c* cations (c) of valence *z_c*. *c_s* is the salt concentration in mol cm⁻³, *N* is Avogadro's number, *V* is the solution volume and *v_n⁽ⁱ⁾(t)* (*i* = a, c) denotes the velocity of particle *n* of constituent *i* at time *t*. The velocities *v_n⁽ⁱ⁾(t)* are measured relative to the laboratory (or cell) coordinate system; they are vector quantities, but for simplicity we omit vector notation. As usual the pointed brackets represent the ensemble average.

The three independent quantities given by eqn (1) and (2) were calculated from experimental values of the equivalent conductance, Λ , the transport number of the cation, *t_c*, and the mutual diffusion coefficient of the salt against water, *D_{sw}*. The quantity *D_{sw}* describes the flux of a neutral substance, the dissolved salt, whereas the transport number is a quantity which describes the motion of a single ionic species under the action of the electric field; the microscopic representation of the electric current consists of the separate motion of ionic species. In order to incorporate the mutual diffusion data in the treatment it was necessary to generalize the concept of a molecule to a solution of a strong electrolyte, *i.e.*, to a situation where the intramolecular distances of the anions and cations are not constant. For the transport properties considered here, the velocity of the salt molecule is of particular interest; this velocity will be given in terms of the velocities of the cations and anions belonging

to the molecule. In our previous work we used the following expression connecting the instantaneous ionic velocities with the instantaneous molecular velocity

$$v_n^{(s)}(t) = \frac{\left(\sum_{i=1}^{v_c} v_i^{(c)}(t)\right) D_c^{-\frac{1}{2}} + \left(\sum_{j=1}^{v_a} v_j^{(a)}(t)\right) D_a^{-\frac{1}{2}}}{\left\{ (v_c + v_a) \left(\frac{v_a}{D_a} + \frac{v_c}{D_c} \right) \right\}^{\frac{1}{2}}} \quad (3)$$

where D_c and D_a are the self-diffusion coefficients of the cation and anion, respectively.

$$D_i = \frac{1}{3} \int_0^{\infty} \langle v_1^{(i)}(0) \cdot v_1^{(i)}(t) \rangle dt \quad i = c, a. \quad (4)$$

Eqn (3) was chosen in such a form that in the limit of high salt dilution the correct limiting value for D_{sw} results:

$$\lim_{c_s \rightarrow 0} D_{sw} = \frac{(v_a + v_c) D_a D_c}{v_a D_c + v_c D_a} \quad (5)$$

which represents the well-known Nernst limiting formula when the self-diffusion coefficients are replaced by the ionic equivalence conductances λ_i using the relation *

$$D_i = \lambda_i^{\circ} RT / |z_i| F^2 \quad (i = c, a)$$

where F is the Faraday constant.

Thus there is no doubt that eqn (3) is correct at very low salt concentrations; however, it is not yet clear which condition

$$v_n^{(s)}(t) = v_n^{(s)}[v_1^{(c)}(t), v_2^{(c)}(t), \dots, v_1^{(a)}(t), v_2^{(a)}(t), \dots]$$

has to apply at high salt concentrations. In the meantime this condition has been worked out for 1-1 electrolytes.⁵ We require that the quantity

$$\Delta = \frac{f_{cc}}{D_c} - \frac{f_{aa}}{D_a} \quad (6)$$

must vanish at all concentrations, *i.e.*,

$$\Delta = 0 \quad 0 \leq c_s \leq c_{sat} \quad (7)$$

where c_{sat} is the saturation concentration of the salt. The validity of eqn (7) is a consequence of the requirement that the salt molecule is electrically neutral; thus in a homogeneous solution ($c_s = \text{const.}$) there cannot be any mass transport under the action of electric field strength. It appears⁵ that the application of the molecular velocity definition eqn (3) in general does not satisfy eqn (7). Only in the case that the cations and anions involved are not strongly hydrated was eqn (7) found to be approximately fulfilled. These are the ions K^+ , Cs^+ , Cl^- and I^- , typically those ions which are usually characterized as being structure-breaking. The chlorides of Na^+ , Li^+ , Ca^{2+} and Ba^{2+} showed distinct deviations from eqn (7).

It has been shown elsewhere⁵ that for symmetrical electrolytes the quantities D_c and D_a in the numerator of eqn (3) have to be replaced by*

$$D_i + \delta^* \quad i = c, a \quad (8)$$

where

$$\delta^* = \frac{f_{cc} D_a - D_c f_{aa}}{D_a + f_{aa} - D_c - f_{cc}} \quad (9)$$

in order to guarantee the validity of eqn (7) for all concentrations.

* In ref. (5) the quantity δ^* is denoted by δ .

The present paper has three purposes: (i) To generalize the correction given in eqn (8) in such a way that we write:

$$D_c + \delta_c \quad \text{and} \quad D_a + \delta_a. \quad (8a)$$

In particular we shall investigate the choice

$$\begin{aligned} \delta_c &= \delta \\ \delta_a &= -\delta. \end{aligned} \quad (8b)$$

The use of eqn (8a) and (8b) rather than eqn (8) has only practical reasons; in this way singularities of the function $(D_i + \delta^*)^{-1}$ are avoided. (ii) To work out the correct formulae for non-symmetric electrolytes. (iii) To recalculate the velocity correlation coefficients f_{aa} , f_{cc} , f_{ac} as defined by eqn (1) and (2) using the new definition of the molecular velocity for the salts NaCl, LiCl, CaCl₂ and BaCl₂. The behaviour of the new f_{ij} remains practically the same as previously reported.^{2, 3}

THEORETICAL

MASS FLUX AND ELECTRIC CURRENT DENSITY: GENERAL

We consider a binary electrolyte solution consisting of any polyvalent electrolyte and water. In the microscopic representation of this system the instantaneous velocities of the cations are

$$v_1^{(c)}, v_2^{(c)}, v_3^{(c)}, \dots \quad v_{v_c N_s}^{(c)}$$

and the instantaneous velocities of the anions are

$$v_1^{(a)}, v_2^{(a)}, v_3^{(a)}, \dots \quad v_{v_a N_s}^{(a)}$$

where $N_s = Vc_s N$.

There may be a macroscopic (*i.e.*, observable) mass flux of the solute, $j_s^* = j_s^*(r, t)$, in the system; j_s^* is defined by the relation

$$\frac{\partial \rho_s}{\partial t} = -\text{div } j_s^* \quad (10)$$

together with $j_s^* = 0$ at those positions where $\text{grad } \rho_s = 0$ and ρ_s is the partial mass density of the solute. According to eqn (10) j_s^* is defined in the laboratory (or cell) coordinate system. Having j_s^* at each point, it is easy to transform j_s^* to a centre of volume fixed reference frame;⁶ the solute mass flux is then denoted by j_s .

