Macromolecules **2002,** *35,* 4531−4538

Phase Diagram of Diblock Polyampholyte Solutions

M. Castelnovo* and J. F. Joanny

Institut Charles Sadron, 6 Rue Boussingault, 67083 Strasbourg Cedex, France;
Physico-Chimie, Institut Curie, 11 Rue P. et M. Curie, 75231 Paris Cedex 05, France

Received December 3, 2001; Revised Manuscript Received March 7, 2002

ABSTRACT: We discuss in this paper the phase diagram of a diblock polyampholyte solution in the limit of high ionic strength as a function of concentration and charge asymmetry. This system is shown to be very similar to solutions of so-called charged-neutral diblock copolymers: at zero charge asymmetry, the solution phase separates into a polyelectrolyte complex and almost pure solvent. Above a charge asymmetry threshold, the copolymers are soluble as finite size aggregates. Scaling laws of the aggregates radius as a function of pH of the solution are in qualitative agreement with experiments.

1. Introduction

Mixtures of oppositely charged polyelectrolytes have been studied quite extensively over the last 30 years by various experimental groups.[1−3] There are numerous motivations for these studies such as the similarities with biological systems or the applications to cosmetics and food industries. Depending on the stoichiometry of the mixture, (the relative concentrations, the relative chain lengths, and charge densities), one observes mainly two types of behavior: a macroscopic phase separation between the solvent and the polymers, or a partial aggregation of the polymer chains.[3] In both cases, one speaks about polyelectrolyte complexation. The electrostatic attraction between chains of opposite signs is clearly responsible of this behavior. Despite this simple statement, there is no deep understanding of the underlying mechanisms of polyelectrolyte complexation. The introduction of the polyelectrolyte multilayers concept almost 10 years ago has revived the activity of this research area, mainly due to the numerous potential applications of the multilayers.[4] The principle of the polyelectrolyte multilayers growth is to adsorb sequentially polyelectrolytes of opposite signs on a charged substrate. The adhesion between two consecutive layers is attributed to the complexation between the oppositely charged polyelectrolytes at the interface between layers where they strongly interpenetrate.[5,6]

In a bulk solution, the complex formation is very similar to the demixing phase transition of a neutral polymer solution under poor solvent conditions if the polyelectrolyte mixture is symmetric in charge, i.e., if the polycations and poyanions carry the same charge in absolute value, and their total concentrations are the same: there is a polymer−solvent phase separation. If the mixture is no longer symmetric in charge, soluble complexes carrying a net charge can exist in solution.[3] The aggregation process depends on the charge asymmetry between the polyelectrolytes, but also on the relative concentrations of the polyions. Because of the large number of degrees of freedom, a comprehensive study of an asymmetric polyelectrolyte mixture is quite difficult. Everaers et al. have performed recently a study of solutions of random polyampholytes which are very similar systems.[7] They have allowed both for a macroscopic phase separation and for a finite size aggregation process, but they have restricted themselves to some specific limits for a sake of simplicity. In the case of a mixture of oppositely charged polyelectrolytes, one can suppress 1 degree of freedom by considering diblock polyampholyte solutions. These copolymers are made of two oppositely charged polyelectrolytes chemically linked by one end. The concentrations of polycations and polyanions in the solution are then equal. In particular, each aggregate is characterized by a single aggregation number. In the equivalent polyelectrolyte mixture, where the polyions are not bound, the aggregates are characterized by two aggregation numbers, the number of polycations and polyanions, respectively.

Our aim in this article is to study the phase diagram of diblock polyampholyte solutions as a function of the copolymers charge asymmetry. This is a first step toward a more precise understanding of aggregation processes in mixtures of oppositely charged polyelectrolytes. Diblock polyampholyte solutions have been far less studied experimentally than the equivalent mixture of free polyions. Nevertheless, recent experiments have shown that the aggregates in solution are roughly spherical; they adsorb on charged substrate mostly as micelles, and not as isolated molecules.[8−10] The aggregate sizes can be measured by dynamic light scattering experiments and are of the same order as the size of an adsorbed aggregate. To our knowledge, in all of the existing experiments, the charged groups on the copolymers are pH-dependent. In particular, the copolymer has an isoelectric point at a value pH_i of the pH, where the net charge vanishes. Around the isoelectric point, the solution is not stable: there is a macroscopic phase separation which is attributed to the complexation of the copolymers. For pH values not too close to pH_i, aggregates of diblock polyampholytes form in the solution, but the solution is macroscopically stable. Therefore, our theoretical description must consider both possibilities of macroscopic phase separation and of partial aggregation of the chains in the supernatant. This is achieved in several steps.

In a first step (section 2),[7] we neglect the influence of the supernatant content on the properties of the dense phase for diblock polyampholytes with a quenched homogeneous charge distribution. It has been realized quite early that the properties of polyelectrolyte com-

---

* Corresponding author. Present address: Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, CA 90095.

10.1021/ma012097v CCC: $22.00

plexes can be described in the low charging limit by an equilibrium between the attraction induced by charge fluctuations and the hard core interactions:[2] due to the very low mixing entropy of polymers, polymer mixtures are very sensitive to small interactions.[11] This low mixing entropy is, for example, responsible for the so-called "incompatibility" between neutral polymers. In polyelectrolyte mixtures, the phase diagram is determined by a subtle balance between the incompatibility and complexation transitions.[12] Using our previous results on the complexation between oppositely charged polyelectrolytes in a symmetric mixture, we describe the swelling of the dense phase by increase of the counterion excess osmotic pressure with the asymmetry of the copolymers.[6] In a second step (cf. section 3), the aggregation process is described in the absence of any macroscopic phase separation. By analogy with the associating behavior of charged-neutral diblock copolymers (ionized hydrophilic block−neutral hydrophobic block), we propose that the copolymers form spherical micelles with a neutral core made of symmetric polyelectrolyte complex, and branches carrying the net charge of the aggregates. Finally, the phase diagram is drawn by combining all these results in section 4. We also discuss in this section the effect of "charge annealing" on the properties of the aggregates in the case where the ionizable groups along the blocks are weak acids and weak bases. All the energies in this paper are measured in units of the thermal excitation k_BT.

