

Scientific paper

The Distribution of Ions between a Bulk Electrolyte Solution and Charged Microcapillaries in Solvents with Low Dielectric Constant

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Abstract

The distribution of ions between charged cylindrical micropores modeling an adsorbing material and a bulk electrolyte was calculated. For this purpose the Grand Canonical Monte Carlo method and the method based on solution of the non-linear Poisson-Boltzmann equation were utilized. The focus was on the effect of the solvent, characterized here merely by its dielectric constant. The Donnan exclusion coefficient and mean activity coefficient of an electrolyte confined in a microcapillary were calculated as functions of the electrolyte concentration and the dielectric constant of the solvent. The exclusion coefficient was found to decrease with increasing electrolyte concentration and with decreasing dielectric constant of the solvent. In other words, the desalination mechanism becomes very inefficient in solvents with dielectric constant lower than that of water. In comparison with Monte Carlo simulations the Poisson-Boltzmann theory was able to predict correct trends for the Donnan exclusion coefficient, but it grossly overestimated Monte Carlo results. The microscopic picture which emerged on the basis of the distributions of small ions in the microcapillary was helpful in explaining these results.

Keywords: Electrolytes, microcapillary, dielectric constant of solvent, Donnan equilibrium, Monte Carlo simulation, Poisson-Boltzmann theory

1. Introduction

Material containing charged microcapillaries surrounded by a low-molecular weight electrolyte usually contains a different concentration of electrolyte than the surrounding equilibrium solution^{1,2} (for a review of earlier works see³). The ability of charged microporous material to exclude electrolyte forms the basis of important separation processes such as ultrafiltration and reverse osmosis. For this reason the problem of electrolyte exclusion from porous media continues to be of interest to many researchers.⁴⁻²²² In these studies the electrokinetic problem is essentially reduced to determination of the ionic profile inside the microcapillary. In most such studies the solution of the nonlinear Poisson-Boltzmann equation, despite its well known deficiency (see, for example^{3,7}), is utilized for this purpose. Knowledge of the ionic distribution within the charged microporous material therefore represents

the first step toward better understanding and design of separation processes. Note that studies of this phenomenon are important for the biological sciences as well.²³

In a series of papers we investigated the equilibrium distribution of ions, most often modeled as charged hard spheres in a dielectric continuum representing the solvent, between a charged cylindrical microcapillary and the external (bulk, isotropic) electrolyte.²⁴⁻³⁰ The Grand Canonical Monte Carlo method was applied²⁵ to test the theory based on the numerical solution of the non-linear Poisson-Boltzmann equation. The results indicate that the latter approximation is reasonably accurate for a +1:-1 electrolyte present in the microcapillary. Qualitative and quantitative differences between the two types of calculation were noticed for +2:-2 electrolytes. We have shown in one of the more recent papers²⁹ that a modified Poisson-Boltzmann equation yields improved agreement with the simulation results. The computer simulations and Poisson-Boltzmann theory were extended to treat asym-

metric +1:–2 and +2:–1 electrolytes.²⁷ The model was further generalized²⁸ to mixtures of +2:–1/+1:–1 in order to account for the ion-selectivity effects in such mixtures. In both cases the results were in qualitative or semi-quantitative agreement with experimental data. More recently computer simulations of a strongly coupled system, where the model microcapillary was in equilibrium with a +3:–3 electrolyte, were presented.³⁰ In agreement with some experimental data^{4,6,31} we found that in the case of multiply charged counterions the strong ion-ion correlation may yield a "negative rejection", that is, an increase of the electrolyte concentration in the micropore. Boda and coworkers³² performed simulations of electrolytes at an electrode. They found that negative adsorption can occur at low temperatures (for high ionic coupling). This finding is at variance with the result predicted by the traditional Poisson-Boltzmann theory. Note, however, that a modified Poisson-Boltzmann equation^{33,34} which explicitly includes the ion-ion correlations, correctly predicts this effect. The dielectric constant of the solvent in the calculations presented in this paper plays a similar role as temperature in the aforementioned studies.^{32–34}

