

Polyelectrolyte hydration: Theory and experiment*

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Abstract: A short review of recent theoretical and experimental advances in studies of polyelectrolyte solutions is presented. The focus is on ion-specific effects as revealed in measurements of osmotic pressure and enthalpy of dilution. We review the experimental results for two different polyelectrolyte systems: (i) salts of polyanetholesulfonic acid, and (ii) aliphatic ionenes (polycations) in aqueous solution with various counterions. A theoretical approach based on the extension of Wertheim's integral equation theory [*J. Stat. Phys.* **35**, 19 (1984)] is used to analyze the experimental data. Preliminary results, based on the all-atom simulation of model 3,3 ionene oligomers, are discussed in the light of polyelectrolyte hydration.

Keywords: polyelectrolytes; osmotic pressure; enthalpy of dilution; polyanetholesulfonic; ionenes; integral equation approach; hydration; polyelectrolyte hydration; osmotic coefficient; molecular dynamics.

INTRODUCTION

Polyelectrolytes are polymers consisting of monomers having groups which ionize in water. Well-known representatives of this class are biopolyelectrolytes such as DNA, RNA, and polysaccharides. Synthetic polyelectrolytes are important too; they find application in the food industry and cosmetics and are used for coating surfaces, as superabsorbers in the paper industry, and in waste-water management [1]. Polyelectrolytes come in various shapes: DNA is rod-like, synthetic polyelectrolytes are flexible (chain-like), and some are globular such as fullerene derivatives, or micelles and colloids. They may contain charged and hydrophobic groups and therefore possess a very rich physical behavior. In addition to large polymeric ions termed "polyions", such a solution also contains an equivalent number of low-molecular-weight ions having charges of opposite sign to the polyions, called counterions. In a mixture with a low-molecular-weight electrolyte, an additional ionic species, the coion, having the same charge sign as the polyions, is present in the solution. For example, for the sodium salt of polystyrene-sulfonic acid (HPSS) (having an $-\text{SO}_3$ group attached to the backbone) in a mixture with NaCl, the Na ion is the counterion and Cl the coion.

The physicochemical properties of aqueous polyelectrolyte solutions are not intermediate to the properties of low-molecular-weight electrolytes and those of uncharged polymers; quite the opposite, they differ significantly from both of these materials [2–5]. Their properties can be briefly summarized as follows. The activity and mobility of the counterions are reduced below the bulk values; note that a

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low osmotic pressure means a high activity (high vapor pressure) of water. When an external field is applied to such solution, a fraction of the counterions travels as an integral part of the polyion. In contrast to low-molecular-weight electrolytes, the non-ideality increases upon dilution in the experimentally accessible concentration range. Further, the reduced viscosity increases upon dilution, just the opposite as for uncharged polymers. For the heats of dilution, electrostatic theories predict an exothermic effect, while experimental values can be positive or negative. This suggests that the ion-specific effects, brought about by water rearrangement upon dilution, can significantly affect the measurable properties.

Polyelectrolyte properties depend strongly on the distribution of small ions in the vicinity of the charged polyions. It has been suggested [6] that there are two types of “binding” of counterions to polyions: (i) one caused by the Coulomb attraction of counterions to polyions; and (ii) the other, which involves specific charged sites on the chain and was referred to as “site-binding”. Due to the first effect (i), the counterions are trapped in the electrostatic field around the polyions, making the osmotic coefficients of these solutions very low. The second effect (ii) may be accompanied by displacement of the water molecules between the interacting charges, and as such it is ion-specific. The nature of the counterion and the charged group on the polyion, as well as the presence of hydrophobic groups, influences the water rearrangement between the approaching charges. In other words, not only the magnitude of the charge but also the chemical nature of the counterions and the charged (and uncharged) groups on the polyion play a role. These effects are crucial for understanding processes involving biological polyelectrolytes (see, e.g., [7] and refs. therein) and also some industrial applications [8]. The ion-specific effects are observable even with strong polyelectrolytes [6]. For cesium poly(styrenesulfonate) at 0 °C, for example, even the sign of the enthalpy of dilution is not predicted correctly by popular theories [9]. Examples showing the importance of the ion-specific interaction are given in refs. [6,9–13]; the enthalpies of dilution, ΔH_D , of polyelectrolyte solutions were found to be either negative or positive, depending on the temperature of observation and the nature of the counterions and charged groups on the polyion. Classical models [3,4,14–16], treating the solvent as a dielectric continuum, the polyions as charged hard cylinders (or a line charge), and ions as charged points (or charged hard spheres), predict the enthalpy of dilution to be negative under all conditions.

The ion-specific effects can be explained as a result of effects caused by restructuring of water between the interacting charges. Chain-like polyelectrolytes in solution are difficult to model in such detail; for a review of theoretical developments, see ref. [17]. The present state of theory is such that thermodynamic properties can only be calculated for simplified solvation models [18,19]. In recent years, explicit solvent molecular dynamics (MD) simulations of short oligoions [20–23] have become available. In what follows, we will review some of the experimental and theoretical advances with the purpose of better understanding polyelectrolyte hydration and the origins of the ion-specific effects in these systems.

