

Velocity Correlations in Aqueous Electrolyte Solutions from Diffusion, Conductance and Transference Data: Application to Concentrated Solutions of Nickel Chloride and Magnesium Chloride

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Velocity cross-correlation coefficients have been calculated for aqueous solutions of NiCl₂ and MgCl₂ up to concentrations of 4M. Examination of the concentration-dependence of these coefficients show that it is very similar for the two salts. There is no evidence for any special structural characteristics in NiCl₂ solutions. The velocity correlation technique is apparently not sensitive enough to detect the small amount of complexation that is thought to be present in NiCl₂ solutions.

KEY WORDS: Nickel chloride; magnesium chloride; velocity cross-correlation coefficients; concentrated solutions; aqueous solutions; transport coefficients; complex formation.

1. INTRODUCTION

In previous papers on this subject⁽¹⁻³⁾ we have demonstrated that macroscopic transport coefficient data can be used to give information about microscopic motions in concentrated electrolyte solutions. In this type of approach, diffusion, conductance and transference data are transformed into velocity cross-correlation coefficients which have their definition in linear response theory. The framework for the calculation of velocity cross-correlation coefficients for 1:2 electrolytes, in particular, is given in one of these papers.⁽³⁾ Recently the treatment has been improved in several ways.^(4,5)

We have chosen to extend these studies to NiCl₂ for several reasons. In the first place although we have calculated velocity cross-correlation coefficients for 1:2 electrolytes such as BaCl₂ and CaCl₂ we have not yet studied a case where the cation is a transition metal ion.

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As these coefficients describe the extent of specific interaction between two species it should be interesting to see how such interaction is affected by the presence of d bonding orbitals and in particular whether complexation occurs. The question whether the nickel ion forms inner-sphere chloride ion complexes has been under debate; a recent summary is given by Weingärtner *et al.*⁽⁶⁾ A second very pertinent reason for studying NiCl_2 is that there have been recently two studies which suggest that there is a specific structure in concentrated solutions of this salt. Enderby and coworkers^(7,8) have conducted neutron scattering experiments on NiCl_2 solutions and suggested that there may be some kind of nickel-nickel ordering present. More recently, Maisano *et al.*,⁽⁹⁾ on the basis of viscosity and density measurements have conjectured that there may be a structure change in nickel chloride solutions at a concentration of about 1 M .

If any of the effects mentioned above are present they ought to be reflected in some of the velocity cross-correlation coefficients for the various binary combinations. It is of considerable interest then to calculate the coefficients and examine their concentration-dependence. In one of the above mentioned papers⁽⁶⁾ certain properties of NiCl_2 and MgCl_2 solutions were directly compared. It was felt that it would be instructive to apply the same type of comparison in this study. Generally an aqueous MgCl_2 solution is considered to be a strong electrolyte system which, apart from the presence of strongly hydrated cations, has no anomalous properties.³

2. EXPERIMENTAL DATA

Experimental data for conductance, transference numbers, tracer-diffusion and mutual diffusion in NiCl_2 are contained in a recent publication by Stokes *et al.*⁽¹⁰⁾ Sources of data for MgCl_2 solutions are as follows: conductances,⁽¹¹⁾ transference numbers,⁽¹¹⁾ tracer-diffusion,⁽¹²⁾ mutual diffusion.⁽¹³⁾ Activity coefficient data needed in the calculations were taken from Robinson and Stokes⁽¹⁴⁾ in both cases.

3. RESULTS

In Fig. 1 we show the concentration dependence of the three

³A recent publication [K. Lee and R. L. Kay, *Aust. J. Chem.* 33, 1895 (1980)] dealing with transference data for aqueous MgCl_2 confirms this assumption.

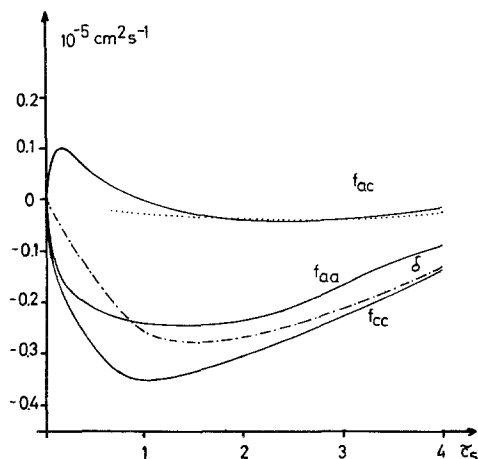


Fig. 1. Velocity cross-correlation coefficients f_{aa} , f_{cc} , and f_{ac} for NiCl_2 solutions as a function of the salt concentration ζ_s . δ is the molecular position parameter and the dotted curve represents the calculated standard coefficient, f_{ac}^0 .