There may also exist an electric current density j_q at each point of the system. j_q is connected with the rate of increase of the local internal energy; it may be measured *via*, *e.g.*, its magnetic field. The microscopic representation of the instantaneous electric current density of the system is

$$J_q = \frac{1}{V} (q_c v_1^{(c)} + q_c v_2^{(c)} + q_c v_3^{(c)} + \dots + q_a v_1^{(a)} + q_a v_2^{(a)} + q_a v_3^{(a)} + \dots). \quad (11)$$

q_c and q_a are the electric charges of the cation and anion, respectively. We have

$$q_c = z_c e, \quad q_a = -z_a e \quad (12)$$

where $-e$ is the charge on the electron. z_c and z_a are related to one another

$$z_c v_c = z_a v_a$$

so that the salt molecule is electrically neutral. The velocities in eqn (11) are not

entirely independent: a volume element which is macroscopically small has to remain electrically neutral

$$z_c c'_c(t) = z_a c'_a(t)$$

where $c'_i(t)$; $i = c, a$, are the instantaneous number densities of cations and anions.

The instantaneous mass flow density in the microscopic representation is given by the relation

$$J_s = \frac{1}{V} (v_c m_c + v_a m_a) \{v_1^{(s)} + v_2^{(s)} + v_3^{(s)} + \dots\} \quad (13)$$

where m_c and m_a are the masses of the cation and anion, respectively. $v_k^{(s)}$ is the instantaneous velocity of the k th molecule. Now, as has already been described in the introduction [see eqn (3), (8), (8a) and (8b)], we write $v_k^{(s)}$ in terms of the instantaneous velocities of the v_c cations and v_a anions as the following relation:^{1, 3}

$$v_k^{(s)} = [(v_c + v_a)(v_c D_c^{-1} + v_a D_a^{-1})]^{-\frac{1}{2}} \left\{ \sum_{i=1}^{v_c} v_{ki}^{(c)} + \sum_{j=1}^{v_a} v_{kj}^{(a)} \right\}. \quad (14a)$$

This then implies that the microscopic representation of the instantaneous solute mass flux is defined as the quantity:

$$J_s = \frac{(v_c m_c + v_a m_a)}{V[(v_c + v_a)(v_c D_c^{-1} + v_a D_a^{-1})]^{\frac{1}{2}}} \left\{ \sum_{k=1}^{N_s} \sum_{i=1}^{v_c} v_{ki}^{(c)} + \sum_{k=1}^{N_s} \sum_{j=1}^{v_a} v_{kj}^{(a)} \right\}. \quad (14b)$$

In eqn (14a) and (14b) $\delta \rightarrow 0$ as $c_s \rightarrow 0$; then these expressions lead to the correct limiting behaviour for $c_s \rightarrow 0$ as given in eqn (5).^{1, 3}

According to the results of the linear response theory⁷ the observable mean electric current density is

$$j_q = \frac{1}{3kT} \int_0^\infty \langle J_q(0) \dot{A}(t) \rangle dt \quad (15)$$

and likewise the observable mean mass flow density is

$$j_m = \frac{1}{3kT} \int_0^\infty \langle J_s(0) \dot{A}(t) \rangle dt \quad (16)$$

where \dot{A} is the time derivative of the effective perturbation energy connected with the flux in question, the time dependence being given by the microscopic motion of the system in the equilibrium state.

We consider here two kinds of perturbation energy: (1) the electrostatic one

$$A_{el} = (q_c r_1^{(c)} + q_c r_2^{(c)} + \dots + q_a r_1^{(a)} + q_a r_2^{(a)} + \dots) \mathcal{E} \quad (17)$$

where $r_l^{(i)}$ ($i = c, a$) is the position of the l th cation or anion, \mathcal{E} is the gradient of the macroscopic electric potential (*i.e.*, the electric field strength); (2) the thermodynamic one

$$A_m = -(v_c m_c + v_a m_a) (y_1 + y_2 + y_3 + \dots) \text{grad } \mu_s^* \quad (18)$$

where the meaning of the y_k is that the mass of the k th molecule is to be placed at y_k , $k = 1, 2, \dots, N_s$. μ_s^* is the specific chemical potential of the solute. Since the gradient of the latter quantity is always connected with the gradient of the specific

chemical potential of the solvent, A_m contains a factor $1 + \rho_s/\rho_w$ which we omit for simplicity.⁶ ρ_w is the partial mass density of the solvent water. Now we may insert both the quantities eqn (17) and (18) in eqn (15). This then gives two kinds of electric current density: one connected with \mathcal{E} and another with $\text{grad } \mu_s^*$. Likewise, substitution of eqn (17) and (18) in eqn (16) yields the corresponding two kinds of mass flux. We begin with eqn (16).

MASS FLUXES

First we must find A_{e1} . It follows from eqn(13) and (14a) that the position of the k th salt molecule is

$$y_k = [(v_c + v_a)(v_c D_c^{-1} + v_a D_a^{-1})]^{-\frac{1}{2}} \left\{ \frac{\sum_{i=1}^{v_c} r_{ki}^{(c)}}{(D_c + \delta)^{\frac{1}{2}}} + \frac{\sum_{j=1}^{v_a} r_{kj}^{(a)}}{(D_a - \delta)^{\frac{1}{2}}} \right\} \quad k = 1, 2 \dots N_s \quad (19)$$

where $r_l^{(c)} = r_{ki}^{(c)}$, $r_l^{(a)} = r_{kj}^{(a)}$ are the positions of the l th cation and anion, respectively; then $\dot{r}_{ki}^{(j)} = v_{ki}^{(j)}$, $\dot{y}_k = v_k^{(s)}$, where vector notation has again been dispensed with for simplicity. However, according to eqn (17) the contribution to the potential energy of a salt molecule due to the electric field strength \mathcal{E} is

$$E_{\text{pot}} = z_c e \sum_{i=1}^{v_c} r_{ki}^{(c)} \mathcal{E} - z_a e \sum_{j=1}^{v_a} r_{kj}^{(a)} \mathcal{E}. \quad (20)$$

