Pure & Appl. Chem., Vol. 55, No. 10, pp. 1563-1572, 1983.
Printed in Great Britain.

0033-4545/83 $3.00+0.00
Pergamon Press Ltd.

MICELLE FORMATION BY BLOCK COPOLYMERS IN ORGANIC SOLVENTS

Colin Price

Department of Chemistry, University of Manchester,
Manchester M13 9PL, U.K.

Abstract - It has been known for many years that amphiphiles such as synthetic surfactants aggregate reversibly in water to form micelles. More recently it has been recognised that when a block copolymer is dissolved in a liquid that is a 'solvent' for only one of its polymeric components, the block copolymer may also form stable colloidal particles. In this contribution aspects of the association behaviour of block copolymers in selective organic solvents are compared with the behaviour of synthetic surfactants in water.

Evidence is presented from gel permeation chromatography and electron microscopy which shows that like amphiphiles block copolymers can form globular micelles having narrow size distributions. Another similarity is that both types of system can, under suitable conditions, form extended or worm-like micelles.

However, the thermodynamic factor responsible for the association of block copolymers in organic liquids is different from that for amphiphiles in aqueous media. Micelle formation by amphiphiles is mainly due to a positive standard entropy of micellization. On the other hand, results obtained for a polystyrene-b-poly(ethylene/propylene) block copolymer in n-decane show that for this case it is the enthalpy contribution to the free energy change that is solely responsible for association taking place.

INTRODUCTION

The reversible aggregation of amphiphiles, which are molecules that contain both hydrophobic and hydrophilic components, has been studied extensively since the early part of this century (Ref. 1 & 2). The topic still continues to attract enormous attention. One of the earliest workers in the field was McBain (Ref. 3) who recognised that simple surfactants could aggregate reversibly in water. The products of the association process he termed micelles. However, when the concept was first proposed it was greeted with much scepticism and did not become properly established until the basic structural features of surfactant micelles were worked out by Hartley in a series of classic studies (Ref. 4).

It is now recognised (Ref. 5) that micelle formation occurs as the result of two opposing forces. These are an attractive force leading to association of the molecules and a repulsive force that prevents unlimited growth of the micelles to a distinct macroscopic phase. Micelles formed by amphiphiles consist of a hydrophobic core surrounded by polar or ionic groups which protrude into the aqueous medium. In amphiphiles containing ionic head groups the repulsive force arises primarily from electrostatic interactions. In amphiphiles containing non-ionic head groups, such as poly(oxyethylene), it is the preference for hydration as opposed to self-association that is the main factor involved. The attractive force stems from the hydrophobic effect, the origin of which is the structural adjustment which takes place in water when hydrophobic units are separated from it (Ref. 5 & 6). The separation leads to an overriding increase in entropy and hence a reduction in free energy.

It has been shown that synthetic surfactants can form both globular and elongated micelles (Ref. 7-10). The majority of investigations, however, have been carried out on systems containing predominantly globular micelles.

The latter, which typically might have association numbers of the order of 50-100, are believed to have narrow size distributions. It has been found that regardless of the shape of the micelles the cores of surfactant micelles contain very little water and are liquid-like provided the molecular weight of the hydrophobic group is not too high (Ref. 11 & 12). It is still not fully understood, however, how the relatively stiff hydrocarbon chains (which form the hydrophobic group in many surfactants) can uniformally fill the space in a roughly spherical or cylindrical core. One possible explanation has recently been put forward by Fromherz (Ref. 13) who argues that there is some parallel stacking of the chains in the micellar cores.

When polymer chemists started to prepare and fractionate graft and block copolymers in the 1950's, they noticed the formation of stable aggregates in certain organic liquids. This occurred whenever the organic liquid was a 'non-solvent' for one of the components of the copolymer but a good solvent for the other. It was argued by Merritt (Ref. 14) and later by Benoit et al (Ref. 15-17) that these copolymer micelles had structures similar to surfactant micelles.

In the present contribution consideration will be given to the shape and solution behaviour of micelles formed by a number of well characterized block copolymers in selective solvents. The results will be compared and contrasted with the behaviour of micelles formed by synthetic surfactants in aqueous solution.

