AIP The Journal of Chemical Physics

Effect of ion pair formation on the structure of polymer micelles with ionic amphiphilic coronae

A. M. Rumyantsev and E. Yu. Kramarenko

Citation: J. Chem. Phys. **138**, 204904 (2013); doi: 10.1063/1.4807005
View online: http://dx.doi.org/10.1063/1.4807005
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v138/i20
Published by the American Institute of Physics.

THE JOURNAL OF CHEMICAL PHYSICS **138**, 204904 (2013)

Effect of ion pair formation on the structure of polymer micelles with ionic amphiphilic coronae

A. M. Rumyantsev and E. Yu. Kramarenko[a)]
Physics Department, Moscow State University, Moscow 119991, Russia

(Received 26 February 2013; accepted 3 May 2013; published online 24 May 2013)

We report a theoretical study of micelles from diblock copolymers with an insoluble core-forming block and an amphiphilic ionic corona-forming block. We calculate the micelle structural parameters depending on the composition of the coronal block (ratio between the non-polar and ion-containing groups) as well as solvent quality and polarity for the coronal block. We focus on the effect of ion pair formation in a low polar corona medium and predict the existence of novel micelles with ionomer-type coronae. In these micelles most part of counterions is bound with ions in polymer chains. Two consecutive jump-like first-order phase transitions between different-type micelles can take place in the solution upon change of hydrophobic/polyelectrolyte balance within the micelle corona: large micelles with polyelectrolyte collapsed coronae → large micelles with ionomer-type coronae → small micelles with polyelectrolyte swollen coronae. These transitions are accompanied by non-monotonous change in the micelle aggregation number. New insight into the role of counterions is important for design of stimuli responsive systems. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4807005]

I. INTRODUCTION

Self-assembling behavior of block copolymers in selective solvents has been attracting a considerable attention for many years.[1–3] A special interest has been paid to amphiphilic ionic diblock copolymers that in aqueous solutions form micelles with hydrophobic non-ionic cores and hydrophilic polyelectrolyte (PE) coronae. Their solubility in water, diversity of morphologies, fast controllable response to various environmental conditions (such as pH, salt concentration, temperature, light, etc.), ability to solubilize hydrophobic substances make them very promising for many practical applications, in particular, for gene and drug delivery.[4]

During the last decades considerable progress has been made in understanding physical factors underlying the self-assembling behavior of ionic block copolymers and governing the structure and morphology of micelles with hydrophobic core/hydrophiphilic ionic corona. Block copolymers with both strongly and weakly dissociating (pH-sensitive) ionic blocks have been studied extensively and important role of counterions has been elucidated. The review of the main theoretical results and their comparison with the experimental data can be found, for instance, in Ref. 3.

The new direction in this field is the development of micelles with heterogeneous cores or coronae. This can be done, for instance, either by introduction of ion-containing groups into the hydrophobic core of the micelles[5,6] or hydrophobic modification of the polyelectrolyte corona of the micelle.[7–9] The amphiphilic nature of one of the micelle domains gives a possibility of an additional subtle control of micellar stability, more pronounced responsiveness and special interactions with complexing agents.

In this paper we study theoretically the structure of micelle with the corona, formed by statistical copolymer containing non-polar monomer units which are poorly soluble in the solvent and polar groups capable to ionization in polar solvents and providing micelle solubility. Experimentally such systems have been studied, for instance, in Ref. 7 where micelles with hydrophobic polystyrene (PS) core and ionic amphiphilic corona from charged N-ethyl-4-vinylpyridinium bromide (EVP) and uncharged 4-vinylpyridine (4VP) units were considered. It has been shown that at some critical fraction of EVP units a jump-like transition between different-type micelles takes place in the solution. A simple theoretical approach to explain the experimental results has been proposed.[7]

In this paper, we generalize the theory developed in Ref. 7 to focus on the effect of counterion binding with ion pair formation within the corona domain. As it has been shown in Ref. 7 when the solvent is slightly poor for the coronal non-polar monomer units, the concentration of low-polar polymer within the corona could be rather high, thus, decreasing the average dielectric constant of the corona media and promoting ion pairing.

The importance of ion pair formation has been previously demonstrated for various polyelectrolyte systems: the low polymer polarity and extensive ion binding can promote the formation of ionomer-type state within the microgel particles as well as macroscopic gels,[10–13] can significantly influence the phase behavior of polyelectrolyte solutions,[14] singe molecules can also demonstrate dual polyelectrolyte-ionomer behavior in low polar solvents.[15,16] Recently, the formation of micelles with ionomer-type cores has been predicted theoretically and confirmed experimentally.[6] In this paper, we

---

[a)]Author to whom correspondence should be addressed. Electronic mail: kram@polly.phys.msu.ru

demonstrate that ion pair formation within the heterogeneous micellar corona can also lead to a number of novel striking phenomena.

In Sec. II, we describe the theoretical model, then we discuss the obtained results (Sec. III) and formulate the main conclusions (Sec. IV).

II. THEORETICAL MODEL

We consider a dilute solution of an A-B diblock copolymer with N_A and N_B statistical segments in the A and B blocks, respectively. Both blocks are flexible chains with the same statistical segment length a. The A block is assumed to be insoluble while for the monomer units of the B block, the solvent is θ or slightly poor. Furthermore, the B block contains a fraction β of polar groups that can become charged in the course of dissociation with the release of low-molecular-mass counterions. Attraction between the insoluble A monomer units provides the self-assembling behavior of the diblock copolymer chains while the presence of charged groups in the B block ensures its solubility in polar solvents and formation of finite-size aggregates in the solution instead of macroscopic phase separation.

Thus, above the so-called critical micelle concentration, the A-B chains associate and form micelles of an average aggregation number m. We restrict ourselves to the case of a relatively long coronal B block, $N_B \geq N_A$, then the spherical micellar core-corona morphology is the most favorable.[17] The core consists of the insoluble A blocks, surrounded by a corona of the charged B blocks (see Fig. 1). We do not consider any phase separation within the corona possible at some conditions. It has been shown for star-branched molecules in Ref. 18.

We suppose that the A and B blocks are strongly incompatible. Thus, the width of the core/corona interface is small compared to the size of the micelle, so that the A and B blocks are envisioned as grafted to the core surface. Let us denote as R_A, R_B, and $R = R_A + R_B$ the core radius, the width of the corona, and the total micelle radius, respectively (see Fig. 1).

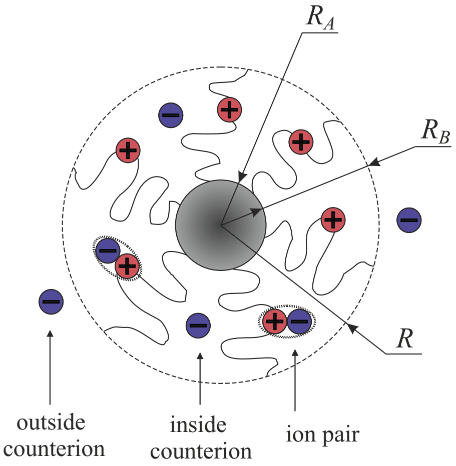

FIG. 1. Schematic representation of a micelle with a charged corona. Three types of counterion states are distinguished: bound counterions forming ion pairs, free counterions within the micelle corona and in the outer solution.

If the A blocks are completely insoluble, the micelle core contains no solvent and its radius is equal to

$$R_A = a\left(\frac{3}{4\pi} m N_A\right)^{1/3}. \tag{1}$$

This formula can be easily generalized for the case when the micelle core contains some amount of solvent.