In studies presented so far we independently varied the main parameters of the model such as the charge density and radius of the microcapillary, and the concentration and composition of the invading electrolyte. All these investigations apply to aqueous solutions at 298 K, and no calculations for other conditions were published. An important model parameter, the influence of which has not been yet explored, is the dielectric constant of the solvent. Note that in continuum-solvent models all the properties of the solvent are subsumed in its dielectric constant. By varying this quantity we can influence the Coulomb interactions in the external (bulk) electrolyte, as well as its interaction with the surface charge. By decreasing the dielectric constant of the solvent, we equally increase the ion-ion and ion-capillary interactions. For this reason the influence of the solvent on the equilibrium distribution of electrolyte should be different than, for example, the influence of the variation of the surface charge density. The solvent effect as brought about by the dielectric constant variation therefore deserves a separate evaluation. In addition, the accuracy of the Poisson-Boltzmann approximation has not yet been tested under these conditions and this is another goal of present study. Since no experimental data is available for ionic adsorption from solvents with lower dielectric constant than water, the results presented here provide useful estimates of the dielectric constant effects on the electrolyte adsorption.

2. Methods of Calculation

2.1. Model

The interaction potential between two ions of species i and j separated by a distance r_{ij} is given by

$$u_{ij}(r_{ij}) = \begin{cases} \frac{z_i z_j L_B}{r_{ij}}, & \text{if } r_{ij} \geq a_{ij} \\ \infty & \text{if } r_{ij} < a_{ij}, \end{cases} \quad (1)$$

where $a_{ij} = (a_i + a_j)/2$, with a_i being the diameter of a particle of type i . In this paper we treat only symmetric electrolytes so $a_i = a_j = a$. We define the Bjerrum length as

$$L_B = \frac{e_0^2}{4\pi\epsilon_0\epsilon_r}. \quad (2)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of the system, z_i is the valency of ion type i , and e_0 is the proton charge. The fixed charge q is assumed to be smeared uniformly over the inner surface of the capillary with charge density σ

$$\sigma = \frac{q}{2\pi R_c h}, \quad (3)$$

where $R_c (= R + a/2)$ and h are the radius and length, respectively, of the microcapillary (cf. Fig. 1, of Ref.²⁹). In this model the centres of the ions can approach up to the distance $a/2$ (ionic radius) from the charged surface.

2.2. The Poisson-Boltzmann Equation

The Poisson equation, which relates the electrostatic potential $\psi(r)$ to the charge density $\rho_e(r)$, is the fundamental equation of this approach. In cylindrical geometry this equation reads

$$\frac{1}{r} \frac{d}{dr} \left[r \frac{d\psi}{dr} \right] = -\frac{\rho_e(r)}{\epsilon_0\epsilon_r} \quad (4)$$

where $\rho_e(r)$ at distance r is given by:

$$\rho_e(r) = e_0 \sum_i z_i \rho_i(r) \quad (5)$$

Each $\rho_i(r)$ can be approximated as:

$$\rho_i(r) = \rho_i(0) \exp[-e_0 z_i \beta \psi], \quad (6)$$

where i can be either +, or –, e_0 is the elementary charge, $\epsilon_0\epsilon_r$ the dielectric constant and $\beta = (k_B T)^{-1}$. Further, $\rho_i(0)$ is the number density of the ionic species i at the position $r = 0$ (see Fig. 1, of Ref.²⁹), where the electrostatic potential $\psi(r)$ is chosen to be zero. Note that the condition of electroneutrality may not necessarily be satisfied locally^{10,11} (at $r = 0$, $\rho_+(0) \neq \rho_-(0)$), though of course is satisfied globally within the infinite microcapillary. An analytical solution for this differential equation only exists for $|e_0 z_i| \beta \psi \ll 1$, and the equations above need to be solved numerically. The boundary conditions are prescribed by the Gauss statement (for details see, Ref.²⁴).

Table 1: Calculated^{37,38} negative logarithm of the mean-activity coefficient of bulk electrolyte, $-\ln \gamma_{\pm}^b$, as a function of the electrolyte concentration c_b at different values of L_B/nm .

