Velocity Correlations in Aqueous Electrolyte Solutions from Diffusion, Conductance, and Transference Data. Part 2, Applications to Concentrated Solutions of 1−1 Electrolytes

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Velocity Correlations in Aqueous Electrolyte Solutions from Diffusion, Conductance, and Transference Data.
Part 2, Applications to Concentrated Solutions of 1-1 Electrolytes

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Diffusion / Elektrochemie / Lösungen / Transporterscheinungen

In the preceding paper [1] in this volume, a formulation using the velocity correlation approach has been developed to describe micro-dynamical behaviour in electrolyte solutions. In this paper it is applied to aqueous electrolyte solutions of LiCl, NaCl, KCl, CsCl and KI in the range 0 – 3 molar.

In der vorhergehenden Arbeit in dieser Zeitschrift [1] wurde die Berechnung von Geschwindigkeitskorrelationskoeffizienten beschrieben mit dem Ziele, eine Beschreibung des mikrodynamischen Verhaltens von Elektrolytlösungen zu geben. In der vorliegenden Arbeit wird diese Methode auf wäßrige Lösungen von LiCl, NaCl, KCl, CsCl und KI im Konzentrationsbereich 0 – 3 molar angewendet.

1. Introduction

In the preceding paper [1] (in the following denoted as part 1) one of the present authors derived formulae from which velocity cross correlation coefficients can be calculated for the various components in an electrolyte solution. These coefficients f_{aa}, f_{cc}, f_{ac}, f_{ss}, f_{sw} and f_{ww} representing anion-anion, cation-cation, anion-cation, salt-salt, salt-water and water-water velocity correlations respectively are expressed in terms of measurable experimental quantities in the above formulae. In the present paper we apply the formulae given in part 1 to a number of systems for which sufficiently accurate experimental results are available. At the same time these are some of the simplest and most typical representatives of 1-1 electrolytes. It will be seen that, in particular, the concentration dependence of the equivalent conductivity is seen from quite new and interesting aspects.

The systems considered are aqueous solutions of LiCl, NaCl, KCl, CsCl and KI all in the concentration range $0 < \tilde{c}_s \leq 3\,\text{M}$.

2. Some Comments Regarding the Self-Diffusion Coefficient of Ions

It will be useful to compare the velocity correlation coefficients f_{aa}, f_{cc}, and f_{ac} to be calculated in the following sections with the self-diffusion coefficients of the various ions. These

are shown in Fig. 1. In some cases experimental data were available from different sources and only for limited concentration ranges. In these situations we applied a suitable averaging and smoothing procedure. The numerical values which we used for our computation are presented in table 1. The experimental error in D for low concentrations is a fraction of a per cent, at high concentrations in some cases it is greater. The inset of Fig. 1 gives the low concentration behaviour of the electrolytes studied on a relative scale. The dashed line shows the estimated relative decrease of a representative self-diffusion coefficient. This estimate, which is helpful for the discussion later in the paper and which may be considered as a very simple alternative to the more sophisticated Onsager limiting law, is based on the following arguments:

The self-diffusion coefficient of a given ion can be expressed as [13, 15 – 17]

$$D = (1 - w^+)D_0 + D_b w^+ + b, \tag{1}$$

where D_0 is the self-diffusion coefficient of the free ion, D_b is the self-diffusion coefficient of the same ion when another ion is attached to it. w^+ is the probability that the other ion is attached to the reference ion for a sufficiently long time, such that a self-diffusion coefficient D_b can be defined. b is the contribution of all the other ions, we denote b as the background effect. For w^+ we may write [16, 17]

$$w^+ = 4\pi c_s N_0 \int_a^{r_1} e^{-E(r,a\kappa)/kT}(1 - e^{(E(r,a\kappa)-\Delta E)/kT})r^2\,dr \tag{2}$$

Table 1
Self-diffusion coefficients D_c, D_a[a]) of ions in aqueous electrolyte solutions (25°C)

Solution	Ion	$\tilde{c}_s$[b]): 0[c])	0.05	0.1	0.2	0.5	1	2	3	References
LiCl	Li$^+$	1.029	0.9925	0.978	0.9625	0.9452	0.918	0.83	0.75	[3, 4]
	Cl$^-$	2.032	1.970	1.935	1.884	1.795	1.666	1.51	1.34	[5] see also [6]
NaCl	Na$^+$	1.333	1.295	1.285	1.283	1.279	1.233	1.130	1.035	[7, 8] see also [9 – 11]
	Cl$^-$	2.032	1.982	1.952	1.913	1.850	1.771	1.62	1.45	[5] see also [6]
KCl	K$^+$	1.956	1.914	1.900	1.890	1.876	1.865	1.861	1.825	[12]
	Cl$^-$	2.032	1.966	1.958	1.950	1.941	1.931	1.902	1.874	[13]
CsCl	Cs$^+$	2.055	2.003	1.983	1.970	1.960	1.947	1.891	1.812	[13] see also [14]
	Cl$^-$	2.032	1.993	1.980	1.970	1.964	1.980	2.016	1.982	[13] see also [11]
KI	K$^+$	1.956	1.937	1.928	1.930	1.966	1.983	1.985	1.955	[12]
	I$^-$	2.044	2.011	2.004	1.992	1.440	1.993	1.966	1.925	[12]

