Structure and reactivity of ion hydration complexes in solution
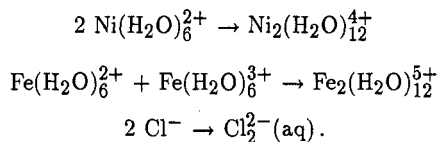
Harold L. Friedman, Fernando O. Raineri and Hua Xu

Department of Chemistry, State University of New York, Stony Brook N. Y. 11794, USA

Abstract - Hydration complexes, long an object of study in the coordination chemistry field, can now be studied more directly by new and powerful methods. Among the new experimental methods are the refined neutron scattering methods developed by J. E. Enderby, G. Neilson and co-workers. Another is the study of ion-solvent clusters in molecular beams, especially by spectroscopic techniques. Some important new theoretical studies begin with calculating the Born-Oppenheimer potential surfaces for very small ion-water clusters. Then one of the available statistical mechanical techniques is applied to generate solvent-averaged ion-ion pair potentials from which measurable equilibrium solution properties can be calculated. In another new development, the same solvent-averaged models are dressed with bare ionic self diffusion coefficients and with the ion-ion hydrodynamic interactions. From such models one can calculate some of the solution transport coefficients for comparison with real systems. Illustrations of both consistencies and contradictions are found.

INTRODUCTION

The last decade has witnessed impressive advances in our methods of investigating the molecular structures around ions in aqueous solutions. These advances are based on neutron diffraction experiments by Enderby, Neilson, and co-workers [1], together with important advances in calculating those average properties of model systems that can be compared with experimental data. Thus it becomes practical to apply these developments in statistical mechanics to assess the degree to which various models are realistic.

At the same time evidence has been accumulating for a surprising type of chemical reactivity of some ion hydration complexes; they dimerize even in the face of large accumulations of coulombic energy. Here are some examples of proposed dimerization processes expressed as chemical reactions

$$2\,Ni(H_2O)_6^{2+} \rightarrow Ni_2(H_2O)_{12}^{4+}$$

$$Fe(H_2O)_6^{2+} + Fe(H_2O)_6^{3+} \rightarrow Fe_2(H_2O)_{12}^{5+}$$

$$2\,Cl^- \rightarrow Cl_2^{2-}(aq).$$

The evidence for the nickel dimer comes from neutron diffraction experiments which will be discussed below [2]; they show that in a $4.35m$ aqueous $NiCl_2$ solution a major fraction of the nickel ions is within 5Å center to center of another nickel ion. The evidence for the ferrous-ferric complex is based on applying Marcus theory to calculate the rate constant for the electron exchange in solution, together with certain NMR relaxation data [3].The evidence for the chloride ion dimerization comes from model calculations done by Kusalik and Patey [4] and, for a different model, by Pettitt and Rossky [5]. According to these theories the fluoride ion dimer is even more stable [4,5]; it is also is more amenable to investigation by NMR techniques. Indeed Hertz and Rädle found enhanced NMR relaxation of ^{19}F in F^- solutions which they attribute to F^--F^- interactions [6]. Besides these aquo-ion dimers with similar charge sign within the pair, there is also evidence for pairwise association of the oxo cations such as UO_2^{2+}, NpO_2^+ and VO_2^+ [7].

In this report we limit ourselves to describing the evidence, both pro and con, that chloride ions in aqueous solution form dimers, presumeably stabilized by hydrogen bonds [5,8]. While the questions regarding the stability of these dimers are not all answered, it is surely an interesting exercise to see which experiments will provide a measure of their importance in dilute solutions. So we turn our attention to the proposition that in 1M aqueous NaCl solution a substantial fraction of the chloride ions is distributed as close pairs Cl_2^{2-}, contrary to what Arrhenius concluded 103 years ago.

Ion hydration complexes in solution are traditional objects of study in coordination chemistry [9]. At the most basic level a hydration complex is characterized by the hydration number and its lifetime. The former specifies the stoichiometry of the complex, while the latter corresponds to the average time a water molecule lives in the complex before exchanging with an outside water molecule. In some cases hydration complexes found in salt hydrate crystals can be shown to persist in solution on the basis of comparison of electronic

spectra. Then one may be able to infer some details of the geometry of the complex in solution. But more generally the study of ion hydration phenomena and the structure of electrolyte solutions must be based on the ion-ion, ion-water and water-water forces.

From this general perspective we find that the distinction between a Born-Oppenheimer (BO) picture, in which solute and solvent are treated symmetrically, and a McMillan-Mayer (MM) solvent-averaged picture is very useful [10]. Thus the ion-ion interaction phenomena, responsible for the concentration dependence of the thermodynamic and transport properties of electrolyte solutions, are often advantageously discussed in terms of <u>solvent averaged</u> ion-ion forces. On the other hand it is only in the BO picture that one sees the arrangement of water molecules around an ion. Important information concerning both levels of description is provided by the refined neutron diffraction methods [1], and the results achieved by this method are relevant to the chloride-chloride complex formation. These experiments, however, are mostly made in the solution concentration range above 1M; there is still a need for statistical mechanical model calculations to estimate the changes in solution structure as the concentration is changed from infinite dilution to the molar range. The relevant theory, described in the sections on BO and MM models and their applications, most directly (MM-level) leads to osmotic coefficients (~ excess free energies) as functions of the concentration of NaCl. The calculation of transport coefficients in electrolyte solution gives another set of coefficients which may be used to test the models. In new work that is briefly summarized here, a theory of liquid junction potentials is developed and applied to the chloride dimer problem, with striking results. In the concluding section the various calculations already described are brought together to see what degree of dimerization of the aqueous chloride ion is consistent with the various experimental data.

