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Z. Tuzar[a]
[a] Institute of Macromolecular Chemistry, Czech. Acad. Sci., Prague, Czechoslovakia

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EXPERIMENTS ON ASSOCIATION OF BLOCK COPOLYMERS IN SOLUTION

Z. Tuzar

Institute of Macromolecular Chemistry,
Czech. Acad. Sci., 16206 Prague, Czechoslovakia

ABSTRACT

Block copolymers in dilute and semidilute solutions in selective solvents self-associate forming multimolecular spherical micelles, cores of which are formed by insoluble blocks and shells by soluble blocks. In this paper experimental approaches are surveyed concerning structure and hydrodynamic properties of block copolymer micelles, thermodynamics of micelle formation, kinetics of micelle formation and dissociation, and dynamics of micellar equilibria. Some problems of present interest are briefly mentioned, like anomalous micellization or "tentacled" micelles.

INTRODUCTION

Colloidal properties of block copolymers in selective solvents (good for one block, bad for the other) recall those known from aqueous solutions of soaps and surfactants: Block copolymers form fairly uniform spherical micelles, cores of which are formed by insoluble blocks, while soluble blocks form protective shells. These micelles can solubilize or "compatibilize" otherwise insoluble substances, stabilize particles of colloidal dimensions, form microemulsions, etc.

Micellization of block copolymers obeys the model of closed association characterized by an equilibrium between unimer (molecularly dissolved copolymer) and micelles. Micellar association number (i.e., the number of copolymer molecules forming a micelle) is typically several tens, in some cases even hundreds.

Due to increasing interest of both chemists and physicists in the field of polymeric micelles, the number of relevant papers has been increasing in the last decade. Several works reviewing the accumulated experimental data on block and graft copolymer micelles should be mentioned here: Price's chapter in a book on block copolymers[1], the article of Riess et al.[2] in the Encyclopedia of Polymer Science and Engineering, and two reviews by Tuzar and Kratochvil[3,4].

The aim of my contribution is to survey experimental approaches to micellar structure, thermodynamics of micelle formation, kinetics of micelle formation and dissociation, and dynamics of the unimer $\rightleftarrows$ micelle equilibria. In the end I will try to expose some topical or unresolved problems, such as the so called anomalous micellization, the micellization of ABA block copolymers in solvents selectively good for block B, and the bimodal distribution of micelles.

MICELLAR MOLAR MASS AND STRUCTURE

Micellar molar mass is usually measured by static light scattering (SLS), provided the unimer $\rightleftarrows$ micelles equilibrium is shifted towards micelles. If the unimer is present in a substantial amount, SLS provides - at a finite copolymer concentration - only an apparent molar mass, for the closed association model defined as

$$M_w^{app} = M_w^{(u)} w^{(u)} + M_w^{(m)} w^{(m)} \tag{1}$$

where superscripts (u) and (m) stand for unimer and micelles, respectively, and w is the weight fraction. Since the $M_w^{(u)}$ value can easily be determined by SLS in a good solvent, and w values either from sedimentation velocity or from quasielastic light scattering (QELS), $M_w^{(m)}$ can be calculated. A constant value of $M_w^{(m)}$ at different copolymer concentration (and various $w^{(u)}/w^{(m)}$ values for a given block copolymer-selective solvent system, was considered to provide an experimental proof of the applicability of the closed association model for the block copolymer association.

The essentially uniform character of micelles has been verified by electron microscopy, by QELS (single-exponential decay curves), by sedimentation velocity (sharp concentration boundaries), and by the small-angle X-ray scattering (SAXS) or the small-angle neutron scattering (SANS) (prominent side maxima on scattering curves).

