Spontaneous Charge Inversion of a Microgel Particle by Complexation with Oppositely Charged Polyelectrolytes

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Received March 13, 2006

ABSTRACT: A combination of the mean-field theory and the random phase approximation is used to describe the effect of charge inversion (overcharging) of a spherical penetrable microgel particle by oppositely charged multiarm star polyelectrolytes in dilute solution. The overcharging is shown to occur due to the gain in the electrostatic self-energy and in the elastic free energy of the star macromolecules, while counterions can either promote or suppress the effect. It is shown that many parameters, such as the densities of the microgel and the stars, the fraction of charged units, etc., control the overcharging.

1. Introduction

The effect of overcharging of macroions by oppositely charged polyelectrolytes plays a very important role in many biological processes[1] and practical applications.[2−4] One of the examples is the concept of “gene delivery”.[5,6] Since the molecule of DNA carries the charge of the same sign as that of the membrane of a living cell, it has to be overcharged via complexation with oppositely charged macroion to penetrate through the membrane. As a vehicle for DNA such objects as proteins, dendrimers, micelles, microgel particles, etc., can be used. The formation of complexes DNA−cationic liposomes, when the nucleic acids are completely encapsulated within the positively charged lipid bilayers, is another example of the overcharging.[7−9] The reversal electrophoretic mobility of the complexes formed by the protein pepsin with strong polyelectrolytes can also be attributed to the charge inversion.[10] The study of complexation of the DNA molecules with positively charged dendrimers[11] demonstrated that the increase of the concentration of the dendrimers results in the entire screening of negative charge of the DNA and that the complexes become positively charged.

The binding of polyelectrolytes to small oppositely charged micelles was observed in refs 12−14. The critical conditions for the micelle−polyelectrolytes complex formation were found to be strongly depended on the ionic strength of the solution that emphasized the electrostatic nature of this effect.[12] Coacervation and precipitation in solutions of the micelles−polyelectrolytes complexes were studied in ref 13. This system also revealed the phenomenon of charge and mass overcompensation.[14] Very important result of ref 14 comprised penetrability of the polymer micelles for polyelectrolyte chains. The same conclusion was made in ref 15 for the case of dendrimers, which are permeated by flexible polyanions. Therefore, the penetrability of porous macroions has to play a key role in the theoretical analysis of the overcharging.

Up to now most of the theoretical models examined the case of polyelectrolytes interacting with oppositely charged hard, impenetrable spheres or cylinders.[16−21] The practical importance of such studies was primarily connected with the understanding of the physical reasons of the DNA−histone complexation.[8] In our earlier work,[23] the charge inversion of a spherical penetrable polyanion by spherical polycations was analyzed within the framework of the simple model of structureless macroions of the fixed volume. Electrostatic interactions and the translational motion of counterions were taken into account. It was shown that the inversion of the charge of a large polyanion by smaller polycations, which are able to enter into the polyanion, is always driven by Coulomb interactions: excess polycations possess smaller electrostatic self-energy within the complex because of the “smearing” of the charge of the polycations throughout the whole volume of the complex. Counterions were shown to play a dual role: they can both promote and suppress the overcharging.

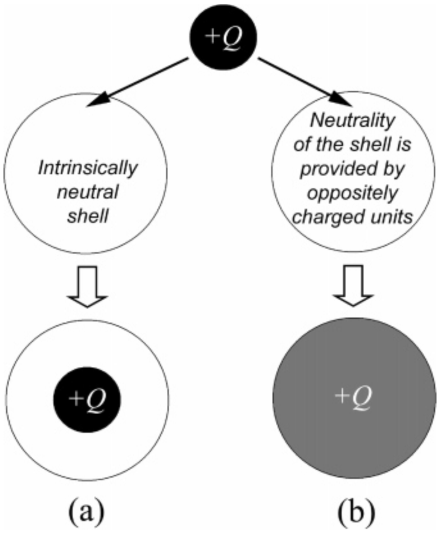

Figure 1. Distribution of the charge of the droplet within intrinsically neutral shell (a) and within the shell having equal amount of oppositely charged units (b). The charge density is characterized by the color: higher density (black) and lower density (gray). The electrostatic energy of the state (b), $E_b = 3Q^2/5R$, is lower than the energy of the state (a), $E_a = 3Q^2/5r$, $E_b < E_a$.

The energetic mechanism of the overcharging proposed in ref 23 can be illustrated by a simple example of the spherical charged droplet of the charge Q and of the radius r which is able to enter into a neutral shell of the radius R, $R > r$ (Figure 1). If the interior of the shell is intrinsically neutral (“empty” shell), the Coulomb energy of the droplet within the shell is

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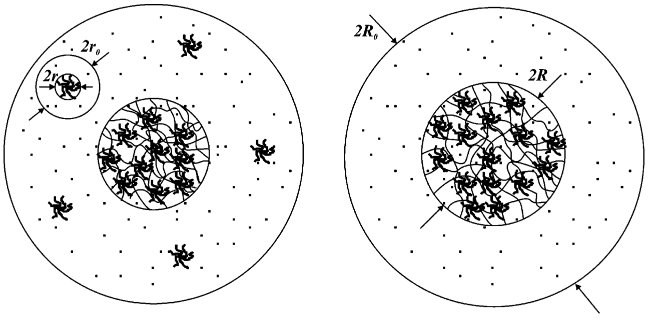

Figure 2. Schematic representation of two states of the system: a neutral PA−PCs complex coexisting with the unbound excess polycations (left) and swollen overcharged complex (right).

the same as that of the droplet in the infinite space, $E_a = 3Q^2/5r$ (Figure 1a). However, if the electric neutrality of the shell is provided by equal amount of oppositely charged units (full shell), the spreading of the charge of the droplet throughout the volume of the shell is energetically favorable because it reduces the electrostatic energy up to the value $E_b = 3Q^2/5R$ (Figure 1b). Since E_b is smaller than the Coulomb energy of the unbound droplet, one can say that the electrostatic interactions promote the overcharging.

