SMALL-ANGLE NEUTRON SCATTERING STUDY OF POLY(OXYETHYLENE)-*block*-POLY(OXYPROPYLENE)-*block*-POLY(OXYETHYLENE) IN AQUEOUS SOLUTIONS

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Solutions of a triblock copolymer, poly(oxyethylene)-*block*-poly(oxypropylene)-*block*-poly(oxyethylene) (POE–POP–POE), in deuterated water were studied by small-angle neutron scattering (SANS) in the temperature range from 20 to 45 °C. Radius of gyration, molecular weight, second virial coefficient for both unimers and micelles, critical micelle concentration and unimer concentration were determined from the scattering data. Under assumption of the spherical core/shell micellar model structural parameters were estimated. Degree of swelling of the micellar core was evaluated from the mean-square fluctuation of scattering density.

It is a well-known fact that block copolymers in selective solvents (good solvents for one type of block precipitants for the other) form micelles[1] consisting of a dense core which contains mainly the insoluble blocks, and a shell composed of the swollen soluble blocks.

For the oxyethylene-oxypropylene block copolymers in water, the quality of solvent can easily be modified by changing the temperature. At low temperatures, the copolymer in molecularly dispersed (unimers) while at higher temperatures both multimolecular associates (micelles) and unimers are present[2].

We have investigated a commercial triblock POE–POP–POE copolymer Pluronic L64 (also known as Poloxamer 184) in heavy water. Several papers on this or similar copolymers have been published. Most of them are based on static and dynamic light scattering data[3-7].

One of the novel promising applications of block copolymer micelles in an uptake and controlled release of organic substances from and into aqueous media. The uptake/release phenomena are controlled by many factors (e.g. core/shell dimensions and thermodynamic parameters of the system), but mainly by the swelling of micellar cores. Therefore, the determination of the degree of swelling is desirable.

The aim of our study is to get a more detailed information on the Pluronic micelles from SANS experiments. This method is sensitive also to such factors as swelling of micelles or the presence of a molecularly dispersed copolymer, which are frequently not taken into account in the studies dealing with micellar systems. The reason for the use of neutron scattering was a much higher contrast in the comparison with that of X-rays.

EXPERIMENTAL

Samples

Triblock copolymer Pluronic L64 contains a total of 26 oxyethylene units in the two hydrophilic end blocks and 30 oxypropylene units in the hydrophobic middle block. The molecular weight of the copolymer was 2 900. Solutions for SANS measurements were prepared by dissolving the polymer in heavy water (isotopic purity 99.6 atom % D). Minor components of the copolymer sample richer in POP, which are believed to be responsible for what is called anomalous micellization[2], were removed by filtering a solution of concentration 0.109 g cm^{-3} at T = 25 °C.

Partial specific volumes have been calculated from the concentration dependence of the density of solutions as measured by an Anton Paar DMA-602M vibrating densitometer.

Small-Angle Neutron Scattering (SANS)

SANS measurements were performed using the time-of-flight small-angle neutron spectrometer MURN at the IBR-2 pulse reactor in the Joint Institute for Nuclear Research, Dubna[8]. The solution was placed in optical quartz cell with a path length 1 mm. The incoherent contribution to the scattering was estimated by measuring the scattering from H_2O/D_2O mixtures. All measurements were corrected for background scattering and normalized using a vanadium standard[9].

The mass-average molar mass, M_w, was calculated using the relation

$$\frac{c(\Delta b)^2}{N_A \frac{d\Sigma}{d\Omega}(0)} = \frac{1}{M_w} + 2A_2 c, \qquad (1)$$

where $\frac{d\Sigma}{d\Omega}(0)$ is the differential cross-section of the coherent scattering per unit sample volume (cm^{-1}) extrapolated to zero scattering angle, c is the copolymer concentration (g cm^{-3}), N_A is the Avogadro constant, A_2 is the second virial coefficient (cm^3 mol g^{-2}), $\Delta b = b - \bar{v}\,\rho_0$ is the excess scattering amplitude (cm g^{-1}), b is the scattering amplitude, $\bar{v}$ is the partial specific volume (cm^3 g^{-1}) of dissolved compound and ρ_0 is the scattering density of solvent (cm^{-2}).