velocity cross-correlation coefficients for NiCl_2 . The definition of these coefficients has been given elsewhere^(1,3-5) so that here it is sufficient to sketch their qualitative physical significance. The coefficient f_{ac} characterizes the correlations between anions and cations. If the velocities of the cations were strictly uncorrelated relative to the velocity of an anion selected at random, then $f_{ac} = 0$. In contrast to this, if both types of ions were tightly coupled so as to form a rigid molecule in the conventional sense, then f_{ac} would be approximately equal to the self-diffusion coefficient of this molecule, *i.e.* in this case $f_{ac} > 0$. In principle, the same rules hold for the coefficients f_{cc} and f_{aa} . However, since the subscripts *cc* and *aa* mean 'cation-cation' and 'anion-anion' correlation, tight binding between equally charged ions will never occur. Generally the velocity cross-correlation coefficients will be negative. Thus, there is a negative correlation between the velocities of the ions (and molecules) which means that if one ion moves in a given direction, then the mean velocity of the other ions is in the opposite direction. This is a simple consequence of the conservation of momentum. In order to give some feeling for the order of magnitude of the velocity correlation effects which occur, we should mention that the self-diffusion coefficients of the ions present in the solution under consideration range between $2 \cdot 10^{-5}$ and $0.15 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$.

The curves presented in Figs. 1 and 2 have been calculated using Eqs. (58) and (59) of Ref. 5 and by applying the procedure described in

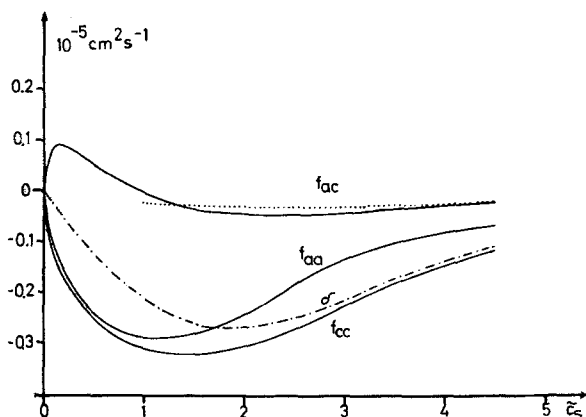


Fig. 2. Velocity cross-correlation coefficients f_{aa} , f_{cc} , and f_{ac} for MgCl_2 solutions as a function of the salt concentration \bar{c}_s . δ is the molecular position parameter and the dotted curve represents the calculated standard coefficient, f_{ac}^0 .

that paper. As has been shown in the same paper, the f_{cc} , f_{aa} , f_{ac} can also be computed using a simpler procedure; the results differ little and qualitative features are preserved.

Inspection of Fig. 1 shows that in fact most of the velocity cross-correlation coefficients are negative. Only f_{ac} is positive in the range $0 < \bar{c}_s \leq 1$ M. The maximum value of f_{ac} is slightly larger than one tenth of the cation self-diffusion coefficient. Since in this range there are positive velocity correlations, here we must have association between cations and anions. At higher concentrations there may be ion association as well. However, the effect of momentum conservation is stronger and consequently f_{ac} is slightly negative.

Let us now turn to Fig. 2 which gives f_{aa} , f_{ac} and f_{cc} for the MgCl_2 solutions. It may be seen immediately that the general appearance of this diagram is almost identical to that for the NiCl_2 system. Thus, we can conclude that, as judged from the point of view of velocity correlations between the ions, the NiCl_2 solution has no special features distinguishing it from the 'normal' MgCl_2 system. Finally, we may mention that also the coefficients found for the aqueous CaCl_2 and BaCl_2 systems have practically the same pattern.⁽³⁻⁵⁾

Next we have to discuss the parameter δ whose concentration dependence is also included in Figs. 1 and 2. The primary physical significance of δ lies in the fact that it is a magnification or reduction factor of the instantaneous ionic velocities which determines their separate contributions to the solute mass flux in the presence of a concen-