The essential feature of eqn (14a) is the redistribution of weights of the cationic and anionic velocities. Usually the cation is strongly hydrated and as a consequence the thermal motion is more strongly damped. To compensate partly for this effect, in the expression for the total solute mass flux, the instantaneous cation velocity contribution is increased by a factor

$$\left(\frac{D_a - \delta}{D_c + \delta} \right)^{\frac{1}{2}}$$

relative to that of the anions. Thus, the dynamical variable "mass flux of the salt", apart from a multiplication by the mass, consists of a redistribution of weights to the instantaneous ionic velocities. However, if the velocities have different weights, then the forces must also be modified in the corresponding way. Thus, the effective potential energies of the cations and anions with respect to the dynamical variable mass flux are

$$E_{\text{pot,eff}}^{(c)} = z_c e \left[\frac{(D_c + \delta)^{-1}}{(v_a + v_c)(v_a D_a^{-1} + v_c D_c^{-1})} \right]^{\frac{1}{2}} r_{ki}^{(c)} \cdot \mathcal{E} \quad (21)$$

$$E_{\text{pot,eff}}^{(a)} = -z_a e \left[\frac{(D_a - \delta)^{-1}}{(v_a + v_c)(v_a D_a^{-1} + v_c D_c^{-1})} \right]^{\frac{1}{2}} r_{kj}^{(a)} \cdot \mathcal{E} \quad (22)$$

and, in order to obtain the total effective potential energy of the molecule, one must replace the field strength in eqn (20) by the effective field strengths which occur in eqn (21) and (22) as the factors of $z_c e r_{ki}^{(a)}$ and $-z_a e r_{kj}^{(c)}$. So we arrive at the effective perturbation energy of the system of N_s points described by eqn (19):

$$A_{e1} = [(v_a + v_c)(v_c D_c^{-1} + v_a D_a^{-1})]^{-\frac{1}{2}} e \left\{ \frac{z_c \sum_k^{N_s} \sum_i^{v_c} r_{ki}^{(c)}}{(D_c + \delta)^{\frac{1}{2}}} - \frac{z_a \sum_k^{N_s} \sum_j^{v_a} r_{kj}^{(a)}}{(D_a - \delta)^{\frac{1}{2}}} \right\} \mathcal{E}. \quad (23)$$

We now form the time derivative of eqn (17) in which $\mathcal{E} = \text{const}$. With eqn (23) the result is :

$$A_{e1} = [(v_a + v_c)(v_c D_c^{-1} + v_a D_a^{-1})]^{-\frac{1}{2}} e \left\{ \frac{z_c \sum_k^{N_s} \sum_i^{v_c} v_{ki}^{(c)}}{(D_c + \delta)^{\frac{1}{2}}} - \frac{z_a \sum_k^{N_s} \sum_j^{v_a} v_{kj}^{(a)}}{(D_a - \delta)^{\frac{1}{2}}} \right\} \mathcal{E} \quad (24)$$

and we can introduce eqn (13), (14b) and (24) into eqn (16) to obtain :

$$j_{m\mathcal{E}} = \frac{m_s e}{(v_a + v_c)[v_a D_a^{-1} + v_c D_c^{-1}]3kTV} \{ (z_c v_c N_s \langle v_{11}^c v_{11}^c \rangle + z_c v_c (v_c - 1) N_s \langle v_{11}^c v_{12}^c \rangle + z_c v_c^2 N_s^2 \langle v_1^c v_2^c \rangle) (D_c + \delta)^{-1} + (z_c v_c v_a N_s \langle v_{11}^a v_{11}^c \rangle + z_c v_c v_a N_s^2 \langle v_1^a v_1^c \rangle - z_a v_c v_a N_s^2 \langle v_1^c v_1^a \rangle - z_a v_c v_a N_s \langle v_{11}^a v_{11}^c \rangle) [(D_c + \delta)(D_a - \delta)]^{-\frac{1}{2}} - (z_a v_a^2 N_s^2 \langle v_1^a v_2^a \rangle + z_a v_a (v_a - 1) N_s \langle v_{11}^a v_{12}^a \rangle + z_a v_a N_s \langle v_{11}^a v_{11}^a \rangle) (D_a - \delta)^{-1} \} \mathcal{E}; \quad (25)$$

$j_{m\mathcal{E}}$ is the mass flux arising from the gradient of the electrical potential \mathcal{E} ; $m_s = v_c m_c + v_a m_a$. Furthermore, we have introduced the abbreviations

$$\langle v_{11}^i v_{11}^j \rangle = \int_0^\infty \langle v_{11}^{(i)}(0) \cdot v_{11}^{(j)}(t) \rangle dt \quad i, j = c, a \quad l = 1, 2$$

for the intramolecular velocity correlations and

$$\langle v_1^i v_1^j \rangle = \int_0^\infty \langle v_1^{(i)}(0) \cdot v_1^{(j)}(t) \rangle dt \quad i, j = c, a \quad l = 1, 2$$

for the intermolecular velocity correlations.

Consider the case that all $v_c + v_a$ ions are tightly bound so as to form a molecule in the conventional sense.

Then we have

$$D_c = D_a = \frac{1}{3} \langle v_{11}^i v_{11}^j \rangle \quad i, j = c, a \quad l = 1, 2$$

and

$$\langle v_1^c v_2^c \rangle = \langle v_1^c v_1^a \rangle = \langle v_1^a v_1^c \rangle = \langle v_1^a v_2^a \rangle.$$

We set $\delta = 0$ and introduction of these relations into eqn (25) yields

$$j_{m\mathcal{E}} = 0. \quad (26)$$

If there is an electrical field strength acting on a system containing dissolved neutral molecules, then no mass flux of the solute is observed; this is a well-known result.

When we insert the velocity correlation coefficients f_{cc} , f_{aa} and f_{ac} , defined in the introduction, in eqn (25) and neglect the terms involving products of N_s and intramolecular cross-correlation coefficients, i.e., those containing $\langle v_{11}^{(i)} v_{12}^{(j)} \rangle$ ($i = c, a$), the result is :

$$j_{m\mathcal{E}} = \frac{M_s F D_a D_c c_s}{(v_a + v_c)(v_a D_c + v_c D_a) RT} \left\{ \frac{v_c z_c (D_c + f_{cc})}{D_c + \delta} + (z_c - z_a) \frac{v_a f_{ac}}{(D_c + \delta)^{\frac{1}{2}} (D_a - \delta)^{\frac{1}{2}}} - \frac{v_a z_a (D_a + f_{aa})}{D_a - \delta} \right\} \mathcal{E} \quad (27)$$

where $M_s = N(v_a m_a + v_c m_c) = N m_s = v_a M_a + v_c M_c$.

We now choose δ such that we obtain $j_{m\mathcal{E}} = 0$. If $z_c = z_a$ and if $z_c \neq z_a$ but $f_{ac} = 0$, then we find from the requirement $j_{m\mathcal{E}} = 0$ according to eqn (27)

$$\delta = \delta^0 = \frac{D_a f_{cc} - D_c f_{aa}}{D_c + f_{cc} + D_a + f_{aa}}. \quad (28)$$

In the general case we proceed as shown below.