DIFFRACTION BY SOLUTIONS

The equilibrium structure of a fluid system is mainly expressed in terms of pair correlation functions $g_{AB}(r)$. These functions are defined so that the average local concentration of a particle of species B at a distance r from a A particle is $c_B g_{AB}(r)$ (where c_B is the over-all concentration of particles of species B). Most generally, the equilibrium structure of a hydrated ion of species α is given by $g_{\alpha O}(r)$ and $g_{\alpha H}(r)$. Unfortunately such <u>detailed</u> information is not always available, only the hydration number being at hand. In terms of the pair correlation functions the hydration number of the ionic species α is the running coordination number

$$n_{Y/\alpha}(R_Y) = c_Y \int_0^{R_Y} g_{\alpha Y}(r) \, 4\pi r^2 dr \tag{1}$$

if Y=O, or half the running coordination number if Y=H. In either case the appropriate cut-off R_Y is the minimum beyond the first peak in $g_{\alpha Y}(r)$ [1].

It must be admitted that very often thermodynamic, transport, or relaxation data have been interpreted to reach conclusions about hydration numbers of solute ions. Unfortunately such determinations are unreliable, as shown most obviously by results depending on the kind of data [11]. On the other hand, the most straightforward method for determining structure in chemical systems, namely X-ray diffraction, is not nearly so powerful when applied to fluid systems as when applied to crystals [12]. To see why, we need to take a look at the theory of the diffraction of X-rays or neutrons by a fluid. The experimental data in a neutron diffraction experiment can be reduced to yield a weighted average

$$F(k) = \rho \sum_A \sum_B f_A f_B x_A x_B \, \tilde{h}_{AB}(k) \,, \tag{2}$$

of the partial structure factors

$$\tilde{h}_{AB}(k) = \int [g_{AB}(r) - 1] \, e^{i\mathbf{k}\cdot\mathbf{r}} d^3 r \,. \tag{3}$$

In Eq. (2) ρ is the total atom concentration, while x_A and x_B are the fractions of the nuclear species A and B, respectively. The sums are over all of the nuclear species in the system, and the f's are the neutron scattering lengths.

While a direct measure of the structure, $F(k)$ is not of much use by itself because even in the simplest ionic solution, say 1M NaCl in water, it can be expressed as the sum of ten terms due to the ten atomic species pairs OO, OH, HH, NaO, NaNa, ... The composition dependence appears implicitly in the $\tilde{h}_{AB}(k)$ alongside the secular dependence carried by the factors $x_A x_B$. In dilute solutions, due to the secular dependence in Eq. (2), the water-water terms overwhelm the remaining ion-ion and ion-water terms. Therefore it was a great advance when Enderby and coworkers showed [13] that the measurements could be made so exactly that the differences in $F(k)$ due to change of isotopic species were measurable. Thus an isotopic substitution of the ionic species α by $\underline{\alpha}$ yields

$$\Delta_\alpha(k) = F_\alpha(k) - F_{\underline{\alpha}}(k) = \rho \, (f_\alpha^2 - f_{\underline{\alpha}}^2) \, x_\alpha^2 \, \tilde{h}_{\alpha\alpha}(k) + \rho \, (f_\alpha - f_{\underline{\alpha}}) \, x_\alpha \sum_{B \neq \alpha} f_B x_B \tilde{h}_{\alpha B}(k) \tag{4}$$

if we may assume that isotopic substitution does not change the structure, i.e. $\tilde{h}_{\underline{\alpha}B}(k) = \tilde{h}_{\alpha B}(k)$. Due to the different magnitude of the atomic fractions x_A, the first order difference method gives information about the detailed arrangement of water molecules around the ion α [1,2,13].