[a]) $D_{c,a}$ in 10^{-5} cm^2/sec
[b]) $\tilde{c}_s$ in mole/l
[c]) Calculated from limiting conductivity data [2].

where c_s is the salt concentration (mol/cm^3)*), N_0 is Avogadro's number, and $E(r, a\kappa)$ is the Debye-Hückel potential of mean force [2]:

$$E(r, a\kappa) = -\frac{e^2}{\varepsilon} \frac{e^{\kappa(a-r)}}{(1 + a\kappa)r}. \tag{3}$$

ε is the dielectric constant and κ is the well known ion cloud parameter

$$\kappa = \left(\frac{8\pi e^2 c_s N_0}{\varepsilon kT} \right)^{1/2}$$

(here $z^+ = z^- = 1$), a is the closest distance of approach between the ions and r is the separation between the ions.

$$(1 - e^{(E(r,a\kappa) - \Delta E)/kT}) = \phi(E(r), \Delta E) \tag{4}$$

is the probability that the relative kinetic energy of the ion attached to the reference ion is less than $|E(r, a\kappa)| - |\Delta E|$. It has been shown elsewhere [16] that $\Delta E \approx -kT$ is a good approximation. r_1 defines the range of integration in Equation (2), it is to be chosen such that $|E(r, a\kappa)| \geq kT$ for all $r, a < r \leq r_1$. Then r_1 decreases as the salt concentration c_s increases, because $\kappa a \sim c_s^{1/2}$. However, in order also to take into account the background contribution b in an approximate way we set $r_1 = $ const. $= \frac{1}{2}(a + r_1(c_s \to 0))$ and we omit the r dependence of $E(r, a\kappa)$, putting $E(r, a\kappa) = $ const. $= E(a, a\kappa)$. Finally we set for the self-diffusion coefficient of the aggregate:

$$D_b = \frac{1}{2}D_0.$$

With these simplifications combination of Equations (1) and (2) yields:

$$\frac{D}{D_0} = 1 - 2\pi c_s N_0 (r_1^3 - a^3)[e^{-E(a, a\kappa)/kT} - e^{0.9}]. \tag{5}$$

Considering a typical example of a net structure breaking salt (e. g. CsCl) we set $a = 3.5$ Å, then $e^2/\varepsilon a kT = 2$ at 25°C and $r_1 = 5.5$ Å. With these numerical values Equation (5) yields the dashed line drawn in the inset of Fig. 1. The most important feature expressed by this relation is the fact that the probability of finding a counter ion firmly bound to the reference ion

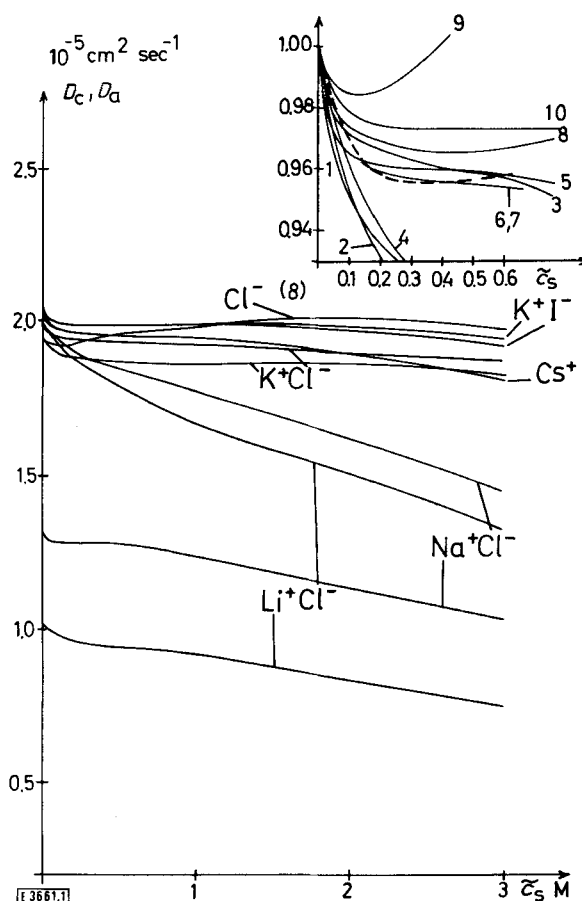*) c_s concentration in mol/cm^3, $\tilde{c}_s$ concentration given in the molarity scale, i.e. mol/l.