REVIEW OF THE EXPERIMENTAL DATA

To illustrate the rich and diverse behavior of polyelectrolyte solutions, we will discuss the thermodynamic properties of one anionic (salts of polyanetholesulfonic acid) and one cationic (ionene) strong polyelectrolyte.

Osmotic coefficient

The osmotic pressure is one of the most often measured properties of polyelectrolyte solutions (see, e.g., refs. [2,4,24–31]). Lipar and coworkers [31] recently determined the osmotic coefficients of lithium, sodium, potassium, and cesium salts of polyanetholesulfonic acid (CsPAS). Measurements were made in salt-free solutions; in other words, no additional low-molecular electrolyte (no coions) was present in the system. The results were compared with the osmotic pressure data for the salts of

HPSS already published [26]. The osmotic coefficient, defined as $\varphi = \Pi/\Pi_{\text{ideal}}$, where Π_{ideal} denotes the ideal osmotic pressure, was found to vary from 0.2 to 0.45 in the concentration range between 0.001 and 0.30 monomole/dm³. The latter quantity, φ , is in the language of continuum-solvent theories [4,14] interpreted as the fraction of “free” counterions. Thermodynamically, however, the osmotic coefficient is related to the activity of water, a_1 , as

$$\varphi n_2 = -n_1 \ln a_1 \tag{1}$$

where n_1 is the number of moles of water, and n_2 the number of moles of solute. The activity of water is reflected in its vapor pressure; note that this effect is utilized (vapor pressure osmometry) to determine osmotic coefficients. An increase of the osmotic coefficient can be interpreted as a decrease of the water activity, that is, an increasing hydration of all solutes.

The osmotic coefficient, as indicated by these and previous measurements, is not very sensitive to the nature of the counterions (see, e.g., Fig. 2 of [31]). One exception seems to be CsPAS, which gives lower values of φ than the other alkaline salts. This is not surprising, since hydrated cesium ions lose water more easily than the other alkaline ions, and may therefore approach closer to the sulfonic group. What is a surprise is perhaps the magnitude of this “deviation”, which will be further discussed in the section “Theoretical advances: Continuum-solvent approaches”. Osmotic coefficient measurements also indicate that this quantity is only marginally dependent on temperature [24].

Before continuing this review, it is worthwhile to define the parameters that characterize polyelectrolyte solutions. The most important quantity in theory of polyelectrolyte solutions is the so-called charge-density parameter λ , defined as

$$\lambda = e_0^2 / (4\pi\epsilon_0\epsilon_r k_B T b) \tag{2}$$

where e_0 is the proton charge, ϵ_0 is the permittivity of a vacuum, and ϵ_r the relative permittivity of the solvent under the conditions of observation, k_B is Boltzmann’s constant, and T the absolute temperature. Parameter b measures the distance between the two charges projected on the z -axis of the polyion, and it therefore determines the linear charge “density” of the polyion. For polyanetholesulfonic acid and its salts discussed here, b is taken to be 0.27 nm, a value which in aqueous solutions at 298 K yields $\lambda = 2.74$. Osmotic coefficients of the HPAS salts are generally higher than the corresponding salts (X^+) of polystyrenesulfonic acid ($\varphi_{\text{XPAS}} > \varphi_{\text{XPSS}}$), as demonstrated in ref. [31].

We turn now to discuss the properties of the representative strongly charged cationic polyelectrolyte, popularly called ionene. In this case, polyions with various (average) distances b between the charged groups on the polymer backbone can be synthesized, and therefore polyelectrolytes with different charge densities λ can be studied. The monomer unit of such a polyelectrolyte is schematically shown in Fig. 1. The notation “ x,y ionene A^- ” represents a polyion with a different number of CH_2 groups between the quaternary nitrogen atoms and A^- as the counterion. The x,y combinations usually studied are: 3,3; 4,5; 6,6; and 6,9. Note that for 3,3 ionenes $b = 0.498$ nm, for 4,5 $b = 0.685$ nm, for 6,6 $b = 0.879$ nm, and for 6,9 $b = 1.063$ nm. For aqueous solutions at $T = 298$ K, the linear charge-density parameter λ varies from 1.43 (via 1.04 and 0.81) to 0.67.

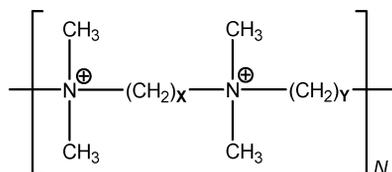


Fig. 1 Formula of x,y ionene.

The fact that these polyelectrolytes can be prepared with a hydrophobic portion of varying length makes ionenes suitable for a wide range of applications. In addition, they are excellent materials for studying the effects of polyion charge density and hydrophobicity on physicochemical properties. Ionene solutions have been characterized experimentally in several papers: Minakata and coworkers [32–34] measured the conductance and activity coefficients of 3,3; 4,5; 6,6; and 6,9 ionene solutions, while heats of dilution and osmotic coefficients were determined by Pohar and coworkers [13,35]. These measurements indicate strong deviations from theoretical predictions based on the continuum-solvent models [3,4,14] of a polyelectrolyte solution. For example, the measured activity and osmotic coefficients are much lower than theoretically predicted [32,35], and the deviations are stronger for more hydrophobic 6,6 and 6,9 ionenes. The osmotic coefficients of ionene solutions with Bz^- ions as counterions were slightly (but significantly beyond the range of experimental uncertainty) lower than the corresponding chloride solutions. In both cases, the osmotic coefficients were insensitive to concentration variation, being practically constant over two decades of polyelectrolyte concentration [35]. The conductance of ionenes measured in the presence of additional electrolytes deviated from the additivity rule, depending on the ionene charge density (x,y values), and also on the nature of the counterion [32]. Ion-specific effects were also noticed in the viscosity measurements [32].

