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Counterion condensation as saturation effect under the influence of ion hydration

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Abstract

Polyelectrolyte solutions are often described by structural theories. These theories in some cases yield values for the counterion concentration at the charged monomer surface that exceed the saturation concentration. This means a change of the ion properties due to ion immobilization or ion condensation in close vicinity to the polymer chain. The extent of this counterion condensation (CIC) and the respective surface potential are calculated from the saturation concentrations of the electrolyte involved including the influence of ion hydration on the effective dielectric number. In this paper, we shall consider all these influences by a fundamental differential equation and a set of explicit formulae yielding quantitative expressions without linearization. All calculations are based on the abstraction of an idealized elementary cell. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Counterion condensation; Saturation effect; Polyelectrolyte; Ion binding; Hydration, Poisson–Boltzmann equation

1. Introduction

In principle, it is possible to calculate the number of fixed charges at a polymer from measurements of ion binding, osmotic pressure, electric potential, ion activity, or other effects by applying the Donnan equilibrium theory. Such calculations, however, give distinct deviations from the number of polymer charges assuming a completely dissociated polymer and simply counting the charged groups. These deviations often clearly exceed the error margin of the experiments. The first attempt to explain this discrepancy was the assumption of Manning [1–3] that counterion condensation (CIC) reduces the effective polymer charge.

The cell model of a polyelectrolyte [4–7] con-

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siders the inner structure of the polymer solution by the approximation of the polymer chain as charged cylinder in a concentric cylindrical electrolyte environment. In the framework of this model the inhomogeneous ion distribution is described by the Poisson–Boltzmann (PB) equation. Gunnarson [8] explained differences between experimental values and chemically expected values for the polymer charge only from the inhomogeneities of the ion distribution without counterion condensation effects. However, this appears to be in contrast to independent experiments (e.g. using NMR spectroscopy [8–11]) reporting a certain amount of counterions that are immobilized at the polymer chain. By considering ions within a restricted cylinder as bound to the polymer, Gunnarson resolved this contradiction within the cell model [8].

Furthermore, there are deviations of the ion activities in a polymer solution predicted by the cell system from those estimated experimentally, even for binary monovalent electrolytes. According to Vlachy and Haymet [12] and Mills et al. [13], the reason for these deviations is in particular that all ions are considered as point charges in the PB theory. The authors performed grand canonical Monte Carlo simulations, in which the ions are represented by hard spheres with a defined radius. This yields a distinct improvement of the agreement between theory and experiment, but nevertheless, a considerable deviation remains. Patra and Yethiraj [14,15] used refined theoretical tools (density functional theory, hypernetted chain integral equation theory) and compared the resulting ion distributions with that from other theories but not with experimental results. They found obvious differences in the results of different theoretical approaches for polyvalent salt solutions. It is common to all described theoretical approaches that counterion accumulation accompanied by an exclusion of coions from the close vicinity of the polymer cylinder occurs. However, these approaches do not distinguish qualitatively between properties of ions close to the charged polymer vs. ions far away in the bulk phase. Otherwise, Deserno et al. [16] used the existence of an inflection point in the counterion distribution plotted against the logarithmic distance from the polyelectrolyte as a criterion to quantify counterion condensation. Gelbart et al. [17] and Gronbech-Jensen et al. [18] explained the nature of strong attractive interactions of highly charged macroions as DNA from CIC. The effect of CIC leads to an attenuation of the repulsive forces between densely packed DNA rods that was measured experimentally [19,20].

Groot [21] calculated the dependence of CIC on the particle charge for multiply charged colloidal particles within a cell model. He compared the results with the results of the linearized Debye–Hückel equation (Manning-condensation-theory), the non-linear Poisson–Boltzmann equation and the weighted density approximation theory. The latter, also developed by Groot, includes ionic interactions, which are neglected in the PB theory. However, as in the classical PB theory, the polarization saturation of water in the central field of the ions was not included in this treatment, even though polarization saturation represents the main reason for the failure of classical theories for strong electrolytes even at moderate concentrations [22].

More recently, some attempts were undertaken to connect the spatial distribution of counterions in an electrolyte solution of a polymer with related changes of the local dielectric number in the vicinity of charged polymer structures. Pack et al. [23] calculated the counterion distribution around an all-atom-model of DNA using a variable dielectric coefficient and found a strong dependence on the dielectric properties of the solvent.

Lamm and Pack [24] investigated the dependence of the local dielectric number on the distance from the polymer surface in a cylindrical cell model adapted from the planar case considering three influencing effects: (i) the orientation of a certain number (approx. 5) of water molecules in the central field of the counter ions resulting in a diminished polarizability of solvated ions; (ii) the polarization saturation of water in the field of the polymer charge; and (iii) changes in the water binding structure. They showed that the influence of (i) is clearly dominant over (ii) and (iii).

Another attempt is that of Blackburn and Kilpatrick [25]. These authors considered the field dependence of the dielectric number in the basic electrostatic equation as well as in the electrochemical potential instead of using empiric activity coefficients. However, in their approach the polarization saturation of water in the central field of ions is neglected without giving further quantitative reasons.