Fig. 1
Self-diffusion coefficients of ions in various aqueous electrolyte solutions at 25°C (M: molarity scale). The two ion symbols which are written together indicate the dissolved salt, Cs$^+$ and Cl$^-$ (8) denote the respective self-diffusion coefficients in CsCl solution. Inset: Self-diffusion coefficients at low concentrations in a relative scale: 1,2: LiCl, 3,4: NaCl, 5,6: KCl, 7,8: CsCl, 9,10: KI, odd and even numbers denote cations and anions, respectively. Dashed line: D/D_0 as calculated from Equation (5)

first increases steeply as the concentration increases from $c_s = 0$, however, due to the $\sqrt{c_s}$ dependence in the denominator of Equation (3) ($r = $ const. $= a$) this increase is stopped very drastically so that w^+ reaches a maximum. $\Delta E = -0.9 kT$

instead of $\Delta E = -kT$ has been introduced in Equation (5) in order to give a slight shift of the maximum in w^+ towards $\tilde{c}_s = 0.5$ M. In fact, for $\tilde{c}_s > 0.5$ M w_I^+ decreases with increasing concentration as the electrostatic retardation effect more and more becomes a background effect, and Equation (5) is no longer valid. However, Equation (5) also becomes invalid for another reason as $\tilde{c}_s \geq 0.5$ M: Now the structure breaking and structure forming effect of the ions on the solvent increasingly become the cause for acceleration and retardation of the motion of the ion as c_s increases. This has already been extensively discussed for the structure breaking ions by two of the present authors in two previous papers [12,13]. A corresponding communication regarding the structure forming effect is in preparation [18].

3. Velocity Correlation Coefficients

3.1. Anion-Cation Correlations

Now we have a qualitative understanding of the concentration dependence of the self-diffusion coefficients and we can turn to the discussion of the concentration dependence of the velocity cross correlation coefficients.

The experimental data, apart from the self-diffusion coefficients, for the LiCl, NaCl and KCl solutions needed for the evaluation according to Equations (84)–(87) of part 1 are taken from the compilations in Miller's work [19] and those
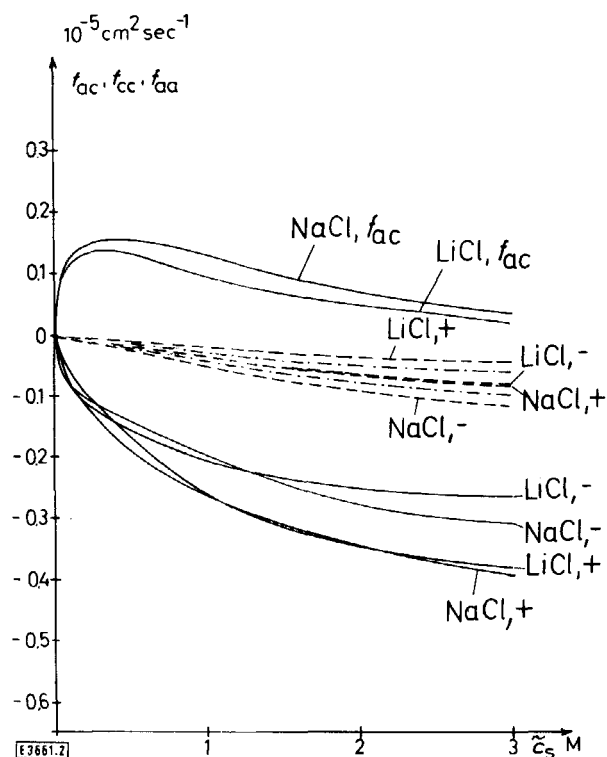
Fig. 2

Solid curves: Velocity correlation coefficients f_{ac}, f_{aa}, and f_{cc} for LiCl and NaCl solutions as a function of the salt concentration. Dashed curves: Standard values of anion-anion and cation-cation velocity correlation coefficients f_{aa}^0, f_{cc}^0. A symbol + or − attached to that of the salt means, cation, or anion of this salt, respectively. A dot-dashed curve between two dashed curves gives the corresponding standard coefficient f_{ac}^0 (25 °C)

for CsCl are taken from the paper of Dunsmore, Jalota, and Paterson [20]. For the KI solutions the sources of experimental data were the following: Equivalent conductivities, see Ref. [21]; mutual diffusion coefficients and activity data, see Ref. [22]; transport numbers, see Ref. [23,24]*). Using all these data Equations (84)–(87) of part 1 yielded the velocity correlation coefficients f_{ac}, f_{cc}, and f_{aa} as shown in Figs. 2 and 3. The dot-dashed and dashed curves in these figures represent the expected or standard values of f_{ac}, f_{cc}, and f_{aa}, i.e. f_{ac}^0, f_{cc}^0, and f_{aa}^0, respectively. These quantities were calculated according to Equations (99), (94), and (95) of part 1.
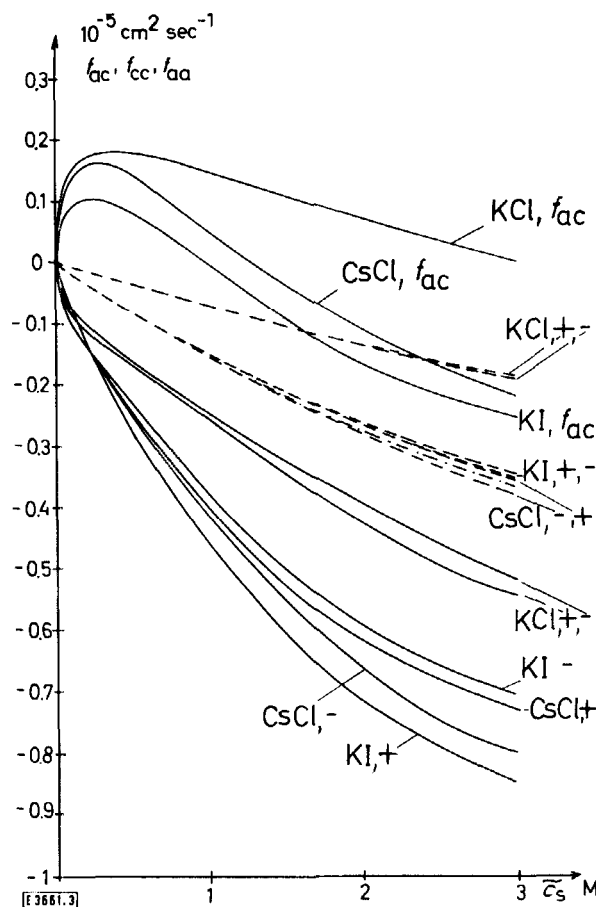
Fig. 3

