

Scientific paper

# Thermodynamics and Structural Properties of the Model Polyelectrolyte-electrolyte Mixture

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## Abstract

Structural and thermodynamic properties of linear polyelectrolyte solutions in presence of a low-molecular electrolyte are studied using Monte Carlo simulation techniques in conjunction with the cylindrical cell model where a uniformly charged hard cylinder mimics the linear polyion situated in its own cylindrical cell. The simulation data are complemented with the results of the Poisson-Boltzmann theory for the same model, while Manning's theory for mixing enthalpies is compared with the corresponding simulation results. The reported results suggest a strong influence of added low-molecular electrolyte on the various distribution functions. The influence of electrolyte addition on thermodynamic properties such as the enthalpy of dilution, enthalpy of mixing, and the osmotic coefficient is examined. These latter results are seen to be consistent with an empirical finding, the so called "additivity rule" for osmotic pressure. The calculated enthalpies of dilution and of mixing are in qualitative agreement with experimental data. The Poisson-Boltzmann results are in semi-quantitative agreement with Monte Carlo simulation results. The same holds true for the enthalpies of dilution and of mixing as calculated via the Manning limiting-law formula.

**Keywords:** Polyelectrolytes, electrolytes, enthalpy of dilution, osmotic coefficient

## 1. Introduction

Mixtures of polyelectrolyte and low-molecular electrolytes are commonplace in many systems of biological and industrial relevance.<sup>1</sup> Yet, a majority of polyelectrolyte studies are concerned with the Coulomb interaction in salt-free solutions, where only the polyions and related counterions are present. Important previous studies of the polyelectrolyte-electrolyte mixtures include, among others, the seminal papers of Alexandrowicz, Katchalsky and coworkers,<sup>2-4</sup> Strauss and Gross<sup>5</sup>, and others.<sup>6-8</sup> Previous theoretical contributions, relevant for this paper, are to be found in the references.<sup>9-21</sup>

Recently, in a series of papers,<sup>22-24</sup> we have explored the ion-ion correlation in the electrical double-layer around a cylindrical polyion. More precisely, we studied this correlation by calculating the canonical average of the ion-ion distribution function  $\langle g_{ij}(\mathbf{r}_i - \mathbf{r}_j) \rangle$  over the cylinder that modeled the polyelectrolyte solution.<sup>22-24</sup>

This important structural feature has received little attention in the literature though it forms the basis for understanding the catalytic effects<sup>25-32</sup> in the polyelectrolyte-electrolyte mixtures.<sup>24,33,34</sup> This topic was a major theme of our recent study.<sup>24</sup>

In the present paper we will extend our study to look more closely at the influence of ion-ion correlation on thermodynamic properties in situations when an additional low-molecular electrolyte is present in the system. Polyelectrolyte-electrolyte mixtures are, of course, more naturally occurring and the presence of an extra ion, co-ion, often leads to interesting effects resulting from more efficient screening of the polyions. In this paper we will examine variations of two important thermodynamic parameters, namely, the enthalpy of dilution and the osmotic pressure, with the concentration of added low-molecular electrolyte. The results are explained vis-a-vis the various distribution functions involving the species in the solution. For this purpose the

canonical Monte Carlo method and the Poisson-Boltzmann theory are applied to a model polyelectrolyte solution. The polyions are pictured as long uniformly (negatively) charged cylinder surrounded by positive and negative microions modeled as rigid charged spheres moving in a continuum dielectric. The theoretical results are analyzed in view of the experimental data for these properties,<sup>35</sup> the validity of the empirical additivity rule<sup>4</sup> for the osmotic pressure is tested. The calculations are performed varying the polyelectrolyte and electrolyte concentrations. In the present study only the polyelectrolyte mixtures with charge and size symmetric electrolyte +1:–1 are treated.

