

Formation of block copolymer micelles: a sedimentation study

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The formation of block copolymer mixed micelles has been studied in solutions of polystyrene-*block*-polyisoprene and polystyrene-*block*-poly(ethylene-*co*-propylene) in decane, a selectively poor solvent for polystyrene blocks. The rate of mass exchange between two types of micelles, studied by the sedimentation velocity method, depends strongly on the rates of micelle formation and dissociation processes, which can be controlled by temperature.

(Keywords: block copolymers; micelles; sedimentation velocity)

Introduction

Block copolymers in dilute solutions in selective solvents (good for one block, poor for the other) self-associate to form multimolecular spherical micelles (fairly uniform in mass and size), with cores of insoluble blocks and shells of soluble blocks¹. Like soap and surfactant micellization in water, block copolymer micellization obeys a model of closed association characterized by an equilibrium between unimer (molecularly dissolved copolymer) and micelles².

Unimer-micelles equilibrium represents a dynamic process in which copolymer molecules migrate at a given rate between micellar and unimer states, i.e. also between micelles themselves. Using fluorimetry^{3,4} and sedimentation velocity⁵⁻⁸ it has been shown that the mass exchange is orders of magnitude slower in block copolymer micellar systems in comparison with soap and surfactant aqueous solutions. In some cases, the equilibrium may become frozen, as in the case of micelles with polystyrene cores in water or aqueous buffers⁶⁻⁸.

In this study we report on the formation of mixed micelles from two different micellizing copolymer samples, with chemically identical cores (polystyrene) and different shells (polyisoprene and hydrogenated polyisoprene) in decane using the sedimentation velocity method.

Experimental

Copolymer samples. Polystyrene-*block*-poly(ethylene-*co*-propylene) (PS-PEP), is a narrow fraction, free of polystyrene, of a commercial Kraton G 1701 (Shell Co), $M_w = 1.05 \times 10^5 \text{ g mol}^{-1}$, 37 wt% of polystyrene,

$M_w/M_n = 1.07$. Polystyrene-*block*-polyisoprene (PS-PI), was prepared by anionic polymerization, as described in ref. 9, $M_w = 1.02 \times 10^5 \text{ g mol}^{-1}$, 34 wt% of polystyrene, $M_w/M_n = 1.08$.

Micellar solutions. Both samples were dissolved in decane and heated for 30 min to 100°C in sealed ampoules. Static light scattering measurements indicated that association numbers of both micellar samples were similar (about 80). Fortunately, sedimentation coefficients at finite concentrations for both micelles differed enough to make a study of mixed micelle formation possible. Sedimentation coefficients of both pure micelles at finite concentrations ($c = 5 \times 10^{-3}$ and $2.5 \times 10^{-3} \text{ g ml}^{-1}$) at 25, 30 and 35°C are given in Table 1.

Ultracentrifugation. Sedimentation velocity measurements were performed using a MOM 3170 analytical ultracentrifuge (Hungarian Optical Instruments) with Schlieren optics. Apparent sedimentation coefficients at finite concentrations and actual temperatures, s , were evaluated using the standard technique of plotting $\ln(r_m)$

Table 1 Apparent sedimentation coefficients, s , of pure micellar species at finite concentrations and various temperatures

Sample	Concentration ($10^{-3} \text{ g ml}^{-1}$)	Apparent sedimentation coefficient, s (10^{-12} s^{-1}) at different temperatures		
		25°C	30°C	35°C
PS-PEP	2.5	2.38	2.87	3.08
	5.0	1.72	1.92	2.18
PS-PI	2.5	4.17	4.78	5.27
	5.0	3.01	3.49	3.93

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versus $\omega^2 t$, where r_m is the distance of the peak maximum from the axis of rotation at time t and ω is the angular velocity of the rotation. The rotor, with a single-sector 10 mm cell, was operated at $40\,000\text{ rev min}^{-1}$ in the temperature range $20\text{--}35^\circ\text{C}$.

Results and discussion

The copolymer/solvent system was chosen as appropriate for the sedimentation study of the formation of mixed micelles for the following reasons. (1) Both samples form multimolecular micelles with polystyrene cores in decane. Micellization equilibrium is, in both cases, shifted considerably in favour of micelles. (2) Sedimentation coefficients of the two micellar species differ considerably from each other in the concentration region, which was used for kinetic measurements, and change only little between 20 and 35°C . (3) Rates of micelle formation and dissociation, which control the re-equilibration of the system after mixing two different micellar samples, increase significantly with increasing temperature.

Sedimentation experiments were performed as follows. Two micellar solutions ($c = 5 \times 10^{-3}\text{ g ml}^{-1}$) were mixed (1:1 by volume) and kept at a given temperature. At given intervals, the micellar solution was transferred from a thermostat to a sedimentation cell and ultracentrifugation measurements were performed. The minimum time for the experiment preparation was 20 min; the average time of ultracentrifugation runs was 40 min. No attempt has been made to standardize the measured quantities, because the viscosity and density of the solvent change with temperature, the association number of micelles decreases slightly with increasing temperature, and differences in refractive index increments change slightly during the formation of mixed micelles.