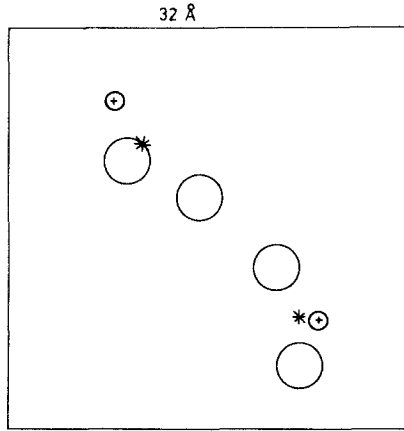


Fig. 3. Projection of a cubical volume element of dimension $(32 \text{ \AA})^3$. Circles represent positions of ions, their positions are in the respective centers and stars represent positions of NiCl_2 molecules, $\bar{z}_s = 0.1 m$.

tration gradient. Another requirement which is also fulfilled by the correct choice of δ is that the solute mass flux is zero if a gradient of electrical potential exists in the system.^(4,5) Let the instantaneous solute mass flux be

$$J_s = m_{\text{NiCl}_2} (v_i^{*(c)} + v_i^{*(a)}) / V \quad (1)$$

with

$$v_i^{*(c)} = [(D_c + \delta)^{-1} / 3(D_c^{-1} + 2D_a^{-1})]^{1/2} v_i^{(c)} \equiv A v_i^{(c)}$$

$$v_i^{*(a)} = [(D_a + \delta)^{-1} / 3(D_c^{-1} + 2D_a^{-1})]^{1/2} v_i^{(a)} \equiv R v_i^{(a)}$$

$$m_{\text{NiCl}_2} = m_{\text{Ni}^{2+}} + 2m_{\text{Cl}^-}$$

where $m_{\text{Ni}^{2+}}$ and m_{Cl^-} are the masses of the Ni^{2+} and the Cl^- ions, respectively, V is the volume of the system, $v_i^{(c)}$, $v_i^{(a)}$ are the instantaneous velocities of the cation and anion, respectively, $i = 1, 2, 3 \dots N_c$, $i = 1, 2 \dots N_a = 2N_c$, N_c is the total number of cations in the system, and D_a and D_c are the self-diffusion coefficients of the anion and cation, respectively. From the experimental data and the results for δ given in Figs. 1 and 2 one finds, for example that $A = 0.44$ and $R = 0.27$ for NiCl_2 at $\bar{z}_s = 0.1 M$. Considering that there are two anions to each cation, we see that the contributions of the cationic and anionic instantaneous velocities to the solute mass flux are about equal. In a NiCl_2 solution at $\bar{z}_s = 4 M$, one finds $A = 1.062$ and $R = 0.24$. So here,

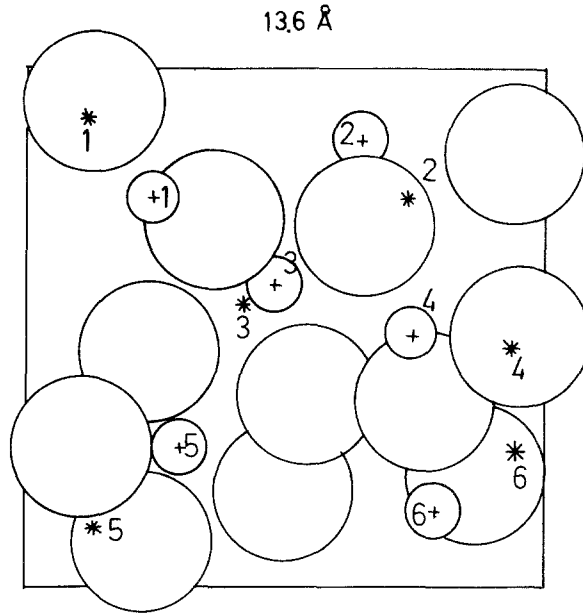


Fig. 4. Projection of a cubical volume element of dimension $(13.6 \text{ \AA})^3$. Circles represent positions of ions, their positions are in the respective centers and stars represent positions of NiCl_2 molecules, $\bar{z}_s = 4 m$.

since $A > 1$ we have in effect an amplification of the contribution of the cationic instantaneous velocities to the solute mass flux. In a MgCl_2 solution at $\bar{z}_s = 4 M$ one finds $A = 1.31$, thus the amplification is even greater here.