The corona of the micelle is considered as a semidilute polymer solution with the volume fraction Φ of the uniformly distributed B monomer units. In the first approximation, the gradient in the coronal polymer density distribution in the collapsed corona state is negligible and we ignore it in the swollen state also. Therefore, the space-filling condition reads

$$m\left(N_A + \frac{N_B}{\Phi}\right) a^3 = \frac{4\pi}{3} R^3, \tag{2}$$

where the average polymer volume fraction Φ in the corona can vary over a wide range depending on the block copolymer composition and the solvent quality.

The counterions and the ions on the B coronal blocks are assumed to be monovalent, carrying the elementary charges $\pm e$. Thus, the number of the mobile counterions per micelle is equal to the number of the charges in the coronal blocks, $N_B m\beta$. For simplicity, we consider a salt-free solution, with the counterions of the B blocks being the only source of mobile ions. A fraction α of the counterions leaves the corona due to entropic reasons, resulting in a nonzero electric charge of the micelle $Q = emN_B\beta\alpha$. We also suppose that some counterions can associate into ion pairs with the oppositely charged ions on the chains (see Fig. 1).

The free energy of the micellar solution per one diblock copolymer chain in kT units can be written as follows:

$$F_{tot} = F_{el}^{core} + F_{el}^{corona} + F_{surf} + F_{el-st} + F_c + F_{agg} + F_{int}. \tag{3}$$

The first and the second terms are responsible for the elastic stretching of the A and B blocks in the core and the corona regions, respectively:[19,20]

$$F_{el}^{core} = \frac{3\pi^2}{80} \frac{R_A^2}{N_A a^2}, \tag{4}$$

$$F_{el}^{corona} = \frac{3}{2} \frac{R_B^2}{N_B a^2}. \tag{5}$$

The F_{surf} term is the energy per chain of the core-solvent interface

$$F_{surf} = \frac{4\pi R_A^2}{m} \frac{\gamma}{kT} \tag{6}$$

and γ is the surface tension coefficient, so that $\gamma a^2/kT$ is the dimensionless parameter. As mentioned above, the A block is insoluble and incompatible with the B block. Let the strength of interactions between the A block and the solvent molecules is close to the one between the A and B blocks of the copolymer. In this case, γ does not depend on the polymer volume fraction Φ in the corona and can be considered as a constant.[3] Taking into account the corona-solvent interfacial energy in the case of the collapsed corona results in some renormalization of γ and does not change qualitatively the behavior of the system. Moreover, this correction is negligible due to a moderate insolubility of the corona chains and is omitted.

The next term in (3), F_{el-st}, is the electrostatic energy per chain of the charged micelle. It can be estimated as the energy of a uniformly charged ball of the radius R:

$$F_{el-st} = u_0 m \frac{(\beta \alpha N_B)^2}{R/a}. \tag{7}$$

Here u_0 is the dimensionless parameter, $u_0 = e^2/\epsilon_0 akT$, ϵ_0 being the dielectric constant of the solvent. In Eq. (7), we omit the numerical coefficient that is of the order of unity.[21,22] This assumption hardly influences main results.

The term F_c in Eq. (3) accounts for the translational entropy of the mobile counterions inside and outside the micelle corona

$$F_c = N_B \beta \left[(1-\alpha)\ln((1-\alpha)\beta\Phi) + \alpha \ln\left(\frac{\alpha\beta N_B C}{N_A + N_B}\right)\right]. \tag{8}$$

In this expression, C is the total polymer volume fraction in the solution, thus, $(N_A + N_B)a^3/C$ is the volume per one molecule.

The term F_{agg} in (3) describes the reversible association-dissociation process between the ions in the B blocks and the counterions. The concentrations of the charges on the polymer chains and the counterions within the corona equal to $\beta\Phi$ and $(1-\alpha)\beta\Phi$, respectively. We suppose a fraction p of the ionizable groups on the B block stays in ion pairs while the fraction $(1-p)$ dissociates with the release of counterions. The F_{agg} term was calculated following our earlier publication:[14]

$$F_{agg} = N_B \beta \left[p + \ln(1-p) + (1-\alpha)\ln\left(1 - \frac{p}{1-\alpha}\right)\right]. \tag{9}$$

The fraction of the ion pairs p is defined as

$$p = 1 - \frac{\alpha}{2} + \frac{1}{2k\Phi\beta} - \sqrt{\left(\frac{\alpha}{2} - \frac{1}{2k\Phi\beta}\right)^2 + \frac{1}{k\Phi\beta}}. \tag{10}$$

Here k is the dimensionless association constant of the thermoreversible ion association-dissociation reaction, $k = exp(u)$.[14] The parameter u describes the strength of electrostatic attraction between two oppositely charged monovalent ions in an ion pair formed in a media with the dielectric constant ϵ: u is the ratio between the Coulomb energy of ion interaction in an ion pair, $e^2/(a\epsilon)$, to the thermal energy (we assume that the distance between ions in an ion pair is of the order of the characteristic size of the monomer units a). Since the solvent is supposed to be poor for the coronal B blocks, the concentration of the B monomer units within the micelle corona can be rather high resulting in a smaller value of the corona dielectric constant in comparison with that of the pure solvent, thus, promoting ion pair formation. As in our previous calculations,[10,11] the dielectric constant of the corona media is adopted to be a linear function of the polymer volume fraction Φ:

$$\epsilon = \epsilon_0(1 - \delta\epsilon\Phi), \tag{11}$$

where $\delta\epsilon = (\epsilon_0 - \epsilon_p)/\epsilon_0$, ϵ_p being the dielectric constant of the pure B polymer.

Thus, the association constant reads

$$k = \exp\left(\frac{u_0}{1 - \delta\epsilon\Phi}\right). \tag{12}$$

One can see that the association constant and, thus, the fraction p of ion pairs significantly depend on the concentration of the low-polar polymer in the corona.

Finally, the last term in the energy (3), F_{int}, accounts for the short-range interactions in the micellar corona region. This contribution can be written in the framework of the Flory-Huggins lattice theory.[20,23,24] We suppose that non-polar monomer units of the B block and the ion pairs interact differently with each other and with the solvent molecules and calculate the F_{int} term for this case in the Appendix. The resulting free energy is dependent on the fraction p of ion pairs:

$$F_{int} = \frac{N_B}{\Phi}\left[(1-\Phi)\ln(1-\Phi) - \chi(1-p\beta)^2\Phi^2\right], \tag{13}$$

where χ is the Flory-Huggins interaction parameter between the non-ionic monomer units of the B block and the solvent molecules.

It should be noted that in our approach, we neglect the electrostatic interactions of ions not associated into ion pairs within the micelle corona, in Debye-Huckel approximation they give much smaller contribution to the free energy than that of translational motion of counterions.[25]

Besides, in our consideration, we neglect the entropy of the translational motion of the micelles themselves. This contribution is much smaller than the entropy of the low-molecular-weight counterions because the total number of the counterions in the solution exceeds by far the total number of micelles: $mN_B\beta \gg 1$.

III. RESULTS AND DISCUSSION

We study conformational transitions in polymer micelles caused by increasing fraction of the charged groups, β, within the corona block. The total free energy defined by Eqs. (3)–(13) is a function of three independent variables m, Φ, and α. The equilibrium free energy per molecule in the micelle is calculated via minimization of expression (3) with respect to these three parameters.

