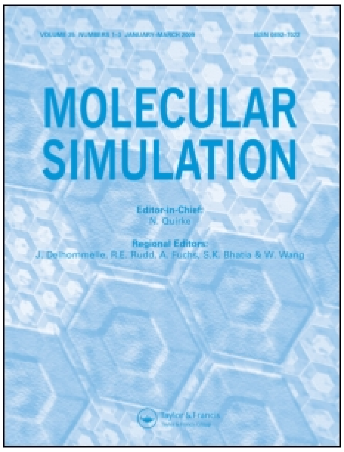

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Direct Calculation of the Electric Potential Distributions around Ions from High Precision Canonical Ensemble Monte Carlo Simulations of Some Primitive Model Electrolyte Systems

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To cite this Article Øsrensen, Torbens Smith(1993) 'Direct Calculation of the Electric Potential Distributions around Ions from High Precision Canonical Ensemble Monte Carlo Simulations of Some Primitive Model Electrolyte Systems', Molecular Simulation, 11: 5, 267 — 303

To link to this Article: DOI: 10.1080/08927029308022514

URL: http://dx.doi.org/10.1080/08927029308022514

Molecular Simulation, 1993, Vol. 11(5), pp. 267–303
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DIRECT CALCULATION OF THE ELECTRIC POTENTIAL DISTRIBUTIONS AROUND IONS FROM HIGH PRECISION CANONICAL ENSEMBLE MONTE CARLO SIMULATIONS OF SOME PRIMITIVE MODEL ELECTROLYTE SYSTEMS

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(Received February 1993, accepted February 1993)

The conditional electric potential around the ions are found by Poisson integration of the conditional charge densities calculated from the radial distribution functions found by the high precision canonical ensemble Monte Carlo simulations of some Z:Z,2:1 and 1:1:1 primitive model electrolyte systems described in earlier studies. In most cases, the correspondance with the solution given by solving the linear Poisson-Boltzmann equation is very nearly perfect - at least not too far from contact. This is so in spite of the fact, that the linearisation condition of Debye and Hückel is violated near to contact in dilute solutions and in spite of the anticipation that the Debye-Hückel approximation should be of little relevance in more concentrated systems, where the Debye length is of the same order of magnitude as the ionic diameters. The linear Poisson-Boltzmann equation even continues to be of relevance in zones around ions of different sizes, where only part of the ions appearing in the solution should be able to come. This parallels the earlier finding, that - not too far from contact - the electric contribution to the potentials of mean force do also very closely follow the Debye-Hückel expressions (the DHX model). The present findings do not mean, that the Debye-Hückel expressions for the thermodynamic quantities are correct (except for low Bjerrum parameters). The surface potentials on the ions calculated by the Debye-Hückel approach are quite correct, but the classical charging procedures (Debye or Güntelberg) are not. The relative success of the DHX + hard sphere model is explained by the numerical fact, that the linear DH potential is a quite accurate »eigen-function« when used as potentials of mean forces in the Poisson integral operator.

KEY WORDS: Primitive model electrolytes, electric potential distribution, Debye-Hückel, DHX model, Monte Carlo

INTRODUCTION

Since the famous approach of Debye and Hückel to the treatment of the thermodynamics of electrolyte solutions [1] now found in every elementary textbook on electrochemistry, there has been much speculation about the validity of the approximations made - especially in connection with their application of the linearized Poisson-Boltzmann equation. Consequently, there is a continuous stream in the physico-chemical literature of papers concerning the nonlinear Poisson-Boltzmann equation in different situations and geometries as well as more rigorous statistical-mechanical integral equation solutions and Monte Carlo simulations. In some recent papers, I have explored the deviation of a multitude of thermodynamic parameters from the Debye-Hückel values in the dilute regime of the primitive electrolyte model [2–5] using refinements of the Monte Carlo techniques first initiated by Poirier [6] Vorontsov-Vel'yaminov *et al.* [7, 8], Card and Valleau [9] and Widom [10, 11]. It seems that nobody has attempted a direct calculation from MC radial distribution functions of the (conditional) electric potential around the ions (with the ion as a »central ion« placed in *Origo*). It should be mentioned, however, that in the very early MC paper of Poirier [6] – using very few ions and configurations – the potential was sampled directly as the mean electrostatic potential between the »moving« MC ions and certain points in space at equidistant intervals of separation from a given fixed ion. This method appears to be somewhat questionable, however. What about the singularities arising, when the center of one of the mobile ions comes arbitrarily close to one »measuring point«?

The purpose of the present paper is to demonstrate an alternative and more reliable route to direct calculation of the potential distribution around the ions, namely *Poisson integration* of the conditional space charge distribution found from the radial distribution functions (RDF's) of high precision canonical ensemble Monte Carlo calculations. A similar technique was used very recently in a paper concerning the ion and potential distribution of ions in charged, spherical micropores [12]. Like in the previous paper in *Molecular Simulation* [5], dilute Z:Z and 2:1 electrolyte systems and moderately concentrated 1:1 electrolyte mixtures with a common ion will be treated. It will be demonstrated, that the solution to the *linear* Poisson-Boltzmann equation is an excellent approximation to the MC electric potential *especially* close to contact, where the linearisation condition of Debye and Hückel is violated! The linear P.B. potential is *also* a very good approximation in moderately concentrated electrolyte mixed solutions in spite of the fact that the ion diameters and the Debye length are of the same size, so that the ions can hardly be sudposed to be »point particles« as supposed in the classical Gouy-Chapman-Debye-Hückel approach! These findings seem to match the findings in Reference [5], that the *electric* contributions to the *potentials of mean force* were also Debye-Hückel. This demonstration of the *unreasonable efficiency of the Debye-Hückel approach* might (with many reservations, see the discussion) be seen as an example of the »principle of unreasonable utility of asymptotic estimates« advocated by Stell in 1977 [13].

FORMULAE FOR DIRECT CALCULATION OF THE ELECTRIC POTENTIAL

The RDF's were sampled in the Canonical Ensemble Monte Carlo Metropolis Markov chain in the manner described in the »Appendix on Methodology« of Reference [5]. To evaluate the electric potential around a given »central ion« of species no. i, use is made of the following general solution of the equation of Poisson for any spherically symmetric charge distribution (see the »Appendix on Poisson integration« in the present paper):

$$\psi_i(r) - \psi_i(\infty) = (1/r)\int_{a_{i,\min}}^{r} s^2\,[\rho_{q,i}(s)/\varepsilon]\,ds + \int_{r}^{\infty} s\,[\rho_{q,i}(s)/\varepsilon]\,ds + q_i/(4\pi\varepsilon r) \tag{1}$$

The contact distance $a_{i,\min}$ is the *minimum* contact distance of the central ion against any of the other species present (including species no. i itself). Below this distance we have $\rho_{q,i}(r) = 0$. In Equation (1), q_i is the charge of the central ion and ε is the dielectric permittivity of the medium (assumed to be independent of the radial separation - r - in the primitive model).

Now, introduce the RDF's $g_{ij}(r)$:

$$\rho_{q,i}(r) = \sum_j z_j e_o \rho_{j,o} g_{ij}(r) \tag{2}$$

The valency and the bulk density of the j'th species is z_j, respectively $\rho_{j,o}$. The elementary charge is e_o. Introducing also the mean *contact distance*

$$a \equiv (1/n) \sum_j a_{jj} \tag{3}$$

(n being the number of different ionic species), the *dimensionless separation*

$$t \equiv r/a \tag{4}$$

the *reduced Bjerrum parameter* (λ_B is the *Bjerrum length)*

$$B_r \equiv e_o^2/(4\pi\varepsilon kTa) = \lambda_B/a \tag{5}$$

the dimensionless bulk densities

$$\rho_j^* \equiv a^3 \cdot \rho_{j,o} \tag{6}$$

the dimensionless *total* ion density ρ^* and $\psi_i(\infty) = 0$ into Equation (1) we obtain for a single z:z electrolyte (Bjerrum parameter $B \equiv z^2 B_r$):

$$z_i e_o \psi_i(t)/kT = +B/t + (1/2)(\kappa a)^2 \left\{ (1/t) \int_{t_{i,\min}}^{t} s^2 |g_{i+}(s) - g_{i-}(s)| ds + \int_t^\infty s \cdot |g_{i+}(s) - g_{i-}(s)| ds \right\} \tag{7}$$

$$\kappa a \equiv (4\pi B \rho^*)^{1/2} \qquad (z{:}z \text{ electrolytes}) \tag{8}$$

For a 2:1 electrolyte (with a doubly charged cation) one obtains:

$$e_o \psi_+(t)/kT = +2B_r/t + (1/3)(\kappa a)^2 \left\{ (1/t) \int_{t_{+,\min}}^{t} s^2 [g_{++}(s) - g_{+-}(s)] ds + \int_t^\infty s \cdot [g_{++}(s) - g_{+-}(s)] ds \right\} \tag{9}$$

$$e_o \psi_-(t)/kT = -B_r/t + (1/3)(\kappa a)^2 \left\{ (1/t) \int_{t_{-,\min}}^{t} s^2 [g_{-+}(s) - g_{--}(s)] ds + \int_t^\infty s \cdot [g_{-+}(s) - g_{--}(s)] ds \right\} \tag{10}$$

$$\kappa a \equiv (24\pi B_r \rho_+^*)^{1/2} \qquad (2{:}1 \text{ electrolytes}) \tag{11}$$

In these formulae, κ is the *inverse Debye length.*

Since we have from computer experiments only reliable RDF's up to a certain maximum distance, we calculate only the *potential differences*, for example in a 2:1 electrolyte for the anion:

$$\Delta e_o\psi_-(t)/kT \equiv e_o\psi_-(t)/kT - e_o\psi_-(t_{\max})/kT = -B_r/t + B_r/t_{\max} + (1/3)(\kappa a)^2\left\{(1/t)\int_{t_{-,\min}}^{t} s^2\Delta g_-(s)ds - (1/t_{\max})\int_{t_{-,\min}}^{t_{\max}} s^2\Delta g_-(s)ds + \int_{t}^{t_{\max}} s\cdot\Delta g_-(s)ds\right\} \tag{12}$$

$$\Delta g_-(s) \equiv g_{-+}(s) - g_{--}(s) \tag{13}$$

In this paper, I shall further investigate a mixture of two 1:1 electrolytes with a common cation and two different anions (1 – and 2 –) with a fraction X of anion no. 1. In that case we have – with Equation (8) for κa:

$$\Delta g_+(s) \equiv g_{++}(s) - X\cdot g_{+1-}(s) - (1-X)\cdot g_{+2-}(s) \tag{14}$$

$$\Delta g_{1-}(s) \equiv g_{+1-}(s) - X\cdot g_{1-1-}(s) - (1-X)\cdot g_{1-2-}(s) \tag{15}$$

$$\Delta g_{2-}(s) \equiv g_{+2-}(s) - X\cdot g_{1-2-}(s) - (1-X)\cdot g_{2-2-}(s) \tag{16}$$

$$\Delta e_o\psi_+(t)/kT = B/t - B/t_{\max} + (1/2)(\kappa a)^2\left\{(1/t)\int_{t_{+,\min}}^{t} s^2\Delta g_+(s)ds - (1/t_{\max})\int_{t_{+,\min}}^{t_{\max}} s^2\Delta g_+(s)ds + \int_{t}^{t_{\max}} s\cdot\Delta g_-(s)ds\right\} \tag{17}$$

$$\Delta e_o\psi_{1-}(t)/kT = -B/t + B/t_{\max} + (1/2)(\kappa a)^2\left\{(1/t)\int_{t_{1-,\min}}^{t} s^2\Delta g_{1-}(s)ds - (1/t_{\max})\int_{t_{1-,\min}}^{t_{\max}} s^2\Delta g_{1-}(s)ds + \int_{t}^{t_{\max}} s\cdot\Delta g_{1-}(s)ds\right\} \tag{18}$$

$$\Delta e_o\psi_{2-}(t)/kT = -B/t + B/t_{\max} + (1/2)(\kappa a)^2\left\{(1/t)\int_{t_{2-,\min}}^{t} s^2\Delta g_{2-}(s)ds - (1/t_{\max})\int_{t_{2-,\min}}^{t_{\max}} s^2\Delta g_{2-}(s)ds + \int_{t}^{t_{\max}} s\cdot\Delta g_{2-}(s)ds\right\} \tag{19}$$

Thus, the electric potential distribution around each ion can be found (except for an additive constant) from *smoothing* numerical integrals over the sampled radial distribution functions. In that way, the precision of the calculated potentials will increase compared to the the precision of the sampled RDF's and charge densities, see the similar discussion in Reference [12].

THE DEBYE-HÜCKEL POTENTIALS

The potentials of mean force and the electric potentials calculated from the MC data will be compared with the solution to the *linearized Poisson-Boltzmann equation*

(LPB), *i.e.* the solution to the equations

$$\nabla^2\Psi = -\rho_q/\varepsilon \approx \kappa^2\Psi \tag{20}$$

When the charge distribution around a »central ion« (of type *i*) is normalized, the solution is of the usual Debye-Hückel form:

$$e_o\Psi_i(t)/kT \approx z_i[\exp(\kappa a_i^*)/(1+\kappa a_i^*)]\cdot[B_r\exp(-\kappa a t)/t] \tag{21}$$

It should be noticed, that the appearance of the mean ionic diameter (a) in $\exp(-\kappa a t)$ has no physical significance, since $\kappa a t = \kappa r$. Similarly, $B_r/t = \lambda_B/r$ and the last square bracket in Equation (21) does not depend on any ionic diameters. In the first square bracket, which stems from the requirement, that the charge on the central ion should be neutralized by the total charge in the »ionic cloud«, the appearance of some »contact distance« (a_i^*) is essential, however. In the case of differently sized ions, we have for the *electric potential* the question, which contact distance should then be used. It will be shown later - by comparison with the MC potentials - that the mean contact distance is a very good approximation. Thus I shall put

$$a_i^* \approx a \qquad (i = 1, 2 \ldots n) \tag{22}$$

In case of comparison of the Debye-Hückel solution with the *potentials of mean force* as in Reference [5] this problem does not exist, since the interactions are now *specific* between two ions. Thus, the generalisation of the DHX theory made in Reference [5] followed naturally (and was shown there to be a good or excellent approximation!). The DHX dimensionless potentials of mean force (units of kT) are given as:

$$W_{ij}(t) \approx z_i z_j[\exp(\kappa a_{ij})/(1+\kappa a_{ij})]\cdot[B_r\exp(-\kappa a t)/t] \tag{23}$$

where a_{ij} is the contact distance between ions of types i and j.

RESULTS FOR A 1:1 ELECTROLYTE WITH B = 1.546 AND EQUAL RADII

The first demonstration of the »unreasonable efficiency of the the Debye-Hückel approximation« will be given for the case of a moderately dilute 1:1 electrolyte with equally sized cation and anion. The Bjerrum parameter is $B = 1.546$ and $\kappa a = 0.139383$. At 25°C in water with a relative permittivity = 78.34, the Bjerrum length is 0.7158 nm and the diameters of the ions are 0.4630 nm. The salt concentration corresponds to 0.008366 mol/L.

