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On the influence of molecular structure on the conductivity of electrolyte solutions — sodium nitrate in water*

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Theoretical calculations of the conductivity of sodium nitrate in water are presented and compared with experimental measurements. The method of direct correlation force in the framework of the interionic theory is used for the calculation of transport properties in connection with the associative mean spherical approximation (AMSA). The effective interactions between ions in solutions are derived with the help of Monte Carlo and Molecular Dynamics calculations on the Born–Oppenheimer level. This work is based on earlier theoretical and experimental studies of the structure of concentrated aqueous sodium nitrate solutions.

Key words: *electrolytes, aqueous sodium nitrate, structural and transport properties, conductance*

PACS: *05.70.Ln, 61.20.Ja, 61.20.Gy, 61.20.Lc, 77.22-d, 82.45.Gj*

1. Introduction

Over the years a fruitful collaboration with my old friend Myroslav Holovko was devoted to the study of liquids and solutions using the methods of Theoretical Physics, the Statistical Mechanics of many body systems. There are not so many places in the world, where this can be done with the same power and inspiration as in the Institute of Condensed Matter Physics in Lviv, Ukraine, and an early sign of this kind of research is the famous book by Ihor Yukhnovsky and Myroslav Holovko "Statistical Theory of Classical Equilibrium Systems" [1] which appeared over 30 years ago in the former Soviet Union (which was perhaps the reason, that it was never translated into English). One of the most interesting goals already in those times was to study the classical systems of charged particles, and the collective coordinate description derived for these systems provided an important basis for the treatment of chemical subjects such as electrolyte solutions. Electrolyte solutions are always around us in everyday life. They govern biochemical processes in living cells, being essential in many kinds of technological processes. Studying the different properties of these systems by experimental and theoretical methods is important in order to taylor useful solvents for practical goals [2]. Concentrated sodium nitrate solutions in water at ambient pressure and 25°C belong to the systems for which very different structural and dynamical properties were derived from measurements. We have recently contributed to these studies by neutron- and x-ray diffraction measurements for a set of four different $NaNO_3$ solutions [22]. Structural information gained from the diffraction experiments is supported by computer simulations and from many body theory. Dynamical properties of electrolyte solutions (diffusion coefficients, conductivity, dielectric relaxation spectra) are also derived from measurements, simulations and theoretical considerations.

Molecular Dynamics (MD) simulations on Born–Oppenheimer (BO) level were performed using the DLPOLY–MD code from Daresbury [23]. We also made Monte Carlo (MC) simulations with the help of the program system MCFLUID, developed by our group [9], to compare the structural correlation functions

*Dedicated to Prof. Dr. Myroslav Holovko on the occasion of his 70$^{\text{th}}$ birthday
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with the results of the diffraction measurements. The simulations gave us the spatial distribution functions for pairs of interacting sites of various components of the solution. Various data allowed us to refine our structural picture and the potential parameters of our model as well. From the simulation we also derived the values for the dielectric constants of the solutions, which can be compared with experimental values, e.g., from dielectric relaxation measurements [26]. The decrease of the dielectric constant of the solution with an increasing solute concentration gives a hint of ion association.

The MD simulations give us also the values for the self-diffusion constants D_i, $(i=+,-)$ of the ions in the concentrated solutions. These diffusion constants of the ions can be compared with the measured values. They also allow us to estimate an approximate value of the specific electrolytic conductivity σ via the Nernst–Einstein equation [2, 20]:

$$\sigma^{\mathrm{NE}}(c) = \frac{e^2}{k_{\mathrm{B}}T}\left[\rho_+ z_+^2 D_+(c) + \rho_- z_-^2 D_-(c)\right], \qquad (1)$$

where k_{B} is the Boltzmann constant, T the temperature, $\rho_i = N_A c_i$ are the number densities of the ions, c_i the corresponding concentrations, and $e_i = z_i e$ are the ionic charges. The equation (1) is correct in the case of infinite diluted solutions ($c_i \to 0$). On the other hand, new theoretical and experimental studies of ionic liquids, which can be seen as limiting cases of concentrated electrolyte solutions, show that the Nernst–Einstein equation is valid for these systems in the case of cross correlations between the moving ions being negligible. We study its approximate use for our concentrated solutions and compare it with the measured values of the equivalent conductivity of concentrated aqueous sodium nitrate solutions.

On the other hand, conductivity belongs to the excess properties of ionic solutions with respect to infinite dilution, such as osmotic pressure or mean activity coefficients. These quantities can be calculated by means of Statistical Mechanics from the effective ionic interactions [the ion–ion potentials of mean forces (pmf) at infinite dilutions] in the framework of the so-called interionic theory. According to such a description, the ions are considered to be structured particles interacting by effective (average) forces and moving in a structureless solvent. The solvent is solely characterized by macroscopic parameters such as viscosity η, dielectric constant ε_r and mobilities ζ_i of the ions. This corresponds to a transition from the so-called Born–Oppenheimer (BO) level of the solution, where all molecules and ions are treated on equal footing, to a solvent-averaged or McMillan–Mayer (MM) level, in which only the ions are the subjects of a statistical description [2, 18].

The introduction of a chemical picture makes it possible to consider the ion association on the MM level. Ion pairs are introduced as a new species, and the interactions between free ions and the pairs have to be specified accordingly. The reduction to the MM level and to a chemical picture considerably simplifies the statistical mechanical calculations. It allows us to calculate the properties of not excessively concentrated electrolyte systems starting with the model of charged particles and interacting with essentially weak Coulomb interactions. However, having a fine structure of the interaction of solvated ions (the ion–ion pmfs in infinite dilution), one has to start with the BO level. We have recently made such a study for the solution of sodium chloride in water-1,4-dioxane mixtures [21], and we continue with the consideration of sodium nitrate in water in this article. For this system we have compared the structural properties derived from x-ray and neutron diffraction measurements with the theoretical predictions from molecular models for solvent and soluted ions [22].

