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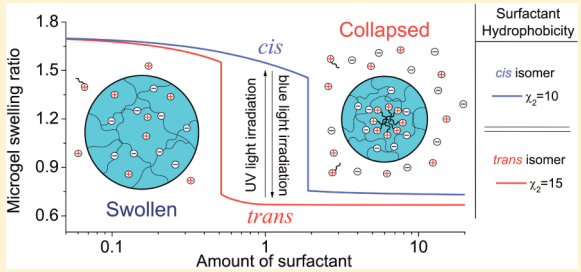
Theory of Collapse and Overcharging of a Polyelectrolyte Microgel Induced by an Oppositely Charged Surfactant

Artem M. Rumyantsev,[†] Svetlana Santer,[‡] and Elena Yu. Kramarenko*[,†]

[†]Physics Department, Moscow State University, 119991 Moscow, Russia

[‡]Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

ABSTRACT: We report on the theoretical study of interaction of ionic surfactants with oppositely charged microgel particles in dilute solutions. Two approaches are proposed. Within the first approach, the micellization of the surfactants inside the microgel is taken into account while the second model focuses on the hydrophobic interactions of the surfactant tails with the hydrophobic parts of microgel subchains. It has been shown that microgels effectively absorb surfactant ions. At low surfactant concentration this absorption is realized due to an ion exchange between microgel counterions and surfactant ions. The ion exchange is significantly affected by the amount of the microgel counterions initially trapped within the microgel particles which depends on the size of the microgel, its ionization degree, cross-linking density as well as polymer concentration in the solution. Increase of the surfactant concentration causes contraction of the microgels, which can be realized as either a continuous shrinking or a jump-like collapse transition depending on the system parameters. In the collapsed state additional absorption of surfactants by microgels takes place due to an energy gain from micellization or hydrophobic interactions. This leads to microgel precipitation and successive microgel overcharging at an excess of the surfactant in the solution. The theoretical results are compared with the existing experimental data, in particular, on photosensitive surfactant/microgel complexes.



INTRODUCTION

Polyelectrolyte (PE) gels are well-known to be highly responsive systems able to undergo volume phase transitions under change of various environmental conditions. Their properties have been reviewed many times.[1,2] The rate of gel volume change is mainly defined by diffusion processes which are time-consuming for large macroscopic gel samples, the equilibrium state is often reached after days or even months, this fact limiting their practical applications. The rate of the gel swelling/shrinking decreases with its geometrical dimensions.[3] In this respect, polymer micro- and nanogels are of great interest due to their ability to respond fast to external stimuli. These systems are widely studied nowadays being promising for drug and gene delivery, sensor design.[4−6]

One of the possible ways to control the PE gel swelling and hydrophobicity of the gel medium is to use surfactant. The collapse of the PE macroscopic gels caused by complexation with an oppositely charged surfactant was first theoretically described and experimentally observed at the end of the 20th century.[7−10] It has been shown theoretically[10] that a PE gel absorb effectively surfactant due to an ion exchange between gel counterions and surfactant ions. As a result, the surfactant concentration within the gel can be much higher than in the outer solution. Another important theoretical prediction was a preferable surfactant micellization within the gel rather than in the outer solution. Indeed, aggregation of ionic surfactant in solvent medium outside the gel is accompanied by immobilization of surfactant counterions in the vicinity of charged micelles and, thus, by a loss in counterion translational entropy. In the gel interior micelle excess charge is neutralized by network subchains while counterions are still able to move freely, resulting in a decrease of CMC inside the PE gel by several orders of magnitude.[10] Thus, when the concentration of surfactant inside the gel exceeds new reduced CMC, intense formation of micellar aggregates in the gel interior results in a drop of exerting osmotic pressure and induces gel continuous shrinking or abrupt collapse.[10] These theoretical predictions were confirmed by experimental studies.[11]

It is natural to expect that the behavior of PE microgels and macroscopic networks in the presence of ionic surfactants might be quite different because the electroneutrality condition is fulfilled only for large gel samples, while small polymer particles are able to release some fraction of counterions into the external solution.[12] Nonzero microgel electric charge promotes or suppresses surfactant trapping depending on the sign. Coulomb interactions, manifesting themselves only in the case of small polymer particles, become the second driving force of surfactant sorbtion, while hydrophobic interactions are the first one. So, the case of PE microgels requires a separate detailed consideration.

In this paper, we develop a first, to our knowledge, theoretical model of interaction of PE microgels with

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oppositely charged surfactants, though significant amount of experimental data have been accumulated for the past decade. For instance, a number of works were devoted to microgel shrinking[13−20] and charge-reversal[16−20] induced by oppositely charged surfactants. In the present paper, these results are explained in the framework of our theory.

Furthermore, there is an increased interest in photosensitive azobenzene-containing surfactants, the hydrophobicity of which can be adjusted by illumination with light of appropriate wavelength.[19−22] The azobenzene molecule bridges the hydrophobic tail and the charged headgroup of the surfactant. Under UV-irradiation, the azobenzene undergoes photoisomerization from a trans- to a cis-conformation which can be reversed by irradiation with blue light. It was shown that the interaction of such surfactants with soft microgel particles allows one to control their size.[19,20] When the photosensitive surfactants are added to a corresponding soft colloid dispersion, the surfactants diffuse into the microgel matrix and cause it to contract as its electrostatically repelling charge groups are effectively screened, the microgel colloids shrink. After irradiation the surfactant becomes hydrophilic since the cis-isomer has a larger dipole moment, the surfactant is expelled from the hydrogel particles into bulk solution, and the particles swell back to their original size. This process is reversible and can be carried out repeatedly.[19] In this study, microgel transitions induced by irradiation are considered from theoretical point of view.

The exact structure of surfactant aggregates inside the microgels is not absolutely clear. In order to clarify the mechanism of interactions dominating inside the microgel particle, we propose two theoretical approaches aimed at description of interaction between oppositely charged PE microgel and ionic surfactants. The first approach considers explicitly the micelle formation inside the microgel. We just generalize the theory developed in ref 10 for a macroscopic gel in a surfactant solution taking into account possible nonzero charge of microscopic gel particles and, hence, quite different redistribution of small ions in such a system in comparison with the case of a macroscopic gel sample.

Within the second approach, we focus on the hydrophobic interactions between the hydrocarbon tails of the surfactants and the hydrophobic parts of the microgels. The interactions between all system components are written in terms of the Flory−Huggins lattice theory and the relative contribution of the hydrophobic interactions on the surfactant absorption as well as the microgel collapse is elucidated.

The paper is organized as follows. In the next section, we formulate the theoretical model describing the effect of surfactant micellization within the microgel and perform comparative analysis of the microgel swelling and surfactant absorption depending on the microgel size (microgel vs macrogel) and other microgel parameters. The existing experimental data are discussed with respect to theoretical predictions. In the third section, the theory is modified in order to account for hydrophobic interactions and their role is analyzed. The main results are summarized in the Conclusion.

