Thermodynamics of micellisation of a diblock copolymer of ethylene oxide and styrene oxide in water

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Received 15th August 2001, Accepted 17th October 2001
First published as an Advance Article on the web

Aqueous solutions of block copolymer $S_{13}E_{60}$ were studied by surface tensiometry. [E denotes an oxyethylene unit, OCH_2CH_2, and S an oxyphenylethylene unit, $OCH_2CH(C_6H_5)$.] Critical micelle concentrations were determined at several temperatures and thereby values of the standard enthalpy of micellisation, $\Delta_{mic}H^\circ$. It was found that the copolymer underwent almost athermal micellisation. This unusual behaviour in block copolymer systems is attributed to the hydrophobic block being tightly coiled in the molecular state, so that interaction of its units with water (hydrophobic bonding) is minimised, with the resulting small positive contribution to $\Delta_{mic}H^\circ$ being essentially balanced by a negative contribution from dispersion interactions of B units in the micelle core.

1. Introduction

The association properties of block copolymers of ethylene oxide and propylene oxide in aqueous solution have been extensively studied, mainly the commercially available triblock copolymers of type EPE,[1] but also other architectures (including diblock EP and triblock PEP) as summarised recently.[2] We use the notation E = oxyethylene, OCH_2CH_2, and P = oxypropylene, $OCH_2CH(CH_3)$. A similar range of architectures has been studied for block copolymers of ethylene oxide and 1,2-butylene oxide, EB, EBE and BEB,[2] B = oxybutylene, $OCH_2CH(C_2H_5)$. It is established, both experimentally[2] and theoretically,[3] that diblock copolymers micellise more readily and form micelles with larger hydrophobic cores than corresponding triblock copolymers. Consequently, diblock copolymers have advantages in many applications, not least in the solubilisation of sparingly-soluble substances, including drugs. The solubilisation of certain aromatic drugs is a particularly difficult problem, and we have shown recently that diblock copolymers of ethylene oxide and styrene oxide, ES where S = oxyphenylethylene, $OCH_2CH(C_6H_5)$, are particularly efficient in this respect.[4] To date the association properties in aqueous solution of only four such copolymers have been reported; a series $E_{50}S_{3.5}$, $E_{50}S_{5.1}$ and $E_{51}S_{6.5}$,[5] and a copolymer polymerised in reverse order, $S_{13}E_{60}$.[6,7] (In these formulae the subscripts denote number-average block lengths.) The report on the $E_{50}S_n$ series[5] included the critical micelle concentration (cmc) as a function of temperature, micelle association numbers and radii, and determination of hard gel boundaries. The studies of $S_{13}E_{60}$ included association numbers and radii,[6] the rheological properties of micellar solutions in fluid and gel states,[6,7] and the structure of the hard gel,[7] but no information on critical micellisation behaviour. This short paper remedies the omission.

2. Experimental section

2.1 Copolymer

Copolymer $S_{13}E_{60}$ was prepared by sequential anionic polymerisation of styrene oxide followed by ethylene oxide. Details of the preparation and characterisation of the copolymer have been reported.[4,6] Chains were initiated by 2-(2-methoxyethoxy)ethanol, which meant that each S block started with two E units. This minor perturbation of the structure is ignored in what follows. Gel permeation chromatography (GPC) was used to confirm a narrow chain length distribution and determine the ratio of number-to-mass-average molar mass (M_w/M_n). The GPC curves obtained for the copolymer had a narrow main peak with a minor peak at lower elution volume related to a proportion (some 13 wt.%) of homopoly(oxyethylene). Analysis showed that the width of the molar mass distribution of the copolymer itself to be 1.03 ± 0.01. ^{13}C NMR spectroscopy was used to obtain an absolute value of M_n for the diblock copolymer of 4290 ± 90 g mol^{-1}.

2.2. Surface tension

Surface tensions (γ) of dilute aqueous solutions were measured at four temperatures in the range 20–50 °C by detachment of a platinum ring using a temperature-controlled (± 0.2 °C) surface tensiometer (Kruss, Model K8600). The instrument was well protected from vibration and draughts. Copolymer solutions in deionised and doubly distilled water were made by dilution of a stock solution. A new solution was first equilibrated at the lowest temperature for 24 h and then γ was measured every 30 min until consistent readings were obtained. Thereafter the temperature was raised, the solution was re-equilibrated (24 h), and the measurement procedure was repeated. Before using a new solution the ring was washed successively with dilute HCl and water. The accuracy of measurement was checked by frequent determinations of the surface tension of pure water.