The instantaneous velocity is the time derivative of an instantaneous position of the particle in question. This means in our case that the position of the salt molecule is given by the vector

$$\mathbf{r} = A\mathbf{r}^{(c)} + R(\mathbf{r}_1^{(a)} + \mathbf{r}_2^{(a)}) \quad (2)$$

where $\mathbf{r}^{(c)}$ is the position of the cation and $\mathbf{r}_i^{(a)}$ ($i = 1, 2$) are the positions of the two anions. In Fig. 3 we show a volume element, a cube with edges of 32 \AA . At $\bar{z}_s = 0.1 M$ this volume element on the average contains two NiCl_2 molecules. We choose the origin of the coordinate system to be the center of the cube. The circles give the instantaneous positions of the ions. Then the stars give the positions of the molecules as calculated from Eq. (2). Here and in the following example Eq. (2) has been applied to the projections of \mathbf{r}_i on the drawing plane.

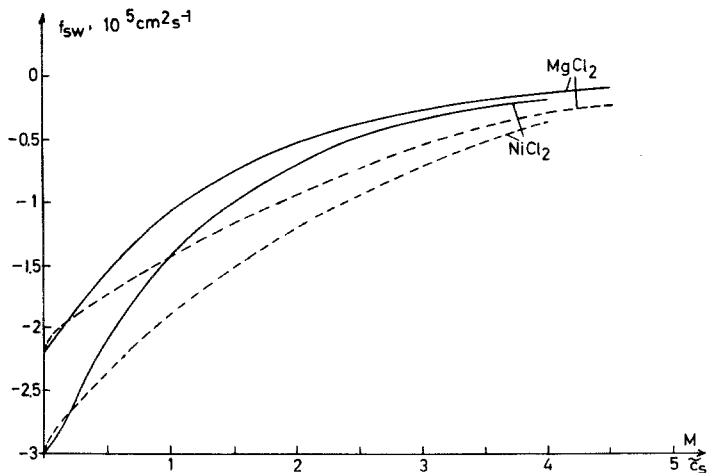


Fig. 5. Velocity cross-correlation coefficients, f_{sw} for MgCl_2 and NiCl_2 solutions as a function of the salt concentration \bar{c}_s . The dashed lines are the standard coefficients, f_{sw}^0 .

In Fig. 4 the cube has edges of 13.6 \AA . At $\bar{c}_s = 4 \text{ M}$ this volume element on the average contains six NiCl_2 molecules all of which are shown in the figure. Again the circles give the instantaneous positions of the ions, the stars are the positions of the molecules, and the origin is at the center. It is required that all the molecules lie within the volume element. This has to be achieved by a proper combination of cation and anion vectors. For instance, cations 2 and 6 would lead to molecular positions outside the cube if we connect them with the anions which are their closest neighbors. Therefore, we exchange the anions close to 2 and 6 such that the anions around cation 6 are combined with cation 2 and vice versa. Since there is no observable quantity which is sensitive to the positions of the ions belonging to a molecule, this procedure is legitimate. The only observable which enters is that on the average 6 molecules are in the cube, this requirement has to be fulfilled. One sees from Figs. 3 and 4 that at low concentrations the position of the molecule is close to the point that one would intuitively mark as being the 'center' of the set of ions in question, whereas at high concentration the position of the molecule is closer to the position of the cation. It is somewhere around the cation but the position is indefinite due to the requirement that it has to be inside the cube. However, the latter behavior is found only for salts with strongly hydrated cations; for other salts δ remains almost zero, which means that we always have the low concentration behaviour of the center of the molecule.

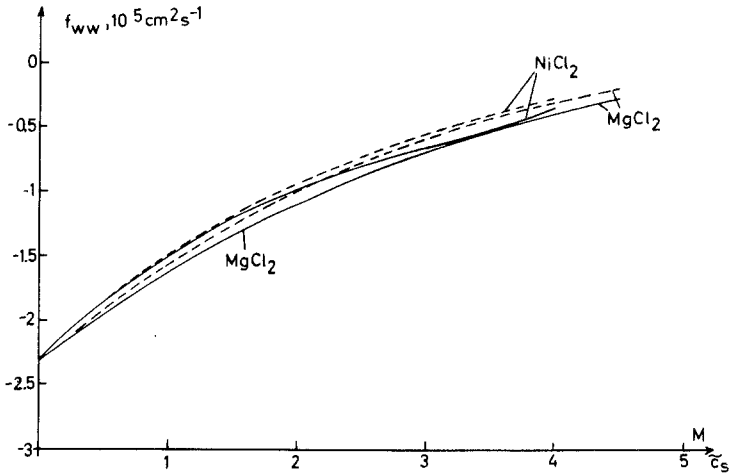


Fig. 6. Velocity cross-correlation coefficients, f_{ww} for MgCl_2 and NiCl_2 solutions as a function of the salt concentration z_s . The dashed lines are the standard coefficients, f_{ww}^0 .