MICELLIZATION OF SURFACTANT WITHIN AN OPPOSITELY CHARGED MICROGEL PARTICLE

Theoretical Model. We consider a polyelectrolyte microgel particle immersed in a solution of an oppositely charged ionic surfactant (Figure 1). The microgel consists of ν subchains each of N monomeric units. Furthermore, the microgel subchains contain a fraction f of ionogenic groups that dissociate with a release of mobile counterions each of the elementary charge e. The polymer is assumed to be strongly dissociating and the value of f to be fixed and independent of the environmental conditions. We restrict ourselves to the case of a slightly charged polyelectrolyte ($f \ll 1$) immersed in a high polar solvent (water) and neglect the effect of an ion pair formation between any oppositely charged ions. Under chosen conditions this presumption seems to be reasonable, while charge renormalization effects was shown to play a crucial role in the case of low polar solvents,[24−26] for highly charged[24] or pH-dependent polyelectrolytes.[27,28]

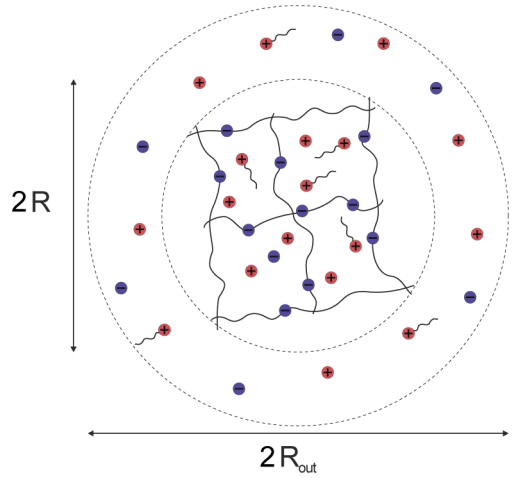

Figure 1. Schematic representation of the solution elementary cell. R and R_{out} are the equilibrium radius of the microgel and the radius of the solution elementary cell, respectively.

Let, for instance, the microgel subchains be negatively charged while the counterion charges are positive. We consider a salt-free case, thus, the counterions of the microgel particles, surfactant ions, and surfactant counterions are the only mobile ions in the system.

In the initial state conformations of the microgel subchains are Gaussian coils and the particle size can be estimated as $R_0 \sim aN^{1/2}\nu^{1/3}$. The equilibrium microgel size R is defined through the swelling ratio $\alpha = R/R_0$. The average distance between two adjacent microgel particles in the dilute solution R_{out} defined by the polymer concentration is by far larger than the equilibrium microgel size R. We introduce a dimensionless parameter $\gamma = R_0/R_{out}$ characterizing the degree of dilution of the microgel solution, $\gamma \ll 1$. The volume of the solution elementary cell, i.e. the volume of the solution per one microgel particle, can be estimated as $V_{out} \sim R_{out}^3$. So, the fraction of the solution elementary cells occupied by the microgel particles is $V_{gel}/V_{out} \sim R^3/R_{out}^3 \sim \alpha^3\gamma^3$.

The total number of the charged polymer units in a single microgel particle equals to the number $fN\nu$ of the counterions in the solution elementary cell. The counterions distribute inhomogeneously in the solution. Following two-zone model (Figure 1), the fraction β of the counterions is held inside the particle while a fraction $(1 - \beta)$ of network counterions leaves the interior of the microgel due to entropic reasons and moves freely in the outer solution.

We denote as Z the number of surfactant molecules in the solution per one charged group on polymer subchains, thus $ZfN\nu$ is the number of the surfactant molecules in the solution elementary cell and the average surfactant concentration in the solution is defined as $n = 3Zf\gamma^3/4\pi a^3N^{1/2}$. The surfactant

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molecules are ionized; they carry a unit charge which is opposite to the charge of the polymer subchains. Thus, according to our previous assumptions, surfactant ions are positively charged while their counterions are negatively charged.

Similar to the microgel counterions, the surfactant ions and surfactant counterions are distributed nonuniformly in the system, s and t are their fractions inside the microgel, respectively. We suppose that all microgels in the solution have the same average composition; i.e., surfactant ions distribute evenly among microgels. Although some experimental data on polyelectrolyte/surfactant complexes indicate that in some cases a disproportionation phenomenon can take place in such systems,[29] we do not examine this possibility.

Owing all types of ions are univalent, one can obtain the total electric charge of the particle $Q = eNf\nu(\beta - 1 + sZ - tZ)$ and microgel ζ-potential $\zeta = Q/\epsilon R$, while the charge of the outer cell region equals $-Q$ due to total electroneutrality of the solution.

Since our theory is only the first natural step in theoretical comprehension of PE microgel−surfactant systems, possible phase separation inside the microgel is not examined here, although it had been experimentally observed[30−34] and theoretically discussed[33−36] for the case of macroscopic networks. Thus, we propose that surfactant molecules are homogeneously distributed inside the microgel, and there are no surfactant-rich and surfactant-poor domains in the microgel interior.

To find the equilibrium distributions of ions of different types and the swelling ratio of the microgels we write down the total free energy of the solution per the elementary cell in k_BT units:

$$F_{tot} = F_{el} + F_{el-st} + F_{tr}^{nc} + F_{tr}^{sc} + F_{\text{int}} + F_s \tag{1}$$

The first term, F_{el}, takes into account the elastic energy of both stretching and compression of the microgel subchains:[37]

$$F_{el} = \frac{3}{2}\nu\left(\alpha^2 + \frac{1}{\alpha^2}\right) \tag{2}$$

The second term, F_{el-st}, describes the electrostatic energy of a charged microgel particle. It can be estimated as the energy of a spherical condenser with charge Q and the radii of the plates R and R_{out} (Figure 1):

$$F_{el-st} \sim \frac{Q^2}{\epsilon kT}\left(\frac{1}{R} - \frac{1}{R_{out}}\right) \sim uN^{3/2}f^2\nu^{5/3}$$
$$(\beta - 1 + sZ - tZ)^2(\Phi^{1/3}N^{1/6} - \gamma) \tag{3}$$

The numeric coefficient in this formula is of the order of unity and can be omited.[38,39] The dimensionless parameter u is the ratio of the Bjerrum length l_b to the monomer unit size a, $u = l_b/a = e^2/\epsilon a k_BT$, ϵ is the dielectric constant of the solvent and $\Phi = 1/\alpha^3\sqrt{N}$ is the polymer volume fraction within the particle. Formula 3 assumes that ions interact with the charged microgel via unscreened Coulomb potential. Since we consider salt-free solution and screening of electrostatic interactions is provided predominately by surfactant ions and all counterions, the Debye length λ_D can be estimated through the average surfactant concentration in the solution:

$$\lambda_D^{-1} = \sqrt{8\pi l_b n} = \sqrt{\frac{6uZf\gamma^3}{a^2N^{1/2}}} \tag{4}$$

The range of validity of eq 3 is roughly defined by inequality $\lambda_D \geq R_0$, i.e.

$$Z \leq Z_{scr} \equiv (6uf\gamma^3N^{1/2}\nu^{2/3})^{-1} \tag{5}$$

which is satisfied in subsequent calculations.