If one calculates the ionic strength at the polymer surface within the frame of a structural theory, values are obtained, which often clearly exceed the saturation concentration at conditions that are absolutely realistic and physically relevant. Provided that the approximation of the used structural theory is sufficient, the physically impossible exceeding of the saturation concentration can be understood in that way that ions near the charged polymer are found in a different 'phase state' with respect to that in regular solution, and their behavior is not described by the applied theory anymore. In the present paper, theoretical investigations on the consequences of this phenomenon and of the other effects mentioned above for the behavior of counterions in a polymer solution are described and discussed.

2. Objective

The aim of the present study is the formulation of a unified continuum theory describing all effects given above (solubility saturation, polarization saturation in the central filed of ions, collectively treated properties of strong electrolytes) together with a partial screening of the polymer charge from the electrolyte space by an immobilization or 'condensation' of counterions at the surface of charged polymer structures. The theory that is applicable to different geometries leads to explicit formulae for the extent of counterion condensation and the respective surface potentials. The formulae enable us to discuss the influences of empirically available quantities and the geometry of the elementary cell on the CIC.

In the present paper, the necessary assumptions for such a theory are listed and general and explicit quantitative expressions are presented and discussed. Particularly, the extent of a CIC is calculated assuming that the immobilized counterions form a 'second phase' coexisting with that of the ions in the electrolyte solution. This 'second phase' is comparable to the crystalline phase adjacent to a saturated solution, but not comparable to a localized chemical binding. Finally, we compare our results with the Manning picture, that we take as the extract of many experiments.

Our derivations are suitable not only for polymer solutions, but also for other charged structures immersed in an electrolyte solution containing counterions. For simplicity, we assume monovalent binary electrolytes and the identity of the counterions with one of the ion species of the electrolyte. Additionally, only ideal symmetric structures with approximately constant electric surface displacement are considered.

3. Definitions and fundamental equations

In this chapter the elementary physical laws and relations will be assembled which describe the electrolyte space between the polymer molecules. This is the basis of all further calculations, especially of the derivation of the fundamental generalized PB equation [Eq. (7)] in Section 3.3.

3.1. Elementary cell

The considered polymer solution is divided into elementary cells. A simple elementary cell comprises one polymer element with exactly one elementary charge and the corresponding part of the electrolyte space.

An idealized elementary cell is created by an imaginary pointwise averaging of all similar elementary cells. All following calculations are carried out for such an idealized elementary cell. In spite of its atomic dimensions, the electrolyte space of this idealized cell can be treated as a continuum around a charged central body (mean-field-theory). As in all applications of the PB equation, we assume that all quantities of the idealized cell follow the laws of macroscopic electrodynamics and classical thermodynamics and yield probability statements, if related to real cells. The limits of this assumption can only be determined by a statistical thermodynamic analysis of all effects covered by the mean-field-theory, which exceeds the framework of this paper.

3.2. Basic relations

The thermodynamic equilibrium is maintained in the idealized elementary cell, i.e. spatial constancy of the electrochemical potentials μ_i of each electrolyte ion species is given (for symbols see Appendix A):

$$\mu_i = \mu_i^0 + RT \ln f_i x_i + z_i F \phi = \text{const},$$
$$x_i = c_i / \Sigma c_j. \tag{1}$$

Additionally, the electrodynamic basic relation

$$\nabla D = \rho \tag{2}$$

linking electric displacement D and space charge density ρ is valid. Eqs. (1) and (2) are connected by the relation

$$\rho = F(c_+ - c_-) \tag{3}$$

between space charge density ρ and the concentrations c_i of the electrolyte ions, and by the relation

$$D = -\varepsilon\varepsilon_0 \nabla\phi \tag{4}$$

between D and the electric potential ϕ.

The properties of the electrolyte are assumed to be empirically given. They are described by the dependence of the activity coefficients f_i on the local ionic strength I

$$f_i(I), \quad \text{with} \quad I = \frac{1}{2}(z_+^2 c_+ + z_-^2 c_-), \tag{5}$$

whereby we will only need the values of f for the bulk, the saturation value and an integrated mean over the whole possible range of values, and by the dependence of the local dielectric number ε on the electrolyte composition and on the effective local electric field (Section 3.4).

3.3. Definitions and fundamental differential equation

The PB equation is derived from the basic relations given in Section 3.2, under ideal conditions (i.e. electrolyte is an ideal solution with $f_i = 1$ and ε is spatially constant). For non-ideal conditions, the PB equation must be replaced by a more general fundamental differential equation. However, this equation must also be derived from the basic relations given in Section 3.2. It is written in the simplest form, when the following dimensionless or relative quantities are used instead of the primary descriptive quantities (for all other symbols see Appendix A):

$X_i = c_i / c_0$, relative ion concentration;
$Q = \frac{\rho}{Fc_0} = X_+ - X_-$, relative charge density;
$P = 2I/c_0 = X_+ + X_-$, relative ionic strength (also determining the osmotic pressure);
$\varepsilon_r = \varepsilon/\varepsilon_w$, relative local dielectric number of electrolyte;
$\varphi = \frac{F\phi}{RT}$, relative electric potential;
$\psi = \int_0^{\varphi} \varepsilon_r d\varphi$, dimensionless potential function.