In the present paper we extend the mean-field theory[23] for the case of macroions capable of the swelling and collapse. The overcharging of a microgel particle by oppositely charged multiarm star polyelectrolytes is considered. The polymeric degrees of freedom are shown to introduce a variety in the behavior of the system and can become one of the tools to control the strength of the overcharging. We show that the overcharging is always driven by the decrease of the self-energy of the macroions.

2. Model

Let us consider a large negatively charged spherical microgel particle (polyanion) comprising $m \gg 1$ flexible subchains, each of $N \gg 1$ segments. Each subchain contains a small fraction of charged units, $f = 1/\sigma \ll 1$. It is assumed that all charged units are completely dissociated; i.e., the system comprises $Z = mN/\sigma$ mobile, positively charged counterions. Let us consider the overcharging of the microgel particle by oppositely charged k-arm star macromolecules (polycations) in dilute solution. For the sake of simplicity, we will analyze a special case of the arms having the same length and the fraction of charged units as those of the subchains. The total electric neutrality of the polycations is provided by mobile negatively charged counterions ($z = kN/\sigma \gg 1$ counterions per star molecule). Every charged unit of the system is monovalent of the charge e, and its size, a, coincides with the size of the neutral segments. We assume that the solvent is a Θ-solvent, and we treat it as a dielectric continuum of dielectric constant ϵ.

To demonstrate the overcharging of the polyanion (PA) by the polycations (PCs), we compare the free energies of two states of the system: neutral PA−PCs complex coexisting with unbound excess PCs (state I) and overcharged PA−PCs complex where all excess PCs are localized within the complex (state II) (Figure 2).

2.1. State I. Let us assume that only PCs are responsible for neutralization of the microgel particle (PA): $p = Z/z$ PCs enter into the PA releasing all "own" and PA's counterions into the outer solution. Such substitution is entropically favorable if $z \gg 1$. Denote by n the number of excess PCs. They are immersed in a "gas" of $nz + Z$ negatively charged and Z positively charged counterions.

The total free energy of the system can be written as a sum of two terms:

$$F_I = F_I^{(1)} + F_I^{(2)} \tag{1}$$

The first term, $F_I^{(1)}$, corresponds to the free energy of the excess PCs and counterions. Assuming the spherical shape of the multiarm star macromolecules in the dilute solution and using the two-zone Oosawa model,[24−26] $F_I^{(1)}$ takes the following form:

$$\frac{F_I^{(1)}}{nk_BT} = \frac{3}{10}\frac{l_Bt(\theta)}{r}\left[z(1-\beta) + \frac{Z}{n}(\gamma-\beta)\right]^2 + \left(z + \frac{Z}{n}\right)\left(\beta \ln\frac{\beta c^-}{\theta} + (1-\beta)\ln\frac{(1-\beta)c^-}{1-\theta}\right) + \frac{Z}{n}\left(\gamma \ln\frac{\gamma c^+}{\theta} + (1-\gamma)\ln\frac{(1-\gamma)c^+}{1-\theta}\right) + \frac{3}{2}k\frac{r^2}{a^2N} + kNC\phi_s^{\,2}, \quad t(\theta) = \frac{2-3\theta^{1/3}+\theta}{(1-\theta)^2}, \quad \theta = \left(\frac{r}{r_0}\right)^3, \quad \phi_s = \frac{3kNv}{4\pi r^3} \tag{2}$$

In this model, the total volume of the system (a sphere of the radius R_0) can be imagined as a set of densely packed, neutral spheres (cells) of the radius r_0, $R_0^3 \approx nr_0^3$ (Figure 2). Each cell is divided into two zones. The first zone of the radius r is occupied by the PC. The second zone of the volume $4\pi(r_0^3 - r^3)/3$ is free of the PC. Counterions are distributed inhomogeneously between the zones because of inhomogeneous distribution of the charge of the PC within the cell. This distribution is approximated by a steplike function: the fractions β and γ of negatively and positively charged counterions occupy the first zone so that the number of the corresponding counterions within the PC is equal to $\beta(z + Z/n)$ and $\gamma Z/n$, respectively. The resultant volume charge density of the PC is assumed to be constant and equal to $\rho_1 = e(z(1-\beta) + Z(\gamma-\beta)/n)/(4\pi r^3/3)$. The second zone is charged with the density $\rho_2 = -e(z(1-\beta) + Z(\gamma-\beta)/n)/(4\pi(r_0^3 - r^3)/3)$ due to electrical neutrality of the cell. Calculation of the Coulomb energy of the concentric spheres with constant charge densities can be done in a standard way[23,27]

$$\frac{F_C}{k_BT} = \int d^3x\, \frac{l_B(\nabla w(x))^2}{8\pi}, \quad \Delta w(x) = -\frac{4\pi\rho(x)}{e}, \quad \rho(x) = \begin{cases}\rho_1 & 0 < x < r\\ \rho_2 & r < x < r_0\end{cases} \tag{3}$$

resulting in the first term of eq 2. Here l_B is the Bjerrum length, $l_B = e^2/\epsilon k_BT$. The next two terms of eq 2 are the contributions of the translational motion of negatively and positively charged counterions, respectively. c^- and c^+ are the corresponding average volume fractions of the counterions, $c^- = (z + Z/n)\cdot v/(4\pi r_0^3/3)$ and $c^+ = Zv/(4\pi r_0^3 n/3)$. The excluded volume of the counterion, v, coincides with the excluded volume of the monomer unit, $v \approx a^3$. Owing to the condition $z \gg 1$, the energy of the translational motion of the PCs can be neglected in comparison with the energy of the counterions.