## 2. Model

The polyelectrolyte solution is depicted as an assembly of identical, independent electroneutral cylindrical cells each of which is of radius  $R$  and length  $h$  (see, for example, reference<sup>4</sup>). The cells are assumed to be mutually independent so that one needs to treat only one such cell. The cylindrical polyion with radius  $a$  and length  $h$  is placed along the  $z$ -axis of the cell. The radius  $R$  of the cell is determined by the polyelectrolyte concentration  $c_m$  expressed in monomer molar units,  $c_m^{-1} = \pi(R^2 - a^2)N_A b$ , where  $b$  ( $h = Nb$ ) is the length of the monomer unit, and  $N_A$  is the Avogadro number. In this work we consider polyelectrolyte solutions with added salt so that both counterions and coions are present, and will be represented by rigid ions of diameter  $d$ . The system as a whole is treated as a dielectric continuum characterized by relative permittivity  $\epsilon_r$ .

The interaction between two ions as a function of the separation distance  $r_{ij}$  is given by

$$\begin{aligned} \beta u_{ij}(r_{ij}) &= \frac{z_i z_j L_B}{r_{ij}} & r_{ij} > d \\ u_{ij}(r_{ij}) &= \infty & r_{ij} \leq d \end{aligned} \quad (1)$$

where the Bjerrum length  $L_B$  is given by

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

In the equations above  $\beta = 1/(k_B T)$ , where  $k_B$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $e$  the proton charge, and  $\epsilon_0$  and  $\epsilon_r$  are the vacuum and relative permittivities, respectively. Note that in this work, all the small ions are monovalent, viz.,  $|z_+| = |z_-| = 1$ . The interaction potential  $u_{pi}(r)$  between the polyion ( $p$ ) and an ion of species  $i$  as function of the perpendicular distance  $r$  from the polyion long axis is given by (see, for example,<sup>18,22</sup>)

$$\beta u_{pi}(r) = 2z_i \lambda \log_e \left[ \frac{h}{2r} + \left( 1 + \frac{h}{2r} \right)^{1/2} \right] \quad (3)$$

where  $\lambda = L_B/b$ .

The Monte Carlo simulations were performed in the canonical ensemble at 298 K and  $\epsilon_r = 78.5$ , the details of the computer simulations are given elsewhere (see, for example, references<sup>22–24</sup>). Note that the distance of closest approach of an ion to the polyion is given by  $a_p = a + d/2$ . The Poisson-Boltzmann equation for the cylindrical cell model in case of the polyelectrolyte-electrolyte mixture was solved numerically by the 4<sup>th</sup> order Runge-Kutta method. The boundary condition at  $r = a_p$ , given by the Gauss Law was satisfied using the trial-and-error procedure.<sup>10,11,36</sup>

## 3. Results and Discussion

All the calculations in this study pertain to the monovalent counterions and coions. The following model parameters were used; polyion radius  $a = 10 \times 10^{-10}$  m, ion diameter  $d = 4 \times 10^{-10}$  m and  $d = 8 \times 10^{-10}$  m, the Bjerrum length  $L_B = 7.14 \times 10^{-10}$  m, and the charge density parameter  $\lambda = L_B/b = 4.2$ . These values of  $b$  and  $a$  are most often used to describe DNA in solution and correspond to a surface charge density on the polyion of 0.15 C/m<sup>2</sup>. Calculations were performed for: (a) fixed salt concentrations of  $c_s = 0.0005$  mol/dm<sup>3</sup>, 0.001 mol/dm<sup>3</sup> and 0.005 mol/dm<sup>3</sup>, while the polyion concentration (in moles of monomer units) was varied from 0.0005 to 0.04 mol/dm<sup>3</sup>. Another set of calculations (b) applies to fixed polyion concentration of  $c_m = 0.002$  mol/dm<sup>3</sup> or 0.005 mol/dm<sup>3</sup> and variable salt concentration ranging from 0.0005 to 0.01 mol/dm<sup>3</sup>. The number of monomer units,  $N$ , was always 1000 in this set of calculations, while the total number of small ions ranged from 1,000 at salt-free conditions to 41,000 at the highest salt concentration used. The number of passes was  $10^8$ .