Next we give the expression for the mass flux which arises from the gradient of the specific chemical potential. With eqn (18) and (19) we have:

$$\dot{A}_m = -\frac{m_s}{[(v_c + v_a)(v_c D_c^{-1} + v_a D_a^{-1})]^{\frac{1}{2}}} \left\{ \sum_k \sum_{i=1}^{N_c} v_{ki}^{(c)} + \sum_k \sum_{j=1}^{N_a} v_{kj}^{(a)} \right\} \text{grad } \mu_s^*. \quad (29)$$

This expression we insert in eqn (16) together with eqn (13) and (14a) which gives the result for the mass flux (taking into account the factor $1 + \rho_s/\rho_w$)

$$-j_s = \left(1 + \frac{\rho_s}{\rho_w}\right) \frac{M_s^2 D_a D_c c_s}{(v_a + v_c)(v_a D_c + v_c D_a) RT} \left\{ \frac{v_c (D_c + f_{cc})}{D_c + \delta} + \frac{2v_a f_{ac}}{[(D_c + \delta)(D_a - \delta)]^{\frac{1}{2}}} + \frac{v_a (D_a + f_{aa})}{D_a - \delta} \right\} \text{grad } \mu_s^*. \quad (30)$$

ELECTRIC CURRENT DENSITY

So far, we have given expressions for the mass fluxes. Next we turn to the corresponding formulae for the electric current density, see eqn (15).

The instantaneous electric current density is given by eqn (11). If we consider the mean electric current connected with the gradient of the electric potential, then the potential energy involves direct coupling with each individual ion and not with a point representing a part of the molecule. Thus, we can apply eqn (17) as it stands and we have

$$\dot{A}_{e1} = [ez_c(v_1^{(c)} + v_2^{(c)} + \dots) - ez_a(v_1^{(a)} + v_2^{(a)} + \dots)]\mathcal{E}. \quad (31)$$

Then combination of eqn (11), (15) and (31) yields

$$j_q = \frac{F^2 z_c^2 v_c c_s}{3RT} \left\{ \langle v_1^c v_1^c \rangle + v_c N_s \langle v_1^c v_2^c \rangle - 2v_c N_s \langle v_1^a v_1^c \rangle + \frac{z_a}{z_c} (v_a N_s \langle v_1^a v_2^a \rangle + \langle v_1^a v_1^a \rangle) \right\} \mathcal{E} \quad (32a)$$

$$= \frac{F^2 z_c^2 v_c c_s}{RT} \left\{ D_c + f_{cc} - 2f_{ac} + \frac{z_a}{z_c} (f_{aa} + D_a) \right\} \mathcal{E} \quad (32b)$$

$$= \kappa \mathcal{E}. \quad (33)$$

From eqn (32a) and (33) we obtain the expression for the reduced equivalent conductivity:

$$\Lambda^* \equiv \frac{\Lambda RT}{z_c F^2} = D_c + f_{cc} - 2f_{ac} + \frac{z_a}{z_c} (f_{aa} + D_a). \quad (34)$$

We now consider $j_{q\mu_s^*}$, the electric current density arising from the gradient of the specific chemical potential.

\dot{A}_m is given by eqn (29) and needs no further comment. In eqn (11) we write for the velocities of the single ions:

$$v_{ki}^{(\lambda)} = \dot{y}_k + v_{ki}'^{(\lambda)} \quad \lambda = c, a \quad (35)$$

where \dot{y}_k is the time derivative of the position given in eqn (19).

$$v_{ki}'^{(\lambda)} = v_{ki}^{(\lambda)} - \dot{y}_k$$

is the velocity of the ion ki relative to the velocity of the point y_k . Since all microscopic velocities occurring in the treatment are taken at equilibrium, the system is fully isotropic and thus we have

$$\langle v_{ki}'^{(\lambda)} \rangle = 0.$$

As a consequence, the mean microscopic electric current density carried by the $v_c N_s$ representative points $x_i^{(c)}$ and the $v_a N_s$ representative points $x_i^{(a)}$ is

$$J_q = \frac{1}{V} [(v_a + v_c)(v_c D_c^{-1} + v_a D_a^{-1})]^{-\frac{1}{2}} e \left\{ \frac{z_c}{(D_c + \delta)^{\frac{1}{2}}} (v_1^{(c)} + v_2^{(c)} + \dots) - \frac{z_a}{(D_a - \delta)^{\frac{1}{2}}} (v_1^{(a)} + v_2^{(a)} + v_3^{(a)} + \dots) \right\} \quad (36)$$

Combination of eqn (15), (29) and (36) then gives the result:

$$-j_{q\mu_s^*} = \frac{M_s F D_a D_c c_s}{(v_a + v_c)(v_c D_a + v_a D_c) RT} \left\{ \frac{v_c z_c (D_c + f_{cc})}{D_c + \delta} + (z_c - z_a) \frac{v_a f_{ac}}{[(D_c + \delta)(D_a - \delta)]^{\frac{1}{2}}} - \frac{v_a z_a (D_a + f_{aa})}{D_a - \delta} \right\} \text{grad } \mu_s^* \quad (37)$$

Apart from the gradient of the chemical potential this is the same expression as eqn (27). Thus, if the quantity δ is chosen such that the mass flux connected with the gradient of the electric potential vanishes, then, at the same time, the electric current connected with the gradient of the chemical potential vanishes.

TRANSPORT NUMBERS

For the total analysis we need the transport numbers which we introduce in the following way. If the boundary arrangements of the electrolyte solution are constructed suitably (*i.e.*, if there are electrodes), then in the presence of the electric current density j_q and in the non-uniform parts of the system, a variation of the solute partial density with time, $\partial \rho_s / \partial t$, may be observed. We write this quantity in the form:

$$\frac{\partial \rho_s}{\partial t} = -\text{div } j_s^* - \frac{j_q}{F v_c z_c} [v_c M_c \text{ grad } t_c - v_a M_a \text{ grad } t_a]. \quad (38)$$

The two quantities t_c and t_a are the transport numbers for the cation and anion, respectively. We consider them to be defined by a pair of excess constituent mass fluxes, j_c' and j_a'

$$j_c' = \frac{t_c M_c}{F z_c} j_q \quad (39)$$

$$j_a' = -\frac{t_a M_a}{F z_a} j_q \quad (40)$$

We emphasize that our choice of a microscopic representation of the mass flux j_s^* is such that $j_s^* = 0$ when $\text{grad } \mu_s^* = 0$ even if $\mathcal{E} \neq 0$. In contrast to this, the excess constituent mass fluxes j'_i ($i = c, a$) do not have this property; they are proportional to j_q . Thus $j'_i \neq 0$ if $\mathcal{E} \neq 0$. This is the justification of the designation "excess constituent mass flux". The strict coupling between the two excess constituent fluxes is given by the relation

$$t_a + t_c = 1 \quad (41)$$

which is a consequence of the requirement of electrical neutrality. With eqn (39)-(41), eqn (38) becomes:

$$\begin{aligned} \frac{\partial \rho_s}{\partial t} &= -\text{div } j_s^* - \text{div } j'_c - \text{div } j'_a \\ &= -\text{div } j_s^* - \frac{j_q}{F z_c v_c} (v_c M_c + v_a M_a) \text{grad } t_c. \end{aligned} \quad (42)$$