The fourth term of eq 2 is the elastic free energy taken in the Flory form.[28] Here we assume homogeneous stretching of the star arms if the value of k is not so high.

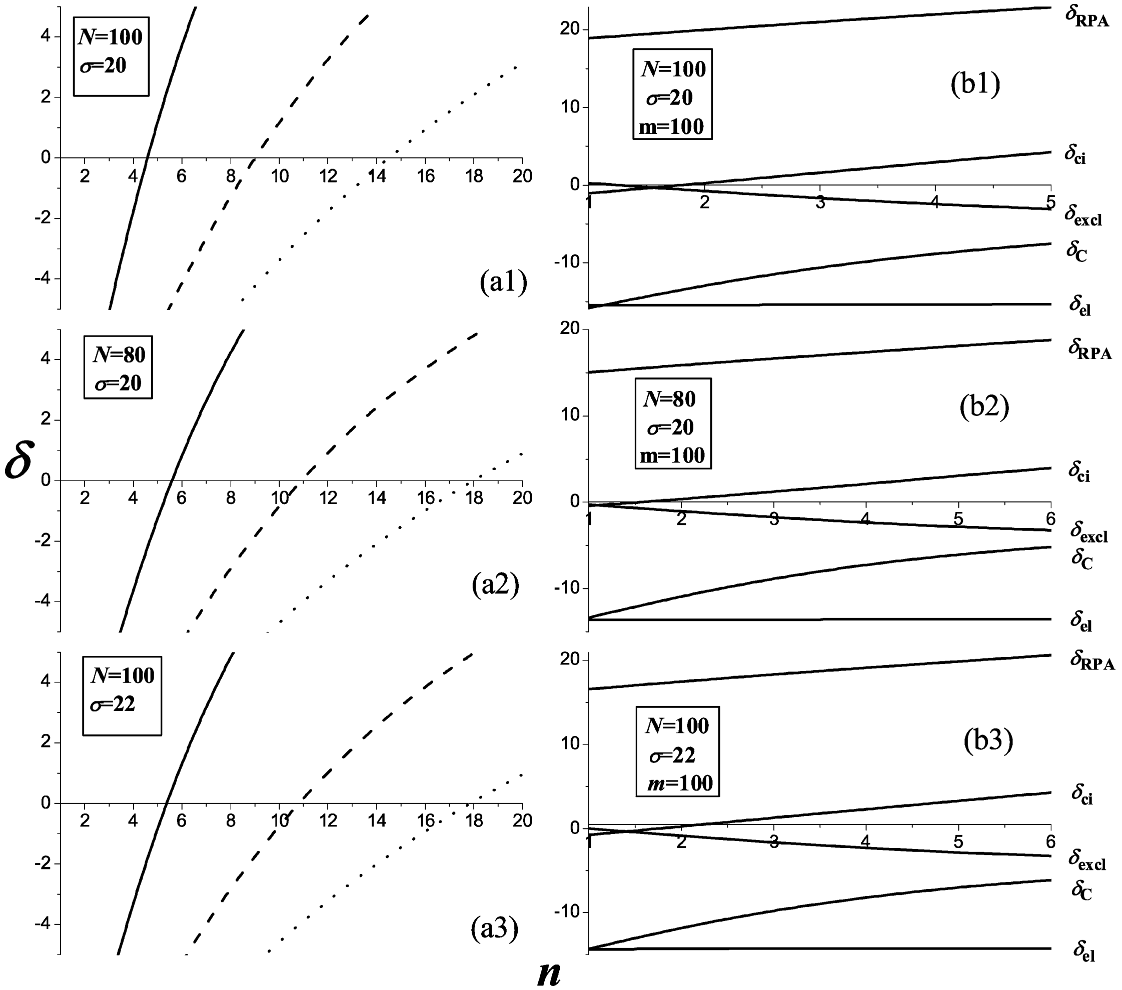

Figure 3. Difference of the free energies, $\delta = (F_{\rm II} - F_{\rm I})/(nk_BT)$, as a function of the number of excess polycations, *n*, for various sets of the parameters of the system a1−a3. Relative mean-field electrostatic energy (δ_C), the energy of the translational motion of counterions ($\delta_{\rm ci}$), the elastic free energy ($\delta_{\rm el}$), the energy of excluded volume interactions ($\delta_{\rm excl}$), and the RPA electrostatic energy ($\delta_{\rm RPA}$) vs *n* in the range of the values of *n* where the overcharged complex is stable, $\delta = \delta_C + \delta_{\rm ci} + \delta_{\rm el} + \delta_{\rm excl} + \delta_{\rm RPA} < 0$. We use $R_0 = 150 l_B$, $k = 5$, $m = 100$ (solid), $m = 200$ (dashed), and $m = 300$ (dotted).

The last term of eq 2 is the third virial contribution with the dimensionless coefficient $C \approx 1$; ϕ_s is the volume fraction of monomer units within the star molecule. The equilibrium value of $F_{\rm I}^{(1)}$ is found by minimization with respect to the parameters β, γ, and r.

The second contribution to the free energy (1) comes from the free energy of the neutral PA−PCs complex. We assume that neutralization of the complex in the dilute solution is achieved only by PCs. Therefore, the average polymer volume fraction of the microgel, φ, coincides with that of the stars localized inside the complex.