SIZE DISTRIBUTIONS OF MICELLES

Let us first consider the type of process involved in micelle formation:

$$M_1 + M_1 = M_2$$

$$M_2 + M_1 = M_3$$

$$M_3 + M_1 = M_4$$

$$M_{N-1} + M_1 = M_N$$

As shown, formation of an N-mer, M_N, in dilute solution from unassociated chains, M_1, must occur through a multistage addition process. (Note: whilst the solvent plays an essential role in these stages, it has been omitted here for ease of presentation.) If the equilibrium constants for each stage were approximately equal the associated species would have a broad size distribution. This extreme case is often termed open association (Ref. 18). An example of this type of behaviour is provided by solutions of simple surfactants in hydrocarbon solvents (Ref. 19).

At the other extreme is the case where only a narrow range of associated species are present in significant proportions. For thermodynamic purposes it is then sometimes assumed as a first approximation that there is just a single equilibrium between unassociated molecules and micelles of fixed size:

$$nM_1 = M_m$$

where m is taken to be the aggregation number of the most abundant micelles in the narrow distribution. The single stage process is often termed closed-association (Ref. 18).

In the case of block copolymer micelles conventional techniques such as gel permeation chromatography (Ref. 20-22) and ultracentrifugation (Ref. 23) have been used to determine the size distributions. These direct methods are possible because the rate of relaxation of micelles to free-chains (i.e. unassociated chains) can be extremely slow (Ref. 24).

In Fig. 1, gel permeation chromatograms are shown for a polystyrene-b-polyisoprene block copolymer, designated PStPIp, for which in the unassociated state $\bar{M}_w$ = 43,000, $\bar{M}_w/\bar{M}_n$ = 1.05 and $\bar{M}_w$ (polystyrene block) = 34,000. Chromatograms are recorded for the copolymer in N,N-dimethylacetamide at 26°C, 60°C and 110°C (Ref. 20). Rigid poly(styrene-divinyl benzene) gel was the packing material used in the columns. The single sharp peak of low elution volume observed at 26°C (see Fig. 1a) indicated that micelles having a very narrow size distribution were present in the solution and that the micelle/free-chain equilibrium was predominantly in favour of micelle formation. The reverse flow method of correction for instrumental spreading showed that $\bar{M}_w/\bar{M}_n < 1.02$.

Since N,N-dimethylacetamide is a selectively bad solvent for polyisoprene, we can assume as a first approximation that the micelles consisted of a core of swollen polyisoprene blocks and an outer fringe of polystyrene blocks. A more realistic model, however, would be one in which there was a smoother change in average segment composition on moving outwards from the middle of the micelle. That the size distribution is narrowed on micelle formation is not surprising and is predictable from statistical arguments for closed association (Ref. 25). Since the majority of the micelles remained intact as they passed through the columns over a period of hours, the rate of dissociation of the micelles to free chains must have been very slow at 26°C.

On raising the temperature of the solution the equilibrium shifted progressively in favour of the free-chain form. The chromatograms indicated the presence of both micelles and free chains in the temperature range 50-65°C. Figure 1b shows the chromatogram for 60°C. The spreading between the micelle peak ($V_e \cong 127$ cm^3) and the free chain peak ($V_e \cong 160$ cm^3) can be attributed to the effect of dilution on the micelle/free-chain equilibrium together with a relaxation time at this temperature which was comparable with the elution time. The extensive spreading which occurred at high elution volumes (up to $V_e = 180$ cm^3 and beyond) was due to strong absorption of the free chains on to the gel matrix.

At 70°C and above the chromatograms showed only a single peak due to free chains. The chromatogram for 110°C is shown in Fig. 1c.