Integration of eqn (42) with respect to x gives

$$\int_{x_0}^{x_1} \frac{\partial \rho_s}{\partial t} dx = - \int_{t_{x_0}}^{t_{x_1}} \text{div } j_s^* dx - \frac{j_q}{F v_c z_c} (v_c M_c + v_a M_a) t_i \quad (i = c, a) \quad (43)$$

x_0 and x_1 are two coordinates given by the apparatus. This equation allows the measurement of t_c . One possibility is to measure the left-hand side and to arrange the set-up by adding another cationic species such that

$$\int_{x_1}^{x_2} \text{div } j_s^* dx = 0$$

in the range of interest $x_1 < x < x_2$. Now in eqn (43) $t_i = t_c$. This is the moving boundary method. Or we may have

$$\int_{\delta x} \frac{\partial \rho_s}{\partial t} dx = 0$$

where the integration range δx is a very thin layer at the electrode and j_s^* may be measured. Now in eqn (43) $t_i = t_a = (1 - t_c)$. This is the Hittorf method. Having thus established the procedure to measure the constituent excess mass fluxes, we need a microscopic representation of these fluxes. In order to find the correct answer we return to eqn (11) and write this expression in the following form:

$$\begin{aligned} J_q^* &= \frac{q_c^*}{V} (v_1^{(c)} + v_2^{(c)} + v_3^{(c)} + \dots) + \frac{q_a^*}{V} (v_1^{(a)} + v_2^{(a)} + v_3^{(a)} + \dots) \\ &= J_q^{(c)} + J_{q,a}^{(a)}. \end{aligned} \quad (44)$$

In the same way as each ion carries a fixed charge, so each ion also carries a fixed microscopic mass. Thus, the instantaneous electric current density is rigidly coupled with an instantaneous mass flow density. As a consequence, the microscopic representation of the electric current density is at the same time a microscopic representation of some kind of mass flux. In particular, let us consider the two contributions $J_q^{(c)}$ and $J_q^{(a)}$ as defined in eqn (44) separately. We can then say: the $J_q^{(i)}$ ($i = c, a$), converted from a charge-characterized to a mass-characterized form, are the microscopic representations of the excess constituent mass fluxes:

$$J_m^{(c)} = \frac{m_c}{q_c} J_q^{(c)} = \frac{m_c}{V} (v_1^{(c)} + v_2^{(c)} + v_3^{(c)} + \dots) \quad (45a)$$

$$J_m^{(a)} = \frac{m_a}{q_a} J_q^{(a)} = \frac{m_a}{V} (v_1^{(a)} + v_2^{(a)} + v_3^{(a)} + \dots). \quad (45b)$$

Of course, in the equilibrium state we have $J_m^{(c)} = J_m^{(a)} = 0$. The potential energy which acts as perturbation in order to cause $J_m^{(i)} \neq 0$ is again for each particle the product of the gradient of the electric potential with the corresponding coupling parameter, *i.e.*, the electric charge. Thus, in order to calculate the mean value of $J_m^{(c)}$, we have to apply eqn (16) with the perturbation eqn (17) and the dynamical variable eqn (45a). The result is

$$j'_c = \frac{F z_c v_c M_c c_s}{3RT} \{ \langle v_1^c v_1^c \rangle + v_c N_s \langle v_1^c v_2^c \rangle - v_c N_s \langle v_1^a v_1^c \rangle \} \mathcal{E} \quad (46a)$$

$$= \frac{F M_c c_s z_c v_c}{RT} (D_c + f_{cc} - f_{ac}) \mathcal{E} \quad (46b)$$

when the definitions of the velocity correlation coefficients are introduced. Equating this with the macroscopic definition of the excess constituent mass flux [eqn (39)], we obtain

$$t_c j'_c = \frac{F^2 z_c^2 v_c c_s}{RT} (D_c + f_{cc} - f_{ac}) \mathcal{E}. \quad (47)$$

Finally, the combination of eqn (47) with eqn (32b) yields

$$t_c = \frac{D_c + f_{cc} - f_{ac}}{D_c + f_{cc} - 2f_{ac} + (z_a/z_c)(D_a + f_{aa})}. \quad (48)$$

Note that the mean values of the excess constituent fluxes are not themselves directly observable quantities. Only the fact that the divergence of j'_c is strictly coupled with the divergence of j'_a

$$\frac{z_c}{M_c} \operatorname{div} j'_c = \frac{z_a}{M_a} \operatorname{div} j'_a$$

which gives

$$\operatorname{grad} t_c = -\operatorname{grad} t_a$$

leads to $\partial \rho_s / \partial t$ or j_s [via eqn (43)] as quantities concerning the neutral solute, thus allowing the determination of t_c .

MUTUAL DIFFUSION COEFFICIENT

Finally, the mass flux j_s given by eqn (30) has to be connected with the experimental quantity $\partial \rho_s / \partial t$ introduced in eqn (10). The mass flux j_s^* measured in the cell-coordinate system is

$$-j_s^* = D_s^* \operatorname{grad} \rho_s \quad (49)$$

where D_s^* is the mutual diffusion coefficient in the cell-coordinate system. On the other hand, j_s in eqn (30) may be written as ⁶

$$\begin{aligned}
 -j_s &= \Omega_{ss}(1 + \rho_s/\rho_w) \text{grad } \mu_s^* \\
 &= D_s \text{grad } \rho_s \\
 &= \Omega_{ss}(1 + \rho_s/\rho_w) \frac{\partial \mu_s^*}{\partial \rho_s} \text{grad } \rho_s
 \end{aligned} \tag{50}$$

where Ω_{ss} is the phenomenological coefficient and D_s is the diffusion coefficient of the solute in the local centre-of-mass fixed reference frame. The mutual diffusion coefficient in the volume fixed reference frame is

$$D_{sw} = \rho \bar{V}_w^* D_s \tag{51a}$$

and

$$D_s^* = D_{sw} \tag{51b}$$

if volume changes during diffusion are absent. \bar{V}_w^* is the partial specific volume of the solvent water. Combination of eqn (50), (51a) and (30) yields, after some rearrangement:^{1, 3}

$$\begin{aligned}
 D_{sw} &= \frac{\rho(c_s^* M_s + 1)}{c_s/c_s^*} \left(1 + c_s^* \frac{d \ln \gamma^\pm}{dc_s^*} \right) \frac{D_a D_c}{(v_a D_c + v_c D_a)} \times \\
 &\quad \left\{ v_c \frac{D_c + f_{cc}}{D_c + \delta} + \frac{2v_a f_{ac}}{[(D_c + \delta)(D_a - \delta)]^{\frac{1}{2}}} + v_a \frac{D_a + f_{aa}}{D_a - \delta} \right\}
 \end{aligned} \tag{52}$$

and considering eqn (51b), (49) and (10) one sees that D_{sw} is a measurable quantity. c_s^* and c_s are the solute concentrations given in mol g⁻¹ and mol cm⁻³, respectively, ρ is the total density of the solution (g cm⁻³) and γ^\pm is the mean activity coefficient of the solute.

