

Temperature Dependences of the Critical Micelle Concentrations of Diblock Oxyethylene/Oxybutylene Copolymers. A Case of Athermal Micellization

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Introduction. Block copolymers prepared by sequential anionic polymerization of ethylene oxide and 1,2-butylene oxide are available on a commercial basis from The Dow Chemical Co., Texas Operations, in both diblock (E_mB_n) and triblock ($E_mB_nE_m$) form.¹ Here E denotes an oxyethylene unit, OCH_2CH_2 , and B an oxybutylene unit, $OCH_2CH(C_2H_5)$. Over the past few years, a wide range of E/B copolymers, including $B_nE_mB_n$ and *cyclo*- B_nE_m architectures, has been synthesized for research purposes in Manchester and Texas, as summarized in a recent review.² An early study³ showed that the critical micelle concentration (cmc) of triblock copolymer $E_{58}B_{17}E_{58}$ was only weakly temperature dependent. For example, relating the cmc to temperature by a van't Hoff plot, i.e., $\log(\text{cmc})$ against $1/T$, gave a standard enthalpy change (ΔH°) for the micellization of $E_{58}B_{17}E_{58}$ of only 37 kJ mol⁻¹ compared with values of 200 kJ mol⁻¹ or more for the well-researched oxyethylene/oxypropylene triblock copolymers, $E_mP_nE_m$, $P = OCH_2CH_2(CH_3)$.^{4–6} This occurred despite the considerably lower cmc of $E_mB_nE_m$ copolymers compared with those of $E_mP_nE_m$ copolymers: we estimate that a B unit is 4 times more hydrophobic than a P unit.⁷ Subsequent work using diblock E_mB_n copolymers with B blocks in the range B_5 to B_{10} confirmed the effect,^{8–10} and also indicated an inverted relationship between ΔH° and B-block length n . The present study extended this field of investigation to copolymers with B_{16} blocks, and it was found that they underwent almost athermal micellization. To the best of our knowledge, this result is unique for block copolymers in aqueous solution.

Experimental Section. Copolymers. Diblock copolymers $E_{106}B_{16}$ and $E_{210}B_{16}$ were prepared by sequential anionic polymerization of ethylene oxide (EO) followed by 1,2-butylene oxide (BO). The monofunctional initiator was 2-(2-methoxyethoxy)ethanol activated by reaction with potassium metal (mole ratio OH/K = 15). Vacuum line and ampule techniques were used throughout. Characterization of the intermediate poly(oxyethylene) and the final copolymer was by gel permeation chromatography (GPC) and ¹³C NMR spectroscopy: GPC (calibrated by poly(oxyethylene) standards) for distribution width; NMR for number-average molar mass, composition, and block structure. Details of the preparation and characterization of the copolymers have been published elsewhere in connection with a study of their adsorption on hydrophobic surfaces.¹¹ A summary of molecular characteristics is given in Table 1.

Table 1. Molecular Characteristics of the Copolymers^a

copolymer	M_w/M_n (GPC)	mol % E	wt % E	$M_n/\text{g mol}^{-1}$ (NMR)	$M_w/\text{g mol}^{-1}$
$E_{106}B_{16}$	1.03	86.9	80.2	5820	5990
$E_{210}B_{16}$	1.03	92.9	88.9	10400	10700

^a M_n = number-average molar mass, M_w = mass-average molar mass calculated from M_n and M_w/M_n . Estimated uncertainties: block lengths, M_n and M_w/M_n to 2%; M_w to 3%.

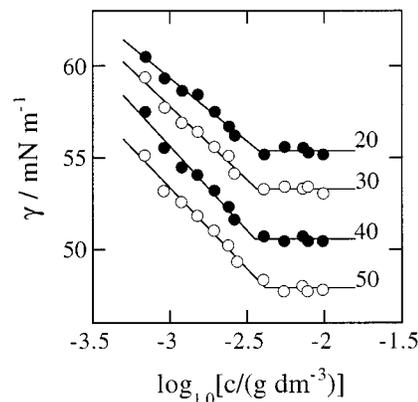


Figure 1. Surface tension (γ) versus concentration for aqueous solutions of block copolymer $E_{210}B_{16}$ at the temperatures ($^\circ\text{C}$) indicated.

