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A Statistical Theory of Globular Polyelectrolyte Complexes

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ABSTRACT: A microscopic statistical theory of a symmetrical polyelectrolyte complex (PEC) is developed. PEC is shown to form a polymer globule. The equilibrium density of PEC, the width of a PEC surface layer, and the surface tension of PEC are calculated as a function of salt concentration. Description of PEC as a polymer globule enables us to simplify theoretical treatment of the phenomenon of phase separation in polyelectrolyte solutions (complex coacervation). Numerous experimental facts concerning complex coacervation are easily explained within this approach. Complex coacervation is considered as precipitation of polymer globules owing to minimization of surface energy. The theory is based on the Lifshitz–Grosberg theory of polymer globules and our previous work concerning the equation of state of polyelectrolyte solutions. It is limited to the case of polyions with the low linear density of charge, which is most clear from the theoretical point of view and is also of practical and, in particular, of biological interest.

I. Introduction

It is well-known that oppositely charged macromolecules in a solution form polyelectrolyte complexes (PEC). Their theoretical investigation is important for the development of a theory of phase separation in a polyelectrolyte (PE) system containing polyions of opposite charges. This phenomenon studied for the first time by Bungenberg de Jong[1] was called complex coacervation (see also refs 2–4). Parts of the condensed phase (coacervate) are usually called coacervate drops and are often considered as model systems for precellular structures.[5] The numerous phenomena that occur in the PE solutions are complicated, and generally their theoretical interpretation is qualitative and controversial. Therefore, it is reasonable to start the consistent consideration of these systems with the most simple solvable model, where main qualitative features are already seen.

As the first step in the study of PEC properties we shall consider in this paper a symmetric PEC, formed by two flexible oppositely charged polyions with the same degree of polymerization N and each having one charge per m monomers (each polyion has charges of one sign). Charges should be distributed more or less uniformly along the chain (for example, randomly). Only for simplicity we consider polyions as flexible filaments on which interacting monomers are strung (the model "beads on a filament"[6]) with Gaussian correlations between adjacent monomers and the mean-square distance, a^2, between them. All the monomers interact by means of non-Coulombic forces of the van der Waals type. These assumptions are typical for the theoretical consideration of this kind[2–4] and can be easily generalized.

The influence of ionic bonds between oppositely charged monomers is supposed to be small (for example, the energy of an ionic bond is small in comparison with temperature T, given in energy units). Thus PEC is formed, owing to fluctuation electrostatic energy. This energy was calculated in ref 7 for polyelectrolyte solution (PES) containing weakly charged macromolecules. (Polyions are called weakly charged when the parameter $u/m^{1/2}$ is small, where $u = l/a$, $l = e^2/\epsilon T$ is the Bjerrum length (see also ref 8), and ϵ is the dielectric constant of the solvent. It was also shown[7] that Coulombic and nonelectrostatic contributions to the free energy may be of the same order of magnitude, which can lead to PEC formation. Weakly charged PE are of

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biological significance, since many of the biological PE are weakly charged,[2] and the linear density of charge of the macromolecules can be regulated by the pH in the solution. Moreover, the assumption of weakly charged PE permits us to calculate rigorously the PEC structure and to describe at the same time many phenomena that seem to be common for different types of PEC. Therefore, in the present paper we shall consider only weakly charged polyions.

The small value of the linear density of charge permits us to both neglect the appearance of the electrostatic persistent length[9] and not take into account the possibility of ionic (possibly, cooperative) bonding between several neighboring charged monomers of different chains. This is an important condition, for if such bonding takes place, the structure of the PEC will be determined by a network of strong bonds and will depend strongly on stoichiometric constraints. This case, where thorough consideration of chemical equilibrium with respect to these bonds is necessary, will not be considered here.

One of the major points of our approach to the PEC structure is the consideration of PEC as a polymer globule. The main difference between the polymer coil and globule appears most clearly when the degree of polymerization of the chain, N, is sufficiently large.[6,15] The equilibrium globule density of monomers, ρ, characterizing its spatial structure takes an approximately constant in space value, which is determined by the balance between forces of attraction and repulsion and is independent of N. On the contrary, in a polymer coil ρ decreases to zero when $N \Rightarrow \infty$.

It will be shown later that in our case the independent of N (in the limit $N \Rightarrow \infty$) equilibrium PEC density also exists and is determined by the balance between fluctuation electrostatic attraction and excluded-volume repulsion. Therefore, PEC is the polymer globule. From this point of view our approach differs from the previous ones,[2-4] which considered PEC as a more or less contracted coil. Description of PEC as a polymer globule not only enables us to use the statistical theory of polymer globules (see ref 6) and thus to calculate equilibrium properties of PEC (monomer density, surface tension, etc.) but also provides a natural framework to account for the various experimental facts (e.g., salt effects), which could not be readily understood from other points of view.[2-4] The globular character of PEC seems to be supported experimentally.[10]

In section II we give a simple qualitative description of the phase-separation phenomenon in PES containing oppositely charged polyions and compare our approach with other ones. Then we briefly consider the theory of polymer globules. In section III the theory of globular PEC is developed in the "volume approximation". In section IV surface properties of PEC are considered. In section V we use our theory to consider some features of complex coacervation. Conclusions are summarized in section VI.

For simplicity in section II we choose for the fluctuation Coulombic energy the Debye–Huckel (DH) expressions.[11] The DH approximation is not always valid for PES,[7] but it permits us to concentrate our attention on the general features of a polyelectrolyte globule. In section III we show the difference between the predictions of the DH approximation and of the more rigorous approach.[7]

II. PEC as a Polymer Globule

A. General Consideration. Let us consider for simplicity thermodynamic properties of a semidilute weakly charged symmetric PES, which contains equal numbers of oppositely charged polyions (polyions with the same charge being identical, each chain having charges of the same sign). The electrostatic interaction in this system may be naively included by adding the DH correction[11] obtained for the equivalent system of separated charged monomers[6,7] to thermodynamic properties of a polymer solution without the Coulombic interaction. Proper consideration of fluctuation Coulombic energy will be given in section III. Here we use the DH expression for Coulombic energy only to illustrate general ideas of our approach. Then for the osmotic pressure of a salt-free PES, which in the absence of electrostatic interaction would be described by the Flory–Huggins theory,[12,13] one can easily obtain

$$\nu P/T = -\ln(1-\phi) - \phi(1-N^{-1}) - \chi\phi^2 - \nu\pi^{1/2}(\rho l/m)^{3/2}/3 \tag{1}$$

where ν is the excluded volume, ρ is the total concentration of monomers (both charged and neutral), $\phi = \nu\rho$ is the volume fraction, and χ is the Flory–Huggins parameter. For a low molecular weight electrolyte ($N = m = 1$) eq 1 takes the form of the Vant–Goff equation with the DH correction:

$$P/T = \rho - \pi^{1/2}(\rho l)^{3/2}/3 \tag{2}$$

Note that the condition when this correction is negligible in comparison with the Vant–Goff pressure

$$\rho l^3 \ll 1 \tag{3}$$

coincides with the condition of applicability of the DH approximation.[11]