The mean square fluctuation of scattering density, $\overline{(\Delta\rho)^2}$ is related to the scattering cross-section, $\frac{d\Sigma}{d\Omega}(q)$, by the relation

$$\frac{\overline{(\Delta\rho)^2}}{c} = \frac{1}{2\pi^2}\int_0^\infty \frac{1}{c}\frac{d\Sigma}{d\Omega}(q)\, q^2\, dq, \qquad (2)$$

where $q = (4\pi/\lambda)\sin(\theta/2)$ is the length of the scattering vector, λ is the wavelength of the radiation, θ is the scattering angle.

The parameter $\overline{(\Delta\rho)^2}$ characterizes the total scattering power of the system. For a particle consisting of N domains differing in the constrast (in case of a micelle with core/shell structure $N = 2$), $(\Delta\rho)^2/c$ can be written[10,11]

$$\frac{\overline{(\Delta\rho)^2}}{c} = \sum_{i=1}^{N} \frac{w_i (\Delta b_i)^2}{\bar{v}_i Q_i} - c\left(\sum_{i=1}^{N} w_i (\Delta b_i)\right)^2, \qquad (3)$$

where Q_i is the swelling factor of the i-th component, w_i is the weight fraction. The last equation is a basis for the determination of the swelling factors.

RESULTS AND DISCUSSION

Micellization

At low temperatures, the scattering intensity is small and does not vary with temperature significantly. We will see later that in this region the copolymer is molecularly dispersed. As an example, variation of the scattering curves with temperature for a 4% solution is shown in Fig. 1. Above a certain critical temperature which depends on copolymer concentration, scattering intensity begins to increase. This increase in intensity is due to the formation of multimolecular associates, micelles.

Figure 2 shows relation between the SANS-determined critical micelle concentration (*cmc*) and temperature. This result was obtained from the breakpoint on the plot of the integrated scattering data as a function of temperature for several copolymer concentrations. Below the $c(T)$ curve, the copolymer is molecularly dispersed, while above the

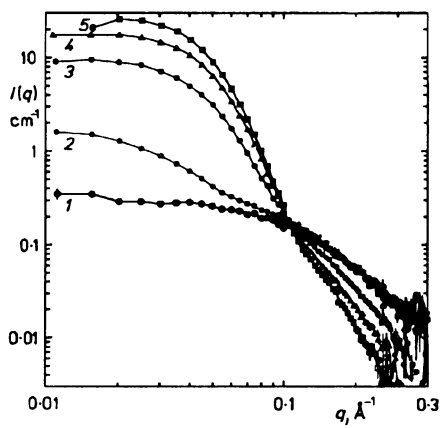

FIG. 1

SANS scattering curves ($\log I(q)$ vs $\log q$) for Pluronic L64 in D_2O (c = 0.045 g cm^{-3}) at various temperatures. *1* 20 °C, *2* 30 °C, *3* 35 °C, *4* 40 °C, *5* 45 °C

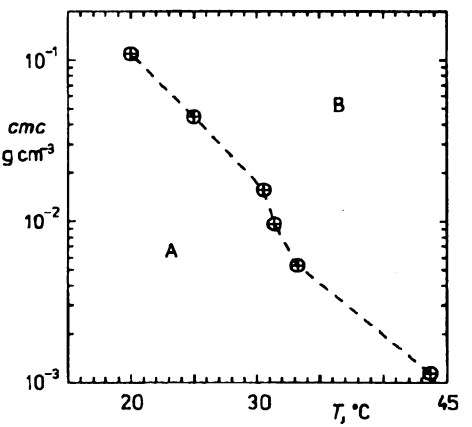

FIG. 2

Temperature dependence of critical micelle concentration (*cmc*). A unimers, B unimers and micelles

curve both micelles and unimers are present in the solution. The temperature dependence of *cmc* is very steep. By increasing the temperature from 20 to 45 °C, the critical micelle concentration decreases by two orders of magnitude.

It can easily be shown that the copolymer is present as unimers in aqueous solution at low concentrations and low temperatures. We measured SANS scattering curves at 20 °C for several copolymer concentrations and extrapolated the scattering intensity to $q = 0$, i.e. to zero scattering angle. From Eq. (*1*), the second virial coefficient ($A_2 = 2.81 \cdot 10^{-3}$ cm^3 mol g^{-2}) and the molecular weight of the particles were calculated.

The obtained value of M_w (2 700) is very close to the label value of the copolymer. So, the particles observed at low concentrations and low temperatures can be identified with single macromolecules, unimers. The radius of gyration extrapolated to infinite dilution was 15.9 ± 0.3 Å.