Surface Tension. Surface tensions (γ) of dilute aqueous solutions were measured at four temperatures in the range 20–50 $^\circ\text{C}$ by detachment of a platinum ring using a temperature-controlled (± 0.2 $^\circ\text{C}$) surface tensiometer (Kruss, Model K8600). The instrument was well protected from vibration and drafts. Copolymer solutions in deionized 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 and the procedure repeated. Before a new solution was used, 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.

Light Scattering. Micellar molar masses were determined by static light scattering using a Brookhaven BI-200SM instrument with vertically polarized incident light of wavelength 488 nm supplied by an argon-ion laser (Coherent Innova 90) operated at 500 mW. Hydrodynamic radii were determined by dynamic light scattering using the same instrument combined with a Brookhaven BI9000AT digital correlator. A detailed account of the methods employed, including clarification of solution, measurement of intensity, and analysis of data, has been published recently in this journal.¹²

Results and Discussion. Plots of surface tension against the logarithm of concentration for aqueous solutions of copolymer $E_{210}B_{16}$ are shown in Figure 1. Each data set can be well fitted by two straight lines, with the concentration at the intersection assigned to the cmc. Similar plots were obtained for solutions of copolymer $E_{106}B_{16}$.

In each case the nature of the association to micelles in dilute solution above the cmc was checked by dynamic light scattering. As an example, the intensity distribu-

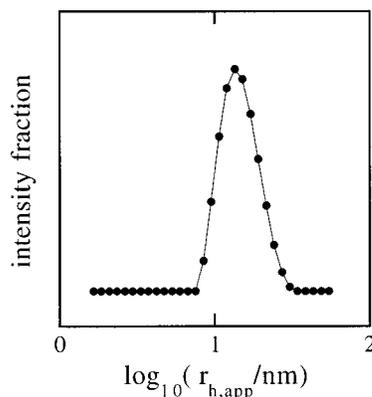


Figure 2. Dynamic light scattering. Intensity fraction distribution of the logarithm of the apparent hydrodynamic radius for a 2.56 g dm⁻³ aqueous solution of copolymer E₂₁₀B₁₆.

Table 2. Critical Micelle Concentration and Surface Properties for Aqueous Solutions of E_mB_n Block Copolymers^a

copolymer	T/°C	cmc/mg dm ⁻³	γ _{cmc} /mN m ⁻¹	a _{cmc} /nm ²
E ₁₀₆ B ₁₆	20	4.7	48.7	0.79
	30	4.1	46.6	0.76
	40	4.6	44.1	0.80
	50	4.5	41.6	0.74
E ₂₁₀ B ₁₆	20	3.8	55.3	1.36
	30	3.7	53.3	1.21
	40	3.6	50.6	1.09
	50	4.2	47.9	1.18

^a Estimated uncertainties: log(cmc), ±0.1; cmc, ±20%; γ_{cmc}, ±1%; a_{cmc}, ±7%.

tion of the logarithm of apparent hydrodynamic radius found for micelles of copolymer E₂₁₀B₁₆ in dilute solution is shown in Figure 2: the narrow distribution peaking at r_{h,app} ≈ 14 nm is typical of the closed association process characteristic of this type of copolymer.⁸⁻¹⁰

Values of the cmc are listed in Table 2, together with the surface tension at the cmc (γ_{cmc}), and the area per molecule at the cmc (a_{cmc}) calculated from the slope of the line below the cmc via the Gibbs equation.¹³ The higher values of γ_{cmc} recorded for the copolymer with the longer E block are consistent with the larger surface area per molecule, since this means a reduced surface fraction of hydrophobic units at the surface.