By introducing these quantities into Eqs. (2)–(4), inserting Eqs. (3) and (4) into Eq. (2) and using the Debye–Hückel constant κ

$$\kappa^2 = \frac{2F^2 c_0}{\varepsilon_w \varepsilon_0 RT} \tag{6}$$

we obtain the following equation, which is the desired fundamental differential equation in its general form:

$$\Delta\psi = -\frac{\kappa^2}{2} Q \tag{7}$$

This equation is the basis for all following calculations.

The potential function ψ turns into φ, if $\varepsilon = \varepsilon_w = \text{constant}$ or $\varepsilon_r = 1$ are valid. If, furthermore, $f_i = 1$ is valid (ideal conditions), then Q turns into Q_{PB} (for definition see below) and the fundamental equation [Eq. (7)] turns back into the ideal PB-equation

$$\Delta\varphi = -\frac{\kappa^2}{2}Q_{\mathrm{PB}}. \tag{8}$$

For larger values of P and $|Q|$, the difference between ψ and φ becomes important and can be as large as one order of magnitude.

For solving the fundamental equation [Eq. (7)] the potential dependence of Q following from Boltzmann's partition law is needed. From the equilibrium condition of thermodynamics (spatial constancy of the electrochemical potentials in thermodynamic equilibrium) Boltzmann's partition law

$$\frac{x_\mathrm{i}}{x_{\mathrm{i}0}} = \frac{f_{\mathrm{i}0}}{f_\mathrm{i}}\exp(-z_\mathrm{i}\varphi), \quad \text{ideal: } \frac{x_\mathrm{i}}{x_{\mathrm{i}0}} = \exp(-z_\mathrm{i}\varphi), \tag{9}$$

results, which is used in all further derivations. It yields

$$Q = \frac{f_{+0}}{f_+}\exp(-\varphi) - \frac{f_{-0}}{f_-}\exp\varphi, \quad \text{ideal: } Q_{\mathrm{PB}} = -2\sinh\varphi \tag{10}$$

and

$$P = \frac{f_{+0}}{f_+}\exp(-\varphi) + \frac{f_{-0}}{f_-}\exp\varphi, \quad \text{ideal: } P_{\mathrm{PB}} = 2\cosh\varphi \tag{11}$$

by using the definitions of Q and P (index 0 is related to the bulk).

Thereby, all our results are in agreement with Boltzmann's partition law. In its general form it contains the influence of solvation of the ions, the influence of ion interactions and further influences present in strong electrolytes.

Since the activity coefficients are empirical functions of P, one needs a relation between Q and P, which results directly from the definitions of P and Q.

$$P^2 - Q^2 = 4\left(\frac{f_0}{f}\right), \text{ with } f^2 = f_+f_-, \quad \text{ideal: } P^2 - Q^2 = 4 \tag{12}$$

This relation will be used for solving Eq. (2.9) in Appendix B and in the derivation of the resulting equations.

3.4. Dependence of the dielectric number on the electrolyte concentration

The fundamental differential equation [Eq. (7)] is expressed for the integral potential ψ. According to the definition of ψ, the local dielectric number ε_r of the electrolyte is used for the calculation of ψ. The value ε_r can be estimated in the following manner.

The dielectric number of pure water is essentially determined by the fact that water is arranged in clusters, that are orientating in an outer electric field. While clusters of pure water have a large dipole moment due to their parallel orientation, water molecules in the vicinity of an ion are orientated spherosymmetrically. This leads to an almost complete loss of the resulting dipole moment. Independently, the energy required for a certain change in the orientation of a single water molecule is increasing with decreasing distance to an ion. This leads to a decreasing polarizability in an outer electric field (water is 'orientationally freezing' [24]).

Altogether, these effects are described by an effective hydration number $w_\pm$. This value represents the number of water molecules near an ion, which are not accessible to polarization. For this, a real chemical hydration is not necessarily assumed. The small influence of the central body field tends in the same direction and can be effectively included in the definition of $w_\pm$. The possible influence of ion association, which would lead to an increase of the dielectric number of an electrolyte, can be neglected in the environment of the monomer cylinder, because associated ion pairs do not appear here due to the low co-ion concentration in practice.

According to all these ideas, the electrolyte in the field of the central body of the elementary cell is electrostatically treated as a mixture of pure water, having the dielectric number ε_w, and hydrated or solvated ions. In this conception, the averaged local dielectric number ε is calculated as weighted mean of the total value ε_w of pure water and the saturation value 1 for an unpolarizable medium according to the respective parts in the solution. For the relative dielectric number ε_r one obtains

$$\varepsilon_r = 1 - (x_0 w_+ X_+ + x_0 w_- X_-)(1 - \varepsilon_s). \tag{13}$$

This relationship is only valid for resulting values larger than the saturation value $\varepsilon_s = 1/\varepsilon_w$. For values smaller than the saturation value it must be set $\varepsilon_r = \varepsilon_s = \text{constant}$.

This approach for the relative dielectric number of the electrolyte is not contradictory to the thermodynamic partition law. Instead, it is a necessary condition for the spatial ion distribution and the potential in Eq. (7).

The chosen definition of the polarization hydration number w_i allows the inclusion of the residual polarizability of hydrated ions as well as the inclusion of the small influence of the strength of the central body field on the dielectric number of water. In principle, this can be done by regarding w_i as empirically determined in analogy to the activity coefficients.