### 3. 1. Thermodynamic Properties

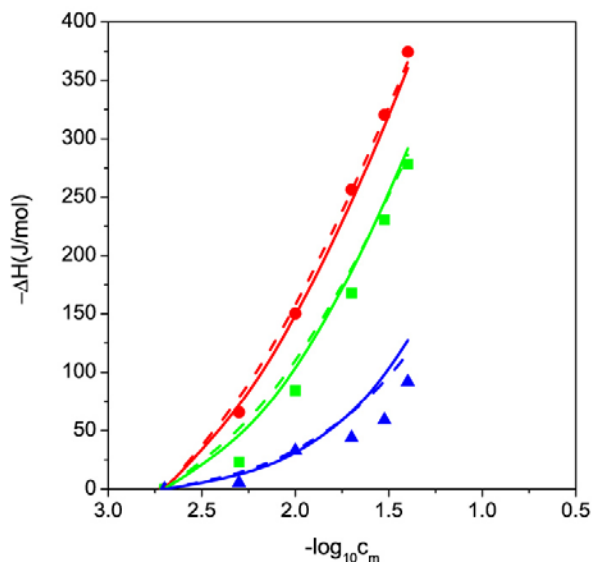
We begin this discussion by presenting the results for perhaps two of the most widely studied thermodynamic properties in polyelectrolyte solutions, that is, for enthalpy of dilution,  $\Delta H_d$ , and the osmotic coefficient  $\phi$ . Since we model the DNA solution the polyions are taken to be negatively charged and the counterions positively charged.

#### 3. 1. 1. Enthalpies of Dilution and Mixing

Here we study the enthalpy changes when polyelectrolyte is mixed with water or low-molecular electrolyte. Conventionally, the heat effect produced by mixing with

water is called the enthalpy of dilution,  $\Delta H_d$ , while the heat effect upon mixing polyelectrolyte with an electrolyte is called enthalpy of mixing and denoted  $\Delta H_{mix}$ . We will adopt such a terminology throughout this paper. Notice that the enthalpy of dilution is theoretically approximated as the energy difference between the final (diluted) and initial (concentrated) state:  $\Delta H_d \approx \Delta E_d = E_{c=0.002M} - E_c$ . Similarly, the enthalpy of mixing is approximated by the energy of mixing.

Experimental results for  $\Delta H_d$  were published by Dolar<sup>35</sup> with coworkers. In their paper the measurements of the enthalpy of dilution for lithium and sodium salts of the polystyrenesulfonic acid in mixture with LiCl and NaCl were presented. The dilution enthalpies from a certain concentration  $c_m$  to  $c_m = 0.001 \text{ mol/dm}^3$  (at constant electrolyte concentration  $c_s$ ) are shown in figures 2 and 3 of their paper.<sup>35</sup> In addition the Poisson-Boltzmann cell model results for  $\Delta H_d$  were presented (cf Fig. 1 of that study). A reasonable agreement between the Poisson-Boltzmann calculation and experimental data was obtained for LiCl/LiPSS mixtures but not for the NaCl/NaPSS system. In the latter case, the experimental values for  $\Delta H_d$  are smaller than the calculated values and the  $c_m$  concentration dependence exhibits a maximum.<sup>35</sup>



**Figure 1:** The negative of the enthalpy of dilution as a function of the negative decade logarithm of  $c_m$ ; the final  $c_m$  value is always  $0.002 \text{ mol/dm}^3$ . The symbols denote Monte Carlo data: (circles)  $c_s = 0.0005 \text{ mol/dm}^3$ , squares  $c_s = 0.001 \text{ mol/dm}^3$  and the triangles  $c_s = 0.005 \text{ mol/dm}^3$ ;  $d = 4 \text{ \AA}$ . The Poisson-Boltzmann results are given by the continuous lines and the results of the Manning approach (Eq. 4) by broken lines.