The formation of the neutral polyelectrolyte complexes cannot be described at the mean-field level: the Coulomb term is equal to zero at this level. One has to include at least fluctuations around the electroneutral state to describe the complexation. The simplest way to do it is the RPA formalism.[29−31] The RPA free energy of the complex is written

$$\frac{F_{\rm I}^{(2)}}{nk_BT} = \frac{mN}{n\varphi}\left(C(2\varphi)^3 + \frac{\sqrt{2}v}{12\pi}\left(\frac{24\varphi l}{v\sigma^2 a^2}\right)^{3/4}\right) \qquad (4)$$

The first term of eq 4 describes hard-core repulsive interactions of monomer units in the Θ-solvent. The second term is the RPA correction to the mean-field free energy. It is responsible for the fluctuation-induced attraction of charged units. Calculation of this term is done in the Appendix. Notice that the translational entropy of PCs is neglected in eq 4. The equilibrium value of the free energy $F_{\rm I}^{(2)}$ is found by minimization with respect to the fraction φ:

$$\frac{F_{\rm I}^{(2)}}{nk_BT} = \frac{9}{4\pi}\left(\frac{8\pi C}{9}\right)^{1/9}\frac{mN}{n}\left(\frac{l}{a\sigma^2}\right)^{2/3}, \quad \varphi = \frac{1}{8}\left(\frac{64}{3\pi^4 C^4}\right)^{1/9}\left(\frac{l}{a\sigma^2}\right)^{1/3} \qquad (5)$$

The value of φ coincides with that of diblock polyampholyte complexes calculated within the framework of the scaling approach.[32] On the other hand, in contrast to the scaling theory,[32] the energy of the complex $F_{\rm I}^{(2)}$ is positive. This difference is connected with the sign of the term of the fluctuation-induced attraction, eq 14. This term is always positive.

2.2. State II. Let us consider the overcharged complex where all *n* excess PCs are trapped within the PA. The key assumption of our model is that the whole excess charge of the complex is smeared out throughout the volume of the complex. It becomes possible because of the collective effect: excess and neutralizing PCs tend to be rearranged within the complex in such a way as to remove charge (spatial) inhomogeneities of the complex. These inhomogeneities could be originated by the excess PCs in the case if the neutralizing PCs would be immobile. Such rearrangement is favorable: homogenization of the PCs within the complex minimizes the energy of electrostatic interactions.

The total free energy of the overcharged complex is derived in a similar way as eqs 2 and 4:

$$\frac{F_{\mathrm{II}}}{nk_{\mathrm{B}}T} = \frac{3}{10}\frac{l_{\mathrm{B}}t(\Theta)}{nR}[nz(1-B) + Z(\Gamma - B)]^2 + \left(z + \frac{Z}{n}\right)\left(B\ln\frac{Bc^-}{\Theta} + (1-B)\ln\frac{(1-B)c^-}{1-\Theta}\right) + \frac{Z}{n}\left(\Gamma\ln\frac{\Gamma c^+}{\Theta} + (1-\Gamma)\ln\frac{(1-\Gamma)c^+}{1-\Theta}\right) + \frac{4\pi R^3}{3nv}\left(C(\bar{\varphi}_{\mathrm{s}} + \varphi_{\mathrm{m}})^3 + \frac{\sqrt{2}v}{12\pi}\left(\frac{12(\bar{\varphi}_{\mathrm{s}} + \varphi_{\mathrm{m}})l}{v\sigma^2a^2}\right)^{3/4}\right), \quad \Theta = \left(\frac{R}{R_0}\right)^3, \quad \bar{\varphi}_{\mathrm{s}} = \frac{3Nk(p+n)v}{4\pi R^3}, \quad \varphi_{\mathrm{m}} = \frac{3Nmv}{4\pi R^3} \quad (6)$$

Here the first term is the mean-field electrostatic energy of the excess charge of the complex. The next two terms describe the translational entropy of counterions inhomogeneously distributed between the complex and the outer solution. The overcharged complex collapses if the excess charge is not so high. The last term of eq 6 is responsible for the collapse. It comprises the third virial contribution $\sim C$, which is necessary to ensure the stability of the complex, and the RPA free energy providing the fluctuation-induced attraction. The latter is derived in the Appendix, eq 20. Notice that fluctuations of the excess charges also contribute to the attraction of charged units in the complex.

The equilibrium fractions of the counterions within the complex, B, Γ, and the radius of the complex, R, are found by minimization of eq 6.

3. Results and Discussion

The difference of the free energies of the two states, $\delta = (F_{\mathrm{II}} - F_{\mathrm{I}})/(nk_{\mathrm{B}}T)$, as a function of the number of excess PCs, n, for various values of the parameters m, N, and σ is presented in Figure 3. These curves are obtained by numerical minimization of eqs 1 and 6. It is seen that stability of the overcharged complexes (negative values of δ) is possible if the number of the excess PCs is smaller some certain value n^*, $\delta(n^*) = 0$. This value increases with m for all cases depicted in Figure 3a1–a3. However, the strength of the overcharging, $\alpha = n^*k/m$ (the ratio of the excess charge, n^*z, to the bare charge of the microgel, Z), weakly depends on m (at least for the parameters analyzed), $\alpha \approx 0.22-0.24$ (a1, a3), $0.27-0.3$ (a2). Simultaneous decrease of the bare charge of the PA and PCs via shortening of the subchains and the arms, N, Figure 3a1,a2, or via decrease of the fraction of charged units, $f = 1/\sigma$, Figure 3a1,a3, leads to the increase of n^*.