A. Micelles in the absence of ion pair formation

Let us consider first a simple case when there is no association between mobile counterions and ions on polymer chains, thus, all the polar groups in the B blocks are dissociated. The free energy per molecule is described by Eq. (3) with $p = 0$ and therefore $F_{agg} = 0$. The counterions redistribute between the interior of the micelle and the outer solution. It should be mentioned that similar situation has already been briefly considered theoretically in Ref. 7 to explain the experimental results.[7] Now we propose a more general theoretical model, in particular, we do not restrict ourselves by only star-like micelle conformations and take into account difference in short-range interactions between non-polar and polar groups within the micellar corona. Furthermore, we

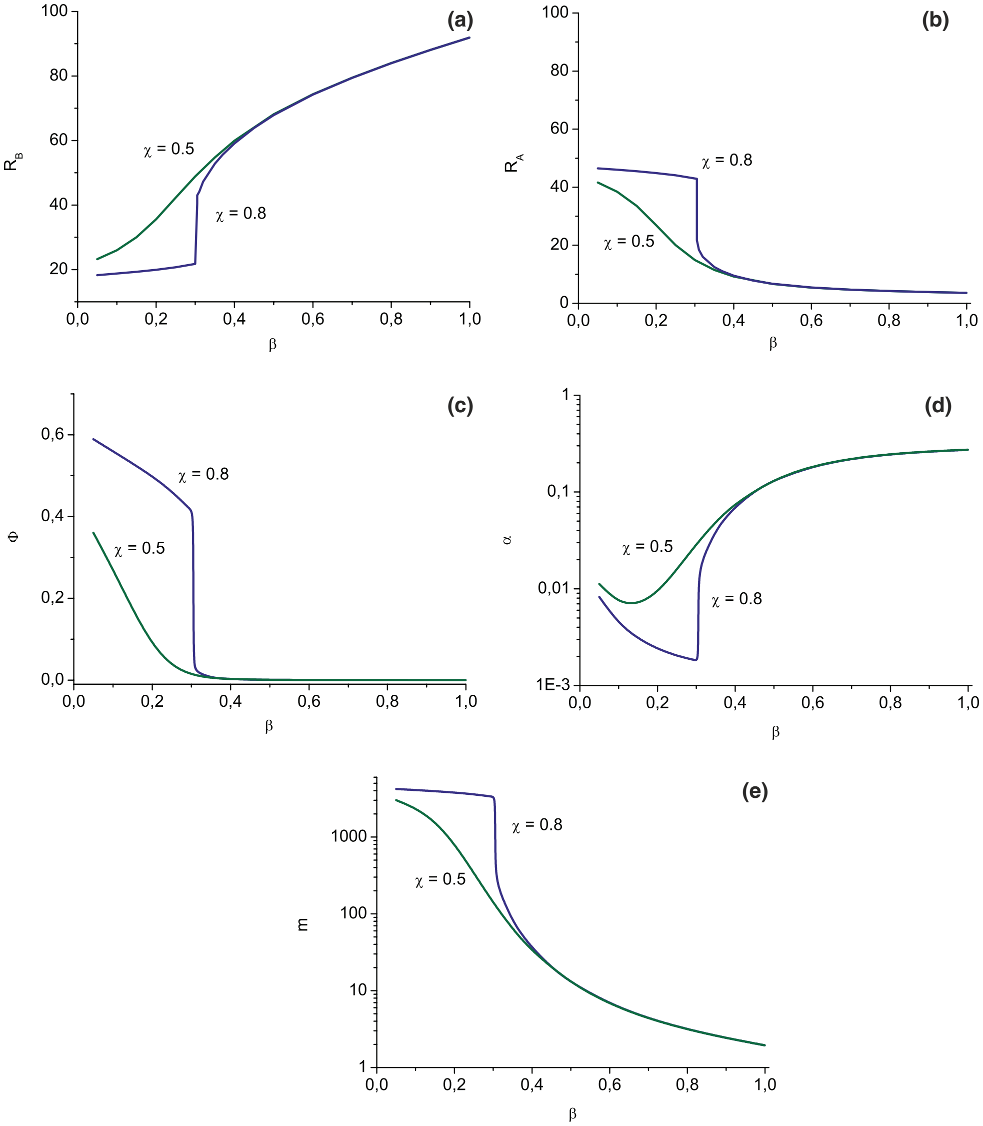

FIG. 2. Corona thickness R_B (a) and core radius R_A (b) in a units, polymer volume fraction Φ in corona (c), fraction of counterions in the outer solution α (d) and aggregation number m (e) as functions of β for $N_A = N_B = 100$, $u_0 = 2$, $\gamma a^2/kT = 4.1$, and $C = 10^{-5}$. Curves correspond to $\chi = 0.5$ and $\chi = 0.8$.

discuss in detail the main physical features of the system under consideration. This discussion helps to understand the effect of ion pair formation on the system behavior analyzed in Sec. III B.

To find the counterion localization as well as the micelle aggregation number as functions of the fraction of charges in the polymer chains and the solvent quality, the system of three equations: $dF_{tot}/dm = 0, dF_{tot}/d\Phi = 0, dF_{tot}/d\alpha = 0$ has been solved numerically for $N_A = N_B = 100, u_0 = 2, \gamma a^2/kT = 4.1, C = 10^{-5}$ and for various values of χ and β. Analysis shows that the character of the micellar structural rearrangement with β depends essentially on the Flory-Huggins parameter χ.

The dependences of all the main micelle parameters on the fraction of the charged groups in the B block are shown in Fig. 2 for two different values of χ: $\chi = 0.5$ corresponding to the Θ-solvent and $\chi = 0.8$ corresponding to a poor solvent.

The ionic micelle behavior in the case of good or Θ-solvent conditions for the coronal block was analyzed in many theoretical papers and is reviewed, for instance, in Ref. 3. All the main tendencies observed in Fig. 2 for $\chi = 0.5$ correspond well to the previous results. In particular, the coronal radius R_B increases while the micelle aggregation number m as well as the core radius R_A decrease with β (Fig. 2(e)). This behavior is due to increasing effective repulsion of the charged monomer units in the corona.

The nature of this repulsion is different for large and small micelles. It has been previously shown[3] that large micelles retain the majority of the counterions ($\alpha \sim 0$), and the repulsion between the coronal blocks is mainly caused by the osmotic pressure of counterions (so-called osmotic regime). In the opposite case when the aggregation number of micelles is small, counterions leave for the outer solution ($\alpha \sim 1$, so-called Pincus regime), then there is Coulomb repulsion of the uncompensated charges in the corona, and the micelles tend to lower the aggregation number because of high electrostatic energy per molecule (7). Scaling estimates of the micellar parameters on the block length, surface tension coefficient of the core-solvent interface and degree of ionization for the osmotic and Pincus regimes can be found, for instance, in review.[3]

In general, α adopts intermediate values between zero and unity, thus, in a wide range of ionization degree, β, none of the limiting cases (osmotic or Pincus) is realized (see Fig. 2(d)). The fraction of counterions in the solution grows with β, smaller micelles possess lower total charge and thus, more counterions are able to leave the micelle corona at high β.