2. Complexation Thermodynamics of an Asymmetric Polyelectrolyte Mixture

We consider in this section a monodisperse solution of diblock polyampholytes of total degree of polymerization N. We assume that all the chemical properties of the blocks are identical except their charge that are of opposite signs. Let N_+, f_+ and N_-, f_- be respectively the degrees of polymerization and charge densities of the polycationic and polyanionic blocks of the copolymer. We neglect in this paper the effects of charge distribution and assume that the total charge of each block is smeared out along chain. We assume that the solvent is a Θ-solvent and we treat it as a dielectric continuum of dielectric constant ϵ. The monomer size is denoted by a. It is also convenient to introduce the Bjerrum length $l_B = e^2/4\pi\epsilon k_BT$, which represents the typical distance between two elementary charges having an electrostatic energy of k_BT. When the polyampholyte is symmetric in charge, i.e., $N_+f_+ = N_-f_-$, the solution phase separates into a dense phase containing almost all the copolymers and a dilute phase composed mainly of solvent. Within the dense phase, the diblock copolymer concentration (expressed as a number of chains per unit volume) c_{dense} is related to cationic and anionic monomer concentrations c_+ and c_- by $c_+ + c_- = c_{\text{dense}}N$. When $N_+f_+ \neq N_-f_-$, there is an excess charge in the dense phase, which is neutralized by the small ions of the solution. The difference in translational entropy of these ions between the two phases produces an excess osmotic pressure which tends to swell the dense phase. Following the results of ref 6, it is possible to describe the effect of a charge excess in the dense phase by a generalized two phases model. The dense phase is mainly composed of polyampholytes, while the dilute phase is modeled as a simple electrolyte. This amounts to neglecting the formation of finite size aggregates in the supernatant of the solution. This approximation is discussed in the next section. The concentrations of monovalent small ions in the dense phase and in the dilute phase are respectively $n_\pm$ and $n_{\pm 0} = n_0$. The conditions for equilibrium between the two phases are given by the equality of various small ions chemical potentials in the two phases, and the equality of the osmotic pressures. Therefore, we need to compute the free energies in the two phases to write the equilibrium conditions.

As previously mentioned, the formation of polyelectrolyte complexes in symmetric polyelectrolyte mixtures cannot be described at the simplest mean field level: because of the global electroneutrality, there is no pure Coulombic term in the mean field free energy. One has to include at least fluctuations around the electroneutral state at the lowest level to describe the complexation. This can be done within the RPA formalism.[13,14] In the case of a diblock polyampholyte solution, we will assume in a first approximation that the RPA correction to the mean field free energy of the dense phase is the same as that of the equivalent polyelectrolyte mixture where the two blocks are not linked: our aim in this paper is just to describe qualitatively the phase diagram at the level of scaling laws. Nevertheless, it seems possible to calculate more precisely the RPA free energy of the copolymers by using the results of ref 12. This will be the topic of a future work. The RPA free energy density of the dense phase is written

$$F_{\text{dense}} = \frac{w^2}{6}(c_+ + c_-)^3 + \sum_i n_{\text{i}} \log n_i + \Delta F_{\text{dense}} \qquad (1)$$

The first term of eq 1 is the third virial contribution. This is the first hard core repulsive interaction for a polymer in a Θ-solvent. This contribution is necessary to ensure the stability of the complex. The second term is the translational entropy of small ions in the dense phase. Notice that the translational entropy of the copolymers has been neglected because it is of order $1/N$. Finally the last term is the RPA correction to the mean field free energy. It is calculated by associating a Gaussian statistical weight to the concentration fluctuations neglected in the mean field theory.[13] In the case of a symmetric mixture ($f_+c_+ = f_-c_-$), the exact result reads

$$\Delta F_{\text{dense}} = -\left(\frac{\xi_w^{-3}}{12\pi} + \frac{q_*^{3}(s-1)(s+2)^{1/2}}{12\pi}\right) \qquad (2)$$

We introduced in the last equation three characteristic lengths ξ_w, q_*^{-1},κ^{-1} which are defined as follows:

$$\xi_w^{-2} = \frac{12w^2(c_+ + c_-)^2}{a^2}, \quad q_*^{4} = \frac{48\pi l_B(f_+^{2}c_+ + f_-^{2}c_-)}{a^2}, \quad \kappa^2 = 4\pi l_B\left(\sum_i n_i\right)$$

The first length is the correlation length of the equivalent neutral polymer mixture in a Θ-solvent. The two other lengths are associated respectively to the screening of electrostatic interactions by the polyelectrolytes and by the small ions. The dimensionless ratio of these two lengths is denoted $s = \kappa^2/q_*^2$. Notice that, in the symmetrical case, the contribution of fluctuations associated, respectively, with the third virial term and the electrostatics are not coupled. The free energy density of the dilute phase is simply given within the RPA by the Debye−Hückel theory[15]

$$F_{\rm dilute} = \sum_i n_{i0} \log n_{i0} - \frac{\kappa_0^{\;3}}{12\pi} \tag{3}$$

with $\kappa_0^2 = 4\pi l_{\rm B}(\sum_i n_{i0})$. In the limit of high ionic strength, one can solve the equilibrium equations using an expansion in the small parameter s_0^{-1}. Additionally, an expansion up to first order in $\kappa_0 l_{\rm B}$ ensures that the Debye−Hückel approach is valid. In the symmetric case, the osmotic balance between the two phases reads the lowest nontrivial order

$$\Delta\Pi = \frac{\bar{w}^2}{3}(c_+ + c_-)^3 - \frac{\kappa_0^{\;3} s_0^{\;-3}}{12\pi} = 0 \tag{4}$$

The effect of fluctuations associated with the third virial term can be absorbed by a renormalization of w. The renormalized third virial term is denoted $\bar{w}$. This osmotic balance lead us to introduce the notion of "complexation blobs":[6,16] by analogy with neutral polymers under poor solvent conditions, the dense phase can be viewed as a compact packing of complexation blobs of size $\xi_{\rm c} \sim \kappa_0^{-1}s_0$. At length scales below $\xi_{\rm c}$, the concentration fluctuations induced attraction is not relevant compared to the thermal energy $k_{\rm B}T$, while it is dominant at larger length scales. This interpretation of the structure of the dense phase will be used in the next section to discuss the formation aggregates.