Situation is completely different for semidilute PES. In this case one can get from eq 1 neglecting all ϕ^3 and higher orders of ϕ

$$P/T = \rho/N + B\rho^2 - \pi^{1/2}(\rho l/m)^{3/2}/3 \tag{4}$$

where $B = (\nu/2)(1 - 2\chi)$ is the second virial coefficient of the monomer–monomer interaction in the solution. When N is large, the first (Vant–Goff) term in eq 4 becomes small compared with the low molecular weight case, so the DH correction begins to play the dominant role. This can lead to the phase separation in the PES. Indeed, it can be easily seen that when $N \Rightarrow \infty$, the monomer concentration in the PES cannot be lower than ρ_g, which is determined by the condition of the osmotic pressure being equal to zero:

$$P(\rho_g)/T = B\rho_g - \pi^{1/2}(\rho_g l/m)^{3/2}/3 = 0 \tag{5}$$

Further dilution would lead to separation of PES into two phases, with the monomer concentration, ρ_g, in one phase and zero in the other. (Factually the concentration in the dilute phase is never equal to zero, since the value of N is large but finite.)

The phase separation in an uncharged polymer solution usually leads to the incompatibility of polymers, i.e., to separation of polymer components into different phases. On the contrary for the case of PES the electroneutrality condition demands that both polymer components (oppositely charged polyions) should precipitate in the same phase.[2,13] According to the theory of polymer globule,[6] the phase separation in the symmetric PES occurs by means of the formation of globular complexes composed of oppositely charged polyions, which then precipitate. This becomes still more evident if one considers the process of dissolution of the condensed phase (coacervate).

As was mentioned above, the concentration of the dilute phase is so small at large N that one can neglect the osmotic pressure of the dilute polyions equaled to the osmotic pressure of the coacervate. Therefore, the volume of the coacervate, determined by the well-known Maxwell rule,[11] decreases with the decrease of the mean (taken over the total volume, V) concentration of monomers. Owing to the condition of electroneutrality, the dissolution of the coacervate occurs by detaching from it electroneutral complexes, which have equal number k of oppositely charged polyions.

When $N \gg 1$, these complexes become macroscopic systems themselves and consequently can be considered as coacervate drops with the monomer concentration also determined by eq 5, that is, by the balance between the DH attraction and the excluded-volume repulsion of monomers. (This last statement corresponds to the so-called large globule or volume approximation,[6] which is valid when the ratio L_s/R_g is small; here $R_g = (N/\rho_g)^{1/3}$ is the radius of the globular complex, and L_s is the width of the surface layer independent of N. Detachment of such a complex does not change the volume part of the free energy of the system and merely increases its surface energy and the configurational entropy. So the maximum of distribution of these complexes in k moves toward $k = 1$ with increasing V. Thus in the limit of complete coacervate dissolution the solution will contain electroneutral polymer globules and not electrostatically swelled polymer coils.

Now let us compare our approach to the PEC structure with that of refs 2–4. Although in refs 2–4 the dilute phase is also described as a solution of complexes of oppositely charged polyions, these complexes are considered not as the globules but as swelled or contracted Gaussian coils. The expansion factor of the coil is determined by minimization of its free energy. This approach, which was natural for the pioneer work on the coil-globule transition,[14] is inadequate after the development of the theory of polymer globules because the former overestimates substantially the entropy loss due to contraction of the coil to a globule and consequently overestimates the radius of a complex.

Different descriptions of PEC structure lead to different interpretations of the mechanism of complex coacervation. In refs 2–4 coacervation is considered to be a result of the attraction of the neutral PEC due to the modified Flory–Krigbaum potential, which takes into account the Coulombic interaction. The radius of a complex is a characteristic scale of this potential, but it is overestimated in these approaches, so the interaction is also overestimated. From the point of view of the polymer globule,[6] the coacervation of globular PEC is the surface coagulation, which results from the condition of minimization of surface energy of all PEC. This description will be shown (section V) to be much simpler. For example, salt effects in ref 4 are treated using a rather sophisticated modification of the Flory–Krigbaum potential, the quantity of salt bounded by PEC being an adjustable parameter. Within our approach this parameter can be easily calculated.

Another important difference of our approach from that of refs 2–4 is a rigorous accounting for the fluctuation Coulombic energy, which in general does not coincide with the DH approximation.

B. On the Theory of Polymer Globules. We describe the PEC structure within the framework of the theory of polymer globules of Lifshitz and Grosberg[15,16] (see also refs 6 and 17). Now we recall some details of this theory, which are necessary for further consideration. Let us begin with a large globule (volume) approximation. In this approximation the monomer concentration in a globule can be considered constant and equal to that in the center of the globule. Then the conditions of the thermodynamic equilibrium of a globule in a solvent (which we assume to be incompressible) have the form

$$P^*(\rho_g) = P(\rho_g,c_g) - P(c_s) = 0 \qquad (6)$$

$$\mu_s(c_s) = \mu_s(\rho_g,c_g) \qquad (7)$$

where ρ_g is the monomer concentration in a globule, c_g and c_s are salt concentrations in a globule and in the solution, respectively (for simplicity we consider a 1 + 1 salt and c_g is the total concentration of positively and negatively charged ions), $P(c_s)$ is the osmotic pressure of salt in the solution, $P(\rho,c_g)$ is the osmotic pressure of monomers and salt in the globule (which coincides[6] with the osmotic pressure of a salt containing semidilute PES at $N \Rightarrow \infty$), $\mu_s(c_s)$ and $\mu_s(\rho,c_g)$ are the chemical potentials of salt ions in the solution and in the globule respectively, and $P^*(\rho)$ is the effective osmotic pressure of monomers in the globule. Equations 6 and 7 describe properties of a globule in the volume approximation.