2. Computer simulations

The interaction of the molecule sites are modelled with a 12–6–1 Lennard-Jones–Coulomb potential. For water we used the well known simple SPC/E model of Berendsen et al. [8]. For alkali ions we used, as in the paper [21], the model potentials of Palinkas et al. [7]. For the nitrate ion we used the values given in [22]. In addition to the MD simulations for the four solutions studied in [22] we have also performed MD and MC simulations of aqueous sodium nitrate solutions with concentrations of $c = 0.65$ mol·dm^{-3} [24] and of $c = 6.67$ mol·dm^{-3} [25].

Pair correlation functions, energies and other structural quantities were calculated for the model systems, and we found a satisfactory agreement with the structural information derived from x-ray and from neutron diffraction measurements for the real solutions [22]. In addition to the correlation functions presented in [22] here we show our results for the ion–ion correlations from MD and MC simulations for six solutions of different concentrations. In the case of molecular ions, we consider every atom of the NO_3-ion to be one site with a partial charge.

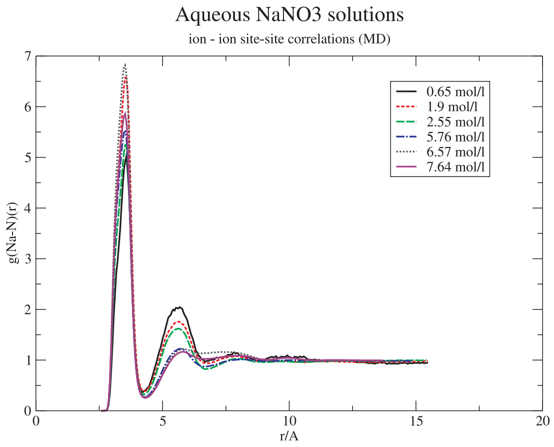


Figure 1. (Color online) Cation–anion pair correlations $g_{\mathrm{Na-N}}(r)$ for six different solutions from MD simulations (see text for a discussion).

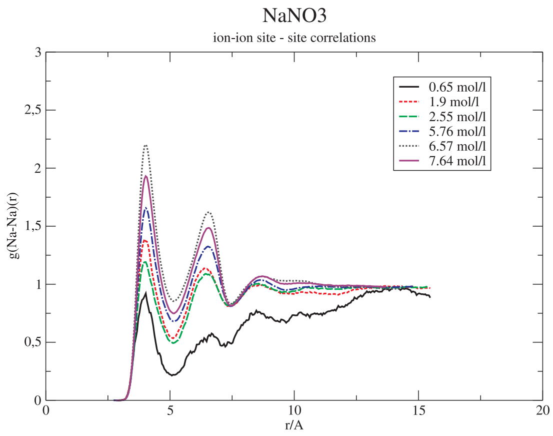


Figure 2. (Color online) Cation–cation pair correlations $g_{\mathrm{Na-Na}}(r)$ for six different solutions from MD simulations.

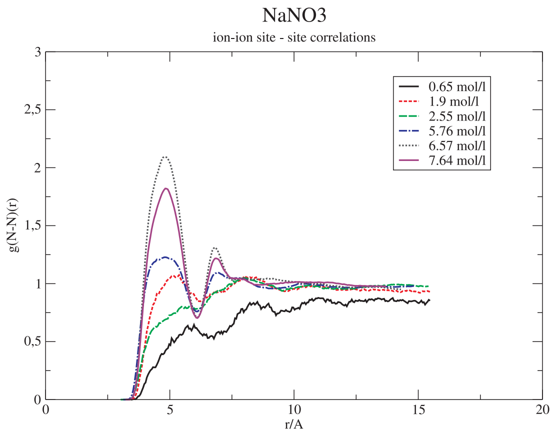


Figure 3. (Color online) Anion–anion pair correlations $g_{\mathrm{N-N}}(r)$ for six different solutions from MD simulations.

Due to the symmetry of the nitrate potential model, figures 1–3 also represent the center–center correlations $g_{ij}(r)$, $(i=+,-)$, of the ions in the solutions. From these correlations the corresponding ion-ion potentials of the mean forces (pmf's) $W_{ij}(r)$ are derived:

$$W_{ij}(r) = -k_{\mathrm{B}}T\ln\left[g_{ij}(r)\right]. \tag{2}$$

These functions show a great manifold of structures. This can be seen from figure 4, where the MC and MD simulations for the ion–ion pmf's in a 5.76 molar sodium nitrate solution are compared.

