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An Introduction to Polyelectrolytes Via the Physical Chemistry Laboratory

Polyelectrolytes are of fundamental interest because they have the combined properties of polymers and of electrolytes. These ion-containing macromolecules are of interest to biologists and biochemists since many polyelectrolytes are involved in biological phenomena. A few such biopolyelectrolytes include proteins and salts of deoxyribonucleic acid, chondroitin sulfate, heparin, hyaluronic acid, pectinic acid, alginic acid, and carboxymethyl cellulose. Among the synthetic polyelectrolytes most thoroughly investigated are salts of polyacrylic acid, polyphosphate, polystyrenesulfonate, and polyvinylalcohol sulfate (1). While many of the polyelectrolytes are polyanions, i.e., the repeating monomer unit has a pendant negative ionic group such as carboxyl, sulfate, sulfonate, and phosphate, proteins are polycations at appropriate conditions and polyquaternized imines are unique inasmuch as the ionic group is in the polymer backbone and not pendant from the chain. Other polycations are known (2, 3).

Because of their importance to several scientific disciplines and to many industries, undergraduate science majors should be introduced to the solution behavior of polyelectrolytes. Chemistry majors in the physical chemistry laboratory course study the simple ion-polyion interaction of sodium polystyrenesulfonate (NaPSS) in several aqueous salt solutions utilizing simple viscosity measurements. While NaPSS was found to be a convenient polyelectrolyte for use in our undergraduate physical chemistry laboratory, sufficient literature results are available for other polyelectrolytes so they could be used (4, 5). Also, biology majors taking physical chemistry have gained an introduction to the behavior of biological polyelectrolytes, from measuring the viscosity of aqueous sodium iota-carrageenan solutions (NaCarr) containing different simple salts. As will be described below, the analysis of the results obtained by the chemistry majors is more demanding than for the biology majors.

The unique solution properties of polyelectrolytes as compared to simple electrolytes is that because of the proximity of the constrained charges on the chain, a large potential is present which traps the oppositely charged counterions in the vicinity of the chain. Because of this large potential, it has been fairly well established that a fraction of the counterions bind (site-bind, condense) onto the charges of the chain and the remaining counterions exist in an ionic atmosphere surrounding the chain. It has been demonstrated that several properties of polyelectrolyte solutions, such as single ion and mean activity coefficients of small ions, and electrical transport parameters and diffusion coefficients of small ions, are independent of the molecular weight of the polyelectrolyte. These properties depend on the linear charge density of the polyelectrolyte chain and the distribution of the small ions, principally the counterions surrounding the polyion. Since polyelectrolytes are generally coiled in aqueous salt solution, the ionic atmosphere surrounding chain segments is cylindrical about the polyion. The distribution of ions in the ionic atmosphere will be affected little by the coiling of the chain provided that the local radius of curvature of the coil is small compared to the size of the Debye-Hückel atmosphere of cylindrical symmetry about the axis of the polyion, as illustrated in the figure. Then the appropriate physical model should be approximated by a fully stretched out rod with a fraction of the counterions bound or condensed onto charged sites on the
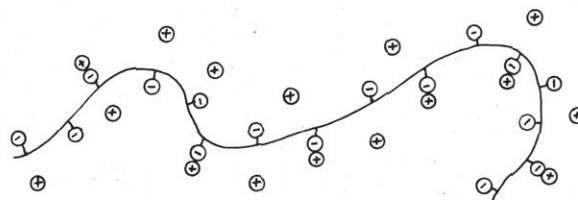
Schematic representation of a portion of a polyelectrolyte in a salt-free solution showing condensed and uncondensed counterions.

polyion analogous to Bjerrum ion pairs, and the remaining fraction of counterions held coulombically in the Debye-Hückel atmosphere.