Heats of mixing were extensively studied by Škerjanc and coworkers,<sup>37,38</sup> in the context of the present work the Ref.<sup>38</sup> is of importance. In their work the enthalpies of mixing of aqueous solutions of alkali metal polystyrene-

sulfonates (XPSS; X stands for Li, Na, K, or Cs) with solutions of the corresponding alkali metal chlorides were determined at 298 K. The experiments were performed at constant concentration of the common cation and the enthalpies of mixing were calculated as a function of the mole fraction of the polyelectrolyte (viz., Figs. 1–3 of Ref.<sup>38</sup> In this way  $\Delta H_{mix}$  assumed value zero for  $c_m = 0$  and  $c_s = 0$ . The results strongly depend on the nature of the counterions; mixing of LiCl with LiPSS yielded a parabola with positive  $\Delta H_{mix}$  values. In contrast, the enthalpies of mixing for CsCl with CsPSS are negative under these conditions (temperature, concentration) for all mole fractions of the polyelectrolyte. A similar set of experimental data has been presented by Boyd and coworkers,<sup>39</sup> who measured enthalpy of mixing, of polyelectrolytes and low-molecular electrolytes with a common cation. In particular they studied the heat transferred in mixing of NaCl with NaPSS.

The experimental results mentioned above<sup>38,39</sup> were compared with predictions of the infinite line charge theory (see Eq. 4 below) and compared well when corrected for the enthalpy of dilution of salt.

$$\Delta H_{mix} = -\frac{RT}{2\lambda} \left[ 1 + \frac{d \log_e \epsilon}{d \log_e T} \right] \log_e \left( \frac{c_m^f + 2\lambda c_s^f}{c_m^i + 2\lambda c_s^i} \right) \quad (4)$$

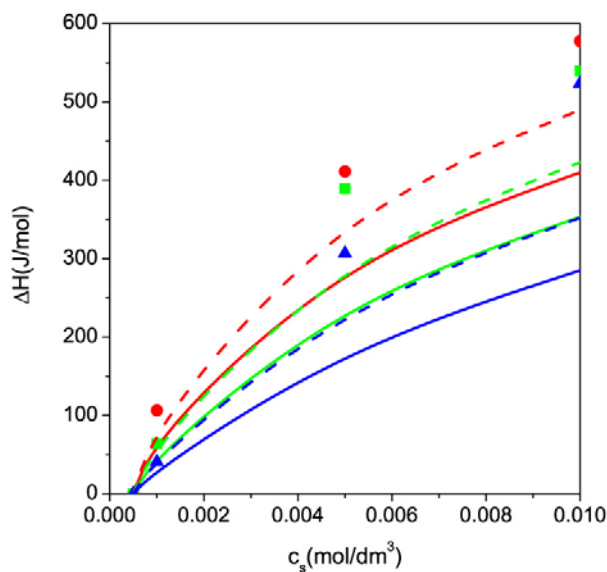
where  $i$  applies to initial and  $f$  to the final concentrations. From this formula, which is an extension of Eq. 5b, given by Boyd and coworkers,<sup>39</sup> the enthalpies of dilution,  $\Delta H_d$ , or mixing,  $\Delta H_{mix}$ , can be calculated.

We discuss first the results presented in our Figure 1 where the  $\Delta H_d$  values for the dilution from  $c_m$  to  $c_m = 0.002 \text{ mol/dm}^3$  are presented for three different electrolyte concentrations  $c_s$ . The simulation (symbols) and Poisson-Boltzmann results (full lines) calculated in this paper are in qualitative agreement with experimental results for LiCl/LiPSS mixture presented by Dolar and coworkers.<sup>35</sup> The results obtained from the Manning limiting law are shown by the broken lines. There are two features, which are reproduced correctly by the theory, i)  $\Delta H_d$  is negative and increases in magnitude with the increasing polyelectrolyte concentration, ii) the effect of electrolyte addition is such that  $\Delta H_d$  becomes less negative (smaller in magnitude). The results of the Manning limiting law for enthalpy, given by the Eq. 4, are denoted by broken lines.

The main conclusion of this part is that the enthalpy of dilution,  $\Delta H_d$ , which is a negative quantity decreases in magnitude with increased content of low-molecular electrolyte. For high  $c_s/c_m$  ratios  $\Delta H_d$  goes to zero. This is a consequence of the increased screening of the polyelectrolyte charge with increasing electrolyte concentration. The Monte Carlo, Manning limiting law and Poisson-Boltzmann results are in fair agreement in view of the fact that the error bars in the Monte Carlo simulations are relatively large. As mentioned earlier,<sup>23</sup>  $\Delta H_d$  results from sub-

