

Scientific paper

Simulation of Polyelectrolyte-Catalysed Reaction between Divalent Ions

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Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

Catalytic potential of linear polyelectrolyte solutions in presence of +2:–2 salts, as evidenced through ionic correlations in the inhomogeneous atmosphere around a polyion, is studied using Monte Carlo simulation techniques and the traditional non-linear Poisson-Boltzmann approach. The simulations are performed on the cylindrical cell model where a uniformly charged hard cylinder mimics the linear polyion caged in a cylindrical cell containing divalent counterions and co-ions. Cell (volume) average of the inter-ionic correlations, as reflected in the pair-correlation functions, is presented as function of the polyion concentration, the low-molecular electrolyte concentration, and the ion radius. The volume average of the doublet pair distribution function between counterions is found to be sensitive to variation of model parameters. The results indicate large enhancement in the reaction rate between the counterions, while a decrease in the coion-coion and the coion-counterion reaction rate is noted, all in comparison with pure electrolyte solutions. The agreement between the predictions of the Poisson-Boltzmann theory and the simulation results is merely qualitative in most instances.

Keywords: : Polyelectrolytes, +2:–2 electrolytes, catalytic effect, Monte Carlo method, Poisson-Boltzmann theory

1. Introduction

Review of experimental data reveals that thermodynamic and transport properties of polyelectrolyte solutions depend strongly on the charge of the polyion, the valency of counterions (ions having the opposite charge sign to that of the polyions), and the concentration of any added low-molecular electrolyte.^{1–8} The counterions are attracted to the polyions and form an ionic cloud around them. On the other hand, the ions having the same charge sign as that of the polyions, viz., the co-ions, are pushed away from the polyions and move relatively "freely". These effects have several important consequences. For example, the osmotic coefficient of such solutions is low,^{1–3} and under the influence of an external electric field a fraction of the counterions move in concert with the polyions.^{9–12} The polyion-counterion attraction is especially strong in case of divalent counterions;^{3,13–18} in such situations the solution becomes less stable and precipitation may occur¹⁵.

There is an important practical aspect of high accumulation of counterions close to polyions pointed out first by Morawetz^{19–22} and subsequently developed by others.^{23–27} Due to the high concentration of counterions next to the polyion their collision frequency increases, which can lead to a strong acceleration (10^3 to 10^5 times) of the chemical reaction between counterions. In this way polyelectrolytes can be used to catalyze efficiently chemical reactions between equally charged ions.^{19–22} By the same token repulsion between the polyions and the co-ions causes the counterions and co-ions to get spatially separated, which can be used to inhibit chemical reaction between these species.²³ Notice that the rate of reaction between coions themselves is only marginally affected. Types of homogeneous reactions investigated experimentally comprise the hydrolysis of organic esters, redox reactions of metal ions, and polymerization reactions.⁶

Recently, in a series of papers^{28–31} we have explored the correlations in the charged atmosphere around a polyion. Because of the nature of the quantity, the doublet

correlation function, $g(\mathbf{r}_1, \mathbf{r}_2)$, which describes the correlation between two ions at positions \mathbf{r}_1 and \mathbf{r}_2 measured from the polyion, respectively, is difficult to evaluate. We have calculated the average value of this function and related its contact value to the catalytic effect caused by the presence of the polyion. To date, we have reported calculations for salt-free polyelectrolyte solutions and polyelectrolyte in mixture with +1:–1 electrolytes. The results have been rich and revealing. The inter-ionic correlations shape the double layer structure around a polyion, while the contact values of the same functions relative to that in a pure electrolyte are good indicators of the catalytic potential of polyions. These properties were also seen to be strongly influenced by physical parameters such as polyion and added electrolyte concentrations, the polyion charge density parameter, and the ionic diameter. We therefore thought it of interest to extend the calculations to examine the effect of higher valencies on the simple ions when the mutual interactions among all the charged species are substantial.

Here we will build upon the earlier analysis^{28–30} to explore situations when a +2:–2 valency salt is mixed with a polyelectrolyte solution containing divalent counterions. Experimental results suggest²⁴ that in such cases the effect of polyelectrolyte addition to the reaction rate is particularly strong. As in the previous papers of this series^{28–30} we will use the Monte Carlo (MC) simulation approach^{32–36} to obtain the desired canonical averages of $\langle g(|\mathbf{r}_1 - \mathbf{r}_2|) \rangle \equiv \langle g_{ij}(r_{ij}) \rangle$ and $\langle g(|\mathbf{r}_1 - \mathbf{r}_2|)_{\text{c=d}} \rangle \equiv \langle g_{ij}(d_{ij}) \rangle$, where d_{ij} is the collision diameter of ionic species i and j and angular brackets denote the canonical cell-average. In this calculation the diameters of counterions and co-ions are equal so $d_{ij} = d$ for all i, j pairs. The increase or decrease in collision frequency above or below the polyelectrolyte-free pure salt solution was taken as a measure of the catalytic effect caused by polyelectrolyte addition.²⁶ The conjecture is based on the theory of bimolecular reactions,³⁷ and was initially proposed by Reščič and Vlady,²⁶ viz.,

$$\frac{k_{ij}}{k_{ij,0}} = \frac{\langle g_{ij}(d_{ij}) \rangle}{\langle g_{ij}^0(d_{ij}) \rangle}, \quad (1)$$

where k_{ij} and $k_{ij,0}$ are the reaction rate constants between interacting ion pairs i and j in presence and absence of polyelectrolyte, respectively. For simplicity the collision diameter of the pair is taken to be the distance of closest approach between them so that $g_{ij}(d_{ij})$ and $g_{ij}^0(d_{ij})$ are essentially the contact values of pair function with the superscript '0' denoting a pure electrolyte solution.