Surface properties of a globule are determined by the chemical potential of monomers in a globule $\mu_m(\rho,c_g(\rho))$ (further designated as $\mu_m(\rho)$), where the function $c_g(\rho)$ is the solution of eq 7. This chemical potential also coincides with the one of a semidilute PES, i.e., chemical potential of monomers with the degree of polymerization of solution $N \Rightarrow \infty$. Equations that determine a profile of a monomer and salt concentrations in a globule have the form[6]

$$\hat{g}\psi = \lambda\nu(\psi); \quad \rho = \psi\nu(\psi); \quad \nu = \rho^{1/2}\exp(\mu/2T) \qquad (8)$$

where $\lambda = \exp(-\mu_m(\rho_g)/T)$, operator $\hat{g}\psi = \int g(x-y)\,\psi(y)\,d^3y$, and $g(x) = (3/2\pi a^2)^{-3/2}\exp(-3x^2/2a^2)$ is a function of linear memory for the model "beads on a filament",[6] ρ being the monomer concentration in a globule in the volume approximation. Equation 8 was obtained in refs 15 and 16 for a single macromolecule, but they can be applied for globular complexes containing two or more macromolecules, if only the degree of polymerization, N, of globule components is not too small: $R \gg L_s$.

The free energy of a globule (more exactly the increment of the free energy with respect to the free energy level of an ideal coil) can be easily obtained[6]

$$F/T = -N\ln\lambda + 4\pi R_g^{\,2}\sigma(T) \qquad (9)$$

where R_g is the radius of the globule and

$$\sigma(T) = -\int_{-\infty}^{+\infty} P^*(\rho(x))\,dx \qquad (10)$$

is the surface tension of the globule. Integration in eq 10 is one-dimensional over the globule radius and the function $\rho(x)$ is determined as the solution of eq 8. The quantity $P^*(\rho(x))$ differs from zero only in the surface layer, since $P^*(\rho_g) = 0$ (see eq 6).

Under the condition $R_g \gg L_s \gg a$, which is assumed to hold in our case, eq 8 becomes one-dimensional:

$$(a^2/6)(d^2\psi/dx^2) = \lambda\,\nu(\psi) - \psi \qquad (8a)$$

From eq 8a one can calculate the width of the surface layer $L_s = L_1 + L_2$, where

$$L_1 = a/(\lambda - 1)^{1/2}; \quad L_2 = a/(\lambda(\partial\nu/\partial\psi) - 1)^{1/2} \qquad (11)$$

Using eqs 8 and 8a we finally arrive at

$$\lambda\,\partial\nu/\partial\psi = [1 + (\rho/T)(d\mu/d\rho)]/[1 - (\rho/T)\,(d\mu/d\rho)] \qquad (11a)$$

and the surface tension can be obtained from eqs 8, 8a, and 10 in the form

$$\sigma(T) = aT\int_0^{\rho_g}[A(\rho)\,(1-2(\rho/T)\,(\mathrm{d}\mu_m/\mathrm{d}\rho))\times \exp(-\mu_m(\rho)/2T)\,\mathrm{d}\rho/2\rho^{1/2}]/[\{(\rho+A(\rho))\times \exp(-\mu_m(\rho_g)/T)-\rho\exp(-\mu_m(\rho)/T)\}^{1/2}] \quad (12)$$

where

$$T\,A(\rho) = \int_0^{\rho}\mu_m(\rho')\,\mathrm{d}\rho' - \rho\,\mu_m(\rho) \quad (12a)$$

and ρ_g is determined from eqs 6 and 7.

The value of σ can be estimated from the following simple expression, which is readily derived from eq 10:

$$\sigma \simeq \mu(\rho_g)\,\rho_g L_s \quad (12b)$$

For further consideration of PEC properties we need explicit expressions for $\mu_m(\rho)$, $\mu_s(\rho,c)$, and $P(\rho,c)$ for the case of semidilute weakly charged PES (in the limit $N \Rightarrow \infty$). This problem has been solved by the authors in ref 7.

III. PEC in the Volume Approximation

A. Equation of State for Semidilute Weakly Charged PES. To facilitate understanding of this paper, recall now some relevant results, obtained in ref 7. Free energy of a semidilute PES consists of the free energy F_o of the basic polymer solution (the solution equivalent to the original polyelectrolyte one but in which all charges are supposed to be equal to zero) and of the Coulombic fluctuation contribution, ΔF_{cl}. Depending on the value of perturbation parameter

$$\eta = (B/a^3)/(B\rho)^{1/2}$$

(see refs 13 and 18) the basic polymer solution can be described in the Flory–Huggins approximation (if $\eta \ll 1$) or it can be chosen in the scaling form $F_o = VT/\xi^3$ (if $\eta \gg 1$).[13] ξ is the correlation radius of the basic polymer solution.

It is convenient to characterize a PE solution in terms of the following parameters (interpolation expressions are given, which hold for all the range of η; these expressions correspond to the case of weakly fluctuating basic polymer solution,[7] described by Edwards,[18] when $\eta \ll 1$, and to the scaling case,[13,19] when $\eta \gg 1$):

$$\xi = a(1+\eta)^{1/2}/(24B\rho)^{1/2} \quad (13)$$

is the correlation radius of the basic polymer solution (here and below the polymer volume fraction is assumed to be small).

$$r_s = [4\pi ua(c+\rho/m)]^{-1/2} \quad (14)$$

is the radius of DH screening by salt and by the polymer system of "separate monomers"[7] (the system where all bonds between monomers are considered to be broken).

$$r_o = a[m^2(1+\eta)^{1/2}/(48\pi\rho a^3)]^{1/4} \quad (15)$$

is the radius of specific polymer screening. It is also useful to determine the dimensionless parameters:

$$s = r_o^2/r_s^2 \qquad t = r_o^2/\xi^2 \quad (16)$$

For consideration of the coacervation phenomena only those values of s and t are essential, which correspond to the region where the sum of the contribution to the osmotic pressure of the basic polymer solution and the electrostatic interaction one approximately equals zero. It was shown in ref 7 that in this region the inequality $r_o \ll \xi$ is fulfilled. Moreover the width of the PEC surface layer L_s will be shown below to be of the order of $L_s \cong \xi$. So the condition $r_o \ll \xi$ is equivalent to $r_o \ll L_s$ and enables us to use for $\mu_m(\rho)$ the expressions obtained for a semidilute solution in ref 7. Indeed, r_o is a characteristic scale of averaging for $\mu_m(\rho)$ and $\sigma_o \ll L_s$. This condition leads to $t \ll 1$ and so we can let $t = 0$. (For scaling regimes this leads only to a change of numerical multipliers for this regime.) Then as was shown in ref 7 Coulombic contribution to the free energy of the system equals

$$\Delta F_{cl} = VT(1-s)(2+s)^{1/2}/(12\pi r_o^3) \quad (17)$$

When $s \ll 1$, eq 17 coincides with the well-known DH expression.[7,11]