There are regions of additional attractions as well as repulsions between the ions, while in the overlap range of the solvation shells specific interactions occur, which will be referred to as solvation potentials. However, it is clear that the long range parts of the effective interactions between the ions will be of screened Coulomb- or Debye-type in dilute solutions, i.e., of Coulomb-type in the infinite dilution, with the dielectric constant ε_r of the solvent

$$\lim_{r\to\infty,c\to 0} W_{ij}(r) \to W_{ij}^{\infty,\mathrm{Coul}}(r) = \frac{z_i z_j e^2}{4\pi\varepsilon_0\varepsilon_r r}.$$

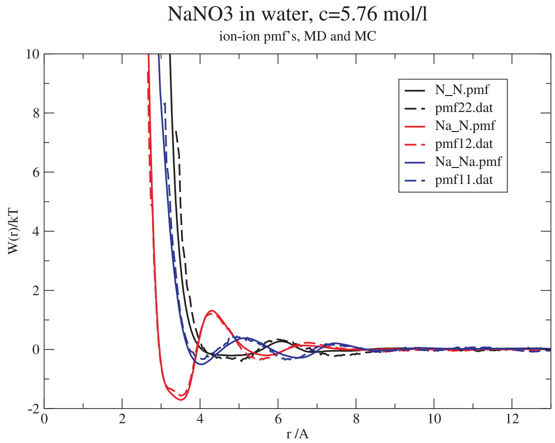


Figure 4. (Color online) Potentials of mean forces between ions in a 5.76 molar aqueous sodium nitrate solution from MD simulations (full lines) and from MC calculations (broken lines).

The short range parts of the effective ionic interactions result from the overlap of solvation shells. This effect depends only very weakly on the concentration of the solution, as can be seen in figures 1–3, which show the ion–ion pair correlation functions for the six solutions studied between 0.65 and 7.5 mol/l. The first maximum in the (+−) pair correlation function, and hence the first minimum of the corresponding pmfs, is always in the neighbourhood of 3.5 Å, nearly independent of the concentration of the ions. This will be helpful in constructing simplified effective ionic interactions for the calculation of conductance in the framework of the solvent averaged McMillan–Mayer theory.

The mean excess internal energies $U^{\text{ex}} = -E^{\text{C}}$ as well as the solvation energies of cations and anions calculated from the MC simulations are shown in table 1 for five of the systems studied.

Table 1. Internal excess and solvation energies in aqueous sodium nitrate solutions (from MC simulations).

System	Eex[kJ/mol]	E(Cation.Solv.)	E(Anion.Solv.)
1 ($c = 7.64$)	–132.92	–169.54	–167.55
2 ($c = 6.67$)	–120.54	–186.46	–169.85
3 ($c = 5.76$)	–111.30	–215.66	–194.85
4 ($c = 2.55$)	–75.76	–313.03	–307.72
5 ($c = 1.9$)	–68.16	–382.24	–347.22

In figure 5 the self-diffusion coefficients from our MD simulations are shown for the solvent water and for the sodium and nitrate ions for the six systems studied.

The concentration dependence of the self-diffusion coefficients is very similar to other concentrated aqueous ionic systems [24]. Using the Nernst–Hartley formula [2],

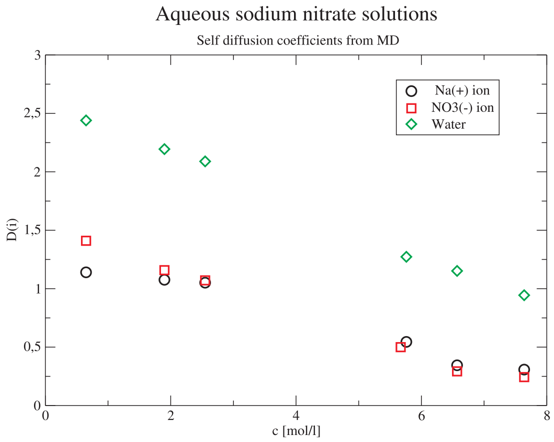
$$D_{\text{NH}}^{\infty} = \frac{D_{+}^{\infty} D_{-}^{\infty} (q_{+}^{2} + q_{-}^{2})}{q_{+}^{2} D_{+}^{\infty} + q_{-}^{2} D_{-}^{\infty}}, \qquad q_i^2 = \frac{z_i^2 e^2}{\varepsilon_0 \varepsilon_r k_{\text{B}} T} N_A c_i, \tag{3}$$

which is valid for the limiting values of the diffusion coefficients as an approximate description for the chemical diffusion coefficient D in the concentrated solution,

$$D_{\text{NH}}(c) = \frac{2D_{+}(c) D_{-}(c)}{D_{+}(c) + D_{-}(c)}, \qquad q_{+}^{2} = q_{-}^{2} \tag{4}$$

one finds the situation depicted in figure 6.

The experimental values are from [27]. As can be seen from the figure, one has the situation, where the D_{NH} are not a good approximation for the chemical diffusion coefficients at higher concentrations.



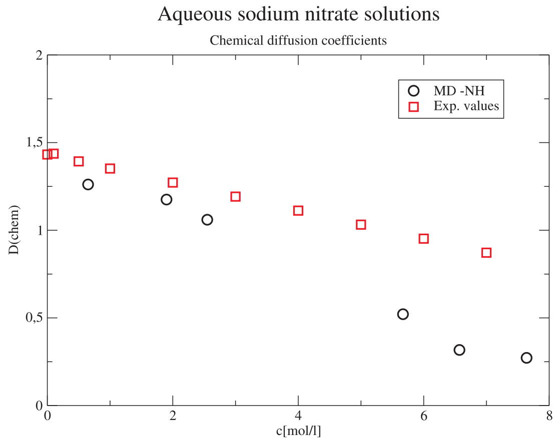


Figure 5. (Color online) Self-diffusion coefficients of water (diamonds), of Na^+-ions (circles) and NO_3^--ions (squares) in the solutions (MD simulations).

Figure 6. (Color online) Chemical diffusion coefficients in aqueous sodium nitrate solutions (squares) and Nernst–Hartley diffusion coefficients from MD simulations (circles).