The next two terms in eq 1 account for the entropy of translational motion of the network and surfactant counterions, respectively:

$$F_{tr}^{nc} = fN\nu\left[\beta\ln(\beta f\Phi) + (1-\beta)\ln\left(\frac{(1-\beta)f\Phi\gamma^3}{\Phi N^{1/2} - \gamma^3}\right)\right] \tag{6}$$

$$F_{tr}^{sc} = ZfN\nu\left[t\ln(Ztf\Phi) + (1-t)\ln\left(\frac{Z(1-t)f\Phi\gamma^3}{\Phi N^{1/2} - \gamma^3}\right)\right] \tag{7}$$

The term F_{int} in 1 describes the volume interactions of the microgel monomer units. In case of low polymer concentration the virial expansion can be used:

$$F_{\text{int}} = N\nu\left(\frac{B}{a^3}\Phi + \frac{C}{a^6}\Phi^2\right) \tag{8}$$

Here B and C are the second and the third virial coefficients, respectively, $B \sim \tau a^3$ and $C \sim a^6$, τ is the relative temperature deviation from the Θ-point. In a good solvent when the microgel swells the main contribution is due to pairwise interactions of monomer units, $\tau \sim 1$ and $B \sim a^3$. Near the Θ temperature, B is close to zero, and the triple interactions can give the leading contribution to the interaction energy. The triple interactions should be also taken into account well below the Θ point where the monomer unit concentration is not so low. It should be noted that in this approach we neglect the interactions of all other species in the solution owing to their small concentrations.

The last term, F_s, in the free energy is connected with the presence of surfactant ions in the system. Following the experimental results and our previous theoretical treatment of macrogel−surfactant interactions let us consider the case of low (below CMC) surfactant concentrations in the solution. Then there is no micellization outside the microgel particles. However, the concentration of the surfactant ions within the microgels can be much higher than in the solution due to the reasons discussed above for the case of macroscopic gels.[10] Thus, in the general consideration micellization within the microgels should be taken into account. For the sake of simplicity we do not go into details of the interior structure of microgel/surfactant complex here, though different ordered structures with correlated location of surfactant aggregates inside macroscopic charged network have been observed.[40−44] In our model, the free energy F_s only includes contributions from the entropy of mobile surfactants ions as well as the aggregation free energy due to micelle formation, thus, F_s is the sum of two terms:

$$F_s = F_s^{tr} + F_{agg} \tag{9}$$

The first term in 9 is the free energy of translational motion of surfactant ions inside and outside the polymer particle:

$$F_s^{tr} = ZfN\nu\left[s\ln(Zsf\Phi) + (1-s)\ln\left(\frac{Z(1-s)f\Phi\gamma^3}{\Phi N^{1/2} - \gamma^3}\right)\right] \tag{10}$$

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To describe possible aggregation of the surfactant we consider their micellization as a thermoreversible self-organization of surfactant ions into micelles of a fixed optimal aggregation number m, $m \gg 1$ (Figure 2):

$$mA \rightleftarrows A_m \tag{11}$$

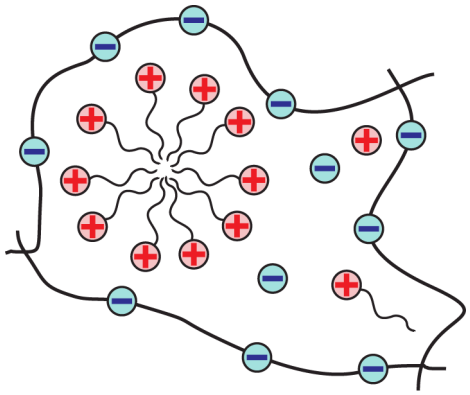

Figure 2. Schematic representation of the microgel interior.

For the sake of simplicity the volume of the surfactant ion is assumed to be of the order of the volume of the monomer unit, i.e., a^3. The gain in free energy due to micelle formation per one molecule in k_BT units is denoted as ΔF. Then the fraction q of the aggregated surfactants is given by generalization of the mass action law:[45,46]

$$\frac{q}{(1-q)^m} = (\Phi sZf)^{m-1} m \exp(\Delta F m) \tag{12}$$

The corresponding free energy has the following form:[45,46]

$$F_{agg} = N\nu Zfs\left[\ln(1-q) + \frac{m-1}{m}q\right] \tag{13}$$

Note that according to ref 10, CMC inside and outside the microgel can be estimated as follows

$$\mathrm{CMC}_{in} \sim \frac{1}{a^3}\exp(-\Delta F - 1) \tag{14}$$

$$\mathrm{CMC}_{out} \sim \frac{1}{a^3}\exp\left(-\frac{\Delta F}{2} - 1\right) \tag{15}$$

One can deduce the estimation for CMC_{in} directly from eq 12 by substituting $q = {}^1/_2$, while to obtain CMC_{out} it is necessary to

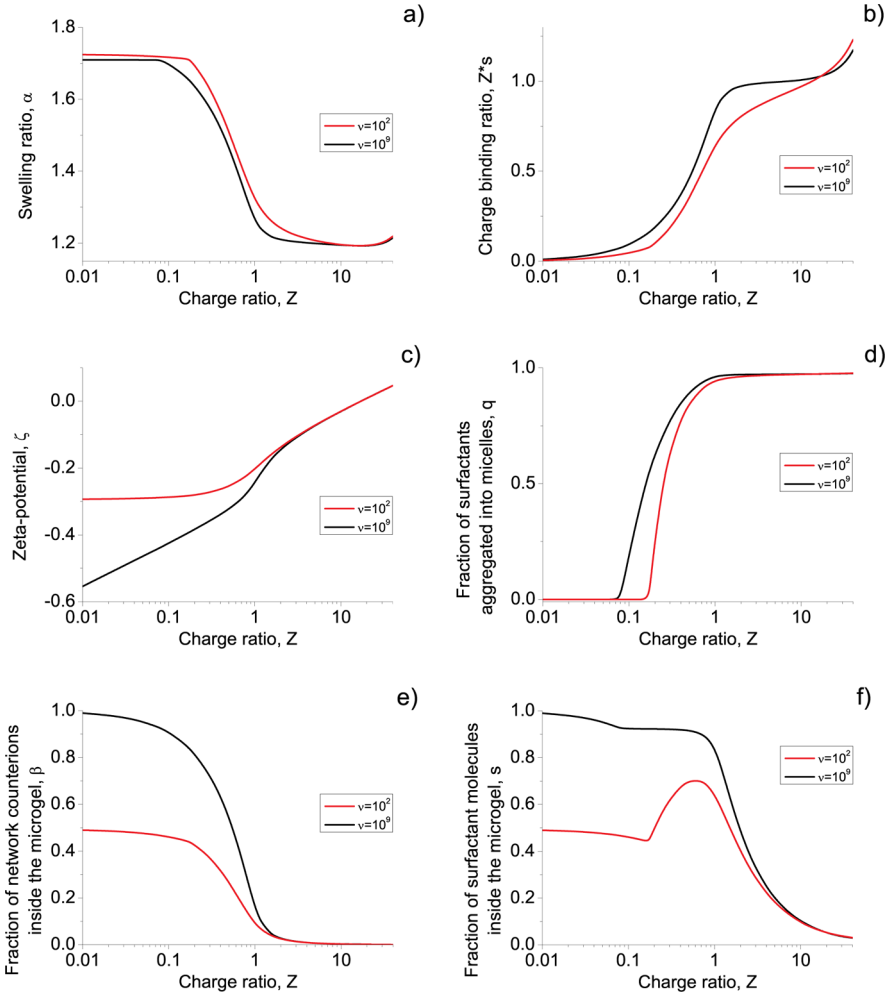

Figure 3. Swelling ratio α (a), charge binding ratio $Z^* s$ (b), ζ-potential ζ (c), fraction of surfactant molecules aggregated into micelles inside the gel q (d), fraction of trapped network counterions β (e), fraction of surfactant molecules inside the microgel s (f), as functions of ratio Z. Comparison of small ($\nu = 10^2$) and large ($\nu = 10^9$) microgels.