3. Results and discussion

Plots of surface tension against the logarithm of concentration for aqueous solutions of the copolymer $S_{13}E_{60}$ at 20, 30, 40 and 50 °C are shown in Fig. 1. For clarity the plots are displaced on the ordinate scale. The curvature in the plots at low concentrations is ascribed to the distribution of S-block lengths

DOI: 10.1039/b107374e

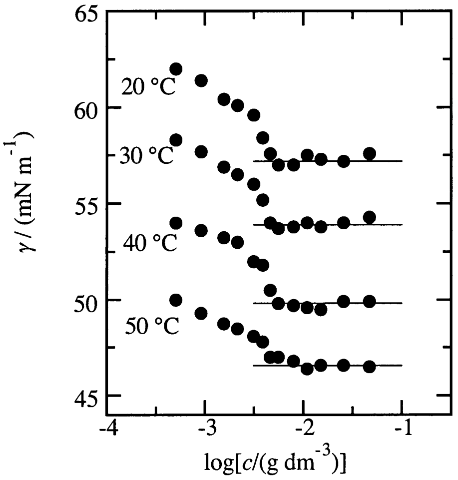

Fig. 1 Surface tension (γ) *versus* concentration for aqueous solutions of block copolymer $S_{13}E_{60}$ at the temperatures indicated. For clarity, 6, 4 and 2 mN m^{-1} have been added to the data points for 20, 30 and 40 °C respectively. The concentration scale is not corrected for the poly(oxyethylene) impurity.

Table 1 Critical micelle concentrations (cmc) and surface tensions for aqueous solutions of block copolymer $S_{13}E_{60}$

T/°C	cmc/g dm^{-3}	γ_{cmc}/mN m^{-1}
20	0.0048	51.5
30	0.0049	50.0
40	0.0049	47.6
50	0.0050	46.6

Estimated uncertainties: log(cmc) ± 0.1, γ_{cmc} ± 1%.

in the sample. Following previous practice[8,9] the cmc was assigned to the concentration at which surface tension reached a steady value, as indicated by the horizontal lines drawn on the diagram. Small corrections were made to the cmc to allow for the fact that the homopoly(oxyethylene) in the samples does not micellise. The values of the cmc so obtained are listed in Table 1, together with the surface tension at the cmc (γ_{cmc}).

Comparison with results for the $E_{50}S_n$ series is shown in Fig. 2, *i.e.*, log(cmc) at 30 °C expressed in molar units *versus* S-block length (n). This plot confirms that the measured cmc fits the pattern reported previously.[5] Also included in Fig. 2 are data for aqueous solutions at 30 °C of diblock copolymers of ethylene oxide and styrene: $St_{16}E_{155}$, $St_{14}E_{160}$ and $St_{10}E_{68}$ (where St denotes a phenylethylene unit).[10–12] Judged by the cmc, the hydrophobicity of a phenylethylene unit is very similar to that of an oxyphenylethylene unit. A previous comparison of association numbers measured for $S_{13}E_{60}$ and $St_{10}E_{68}$ provides some support for this conclusion.[6]

For closed association to micelles with a narrow distribution of association number (N) the equilibrium between copolymer molecules (A) and micelles (A_N) can be written (concentration in mol dm^{-3})

$$K_c = [A_N]_{eq}^{1/N}/[A]_{eq} \qquad (1)$$

If the association number is large, and Hall in his detailed study[13] of associating systems suggests $N > 50$, then the equilibrium constant is well approximated by

$$K_c = 1/[A]_{eq} \qquad (2)$$

where $[A]_{eq}$ can be considered to be the cmc. Accordingly, for the forward reaction in eqn. (1),

$$\Delta_{mic}G^\circ = -RT \ln K_c = RT \ln(\text{cmc}) \qquad (3)$$

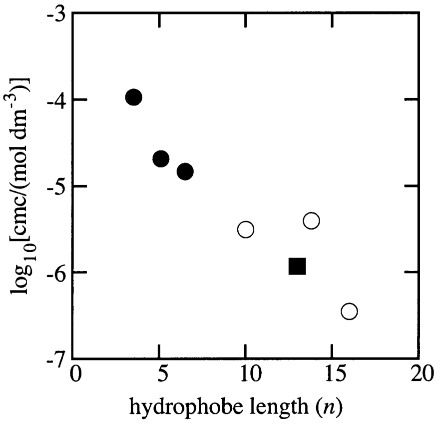

Fig. 2 Logarithm of cmc (in mol dm^{-3}) *versus* hydrophobe length (n) for aqueous solutions at 30 °C of diblock copolymers: (●) E_mS_n (ref. 5); (■) $S_{13}E_{60}$ (present work); (○) St_nE_m (refs. 10–12).

and

$$\Delta_{mic}H^\circ = -RT\, \text{d}\ln(K_c)/\text{d}(1/T) = -RT\, \text{d}\ln(\text{cmc})/\text{d}(1/T) \qquad (4)$$

The process referred to is copolymer chains in their standard state of an ideally dilute solution at unit concentration (1 mol dm^{-3}) going to copolymer chains in the micellar state. (Within the logarithmic terms, dimensionless values are relative to 1 mol dm^{-3}.) For eqn. (4) to apply to equilibrium (1) it is necessary that eqn. (2) is a good approximation of eqn. (1) at all temperatures. Even though N is temperature dependent, if it is sufficiently large in value then the required condition applies. For copolymer $S_{13}E_{60}$, static light scattering has been used to determine the mass-average association numbers (N_w) at 20, 30 and 40 °C of 102, 106 and 111 respectively.[6] Within the temperature range studied, it is clear that N_w is large and does not change significantly in value, so eqn. (4) is valid.