To demonstrate the driving force for the overcharging, let us plot the dependence of the relative mean-field electrostatic energy (δ_{C}), the energy of the translational motion of counterions (δ_{ci}), the elastic free energy of the star arms (δ_{el}), the energy of excluded-volume interactions (δ_{excl}), and the RPA electrostatic energy (δ_{RPA}) on n in the range of the values of n where the overcharged complex is stable, $\delta = \delta_{\mathrm{C}} + \delta_{\mathrm{ci}} + \delta_{\mathrm{el}} + \delta_{\mathrm{excl}} + \delta_{\mathrm{RPA}} < 0$ (Figure 3b1–b3). It is seen that δ_{C} and δ_{el} are always negative; i.e., the mean-field electrostatic interactions and the elastic free energy of the star arms stabilize the overcharged complex. The physical reason for this kind of stabilization is the gain in the self-energy of the trapped PCs: the charge of the complex is distributed homogeneously throughout the volume, reducing the charge density of the excess PCs compared to that in the solution. As a result, the swelling of the excess PCs within the complex reduces, too. The excluded-volume interactions of monomer units also play a stabilizing role, $\delta_{\mathrm{excl}} < 0$: Despite the rise of the number of monomer units within the overcharged complex, the mean-field electrostatic repulsion of charged units reduces the concentration of the overcharged complex in comparison with that of the neutral complex.

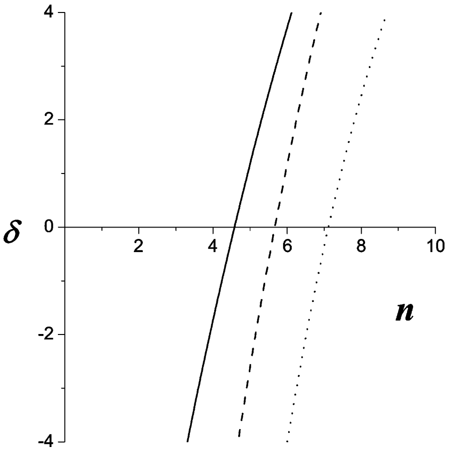

Figure 4. Difference of the free energies, $\delta = (F_{\mathrm{II}} - F_{\mathrm{I}})/(nk_{\mathrm{B}}T)$, as a function of the number of excess polycations, n, for various values of the number of the arms k: $k = 5$ (solid), $k = 7$ (dashed), and $k = 9$ (dotted). We use $R_0 = 150l_{\mathrm{B}}$, $N = 100$, $m = 100$, and $\sigma = 20$.

If the number of the excess PCs in the system is not so high, counterions stabilize the overcharged complex ($\delta_{\mathrm{ci}} < 0$ in Figure 3b1–b3). This effect is connected with the gain in the translational entropy due to the partial release of those counterions which are trapped within the excess PCs in the unbound state. On the other hand, if the number of the excess PCs is high enough, the entropic mechanism does not work anymore, $\delta_{\mathrm{ci}} > 0$ (Figure 3b1–b3): the high number of the excess PCs within the complex (high charge of the complex) is able to keep more counterions (per one PC) than it would be in the unbound state.

The overcharging is very sensitive to the number of the star arms, k (Figure 4): n^* increases with k, and the strength of the overcharging $\alpha = n^*k/m$ can become high enough, $\alpha \approx 0.64$ at $k = 9$. Such behavior is determined by the increase of the self-energy of the unbound excess PCs with k. Therefore, a larger number of the excess PCs are able to come into the complex.

Under dilution of the system (the increase of R_0) the stabilizing role of the counterions diminishes (Figure 5) and disappears in the limit of infinite dilution ($R_0 \to \infty$). In this case a very simple quantitative criterion for the charge inversion can be obtained if we set β, γ, B, Γ, θ, $\Theta = 0$ in eqs 1 and 6:

$$\frac{F_{\mathrm{I}}}{nk_{\mathrm{B}}T} \approx 9N\left(\frac{u}{\sigma^2}\right)^{2/3}\left(\frac{5^{1/3}k^{5/3}}{10} + \left(\frac{C}{72\pi^2}\right)^{1/9}\frac{m}{n}\right) + T_0, \quad r \approx aN\left(\frac{uk}{5\sigma^2}\right)^{1/3} \gg aN^{1/2}, \quad \frac{F_{\mathrm{II}}}{nk_{\mathrm{B}}T} = \frac{3l_{\mathrm{B}}n}{5R}\left(\frac{Nk}{\sigma}\right)^2 + \frac{9}{16\pi^2}\frac{Ca^6N^3s^3}{nR^6} + \frac{4}{\sqrt{3}n}\left(\frac{NsRu}{\sigma^2a}\right)^{3/4} + T_0, \quad s = 2m + kn \quad (7)$$

where $u = l_{\mathrm{B}}/a$, $T_0 = (z + Z/n)\ln c^- + (Z/n)\ln c^+$, and equilibrium values of F_{I} and F_{II} are found by minimization with respect to the radius of the PC, r, and of the overcharged complex, R. The equation $\delta(n^*) = 0$ has a solution only under the condition $m \gg kn$ (the case $k \gg 1$ is excluded from the

