Osmotic Properties of Aqueous Ionene Solutions

K. Arh, C. Pohar,* and V. Vlachy

Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1001 Ljubljana, Slovenia

Received: March 29, 2002; In Final Form: July 12, 2002

Osmotic coefficients of aqueous solutions of 3,3-, 4,5-, 6,6-, and 6,9-ionenes with bromide and chloride counterions were measured at 298 K and in the concentration range from 0.001 to 0.1 mol/dm³. The measured osmotic coefficients are very low, indicating large deviations from ideality caused by strong interactions in these systems. The solutions with chloride counterions have a higher osmotic coefficient than the corresponding bromide solutions, which is in agreement with experimental data for the counterion activity coefficient of these solutions. The experimental results for osmotic coefficients were analyzed using a cylindrical cell model where a fixed charge is assumed to be uniformly distributed along the z-axis of a rigid and impenetrable polyion, in conjunction with the classical Poisson–Boltzmann equation. More refined models in which discrete charges are located periodically along the z-axis of the polyion were also studied. In the latter case the canonical Monte Carlo method was used to calculate the osmotic coefficient. In agreement with previous studies of weak and moderately charged polyelectrolytes, we found the theoretically predicted osmotic coefficients to be too high in comparison with the experimental data for aqueous ionene solutions.

1. Introduction

Ionenes are cationic polyelectrolytes with charged groups located on the main polymer chain.[1,2] Ionenes with various distances between the charged groups on the polymer backbone can be synthesized, and in this way polyelectrolytes with different charge densities can be obtained. This property of ionenes makes them suitable for a wide range of applications: ranging from use as solid polymer conductors,[2,3] or for flocculation of clays in solution,[4] to modifiers of polymer-coated packing materials for capillary electrochromatography.[5] From the theoretical point of view the ionenes seem to be appropriate materials for studying the effect of polyion charge density on thermodynamic and transport properties. Despite the wide range of applicability of these systems and the theoretical interest mentioned above, aqueous solutions of ionenes have not been extensively studied so far. An important contribution toward understanding of thermodynamic and transport properties of aliphatic ionenes was made by Nagaya and co-workers.[1,6,7] These authors studied the conductance and counterion activity of 3,3-, 4,5-, 6,6-, and 6,9-ionenes with various counterions. One conclusion of their study is that the measured counterion activity coefficient is lower than that theoretically predicted.[1]

Polyelectrolyte solutions display strongly nonideal behavior due to electrostatic interactions between the highly charged polyions and small ions in solution. Valuable information about these interactions is obtained from measurements of osmotic pressure.[8–13] The practical osmotic coefficient, defined as $\Phi = \Pi/\Pi_{id}$, is a measure of this nonideality. Note that Π_{id} is the ideal contribution to osmotic pressure. Here we present the results of osmotic pressure measurements of aqueous solutions of 3,3-, 4,5-, 6,6-, and 6,9-ionenes with bromide (Br) and chloride (Cl) counterions. The data were obtained for salt-free polyelectrolyte solutions at 298 K and in the concentration range from a polyelectrolyte concentration $c_m = 0.001$ to 0.1 mol/dm³. The osmotic pressure measurements were mostly per-

formed by a vapor pressure osmometer, and in a few cases at concentrations below 0.02 mol/dm³, also by a membrane osmometer.

Theoretical modeling of polyelectrolyte systems is difficult, in part due to the need to deal effectively with both the long-range Coulombic forces and the short-range solvent effects.[14] In addition, the polyions are more or less flexible and change their conformation due to their interaction with the ionic environment. Considering the complexity of these systems, it is not surprising that popular polyelectrolyte models[15–18] ignore all conformations other than the fully extended one. Further, they neglect the effect of specific interactions, treating the solution as a purely Coulombic fluid, where the charges are embedded in a dielectric continuum. There are a few exceptions in this respect,[19,20] for example, Jayaram and Beveridge[19] used a modified model that included a Gurney correction term for desolvation[21,22] to interpret the experimental data. In a similar study, Rebolj et al.[20] used the Gurney model to analyze the experimental results for ion binding in lithium and cesium poly(styrenesulfonate) solutions at various temperatures.

In the present work we present measurements of the osmotic coefficient of Br and Cl ionene solutions in water. In the theoretical part, several different models of the polyion–counterion interaction were examined and their predictions compared to the experimental data. According to the first model, the polyion is treated as an infinitely long cylinder with the charge uniformly distributed along the z-axis, whereas the solvent is treated as a continuum dielectric with permittivity ϵ_r. This model is examined by solving an appropriate Poisson–Boltzmann equation. Note that the separation between the charges on the polymer backbone (length of the monomer unit b) is rather large, for example, for 3,3-ionene it is 0.498 nm and for 6,6-ionene $b = 0.879$ nm.[1] Accordingly, a uniform distribution of charge on the polyion is not a very realistic approximation for these polyelectrolytes. To correct for this deficiency, in the second model discrete charges are assumed to be fixed along the z-axis to mimic the charged groups on the
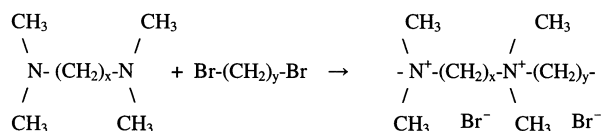
9968 *J. Phys. Chem. B, Vol. 106, No. 38, 2002*

Arh et al.

polyion. Only Coulombic interactions were included in this computation. Finally, in the third model the counterion–counterion and the fixed charge–counterion interactions are modeled using the interaction potential of Ramanathan and Friedman[22] to account for solvation phenomena.[20] The canonical Monte Carlo method was utilized to obtain numerical results for the discrete-charge models.[23-27]

The outline of this paper is the following. After the Introduction (section 1) we describe the experimental procedure and present the results for osmotic coefficients in section 2. Polyelectrolyte models and methods of calculation are introduced in section 3. The comparison of experimental data with the numerical results obtained by the Poisson–Boltzmann theory and the Monte Carlo method is given in section 4. Finally, the conclusions are summarized in section 5.