At $\beta \to 0$ micelles are not charged, and our results for the case of the Θ-solvent coincide with scaling estimations for neutral aggregates.[3,26,27] It should be noted that at low β, some decrease of α with β is observed (Fig. 2(d)). A similar effect usually takes place upon charging of a colloidal particle,[28] a star-branched polyelectrolyte molecule[29] or a polymer microgel particle,[30] increasing β just causes counterion condensation on a charged object and, thus, reduces the fraction α of free counterions. However, in case of ionic micelles, a growth of β induces also a micelle reorganization accompanied by an aggregation number decrease. As a result, at some β, the total micelle charge begins to decrease that allows more counterions to escape the corona. An interplay between these two effects makes the dependence of α on β nonmonotonic (Fig. 2(d)). This peculiarity is well-pronounced in the case of a poor solvent ($\chi = 0.8$, $\beta < 0.3$) because at low β, the amount of charged groups is insufficient to affect significantly collapsed corona and to induce micelle reorganization.

The main micelle parameters change continuously with β in Θ-solvent. However, if the solvent is poor for the B block a jump-like transition between large and small micelles takes place at some critical value of the ionization degree of the coronal blocks (see Fig. 2, $\chi = 0.8$). It is the jump-like character of the transition that is the main feature of the micelle structural behavior in the poor solvent, all other qualitative regularities that were obtained for the case of the Θ-solvent are valid for poor solvent too.

The corona media is similar to both PE microgels and single charged molecules in a poor solvent. It has been previously shown that the presence of charges in polymer chains causes an appearance of a second minimum of the free energy and charging results in abrupt transition from the collapsed to the swollen state (corresponding to two minima of the free energy) for both gels[25] and single chains.[31] Similar situation is realized in micelles with ionic amphiphilic corona. At small β short-range attraction dominates and the micellar corona is in the collapsed state, the polymer volume fraction Φ mainly defined by the volume interactions is much higher than that in the Θ-solvent (see Fig. 2). This leads to smaller elongation of the coronal chains and promotes the formation of larger micelles. On the contrary, at high values of β, the volume interactions in swollen corona are negligible and the micellar parameters adopt quite the same values for both Θ and poor solvent conditions. At some conditions (in particular, smaller surface tension of the core-solvent interface) micelle decay into single molecules can take place in this region (see Fig. 2(e)).

These results, namely, a jump-like change of the micelle parameters with the ionization degree, are in qualitative agreement with the experimental studies as well as their theoretical interpretation in Ref. 7. Note that due to the presence of two minima in the free energy a jump-like transition can be also realized upon change of other system parameters, in particular, the solvent quality.

B. Effects of ion pairing

Let us analyze now effects of possible counterion binding and ion pair formation within the low-polar shrunken corona media. In Fig. 3, we plot the dependences of the main micelle parameters on the fraction of the ionizable groups in the corona chains. The curves are calculated for a fixed solvent quality (the solvent is slightly poor, $\chi = 0.55$) but for various values of the parameter $\delta\epsilon$ describing the difference in polarity between the B coronal polymer and the solvent. The corresponding curves obtained with disregard of ion pairing (for $p = 0$) are also presented in Fig. 3 for comparison.

The system behavior depends essentially on the B polymer dielectric constant. At low values of $\delta\epsilon$ when there is no considerable difference in solvent and polymer polarities accounting for ion pair formation does not cause any considerable change of the system behavior, compare curves 1 and 2 in Fig. 3. Some counterion binding takes place within the corona of large micelles (at $\beta < 0.3$, the fraction of ion pairs reaches 25%) leading only to a quantitative change of the micelle parameters in the region where the value of p is maximum.

However, in a low-polar corona media, the ionic association constant becomes high and the self-assembling behavior of the micelle solution changes qualitatively. Namely, when $\delta\epsilon$ exceeds some critical value $\delta\epsilon^*$, a new type of micelles appear in the solution at intermediate fraction of ion-containing groups (see curves 3 and 4). These new type micelles have rather dense coronae (Fig. 3(d)) with almost all counterions being bound in ionic pairs (the value of p is close to unity, see Fig. 3(c)) demonstrating ionomer-type behavior.

The ionomer-type state of the micelle corona is analogous to that found in polyelectrolyte gels and microgel particles. Recently it has been also predicted theoretically and observed experimentally for the micelles with hydrophilic non-ionic coronae but ion-containing cores.[6] The reason for the ionomer-type behavior is the high energy gain ΔE from ion pairing within low-polar polymer media. According to (11), in a dense corona $\epsilon(\Phi) \simeq \epsilon_p$ and the following estimation for ΔE is valid:

$$\Delta E \sim \frac{e^2}{\epsilon(\Phi)a} \sim \frac{e^2}{\epsilon_p a}. \tag{14}$$

The lower is the value of ϵ_p , the higher the association constant and the higher the fraction of ion pairs are.

Ion binding is accompanied by a loss in the translational entropy of mobile counterions. At low ionization degree, the counterion entropy dominates and large micelles with collapsed polyelectrolyte-like coronae are more favorable in the solution. Then at some critical β^* the energy gain from ion pair formation becomes larger and the micellar corona transforms into the collapsed ionomer-type state. However, when β exceeds β^{**} transition to ordinary small micelles with polyelectrolyte swollen coronae takes place in the solution.