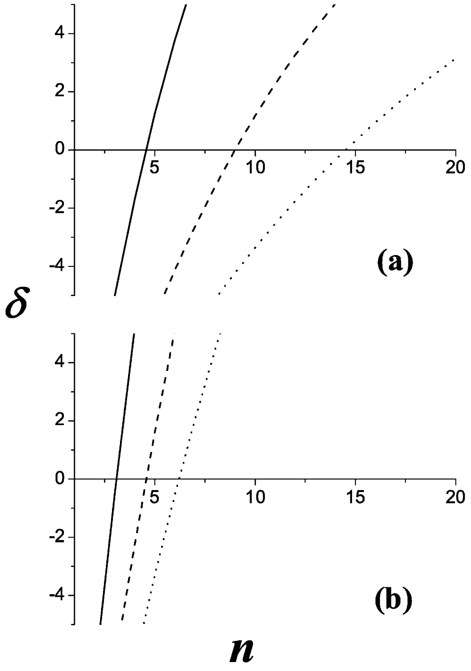

Figure 5. Difference of the free energies, $\delta = (F_{\mathrm{II}} - F_{\mathrm{I}})/(nk_{\mathrm{B}}T)$, as a function of the number of excess polycations, n, for various values of the concentration of PAs ($\sim 1/R_0^3$): (a) $R_0 = 150l_{\mathrm{B}}$ and (b) $R_0 = 300l_{\mathrm{B}}$. We use $N = 100$, $\sigma = 20$, $m = 100$ (solid), $m = 200$ (dashed), and $m = 300$ (dotted).

analysis). In this limit the first term of F_{II} is small, and we can use a perturbation theory to minimize with respect to R:

$$\frac{F_{\mathrm{II}}}{nk_{\mathrm{B}}T} \approx \frac{9Ns}{2n}\left(\frac{u}{\sigma^2}\right)^{2/3}\left(\left(\frac{C}{72\pi^2}\right)^{1/9} + \frac{2}{15}\left(\frac{8\pi^2}{9\sqrt{3}C}\right)^{4/27}\left(\frac{Nu^{2/3}n^3k^3}{s^2\sigma^{4/3}}\right)^{2/3}\right) + T_0,$$

$$R \approx \left(\frac{27C}{8\sqrt{3}\pi^2}\right)^{4/27} a\left(\frac{Ns\sigma^{2/3}}{u^{1/3}}\right)^{1/3} \quad (8)$$

and n^* has the value

$$n^*k \approx \frac{15}{2}\left(\frac{27C}{8\sqrt{3}\pi^2}\right)^{4/27}\left(\left(\frac{k}{5}\right)^{2/3} - \left(\frac{C}{72\pi^2}\right)^{1/9}\right)\left(\frac{2m}{N^2}\right)^{1/3}\left(\frac{\sigma^2}{u}\right)^{4/9} \quad (9)$$

In this regime n^* can be high enough, $n^* \sim m^{1/3}$, but the strength of the overcharging becomes small, $\alpha = n^*k/m \sim \sigma^{8/9}/(mN)^{2/3} \ll 1$. Similarly to the system with the macroions of fixed size,[23] the condition (9) can be rewritten in terms of the radii of the unbound PCs, eq 7, and of the overcharged complex, eq 8:

$$n^* = \frac{R}{\mu r}, \quad \mu = \frac{2}{3}\frac{1}{1 - \left(\dfrac{5^6C}{72\pi^2k^6}\right)^{1/9}} \quad (10)$$

Therefore, the number of the excess PCs is proportional to the radius of the complex.

Using the results for the regime of infinite dilution, let us discuss the following aspect of the model. Derivation of the free energy of the unbound PCs in the state I, eq 2, was done on the mean-field level neglecting the RPA term. Indeed, in contrast to the neutral or overcharged complex, the fluctuation-induced electrostatic energy of the swollen arms is much more smaller than the electrostatic mean-field energy of the PC. To demonstrate this, let us address to the scaling concept. It is known that the mean-field description of the weakly charged chain swollen in the Θ-solvent coincides with the scaling description where the chain is considered as a sequence of electrostatic blobs, each of the size $\xi_{\mathrm{el}} \approx a\sigma^{2/3}/u^{1/3}$ and of the number of the segments $g_{\mathrm{el}} \approx \sigma^{4/3}/u^{2/3}$ ($\xi_{\mathrm{el}} \approx ag_{\mathrm{el}}^{1/2}$).[35,36] The end-to-end distance of the chain scales as $r_{\|} \approx N\xi_{\mathrm{el}}/g_{\mathrm{el}} \approx aNu^{1/3}/\sigma^{2/3}$, and the electrostatic energy is proportional to the number of the blobs, $F_{\mathrm{chain}}/k_{\mathrm{B}}T \approx N/g_{\mathrm{el}} \approx Nu^{2/3}/\sigma^{4/3} \gg 1$. These results coincide with those of eq 7 (the first term of F_{I} and the value of r at $k \sim 1$). To estimate the fluctuation-induced electrostatic energy, one has to take into account lateral fluctuations of the chain of the blobs.[33] In the Θ-solvent, the characteristic length scale of the fluctuations is $r_{\perp} \approx (N/g_{\mathrm{el}})^{1/2}\xi_{\mathrm{el}} \approx aN^{1/2}$. Let us introduce the second kind of blobs of the size $r_{\|}$ so that the chain can be viewed as a straight-line row of the blobs whose number is $r_{\|}/r_{\perp} \gg 1$. Within such blob the electrostatic blobs do not fluctuate (they are absolutely correlated, i.e., one can say about "persistence length" of the chain of the electrostatic blobs), and fluctuation-induced interactions are dominant at the length scales larger than $r_{\perp}$. Thus, the fluctuation-induced electrostatic energy can be estimated as $F_{\mathrm{fluc}}/k_{\mathrm{B}}T \approx r_{\|}/r_{\perp} \approx (Nu^{2/3}/\sigma^{4/3})^{1/2}$, i.e., $F_{\mathrm{fluc}} \ll F_{\mathrm{chain}}$.

Examination of the system is confined by a demonstration of the stability of the overcharged complexes and by the description of the mechanisms responsible for the overcharging. Phase behavior of the solution of the microgel particles and multiarm stars, which can embrace coexistence of the states I and II or precipitation of the neutral complexes, will be described in a forthcoming publication.