2. Experimental Section

2.1. Materials. All investigated polyelectrolyte ionene salts were synthesized in our laboratory following the procedure described by Rembaum et al.[1,6,7,28-30] Bromide salts of aliphatic *x*,*y*-ionenes (3,3-, 4,5-, 6,6-, and 6,9-ionene) were prepared in dimethylformamide (DMF) using appropriate reagents. A solution of N,N,N',N'-tetramethyl-1,*x*-diaminoalkane was mixed with a solution of a 1,*y*-dibromoalkane in a 1:1 molar ratio and the mixture was stirred at room temperature (about 22 °C) under an argon atmosphere. The following reaction took place:

$$
\begin{array}{l}
\text{CH}_3 \quad\quad \text{CH}_3 \\
\;\;\backslash \quad\quad\quad / \\
\text{N- (CH}_2)_x\text{-N} \;\; + \text{Br-(CH}_2)_y\text{-Br} \;\; \rightarrow \\
\;\; / \quad\quad\quad \backslash \\
\text{CH}_3 \quad\quad \text{CH}_3
\end{array}
$$

$$
\begin{array}{l}
\text{CH}_3 \quad\quad\quad \text{CH}_3 \\
\;\;\backslash \quad\quad\quad\quad / \\
\text{- N}^+\text{-(CH}_2)_x\text{-N}^+\text{-(CH}_2)_y\text{-} \\
\;\; / \quad\quad\quad\quad \backslash \\
\text{CH}_3 \;\; \text{Br}^- \;\; \text{CH}_3 \;\; \text{Br}^-
\end{array}
$$

After 48 h, the precipitated polymer ionenes were filtered using Teflon filters, washed with a large amount of acetone, and dried under vacuum at 40 °C. The sample solution was exhaustively dialyzed (applying cellulose bags SIGMA; MWCO = 12 000) against water, which was checked every day by conductivity measurements. Chloride salts were prepared from hydroxides by neutralization with HCl. Hydroxides were obtained from the bromides by ion exchange. Because of the instability of the basic (OH⁻) form, ion exchange was carried out just before the preparation of the chloride form. Sample solutions were concentrated by vacuum evaporation before use. The concentrations of stock solutions were determined by a standard potentiometric titration of the halogenide counterion with AgNO₃, using a corresponding halogenide ion-sensitive electrode and a saturated mercury sulfate electrode as a reference. The structure and purity of the polymeric products were checked by NMR analysis, which showed the absence of the monomer reactants in all final products.

2.2. Osmotic Coefficients. The osmotic coefficient measurements were performed at 25 °C with a Knauer vapor pressure osmometer (Model K-7000) and a Knauer membrane osmometer (Model 7310100000). A detailed description of the osmometers and the experimental procedure has been given elsewhere.[31-34] The vapor pressure osmometer was calibrated with standard KCl solutions. In the membrane osmometer cellulose triacetate membranes with MCO 10000 (Sartorius, AG, Goettingen, Germany), were used.

We start our discussion with the results for 3,3-, 4,5-, 6,6-, and 6,9-ionenes with bromide counterions shown in Figure 1. The data for concentrations lower than 0.02 mol/dm³ were obtained by the membrane osmometer and the others by the vapor pressure instrument. The reason for using the membrane
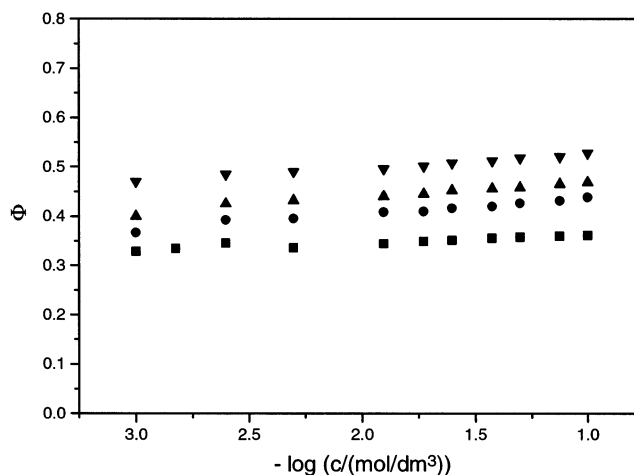
Figure 1. Experimental values of osmotic coefficients of 3,3- (■), 4,5- (●), 6,6- (▲), and 6,9- (▼) ionene bromide solutions as a function of the negative logarithm of the molar concentration.
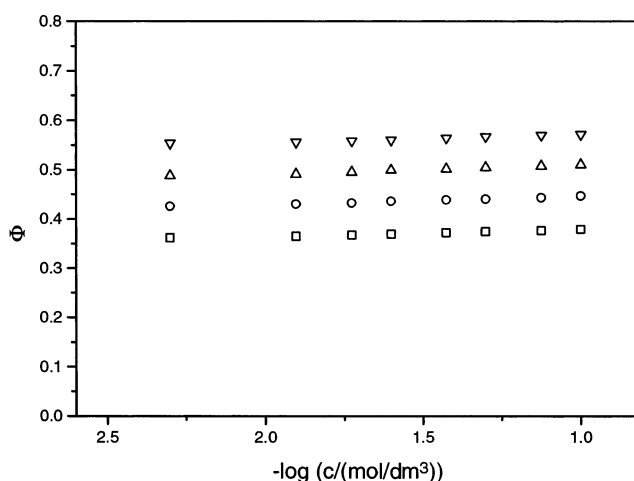
Figure 2. Experimental values of osmotic coefficients of 3,3- (□), 4,5- (○), 6,6- (△), and 6,9- (▽) ionene chloride solutions as a function of the negative logarithm of the molar concentration.