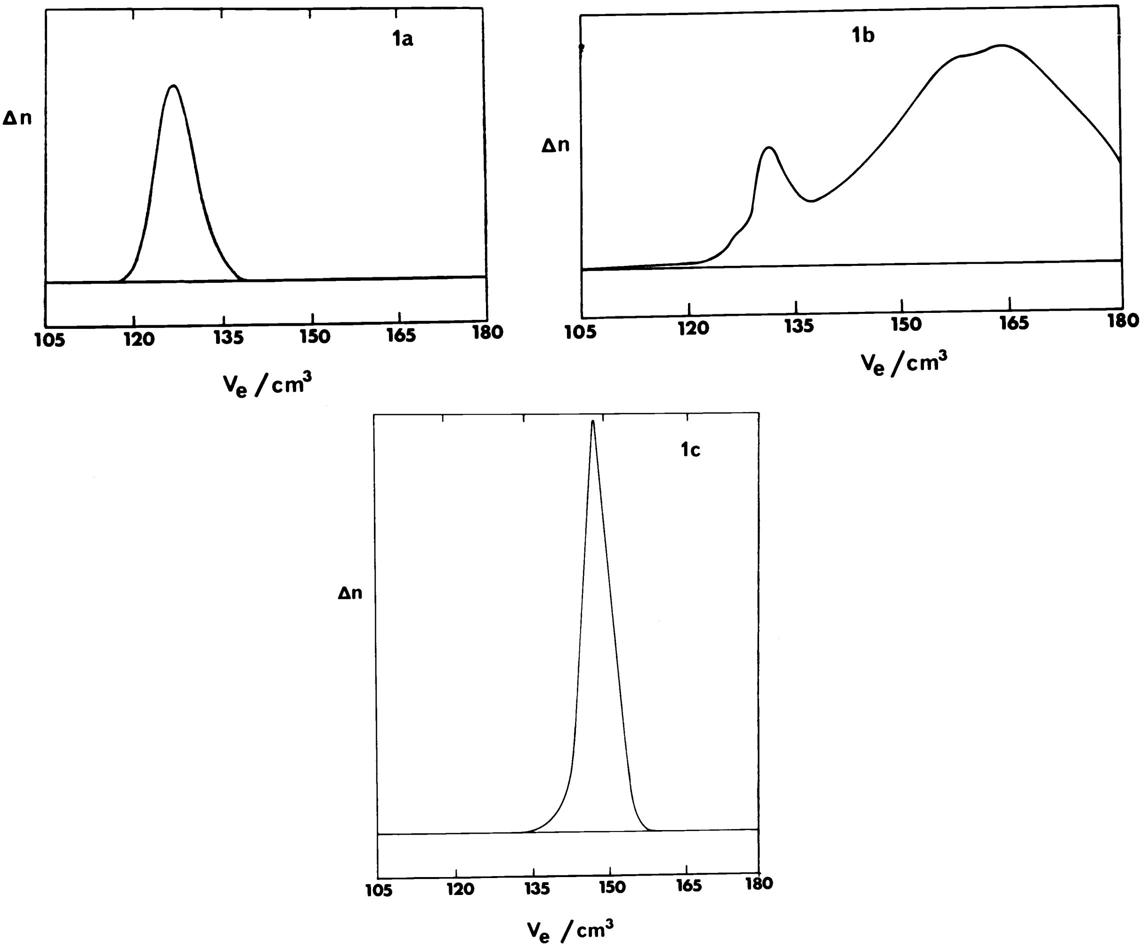

Fig. 1. Gel permeation chromatography plots of refractive index difference between solution and pure solvent (Δn) against elution volume (V_e) for block copolymer PStPIp in N,N-dimethylacetamide at (a) 26°C, (b) 60°C and (c) 110°C.

The very narrow size distribution of micelles formed by PStPIp in N,N-dimethylacetamide was confirmed by ultracentrifugation (sedimentation velocity analysis) and by electron microscopy (Ref. 20 & 24). Only the latter results will be considered here.

Specimens were prepared for electron microscopy by allowing drops of solution to spread and evaporate on a carbon substrate. As the solvent evaporated the micelles collapsed to form particles having a density similar to that of bulk polymer. From shadowing it was deduced that the spherical micelles became approximately disc shaped during isolation because they tended to flow and wet the carbon substrate. A typical electron micrograph of micelles isolated from PStPIp in N,N-dimethylacetamide is shown in Fig. 2.