In Fig. 1 we show $\bar{G}_A(r)$, the inverse Fourier transform of $\Delta_A(k)$, for a $1.46m$ solution of $NiCl_2$ in D_2O in the case in which A=Ni, i.e. one Ni isotope has been changed to another. $\bar{G}_{Ni}(r)$ is a linear combination of the pair correlation functions $g_{NiO}(r)$ and $g_{NiD}(r)$. In the figure we compare the experimental function [1] with that obtained from a model calculation [14]. The comparison shows that the diffraction data may be used to see how realistic a BO model is, but of course it would be more definitive if we had a theory of the concentration dependence of $g_{AB}(r)$.
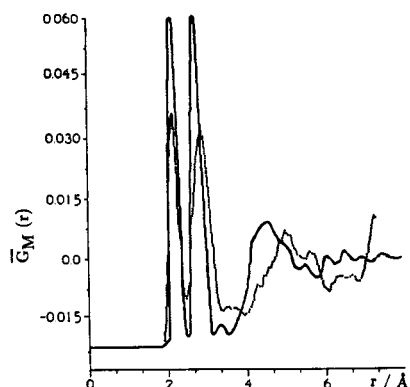

Fig. 1. $\bar{G}_{Ni}(r)$ in water. The heavy line is the function experimentally determined in $1.46m$ $NiCl_2$ [1] while the light line comes from a model calculation with one ion and 100 water molecules [14].
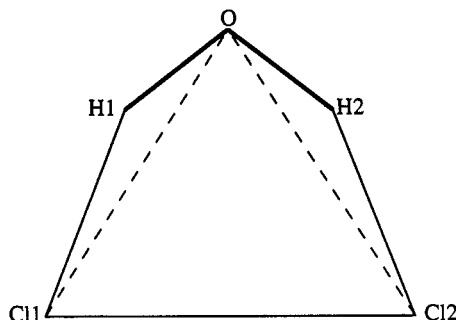

Fig. 2. Geometry of a Cl_2^-(aq) complex that is consistent with observed $\bar{G}_{Cl}(r)$.

The neutron diffraction first difference method can be extended by making a larger number of isotopic substitutions. For example in the second order difference method [2,13], with two substitutions of the Ni isotope (three Ni isotopes altogether) one can determine $\tilde{h}_{NiNi}(k)$. Its Fourier transform shows that two Ni^{2+} ions in $4.35m$ $NiCl_2$ easily approach each other to give a center-to-center separation of scarcely more than 4Å. Since the hydration shells of the ions are not displaced [2], they must interpenetrate to give a shoulder in armpit configuration [3].

These results are relevant to the theory of the ferrous-ferric electron exchange in water [3] even without a theory for predicting the change in $h_{NiNi}(r)$ as one goes from $4.35m$ $NiCl_2$ solution to dilute solutions. More generally, the first difference neutron diffraction method as developed by Enderby has only been applied to very few solutions and the second difference method to even fewer pairs of ions.

For diffraction by X-rays the structure factor is again given by Eq. (2), but now the form factors f_A are functions of the wavevector k. Enderby and coworkers [1,15] have devised a system by atomic substitution based on the "isomorphism" of some pairs of hydrated ions. By this technique it may be again possible to reduce Eq. (2) to fewer terms.

The neutron first difference function $\bar{G}_{Cl}(r)$ has been measured in more than ten solutions [1,13,16]. Remarkably, this measure of the hydration structure of the Cl^-(aq) is insensitive to the medium. For example the Cl-D peak at 2.3Å and the Cl-O peak at 3.2Å scarcely shift or broaden as one changes the concentration or the counterion species. This insensitivity is qualitatively inconsistent with Cl_2^{2-} being an important species as we now explain with the help of Fig. 2. Suppose that Cl1:H1:O:H2 represents the average geometry of the chloride ion hydration as determined by $\bar{G}_{Cl}(r)$. A second chloride ion Cl2 at an arbitrary point in the vicinity of Cl1 would give rise to new Cl-O and Cl-H peaks in $\bar{G}_{Cl}(r)$, unless it is placed in the Cl1-H1-O-H2 plane in a location that is symmetric under C_2 with respect to Cl2 (Fig. 2). While this site exists, it is 5Å away from Cl1.

The Pettitt and Rossky theory [5] that makes us look for the Cl_2^{-2} predicts a 3.5Å separation between the two chloride ions. As calculated from the experimental data [1,13,16] there is no 3.5Å peak in any $\bar{G}_{Cl}(r)$ except in cases where there is also some inconsistency in the correlation distances and angles.

MODELS

Born–Oppenheimer level

Great progress has been made in calculating BO-level potentials from first principles, i.e. from the Schrödinger equation [17]. A water-water potential is calculated by integrating the Schrödinger equation over the electron coordinates to obtain the energy of a given configuration of two water molecules. With a suitable selection of nuclear configurations one can in this way generate an important piece of the electronic ground state BO

potential energy surface on which the two oxygens and four hydrogens move. Most often this BO surface is parametrized in terms of an interaction site model (ISM). Three or more sites [17,18] are chosen in a water molecule and the potential energy of interaction $u(1\,2)$ between two molecules is expressed as the sum of the potential energy over pairs of interaction sites

$$u(1\,2) = \sum_{A\in 1}\sum_{B\in 2} u_{AB}(r_{AB}) \,. \tag{5}$$

One of the most useful forms is

$$u_{AB}(r_{AB}) = \frac{A_A A_B}{r^{12}} - \frac{C_A C_B}{r^6} + \frac{q_A q_B}{r} \,, \tag{6}$$

where r_{AB} is the distance between site A in one water and site B in the other. The 6-12 coefficients A_A and C_A and the site charges q_A are adjusted to fit the BO potential surface generated from Schrödinger-level calculation.