Figure 1 compares the MC results for the Poisson integrated electric potential around an ion with the DH expression (21-22) for radial separations between contact ($t = 1$) and $t = 7$. Numerical integration has been performed according to Equation (7), and the *potential differences relative* to $t = 6.95$ are calculated. In this t-window, the correspondence between the MC electric potential (rectangles) and the DH potential (full curve) seems to be *practically exact* even though the usual linearisation condition of Debye and Hückel ($e_o\Psi_i(t)/kT \ll 1$) is far from fulfilled close to contact! The MC calculations are the calculations reported earlier in Ref. [2] with the number of ions N equal to 32, 44, 64, 100, 150, 350, 512, 700

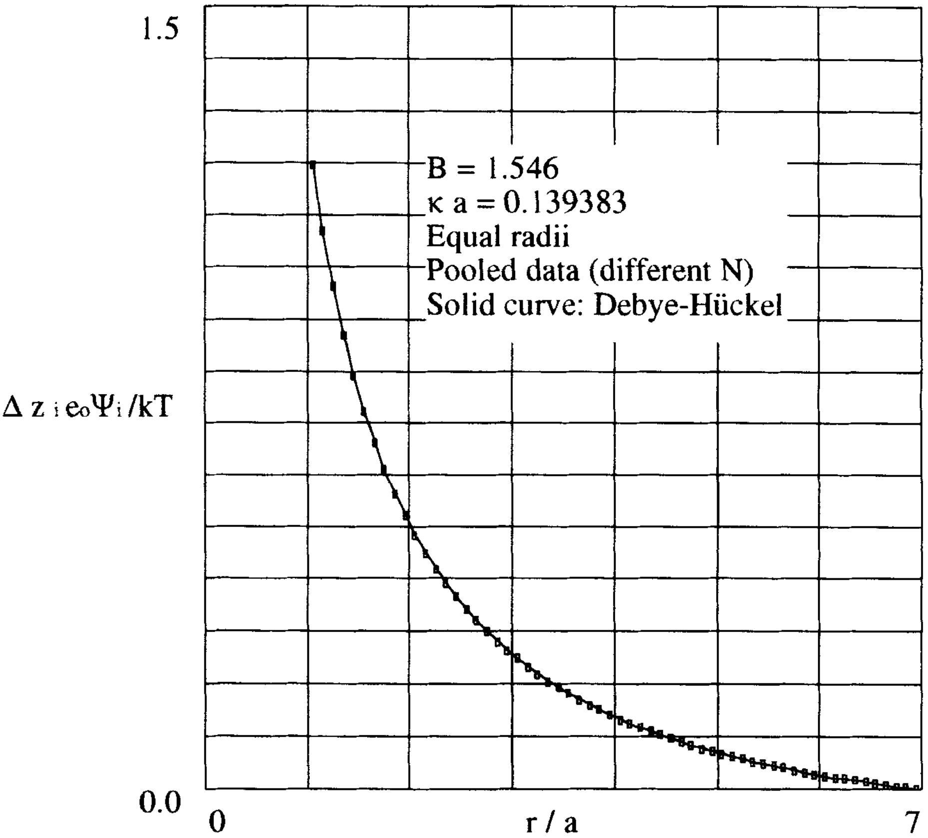

Figure 1 The Poisson integrated dimensionless electric potential around the cation/anion (rectangles) for a 1:1 electrolyte with Bjerrum parameter $B = 1.546$ and $\kappa a = 0.139383$. Both ions have diameter $= a$. The potentials are calculated from the dimensionless, scaled charge densities around the ions obtained by the pooled Monte Carlo simulations shown in Figure 2. Formula (7) was used, and Δ means the difference between the potential at r and the potential at $r = 6.95$. The coincidence with the Debye-Hückel approximation Equations (21-22), solid curve, seems perfect.

and 1000. All these simulations (each using ≈ 2 millions of configurations) have been averaged to improve the precision of the values of the radial distribution functions (especially the RDF between ions of like charge). No significant dependence on the size of the MC simulation box is seen up to $t = 7$, so it is not necessary to perform any extrapolations to the thermodynamic limit as the case is with the thermodynamic quantities [2-5]. (It should be noticed, that the Debye length is ≈ 7.17 hard sphere diameters and the ratio between the side length of the cubic simulation box and the Debye length is between 4.42 for $N = 32$ and 13.94 for $N = 1000$). Figure 2 shows the MC results for the conditional charge density around an ion from which the potential differences in Figure 1 were calculated.

In Figure 3 the MC results for the *dimensionless potential of mean force* $W_{ij}(t) \equiv -\ln g_{ij}(t)$ between like as well as between unlike charges are compared

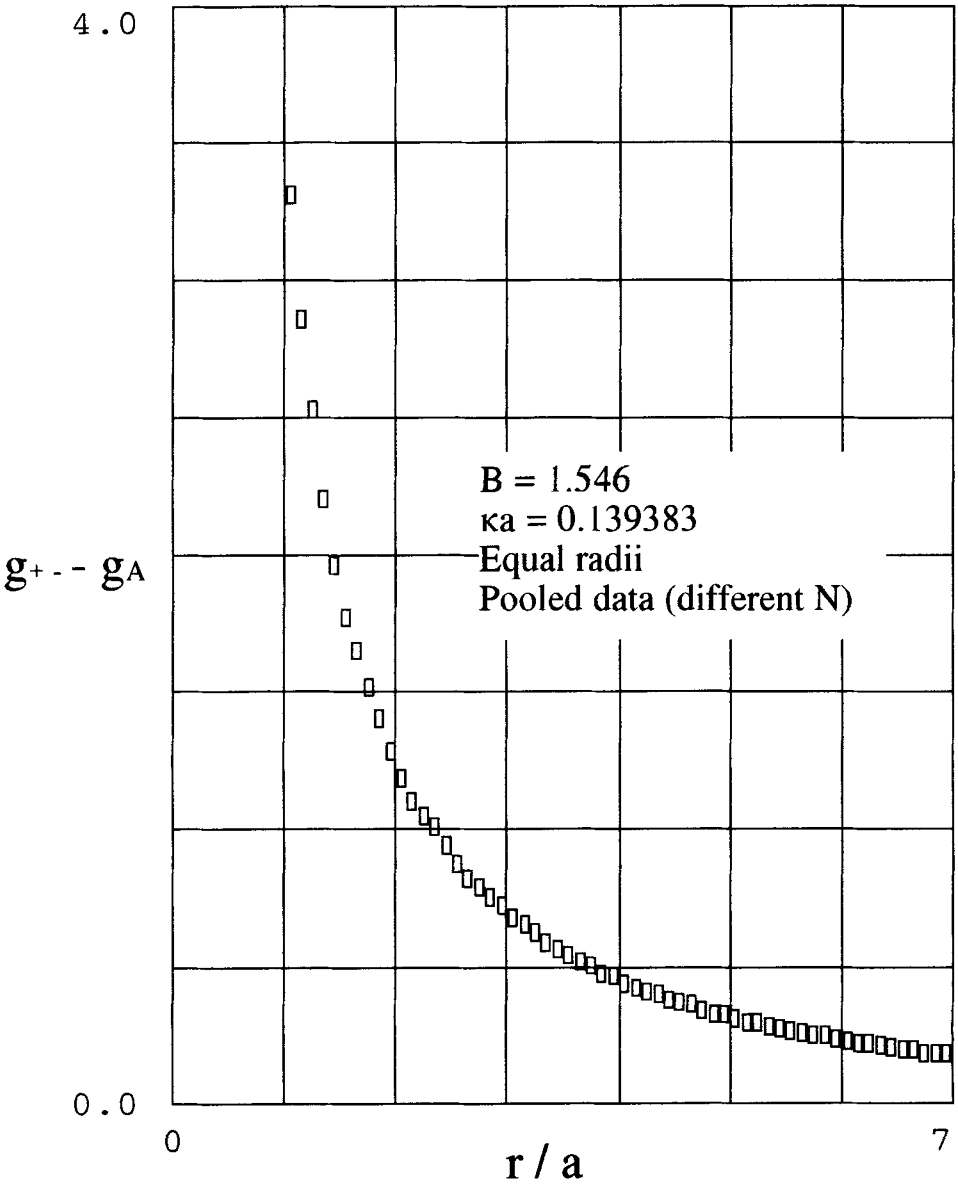

Figure 2 The scaled, dimensionless charge density around an anion calculated from Monte Carlo RDF's for a primitive model 1:1 electrolyte with equal ionic diameters, $B = 1.546$ and $\kappa a = 0.139383$. In order to minimize fluctuations, the RDF's of simulations with a total number of ions $N = 32$, 44, 64, 100, 150, 350, 512, 700 and 1000 have been averaged. Each simulation with ≈ 2 millions of configurations. We have defined $g_A \equiv g_{++} = g_{--}$.

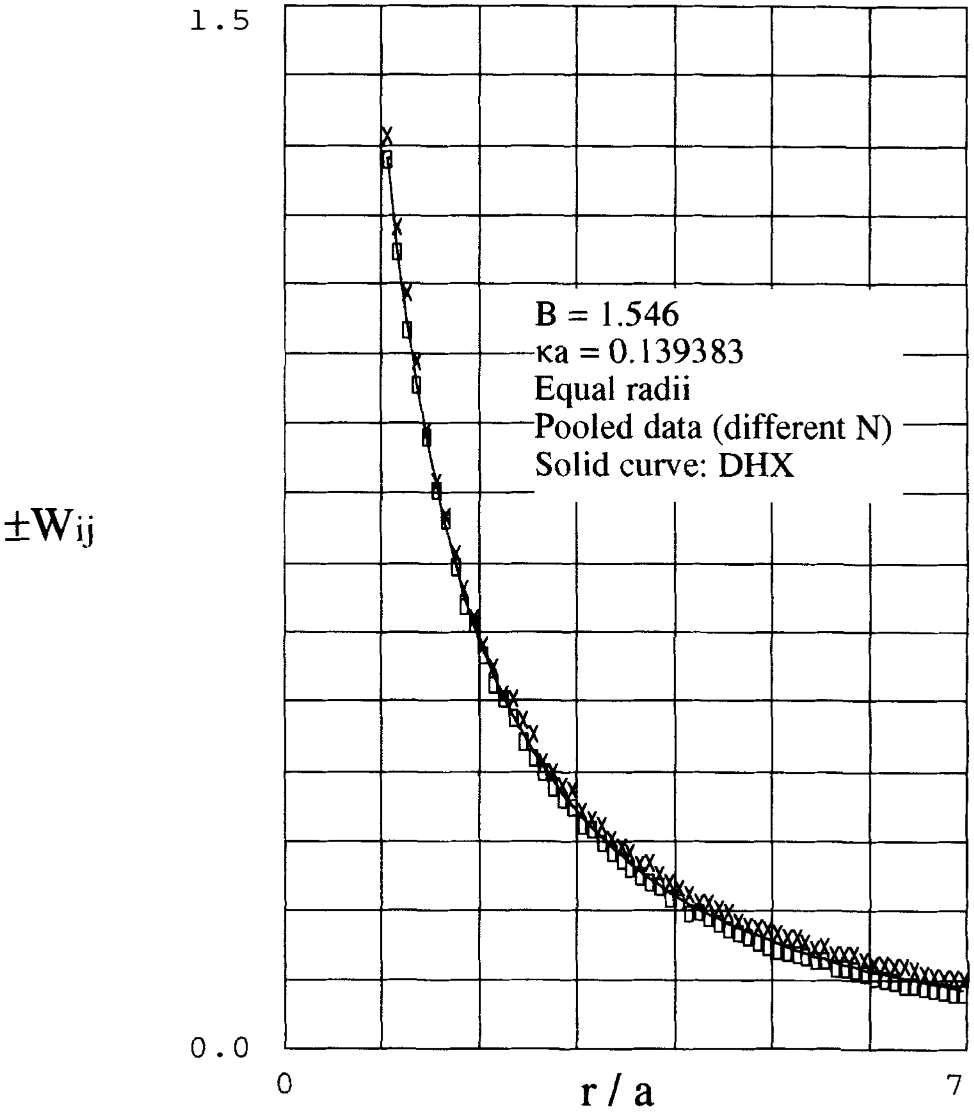

Figure 3 The potentials of mean force between like charges (positive sign and xxxxx) and between unlike charges (negative sign and rectangles) for the same electrolyte as in Figures 1–2. The solid curve is the DHX approximation, Equation (23) with $\kappa a_{ij} = \kappa a = 0.139383$.

to the DHX expression Equation (23) with $a_{ii} = a$. The correspondence is almost perfect although a very small deviation can be seen for the larger t-values for $W_{\pm -}(t)$ (~rectangles), and a somewhat larger deviation can be seen for $W_{++}(t) = W_{--}(t)$ (~crosses) at the larger t-values. This is similar to the findings in Reference [5] for Z:Z, 2:1 and 1:1:1 electrolytes.

RESULTS FOR B = 1.546 AND UNEQUAL RADII

In Reference [2], other simulations were reported for $B = 1.546$, $\kappa a = 0.139383$ and $a_{++}/a_{--} = 3$. Simulation results for the RDF's have been pooled as in the previous section ($N = 32$, 44, 50, 64, 70, 80, 100, 120, 150, 180, 216, 350, 512 and 1000, each with ≈ 2 millions of configuration). Again, no significant dependence on system size could be traced in the sampled RDF's (t below ≈ 7).

Figure 4 exhibits the MC result for the conditional (and scaled) charge density around the small anion. There is a *discontinuity* at $t = 1$ *i.e.* $r = a_{+-} = a$. Below this distance and down to $t = 1/2$, only the small anions are present with a negative charge density as a result. For $t > 1$ the cations dominate of course, and the charge density is positive.

Figure 5 shows the similar discontinuity in the conditional charge density around the cation. Between $t = 1$ and $t = 3/2$, only the anions are present, but for $t > 3/2$ cations (co-ions) are also present. This increases the charge density which is still negative after the increase, however.

In Figure 6 the integrated electric potential *differences* (relative to the value at $t = 6.45$) around the small anion are shown (rectangles). Equation (7) has been used for the numerical integration with $t_{-,\mathrm{min}} = 0.5$. The solid curve is the DH-approximation (21-22). The correspondence in the window from $t = 0.5$ to $t = 6.5$ seems to be practically exact, although $e_0\Psi_-(t)/kT$ is ca. -2.5 at contact. Also, there is *no sign of the charge density dicontinuity* in the potential distribution, although due respect has been paid to this discontinuity during the numerical integration - of course. The Poisson integration smooths the potential nicely out, and the Debye-Hückel solution reigns even in the region from $t = 0.5$ to 1.0, where only the anion can come. The latter phenomenon seems quite contra-intuitive!

Figure 7 demonstrates the conditional electric potential around the large cation. Equation (7) has been used for the numerical integration with $t_{+,\mathrm{min}} = 1.0$. Once more, the DH solution is exact in the t-window and there is no sign of the charge density discontinuity at $t = 1.5$.

Figures 8-10 demonstrate that the DH solutions given by Equation (23) are *also* very well in accordance with the MC results for the potentials of mean force except for a small deviation at the larger t-values - most pronounced for $W_{++}(t)$ (Figure 9).

RESULTS FOR AN EXTREMELY DILUTE 2:1 ELECTROLYTE

Next, an extremely dilute 2:1 electrolyte is considered. The reduced Bjerrum parameter is $B_r = 1.546$ and $\kappa a = 0.0482837$. The cation is doubly charged and has the same size as the anion with a single charge. Only one simulation has been involved here, but with $N = 999$ (333 cations and 666 anions) and as much as 20 million configurations. The RDF's were simulated in 60 spherical shells from contact ($t = 1$) to $t = 60$. The first couple of values (closest to contact) are omitted, since there is here an appreciable discretisation error (apart from larger uncertainty).

The conditional charge densities around the cation and anion were calculated from the RDF's. Using Equations (9-11) or Equation (12) and its analogue for the cation, the electric potential *differences* (relative to the potential at $t = 60.5$) are

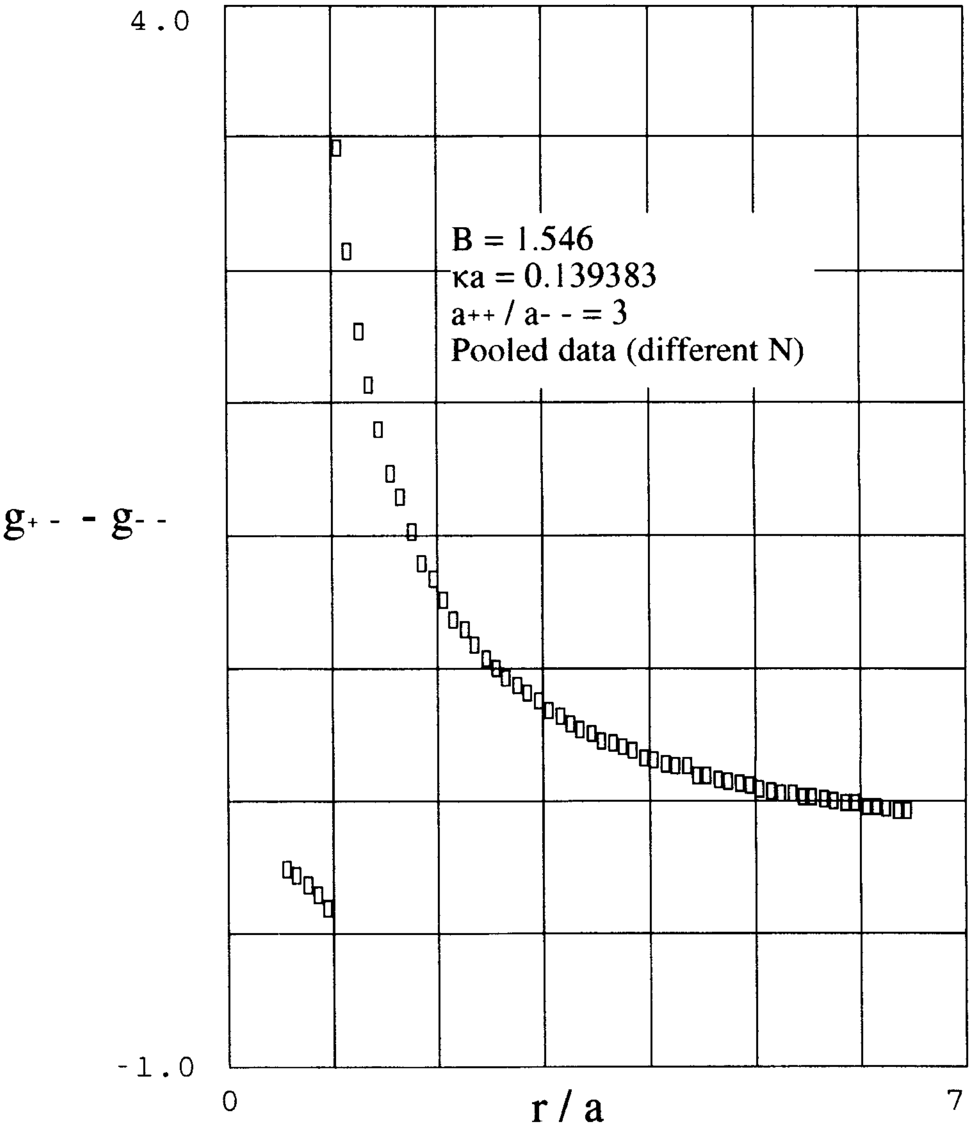

Figure 4 The scaled, dimensionless charge density around the small anion for a primitive model 1:1 electrolyte with cations three times larger in diameters than the anions, $B = 1.546$ and $\kappa a = 0.139383$. $a_{++}/a = 1.5$, $a_{+-}/a = 1$, $a_{--}/a = 0.5$. In the zone from $r/a = 0.5$ to $r/a = 1$, there are only co-ions of negative charge resulting in a negative space charge density. For $r/a > 1$ there are also counterions, and the space charge is positive. The RDF's of simulations with a total number of ions $N = 32, 44, 50, 64, 70, 80, 100, 120, 150, 180, 216, 350, 512$ and 1000 have been averaged. Each simulation with ≈ 2 millions of configurations.