For the scaling regime of a basic polymer system with a high salt concentration it is necessary to use another expression obtained in the Appendix 2 of ref 7. The characteristic scale of specifically polymer screening is also slightly changed in this case (critical indexes are chosen in the Flory approximation[13]):

$$r_{of} = a(m^2/u\rho a^3)^{3/11}(B/a^3)^{1/11}; \quad s_f = r_{of}/r_s \quad (18)$$

and

$$\Delta F_{cl} = -(VT/12\pi r_s^3) + (VT/r_{of}^3)(s_f^{-1/3} - s_f^{-9/5}) \quad (19)$$

Equations 17 and 19 for the Coulombic contribution to the free energy were obtained in ref 7 in the random-phase approximation (RPA), which coincides with the DH one for low molecular weight electrolytes, and are valid when the basic polymer system is relatively homogeneous, i.e., when the electrostatic blobs (fragments of chains with electrostatic energy being of the order of T) overlap (see refs 7 and 8), which implies

$$\rho > \rho^* = u(1+\zeta)^{-5/7} \quad (20)$$

where

$$\zeta = (Bm^{2/3})/(a^3u^{1/3})$$

The RPA is also valid when the salt concentration is sufficiently high

$$r_s \geqslant D = am^{2/3}(1+\zeta)^{2/7}/u^{1/3} \quad (20a)$$

where D is the radius of an electrostatic blob[7,8] and r_s is defined by eq 14. It will be shown below that for PEC at least one of the conditions (20),(20a) is fulfilled.

B. Diagram of States. Thus the expressions for the free energy of a semidilute PES are known; therefore, all the necessary functions P, μ_s, and μ_m can be obtained by conventional methods, and eqs 6 and 7 can be solved. It is convenient to introduce dimensionless concentrations of monomers and salt

$$\tilde{\rho}_g = 4\pi\rho_g ua^3/3 \qquad \tilde{c}_s = 4\pi c_s mua^3/3 \quad (21)$$

and the parameters

$$g = 3^{1/2}u/(2m^{1/2}); \quad \zeta = (Bm^{2/3})/(a^3u^{1/3}); \quad u = 1/a = e^2/(\epsilon Ta) \quad (22)$$

It is also convenient to construct a diagram of states at a fixed value of g within the variables (the dimensionless salt concentration in the solution $\tilde{c}_s$ vs the reduced solvent quality ζ) (Figure 1). When the dimensionless variables eqs 21 and 22, the Flory–Huggins approximation for F_o, and eq 17 for ΔF_{cl} are used, eqs 6 and 7 take the form:

$$\kappa^{-1/2}\tilde{\rho}_g^{\,2} + 3\epsilon\tilde{c}_s/g = \frac{1+s^{-1}+s^{-2}}{(1+2s^{-1})^{1/2}}[(\tilde{\rho}_g+\tilde{c}_g)^{3/2} - \tilde{c}_s^{\,3/2}] \quad (23)$$

$$\ln(1+\epsilon) = g\left[\frac{1+s^{-1}}{(1+2s^{-1})^{1/2}}(\tilde{\rho}_g+\tilde{c}_g)^{1/2} - \tilde{c}_s^{\,1/2}\right] \quad (23a)$$

$\tilde{c}_g$ and $\tilde{c}_s$ are total reduced concentrations of salt ions in

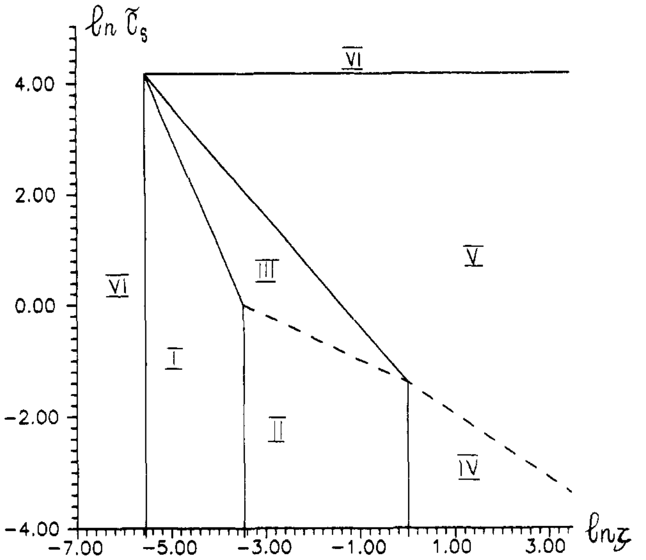

Figure 1. Diagram of states for globular PEC in the dimensionless variables: salt concentration vs reduced solvent quality ($\ln \tilde{c}_s$ vs $\ln \zeta$) for the case $g = 0.125$. The lines divide the regions with different salt (dashed) and fluctuation (solid) regimes.

a globule and solution, respectively ($\tilde{c}_g = \tilde{c}_s(1 + \epsilon)$) and

$$\kappa = [2\pi u^2 a^3/B]^2/(3m)^3 = 2.36 g^{10/3}/\zeta^2 \tag{24a}$$

$$s = (\tilde{\rho}_g + \tilde{c}_g)/2\tilde{\rho}_g^{1/2} \tag{24b}$$

We suppose for simplicity that the interaction of the ions of salt is purely electrostatic and terms of the order of ϕ_g^3 in eqs 23 and 23a are negligible. It can be easily seen from eq 23a that $\epsilon > 0$. It means certain absorption of salt by a globule, which creates an additional osmotic pressure, playing an essential role in PEC formation. Note that the surplus salt concentration ϵ is always of the same order of magnitude as the polymer volume fraction in a globule. Since the latter is supposed to be small, it is sufficient to retain in eqs 23 and 23a only terms of the first relevant order in ϵ. This gives $s = (\tilde{\rho}_g + \tilde{c}_s)/2\tilde{\rho}_g^{1/2}$, and from eqs 23 and 23a we get

$$\tilde{\rho}_g^2 \kappa^{-1/2} - \left[\frac{1 + s^{-1} + s^{-2}}{(1 + 2s^{-1})^{1/2}}(\tilde{\rho}_g + \tilde{c}_s)^{3/2} - \tilde{c}_s^{3/2}\right] + 3\tilde{c}_s\left[\frac{1 + s^{-1}}{(1 + 2s^{-1})^{1/2}}(\tilde{\rho}_g + \tilde{c}_s)^{1/2} - \tilde{c}_s^{1/2}\right] = 0 \tag{25}$$

Let us consider now the solutions of eq 25 $\tilde{\rho}_g(\tilde{c}_s)$ in different characteristic regions of the diagram ($\tilde{c}_s - \zeta$) (see Figure 1). The diagram of states considered in this paper should not be confused with the phase diagram. The regions of the diagram of states correspond not to the different phases of PEC but to the different fluctuation regimes of the system, accordingly the boundary lines are not the phase-transition lines but only the crossover ones.