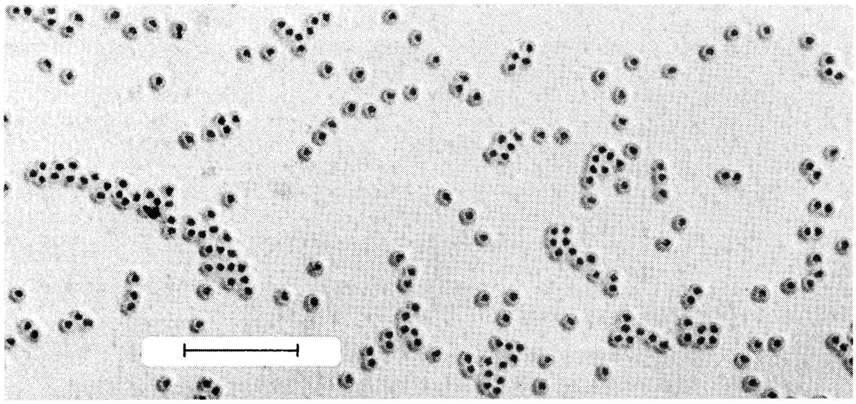

Fig. 2. An electron micrograph of collapsed micelles isolated from a micelle solution of block copolymer PStPIp in N,N-dimethylacetamide. Scale mark indicates 200 nm.

The micelles were stained in solution with osmium tetroxide prior to isolation. The osmium tetroxide selectively reacted with the olefinic bonds of the polyisoprene. The polyisoprene appears black in the micrograph and the polystyrene dark grey.

Results from gel permeation chromatography, ultracentrifugation, and electron microscopy have been obtained by us for a variety of block copolymers in different solvents (Ref. 24). Taken together they show unequivocally that block copolymers in selective organic solvents can form micelles having very narrow size distributions.

Over the years workers have found it much more difficult to obtain detailed information concerning the size distribution of micelles formed by synthetic surfactants, although it is believed that such systems do have fairly narrow size distributions. The problem stems basically from the rate at which such micelles can dissociate and reform. Kinetic studies on a number of simple cationic and anionic surfactants have revealed two relaxation times (Ref. 26 & 27). One is in the range 10^{-2}-$10^{-4}$$s^{-1}$ and the other in the range 10^{-4}-$10^{-7}$$s^{-1}$. According to the theory of Aniannson and Wall (Ref. 28) the first relates to the overall equilibrium process and the second to the removal of individual molecules from a micelle. In such circumstances, gel permeation chromatography and electron microscopy techniques are not very useful for investigating size distributions because they all involve concentration changes during the experiment. The length of the unassociated molecule is undoubtedly an important factor in governing relaxation rates. Recently in our laboratory we investigated micelle formation by the non-ionic surfactant, $CH_3(CH_2CH_2O)_{27}(CH_2)_{17}CH_3$ in water (Ref. 29). With this relatively high molecular weight surfactant it was found possible to apply gel permeation methods directly and the micelles were found to have a narrow size distribution.

FORMATION OF WORM-LIKE MICELLES

Large changes in light-scattering dissymmetry indicating the formation of extended micelles were reported thirty years ago for amphiphiles in aqueous media (Ref. 7). It has been argued that such micelles are basically rod-like possessing a singly connected core and a continuous surface, but that the rods must possess considerable flexibility (Ref. 9 & 10). There is now

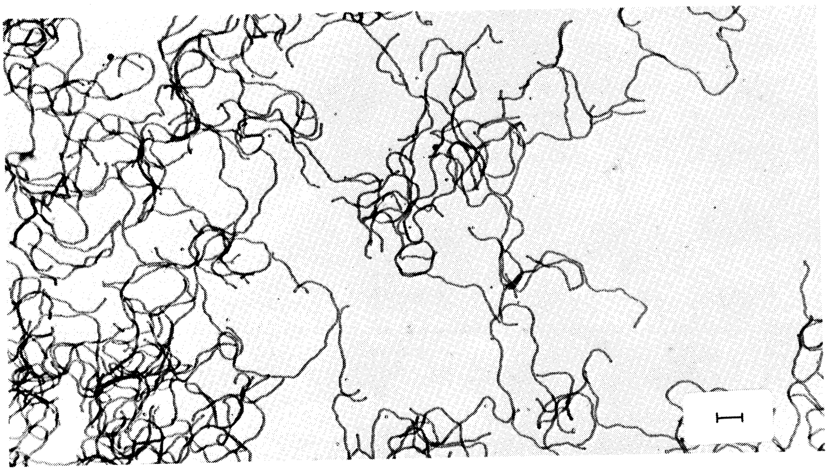

Fig. 3. An electron micrograph of collapsed worm-like micelles. The specimen was stained in solution prior to isolation with OsO_4. Scale mark indicates 400 nm.