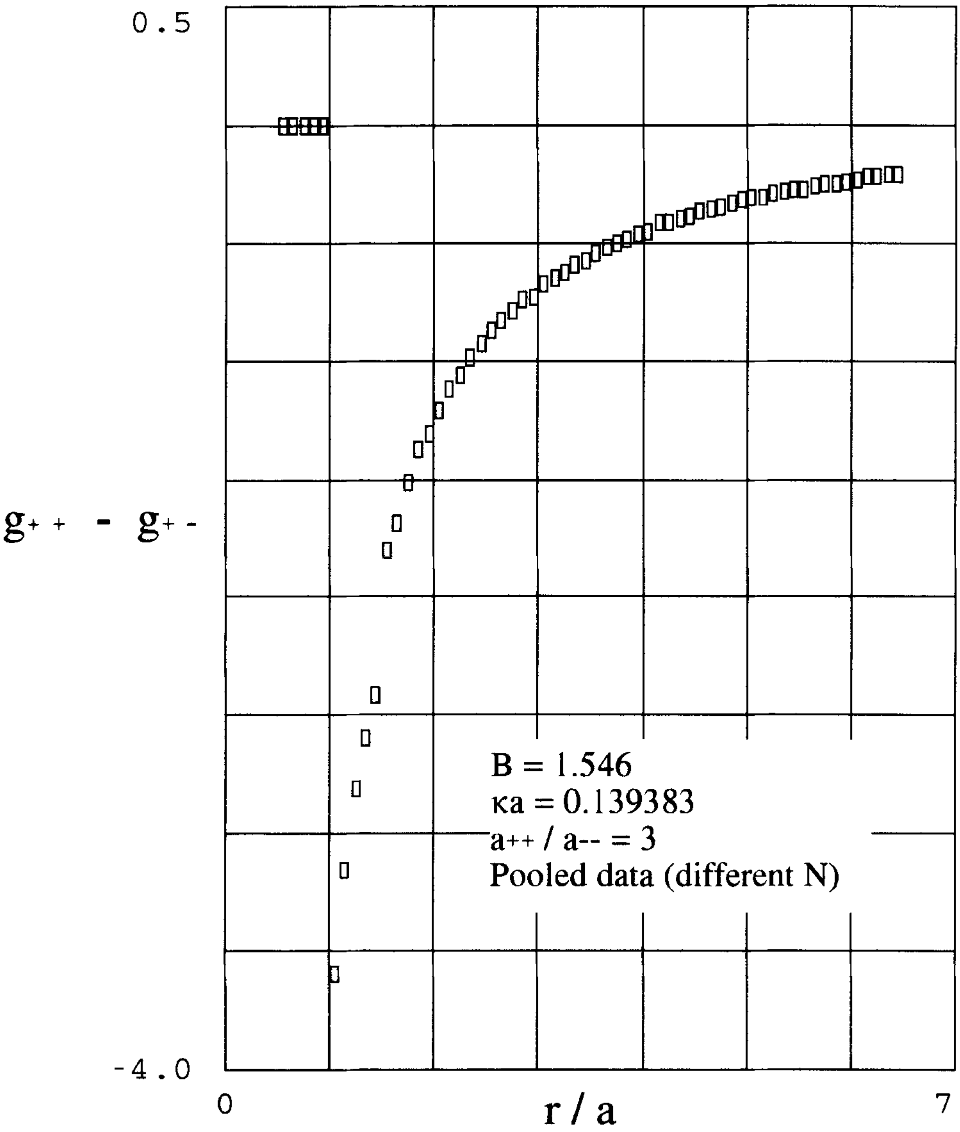

Figure 5 The scaled, dimensionless charge density around the large cation in the same system as in Figure 4. There is a discontinuity at $r/a = 1.5$. Below this distance, large co-cations cannot come.

found by numerical integration, see Figures 11-12. The correspondence with the DH approximation (21-22) seems *practically exact* in the t-window examinated even though the DH linearisation condition is violated - especially for $e_o\Psi_+(t)/kT$ close to contact. The *potentials of mean force* were shown in Reference [5] to be in good agreement with the DHX model, Equation (23), except at large separations, where the percentage deviations are appreciable. The electric potentials around the

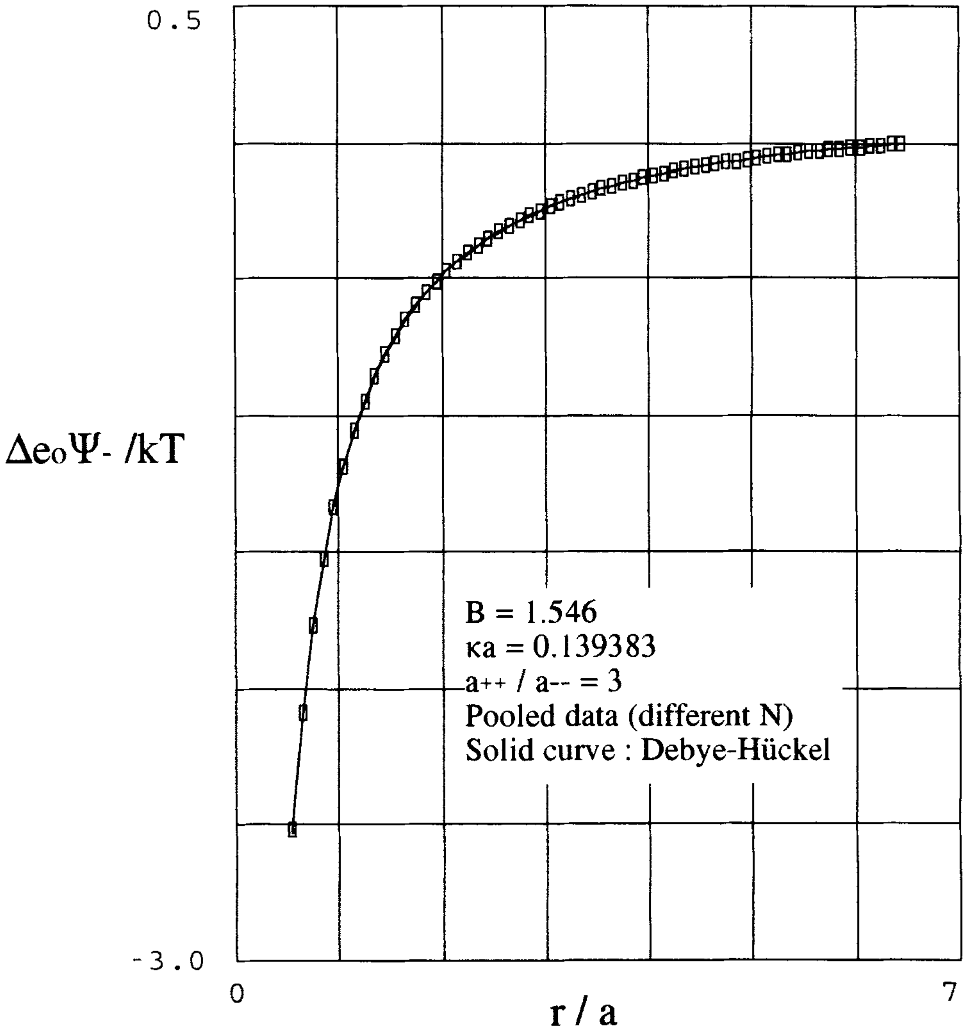

Figure 6 The Poisson-integrated potential (rectangles) around the small anion corresponding to the charge density in Figure 4. There is no sign left of the discontinuity at $r/a = 1$, and there is perfect fit to the Debye-Hückel approximation, Equations (21–22) even in the cation-free zone (0.5–1.0). The potential differences are relative to the potential at $r/a = 6.45$

cations and the anions (Figures 11–12) seem to be in accordance with the Debye-Hückel theory even in the »far tail«, however!

It should be noticed, that half of the edge length of the cubic simulation box is ≈ 128 hard sphere diameters. The Debye length is ≈ 20.7 diameters, so there ought not be any detectable influence from the periodic boundary conditions and the energy cut-off.

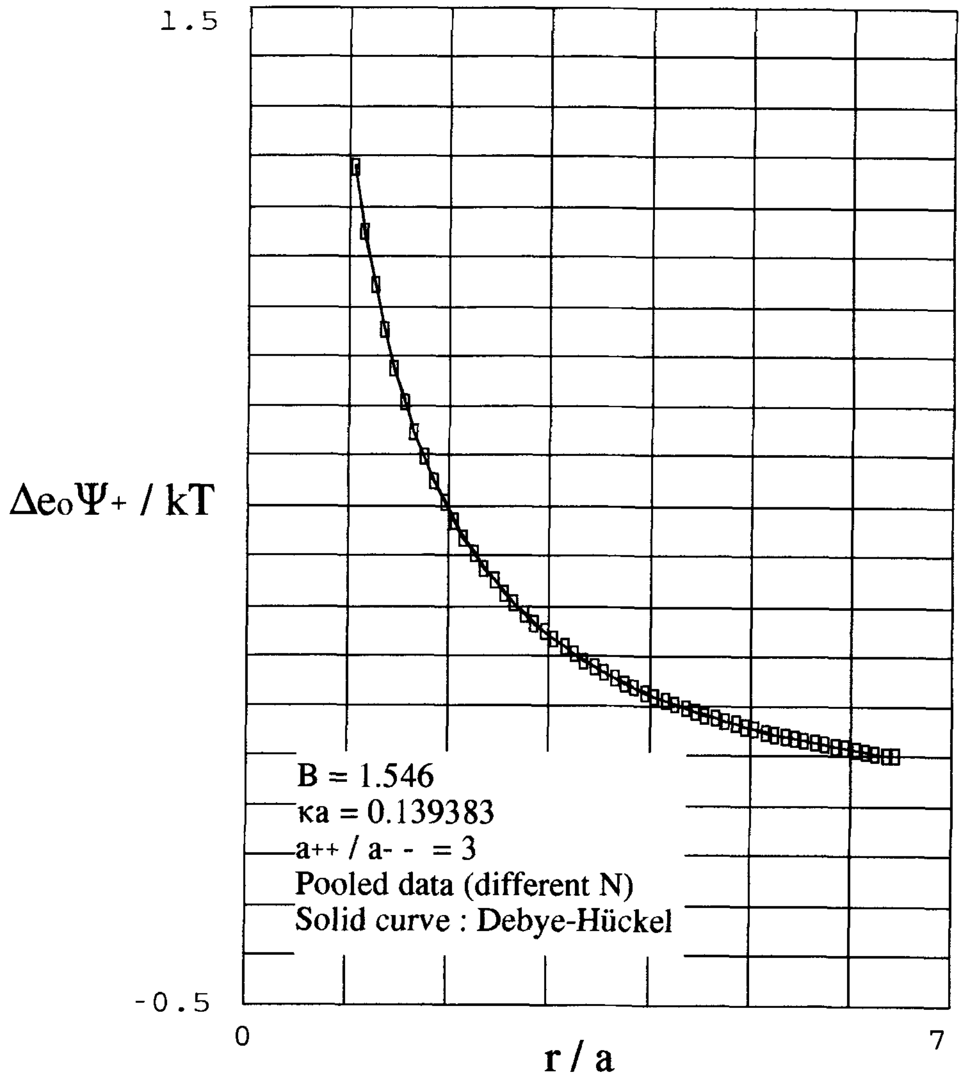

Figure 7 The Poisson-integrated potential (rectangles) around the large cation for the same system as in Figures 4-6. There is no sign left of the discontinuity at $r/a = 1.5$ (Figure 5), and there is perfect fit to the Debye-Hückel approximation, Equations (21-22) even in the co-cation-free zone (1.0-1.5). The potential differences are relative to the potential at $r/a = 6.45$.

RESULTS FOR AN EXTREMELY DILUTE 2:2 ELECTROLYTE

In References [3, 5], a 2:2 electrolyte with $B = 6.8116$ and $\kappa a = 0.0276382$ and equally sized cation and anion was simulated. Consider here a simulation using 1728 ions and 15 millions of configurations.

The RDF's were sampled in 60 spherical shells between contact ($t = 1$) and

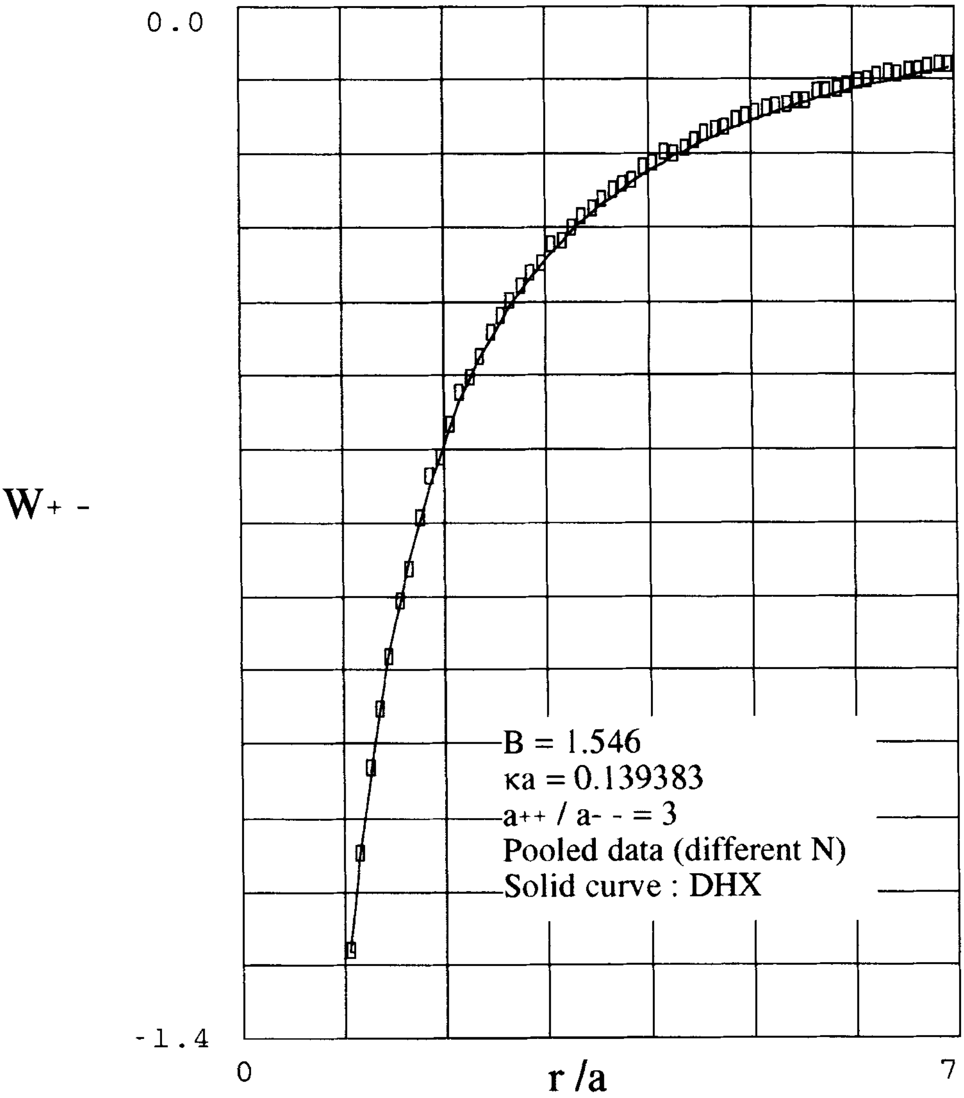

Figure 8 The potential of mean force between the large cation and the small anion (rectangles) for the same electrolyte as in Figures 4-7. The solid curve is the DHX approximation, Equation (23) with $\kappa a_{+-} = \kappa a = 0.139383$. The fit is perfect, except for large separations.

