Electrostatics in the self-assembly of macromolecular surfactants

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Abstract. – We report on a small-angle neutron scattering (SANS) study of dilute solutions of neutral and charged polystyrene-polyisoprene (PS-b-PI) diblock copolymers in dimethyl acetamide (DMAc), a polar selective solvent for PS. This is a model macromolecular surfactant system: the low glass temperature of the PI block ensures that thermodynamic equilibrium can be attained; the ionic character of the copolymers is provided by a single sulfonate group at the free chain end of the PI block. The crossover from ionic to non-ionic behaviour is investigated by addition of salt. The results are compared to theoretical predictions for micellization of these model macromolecular systems.

Micellization of diblock copolymers in a selective solvent [1] constitutes a macromolecular paradigm for self-assembly in solutions: not only the size and geometry of the aggregates can be fine-tuned by tailoring the asymmetry and chemical nature of the copolymers, but also many possibilities may be explored beyond the classical hydrophobic/hydrophilic categories [2]. A single copolymer chain in a selective solvent adopts a tadpole configuration with a collapsed head and a swollen tail. The collapsed head provides the driving force for aggregation by seeking for protection against poor solvent exposure in the commonly shared volume of the micelle core. The swollen tails form a corona around the micellar core. They play a triple role in the stability of the aggregates by ensuring their solubility, by limiting the growth of the core size and by sterically stabilizing the micelles against Van der Waals attractive forces [3], [4]. A distinctive feature of macromolecular surfactants is the large typical energy scale for aggregation, measured, for instance, by the surface energy, F_s, of a single collapsed head $F_s = 4\pi R^2 \gamma$. Here γ is the surface tension and R the radius of the core. F_s is of the order of $30 k_B T$ for a collapsed block of 100 monomers. Such a large energy leads to critical
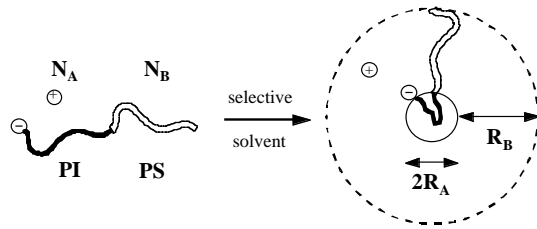
Fig. 1. – Schematic representation of the monofunctionalized PS-b-PI diblock copolymer of N_A and N_B monomers of PI and PS, respectively, and the formation of a spherical micelle in a selective solvent for PS. Because of the high polarity of the solvent, the charge at the chain end is expected to reside at the surface of the core, folding the PI chain. R_A and R_B are the radii of the core and the swollen shell, respectively.

micellar concentration and polydispersity values much smaller than those of low-molecular-weight surfactants. Another important consequence of the large energy value is the decrease of the kinetic rates for micelle/unimer exchange. Typical exchange times in diblock copolymer micelles can be of the order of minutes [5]. If the core of the micelles has a glassy nature, such small exchange rates can be even further reduced to a point where thermodynamic equilibrium can no longer be achieved [6]. As we will see below, this problem can be circumvented by choosing a system with a molten liquid core.

In polar solvents, the presence of ionic groups introduces an electrostatic interaction to the dispersion and micellization of surfactants. For conventional surfactants, the dissociation energy of the ion pair increases the solubility of the molecule and the strength of electrostatic repulsion between heads strongly influences the aggregate geometry. Control of the electrostatic strength can be exerted by using salt to screen the interactions. Ternary phase diagrams solvent-surfactant-salt usually exhibit complex behavior, and subtle variations of the aggregation geometry can be observed as a function of salt and surfactant concentration.

In this letter we undertake a fundamental study of the role of electrostatics on micellization of a model macromolecular surfactant system. We focus on a region of the phase diagram where spherical micelles are formed. The chosen macromolecule is a symmetric poly(styrene-block-isoprene) (PS-b-PI) diblock copolymer dispersed in dimethyl acetamide (DMAc) which is a selective solvent for polystyrene [7], [8]. The glass transition temperature for the PI block is about 273 K, allowing for thermodynamic equilibration of the micellar core at room temperature. The electrostatic interaction is introduced by an ionic sulfonate group at the free chain end of the PI block (see fig. 1). The role of electrostatics in the self-assembly of this model system in dilute solution, in the absence and presence of added salt, is investigated using small-angle neutron scattering (SANS). Micelles formed by the non-ionic symmetric PS-b-PI of identical mass and block size are studied as a reference. The micelle core radii and aggregation numbers, obtained from a fit of the data, are compared to theoretical predictions for copolymer micellization.