4. Conclusions

We have studied in this paper the overcharging of the weakly charged penetrable microgel particle (PA) by oppositely charged multiarm star polyelectrolytes (PCs) in dilute solution. For this purpose we have developed a simple theory that combines both the mean-field approximation and the random phase approximation (RPA) to take into account fluctuation-induced attraction of charged units in the complex. The main physical reason for the overcharging was shown to be the gain in the self-energy of the excess PCs because of localization of them within the neutral complex. The self-energy of the PC comprises two dominant contributions: (i) the electrostatic self-energy and (ii) the energy of the stretching of the arms due to unscreened repulsion of the charged units. The electrostatic self-energy "release" in the complex occurs because of the collective effect: neutralizing and excess PCs are rearranged within the complex in such a way as to homogenize the total charge of the complex. As a result, the excess charge of the complex becomes "smeared out" throughout larger volume than it is in the unbound PCs; i.e., the electrostatic self-energy reduces. The screening of the electrostatic repulsion between the charged units of the excess PCs within the complex leads to the shrinkage of the star arms. This explains the gain in the elastic free energy.

The counterions have been found to play a dual role. If the number of the excess PCs is small, the counterions, which are trapped within the PCs, promote the overcharging due to the release of the part of them after localization of the PCs within the complex. If the number of the excess PCs is larger, the complex gets higher charge and is able to retain more counterions in comparison with the unbound PCs. The fluctuation-induced interactions of the charged units prohibit the overcharging because they are aimed to reduce the size of the complex.

We have shown that the overcharging is sensitive to the concentration of the polyanions and to the number of the arms of the polycations. Dilution of the solution diminishes the overcharging. To get higher inverse charge of the complex, one has to increase the number of the arms of the PCs.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft within the SFB 569 and by the Russian Agency of Science and Innovations.

Appendix

Neutral Complex. Let us consider a neutral PA−PCs complex which is free of counterions. It is assumed that the subchains and the star arms of the complex have Gaussian statistics. Denote by $\psi_m(\mathbf{x}) = \rho_m(\mathbf{x}) - \varphi/v$ and $\psi_s(\mathbf{x}) = \rho_s(\mathbf{x}) - \varphi/v$ the small density fluctuations of monomer units of the microgel and the stars, respectively, $|\psi_m(\mathbf{x})| \ll \varphi/v$, $|\psi_s(\mathbf{x})| \ll \varphi/v$. In the main approximation they contribute to the free energy functional as

$$\frac{\delta F_n(\psi_m,\psi_s)}{k_\mathrm{B}T} = \frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[\frac{l}{q^2}\left|\frac{\psi_s(\mathbf{q})}{\sigma} - \frac{\psi_m(\mathbf{q})}{\sigma}\right|^2 + v\frac{a^2q^2}{12\varphi}(|\psi_s(\mathbf{q})|^2 + |\psi_m(\mathbf{q})|^2)\right] \quad (11)$$

where we used Fourier-transformed amplitudes ψ; $\mathbf{q}$ is the wave vector and $|\psi_m(\mathbf{q})|^2 \equiv \psi_m(\mathbf{q})\psi_m(-\mathbf{q})$. The first term of eq 11 corresponds to the electrostatic interactions. The parameter l is proportional to the Bjerrum length, $l = 4\pi l_\mathrm{B}$. This term vanishes in the limit $q \to 0$ because of the macroscopic electric neutrality of the complex. The second term of eq 11 is the structural contribution. The effect of cross-links of the microgel and the stars on the density fluctuations is negligible in comparison with that of the subchains and the arms. Therefore, we use the approximation for the mixture of linear chains (the translational motion of the PCs is neglected).[33]

The electrostatic free energy of the weakly fluctuating charges can be found following a standard procedure:

$$\frac{F_n}{k_\mathrm{B}T} = -\ln\int \mathscr{D}\psi_m\mathscr{D}\psi_s \exp\left\{-\frac{\delta F_n(\psi_m,\psi_s)}{k_\mathrm{B}T}\right\} + \ln\int \mathscr{D}\psi_m\mathscr{D}\psi_s \exp\left\{-\left.\frac{\delta F_n(\psi_m,\psi_s)}{k_\mathrm{B}T}\right|_{l=0}\right\} \quad (12)$$

where $\mathscr{D}\psi_m\mathscr{D}\psi_s \equiv \Pi_\mathbf{q}\mathrm{d}\psi_m(\mathbf{q})\ \mathrm{d}\psi_s(\mathbf{q})$ is a product of differentials. The details of calculation of similar Gaussian integrals can be found in ref 34. In the case of the functional 11, eq 12 takes the form

$$\mathscr{F}_n = \frac{F_n}{k_\mathrm{B}TV} = \frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\ln\left(1 + \frac{24l\varphi}{va^2q^4\sigma^2}\right) \quad (13)$$

where V is the volume of the complex. Equation 13 comprises both the energy of fluctuation-induced interactions between the charges and the self-energy of the chains. In contrast to the systems with low-molecular-weight ions,[29,30] the integral in eq 13 is convergent at $q \to \infty$:

$$\mathscr{F}_n = \frac{\sqrt{2}}{12\pi}\left(\frac{24\varphi l}{v\sigma^2a^2}\right)^{3/4} \quad (14)$$

To extract the contribution of intercharge interactions, let us calculate the osmotic pressure:

$$\pi_n = \varphi\frac{\partial\mathscr{F}_n}{\partial\varphi} - \mathscr{F}_n = -\frac{\sqrt{2}}{48\pi}\left(\frac{24\varphi l}{v\sigma^2a^2}\right)^{3/4} \quad (15)$$

It is negative and decreases with the increase of φ; i.e., the fluctuation-induced electrostatic interactions are attractive.