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take into account trapping of m surfactant counterions by a charged micelle.[10]

In the calculations below we avoid the case of micelle formation in the outer solution considering the range of low surfactant concentrations well below the CMC_{out}, $n < CMC_{out}$.

It is important to point out that in the proposed simple mean field consideration we omit short-range electrostatic interactions between highly charged micelles and oppositely charged microgel subchains favoring microgel collapse and formation of dense polyion/micelle complex.[34,47] This attraction can be treated, for instance, as an adsorption of a polyelectrolyte on an oppositely charged sphere.[48] Similar to multivalent counterions,[49−51] charged micelles should promote additional microgel shrinking and surfactant trapping. Account for these charge correlations and dense complex formation inside deswollen microgel is a prospective way for the model improvement, especially in case of highly charged networks ($f \sim 1$).[47] Disregard for the above effect is partially compensated though by also omitted excluded volume of surfactants as well as surfactant aggregates. This short-range repulsion hinders formation of microgel dense collapsed conformations and even is able to cause reentrant swelling. These are excluded volume effects that result in PE microgel reswelling under increasing salt concentration, as was demonstrated by de la Cruz and co-workers in ref 52.

Thus, the total free energy of the solution, $F_{tot}(\alpha, \beta, s, t)$, as a function of the four independent variables is defined. The equilibrium values of the microgel swelling ratio as well as surfactants and counterions fractions within the microgel can be obtained via minimization of the total free energy with respect to α, β, s, and t.

Analysis of the Surfactant Sorption and the Microgel Collapse. Let us start the analysis with the comparison of the macrogel and the microgel interactions with surfactant.

As it has been mentioned above the main difference in these two systems is in the counterion distribution. The effect of the microgel molecular mass on its swelling and counterion distribution was analyzed in detail in ref 12. It has been shown that microgels of a low molecular mass and thus, a low total charge cannot keep their counterions, the most of the counterions leave for the outer solution to gain in entropy. The microgel swelling in this case is realized due to electrostatic repulsion of unscreened microgel charges and $\alpha_{el-st} \sim N^{1/2}u^{1/3}f^{2/3}\nu^{2/9}$. With increasing molecular mass the total charge on the microgel increases and more and more counterions concentrate within the microgel to minimize the Coulomb energy. In the limiting case of the macroscopic gel all the counterions are kept within the gel and its swelling is realized due to osmotic pressure of counterions, $\alpha_{osmotic} \sim (Nf)^{1/2}$. It has been shown that the osmotic swelling is much higher than the electrostatic swelling at $\nu \sim 1$, $\alpha_{osmotic} \gg \alpha_{el-st}$. Besides, the fraction β of trapped counterions within the microgel particle increases monotonously with its molecular mass (i.e., with ν), while its swelling degree changes nonmonotonously having a maximum at some ν when β is close to 0.5.

According to these results,[12] one can expect that the ion exchange reaction in microgel/surfactant solution and thus, the microgel response to the surfactant addition should depend on the microgel molecular mass. In Figure 3, we plot the dependences of all the main solution parameters on the amount of surfactant for two different values of ν. The calculations were performed for $u = 1$ (aqueous solution), $N = 25$, $f = 0.1$, $\gamma = 0.1$, $B/a^3 = 0$ (Θ solvent), $C/a^6 = 1$ and $\Delta F = 8$. Although the surfactant aggregation number depends on surfactant concentration as well as properties of the surrounding medium, e.g., degree of gel ionization and degree of gel swelling,[53−55] the value of the aggregation number $m = 50$, typical for such commonly used surfactants as sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC), is also fixed in all subsequent calculations. This assumption is justified by insignificant influence of m on the system behavior within our approach. Two values of the number of subchains $\nu = 10^2$ and $\nu = 10^9$ were chosen. The small microgel with $\nu = 10^2$ is incapable of trapping the most part of counterions. In the absence of surfactant molecules in the solution, only half of the counterions are held within the microgel ($\beta \approx 0.5$ at $Z \to 0$, see Figure 3e), while the second half is able to move freely in the outer solution. On the contrary, the larger microgel ($\nu = 10^9$) can be treated as a macroscopic gel sample. The electroneutrality of this gel is provided by a high charge of the polymer network (despite limitation 5 is not fulfilled) and electroneutrality condition can be expressed by inequality $|\beta - 1 + Z(s - t)| \ll 1$; i.e., the network charge exceeds by far the total charge of the gel. At $Z = 0$, almost all counterions are located inside the gel ($\beta \simeq 1$); concentration of these ions in the outer solution is extremely low.

Addition of surfactant molecules into the microgel solution induces the reaction of an ion exchange, i.e., counterions within the microgel are substituted by surfactant ions. This process is accompanied by the gain in translational entropy of escaping counterions. The amount of the absorbed surfactants increases with decreasing of the microgel counterions concentration in the external solution. Thus, the larger gel binds more surfactant ions than the smaller microgel per one charged network unit. At low Z there is no micellization, the surfactant ions acts just as a simple salt screening the electrostatic interactions and, thus, slightly reducing the swelling ratio, α.

However, one can see in Figure 3 that absorption of surfactant ions by the microgel is rather effective, their concentration within the microgel particle increases strongly with Z and exceeds CMC_{in} already at $Z < 1$. As has been mentioned above the absorption efficiency at small charge ratios increases with an increase of the microgel molecular mass and the micelle formation within the gel starts at smaller values of Z for larger particles. The highest rate of the surfactant binding corresponds to the micellization onset, thus, the CAC coincides with the CMC_{in}.

Figure 3d allows one to determine the value of CMC_{in}, which does not fully coincide for the small particle with the estimation 14 obtained for macroscopic gel sample because of the microgel nonzero electric charge.

Micelle formation causes a drop in osmotic pressure inside the microgel and a shrinking of the gel takes place. In the vicinity of $Z = 1$ practically all counterions in microgels are replaced by surfactant ions and the fraction of the surfactant forming micelles becomes close to unity. Further surfactant sorption is due to an energy gain from micelle formation and at high Z it causes the microgel charge inversion and surfactant trapping by the microgel becomes less favorable because of increasing microgel charge and thus, electrostatic energy. The larger gel which is close to the macroscopic limit is electrically neutral in the whole range of Z (Figure 3c). It should be noted that at $Z > 1$, these are smaller microgels that are better surfactant absorbers because in the case of a macroscopic gel surfactant binding should be accompanied by entropically

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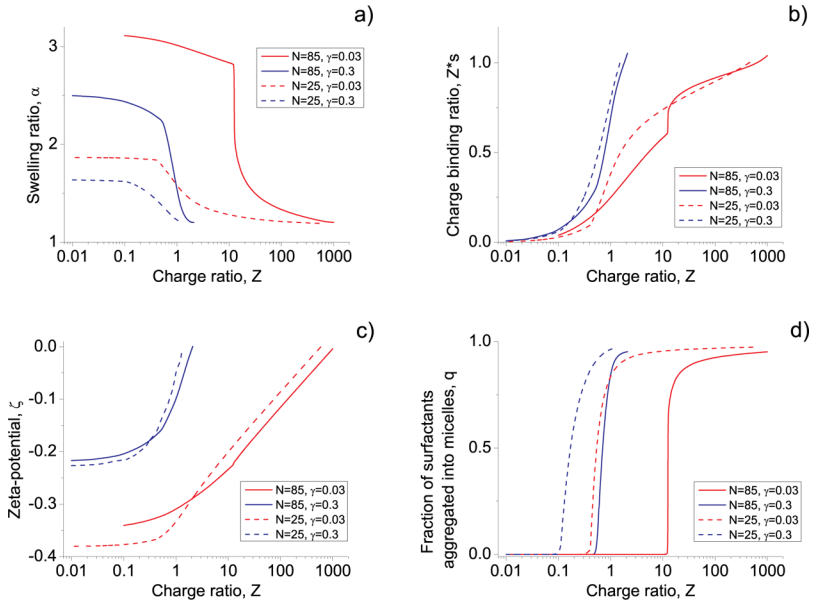