Enthalpy of dilution

The values of the enthalpy of dilution ΔH_D , as amply documented in the literature [9–13], are very sensitive to the nature of the counterion-charged group combination. Recently, Lipar and coworkers [31] published measurements of enthalpies of dilution for alkaline salts of polyanetholesulfonic acid. The heat released upon dilution from a certain concentration m_m (in moles of monomer units per kg) to $m_m = 0.0044$ monomol/kg was measured. The resulting ΔH_D values were exothermic, with the acid producing the strongest and the cesium salt the weakest effect. These results were consistent with the previously published ΔH_D data for polystyrenesulfonic acid and its alkaline salts. The ion-specific effects are clearly shown in Fig. 6 of ref. [31]. In this figure, the authors presented deviations between the experimental values and Monte Carlo (MC) cell model calculations for ΔH_D . In the analysis leading to this figure, it has been assumed [31] that MC results provide good estimates for the Coulomb part of the dilution effect. With this assumption, we supposed that all the deviations from the MC result ($\Delta H_D - \Delta H_{MC}$) may be ascribed to effects other than Coulomb forces. It is shown in this graph (Fig. 6 of ref. [31]) that strongly hydrated ions such as Li^+ and H^+ show positive deviations from the MC “baseline”, while the Cs^+ ion exhibits a strong negative deviation from it. The actual measurements and calculations apply to 298 K, while for a lower temperature we expect for the latter effect to be more pronounced [9,12].

Even more interesting are the heats of dilution for ionene solutions: the experimental results reprinted from ref. [13] are shown in our Fig. 2 (x,y ionene bromide) and Fig. 3 (x,y ionene chloride) solutions. We will focus on the initial slope of the curves; for the more highly charged 3,3 and 4,5 ionenes ($\lambda > 1$), the measurements indicate an endothermic effect, just the opposite to the predictions of classical theories (see also eq. 7 of the next section) [4,14]. Heat is therefore consumed upon dilution of these salts, and the effect is much stronger in the case where bromide ions neutralize the polyions. On the other hand, for more hydrophobic 6,6 and 6,9 ($\lambda < 1$) ionenes, ΔH_D is exothermic and rather insensitive to the nature of the counterion present in the system.

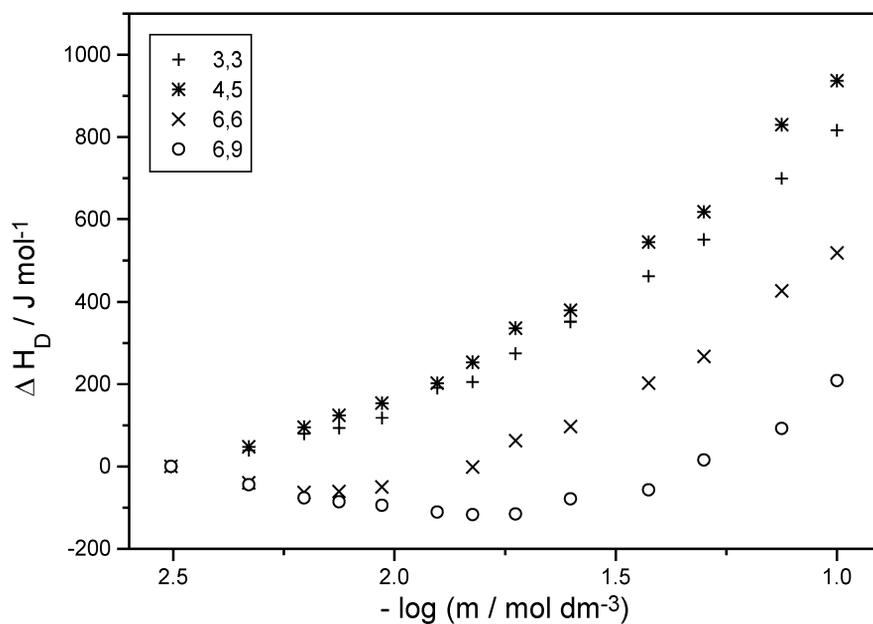


Fig. 2 Enthalpies of dilution of aqueous solutions of x,y ionene-Br at 25 °C. Legend: (+) 3,3 ionene; (*) 4,5; (x) 6,6 and (o) 6,9 ionene. Reprinted from ref. [13].