Are there ion pairs in the concentrated sodium nitrate solutions? Our simulations really show decreasing dielectric constants for the higher concentrated solutions, which is in agreement with the experimental data [26]. This is depicted in figure 7, where the concentration dependent dielectric constants for aqueous sodium nitrate solutions are shown, [26], together with our MD simulation values [22, 24, 25]. Thus, the idea of ion association due to Coulomb forces arises, and a simplified theoretical description in the framework of the interionic theory should consider this aspect.

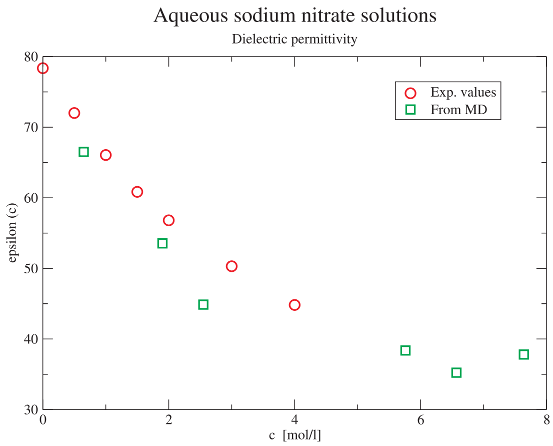


Figure 7. (Color online) Concentration dependent dielectric constants of aqueous sodium nitrate solutions: circles — experimental values; squares — from MD simulations.

A comparison of the molar conductance $\Lambda_{\mathrm{NE}}(c)$, derived from the MD self-diffusion coefficients according to equation (1) and the relation

$$\Lambda_{\mathrm{NE}}(c) = \frac{\sigma_{\mathrm{NE}}(c)}{c}\,, \qquad \Lambda_{\mathrm{NE}}^{\infty} = \lim_{c\to 0} \Lambda_{\mathrm{NE}}(c) \tag{5}$$

with the experimental values of the conductance of the concentrated solutions from [27] are shown in figure 8.

We see, that in the case of very concentrated solutions, a situation similar to the molten salt or ionic liquid case occurs. It has been shown, that the Nernst–Einstein equation (1) is a good approximation for

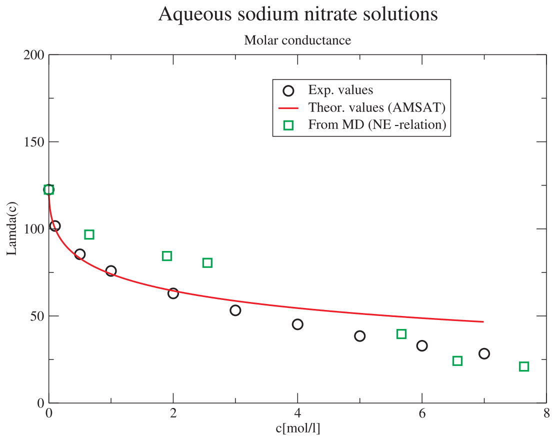


Figure 8. (Color online) Molar conductance of sodium nitrate solution: Circles: experimental values; Line: theoretical calculation from the AMSA theory for transport with R=3.5 Å; Squares: Results from MD-diffusion coefficients via the Nernst–Einstein equation.

the conductivity of some systems [28–30]. The correct conductivity formula is given by [20]

$$\sigma^{\mathrm{NE}}(c) = \frac{1}{k_{\mathrm{B}}T}\sum_i \rho_i z_i^2 D_i(c)[1-\Delta(c)]. \tag{6}$$

If $\Delta(c)$ is not zero, cross correlations between the ions become important. If the ratio between the experimental value of σ and the conductivity calculated from the Nernst–Einstein equation is smaller than unity, then a significant fraction of oppositely charged ions is assumed to move together in the time scale of diffusive motion [29]. $\Delta(c) > 0$ means, that the movement of an ion pair in the same direction contributes to the self-diffusion, rather than to the electric current [20].

With simplified interaction models for the ions, e.g., with the approximation that the N-particle potential of the mean force of the ions at infinite dilution $W_N^{\infty}(\mathbf{r}^N)$ is written as a sum of pair interactions

$$W_N^{\infty}(\mathbf{r}^N) = \sum_{i<j} W_{ij}^{\infty}(\mathbf{r}_i, \mathbf{r}_j) \tag{7}$$

one is able to create a transport theory for electrolytes, which contains elements of statistical mechanics and phenomenological hydrodynamics in the sense of the classical works by Debye, Onsager, Falkenhagen and others, see e.g., [12, 13]. One can further assume that ions associate into neutral pairs

$$C^{z_+} + A^{z_-} \Rightarrow [C^{z_+}A^{z_-}]^o \tag{8}$$

and that a mass action law governs the concentration of free ions defining a degree of dissociation α.

The theory has been published in full in the textbook by Barthel et al. [2]. We have recapitulated it and added some features concerning the effect of ion association on equilibrium and transport properties of electrolytes in systems with low dielectric constants in a recent article [21], so we will recapitulate it here only in a short form in the appendix.

The impressive feature of this approach is that a simple potential model of charged hard spheres in a continuum

$$W_{ij}^{\infty}(r) = \frac{z_i z_j e^2}{4\pi\varepsilon_0\varepsilon_r r}, \qquad r > R, \tag{9}$$

$$W_{ij}^{\infty}(r) = \infty, \qquad r \leqslant R \tag{10}$$

can be used for the free ions, which gives analytical results for the transport properties in the framework of the Mean Spherical Approximation for Transport (MSAT) [15, 16, 33] and of the Associative Mean Spherical Approximation (AMSA) [3–5, 17, 31, 32, 34]. The inclusion of a mass action law (MAL) into the transport theory is also briefly discussed in the appendix.