Region I. The DH Approximation. In this region, $\kappa \gg 1$, $\tilde{\rho}_g \gg 1$, and $s \gg 1$. This case corresponds in fact to the DH approximation for the Coulombic contribution ΔF_{cl} (i.e., s is set equal to infinity in eq 25). The solution of eq 25 in this approximation has the form

$$\tilde{\rho}_g(\tilde{c}_s) = \begin{cases} \kappa - 3\tilde{c}_s & \tilde{c}_s \ll \kappa \\ 6(\tilde{c}_* - \tilde{c}_s)/7 & \tilde{c}_s - \tilde{c}_* \ll \kappa \\ 0 & \tilde{c}_* \leq \tilde{c}_s \end{cases} \tag{26}$$

where $\tilde{c}_* = 9\kappa/16$. The solution is plotted in Figure 2 (solid line 1). It can be seen that in the DH approximation a globule exists only when $\tilde{c}_s = \tilde{c}_*$. Therefore, the line $\tilde{c}_s = \tilde{c}_*$ (boundary of regions I–III) is the line of phase transition where PEC is expected to dissociate into single polyions. This result, however, is an artifact of the DH approximation. In fact this line is just a crossover line (see below), where the asymptote (eq 26) transforms to the asymptote of region III. Representation (eq 26) is valid only in region I.

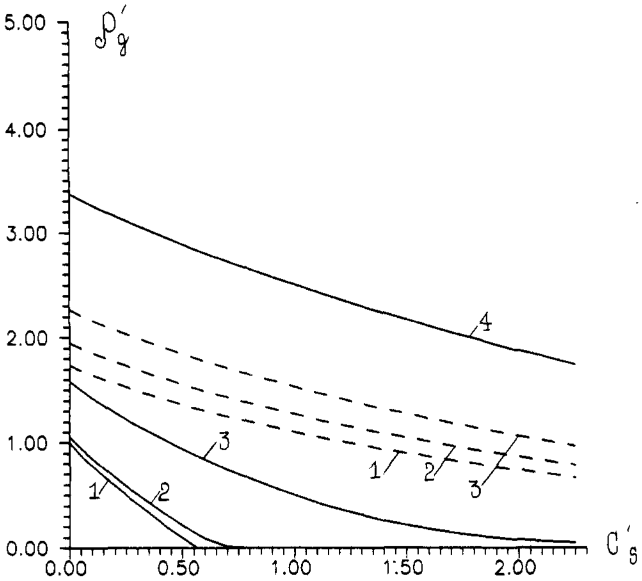

Figure 2. Numerical solutions of the eq 25 for the dimensionless monomer concentration in the globule ρ_g' as a function of the dimensionless salt concentration c_s'. For solid lines $\rho_g' = \tilde{\rho}_g/\kappa$, $c_s' = \tilde{c}_s/\kappa$; for dashed lines $\rho_g' = \tilde{\rho}_g/\kappa^{2/5}$, $c_s' = \tilde{c}_s/\kappa^{1/5}$. Solid lines 1–4 correspond to $\kappa = \infty$ (the DH limit), 160, 9, and 1, respectively. Dashed lines 1–3 correspond to $\kappa = 0$ (parametrization (eq 32)), 2^{-10}, and 2^{-5}, respectively.

A numerical solution of eq 25 at certain values of κ is shown in Figure 2. It can be seen that the systematic error of the DH approximation (eq 26) increases with the decrease of κ. The DH approximation underestimates coacervate density and overestimates PEC swelling by salt in comparison with the results of the rigorous treatment. This discrepancy is readily understood if one recalls that the DH attraction, which plays the key role in these phenomena, is mainly determined by spatial fluctuations of the charge density. The attraction increases with an increase of fluctuations; thus the former may be called fluctuational. The difference between factual correlations of these fluctuations in PES and those in the DH approximation was shown[7] to increase with a decrease of s, at small s fluctuations being solely a polymeric effect. Fluctuations for polyelectrolyte are stronger than those for unconnected charges, and thus the fluctuation attraction is also stronger than in the DH case.

Boundaries of region I are determined as follows. For I–II, $\kappa \cong 1$ or $\zeta \cong g^{5/3}$ (in region II the DH approximation is not applicable). For I–III, $\tilde{c}^* = \tilde{c}_s$ or $\tilde{c}_s = g^{10/9}/\zeta^2$. For I–IV, see below.

Regions II and III. In these regions the basic polymer system can be considered in the mean-field approximation, but the fluctuation electrostatic attraction is substantially renormalized by the influence of the linear memory of macromolecules.

In region II $\kappa \ll 1$, $\tilde{\rho}_g \ll 1$, $s \ll 1$, and $\tilde{c}_s \ll \kappa^{1/5}$. Using eq 25, we obtain the solution, which is valid in the internal part of region II:

$$\tilde{\rho}_g(\tilde{c}_s) = 1.74\kappa^{2/5} - 1.19\kappa^{1/5}\tilde{c}_s \tag{27}$$

Reducing eqs 26 and 27 to more conventional notation, we obtain the following expression for the coacervate volume fraction:

$$\phi_g = B\rho_g = \begin{cases} \pi l^3/9Bm^3 & \kappa \gg 1 \\ (Bl^3/12\pi m^6 a^6)^{1/5} & \kappa \leq 1 \end{cases} \tag{28}$$

It can be seen that ϕ_g decreases with an increase of B or with a decrease of the electrostatic interaction parameter g. However, in region II, where $\kappa \ll 1$, linear memory of polymer results in a much slower decrease of ϕ_g and also in its dependence on the statistical segment length a.