$c_b/(\text{mole}/\text{dm}^3)$	$L_B/\text{nm} = 0.714$	$L_B/\text{nm} = 1.428$	$L_B/\text{nm} = 2.142$	$L_B/\text{nm} = 2.856$
0.025	0.1452	0.4106	0.7536	1.299
0.050	0.1852	0.5231	0.9436	1.431
0.100	0.2267	0.6466	1.151	1.721
0.150	0.2480	0.7199	1.228	1.896
0.200	0.2595	0.7699	1.365	2.020

2. 3. Grand Canonical Monte Carlo Approach

The Poisson-Boltzmann theory treats the ions as pointlike charges and ignores their mutual correlation. This may lead to substantial errors when divalent or trivalent ions are present in the system.^{3,24,26,29,30} Computer simulations are free of this approximation. The Grand Canonical Monte Carlo method proved to be very useful in such calculations^{24,35} and has been used many times before, most recently in Ref.³⁶ where the details of the method were outlined. The advantage of this approach is that by sampling at constant chemical potential the bulk phase is defined unambiguously. To calculate the Donnan exclusion coefficient Γ as a function of c_b , we need to know the mean activity coefficient, γ_{\pm}^b , of the equilibrium bulk electrolyte at concentration c_b . This information can be obtained by a separate Grand Canonical Monte Carlo (GCMC) computer simulation of an isotropic electrolyte or from the solution of the hypernetted-chain integral equation for such a system. As many times before,³⁷ we used the latter method to calculate γ_{\pm}^b in conjunction with the approximate expression proposed by Belloni.³⁸

3. Numerical Results

In the present study the following values of model parameters were used: $a = 0.425$ nm, $R = 3.825$ nm, $\sigma = 0.0711$ As/m² and L_B was varied from 0.714 nm over 1.428 nm and 2.142 nm to 2.856 nm. Experimentally the variation of the dielectric constant (and therefore L_B) can in this range be obtained by mixing water with 1,4-dioxane (see, for example, Ref.³⁹⁻⁴⁴).

First in Table 1 we present the results for the logarithm of the mean-activity coefficient of bulk electrolyte, $\ln \gamma_{\pm}^b$, as obtained from the HNC calculations.³⁸ This quantity is needed as input to the Grand Canonical Monte Carlo simulation. The calculations apply to five different concentrations of bulk electrolyte in the range from 0.025 to 0.200 mole/dm³. The accuracy of the integral-equation results for $L_B = 2.156$ nm was checked against the GCMC calculation. The agreement between the integral-equation theory based on the HNC approximation and the Grand Canonical Monte Carlo simulation is very good in this

range of parameters so only the HNC results are tabulated here.

Accurate measurements of the molal mean activity coefficients of NaCl in dioxane-water mixtures were provided by Dolar and Bešter.⁴¹ Our calculations agree qualitatively with the measured data; the mean activity coefficient γ_{\pm}^b decreases sharply with increasing L_B , that is with increasing percentage of 1,4-dioxane in mixture.

3. 1. Exclusion Coefficient

The Donnan exclusion coefficient, which is the principal result of this study, is defined as:

$$\Gamma = \frac{c_b - \langle c \rangle}{c_b} \quad (7)$$

where c_b is the concentration of co-ions in the bulk electrolyte solution and $\langle c \rangle$ their average concentration in the microcapillary. The coefficient Γ reflects how much of the electrolyte (co-ions) is "rejected" by a charged microcapillary. In most cases $\Gamma > 0$; if the majority of the co-ions are expelled from the microcapillary Γ approaches 1.

The GCMC results for the exclusion coefficient Γ as a function of c_b are shown in Fig. 1. As we see from this figure Γ decreases with increasing electrolyte concentra-

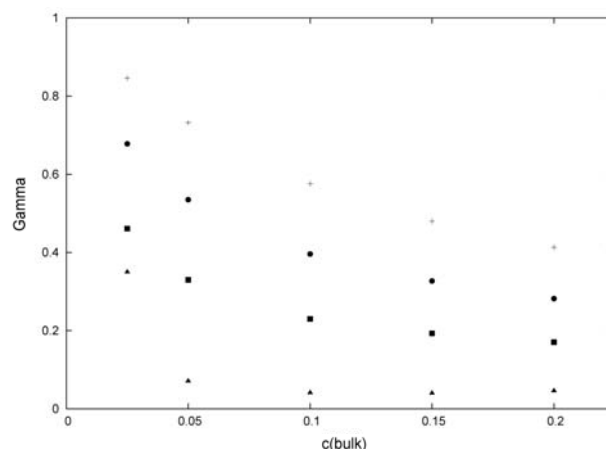


Fig. 1: GCMC results for the exclusion coefficient Γ as a function of the external electrolyte concentration. From top to bottom $L_B = 0.714$ nm (water at 298 K), 1.428 nm, 2.142 nm and 2.856 nm.

tion c_b , as also with increasing value of L_B (decreasing dielectric constant of the solvent). In one case, for $c_b = 0.2 \text{ mol/dm}^3$, we calculated Γ for $L_B = 0.357 \text{ nm}$, that is for a dielectric constant larger than that of water. The result for Γ was 0.58 under this condition. The concentration dependence is relatively easy to understand; the decrease in Γ (increase in $\langle c \rangle$) is due to the increased screening of the surface charges by electrolyte ions at higher concentration. The same functional dependence has been observed before (see, Fig. 4 of Ref.²⁷).