In addition to the Monte Carlo simulation the classical Poisson-Boltzmann (PB) theory^{2–4} is applied to this problem. In both cases the calculations are based on the cylindrical cell model.^{1,3} This is a useful model and has been utilized earlier in the literature in conjunction with different theoretical approaches such as the hypernetted

chain/mean spherical approximation (HNC/MSA),^{38,39} the PB/mean spherical approximation (PB/MSA),⁴⁰ and the modified Poisson-Boltzmann theory (MPB)^{35,36} and others. Within the Poisson-Boltzmann theory, due to the nature of the approximation, the interionic correlations $\langle g(|\mathbf{r}_1 - \mathbf{r}_2|) \rangle$ and $\langle g(|\mathbf{r}_1 - \mathbf{r}_2|)_{\text{c=d}} \rangle$ leading to Eq. 1 cannot be readily calculated. To circumvent this problem Morawetz *et al.* suggested a mean-field expression^{19–22} to evaluate an increase in collision frequency upon addition of polyelectrolyte. The equation is easy to use and in many situations it yields good agreement with Eq. 1.^{8,27}

The principal goals of this paper are: (i) A study of the doublet distributions for g_{++} , g_{+-} , and g_{--} in the inhomogeneous domain of a cylindrical polyion, (ii) evaluation of the contact values of these distributions and hence calculation of the binary reaction rate ratio $k_{ij}/k_{ij,0}$, and (iii) a characterization of the influence of polyelectrolyte addition to a +2:–2 electrolyte solution at several polyelectrolyte and electrolyte concentrations. We will also present results for two different sizes of ions. To the best of our knowledge, no such calculations have been conducted so far.

2. Model and Methods

In the classical cell model, the polyelectrolyte solution is depicted as an assembly of identical and electroneutral cylindrical cells each of which is of radius R and length h . Because of their independent nature, it is enough to treat 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,

$$c_m^{-1} = \pi(R^2 - a^2)N_A b, \quad (2)$$

where b is the length of the monomer unit, while the length of the polyion, $h = Nb$ (N being the number of monomer units), and N_A is the Avogadro's number.

In this work we consider polyelectrolyte-electrolyte mixtures so both counterions and coions are present in the cell. These small, simple ions are represented by rigid ions of diameter $d = 4.0 \times 10^{-10}$ or 8.0×10^{-10} m. Neglecting dielectric discontinuities at the polyion and cylindrical cell boundaries, the system is treated as ions moving in a dielectric continuum characterized by relative permittivity ϵ_r . The model has been explained in several previous papers, so details such as the exact forms of the ion-polyion and ion-ion potentials, are omitted here. We refer the interested reader to our previous papers for the relevant details.^{28–31}

An important quantity in theory of polyelectrolyte solutions is the, so-called, linear charge density parameter $\lambda = L_B/b$, where the Bjerrum length L_B is given by

$$L_B = \frac{e^2}{4\pi k_B \epsilon_0 \epsilon_r T}, \quad (3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, e the proton charge, and ϵ_0 is the vacuum permittivity. Note that in this work, the magnitude of the counterion and coion valencies is two. The distance of closest approach of a simple ion to the polyion is denoted by $a_c = a + d/2$.

2. 1. Monte Carlo Method

The Monte Carlo simulations were performed in the canonical ensemble on the cylindrical cell model at 298 K and $\epsilon_r = 78.5$ using the standard Metropolis algorithm. A drawback of cell models is the fact that all ionic correlations beyond the cell boundary are neglected. This approximation may be especially severe when multivalent counterions and coions are treated. Since a single cell is treated, the interactions are truncated at the cell boundary and do not extend beyond it. In other words the electrolyte present at the cell boundary does not feel any interaction from the outside world. This broken symmetry creates a surface effect, similar to that found in the electrical double-layer studies.⁴¹ As a consequence, the singlet distribution functions for counterions and coions is found to be too low in that region, as pointed out by Das *et al.*³⁶ The contributions to $\langle g(|\mathbf{r}_1 - \mathbf{r}_2|)_{r=0} \rangle$, as discussed in some detail before,²⁹ come mostly from the volume close to the polyion so the $k_{ij}/k_{ij,0}$ obtained via the Monte Carlo method should be only marginally affected by this cell-model approximation. We believe that under these circumstances Eq. 1 represents a more accurate measure of the ion-polyion correlation than the osmotic coefficient. The latter is proportional to the sum of the counterion and coion concentrations at the cell boundary,³¹ where the "surface effect" is the largest.³⁶

In a Monte Carlo simulation the polyion length is necessarily finite. In the present context the number of monomer units is $N = 1000$. The corrections due to a finite polyion were taken into account by replicating the central Monte Carlo cell along the long polyion axis as explained elsewhere.^{35,36} The residual N dependence was thoroughly examined and found to be negligible²⁸ for N of the order $\sim 10^3$. The statistical errors in the simulated ion-ion distributions and the reaction rate ratios were estimated to be from $\pm 5\%$ to $\pm 10\%$. The number of passes needed to obtain such accuracy was 200×10^6 . The contact values of the pair distribution functions for ions in absence of polyelectrolyte, $\langle g_{ij}^0(d_{ij}) \rangle$ were calculated via the MPB theory,⁴² the HNC approach,⁴³ and Monte Carlo simulations of the bulk electrolyte. The calculations agree within the numerical uncertainty of the simulations, that is $\sim \pm 10\%$. The bulk simulations, due to the poor statistics between like charge ions require extremely long runs. In the actual calculations of the reaction rates we used the simulation data for $\langle g_{ij}^0(d_{ij}) \rangle$.