Figure 4. Swelling ratio α (a), charge binding ratio $Z^* s$ (b), ζ-potential ζ (c) and fraction of surfactant molecules aggregated into micelles inside the gel q (d) on the charge ratio Z. Influence of microgel concentration ($\gamma = 0.03$, red; $\gamma = 0.3$, blue) and cross-linking density ($N = 85$, solid line; $N = 25$, dashed line).

unfavorable trapping of surfactant counterions to provide total gel electroneutrality, while small microgels are able to possess a nonzero electric charge.

In the vicinity of $Z = 1$, the charge of the microgel is close to zero, thus, in case of a poor solvent microgel/surfactant complexes can precipitate, while at $Z < 1$ and $Z > 1$ the excess charge on the microgel stabilizes the dispersion. This was indeed observed experimentally.[17,19,20]

It should be emphasized that the developed theory allows one to describe the complex formation between linear polyelectrolyte chains and oppositely charged surfactant in dilute solutions. The free energy for the linear chain is described by the introduced above free energy for $\nu = 1$ (a microgel with one subchain). In this limiting case, all the chain counterions will escape for the outer solution and due to a shift of the ion exchange the formation of polymer/surfactant complex will start at a higher charge ratio. In ref 56, Nilsson and Hansson have demonstrated that macroscopic gels absorb more surfactant ions than linear polyelectrolytes in solution at the same average concentration. Recently new studies of the complexes between linear synthetic and natural (DNA) polyelectrolytes with surfactants have been performed and a phase diagram containing regions of surfactant effective sorption and chain shrinking, solution precipitation and chain redissolution due to overcharging has been constructed.[21,22] Earlier surfactant-induced charge-reversal of hydrophobically modified sodium salt of poly(styrenesulfonate) (NaPS) was observed by the group of Osada.[23] All these phenomena are common for single polyelectrolyte chains as well as microgel/surfactant solutions and are explained by our theory.

It is important that the ion exchange and thus, the composition of microgel/surfactant complexes and their dispersion stability is significantly influenced by the polymer concentration. In Figure 4, we plot the dependences of the swelling ratio α, the charge binding ratio $Z^* s$, ζ-potential and the fraction of the surfactant ions aggregated into micelles inside the gel q on the charge ratio Z for different microgel concentrations ($\gamma = 0.3$ and $\gamma = 0.03$) and cross-linking density ($N = 25$ and $N = 85$).

The more dilute the solution, the larger the fraction of released counterions. An increase of the microgel concentration results in a decrease of the volume of the elementary cell inducing counterion trapping by microgels.[12] As a result, the ion exchange reaction in microgel−surfactant solution shifts and the CMC_{in} is reached earlier. Therefore, in more concentrated solutions microgel collapse occurs at lower values of Z (Figure 4a). This result is fully supported by experimental data.[19]

Furthermore, similarly to macroscopic gels[10] increasing the volume of the elementary cell, i.e., the solution volume per microgel, can change the character of the collapse transition. It is clearly seen in Figure 4 that in case of high dilution ($\gamma = 0.03$) the collapse transition can be realized as a jump-like first-order phase transition, in the swollen state surfactant concentration is much smaller than CMC while in the collapsed state it exceeds CMC. From Figure 4, it is clear that if we fix Z, for instance, consider stoichiometric mixtures, $Z = 1$, and start to dilute the solution, we could induce micelle dissociation within microgels and their swelling.

Other important microgel parameters influencing the surfactant sorption as well as microgel swelling are the ionization degree of the microgel and its degree of cross-linking. These parameters affect the total charge of the microgel, its elasticity and the amount of released counterions. The swelling in a surfactant-free solution is higher for less cross-linked microgel particles carrying more charges, this follows from the presented above estimations for $\alpha_{osmotic}$ and α_{el-st} and from Figure 4 where the solid and dashed lines show the swelling of the microgels with different length of the subchain $N = 85$ and $N = 25$ (varying f gives a similar effect, the corresponding curves are not shown to avoid cluttering of the graph). The same tendency is true for low surfactant concentrations $Z < Z_{cr}$. On the other hand, in the collapsed state the swelling degree of the microgel is mainly defined by the volume interactions dependent on solvent quality rather

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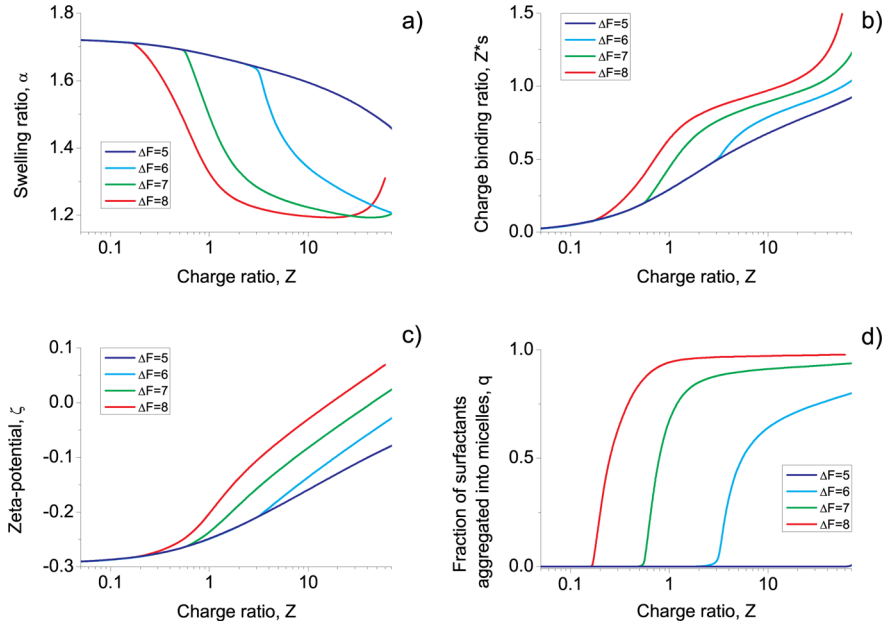

Figure 5. Swelling ratio α (a), charge binding ratio $Z^* s$ (b), zeta-potential ζ (c) and fraction of surfactant molecules aggregated into micelles inside the gel q (d) as functions of the charge ratio Z. Effect of surfactant hydrophobicity (ΔF = 5, 6, 7, and 8).

than on the amount of charges on polymer subchains and their length. As a result, the change in volume upon transition is more pronounced for highly charged lightly cross-linked particles (see Figure 4).