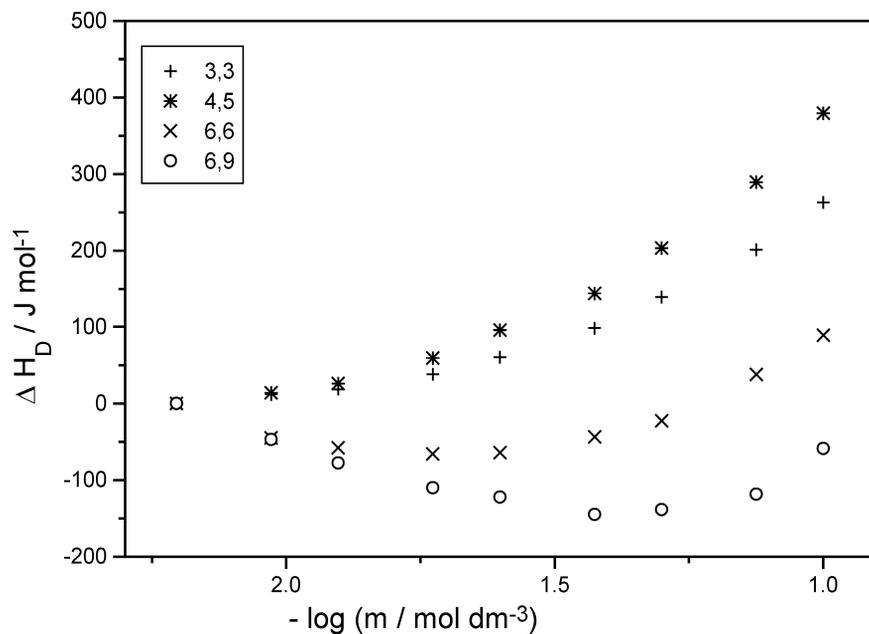


Fig. 3 Enthalpies of dilution of aqueous solutions of x,y ionene-Cl at 25 °C. Legend as for Fig. 2. Reprinted from ref. [13].

These results suggest strong ion-specific effects, reflecting the influence of various charges, as well of the methyl and methylene groups on water. In particular, the exothermic effect of the 6,6 and 6,9 ionenes, and their insensitivity to the nature of the counterions, point toward hydrophobic hydration for which $\Delta H_D < 0$. Very recently, the enthalpy of dilution of ionene solutions containing F^- ions was measured. The preliminary results [36] for 3,3 ionene fluorides indicate that ΔH_D values are negative for this salt; moreover, the measurements are in quantitative agreement with predictions of continuum-solvent theories [4,14].

THEORETICAL ADVANCES

Many of the effects described in the previous paragraph are connected with the properties of the solvent, which is water in most cases. Traditional theories of polyelectrolyte solutions treat the solvent as a dielectric continuum ignoring its molecular nature. The advantage of this, the so-called McMillan–Mayer approximation (see, e.g., ref. [37]), is that by studying dilute fluids (it is the solvent which makes the system dense) we make the theoretical calculations (and also the simulations) much easier.

Continuum-solvent theories

Interpretation of measurable quantities in solutions of linear polyelectrolytes is most often based on the Manning condensation theory [14,15], which is very attractive to use because it possesses an analytical solution. It is the linear charge-density parameter λ which plays a special role in the Manning theory [14,15]. According to the latter approach, the properties of a solution of infinitely long polyions at high dilution change qualitatively when λ is larger than unity for monovalent counterions. In particular, the osmotic coefficient can be written as

$$\varphi = \frac{1}{2\lambda}, \quad \lambda \geq 1 \quad (3)$$

$$\varphi = 1 - \frac{\lambda}{2}, \quad \lambda \leq 1 \quad (4)$$

Notice that according to the Manning theory (eqs. 3 and 4), the 3,3 and 4,5 ionenes with $\lambda = 1.43$ and 1.04 exhibit behavior different from 6,6 and 6,9 ionenes having $\lambda = 0.81$ and 0.67. This theory is often in good agreement with experimental data for strong polyelectrolytes and is able to explain many important phenomena in biological systems.

An alternative to the Manning theory is the cylindrical cell model, which has most often been used with the Poisson–Boltzmann approach (see, e.g., ref. [3,4]). The same model has also been utilized in conjunction with other approaches such as the modified Poisson–Boltzmann [38–40] equation, the hypernetted chain/mean spherical approximation theory [41,42], the density-functional approach [43], and computer simulations [16,38,40,44–48]. Within the cell model approximation, the polyelectrolyte solution is viewed as an assembly of mutually independent, electroneutral cylindrical cells of radius R and length h . The cylindrical polyion with a certain diameter and of length h is placed along the long cell axis. The model polyion contains N monomer units: $N \rightarrow \infty$ in theory, while in simulations N is typically of the order of 1000. Each monomer unit of length b ($h = Nb$) carries one elementary charge. The cell radius is determined by the polyelectrolyte concentration given in moles of monomer units per volume. In the Poisson–Boltzmann approach, the counterions were assumed to be point-like and the solvent is treated as a dielectric continuum, similarly as in the Manning theory mentioned before. For such a situation, an analytical solution exists [4,49,50]. An advantage of the Poisson–Boltzmann approach vis-a-vis the Manning theory is that it provides the concentration dependence for various thermodynamic properties. In fact, some of the Manning limiting law results can be derived from the

Poisson–Boltzmann cell model theory in the limit of infinite dilution with respect to the polyelectrolyte component.