For asymmetric mixtures ($f_+c_+ \neq f_-c_-$), the calculation of $\Delta F_{\rm dense}$ is more complicated. Nevertheless we are looking for the effect of a small charge asymmetry on the structure of the dense phase. The calculation can be therefore simplified by expanding the RPA correction term with the charge asymmetry.[16] The main difference with the symmetric calculation of $\Delta F_{\rm dense}$ is the appearance of a new term coupling the fluctuations associated with the third virial coefficient and the electrostatic interactions. It can be shown a posteriori that this term simply renormalizes the prefactors in the osmotic balance. It will be therefore neglected. The equilibrium of the small ion chemical potentials between the two phases requires the introduction of a Donnan potential, because of the electroneutrality constraint in the two phases.[17] Therefore, the concentrations of small ions in the dense phase are related by

$$n_+n_- = n_0^{\;2}\exp[-2\Delta\mu_{\rm pol}] \tag{5}$$

with the chemical potential difference due to the polarization energy (RPA correction term) $\Delta\mu_{\rm pol} = \partial/\partial n_\pm(\Delta F_{\rm dense} - \Delta F_{\rm dilute})$. This equation in n_+ can be solved with the constraint of electroneutrality at the first order in $\kappa_0 l_{\rm B}$. Finally, the osmotic balance between the two phases reads at the lowest nontrivial order

$$\Delta\Pi = \frac{w^2 c_{\rm dense}^{\;\;3} N^3}{3} + \frac{c_{\rm dense}^{\;\;2}(f_+N_+ - f_-N_-)^2}{4n_0} - \frac{\kappa_0^{\;3} s_0^{\;-3}}{24\pi} \tag{6}$$

We used in the preceding equation the definition of the monomer concentrations in the dense phase $c_\pm = c_{\rm dense}N_\pm$. The first and third terms of this equation are reminiscent of the osmotic pressure of a symmetrical complex. The second term is of purely entropic origin: the difference in translational entropy of the small ions between the two phases induces an excess osmotic pressure inside the dense phase. The excess charge per copolymer is conveniently measured by the introduction of the *average net charge* per monomers

$$q \equiv \frac{f_+N_+ - f_-N_-}{N} \tag{7}$$

This is the net charge of a copolymer redistributed on all the monomers. In the limit of low asymmetry, the third virial term dominates over the osmotic term. The copolymer concentration inside the dense phase is therefore given by its value in the symmetrical case

$$c_{\rm dense}a^3N = \frac{3}{2\pi^{2/3}}\,\frac{f_+f_-}{n_0a^3\left(\frac{w^{1/3}}{a}\right)^4} \tag{8}$$

The number of monomers inside a complexation blob reads

$$g_{\rm c} \sim \frac{(n_0a^3)^2\left(\frac{w^{1/3}}{a}\right)^2}{(f_+f_-)^2} \tag{9}$$

The size of the complexation blob is given by $\xi_{\rm c} \sim g_{\rm c}^{1/2}a(w^{1/3}/a)$. Neglecting all numerical prefactors, a careful analysis of eq 6 shows that the third virial contribution dominates over the osmotic one if

$$q < (f_+f_-)^{1/2}\left(\frac{w^{1/3}}{a}\right) \tag{10}$$

This inequality is valid as long as $|f_+ - f_-|w^{1/3}/a \lesssim (f_+f_-)^{1/2}$. It means that the properties of the dense phase are well described by eqs 8 and 9 if $q/f \lesssim 1$, where f is the geometric average of charge densities. If $q/f \gtrsim 1$, the osmotic term dominates over the third virial term, and the copolymer concentration of the dense phase can be calculated using the osmotic balance eq 6. However, as will be shown in the next sections, finite size aggregates are more favorable in this range of parameters.

3. Micelle Formation

We propose in this section a model for the aggregates in the supernatant. It has been shown in the last section that the polymeric net charge in the dense phase induces an excess osmotic pressure which tends to swell this phase. By analogy with the associating behavior of diblock copolymers charged hydrophilic/hydrophobic, we will assume that spherical micelles are formed in solution:[18] the polymeric net charge of the core vanishes, and the excess charge is localized on the surrounding arms in the corona of the micelle (cf. Figure 1).

For a positive excess charge per copolymer, the number of cationic monomers in the core $N_{\rm c+}$ is given by the electroneutrality condition $N_{\rm c+}f_+ = N_-f_-$. The total number of monomers per chain in the core is denoted by $N_{\rm c} = N_{\rm c+} + N_-$. The excess charge of the corona per copolymer is Nq. In this geometry, the noncompensated charges of the arms are further away from each other than in a single homogeneous dense phase. It is also the case for charged-neutral diblock copolymers where this geometry has been observed experimentally.[19] When the charge asymmetry is small enough, we expect other aggregate geometries to be

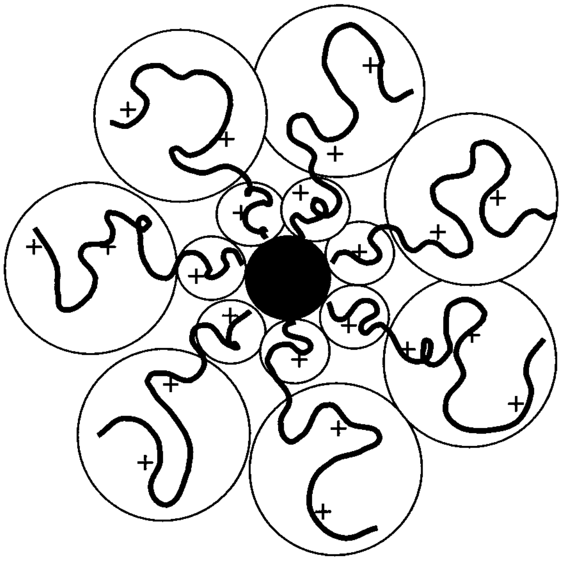

Figure 1. Copolymer micelle. The circles of growing diameters are the compact packing blobs of the Daoud−Cotton model. For the sake of simplicity, only charges of the arms are explicitly sketched.