Boundaries of region II are determined as follows: II–III, $\tilde{c}_s \cong \kappa^{1/5}$ or $\tilde{c}_s \cong g^{2/3}/\zeta^{2/5}$; II–IV, $\zeta \cong 1$ (see below).

In region III $\tilde{\rho}_g \ll 1$, $\tilde{\rho}_g \ll \tilde{c}_s$. Performing the necessary simplifications we get from eq 25

$$\tilde{\rho}_g = 64\kappa/\tilde{c}_s^{\,3} \tag{29}$$

This asymptote is valid in the internal part of region III. Crossover from region I to region III is described by the following asymptote, obtained from eq 25:

$$\tilde{\rho}_g(\tilde{c}_s) = \begin{cases} 6(\tilde{c}_* - \tilde{c}_s)/7 & 1 \ll \tilde{c}_* - \tilde{c}_s \ll \kappa \\ 6.94\kappa & \tilde{c}_s = \tilde{c}_* = 9\kappa/16 \\ 64\kappa/[\tilde{c}_s^{\,2}(\tilde{c}_s^{\,1/2} - \tilde{c}_*^{\,1/2})^2] & \tilde{c}_s - \tilde{c}_* \gg 1 \end{cases} \tag{30}$$

For a description of regions II and III (where $\tilde{\rho}_g \ll 1$) a convenient parametrization can be obtained

$$\tilde{\rho}_g^{\,5/4} = 2\kappa^{1/2}\{1 - 2\alpha[\alpha + 1 - ((\alpha + 1)^2 - 1)^{1/2}]\}/(1 + \alpha/2)^{1/2}$$

$$\tilde{c}_s = 2\alpha\rho_g^{\,1/2} \tag{31}$$

with $0 \leq \alpha < \infty$. The limits of the validity of this parametrization can be seen from Figure 2.

Thus while in the DH approximation globular PEC and hence a coacervate can exist only in the region separated from the rest of the diagram by the second-order phase-transition line; in a more rigorous consideration this line appears to be merely a crossover line, and the region of PEC existence broadens substantially.

Until now we have been considering the structure of PEC in the volume approximation under the assumption of a weakly fluctuating basic polymer solution ($\eta = (B/a^3)/(B\rho)^{1/2} \ll 1$). This assumption fails when $\eta = g^{2/3}\zeta^{1/2}/\tilde{\rho}_g^{1/2} \leq 1$, at low salt concentrations (see eqs 20 and 21). Using eq 27, we can get that in region II $\zeta \leq 1$. The boundary II–IV is given by the condition $\zeta \leq 1$. When the salt concentration is high, the monomer concentration ρ_g is determined by eq 29 and the condition $\zeta \cong 1$ reduces to $\tilde{c}_s \cong g^{2/3}/\zeta$, which results in the equation for the boundary III–V.

Regions IV and V. As has been mentioned above, here the basic polymer system is in a scaling regime $\eta \gg 1$. Let us consider first the low salt concentration case ($s \ll 1$, region IV). Then eq 6 with regard for eqs 13, 15, and 17 reduces to

$$P_*(\rho_g)/T = \xi^{-3} - r_o^{-3} \tag{32}$$

where in scaling regimes all numerical multipliers are omitted. From eq 32 we get the solution

$$\tilde{\rho}_g = g^{4/3}/\zeta^{5/7} \tag{33}$$

It is useful to compare this expression for $\tilde{\rho}_g$ with one in the region II; see eq 27. In the region IV the decrease of $\tilde{\rho}_g$ with an increase of ζ is slower. For $\zeta \cong 1$ both expressions coincide.

Now let us consider the scaling regime at high salt concentrations, $s \gg 1$ (or, which is the same according to eq 18, $s_f \gg 1$). In this regime (region V) the Coulomb contribution to the free energy is determined by eq 19. Using the conventional formula, we can transform eqs 6 and 7 to

$$\xi^{-3} + c_g - c_s - (3r_{of}^{\,3}s_f)^{-1} + (3r_{of}^{\,3}s_f^{\,9/5})^{-1} = 0$$

$$c_g - c_s - (3r_{of}^{\,3}s_f)^{-1} = 9/[5r_{of}^{\,3}s_f^{\,9/5}] \tag{34}$$

In eq 34 numerical constants are retained because in this case only their relative values are important. Indeed due to sucking of salt into the PEC, term $(3r_{of}^{\,3}s_f)^{-1}$ in the first part of eq 34 is canceled with the same term from the second part of eq 34. Then the equation of equilibrium for the globule takes the form

$$\xi^{-3} = 4/[5r_{of}^{\,3}s_f^{\,9/5}] \tag{35}$$

and finally gives

$$\tilde{\rho}_g(\tilde{c}_s) = g^4/[\tilde{c}_s^{\,4}\zeta^3] \tag{36}$$

On the boundary III–V eq 36 coincides with eq 29 obtained in the mean-field approximation. Thus in the scaling regime V the monomer concentration in PEC decreases with an increase of salt concentration faster than in region III. The condition $s \cong s_f \cong 1$, which results in $\tilde{c}_s \cong g^{2/3}/\zeta^{4/7}$, determines the boundary IV–V.

Region VI. In this region the DH approximation is violated from the high concentration side. Indeed, the salt concentration can not be too high and must satisfy to the inequality $c_s a^3 u^3 \ll 1$ (see ref 11) or $\tilde{c}_s \ll g^{-2}$ (this gives the boundary V–VI). For small B (i.e., ζ) PEC becomes very dense, and the DH approximation fails from the high ρ side; the density of charged monomers becomes high. Using eq 26 this gives similar to the salt case $\zeta \geq g^{8/3}$ (the boundary I–VI). In region VI the equation of state of PES should be obtained using a more sophisticated approximation than the random-phase one.