It seems to be more difficult to explain the L_B dependence presented in the same figure. For this reason it is instructive to re-visit some of the earlier results. In one of the preceding contributions²⁷ we examined the behaviour of the exclusion coefficient for microcapillaries of various charge density σ (see Eq. 3). As shown in Fig. 3 of Ref.²⁷, the Γ coefficient for solutions with monovalent counterions increases (see also Table I of²⁵) with increasing charge density and it levels off for higher σ values. The initial increase is due to the increased "coupling" between the charged inner surface of the microcapillary and electrolyte ions. The ion-surface interaction is proportional to σ , while the ion-ion "coupling" (see Eq. 1) does not change. Notice, however, that by increasing σ we also increase the concentration of counterions in the microcapillary. The "saturation" in Γ as seen in the GCMC and Poisson-Boltzmann results may be attributed to increased screening due to the increased concentration of the invading electrolyte.

Now consider the situation where monovalent counterions in the system are replaced by divalent ones. In such a case a significant decrease of Γ is observed, as inferred by comparing Fig. 4 of Ref.²⁷ with Fig. 7 of the same paper. In general, by replacing a +1:-1 electrolyte by a +2:-2 electrolyte the ion-ion interaction is increased fourfold while the ion-surface interaction only twofold. The strong ion-ion correlation between the divalent coun-

terions causes the exclusion coefficient to decrease in comparison with the case of a +1:-1 electrolyte.^{3,25,27}

Here the situation of interest is the one where by changing the solvent we decrease the dielectric constant (and accordingly increase L_B) in the model system. In such a case the strength of the ion-ion and ion-surface interactions both change proportionally to L_B . This produces qualitatively the same effect as an increase of the inter-ionic correlation in solutions with divalent counterions described above. We will discuss this issue further in connection with the ionic distributions presented in Fig. 6 and 7. Notice that for the value of charge density σ studied here, the counterion concentration, needed to neutralize the surface charge, in most cases exceeds the co-ion concentration.

The simplest estimate of capillary electrolyte rejection follows from the classical work of Donnan (see, for example, Ref.,³⁹ p. 410). The assumptions of the theory are the following: i) ion activities inside and outside (bulk) the microcapillary are equal to their concentrations; ii) the electroneutrality condition is satisfied in both the inside and outside solution. As shown in several papers^{28,36} the approach is at best only qualitatively correct. The main deficiency of the classical theory is that it cannot account for different L_B values; in other words it returns the same result regardless of the value of the dielectric constant of the solvent. We also need to say that this simple approach provides the correct trend for the concentration dependence of Γ .

A considerably more accurate approach is provided by the solution of the Poisson-Boltzmann equation (see, for example,³). Once the mean electrostatic potential is obtained from Eq. 4 the concentration $\langle c \rangle$ of the absorbed electrolyte and the coefficient Γ can be easily calculated. These results are shown in Fig. 2, which parallels Fig. 1, except that all the results were obtained by the Poisson-Boltzmann theory. The exclusion coefficient is

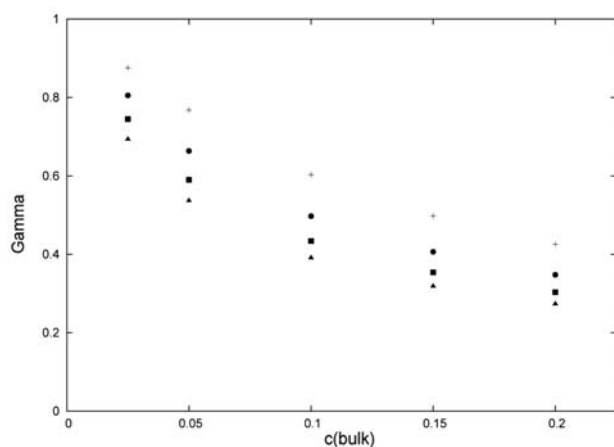


Fig. 2: Poisson-Boltzmann results for the exclusion coefficient Γ as a function of the external electrolyte concentration; legend as for Fig. 1