As seen in Table 1, the cmc is almost independent of temperature for the copolymer $S_{13}E_{60}$ in water. Taking into account the uncertainty in the values of the cmc, the standard enthalpy of micellisation is obtained as $\Delta_{mic}H^\circ = 0 \pm 4$ kJ mol^{-1}. The plot of the standard enthalpy of micellisation per S unit ($\Delta_{mic}H^\circ/n$) against n including copolymer $S_{13}E_{60}$ and the copolymers of the $E_{50}S_n$ series (see Fig. 3) shows a regularity of behaviour. A similar effect of hydrophobe block length on the standard enthalpy of micellisation per B unit has been found for diblock E_mB_n copolymers,[14] but corresponding results for diblock E_mP_n copolymers show a weak dependence of the

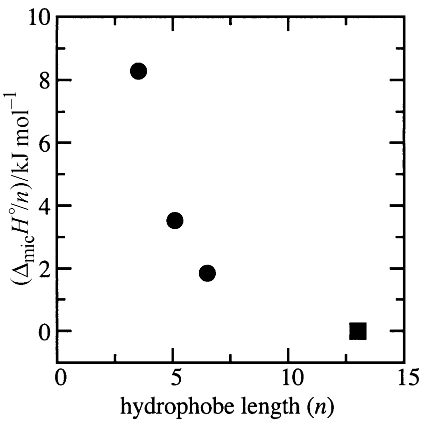

Fig. 3 Standard enthalpy of micellisation per S unit ($\Delta_{mic}H^\circ/n$) for aqueous solutions of (●) E_mS_n (ref. 5) and (■) $S_{13}E_{60}$ (present work).

standard enthalpy of micellisation per P unit on block length.[15,16]

As discussed for the EB copolymers,[14] the low standard enthalpy change associated with the S_{13} block is attributable to the block being tightly coiled in the dispersed molecular state, so that the interaction of an S unit with water (hydrophobic interaction)[17] is much reduced in comparison with the interaction enthalpies of the units of short blocks, which are relatively extended in the molecular state. An unassociated copolymer with its hydrophobic block in such a tightly coiled state is often called a monomolecular micelle. From eqn. (3) and the value of the cmc in Table 1, $\Delta_{\mathrm{mic}}G^\circ = -34$ kJ mol^{-1} at 30 °C which, with $\Delta_{\mathrm{mic}}H^\circ = 0$, implies $T\Delta_{\mathrm{mic}}S^\circ = 34$ kJ mol^{-1}, *i.e.*, a small positive standard entropy of micellisation arising mainly from the reduced hydrophobic effect. The fact that $\Delta_{\mathrm{mic}}H^\circ = 0$ means that the corresponding small positive contribution to the enthalpy of micellisation from the hydrophobic effect must be compensated by a negative contribution.

The balance of the contributions to $\Delta_{\mathrm{mic}}G^\circ$ has been discussed many times, very recently by del Rio and Jones.[18] Recognised contributions to $\Delta_{\mathrm{mic}}H^\circ$ are

$$\Delta_{\mathrm{mic}}H^\circ = \Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{HP}} + \Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{S}} + \Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{D}} + \Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{E}}$$

where $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{HP}}$ is associated with the hydrophobic effect, $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{S}}$ with formation of the core–corona interface, $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{D}}$ with enhanced van der Waals (dispersion) interactions between the units of the B blocks in the core, and $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{E}}$ with transfer of E blocks to a more concentrated solution in the micelle corona. In the micellisation of nonionic block copolymers the last three contributions to $\Delta_{\mathrm{mic}}H^\circ$ are usually small in comparison with that from the hydrophobic effect, and assume significance only when $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{HP}}$ is small. $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{E}}$ relates to the reverse of the enthalpy of dilution of dilute aqueous poly(oxyethylene) solution, and will be small and positive.[19] $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{S}}$ is also likely to be small and positive. However, $\Delta_{\mathrm{mic}}H^\circ{}_{\mathrm{D}}$ is indisputably negative, and we attribute the low value of $\Delta_{\mathrm{mic}}H^\circ$ to, essentially, a balance between the contributions of hydrophobic and dispersion interactions.

Acknowledgements

We are pleased to acknowledge valuable discussions with Dr M. N. Jones.

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