We have made calculations according to the AMSA theory for transport of various aqueous sodium nitrate solutions. The input parameters are the friction coefficients of the ions in water ζ_i, which also define the single ion conductivities at infinite dilution λ_i^∞, the viscosity of water η and its dielectric constant ε_r.

Beside these parameters, the distance of the closest approach R between free ions is the only parameter in this theory. From the diffraction experiments and our simulation results described in figures 1–4 we see that the value of $R = 3.50$ Å is the value of the closest approach for Na^+- and NO_3^--ions in our solutions. The degree of dissociation $\alpha(c)$ is calculated from these input parameters in the framework of the AMSA theory (see Appendix). The result is shown in figure 9.

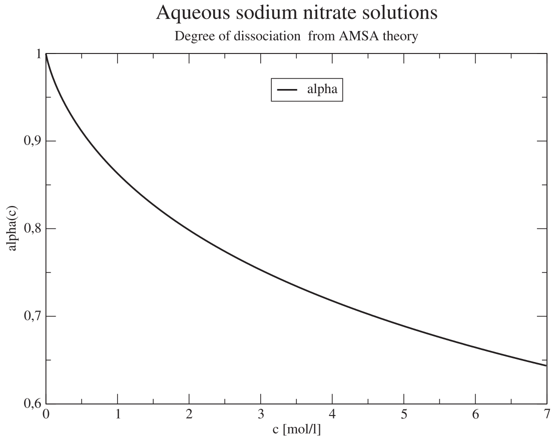


Figure 9. Concentration dependent degree of dissociation of aqueous sodium nitrate solution (from the AMSA theory).

$\alpha(c)$ decreases in the solutions of higher concentrations. Therefore, the calculation of the conductance including association is appropriate. Then, we get the molar conductance Λ as

$$\Lambda = \alpha\Lambda^\infty [(1 + S_1(\alpha) + S_2(\alpha) + S_3(\alpha) + S_4(\alpha)] \tag{11}$$

with the S functions given in [2, 16, 17, 21].

With these data, the experimental molar conductivity can be described up to concentrations of several moles per liter, as can be seen in figure 8, where the experimental values from [27] are compared with the theoretical predictions from the AMSAT theory.

3. Conclusions

The design of special electrolytes for a wide variety of applications is an important goal. Physical and chemical properties of such systems are studied by a variety of experimental and theoretical methods. The combination of simulations, experiment and theory reduces the number of free parameters used for explaining the conductivity data in the solvent. The estimation of the conductance of sodium nitrate in water is one further example for this kind of studies.

A theory based on a very simple potential model with only one parameter (the distance R, which can be approached by free ions) is needed in solutions having no excessive concentrations to describe the molar conductivity of aqueous solutions of sodium nitrate. This parameter should be derived from the studies on the Born–Oppenheimer level, where all constituents of the solutions are treated on an equal level. For concentrated solutions, approximative values for the conductance — at least in our example studied — are derived from the Molecular Dynamics self-diffusion coefficients of the ions with the help of the Nernst–Einstein equation.

Acknowledgements

Most of the MD calculations were started by Emanuel Peter in the course of his diploma work several years ago. His contribution is greatly acknowledged.

Appendix — conductance on MM level

When an external force $\mathbf{F}_i^{\text{ext}}$ caused by a homogeneous electric field $\mathbf{E}$

$$\mathbf{F}_i^{\text{ext}} = e_i \mathbf{E} \tag{12}$$

acts on ions in a solution, their one-particle flow $\mathbf{J}_i$ yields Ohm's law for the current density $\mathbf{j}$:

$$\mathbf{j} = \sum_i e_i \mathbf{J}_i = \sigma \mathbf{E}. \tag{13}$$

The equation for the one-particle flow $\mathbf{J}_i(\mathbf{r}_1)$ with $\rho_i = N_i/V$ as the number density of species i is

$$\mathbf{J}_i(\mathbf{r}_1) = \frac{\rho_i}{\zeta_i}\left[\mathbf{F}_i^{\text{ext}}(\mathbf{r}_1) + \mathbf{F}_i^{\text{rel}}(\mathbf{r}_1) + \mathbf{F}_i^{\text{el}}(\mathbf{r}_1)\right] = \frac{\rho_i}{\zeta_i}\mathbf{F}_i^{\text{tot}}(\mathbf{r}_1). \tag{14}$$

The total force acting on the ions is in the direction of the field $\mathbf{E}$:

$$\mathbf{F}_i^{\text{tot}} = F_i^{\text{tot}}\frac{\mathbf{E}}{E}, \qquad F_i^{\text{tot}} = e_i E + F_i^{\text{rel}} + F_i^{\text{el}}. \tag{15}$$

The specific conductivity σ is then expressed as

$$\sigma = \sum_i \frac{\rho_i e_i^2}{\zeta_i}\left[1 + \frac{F_i^{\text{rel}}}{e_i E} + \frac{F_i^{\text{el}}}{e_i E}\right]. \tag{16}$$

The additional forces in equation 14 are the relaxation force $\mathbf{F}_i^{\text{rel}}(\mathbf{r}_1)$ and the electrophoretic force $\mathbf{F}_i^{\text{el}}(\mathbf{r}_1)$. $\mathbf{F}_i^{\text{rel}}(\mathbf{r}_1)$ expresses the additional force acting on an ion of species i due to the asymmetry of the ion distribution around it. It is the average of the interaction force acting on ion i at $\mathbf{r}_1$ which is obtained by means of the pair distribution function $g_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ in the non-equilibrium case:

$$\mathbf{F}_i^{\text{rel}}(\mathbf{r}_1) = -\sum_j \rho_j \int \nabla_1 W_{ij}^{\infty}(\mathbf{r}_1,\mathbf{r}_2)\, g_{ij}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_2\,. \tag{17}$$