osmometer is the relatively low accuracy of the vapor pressure apparatus for dilute polyelectrolyte solutions. In the region where accurate results could be obtained, the two methods agree within the experimental uncertainties, i.e., about 4%. Figures 1 and 2 show that ionene solutions exhibit large deviations from ideality, which are reflected in the low values of the osmotic coefficient. As expected, the osmotic coefficient monotonically increases from 3,3- through 4,5- to 6,9-ionenes, i.e., in the direction of increasing distance *b* (length of the monomer unit) between two consecutive charged groups on the polyion. However, as we will see later, the increase of the osmotic coefficient as a function of a polyion charge density is much less than expected on the basis of popular electrostatic theories.

The osmotic coefficient results for 3,3-, 4,5-, 6,6-, and 6,9-ionenes with chloride counterions are shown in Figure 2. The values of osmotic coefficients are slightly higher than for bromide solutions of the same concentrations. This observation is in agreement with the measurements of the counterion activity coefficient of ionene solutions performed by Nagaya and co-workers,[1] as also with experimental results for aqueous solutions of tetraalkylammonium halides.[35]

3. Theoretical Analysis

3.1. Ion-Condensation Theory. Manning's ion-condensation theory[17,18] has proved on many occasions to be very successful

Osmotic Properties of Aqueous Ionene Solutions

J. Phys. Chem. B, Vol. 106, No. 38, 2002 **9969**

in interpreting experimental data on polyelectrolyte solutions. The model of polyelectrolyte solution is based on the following assumptions:[17] (a) the real polyion is replaced by an infinite line charge, (b) interactions between two or more polyions are neglected, and (c) the dielectric constant is taken equal to that of water. The most important parameter of the theory is the linear charge density ξ, equal to $e_0^2/(4\pi\epsilon_0\epsilon_r k_B T b)$. As usual, k_B is the Boltzmann constant and T is the absolute temperature, ϵ_r is the dielectric constant of the solvent relative to a vacuum, e_0 is the elementary charge, and b is the length of the monomer unit carrying charge e_0. The theory is based on the observation that the statistical-mechanical phase integral for an infinite line charge model diverges for the values of the charge density on the polyion, which yield $\xi > 1$. The physical interpretation of the divergence of the phase integral is that for $\xi > 1$ the system becomes unstable and sufficiently many counterions have to "condense" on a polyion to reduce the charge density. The condensed layer cannot be diluted from the polyion. A short, but illuminating, review of the characteristic properties of polyelectrolyte solutions in light of this theory has recently been given by Manning and Ray.[18] According to this approach the osmotic coefficient Φ, for solutions with monovalent counterions, is given by

$$\Phi = 1 - \frac{\xi}{2} \qquad \xi \leq 1 \tag{1}$$

$$\Phi = \frac{1}{2\xi} \qquad \xi \geq 1 \tag{2}$$

Note that the osmotic coefficient behaves dramatically different for values above (or below) the critical value of ξ, which for solutions with monovalent counterions is unity. This approach often yields good agreement with experimental results for thermodynamic and transport properties of polyelectrolyte solutions.

3.2. Poisson−Boltzmann Cell Model. The polyelectrolyte solution is modeled as a system of a large number of cylindrical cells of length $h = Nb$, equal to the length of the polyions. The polyions contain N monomer units of length b ($N \gg 1$). The cell radius R is determined by the concentration of monomer units c_m (eq 3), where N_A is Avogadro's number. Each polyion

$$c_m = \frac{1}{\pi R^2 b N_A} \tag{3}$$

is placed along its own cylindrical cell. The interactions between the particles in the adjacent cells are neglected. In this model the fixed charge is assumed to be smeared uniformly along the long polyion axis and a is the counterion−polyion contact distance. The pointlike counterions are distributed within the free volume of the cell, and no additional simple electrolyte is present. For simplicity, a uniform permittivity was assumed throughout the solution. This model is very popular and has been widely studied using the Poisson−Boltzmann (PB) equation,[15,16] the modified PB theory[23−27] by computer simulations,[23,27,36] and also by the density functional approach.[37] The osmotic coefficient within the cell model can be expressed as the ratio of the ion concentration at the cell boundary $c_-(R)$ and the average concentration of counterions c_- in the cell, as given by

$$\Phi = \frac{c_-(R)}{c_-} \tag{4}$$

Using the analytical solution of the Poisson−Boltzmann equation in cylindrical symmetry, the osmotic coefficient Φ can be written in the form

$$\Phi = \frac{1 - \beta^2}{2\xi}(1 - e^{-2\gamma}) \tag{5}$$

where $\gamma = \ln(R/a)$ and β is an integration constant following from the solution of the Poisson−Boltzmann equation.[15,16] Note that in the Poisson−Boltzmann theory the ions are treated as pointlike charges and their size is reflected merely in the polyion−counterion contact distance a ($=0.335$ nm). An expression for the osmotic coefficient equivalent to eq 5, but based on the virial theorem, has also been proposed.[38]