more favorable than the spherical one, such as cylindrical micelles or lamellae (planar geometry).[20] However it can be shown a posteriori that those geometries are less favorable at the level of scaling laws than a macroscopic phase separation for low charge asymmetry.[16] Therefore, we will not consider explicitly those geometries further. Before drawing the full phase diagram of the solution, we first consider in this section, the properties of the optimal spherical micelle, which minimizes the free energy per copolymer. We suppose therefore that all the required conditions for the formation of spherical micelles are met. The main contributions to the micelle free energy per copolymer are the surface tension of the core and the electrostatic free energy of the corona. In the range where spherical micelles are favorable, the stretching energy of the chains in the core is negligible.[21]

The "neutral" core of the micelle can be viewed as a symmetrical polyelectrolyte complex. Using the interpretation of its structure in terms of complexation blobs in the limit of high ionic strength, its negative free energy is evaluated with the ansatz "k_BT per blob". Similarly, the interfacial tension between the complex and the surrounding solvent is estimated by associating an energy k_BT per blob on the surface of the core. Therefore, the surface tension reads $\gamma a^2 \sim k_BTa^2/\xi_c^2 \sim k_BT/g_c$. For an aggregate containing p chains, the core size R_c is given by $R_c^3 \sim pN_cg_c^{1/2}a^3$. The interfacial free energy per copolymer reads

$$F_{\text{surf}} \sim \frac{\gamma a^3 N_c g_c^{1/2}}{R_c} \sim \frac{aN_c}{R_c g_c^{1/2}} \tag{11}$$

In the limit of high ionic strength $n_0a^3 > f_+^{4/3}/(l_B/a)^{1/3}$, it has been shown that the corona of a charged micelle can be described by the Daoud−Cotton model for neutral star branched polymers.[22] This comes from the fact that in the high ionic strength limit, the electrostatic interactions are strongly screened. This effective short-range interaction is equivalent to an excluded volume interaction with an electrostatic excluded volume parameter $v_{\text{el}} \sim f_+^2/n_0 \sim \bar{v}_{\text{el}}a^3$. According to the Daoud−Cotton model, the star is composed of a compact packing of correlation blobs of size $\xi(r)$, where r is the distance to the center of the star.[23] This condition implies $\xi(r) \sim r/p^{1/2}$. The chain statistics of inside a blob the excluded volume statistics $\xi(r) \sim g(r)^{3/5}v_{\text{el}}^{1/5}a^{2/5}$. The monomeric concentration profile of the corona is then given by $c(r)a^3 \sim p^{2/3}/\bar{v}_{\text{el}}^{1/3}(r/a)^{4/3}$. The extension of the arms and the free energy per chain are calculated by counting the number of blobs, or equivalently by

$$(N_+ - N_{c+})p = \int_{R_c}^{R} \mathrm{d}r\, 4\pi r^2 c(r) \tag{12}$$

$$F_{\text{corona}}p = \int_{R_c}^{R} \mathrm{d}r \frac{4\pi r^2}{\xi^3(r)} \tag{13}$$

Let $N_b = N_+ - N_{c+}$ be the number of monomers per branch in the corona. In the limit $R/R_c \gg 1$, where the spherical aggregate is the most favorable geometry, one finds for the corona extension the same result as in a Flory-like mean field evaluation balancing the osmotic pressure due to the salt in the micelle and the stretching of the arms $R \sim aN_b^{3/5}p^{1/5}\bar{v}_{\text{el}}^{1/5}$. The Daoud−Cotton model takes into account excluded volume correlations and therefore leads to a more accurate result for the free energy than the mean-field prediction. The free energy per copolymer reads

$$F_{\text{corona}} \sim p^{1/2} \log \frac{N_b^{3/5} p^{1/5} \bar{v}_{\text{el}}^{1/5} a}{R_c} \tag{14}$$

It depends only very weakly on N_b (logarithmically).

The minimization of the total free energy per copolymer leads to the following radius, aggregation number and free energy for the spherical micelle

$$R \sim a \frac{N_b^{3/5} N_c^{4/25} \bar{v}_{\text{el}}^{1/5}}{g_c^{4/25}\left(\log \frac{R}{R_c}\right)^{6/25}} \tag{15}$$

$$\bar{p} \sim \frac{N_c^{4/5}}{g_c^{4/5}\left(\log \frac{R}{R_c}\right)^{6/5}} \tag{16}$$

$$F_{\bar{p}} \sim \left(\frac{N_c}{g_c}\right)^{2/5}\left(\log \frac{R}{R_c}\right)^{2/5} \tag{17}$$

It can be shown that the spherical geometry is favored if one ignores macroscopic phase separation if $q/f_+ \gg N_c^{11/15}g_c^{1/10}/N\bar{v}_{\text{el}}^{1/3}$. This condition is also equivalent to $R/R_c \gg 1$.