Velocity correlation coefficients f_{ac}, f_{aa}, f_{cc}, and standard coefficients f_{ac}^0, f_{aa}^0, f_{cc}^0 for solutions of KCl, CsCl, and KI. All details are as explained for Fig. 2. Standard values f_{ac}^0 for KCl and KI are not given; they lie between the corresponding f_{aa}^0 and f_{cc}^0 (25 °C)

Let us first discuss f_{ac}, the anion-cation velocity correlation coefficient. It may be seen from the figures that f_{ac} increases very rapidly with increasing concentration when $\tilde{c}_s \approx 0$. As the salt concentration increases further, f_{ac} goes through a maximum. For KI and CsCl f_{ac} becomes negative at concentrations around 1 M.

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*) Three of the authors (K. H., R. M., and L. A. W.) believe that a frame of reference correction is needed for the transport number data. This alters the position of the f_{aa} and f_{cc}'s slightly but does not affect the general qualitative conclusions of the paper.

As all time correlation functions, such as $\langle v_1^{(a)}(0) \cdot v_1^{(c)}(t) \rangle$ may be written in the form:

$$\langle v_1^{(a)}(0) \cdot v_1^{(c)}(t) \rangle = \int p(v_{10}^{(a)}) P(v_{10}^{(a)}, v_1^{(c)}, t) v_{10}^{(a)} \cdot v_1^{(c)} dv_{10}^{(a)} dv_1^{(c)} \quad (6)$$

where $p(v_{10}^{(a)}) dv_{10}^{(a)}$ is the probability that an anion selected at random (and numbered as 1) has the velocity $v_{10}^{(a)}$ at time $t = 0$. ($p(v_{10}^{(a)})$ is essentially the Maxwell distribution law). $P(v_{10}^{(a)}, v_1^{(c)}, t) dv_1^{(c)}$ is the probability that a given cation (numbered as 1) has the velocity $v_1^{(c)}$ at time t if we know that the anion 1 had the velocity $v_{10}^{(a)}$ at time $t = 0$. Next we split $P(v_{10}^{(a)}, v_1^{(a)}, t)$ in two parts

$$P(v_{10}^{(a)}, v_1^{(c)}, t) = P_b(v_{10}^{(a)}, v_1^{(c)}, t) + P_u(v_{10}^{(a)}, v_1^{(c)}, t) \quad (7)$$

(b = bound, u = unbound)

with

$$P_b(v_{10}^{(a)}, v_1^{(c)}, t) = \frac{w^+}{N_c} P_{as}(v_{10}^{(a)}, v_1^{(c)}, t) \qquad N_c = c_s N_0, \quad (8)$$

where $P_{as}(v_{10}^{(a)}, v_1^{(a)}, t) dv_1^{(a)}$ is the probability that an anion being bound to the cation has the velocity $v_1^{(a)}$ at time t if we know that the same anion (also in the bound state) had the velocity $v_{10}^{(a)}$ at $t = 0$. Then with Equations (2) and (16) of part 1 and with Equations (6) and (7) one obtains:

$$f_{ac} = w^+ D_b + \frac{c_s N_0 V}{3} \int_0^\infty \{\int p(v_{10}^{(a)}) P_u(v_{10}^{(a)}, v_1^{(c)}, t) \cdot$$
$$\cdot v_{10}^{(a)} \cdot v_1^{(c)} dv_{10}^{(a)} dv_1^{(c)}\} dt. \quad (9)$$

D_b, the self-diffusion coefficient of the bound pair, is about $1 \cdot 10^{-5}$ cm^2/sec and if for small concentrations (where f_{ac} has its maximum) we set the second term on the right-hand side of Equation (9) = 0, from the results shown in Figs. 2 and 3 we get $w_1^+ \approx 0.1 - 0.2$ at the maximum. This is in fair agreement with the w^+ value estimated from Equation (2) which then yielded the D/D_0 values corresponding to Equation (5). Thus, at low concentrations the second term of Equation (9) which represents the contribution of the ions which are not direct pair partners in the sense that their binding energy is greater than $-kT$, obviously is fairly small.

