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Properties

Counter-Ion Activity in a Cationic Polyelectrolyte Solution

C. A. Kienzle-Sterzer, G. Bakis, D. Rodriquez-Sanchez and C. K. Rha

Biomaterials Science and Engineering Laboratory, Department of Nutrition and Food Science, Room 56-137, Massachusetts Institute of Technology, Cambridge Mass. 02139, USA

Summary

The counterion transport properties, represented by the chloride ion activity coefficient in cationic polyelectrolyte solutions were studied. The effect of polymer concentration and ionic strength of the media in non-dilute regime were examined. The relative counterion activity coefficient (γ/γ_o) decreased with a decrease in ionic strength, but remained unchanged with polymer concentrations. Chloride ions bound per monomer of polymer (n) were estimated from the activity coefficient. The bound ion (n) decreased with decreases in ionic strength and increases in polymer concentration. This phenomenon demonstrates the effect of intermolecular interactions in polyelectrolytes on the charge shielding process of polyions.

Introduction

Polyelectrolytes are macromolecules with potentially ionizable groups along their backbone. Polyelectrolytes behave as noncharged polymers in non-ionizing solvent, but they ionize to form macroions in polar solvents. It has been shown (1-3) that the high charge density of the polyions result in stronger interaction with the counterions. The stronger interaction between ions and polyions changes counterion transport properties, such as self-diffusion and activity coefficients. The interactions of counterions, coions and charged polyelectrolytes in dilute aqueous solutions have been thoroughly studied theoretically and experimentally (4-10). Our attempt is to extend the study of counterion-polyion interactions and the transport properties of counterions in polyelectrolyte solutions to the semiconcentrated region. Polyion-polyion overlap should affect counterion-polyion interactions (11,12) in non-dilute regimes when polymer concentration is equal to or greater than the overlapping concentration, C_p^*, defined as:

$$C_p^* = 0.5/[\eta]$$

The overlapping concentration is defined based on potentiometric data which indicates that above this concentration the degree of ionization is affected by the polymer concentration (18).

In this study, chitosan, a polycationic biopolymer was used. Chitosan, its dilute, semiconcentrated, and network forming properties, as well as its varied functional properties, have been subjected to examination (13-15).

Materials and Methods

Chitosan [(1-4)-2 amino- 2 deoxy -β-D glucan] (Madera, Bio-Shell Products Inc., Albany, Oregon) obtained from Tanner (snow) crab, Chionecetes Bairdi, with less than 1% of protein and ash, and with 80% deacetilation was used in this study. The estimated molecular weight of chitosan was obtained from intrinsic viscosity in 1% acetic acid with 2% LiCl at 25°C (16). The molecular weight was estimated to be 1.3×10^5 daltons.

Chitosan was stirred in 0.4M HCl at room temperature until complete dissolution. To obtain a good dispersion, chitosan powder was sifted slowly onto the surface of the vortexing acid solution in order to minimize agglomeration. After complete solubilization, the chitosan solutions were stored overnight. Then, NaCl was added to adjust the counterion concentration between .05M and 0.4M.

Measurement of the cell potential (in mV) of the chitosan solutions, with an accuracy of 0.1 mV, were performed with an Orion Microprocessor pH/millivoltmeter model 811 (Orion Research, Cambridge, MA). An Orion combination chloride electrode model 96-17B in conjunction with an Orion double junction reference electrode model 90-02 were used for the measurement of chloride ion activity coefficients. All measurements were carried out at constant temperature (25.0 ± 0.1°C) while nitrogen gas was bubbled through the solutions. Calibration curves were determined before and after every series of measurements on both polyelectrolyte and blank solutions with standard HCL solutions in order to test for Nerstian electrode slopes.

The chloride ion activity coefficient is the ratio of its activity obtained from e.m.f. values to its concentration. The reported values are the ratio of the measured ion activity coefficients in the presence of chitosan to that in the blank solution under similar experimental conditions.

Several chitosan concentrations between 1.0 g/l and 2.0 g/l were tested in order to evaluate the effect of chitosan concentration on the chloride activity coefficient.

It must be pointed out that the values of e.m.f. obtained in the range of chloride ion concentration investigated, $.05M \leq C_{Cl^-} \leq 0.5M$, were independent of pH for $pH \leq 4.5$. This phenomenon is in agreement with the independency of $[\eta]$ and degree of ionization with pH for pH values below 4.5 (18).