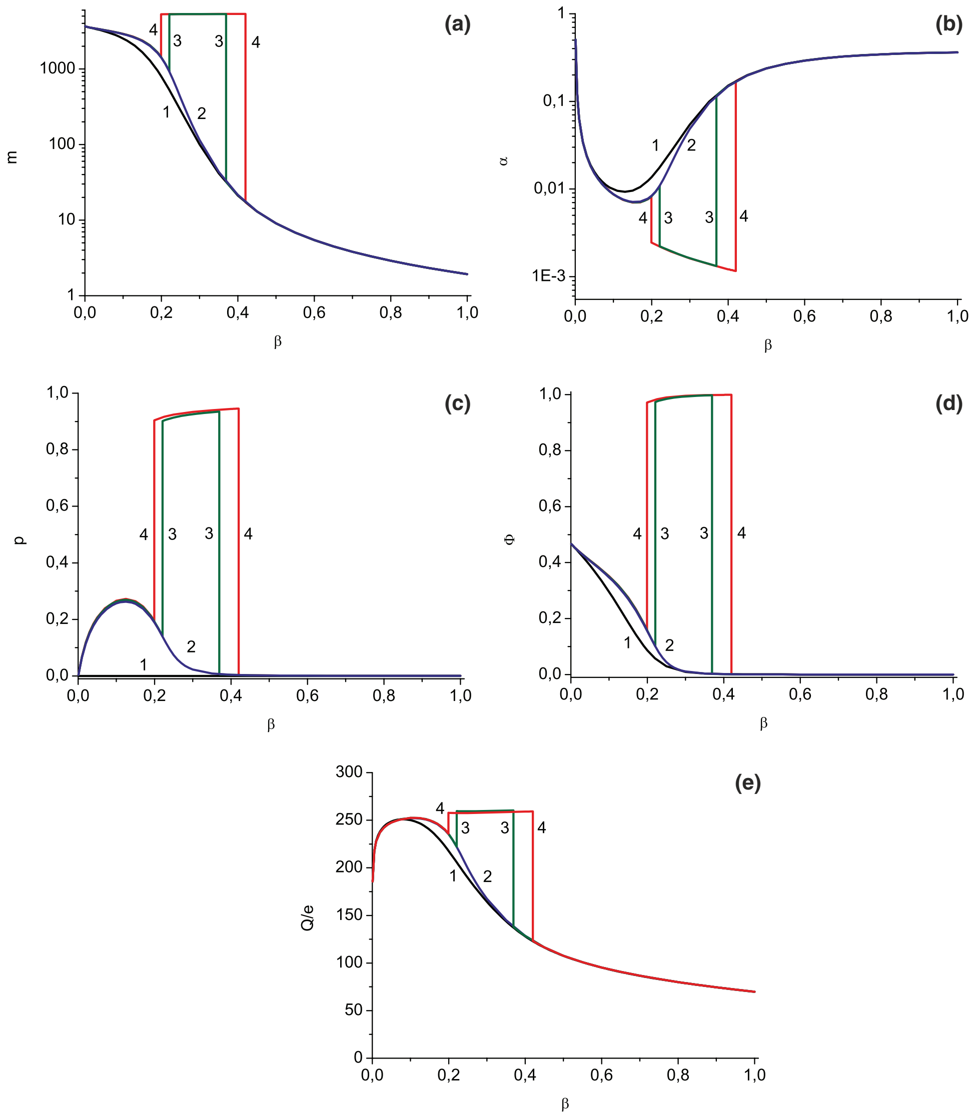

FIG. 3. Aggregation number m (a), fraction of counterions in the outer solution α (b), fraction of ion pairs p (c), volume fraction of the polymer in corona Φ (d), and total micelle charge in e units (e) as the functions of β for $N_A = N_B = 100$, $u_0 = 2$, $\gamma a^2/kT = 4.1$, $\chi = 0.55$, $C = 10^{-5}$. Curves correspond to the case of no ion binding $p = 0$ (1) and $\delta\epsilon = 0.67$ (2), $\delta\epsilon = 0.69$ (3), and $\delta\epsilon = 0.7$ (4).

At high β due to the presence of a considerable fraction of charged groups in the B blocks interacting through long-range electrostatic interactions, the short-range volume interactions play no role in the system behavior. The polymer concentration in the swollen corona is low thus the value of the dielectric constant is close to that of the pure solvent and there is no ion pairing in this regime, the mobile counterions distribute homogeneously in the solution.

Thus, due to existence of a new micelle state at $\delta\epsilon > \delta\epsilon^*$, two types of the jump-like first-order phase transitions can be realized in the solutions with increasing β: large micelles with PE collapsed coronae → large micelles with ionomer-type coronae → small micelles with PE swollen coronae (see Fig. 4). Conformational transitions in micelles are caused by changes in the balance of interactions in the micelle corona and are accompanied by a non-monotonous change in the micelle aggregation number. This non-monotonous behavior is rather unusual for micelles with ionic corona, though it has been observed recently for micelles with ionic cores.[6]

As it could be expected an increase of $\delta\epsilon$ favors the ion pairing in the corona and results in a widening of β-values area, where the new ionomer state is realized (compare curves 3 and 4 in Fig. 3).

The polarity of the pure solvent is described by the parameter u_0. In Fig. 5, we plot the dependences of the micelle parameters on β for various values of u_0. We fix the value of the relative dielectric constant $\delta\epsilon = 0.7$ for all curves, and thus, change of u_0 means a change of the polymer polarity too. It is quite natural that the area of ionomer-type micelles becomes wider in media of lower polarity (high values of u_0).

Another important parameter defining the behavior of the micellar solution in the Flory-Huggins parameter describing short-range interactions within the micelle corona. The higher the χ-values, i.e. the more attractive the interactions are, the denser and thus, less polar the micellar corona is, this fact leading to an enlargement of the region where ionomer micelles are formed (see Fig. 6). Besides, the type of the phase transition between large PE and ionomer-type micelles

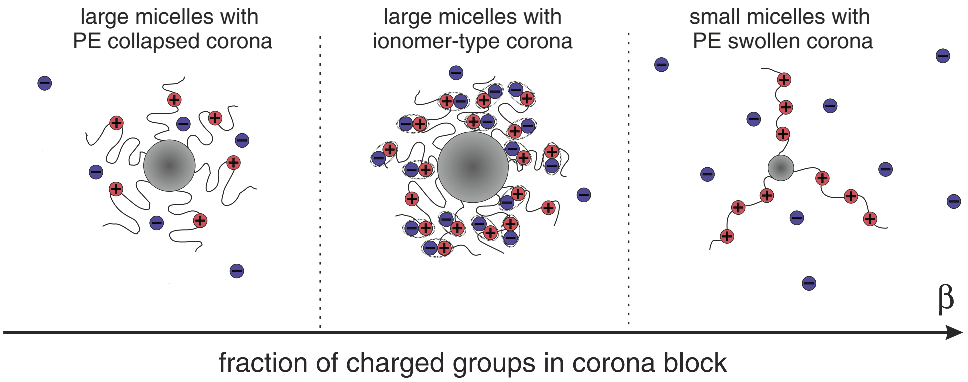

FIG. 4. Schematic representation of two consecutive transitions in micelles induced by corona block charging.

changes with χ (Fig. 6). When the solvent becomes poorer, the sharp transition turns into continuous. Corona density in large PE micelles increases with an increase of Flory-Huggins interaction parameter χ. Therefore, the solvent deterioration reduces distinctions (e.g., Φ) between micelle corona in collapsed PE and ionomer states.

It is possible to induce transitions between all three types of micelles by changing not only β but also the solvent quality. In Fig. 7, we plot m and p as functions of χ for a fixed fraction of ionizable groups in corona blocks. Note, that aggregation number and fraction of ion pairs are monotonous functions of the Flory-Huggins interaction parameter χ (see Fig. 7). It is quite natural that worsening of the solvent quality (increase of χ) causes shrinking of the corona and thus increase of m. Then the avalanche-type process of counterion condensation[10,11] sets in and a second transition into ionomer state takes place.

C. Diagrams of micelle states

Let us summarize the results determining the region of the system parameters where the new micelle state can exist. The boundary of this region is defined by equating the free energies per molecule in different types of micelles. In all our calculations, we fix $N_A = N_B = 100, \delta\epsilon = 0.7, \gamma a^2/kT = 4.1, C = 10^{-5}$. The other parameters controlling the phase behavior are u_0, β, and χ.

A typical diagram of the possible micelle states in terms of u_0 and β is presented in Fig. 8. It is calculated at a fixed value of the Flory-Huggins interaction parameter χ corresponding to poor-solvent conditions for the coronal block. As we discussed above, we distinguish two types of micelles in the polyelectrolyte regime where ion pair formation is insignificant, $p \approx 0$. These micelles differ in aggregation number and counterion distribution between the micelle interior and the solution:

- so-called small PE micelles with rather low aggregation number do not keep their counterions, a large fraction of counterions leave for the outer solution, $\alpha \sim 1$;
- large PE micelle with high aggregation numbers, almost all counterions are trapped within the corona, $\alpha \sim 0$.

At u_0 less than a critical value u_0^* only these two types of the micelles exist in the solution. A continuous transition from large to small micelles takes place upon increase of the amount of polar groups in the coronal block.