Manning's model of polyelectrolyte solutions is simple and useful (6, 7). The polyelectrolyte is represented by an infinite line charge with the stoichiometric average distance between charges on the polyelectrolyte b defining the stoichiometric linear charge density parameter ξ

$$\xi = \frac{e^2}{\epsilon k T b} \qquad (1)$$

where e is the proton charge, ϵ is the bulk dielectric constant of the solvent, k is the Boltzmann constant, T is the absolute temperature. For aqueous solutions at 25°C, $\xi = 7.15/b$, with b in Angstrom units. For helical DNA $b = 1.7$Å and $\xi = 4.2$, and for NaPSS, $b = 2.85$ Å and $\xi = 2.5$. If ξ is greater than a critical linear charge density ξ_c

$$\xi_c = \frac{1}{|Z_1|} \qquad (2)$$

where Z_1 is the charge of the counterion (subscript 1), counterions condense onto polyion chain sites until the effective value of ξ_c is reached and the remaining counterions are in the Debye-Hückel atmosphere and interact with the polyion electrostatically. Denoting the charge numbers ν and ν_c as the number of ionizable groups on the polyelectrolyte stoichiometrically and at the critical point, respectively. The fraction of counterions condensed onto the polyion is given by (7, 8).

$$\frac{\nu - \nu_c}{\nu} \approx \frac{\xi - \xi_c}{\xi} = 1 - \frac{\xi_c}{\xi} \qquad (3)$$

which by eqn. (2) gives as the fraction of counterions condensed $(1 - \xi^{-1})$ for univalent counterions and $(1 - (2\xi)^{-1})$ for divalent counterions. Thus, Na^{+1} ions will condense onto a given polyelectrolyte to a lesser extent than will Ca^{+2} ions. Conversely, the degree of dissociation of a polyelectrolyte is $[1 - (1 - \xi_c/\xi)]$ or ξ_c/ξ. Note that this depends only on the valence of the counterions and the structural value of b for the polyelectrolyte. For a polyelectrolyte with Na^+ ions as the only counterion, ξ^{-1} is the degree of dissociation for Na^+ ions and $(2\xi)^{-1}$ for Ca^{+2} ions. In a salt-free polyelectrolyte solution, if n_p is the equivalent concentration of polyelectrolyte, the equivalent concentration of charges on the polyelectrolyte is $\xi^{-1}n_p$ and the effective concentration of dissociated Na^+ ions is $\xi^{-1}n_1$. In a polyelectrolyte solution containing simple salt of concentration n_s, the effective counterion concentration is $(n_s + \xi^{-1}n_p)$ and the effective polyelectrolyte concentration is $\xi^{-1}n_p$. If $\xi < \xi_c$, there is no counterion condensation onto

the charge sites of the polyion and all small ions interact with the fully dissociated polyion in the Debye-Hückel atmosphere.

Since the intrinsic viscosity of a polyelectrolyte in an aqueous salt solution is a measure of hydrodynamic size of the molecule, such a measurement should give a measure of the elongation (or coiling) of a polyelectrolyte in different salt solutions. The intrinsic viscosity of a given polyelectrolyte in 0.010 M NaCl should be higher than in 0.10 M NaCl. The lower is the simple salt concentration, the larger is the Debye-Hückel atmosphere (κ^{-1} varies inversely with the square root of the ionic strength), thereby affording less screening of the polyion charges which causes repulsion between the polyion charges with a concomitant elongation of the polyion coil and a larger intrinsic viscosity. Note that the degree of dissociation of counterions is fixed (see eqn. 3). Also when Ca^{+2} is the counterion instead of Na^{+1}, more Ca^{+2} counterions will condense as compared to Na^{+1}, neutralizing more charges on the polyion as compared to Na^{+1}. This, combined with greater Debye-Hückel interaction of Ca^{+2} with the polyion, will cause greater coiling and a lower intrinsic viscosity.

The intrinsic viscosity $[\eta]$ can be calculated from extrapolations of the plots of η_{sp}/C_p (or $\ln \eta_{rel}/C_p$) versus C_p to $C_p = 0$, (9)

$$[\eta] = \lim_{C_p \to 0} \eta_{sp}/C_p = \lim_{C_p \to 0} (\ln \eta_{rel}/C_p) \quad (4)$$

where

$$\eta_{sp} = \eta_{rel} - 1 = \frac{t}{t_0} - 1 \quad (5)$$

where t and t_0 are the flow times of the polyelectrolyte solution and solvent, respectively. When a macromolecule is a polyelectrolyte, usually the solvent is water or an aqueous salt solution. From the Mark-Houwink equation

$$[\eta] = KM^a \quad (6)$$

where M is the average molecular weight and K and a are constants for a given polymer-solvent system, the value of M is calculated. At 25°C for NaPSS in aqueous NaCl solutions the parameters of eqn. (6) are in the table.