3.5. Boundary conditions

The above mentioned relations are completed by boundary conditions at the central body (index 2) and at the outer interface of the elementary cell (index 1).

Firstly, we demand the equality of the chemical potential of the dissolved counterions at the central body surface and the chemical potential of counterions in the condensed phase. We assume the constancy of the chemical potential in this phase similar to the case of phase equilibrium between a crystalline phase and a saturated solution.

It follows that the counterion concentration c_2 at the central body surface is not allowed to exceed a certain saturation value. This is expressed in relative quantities as

$$X_2 \le X_s.$$

The saturation concentration c_s is equivalent to the solubility hydration number u. It is a descriptive representation of the number of water molecules per counterion that are necessary for one ion to behave like in free solution. Its value can be estimated by

$$u = \frac{c_w}{c_s}$$

using c_w and c_s of a saturated solution. We understand u as an empirically determined effective value in the sense of the mean-field-conception as we did with the activity coefficients. The relative saturation concentration X_s is written as

$$X_s = \frac{1}{x_0 u}. \tag{14}$$

For not too high bulk concentrations, in combination with Eq. (12) this yields

$$P_2 \approx X_2 \approx |Q_2| \gg 2. \tag{15}$$

Secondly, assuming that the total charge e in the central body is reduced to q by CIC and, furthermore, assuming homogeneous symmetrical distribution of q in the central body, the relation $AD_2 = q$ or with relative quantities (b Bjerrum length)

$$\frac{A|\nabla\psi|_2}{4\pi b} = \frac{q}{e} \tag{16}$$

must be valid for the electric displacement at the surface A of the central body.

Thirdly, the electric field strength must equal zero at the surface of the elementary cell. Assuming wide elementary cells, also the electric potential, which is standardized to be zero in the far bulk, vanishes at the cell surface:

$$|\nabla\psi|_1 = 0 \quad \text{or} \quad |\nabla\varphi|_1 = 0 \tag{17}$$

$$\psi_1 \approx 0 \quad \text{or } \varphi_1 \approx 0 \tag{18}$$

4. Field calculation in elementary cells — general relations

It is possible to solve the differential equation [Eq. (7)] for a given geometry using the relations listed in Section 3. The solution of Eq. (7) yields the ion concentration (or ionic strength) and the potential at each point in the elementary cell. However, to determine the extent of CIC it is sufficient to know the respective values at the surface of the central body. With some reasonable assumptions, this is possible without any linearization. This is a fundamental result of the present study.

The determination of the surface values at the central body is carried out by multiplying the non-linear basic equation [Eq. (7)] with $\nabla\psi$ and integrating it along a line of force from the central body surface to the outer boundary of the elementary cell (see Appendix B). This is possible without general linearization but needs some other approximations. The result comes up by applying the boundary conditions and by using the following abbreviations:

$$\xi = \left|\frac{e}{q}\right|, \quad \text{extent of counterion condensation,} \tag{19}$$

with q being the effective charge of the central body and with

$$\xi_0 = \frac{2\pi r_2 b}{A}, \quad \text{generalized Manning parameter,} \tag{20}$$

where

$$b = \frac{e^2}{4\pi\varepsilon_w\varepsilon_0 kT}, \quad \text{Bjerrum length,} \tag{21}$$

A is the central body surface area adjacent to the electrolyte, and r_2 is the central body radius (to be chosen freely in the planar case).

For cylindrical symmetry, the parameter ξ_0 turns into the well-known Manning parameter. It provides the possibility to compare the Manning picture with the structural theory.

In the realistic case $P_2 \gg 2$, the following equation results (see Appendix B).

$$\frac{\xi_0}{\xi} = \frac{1}{2}\kappa r_2 \alpha\sqrt{EP_2}\,. \tag{22}$$

Eq. (22) relates the extent of CIC, ξ, to the relative ionic strength P_2 of counterions at the central body surface, to the central body radius r_2 and, by ξ_0, to the central body surface area A. This general resulting equation is the basis of all further discussions.

The factors α and E have values near 1. The correction factor α results from integration of $\Delta\psi\ \nabla\psi$ in the case of central bodies with curved surfaces (lamellas: $\nu = 0$; cylinders: $\nu = 1$; spheres: $\nu = 2$) to

$$\alpha = 1 + \frac{\nu}{1 + \kappa r_2\sqrt{\dfrac{P_2}{E}}}\,. \tag{23}$$

E describes the properties of a strong electrolyte

$$E \approx \frac{1}{2} + \frac{f_2}{2f_1}\varepsilon_{r_2} - \frac{2}{P_2}\frac{f_0}{f_1} \tag{24}$$

with the activity coefficients f_i of the electrolyte (index 0 — bulk; index 1 — integral mean over the whole electrolyte space between the polymer structures; index 2 — at the central body surface). For physiological NaCl solution it holds $f_0 \approx 0.85$, $f_1 \approx 0.70$, $f_2 \approx 0.80$ [22]. ε_{r_2} is the relative dielectric number of the electrolyte at the central body surface given by

$$\varepsilon_{r_2} = 1 - x_0 w P_2 \geq \varepsilon_s, \quad \varepsilon_s \ll 1. \tag{25}$$

As before, w is the polarization hydration number of the counterions. For NaCl $w \approx 5$ is a reasonable value [24].