The third type of micelles can exist in the solution only when u_0 exceeds the critical value u_0^*, i.e., the solvent is not so polar. These micelles are in ionomer regime, their aggregation number is as large as that of the large PE micelles, but nearly all counterions are kept within the corona and are bound with the charges on the polymer chains, i.e., the fraction of ion pairs is close to unity, $p \approx 1$. The bold line in Fig. 8 defines the region of stability of these ionomer-like micelles

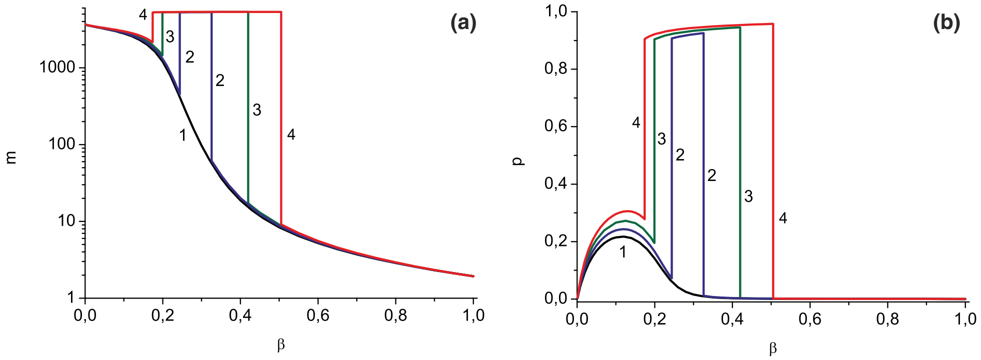

FIG. 5. Aggregation number m (a) and fraction of ion pairs p (b) as functions of β for $N_A = N_B = 100, \delta\epsilon = 0.7, \gamma a^2/kT = 4.1, \chi = 0.55, C = 10^{-5}$. Curves correspond to $u_0 = 1.8$ (1), $u_0 = 1.9$ (2), $u_0 = 2$ (3), $u_0 = 2.1$ (4).

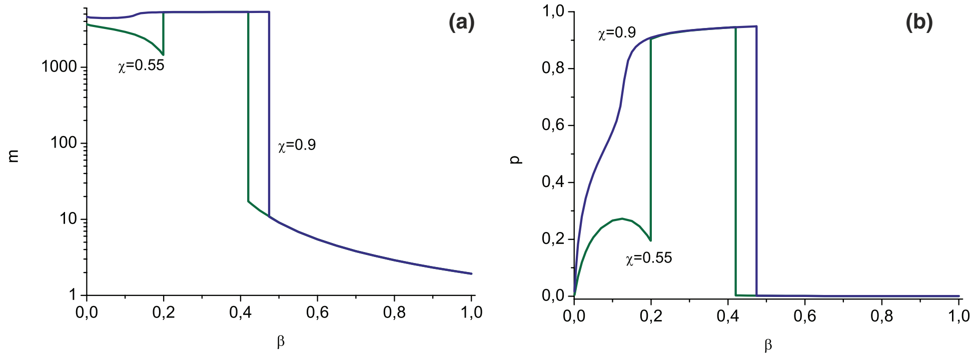

FIG. 6. Aggregation number m (a) and fraction of ion pairs p (b) as functions of β for $N_A = N_B = 100, u_0 = 2, \delta\epsilon = 0.7, \gamma a^2/kT = 4.1, C = 10^{-5}$. Curves correspond to $\chi = 0.55, \chi = 0.9$.

and shows where the jump-like first-order phase transition between different-type micelles takes place.

Thus, if u_0 is slightly higher than u_0^*, the growth of the ionization degree results in the emergence of two successive first-order phase transitions: large PE micelles with collapsed corona → ionomer-type micelles with supercollapsed corona → small PE micelles with swollen corona. There is no formation of ionomer-type micelles in high polar media ($u_0 < u_0^*$) because the ion pairing is unfavorable.

It should be noted that in our theoretical model, we assumed that the dielectric constant of the polymer, ϵ_p, is smaller than the dielectric constant of the solvent ϵ_0. This assumption is valid only when the fraction of ion-containing groups in the coronal block is much less than unity, since ion pairs possess permanent dipole moments and give a contribution into the average value of the dielectric constant of the media within the micelle corona. Thus, in Fig. 8, we restrict the diagram by $\beta < 0.5$.

The bold line in the diagram depicting the location of the first-order phase transition terminates at β^{cr}, u_0^{cr}. It means that two minima of the free energy corresponding to the large PE micelles and ionomer micelles merge, and the transition between the two types of micelles becomes continuous with a sharp but continuous growth of the ion pair fraction upon β increase.

In Fig. 9, we plot a series of the first-order phase transition lines for various values of the the Flory-Huggins interaction parameter χ. An increase in χ, i.e., worsening of the solvent quality results is the downward shift of these lines. This effect has a clear physical meaning. Both solvent quality and solvent polarity decrease make the formation of a dense micelle corona as well as counterion binding more favorable. Thus, the ionomer-type micelles remain thermodynamically equilibrium even in a polar solvent (at rather low values of u_0), if the χ value is high enough.

It is clear that if the solvent is poor for the coronal block then at small fraction of charges the micellar dispersion could be unstable and micelles could precipitate from the solution. Besides, at some conditions other micelle morphologies (i.e., cylinders or lamellar structures) could be more favorable. Though the analysis of aggregate diverse morphologies and macroscopic phase separation is not the main objective of our study, it is useful to give some remarks on this issue supporting spherical micelle model. First, direct experimental observations of micelles with hydrophobic ionic coronae have lately demonstrated stability of spherical aggregates in the case of equal lengths of the blocks.[7] Second, a recent theoretical consideration showed that the presence of charged groups in the soluble block enhances vastly the stability of spherical micelles at low polymer concentration versus cylindrical, lamellar structures and precipitate. Even though the length of core block exceeds the length of the corona one by several times, spherical micelles are still thermodynamically stable.[17] Furthermore, according to our results both the ionomer-type and PE micelles carry a significant electric charge (see Fig. 3(e)) promoting their stability in the solution.

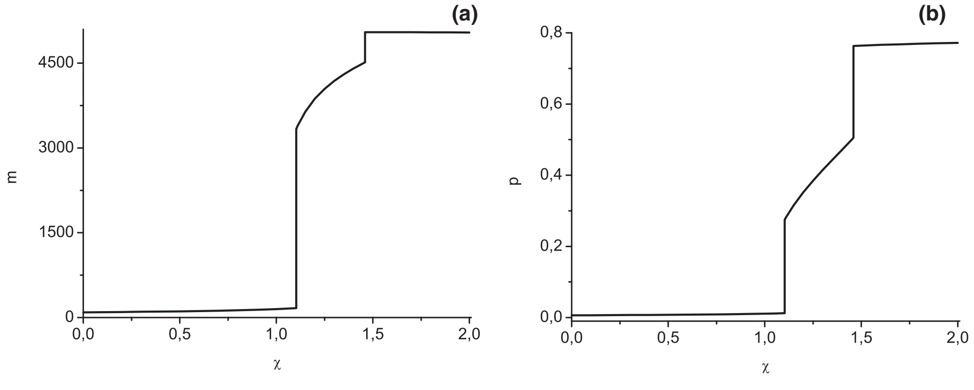

FIG. 7. Aggregation number m (a) and fraction of ion pairs p (b) as functions of χ for $N_A = N_B = 100, u_0 = 1, \delta\epsilon = 0.78, \gamma a^2/kT = 4.1, \beta = 0.25, C = 10^{-5}$.