strong evidence that under favourable conditions block copolymers also form extended micelles, which are worm-like in nature (Ref. 30-34). When this occurs the micelle molecular weights are very high and the size distributions are broad. An electron micrograph of worm-like micelles is shown in Fig. 3. The specimen was isolated from a solution of a polystyrene-b-polyisoprene block copolymer in N,N-dimethylacetamide using a procedure similar to that described earlier; the unassociated copolymer had a weight average molecular weight of 29,000 g mol^{-1} and contained 28.5% by weight polystyrene (Ref. 35).

THE THERMODYNAMICS OF MICELLE FORMATION

If it is assumed the associated solution is ideal except for intramicellar interactions, the equilibrium constant for the formation of an m-mer from unassociated chains,

$$K_m = [A_m] / [A_1]^m = \exp(-m\,\Delta G^\circ/RT)$$

where ΔG° is the standard free energy change per molecule in the m-mer, and $[A_m]$ and $[A_1]$ are the concentrations of m-mer and unassociated chains respectively. If the micelles have a narrow size distribution and the association numbers are large, it has been shown

$$\Delta G^\circ \cong RT \ln(\text{c.m.c.})$$

where c.m.c. is the critical micelle concentration. The c.m.c. is effectively the concentration at which the presence of micelles is just detectable by the experimental method in use. Each experimental method (light scattering, osmometry etc) will give a slightly different value for this concentration. The relationship has been used extensively over the years in investigations of amphiphilic micelles.

Two approaches have been used for resolving the free energy of micellization into its enthalpy and entropy components. The most satisfactory approach from a thermodynamic standpoint involves the determination of the standard enthalpy of micellization, ΔH°, from direct calorimetric measurements (Ref. 36-38). It becomes increasingly difficult to apply, however, as the c.m.c. of the system under investigation decreases. The second approach involves determining ΔH° from the temperature dependence of the c.m.c. (Ref. 39).

Assuming m is independent of temperature it has been shown via the van't Hoff equation that

$$\Delta H^\circ \cong -RT^2 d\ln(\text{c.m.c.})/dT$$

If ΔH° is taken to be independent of temperature, the above relation yields on integration

$$\ln(\text{c.m.c.}) \cong \Delta H^\circ/RT + \text{constant}$$

and ΔH° may be determined from the gradient of a plot of ln(c.m.c.) against T^{-1}. We have used this approach in our laboratory in the study of micelles

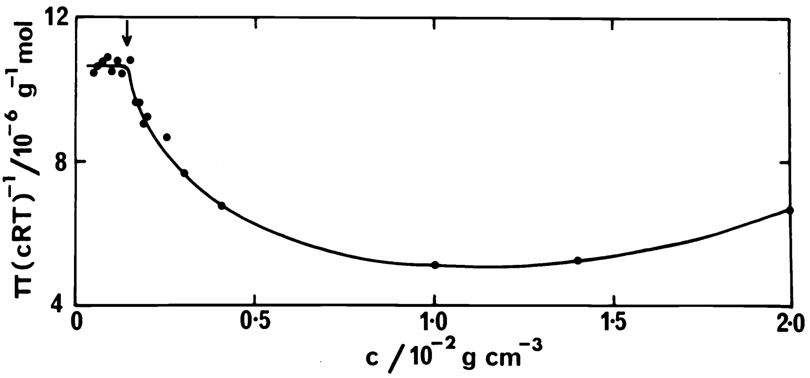

Fig. 4. A plot of the reduced osmotic pressure, $\pi(cRT)^{-1}$, against concentration for the PStPEp block copolymer in n-decane at 97.1°C. The arrow indicates the critical micelle concentration.