The ionic strength P_2 at the central body surface is always directly related to the surface potential φ_2:

$$|\varphi_2| = \ln P_2 + \ln \frac{f_2}{f_0} \tag{26}$$

5. Counterion condensation as a consequence of saturation effects

For the interpretation of the resulting Eq. (22) we have to distinguish between two different cases.

Case 1: In the case, that P_2 does not reach its saturation value P_s, Eq. (22) yields the relative ionic strength P_2 (of counterions) for $\xi = 1$ at the central body surface and the relative surface potential φ_2.

Case 2: The saturation value P_s is reached. Then Eq. (22) yields for $P_2 = P_s$ the extent of CIC, ξ. A resulting $\xi > 1$ is the criterion for the occurrence of CIC. In this case, the relative surface potential φ_2 has the constant saturation value φ_s determined by P_s. It is not allowed to apply case 2 for $\xi < 1$. With the definition of the solubility hydration number u for counterions at the central body surface (NaCl: $u \approx 10$) and with $P_s \approx X_s$, the relative ionic strength saturation value P_s is written as

$$P_s = \frac{1}{x_0 u}. \tag{27}$$

For an initial approximation, we assume $\xi = 1$ (case 1) to be fulfilled and use Eq. (22) to obtain a certain P_2 value. Under usual conditions, this P_2 value is several times larger than the ionic strength at the saturation concentration. For example, for physiological NaCl solution with Debye–Hückel length of 0.8 nm, cylindrical central body with monomer radius r_2 of 0.2 nm and monomer distance of 0.4 nm, we obtain $\xi_0 = 1.77$. The saturation concentration is 5.5 mol/l. With $E = 1$ and the above given values one obtains by iteration $P_2 \approx 125$, while $P_s \approx 35$. From the physical point of view, values higher than the saturation value are not possible, unless the ions at the monomer cylinder have extremely different properties compared to that in free solution. This is another description of counterion condensation of whatever nature. Therefore we turn to case 2.

With $P_2 = P_s$ the above discussed equation turns into a determination equation for the CIC extent ξ with respect to the generalized Manning parameter ξ_0:

$$\frac{\xi_0}{\xi} = \frac{1}{2} \kappa_w r_2 \alpha \sqrt{\frac{E}{u}}. \tag{28}$$

In this equation the following abbreviations are used:

$$\kappa_w^2 = \frac{2 c_w F^2}{\varepsilon_w \varepsilon_0 RT}, \quad \text{general constant } (c_w \text{water concentration}) \tag{29}$$

$$E = \frac{1}{2}\left(1 + \frac{f_s}{f_1} \varepsilon_{r_2} - 4 x_0 u \frac{f_0}{f_1}\right), \quad \text{'hydration factor' of electrolyte} \tag{30}$$

$$\varepsilon_{r_2} = 1 - \frac{w}{u}, \quad \text{relative dielectric number of electrolyte} \tag{31}$$

$$\alpha = 1 + \frac{\nu}{1 + \frac{\kappa_w r_2}{\sqrt{Eu}}}, \quad \text{correction factor of central body geometry.} \tag{32}$$

As before, it holds $\nu = 1$ for cylindrical geometry. The result [Eq. (28)] shows that under special but often realistic (see below) conditions the extent of CIC agrees with the Manning parameter. However, this is not necessarily the case.

The determination equation for ξ is connected with the relation

$$\varphi_s = \ln\frac{1}{x_0 u} + \ln\frac{f_s}{f_0} \tag{33}$$

for the saturation surface potential. The surface potential cannot exceed the value φ_s.

For NaCl as electrolyte ($x_0 \approx 0.0027$, $u \approx 10$), the second term in Eq. (33) approximately vanishes. Here, Eq. (33) yields $\varphi_s \approx 3.6$ or $\phi_s \approx 75$ mV. It is remarkable that this value is independent of any assumptions about the dielectric number of the electrolyte.

We now define a special scaling quantity ρ_0 by the relation

$$\left(\frac{b}{\rho_0}\right)^2 = \frac{1}{4}\kappa_w b\sqrt{\frac{E}{u}} \approx 1.36\sqrt{E}, \quad E \approx 1 - \frac{w}{2u} \tag{34}$$

ρ_0 nearly equals the Bjerrum length b. By the use of ρ_0, ξ can be written extremely simply as

$$\frac{1}{\xi} = \frac{A\alpha}{\pi\rho_0^2}. \tag{35}$$

These simple equations easily allow the discussion of possible influences on the extent of CIC. First of all, ξ depends on the central body surface area A. In the cylindrical case A is defined by $A = 2\pi r_2 d$ with the charge distance or central body length d. Here, Eq. (35) reveals that CIC can only be expected, if the central body diameter $2r_2$ and the charge distance d at the polymer molecule are essentially smaller than the Bjerrum length of 0.71 nm. However, it is remarkable that the used approximation of homogeneously spread charge is invalid for $d > 2r_2$. Therefore, CIC is in principle also possible for larger d values, if some further conditions are fulfilled. The inclusion of polarization saturation ($E \approx 0.5$) yields an extent of CIC that is 1.4 times higher than that predicted by equivalent PB calculations without the assumption of polarization saturation ($E = 1$). This means that in some cases calculations carried out with polarization saturation give considerable extents of CIC, while from PB calculations no CIC is obtained. In the same limits, the scaling quantity ρ_0 has values between $\rho_0 = b = 0.71$ nm in the case of total polarization saturation ($u = w$) and $\rho_0 = 0.86b = 0.61$ nm in the PB case. The realistic case is found in between ($w \approx u/2$). The influence of activity coefficients different from 1 is relatively small.