The main surfactant parameter altering the system behavior is the surfactant tail hydrophobicity. In our theory it is governed by the value of the energy gain from micellization ΔF, that increases, in particular, with the length of the surfactant tail. To reveal the effect of the surfactant type on the microgel collapse, we plot the swelling curves, the surfactant binding ratios, zeta potentials and fractions of aggregated surfactant vs Z calculated for various values of ΔF: ΔF = 5, 6, 7, 8. (see Figure 5). At ΔF = 5 the energy gain from micellization is too small to compete with the loss in the translational entropy of the surfactant. Thus, surfactant ions do not aggregate at any concentration and act just as salt ions causing a certain screening of electrostatic interactions in the solution. In this case a kind of salting-out phenomenon is observed, the volume of the microgel is slightly decreasing with Z, this behavior is similar to a polyelectrolyte microgel shrinking in a salt solution.[57]

Increasing ΔF causes micelle formation within the gel. The higher the energy gain ΔF, the smaller amount of surfactant is needed to induce micellization and, thus, collapse of the microgel. It should be stressed that micelle formation within the microgel takes place at surfactant concentrations much less than CMC in solution. Thus, micelles are formed only inside the microgel, $CMC_{in} < CMC_{out}$ (see estimations above). Owing to the energy gain from micellization, more surfactants are trapped by the microgel, so that at high ΔF the charge binding ratio Z^*s can exceed unity. As has been mentioned above the surfactant sorption can lead to a microgel overcharging at large Z (Figure 5, red curve) providing dispersion stability of the microgel−surfactant solution.

The behavior of the charge binding ratio and ζ-potential predicted by the theory and the main tendencies found for various ΔF values (Figure 5) are in good agreement with experimental data. In particular, in refs 17 and 20 the interaction between poly(*N*-isopropylacrylamide-*co*-acrylic acid) microgel particle and modified organic salts containing hydrocarbon chains of different lengths was studied. It has been found that the surfactant uptake by the microgels increases with the length of the surfactant tail. As a consequence, in order to induce microgel collapse one needs less surfactants with longer tail. It was also shown that the longer the surfactant tail, the more pronounced the microgel overcharging.

It should be noted again that according to the presented model the main driving force of the gel contraction is a drop in the microgel charge and osmotic pressure in the course of micellization: aggregated surfactant lose their translational entropy and cease to create the osmotic pressure within the gel, simultaneously neutralizing the microgel charge. Thus, the volume of the fully neutralized microgel/surfactant complex is mainly defined by the solvent quality for the microgel and does not depend on the nature of the surfactant. As has been shown above, the parameter ΔF defines the surfactant hydrophobicity with respect to the solvent and, thus, its CMC. The value of ΔF only shifts the transition point and does not affect the polymer volume fraction within the collapsed particle.

However, there are experiments both on macroscopic gels as well as microgels demonstrating that the PE gel/surfactant complex is somewhat denser than network neutral analogue[11] and that the surfactant hydrophobicity influences the equilibrium gel volume.[17,53,58] The importance of the hydrophobic attraction between surfactant hydrocarbon tails and gel hydrophobic units was discussed in refs 17, 59, and 60.

Thus, in the next section we modify our model to describe this effect.

EFFECT OF HYDROPHOBIC INTERACTIONS BETWEEN THE SURFACTANT TAIL AND MICROGEL MONOMER UNITS

Modified Free Energy. To take into account the hydrophobic interactions between the surfactant tail and the microgel monomer units we have to modify the last two terms in the free energy (eq 1) corresponding to the volume

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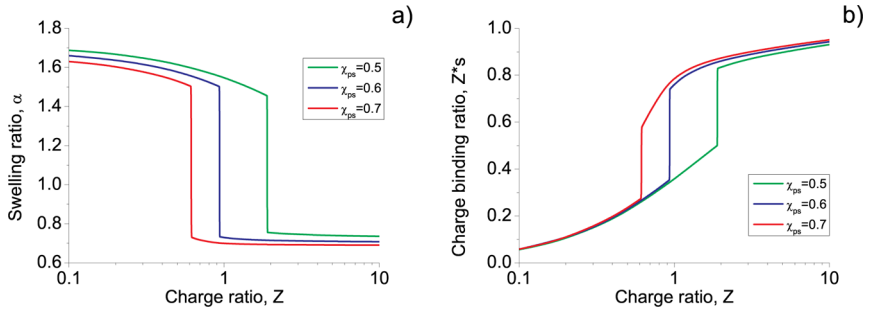

Figure 6. Swelling ratio α (a) and charge binding ratio Z^*s (b) on the charge ratio Z. Effect of solvent quality (χ_{ps} = 0.5, 0.6, and 0.7).

interactions as well as surfactant translational entropy and aggregation energy.

Flory–Huggins lattice theory is used to describe a microgel particle as a ternary system polymer–surfactant–solvent as well as a two-component surfactant–solvent mixture outside the microgel.[37,61,62] Owing to the difference between the interior of the microgel and the outer solution, $F_{int} + F_s$ is written as the sum of two terms, corresponding to these two regions:

$$F_{\text{int}} + F_s = F_s^{gel} + F_s^{out} \tag{16}$$

In our consideration, we neglect the volume interactions of small counterions. The total volume of the system is divided into cells of size a^3. The surfactant molecule can be represented as a dimer, i.e. as a couple of bound cells with different interaction parameters. These cells correspond to the headgroup and the tail of the surfactant molecule. The headgroup is considered to be charged and hydrophilic, while the hydrophobicity of the tail depending on its length and the chemical structure is described by the value of the interaction parameters. In such consideration, the surfactant volume is equal to $2a^3$. Since in the framework of the Flory–Huggins solution theory molecules of all mixture constituents are considered to be randomly distributed on the lattice, it is supposed that there is no micelle formation both inside and outside the microgel particle.

We use the following notations for the Flory–Huggins interaction parameters: χ_{st} for solvent-tail; χ_{sh} for solvent-head; χ_{th} for tail–head; χ_{ps} for polymer–solvent; χ_{pt} for polymer-tail; χ_{ph} for polymer-head. Though we have introduced six parameters, the system behavior is governed by only three independent parameters which are the following combinations of the introduced ones: χ_{ps}, $\chi_1 = \chi_{th}/2 - \chi_{st} - \chi_{sh}$ and $\chi_2 = \chi_{th}/2 - \chi_{pt} - \chi_{ph}$. Moreover, it is naturally to assume $\chi_1 - \chi_2 = \chi_{pt} + \chi_{ph} - \chi_{st} - \chi_{sh} < 0$ because surfactant molecules prefer microgel medium rather than pure solvent.

The volume fractions ψ_{out} and ψ_{in} of the surfactant outside and inside the microgel particle equal

$$\psi_{out} = 2Z(1 - s)f\Phi\frac{\gamma^3}{\Phi N^{1/2} - \gamma^3} \tag{17}$$

$$\psi = 2Zsf\Phi \tag{18}$$

Then using the introduced notations we can write the surfactant contributions to the free energy of the outer solution, F_s^{out}, and to the free energy of the microgel interior, F_s^{gel}, as

$$\frac{F_s^{out}}{N\nu} = Zf(1 - s)\ln\psi_{out} + \left(\frac{\Phi N^{1/2} - \gamma^3}{\Phi\gamma^3} - 2Zf(1 - s)\right)\ln(1 - \psi_{out}) + \chi_1 Zf(1 - s)\psi_{out} \tag{19}$$

$$\frac{F_s^{gel}}{N\nu} = Zfs\ln\psi + \left(\frac{1}{\Phi} - 2Zs - 1\right)\ln(1 - \Phi - \psi) - \chi_{ps}\Phi + \chi_1 Zfs\psi + \left(\frac{\chi_1 - \chi_2}{2} - \chi_{ps}\right)\psi \tag{20}$$

These two terms take into account the entropy of the translational motion of the surfactant and solvent molecules as well as the volume interactions of the microgel monomer units both with each other and with the surfactant.