tracting two relatively large numbers. The uncertainties in the Monte Carlo values for this quantity are around  $\pm 5\%$ , while the Poisson-Boltzmann calculations are relatively more accurate with errors in the numerical solution being around  $\pm 1\%$ . Of course our modeling takes into account only the electrostatic contribution to the  $\Delta H_d$  and therefore cannot account for the deviations in the NaCl/NaPSS mixture. The heat of dilution is very sensitive to the nature of counterion present in the solution (see, for example,<sup>40</sup>). In view of the reasonable agreement between the Monte Carlo simulation and Poisson-Boltzmann equation presented here, the disagreement between the theory and experiment (cf. Ref.<sup>35</sup>), cannot be attributed to the statistical-mechanical approximations of the theory but rather to imperfections of the model. The ion-specific effect can only be explained by the theories which treat water molecules explicitly<sup>41–44</sup>.

Next we discuss the results presented in Figure 2, where the enthalpy of mixing of polyelectrolyte at  $c_m$  with a simple electrolyte ( $c_s$ ) is considered. The initial  $c_s$  value was always  $0.0005 \text{ mol/dm}^3$  and the polyelectrolyte concentration,  $c_m$  was constant during the mixing. The study was performed for three different  $c_m$  values. Again the Poisson-Boltzmann and the Manning limiting-law results are tested against the new computer simulation results. Interestingly, here the Manning theory is in slightly better agreement with the machine simulations, though, strictly speaking, the theory on which Eq. 4 is based is valid only at very low concentrations.<sup>39</sup> Both theories are, however, in substantial disagreement with the Monte Carlo data.



**Figure 2:** The enthalpy of mixing as a function of the concentration  $c_s$ : the initial  $c_s$  value is  $0.0005 \text{ mol/dm}^3$ . The symbols denote Monte Carlo data: (circles)  $c_m = 0.002 \text{ mol/dm}^3$ , squares  $c_m = 0.005 \text{ mol/dm}^3$  and the triangles  $c_m = 0.01 \text{ mol/dm}^3$ ;  $d = 4 \text{ \AA}$ . The Poisson-Boltzmann results are given by the continuous lines and the results of the Manning approach (Eq. 4) by broken lines.

The question can be raised why the agreement between theories and machine calculations is much better for the enthalpy of dilution (Fig. 1) than for enthalpy of mixing (Fig. 2). To answer this question we have to understand the definition of  $\Delta H_{mix}$ . In order to determine this quantity experimentally we mix certain amounts of low-molecular electrolyte and polyelectrolyte solutions. In this process the polyelectrolyte and electrolyte get diluted from initial to final concentrations.

The Poisson-Boltzmann equation and Manning approach (Eq. 4) are, due to their mean-field nature, unable to account for the dilution of low-molecular electrolyte. In order to obtain good agreement between these theories and Monte Carlo simulation the theoretically (or experimentally) obtained heat of dilution of simple electrolyte has to be subtracted from the simulation results presented in Fig. 2. The same procedure has been adopted to bring the  $\Delta H_{mix}$  measurements into agreement with the Poisson-Boltzmann<sup>35</sup> and Manning theory.<sup>39</sup>

### 3. 1. 2 Osmotic Pressure

The osmotic coefficients of the polyelectrolyte-electrolyte mixture as obtained from the Monte Carlo and Poisson-Boltzmann calculations are presented in Table 1. In both cases  $\phi$  was calculated using the standard equation

$$\phi = \frac{c_+(R) + c_-(R)}{c_m + 2c_s} \quad (5)$$

where  $c_+(R)$  and  $c_-(R)$  are the concentrations of the monovalent counterions and coions at the cell boundary. In case of the simulations these concentrations,  $c_i(R)$ , were determined via the histogram method.

**Table 1a:** The osmotic coefficient  $\phi$  as obtained from the Monte Carlo simulation of the polyelectrolyte-electrolyte mixture and from the Poisson-Boltzmann theory ( $\phi_{PB}$ ).