Results and Discussion

Chitosan is a hydrophilic polyelectrolyte that is insoluble in pure water, but soluble in dilute acid conditions (17). The polyelectrolyte behavior of chitosan has been demonstrated both in solution, as well as in films (13-15). Also the effect of solution conditions, pH and ionic strength on the hydrodynamic behavior and charge density of chitosan molecules has been examined (22). The results of these studies indicated that both the intrinsic viscosity and the degree of ionization remain constant at pH below 4.5 independent of the ionic strength. In this study, in order to analyze the effect of polymer and counterion concentrations, counterion activity coefficients in chitosan solutions (5×10^{-3} mono M to 11×10^{-3} mono M) were studied at ionic strengths between 0.05M and 0.4M, and pH values below 4.5. Relative chloride ion activity coefficient, represented as the ratio of the chloride ion activity coefficient in the polyion solution (γ_{Cl^-}) to the correspondent chloride ion activity coefficient in polyelectrolyte free solution ($\gamma^o_{Cl^-}$), is shown in Figure 1. Figure 1 shows that the relative counter ion activity coefficient ($\gamma_{Cl^-}/\gamma^o_{Cl^-}$) decreases with decreasing ionic strength, but is unaffected by polymer concentration.

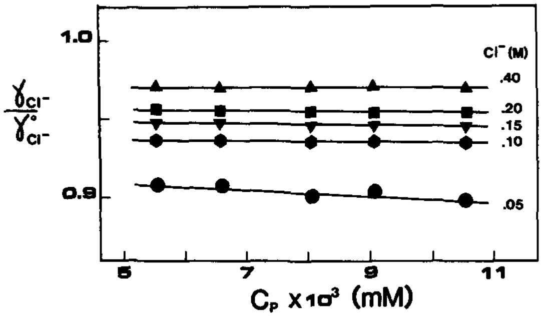

Figure 1.
Relative counterion activity coefficient in semiconcentrated chitosan solutions as affected by polymer concentration and counterion concentration.

The high values of the relative counterion activity coefficient ($\gamma_{Cl^-}/\gamma^{o}_{Cl^-}$) indicates enhanced shielding of the charges on the chitosan backbone due to the relative high counterion concentration. Meanwhile, the fact that the counterion activity coefficient is independent of the polymer concentration indicates that the shielding effect is sufficiently extensive. However, with ionic strength of the media significantly decreased, the relative counterion activity coefficient decreases. This confirms that at constant polymer concentration,increasing the counterions results in an increase in the interactions between counterion-polyion. Similar behavior in the counterion activity coefficient has been observed for charged heparin (19) and for λ and κ carraginan at high salt concentrations (5).

Counterion activity coefficient approximates the fraction of free counterions in polymer solutions (21). Therefore, we calculated "n", defined as the bound chloride ion concentration divided by the monomolar chitosan concentration, by the expression:

$$n = \frac{\Delta C_{Cl^-}}{C_p}$$

Cp is the polymer concentration, and ΔC_{Cl^-} represents the bound chloride concentration obtained by:

$$\Delta C_{Cl^-} = C_t - C_t \gamma_{Cl^-}/\gamma^{o}_{Cl^-}$$

where C_t is the total counterion concentration.

Figure 2 shows the relationship between "n", counterion and chitosan concentration. Straight lines with an inflection point at approximately 0.13M chloride concentration. This change in the slope of the straight lines may be due to the transition of chitosan molecules from an extended configuration at low ionic strength to a globular compact shape at high ionic strength. This transition effect was also clearly indicated in our earlier study by the inflection point (0.10-0.15M Cl⁻ conc.) in the relationship between the local viscosity and counterion concentration.

The similarity in the shape of the relationship between "n" and counterion concentration for different chitosan concentrations suggests that the ion binding mechanism remains unaltered with the polyelectrolyte concentration.

Figure 2 shows that the number of bound counterions per monomer

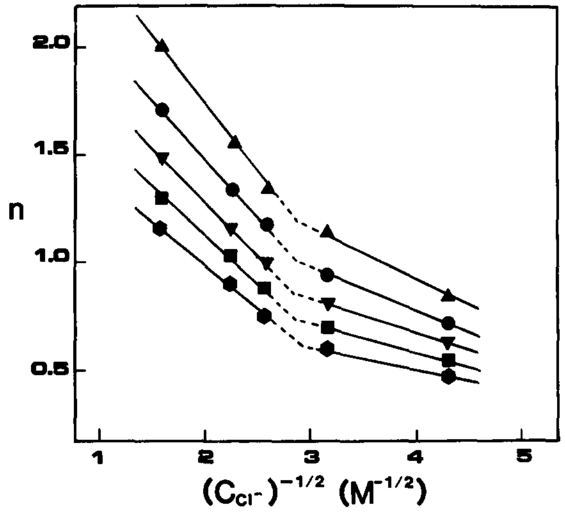

Figure 2.
Effect of counterion concentration on the number of counterion bound per monomer of chitosan "n" for a given chitosan concentration.
Symbols:
⬢ = 10.58×10^{-3}mM;
■ = 9.00×10^{-3}mM;
▼ = 8.00×10^{-3}mM;
● = 6.50×10^{-3}mM and
▲ = 5.60×10^{-3}mM.

increases with increasing counterion concentration and decreases with increasing polymer concentration. This indicates the repulsive effect on the bound counterion sheath around the polyion molecules as intermolecular interactions start to appear.