$t = 120$. The Poisson integrated potential *differences* (relative to the potential at $t = 120$) around a cation or anion is shown in Figure 13. Now, an appreciable deviation from the DH potentials is seen, although the values at contact are probably quite close to each other. The deviation seen may be the result of tiny deviations between the DH and the MC charge densities in the »far tails« of the RDF's, however. This is visualized in Figure 14, where the reference for the potential

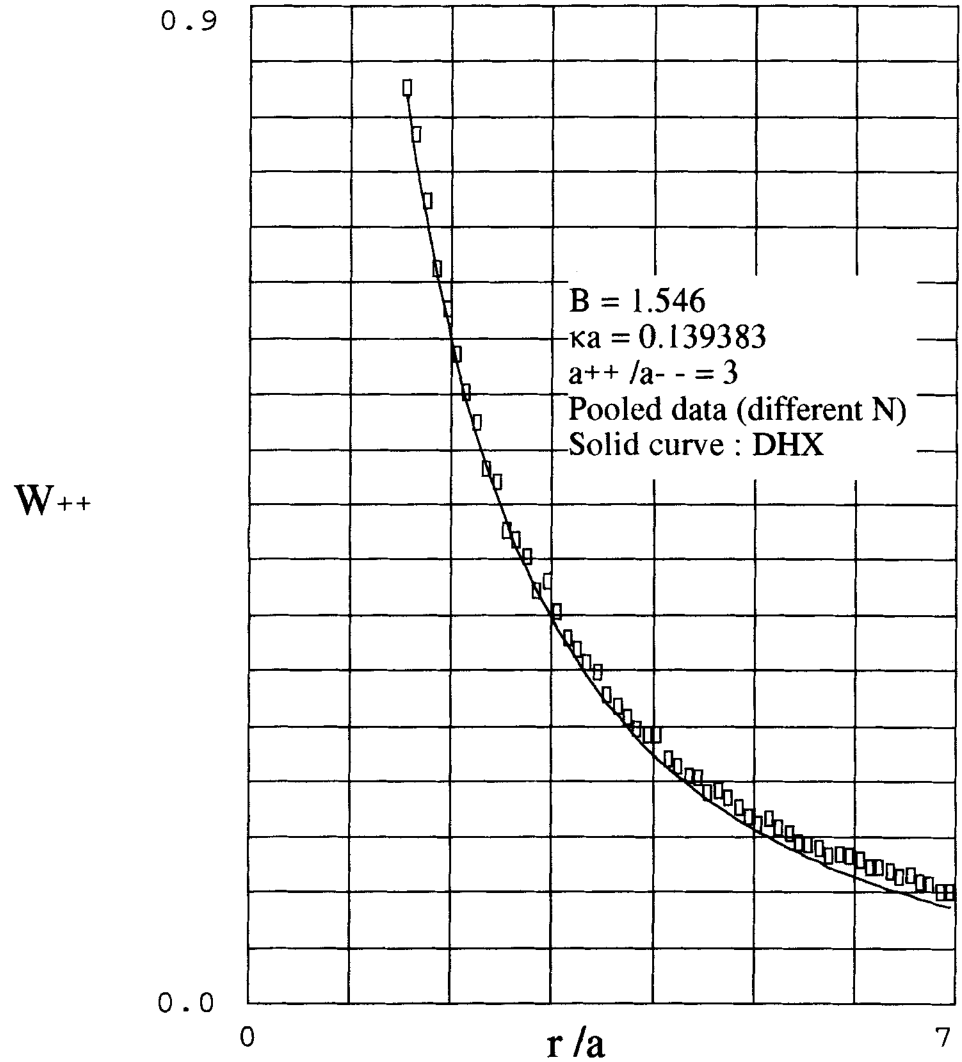

Figure 9 The potential of mean force between the large cations (rectangles) for the same electrolyte as in Figures 4-8. The solid curve is the DHX curve, Equation (23) with $\kappa a_{++} = 1.5 \cdot \kappa a$. The fit is only perfect close to contact.

differences is taken at $t = 24$ instead of at $t = 120$ as in Figure 14. Now, the correspondance between DH and MC in the window up to $t = 24$ is quite good. Since we have in the latter case not used any information outside $t = 24$, there are all reasons to believe, that the DH-approximation (21-22) is a good approximation for the electric potential close to contact even for dilute 2:2 electrolytes, where the Debye-Hückel linearisation condition is grossly violated! The *potentials of mean force* were discussed in Reference [5].

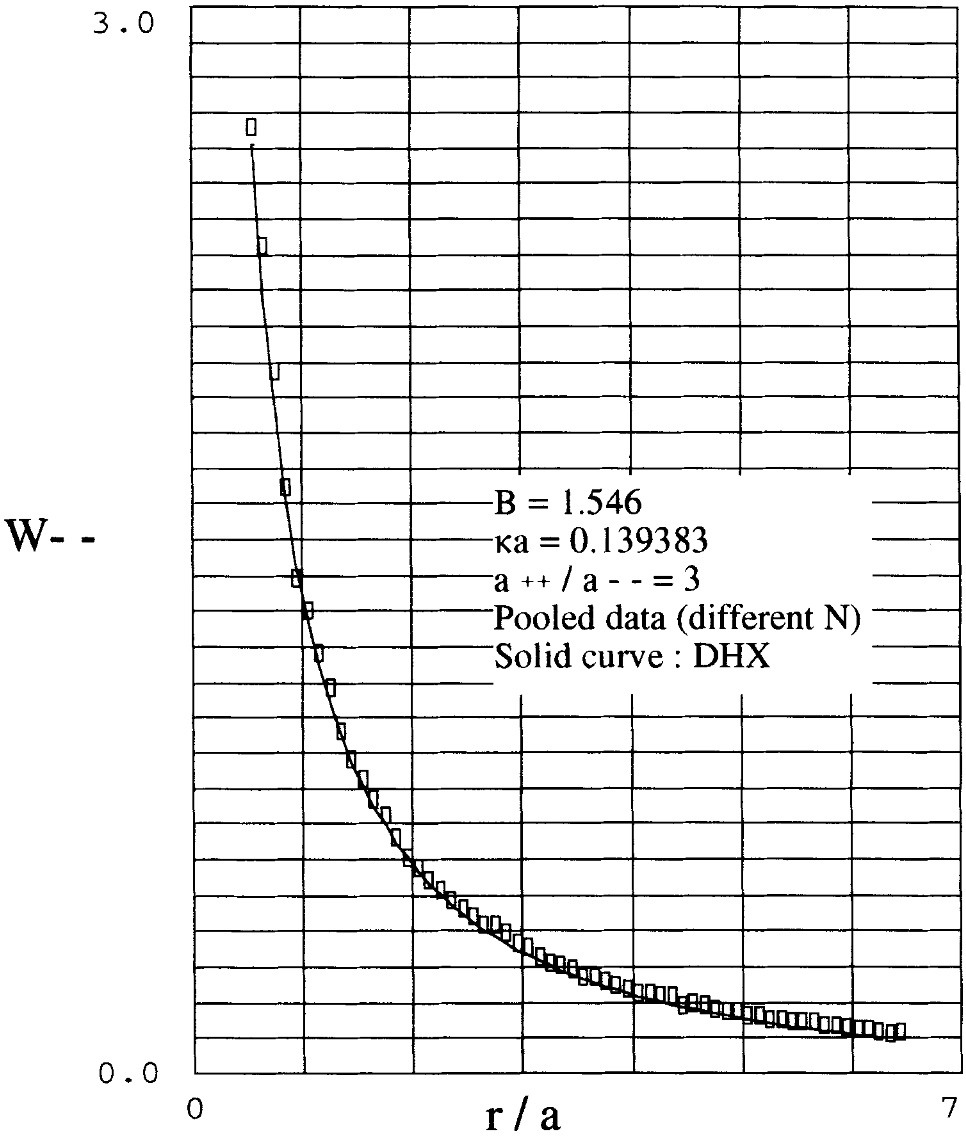

Figure 10 The potential of mean force between the small anions (rectangles) for the same electrolyte as in Figures 4–9. The solid curve is the DHX curve, Equation (23) with $\kappa a_{--} = 0.5 \cdot \kappa a$. There is some deviation at large separations, less than for W_{++} (Figure 9) but more than for W_{+-} (Figure 8).

RESULTS FOR A MODERATELY CONCENTRATED 1:1:1 MIXTURE

In Reference 14, the KCl-KF system was studied experimentally as well as theoretically and single ion activity coefficients were found by the technique of Widom [9–10]. The mean ionic activity coefficients were compared to values

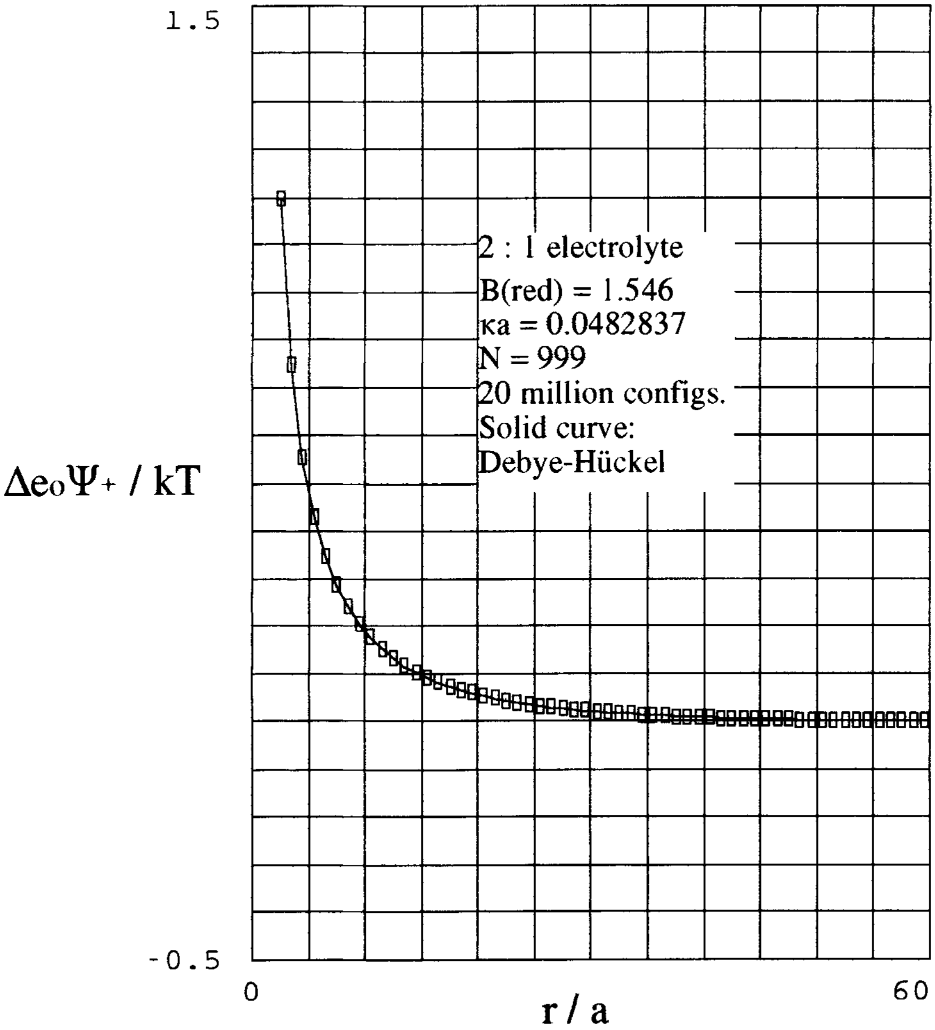

Figure 11 The Poisson-integrated potential around the doubly charged cation (rectangles) of a dilute 2:1 electrolyte with equally sized ions. The reduced Bjerrum parameter is $B_r = 1.546$ and $\kappa a = 0.0482837$. Number of ions: $N = 999$ (333 cations and 666 anions). Number of configurations: 20 millions. The solid curve is the Debye-Hückel approximation (21-22). The correspondence seems perfect. All potential differences are relative to the potential at $r/a = 60.5$. Equation (9) is used for the integration.

measured in real KCl-KF solutions (using Valinomycine, LaF_3 and Ag/AgCl electrodes) and to mean spherical approximation (MSA) calculations. In reference [5] the MC simulations for this system were further developed and more refined and corrected values for the thermodynamic quantities were calculated (for example, the correction formula described in Reference [3] were used in the extrapolation of the

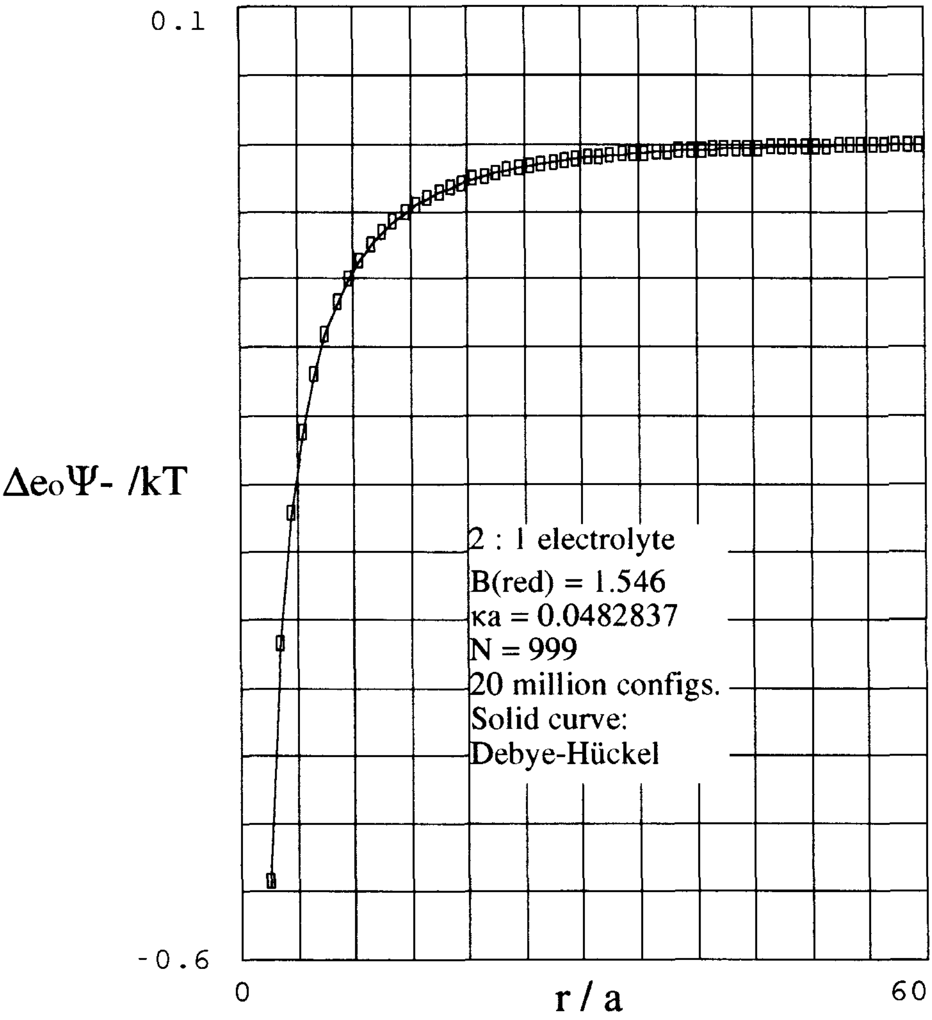

Figure 12 The Poisson-integrated potential around the singly charged anion (rectangles) of a dilute 2:1 electrolyte with equally sized ions. Same system as in Figure 11. Equation (10) - or Equation (12) - is used for the integration. The solid curve is the Debye-Hückel approximation (21-22). The correspondence seems perfect. All potential differences are relative to the potential at $r/a = 60.5$.

single ion activity coefficients). Furthermore, a long run simulation (4 millions of configurations) in a moderately concentrated mixed electrolyte system (1 mol/L total ionic strength) was singled out for analysis of the potentials of mean force. The same system will be considered here to investigate the electric potentials around the three kind of ions.