The correction factor α measures the deviations of the results, if one considers planar instead of cylindrical geometry. With the above given values one can conclude from Eq. (28) that the extent of CIC agrees with the original Manning parameter b/d, if the central body diameter has a value of approximately 0.30 nm for the case of polarization saturation and 0.18 nm resulting from PB-calculations. For these cases one obtains α values between 1.24 and 1.42. It has to be noticed that $\xi = \xi_0$ was chosen for orientation but not as a necessary condition.

For an assumed central body radius of approximately 0.4 nm, PB calculations do not show CIC anymore ($\xi \leq 1$ or in our example $\xi_0/\xi \geq 1.77$), whereas the assumption of total polarization saturation yields an CIC extent of $\xi = 1.49$ or $\xi_0 = 1.19$. This means that in this case 33% of the central body charge is neutralized by CIC. In reality, a value in between is expected.

6. Discussion

Generalized theories describing charged polymers in electrolyte solutions have to include the structure of the polymer and, therefore, also spatial inhomogeneities of the ion distribution. In the present paper, such a generalized theory was developed, that additionally includes hydration- and saturation effects. This theory is applied to an idealized mean 'elementary cell' consisting of a symmetrical charged 'central body' (total charge e) in an electrolyte environment, which contains the counterions of the central body charge. Further, we assume that counterions can condense at the central body surface into a different phase state with a constant chemical potential. Starting from a generalized PB equation Eq. (7), in Eq. (22) and the following Eq. (28) or Eq. (35) we derived a criterion for the occurrence ($\xi > 1$) or no occurrence ($\xi \leq 1$) of counterion condensation and a measure for its extent.

The developed theory is a consequent mean field theory, in which the properties of the electrolyte are given by empirically defined quantities (activity coefficients, solubility hydration number and polarization hydration number). The properties of the polymer molecule are given by its geometric dimensions. Both hydration numbers are effective values, which include the ion hydration as well as some smaller effects, so that the results can be adapted to independent experiments, which directly measure the extent of CIC (e.g. special NMR experiments). Up to now we only give the theoretical basis for this way. The results are given in simple explicit formulae, which show the influence of the considered effects. Only results for symmetric elementary cells are given in this paper. However, more general applications of our theory are possible.

The presented equations allow the following conclusions: due to the paradigm that the ionic strength of the electrolyte must not exceed the saturation value, counterion condensation of whatever nature may occur also within the scope of a generalized theory. Our results can be adapted to different structural theories (e.g. PB theory). The extent of counterion condensation calculated by our equations can be different from that predicted by Manning's parameter ξ_0, above all in the case of ideal PB calculations. This means that situations are possible, that necessitate counterion condensation in Manning's picture, but do not necessitate counterion condensation in the frame of a structural theory. This statement holds in an analogous sense also for the comparison of the generalized structural theory with the PB theory.

While the dependence of counterion condensation on the electrolyte concentration and the polymer concentration is rather negligible in our resulting equations, the influence of the structural parameters of the polymer (central body surface A, charge distance d and central body radius r_2) is crucial, especially that of d. Furthermore, counterion condensation starts abruptly at $\xi = 1$, if it is explained by hydration and saturation effects. Beyond $\xi = 1$, there is no effect. This is in accordance with the theory by Manning, but it is in contrast to the explanation of CIC by invoking purely structural effects. Here, an effective reduction of the polymer charge with respect to the Donnan system occurs over the whole range of the used structure parameter. Assuming an identical central body surface area A, the extent of CIC is lower in the case of spheres than in the cylindrical case because of the dependence of the geometry correction factor α on curvature dimension ν.

In all cases, the extent of counterion condensation is determined essentially by the assumptions made for the monomer radius, which further imply assumptions about the hydration of ions and charged groups. The smaller the assumed monomer radius, the more the ionic strength calculated at the monomer surface exceeds its saturation value and reaches a physically unrealistic range. So far, in a first step the supposed counterion condensation is a helpful construction, which describes effects out of the validity range of the used basic equation. Only by experiments independent of the underlying theoretical ideas, one can compare and assess different structural theories and assign a physical meaning to the counterion condensation analogous to the condensation of a liquid from its gas phase.

The Manning parameter ξ_0 can be understood as summarized expression for results on ion binding, which were collected empirically and evaluated by means of the Donnan equilibrium theory. Thus, from a known ξ_0 value, one can re-calculate the corresponding ion binding and take this as empirically given. Then, the necessary counterion condensation can be estimated using a structural theory and a relationship between ξ and ξ_0 can be obtained as sketched in Appendix C:

$$\frac{\xi_0}{\xi} = 1 + \frac{\varepsilon_r}{16}(\kappa r_2)^2 \varphi_s^3 \frac{\xi}{\xi_0} \tag{36}$$

Eq. (36) must not be used for $\xi < 1$. The saturation surface potential φ_s is given by Eq. (33). It only depends on the bulk concentration and the solubility hydration number but does not depend on any assumption about the dielectric number of the electrolyte.