3.3. Discrete Charge Models. Again, the solution is divided into cylindrical cells as described before. The main difference to the model described in section 3.2 is that we assume that the charges on the polyion are located periodically (at distance b) along the z-axis. The centers of counterions are not allowed to penetrate within the cylinder of radius a, here chosen to be 0.335 nm. Two different discrete-charge models were examined. In the first case the interaction potential between the various charged groups is given by

$$u_{ij}(r) = \frac{e_i e_j}{4\pi\epsilon_0\epsilon_r r_{ij}} \qquad r_{ij} \geq r_{ij}^* \tag{6}$$

$$u_{ij}(r) = \infty \qquad r_{ij} < r_{ij}^*$$

where $r_{ij}^* = (r_i^* + r_j^*)/2$ and i (j) denotes a charged group on the polyion (P) or the counterion (c). The model above is an analogue of the so-called primitive model, often used to describe electrolyte solutions. The parameters used in the actual calculations are given in section 4.1.

In the second, more refined model, the solvent-averaged potential energy between the two charges is given by[22]

$$u_{ij}(r) = \frac{e_i e_j}{4\pi\epsilon_0\epsilon_r r_{ij}} + CAV_{ij} + COR_{ij} + GUR_{ij} \tag{7}$$

where e_i (e_j) is the charge of a particular ionic species. The first term in eq 7 represents the Coulomb interaction. The term CAV_{ij} is zero for our model of a continuous dielectric. The core repulsion term COR_{ij} is given by eq 8 where r_i^* (r_j^*) is the Pauling radius of an ion of species i (j).[39] Further, F_m is the Madelung constant and σ is the coordination number.

$$COR_{ij} = B_{ij}\left(\frac{r_i^* + r_j^*}{r_{ij}}\right)^9 \tag{8}$$

$$B_{ij} = F_m\frac{|e_i e_j|}{\sigma 4\pi\epsilon_0}\frac{1}{9(r_i^* + r_j^*)}$$

According to Gurney,[21] the isolated ion is surrounded by a co-sphere of water of thickness w, in which water has different properties than in the bulk. When two ions come close enough, the sum of their co-sphere volumes is reduced by overlap. The water contained in the overlap volume V_s must return to its unperturbed state and A_{ij} is the change in the molar free energy associated with this process. This Gurney term (GUR_{ij}) for a pair of ions i and j is given by the expression

$$GUR_{ij} = A_{ij}\frac{V_s(r_i^*+w, r_j^*+w, r_{ij})}{V_w} \tag{9}$$

9970 *J. Phys. Chem. B, Vol. 106, No. 38, 2002*

Arh et al.

where V_w is the molar volume of bulk water and V_s is the mutual volume function.[22] The parameters used in our study are the Madelung constant $F_m = 1.76$, the coordination number $\sigma = 6$, $w = 0.276$ nm, and again $a_p = 0.335$ nm. The Gurney parameters A_{cc} and A_{pc} are not known in advance: in principle, they can be obtained from fitting of the measured data.[22,40,41] The Monte Carlo method has been utilized to obtain results for the models described in section 3.3.

3.4. Monte Carlo Method. The canonical Monte Carlo method has been applied to polyelectrolyte solutions before and it is described in several articles.[23–26] In the Metropolis scheme,[42] a sequence of configurational states is generated according to the condition

$$f \leq \min[1, e^{-\beta \Delta U}] \tag{10}$$

where f is a random number and ΔU is the difference in the configurational energy between the trial configuration and the previously accepted configuration. The central cell in the simulations is represented by a cylindrical box of height Nb and radius R. In all calculations presented in our study, the number of monomer units included in the central cell was $N = 1000$. Corrections due to the finite number of particles in the Monte Carlo cell were evaluated as suggested by Bacquet et al.[25] The counterion concentration at the cell boundary $c_-(R)$ (cf. eq 4), needed to evaluate the osmotic coefficient, was calculated in two different ways. One is the conventional method; $c_-(R)$ was obtained by extrapolation from the histogram points, where each bin has a width δr and extends from $r + \delta r$. In addition, the modified "test particle method"[43,44] was also used. In both cases the z-dependencies due to the discrete charges on a polyion were averaged out. The results obtained by the two alternative methods agreed within the numerical uncertainty of the simulation. The statistics were collected over 16 million or more of attempted configurations, after an equilibration run of at least 5 million configurations. The uncertainty in the calculated values of the osmotic coefficient is estimated to be about ±2%.

4. Numerical Results and Comparison with Experimental Data

4.1. Results for 3,3-Ionenes. In this section we present numerical results for the models and methods described in section 3. Our analysis first focuses on modeling 3,3- and 6,6-ionene bromides. First, in Figure 3 we present the osmotic coefficients for model 3,3-ionene solutions as calculated by the Poisson–Boltzmann equation (eq 5). In this calculation the polyion is represented as a cylinder of diameter 0.335 nm, whereas the counterions are assumed to be point charges. The fixed charge is actually modeled as a continuous line of charge on the z-axis of the cylinder. All calculations for 3,3-ionene solutions in water apply to $T = 298$ K and $b = 0.498$ nm, where $\xi = 1.43$ ($\epsilon_r = 78.3$). These results are shown in Figure 3 by a dotted line. An increase of parameter ξ from theoretical value 1.43 to 2.00 brings the Poisson–Boltzmann theory in agreement with the experiment.

