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Abstract

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ON THE THEORY OF THE CONFIGURATIONAL PROPERTIES OF POLYELECTROLYTE MOLECULES

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It was shown by one of us ([1]) that the theory of the configurational properties of polyelectrolyte molecules can be reduced to the corresponding theory for uncharged macromolecules with long-range interactions. This made it possible to relate the mean dimensions of polyelectrolyte molecules $\overline{h^2}$ to their molecular weight M and to the mean effective excluded volume of a segment v_0, expressed through the second virial coefficient A_2 ([1]). The theoretically established relation between $\overline{h^2}$, M, and A_2 agrees with experiment; however, an attempt to calculate v_0 from the Debye-Hückel potential for each charged molecular unit led to values of v_0, and consequently also of $\overline{h^2}$, which at not very small degrees of ionization diverge sharply from experiment. A recent detailed study ([2]) of the intrinsic viscosity of fully ionized polyacrylic acid confirmed that the experimental values of v_0 exceed the theoretical ones by tens and hundreds of times; moreover, $v_0 \sim 1/\sqrt{c_s}$ (c_s is the ionic strength of the solution), whereas according to the theory ([1]), $v_0 \sim 1/c_s$.

We shall show that the discrepancy between theory and experiment can be removed if one takes into account that, at not very small degrees of ionization, the strong interaction of two monomer units necessarily entails the interaction of their neighbors as well, so that in fact it is not individual monomer units that interact, but groups of them, whose sizes are determined by the radius over which the electrostatic repulsion forces decay. Therefore the minimum size of the segments considered in the usual theories of long-range interaction in macromolecules (see, for example, ([3])) must coincide with the size of this group, and any further reduction of the segment size to that of a monomer unit in the case of polyelectrolytes is devoid of physical meaning.

For the swelling coefficient of a macromolecule $\alpha = (\overline{h^2}/h_0^2)^{1/2}$ under the influence of long-range interactions, the approximate equation ([4,5]) is valid: $\alpha^3 = 1 + 2z$, where

$$z = (3/2\pi)^{3/2}\sqrt{N}v_0/A^3 = (3/2\pi)^{3/2}\sqrt{n}v_0/m^2a^3,$$

N is the number of segments, $A = (h_0^2/N)^{1/2}$ is the effective length of a segment, v_0 is the effective excluded volume of a segment, n is the degree of polymerization, m is the number of monomer units in a segment, and $a = (h_0^2/n)^{1/2}$ is the effective length of a monomer unit. Thus, experiment determines the quantity $\beta = v_0/m^2$, which has the meaning of the effective excluded volume of a monomer unit. In comparing theory with experiment in ([1]), it was assumed that each segment contains one charge, i.e., $m = 1/i$ (i is the degree of ionization), and v_0 was calculated with the aid of the Debye–Hückel potential.

In reality, around a chain that is not very weakly ionized there is formed a "shell" of counterions tightly bound to it, owing to which the density of the uncompensated charge of the chain proves to be independent of i (see, for example, ([6])). Owing to this, at not very small i, v_0

does not depend on i, and it may be assumed that $v_0 \sim r_0^3$, where r_0 is the range of the forces of mutual electrostatic repulsion, and $m \sim r_0/d$, where d is the length of a monomer unit. Consequently, $\beta \sim r_0 d^2$. It is reasonable to suppose that the range of the electrostatic repulsion forces r_0 is close to $1/\varkappa$, where $\varkappa$ is the Debye–Hückel screening constant, proportional to $\sqrt{c_s}$. Then $\beta = \gamma d^2/\varkappa$, where γ is a numerical factor of the order of several units. For the aqueous salt solutions of polyacrylic acid studied in ([2]), we have $\beta \simeq 6\gamma/\varkappa \simeq 18\gamma/\sqrt{c_s}$, which at $\gamma \simeq 2.5$ agrees with the empirical formula describing the results of ([2]). Thus, taking into account the collective character of the interaction of monomer units explains both the order of magnitude of v_0 for strongly ionized chains and the character of its dependence on the ionic strength of the solution.

According to what has been said above, at not very small i, β, and therefore $\overline{h^2}$, should in the first approximation not depend on i. This, at first sight paradoxical, result, which is a consequence of counterion binding, is confirmed by the experimental data of Orofino and Flory for polyacrylic acid with $i \simeq 1/3$ and $i \simeq 1$ ([7]). At sufficiently small i, when counterion binding no longer takes place, one should have $m = 1/i$ and $\beta \simeq 10^3 i^2/2N_A c_s$, in agreement with the results of ([1]).

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[1] O. B. Ptitsyn, *Vysokomolek. soed.*, **3**, 1251 (1961).
[2] A. Takahashi, M. Nagasawa, *Excluded Volume of Polyelectrolyte in Salt solutions* (Preprint).
[3] O. B. Ptitsyn, *Vysokomolek. soed.*, **1**, 715 (1959).
[4] O. B. Ptitsyn, *Vysokomolek. soed.*, **3**, 1673 (1961).
[5] M. Fixman, *J. Chem. Phys.*, **36**, 3123 (1962).

[6] F. T. Wall, H. Terayama, S. Techakumpuch, *J. Polym. Sci.*, **20**, 477 (1956).
[7] T. Orofino, P. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

Note: Figure translations are in progress. See original paper for figures.