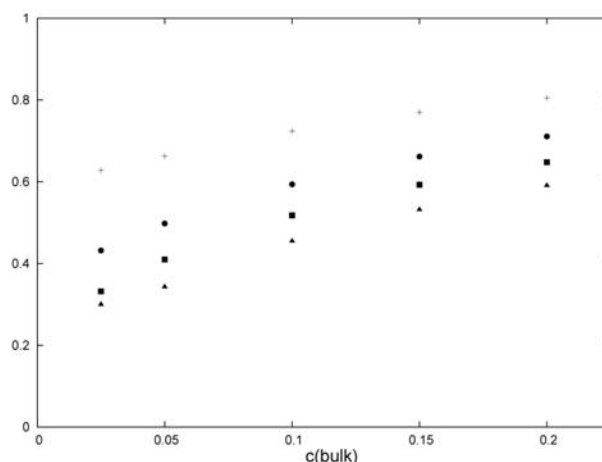


Fig. 3: GCMC results for the $Y = \gamma_{\pm} / \gamma_{\pm}^b$ ratio as a function of the external electrolyte concentration. From top to bottom $L_B = 0.714 \text{ nm}$, 1.428 nm , 2.142 nm and 2.856 nm .

plotted as a function of concentration and for four different values of the Bjerrum length L_B . By comparing Fig 2 (Poisson-Boltzmann result) with Fig. 1 (Grand Canonical Monte Carlo data) we notice a qualitative agreement between the two calculations. A closer inspection of data reveals that for the values of the model parameters studied here, the Poisson-Boltzmann theory overestimates the exclusion coefficient. As expected, the discrepancies increase with increasing strength of the interaction, as reflected in the Bjerrum length.

3. 2. Mean Activity Coefficient of a Confined Electrolyte

It is of some interest to present numerical results of the Grand Canonical Monte Carlo approach and the Poisson-Boltzmann theory for the mean activity coefficient of the electrolyte in such microcapillaries. Note that

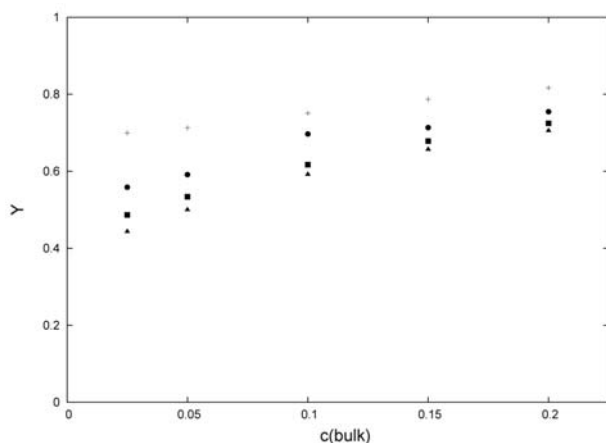


Fig. 4: Poisson-Boltzmann calculation results for the $Y = \gamma_{\pm} / \gamma_{\pm}^b$ ratio as a function of the external electrolyte concentration; legend as for Fig. 3

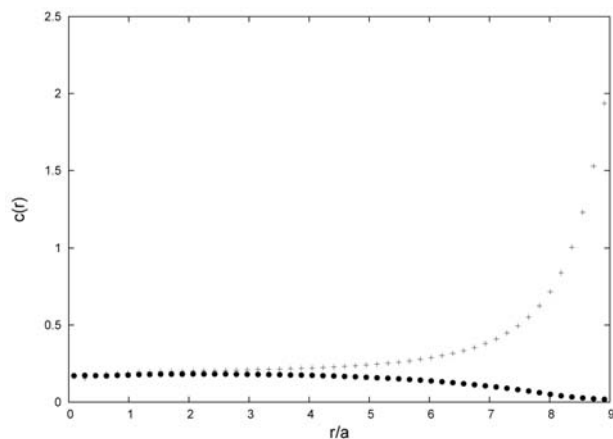


Fig. 5: Monte Carlo calculation results for ionic distributions inside a microcapillary; counterions (+), co-ions (●), $c_b = 0.2$ mole/ dm³, $L_B = 0.714$ nm.

according to the approximation inherent to the Donnan approach, the mean activities of the electrolytes in the inside and outside solution are the same, $\gamma_{\pm} = \gamma_{\pm}^b$.