2. 2. The Morawetz Equation and Poisson-Boltzmann Theory

Morawetz^{19–22} suggested that the catalytic effect of a polyelectrolyte addition to a low-molecular electrolyte may be estimated from the following equation

$$\frac{k_{ij}}{k_{ij,0}} = \frac{V^{-1} \int_v dV \rho_i(r) \rho_j(r)}{[V^{-1} \int_v dV \rho_i(r)][V^{-1} \int_v dV \rho_j(r)]}. \quad (4)$$

Here V is the volume per monomer unit, and $\rho_i(r)$ is the number density of ions,

$$\rho_i(r) = \rho_i(R) \exp[-\beta z_i e (\psi(r) - \psi(R))], \quad (5)$$

with $\psi(r)$ being the solution of the Poisson-Boltzmann equation for the mean electrostatic potential in polyelectrolyte–electrolyte mixture. The Morawetz equation is quite general and can be applied for all i, j combinations; note that $|z_i| = |z_j| = 2$ in our case. The basic drawback of this mean field approach is that the ionic distributions $\rho_i(r)$, evaluated via Eq. 5 have limited validity in case of divalent ions. The non-linear Poisson-Boltzmann equation for the cylindrical cell model was solved numerically by the 4th order Runge-Kutta method. The boundary condition at the surface of the polyion, $r = a_c$, given by the Gauss Law was satisfied using the 'shooting method'.³²

As noted by Ishikawa,²⁴ Eq. 4 can be cast into a more general form

$$\frac{k_{ij}}{k_{ij,0}} = \frac{f_i f_j}{f_X} \quad (6)$$

where f_i is the single ionic activity coefficient⁴⁴ and X denotes the activated complex. A more accurate approach would therefore involve Eq. 6 together with a formal statistical mechanical treatment such as the MPB theory.^{35,36} It ought to be emphasized though that the Morawetz equation (Eq. 4 or its general form Eq. 6) has the appealing feature of being universal in that it can be used with any relevant theory or even simulation data for $\rho_i(r)$.

3. Results and Discussion

All calculations in this study pertain to a polyelectrolyte with divalent counterions and an added +2:–2 salt. The following physical parameters were used; polyion radius $a = 10 \times 10^{-10}$ m, ion diameter $d = 4 \times 10^{-10}$ m or $d = 8 \times 10^{-10}$ m, and the Bjerrum length $L_B = 7.14 \times 10^{-10}$ m. In a majority of the calculations the charge density parameter was taken to be $\lambda = L_B/b = 4.2$. Thus the polyion-simple ion distance of closest approach $a_c = 12 \times 10^{-10}$ m or 14×10^{-10} m. These values of b and a are typical model parameters used to describe DNA–electrolyte mixture²⁵ and

correspond to a surface charge density on the polyion of -0.15 C/m^2 . Calculations were performed for: i) fixed salt concentrations of $c_s = 0.002 \text{ mol/dm}^3$ or 0.005 mol/dm^3 and variable polyion concentration, ranging from 0.0005 to 0.02 mol/dm^3 , and ii) fixed polyion concentration of $c_m = 0.002 \text{ mol/dm}^3$ or 0.005 mol/dm^3 and variable salt concentration ranging from 0.0005 to 0.02 mol/dm^3 . We have also done a set of calculations with varying b to investigate its influence (via the charge density parameter λ) on the reaction rate ratio $k_{ij}/k_{ij,0}$.

3. 1. Ion-ion Correlation

The ion-ion correlation will be represented through a polyion-free cell volume average of the ion ion radial distribution function $\langle g(r_{12}) \rangle$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The counterion-counterion $\langle g_{++}(r) \rangle$, counterion-coion $\langle g_{+-}(r) \rangle$, and coion-coion $\langle g_{--}(r) \rangle$ correlation functions