In summary it is convenient to list all the equations for the boundaries (see Figure 1):

$$\begin{gathered} \text{I–II: } \zeta \cong g^{5/3} \qquad \text{I–III: } \tilde{c}_s \cong g^{10/3}/\zeta^2 \\ \text{I–VI: } \zeta \cong g^{8/3} \qquad \text{II–III: } \tilde{c}_s \cong g^{2/3}/\zeta^{2/5} \\ \text{II–IV: } \zeta \cong 1 \qquad \text{III–V: } \tilde{c}_s \cong g^{2/3}/\zeta \\ \text{IV–V: } \tilde{c}_s \cong g^{2/3}/\zeta^{4/7} \qquad \text{V–VI: } \tilde{c}_s \cong g^{-2} \end{gathered} \tag{37}$$

C. Applicability of the Random-Phase Approximation (RPA). Parameters of PEC were obtained in the volume approximation based on the expressions for the free energy of PES, which are valid only in the RPA. It was shown in IIIA that the RPA holds when at least one of eqs 20 or 20a is valid, which in dimensionless variables gives

$$\tilde{\rho}_g \geq \tilde{\rho}_* = g^{4/3}(1 + \zeta)^{-5/7}; \quad \tilde{c}_s \geq g^{2/3}(1 + \zeta)^{-4/7} \tag{38}$$

From eq 37 it can be seen that the second inequality is valid in the part of region I and in regions III and V. In region I from eqs 24 and 26 and the condition $\zeta \leq g^{5/3} \ll 1$ we obtain $\tilde{\rho}_g \simeq g^{10/3}/\zeta^2 \gg \tilde{\rho}_*$, so the first inequality in eq 38 is valid. In the region II using eqs 24 and 27 and the condition $\zeta \ll 1$, we obtain $\tilde{\rho}_g \simeq g^{4/3}/\zeta^{4/5} \gg \tilde{\rho}_*$, so eq 38 is also valid. In region IV eq 33 gives $\rho_g \simeq \rho_*$ or $\xi \simeq r_o$. Therefore, in this region the RPA is valid only to within a numerical multiplier, which is quite natural and satisfactory for the theory of scaling type.[13] Thus the RPA can be applied to the theory of globular PEC.

In this paper we assume that the polymer volume fraction is small. This condition can be violated only in region I. But it can be shown that the conditions $\phi_g \simeq 1$

and $\zeta \simeq g^{8/3}/m$ are equivalent. So if the RPA is valid, ϕ_g will always be small.

IV. Surface Properties of PEC

Let us consider now properties of the PEC surface layer, assuming first that $\eta \ll 1$ (the basic polymer solution is weakly fluctuating). Then using eq 17 for the free energy we obtain the chemical potential of monomers (in the limit $N \Rightarrow \infty$) in the form:

$$\frac{\mu_m(\tilde\rho)}{T} = \frac{2g}{3m\kappa^{1/2}}\left[\tilde\rho + \frac{3\kappa^{1/2}[1 - \tilde\rho^{1/2}(1+s)/2]}{\tilde\rho^{1/4}(1+s/2)^{1/2}}\right] \equiv \frac{2g\tilde\mu_m(\tilde\rho)}{3Tm\kappa^{1/2}} \tag{39}$$

It is easy to see that when $\tilde\rho = \tilde\rho_g$, both right-hand terms in eq 39 are of the same order of magnitude and hence $\mu_m(\rho_g)/T = \phi_g \ll 1$. So from eqs 12 and 12a it follows that $L_s \approx L_1 \approx L_2 \approx a/\phi_g^{1/2}$; that is, the width of surface layer coincides with the correlation radius, ξ, of the basic polymer system. This is also valid for scaling regimes in the regions V and IV.

It has been shown in IIA that eq 39 can be used to determine surface properties of PEC if L_s is much larger than the characteristic scale of screening. It is clear that L_s increases and the scale of the screening, on the contrary, decreases when the salt concentration increases, which corresponds to globule swelling. Hence, it is sufficient to verify the above-mentioned inequality for $c_s = 0$. In this case the radius of screening is r_o (see eq 15), and it follows from eqs 24, 26, and 27 that $t = r_o^2/\zeta^2 = \tilde\rho_g^{1/2}\zeta/g^{2/3}$, and in the region I, $t \approx g \ll 1$ (since $\xi \ll 1$). Hence, $r_o \ll L_s$.

Using $\tilde\mu_m(\tilde\rho)$ and eq 12, we can now calculate surface tension, σ. It is necessary to point out that eq 39 is valid only for not too small ρ (see eq 38). On the PEC boundary $\rho \to 0$ and eq 38 is violated. If $\tilde c_s > g^{2/3}$, eq 39 can be used for all ρ. This is true in certain parts if the regions I and II and in region III. For $\tilde c_s \leqslant g^{2/3}$ the eq 39 is valid until $\tilde\rho \geqslant \tilde\rho_*$. Nevertheless, eq 39 can be used for calculation of σ, since the width of surface layer where $\tilde\rho \ll \tilde\rho_*$ is small ($\tilde\rho_g \gg \tilde\rho$, see section IIIC) and its contribution leads to the minor changes of the numerical coefficient in the expression for σ.

Thus, it is reasonable to begin with a simple estimation of σ using eq 12a, which with regard to eq 39 gives

$$\sigma = \alpha a T B^{1/2}\rho_g^{3/2} = 0.1\alpha T\zeta^{1/2}\tilde\rho_g^{3/2}/(a^2 m g^{4/3}) \tag{40}$$

where α is a numerical constant of the order of unity. As it was argued above it cannot be defined exactly for all the regions of diagram of states. Using eq 12 and retaining only the terms of the relevant order in ϕ, we obtain

$$\alpha = \int_0^{\rho_g} \frac{d\tilde\rho/(2\tilde\rho)^{1/2} TA(\tilde\rho)}{\tilde\rho_g^{3/2}\{TA(\tilde\rho)\}^{1/2}} \tag{41}$$

where $A(\tilde\rho)$ is determined by eq 12a with the change $\rho \to \tilde\rho$ and $\mu_m(\rho) \Rightarrow \tilde\mu_m(\tilde\rho)$.

Numerical calculations show that in the regions I and III α is approximately constant and is equal to 0.33. In region II α increases up to 0.67, which may be connected with some inaccuracy of eq 39 in this region.

Until now the surface properties of PEC were discussed only in regions I–III, where the basic polymer solution is weakly fluctuating. In the regions IV–V the basic polymer system is in the scaling regime. So taking into account the estimation (eq 12a) for σ and the fact that in the scaling regimine $\mu_m(\rho)/T \simeq 1/(\rho\xi^3)$ and $L_s \cong \xi$, we obtain (see also ref 13)

$$\sigma \cong T/\xi^2 = aTB^{1/2}\rho_g^{3/2} = T\zeta^{1/2}\tilde\rho_g^{3/2}/(a^2 m g^{4/3}) \tag{42}$$

This estimation can be seen to coincide with the one in the mean-field approximation (eq 40). Thus estimations (eqs 40 and 42) are valid in the whole range of parameters within the numerical constant precision α (which was calculated above).