The Poisson–Boltzmann cell model is relatively successful in explaining the thermodynamic and transport properties of polyelectrolyte solutions containing monovalent counterions. It can correctly predict the concentration dependence of the osmotic coefficients (see, e.g., ref. [4]), as well as some transport and other properties [51–53]. Due to the shortcomings of the Poisson–Boltzmann equation, which ignores ion–ion correlations, this approach is less successful for divalent counterions [38–42]. To obtain quantitative agreement between theory and experiment, it is most often necessary to treat λ as an adjustable parameter. Practically in all cases a higher than structural value (based on the length of the monomer unit b) of λ is required to fit the experimental data (see, e.g., refs. [4,48]). A notable exception to this “rule” was pointed out in our recent paper [31] where the measurements of the osmotic coefficient of the CsPAS were presented. In this case, the λ value which provided a good fit to the measurements was lower than the structural value of this quantity. This finding (for details and comparisons with the results for polystyrenesulfonate salts, see ref. [31]), could perhaps be explained by the influence of the extra hydrophobic groups present on the polyanetholesulfonic polyion.

The osmotic coefficient is related to the activity of solvent via eq. 1. An increase of the osmotic coefficient can be interpreted as a decrease of water activity or vice versa. In fact, measurements of the osmotic coefficient of ionenes indicate that the osmotic coefficient is constant over several decades in concentration. This means that the increase in concentration of solute (cf. eq. 1) is almost exactly balanced by the decrease in the logarithm of water activity. This behavior is relatively well fitted by the theory. Despite a certain success of the continuum-solvent theories described above, there are still many unsolved questions. In particular, these theories cannot adequately explain the ion-specific effects, for example, the difference in the osmotic coefficients between the bromide and chloride salts of ionene. The only parameter which can be varied to model such behavior is the distance of closest approach of the counterion to the polyion (radius of the polyion), but this can only account for a smaller part of the effect. In Fig. 4, we present a compilation of osmotic coefficient data for various polyelectrolytes. The graph is taken from ref. [35] and shows the osmotic coefficient as a function of the charge-density parameter λ for various cationic and anionic polyelectrolytes (for details, see the legend). It seems that the osmotic coefficient does not approach unity when λ approaches zero. For example, if we speculate and extrapolate the experimentally obtained osmotic coefficient to $\lambda \rightarrow 0$, we obtain a value of φ for a hypothetical uncharged “polyion” to be somewhere between 0.75 and 0.85. The continuum-solvent theories significantly overestimate the osmotic coefficient for small λ values. Accordingly, there must be another source of nonideality, which is not accounted for by the electrostatic theories. We note in passing that weakly charged polyelectrolytes, containing charged and hydrophobic groups, and possibly exhibiting conformational transitions, can serve as models for more complicated biological polyelectrolytes.

As already mentioned (see also Figs. 2 and 3), the enthalpy of dilution is more sensitive to ion-specific effects. This quantity in the McMillan–Mayer theory (continuous-solvent models) is approximated by the excess internal energy difference between the final and initial concentration. The excess internal energy within this approximation is calculated as a canonical average of terms

$$\frac{\partial \beta u_{ij}}{\partial \beta} = u_{ij} \left(1 + \frac{\partial \ln u_{ij}}{\partial \ln \beta} \right) \quad (5)$$

where $u_{ij}(r;P,T)$ is the isothermal reversible work needed to bring the particles i and j from infinity to the distance r , averaged over all possible orientations of solvent molecules, consistent with P and T [54,55]. The excess internal energy is therefore composed of two parts; the term proportional to u_{ij} , which is the free energy change for this process, and the part containing the derivative of the logarithm of the potential $u_{ij}(r;P,T)$ with respect to the temperature (entropic term). For the class of models in which the solvent is represented as a continuum dielectric, and the polyions and counterions as hard bodies, the only temperature- and pressure-dependent parameter in the pair potential functions is the