In the same figure we also present the results of the Monte Carlo method applied to the discrete charge model described in section 3.3 (cf. eq 6). As before, the counterions are excluded from the cylinder with radius $a = 0.335$ nm and $b = 0.498$ nm. The Pauling radius[39] r_c for a bromide ion is 0.181 nm, and the same quantity for the model "charged group" on a polyion, r_p, is chosen to be 0.195 nm. This means that the distance of closest approach of a counterion to the charge on the backbone is (0.181 nm + 0.195 nm) = 0.376 nm. The Monte Carlo data are
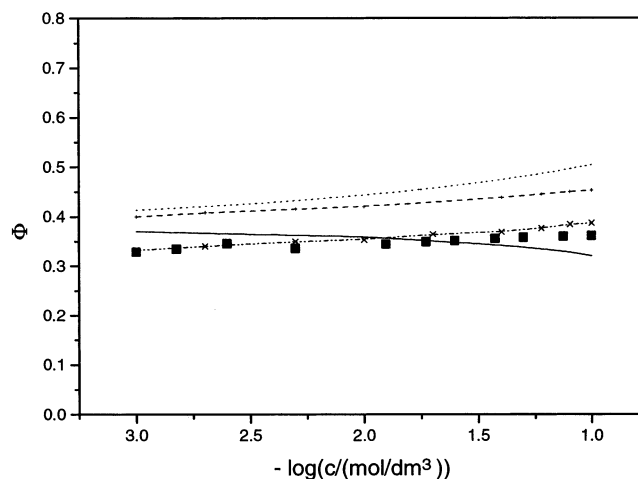

Figure 3. Calculated and measured values of the osmotic coefficient for 3,3-ionene Br⁻ solution at 25 °C: (■) experimental points; (dotted line) Poisson–Boltzmann results; (dashed line) Monte Carlo results for the discrete charge model with $\xi = 1.43$; (dash–dotted line with ×) Monte Carlo data for $\xi = 1.75$. The full line represents the results of the refined model with Gurney parameters $A_{pc} = -1065$ J/mol and $A_{cc} = 0$.

presented in Figure 3 by a dashed line just below the dotted line. This result suggests that the discrete-charge model predicts stronger binding (smaller osmotic coefficient) than the Poisson–Boltzmann equation. Also, the discrete-charge model concentration dependence of Φ is slightly weaker than predicted by the Poisson–Boltzmann smeared-charge model calculation. A similar discrepancy has been found for other thermodynamic properties, for example, D/D_0,[20,45] or the Donnan exclusion coefficient[36] and can, in part, be attributed to neglect of the interionic correlation by the Poisson–Boltzmann theory. To bring the discrete-charge model into agreement with experiment, a considerably higher value of the charge density parameter ξ must be used in the calculation. This finding is consistent with previous studies of poly(styrenesulfonate) solutions.[8] The Monte Carlo results for $\xi = 1.75$ are shown in Figure 3 by crosses connected by a dash–dotted line. An increase of parameter ξ from theoretical value 1.43 to 2.00 brings the Poisson–Boltzmann theory into agreement with experiment.

In this part we discuss the results for the refined (also called Gurney) model. Again, these results were obtained by the Monte Carlo method. The potential function described by eqs 7–9 contains several parameters. Again the (Pauling) radius of a bromide ion is taken to be 0.181 nm, r_p is 0.195 nm, and $a = 0.335$ nm and for ξ a structural value equal to 1.43 is used. Two unknown parameters of the refined model are the so-called Gurney coefficients for the counterion–counterion, A_{cc}, and the charged group (polyion)–counterion interaction, A_{pc}. These coefficients can be used as fitting parameters to bring the theory and experiment into agreement.[22,40,41] Fortunately, as found before,[20] an exact value of the coefficient A_{cc} seem to be less important for the analysis. Namely, this coefficient has much less effect on the calculated values of thermodynamic properties than A_{pc}. For simplicity we choose the c–c Gurney parameter $A_{cc} = 0$, though some other combination of Gurney parameters could yield better agreement with experimental data.[22] With this approximation, the only parameter left is A_{pc}, which can be adjusted for the maximum agreement between the measured and calculated data.

The theoretical results for the refined model are shown in the same figure (Figure 3) by a full line. For this calculation we set $A_{pc} = -1065$ J/mol at 25 °C, whereas the other
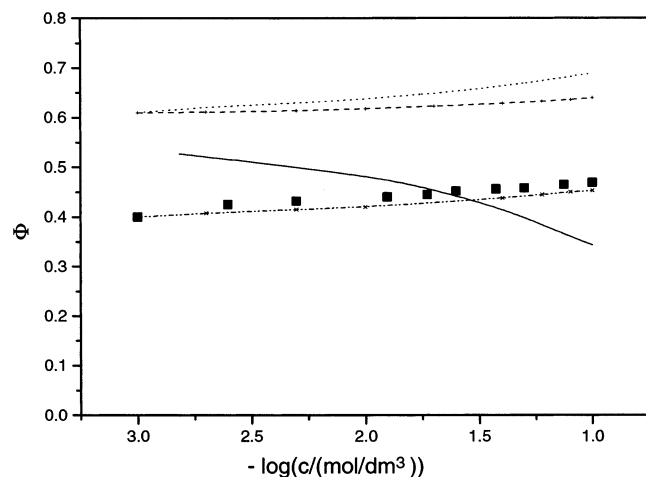
Osmotic Properties of Aqueous Ionene Solutions

J. Phys. Chem. B, Vol. 106, No. 38, 2002 **9971**

Figure 4. Calculated and measured values of the osmotic coefficient for 6,6-ionene Br$^-$ solution at 25 °C. Notation as for Figure 4.