V. Complex Coacervation

It is not the aim of the present work to investigate in detail such a complicated problem as complex coacervation. We shall just consider some aspects, which can be understood on the basis of our concepts at least qualitatively.

Coacervation as Precipitation of Globules. Complex coacervation for symmetrical PES was described as precipitation of globules in IIA. Here we shall consider this problem in more detail.

Our approach to the complex coacervation is based on the volume approximation, which is valid at sufficiently high degrees of polymerization of polyions; that is, $R_g \cong (N/\rho_g)^{1/3} \gg L_s$. In this situation the precipitation of globules leads to a gain in the free energy due to the decrease of area of the interface between the globular phase and solvent σR_g^2. However, there is a loss in the free energy of the relative motion of globules $\cong T \ln(\rho_g/\rho_s)$, where ρ_s is the average concentration of monomers in the uncondensed phase (since the volume fraction of globules in the solution equals $\rho_g/\rho_s = \rho_s R_g^3/2N$). Thus, to a precision of a numerical constant

$$\ln(\rho_g/\rho_s) = (\sigma/T)(N/\rho_g)^{2/3} \tag{43}$$

and using eq 40, we get the expression for ρ_s

$$\rho_s = \rho_g \exp\{-\gamma\zeta^{1/2}\rho_g^{5/6}(N/gm)^{2/3}\} \tag{44}$$

where γ is an unknown numerical constant.

An increase of the salt concentration leads to a decrease of ρ_g and σ and to the increase of the width of the PEC surface layer (the swelling of PEC). Obviously, this makes PEC less likely to precipitate and results in an increase of ρ_s, which is a well-known phenomenon of complex coacervation suppression by salt.[2]

However, the eq 44 can be used only until the globule swelling is not too large ($L_s \ll R_g$), which surely does not hold near the critical salt concentration, where complex coacervation is completely suppressed. For a description of PEC precipitation near the critical salt concentration, it is already insufficient to consider PEC as a globule, since the terms on the order of $1/N$ now become significant. Following ref 13, we estimate the critical salt concentration using the Flory–Huggins approximation. Applying conventional methods of calculations,[13] we arrive at the result that the coacervation is suppressed when the monomer volume fraction in the coacervate (or PEC) ϕ_g is on the order of $N^{-1/2}$. When the dependence $\phi_g(c_s)$, which is provided by our theory of PEC is used, it is possible to obtain critical values of c_s, corresponding to suppression of complex coacervation for each region of the diagram in Figure 1.

It is known[2] that salt can cause not only suppression of coacervation but also its enhancement. From our point of view this phenomenon can be explained taking into account the nonelectrostatic van der Waals interaction between monomers and salt ions (neglected in this paper). The methods of accounting for this interaction were presented in ref 7, and it has been shown that this interaction leads to selective absorption of salt ions on previously uncharged monomers and thus induces an effective charge, which depends on the salt concentration. This changes PEC parameters, which results in changes of σ and ρ, and can lead to coacervation enhancement by salt. More thorough investigation of this effect is outside the scope of the present paper.

Effect of Polydispersity. The most simple generalization of the considered symmetrical monodisperse PES is a symmetrical polydisperse PES. In the solution of this kind for every polyion of a certain charge with the degree of polymerization, N, there exists a polyion with the same N and with equal charge of the opposite sign. Experiments for such a solution were described in ref 2. In this case neutral globular PEC of different sizes are formed. PECs with the largest degree of polymerization precipitate first (see eq 44). The increase of ρ_s will lead to precipitation of PEC with smaller N, and thus the selective precipitation of PEC with respect to the degree of polymerization will occur, which is just the case, observed experimentally in ref 2.

It is also easy to explain the so-called "electroneutrality" of a coacervate (see ref 2), i.e., the fact that complexes are not usually formed of polyions with significantly different charges in which case charge compensation could take place through sucking of counterions into PEC. Indeed, the entropy of counterions is enormous as compared with that of charged monomers in a chain. Therefore, their binding to PEC creates a surplus osmotic pressure destroying PEC. The maximal number of counterions N_c that can be bound to PEC without its destruction can be estimated as $N_c \cong \rho_g^2 B/R_g^3$, which corresponds to approximate equality of the surplus osmotic pressure of counterions TN_c/R_g^3 to the fluctuation Coulombic attraction $T\rho_g^2 B$.

For asymmetric PEC formed by polyions with unequal charges beside the phenomenon of counterion binding there can exist a surplus surface charge of PEC. This charge can suppress complex coacervation to some extent, because it effectively decreases the surface tension. When asymmetry of PEC is increased, the structure of the complex can change drastically. For example, a surplus charge can create a rodlike tail coming from the PEC globular core.

Microstructure of PEC. If polyions forming PEC are thermodynamically incompatible due to short-range interaction, microphase separation into small oppositely charged domains can occur (see ref 7). If the size of the domains is smaller than the PEC size, the microstructure of PEC can be observed experimentally. Moreover, it can be observed in the coacervate phase. Some indications of such observations were given in ref 2.

VI. Conclusions

In this paper we have described the structure of symmetrical polyelectrolyte complexes using the concept of polymer globules. Globular structure is formed owing to the balance between the excluded-volume interaction and the fluctuation contribution of Coulombic interaction to free energy, which was previously calculated by us for polyelectrolyte solution.[7] Linear memory of polymers was shown to play the essential role in determination of this fluctuation energy; namely, in the limit $N \Rightarrow \infty$ it always leads to the coacervation in contrast with DH approximation, where the coacervation is erroneously described as the phase transition. The equilibrium monomer concentration, the width of the PEC surface layer, and the surface tension were also calculated. The diagram of the various fluctuation regimes (the diagram of states) was constructed. The different regions of the diagram correspond to the different dependencies of PEC density on the salt concentration.

We considered only the case of PEC with sufficiently high degree of polymerization N. When the density of PEC decreases (e.g., salt concentration is high), the globule approximation fails, and more thorough treatment is needed, in particular, to determine the region of PEC stability for finite N (we determined this region only qualitatively in section V).

The consideration of PEC from the polymer globule point of view simplies the treatment of the effects of the phase separation in polyelectrolyte solutions (complex coacervation). In particular some well-known qualitative features of complex coacervation[2] were naturally explained. Nevertheless, complex coacervation is a complicated problem in which the effects of polydispersity are of great importance. More theoretical and experimental results are needed for a thorough description of the complex coacervation phenomena.

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