The system is a three ion system with a cation and an anion of diameter 0.29 nm (K^+ and Cl^-, say) and another anion of diameter 0.37 nm. The latter we call F^-

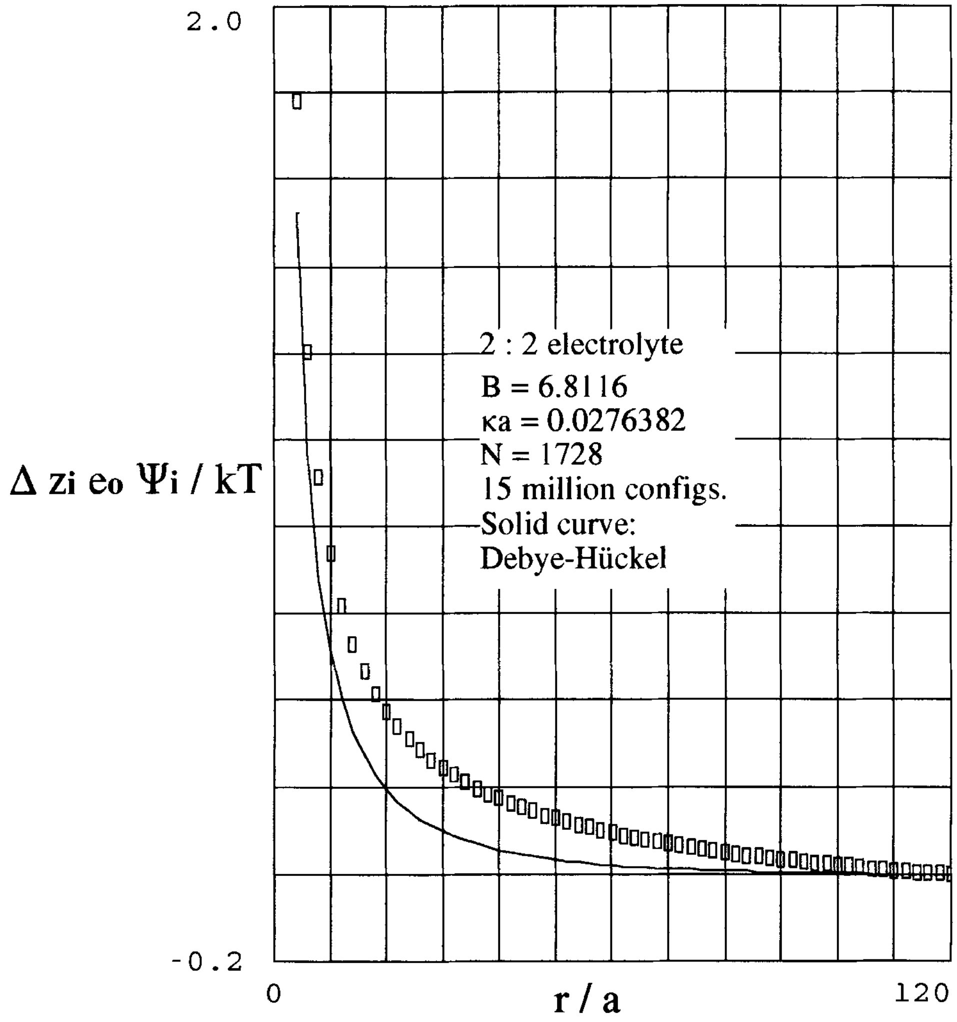

Figure 13 The Poisson-integrated potential around the cation (or anion) in a dilute 2:2 electrolyte with equally sized cations and anions and $B = 6.8116$, $\kappa a = 0.0276382$. Number of ions: $N = 1728$. Number of configurations: 15 millions. The MC data (rectangles) deviate appreciably from the DH approximation (full curve). All potential differences are relative to the potential at $r/a = 120$. The deviations are mostly due to large relative deviations of the MC and DH charge denities in the tail of the distribution.

even if it was found in Reference 14, that »real« F^- rather has an »effective diameter« ≈ 0.34 nm. (This »exaggerated« KF-KCl system was also studied in References [5, 14] as well as the »normal« KF-KCl system). The specific MC system studied has 456 (exaggerated) F^- ions, 38 Cl^- ions and 494 K^+ ions. In the Equations (14–19), anion no. 1 is Cl^-, anion no. 2 is F^- and $X = 1/13$. The mean contact distance $a = 0.316666\ldots$ nm. The 6 different RDF's were sampled in 60 spherical shells of equal thickness between contact and $r \approx 7a$.

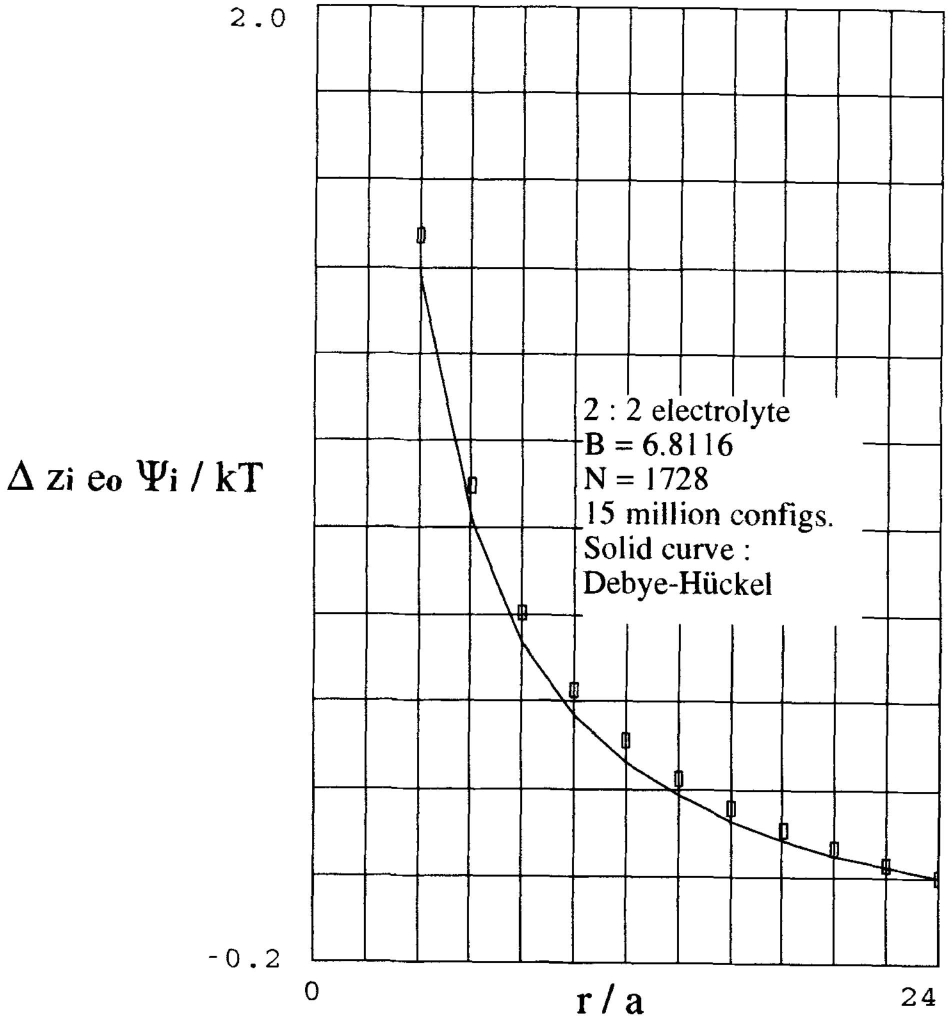

Figure 14 Basically the same integration as in Figure 13, but now only RDF-values up to $r/a = 24$ have been included (rectangles). All potentials are relative to the potential at this separation. Now, the correspondence with the Debye-Hückel expression (full curve) is quite good. The conclusion is, that the Debye-Hückel potential is best close to contact (where the DH linearisation condition is mostly violated!).

Figure 15 shows the Poisson-integrated potential *differences* around the K^+ ion (rectangles) compared to the DH result from Equation (21–22). The correspondance is practically perfect even at this relatively high concentration where *the Debye length is approximatey equal to the diameter of the ions* ($\kappa a = 1.04071$). The ionic cloud concept of Debye and Hückel should refer to *point ions* surrounding a central ion with forbidden volume, and the fit here is quite »unreasonable« but it parallels the findings in Reference [5], that the *electric* contribution to the potentials of mean force are well fitted by Equation (23) for the present system.

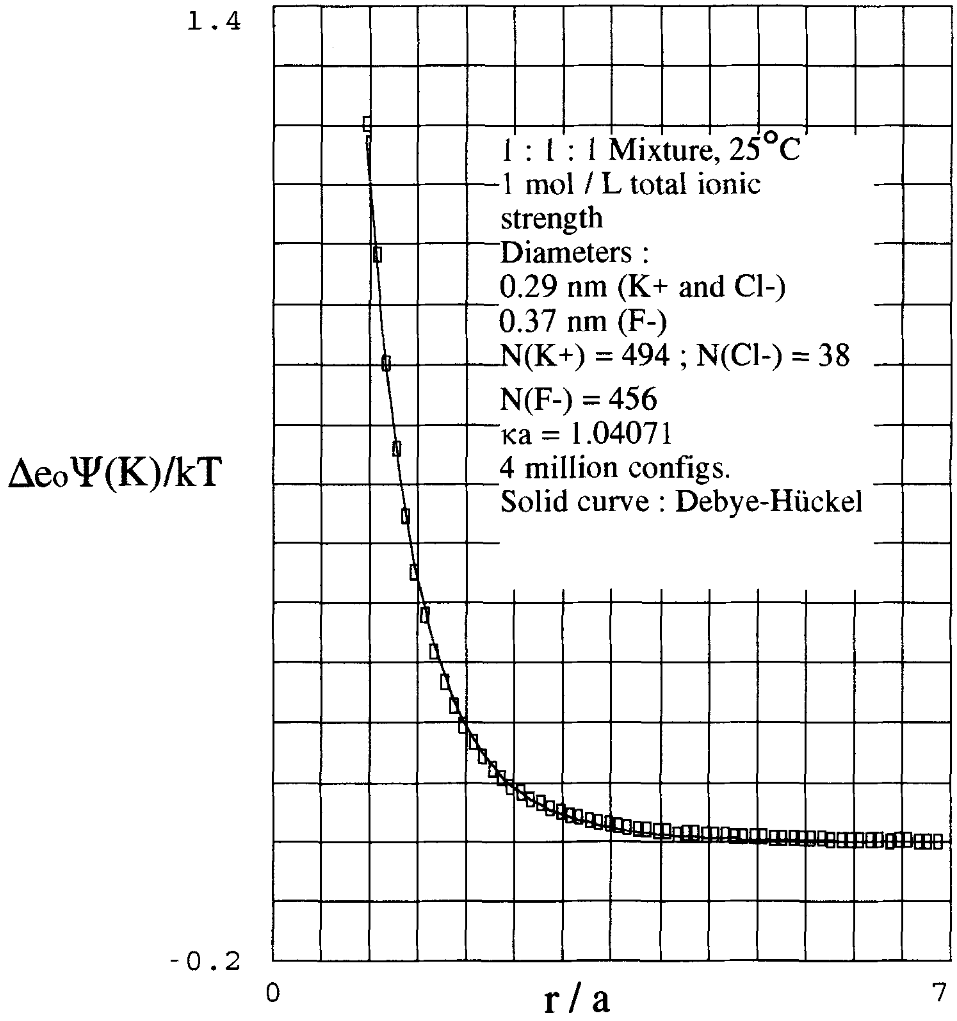

Figure 15 The Poisson-integrated potential around the K^+ ion in a 3-ion system with 494 »K^+ ions« (diameter 0.29 nm), 38 »Cl^- ions« (diameter 0.29 nm) and 456 »F^- ions« (diameter 0.37 nm). The mean diameter $a = 0.3166666\ldots$ and the concentration (in »water« with dielectric constant 78.34 at 25°C) is 1 mol/L, $\kappa a = 1.04071$, $B = 2{,}2533$. Number of configurations: 4 millions. The correspondence between the MC data (rectangles) and the Debye-Hückel approximation (full curve) seems excellent. There is no sign left of the charge density discontinuity shown in Figure 16. All potentials are relative to the potential at $r/a = 6.865789$.

From separations equal to 0.29 nm ($t = 0.29/0.31666\ldots \approx 0.915$) to 0.33 nm ($t \approx 1.042$) only K^+ co-ions and Cl^- counterions are able to come, and since there are only few Cl^- ions, the charge density around the K^+ ion in this zone is positive. From $t \approx 1.042$ and above also the F^- ion can come, and the charge density in the ionic cloud changes to the normal negative values (the central ion being positive). This is shown in Figure 16. There is *no trace of this discontinuity* in the

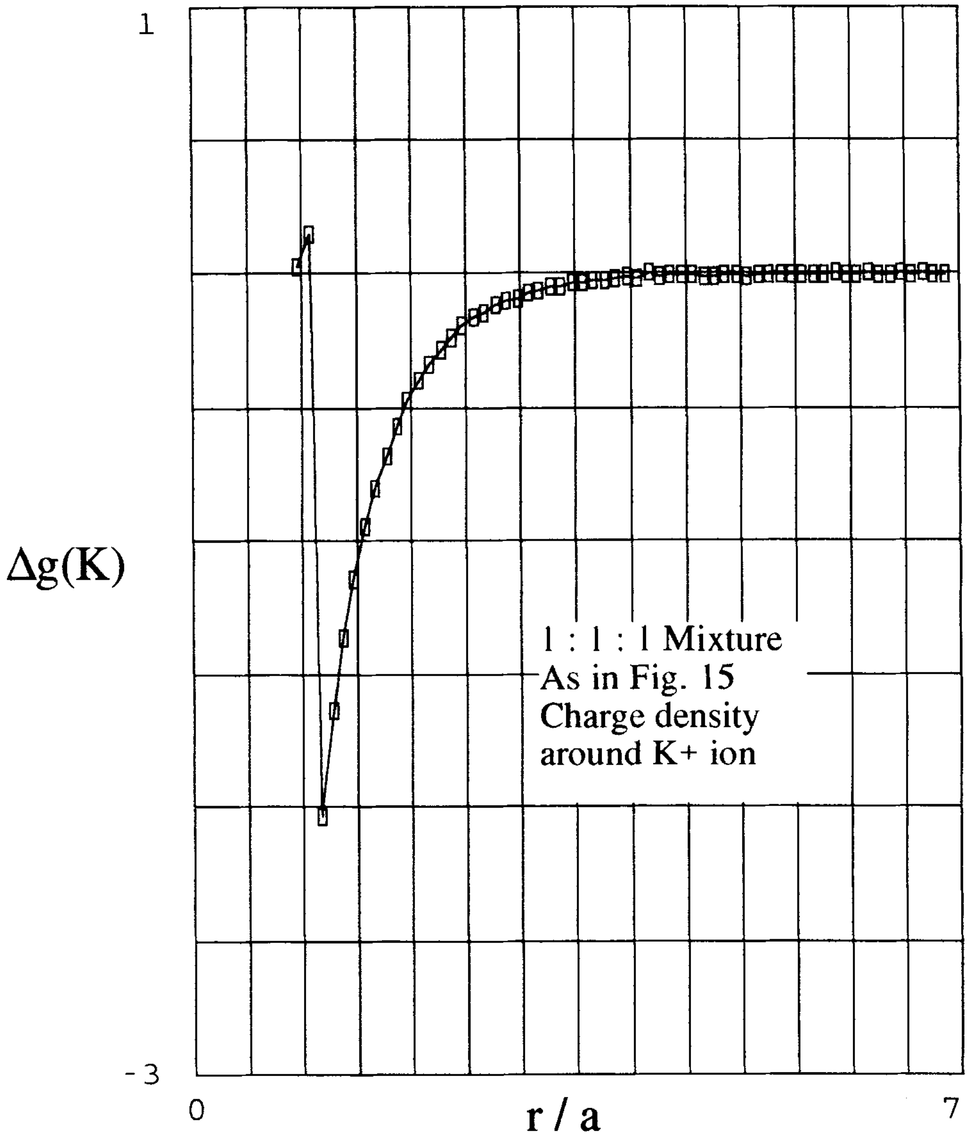

Figure 16 The scaled and dimensionless charge densities around a K^+ ion calculated from RDF's. Same system as in Figure 15. From $r/a \approx 0.915$ to $r/a \approx 1.042$ only K^+ and Cl^- can come. Since there are only few chloride ions in the mixture, the net result is a positive space charge in this zone. After the discontinuity at $r/a \approx 1.042$ fluoride counter ions are also present, and the charge density is negative (to balance the charge on the positive K^+).