This is different at higher concentrations for two reasons: (1) The standard value of f_{ac}, f_{ac}^0, is negative as may be seen from Figs. 2 and 3, and its magnitude increases as c_s increases. As has been shown in part 1 this is a consequence of the conservation of momentum. Thus the second term on the right-hand side of Equation (9) becomes negative as c_s increases and partly compensates for the positive correlation term or even becomes dominant. (2) Due to mutual averaging out of electrostatic forces the tendency of pair formation with a sufficiently deep potential well disappears as c_s becomes larger *).

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*) Note the difference between Bjerrum's treatment of ion association (see e.g. [2]) and our treatment: In Bjerrum's approach the Debye-Hückel potential Equation (3) is replaced by the concentration independent potential $e^2/\varepsilon r$. This has the effect that according to Bjerrum the degree of ion-ion association does not decrease with increasing concentration. On the other hand r_1, the radius defining ion association, is larger in our treatment than in Bjerrum's, this causes an increase of the number of pairs of ions which have to be reckoned as associated ones.

3.2. Cation-Cation and Anion-Anion Correlation

Next we turn to the cation-cation and anion-anion velocity correlation coefficients which are also shown in Figs. 2 and 3. For ions of equal charge we certainly have $w^+ = 0$, thus

$$f_{cc} = \frac{c_s N_0 V}{3} \int_0^\infty \{\int p(v_{10}^{(c)}) P(v_{10}^{(c)}, v_2^{(c)}, t) v_{10}^{(c)} \cdot v_2^{(c)} dv_{10}^{(c)} dv_2^{(c)}\} dt \quad (10)$$

$$P = P_u$$

and a corresponding expression for f_{aa}.

At time $t = 0$, $P(v_{10}^{(c)}, v_2^{(c)}, 0)$ represents a velocity pair distribution for which the region "opposite to $v_1^{(c)}$", i.e. the region $v_2^{(c)} \approx -v_{10}^{(c)}$ is slightly more populated than the region around $v_2^{(c)} \approx v_{10}^{(c)}$, which again is a consequence of momentum conservation. As the time goes on, $P(v_{10}^{(c)}, v_2^{(c)}, t)$ becomes isotropic with respect to $v_2^{(c)}$ and the correlation function vanishes. These arguments led us to the formulae for the standard correlation coefficients f_{cc}^0 and f_{aa}^0, Equations (94), (95) of part 1. However, as may be seen from Figs. 2 and 3, the observed velocity correlation coefficients f_{cc} and f_{aa} are much more negative than the expected ones (i.e. the standard coefficients). One reason for this behaviour is that the approach towards an isotropic distribution of $P(v_{10}^{(c)}, v_2^{(c)}, t)$ goes much slower than that of $P(v_{10}^{(c)}, v_1^{(c)}, t)$, the corresponding propagator in velocity space for the self-correlation function which led to the standard values f_{cc}^0, f_{aa}^0 (according to Equation (93) of part 1. In fact, the ions of like charge are relatively far apart, and if, for example, a cation has left a given surroundings (having a velocity $v_1^{(c)}$, say), then it takes a long time for another cation to diffuse into the disturbed surroundings in order to replace the one which has left. Thus, the time correlation function $\langle v_1^{(c)}(0) \cdot v_2^{(c)}(t) \rangle$ decreases towards 0 fairly slowly. Whereas the velocity self-correlation function $\langle v_1^{(c)}(0) \cdot v_1^{(c)}(t) \rangle$ goes to zero after a time $\approx 10^{-12}$ sec, $\langle v_1^{(c)}(0) \cdot v_2^{(c)}(t) \rangle$ may have a correlation time $10^{-10} - 10^{-9}$ sec, depending on the concentration. Measurements of the frequency dependence [25] of the conductance should supply the answer here, unfortunately the problem arises of overlap of the relaxation of the ion cloud with the solvent molecule relaxation.

It is interesting that we do not find a large positive contribution to f_{ac} which would arise from long distance migration. Thus, if in an instantaneous configuration the cation and anion are relatively far apart and if from this configuration the cation, say, from its surrondings receives a large momentum so as to "leave" the pair partner, then, obviously the anion does not follow the cation, rather, another cation migrates into the region where the first cation originally was. And, since the velocity cross correlation function is negative, this other cation mainly comes from that direction towards which the first cation has left the anion, not from the opposite direction, here the anion exerts a certain screening action. If, however, we have a pair configuration where the anion is close to the cation, then, as we have seen, in the event that the cation has a finite velocity, the anion follows that cation immediately and this gives the small positive contribution to f_{ac}. It should be noted that there might be a cancellation effect of a positive and a negative contribution to f_{ac}, since for tight binding one part of f_{ac} is >0 and another part of $f_{ac} < 0$

and approaches f_{aa} and f_{cc}. However, we feel that in 1:1 electrolyte systems the positive part of f_{ac} is too small for such an effect to occur.

There is, however, another effect which in certain cases is very likely to contribute to the large negative value of f_{cc} and f_{aa}. This is the effective or dynamical mass of the ion considered. It is very likely that for a given ion the mass of the water molecules which are bound to it through a potential well deeper than kT together with the ion mass constitute the dynamical mass of the ion. Thus, for Li^+ one has to use a mass of $7 + 4 \cdot 18 = 79$ and thus $M_s = 35.5 + 79 = 114.5$. The dashed line in Fig. 2 has been calculated with the formal or chemical mass $M_s = 42.5$ using Equation (94) of part 1.