Using the value $r_2 = 0.4$ nm for the central body radius as in our example at the end of Section 5, Eq. (36) yields ξ_0/ξ values rising from 1.0 in the case of total polarization saturation to 1.49 in the PB case in good agreement with the interval discussed above. For smaller radius the agreement will be better. These results confirm our hypothesis, that saturation effects can produce counterion condensation. If one looks carefully, it is evident that the mean radius is not known for the experiments that Manning based his theory on. So, if we identify ξ_0/ξ in Eqs. (28) and (36), we obtain a relation between the degree of polarization saturation described by E and the central body radius r_2. Here the radius decreases from 0.33 to 0.21 nm, if one proceeds from the case of total polarization saturation ($E \approx 0.5$) to the ideal PB case ($E = 1$). Because in this range a smaller radius seems to be less realistic, we conclude that the influence of polarization saturation, which is not covered by the PB theory, plays an important role and must not be neglected. Our results are in accordance with the tendency concluded by Deserno et al. [16] from molecular dynamics simulations, which also gave stronger condensation than that predicted by the PB theory.

It is remarkable that in the cylindrical case the polymer properties only contribute to the equations by the geometric parameters monomer distance d and effective monomer radius r_2. Besides, the influence of the electrolyte is expressed by the effective hydration numbers w and u of the counterions. The possible variance of the monomer radius r_2 is relatively small. So in agreement with the theory by Manning the monomer distance included in ξ_0 becomes the most determinant factor. Therefore, our results show that at ξ_0 values distinctly higher than 1.5 the spatial inhomogeneous ion distribution within the polyelectrolyte alone is not sufficient for the explanation of counterion condensation postulated by Manning and indicated by NMR experiments. Rather, a remarkable immobilization of counterions or some other kind of ion condensation at the polymer chain has to be considered.

The derivation of Eq. (22) and the equations concluded from this basic equation was initially done for an electrolyte concentration ranging between low values of P_1 or Q_1 and high values of P_2 or Q_2, respectively. That means concentrations comparable to physiological conditions. The obtained equation Eq. (35) is indeed approximately independent of c_0, what enables us to obtain results for isolated polymer solutions without any contact to an electrolyte bath. On the other hand, this transition is not possible for the Eq. (36), which was used for comparison, because in this case the used concept of ion binding in the sense of titration experiments (charged polymer solution in direct contact with an electrolyte) becomes meaningless.

The use of a cylinder model for monomers implies the assumption, that the monomer distance d equals the charge distance at the polymer chain and is comparable to the monomer diameter $2r_2$. For weakly charged polymers with much larger charge separation, the charge distance d in the parameter ξ_0 has to be replaced by $2r_2$, which is the diameter of the in this case charged polymer link. This replacement means the transition to a sphere model and can cause counterion condensation in cases, where the Manning picture of the same situation does not. In the case of flat networked and highly charged polymers, a transition to a plate model is appropriate, if the charge distance is not too high. All given statements are limited to wide elementary cells, i.e. not too high polymer concentrations. Neighbouring polymer chains must have a spacing of at least 4 Debye–Hückel lengths.

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Appendix A. Used symbols of primary quantities

ε	local dielectric number of electrolyte solution
ε_0	permittivity of vacuum
ε_w	dielectric number of pure water
ρ	local charge density
κ	Debye-Hückel constant
ϕ	electric potential
A	central body surface area, through which the force lines of central body charge go into electrolyte
b	Bjerrum length
c_0	bulk concentration of the electrolyte, also as $x_0 = c_0/c_w$
c_i	local concentration of the i-th ionic species of electrolyte
c_w	concentration of pure water
d	charge distance at polyelectrolyte molecule
e	elementary charge
F	Faraday constant,
f_i	activity coefficient of the i-th ionic species of electrolyte
k	Boltzmann constant
N_A	Avogadro constant
R	universal gas constant
r_2	central body radius
u	solubility hydration number of counterions
w	polarization hydration number of counterions
x_i	molar ratio of the i-th ionic species of electrolyte
z_i	valency of the i-th ionic species of electrolyte

Appendix B. Integration of the fundamental differential equation [Eq. (7)]

The integration of the non-linear basic differential equation [Eq. (7)]

$$\Delta\psi = \psi'' + \frac{\nu}{r}\psi' = -\frac{\kappa^2}{2}Q, \quad \psi' = \frac{d\psi}{dr},$$

$$\psi'' = \frac{d\psi'}{dr} \tag{2.1}$$

for symmetrical elementary cells (r radius variable, ν curvature dimension) along a line of force from inner (2) to outer (1) boundary of the electrolyte space of the elementary cell after multiplying by $\nabla\psi$ gives

$$\int_{\psi'_2}^{0} \psi' d\psi' + \nu\int_{r_2}^{r_1} \frac{\psi'^2}{r} dr = -\frac{\kappa^2}{2}\int_{\varphi_2}^{\varphi_1} \varepsilon_r Q d\varphi \tag{2.2}$$