Above a critical micelle concentration, polymolecular micelles coexist with unimers. When calculating the structure parameters of micelles, the presence of unimers must be taken into account. In our case, it was possible to estimate the unimer concentration directly from the scattering curves. The experimental scattering intensity can be expressed as a sum of two terms which correspond to contributions of micelles and unimers, respectively

$$\frac{d\Sigma}{d\Omega}(q) = w_u I_u + w_m I_m , \qquad (4)$$

where w_u is the weight fraction of unimers and $w_m = 1 - w_u$ is the weight fraction of micelles. It follows from the theory and from the scattering data shown in Fig. 1, that at large angles the scattering curves are expected to vary as $I_u \sim q^{-2}$ for unimers and as $I_m \sim q^{-4}$ in the case of micelles.

By resolving the tails of the experimental scattering curves into the above-mentioned contributions, we were able to calculate the concentrations of micelles and unimers. The results of such a fitting are in Fig. 3. Temperature dependences of the weight fraction of unimers for copolymer concentrations c = 0.016, 0.045, 0.109, 0.177 and 0.313 g cm^{-3} are shown in Fig. 4. We can see again that the association behaviour of this copolymer is very sensitive to temperature and concentration. For example, in a 2% solution essentially only unimers are present below 35 °C, while for a 10% solution, the onset of micellization is already observed somewhat between 20 °C and 25 °C.

Micellar Structure

The next step was the determination of the structural parameters of the micelles. We will discuss the results for 45 °C. Structure properties of micelles derived from SANS measurements by extrapolation to infinite dilution are summarized in Table I.

Mean-square fluctuation of scattering density determined from the integrated scattering intensity is of great importance in micellar studies because it contains information on the degree of swelling of particles, virtually inaccessible by other methods.

A structure model must be adopted to estimate size of micelles. We used a very simple concentric-sphere core/shell model. We assume that the core contains poly(oxypropylene) blocks and the shell is composed of soluble poly(oxyethylene) blocks. Both parts are swollen by water. The swelling factor Q is defined as a ratio of the volume of swollen particle to that of dry polymer. The starting quantities are the micellar molecular weight, radius of gyration and mean-square fluctuation of scattering density. The relations between these quantities and the model parameters can be derived using

TABLE I
Structure parameters of Pluronic L64 micelles in D_2O

Parameter	Value
Molecular weight, M_w	$(358 \pm 20) \cdot 10^3$
Second virial coefficient, A_2	$4.09 \cdot 10^{-5}$ cm^3 mol g^{-2}
Association number	120
Radius of gyration, R_g	57.0 ± 0.5 Å
$\lim_{c \to 0} \overline{(\Delta \rho)^2}/c$	$(17.9 \pm 0.3) \cdot 10^{20}$ cm^{-1} g^{-1}

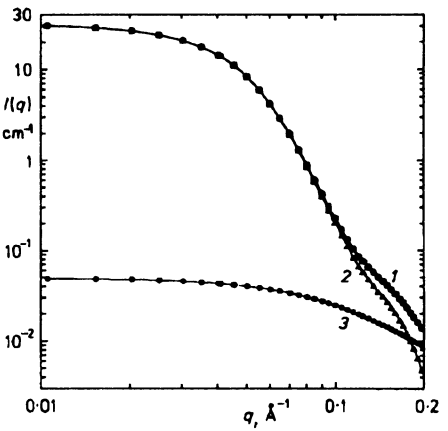

FIG. 3
Determination of the concentration of unimers by SANS scattering. The scattering contributions of the micelles and unimers were calculated from Eq. (4). *1* unimers and micelles, *2* micelles, *3* unimers.

