

# Association Behavior of Diblock (Oxyethylene/Oxybutylene) Copolymer $E_{18}B_{10}$ in Aqueous Solution

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**ABSTRACT:** The association properties of block copolymer  $E_{18}B_{10}$  in aqueous solution have been studied. We use E to denote an oxyethylene unit and B an oxybutylene unit and  $m$  and  $n$  to denote block lengths in chain units. The samples had E blocks terminated by methoxy groups but B blocks terminated either with hydroxy or with methoxy groups. Surface tensiometry was used to determine the critical micelle concentrations of the samples at several temperatures and thereby values of the enthalpy of micellization. Dilute solution viscometry was used to investigate the geometry of micelles in solution. Critical micelle temperatures were found to be insensitive to the B-block end group and to the geometry of the micelles, whether spherical or wormlike.

## 1. Introduction

A range of block copolymers of ethylene oxide and 1,2-butylene oxide are available commercially from The Dow Chemical Co., and their association properties in dilute aqueous solution are included in recent reviews.<sup>1,2</sup> One of these copolymers, coded BM45-1600 by the company, is the subject of this short paper. The sample used has molecular formula  $E_{18}B_{10}$ , where E denotes oxyethylene,  $OCH_2CH_2$ , B denotes oxybutylene,  $OCH_2-CH(C_2H_5)$ , and the subscripts denote number-average block lengths in chain units. Its association properties in dilute aqueous solution have been studied by light scattering,<sup>3</sup> small-angle neutron scattering (SANS),<sup>4</sup> and surface tension,<sup>5</sup> but none provide the temperature dependence of the critical micelle concentration (cmc) and thereby access to the standard enthalpy of micellization. This gap in the literature of block copolymer (oxyalkylene)s is addressed in this paper.

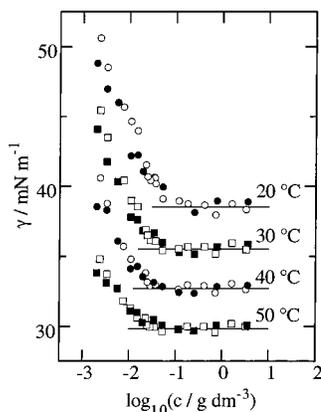
Because of the monomer sequence used in the oxyanionic polymerization of  $E_{18}B_{10}$ , ethylene oxide followed by butylene oxide, the E block is methoxy-ended while the B block is hydroxy-ended. As the presence of a terminal hydroxy group on the B group could well affect the critical micellization concentration, we included a methylated version of  $E_{18}B_{10}$  in our study. This copolymer, denoted  $E_{18}B_{10}M$  to distinguish it from the parent copolymer  $E_{18}B_{10}H$ , was prepared recently and used in a study of micelle properties by light scattering.<sup>6</sup> While both copolymers formed spherical micelles in dilute aqueous solution at 30 °C, and the same geometry held for solutions of copolymer  $E_{18}B_{10}H$  at 40 °C, the association number and radius of micelles of copolymer  $E_{18}B_{10}M$  were remarkably high, indicative of a transition from spherical to wormlike micelles. The sphere-to-worm transition in micellar solutions of copolymer  $E_{18}B_{10}H$ ,

as detected by SANS, does not occur until the temperature approaches 50 °C, i.e., at least 10 °C higher.<sup>4</sup> It is likely that the internal structure of the micelle core differs considerably between the two copolymers, that of  $E_{18}B_{10}M$  being relatively free of water (a B unit is highly hydrophobic)<sup>2</sup> and that of  $E_{18}B_{10}H$ , with terminal hydroxy groups concentrated at the center of the micelle core, containing a considerable fraction of water (as revealed by SANS on a related copolymer),<sup>7</sup> i.e., having the character of a primitive vesicle. Consequently, it was not possible to predict the effect of methylation on the cmc, and the present experiments provided an opportunity to find out.