Measurable averages, such as $g_{OO}(r)$, calculated from a model water-water potential by Monte Carlo (MC) or Molecular Dynamics (MD) simulation mostly show rough agreement with laboratory data. We recall that Kuharski and Rossky [19] showed that models treated by classical mechanics should not agree too closely with the laboratory data because the latter carry quantum effects. It seems worth remembering that turning on the quantum dispersion changes $g_{OO}(r)$ roughly as much as raising the temperature of classical water from $300\,K$ to $350\,K$ [19].

Ion-water potentials can be evaluated by calculating average properties of small clusters of water molecules around one ion and comparing the results with thermodynamic data for the same clusters in ion beams [20]. Spectroscopic data for vibrational modes of these clusters can now be measured [21] and may be expected to be even more useful for evaluating model solute-water BO surfaces like those in refs. [18(b)] and [22].

In recent years there have been attempts to obtain the structure of pure water from models treated by approximate statistical mechanical theories. Solving the hypernetted chain (HNC) approximation [10] (see following section) for the "ionic" or central force model for water [23] gives very poor results for the short range structure, although the structure factor $F(k)$ for X-ray diffraction is satisfactory [24(a)]. More recently it has been reported that far better results can be obtained for the short-range structure by including the so-called bridge functions of a simple hard sphere fluid (at appropriate density) [24(b)]. In particular the peak locations and coordination numbers are much better than those given by simple HNC for the same model. Other approaches to the structure of water are due to Kusalik and Patey [25] using the reference HNC theory for water modeled as polarizable hard spheres with embeded multipoles and by Pettitt and Rossky [26] by applying the extended RISM theory to the TIPS interaction site model [17(b)].

McMillan–Mayer level

These models specify the interaction laws $\bar{u}_{\alpha\beta}(r)$, the potential of average force between solute particles at infinite dilution, and are the input for most theoretical calculations of the ion distributions and of the concentration dependence of thermodynamic and transport properties.

At the MM-level the molecular solvent is variously described as averaged out, projected out, or replaced by a dielectric, viscous continuum. The basis in statistical mechanics for projecting out the solvent is well known [10,27,28] for equilibrium systems. It is implicit already in the theory of the concentration dependence of transport coefficients developed by Debye, Hückel, Onsager, and Falkenhagen [29].

Quite generally one can distinguish between those models that are introduced more or less ad-hoc from those that are derived under given approximations from BO statistical mechanical calculations. The first group comprises the primitive model (charged hard spheres with omission of the image terms of order $1/r^4$) and other more refined charged hard core models like the square well or mound model [30]. Included in this group are also the solvent-averaged pair potentials of the form [31]

$$\bar{u}_{\alpha\beta}(r) = \frac{A_{\alpha\beta}}{r^9} + \frac{q_\alpha q_\beta}{\epsilon r} + \mathrm{CAV}_{\alpha\beta}(r) + \mathrm{GUR}_{\alpha\beta}(r) \,, \tag{7}$$

where $A_{\alpha\beta}$ is a repulsive coefficient that is selected to be consistent with the diameters of ions of species α and β and ϵ is the dielectric constant of the medium. The $\mathrm{CAV}_{\alpha\beta}(r)$ term is the leading correction for image effects [31]. The Gurney term $\mathrm{GUR}_{\alpha\beta}(r)$, is a bland adjustable term that is tuned to reproduce some property, usually the osmotic coefficient, as a function of concentration up to 1M or so. Often referred to as vanilla (V) models because they are reduced to essentials (core repulsion, coulomb tail, tunable middle section), these soft core models (like the primitive and the other hard core models) might be realistic if the real molecular solvent were replaced by a continuous dielectric medium.

A more realistic model, however, should exhibit spatial oscillations due to the granularity of the solvent, as remarked long ago by Guggenheim [32(a)] and recently by Ciccariello [32(b)]. Such oscillatory features appear naturally in solvent-averaged pair potentials derived from BO level calculations. The latter approach includes the oustanding contributions by Kusalik and Patey [4] and by Pettitt and Rossky [5] mentioned in
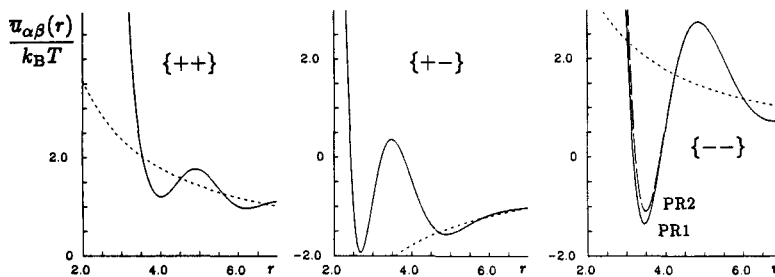
Fig. 3. Solvent averaged pair potentials $\bar{u}_{\alpha\beta}(r)/k_B T$. We have in turn $\alpha, \beta = $ Na$^+$-Na$^+$; Na$^+$-Cl$^-$; and Cl$^-$-Cl$^-$. The broken line represents the coulombic contribution to the potentials. The abcisa is r is in units of Å.

the introduction. As an example Fig. 3 shows the Pettitt-Rossky (PR) [5] solvent averaged pair potentials of NaCl(aq). For the Cl$^-$-Cl$^-$ pair potential, PR1 is the original Pettitt-Rossky potential while PR2 is a slight modification to improve the agreement of the MM calculations with the experimental osmotic coefficient data [33].