At 20°C , the pattern of two sharp peaks for both individual micellar components (the fast one for PS-PI and the slow one for PS-PEP) did not change with time, even when the experiment was run for 40 days. It can be concluded that there is no exchange of mass between the

two micellar species and the micellar equilibrium is frozen. A similar case has been described for micelles with polystyrene cores and poly(methacrylic acid) shells in water or aqueous buffers⁵. At 35°C , a single sharp peak, corresponding to a sedimentation coefficient value between those of the original micelles, appeared at a minimum possible time (20 min). This value did not change after heating to 100°C for 20 min and recooling to 35°C . This means that the complete formation of mixed micelles occurred within this time.

Sedimentation diagrams of the mixture at 29°C , taken at different time intervals after mixing, at constant rotational velocity of $40\,000\text{ rev min}^{-1}$ and constant sedimentation time (20 min), are shown in Figure 1. The position of the fast peak does not change appreciably, but the peak area, i.e. the concentration of this component, decreases considerably with increasing time. The changing position and the area of the slower peak show that the sedimentation coefficient of this component increases with increasing time after mixing, and that its concentration grows. The insert in Figure 1 shows both sedimentation coefficients as a function of time. The time dependence of the sedimentation coefficient of the slower component corresponds to an S-shaped curve, which suggests a mechanism with a certain induction period. This is slightly surprising as we do not see any reason for such behaviour. Similar S-shaped curves were always obtained between 27 and 29°C . On the basis of a very limited knowledge of the highly complex processes involved in the formation of mixed micelles, we cannot make any conclusions concerning the shape of experimental curves.

The sedimentation velocity pattern and sedimentation coefficients of both components (insert) measured at 31°C are shown in Figure 2. At this temperature, the formation of mixed micelles proceeds much faster than at 29°C . The sedimentation coefficient of the fast component again remains constant within the range of experimental error, but the concentration of this species diminishes quickly. There is no induction period in the curve for the fast

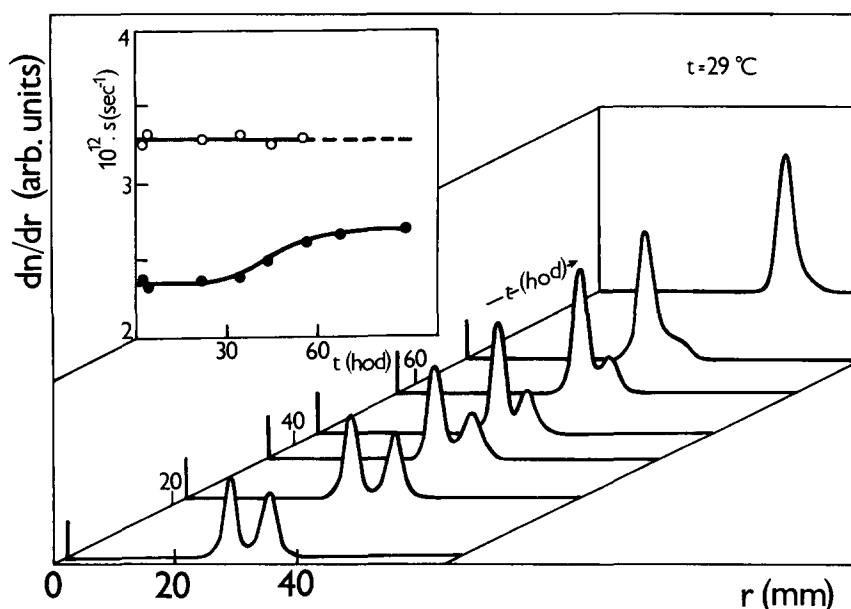


Figure 1 Sedimentation velocity diagrams, (dn/dr) versus r (where n is the refractive index and r the position in the cell) for a mixture of PS-PI and PS-PEP micelles (1:1) at 29°C ($40\,000\text{ rev min}^{-1}$, 20 min of sedimentation, total copolymer concentration, $c_{\text{tot}} = 5 \times 10^{-3}\text{ g ml}^{-1}$). The oblique axis represents the time, t , after mixing the pure components. The insert depicts the apparent sedimentation coefficients, s , as a function of time, t , after mixing the pure components: ○, fast sedimenting micelles (PS-PI); ●, slowly sedimenting micelles (PS-PEP)