formed by a polystyrene-b-poly(ethylene/propylene) block copolymer (designated here PStPEp) in n-decane (Ref. 40). The block copolymer was provided by Shell Research Ltd. It had been prepared by hydrogenating the polyisoprene block of a polystyrene-b-polyisoprene block copolymer. U.v. spectroscopy showed the copolymer contained 38.5 ± 3.0% by weight of polyisoprene. Its number-average molecular weight (determined by membrane osmometry using toluene which is a good solvent for both components) was 97,000 g mol^{-1}. Gel permeation chromatography gave the ratio of the weight-average to number-average molecular weight, $\bar{M}_w/\bar{M}_n$, to be 1.14. Electron microscopy studies showed that the micelles formed by the block copolymer in n-decane were of the globular type and had a narrow size distribution. Since n-decane is a selectively bad solvent for polystyrene, this component would have formed the cores of the micelles.

The c.m.c. of block copolymer PStPEp in n-decane at different temperatures was determined by two separate methods: membrane osmometry and light scattering. In the first case the c.m.c. at four different temperatures was deduced from plots of the reduced osmotic pressure, π/cRT, against c, where c is the concentration of the solution (see Fig. 4). In the second case, light scattering intensity against temperature plots for solutions of fixed concentration were used to locate the temperature at which a solution had a given c.m.c. (see Fig. 5). Plots of ln(c.m.c.) against T^{-1} are shown in Figs. 6 and 7. The osmotic pressure data gave a value for ΔH° of

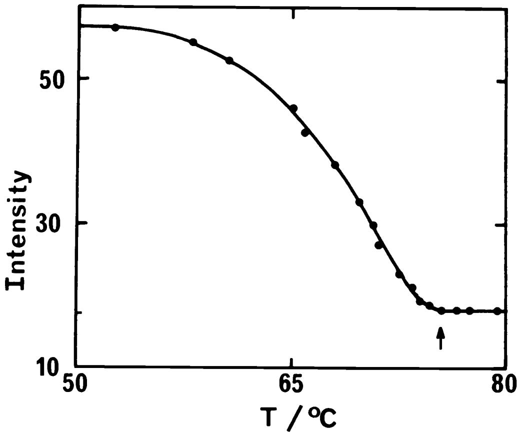

Fig. 5. A plot of relative light scattering intensity against temperature for the PStPEp block copolymer in n-decane. The concentration of the solution was 3.85×10^{-5}g cm^{-3} and the angle of scatter 60°. The arrow indicates the critical micelle concentration.

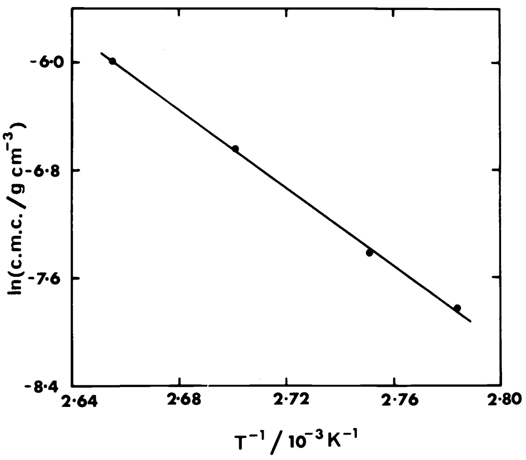

Fig. 6

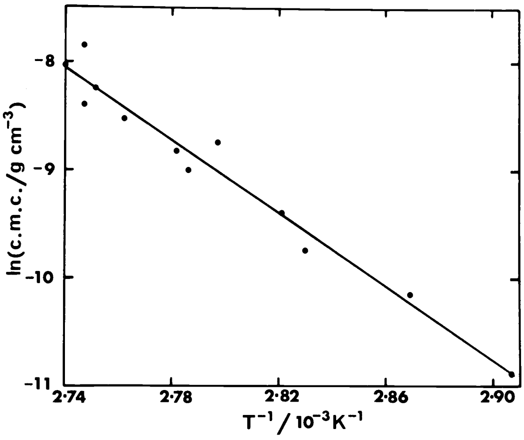

Fig. 7

Fig. 6. A plot of the logarithm of the critical micelle concentration against the reciprocal of the absolute temperature. The data were obtained by membrane osmometry for the PStPEp block copolymer in n-decane.