Here in Fig. 3 and 4 we present the mean activity coefficient ratio $\gamma_{\pm} / \gamma_{\pm}^b$ as obtained by the two numerical methods. Again we notice the same trends; the mean activity coefficients ratio increases with increasing concentration of the external electrolyte. The Poisson-Boltzmann calculation yields $\gamma_{\pm} / \gamma_{\pm}^b$ values which are too high in comparison with the machine calculations. The disagreement between the two types of calculation increases with increasing coupling, i.e. with decreasing value of the dielectric constant of the solvent.

3. 3. Ionic Distributions

In this section we present local distributions of ions, $c(r/a)$, which may help us in understanding the exclusion

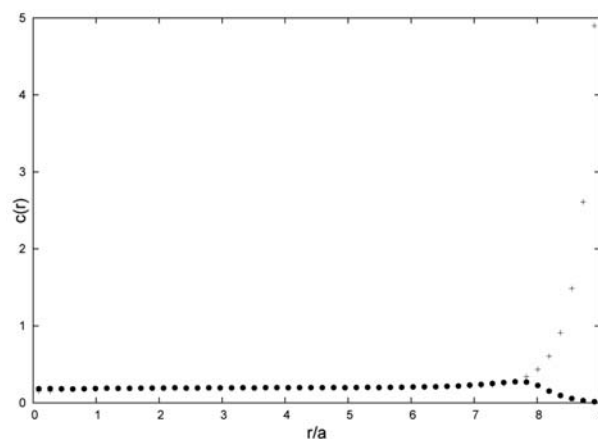


Fig. 6: Monte Carlo simulation results for ionic distributions inside a microcapillary; $L_B = 2.856$ nm other parameters as for Fig. 5

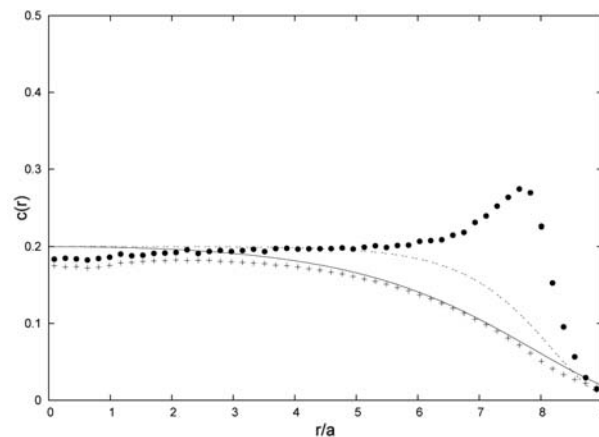


Fig. 7: Monte Carlo (symbols) and Poisson-Boltzmann (lines) results for the co-ion distributions inside a microcapillary; $L_B = 0.714$ nm (+; lower curve), $L_B = 2.856$ nm (ε; upper curve) other parameters as for Fig. 5.

coefficient data presented above. In Fig. 5 we present the counterion (+) and coion (•) distributions in the microcapillary. The x-axis, r/a , has its origin in the middle of the microcapillary. The results in Fig. 5 apply to $L_B = 0.714$ nm and those plotted in Fig. 6 to $L_B = 2.856$ nm: the external electrolyte concentration was 0.2 mole/dm^3 in both examples. In the latter example of higher coupling there is a much stronger accumulation of counterions next to the charged surface of the microcapillary. This in turn affects the distribution of co-ions, as is more clearly presented in Fig. 7, discussed next.

In comparison with the Poisson-Boltzmann calculation we only focus on the co-ion-surface distribution, which in our view most clearly explains the behaviour of the exclusion coefficient. As a consequence of the accumulation of counterions next to the surface of the microcapillary and the strong electrostatic coupling between counterions and co-ions for $L_B = 2.856$ nm, there is an increased concentration of co-ions in the next layer (overcharging). The Monte Carlo distribution of co-ions for $L_B = 2.856$ nm has a noticeable peak at $r/a \approx 7.8$. No such peak can be observed for lower couplings; at $L_B = 0.714$ nm, the co-ion distribution is monotonic. These kinds of co-ion distributions have previously been observed in solutions with divalent and trivalent counterions.^{25,30}

Fig. 7 also reveals the source of the discrepancy between the mean-field (Poisson-Boltzmann) theory and essentially exact computer simulations. The ionic distributions calculated via the Poisson-Boltzmann theory in this figure are shown by lines. As we can see, the Poisson-Boltzmann equation predicts the co-ion profiles to be monotonic in both cases. This is another example showing the deficiency of the mean-field theory, which does not account properly for the ion-ion correlations in the electrical double layer. These correlations yield an increased concentration of co-ions in the microcapillary and lead to a significant decrease of the Donnan exclusion coefficient, as indicated in Fig. 1. In the case of multivalent counterions the effect may be so strong that it actually yields negative Γ values, as shown theoretically in Ref.³⁰ This effect also causes the Poisson-Boltzmann predictions of Γ to be too high, and increasingly less accurate for higher L_B values.