$c_m/M$	$c_s/M$	$d = 4 \text{ \AA}$		$d = 8 \text{ \AA}$	
		$\phi_{PB}$	$\phi$	$\phi_{PB}$	$\phi$
0.002	0.0005	0.46	0.45	0.46	0.46
	0.001	0.60	0.59	0.60	0.60
	0.005	0.87	0.85	0.87	0.86
	0.010	0.93	0.91	0.93	0.92
	0.020	0.97	0.94	0.97	0.95
	0.030	0.98	0.95	0.98	0.97
0.005	0.0005	0.33	0.32	0.33	0.33
	0.001	0.43	0.42	0.44	0.43
	0.005	0.75	0.73	0.75	0.74
	0.010	0.85	0.82	0.86	0.84
	0.020	0.92	0.89	0.92	0.91
	0.030	0.95	0.91	0.95	0.94
0.010	0.040	0.96	0.92	0.96	0.95

**Table 1b:** The osmotic coefficient  $\phi$  as obtained from the Monte Carlo simulation of the polyelectrolyte-electrolyte mixture and from the Poisson-Boltzmann theory ( $\phi_{PB}$ ).

$c_m/M$	$c_s/M$	$d = 4 \text{ \AA}$		$d = 8 \text{ \AA}$	
		$\phi_{PB}$	$\phi$	$\phi_{PB}$	$\phi$
0.0005	0.002	0.91	0.90	0.92	0.90
0.001		0.84	0.83	0.84	0.83
0.002		0.74	0.72	0.74	0.73
0.004		0.61	0.59	0.61	0.60
0.005		0.57	0.55	0.57	0.56
0.006		0.53	0.51	0.53	0.52
0.008		0.48	0.46	0.48	0.47
0.010		0.44	0.43	0.45	0.44
0.0005	0.005	0.96	0.95	0.96	0.95
0.001		0.93	0.91	0.93	0.92
0.002		0.87	0.85	0.87	0.86
0.004		0.78	0.76	0.78	0.77
0.005		0.75	0.73	0.75	0.74
0.006		0.71	0.69	0.72	0.71
0.008		0.66	0.64	0.67	0.65
0.010		0.62	0.60	0.63	0.61

The measurements have shown<sup>4</sup> that osmotic pressure of polyelectrolyte solution can be reasonably well approximated by the equation

$$\Pi_a = RT [\phi_0 c_m + 2\phi_s c_s] \quad (6)$$

In the equation above  $\phi_0$  denotes the osmotic coefficient of pure polyelectrolyte solution (for  $c_s = 0$ ) and  $\phi_s$  osmotic coefficient of the +1:-1 electrolyte at  $c_s$  and in absence of polyelectrolyte. The osmotic coefficient is defined as  $\phi = \Pi/\Pi_{id}$ , where  $\Pi_{id}$  denotes an ideal pressure. The additivity approximation,  $\phi_a$ , for the osmotic coefficient of the mixture then reads<sup>4</sup>:

$$\phi_a = \frac{\phi_0 c_m + 2\phi_s c_s}{c_m + 2c_s} \quad (7)$$

The above expression has two limiting values. For  $c_s = 0$  we obtain the  $\phi_a = \phi_0$  while in the absence of the polyelectrolyte the result for osmotic coefficient of pure electrolyte,  $\phi_s$  is obtained.

The osmotic coefficient of pure +1:-1 electrolyte can be obtained via the hypernetted-chain approximation,<sup>45</sup> or the modified Poisson-Boltzmann equation,<sup>46</sup> both are known to be excellent approximations in such situations. In the present work we have obtained the  $\phi_s$  through the Monte Carlo simulations of the pure electrolyte and indeed the corresponding modified Poisson-Boltzmann results were found to be within the statistical uncertainty of the simulation data. The osmotic coefficient of the salt-free polyelectrolyte,  $\phi_0$ , have been earlier obtained by the separate Monte Carlo simulation of the electrolyte-free polyelectrolyte solutions.<sup>22</sup>

The results are presented in Tables 1a, 1b and 2. First in Tables 1a and 1b we show the simulation results

for the osmotic coefficient  $\phi$  as obtained for the polyelectrolyte-electrolyte mixtures characterized by the various  $c_m$  and  $c_s$  values. The Poisson-Boltzmann calculations are presented in the same table. It is easy to see that, consistent with previous electrolyte-free studies, the agreement between the two types of calculations is reasonably good. It has to be stressed, however, that the Poisson-Boltzmann theory overestimates the actual osmotic coefficient. Note that the Poisson-Boltzmann theory ignores the ion-ion correlations and thus it necessarily yields wrong result under the excess of salt condition ( $c_m \ll c_s$ ).