4. Phase Diagram

Our aim in this section is to link the results of the two previous sections: in section 2, we have studied the macroscopic phase separation of the solution by assuming a macroscopic phase separation ignoring the finite size aggregation in the supernatant; in section 3, we have evaluated the optimal properties of a spherical aggregate, neglecting any concentration effect. In fact, a diblock polyampholyte solution should be fully described by a model allowing both for macroscopic and mesoscopic phase separations. Let ϕ, c_{dense}, n_+, and n_- be, respectively, the volume fraction, the copolymer concentration, and the positive and negative small ion concentrations in the dense phase of a macroscopically separated solution. In the dilute phase, we define respectively c_p, n_{+0}, and n_{-0} the concentrations of p chains aggregates and of positive and negative small ions. The free energy density of the solution reads

$$F = \phi F_{\mathrm{dense}}(c_{\mathrm{dense}}, n_+, n_-) + (1 - \phi)F_{\mathrm{dil}}(\{c_p\}, n_{+0}, n_{-0}) \tag{18}$$

with the free energy density of the dense phase

$$F_{\mathrm{dense}} = c_{\mathrm{dense}}(\log c_{\mathrm{dense}} - 1) + \sum_{i=\pm} n_i (\log n_i - 1) + F_{\mathrm{D}} \tag{19}$$

and the free energy density of the dilute phase

$$F_{\mathrm{dil}} = \sum_{p=1,2...} c_p(\log c_p - 1 + F_p) + \sum_{i=\pm} n_{i0}(\log n_{i0} - 1) + F_{\mathrm{d0}} \tag{20}$$

The quantities F_{D}, F_p and F_{d0} are respectively the free energy of the dense phase, and the free energies of an aggregate of p chains and the Debye Hückel polarization energy of the dilute phase. Within the RPA, F_{D} includes the excluded volume contribution and the polarization energy of the dense phase in eq 2 and depends on the various concentrations. Finally, F_p has been evaluated in section 3. We will keep these very general notations in the following, since they are not model dependent. The equilibrium between the two phases is obtained by minimizing the free energy density with respect to the volume of the dense phase and the various concentrations, with the constraints of mass conservation of copolymers and small ions, and electroneutrality of both phases. The minimization with respect to the volume of the dense phase leads to the osmotic balance. When the contribution of translational entropy and polarization energy of the aggregates are neglected, this leads to the analysis of section 2. This approximation is justified since the translational entropy of an aggregate of p chains is of order $1/pN$, and therefore the contribution to the polarization energy is also negligible. The other equilibrium equations read

$$\begin{aligned} n_+ &= n_{+0} \exp(-\Psi) \exp(-(\mu_i - \mu_{i0})) \\ n_- &= n_{-0} \exp(+\Psi) \exp(-(\mu_i - \mu_{i0})) \\ c_p &= c_{\mathrm{dense}}{}^p \exp(+pNq\Psi) \exp(-(F_p - p\mu_{\mathrm{D}})) \end{aligned} \tag{21}$$

The chemical potentials μ_α in the last equations are obtained by derivation of the free energy densities with respect to the corresponding concentration; they do not include the contributions of the translational entropies; the subscript 0 corresponds to the dilute phase. The electroneutrality constraint in the two phases induce an electrostatic potential difference between the two phases Ψ: this is the so-called Donnan potential. By using the first two equations of (21), we can calculate Ψ at first order in $\kappa_0 l_{\mathrm{B}}$

$$\Psi = \frac{c_{\mathrm{dense}}Nq}{2n_0} + o\left(\left(\frac{c_{\mathrm{dense}}Nq}{2n_0}\right)^2\right) + o((\kappa_0 l_{\mathrm{B}})^2) \tag{22}$$

The last equation of (21) can be rewritten $c_p = c_{\mathrm{dense}} \exp(-\Omega_p)$ with the thermodynamic grand potential

$$\Omega_p = F_p - p(\mu_{\mathrm{D}} + \log c_{\mathrm{dense}} + Nq\Psi) \tag{23}$$

The total copolymer concentration c^{tot} is written as

$$\phi c_{\mathrm{dense}} + (1 - \phi)(\textstyle\sum_p p c_{\mathrm{dense}}\exp(-\Omega_p)) = c^{\mathrm{tot}} \tag{24}$$

This equation shows that the contribution of aggregates is negligible compared to the contribution of the dense phase if $\Omega_p > 0$. In the opposite case $\Omega_p < 0$, the concentration of aggregates becomes relevant. Therefore, we can write a simple solubility criterion: the chains are soluble as aggregates when

$$\frac{F_{\bar{p}}}{\bar{p}} < \mu_{\mathrm{D}} + \frac{c_{\mathrm{dense}}(Nq)^2}{2n_0} + \log c_{\mathrm{dense}} \tag{25}$$

We used in this equality the average aggregation number $p = \bar{p}$ that minimizes the free energy per diblock copolymer. This inequality means that copolymers are soluble when the chain chemical potential in an aggregate is smaller than the chain chemical potential in the dense phase. The dense phase chemical potential has two main contributions: the attractive energy, $-k_{\mathrm{B}}T$ per blob, and the energy associated with the loss of translational entropy of the small ions. A careful analysis of the inequality (25) leads to the simplified criterion

$$\frac{N_{\mathrm{b}}}{g_{\mathrm{c}}} < \frac{c_{\mathrm{dense}}(Nq)^2}{2n_0} \tag{26}$$

Therefore, the chains are soluble when

$$q > f_-\left(\frac{w^{1/3}}{a}\right)^2 \tag{27}$$

(note that the prefactor on the right-hand side must be smaller than one for consistency). At the level of the scaling laws, we found that the dense phase disappears when $q/f \gtrsim 1$, where f is the average charge density of the copolymer. The chains are thus soluble as spherical aggregates when the excess charge per monomer is of the same order of the charge density that induces the collapse of the complex by fluctuations. This value corresponds at the level of scaling laws to the regime where the excess osmotic pressure due to the small ions becomes of the order of the third virial contribution in the analysis of the osmotic balance in section 2. The criterion (27) does not depend on concentration effects. This means that the solution has to be already phase separated or partially aggregated for this criterion to hold. It happens only above some critical copolymer concentration.