EVALUATION

Next we introduce the following abbreviations:

$$u = D_a + f_{aa} \tag{53}$$

$$v = D_c + f_{cc}. \tag{54}$$

Then combination of eqn (34) and (48) yields:

$$f_{ac} = v - t_c \Lambda^* \tag{55}$$

and

$$u = \{v + \Lambda^*(1 - 2t_c)\} \xi^{-1} \tag{56}$$

with

$$\xi = \frac{z_a}{z_c}.$$

Furthermore, in eqn (52) we set:

$$L = \frac{D_{sw}(v_a D_c + v_c D_a)(D_a + D_c)c_s/c_s^*}{\rho(1 + c_s^* M_s)D_a D_c(1 + c_s^* d \ln \gamma^\pm / dc_s^*)}. \tag{57}$$

With these abbreviations and with eqn (53) and (54) eqn (52) can be written in the form:

$$\frac{L}{D_a + D_c} = v_c \frac{v}{D_c + \delta} + 2v_a \frac{v - t_c \Lambda^*}{[(D_c + \delta)(D_a - \delta)]^{\frac{1}{2}}} + v_a \frac{[v + \Lambda^*(1 - 2t_c)] \xi^{-1}}{D_a - \delta} \tag{58}$$

and the requirement

$$j_q \mu_s^* = j_{m\mathcal{E}} = 0$$

according to eqn (27) takes the form :

$$\frac{v}{D_c + \delta} - \frac{[v + \Lambda^*(1 - 2t_c)]\xi^{-1}}{D_a - \delta} = \left(\frac{z_a}{z_c} - 1\right) \frac{v_a}{v_c} \frac{v - t_c \Lambda^*}{[(D_c + \delta)(D_a - \delta)]^{\frac{1}{2}}} \quad (59)$$

L , D_a , D_c , Λ^* and t_c are given as a function of the concentration; they are experimental quantities or directly obtainable from other experimental quantities. The two unknowns v and δ then have to be determined such that they fulfil both eqn (58) and (59). For symmetrical electrolytes the situation simplifies. Now the right-hand side of eqn (59) equals zero and $\delta = \delta^\circ$ [see eqn (28)]. In this situation $\delta = \delta^\circ$ according to eqn (28) can directly be introduced into eqn (58). The result is:

$$\frac{L}{u + v} - (v_c + v_a) = \frac{2v_a(v - t_c \Lambda^*)}{(uv)^{\frac{1}{2}}} \quad (60)$$

or with eqn (56)

$$\frac{L}{v(\xi^{-1} + 1) + \Lambda^*(1 - 2t_c)\xi^{-1}} - (v_c + v_a) = \frac{2v_a(v - t_c \Lambda^*)}{\{v[v + \Lambda^*(1 - 2t_c)]\xi^{-1}\}^{\frac{1}{2}}} \quad (61)$$

From this equation v has to be determined as a function of the salt concentration. When v is available, then f_{aa} , f_{cc} and f_{ac} may be calculated using the set of eqn (53)-(56).

The numerical solution to eqn (61) was achieved by a standard Newton-Raphson iteration. To solve the system of the two non-linear eqn (58) and (59) for v and δ , a subroutine (library IMSL, computer system UNIVAC 1108) based on Brown's method⁸ was used. Tests insured that the stopping criterion for the iteration process gives a numerical accuracy in the results of at least six digits.

FIRST APPROXIMATION FOR THE VELOCITY CORRELATION COEFFICIENTS

So far we have used expression (14b) as the definition of the instantaneous solute mass flux in the molecular picture. The quantity δ occurring in this formula was determined in such a way that the instantaneous electric current density and the instantaneous excess constituent mass fluxes are represented by eqn (11) and (45), respectively, and that at the same time the solute mass flux j_s vanishes if $\text{grad } \mu_s^* = 0$, whatever the electrical potential gradient may be. The electric current density and the solute mass flux are well-defined quantities even if the excess constituent mass fluxes do not exist. This situation occurs in all those arrangements where the mass flux j_s vanishes at the boundaries of the system. For an ordinary mutual diffusion experiment it is clear that, for the electric current density to be non-zero, one has to place the electrolyte solution in a capacitor with insulated plates and to charge the capacitor. During the charging process $j_q \neq 0$ and, of course, if $\text{grad } \mu_s^* = 0$ we also have $j_s = j_{m\mathcal{E}} = 0$ whilst $\mathcal{E} \neq 0$. In this case the excess constituent mass fluxes are undetermined and the mean displacements of a cation and of an anion are both zero. In contrast to this, when we have mass fluxes at the boundaries, excess constituent fluxes also exist and the mean displacement of a given ion does not vanish; for instance, a cation undergoes a displacement in the direction of the cathode.

Having no observation on which to fix the values of the excess constituent mass fluxes

the parameter δ in eqn (14) and (14a) remains undetermined. We may then choose any δ -value with the property $\delta \rightarrow 0$ as $c_s \rightarrow 0$ and, since the results for the velocity correlation coefficients f_{cc} , f_{aa} and f_{ac} depend on this choice, they are no longer uniquely defined. The simplest approximation is to set $\delta = 0$ over the entire concentration range. Then the three unknowns f_{cc} , f_{aa} and f_{ac} are to be determined from the equivalent conductance, eqn (33), from the mutual diffusion coefficient according to eqn (52) (with $\delta = 0$) and from the condition $j_{m\epsilon} = 0$ according to eqn (27) (again with $\delta = 0$). Since we do not need the transport numbers (for which in many cases experimental data for high concentrations are not available) we call the v.c.c. obtained in this way "first approximation velocity correlation coefficients". After some algebraic operations one obtains from eqn (27) with $j_{m\epsilon} = 0$, $\delta = 0$, eqn (33) and eqn (52):

$$1 + \frac{f_{cc}}{D_c} = \frac{\Lambda^* - D_{sw} \frac{z_a}{z_c} (Fv)^{-1} \left[\left(1 - \frac{z_a}{z_c} \right) D_a - 2(D_a D_c)^{\frac{1}{2}} \right]}{\left(\frac{z_a}{z_c} D_a^{\frac{1}{2}} + D_c^{\frac{1}{2}} \right)^2} \quad (62)$$

with

$$F = \frac{\rho(c_s^* M_s + 1)}{c_s/c_s^*} \left(1 + c_s^* \frac{d \ln \gamma^{\pm}}{dc_s^*} \right) \frac{D_a D_c}{(v_a D_c + v_c D_a)}$$

$$v = v_a + v_c$$

$$f_{ac} = \frac{\Lambda^* - (D_c + f_{cc}) \left[1 + \frac{z_a D_a}{z_c D_c} \right]}{\left(1 - \frac{z_a}{z_c} \right) D_a - 2(D_a D_c)^{\frac{1}{2}}} (D_a D_c)^{\frac{1}{2}}. \quad (63)$$

f_{aa} is then given by eqn (32b).