Fig. 7. A plot of the logarithm of the critical micelle concentration against the reciprocal of the absolute temperature. The data were obtained by light scattering for the PStPEp block copolymer in n-decane.

-130 kJ mol^{-1} (per copolymer chain in the micelle) and the light scattering data a value of -140 kJ mol^{-1}. The degree of agreement between these two results was judged to be very satisfactory in view of the arbitrary nature of the c.m.c.

Using the osmotic pressure data and adopting hypothetical standard states of unit mole fraction for the micelles and unassociated chains, values of ΔG° and $-T\Delta S^\circ$ were calculated. The results are recorded in Table 1 for T = 86°C.

The results in Table 1 show that for the PStPEp block copolymer in n-decane it is the enthalpy contribution to the free energy change which is responsible for micelle formation. As could be predicted from simple statistical arguments, the entropy contribution is unfavourable to micelle formation. The negative standard enthalpy of micellization stems from the exothermic

TABLE 1. Thermodynamics of micellization

Solute	Solvent	T (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	$-T\Delta S^\circ$ (kJ mol^{-1})
PStPEp	n-decane	86	-42	-130	88
Sodium n-dodecylsulphate[a]	H_2O	25	-21.1	0.38	-21.5
n-dodecyltrimethylammonium bromide[a]	H_2O	25	-17.9	-1.4	-16.5
n-octyl hexaoxyethylene monoether[b]	H_2O	25	-21.3	20.1	-41.4

a Jones et al (1970), standard states of unit molarity, (Ref. 38)
b Corkill et al (1964), standard states of unit mole fraction, (Ref. 36)

interchange energy accompanying the replacement of (polymer segment)-(solvent) interactions by (polymer segment)-(polymer segment) interactions. At lower temperatures, or higher concentrations, this interchange energy is sufficient to outweigh the entropic factors tending to disperse the copolymer chains freely throughout the solution. The block copolymer micelles are held together by net van der Waals attractions and could meaningfully be described as van der Waals macromolecules or van der Waals complexes. The combined effect (per copolymer chain in the micelle) is an attractive interaction similar in magnitude to that posed by a covalent chemical bond. Although results for only one block copolymer are presented here, the net attractive interaction can be expected to increase with the number of segments in the copolymer chain.

In contrast, for synthetic surfactants in water, it is the entropy contribution to the free energy change which is the thermodynamic factor mainly responsible for micelle formation. The sign of the entropy change has been explained in terms of the hydrophobic effect mentioned in the introduction. The standard enthalpy of micellization for synthetic surfactants is generally small and may be positive or negative depending on the system in question. Included in Table 1 are results for an anionic surfactant a cationic surfactant and a non-ionic surfactant.

THE SOLUTION BEHAVIOUR OF GLOBULAR MICELLES

Detailed studies have been made on a number of block copolymer systems in selective solvents at temperatures that ensure the micelle/free chain equilibrium overwhelmingly favours the globular micelle form down to the lowest concentrations of interest (Ref. 20,41 & 42). In such cases the solutions can be treated as if the solute were simply a large compact macromolecule (Ref. 24). The evidence suggests the micelles have spherically symmetric segment distributions. Light scattering and membrane osmometry can be applied in the normal way to determine the weight-average and number-average molecular weight respectively. Furthermore in such cases dilute solution viscometry can be used to gain a meaningful estimate of the intrinsic viscosity of the micelles. One can also expect such solutions to exhibit upper and in some cases lower critical solution temperature behaviour (Ref. 43). In very special cases it might be possible to pass from an upper to a lower critical solution temperature without the micelle dissociating significantly at any stage.