As expected,⁷ values of the cmc are insensitive to E-block length. Our present interest lies in the essentially constant value of the cmc for a given copolymer across the range of temperature investigated. Within the error of determination, the micellization of each copolymer is athermal. Specifically, the data give ΔH[°] = +0.4 ± 2.7 kJ mol⁻¹ for E₁₀₆B₁₆ and ΔH[°] = -1.7 ± 2.6 kJ mol⁻¹ for E₂₁₀B₁₆. The comparison with previous results^{7-10,14} shown in Figure 3, i.e., the logarithm of the cmc expressed in molar units versus B-block length *n*, confirms that the cmcs themselves (i.e., in the standard Gibbs energy of micellization) fit regularly to the established pattern.⁷ The plot of the standard enthalpy change per B unit (ΔH[°]/*n*) against *n*, shown in Figure 4, shows a regularity of behavior in that property too, and therefore, by implication, in the positive standard entropy change associated with micellization. The effect holds for all block architectures. The low value of ΔH[°] = 34 kJ mol⁻¹ reported for E₅₈B₁₇E₅₈ has been mentioned in the Introduction, and a similarly low value of ΔH[°] = 34 kJ mol⁻¹ has been reported for copolymer B₁₂E₂₆₀B₁₂.¹⁵ A summary of

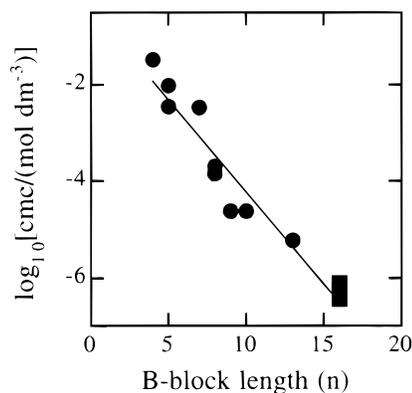


Figure 3. Logarithm of the critical micelle concentration (in mol dm⁻³) versus B-block length for aqueous solutions of E_mB_n copolymers at 30 °C: (■) Results from refs 7-10 and 14; (●) present results.

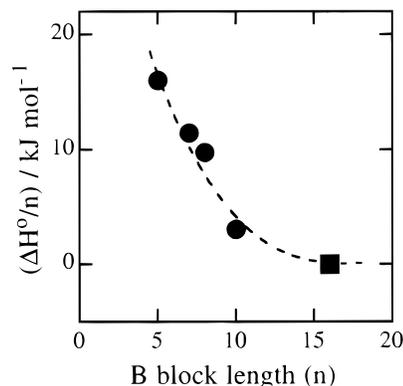
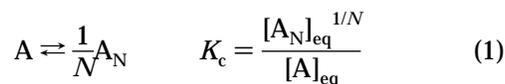


Figure 4. Standard enthalpy of micellization per B unit (ΔH[°]/*n*) for aqueous solutions of E_mB_n copolymers: (■) results from refs 8-10; (●) present results. The dashed curve has no theoretical justification but is drawn to give an asymptotic approach to low values of ΔH[°]/*n* at high values of *n*.

recent work can be found in ref 2. The present results provide the most striking example reported to date.

When the results are considered, the manner in which the obtained standard enthalpy change is related to the micellization process is important. 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)



If the association number is large, and Hall in his detailed study of associating systems suggests *N* > 50,¹⁶ then the equilibrium constant is well approximated by

$$K_c \approx 1/[A]_{\text{eq}} \quad (2)$$

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

$$\Delta G^\circ \approx -RT \ln(K_c) = RT \ln(\text{cmc}) \quad (3)$$

and

$$\Delta H^\circ \approx -R \frac{d \ln(K_c)}{d(1/T)} = R \frac{d \ln(\text{cmc})}{d(1/T)} \quad (4)$$