Microgel Swelling and Surfactant Absorption vs Solvent Quality and Surfactant Hydrophobicity. Let us now analyze the results obtained by the second approach taking into account attractive interactions between the surfactant tails and microgel monomer units. In this case the free energy F_{tot} is described by eqs 1–7 and 16–20.

The system of equations $dF_{tot}/d\alpha = 0$, $dF_{tot}/d\beta = 0$, $dF_{tot}/ds = 0$, $dF_{tot}/dt = 0$ was solved numerically for $u = 1$ (aqueous solution), $N = 25$, $\nu = 100$, $f = 0.1$, $\gamma = 0.1$, $\chi_1 = 0$, and $\chi_2 = 10$ (strongly hydrophobic surfactant tail). It should be emphasized that to compare the results of the two approaches the values of the main microgel parameters are chosen the same as in Figure 3. Concerning the surfactant ions, the hydrophobicity of the surfactant tail is governed by the Flory–Huggins parameter χ_2 while in the first approach it is the energy gain from micellization, ΔF.

In Figure 6 we plot the dependences of the main system parameters on the amount of the surfactant in the solution, Z, for χ_{ps} = 0.5 (Θ solvent as in Figure 3) and slightly poorer solvents χ_{ps} = 0.6, χ_{ps} = 0.7. It is near Θ point that microgels are expected to demonstrate high sensitivity to external stimuli, besides a considerable number of experimental research is also devoted to the microgel behavior in the vicinity of a swelling/contraction transition.

The analysis shows that for the chosen values of the parameters the free energy has two minima corresponding to the swollen and collapsed states of the microgel. The swollen state is realized at low surfactant concentrations while the collapsed state is favorable above some critical charge ratio Z_{cr}.

In the swollen state, i.e., at low values of the charge ratio ($Z < Z_{cr}$), the influence of the surfactant molecules on the microgel behavior is negligible. In the swollen state the polymer volume fraction is quite low, and volume interactions do not play a crucial role. The surfactant binding by swollen microgel is rather weak (Figure 3b,f). Some redistribution of microgel

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counterions and surfactant ions between the particle interior and the outer solution takes place, their behaviors are almost identical ($\beta \simeq s$). The gel swelling is caused both by the osmotic pressure of trapped ions and electrostatic repulsion of not fully neutralized microgel subchains. This regime was discussed in detail in the previous section. All the regularities obtained above for the main system parameters are hardly influenced by the surfactant/microgel hydrophobic interactions.

Hydrophobic interactions play a crucial role in the collapsed state of the microgel. Indeed, the collapsed particle is rather dense, polymer volume fraction reaches 0.65, and the short-range attractive interactions dominate causing strong binding of surfactant ions by the oppositely charged microgel.

The main effect of the hydrophobic interactions is in the nature of the shrunken microgel state. The first approach takes into account surfactant micellization within the microgel and predicts, that the gel dimensions decrease because the surfactant ions lose their translational entropy in the course of micellization and the osmotic pressure within the gel goes down. In the vicinity of microgel charge neutralization the swelling ratio is close to that of the uncharged microgel defined by the solvent quality. The results presented in Figure 3 were obtained for $B = 0$, i.e., for Θ solvent conditions, thus, the microgel subchains in the shrunken microgel state are close to unperturbed Gaussian coils.[10] Account for hydrophobic attraction between the microgel monomer units and surfactant tails leads to the formation of a much denser collapsed state. In the Θ solvent ($\chi_{ps} = 0.5$) the swelling ratio drops down to approximately 0.7 (Figure 6a). It should be noted that in the collapsed state the fraction of low-polar polymer is rather high and the role of short-range electrostatic correlation effects which are not taken into account in our model, enhance. Since correction for ion−ion correlation is negative, account for these effects shift the transition point toward lower Z. One can also expect that a decreasing dielectric constant of the gel media will cause some additional microgel shrinking.[25,26,52]

It is quite natural that worsening of the solvent quality for the microgel monomer units (increase in χ_{ps}) leads to a higher shrinking of the microgel. Indeed, additional attractive polymer interactions promote the formation of denser conformations, α decreases with growing χ_{ps}. Besides, the transition from the swollen to the shrunken gel is realized at smaller surfactant concentration (Figure 6).

Another effect of the hydrophobic interactions is revealed in the character of the gel contraction. Attraction between the hydrocarbon tails and microgel subchains leads to some sharpening of the gel transition from the swollen to shrunken state upon increase of surfactant concentration. For the same values of the system parameters micellization described by the first approach causes in most of the cases continuous contraction of the microgel while account for hydrophobic interactions predicts an abrupt gel collapse (compare Figures 3 and 6). This is caused by an enhanced cooperativity of the surfactant sorption induced by the hydrophobic attraction: the higher the number of trapped surfactant ions, the more hydrophobic the microgel medium and the more efficient the further sorption proceeds until the microgel charge neutralization.

Because such experimental methods as electrophoretic mobility measurement and DLS allow to observe only average values of microgel particle parameters among members of the ensemble, it is not always possible to observe a discrete collapse transition. Ensemble averaging smoothen the transition and it can be actually observed in experimental studies as a continuous one.[63]

Moreover, experimental investigations of surfactant absorption by PEs containing hydrophobic polystyrene units detected continuous shape of surfactant binding isotherms for linear chains, microgels, and macroscopic networks.[23,53] Discrepancy between these data and results of the second model predicting a break on the charge binding ratio curve (Figure 6b) might be apparently referred to the micelle formation disregard.

Recently it has been reported on a new perspective way to reversibly manipulate the microgel size in a photosensitive surfactant solution by using light.[19] UV light irradiation results in trans−cis isomerization of an azobenzene unit incorporated in the surfactant tail. The cis isomer is more hydrophilic than the trans one. Thus, the light irradiation tunes the hydrophobicity of the surfactant and as a result, has an effect on the surfactant sorption by microgels and the final microgel state.

The developed theory allows to explain and to describe light-induced conformational transitions of microgel/surfactant complexes. In our model the hydrophobicity of the surfactant tail is described by the χ_2 parameter. At a fixed type of the headgroup, the more hydrophobic the surfactant tail, the higher the value of χ_2. In Figure 7, we plot the swelling curves for χ_2 = 15 and χ_2 = 10. Decrease in the tail hydrophobicity (decrease in χ_2-value) results in a shift of the transition point Z_{cr} toward higher values of Z. Thus, there is a range of Z where the microgel size is extremely sensitive to the surfactant hydrophobicity. Varying the χ_2 parameter (having in mind light-induced switching between cis- and trans-isomers) one can induce transition between the swollen and collapsed states of the microgel. This transition is shown in Figure 7 by arrows between the blue and green curves in the vicinity of $Z = 1$.