EQUILIBRIUM STRUCTURE AND ENERGETICS FROM MODELS

The hypernetted chain (HNC) integral equation approximation is accurate enough for many MM studies involving aqueous electrolytes with ion concentrations up to the molar range. Mostly this statement rests on comparisons of treating given models by both HNC and a simulation method, whether MC [34] or BD [35] (Brownian dynamics, in which the ions follow some projected dynamics such as Langevin's or Smoluchowski's. [36]).

The HNC theory for the calculation of the average equilibrium structures of a MM model specifying the pair potentials $\bar{u}_{\alpha\beta}(r)$ may be described as follows [10]. The Ornstein-Zernike equation

$$h_{\alpha\beta}(1\,2) \ = \ c_{\alpha\beta}(1\,2) \ + \ \sum_\eta \int c_{\alpha\eta}(1\,3)\,\rho_\eta\,d(3)\,h_{\eta\beta}(3\,2) \tag{8}$$

may be taken as defining the direct correlation function $c_{\alpha\beta}(12)$. Also α, β, and η are solute species labels, while the integers label coordinates, say r_1, r_2, r_3. The HNC approximation involves a second equation to close the calculation, namely

$$c_{\alpha\beta}(1\,2) \ = \ h_{\alpha\beta}(1\,2) \ - \ \ln[1 + h_{\alpha\beta}(1\,2)] \ - \ \frac{1}{k_B T}\,\bar{u}_{\alpha\beta}(1\,2) \ . \tag{9}$$

With the addition of one more term, the bridge graph sum $\mathcal{B}_{\alpha\beta}(1\,2)$, this equation would be exact and we could solve for the exact structure functions implied by the model potential and the state variables. If we do not neglect $\mathcal{B}_{\alpha\beta}$ completely but instead use $\mathcal{B}_{\alpha\beta}$ calculated for some reference system the theory is called reference-HNC (RHNC) [10].

For MM-level models of aqueous electrolytes the adequacy of the HNC theory leaves little incentive to apply the RHNC theory. An odd result (which is mended by the RHNC) is that in symmetrical models for aqueous CuSO$_4$ in the millimolar range there is a range of concentration in which $g_{++}(r) = g_{--}(r)$ has a peak as a function of r at a separation that corresponds to the like-like distance in the triple ion $+ - +$ [37(a)]. Another striking result for the same model is that the HNC results for the osmotic coefficient agree very closely with results from the non-linear Poisson-Boltzmann equation [37(b)].

To see whether the vanilla (V) and Pettitt-Rossky (PR) models can be distinguished by thermodynamic data we apply the HNC approximation to both models. We find, after some small adjustments of each model [33] that we can fit the osmotic coefficient data up to 1M with high accuracy. Essentially the same result was reported by Pettitt and Rossky [5].

To investigate the thermodynamics more completely we are calculating the mixing rules for some osmotic coefficients of these models. We recover Harned's rule in mixing a vanilla model for NaClO$_4$ with a vanilla model for NaCl, in agreement with experiment. But when we mix a vanilla model for NaClO$_4$ with a PR model for NaCl and with a vanilla model for the Cl$^-$,ClO$_4^-$ pair potential, we find unrealistic deviations from Harned's rule, especially above 1M [37(c)].

The pair correlation function $g_{--}(r)$ for the V and PR models of aqueous NaCl at 1M are shown in Fig. 4. PR1 is the potential before tuning (to PR2) to fit the experimental osmotic coefficient data [33]. Also for comparison $g_{+-}(r)$ for the PR1 model is included. The extensive formation of Cl$_2^{2-}$ predicted by the PR models is evident from the figure.
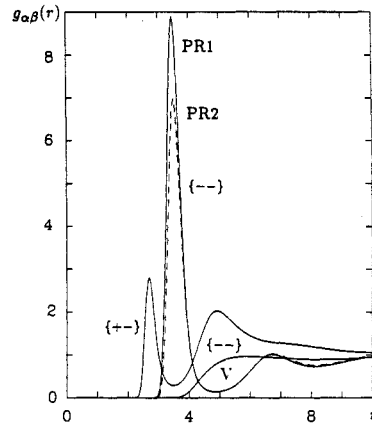
Fig. 4. Pair correlation function $g_{--}(r)$ for V and PR model of aqueous NaCl at 1M. Also included is $g_{+-}(r)$ of the PR1 model. r in units of Å.

In the next two sections we exploit MM-level theories under the HNC approximation in the context of evaluating model properties that correspond to measurable non-equilibrium functions of aqueous NaCl solutions at finite concentrations. We believe that these properties are particularly sensitive probes of the specific ion-ion interactions. The results derived from a vanilla model "tuned" to fit osmotic coefficient data are compared with the results derived from a Pettitt-Rossky models PR1 and PR2.