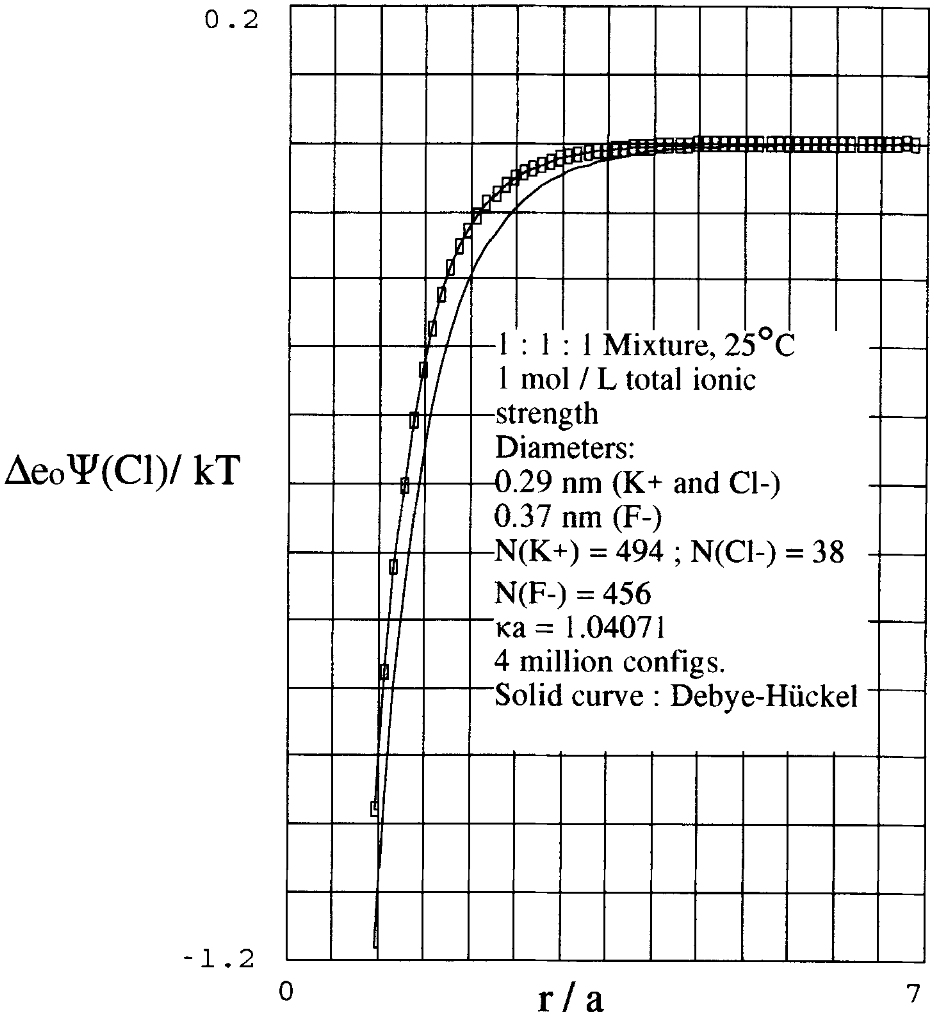

Figure 17 The Poisson-integrated potential around the Cl^- ion in the same 3-ion system as in Figures 15–16. The correspondence between the MC data (rectangles + curve) and the Debye-Hückel approximation (full curve without rectangles) is less good than for the potential around K^+ (Figure 15). All potentials are relative to the potential at $r/a = 6.865789$.

integrated potential, and Figure 15 shows that the Debye-Hückel behaviour prevails even in the volume into which the big ion cannot penetrate!

The conditional potential differences around the Cl^- ion is shown in Figure 17. In this case, there is a certain deviation from the DH curve. Also in this case there is in principle a discontinuity in the space charge distribution at $t \approx 1.042$, but it is not visible on a plot. The reason is, that it is co-ions and not counterions which are excluded below $t \approx 1.042$. Figure 18 shows that also the Poisson integrated potential around the F^- ion deviates a little from the DH approximation (21-22), but less than with Cl^- as central ion. There is no discontinuity in the conditional space charge around the large F^- ion.

DISCUSSION AND CONCLUSIONS

Unreasonable efficiency of linear Poisson-Boltzmann approach

In a very recent paper [12], the »inverse Debye-Hückel« model was investigated by Grand Canonical Ensemble Monte Carlo techniques. The distribution of ions in small spherical pores with a uniform fixed charge density at the surface and a distant, free (primitive) solution of the same ions were investigated as well as the internal distribution of ions, space charge and electric potential. In the case of dilute solutions, the electric potential distribution inside the pores were the solutions of a simple generalisation of Equation (20), where the Poisson-Boltzmann equation was linearized around the potential in the center of the pore rather than around the potential in the distant, free solution (Reference [12], Figures 19-21). One should use also the local mean ionic concentration in the center of the pore to calculate the mean Debye length in the pore. With these natural modifications the results found may also be taken as a confirmation of the unreasonable efficiency of the simple Debye-Hückel approach. For example, in the case of a pore with a radius which is five times the diameter of the ions and with a continuous surface charge equal to five elementary charges, the dimensionless electric potential in the middle of the pore (at Donnan electroneutrality) was found to be ca. 2.7 compared to the value ca. 3.4 at the surface of the pore. The potential difference is 0.7 which cannot be said to be much less than unity, but the solution to the generalized DH equation fits the Poisson integrated MC data quite perfectly see Reference [12], Figure 19, curve (b) and Reference [12], Table 6.

In the present paper we have collected ample documentation, that the Debye length and the solution to the linearized Poisson-Boltzmann equation play a very central role in the normal (external) Debye-Hückel model not only in dilute solutions of 1:1 , 2:1 and z:z electrolytes, but also in solutions up to at least ionic strengths, where the Debye length is of the same order of magnitude as the size of the ions ($\kappa a \approx 1$). The DH solution mostly fits perfectly the electric potential calculated from MC as well as the (electric) potentials of mean force - especially near to contact, where the DH linearisation condition

$$e_0 \Psi / kT \ll 1 \tag{24}$$

is *not* fulfilled! This puzzling finding might - with many reservations - be seen as an example of the *principle of unreasonable utility of asymptotic estimates* put forward by Stell [13] in a fundamental paper on the statistical mechanics of fluids with long range forces. In the introduction this author stated, that »asymptotic estimates of physical quantities are often useful far beyond the range over which they have good mathematical justification«. It is a fascinating principle, which is admittedly not proven in the Reference [13], however. (And I doubt that any general proof can be made, the statement is a little too »philosophical«!). Rather, some demonstrations of the utility are given in the paper in special cases - for example for the primitive electrolyte model. My reservations are mainly, that the demonstration of the unreasonable utility of the linearized Debye-Hückel approach demonstrated in this paper and in Reference [5] for the electric potential as well as for the potential of mean forces seems to be of a much more direct nature than any of the expansions discussed in Reference [13]. Indeed. the most »optimistic« use of the principle of Stell is the MSA (Mean Spherical Approximation) theory. Although this theory does give quite valid results for excess energy and for (single) ion activities at moderate Bjerrum parameters and concentrations, it is as bad for the radial distribution functions as the DH theory (with the exponentials linearized) and exhibit the same deviations from the true thermodynamic values as the simple DH expressions at very low concentrations. Higher level expansions discussed by Stell are for example the LIN-approximation

$$g_{ij}(r) \approx g^{o}_{ij}(r)\cdot[1+\mathrm{Chain}_{ij}(r)] \tag{25}$$

or the EXP-approximation

$$g_{ij}(r) \approx g^{o}_{ij}(r)\cdot\exp(\mathrm{Chain}_{ij}[r]) \tag{26}$$

where $\mathrm{Chain}_{ij}(r)$ are complicated infinite »chain graph sums« and $g^{o}_{ij}(r)$ the discharged RDF's (*e.g.* hard sphere RDF's). These formulae would be in harmony with the *additivity principle* of the hard sphere and the electric potential of mean force demonstrated by direct simulation in Reference [5] and with the DHX model, if we have

$$\mathrm{Chain}_{ij}(r) \approx \begin{cases} \exp(-W_{ij}[r]) - 1 & \text{(LIN)} \quad (27a) \\ -W_{ij}[r] & \text{(EXP)} \quad (27b) \end{cases}$$

with $W_{ij}[r]$ given by equation (23), but these results are not evident from any of the involved expansions given by Stell. Furthermore, the *unreasonable* fit of the Debye-Hückel *electric potential* in (1) regions were the inequality (24) is violated, (2) regions were only some of the ions are able to penetrate and (3) concentrations where the Debye length and the ionic diameters are of the same size, are not explained by such »graphological« exercises. (Indications, that the DHX + hard sphere model was probably a good approximation were given already in 1975 by Olivares and McQuarrie, however [15-16]).

The classical electrochemical charging procedures are not correct

The fact that the DH expression is excellent in many cases for describing the potentials near to contact does not mean that the ordinary DH expressions for the thermodynamic quantities - found in all textbooks on electrochemistry - are also excellent. Previous studies have shown that the DH expressions (including the κa corrections to the limiting laws) are $B \to 0$ limits rather than low concentration limits [2-4]. For example, in an extremely dilute 2:2 electrolyte ($B \approx 6.8$), the excess heat capacity at constant volume may deviate as much as 450% from the DH result, and other quantities also deviate a lot - although less, see Reference 3, Figure 10. Even such enormous deviations as those mentioned are well described by the so-called DHX model. The assumption behind this model is precisely, that the potentials of mean forces are given by the DH expression! A careful check of the thermodynamic consistency of this model for 1:1 electrolytes have been performed in References [2-3]. Thermodynamic quantities calculated from integrals of the type

$$\int_a^\infty g_{ij}(r)r^n dr$$

with $n = 1$ are quite consistent up to at least $B \approx 2$ and $\kappa a \approx 0.5$, whereas Kirkwood-Buff quantities based on integrals with $n = 2$ are much less consistent. This is further evidence for the fact also found in Reference [5], that the potentials of mean force in the far tails are quite non-Debye-Hückelian.

Alternatively, we may say that the *surface electric potential* on the ions seems to be in accordance with the linear Poisson-Boltzmann equation to a very good approximation even up to $\kappa a \approx 1$. If the classical *charging procedures* (*Debye charging or Güntelberg charging*, see References [17-18]) - normally used in electrochemical textbooks - were correct, then the Debye-Hückel expressions for the excess Helmholtz free energy or for the single ion activity coefficients would also be correct. Since this is *not* the case, we may conclude that these charging procedures are somewhat misguiding. These procedures would be correct for the electrostatic energy of charging of macrospheres in a dielectric continuum. In rigorous statistical mechanics, the correct analogue of *e.g.* the Güntelberg charging procedure of a selected ion is a *Kirkwood charging* involving the gradual introduction of the electrostatic interaction including the corresponding change in RDF's during the charging. This procedure involves for electric pair potentials (proportional to *1/r*) double integrals of the form

$$\int_{r=0}^\infty \int_o^1 g_{ij}(r, \lambda_i) r d\lambda_i dr,$$

where λ_i is the Kirkwood coupling parameter of one ion of species *i* to the rest of the ions (of the same and of different species), see for example the formula (13.34) for the chemical potential in Reference [19]. More specifically, simplifiying to to a mixture of ions with different valencies but of the same diameter (a) and using the bulk electroneutrality and the fact that the RDF's are zero for $r < a$ we obtain for the single ion coefficient:

$$\ln y_i = 4\pi B_r z_i \int_o^1 d\lambda_i \left\{ \sum_j z_j \rho_j^* \int_{t=1}^\infty h_{ij}(t; \lambda_i) t\, dt \right\} \tag{28}$$

$$h_{ij}(t; \lambda_i) \equiv g_{ij}(t; \lambda_i) - 1 \tag{29}$$

What we have learned in the present study is that (when we may ignore variations in the RDF due to hard sphere interactions) the dimensionless potentials of mean force and the conditional electric potentials around the ions are to a good approximation given by:

$$W_{ij}(r; \lambda_i) \equiv -\ln g_{ij}(r; \lambda_i)$$

$$\approx \lambda_i z_i z_j B_r [\exp(\kappa a)/\{1 + \kappa a\}] \exp(-\kappa a t)/t \approx e_o z_j \Psi_i(t; \lambda_i)/kT \tag{30}$$

Inserting these potentials of mean force into Equation (28) we obtain a Kirkwood charging version of the DHX theory, which should be much better at higher Bjerrum parameters than the Debye-Hückel theory. This procedure might be seen as an interesting alternative to the DHX-RDF integration to find excess energy, heat capacity and osmotic coefficient as investigated in details in *e.g.* references [2-3]. In passing it may be noticed, that the reason that the DHX model is much better as a low concentration limit than the ordinary DH model - as discussed in the abovementioned references - is that they only assume the *structure* of the electric double layer to be given by the linear Debye-Hückel theory, but *not* the charging procedures! When - for potentials of mean force much smaller than kT - the correlation functions can be approximated by

$$h_{ij}(t;\lambda_i) \approx -W_{ij}(r;\lambda_i) \tag{31}$$

we retain from Equation (28) the usual DH formula

$$\ln y_i = -(B_r/2)z_i^2\kappa a/(1+\kappa a) \tag{32}$$

using

$$(\kappa a)^2 \equiv 4\pi B_r \sum_j z_j^2 \rho_j^* \tag{33}$$

In the Güntelberg charging process, one also charges one ion of the i'th species, keeping the charge of all others constant. However, the statistical mechanical formula Equation (28) is not used. Instead one uses the ordinary formula for the electrostatic energy of charged interacting point charges [20]

$$\text{electrostatic energy} = (1/2)\left[\sum_i z_i e_o \Psi_i'\right] \tag{34}$$

where the dash on the potential signifies the potential from all charges different from the i'th (so that self-energies are avoided). The factor (1/2) is due to the linearity between the charges and the potentials during the charging process. Similarly, the electrostatic *free energy* contribution of charging a single ion at the surface ($r = a$) is in the simple DH approach *postulated* to be given by the charge multiplied by half the surface potential stemming from ions *other* than the central ion:

$$\mu_{i,ex}/kT = \ln y_i = (1/2)z_i e_o\{\Psi_i(a) - z_i e_o/(4\pi\epsilon kTa)\} \tag{35}$$

Inserting for $\Psi_i(a)$ the DH-expression, we obtain once more the formula (32). However, it seen that the correctness of this charging procedure is a special case of the more general Kirkwood charging (28), which has a *nonlinear* relation between the potentials and the excess free energy per ion. Furthermore, the excess chemical potentials are *functionals* of the potential distribution and not only dependent on the surface potential. Only when $e_0 z_j \Psi_i(t)/kT \ll 1$, the relations (30-31) indicate that there is linearity, and the radial integration may be performed and expressed through the surface potential. Only in this case, the Güntelberg charging process is the right one and leads to Equation (32). The same can be said when all the ions are charged simultaneously to obtain the exces Helmholtz free energy (*Debye charging*).

The status of the nonlinear Poisson-Boltzmann equation

Interestingly enough, the *double layer structure* predicted by the linear Poisson-Boltzmann equation seems to be quite correct in many cases, where classical electrochemistry claims that it should fail. Much of the effort in the literature of spherical double layers (polyelctrolyte and colloid thermodynamics) has been concerned with correcting for the *nonlinearities* in the Poisson-Boltzmann equation but according to the preceding analysis this does not seem to be worth the while - or even to be wrong - since the solution of the linear P.B. equation is almost perfect for the potential distribution in the *spherical* double layer. This should be contrasted with the situation in the *plane* electric double layer (with an externally induced electric field), where the *nonlinear* Gouy-Chapman theory seems to be very well in accordance with Monte Carlo simulations for the ionic distribution as well as for the potential distribution, whereas the linear theory is not, see the review paper of Carnie and Torrie [21]. This may explain the succes of the nonlinear Poisson-Boltzmann treatment for such phenomena as *electrode capacitance* and electrocapillarity (although image charges are usually neglected, and a lot of complications are probably swept under the blankets of »Stern layers« and »inner and outer Helmholtz layers«!).