4. Conclusions

The mean activity ratio $\gamma_{\pm}/\gamma_{\pm}^b$ of an electrolyte confined in a microcapillary versus the bulk electrolyte of the same type, decreases with increasing strength of the interaction, measured by the magnitude of the Bjerrum length L_B . The Poisson-Boltzmann calculations are in qualitative agreement with the Grand Canonical Monte Carlo data, but the Poisson-Boltzmann values for γ_{\pm} are considerably too high. The

discrepancy between the two methods increases with increasing L_B , i.e. decreasing dielectric constant. The simulated mean activity coefficient ratio increases with increasing concentration c_b of the equilibrium bulk electrolyte. Again the trend is correctly reproduced by the Poisson-Boltzmann equation.

The other quantity presented in this study, the Donnan coefficient Γ , is considerably more sensitive to variations of dielectric constant of the solvent and therefore to L_B . Note that this quantity measures the amount of electrolyte being rejected from the microcapillary. The concentration dependence is such that the Donnan coefficient becomes smaller with decreasing bulk electrolyte concentration. In other words, the higher the concentration of invading electrolyte, the less efficient becomes the microporous material in rejecting electrolyte. The results can be explained by increased screening of the charged microcapillary at higher electrolyte concentration, which effectively reduces its power to reject the invading co-ions.

The Donnan coefficient Γ sharply decreases with increasing Bjerrum length, that is with decreasing dielectric constant of solvent. The direction of the effect is therefore the same as produced by the increase of electrolyte concentration, but the mechanism leading to it is different. A solvent with a low dielectric constant is able to produce strong correlations between small ions (including ion pairs)^{39,41,42} and ions and the charged inner surface of the microcapillary. As a result a "triple-layer" (cf Fig. 7) may be formed, an effect which grossly increases the concentration of co-ions in the microcapillary, and therefore reduces its rejection power. Another important conclusion of this work is, that the Poisson-Boltzmann equation is merely qualitatively correct under such conditions and cannot be trusted to explain the experimental data.

As already mentioned in Introduction, to our best knowledge, no measurements exist to be directly compared with calculations presented in this study. It is worth mentioning, however, that osmotic pressure and heat of dilution measurements for polystyrenesulfonic acid and its salts in water-dioxane mixtures,^{43,44} indicate strong correlation between the counterions themselves, as also between and counterions and polyions. This correlation is reflected in low values of the osmotic coefficient and in less exothermic enthalpy of dilution as found when pure water has been used to dissolve the polyelectrolyte. The calculations presented in this paper are consistent with the experimental results of Vesnaver and coworkers.^{43,44}

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6. References

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Povzetek

Izračunali smo porazdelitev ionov med porozno fazo, ki jo sestavljajo nabite valjaste mikrokapilare, in nemoteno raztopino elektrolita. V ta namen smo uporabili veleanonično metodo Monte Carlo in pa nelinearno Poisson–Boltzmannovo diferencialno enačbo. Namen dela je bil raziskati vpliv dielektrične konstante topila na porazdelitev ionov elektrolita. Izračunali smo srednji koeficient aktivnosti raztopine znotraj mikropore in tudi Donnanov izključitveni koeficient. Ugotovili smo, da se slednji manjša z rastočo koncentracijo elektrolita in s padajočo dielektrično konstanto topila. Drugegače povedano, desalinacija postane v topilih, ki imajo dielektrično konstanto nižjo od vode, zelo neučinkovita. Teorija na osnovi Poisson–Boltzmannove enačbe pravilno napove odvisnosti posameznih količin od parametrov modela, a so tako izračunane vrednosti, v primerjavi z Monte Carlo simulacijami, močno prevelike. Porazdelitve posameznih ionskih vrst, ki so stranski produkt tega računa, omogočajo boljše razumevanju termodinamičnih rezultatov.