SELF AND DISTINCT DIFFUSION COEFFICIENTS

Historically the development of the theory of ionic solutions has been strongly affected by the progress made in the accurate measurement and theoretical interpretation of mass transport coefficients, above all the electrical conductivity. But the pace of progress slows down considerably when it comes to the interpretation of the transport coefficients of solutions in the molar concentration range. More recently it has been proposed that it might be advantageous to concentrate on just two kinds of "more basic" diffusion coefficients, the self D_α^s and the distinct $D_{\alpha\beta}^d$ diffusion coefficients. They are the basic pieces from which the collective isothermal mass transport coefficients (electrical conductivity, transport numbers and interdiffusion coefficients) are built. The time correlation function expression of the self diffusion coefficients is

$$D_\alpha^s = \frac{1}{3} \int_0^\infty dt \; \{\langle \mathbf{u}_a(t) \cdot \mathbf{u}_a(0) \rangle \}_\infty \;, \tag{10}$$

where $\mathbf{u}_a(t)$ is the velocity of a particle a of species α defined relative to a reference frame that is fixed with respect to the laboratory. Also $\langle \cdots \rangle$ denotes an average over an equilibrium ensemble while $\{\cdots\}_\infty$ indicates the thermodynamic limit operation. In contrast with the D_α^s, but in common with most of the other mass transport coefficients, the internal reference frame to which the $D_{\alpha\beta}^d$ pertain has to be specified. In the solvent-fixed reference frame their time correlation function expression [38] (BO-level) is

$$D_{\alpha\beta}^d = \frac{1}{3} \int_0^\infty dt \; \left\{ (N_\alpha + N_\beta) \langle [\mathbf{u}_a(t) - \hat{\mathbf{v}}_w(t)] \cdot [\mathbf{u}_b(0) - \hat{\mathbf{v}}_w(0)] \rangle \right\}_\infty \;, \tag{11}$$

where $\hat{\mathbf{v}}_w$ is the mean molecular velocity of the solvent [39] (a collective dynamical variable), which is defined relative to the laboratory reference frame. We say that in Eq. (11) $\hat{\mathbf{v}}_w$ plays the role of a microscopic reference velocity [38,39].

For electrolyte solutions the solvent-fixed reference frame is most natural and useful [40], particularly because it generates a closed set of ion-ion $D_{\alpha\beta}^d$ which lends itself to approximate calculation (integral equation theories or Brownian Dynamics computer simulations) using a projected dynamics that operates at the MM level with the solvent-averaged ion-ion pair potentials discussed in the preceding sections. One such scheme is the Altenberger, Zhong and Friedman theory (AZF) [33,41], a type of renormalized Smoluchowski integral equation transport theory in which the bare solute-solute MM forces are replaced by mean field forces, namely the gradients of the equilibrium direct correlation functions $c_{\alpha\beta}(r)$. The bare self diffusion coefficients of the ions D_α^0 (i.e. infinite dilution values) and a model for the bare hydrodynamic interaction of pairs of ions (the Oseen tensor at the simplest level) are further input to the theory.

In fact, if for the moment we neglect the hydrodynamic interactions and the mixture aspect, the AZF theory takes the form of the Smoluchowski-Vlasov equation [42] for one component spherical particles

$$\frac{\partial \delta \rho(1,t)}{\partial t} = D \nabla_1 \cdot \left[\nabla_1 \rho(1,t) - \rho(1,t) \int \nabla_1 c(1\,2)\, d(2)\, \delta\rho(2,t) \right] \;, \tag{12}$$

where $\delta\rho(1,t)$ is the fluctuating part of the particle density field $\rho(1,t)$.

Equilibrium and non-equilibrium Brownian Dynamics simulations to test the validity of the AZF theory were applied to vanilla models for 1M NaCl, 0.5M K_2SO_4 and 0.5M $CuSO_4$ aqueous solutions [35(b),40,43]. In some studies (K_2SO_4) hydrodynamic interactions were included [40]. The AZF theory was found inadequate for the 2-2 electrolyte, but seems quite accurate for the 1-1 and 1-2 electrolyte models, particularly for the self diffusion coefficients and ionic conductivities. Until now, however, the simulations have provided only an incomplete test of the quality of the theory owing to the great difficulty in obtaining accurate values of the distinct diffusion coefficients by simulation.