Analogous to the Boyle temperature for gaseous molecules, polymers in solution have a reference state where long-range forces vanish, called a theta temperature or a theta solvent. In the theta state for polymers, thermodynamic interactions with the solvent are suppressed and local constraints depend on the geometry of the chain due to bond angles and the steric hindrance to rotation about bonds. The average mean square end-to-end distance of a long chain unperturbed by solvent $\overline{r_o^2}$ is (9, 10)

$$\overline{r_o^2} = nl^2 \frac{1 + \cos\theta}{1 - \cos\theta} \frac{1 + \cos\phi}{1 - \cos\phi} = nl^2 C_\infty \quad (7)$$

where n is the number of bonds of length l, θ is the bond angle, ϕ are the internal angles of rotation and C_∞ is a constant called the *characteristic ratio* which is a measure of the chain flexibility characteristic of the polymer only and independent of its molecular weight. The viscosity method for the determination of C_∞ depends on a knowledge of eqn. 6 for a polymer system and upon the Flory relationship (9, 10)

$$[\eta] = \Phi \overline{(r^2)}^{3/2}/M \quad (8)$$

where $\overline{r^2}$ is the average mean-square end-to-end distance of the polymer chains and Φ is 2.66×10^{23}, thought to be constant for all systems, with r in cm and $[\eta]$ in ml/g. For polyelectrolyte solutions, an average value of $\Phi = 2.1 \times 10^{23}$ was suggested (5). Viscosity measurements in a theta solvent gives for eqn. (8)

$$[\eta]_\theta = \Phi(\overline{r_0^2}/M) \quad (9)$$

To calculate C_∞, $[\eta]$ is determined for NaPSS in 0.10 M NaCl, M is calculated from eqn. (6), then the intrinsic viscosity in a theta solvent $[\eta]_\theta$ could be calculated from eqn. (6). The

The Mark-Houwink Equation Constants for NaPP at 25°C with $[\eta]$ in ml/g

NaCl, M	$K \times 10^3$	a
0.0050	2.3	0.93
0.0100	2.8	0.89
0.0200	10.1	0.78
0.0500	13.9	0.72
0.100	17.8	0.68
0.500	18.6	0.64
4.17	20.4	0.50

theta solvent for NaPSS at 25°C is 4.17 M NaCl. From eqn. (7)

$$C_\infty = (\overline{r_o^2}/M)(M_b/l^2) \quad (10)$$

where M_b is the mean molecular weight per skeletal bond of length l. The values of M_b and l for NaPSS are 103 and 1.54 $\times 10^{-8}$ cm, respectively. Equations (9) and (10) give C_∞. For free rotation about bonds in a chain of carbon atoms, eqn. (7) and (10) give $C_\infty = 2$, while polymers are usually in the range 4–10. Our calculated value of C_∞ for NaPSS in NaCl solutions is 9.2 (5).

It is worthwhile for the student to calculate $(r^2)^{1/2}$ and $(r_o^2)^{1/2}$ from eqns. (8) and (9) and linear expansion factor α defined by

$$(\overline{r^2})^{1/2} = \alpha(\overline{r_o^2})^{1/2} \quad (11)$$

which is a function of the molecular weight, the polymer-solvent interaction and the polymer segment-polymer segment interaction of the same chain. Of course, α is given by $([\eta]/[\eta]_\theta)^{1/3}$. For polyelectrolyte solutions containing simple salt, the values of α increase with decreasing simple salt concentration because of a decrease in the screening of the charges on the polyion as the ionic atmosphere size increases. Below are the experimental instructions given to each student.