The pair distribution function has an equilibrium and a non-equilibrium part:

$$g_{ij}(\mathbf{r}_1,\mathbf{r}_2) = 1 + h_{ij}(\mathbf{r}_1,\mathbf{r}_2) = 1 + h_{ij}^{\text{eq}}(r) + h'_{ij}(\mathbf{r}_1,\mathbf{r}_2), \tag{18}$$

where $h'_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ corresponds to the *non-equilibrium contribution* of the total pair correlation function.

The electrophoretic force may be expressed as

$$\mathbf{F}_i^{\text{el}}(\mathbf{r}_1) = \zeta_i \sum_j \rho_j \int \mathsf{T}_{ij}(\mathbf{r}_1,\mathbf{r}_2)\cdot[e_j\mathbf{E} + \mathbf{K}_{ji}(\mathbf{r}_2,\mathbf{r}_1)]\, g_{ij}(\mathbf{r}_1,\mathbf{r}_2)]\, \mathrm{d}\mathbf{r}_2\,. \tag{19}$$

The electrophoretic or hydrodynamic interaction tensor $\mathsf{T}_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ is approximated by its long range part, the Oseen tensor, acting between ions i and j at locations $\mathbf{r}_m$ and $\mathbf{r}_n$:

$$\mathsf{T}_{ij}(\mathbf{r}_m,\mathbf{r}_n) = \frac{1}{8\pi\eta_0 r_{mn}}\left(\mathsf{I}_{ij} + \frac{\mathbf{r}_{mn}\mathbf{r}_{mn}}{r_{mn}^2}\right) \tag{20}$$

(I_{ij} is the unity tensor, $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$ and $\mathbf{r}_{mn}\mathbf{r}_{mn}$ is the dyadic product).

The mean interionic force $\mathbf{K}_{ij}$ between an ion of species i at $\mathbf{r}_1$ and an ion j at $\mathbf{r}_2$ is given by

$$\mathbf{K}_{ij}(\mathbf{r}_1,\mathbf{r}_2) = -\nabla_1 W_{ij}^{\infty}(\mathbf{r}_1,\mathbf{r}_2) - \sum_k \rho_k \int \nabla_1 W_{ik}^{\infty}(\mathbf{r}_1,\mathbf{r}_3) \frac{g_{ijk}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g_{ij}(\mathbf{r}_1,\mathbf{r}_2)} \mathrm{d}\mathbf{r}_3 . \tag{21}$$

In the stationary case $\operatorname{div}\mathbf{j} = 0$, Onsagers continuity equation for the pair distribution functions in the non-equilibrium situation is given by the expression [2]:

$$\nabla_1 \cdot \tilde{\mathbf{J}}_{ji}(\mathbf{r}_2,\mathbf{r}_1) + \nabla_2 \cdot \tilde{\mathbf{J}}_{ij}(\mathbf{r}_1,\mathbf{r}_2) = 0. \tag{22}$$

The reduced two particle flow

$$\tilde{\mathbf{J}}_{ij}(\mathbf{r}_2,\mathbf{r}_1) = \frac{1}{\zeta_i}\left[h_{ij}(\mathbf{r}_1,\mathbf{r}_2)\mathbf{F}_i^{\mathrm{tot}}(\mathbf{r}_1) + \mathbf{C}_{ij}(\mathbf{r}_1,\mathbf{r}_2) + \sum_k \rho_k \int \mathbf{C}_{ik}(\mathbf{r}_1,\mathbf{r}_3) h_{kj}(\mathbf{r}_3,\mathbf{r}_2)\mathrm{d}\mathbf{r}_3 - k_{\mathrm{B}} T \nabla_1 h_{ij}(\mathbf{r}_1,\mathbf{r}_2) \right] \tag{23}$$

contains a direct correlation force $\mathbf{C}_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ with an equilibrium and a non-equilibrium term:

$$\mathbf{C}_{ij}(\mathbf{r}_1,\mathbf{r}_2) = k_{\mathrm{B}} T \nabla_1 c_{ij}^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2) + \mathbf{C}'_{ij}(\mathbf{r}_1,\mathbf{r}_2). \tag{24}$$

A corresponding equation is valid for $\tilde{\mathbf{J}}_{ji}(\mathbf{r}_2,\mathbf{r}_1)$ [19].

At equilibrium, the flows $\tilde{\mathbf{J}}_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ and forces $\mathbf{F}_i^{\mathrm{tot}}(\mathbf{r}_1)$ vanish and equation 23 reduces to the usual OZ equation.

$\mathbf{C}'_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ or, equivalently, the non-equilibrium part of the total correlation function, $h'_{ij}(\mathbf{r}_1,\mathbf{r}_2) = h_{ij}(\mathbf{r}_1,\mathbf{r}_2) - h_{ij}^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2)$ must now be calculated.

For binary electrolytes, $(i,j = +,-)$, the symmetry relations in the linear approximations in $\mathbf{E}$ lead to $\mathbf{C}'_{ii}(\mathbf{r}) = \mathbf{0}$ and $h'_{ii}(\mathbf{r}) = 0$. Also $\mathbf{C}'_{-+}(\mathbf{r},\mathbf{E}) = -\mathbf{C}'_{+-}(-\mathbf{r},\mathbf{E})$ and $h'_{-+}(\mathbf{r},\mathbf{E}) = h'_{+-}(-\mathbf{r},\mathbf{E})$.