The difference between the plane and the spherical case is not just due to difference in surface charge density. A singly charged ion with a diameter of 0.30 nm, for example, has a surface charge density equal to $\sigma = 0.57\,\mathrm{C/m^2}$. For a plane electric double layer and *e.g.* an 0.1 mol/L 1:1 electrolyte, the surface potential only rises linearly with the surface charge density (as prescribed by the linear P.B. approach) up to $\sigma = 0.04\,\mathrm{C/m^2}$. At higher surface charge densities, the nonlinear P.B. surface potential rises gradually more and more slowly with σ (*sublinear* dependence), and the deviation at $\sigma = 0.20\,\mathrm{C/m^2}$ is as much as 100%! (See Reference [21], Figure 2). Comparison with Monte Carlo simulations exhibits the MC surface potentials to deviate even more (in the same direction) from the linear P.B. potentials than the nonlinear P.B. surface potentials ([21], Figures 6-7). Thus, it might still seem somewhat »mysterious« that the linear approach and the DHX model performs so well in *spherical* double layer. I shall attempt an explanation in the next paragraph.

The »DHX mystery« and its possible resolution

Ruff [22] has attempted »a formal mathematical legalization of the exponential Debye-Hückel theory«, but his paper left me in a state even more mystified than before. In short, the strange thing about this model is, that it uses the electric potential of the ordinary DH approach based on the *linear* P.B. equation to estimate the (electric) potential of mean forces. Then these are used as highly *nonlinear* expressions for the ionic distributions - involving exponentials of exponentials divided by the separation. The charge densities calculated by these RDF's should certainly then be in conflict with the linear P.B. equation and with the charge normalisation of the ordinary DH approach. Nevertheless, Olivares and McQuarrie [15-16] showed, that a renormalisation of the DHX RDF's had very little effect on the results.

I think, that the relative success of the DHX theory lies in the remarkable *numerical* fact, that the Debye-Hückel potential distribution happens to be an *almost* perfect »*eigenfunction*« (with »eigenvalue« equal to unity) to the *Poisson integral operator* described in the Appendix, when inserted as the potential of mean forces. Since it is reasonable to assume, that the electric part of the potential of mean forces is dominated by the interactions through the electric potential, the DHX theory is quite consistent without regard to the linearisation condition (24). Let us consider some examples:

Inserting the DHX potential of mean forces given by Equation (23) into the

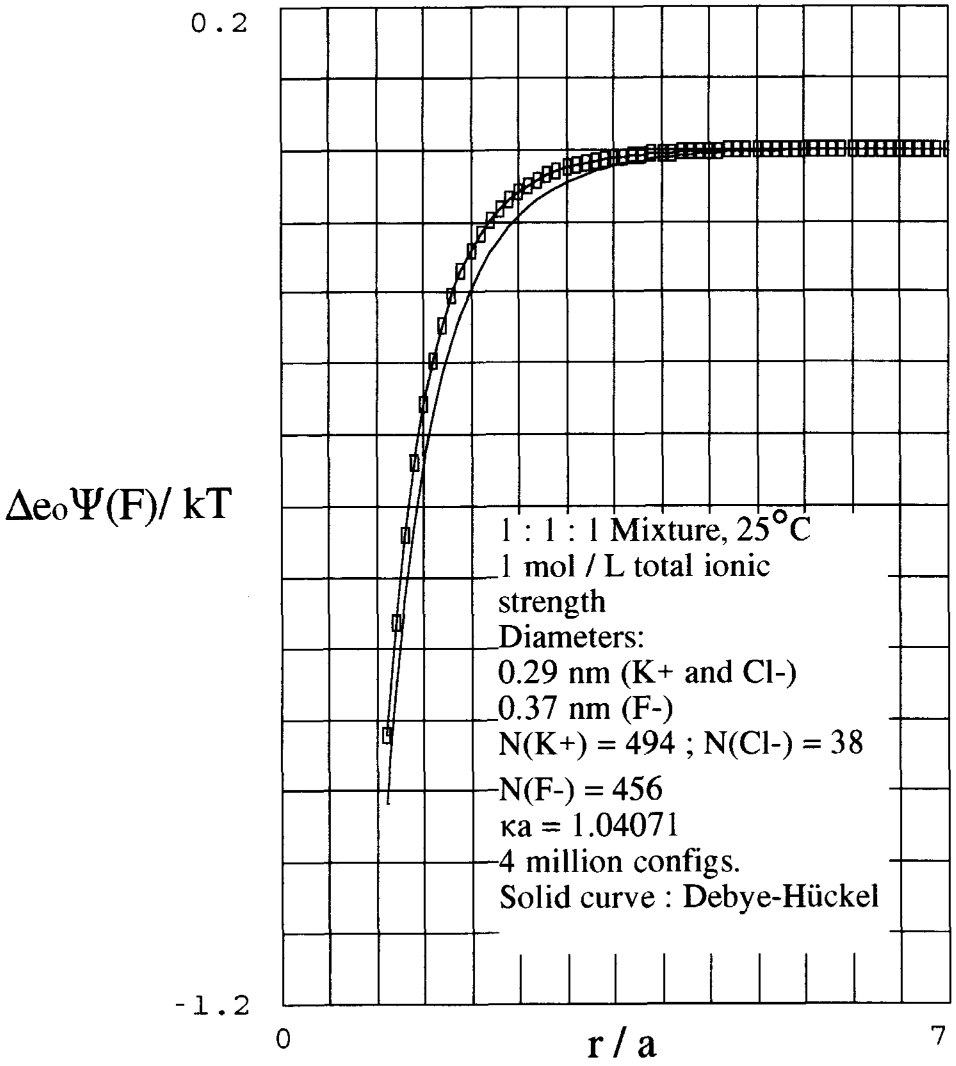

Figure 18 The Poisson-integrated potential around the F^- ion in the same 3-ion system as in Figures 15-17. The correspondence between the MC data (rectangles + curve) and the Debye-Hückel approximation (full curve without rectangles) is less good than for the potential around K^+ (Figure 15), but better than for the potential around Cl^- (Figure 17) All potentials are relative to the potential at $r/a = 6.865789$.

»Poisson operator« given in Equation (1) in the case of $B = 1.546$, $\kappa a = 0.139383$ and equal ion size, the output electric potential distribution is *indistinguishable* from the DH potential (and from the Monte Carlo values) in a plot similar to Figure 1. To see a slight difference, we have to scrutinize the conditions in the far tail by weighting $W_{ij}(t)$ by t, for example. Therefore, the figure will not be shown. Instead, we consider the even more drastically nonlinear example of an ultradilute

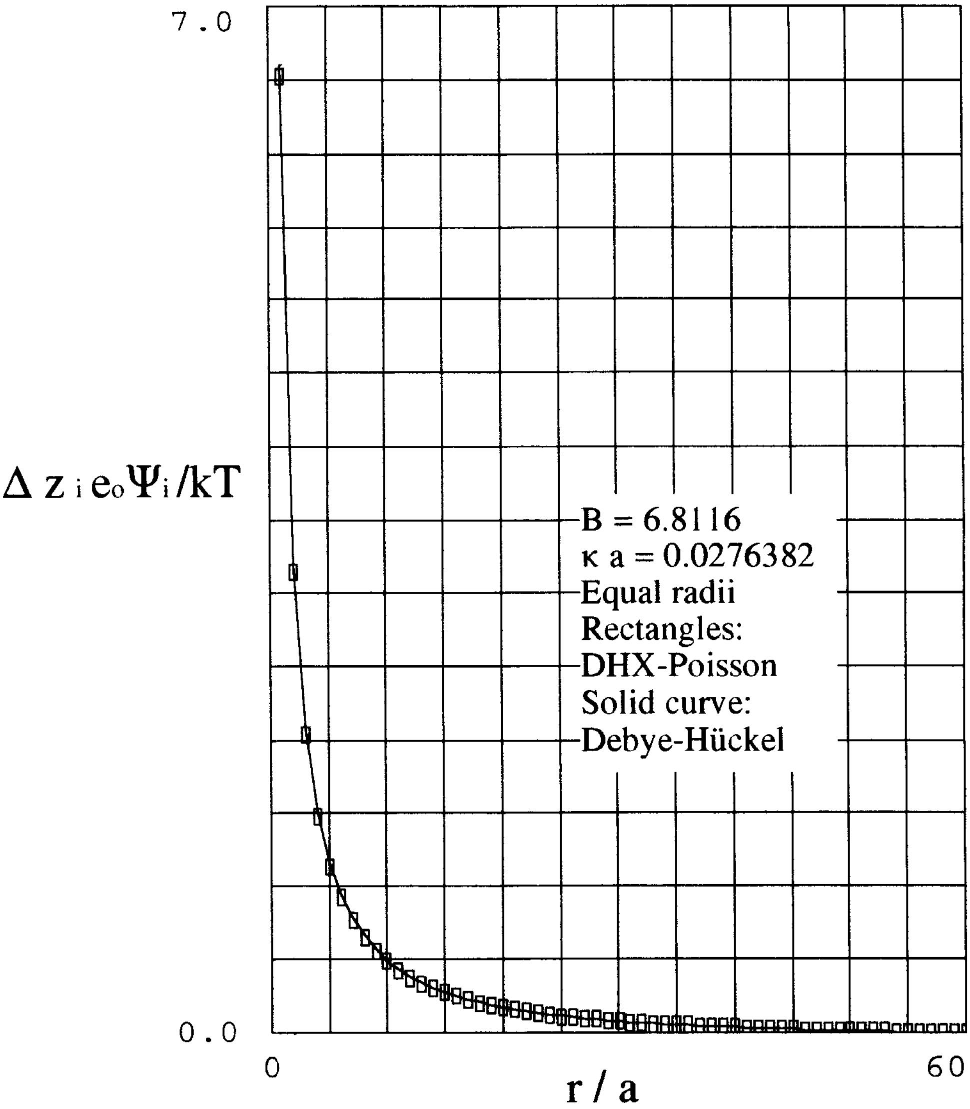

Figure 19 The Debye-Hückel potential is seemingly quite perfectly regenerated, when it is used as the potential of mean forces to calculate the DHX charge density, which is then subjected to Poisson integration. Even in this case of an ultradilute 2:2 electrolyte, where $2e_0|\Psi|/kT$ is close to 7 at contact, which is certainly $\gg 1$! All potentials are relative to the potential at $t = r/a = 60$.

2:2 electrolyte ($B = 6.8116$, $\kappa a = 0.0276382$, equal ion size) in Figure 19. Again, the simple DH potential distribution comes out almost exactly of the Poisson-DHX integrations in the window up to a separation of 60 ion diameters shown in this Figure. Indeed, in this case, the DHX model is much more consistent with itself, than with the Monte Carlo data, as seen in Figures 13–14.

In the abovementioned two cases, the normalisation factors in the DH-potential given as $\exp(\kappa a)/(1+\kappa a)$ is very close to unity, and the difference between the DHX and the EXP model is negligible, so let us consider a 1:1 electrolyte (with equal ion size), $B=2$ and $\kappa a=1$ (Figure 20). The plot of the potential differences against $t=r/a$ exhibits indiscernible Debye-Hückel potentials and DHX-Poisson potentials, and to reveal the small inconsistency in the far tail, the potential differences in Figure 20 have been weighted by t. The correspondence close to contact is still perfect, but the small deviations in the far tail demonstrates, that the »eigenfunction« property of the DH potential is a practical, numerical property and not an exact property. However, there is only $\approx 2.1\%$ more charge in the DHX ion cloud than at the central ion!

In References [5, 12] it was advocated, that the linear P.B. equation should be given the formulation

$$\nabla^2\rho_{q,i} \approx \kappa^2\rho_{q,i} = -\varepsilon\kappa^2\nabla^2\psi_{q,i} \tag{36}$$

which is equivalent to the usual potential formulation for the ordinary Debye-Hückel problem, but allows for an additive potential in cases, where the P.B. equation is linearized around a high non-zero potential as in charged micropores [12]. It would be interesting to see, how far the DHX approximation for the charge density satisfies this linear eigenvalue problem. Figures [21-22] show two examples. It is seen - not surprisingly - that the approximation is only valid in the tail, but fails seriously close to contact. However, the Poisson integration is much more influenced by the conditions in the tail than close to contact, as it was demonstrated also in the insensitivity to the discontinuities in the charge densities close to contact in the MC data for ions of *different* sizes. Therefore, the DH potential is most consistent close to contact!

The same is correspondingly true for the MC potentials of mean forces. Figure 23 shows, that the MC potentials of mean forces are closest to the DHX approximation at *contact* in a transformation of plots 9-10. This was also demonstrated for many other systems in Reference [5].

Hommage to Debye and Hückel

As a result of the studies performed in Reference [5] and in the present paper, we may conclude that one part of Debye's and Hückel 's original conjecture is quite right in the *spherical* case (the surface potentials), whereas the other part (the charging procedure) is quite wrong. There is nothing to blame these *grand old men* of electrochemistry, however, since they developed their theory long before the statistical mechanics of solutions had become mature and long before the McMillan-Mayer status of the primitive model was made clear. Rather, the high precision MC studies performed until now have confirmed the brilliance of the intuition of the founders of electrochemical thermodynamics!

APPENDIX ON POISSON INTEGRATION

For an arbitrary, spherical symmetrical charge distribution in a simple linear dielectric material the Poisson equation can be written:

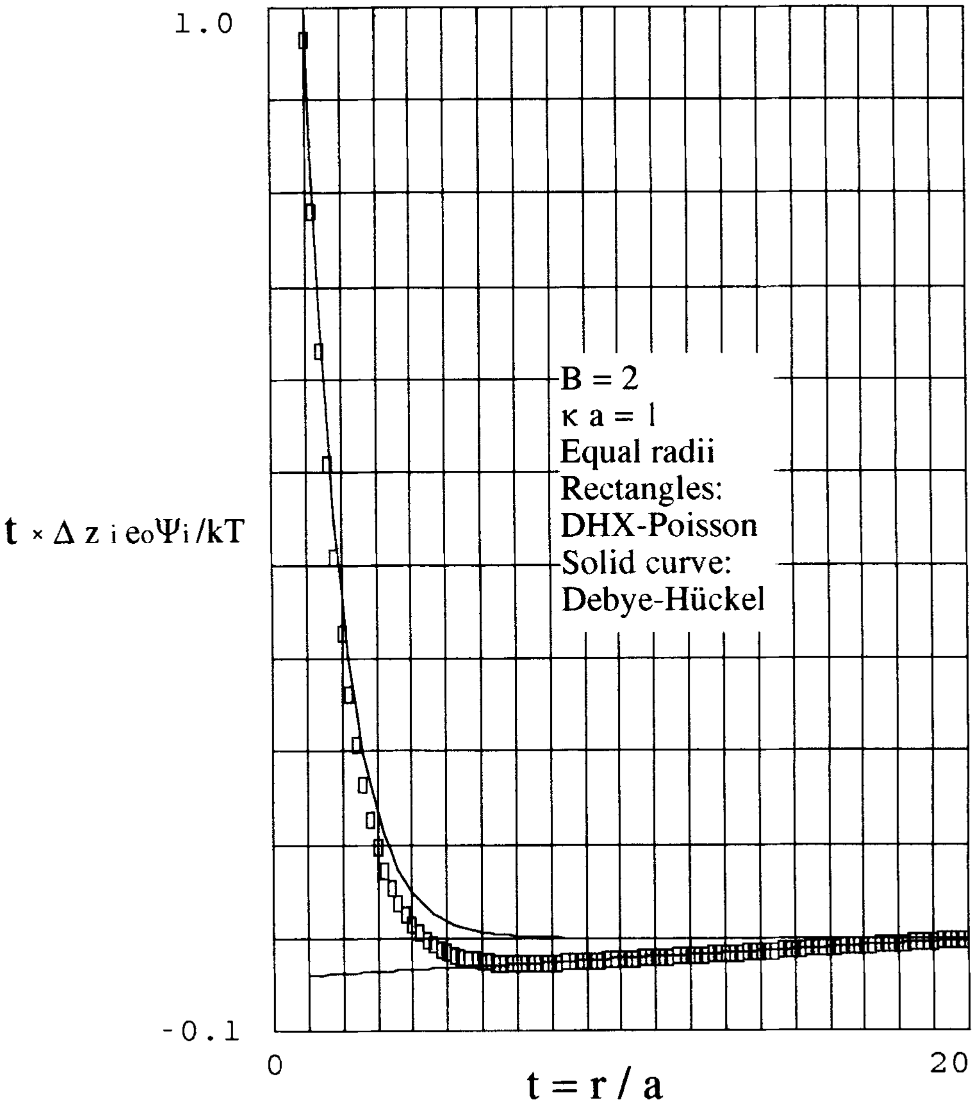

Figure 20 A 1:1 electrolyte at moderate concentration with $B = 2$ and $\kappa a = 1$, where the Debye-Hückel normalisation factor $\exp(\kappa a)/(1 + \kappa a)$ (≈ 1.36) is of importance. In the same kind of plot as in Figure 19, the Debye-Hückel potential seems as perfectly regenerated in the DHX-Poisson integration as for a 2:2 electrolyte. To demonstrate, that the DH potential is not an exact »eigenfunction« of the nonlinear, functional Poisson integration operator, the potential *differences* have been weighted by $t = r/a$. All potential differences are relative to the potential at $t = 20.8$. At large t, the *weighted* potential differences are asymptotic to the solid, straight line shown $= 0.002\ (t - 20.8)$. This corresponds to the dependence $e_0 z_i \Psi_i/kT \approx [z_i e_0 \Psi_i(t = 20.8)/kT + 0.002] - (0.002 \cdot 20.8)/t$. Setting $z_i e_0 \Psi_i(t = 20.8)/kT = -0.002$, this is a Coulomb potential with a radial dependence $-0.0416/t$ compared to the original $+B/t$ from the central ion. Thus, there is only $0.0416/B \approx 2.1\%$ more charge in the DHX ionic cloud than at the central ion. Thus, the DHX charge density is close to be normalized, too!