To include concentration effects in this description, one has to consider the two following asymptotic limits: a micellization with no macroscopic phase separation, and a macroscopic phase separation with no micellization. This allows to compute respectively the critical micellar concentration (cmc) and the critical macroscopic phase separation concentration, and to compare them. In the case of a pure micellization, the total concentration of copolymers is written as

$$c_1 + (\sum_p pc_p) = c^{\mathrm{tot}} \tag{28}$$

The equilibrium conditions between all aggregates can be written as

$$c_p = c_1{}^p \exp[-(F_p - pF_1)] \tag{29}$$

where F_1 is the free energy of one isolated copolymer in solution. This energy contains mainly two contributions: the interfacial tension between the complexed part and the solvent $(N_c/g_c)^{2/3}$, and the attractive energy $-N_c/g_c$. Up to entropic effects, micelles are formed in solution if $F_1 > F_{\bar{p}}/\bar{p}$, where $p = \bar{p}$ minimizes the free energy per copolymer in an aggregate. The cmc is then evaluated by

$$\log c_{\mathrm{mc}} \sim -\left(F_1 - \frac{F_{\bar{p}}}{\bar{p}}\right) \tag{30}$$

For spherical micelles, this concentration can be rewritten as

$$\log c_{\mathrm{mc}} \sim -\left(\left(\frac{N_{\mathrm{c}}}{g_{v_{\mathrm{el}}}}\right)^{2/3} - \left(\frac{N_{\mathrm{c}}}{g_{v_{\mathrm{el}}}}\right)^{2/5}\right) \tag{31}$$

This cmc is exponentially small, as for any diblock copolymer system.

In the limit of a pure macroscopic phase separation, with no micellization, the total copolymer concentration reads

$$\phi c_{\mathrm{dense}} + (1 - \phi)c_1 = c^{\mathrm{tot}} \tag{32}$$

The equality of diblock copolymer chemical potentials between the two phases leads to

$$c_1 = c_{\mathrm{dense}} \exp[-(F_1 - (\mu_{\mathrm{D}} + Nq\Psi))] \tag{33}$$

We introduced in the last equation the Donnan potential that takes into account the loss of translational entropy of small ion in the dense phase. The critical concentration for macroscopic phase separation is thus given by

$$\log c_{\mathrm{sep}} \sim -\,(F_1 - ((\mu_{\mathrm{D}} + Nq\Psi))) \tag{34}$$

This critical concentration is approximately of the same order of the cmc. More precisely, the ratio between those two critical concentrations reads

$$\log \frac{c_{\mathrm{mc}}}{c_{\mathrm{sep}}} \sim \frac{F_{\bar{p}}}{\bar{p}} - (\mu_{\mathrm{D}} + Nq\Psi) \tag{35}$$

The right-hand side of the preceding equation gives our simplified criterion for the solubility of aggregates.

Therefore, we can draw qualitatively the following phase diagram (cf. Figure 2): the macroscopic phase separation takes place first when $q/f \lesssim 1$ and $c^{\mathrm{tot}} > c_{\mathrm{sep}}$. For higher asymmetries $q/f \gtrsim 1$, spherical micelles are formed when $c^{\mathrm{tot}} > c_{\mathrm{mc}}$. We thus predict that the only aggregates to be observable when the solution is macroscopically stable are spherical micelles. This has to be compared to the recent experiments on diblock polyampholyte solutions.[8−10,24] As was mentioned in the Introduction, one observes indeed in those experiments spherical aggregates in solution: their radius is measured by dynamic light scattering or by AFM experiments, since those copolymers mainly adsorb on charged substrates as micelles and not as single molecules.

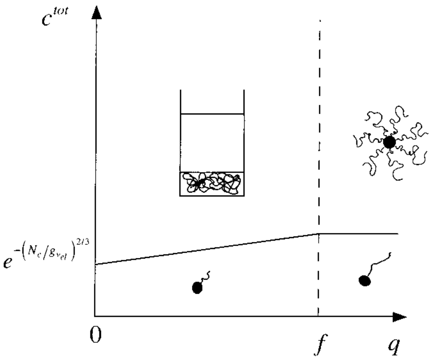

Figure 2. Phase diagram (c^{tot} vs q) in the limit of high ionic strength.

The only available experiments on diblock polyampholytes to our knowledge are performed with weak acidic and basic groups on the two blocks. It means therefore that the excess charge q depends on the local pH of the solution.[25] In particular, the radius of the aggregates varies with the pH. As we shall see below in an appendix, our model predicts qualitatively the same variation if local pH effects are neglected. By local pH effects, we mean inhomogeneities of the solution (such as aggregation) that lead to inhomogeneities of the pH that can take locally a value different than the imposed value. For example, the pH inside an isolated star-branched weak polyelectrolyte is different from the value in the bulk solution.[22] Neglecting local pH effects, we assume in a first approximation, that pH variations in a solution of diblock polyampholytes change only the value of q. Notice that in the most general case, N_{c} and N_{b} depend in a complex manner on q. It is possible to simplify those expressions for two limiting cases of asymmetry ($N_+ = N$ and $f_+ \neq f_-$) and ($N_+ \neq N_-$ and $f_+ = f_-$). We will not analyze those particular cases in this paper. For the sake of simplicity, we consider N_{c} and N_{b} as constants. The charge densities along the two blocks are given by the following action mass laws

$$\frac{f_-}{1 - f_-} = \frac{K_{\mathrm{A}}}{c_{\mathrm{H}^+}} \tag{36}$$

$$\frac{f_+}{1 - f_+} = \frac{K_{\mathrm{B}}}{c_{\mathrm{OH}^-}} = K_{\mathrm{B}} 10^{14} c_{\mathrm{H}^+} \tag{37}$$

with the dissociation constants K_{A} and K_{B} of the acidic and basic groups. The pH of the solution is related to the concentration of H^+ ions by $c_{\mathrm{H}^+} = 10^{-\mathrm{pH}}$. In eq 37, the ionization product of water has been used. For weakly charged polyelectrolytes ($f_+, f_- \ll 1$), the product of charge densities f_+f_- is approximately constant and does not depend strongly on the pH. As was shown in the first section of this paper, the properties of the dense phase (in macroscopically phase separated sample or in the core of a micelle) depend only on f_+f_- (for example $g_{\mathrm{c}} \sim (f_+f_-)^{-2}$). Therefore, pH variations do no affect strongly the core properties of spherical micelles within this very crude model. The only effect of pH variations is to change the corona extension which depends strongly on the charge density of the arms. For a positive excess charge (low pH values), the radius of a micelle vary as

$$R \sim {c_{\mathrm{H}^+}}^{2/5} \tag{38}$$

The radius of a spherical aggregate decreases with the pH. On the contrary, the radius for a negatively charged micelle (high pH values) scales like

$$R \sim {c_{\mathrm{H}^+}}^{-2/5} \tag{39}$$

Therefore, the extension of the micelle increases with the pH. For intermediate values close to the isoelectric point $\mathrm{pH_i}$, the excess charge vanishes and the solution macroscopically phase separates. Notice that eq 15 is no longer valid when $R \sim R_c$ since the logarithmic factor becomes important. In this range of parameters, the solution has already phase separated as discussed at the beginning of this section. Close to this regime, the aggregation number increases again with the pH for $\mathrm{pH} < \mathrm{pH}_i$ and decreases for $\mathrm{pH} > \mathrm{pH}_i$.