The unfunctionalized and sulfonated symmetric PS-b-PI diblock copolymers were synthesized following the procedure described in ref. [9]. The mass of each block is $M_n \sim 12 \, \text{kg mol}^{-1}$. PI and PS polymerization indices are, respectively, $N_A = 176$ and $N_B = 120$. Deuterated dimethylacetamide (DMAc) was purchased from Aldrich and used without further purification. Neutron scattering experiments were performed at spectrometer D11 at ILL and standard procedures of data treatment were applied to the raw data.

In fig. 2 a), scattering data for a dilute solution of the sulfonated block copolymer at a volume fraction of 0.01 is plotted on a log-log scale and compared to that of non-ionic copolymer. The
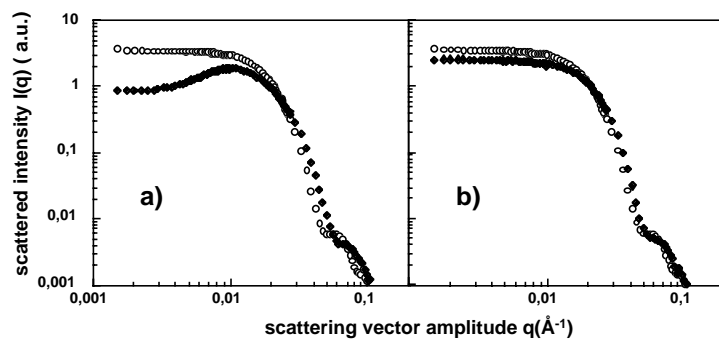
Fig. 2. – a) Comparison of the scattered intensity of the non-functionalized (○) with the mono-functionalized (●) PS-b-PI. b) Comparison of the scattered intensity of the non-functionalized (○) with that of the monofunctionalized (●) PS-b-PI in the presence of added salt. The polymer volume fraction is 0.01 in all the solutions.

scattering of the neutral copolymer shows the typical signature of spherical micelles in a dilute solution [10]-[12] with no strong correlation between neighbouring micelles. An oscillation due to a contrast step between the molten core and the swollen shell can be observed at high scattering amplitudes. When one electric charge is added to the PI chain ends the scattering curve exhibits a broad correlation maximum at wavevector $q \sim 0.01$ Å^{-1} and a reduced scattering intensity at small angles. Further features are a shift towards higher scattering vectors and a decrease of the high q oscillations. The scattering peak is the signature of long-range Coulomb interactions. It shows that the functional ionic group attached to the end of the core PI block dissociates in DMAc (dielectric constant $\epsilon = 40$). The shift of the scattering curves towards higher q values indicates a decrease of the core size of the micelles. The electrostatic interactions therefore play the double role of increasing the intermicellar interactions and decreasing the micelle aggregation number.

Addition of salt leads to screening of the Coulomb interactions. In fig. 2 b) we plot both the scattering curve from a solution of the anionic copolymer with added LiCl and the reference scattering curve of the non-ionic copolymer. LiCl was added to the solution until saturation was reached. The general shape of the scattering curve of the ionic copolymer in the presence of salt is similar to that of the non-functionalized copolymers. The absence of the correlation peak confirms that the long-range Coulomb interactions have been screened. However, the inner structure of the charged micelles does not completely relax to that of the non-functionalized species. The spectrum is slightly shifted towards higher scattering vectors and the low-angle scattering intensity is smaller. This suggests that the aggregation number of the ionic micelles in the presence of salt remains smaller than that of the neutral micelles.

The scattered intensity can be written as $I(q) = S(q) P(q)$, with $P(q)$ the form factor of a diblock copolymer micelle [2], [4] and $S(q)$ the structure factor of the micellar solution. In the absence of strong micelle-micelle correlations, the structure factor $S(q)$ is featureless over the whole wavevector range. Thus, for both, non-ionic and screened micelles, the scattering intensity can be described by $I(q) = N P(q)$ with N the number of micelles per unit volume. For the charged micelle case, where a correlation peak is present, the structure factor $S(q)$ has to be taken into account in order to describe the full scattering range. However, structural information can still be obtained from the high wavevector range where $S(q)$ approaches a constant value. Fitting data in this high q-range with $P(q)$ only is further supported by polydispersity, related effects that damp oscillations in $S(q)$. Finally, an experimental $S(q)$
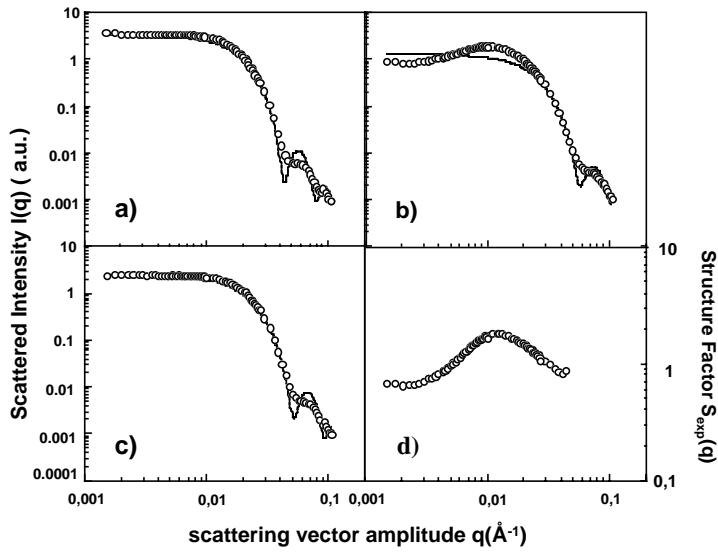
Fig. 3. – Fit of experimental data with the form factor of spherical micelles described in eq. (1). a) Non-functionalized PS-b-PI; b) monofunctionalized PS-b-PI without added salt: only data beyond $q = 0.03$ Å^{-1} was used for the fitting. c) Monofunctionalized PS-b-PI in the presence of added salt; d) Structure factor obtained by dividing data for monofunctionalized PS-b-PI (without salt) by the form factor as obtained from the fit in c).