In fig. 5 we compare the experimental Cl^--Cl^- distinct diffusion coefficient in the solvent-fixed reference frame (calculated from the data of refs. [44]) with predictions by the AZF theory for the V and PR models [33,45]. We conclude that the PR model for NaCl(aq) has an unrealistically strong attraction between two Cl^- ions near contact, as reflected in the D^d_{--} becoming positive at rather low concentration, in contrast with the experimental data.
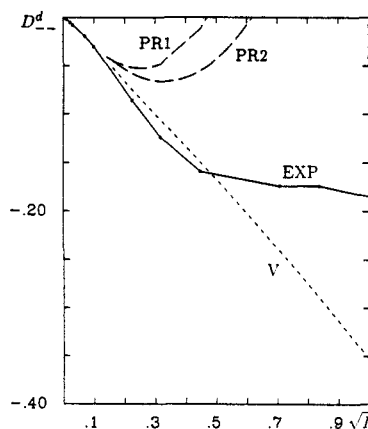

Fig. 5. Distinct diffusion coefficient D^d_{--} (solvent-fixed reference frame) for Cl^--Cl^- in NaCl(aq) as a function of the square root of the molar ionic strength [33,45]. PR1 and PR2: Pettitt-Rossky models as in Figs. 3 and 4; EXP: experimental; V: vanilla model.

THE LIQUID JUNCTION POTENTIAL

We now turn our attention to an apparently unrelated problem, namely the distributions of charge and electrical potential through the junction between two electrolyte solutions of different composition that are mixing by diffusion. We have recently developed a molecular theory [46] for the special case of a liquid junction formed between solutions of the same binary electrolyte. The theory of linear response to thermal perturbations (McLennan [47(a)] and Mori [47(b)]) is generalized to inhomogeneous electrolyte solutions. A novel aspect of the theory is that it is formulated in a salt representation [48]; the system is viewed in terms of its components in the thermodynamic sense: the "salt" and the solvent. In this way we avoid single-ion thermodynamic state parameters in the nonuniform non-equilibrium system. Only the chemical potential of the neutral "salt" species is needed, while the troublesome single-ion activity coefficients that plague the conventional macroscopic formulations are eliminated in favor of equilibrium static correlation functions. These functions or susceptibilities may be calculated from BO Hamiltonian models. The transport numbers of the ion-constituents, t_+ and t_- (solvent-fixed reference frame), are required as input to the theory; they may be chosen to match those of the system of interest. Under a certain <u>approximation</u> that we call the continuum-solvent, the theory may be simplified to the MM level. We confine our discussion to this approximation.

The most interesting liquid junction characteristic is the liquid junction potential (LJP) Ψ. A surprising result of our theory is that Ψ has direct relevance to the problem discussed in this article. This is due to the dependence of Ψ on the short range <u>specific</u> interactions between the ionic species; indeed Ψ may become a rather useful probe for judging the validity of model particle-particle interaction potentials, a point that we exemplify below, after briefly summarizing the results of the theory for the LJP in the continuum-solvent approximation.

The liquid junction potential is given by [46]

$$\Psi = \frac{4\pi e}{\epsilon_0} \left\{ \frac{\tilde{\chi}_{e\mu}(k)}{k^2} \right\}_{k=0} \frac{\Delta\mu_s}{F} , \qquad (13)$$

where $\Delta\mu_s$ is the difference in the chemical potential (molar units) of the salt at points far from the junction and F is the Faraday constant. Moreover $\tilde{\chi}_{e\mu}(k)$ is the three dimeensional Fourier transform of the
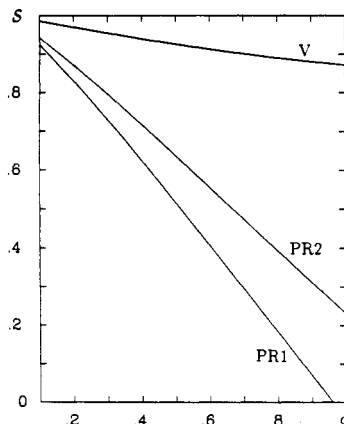
Fig. 6. The correction factor for the LJP calculated for several models described in the text as a function of the molar concentration of NaCl at the final equilibrium state.

charge susceptibility $\tilde{\chi}_{e\mu}(r)$. The latter depends linearly on the transport numbers of the cation and anion constituents and on the mean charge density functions at a distance r from a central ion of species α

$$H_\alpha(r) \equiv z_+\rho_+\, h_{\alpha+}(r) \,+\, z_-\rho_-\, h_{\alpha-}(r) \qquad , \quad \alpha = +,- \ . \tag{14}$$

The correlation functions $h_{\alpha\beta}(r)$ are evaluated at the concentration of the final equilibrium state of the junction; a consequence of the linear character of the theory. The linear relation between $\tilde{\chi}_{e\mu}(k)$ and the $\tilde{H}_\alpha(k)$ implies that $\{\tilde{\chi}_{e\mu}(k)/k^2\}_{k=0}$ is linearly related to the single-ion second moment coefficients

$$H_\alpha^{(2)} \,=\, -\frac{4\pi}{6}\int_0^\infty dr\, r^4\, H_\alpha(r) \ . \tag{15}$$