3.3. Velocity Correlations Involving the Salt Molecule

Next we turn to f_{ss}, the salt molecule-salt molecule velocity correlation coefficients which are depicted in Fig. 4. They have been calculated from Equation (82) of part 1. It may be seen that at high concentrations f_{ss} is negative as it should be as a consequence of the conservation of momentum. However, for small concentrations $f_{ss} > 0$ for all salts which gives strong evidence that this is a real physical effect and not an artefact produced by insufficient accuracy of experimental data. Clearly there are no positive velocity correlations between salt molecules. Rather, as has been shown in section 4 of part 1, the experimental quantity f_{ss} also contains a velocity cross correlation contribution from the ions belonging to the same molecule. Obviously, it is just this little positive hump
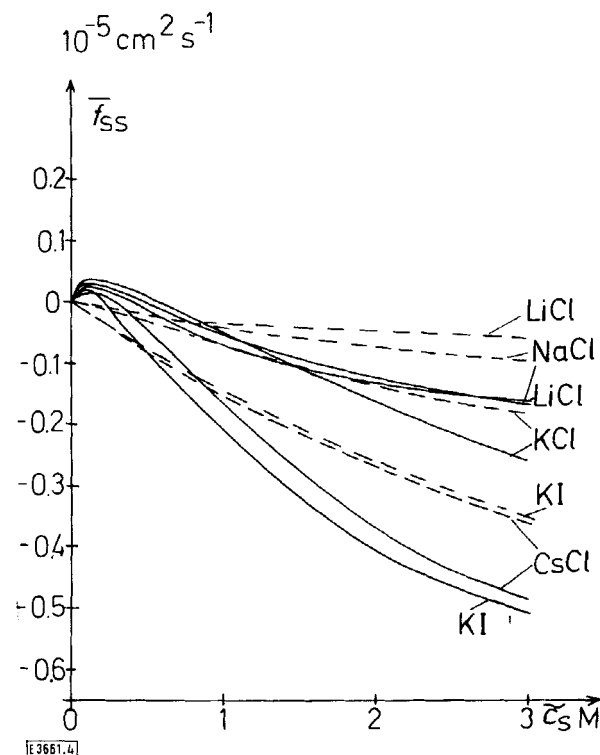
Fig. 4

Salt molecule-salt molecule velocity correlation coefficients for a number of 1-1 electrolytes as a function of the salt concentration (molarity scale) at 25 °C. Dashed lines represent standard values f_{ss}^0

between $\bar{c}_s = 0$ and $\bar{c}_s \approx 0.5$ M which represents the fairly feeble positive velocity correlations between two ions forming a salt molecule. At $\bar{c}_s > 0.5$ M this direct effect of the positive correlations has disappeared, due to momentum conservation the negative contribution becomes increasingly predominant.
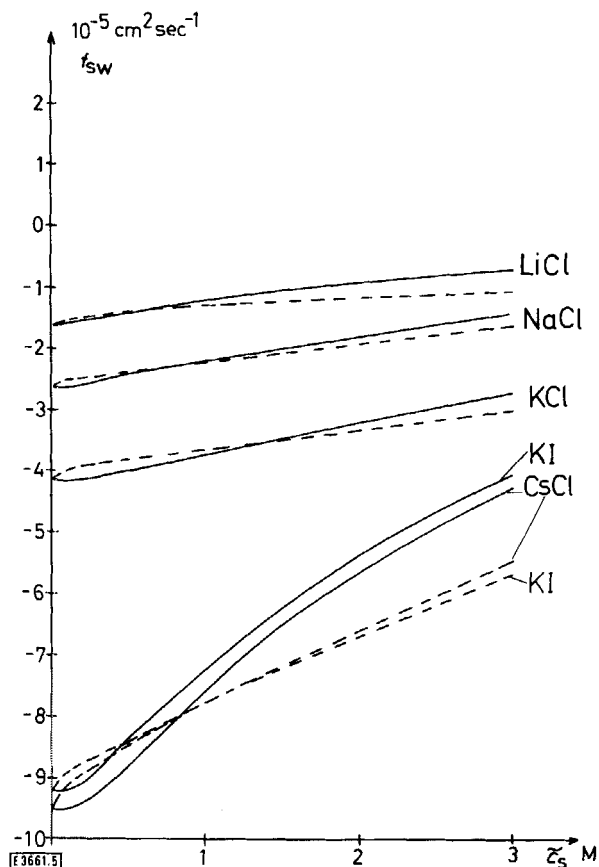

Fig. 5

Salt molecule-water velocity correlation coefficients for a number of 1-1 electrolytes as a function of the salt concentration at 25 °C. Dashed lines represent standard values f_{sw}^0

In Fig. 4 one sees that the experimental f_{ss}'s at high concentrations are markedly more negative than the expected ones which are included in the figure as dashed lines. This is not surprising when we recall that the ionic cross correlation coefficients f_{cc} and f_{aa} are also much more negative than the corresponding standard values.