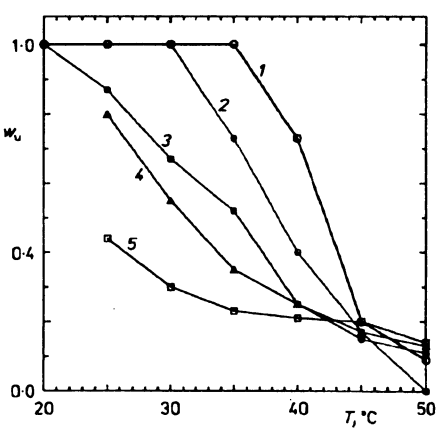

FIG. 4
Temperature dependence of the weight fraction of unimers for various copolymer concentrations. *1* 0.016, *2* 0.045, *3* 0.109, *4* 0.177, *5* 0.313 g cm^{-3}

simple geometrical arguments[12]. For the core/shell model the radius of gyration of the micelles can be written as

$$R_g^2 = \frac{3}{5}\frac{w_c \Delta b_c}{\Delta b} R_c^2 - \frac{3}{5}\frac{w_s \Delta b_s}{\Delta b}\frac{R_m^5 - R_c^5}{R_m^3 - R_c^3} \equiv g(Q_c, Q_s), \quad (5)$$

where $\Delta b_c = -5.97 \cdot 10^{10}$ cm g^{-1}, $\bar{v}_c = 0.99$ cm^3 g^{-1}, $\Delta b_s = -4.76 \cdot 10^{10}$ cm g^{-1}, $\bar{v}_s = 0.83$ cm^3 g^{-1}, $\Delta b = -5.48 \cdot 10^{10}$ cm g^{-1}, and w_c and w_s are weight fractions of core and shell, respectively.

The radius of the core, R_c, can be expressed by the micellar weight and degree of swelling of the core as $R_c^3 \sim Q_c M_w$. A similar relation exists also for the overall radius of the micelle, $R_m^3 - R_c^3 \sim Q_s M_w$.

The second equation for the swelling factors Q_c and Q_s can be written as

$$\left(\frac{\overline{(\Delta\rho)^2}}{c}\right)_{c\to 0} = \frac{w_c (\Delta b)_c^2}{\bar{v}_c Q_c} + \frac{w_s (\Delta b)_s^2}{\bar{v}_s Q_s} \equiv f(Q_c, Q_s). \quad (6)$$

Thus, we have two equations for two unknowns, Q_c and Q_s. A graphic solution of these equations is presented in Fig. 5. The first solid line is described by Eq. (5) with the radius of gyration $R_g = 57.0$ Å and the second one corresponds to $\lim_{c\to 0}(\Delta\rho)^2/c = 17.9 \cdot 10^{20}$ cm^{-1} g^{-1}. The intersect of these two curves defines the swelling factors $Q_c = 1.24$ and $Q_s = 20.4$. As expected, the shell is swollen much more than the core. To assess the uncertainty of the resulting swelling factors, we calculated also the curves for $R_g \pm 3$ e.s.d. and for $\lim_{c\to 0}(\Delta\rho)^2/c \pm 3$ e.s.d. It should be noted that the result is not too sensitive to uncertainty of the starting data.

We would like to emphasize that the scattering data are not compatible with the dry, unswollen micellar core. It can be concluded that water penetrates into the micellar core.

The values obtained from the SANS data at 45 °C for the core radius $R_c = 47$ Å and micelle radius $R_m = 107$ Å agree well with parameters obtained from the light scattering experiments[2,3].

In spite of hydrophobic character of poly(oxypropylene), the core is swollen by water. The volume fraction of water is 20%. One controversial result has been obtained, namely, the shell thickness 56 Å is by 20% higher than the length of the poly(oxyethylene) chain in fully extended conformation. The most plausible explanation of this discrepancy is polydispersity of micelles. The polydispersity leads to an overestimate of the radius of gyration. In such case, the swelling factor and thickness of the shell are overestimated, too. Another possible explanation is that some of hydrophobic poly(oxypropylene) chains are partly pulled out from the core into the shell region.

Intermicellar Interactions

The second virial coefficient A_2 is one of the parameters which are sensitive to the interparticle interference effects. By employing Eq. (*1*), we determined $A_2 = 4.09 \cdot 10^{-5}$ cm^3 mol g^{-2} for the micelles at 45 °C. For a model dispersion of hard spheres, the equivalent radius, R_{eq}, can be written as[13]

$$R_{eq}^3 = \frac{3}{16\pi} \frac{M_w^2 A_2}{N_A} . \qquad (7)$$

For micelles with the structure described above and the experimental value of A_2 we obtained $R_{eq} = 81$ Å. As expected, the value R_{eq} is larger than the core radius (47 Å), but smaller than the micelle radius (103 Å).