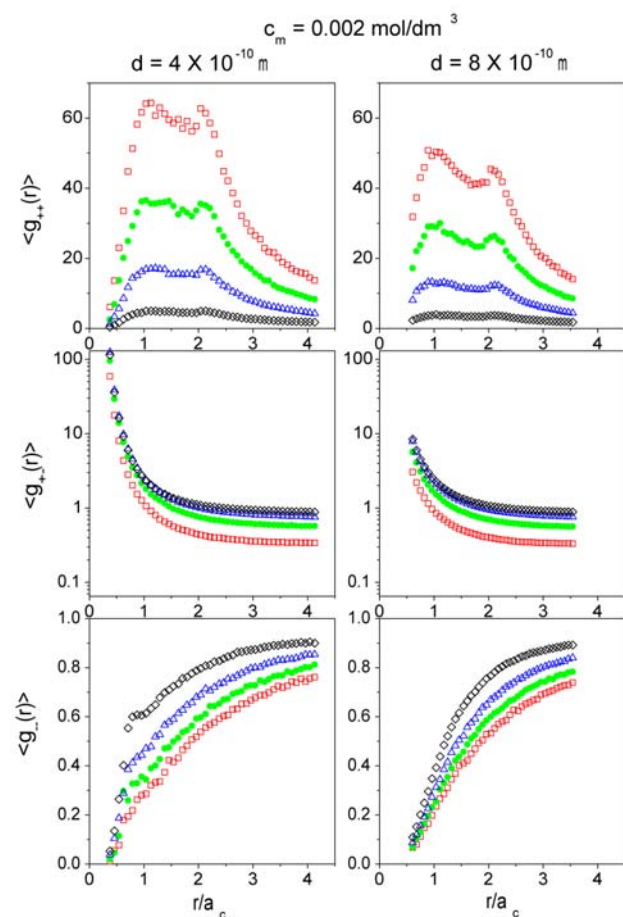


Figure 1: Monte Carlo simulated ion-ion correlation functions $\langle g_{ij}(r) \rangle$ at a fixed polyion concentration $c_m = 0.002 \text{ mol/dm}^3$ and variable added salt concentrations. From top to bottom, counterion-counterion, counterion-coion, and coion-coion correlations. The left and right columns show results for the ionic diameters of 4 and $8 \times 10^{-10} \text{ m}$, respectively: (squares) $c_s = 0.0005 \text{ mol/dm}^3$, (filled circles) $c_s = 0.001 \text{ mol/dm}^3$, (triangles) $c_s = 0.005 \text{ mol/dm}^3$, and (diamonds) $c_s = 0.02 \text{ mol/dm}^3$.

in the electrical double layer around the polyion are shown in Figures 1–4.

First in Figure 1 we present ion-ion correlation functions $\langle g_{ij}(r) \rangle$ in the inhomogeneous double layer surrounding a cylindrical polyion at a fixed polyion concentration and variable salt concentrations. The panels show, from top to bottom, counterion-counterion, counterion-coion, and coion-coion correlations, respectively. The left and right columns show results for the ionic diameters of 4 and $8 \times 10^{-10} \text{ m}$, respectively. The polyion concentration is held fixed at $c_m = 0.002 \text{ mol/dm}^3$, while the symbols represent results for added salt concentrations.

The most prominent feature in the counterion-counterion correlation function is the appearance of two peaks.

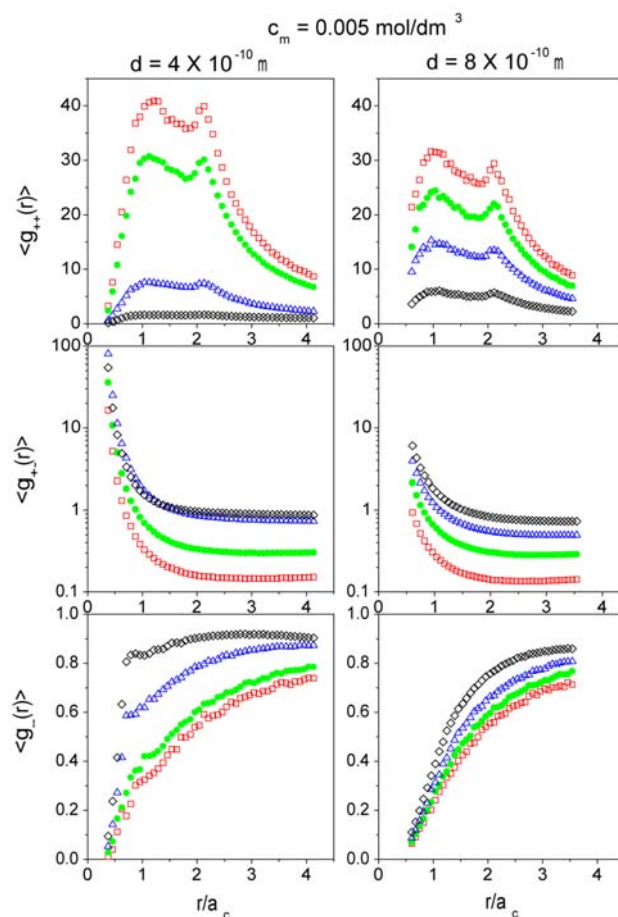


Figure 2: Monte Carlo simulated ion-ion correlation functions $\langle g_{ij}(r) \rangle$. Notation and symbols as in Figure 1 except for $c_m = 0.005 \text{ mol/dm}^3$.

The first one is located at approximately $r/a_c \sim 0.8$, while the second one is located at around $r/a_c \sim 2.2$, which is slightly larger than $r = 2a + d$. Physically, the first peak denotes roughly the upper limit of a correlation hole around a counterion from which other counterions are generally excluded. The second peak and the shape of the curve stem from the tendency of the counterions to cluster