The salt molecule-solvent velocity correlation coefficients f_{sw} have been computed using Equation (34) of part 1 and are shown in Fig. 5. Again, the dashed curves represent the standard correlation coefficients f_{sw}^0 as calculated with the aid of Equation (102). Here the experimental and the standard velocity correlation coefficients agree rather closely: for CsCl at $\bar{c}_s = 3$ M $f_{sw}/f_{sw}^0 = 0.78$ and for LiCl at the same concentration $f_{sw}/f_{sw}^0 = 0.67$. At lower concentrations $f_{sw}/f_{sw}^0 > 1$. The reason for this latter effect is obvious: due to the positive velocity correlations between cations and anions the self-diffusion coefficient of the salt molecule is given by Equation (76) of part 1 and this is slightly greater than $D_s = [D_s]_0$ according to Equation (71). On the other hand, at high concentrations when the salt molecule moves in one direction,

there is always a correlated motion of salt molecules in the opposite direction since $\bar{f}_{ss} < 0$. As already mentioned above, the negative excess of $\bar{f}_{ss}$ as compared with f_{ss}^0 is due partly to the comparatively slow motion even at higher concentrations. Therefore, at high concentrations, f_{sw} comes out more positive than it should be according to simple momentum conservation considerations. In the same way, when the water molecule has a given velocity, the correlation of the motion of the salt molecules has a positive contribution (i.e. it is less negative than it should be) which is a consequence of the relation

$$\langle v_1^{(s)}(0) \cdot v_1^{(w)}(t) \rangle = \langle v_1^{(w)}(0) \cdot v_1^{(s)}(t) \rangle .$$

3.4. Water-Water Velocity Correlation

Lastly we turn to the discussion of the water-water velocity correlation coefficients which have been calculated from Equation (44a) of part 1 and which are shown in Fig. 6. The dashed curves are the standard velocity coefficients which are calculated according to Equation (101) of part 1. The water self-diffusion coefficients have been taken from the following literature references: CsCl [13, 14], KI [13], KCl [13, 14], NaCl [14, 26, 27], LiCl [14, 26]. It may be seen that for NaCl the experimental f_{ww} and the standard value f_{ww}^0 are very close to one another. However, for LiCl f_{ww} is slightly more
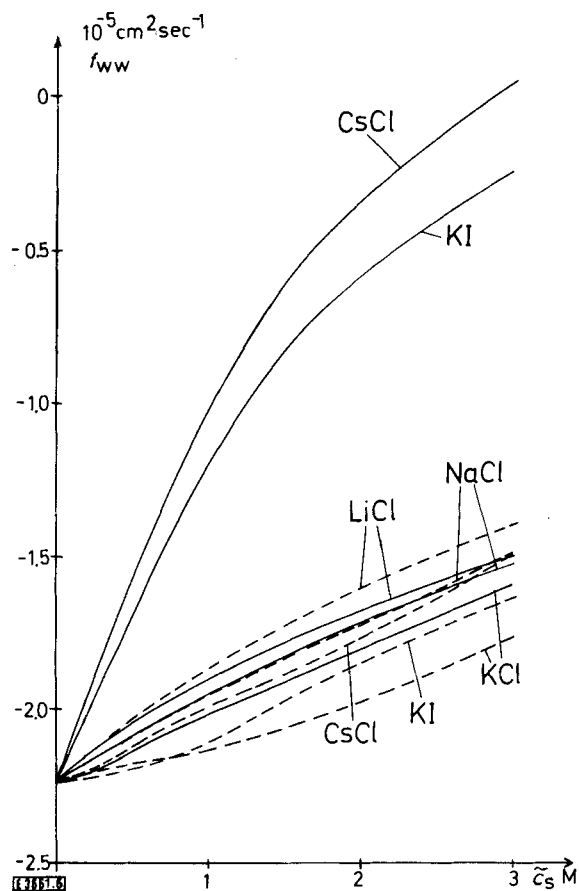

Fig. 6
Water-water velocity correlation coefficients for aqueous solutions of a number of 1-1 electrolytes as a function of the salt concentration at 25 °C. Dashed lines represent standard velocity coefficients f_{ww}^0

negative than f_{ww}^0, especially in the concentration range around $\tilde{c}_s = 2$ M. This observation is interpreted by the fact that M_w in Equation (101) actually is the effective or dynamical mass of water. At $\tilde{c}_s = 0$, M_w is the dynamical mass of pure water, then, as $\tilde{c}_s$ increases the effective mass of water gradually becomes more and more determined by the Li^+ hydration sphere, and this effective mass is just slightly greater than the dynamical mass of water in the pure liquid. For KCl, KI, and CsCl f_{ww} is much less negative than f_{ww}^0. Here the dynamical mass M_w decreases rapidly as the salt concentration decreases. This is probably the most drastic manifestation of the structure breaking effect of these salts. According to Equation (101) f_{ww} should always remain negative whatever the dynamical mass of the water. In the case of CsCl we see that $f_{ww} > 0$ at $\tilde{c}_s \approx 3$ M which cannot be explained in terms of Equation (101). At this time being no simple interpretation for the finding that $f_{ww} > 0$ in CsCl solutions at high concentrations can be given.

4. Conclusions

In summary we list the main pieces of information about the microdynamical behaviour of electrolyte solutions which velocity cross-correlation coefficients can give.