The qualitative behavior of the micelle radius with pH is qualitatively observed in experiments of ref 8. The authors study the adsorption of dilute diblock polyampholyte solutions. As it previously mentioned, AFM experiments on the substrates and dynamic light scattering experiments in solution confirm the presence of spherical aggregates. By studying the adsorption kinetics as a function of the ionic strength of the solution, one can measuer a diffusion coefficient toward the surface which can be used as an alternative mean to determine the size of the aggregates. This radius is found to decrease with added salt, in qualitative agreement with our model which predicts $R \sim {n_0}^{-13/25}$. Notice that no significant variations of the aggregate radius with pH or ionic strength is observed in the experiments of Goloub et al. with another kind of diblock polyampholytes. We believe that this is probably due to the relevance of non electrostatic interactions in this case.[10] It seems thus that diblock polyampholyte aggregates can be described by a very crude model of polyampholytes with quenched charge distribution with no local pH effects. The agreement with the experiments is not quantitative, but all the qualitative trends are predicted. We give some arguments in the appendix of this paper that justify partially this very crude model.

5. Concluding Remarks

We have studied in this paper the phase diagram of monodisperse diblock polyampholyte solutions. In the case of charge symmetry ($N_+f_+ = N_-f_-$), the properties of the solution are very similar to those of an equivalent homopolymer mixture obtained by cutting the junction point between the oppositely charged polyelectrolytes in the copolymer: there is a macroscopic complexation phase separation between the polymers and the solvent. The structure of the dense phase has been here described in terms of complexation blobs. When the charge asymmetry increases, the small ions of the solution are strongly coupled to the copolymers: the electroneutrality of the dense phase requires a finite density of counterions that induces an excess osmotic pressure which tends to swell the complex. Above a charge asymmetry threshold, this excess osmotic pressure is larger than the attractive energy collapsing the complex: the copolymers are soluble in the form of finite size aggregates. We propose in this paper that the chains are aggregated in solution as spherical micelles with a neutral core, the excess charge being carried by the arms of the corona. In the limit of high ionic strength, the micelle corona is described by the Daoud–Cotton model for neutral polymeric stars with an effective electrostatic excluded volume $v_{\mathrm{el}} = 4\pi l_B f^{\,2}/\kappa_0^{\,2}$. The structure of the micelle core is very similar to a neutral polymer solution in a poor solvent and is described using complexation blobs.

The only available experiments that we are aware of on diblock polyampholyte solutions are performed with annealed polyampholytes carrying acidic and basic groups along each blocks. Therefore, the charge distribution along the chain is annealed and depend on the local pH of the solution. By neglecting any local pH effects, it is possible to predict at least qualitatively the variation of the micelle radius with pH and salt amount. In the limit of high ionic strength, this simple model can be partially justified: the charge fluctuations still collapse the core of the micelles and are in fact stronger in the case of an annealed charge distribution. Moreover the pH variations of the buffer are transmitted to the corona and the core of the micelles. Of course this very simple model is not expected to be a quantitative description of the aggregates because of the naive modelization of the annealed effect. The main problem for a more precise modelization comes from the dependencies of some parameters of the complex as a function of the charge asymmetry: the number of monomers in the core and in the corona of the micelle, the charge densities inside the core and on the arms of the corona, etc.

The micellization model proposed in this paper is a first step toward a more precise understanding of asymmetries effects in mixtures of (unbound) oppositely charged polyelectrolytes. In this case, the separation of the polyions produces a new degree of freedom. In particular, the aggregates are characterized by two aggregation numbers. This will the topic of future work.

Acknowledgment. Fruitful discussions with H. Mohrbach and F. Clement (Institut Charles Sadron, Strasbourg, France) are gratefully acknowledged. This research was supported by the Deutsche Forschung Gemeinschaft through the Schwerpunkt program "Polyelektrolyte".

Appendix A

We give briefly in this appendix some arguments justifying the very crude model of charge annealing in the micelles in the limit of high ionic strength.

A.1. RPA Free Energy. To understand the effect of an annealed charge distribution, let us see how the polarization energy driving the complexation is modified. We consider Gaussian chains for the sake of simplicity (no third virial contribution). The general form of the RPA correction term to the free energy is given by

$$\Delta F = \frac{1}{4\pi^2}\int_0^\infty \mathrm{d}q\, q^2 \log\left[\det\left[\frac{\hat{G}_{\mathrm{RPA}}^{-1}}{2\pi V}\right]\right] \tag{40}$$

where ${\hat{G}_{\mathrm{RPA}}}^{-1}$ is the inverse structure matrix matrix at the RPA level.[13] The determinant of this matrix in the case of an annealed charge distribution is exactly the same as in the quenched distribution case if the Debye–Hückel screening length is defined as

$$\kappa^2 = 4\pi l_B\left(\sum_i n_i + f_+(1 - f_+)c_+ + f_-(1 - f_-)c_-\right) \quad (41)$$