In Fig. 5 we present velocity cross-correlation coefficients f_{sw} . This coefficient gives the correlations between the velocity of a salt molecule and the totality of the water molecules. These curves were calculated using Eq. (7) of Ref. 3. It may be seen that the f_{sw} are always negative, and so are totally determined by the requirement of the conservation of linear momentum. The dashed curves give predicted standard values $f_{sw}^{o(1,3,4)}$ based on the law of momentum conservation. The important conclusion to be derived here is that the behaviour of f_{sw} for MgCl_2 and NiCl_2 solutions is entirely analogous and there is no peculiarity in the latter case.

Shown in Fig. 6, is the coefficient f_{ww} which describes the velocity correlation between two different water molecules and contains the following information. Given that a water molecule selected at random has a finite velocity, what is the mean velocity of all other water molecules? The curves were calculated from Eqs. (38) and (41) of Ref. 3, and the expression

$$D_a D_c / (v_a D_c + v_c D_a) + \bar{f}_{ss} \quad (3)$$

eliminated between these two equations. The quantity \bar{f}_{ss} is not needed in the present paper. Again we have negative f_{ww} 's due to the dominant influence of momentum conservation, and almost exact agreement for the curves for both NiCl_2 and MgCl_2 . This demonstrates the absence of structural peculiarities which could be evidenced by solvent

velocity correlations. Compare also the standard coefficients f_{ww}^0 which are derived from the law of momentum conservation.^(1,3,4)

4. DISCUSSION

We have found that the study of velocity cross-correlation coefficients yields almost identical behavior for solutions of NiCl_2 and MgCl_2 . It may be remarked here that velocity self-correlations of all three species in both solutions, as shown by the self-diffusion coefficients, are practically indistinguishable also.

The question that can now be asked is whether there is other evidence of a different behavior for ions and water molecules in the two systems. The answer is that, whereas cation-anion association has never been reported in MgCl_2 solutions, the summary of data reported in Ref. 6 shows that there are observations which point to the definite existence of Ni^{2+} - Cl^- coupling. For one thing, the effect of Ni^{2+} on the Cl^{35} n.m.r. signal is fairly dramatic compared with that caused by Mg^{2+} ⁽¹⁶⁾. However by the standards of a normal complexing electrolyte (e.g. in CdCl_2 solutions) the amount of direct anion-cation contact is small. The probability that a given Cl^- ion is in direct contact with Ni^{2+} is about 25%,^(6,15) and as far as the precision of the n.m.r. method allows, it can be stated that this probability is constant in the concentration range $0 < \bar{c}_s \leq 4 M$. In comparing these results with the velocity correlation data, we discuss the low and high concentration ranges separately.

In NiCl_2 solutions at $\bar{c}_s \approx 0.1 M$, f_{ac} is positive, confirming the occurrence of association. However, in MgCl_2 solutions f_{ac} is also positive at $\bar{c}_s \approx 0.1 M$ and has the same magnitude which would not be expected. In MgCl_2 and NiCl_2 the cation-anion radial distribution functions are different. For NiCl_2 , the closest distance of approach between Ni^{2+} and Cl^- is $\approx 2.6 \text{ \AA}$, which is the sum of the ionic radii whereas in MgCl_2 solutions the closest distance of approach is larger because there is always one water molecule which separates anion and cation. We conclude that the velocity correlation effect extends sufficiently far out into the liquid from a given ion, so that minor differences in the pattern of spatial correlations are of little importance. For further details see Ref. 2.

In the high concentration range, for example at $\bar{c}_s = 4 M$, one calculates standard velocity cross-correlation coefficients $f_{ac}^0 = -0.28$ and -0.23 for NiCl_2 and MgCl_2 , respectively, from the requirement of momentum conservation; the experimental results are $f_{ac} = -0.189$ and

-0.240 for NiCl_2 and MgCl_2 , respectively, so that they are almost equal to the predicted coefficients. We notice that there is one difference. We have $|f_{ac}^o| < |f_{ac}|$ for MgCl_2 and also for the systems CaCl_2 ,⁽³⁾ NaCl ⁽²⁾ and LiCl ,⁽²⁾ but, $|f_{ac}^o| > |f_{ac}|$ for the NiCl_2 solution. The effect is fairly small but real (see also the dotted curve in Figs. 1 and 2). This can be explained as a weak positive contribution to f_{ac} from Ni^{2+} - Cl^- contact. Apart from this, momentum conservation is entirely dominant, practically irrespective, again, of the spatial distribution of the anions relative to the cations. It should be kept in mind that the velocity correlation function⁴ decays very fast; the correlation time is about 10^{-12} s. During this very short time it virtually does not matter whether a Cl^- ion is inside or outside the first coordination sphere of Ni^{2+} as far as velocity correlations are concerned.