In Table 2, the additivity rule is tested against the simulation results obtained for the polyelectrolyte-electrolyte mixture. Comparison between the two osmotic coefficients, namely,  $\phi$  obtained from simulation of the full mixture and  $\phi_a$  calculated with the help of Eq. 7 indicates, that additivity rule is only obeyed semi-quantitatively. For all the polyelectrolyte and electrolyte concentrations studied here  $\phi_a$ , calculated from Eq. 7, is systematically lower than the exact simulation result  $\phi$ . Notice, however that the numerical uncertainty of the Monte Carlo simulation for  $\phi$  is from  $\pm 2$  to  $\pm 4$  %.

**Table 2:** The osmotic coefficient  $\phi$  as obtained from the Monte Carlo simulation of the polyelectrolyte-electrolyte mixture and as calculated from the approximate Eq. 7,  $\phi_a$ .

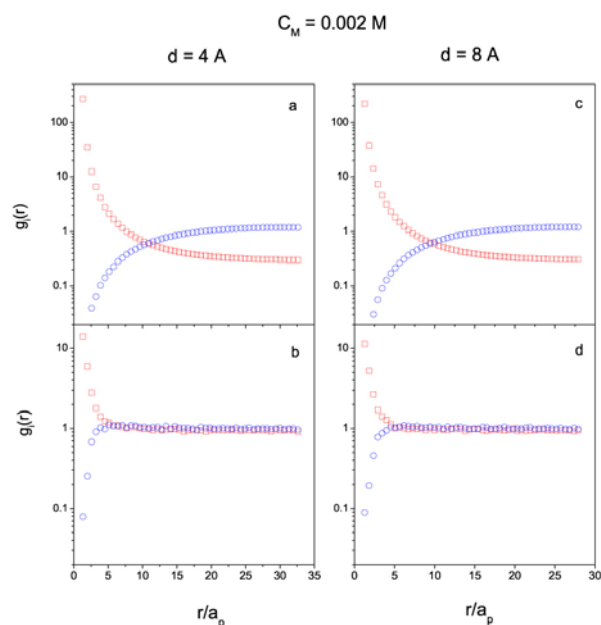
$c_m/M$	$c_s/M$	$d = 4 \text{ \AA}$		$d = 8 \text{ \AA}$	
		$\phi$	$\phi_a(\text{Eq. 7})$	$\phi$	$\phi_a(\text{Eq. 7})$
0.002	0.0005	0.45	0.44	0.46	0.45
	0.001	0.59	0.58	0.60	0.58
	0.005	0.85	0.84	0.86	0.85
	0.010	0.91	0.90	0.92	0.90
	0.020	0.94	0.92	0.95	0.93
	0.030	0.95	0.93	0.97	0.95
	0.040	0.95	0.93	0.97	0.95
0.005	0.0005	0.32	0.31	0.33	0.32
	0.001	0.42	0.41	0.43	0.42
	0.005	0.73	0.71	0.74	0.72
	0.010	0.82	0.81	0.84	0.82
	0.020	0.89	0.87	0.91	0.89
	0.030	0.91	0.89	0.94	0.91
	0.040	0.92	0.90	0.95	0.93

### 3. 2. Distribution Functions

In this part we will discuss the small ion-polyion and ion-ion correlation functions in order to better understand the thermodynamic results calculated above. The ion-ion correlations as evidenced through the canonical average,  $\langle g_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \rangle$ , were presented in details in our earlier study<sup>24</sup> and as such they will not be repeated here.