The mobile charges on the chains contribute to the screening of electrostatic interactions. The quantities n_i are the concentrations of small ions (salt ions, H^+,OH^-). Notice that we will sometimes denote the concentrations of H^+ and OH^- by $n_{H^+} = c_{H^+}$ and $n_{OH^-} = c_{OH^-}$. Therefore, the RPA correction term reads

$$\Delta F = -\frac{{q_*}^3}{12\pi}(s - 1)(s + 2)^{1/2} \quad (42)$$

with $q_*^4 = 48\pi l_B(f_+^2c_+ + f_-^2c_-)/a^2$ and $s = \kappa^2/q_*^2$. It is exactly the same as for quenched distributions, except for the new definition of κ. The mean field contribution to the free energy density is given by

$$\frac{F}{kT} = \frac{c_+ + c_-}{N}\left(\log\frac{c_+ + c_-}{N} - 1\right) + \sum_i n_i(\log n_i - 1) + c_-[f_- \log f_- + (1 - f_-)\log(1 - f_-) + f_-\mu_{A^-} + (1 - f_-)\mu_{AH}] + c_+[f_+ \log f_+ + (1 - f_+)\log(1 - f_+) + f_+\mu_{B^+} + (1 - f_+)\mu_{BOH}] \quad (43)$$

where we take into account the translational entropies of the chains and the small ions in the solution, the mixing entropy of the small ions on the chains, and their equilibrium with a charge reservoir.

A.2. Equilibrium between Two Phases. As in section 2, we neglect the influence of copolymers in the dilute phase. We can write the equilibrium conditions as in section 2. In the limit of high ionic strength, one can solve at the first order in $\kappa_0 l_B$ the equilibrium equations for the small ions concentrations.[16] This leads to introduce a new parameter $\eta = f_+(1 - f_+)c_+ + f_-(1 - f_-)c_-$. In the symmetric case where $f_+c_+ = f_-c_-$, the osmotic balance reads at lowest order in $\kappa_0 l_B$, s_0^{-1} and η/n_0

$$\Delta\Pi = -\frac{{\kappa_0}^3}{24\pi}\left({s_0}^{-3} + \frac{3}{2}\frac{\eta}{2n_0}{s_0}^{-2}\right) \quad (44)$$

Thus, we find that at lowest order that charge annealing leads to an increased attractive term free energy the complex: this is quite natural since there is a new fluctuating variable. Nevertheless, the dominant term is still the same as in the quenched case.

A.3. Local pH Effects. We denote in this section with a “0” subscript the quantities related to the region outside the micelles, namely the bulk solvent properties. In particular, the charge density of an isolated weak polyelectrolyte (no local pH effects) is f_0. In the case of star-branched weak polyelectrolytes, it was shown that the charge density of the arms depends on the pH of the buffer solution like[22]

$$f^2 = \frac{f_0}{c}(c_{H^+0} + n_{sel} + n_{strong\ base}) \quad (45)$$

if $f_{0-}c \gg (c_{H^+0} + n_{sel} + n_{strong\ base})$. Notice that the contribution of the polarization energy has been neglected. In the opposite case, the charge density is $f = f_0$. It means therefore that in the high ionic strength limit, the pH variations in the solution buffer are *entirely* transmitted to the inside of the star.

All the arguments presented above can still be used: in the limit of high ionic strength, local pH effects are very weak, and therefore, they can be ignored in first step of modelization.

References and Notes

(1) Philipp, B.; Dautzenberg, H.; Linow, K. J.; Kotz, J.; Dawydoff, W. *Prog. Polym. Sci.* **1998**, ***14***, 823.
(2) Michaeli, I.; Overbeek, J. T. G.; Voorn, M. J. *J. Polym. Sci.* **1957**, *23*, 443.
(3) Tsuchida. E. *J. Macromol. Sci.—Pure Appl. Chem.* **1994**, *A31*, 1.
(4) Decher, G. *Science* **1997**, *277*, 1232.
(5) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16*, 1249.
(6) Castelnovo, M.; Joanny, J. F. *Langmuir* **2000**, *16*, 7524.
(7) Everaers, R.; Johner, A.; Joanny, J. F. *Macromolecules* **1997**, *30*, 8478.
(8) Walter, H.; Harrats, C.; Muller-Buschbaum, P.; Jerome, R.; Stamm, M. *Langmuir* **1999**, *15*, 1260.
(9) Mahltig, B.; Gohy, J. F.; Jerome, R.; Bellmann, C.; Stamm, M. *Colloid Polym. Sci.* **2000**, *278*, 502.
(10) Goloub, T.; de Keizer, A.; Cohen Stuart, M. A. *Macromolecules* **1999**, *32*, 8441.
(11) de Gennes, P. G. *Scaling concepts in polymer physics.* Cornell University: Ithaca, NY, 1979.
(12) Castelnovo, M.; Joanny, J. F. *Eur. Phys. J. E* **2001**, *6*, 377.
(13) Borue, V. Y.; Erukhimovich, I. Y. *Macromolecules* **1988**, *21*, 3240.
(14) Borue, V. Y.; Erukhimovich, I. Y. *Macromolecules* **1990**, *23*, 3625.
(15) Landau, L.; Lifshitz, E. *Physique Statistique;* Editions Mir: Moscow, 1967.
(16) Castelnovo, M. Charge distribution and complexation of polyelectrolytes. Ph.D. Thesis, University of Strasbourg, Strasbourg, France, 2001.
(17) Hill, T. L. *An introduction to statistical thermodynamics;* Dover Publications: New York, 1986.
(18) Netz, R. R. *Europhys. Lett.* **1999**, *47*, 391.
(19) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(20) Izzo, D.; Marques, C. M. *Macromolecules* **1993**, *26*, 7189.
(21) Sens, P.; Marques, C. M.; Joanny, J. F. *Macromolecules* **1996**, *29*, 4880.
(22) Borisov, O. V.; Zhulina, E. B. *Eur. Phys. J. B* **1998**, *4*, 205.
(23) Daoud, M.; Cotton, J. P. *J. Phys. (Paris)* **1982**, *43*, 531.
(24) Mahltig, B.; Gohy, J. F.; Jerome, R.; Stamm, M. *J. Polym. Sci., B: Polym. Phys.* **2001**, *39*, 709.
(25) Castelnovo, M.; Sens, P.; Joanny, J. F. *Eur. Phys. J. E* **2000**, *1*, 115.

MA012097V