In order to study the effect of both the degree of ionization (α) and the chain overlapping on the number of bound counterions, "n" was plotted against α, and the overlapping parameter, represented by the term C[n], in Figure 3. "n" increases with α , independent of the chitosan and salt concentration, due to an increase in the electrostatic interaction between polyion and counterions when the number of charged points are increased. On the other hand, a reduction in "n" was observed when the overlapping parameter was increased. This effect was due to an increase in the interaction between counterions bound to the polyion molecules, which in turn allow a distribution of the counterions around the charged points on the polymer backbone.

In recent years attention has been given to the development of theoretical treatments in order to predict the activity coefficients of ions in mixtures of polyelectrolytes and simple electrolytes (4,6). It has been found that counterion condensation occurs, when the charge density of the polyion (ξ) is greater than that of the critical charge density ($\xi_c = 1$ for monovalent counterion), until the polyion charge density is equal to the critical one. According to the Manning theory of polyelectrolyte solution, the counterion activity coefficient can be represented by (4).

$$\frac{\gamma_{Cl^-}}{\gamma^o_{Cl^-}} = \frac{\xi^{-1}X + 1}{X + 1} \exp\left[\frac{-0.5\ \xi^{-1}X}{\xi^{-1}X + 2}\right] \quad \text{for} \quad \xi \geq 1$$

where X is the concentration ratio of polyelectrolyte to simple salt.

Similarly, Iwasa et al. (6) predict a counterion activity coefficient, for monovalent counterions, by the equation:

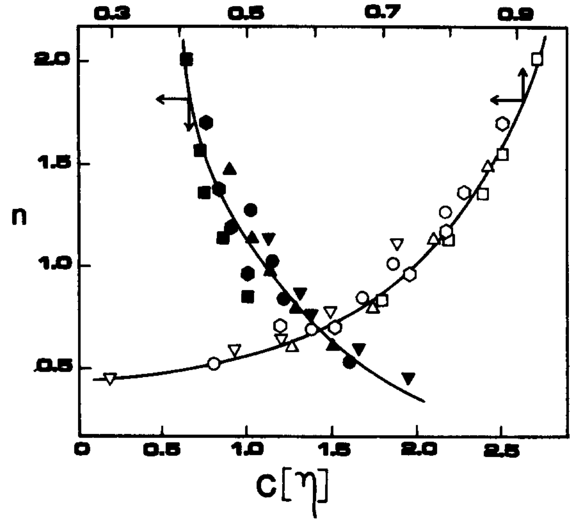

Figure 3.
Number of counterions bound per monomer "n" as affected by the overlapping parameter "c[η]" and degree of ionization "α". The symbols are the same as in Figure 1.

$$\frac{\gamma_{Cl^-}}{\gamma^{o}_{Cl^-}} = \frac{\xi^{-1}X+1}{X+1}\quad \exp\left\langle \frac{\xi^{-1}X}{\xi^{-1}X+2}\left[-0.5+0.39\left(\frac{\xi^{-1}X}{\xi^{-1}X+2}-1\right)\right]\right\rangle$$

for $\xi \geq 1$

Figure 4 shows the relationship between $\gamma_{Cl^-}/\gamma^{o}_{Cl}$ and X for our experimental results which are compared with the theoretical curves obtained from both Manning's and Iwasa's approach with $\xi = \xi_c = 1$. The values obtained from both that of Manning's and Iwasa's theories are higher than the experimental values of the relative counterion activity.

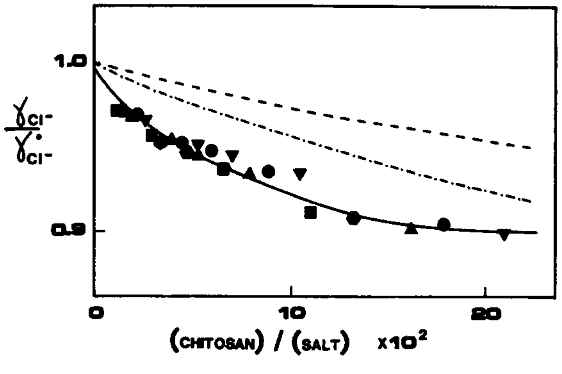

Figure 4
Relative counterion activity coefficient in semi-concentrated chitosan solutions versus dimensionless concentration "[chitosan]/[sal]": ---: theoretical line according to Manning's approach (4); -.-.-: theoretical line according to Iwasa et al.'s approach (6), both calculated for $\xi = \xi_c = 1$. The symbols are the same as those in Figure 1.

Since both theories deal with dilute polymer solutions, the difference between these and our experimental values should represent the intermolecular interactions since our experiment employed overlapping parameters in the range 0.5 to 2.0. In this region the increase in intermolecular interaction will perturb the counterion sheath around polyion molecules, therefore decrease the number of counterions bound per monomer.

Acknowledgments

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