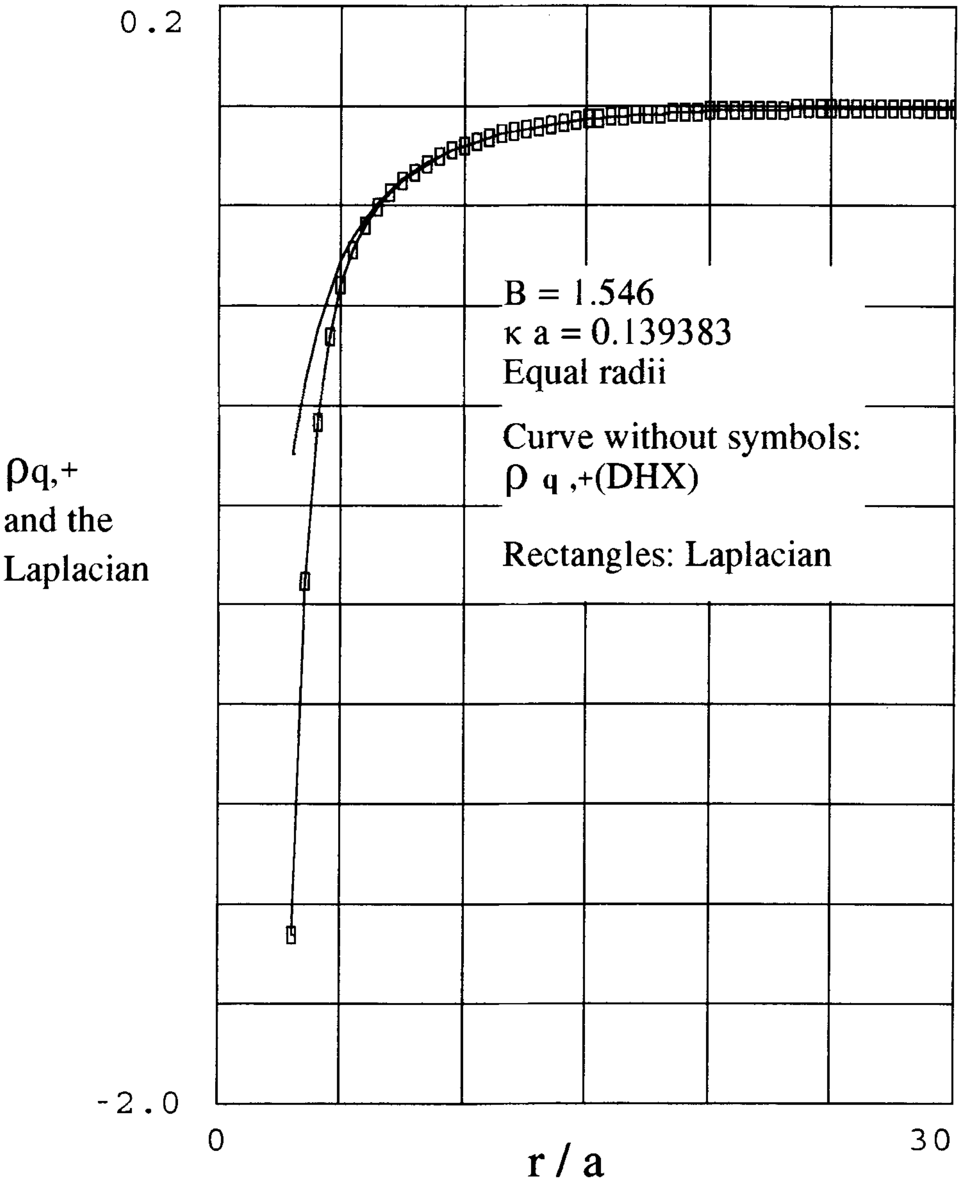

Figure 21 Numeric evaluation of the Laplacian [$= d^2/dt^2 + (2/t)d/dt$] of the dimensionless DHX charge density around the positive ion [$\rho_{q,+} \equiv g_A$(DHX) $- g_{+-}$(DHX)] at different separations for a 1:1 electrolyte with $B = 1.546$ $\kappa a = 0.139383$ and equal ionic radii. The Laplacian has been divided by $(\kappa a)^2$ to test, if the DHX charge density satisfies Equation (36). This is the case for $t = r/a > 5$ or $|\rho_{q,+}| < 0.3$, but closer to contact, Equation (36) is a very bad approximation. Nevertheless, the potential close to contact is the Debye-Hückel potential, since the main contribution to the potential even at contact is stemming from the larger amount of charge in the outer spherical shells than in the shells close to contact.

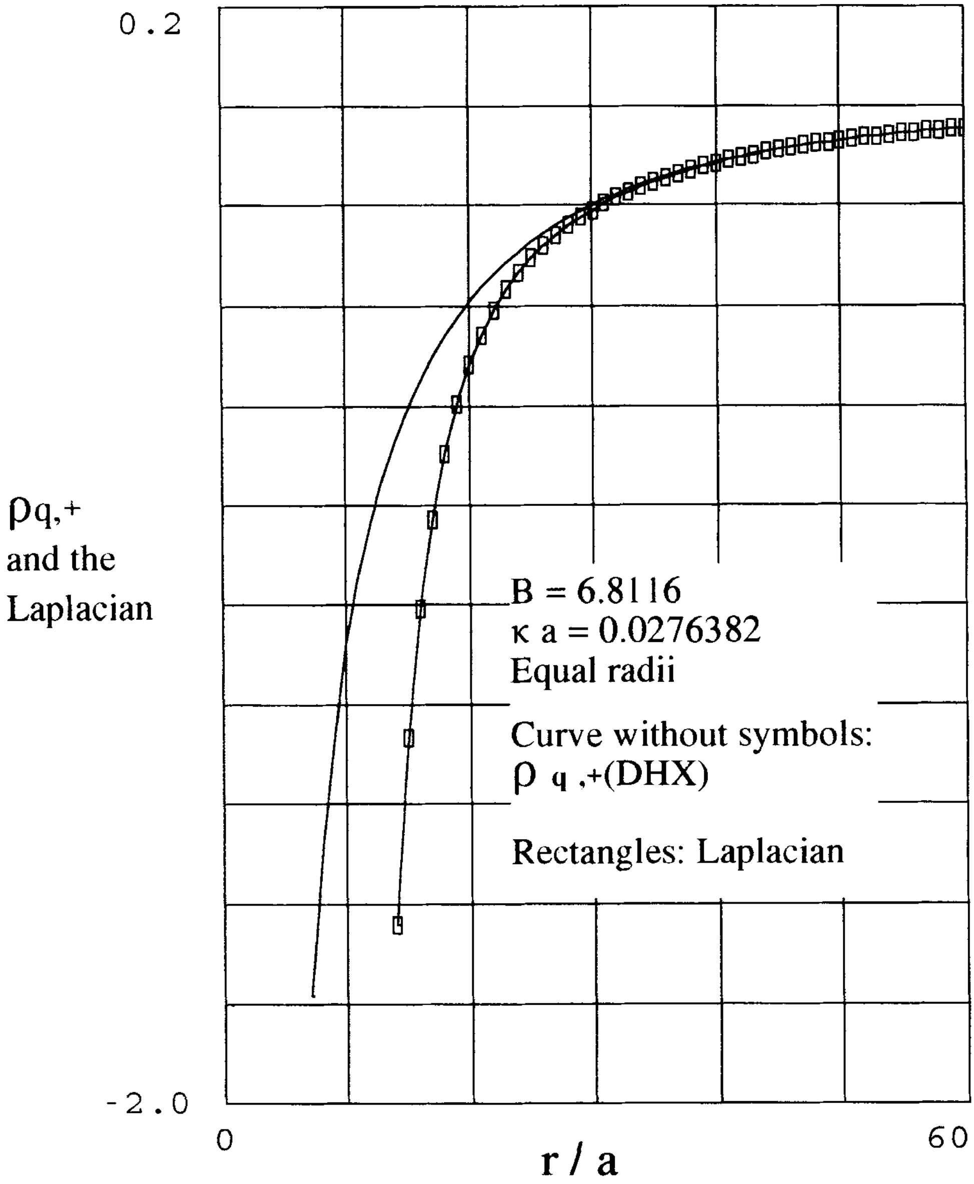

Figure 22 The same kind of plot as in Figure 21, but for an ultradilute 2:2 electrolyte. The DHX charge density satisfies Equation (36) for radial separations > 25 ion diameters. Nevertheless, the DHX-Poisson potential at contact is perfectly Debye-Hückelian!

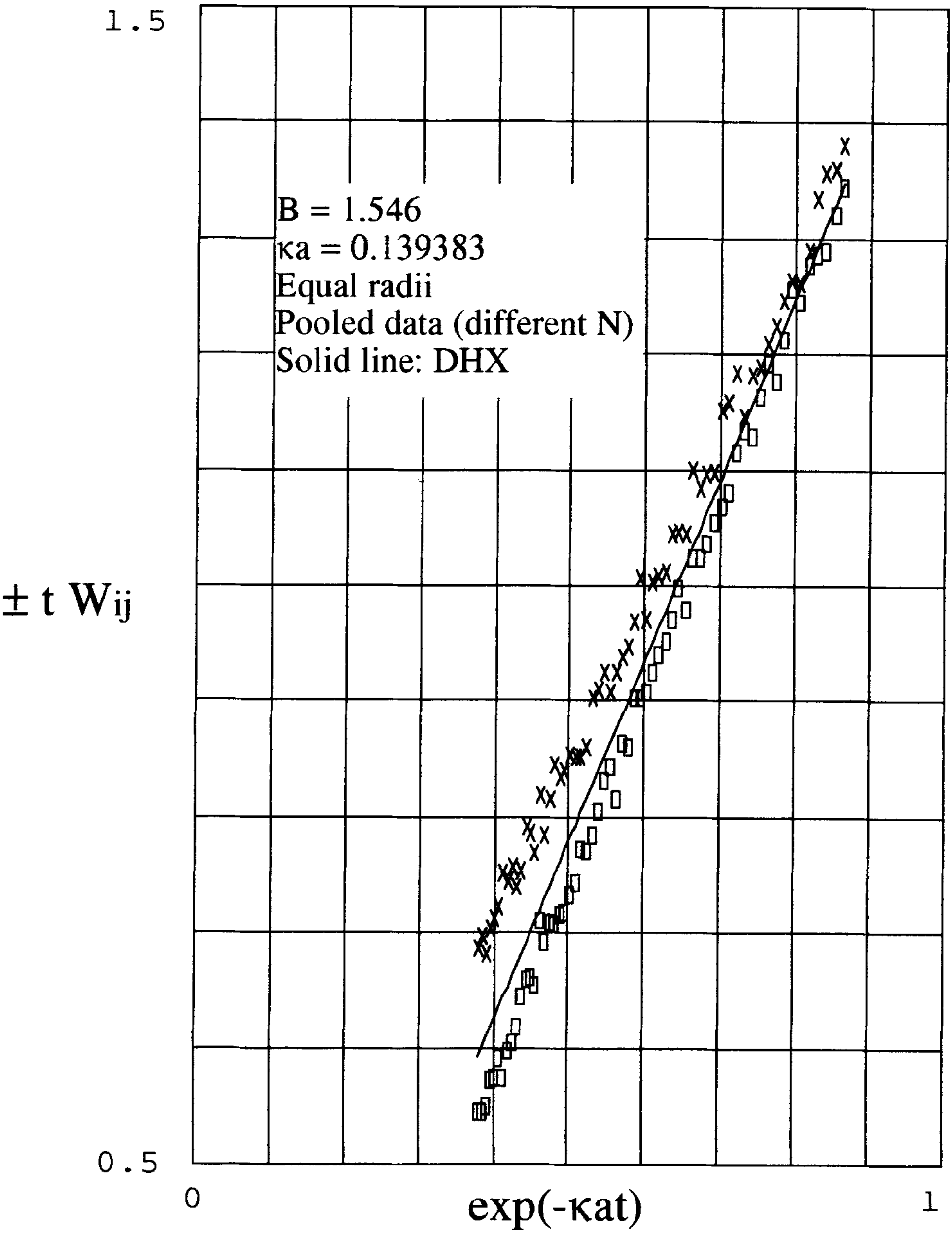

Figure 23 A transformation of the plot in Figure 1 of the Monte Carlo dimensionless potentials of mean forces between like and unlike charges for a 1:1 electrolyte with $B = 1.546$, $\kappa a = 0.139383$ and equal ionic radii. Rectangles represent $t \cdot W_{+-}$ and crosses $t \cdot W_A = t \cdot W_{++} = t \cdot W_{--}$. The DH potential (DHX model) is best at contact. In the range from $t = r/a = 1$ to $t = 7$ better approximations are the following: $-t \cdot W_{+-} = 1.665 \exp(-\kappa at) - 0.092$ (correlation coeff. $r = 0.999$) and $+t \cdot W_A = 1.405 \exp(-\kappa at) + 0.147$ ($r = 0.997$).

$$[d/dr + (2/r)]E = \rho_q(r)/\varepsilon \tag{A1}$$

E is the (outwardly directed) electric field strength, and $\rho_q(r)$ is the space charge density at position r. The solution to the homogeneous differential equation is C/r^2 with C arbitrary. By the method of variation of parameters, a particular solution of the form $K(r)/r^2$ may be sought. We then obtain:

$$dK/dr = r^2\rho_q(r)/\varepsilon \tag{A2}$$

$$K(r) = \text{constant} + \int_o^r x^2[\rho_q(x)/\varepsilon]\,dx \tag{A3}$$

Thus, the general form of the solution (Al) is given as:

$$E(r) \equiv -d\psi/dr = \left\{C + \int_o^r x^2[\rho_q(x)/\varepsilon]\,dx\right\}/r^2 \tag{A4}$$

Setting $\psi(\infty) = 0$, we have by another integration:

$$\psi(r) = (C/r) + \int_{s=r}^{\infty}(1/s^2)\int_{x=0}^{s} x^2[\rho_q(x)/\varepsilon]\,dx \tag{A5}$$

The outmost integral in (A5) may be transformed by partial integration:

$$\int_{s=r}^{\infty}(1/s^2)\int_{x=0}^{s} x^2[\rho_q(x)/\varepsilon]\,dx = \left[-(1/s)\int_{x=0}^{s} x^2[\rho_q(x)/\varepsilon]\,dx\right]_{s=r}^{\infty} + \int_{s=r}^{\infty} s[\rho_q(s)/\varepsilon]\,ds \tag{A6}$$

Thus, using that the charge distribution is *bounded*, or more specifically

$$\int_{x=0}^{\infty} x^2[\rho_q(x)/\varepsilon]\,dx \quad \text{exists} \tag{A7}$$

the general solution may be written:

$$\psi(r) = (C/r) + (1/r)\int_{x=0}^{r} x^2[\rho_q(x)/\varepsilon]\,dx + \int_{x=r}^{\infty} x[\rho_q(x)/\varepsilon]\,dx \tag{A8}$$

The first term will be non-zero if there is a point charge at $r = 0$. Thus, the potential around an ion of charge q_i positioned at $r = 0$ surrounded by a continuous charge distribution is given as (A8) with the constant C given by:

$$C = q_i/(4\pi\varepsilon) \tag{A9}$$

Since the continuous charge density is zero for radial separations less than the minimum contact distance between ion i and the other ions $(a_{i,\min})$, the Equation (1) in the main text follows at once.

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