curve can be extracted by deviding the data by the form factor $P(q)$ obtained from the large wavevector fit.

The form factor of a diblock micelle, $P(q)$, can be written [13] as a sum of four different terms: the self-correlation of the micelle core, F_s; the self-correlation of the chains in the corona, F_c; the cross-term between the spherical core and the corona chains, F_{sc}; and the cross-correlation between different chains in the corona, F_{cc}. Explicitly:

$$P(q) = p^2\rho_s^2 F_s(q, R_A) + p\rho_c^2 F_c(q, R_B) + p(p-1)\rho_c^2 F_{cc}(q, R_A, R_B) + 2p^2\rho_s\rho_c F_{sc}(q, R_A, R_B), \quad (1)$$

where p is the micelle aggregation number and ρ_s and ρ_c are the excess scattering lengths of the core and of the outer chains, respectively. R_A is the micelle core radius and R_B the radius of gyration of the chains in the shell ($R_B = N_B a^2/6$), with N_B the polymerization index of the chain and a the Kuhn length. The first term on the r.h.s. of eq. (1) is written as: $F_s(q, R_A) = \Phi(qR_A)^2$ with $\Phi(x) = 3x^{-3}(\sin x - x\cos x)$, if one assumes a constant density core of radius R_A. An approximate expression for the chains in the corona can be written by considering Gaussian chains: $F_c(q, R_B) = g(q^2 R_B^2/6)$ with $g(x) = 2x^{-2}(\exp[-x] - 1 + x)$. With these approximations the cross-correlation terms are given by $F_{cc}(q, R_A, R_B) = \Psi(qR_B)^2\chi(qR_A)^2$ with $\Psi(x) = x^{-1}(1 - \exp[-x])$ and $\chi(x) = x^{-1}\sin x$; $F_{sc}(q, R_A, R_B) = \Psi(qR_B)\Phi(qR_A)\chi(qR_A)$.

The fitting results displayed in figs. 3 a)-c) were obtained by considering a minimum set of three free parameters: R_A, R_B and p. Polydispersity has not been taken into account. In the cases of neutral (fig. 3 a)) and charged micelles with added salt (fig. 3 c)), eq. (1) fits the whole scattering range reasonably well. More weight was given to points at high scattering vector values to ensure precision in the determination of the radius of the molten core. In the case of charged micelles (fig. 3 b)), the fitting quality at high q values is comparable to that in cases of fig. 3 a) and fig. 3 c) which ensures a good determination of the core radius. At lower
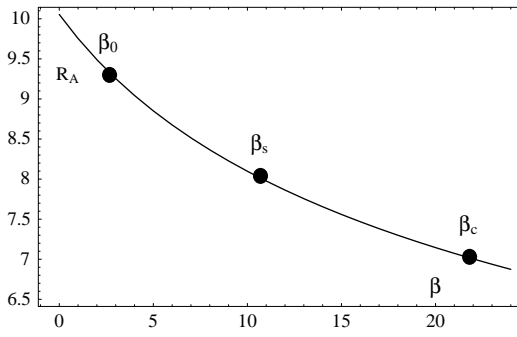
Fig. 4. – Comparison of the experimentally measured (•) and theoretically predicted (——) core radii R_A in nanometers. The parameter β measures both the importance of electrostatic interactions and elastic stretching in the core (see text for details).

q values, deviations are due to the structure factor. An experimental structure factor $S_{\mathrm{exp}}(q)$ exhibiting a soft maximum can be obtained by dividing the scattering data by the fit of the form factor (fig. 3 d)).