All these arguments may also be applied to the water-water and solute-water velocity correlations. The agreement between the standard velocity cross-correlation coefficients and the experimental ones show that the behavior of the velocity correlations is mainly determined by the momentum conservation; the particular distribution of the cations and anions relative to one another is of little importance.

In the introduction, we planned to investigate two effects thought to be present in NiCl_2 solutions by calculating the respective velocity cross-correlation coefficients. These calculations as well as comparison with the corresponding ones for MgCl_2 solutions, gave no evidence of either long-range structure effects at specific concentrations or of appreciable complexation. However as other evidence exists for a small degree of complex formation in MgCl_2 solutions it would seem that the velocity correlation technique is not particularly sensitive to details of the configurational distributions among ions and water. We are at present collecting transport data for CdCl_2 solutions and it should be interesting now to see how the high degree of complexation associated with this electrolyte is reflected by its velocity cross-correlation coefficients.

5. NOTE ADDED IN PROOF

During the publication of this paper, a number of comments were received which in some cases were critical of the procedures and assumptions used here. These criticisms can be grouped under four

⁴It has been assumed here that velocity cross-correlation coefficients have the same time constant as velocity self-correlation functions.^(1,4,16)

headings and answered as follows:

1). One criticism concerned the use of the 'conservation of momentum' principle for deriving standard velocity cross-correlation coefficients (f_{ij}^0) in view of the fact that Kubo-type relations are meant to apply in infinite volume systems. We would comment that in a strongly coupled system such as a molecular or ionic liquid, conservation of momentum must apply locally. But in any event in this paper the principle has been used mainly to calculate standard velocity cross-correlation coefficients. These f_{ij}^0 are intended as a yardstick derived from experiment. As in equilibrium thermodynamics the standards are those applicable to an ideal system and as such can be obtained in a number of ways and without rigorous derivation. Recently Friedman and Mills⁽¹⁷⁾ derived standard velocity cross-correlation coefficients for non-electrolyte systems and these f_{ij}^0 are obtained by essentially guessing at an 'ansatz' between the three f_{ij} which involved the use of fractional mass weighting and also experimental limiting values. Conservation of momentum was not explicitly used. Yet when applied to near ideal mixtures with CCl_4 at 25° , Hertz's⁽⁴⁾ f_{ij}^0 and those of Friedman and Mills fitted the data equally well and so both sets serve equally well as standards.

2). Comments were also made that the assumption, that the time-constants for the decay of self correlations and cross correlations were of the same order, was unjustified. It should be noted that this assumption was only made as an approximation to obtain standard velocity cross-correlation coefficients and not meant to apply generally. In any event, the practical equivalence of the f_{ij}^0 derived with this assumption and the f_{ij} derived from experiment for near-ideal systems leads one to believe that this assumption is not a poor one.

3). Statements were made also that velocity cross-correlation coefficients were either equal to zero or, if finite, should have positive values. Most velocity cross correlations derived from experiment are, of course, negative. Friedman⁽¹⁸⁾ recently derived velocity cross-correlation coefficients using a force correlation approach and indeed showed that the initial slope of the cross correlation function was positive but, it seems certain, that after a positive incursion the f_{ij} must cross the zero line and go deeply negative (in most cases).

4). One other comment concerned the validity of the application of linear response theory to systems of charged particles and it was implied that the subtleties of the problem had not been taken into account. We feel that the procedure, adopted by Hertz⁽¹⁾ in the first paper of this series, demonstrates how these problems can be over-

come by a simple and elegant procedure. The basic principles of this new approach will be found in a recent publication by Hertz.⁽¹⁹⁾

Finally it should be emphasized that this paper uses experimental data (produced in the laboratory of one of the authors) to calculate velocity cross-correlation coefficients through an established procedure. The concentration dependence of these coefficients is then examined with standard velocity cross-correlation coefficients being used only as an aid to detailed interpretation. However, the conclusions reached in this study are independent of this detailed interpretation. These conclusions were, that since NiCl_2 and MgCl_2 are virtually identical in the velocity cross correlation description, then complexation in NiCl_2 must be small and Ni-Ni ordering can scarcely exist.

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