For the salts containing only structure-breaking or structurally indifferent ions the first approximation to the velocity correlation coefficients provides the correct set of f_{cc} , f_{aa} and f_{ac} .^{1, 2, 5}

RESULTS AND DISCUSSION

In fig. 1 and 2 the results of the computation of f_{aa} , f_{cc} , f_{ac} and δ , using eqn (58) and (59) for the unsymmetrical electrolytes, and eqn (61) for the 1-1 electrolyte, together with eqn (53)-(56), are shown. The experimental data are the same as used in our earlier papers,^{2, 3} where literature references are given. It is not the purpose of the present paper to discuss the physical meaning of the shapes of the curves shown in the figures. This has been amply done in the preceding papers of this series.^{1-3, 5} The results shown in fig. 1 and 2 are practically identical with those previously reported.^{2, 3} The dashed curves in these figures represent the previous values in those cases where the deviation allows separate drawing. In all other cases the difference is smaller. So, obviously the fulfilment of the requirement $j_{m\epsilon} = 0$ [eqn (27)] is not of great importance for the final numerical results. We also applied eqn (61), which is only valid for symmetrical electrolytes, to the system CaCl_2 and BaCl_2 . The numerical results for f_{aa} , f_{ac} and f_{cc} again are practically indistinguishable from the exact computations, only δ is different. The δ values of this approach are indicated as dotted curves in fig. 2.

In a further computation we examined the influence of the choice of δ on the final results for the velocity correlation coefficients. Whereas the fully drawn curves in fig. 1 and 2 correspond to the choice $\delta_c = \delta$, $\delta_a = -\delta$ and the dashed curves represent the results for $\delta = 0$ (using the t_c values) we show in fig. 3 the resulting velocity correlation coefficients when one sets $\delta_a = \delta_c = \delta^*$ [see eqn (8) and (9)].

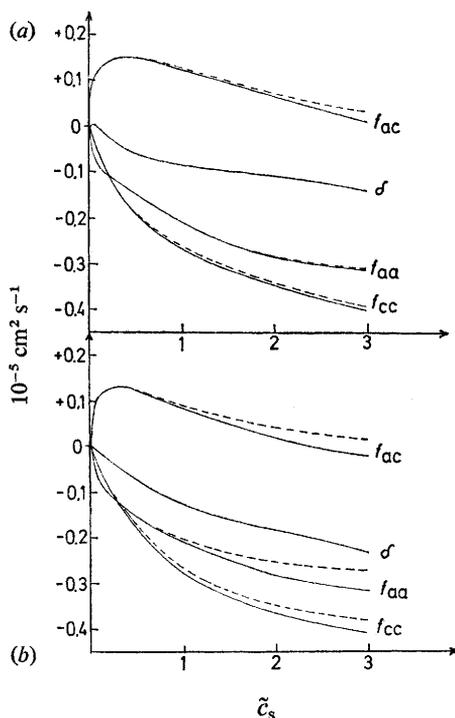


FIG. 1.—Velocity correlation coefficients f_{aa} , f_{ac} and f_{cc} for aqueous NaCl (a) and LiCl (b) solutions at 25°C. The salt molecule location parameter δ is also given. The dashed curves are our previous results² where the condition of vanishing mass flux $j_{m\delta}$ has not yet been fulfilled. \tilde{c}_s is the salt concentration in mol dm⁻³.

The qualitative behaviour is similar to that shown in fig. 1 and 2, but all curves are shifted in the direction of more negative values. However, the $-\delta$ values are much closer to the D_c , D_a values; in the CaCl₂ system at $\tilde{c} = 4$ mol dm⁻³ we have $D_c = -\delta$, which causes a singularity of $(D_c + \delta)^{-1}$. For this reason the choice $\delta_c = \delta$, $\delta_a = -\delta$ is preferred.

Finally, in fig. 4 we give the first approximation to the velocity correlation coefficients as defined in the previous section. It may be seen from fig. 1, 2 and 4 that the f_{ac} are almost identical in both representations, whereas the behaviour of f_{cc} and f_{aa} is only qualitatively similar. In particular, the order of f_{cc} and f_{aa} has changed, in fig. 4 $|f_{aa}| > |f_{cc}|$ in all cases. This is due to the fact that we have $D_a > D_c$ and according to eqn (6) and (7) (which approximately hold also for the 1–2 electrolytes) $f_{aa}/D_a = f_{cc}/D_c$ when the excess constituent mass fluxes are undetermined. In contrast to this, when the excess constituent mass fluxes are fixed, expressed by a knowledge of the transport numbers, then the relative weight of the cations to form

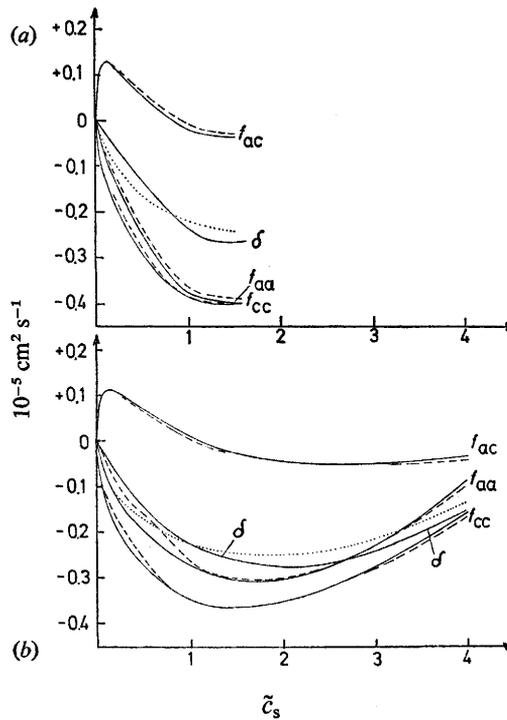


FIG. 2.—Velocity correlation coefficients f_{aa} , f_{ac} and f_{cc} for aqueous BaCl_2 (a) and CaCl_2 (b) solutions together with molecule location parameter δ ($T = 25^\circ\text{C}$). The dashed curves are our previous results³ where the condition of vanishing mass flux $j_m \delta$ has not yet been fulfilled. c_s is the salt concentration in mol dm^{-3} . For other details see text.