Core radii obtained by data fitting are 9.2 nm, 7.0 nm and 8.0 nm, for neutral, charged and charged micelles with salt, respectively. The corresponding aggregation numbers, p, obtained from the fit as free independent parameters are 90, 47 and 60, respectively. The aggregation number of the charged micelles corresponds to an average distance of 64 nm between micelles. This is close to a distance of 63 nm that one can extract from the position of the peak in the structure factor. From the radii and aggregation numbers one can also extract the volume v occupied by one PI monomer in the core $v = (4/3)\pi R_A^3/(pN_A)$. One gets, respectively, 0.20 nm^3, 0.17 nm^3, 0.20 nm^3. The volume of one PI monomer in a bulk polymer sample (monomer mass 68 g mol^{-1} and density 0.97 g cm^{-3}) is 0.12 nm^3. The core thus appears to accomodate 30% to 40% of the solvent. The values for the gyration radius of the chains in the outer shell were found to be, respectively, 4.0 nm, 3.0 nm and 4.0 nm.

The structure of non-ionic diblock copolymer micelles in a selective solvent can be described by considering [3], [4] three contributions to the free energy per chain $\mathcal{F}_p$: the core-solvent interfacial tension, the stretching energy of the chains in the corona and the stretching energy of the chains in the core:

$$\frac{\mathcal{F}_p}{k_{\mathrm{B}}T} = 4\pi\frac{\gamma}{k_{\mathrm{B}}T}\frac{R_A^2}{p} + Ap^{1/2} + \frac{\pi^2}{80}\frac{R_A^2}{N_A a^2}. \tag{2}$$

Here γ is the interfacial tension between the core and the solvent, R_A is the radius of the micelle core, p the aggregation number, N_A the polymerization index of the blocks in the core and a its Kuhn length. A is a logarithmic function of the core and corona radii, we approximate it here by a constant value of order unity. It is convenient to introduce dimensionless variables $r = R_A(\tilde{\gamma}/A)^{-2/5}(4\pi N_A/3)^{-3/5}b^{-1}$ with $\tilde{\gamma} = \gamma b^2/(k_b T)$ and $4\pi b^3/3 = v$. Equation (2) can then be rewritten as

$$\tilde{\mathcal{F}}_p = \frac{3}{r} + \left[\frac{4\pi}{3}r^3\right]^{1/2} + \frac{\pi^2}{80}\beta\, r^2\,, \tag{3}$$

where $\beta = (\tilde{\gamma}/A)^{1/5}A^{-1}(4\pi/3)^{4/5}N_A^{1/5}(b/a)^2$ is a coefficient that measures the relative importance of stretching in the core and in the corona. Minimization of eq. (3) with respect to r for a given β provides an explicit value for the predicted core radius R_A. When a

charge is added to the extremity of the block in the core, that extremity will preferentially be located at the core surface, where the polar environment allows for counterion dissociation. We assume now that all the charges migrate to the core surface, where a fraction α dissociates. This introduces two new contributions to the micelle free energy. The first is an increase of the elastic energy of the core due to the presence of loops (such an increase multiplies the elastic contribution by four). The second is the electrostatic energy of $\alpha\,p$ charges at the core surface. It can be easily checked that eq. (3) still holds if one replaces the coefficient β by a new coefficient $\beta_c = 4\,\beta(1 + \alpha^2 40 a^2 l_B/(3\pi v))$ with $l_B = e^2/(4\pi\epsilon k_B T)$ the Bjerrum length. $l_B = 1.44$ nm for DMAc. In the presence of salt the electrostatic interactions are negligible. We assume that in this limit the charges still migrate to the core surface where they benefit from the polar environment. In this case the coefficient β in eq. (3) is replaced by a new coefficient $\beta_s = 4\,\beta$. We plot in fig. 4 the theoretical prediction of eq. (3) and the experimentally measured radii. Agreement was obtained by setting $\tilde{\gamma} = 0.34$, $A = 0.34$ and $\alpha = 0.23$. The value of $\tilde{\gamma}$ corresponds to a core/solvent interfacial tension $\gamma = 16$ mN m^{-1}, consistent with typical values for polymer/solvent interfacial tensions. Interestingly, the value of the dissociation constant α is similar to values obtained in many micellar systems of low molecular weight surfactants [14]-[16].

In conclusion, we studied the role played by electrostatic interactions in the micellization of diblock copolymers in a selective solvent, when a single charge is introduced at the extremity of the blocks in the core. Our measured core radii for non-charged, charged and salt-screened micelles are quantitatively described by a micellization model that assumes localization of the charges at the core surface.

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