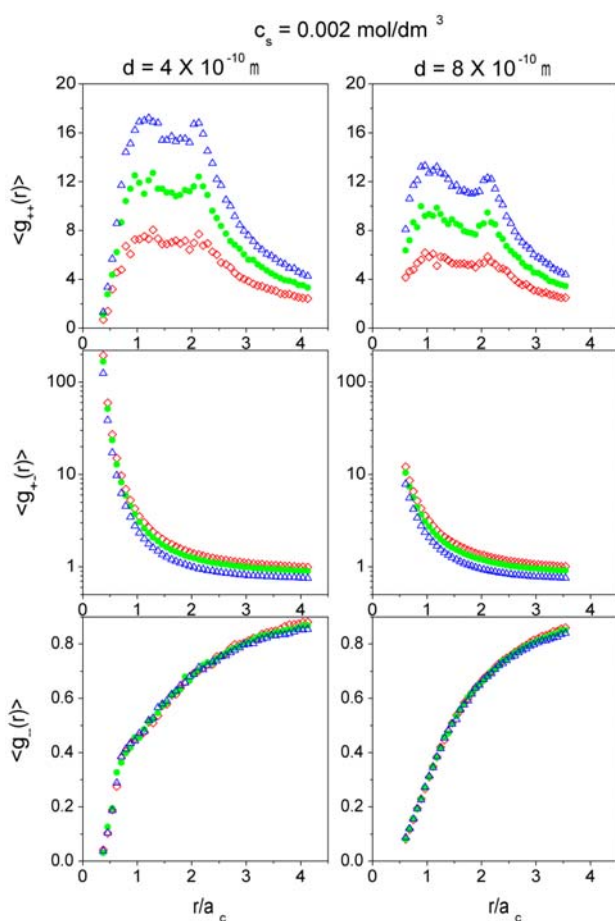


Figure 3: Monte Carlo simulated ion-ion correlation functions $\langle g_{ij}(r) \rangle$ at a fixed added salt concentration $c_s = 0.002 \text{ mol/dm}^3$ and variable polyion concentration. From top to bottom, counterion-counterion, counterion-coion, and coion-coion correlations. The left and right columns show results for the ionic diameters of 4 and $8 \times 10^{-10} \text{ m}$, respectively: (diamonds) $c_m = 0.0005 \text{ mol/dm}^3$, (filled circles) $c_m = 0.001 \text{ mol/dm}^3$, (triangles) $c_m = 0.002 \text{ mol/dm}^3$.

around the polyion while at the same time exhibiting mutual repulsion. The influence of added salt concentration is seen to be quite substantial and has the effect of dampening the correlations due to increased screening effects. It is worth emphasizing that $\langle g_{++}(r) \rangle$ is much more sensitive to the polyelectrolyte and electrolyte concentrations as well as to other model parameters (d and λ) than the commonly studied singlet polyion–small ion distribution functions.^{32–36} Note that (in Figures 3 and 4) the intensity of this correlation increases when the polyion concentration is increased at a fixed salt concentration.

The coion-counterion correlations are shown in the middle panels of Figures 1–4. As can be seen the $\langle g_{+-}(r) \rangle$ function is monotonically decreasing and featureless rather like the analogous coion-counterion distribution in a dilute bulk electrolyte. Increasing the salt content at a constant polyelectrolyte concentration or increasing the polyion content at a constant salt concentration enhances or suppresses the coion-counterion correlations only mar-

ginally. Consequently, as we will see later, little effect is expected on the chemical reaction rate.

The coion-coion correlations in the form of $\langle g_{--}(r) \rangle$ are shown in the bottom panels of Figures 1–4 and again resemble like ion distributions in a dilute bulk electrolyte. Although being quite featureless, like the $\langle g_{++}(r) \rangle$ they show a small increase in magnitude with increasing added salt concentration leading to a modest increase in the reaction rate ratio. The opposite effects occur when the polyion concentration is increased at a particular salt concentration (cf. following sub-section).

As a final remark here we note that the most important effect due to the larger ion radius (the right hand panels of Figures 1–4) is to decrease the heights of the counterion-counterion peaks (top panels). Physically this stems from the fact that two interacting ions are now in relatively less proximity to each other; this effect also makes the electrical double-layer less dense.

3. 2. Catalysis Effect of Polyions

Bimolecular reaction rate theory suggests that reaction rates can be related to the static structure of the solu-

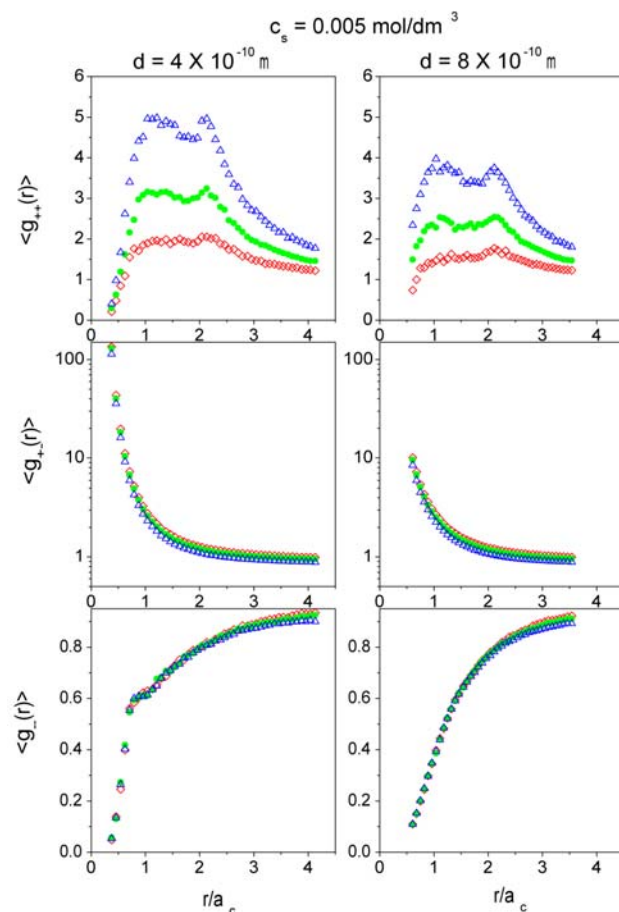


Figure 4: Monte Carlo simulated ion-ion correlation functions $\langle g_{ij}(r) \rangle$. Notation and symbols as for Figure 3 except for $c_s = 0.005 \text{ mol/dm}^3$.