The first integral on the left site can be solved explicitly. The second term is seen as a correction of the first, approximated for $P_2 \gg 2$ by means of

$$\psi' \approx C\frac{\exp(-\kappa' r)}{\sqrt{r}^{\nu}}, \quad C = \text{const} \tag{2.3}$$

and approximately solved. With this, the boundary conditions and after substitution in the right hand integral one obtains

$$|\psi'_2| = \alpha\kappa\sqrt{J}, \quad J = \int_{Q_2}^{Q_1} \frac{\varepsilon_r Q}{Q'} dQ, \quad Q' = \frac{dQ}{d\varphi} \tag{2.4}$$

The correction factor α results together with ψ'_2 from solving the left hand integrals of Eq. (2.2) and is given by

$$\frac{1}{\alpha^2} = 1 - \frac{2\nu}{\nu + 1 + 2\kappa' r_2} \tag{2.5}$$

One obtains κ' by inserting Eq. (2.3) into the differential equation [Eq. (2.1)] and taking this at the central body surface:

$$2\kappa' r_2 - \nu = \kappa^2 r_2 \frac{Q_2}{\psi'_2} = \kappa^2 r_2 \frac{|Q_2|}{\alpha\kappa\sqrt{J}} \tag{2.6}$$

Together, this approximately gives

$$\alpha = 1 + \frac{\nu}{1 + \kappa r_2 \frac{|Q_2|}{\sqrt{J}}} \tag{2.7}$$

In the case of wide cells discussed here, Q_1 vanishes. From the definitions of Q and P one obtains in some steps in good approximation

$$Q' = -P + Q\frac{f}{f_0}\frac{d}{dQ}\left(\frac{f_0}{f}\right)Q' \tag{2.8}$$

With this, the integral J assumes the form

$$J = \int_{Q_2}^{0} \varepsilon_r(P,Q)\frac{Q}{P}\left(1 - Q\frac{d}{dQ}\ln\frac{f_0}{f}\right)dQ \tag{2.9}$$

Here, the dependence of ε_r on X_+ and X_- was substituted by P and Q. Further P is related to Q by Eq. (12). Therefore, it follows:

$$P = \sqrt{Q^2 + 4\left(\frac{f_0}{f}\right)^2} \tag{2.10}$$

When using this in the integral J, we substitute f_0/f in this relation by a constant mean value f_0/f_1, so that J remains unchanged. Because J is above all determined by the mean part of the value interval of ionic strength, where in the case of NaCl solution f is approximately constant, f_1 can be identified with this. Partial integration and application of the mean value theorem of integral calculus neglecting all small terms and using $|Q_2| \approx P_2$ yields

$$J = EP_2, \quad E = \frac{1}{2}\left(1 + \frac{f_2}{f_1}\varepsilon_{r_2} - \frac{4}{P_2}\frac{f_0}{f_1}\right) \tag{2.11}$$

By substituting this with Eq. (2.4) into the boundary condition [Eq. (16)] one obtains the resulting Eq. (22).

Appendix C. Theoretical basis of Eq. (36) used in the discussion

If one connects a polymer solution to an electrolyte bath, the electrolyte concentration in the electrolyte space of the polymer solution increases. In this sense we define ion binding B by

$$2B = \bar{P} - |Q_q| \tag{3.1}$$

and use the term 'ion binding' only in this sense. $\bar{P}$ is the mean of P over the electrolyte space between the polymer molecules, Q_q describes the effective polymeric charge in relation to this space. Because of neutrality it holds

$$Q_q = -\bar{Q} \tag{3.2}$$

In a polymer solution regarded as a continuous Donnan system there is no difference between mean and local values. Therefore Eq. (12), which primarily holds for local values, can be used here for the mean values also. This gives

$$\left(|Q_q| + 2B\right)^2 - Q_q^2 = 4 \tag{3.3}$$

This equation often fails empirically, if one substitutes Q_q by the total polymeric charge Q_e, and also in the case of complete dissociation of the polymer. Manning therefore introduced the assumption of counterion condensation (CIC), which means

$$Q_q = \frac{Q_e}{\xi_0} \quad \text{if} \quad \xi_0 \geq 1 \tag{3.4}$$

and gives, substituted in Eq. (3.3), a determination equation for the expected ion binding from the total polymeric charge and the Manning parameter ξ_0 in the framework of the Donnan theory.

Now, we use the so determined ion binding B to calculate the extent ξ of CIC in the framework of a structural theory. Here, the local quantities P and Q vary in the electrolyte space and Eq. (12) no longer holds for the mean quantities. The needed relation between local and mean quantities can be obtained in a first step by setting Eq. (12) at that point, at which the potential has its mean value, and second by Taylor expansion of P and Q at this point with respect to the potential difference. Then one takes the mean over the Taylor series up to the quadratic term and obtains

$$\frac{\xi_0}{\xi} = 1 + \frac{\xi_0}{Q_e}\overline{\Delta\varphi^2} \tag{3.5}$$

The second term on the right hand side is considered as correction, which allows to calculate it in a similar manner as the correction factor α in Appendix B. We use an exponential approach, but vary the constant κ' for adaptation to the nonlinear equation at the central body surface. By using an asymptotic expansion we obtain in some steps Eq. (36) in Section 4. The details and conditions of derivation will be published later.

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