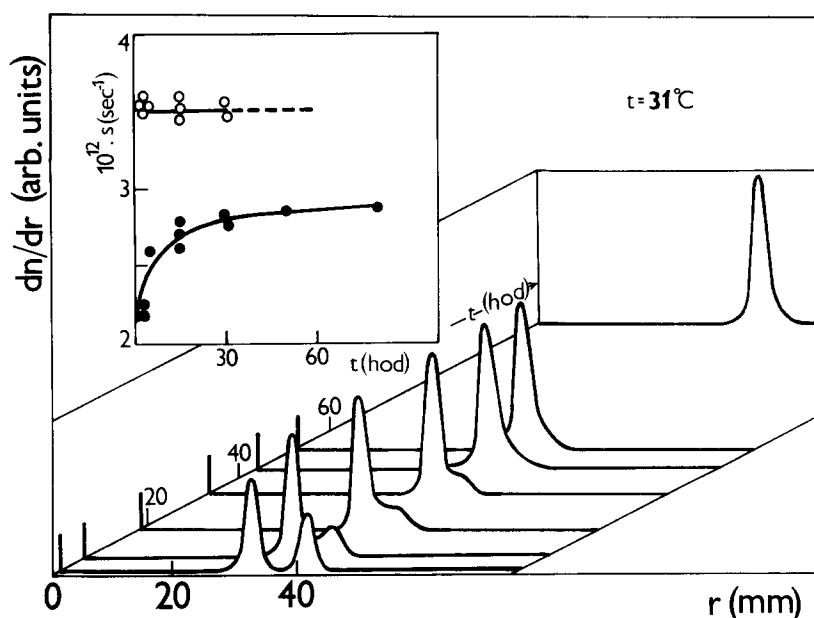


Figure 2 Sedimentation velocity diagrams and sedimentation coefficients (insert) for a mixture of PS-PI and PS-PEP micelles (1:1) at 31°C. The experimental conditions and the meaning of all symbols are the same as in *Figure 1*

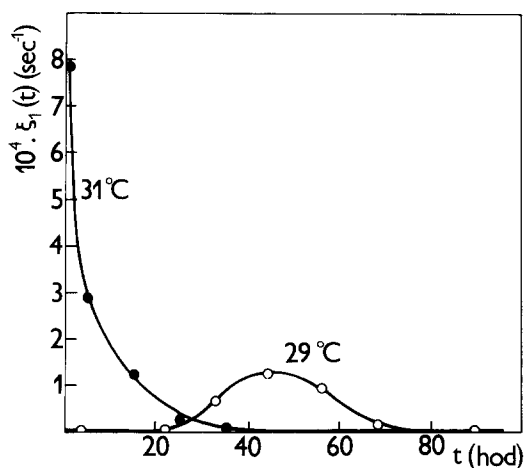


Figure 3 Time dependence of the apparent rate of formation of mixed micelles, $\xi_1(t)$, defined by equation (1), from PS-PI and PS-PEP micellar samples in decane at 29 and 31°C

sedimentation coefficient and its rise is quite steep in comparison with that at 29°C.

A rigorous kinetic interpretation of ultracentrifugation data is neither easy nor straightforward. We propose the following approximate formula which allows assessment of the apparent rate of the overall re-equilibration process, $\xi_1(t)$:

$$\xi_1(t) = -(s_2^0 - s_1^0)^{-1} [w_2(t)(ds_2/dt) - w_1(t)(ds_1/dt)] \quad (1)$$

where (ds_i/dt) are the time derivatives of sedimentation coefficients, $w_i(t)$ are the time-dependent weight fractions of micellar components and the superscript zero refers to $t=0$. The precision of the evaluation of w_i for systems with merging peaks that are not well-separated is much lower than that of s_i (the relation $\sum w_i = 1$ slightly improves the precision of its evaluation). *Figure 3* depicts ξ_1 as a function of time for two representative temperatures, 29 and 31°C.

Apart from a remarkable temperature acceleration of re-equilibration processes after mixing, another

experimental finding is worth mentioning. The transport of unimers from PS-PI micelles into PS-PEP micelles is much faster than the reverse transfer, which results in considerable concentration changes of individual transient species. A similar asymmetric mass transfer between two different micellar species is also described in our recent study⁸. In the present study we assume that micellar cores (which are chemically identical for both micellar species) are influenced by chemically different soluble blocks in the shells. This may modify the escape processes of insoluble blocks and the accommodation abilities of cores of PS-PI and PS-PEP copolymer samples. More extensive and complex experimental studies are in progress, with the aim of making a reliable proposal for the detailed mechanism of this dynamic process.

Conclusions

Copolymer samples of polystyrene-*block*-polyisoprene and polystyrene-*block*-poly(ethylene-*co*-propylene) form mixed micelles with polystyrene cores in *n*-decane at ambient and slightly elevated temperatures.

Mixed micelles may be obtained by mixing two solutions of different micelles. The equilibration process assumes an interchange of unimers between individual micelles.

Ultracentrifugation has been found to be a suitable experimental technique for studying the re-equilibration process following mixing on the time scale of hours and days.

Changes in sedimentation coefficients and relative concentrations of transient micellar species (with not yet fully randomized copolymer chains) enable assessment of the rate of mass exchange. The exchange rate depends strongly on temperature in the range 20–35°C. At 20°C the equilibration processes are totally frozen (i.e. the mobility of unimer-micelles equilibrium is kinetically frozen), whereas at 35°C an almost complete formation of mixed micelles takes place in less than 20 min.

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