Figure 5. Calculated and measured osmotic coefficients of 3,3-, 4,5-, 6,6-, and 6,9-ionene bromides at 0.001 mol/dm^3. The theoretical results are for the Manning theory (eqs 1 and 2) shown by the dashed line, and the Monte Carlo data are presented by the full line connecting circles.

parameters are given in the previous paragraph. As we can see from this plot, the inclusion of the short-range interaction significantly lowers the value of the osmotic coefficient. However, the influence of the short-range potential due to the nonzero (negative) A_{pc} Gurney term, is stronger at higher concentration, which yields an incorrect concentration dependence of the osmotic coefficient.

4.2. Results for 6,6-Ionenes. We have also performed calculations for models mimicking 6,6-ionene solutions in water. We present these results in the next figure, Figure 4. The Poisson−Boltzmann results presented in this figure apply to $\xi = 0.81$ ($b = 0.879$ nm), whereas the other parameters are as for the 3,3- case. These results are shown by the dotted line. The discrepancies between the purely electrostatic Poisson−Boltzmann theory and the experimental results are, as expected, even larger here. The Poisson−Boltzmann calculation can be brought into reasonable agreement with the experiment for $\xi = 1.54$. This finding is in agreement with previous studies of osmotic coefficients of polyacrylic acid[45] and maleic acid/ethylene copolymer solutions.[10] In particular, Kozak[10] studied solutions of the copolymer of maleic acid and ethylene at various degrees of neutralization α. The agreement between the measured and the Poisson−Boltzmann values of the osmotic coefficient is semiquantitative; more precisely, by decreasing the charge on the polymer (low α), the agreement between theory and experiment becomes worse. The same holds true for the Monte Carlo data for the discrete charge model obtained with a structural value of ξ (=0.81), cf. the dashed line in this figure. Theory for the discrete charge model can be brought into better agreement if we increase the value of ξ to around 1.43. These results are shown in Figure 4 by crosses connected with the dashed−dotted line. Finally, we also present the results for the refined model. The two Gurney parameters were chosen to be $A_{pc} = -1860$ J/mol and $A_{cc} = 0$, whereas for the charge density parameter, ξ, a structural value of 0.81 was used. These results are shown by a full line. As already noticed for 3,3-ionenes (Figure 3), the refined model does not correctly predict the concentration dependence of the osmotic coefficient, though, a more complete analysis in which both Gurney parameters would be varied, could yield a better agreement between theory and experiment.

4.3. Effect of the Polyion Charge Density. The ionenes studied in the present work differ significantly in their charge density parameter. For example, for 3,3-ionenes the length of the monomer unit $b = 0.498$ nm, which yields $\xi = 1.43$. On the other hand, for 6,9-ionenes the distance between the two
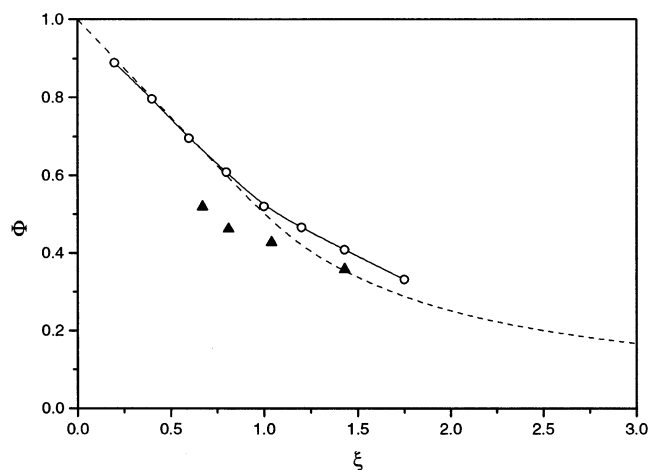
consecutive charges on the polymer backbone $b = 1.06$ nm and therefore $\xi = 0.67$. It is of considerable interest to present the osmotic coefficient data for these solutions as a function of the charge density parameter ξ. These results are shown in Figure 5, where the predictions of various theories are compared to the experimental data here presented by symbols. All the experimental results apply to ionene solutions with Br ions as counterions at a concentration of 0.001 mol/dm^3 and $T = 298$ K. The same holds true for the theoretical results, an exception being Manning's condensation theory (eqs 1 and 2) calculation, which applies to the infinite dilution limit.[17] The latter results are shown in Figure 5 by a dashed line. The predictions of the Manning theory are in good agreement with the measurements for solutions with $\xi > 1$, but for lower values of ξ the calculated values are too high. The same behavior has been noticed previously by Manning (see Figure 5 of ref 17) for the sodium salt of polyacrylic and poly(methacrylic acid) and also by Kozak,[10] who studied maleic acid/ethylene copolymer solutions. The Monte Carlo results are presented in Figure 5 by a full line. The conclusion is that the theories examined here overestimate the osmotic coefficient and that the discrepancies increase with the decreasing charge on the polyion. It is quite clear from this figure that the Coulomb interaction between the counterions and the charges on the infinitely long polyion, as taken into account in this study, is not the only source of nonideal behavior of ionene solutions. The contribution of the interaction not included in modeling to polyelectrolyte nonideality is more important for lower values of ξ. If we are allowed to speculate and extrapolate the ξ dependence of the measured data given in Figure 5 to $\xi = 0$, we obtain a value of the osmotic coefficient for a hypothetical discharged ionene polyion somewhere between 0.75 and 0.85. To show that this is not an isolated result in Figure 6, we present a compilation of osmotic coefficient data for various polyelectrolytes (for details see the legend to this figure) as a function of the charge density parameter ξ. The results for several different weak polyelectrolytes, including maleic acid/ethylene copolymer solutions[10] and poly(acrylic acid)),[10,45] show that the osmotic coefficient does not approach unity as ξ approaches zero. The osmotic pressure results for HPSS solutions (poly(styrenesulfonic acid), a strong polyelectrolyte), where the charge on the polyion is partly blocked by addition of a surfactant,[49] show similar behavior (cf. Figure 6). From the experimental results
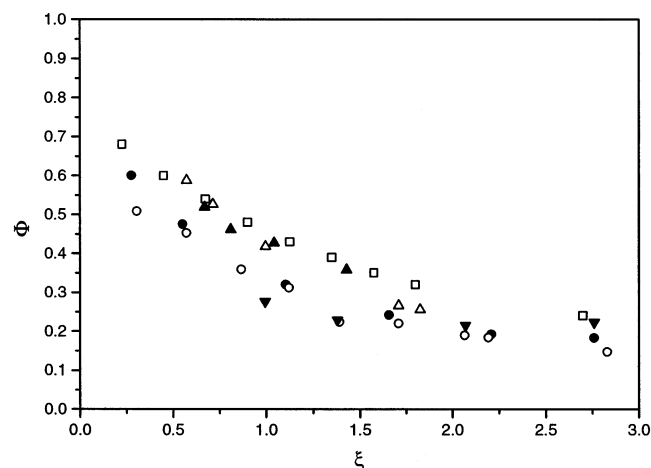
Figure 6. Compilation of osmotic coefficient data for various polyelectrolytes as a function of the linear charge density parameter ξ. Experimental values: ($\bullet$) maleic acid/ethylene copolymer solutions;[10] ($\blacktriangle$) ionenes; ($\bigcirc$) polyphosphates;[46] ($\triangle$) carboxymethyl cellulose;[46] ($\square$) polyacrylates;[47,48] ($\blacktriangledown$) HPSS, where the charge on the polyions was partly blocked by addition of a surfactant.[49] In all cases $c = 0.06$ mol/dm^3.