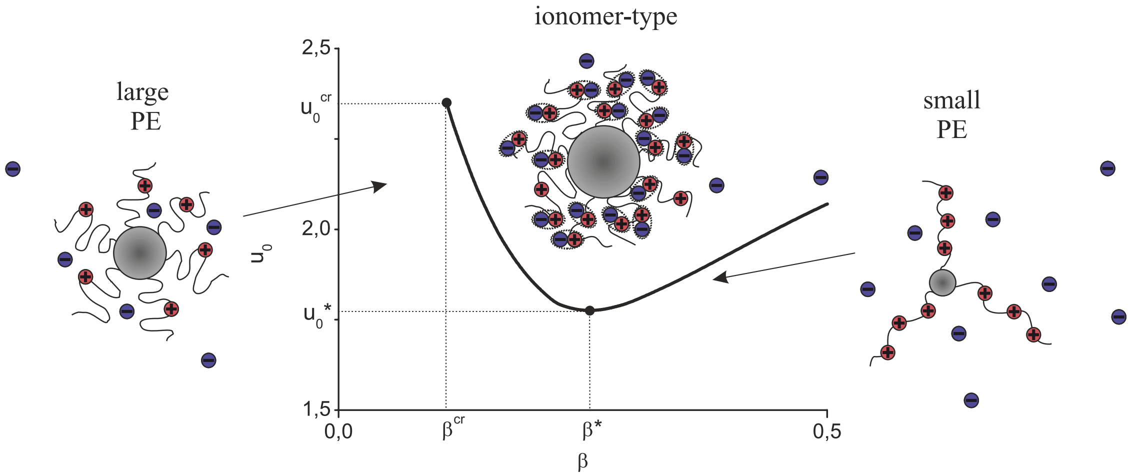

FIG. 8. $\beta - u_0$ diagram of micelle states for the fixed value of Flory-Huggins interaction parameter $\chi = 0.7$. Micelle types (large PE, small PE, ionomer-type) are depicted on the diagram.

In this paper, we restrict ourselves to the case of a salt-free solution. Addition of salt has been recently observed experimentally to promote micelle precipitation.[7,8] The larger the micelle charge is, the higher micelle stability against salt is. We believe that at some conditions addition of salt may induce corona chains shrinking and transition from small PE micelles to aggregates with dense corona similar to salt-induced contraction of polyelectrolytes in poor solvents.[32–35]

In the framework of our theoretical approach, only thermodynamically equilibrium micelles have been examined. However, aggregates with strongly insoluble core block often appear to be kinetically frozen. For instance, polymer micelles with polystyrene core in aqueous solutions are known to be under kinetic control.[1] This fact may lead to some discrepancies between theoretical results and experimental observations.[7]

It is worth noting that finite-size effects may play a noticeable role in micellar solution behavior.[20] According to the presented theory, transitions between different types of micelles are abrupt first-order phase transitions. However, near the transition point, the system may stay in a thermodynamically unfavorable state, i.e., two types of micelles are able to coexist when the difference in free energies of different micelle states is of the order of the temperature. Such experimental methods as light scattering and electrophoretic mobility measurements allow to observe average values of micelle parameters among members of the ensemble. Thus, a jump-like transition is actually observed as continuous one.[36]

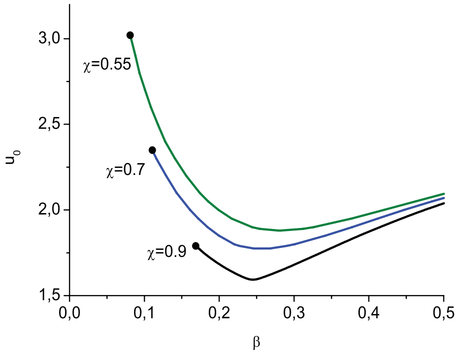

FIG. 9. First-order phase transition lines of the solution for different values of Flory-Huggins interaction parameter χ. Curves correspond to $\chi = 0.55$, $\chi = 0.7$, $\chi = 0.9$. Critical points are depicted by bold dots.

IV. CONCLUSION

We develop a mean-field theory to study the structure of micelles formed by diblock copolymers with insoluble/amphiphilic ionic blocks in a salt-free dilute solution. The core of the micelles comprises the insoluble blocks while the corona has an amphiphilic ionic nature containing non-polar and ionizable groups. We suppose that the solvent is slightly poor for the non-polar monomer units, thus, there is an interplay of the short-range attractive interactions and long-range Coulomb interactions within the corona. We study conformational transitions in the micellar aggregates with the change of the balance between these two types of interactions caused by changes in solvent quality, solvent polarity, and fraction of ionizable groups.

We focus on the role of counterions in the system behavior. Owing to the micelle corona charge, the distribution of counterions in the solution is strongly inhomogeneous. Translational entropy of counterions completes with their attraction to the charged micellar aggregates resulting in accommodation of a large fraction of counterions in the micelles. The novelty of our approach is that we account for counterion binding with ion pair formation within the micellar corona. While in a swollen hydrophilic corona, the fraction of ion pairs is negligible, in a polymer dense hydrophobic corona ion pairing is expected to be significant.

Taking into account a progressive counterion binding within collapsing in a poor solvent micellar corona, we predict a new type of micelles in the solution. The corona of these micelles has an ionomer-type structure, i.e., it contains a large fraction of ion pairs. The region of stability of ionomer micelles increases with a decreasing solvent quality and polarity.

Another important result is the prediction of two first-order phase transitions between different-type micelles upon increase of the fraction of ion-containing groups in the micellar corona: large polyelectrolyte micelles with quasineutral coronae → large ionomer micelles → small charged micelles.

The obtained theoretical results could explain the existence of two types of micelle species from PS-b-P(EVP/4VP) copolymers observed in Ref. 7. Large and small micelles were formed upon addition of water into solutions of these copolymers in dimethylformamide/methanol nonselective solvent. Coexistence of micelles of two different sizes can be attributed to the two minima in the free energy appearing due to ion aggregation within the micelle corona.

Direct observation of ionomer-type micelle is a challenging task. A possible system could include micelles from polycarboxylic acids as coronal blocks perhaps not in aqueous solutions but in a less polar solvent, for example, methanol. Titration, for instance, with sodium methoxide will induce substitution of H^+ ions by Na^+ ions in carboxylic groups. The degree of dissociation of COO^-Na^+ should depend on the local dielectric constant of the corona medium. One could expect that formation of ionomer-type micelles can be triggered by the high binding constant of the Na^+ counterions to the ions on PE coronal chains in a low-polar medium. Instead of Na^+ other counterions with different binding affinity to COO^- groups could be used and the role of counterion nature on the micellar solution structure could be elucidated.

APPENDIX: FREE ENERGY OF SHORT-RANGE INTERACTIONS WITHIN THE MICELLE CORONA

The free energy of the short range interactions in the micelle corona can be expressed in terms of the Flory-Huggins lattice theory.[20,23,24] In general case, when there are k types of molecules in the mixture, with the degrees of polymerization $M_n (M_n \geq 1, n = 1, 2, ...k)$, F_{int} has the following form:

$$\frac{F_{int}}{T}\frac{a^3}{V} = \sum_{n=1}^{n=k} \frac{1}{M_n} \Phi_n \ln \Phi_n + \frac{1}{2} \sum_{n=1}^{n=k} \chi_{nn} \Phi_n^2 + \sum_{n=1}^{n=k} \sum_{\substack{m=1 \\ m<n}}^{m=k} \chi_{nm} \Phi_n \Phi_m, \tag{A1}$$

where the first term accounts for the free energies of translational motion of the various type molecules in the system and the other ones describe their interactions, χ_{mn} are the so-called Flory-Huggins interaction parameters.