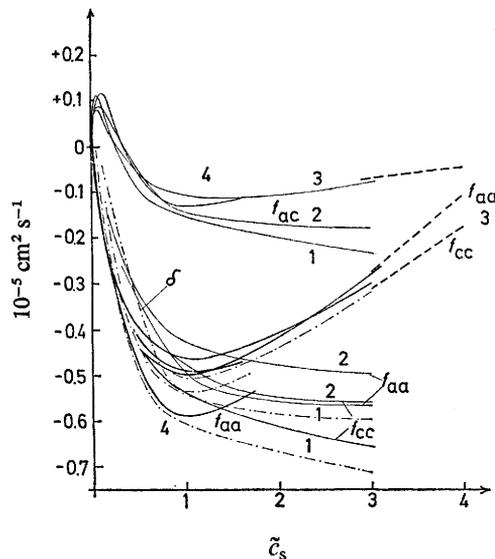


FIG. 3.—Velocity correlation coefficients for aqueous solutions of NaCl (1), LiCl (2), CaCl_2 (3) and BaCl_2 (4) when computed with the location parameter δ^* (dot-dashed curves) according to eqn (8) and (9). Where curves are broken δ^* leads to a singularity ($T = 25^\circ\text{C}$).

the salt molecule is increased compared with that given by the friction property alone. This then also increases the magnitude of f_{cc} relative to f_{aa} .

In summary, the velocity coefficients are not very sensitive to changes in the parameters defining the salt molecule. One can demonstrate clearly the hierarchy of definability of a salt molecule. In equilibrium the definition of a salt molecule is entirely arbitrary, the ions themselves may be considered to be the independent particles. Of course, this holds as long as no equilibrium properties lead to the conclusion that ion pairs should exist.

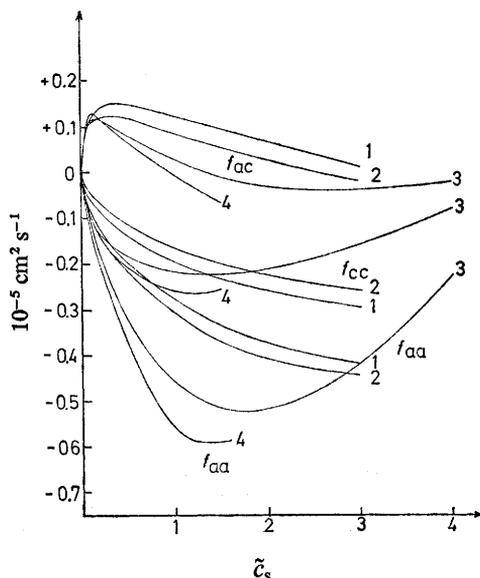


FIG. 4.—First approximation to velocity correlation coefficients for aqueous solutions of NaCl (1), LiCl (2), CaCl_2 (3) and BaCl_2 (4).

In the presence of an electric current, when the system remains uniform, the same statements hold true.

If there is a non-uniformity in the system, mass fluxes occur in the analytical field $c_i(r, t)$ ($i = 1, 2$) represented by the solution. The analytical operation of taking a sample always yields the neutral salt, in spite of the fact that the ionic mobilities differ. This fundamental result requires the definition of the salt molecule. However, the location of the salt molecule is not uniquely specified; in eqn (19) the definition of the position vectors y_k may involve any δ -value, provided $\delta \rightarrow 0$ as $c_s \rightarrow 0$. We have, arbitrarily, chosen the example $\delta = 0$ for all concentrations (fig. 4).

The next requirement is that the excess constituent mass fluxes in the presence of electrodes ($j_a = 0$) are also represented by the concept of the salt molecule. The mass fluxes of the solute towards or from the electrodes are correctly described by the first approximation, but the "rotation" of the salt molecule representing the excess constituent mass fluxes, eqn (39) and (40), has also to be described correctly. In fact, the definition of the molecule does not *a priori* fix the location of the ions belonging to the molecule and we have also to account for the "salt molecule" whose parts are extending over the entire electrolytic cell from the cathode to the anode. At the cathode the anion is formed and at the anode the cation is formed; this

molecule then "rotates" about the point y_k as given by eqn (19) with the δ values show in fig. 1 and 2. This is the second aspect of the concept of a salt molecule: the coherent effects at the cathode and anode, which have the form of two diffusion fluxes of solute towards and away from the electrodes (which in general are asymmetric at the boundaries). Were they symmetric then we would always have $t_c = t_a = \frac{1}{2}$.

Woolf and Harris⁹ have also computed velocity correlation coefficients using the approach based on two ionic fluxes in the solvent at rest as developed by Miller,¹⁰ see also ref. (11) and (12). Miller's phenomenological coefficients l_{ij} are related to the velocity correlation coefficients *via* phenomenological coefficients in the local centre-of-mass fixed coordinate system. Although this treatment in its physical essence is different from ours because mass flux and electric current density are considered to be directly coupled, the final results for the velocity correlation coefficients are very similar to our data presented in fig. 1 and 2. To give a rough estimate, the deviation is of the order of $\pm 10\%$. Thus even here we see that the velocity correlation coefficients are fairly insensitive to the path on which they were derived.

¹ H. G. Hertz, *Ber. Bunsenges. phys. Chem.*, 1977, **81**, 656.

² H. G. Hertz, K. R. Harris, R. Mills and L. A. Woolf, *Ber. Bunsenges. phys. Chem.*, 1977, **81**, 664.

³ H. G. Hertz and R. Mills, *J. Phys. Chem.*, 1978, **82**, 952.

⁴ See, *e.g.*, R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1970).

⁵ H. G. Hertz, in *Protons and Ions Involved in Fast Dynamic Phenomena*, ed. P. Laszlo (Elsevier, Amsterdam, 1978), p. 1.

⁶ See, *e.g.*, D. D. Fitts, *Non-equilibrium Thermodynamics* (McGraw-Hill, New York, 1962).

⁷ See, *e.g.*, E. W. Steele, in *Transport Phenomena in Fluids*, ed. H. J. M. Hanley (Marcel Dekker, New York, 1969).

⁸ K. M. Brown, *SIAM J. Numerical Analysis*, 1969, **6**, 560.

⁹ L. A. Woolf and K. R. Harris, *J.C.S. Faraday I*, 1978, **74**, 933.

¹⁰ D. G. Miller, *J. Phys. Chem.*, 1966, **70**, 2639.

¹¹ D. G. Miller, *Faraday Disc. Chem. Soc.*, 1977, **64**, 295.

¹² R. Paterson, *Faraday Disc. Chem. Soc.*, 1977, **64**, 304 and discussion on p. 349.