collected in Figure 6 we may conclude that the osmotic coefficient does not approach the ideal value when the charge on the polymer backbone decreases toward zero. Accordingly, there must be another source of nonideality present, not accounted for by purely electrostatic polyelectrolyte theories applied in this work.

5. Conclusions

Experimental results for the osmotic coefficients of 3,3-, 4,5-, 6,6-, and 6,9-ionenes with bromide and chloride counterions are presented. The results at 298 K were obtained in part by membrane osmometry (for concentrations below 0.02 mol/dm^3) and with a vapor pressure osmometer at higher polyelectrolyte concentrations. The experimental results indicate strong deviations from ideality for all solutions. In general, osmotic coefficients are in the same range as for other anionic polyelectrolytes of similar charge density. The osmotic coefficients of chloride solutions are slightly higher than for the corresponding bromide solutions.

In the second part of the study various models of polyelectrolyte solutions were applied to analyze the experimental data from osmotic measurements. Main conclusions of the analysis are as follows: The Poisson–Boltzmann approximation, when compared to the experimental data, grossly overestimates the osmotic coefficient. The same holds true for the discrete-charge models studied by the Monte Carlo method. A value of the charge density parameter ξ considerably larger than the structural value must be applied to bring the theory into agreement with the measurements. Manning's condensation theory works well for higher values of the charge density parameter but overestimates the osmotic coefficients for $\xi < 1$. A limited numerical analysis, based on refined models where A_{pc} and A_{cc} are the Gurney coefficients, indicates that these models overestimate the influence of short-range forces at higher polyelectrolyte concentrations.

In general, our experimental data indicate stronger deviations from ideality than predicted by theory. The discrepancies[11,12] may be attributed to the many simplifications in the theoretical models used in this and in many previous studies. In particular, the actual polyion is flexible and not rigid, as modeled here. For flexible polyions with low charge on the backbone,

cylindrical symmetry may not be a good representation of the actual average conformation. The correlation between the polyions and counterions occupying adjacent cells is not included in the calculation. There is some indication that this interaction may increase the nonideality in the system.[50] Further, the models applied in our analysis ignore the molecular nature of the solvent, and also the dielectric discontinuity at the polyion–solution boundary. In addition, the theories used in the present analysis ascribe all the deviations from ideality to the electrostatic counterion–polyion interaction. In other words, for a charge density parameter ξ approaching zero, the polyelectrolyte solution should exhibit ideal behavior. The experimental results for several weakly charged polyelectrolytes presented in Figures 5 and 6 show that this is not the case. An important future goal of the theoretical research in the field of polyelectrolyte solutions should be to explain and quantify this remaining nonideality.