In this paper we present the concentration profiles, that is the singlet distribution function,  $g(r)$ , showing how the counterions and coions are distributed around the polyion. Figure 3 shows the singlet profile at a fixed

polyion concentration  $c_m = 0.005 \text{ mol/dm}^3$  and two electrolyte concentrations  $c_s = 0.0005$  and  $0.04 \text{ mol/dm}^3$ , respectively. Also the results are presented at two ionic diameters  $d = 4$  and  $8 \times 10^{-10} \text{ m}$ , respectively. A glance at the figure reveals the influence of added salt on such distributions at higher (salt) concentrations – the double layer is very compact indicating that range of the influence of polyion is limited to the distances  $r \approx 5a_p$ . We also note from the left and the right panels that the influence of ionic size appears to be minimal.



**Figure 3:** Left panels: the counterion-polyion distribution function is denoted by squares, and the coion-polyion distribution by circles:  $c_m = 0.002 \text{ mol/dm}^3$  in both cases,  $c_s = 0.0005 \text{ mol/dm}^3$  (top panel) and  $c_s = 0.04 \text{ mol/dm}^3$  (bottom panel);  $d = 4 \text{ \AA}$ . Right panels: The same as above except  $d = 8 \text{ \AA}$ .

The upper panel shows the situation where the polyelectrolyte is in excess of the simple electrolyte,  $c_m = 0.002 \text{ mol/dm}^3$  and  $c_s = 0.0005 \text{ mol/dm}^3$ . The figures in the lower panel apply to the situation where  $c_s \gg c_m$ ;  $c_m = 0.002$  and  $c_s = 0.04 \text{ mol/dm}^3$ . In the latter case the electrical double layer is compact, the electrostatic interaction between small ions and polyions is efficiently screened, and the concentration of counterions and coions are equal throughout a substantial portion of the cell. In other words there is a "bulk electrolyte" present in the cell. These figures explain why the enthalpy of dilution is much less negative in presence of the excess of low-molecular electrolyte.

## 4. Conclusions

In this contribution we have presented new theoretical and Monte Carlo results for a polyelectrolyte in mix-

ture with the low-molecular electrolyte. The emphasis is put on the thermodynamic quantities, viz.: i) enthalpy of dilution of electrolyte-polyelectrolyte mixture, ii) enthalpy of mixing of polyelectrolyte with the low-molecular electrolyte, and iii) the osmotic coefficient of such a mixture. In the latter case the empirical additivity rule was tested; the actual osmotic coefficients were systematically a little higher than predicted by this empirical "rule". The calculated enthalpies, based on the cylindrical cell model, are in qualitative agreement with experimental data. The Poisson-Boltzmann equation and the Manning limiting law approach are in semi-quantitative agreement with the computer simulations for these quantities; the disagreement is stronger at higher electrolyte content. This can be explained by the deficiencies of the mean-field theories, which do not take into account the ion-ion correlations. In other words, the contributions due to the dilution effects of the present electrolyte are not accounted for by these theories. The latter effect may strongly influence the enthalpy of mixing when the concentration of added electrolyte exceeds the polyelectrolyte concentration. These and other thermodynamic results can be explained on the basis of the polyion-ion distributions.

## 5. Acknowledgements

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## Povzetek

V predloženem delu smo preučevali strukturne in termodinamične lastnosti mešanice linearnega polielektrolita in nizkomolekularnega elektrolita. V ta namen smo uporabili Monte Carlo računalniško simulacijo in celični model raztopine. Poliion smo obravnavali kot neskončno dolg in enakomerno nabit valj, okoli katerega so porazdeljene nabite toge kroglice – protiioni. Rezultate simulacij smo primerjali z rezultati Poisson-Boltzmannove enačbe in Manningove teorije. Računi potrjujejo pomemben vpliv dodatka navadnega elektrolita na lastnosti raztopine. Raziskali smo vpliv dodane soli na osmozni koeficient in razredčilno entalpijo, oziroma na entalpijo mešanja. Z računalniškimi simulacijami smo potrdili veljavnost empirično dobljenega »pravila aditivnosti« za osmozne koeficiente. Rezultati simulacij se kvalitativno ujemajo z ustreznimi poskusi. Osmozni koeficienti, razredčilne entalpije in entalpije mešanja, izračunane s pomočjo Poisson-Boltzmannove in Manningove teorije, pa se le približno ujemajo z rezultati simulacij.