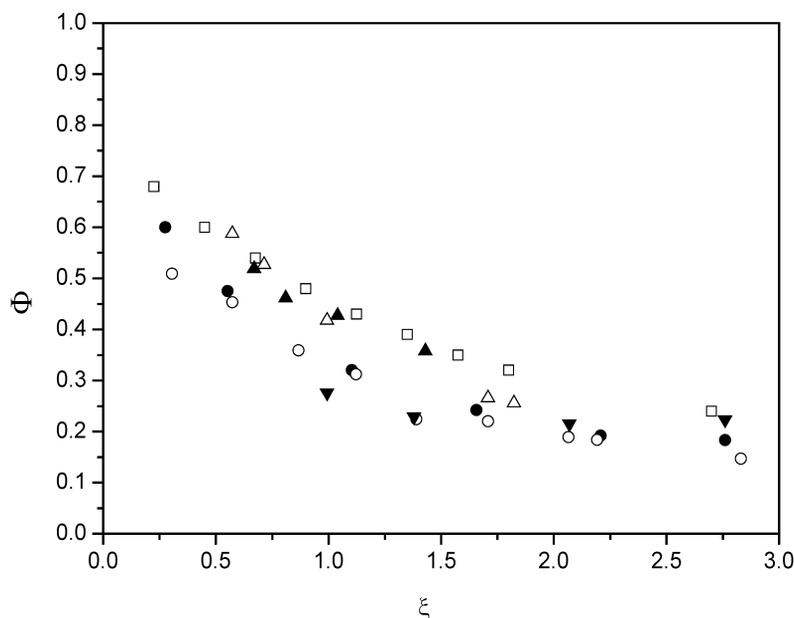


Fig. 4 A compilation of osmotic coefficient data for various polyelectrolytes as a function of the linear charge-density parameter λ (in the original paper denoted by ξ). Experimental values: (●) maleic acid/ethylene copolymer solutions [25]; (▲) ionenes [35]; (○) polyphosphates [2]; (△) carboxymethyl cellulose [2]; (□) polyacrylates [27,28]; (▼) polystyrenesulfonic acid, where the charge on the polyions was partly blocked by addition of a surfactant [29]. In all cases, $c = 0.06$ monomole/dm³. Reprinted with permission from ref. [35]; Fig. 6.

relative permittivity ϵ_r . For such models, the configuration energies obtained either from theory or simulations have to be multiplied by the factor

$$1 + \frac{\partial \ln \epsilon_r}{\partial \ln T} \quad (6)$$

which for water at 298 K equals -0.37 . Notice that this factor determines the sign of the excess internal energy and consequently the sign of the enthalpy of dilution. The solvent-averaged potential between two particles may contain a more realistic, temperature-dependent (see, e.g., ref. [56]), short-range part. In such a case, all temperature-dependent terms of the pair potentials $u_{ij}(r; P, T)$ make their own contributions to the excess internal energy.

For monovalent counterions, the Manning limiting law expression for the enthalpy of dilution reads [4,57]

$$\Delta H_D = -\frac{RT}{2\lambda} \left(1 + \frac{\partial \ln \epsilon_r}{\partial \ln T} \right) \ln \frac{c_2}{c_1} \quad (7)$$

Alternatively, enthalpy of dilution can be calculated via the Poisson–Boltzmann cell model as shown already in refs. [4,9,58,59]. The two theories are in good agreement with measured data for strongly hydrated monovalent ions such as H⁺ and Li⁺ but not for others. The calculated ΔH_D values are always negative, while experimentally determined values of this quantity can be either positive or negative, depending on the polyelectrolyte–counterion pair and the temperature of observation [9,12,13,60]. Poor agreement between the Poisson–Boltzmann theory and experiment for ΔH_D is obtained for solutions containing divalent counterions [59]. It has been demonstrated recently that using a more exact statistical mechanical treatment (e.g., MC simulation) of the model considering polyions as hard cylinders, the

solvent as a dielectric continuum, and ions as charged hard spheres, does not bring the theory any closer to the experimental data [16,48]. As discussed in ref. [31], moderate positive departures from the MC simulations (see Fig. 6 of ref. [31]) can be modeled by exaggerating the size of the counterion. Negative deviations are more difficult to capture quantitatively and the simplest way seems to be by invoking the non-Coulombic counterion–polyion attraction [61]. Attempts have also been made [52,53] to explain the disagreement between theory and experiment for some other properties by augmenting the cylindrical cell model with an additional short-range potential between the polyions and counterions.

Theory: The explicit solvent approach

The effect of solvent is considered to be complex in electrolyte solutions (see an instructive theoretical contribution on this topic in ref. [62]): in the first place, the solvent occupies volume, so the interacting species feel the excluded-volume effect [63]. Secondly, the solvent molecules compete with ions for a position near the charged groups on polyion; we may have either a solvent-separated pair of charges, or the counterion and charged group can come into contact. The present state of theory is such that only simplified models can be evaluated numerically [18,19]: one such approach has recently been proposed by Kalyuznyi and coworkers [19]. In their work, an extension of the product-reactant Ornstein–Zernike theory for polyelectrolyte solution [64–70], which in turn is based on the Wertheim theory [71,72], was extended to cater for the solvent component. Solvent molecules were modeled with four square-well sites so they can coordinate with each other, mimicking hydrogen bonding between water molecules, and to solvate the charges in solution. Chain-like polyions with 120 monomer units and an equivalent number of oppositely charged counterions were present in the system. The strength of the water–counterion interaction was varied, while the water–polyion and water–water interactions were assumed to be constant. Note that these “water” molecules had no charges; the dielectric constant of the solution was assumed to be equal to that of pure water under these conditions. The pair potential for the model was therefore written as the sum of the hard-sphere term, the Coulomb term, and the term describing the association.

The calculations were performed at a temperature of 300 K, where the Bjerrum length defined as $L_B = \lambda b$ (cf. also eq. 2) is 0.714 nm. The oligomeric ions were represented as freely jointed charged hard spheres. Further, each monomer unit of the chain carried one elementary charge, and each counterion one charge of the opposite sign. The numbers of the square-well sites on the counterions and on the chain monomers were four and three, respectively. Values of the water–polyion, water–water, and counterion–polyion interaction parameters were fixed at the beginning of the calculation, while the value of the water–counterion (u_{wc}) parameter was varied from 500 K, over 735 K, and 2400–3500 K. A schematic representation of the model used can be seen in Fig. 1 of ref. [19] where also all the necessary details of the calculation are given. Despite its simplicity, the model was capable of explaining the basic experimental results of real polyelectrolytes as presented in the next two figures.