References and Notes

(1) Nagaya, J.; Minakata, A.; Tanioka, A. *Langmuir* **1999**, *15*, 4129.
(2) Rembaum, A.; Baumgartner, W.; Eisenberg, A. *J. Polym. Sci. B* **1968**, *6*, 159.
(3) Somoano, R.; Yen, A. P. S.; Rembaum, A. *J. Polym. Sci. B* **1970**, *8*, 467.
(4) Casson, D.; Rembaum, A. *J. Polym. Sci. B* **1970**, *8*, 773.
(5) Pirogov, A. V.; Buchberger, W. *J. Chromatogr. A* **2001**, *916*, 51.
(6) Nagaya, J.; Minakata, A.; Tanioka, A. *Rep. Prog. Polym. Phys. Jpn.* **1997**, *40*, 123.
(7) Nagaya, J.; Minakata, A.; Tanioka, A. *Colloids Surf. A* **1999**, *148*, 163.
(8) Dolar, D. In *Polyelectrolytes*; Selegnyi, E., Ed.; D. Reidel: Dordrecht, Holland, 1974; pp 97–113.
(9) Kozak, D.; Kristan, J.; Dolar, D. *Z. Phys. Chem. Neue Folg.* **1971**, *76*, 85.
(10) Kozak, D. *Die Makromol. Chem.* **1976**, *177*, 287.
(11) Deserno, M.; Holm, C.; Blaul, J.; Ballauff, M.; Rehahn, M. *Eur. Phys. J.* **2001**, *E5*, 97.
(12) Blaul, J.; Wittemann, M.; Ballauff, M.; Rehahn, M. *J. Phys. Chem. B* **2000**, *104*, 7077.
(13) Boisvert, J. P.; Malgat, A.; Pochard, I.; et al. *Polymer* **2000**, *43*, 141.
(14) Strauss, U. P. In *Polyelectrolytes*; Selegnyi, E., Ed.; D. Reidel: Dordrecht, Holland, 1974; pp 79–85.
(15) Fuoss, R. M.; Katchalsky, A.; Lifson, S. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 579.
(16) Alfrey, T.; Berg, P. W.; Morawetz, H. *J. Polym. Sci.* **1951**, *7*, 543.
(17) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(18) Manning, G. S.; Ray, J. *J. Biomol. Struct. Dyn.* **1998**, *16*, 461.
(19) Jayaram, B.; Beveridge, D. L. *J. Phys. Chem.* **1991**, *95*, 2506.
(20) Rebolj, N.; Jamnik, B.; Vlachy, V. *Ber. Bunsen-Ges. Phys. Chem.* **1996** *100*, 770.
(21) Gurney, R. W. *Ionic Processes in Solution*; McGraw-Hill: New York, 1953.
(22) Ramanathan, P. S.; Friedman, H. L. *J. Chem. Phys.* **1971**, *54*, 1086.
(23) Bratko, D.; Vlachy, V. *Chem. Phys. Lett.* **1982**, *90*, 434.
(24) Le Bret, M.; Zimm, B. H. *Biopolymers* **1984**, *23*, 271.
(25) Bacquet, R. J.; Rossky, P. J. *J. Phys. Chem.* **1984**, *88*, 2660.
(26) Mills, P.; Anderson, C. F.; Record, M. T. *J. Phys. Chem.* **1985**, *89*, 3984.
(27) Bhuiyan, L. B.; Bratko, D.; Outhwaite, C. W. *J. Phys. Chem.* **1991**, *95*, 336.
(28) Noguchi, H.; Rembaum, A. *Macromolecules* **1972**, *5*, 253.
(29) Rembaum, A.; Noguchi, H. *Macromolecules* **1972**, *5*, 261.
(30) Arh, K.; Pohar, C. *Acta Chim. Slov.* **2001**, *48*, 385.
(31) Burg, D. E. *J. Phys. Chem.* **1963**, *67*, 2590.
(32) *Vapour Pressure Osmometer K-7000 User Manual*; Knauer Instruments Inc.: Berlin, 1999.
(33) Haynes, C. A.; Tamura, K.; Körfer, H. R.; Blanch, H. W.; Prausnitz, J. M. *J. Phys. Chem.* **1992**, *96*, 905.
(34) *Knauer Model 7310100000 Membrane Osmometer operations manual*; Knauer Instruments Inc.: Berlin, 1990.

Osmotic Properties of Aqueous Ionene Solutions

J. Phys. Chem. B, Vol. 106, No. 38, 2002 **9973**

(35) Desnoyers, J. E.; Arel, M.; Perron, G.; Jolicoeur, C. *J. Phys. Chem.* **1969**, *73*, 3346.

(36) Vlachy, V.; Haymet, A. D. J. *J. Chem. Phys.* **1986**, *84*, 5874.

(37) Patra, C. N.; Yethiraj, A. *J. Phys. Chem. B* **1999**, *103*, 6080.

(38) Vlachy, V. *J. Chem. Phys.* **1982**, *77*, 5823.

(39) Pauling, L. *The Nature of Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(40) Barthel, J.; Klein, L.; Kunz, W.; Calmettes, P.; Turq, P. *J. Solution Chem.* **1994**, *23*, 955.

(41) Otrin Debevc, K.; Pohar, C.; Vlachy, V. *J. Solution Chem.* **1996**, *25*, 787.

(42) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(43) Widom, B. *J. Stat. Phys.* **1978**, *19*, 563.

(44) Svensson, B.; Åkesson, T.; Woodward, C. E. *J. Chem. Phys.* **1991**, *95*, 2717.

(45) Kern, W. *Z. Phys. Chem., Abt. A* **1939a**, *184*, 197.

(46) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327.

(47) Conway, B. E.; Barradas, R. G. *Chemical Physics of Ionic Solutions*; Wiley: New York, 1966.

(48) Kakehashi, R.; Yamazoe, H.; Maeda, H. *Colloid Polym. Sci.* **1998**, *276*, 28.

(49) Škerjanc, J.; Kogej, K. *J. Phys. Chem.* **1989**, *93*, 7913.

(50) Rebolj, N.; Kristl, J.; Kalyuzhnyi, Yu. V.; Vlachy, V. *Langmuir* **1997**, *13*, 3646.