Micellar size can be characterized by the radius of gyration $R_G^{(m)}$, (from SLS, SAXS, or SANS), or by the hydrodynamic radius, R_H (from QELS). $R_G^{(m)}$ values are practically always apparent values, since the core and the shell have generally different scattering contrasts with respect to the solvent used.

$$\left(R_{G,app}^{(m)}\right)^2 = Y^{(c)}\left(R_G^{(c)}\right)^2 + Y^{(s)}\left(R_G^{(s)}\right)^2 \tag{2}$$

Superscripts (m), (c), and (s) stand for micelle, core, and shell, respectively, and Y is the contrast. Assuming a simple concentric-sphere model, eq. (2) can be rewritten in terms of geometrical radii of the core, $R^{(c)}$, and of the whole micelle, $R^{(m)}$

$$\left(R_{G,app}^{(m)}\right)^2 = 0.6Y^{(c)}\left(R^{(c)}\right)^2 + 0.6Y^{(s)}(I/J) \tag{3}$$

where $I = (R^{(m)})^5 - (R^{(c)})^5$ and $J = (R^{(m)})^3 - (R^{(c)})^3$. Since $R^{(c)}$ can be determined from the position of the side maximum on the SAXS scattering curve, $R^{(m)}$ and the thickness of the shell, $D^{(s)}$, can be calculated. This experiment has been performed for micelles with hydrogenated polybutadiene cores and polystyrene shells in dioxane[5]. A fairly good coincidence of $R^{(m)}$ and R_H (from QELS) values indicated that micelles in dilute solutions behave like hydrodynamic hard spheres. This finding was confirmed later by other experiments with various block copolymer-selective solvent systems. $R^{(c)}$ and $D^{(s)}$ can also be obtained separately using the contrast-matching technique. However, this method is not generally applicable, since it is difficult and sometimes impossible to find a solvent providing zero contrast for the core or for the shell.

Once $M_w^{(u)}$, $M_w^{(m)}$, copolymer composition, $R^{(c)}$, and $D^{(s)}$ are known, the association number, the average segment densities in the core and in the shell, as well as the average dimensions of the core-forming and shell-forming blocks, can be calculated and compared with theoretical predictions.

THERMODYNAMICS OF MICELLE FORMATION

The micellar equilibrium state is given by a minimum of the Gibbs energy of the system. The basic question arising in the thermodynamics of micelle formation is to determine which term, entropic of enthalpic, contributes more to the decrease of the Gibbs energy. For the closed association model and large values of the association number, it has been shown that the following relations are valid[6] for the standard Gibbs energy change, ΔG°, and the standard Gibbs enthalpy change, ΔH°, per mol of the solute in a micelle:

$$\Delta G^\circ = RT \ln CMC \qquad (4)$$

$$\Delta H^\circ = RT^2 (d\ln CMC/dt) \qquad (5)$$

$$\ln CMC = \Delta H^\circ/RT + const \qquad (6)$$

where CMC is the critical micelle molar concentration. Strongly negative ΔH° values were obtained for a series of copolymers in organic selective solvents using eq. (6), and were confirmed by independent calorimetric measurements, indicating that the micellization of block copolymers is an enthalpy driven process[7]. A comparison with the theoretical model shows (in Ref. 4) that the main contribution to the exothermic process is the formation of the core. The results for these basically organic systems are contrary to those reported for low-molar-mass surfactants in water (e.g.[8]), indicating the "entropy driven" micellization. It may be argued, however, that this effect is caused mainly by the change of water structure, due to the hydrophobic interactions.