The osmotic coefficient was calculated considering an equilibrium distribution of water molecules between the pure aqueous phase and the polyelectrolyte solution. The osmotic coefficient in Fig. 5 (originally presented as Fig. 2 of ref. [19]) is plotted as a function of the monomer number density. The continuous curves from top to bottom labeled with numbers representing different strengths u_{wc} of the counterion–water square-well interaction. Notice that this parameter regulates the solvation of counterions: by changing its value, it is possible to influence the physicochemical behavior of the polyelectrolyte solution. In all cases shown in Fig. 5, the osmotic coefficient ϕ decreases sharply from unity with increasing monomer concentration. The behavior at moderate concentrations critically depends on the parameter u_{wc} . For strongly hydrated counterions (curves 3 and 4), a steep increase of the osmotic coefficient ϕ with increasing concentration is observed. For marginally hydrated counterions (curve 1), the osmotic coefficient assumes unphysical (negative) values, possibly indicating a phase separation. Weakly solvated counterions may approach closer to polyions and cause the precipitation of polyelectrolytes [73]. It is the curve labeled 2 which mimics the typical experimental behavior of a poly-

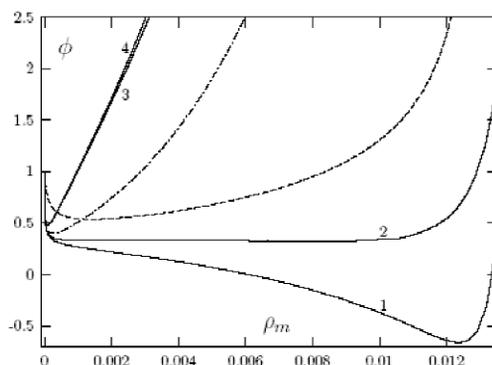


Fig. 5 Osmotic coefficient as a function of the monomer number density: (1) $u_{wc} = 500$ K, (2) 735 K, (3) 2400 K, and (4) $u_{wc} = 3500$ K. The third curve from top to bottom applies to the continuum-solvent calculation (dashed–dotted line), and for the fourth one (dashed line) the solvent is modeled as dipolar fluid [18]. Reprinted with permission from ref. [19].

electrolyte solution with the osmotic coefficient being constant over a substantial concentration range. Our study also indicates [19] that with an increase of polyelectrolyte concentration, the counterions substitute the water molecules next to the polyion charge, which may account for the constancy of the osmotic coefficient.

In ref. [19], we analyzed yet another important thermodynamic property that is the enthalpy of dilution. These results are displayed in Fig. 6 of the present review paper. The $\Delta H_D/N_A k_B T$ values (N_A is the Avogadro number) were calculated before for different u_{wc} values, mimicking in this way differently solvated ions. The curves as before for Fig. 5 are labeled by numbers; let us focus on the initial slopes in this graph. For strongly hydrated counterions (see, e.g., curve 4), we obtained $\Delta H_D < 0$, i.e., heat is released in the process of dilution. For weakly hydrated counterions (curves 1 and 2), we observed the opposite effect: heat is consumed upon dilution. By tuning the u_{wc} value, we can obtain a slope of zero as actually observed in the experimental paper of Hales and Pass [12]. For higher polyelectrolyte concentrations, all the curves exhibit endothermic tendencies as found in the measurements. In summary, our numerical results are consistent with the experimental data analyzed in the previous section (“Review of the experimental data: Enthalpy of dilution”), and also with the osmotic pressure

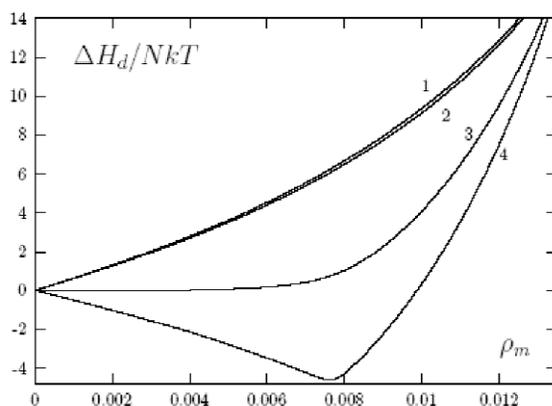


Fig. 6 Enthalpy of dilution as a function of the monomer number density at $T = 300$ K: (curve 1) $u_{wc} = 500$ K, (2) 735 K, (3) 2400 K, and (4) $u_{wc} = 3500$ K. Reprinted with permission from ref. [19].

calculations discussed above. Note that the approach outlined in [19] is fully analytical and does not require a powerful computer.

Molecular dynamics simulations

Ion-specific effects can only be explained satisfactorily by treating the solvent as a separate species. Polyelectrolyte solutions, however, are very difficult to model realistically. Flexible polyions with a degree of polymerization of several thousands change their conformation in accordance with the ionic strength and composition of the solution, thus affecting the thermodynamic properties. In addition to the long-range Coulomb interaction, which shapes the general properties of polyelectrolyte solutions, the ion-specific effects were proved to be important. A good model would therefore need to treat satisfactorily length scales from one to several tens of ionic diameters, an extremely difficult task for today's computers. Note that the even less demanding continuum-solvent simulations, pioneered by Kremer and coworkers [74,75], are currently limited to flexible polyions with around 120 monomer units [70].