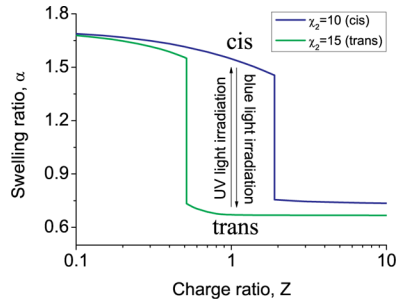

Figure 7. Swelling ratio α on the charge ratio Z at different surfactant tail hydrophobicity; $\chi_2 = 10$ and $\chi_2 = 15$ correspond to cis- and trans-forms of photosensitive surfactant, respectively.

The shift of the transition point, Z_{cr}, upon increase of the surfactant hydrophobicity can also be explained by the surfactant micellization (see the previous section). However, only account for the hydrophobic interactions between surfactant and microgel subchains predicts the formation of a denser microgel state for more hydrophobic surfactants, which was experimentally observed in ref 17.

Finally, both methods predict the following consequence of processes under surfactant molecules addition: microgel collapse or contraction → microgel precipitation (zero of ζ-potential) → microgel overcharging → slight microgel reentrant swelling. These results are in general agreement with experimental studies.[13−20]

In present work we focused on the case of salt-free solutions and restricted ourselves by relatively low surfactant concen-

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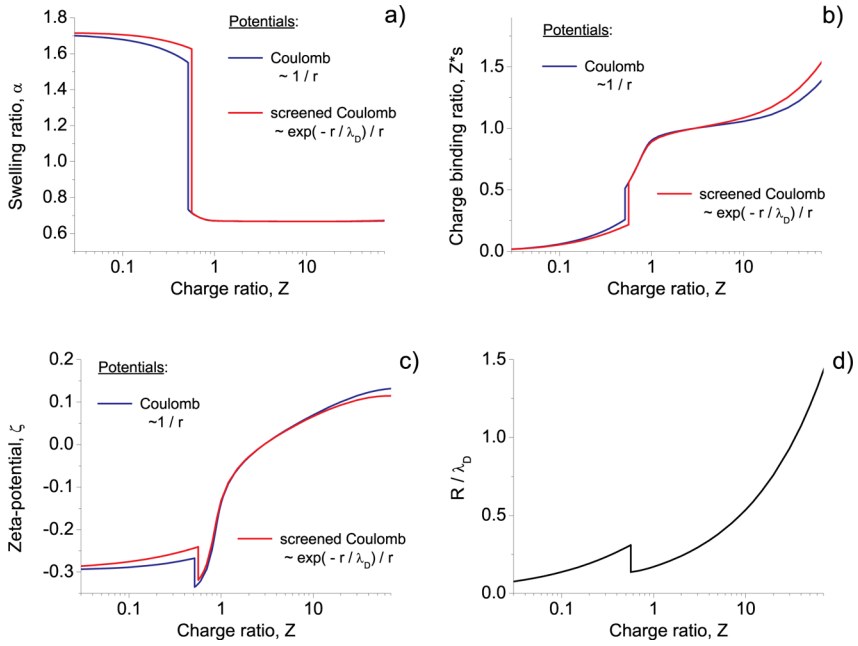

Figure 8. Swelling ratio α (a), charge binding ratio Z^*s (b), ζ-potential ζ (c) and ratio between microgel radius and Debye length R/λ_D (d) on the charge ratio Z. Blue and red curves correspond to Coulomb and modified (screened Coulomb) potentials of microgel, respectively. The values of all parameters are equal to ones in Figure 7, $\chi_2 = 15$.

trations $Z \leq Z_{scr}$ as well as microgels of small dimensions (see eq 5). Namely, the model applies to the particle with sizes about (50−100) nm in the swollen state and solution ionic strength not exceeding (0.1−0.3) mM.

To take into consideration screening effects at higher values of Z and nonzero salt concentrations, electrostatic free energy defined by eq 3 should be modified by substitution of Coulomb potential for the screened one: $1/r \rightarrow \exp(-r/\lambda_D)/r$.[64] In the case of a salt-free solution we used eq 4 for the screening length λ_D and found that this correction results in (i) a slight shift of microgel collapse point toward higher values of Z and (ii) an amplification of surfactant absorption by charge-reversed microgel (see Figure 8). The impact of salt addition on the system behavior is expected to be similar. The first effect coincides with results for the surfactant-induced deswelling of macroscopic networks: at high salt concentrations more surfactant is required to provoke polyelectrolyte gel collapse.[34,65,66] The second one should be referred to the reduction of the excess electrostatic energy of overcharged microgel due to Debye screening. Besides that salt is known to reduce colloidal stability of charged particles. Therefore, broadening of the precipitation Z-range of microgel−surfactant complex in the vicinity of its total electroneutrality at increasing salt concentration should take place as well. The above modification of electrostatic energy is also useful for describing larger microgels, though even without this correction there is the qualitative agreement with experimental studies.

CONCLUSION

In conclusion, we present a comprehensive theoretical study of polyelectrolyte microgel interactions with an oppositely charged surfactant in a dilute solution. Within a mean-field approach, we focus on some important physical effects (such as ion exchange, micellization of surfactant within microgels, hydrophobic interactions) in microgel/surfactant systems.

It has been shown that at low surfactant concentration the sorption of surfactant by microgels is mainly due to an ion exchange reaction between microgel counterions and surfactant ions. With an increase of surfactant concentration both surfactant micellization and hydrophobic interactions between surfactant tails and microgel monomer units contribute significantly to the absorption mechanism. The effect of the microgel parameters, i.e., ionization degree, cross-linking density, microgel size, and polymer concentration on the surfactant uptake and microgel swelling has been elucidated.

Although nonmean-field effects such as charge renormalization and charge correlations are neglected in this first attempt to describe these complex systems, the presented theory gives rather good qualitative agreement with existing experimental data. In particular, a dilution of microgel solution leads to a shift of collapse and charge-reversal regions to higher values of the total surfactant amount in the system, i.e., higher values of Z.[19] Another verification of our theory is the observed effect of the hydrocarbon chain length in modified organic salt surfactant on the swelling behavior of poly(*N*-isopropylacrylamide-*co*-acrylic acid) microgels: a more hydrophobic surfactant induces microgel shrinking and precipitation at lower concentrations than the less hydrophobic one because of a higher absorption rate.[17,20] These results indicate that the main physical effects are described properly.

At the same time, the range of a quantitative agreement between theory and experimental data is restricted to low salt concentrations, small microgel sizes as well as low degree of network ionization. This range could be extended through a modification of the present theory and account for neglected effects, which discussed at length in the body of the article. Further research will hopefully facilitate solution of this challenging task.

The theory also describes the microgel charge inversion at an excess of the surfactant in the solution observed experimentally in refs 14, 16, 17, 19, and 20. The microgel overcharging was shown to be promoted by the surfactant hydrophobicity

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through either micellization or attraction to hydrophobic microgel medium.

The other theoretical predictions, in particular, an increasing abruptness of microgel collapse with increasing fraction of charged groups in the gel, decreasing cross-linking density and microgel concentration, are waiting for experimental confirmation opening new ways to control microgel conformational properties important for uptake and release applications.

AUTHOR INFORMATION

Corresponding Author

*(E.Y.K.) E-mail: kram@polly.phys.msu.ru. Telephone: +7 (495) 9394013. Fax: +7 (495) 9392988.

Notes

The authors declare no competing financial interest.

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