tion as proposed by Eq. 1. Monte Carlo results for the quantity $k_{ij}/k_{ij,0}$ are shown by symbols in Figures 5 and 6. The results obtained via the the Morawetz equation together with the solution of the non-linear Poisson-Boltzmann equation (solid lines) are displayed in the same figures. The results at two fixed salt concentrations, $c_s = 0.002$ (squares) and 0.005 mol/dm^3 (circles) at different polyion concentrations are shown in Figure 5, while the results at two fixed polyion concentrations $c_m = 0.002$ (squares) and 0.005 mol/dm^3 (circles) can be seen in Figure 6. Also, the left and right hand panels of these figures correspond to ion diameters $d = 4 \times 10^{-10} \text{ m}$ and $8 \times 10^{-10} \text{ m}$, respectively.

The distinctive feature of the $k_{++}/k_{++,0}$ behaviour shown in top panel of Figure 5 is the appearance of a maximum similar to that seen in the earlier studies of solutions with monovalent counterions.^{26,27,30} This suggests that increasing the polyion concentration above that of the salt is inefficient as far as the reaction rate is concerned. The catalytic effect is very strong in this case, much stronger than

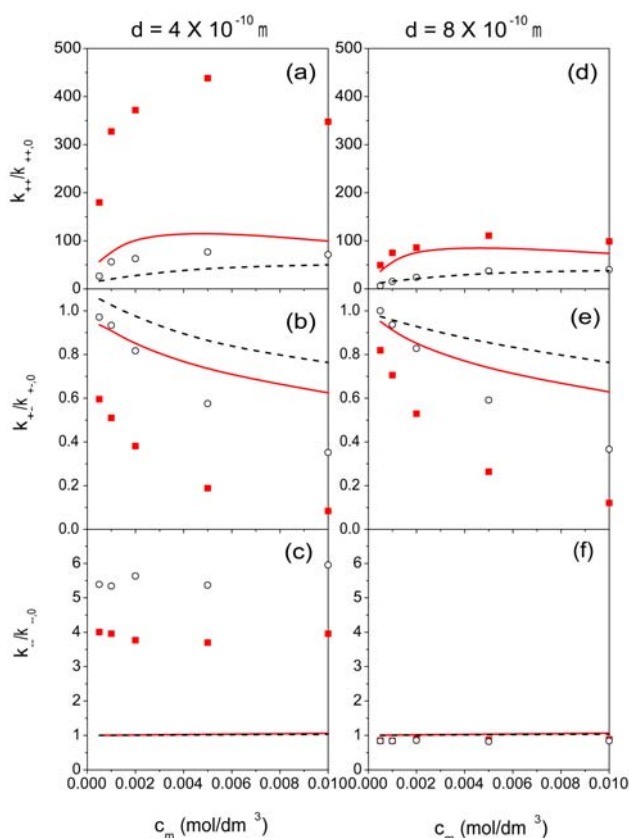


Figure 5: Reaction rate ratio $k_{ij}/k_{ij,0}$ as a function of the polyion concentration at a fixed salt concentration. From top to bottom – interacting counterion-counterion, counterion-coion, and coion-coion pairs, respectively, and the left and right hand panels are for ionic diameters $4 \times 10^{-10} \text{ m}$ and $8 \times 10^{-10} \text{ m}$, respectively. The symbols represent Monte Carlo results, (squares) $c_s = 0.002 \text{ mol/dm}^3$ and (circles) $c_s = 0.005 \text{ mol/dm}^3$, while the solid and dashed lines represent Poisson-Boltzmann-Morawetz results for these two cases, respectively.