The experimental scattering intensity can be written as a product of the particle form factor, $P(q)$ and structure factor, $S(q)$:

$$\frac{d\Sigma}{d\Omega}(q) \sim P(q)\, S(q) . \qquad (8)$$

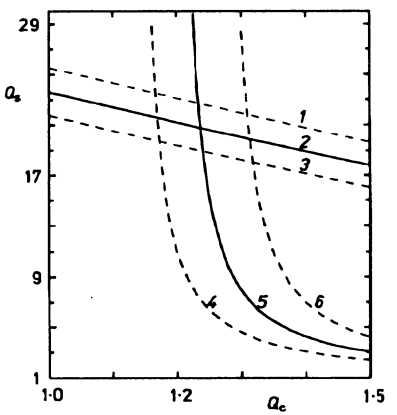

FIG. 5

Determination of the swelling factors $Q_c = 1.24$ and $Q_s = 20.7$. R_g: *1* 58.5; *2* 57.0 (experimental value); *3* 55.5 Å; $\lim_{c \to 0} \overline{(\Delta\rho)^2}/c$: *4* 18.9; *5* 17.9 (experimental value); *6* 16.9 . 10^{20} cm^{-1} g^{-1}. Dashed lines represent the confidence intervals: experimental value ± 3 e.s.d.

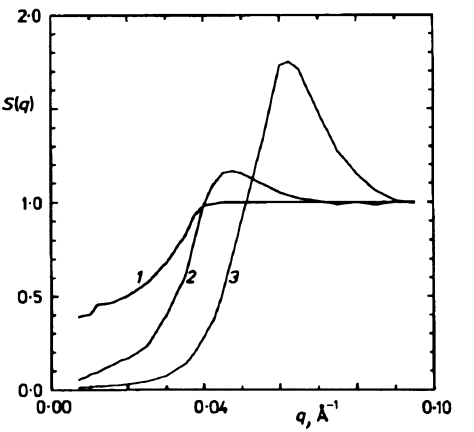

FIG. 6

Structure factor $S(q)$ for various copolymer concentrations at 45 °C. *1* 0.045, *2* 0.177, *3* 0.313 g cm^{-3}

The particle form factor was determined by extrapolation the experimental intensities to infinite dilution and is assumed to be independent of concentration. The structure factor contains information about the interparticle inteactions (Fig. 6). For dilute solutions, $S(q)$ is smaller than unity in the lower q range and approaches unity with increasing q. This behaviour is characteristic of a system of repulsing particles without regular arrangement.

With increasing micellar concentration spatial constraints are more apparent. The volume fraction of micelles (or better, monodisperse particles with an equivalent radius R_{eq}) reaches its maximum theoretical value (0.74) at the concentration $c_{crit} = 0.21$ g cm^{-3}.

It may be expected that a specific distance between micelles is strongly preffered in the region close to the critical concentration, c_{crit}, accompanied by a maximum of the structure factor $S(q)$. The experimental curves (Fig. 6) for $c = 0.177$ and 0.313 g cm^{-3} agree with this expectation. From the position of the maximum on the curve $S(q)$, q^+, using the relation[14]

$$d = 1.22\ 2\pi/q^+ , \tag{9}$$

characteristic distance between micelles was determined

$$d = 160\ \text{Å}\ \ (171\ \text{Å})\ \ \text{for}\ \ c = 0.17\ \text{g cm}^{-3}$$

$$d = 134\ \text{Å}\ \ (140\ \text{Å})\ \ \text{for}\ \ c = 0.31\ \text{g cm}^{-3} .$$

The intermicellar distances calculated from the concentration and micellar molecular weight on the assumption of an expanded close packing structure model (in the parentheses) are in fair agreement with the values obtained from $S(q)$.

CONCLUSIONS

SANS technique has provided a great deal of information on the association behaviour of poly(oxyethylene)-*block*-poly(oxopropylene)-*block*-poly(oxyethylene) (Pluronic L64) in aqueous solutions. The association behaviour is strongly dependent on the copolymer concentration and temperature. At low c and T, the copolymer is molecularly dispersed (unimers). Above a critical temperature or concentration, multimolecular micelles are formed which coexist with the unimers. The scattering contributions of the micelles and unimers were resolved in the SANS curves and structural parameters of both the components were calculated. An analysis of the integrated SANS intensity reveals that the micellar poly(oxypropylene) cores are swollen with water. The radius of equivalent sphere calculated from the second virial coefficient using a hard-sphere model is in reasonable accord with the size characteristics based on the core/shell micellar model.

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