At 30°C globular micelles were overwhelmingly the preferred form for dilute solutions of PStPEp in n-decane. From the light scattering results discussed earlier the c.m.c. at 30°C was estimated to be 2.4×10^{-8} g cm^{-3}. The latter is far below the concentration at which useful light scattering measurements could be made on the block copolymer solution. Light scattering results for the system at 30°C are shown in Fig. 8, where $(Kc/R_\theta)_{\theta=o}$ is plotted against concentration. Since the block copolymer was homogeneous in chemical composition.

$$(Kc/R_\theta)_{\theta=o} = \bar{M}_w^{-1} + 2A_2c + \ldots$$

Extrapolation of the results to zero concentration yielded a value for the weight-average molecular weight of the micelles of 6.6×10^6 g mol^{-1}.

The compact nature of the PStPEp micelles formed in n-decane was reflected by the dependence of the dissymmetry ratio, I(45°)/I(135°), on concentration. As shown in Fig. 9 the dissymmetry ratio fell below unity at $c = 0.8 \times 10^{-3}$ g cm^{-3}. This behaviour can be predicted quite well by assuming that on increasing the concentration the micelles packed together like hard spheres (i.e. the local packing can be described by radial distribution functions for hard spheres). A similar calculation has been described previously by us (Ref. 44). For the present case the effective hard sphere radius was set equal to 46.4 nm. The first part of the dissymmetry curve (indicated by the full line in Fig. 9) was calculated using radial distribution functions obtained from an analytical expression predicted by the Percus-Yevick theory (Ref. 45). Radial distribution functions obtained by Monte Carlo machine calculations (Ref. 46) were used to predict the behaviour at two higher concentrations (indicated by the squares in Fig. 9); the concentrations correspond to hard sphere number densities of $0.298\,{}^n\rho_o$ and $0.372\,{}^n\rho_o$, where ${}^n\rho_o$ is the number density of a close-packed system.

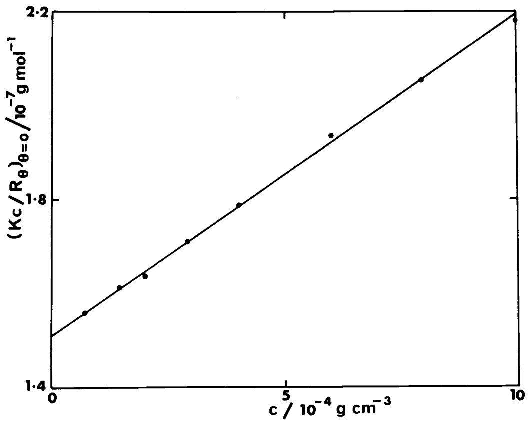

Fig. 8

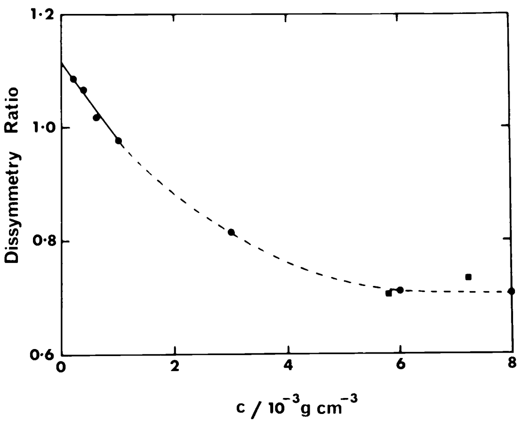

Fig. 9

Fig. 8. Plot of $(Kc/R_\theta)_{\theta=0}$ against concentration for block copolymer PStPEp in n-decane at 30°C.

Fig. 9. Plot of dissymmetry ratio against concentration for block copolymer PStPEp in n-decane at 30°C. The broken curve passes through the experimental points (●). The full curve and the squares (■) indicate behaviour predicted theoretically using a hard-sphere approximation.

The repulsive potential between the micelles stems primarily from the large reduction in entropy when the relatively dense micellar fringes overlap. Dissymmetry ratios below unity are not generally observed for flexible unassociated chains basically because the repulsive potential is much softer and the coils are able to interpenetrate more effectively.

Acknowledgement - The author wishes to thank S.E.R.C. for supporting this programme of research and Shell Research Ltd. for supplying the PStPEp polymers.

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