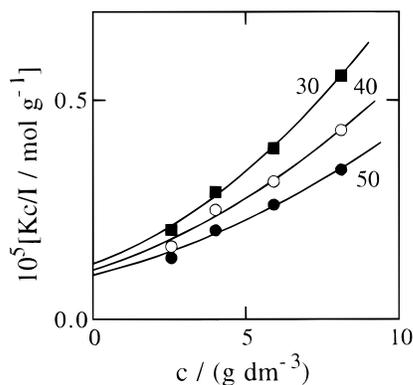


Figure 5. Static light scattering, Debye plots for aqueous micellar solutions of copolymer $E_{210}B_{16}$ at the temperatures ($^{\circ}C$) indicated. The least-squares curves through the data points correspond to the equation: $KcI = 1/M_w + A_2c + A_3c^2$, where K is the appropriate optical constant, I is the excess scattering intensity over that from solvent, and A_2 and A_3 are virial coefficients.

Table 3. Effect of Variation of N with Temperature on the Thermodynamic Quantities

$T/^{\circ}C$	N	$\Delta G^{\circ}/kJ\ mol^{-1}$		$\Delta H^{\circ}/kJ\ mol^{-1}$	
		approx (2)	approx (6)	approx (2)	approx (6)
30	80	-34.8	-34.2		
50	100	-37.1	-36.6	0	+2.1

^a Values calculated for $cmc = 10^{-6}\ mol\ dm^{-3}$ (independent of temperature) and advancement $\alpha = 0.05$. Values of N are for micelles of copolymer $E_{210}B_{16}$.

The process referred to is copolymer chains in their standard state of 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 eq 4 to apply to equilibrium (1) it is necessary that N be independent of temperature.

In the present case, static light scattering has been used to show that $N \geq 50$ for solutions of both copolymers, hence eq 3 is a good approximation for ΔG° . However N changes somewhat with temperature. The effect, monitored by static light scattering, is illustrated by the Debye plots shown in Figure 5 for micellar solutions of copolymer $E_{210}B_{16}$. In the temperature interval 30–50 $^{\circ}C$, the molar mass of the micelles changed from 8×10^5 to $10 \times 10^5\ g\ mol^{-1}$; i.e., N varied (in round figures) from 80 to 100. Similar results were recorded for micelles of copolymer $E_{106}B_{16}$.

Given that the cmc is detected at a fractional advancement in the equilibrium α , then the equilibrium constant can be written exactly as

$$K_c = \frac{\beta}{1 - \alpha} \left(\frac{\alpha}{N\beta} \right)^{1/N} (cmc)^{-1+1/N} \quad \beta = 1 - \alpha + \frac{\alpha}{N} \quad (5)$$

which, for small α , can be well approximated by

$$K_c = \left(\frac{\alpha}{N} \right)^{1/N} (cmc)^{-1+1/N} \quad (6)$$

The effect of correction for this variation of N with T is illustrated in Table 3 using micellar parameters relevant to the present results and assuming that $\alpha = 0.05$. The more correct calculation indicates a value of the $\Delta H^{\circ} \approx 2\ kJ\ mol^{-1}$ for the ideal (constant N) process, a small positive value rather than zero. Changing the value of α within the range 0.01–0.05 makes little

difference. Of course, the temperature dependence of the real micellization process (variable N) is correctly described by $\Delta H^{\circ} \approx 0$. In any event, for the present case of a modest variation in a large value of N , the correction is well within the uncertainty of our measurements.

The low standard enthalpy changes associated with the units of lengthy B blocks have been attributed to the blocks being tightly coiled in the dispersed molecular standard state, so that interaction with water (hydrophobic bonding) is minimized, particularly in comparison with the interaction enthalpies of the units of short blocks, which are relatively extended in the molecular state.^{2,8,9} An unassociated copolymer with its hydrophobic block in such a tightly coiled state has been called a "monomolecular micelle".¹⁷ Transfer of B blocks to the micelle core would then involve little (or no) standard enthalpy change. The transfer of E blocks from solution to a more concentrated state in the micelle fringe must result in a small positive enthalpy change, e.g., as assessed as the reverse of the partial molar enthalpy of dilution,¹⁸ or less directly, as the integral enthalpy of dilution.¹⁹ The present results are consistent with this explanation.

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