In recent years, the first explicit solvent MD simulations of short polyelectrolyte chains were published. Molnar and Rieger [20] used the MD approach to study the solvation of a model polyacrylic acid oligomer with 20 monomer units in interaction with Na^+ and Ca^{++} counterions. In another such contribution, Chialvo and Simonson [21] examined the solvation behavior of short-chain polystyrene-sulfonate in aqueous electrolyte solutions. An atomistic description of water, the polymer chain, and their interaction with ions and other species was used. One finding of this work concerns the Li ion-sulfonic group interaction. They found that this interaction is not strong enough to cause a desolvation of charges, in other words, no contact pair (site-binding) is formed. This result seems to be consistent with both old [4] and new experimental results [31] for lithium salts of polyelectrolytes containing a sulfonic group. In a similar study, Chang and Yethiraj [22] presented an explicit solvent MD simulation of moderately long (degree of polymerization equal to 64) flexible polyions, but the solvent molecules were only treated as uncharged spheres.

Recently, Druchok and coworkers [23] performed an all-atom explicit water study of model 3,3 ionenes. The MD approach was used to examine the solvation behavior of a six monomer units long cationic oligoion in the presence of various electrolytes. More specifically, the interaction between 3,3 ionene and $\text{Na}^+ \text{F}^-$, $\text{Na}^+ \text{Cl}^-$, $\text{Na}^+ \text{Br}^-$, and $\text{Na}^+ \text{I}^-$ salts was modeled in SPC/E [76] water. The simulated system consisted of water molecules, one molecule of ionene (six-mer), the coions and an equivalent number of counterions to satisfy electroneutrality. Modeling the chain with a realistic length ($N \approx 100$) is currently not possible due to computational limitations. During the simulation, various site-site distribution functions were calculated. The results indicate that strongly hydrated ions such as F^- cannot approach close to the nitrogen atom. In contrast, ions with large crystal radii such as I^- accumulate strongly around the oligoion. Of interest is the difference in behavior of the Br^- and Cl^- ions. The MD simulation indicates that the less solvated Br^- ion can approach closer to the nitrogen atom than the Cl^- ion. This finding is in agreement with the osmotic pressure measurements [35]; notice that solutions with Cl^- counterions yield higher osmotic coefficients than the corresponding Br^- salts. The MD results seem to be also consistent with ongoing measurements of the dielectric relaxation and heat capacities for 3,3, 4,5, 6,6, and 6,9 ionene solutions with various counterions [77]. We hope to report these results in future publications.

CONCLUSIONS

Despite the advances in understanding of polyelectrolyte solutions, there are still aspects that pose a challenge. One such aspect is related to the ion-specific effects connected with water as revealed in thermodynamic and transport measurements. These effects, being the subject of the present review, are especially important in biology. Certain ions precipitate proteins in water ("salting out"), while others

help solubilize them (“salting in”). This has been interpreted as a modulation of the hydrophobic effect by salts due to the changes in the water structure brought about by ions [78]. The so-called Hofmeister series is a list of ions rank-ordered in terms of how strongly they affect hydrophobicity; for a review of recent theoretical and experimental results and for a translation of the original Hofmeister paper [79], see a dedicated issue of *Current Opinion in Colloid and Interface Science* **9** (2004), in particular, ref. [80].

Synthetic polymers possess a relatively simple chemical structure that makes them suitable models for the study of much more complicated biological macromolecules. Two such polyelectrolytes, one of anionic and cationic type, were the subject of our analysis. In particular, the second polyelectrolyte, so-called ionene, seems to be interesting since it can be prepared in a controlled way, varying the number of charged and hydrophobic groups on the backbone. Several experimental techniques have been applied to study ionene salt solutions, and the results strongly depend on the nature of the counterions present. Different theoretical approaches have been applied to understand better the underlying microscopic picture. The review presented here proves that the results obtained so far are interesting and that additional studies are warranted.

There seem to be, however, a general problem in the physical chemistry of ionic solutions, which the author wishes to point out. On one hand, we have a rather large body of thermodynamic and transport data as a result of the osmotic coefficient, enthalpy of dilution, conductivity, and other measurements. These data reveal a strong ion-specific effect, where on replacing one ionic species with another the sign of the enthalpy of dilution may be reversed. To understand better the role of water in these processes, measurements probing the vicinity of the charged groups are needed. Such approaches are offered, for example, by dielectric relaxation measurements [81,82] or small angle neutron scattering (see, e.g., ref. [83]), or as a theoretical alternative the all-atom MD simulation may be applied. In our experience and in the light of information gained from literature, these methods reveal relatively small differences between solutions with different counterions; the magnitudes of the effects are often within the experimental or numerical error. In other words, the relatively small differences caused by the water-mediated interaction between charged groups seem to have significant consequences for thermodynamic properties. The current theoretical approaches seem to be unable to bridge the length scales from a few to several hundred angstrom units and consistently connect the two sets of experimental data.

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