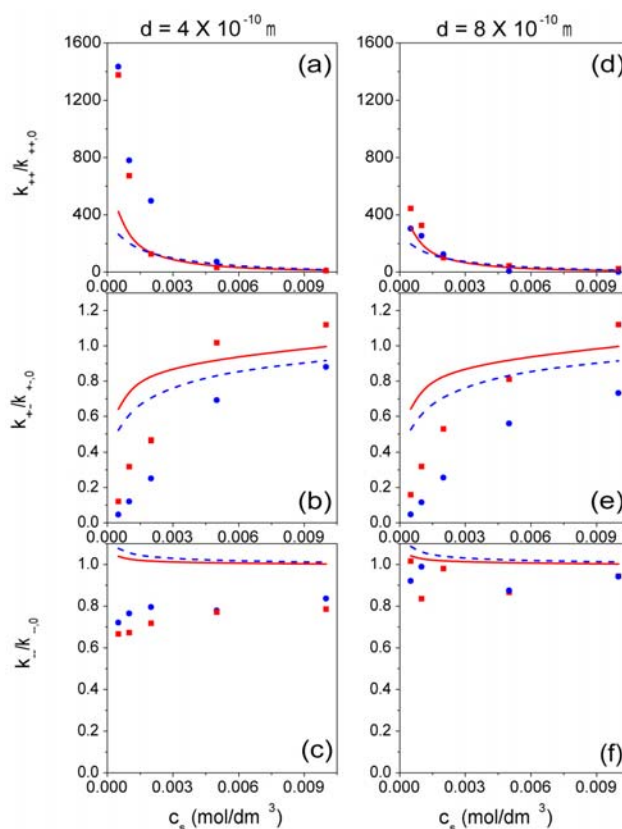


Figure 6: Reaction rate ratio $k_{ij}/k_{ij,0}$ as a function of the added salt concentration at a fixed polyelectrolyte concentration. The symbols represent Monte Carlo results, (squares) $c_m = 0.002 \text{ mol/dm}^3$ and (circles) $c_m = 0.005 \text{ mol/dm}^3$, while the solid and dashed lines are the Poisson-Boltzmann-Morawetz results for these two cases, respectively. The remaining legend as for Figure 5.

observed in the +1:–1 electrolyte solution mixed with the polyelectrolyte under otherwise same conditions (cf Figure 5 of Ref.³⁰, top panel). Note that polyelectrolyte effect on the collision rate is stronger for smaller salt concentration, c_s .

Calculations of $k_{+-}/k_{+-,0}$ for an interacting counterion-coion pair are shown in the middle panel of this figure. In agreement with the previous calculations for the the +1:–1 electrolyte we observe a decrease of the counterion-coion collision frequency upon addition of the polyelectrolyte. The effect is of similar magnitude than found before for the univalent salt.³⁰ The bottom panel of this figure shows the $k_{--}/k_{--,0}$ function, that is, the reaction rate between two coions. The Poisson-Boltzmann-Morawetz results are merely qualitative in all three situations.

Next we present Figure 6, showing the salt concentration dependence of $k_{ij}/k_{ij,0}$ at a fixed polyion concentration. For the counterion-counterions pair (top panel), this function is monotonically decreasing as noticed before for solutions with monovalent counterions,^{27,30} while the $k_{+-}/k_{+-,0}$ function increases monotonically to unity. Both results are clearly related to the screening effects due to

the added salt. The reaction rate between the coions, $k_{--}/k_{--,0}$ is again surprisingly quite different from that obtained in solutions of univalent salts. The effect on the reaction rate is strong. The Poisson-Boltzmann-Morawetz equation is not very good in describing these effects due to the mean field approximations involved in the Poisson-Boltzmann equation. We would like to draw the attention of the reader to the explanations given in this connection in Ref.³⁰

Figure 7 shows $k_{ij}/k_{ij,0}$ as a function of the monomer length b . Note that increasing b is tantamount to decreasing the surface charge density (decreasing λ) on the polyeion. In these calculations the ion radius is held fixed at 2×10^{-10} m, while the polyeion and added salt concentrations are 0.005 mol/dm³ and 0.002 mol/dm³ and 0.002 mol/dm³, respectively. As this has not been investigated before, results for both univalent (circles) and divalent (triangles) simple ions are shown for comparison purposes. Two features are conspicuous in this figure. First, the magnitude of $k_{++}/k_{++,0}$ is much higher for the divalent ion situation than that for the univalent ion case. The situation is reversed in case of $k_{--}/k_{--,0}$ although now the difference in the magnitudes for univalent and divalent ion cases is small. Second, the reaction rate ratio decreases or increases monotonically for the counterion-counterion and coion-counterion pairs, respectively, whereas it is barely affected for the coion-coion pair.

3. 3. Correlation with Experimental Data

From the above discussion it is clear that the catalytic effects in an electrolyte caused by an addition of polyelectrolyte are very strong for divalent counterions. Commercially interesting systems were to a certain degree explored experimentally in several papers^{19,21,45,46} and compared with the Poisson-Boltzmann-Morawetz results in Ref.²⁴

There are several facts we need to be aware of when confronting the calculations against the experimental results. Firstly, (i) the cell model as used here contains only three ionic species, polyeion, counterions and coions, with all the small ions having equal diameter. The experimental systems^{19,21,45,46} are more complicated since they contain two counterion species, which compete for the place near the polyeion. If one of the interacting counterion species is more strongly bound to the polyeion than the other, the collision rate between these species will be affected. In principle there is no obstacle to model such systems, in practice, however, the multi-component computer simulations are quite time consuming. Secondly, (ii) the primitive model used in our paper only includes the electrostatic interaction, any ion-specific effects due to the site-binding of ions are ignored. Thirdly, (iii) while the Morawetz equation provides the ratio $k_{ij}/k_{ij,0}$ directly, in simulations we need to calculate this quantity separately. This is another source of error. The same holds true for experi-