After a Fourier transformation according to

$$\hat{f}(\mathbf{q}) = \int \exp(i\mathbf{q}\cdot\mathbf{r}) f(\mathbf{r})\mathrm{d}\mathbf{r} \tag{25}$$

of the continuity equation, a relation for $\hat{h}'_{+-}(\mathbf{q}) = \hat{h}'_{+-}(q,\theta')$ results in the $\mathbf{q}$-space

$$\begin{aligned} \hat{h}'_{+-}(q,\theta') \quad = \quad & \frac{-\mathrm{i}(w_{+-}F_+^{\mathrm{tot}} - w_{-+}F_-^{\mathrm{tot}})\,\hat{h}_{+-}^{\mathrm{eq}}(q)}{k_{\mathrm{B}} T q[1 - \rho_+ w_{+-}\hat{c}_{++}^{\mathrm{eq}}(q) - \rho_- w_{-+}\hat{c}_{--}^{\mathrm{eq}}(q)]}\cos\theta' \\ & - \frac{\mathrm{i}[1 + \rho_+ w_{-+}\hat{h}_{++}^{\mathrm{eq}}(q) + \rho_- w_{+-}\hat{h}_{--}^{\mathrm{eq}}(q)]}{k_{\mathrm{B}} T q^2[1 - \rho_+ w_{+-}\hat{c}_{++}^{\mathrm{eq}}(q) - \rho_- w_{-+}\hat{c}_{--}^{\mathrm{eq}}(q)]}\mathbf{q}\cdot\hat{\mathbf{C}}'_{+-}(\mathbf{q}). \end{aligned} \tag{26}$$

To derive equation (26), one has to consider the relations between the vectors $\mathbf{E}$, $\mathbf{r}$ and $\mathbf{q}$. One has

$$\frac{\mathbf{r}\cdot\mathbf{E}}{rE} = \cos\theta. \tag{27}$$

Then, the non-equilibrium term $h'_{ij}(r,\theta)$ of the total correlation function can be formulated as

$$h'_{ij}(r,\theta) = \mu_{ij}\, y(r)\cos\theta, \qquad \mu_{ij} = \frac{1}{k_{\mathrm{B}} T}\left(w_{ij}F_i^{\mathrm{tot}} - w_{ji}F_j^{\mathrm{tot}}\right) \tag{28}$$

with the radial part $y(r)$ and w_{ij} defined as

$$w_{ij} = \frac{1}{\zeta_i}\left[\frac{1}{\zeta_i} + \frac{1}{\zeta_j}\right]^{-1}, \qquad w_{ji} = \frac{1}{\zeta_j}\left[\frac{1}{\zeta_i} + \frac{1}{\zeta_j}\right]^{-1}. \tag{29}$$

The three-dimensional Fourier transform of $h'_{ij}(\mathbf{r})$ is denoted by $\hat{h}'_{ij}(\mathbf{q})$ and given by

$$\hat{h}'_{ij}(\mathbf{q}) = \hat{h}'_{ij}(q,\theta') = \mathrm{i}q\mu_{ij}\omega(q)\cos\theta' \tag{30}$$

with the help of function $\omega(q)$ containing the q-dependent part of the transformed nonequilibrium pair correlation function $\hat{h}'_{ij}(\mathbf{q})$. The angle θ' in $\mathbf{q}$-space is defined by

$$\frac{\mathbf{q}\cdot\mathbf{E}}{qE} = \cos\theta'. \tag{31}$$

Due to the angular dependence expressed in equations (28) and (31), one finds for the function $\omega(q)$ defined in equation (30)

$$\omega(q) = -4\pi\frac{1}{q}\frac{\mathrm{d}}{\mathrm{d}q}\left[\int\limits_0^\infty \frac{\sin qr}{qr} y(r)\, r\,\mathrm{d}r\right]. \tag{32}$$

The back transformation of this function yields for the radial part $y(r)$ of $h'_{ij}(r,\theta)$, equation (28):

$$y(r) = \frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{1}{2\pi^2}\int\limits_0^\infty \frac{\sin qr}{qr}\omega(q)\, q^2\mathrm{d}q\right] = \frac{\mathrm{d}}{\mathrm{d}r}\omega(r). \tag{33}$$

As in the case of the equilibrium OZ equation, the second relation between h_{ij} and $\mathbf{C}_{ij}$ is needed to calculate the correlation functions. A non-equilibrium analogue for the HNC closure is [18, 19]

$$\mathbf{C}_{ij}(\mathbf{r}_1,\mathbf{r}_2) = \left[-\nabla_1 W_{ij}^\infty(\mathbf{r}_1,\mathbf{r}_2)\right] g_{ij}(\mathbf{r}_1,\mathbf{r}_2) + h_{ij}(\mathbf{r}_1,\mathbf{r}_2)\sum_k \rho_k \int \mathbf{C}_{ik}(\mathbf{r}_1,\mathbf{r}_3)\, h_{kj}(\mathbf{r}_3,\mathbf{r}_2)\mathrm{d}\mathbf{r}_3 . \tag{34}$$

A simplified closure relation for the nonequilibrium part of the direct correlation force is

$$\mathbf{C}'_{+-}(\mathbf{r}) = -h'_{+-}(\mathbf{r})\nabla\left\{W_{+-}^\infty(r) - k_\mathrm{B}T[h_{+-}^{\mathrm{eq}}(r) - c_{+-}^{\mathrm{eq}}(r)]\right\}. \tag{35}$$

The system of equations equation (26) and equation (34) or equation (35) is solved by numerical methods for general ionic interactions $W_{ij}^\infty(r)$.