The initial positive rise at low concentrations for f_{ac}'s for all the electrolyte solutes considered can be interpreted in terms of ion association. This concept is supported by calculations of the effect of pairing on the concentration dependence of ion diffusion coefficients. Effects in more concentrated solutions (> 0.5 M) would indicate that ion association decreases and this can be attributed to mutual averaging of the electrostatic forces around ions.

The coefficients f_{cc} and f_{aa} are more negative than standard values would lead us to expect. Our interpretation is that the ion cross correlation functions decay more slowly than the self-correlation functions which implies that it takes a comparatively long time for an ion to diffuse into the disturbed surroundings recently vacated by another ion of the same kind.

The sign and concentration dependence of the curves for f_{ss}, f_{sw}, and f_{ww} can also be interpreted in dynamical terms. Some of these effects can be attributed to the hydration of the ions.

We can also qualitatively describe the concentration dependence of the equivalent conductivity in the following way. $\Lambda = \Lambda(\tilde{c}_s)$ is mainly given by the concentration dependence of the ionic self-diffusion coefficients. At very high dilution these self-diffusion coefficients correspond to the independent motion of the ions. Then, as the concentration increases, a sudden retardation occurs partly due to the fact that cations and anions are coupled through an electrostatic potential $|E| > kT$. This potential is quickly averaged out by the presence of other ions close to a given pair and the retardation effect is diminished. However, in the same concentration range, $\tilde{c}_s \approx 0.1 - 0.5$ M the influence of the structural changes of the solvent becomes important, which may further retard the motion or which may give an accelerating contribution, and even lead to an increase of the ion diffusion coefficient, such that D has a maximum at $\tilde{c}_s \approx 2 - 3$ M. Superposed on this dominating effect of the concentration dependence of the self-

diffusion coefficients there is a markedly smaller contribution due to the ion-ion velocity cross-correlation effects. Coming from low concentrations the velocity correlation contribution increases fairly rapidly and reaches about 15% of the D contribution at $\bar{c}_s \approx 0.2$ M. It is a contribution which reduces the equivalent conductivity relative to the effect of the mean self-diffusion coefficient and at 3 M its amount is approximately 25% of the contribution due to D.

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Reaktionen von Molekülen in definierten Schwingungszuständen (IV). Reaktionen schwingungsangeregter Cyan-Radikale mit Wasserstoff und einfachen Kohlenwasserstoffen*)

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Energieübertragung / Freie Radikale / Photochemie / Reaktionskinetik

Gasphasenreaktionen von CN-Radikalen im Schwingungsgrundzustand und angeregten Schwingungszuständen mit molekularem Wasserstoff und einfachen Kohlenwasserstoffen (CH_4, C_2H_4, C_2H_2) wurden im Temperaturbereich von 259 K bis 396 K untersucht. Die CN-Radikale in den verschiedenen Schwingungszuständen $v'' = 0, 1, \ldots, 5$ wurden durch Blitzlichtphotolyse von C_2N_2 in Gegenwart von hohem Reaktandenüberschuß erzeugt und durch kinetische Absorptionsspektroskopie nachgewiesen. — Im System

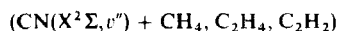$$CN(X^2\Sigma, v'') + H_2 \qquad v'' = 0, 1, \ldots, 5$$
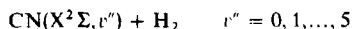
liegt neben der Reaktion

$$CN(v'') + H_2 \longrightarrow HCN + H \tag{1}$$

$$k_1(v'' = 0) = (6 \pm 2) \cdot 10^{13} \exp(-E_A/RT)\,\text{cm}^3/\text{mol sec} \qquad E_A = (22.2 \pm 2.5)\,\text{kJ/mol}$$

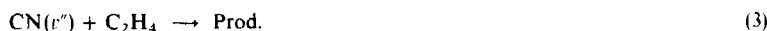auch Relaxation von schwingungsangeregtem CN an H_2 vor. Im Gegensatz dazu wird in den Kohlenwasserstoffsystemen

$$(CN(X^2\Sigma, v'') + CH_4, C_2H_4, C_2H_2)$$

der Verbrauch von CN-Radikalen in allen Schwingungszuständen v'' im wesentlichen durch Reaktion bestimmt. — Für

$$CN(v'') + CH_4 \longrightarrow HCN + CH_3 \tag{2}$$

erhält man

$$k_2(v'' = 0) = (6 \pm 3) \cdot 10^{12} \exp(-E_A/RT)\,\text{cm}^3/\text{mol sec} \qquad E_A = (7.2 \pm 2.5)\,\text{kJ/mol}.$$

Bei

$$CN(v'') + C_2H_4 \longrightarrow \text{Prod.} \tag{3}$$

$$k_3(v'' = 0) = (3 \pm 0.5) \cdot 10^{13}\,\text{cm}^3/\text{mol sec}$$

und

$$CN(v'') + C_2H_2 \longrightarrow \text{Prod.} \tag{4}$$

$$k_4(v'' = 0) = (3 \pm 1) \cdot 10^{13}\,\text{cm}^3/\text{mol sec}$$

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*) Dissertation H. Schacke, Göttingen 1974.