Undergraduate students taking a one semester physical chemistry course are introduced to the structure of aqueous solutions of simple electrolytes, polymers, and polyelectrolytes. Several polyelectrolytes are discussed and the interactions of Na^+, Ca^{+2}, Cl^-, and SO_4^{-2} ions with the polyelectrolyte in solution are discussed in terms of site-binding and ion atmosphere binding. Since the intrinsic viscosity is a measure of the hydrodynamic size of the polymer molecule, its simple experimental evaluation lends itself to the purpose of the experiment. From the determination of $[\eta]$ for NaCarr in 0.0010 M NaCl and 0.10 M NaCl, the students note the affect of the concentration of simple salt on the screening of the charges on the polyelectrolyte. By comparing the $[\eta]$ values in 0.10 M NaCl and 0.050 M $CaCl_2$, the effect of the charge of the counterion on the dimensions of the polyelectrolyte could be understood. Also, a comparison of the $[\eta]$ values in 0.10 M NaCl and 0.10 M Na_2SO_4 should show the student that the charge on the coion has little effect on the dimensions of the polyelectrolyte in dilute solution (11). Many biological polyelectrolytes are available for this experiment.

Experimental Instructions

In preparation for this experiment read Chapter 2 in "Laboratory Preparation for Macromolecular Chemistry" by E. M. McCaffrey.

(1) Prepare 100 ml of 0.010 M and 100 ml of 0.020 M NaCl, which are the solvents.

(2) Prepare 50 ml of approximately 0.1% of sodium polystyrenesulfonate, (NaPSS) of known concentration in a 50 ml volumetric flask by dissolving a known weight of NaPSS in approximately 30 ml of solvent and filling to the mark with solvent after dissolution of the NaPSS. Mix each solution. The solvents are those in (1).

(3) The efflux times should be determined for each solvent and for each solution to a reproducibility of 0.1% in your Ubbelhode viscometer. Each NaPSS solution is filtered just prior to use. Using a volumetric pipette, 10.00 ml of the NaPSS solution is introduced into the viscometer and its efflux time is determined. The efflux times are determined for each of four successive dilutions, made by adding 2 ml of solvent with a volumetric pipette.

(4) Plot η_{sp}/C_p and $\ln \eta_{rel}/C_p$ versus C_p to determine $[\eta]$ for each solvent.

(5) Calculate the pertinent molecular parameters for NaPSS: M, $\overline{(r^2)}^{1/2}$, $\overline{(r_o^2)}^{1/2}$, α, and C_∞.

Literature Cited

(1) Manning, G. S., *Annu. Rev. Phys. Chem.*, **23**, 117 (1972).
(2) Armstrong, R. W., and Strauss, V. P., "Polyelectrolytes" in "Encyclopedia of Polymer Science and Technology," Vol. X, Wiley, New York, N.Y. **1969.**
(3) Eisenberg, A., and King, M., "Ion-Containing Polymers," Academic Press, New York, N.Y. **1977.**
(4) Brandrup, J., and Immergut, E. H., (*Editors,*) "Polymer Handbook," 2nd Edition, Wiley, New York, N.Y., **1975.**
(5) Nagasawa, M., and Takahashi, A., "Light Scattering from Polyelectrolyte Solutions," M. G. Huglin, (*Editor*). Academic Press, New York, N.Y., **1972,** Chapter 16.
(6) Manning, G. S., *J. Chem. Phys.*, **51**, 924 (1969).
(7) Manning, G. S., in "Polyelectrolytes," E. Selegny, *Editor, Reidel Publ. Co., Dordrecht,* Holland, 11 (**1974**).
(8) Magdelenat, H., Turq, P., Tivant, P., Chemla, M., Menez, R., and Drifford, M., J. CHEM. EDUC., **55**, 12 (1978).
(9) Flory, P. J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N.Y. (**1953**).
(10) Flory, P. J., "Statistical Mechanics of Chain Molecules," Interscience, N.Y., (**1969**).
(11) Flory, P. J., and Osterheld, J. E., *J. Phys. Chem.*, **58**, 653 (1954).