If the interaction is represented by that of charged hard spheres of equal diameter R, a natural boundary condition for the relative flows arises at the contact distance R

$$(\mathbf{r}_1 - \mathbf{r}_2)\cdot[\tilde{\mathbf{J}}_{ij}(\mathbf{r}_1,\mathbf{r}_2) - \tilde{\mathbf{J}}_{ji}(\mathbf{r}_2,\mathbf{r}_1)] = 0 \quad \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| = R. \tag{36}$$

Describing the equilibrium parts of the direct and total correlation functions in the Mean Spherical Approximation, one finds for the nonequilibrium contributions in the corresponding MSA conditions [19]:

$$\mathbf{C}'_{+-}(\mathbf{r}) = \mathbf{0} \tag{37}$$

and

$$h'_{+-}(\mathbf{r}) = 0, \qquad r \leqslant R. \tag{38}$$

Defining in the following equations the Debye parameter κ and the Bjerrum parameter b:

$$\kappa^2 = \frac{|z_+z_-|e^2(\rho_+ + \rho_-)}{\varepsilon_0\varepsilon_r k_\mathrm{B}T}, \qquad b = \frac{|z_+z_-|e^2}{4\pi\varepsilon_0\varepsilon_r k_\mathrm{B}TR} \tag{39}$$

in the framework of the Mean Spherical Approximation for Transport (MSAT) for the help function $\omega(r)$ one finds the result which assures the flow condition, equation (36) [15–17]:

$$\omega(r) = \frac{R^3}{2r}\left(b + \frac{1}{3}\right)\exp(-\kappa r) - \frac{1}{2\pi^2}\int\limits_0^\infty \frac{q}{r}\frac{\sin(qr)\, h_{+-}^{\mathrm{eq,MSA}}(q)}{(q^2 + 0.5\kappa^2)}\mathrm{d}q \tag{40}$$

$h_{+-}^{\mathrm{eq,MSA}}(q)$ is the Fourier transform of the equilibrium total correlation function of charged hard spheres in the MSA. With these results, the nonequilibrium pair correlation function $h_{+-}^{\mathrm{MSA}\prime}(r,\theta)$ is calculated as well as the relaxation and electrophoretic contributions to the conductivity.

The results for the MSAT conductance derived in [33, 34] are in agreement with the results by Ebeling and coworkers [15–17].

If it is assumed that the cations and anions form ion pairs, the density of the ionic species i splits into two parts, namely the density of free ions $\alpha\rho_i$, and the density of ion pairs $(1-\alpha)\rho_i$ [3–5, 31, 32] . They are connected by a mass action law (MAL) with Ebeling's mass action constant $K_{\mathrm{A}}^{\mathrm{E}}$ [11, 12] for ion association, which depends only on the ionic charges and the distance of the closest approach R — the ion diameter in the RPM:

$$\frac{1-\alpha}{\alpha^2} = cK_{\mathrm{A}}^{\mathrm{E}}\frac{(y'_\pm)^2}{y'_0}, \qquad K_{\mathrm{A}}^{\mathrm{E}} = 8\pi N_{\mathrm{A}} R^3 \sum_{m=2}^{\infty} \frac{b^{2m}}{(2m)!(2m-3)}\,. \tag{41}$$

In dilute solutions, the mean activity coefficients of the free ions, $y'_\pm$, and the activity coefficients of the ion pairs, y'_0, are substituted by their electrostatic contributions $y_\pm^{\mathrm{el}'}$ and to $y_0^{\mathrm{el}'}$. In the framework of the AMSA these quantities are given by

$$\ln(y_\pm^{\mathrm{el}'}) = -b\frac{\Gamma_{\mathrm{B}}R}{(1+\Gamma_{\mathrm{B}}R)}, \qquad \ln(y_0^{\mathrm{el}'}) = -b\frac{(\Gamma_{\mathrm{B}}R)^2}{(1+\Gamma_{\mathrm{B}}R)^2}\,. \tag{42}$$

In these equations, a new screening parameter Γ_{B} appears, which is connected with the Debye κ and the degree of dissociation α [35]:

$$4\Gamma_{\mathrm{B}}^2(1+\Gamma_{\mathrm{B}}R)^2 = \kappa^2\frac{(\alpha+\Gamma_{\mathrm{B}}R)}{(1+\Gamma_{\mathrm{B}}R)}\,. \tag{43}$$

Equations (41) to (43) are now combined to calculate the concentration dependent degree of dissociation $\alpha(c)$ for the system studied. For $R = 3.5$ Å, its value is given in figure 9.

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Про вплив молекулярної структури на провідність розчинів електролітів — нітрат натрію у воді

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Представлено теоретичні обчислення провідності нітрату натрію у воді, порівняні з експериментальними вимірюваннями. Метод прямої кореляційної сили в рамках міжіонної теорії використано для обчислення властивостей транспорту у зв'язку з асоціативним середньосферичним наближенням (AMSA). Ефективні взаємодії між іонами в розчинах отримані з обчислень методами Монте Карло і молекулярної динаміки на рівні Борна-Оппенгеймера. Ця робота базується на попередніх теоретичних і експериментальних дослідженнях структури концентрованих водних розчинів нітрату натрію.

Ключові слова: *електроліти, водний розчин нітрату натрію, структурні і транспортні властивості, провідність*