KINETICS OF MICELLE FORMATION AND DISSOCIATION

While numerous studies have been devoted to the kinetics of micellization of soaps and surfactants in water, kinetic data on block copolymer micelle formation are scarce. Recently[9], the stopped flow method with light scattering detection was employed to study rates of micelle formation and micelle dissociation with a diblock AB and a triblock ABA copolymers, A being styrene and B hydrogenated polydiene. Micelle formation was realized by mixing a molecular solution in a good solvent with a precipitant, so that the solvent mixture became selectively bad for blocks B. Micelle dissociation was realized by mixing a micellar solution with a good solvent, so that the final solvent mixture became thermodynamically good for both blocks. The results can be summarized as follows: The relaxation time for micelle formation was on the same time scale (tens of ms) for both samples. Relaxation time of micelle dissociation for the diblock copolymer was shorter than 1 ms, while for the triblock copolymer was over 100 ms. The interpretation of these results, taking into account the shapes of the intensity - time dependences was: Micelle formation proceeds in two steps: In the first one, B blocks shrink and copolymer molecules get together. In the second stage, the B blocks in the core rearrange, finding their low-entropy conformations. In case of triblock copolymers, these blocks may get entangled. In the dissociation process, the first step is a rapid influx of solvent molecules into the micellar core, the second step is a separation of copolymer molecules. Dissociation of the triblock copolymer micelles is slowed down by a disentanglement process. A strongly non-single exponential character of the intensity - time dependences in the latter case indicated that the process is accompanied and complicated by a slow exchange of unimers between micelles.

DYNAMICS OF THE MICELLIZATION EQUILIBRIUM

Unimer $\rightleftarrows$ micelles equilibrium represents a dynamics process, in which copolymer molecules migrate at a given rate between micellar and unimer states, i.e. also, between micelles themselves. One prediction could have been made, based on the model of micelle formation and dissociation outlined above[9] : The exchange of unimers between micelles would be a much slower process than the solvent-assisted dissociation, especially for triblock copolymer micelles.

Only two experiments have been done so far, probing the dynamics of micellization equilibria, employing the steady state fluorescence and the sedimentation velocity methods.

In the first study[10], diblock copolymer micelles having polystyrene cores and hydrogenated polyisoprene shells with polystyrene blocks labeled by fluorescence donor (carbazol), were mixed with identical micelles (in the same solvents) labeled by fluorescence acceptor (anthracene). Exchange of copolymer molecules between micelles, i.e., formation of carbazol-tagged and anthracene-tagged mixed micelles, was monitored as the nonradiative energy transfer from carbazol to anthracene groups. Equilibration process proved to be very complex, and was roughly characterized by two relaxation times: a faster (on the time scale of 10^2 s) and a slower one (10^3 s), the concrete values of which depended on the degree of swelling of polystyrene cores.

In the second study[11], two kinds of micelles with different molar masses and sizes (and thus with different sedimentation coefficients) were mixed, and the formation of mixed micelles with an intermediate sedimentation coefficient was monitored with an analytical centrifuge. In case of diblock copolymer micelles, the equilibrium, i.e. the formation of uniform mixed micelles, was established within the time of experiment (below 10^2 s). In case of triblock copolymer micelles, a slow equilibration (10^3 - 10^4 s) has been observed. Two different original concentration boundaries, approaching each other in time, indicated that the equilibration proceeds via exchange of copolymer molecules between smaller and larger micelles. Like in the fluorescence study[10], the equilibration process was relatively fast at the beginning (10^3 s) and then slowed down (10^4 s).

SOME TOPICAL PROBLEMS

From numerous unresolved or puzzling problems arising in experimental studies of various micellar systems, only a few will be mentioned here.

Anomalous micellization. Transient formation of large particles at the onset of micellization has been observed with a relatively large number of various block copolymer - selective solvent systems. As summarized in Ref. 4, there are at least four alternative interpretations of this phenomenon.

Spatial arrangement of micelles. While ABA triblock copolymer micelles in a selective solvent for blocks A form macrolatices in concentrations above 10 wt.%, micelles in a selective precipitant of blocks A show a spatial arrangement above 2 wt.%. A model of the so called "tentacled micelles", explaining the strange behavior in the latter case, has been tentatively proposed[12], but has not been confirmed, yet.

Bimodal distribution of particles in various micellar systems has been reported lately[13,14,15]. It has not been resolved, yet, if the coexistence of micelles and multimicellar particles is of a thermodynamic or a kinetic nature.

Dynamics on the chain or even on a segmental level in a micelle is probably one of the most challenging problems of all. It can be approached e.g., by the high resolution NMR, by the quasi elastic neutron scattering, and by various fluorescence techniques.

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