Overcharged Complex. The overcharged complex can contain some certain fraction of counterions to compensate (partially) the excess charge. Denote by $\psi_m(\mathbf{x}) = \rho_m(\mathbf{x}) - \varphi_m/v$, $\bar\psi_s(\mathbf{x}) = \bar\rho_s(\mathbf{x}) - \bar\varphi_s/v$, and $\xi(\mathbf{x}) = \rho_c(\mathbf{x}) - \varphi_c/v$ the small density fluctuations of the microgel, stars, and counterions, respectively. The contribution of Coulomb interactions to the free energy functional of the overcharged complex can be written as follows:

$$\begin{aligned}\frac{F_\mathrm{C}}{k_\mathrm{B}T} = \frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\frac{l}{q^2}\left|\frac{\bar\rho_s(\mathbf{q})}{\sigma} - \frac{\rho_m(\mathbf{q})}{\sigma} - \rho_c(\mathbf{q})\right|^2 = {}\\ \frac{1}{2}\int \mathrm{d}\mathbf{q}(2\pi)^3 l\frac{\delta(\mathbf{q})\ \delta(\mathbf{q})}{q^2}\left(\frac{\bar\varphi_s}{v\sigma} - \frac{\varphi_m}{v\sigma} - \frac{\varphi_c}{v}\right)^2 + {}\\ \int \mathrm{d}\mathbf{q}l\frac{\delta(\mathbf{q})}{q^2}\left(\frac{\bar\varphi_s}{v\sigma} - \frac{\varphi_m}{v\sigma} - \frac{\varphi_c}{v}\right)\left(\frac{\bar\psi_s(\mathbf{q})}{\sigma} - \frac{\psi_m(\mathbf{q})}{\sigma} - \xi(\mathbf{q})\right) + {}\\ \frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\frac{l}{q^2}\left|\frac{\bar\psi_s(\mathbf{q})}{\sigma} - \frac{\psi_m(\mathbf{q})}{\sigma} - \xi(\mathbf{q})\right|^2\end{aligned} \quad (16)$$

The first term on the right-hand side of eq 16 corresponds to the electrostatic energy of the excess charge homogeneously distributed throughout the volume of the complex. The second term of eq 16 is equal to zero because $\psi_m(\mathbf{q}{=}0) = \int\mathrm{d}\mathbf{x}(\rho_m(\mathbf{x}) - \varphi_m/v) \equiv 0$, etc. The last term comes from the thermodynamic fluctuations of the charged units. Introducing electrostatic potential $w(\mathbf{x})$, which is subjected to the Poison equation, $\Delta w(\mathbf{x}) = -4\pi(\bar\varphi_s/(\sigma v) - \varphi_m/(\sigma v) - \varphi_c/v)$, eq 16 can be rewritten in the conventional form

$$\frac{F_\mathrm{C}}{k_\mathrm{B}T} \approx \int \mathrm{d}^3x\,\frac{l_\mathrm{B}(\nabla w(\mathbf{x}))^2}{8\pi} + \frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\frac{l}{q^2}\left|\frac{\bar\psi_s(\mathbf{q})}{\sigma} - \frac{\psi_m(\mathbf{q})}{\sigma}\right|^2 \quad (17)$$

where integration over the spatial coordinates $\mathbf{x}$ covers the volume of the complex and $\bar\varphi_s/(\sigma v) - \varphi_m/(\sigma v) - \varphi_c/v = [nz(1 - B) + Z(\Gamma - B)]/(4\pi R^3/3)$. We neglect the contribution of the density fluctuations of counterions in eq 17. To argue in favor of this, let us address to macroscopically neutral solution of the mixture of oppositely charged polyelectrolytes with low-molecular-weight ions.[29,30] For this system in the salt-free regime the contribution of counterions is negligible if the condition

$$l\varphi_c{}^2 \ll af^2(\bar\varphi_s + \varphi_m) \quad (18)$$

is held.[29,30] The macroscopic electric neutrality provides the dependence $\varphi_c = f(\bar\varphi_s + \varphi_m)$, leading to $l_\mathrm{B}(\bar\varphi_s + \varphi_m)/a \ll 1$. This inequality is always valid for the case of weakly charged polyelectrolytes. The concentration of the counterions inside the finite-size overcharged complex is smaller than that in the neutral system.[29,30] Therefore, in the case of the overcharged complex the condition (18) has to be held a fortiori.

Taking into account that the average concentrations of monomer units of the microgel and the stars are different, $\bar\varphi_s \neq \varphi_m$, the contribution of the density fluctuations to the free energy functional takes the form

$$\frac{\delta F_{\mathrm{o}}(\psi_m,\psi_s)}{k_{\mathrm{B}}T} = \frac{1}{2}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[\frac{l}{q^2}\left|\frac{\bar{\psi}_s(\mathbf{q})}{\sigma} - \frac{\psi_m(\mathbf{q})}{\sigma}\right|^2 + v\,\frac{a^2q^2}{12\bar{\varphi}_s}|\bar{\psi}_s(\mathbf{q})|^2 + v\,\frac{a^2q^2}{12\varphi_m}|\psi_m(\mathbf{q})|^2\right] \quad (19)$$

The fluctuation-induced electrostatic energy of the overcharged complex is found by eq 12 with the functional (19):

$$\mathscr{F}_{\mathrm{o}} = \frac{\sqrt{2}}{12\pi}\left(\frac{12(\bar{\varphi}_s + \varphi_m)l}{v\sigma^2a^2}\right)^{3/4} \quad (20)$$

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MA0605649