Unlike the global second moment condition $S^{(2)} = z_+\rho_+H_+^{(2)} + z_-\rho_-H_-^{(2)}$ [10], the single-ion second moment coefficients depend not only on the long range coulombic interactions, but also on the specific short range interactions [49]. This dependence is effected through the functions

$$C_\alpha^{\text{s}} \,\equiv\, \rho_+\, \tilde{c}_{+\alpha}^{\text{s}}(0) \,+\, \rho_-\, \tilde{c}_{-\alpha}^{\text{s}}(0) \ , \tag{16}$$

where $\tilde{c}_{\beta\alpha}^{\text{s}}(0)$ is the $k = 0$ value of the Fourier transform of the short range part of the ion-ion direct correlation function. In terms of this result for the single-ion second moment coefficients, the expression that we obtain for the LJP is

$$\Psi \,=\, \Psi^{\text{L}}\mathcal{S} \ , \tag{17}$$

where the quantity Ψ^{L} arises from the contributions of the long range coulombic interactions to the single-ion second moment coefficients

$$\Psi^{\text{L}} \,=\, \frac{\nu RT}{F}\,\frac{z_+t_- + z_-t_+}{z_+^2\nu_+ + z_-^2\nu_-}\,\ln\frac{a_\pm(+\infty)}{a_\pm(-\infty)} \ , \tag{18}$$

in which $\nu = \nu_+ + \nu_-$, R is the gas constant and T is the absolute temperature. Furthermore the $a_\pm$ are the mean activities of the electrolyte at points far from the junction. Ψ^{L} given by Eq. (18) is the expression derived by MacInnes [50] from the classical expression for the diffusion potential by assuming that $a_+ = a_- = a_\pm$ holds for the single-ion activities. Henderson's equation [50] follows as a further approximation to this expression.

But according to our theory (continuum-solvent approximation) there is still another contribution to Ψ which is due to the specific short range ion-ion interactions. It is expressed by the correction factor

$$\mathcal{S} \,=\, 1 + \frac{\Delta^{\text{s}}}{z_+t_- + z_-t_+} \ , \tag{19}$$

in Eq. (17). Here Δ^{s} is a functional of the C_α^{s} which were defined above

$$\Delta^{\text{s}} \,=\, \frac{z_+y_-C_+^{\text{s}} \,+\, z_-y_+C_-^{\text{s}}}{1 - (y_+C_-^{\text{s}} + y_-C_+^{\text{s}})} \ . \tag{20}$$

where y_α is the ionic strength fraction of the ionic species α in the solution in the final equilibrium state.

In Fig. 6 we show $\mathcal{S}$ as a function of the molar concentration for NaCl(aq) according to the vanilla model and the two Pettitt-Rossky models in Fig. 4. These results are interesting because they suggest the LJP, or rather the factor $\mathcal{S}$, as a sensitive measure for probing the soundness of ion-ion solvent averaged pair potential models. The factor indicates a 10% correction to the classical formula Eq. (18) for the vanilla model at 1M. The correction is about 100% for the PR models, being negative for the PR1 model at 1M. This is in contrast with the view (always valid for 1-1 electrolytes) that the faster ions (Cl$^-$) move ahead of the slower ions (Na$^+$) so the dilute side of the junction accumulates a negative charge, as indicated by experiment [50].

THE DIMER OF AQUEOUS CHLORIDE ION

Here we review our results obtained by various tests of whether the PR model for $\bar{u}_{--}(r)$ in aqueous NaCl is realistic.

The analysis of the $\bar{G}_{Cl}(r)$ data is not consistent with Cl_2^{2-} being an important aqueous species. Basically this conclusion depends on the evidence that the geometric arrangement of water around chloride ions is independent of both concentration and counterion [1,13,16,51] (within certain limits) and on the 3.5Å Cl^--Cl^- distance being incompatible with the Cl^- hydration structure revealed by $\bar{G}_{Cl}(r)$.

The experimental osmotic coefficient, conductivity, D_+^s, D_-^s, D_{++}^d and D_{+-}^d are consistent with the PR model in the sense that it fits the experimental data about as well as the vanilla model (the situation changes when mixtures are considered). But D_{--}^d for the PR model is highly unrealistic in the way one would expect if strong Cl^--Cl^- dimerization were present. This effect is absent in the vanilla model, which shows a much better agreement with experiment.

The calculated LJP for the vanilla model is in the range that is consistent with the experimental data. This is not really a very strong claim since the experimental LJP is not known with precision. However the LJP calculated for the PR model strongly deviates from the classical results, as would be expected for a model with strong specific Cl^--Cl^- interactions. At high concentration the PR model predicts that a liquid junction between two concentrated NaCl solutions would charge in the way opposite to that observed in experiment.

Presumably improvements in the BO level model would raise $\bar{u}_{--}$ by $k_B T$ or more, until it is no longer negative. Nothing we have found in the present work suggests that PR models modified in this way would still be unrealistic.

It is interesting to speculate on the source of the error in $\bar{u}_{--}(r)$ for the aqueous chloride pair. It cannot be the extended RISM theory applied by Pettitt and Rossky to the BO model because MD simulations [52] confirm the integral equation results in a very satisfactory way. Therefore the error must come from the models used as input to their theory. It would not be surprising if the error came from the absence of electronic polarizability in the model Cl^-, as suggested by calculations by Foresman and Brooks [53], leading to substantial deviations from pairwise additivity.

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