According to the incompressibility condition

$$\sum_{n=1}^{n=k} \Phi_n = 1. \tag{A2}$$

Let us consider a micelle corona as a solution containing three interacting components taking in mind polymer units not forming ion pairs (non-ionic as well as charged) (p), ion pairs (i), and solvent molecules (s). Describing thus the coronal media, we neglect non-Coulomb interactions of the counterions and their own volume here. Note, that the solvent molecules are unimolar, $M_s = 1$, and the other components do not possess an entropy of independent translational motion within the corona. Thus, the total free energy of the system equals

$$\frac{F_{int}}{T}\frac{a^3}{V} = (1-\Phi)\ln(1-\Phi) + \frac{1}{2}\left[\chi_{ss}\Phi_s^2 + \chi_{ii}\Phi_i^2 + \chi_{pp}\Phi_p^2\right] + \chi_{si}\Phi_s\Phi_i + \chi_{sp}\Phi_s\Phi_p + \chi_{ip}\Phi_i\Phi_p. \tag{A3}$$

Here Φ is the total polymer volume fraction, thus, the volume fraction of the solvent molecules is equal to $\Phi_s = 1 - \Phi$; $\Phi_p = \Phi(1 - p\beta)$ and $\Phi_i = p\beta\Phi$ are the volume fractions of the non-polar monomer units and the ion pairs, respectively; χ_{nm} are the Flory-Huggins parameters of interaction between the mixture components $(n, m = s, i, p)$. After some transformation we get

$$\frac{F_{int}}{T}\frac{a^3}{V} = (1-\Phi)\ln(1-\Phi) - [(1-p\beta)\tilde{\chi}_{sp} + p\beta\tilde{\chi}_{si} + p\beta(p\beta-1)\tilde{\chi}_{pi}]\Phi^2 + \left[\chi_{si}p\beta + \chi_{sp}(1-p\beta) - \chi_{ss}\right]\Phi + \frac{\chi_{ss}}{2}, \tag{A4}$$

where $\tilde{\chi}_{nm} = \chi_{nm} - (\chi_{nn} + \chi_{mm})/2$, $n \neq m$. The Φ-independent term, $\chi_{ss}/2$, in the free energy can be omitted. The linear in Φ term is similar to that accounting for the energy gain from ion pair formation in F_{agg}.

Let $\tilde{\chi}_{si} = 0$ because both ion pairs and solvent molecules are polar. Dielectric constant of the dry polymer is rather low, and the contacts between the nonpolar polymer units on the one side and the polar ion pairs and solvent molecules on the other side are unfavorable. Thereby, it is natural to assume that both $\tilde{\chi}_{sp} > 0$ and $\tilde{\chi}_{pi} > 0$. For the sake of simplicity, we suppose $\tilde{\chi}_{sp} = \tilde{\chi}_{pi} = \chi$. Then the Flory-Huggins free energy reduces to

$$\frac{F_{int}}{T}\frac{a^3}{V} = (1-\Phi)\ln(1-\Phi) - \chi(1-p\beta)^2\Phi^2. \tag{A5}$$

[1] M. Moffitt, K. Khougaz, and A. Eisenberg, Acc. Chem. Res. **29**, 95 (1996).
[2] S. Forster, V. Abetz, and A. H. E. Muller, Adv. Polym. Sci. **166**, 173 (2004).
[3] O. V. Borisov, E. B. Zhulina, F. A. M. Leermakers, and A. H. E. Muller, Adv. Polym. Sci. **241**, 57 (2011).
[4] S. Forster and T. Plantenberg, Angew. Chem., Int. Ed. **41**, 688 (2002).
[5] A. B. Lowe, M. Torres, and R. Wang, J. Polym. Sci., Part A: Polym. Chem. **45**, 5864 (2007).
[6] I. Erel, Z. Zhu, S. Sukhishvili, E. Patyukova, I. Potemkin, and E. Kramarenko, Macromol. Rapid Commun. **31**, 490 (2010).
[7] E. A. Lysenko, A. I. Kulebyakina, P. S. Chelushkin, A. M. Rumyantsev, E. Yu. Kramarenko, and A. B. Zezin, Langmuir **28**, 17108 (2012).
[8] E. A. Lysenko, A. I. Kulebyakina, P. S. Chelushkin, A. M. Rumyantsev, E. Yu. Kramarenko, and A. B. Zezin, Langmuir **28**, 12663 (2012).
[9] K. Jelinek, Z. Limpouchova, F. Uhlik, and K. Prochazka, Macromolecules **40**, 7656 (2007).
[10] A. R. Khokhlov and E. Yu. Kramarenko, Macromol. Theory Simul. **3**, 45 (1994).
[11] A. R. Khokhlov and E. Yu. Kramarenko, Macromolecules **29**, 681 (1996).
[12] O. E. Philippova, N. L. Sitnikova, G. B. Demidovich, and A. R. Khokhlov, Macromolecules **29**, 4642 (1996).
[13] S. G. Starodoubtsev, A. R. Khokhlov, E. L. Sokolov, and B. Chu, Macromolecules **28**, 3930 (1995).
[14] E. Yu. Kramarenko, I. Ya. Erukhimovich, and A. R. Khokhlov, Macromol. Theory Simul. **11**, 462 (2002).

[15] E. Yu. Kramarenko, A. R. Khokhlov, and K. Yoshikawa, Macromol. Theory Simul. **9**, 249 (2000).

[16] E. V. Volkov, O. E. Filippova, and A. R. Khokhlov, Colloid J. **66**, 663 (2004).

[17] S. V. Venev, P. Reineker, and I. I. Potemkin, Macromolecules **43**, 10735 (2010).

[18] O. V. Rud, A. A. Mercurieva, F. A. M. Leermakers, and T. M. Birshtein, Macromolecules **45**, 2145 (2012).

[19] A. N. Semenov, Sov. Phys. JETP **61**, 733 (1985).

[20] A. Yu. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP, New York, 1994).

[21] J. K. Wolterink, F. A. M. Leermakers, G. J. Fleer, L. K. Koopal, E. B. Zhulina, and O. V. Borisov, Macromolecules **32**, 2365 (1999).

[22] F. A. M. Leermakers, M. Ballauff, and O. V. Borisov, Langmuir **24**, 10026 (2008).

[23] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

[24] P. G. de Gennes, *Scaling Concepts in Polymer Chemistry* (Cornell University Press, Ithaca, 1979).

[25] A. R. Khokhlov, S. G. Starodubtzev, and V. V. Vasilevskaya, Adv. Polym. Sci. **109**, 123 (1993).

[26] N. P. Shusharina, I. A. Nyrkova, and A. R. Khokhlov, Macromolecules **29**, 3167 (1996).

[27] T. M. Birshtein and E. B. Zhulina, Polymer **30**, 170 (1989).

[28] S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, P. Pincus, and D. Hone, J. Chem. Phys. **80**, 5776 (1984).

[29] O. V. Borisov, J. Phys. II France **6**, 1 (1996).

[30] E. Yu. Kramarenko, A. R. Khokhlov, and K. Yoshikawa, Macromolecules **30**, 3383 (1997).

[31] A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, Macromolecules **29**, 2974 (1996).

[32] V. V. Vasilevskaya, A. R. Khokhlov, and K. Yoshikawa, Macromol. Theory Simul. **9**, 600 (2000).

[33] V. V. Vasilevskaya and A. R. Khokhlov, Vysokomol. Soedin., Ser. A **28**, 316 (1986).

[34] E. Yu. Kramarenko, O. E. Philippova, and A. R. Khokhlov, Vysokomol. Soedin., Ser. C **48**, 1216 (2006) [Polym. Sci., Ser. C **48**, 1 (2006)].

[35] J. Hua, M. K. Mitra, and M. Muthukumar, J. Chem. Phys. **136**, 134901 (2012).

[36] K. Yoshikawa, M. Takahashi, V. V. Vasilevskaya, and A. R. Khokhlov, Phys. Rev. Lett. **76**, 3029 (1996).