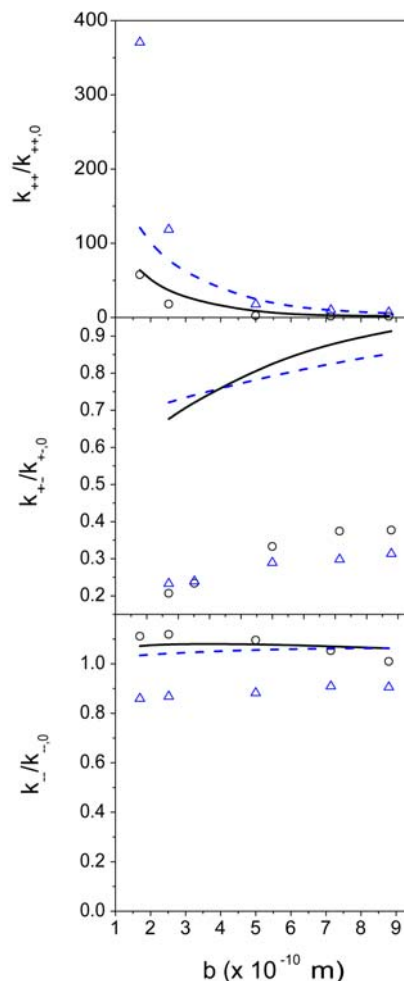


Figure 7: Reaction rate ratio $k_{ij}/k_{ij,0}$ as a function of the monomer length b . The ionic radius is held fixed at 2×10^{-10} m, while the polyeion and added salt concentrations are $c_m = 0.005$ and $c_s = 0.002$ mol/dm³. The circles and the triangles represent Monte Carlo simulation results for univalent and divalent ions systems, while the solid and the dashed lines represent results out of Poisson-Boltzmann-Morawetz equations for the same two cases, respectively. The remaining legend as for Figure 5.

ments, for example, in the analysis of experimental data by Morawetz and Gordimer,⁴⁵ $k_{ij,0}$ was estimated using the Debye-Hückel theory. All these makes the comparison of calculations with experiment rather uncertain.

Yet a good qualitative correlation between the experimental data and theory, based on the Morawetz equation, (see Ref.²⁴) (cf. Eq. 1) can be observed. In particular both the theory and experiment yield a distinct maximum in the counterion-counterion ($k_{++}/k_{++,0}$) enhancement, plotted against polyelectrolyte concentration. This has been confirmed for several experimental systems with varying polyeions and divalent counterions.^{24,45,46} The position of maximum depends on the nature (charge density) of the polyeion and concentration of added simple $-2/+2$ electrolyte. The analysis of experimental data performed by Ishikawa²⁴ indicates that the Morawetz equation under-

estimates the enhancement of the chemical reaction between counterions in practically all situations. For this reason it was important to compare the Monte Carlo results obtained via Eq. 1 with the results of the Poisson-Boltzmann theory and Eq. 4. The comparison given in Figures 5–6 proves that the latter theory also underestimates the computer simulation results.

To the best of our knowledge, there is no experimental evidence about chemical reaction rates between the divalent counterions and divalent coions theoretically studied in Figures 5–6. Ishikawa²⁴ in his Figure 4 presents some results for the $-1:+2$ case. It is clear from that figure that the chemical reaction between the oppositely charged species is decelerated and that the effect increases with increasing polyelectrolyte concentration. The result is in agreement with our simulations.

4. Conclusions

The main achievement of this paper has been an extension of our study of the ionic correlations around a rod-like polyion to when higher valency simple ions are present. In particular we have treated divalent co- and counterions and the results show a substantial influence of stronger Coulomb interactions. For example, the magnitude of the counterion-counterion correlation is much higher than seen earlier for monovalent counterions. These in turn, indicate a strong influence on the reaction rates, viz., counterion-counterion reaction rate increases up to five-fold in one case for the same physical parameters as for $-1:+1$ salts. The volume average of the counterion-counterion correlation function and the collision rate ratio k_{++}/k_{++0} are much more sensitive to the concentrations of all species and model parameters than the counterion-polyion concentration profiles or the thermodynamic properties. Any experimental method reflecting the collision frequency between the counterions would therefore yield valuable information about interaction in the electrical-double layer. The counterion-coion and coion-coion correlations are less affected by the valency and less dependent on concentration variations. The agreement between the predictions of the Morawetz equation, based on the solution of Poisson-Boltzmann theory, and the simulation results is merely qualitative. The deviations are greater at lower electrolyte concentrations. This occurs due to the fact that the differences between theory and simulation depend on the c_s/c_m ratio. When the relative amount of added salt is small, the shielding effect of the salt is small and the electrostatic effects are more pronounced, and hence the bigger deviation. Further extension of the study to cater for mixed valency ions is contemplated for the future.

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6. References

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Povzetek

Raziskali smo sposobnost linearnega polielektrolita da katalizira kemijske reakcije med enako nabitimi ioni v raztopini +2:–2 elektrolita. V ta namen smo uporabili metodo Monte Carlo in celični model raztopine. Polion smo obravnavali kot neskončno dolg in enakomerno nabit valj, okoli katerega so porazdeljene nabite toge kroglice: to so dvovalentni protiioni in koioni. Rezultate simulacij smo primerjali z rezultati Poisson-Boltzmannove teorije v povezavi z Morawetzovo enačbo. Pomemben rezultat simulacije je prostorsko povprečje parske porazdelitvene funkcije za različne ione v električni dvojni plasti okoli poliona. Slednje je precej odvisno od parametrov modela. V primeru, ko raztopini navadnega elektrolita dodamo polielektrolit, opazimo močno povečanje števila trkov med dvovalentnimi protiioni. Ujemanje med rezultati simulacij in teorijo na osnovi Poisson-Boltzmannove enačbe je v večini primerov le kvalitativno.