## 2. Experimental Section

**2.1. Copolymers.** The general methods used in the synthesis of  $E_{18}B_{10}H$  have been described.<sup>8</sup> The sample was characterized as described previously<sup>3</sup> by gel permeation chromatography calibrated with poly(oxyethylene) standards (for width of the size distribution: ratio of mass-average to number-average molar mass,  $M_w/M_n = 1.04$ ) and <sup>13</sup>C NMR (for absolute measurement of number-average molar mass,  $M_n = 1510 \text{ g mol}^{-1}$ , and composition, wt % E = 52), whence the molecular formula. Methylation of the hydroxy group was by a modified Williamson synthesis which gave essentially 100% conversion.<sup>9</sup> Within experimental error, estimated as  $\pm 4\%$ , the block lengths were unchanged by methylation: see ref 6 for details.

**2.2. Surface Tension.** Surface tensions ( $\gamma$ ) of dilute aqueous solutions were measured by detachment of a platinum ring at four temperatures in the range 20–50 °C using a temperature-controlled ( $\pm 0.2$  °C) surface tensiometer (Kruss, model K8600). The instrument was well protected from vibration and draughts. 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  $\gamma$  was measured every 30 min until consistent



**Figure 1.** Concentration dependence of surface tension for aqueous solutions of block copolymers  $E_{18}B_{10}H$  (unfilled symbols) and  $E_{18}B_{10}M$  (filled symbols) at the temperatures indicated. The data points are shifted on the ordinate scale as described in the text.

**Table 1. Critical Micelle Concentrations and Surface Tensions for Aqueous Solutions of Hydroxy- and Methoxy-Ended  $E_{18}B_{10}$  Copolymers<sup>a</sup>**

$T/^\circ\text{C}$	$\log(\text{cmc}/\text{g dm}^{-3})$ (both copolymers)	$\text{cmc}/$ $\text{g dm}^{-3}$	$\gamma_{\text{cmc}}/\text{mN m}^{-1}$ $E_{18}B_{10}H$	$\gamma_{\text{cmc}}/\text{mN m}^{-1}$ $E_{18}B_{10}M$
12	-0.96	0.11		
20	-1.10	0.08	32.5	31.8
30	-1.20	0.06	31.5	30.7
40	-1.40	0.04	30.7	29.9
50	-1.53	0.03	29.8	28.8

<sup>a</sup> Estimated uncertainties:  $\log(\text{cmc}) \pm 0.05$ ,  $\gamma_{\text{cmc}} \pm 0.5 \text{ mN m}^{-1}$ .

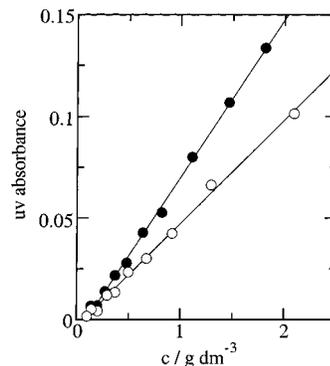
readings were obtained. Thereafter, the temperature was raised and the procedure repeated. Before using a new solution, the ring was washed successively with dilute HCl and water. The accuracy of measurement was checked by frequent determinations of the surface tension of pure water.

**2.3. Dye Solubilization.** The general method was that described Alexandridis et al.,<sup>10</sup> but with the particular procedures used recently in our laboratory.<sup>11</sup> In this method, a Cary 1E UV/vis spectrometer with temperature controller was used to obtain UV spectra of copolymer solutions (prepared as described in section 2.2) containing the hydrophobic dye DPH (1,6-diphenyl-3,5-hexatriene) at a concentration of  $0.008 \text{ mmol dm}^{-3}$ . Solutions covering a range of concentrations were held at  $12 \pm 0.2 \text{ }^\circ\text{C}$ .

**2.4. Specific Viscosity.** Flow times of copolymer solutions were measured in a Schott Geräte AVS 310 unit equipped with an Ubbelohde capillary viscometer. Density and kinetic energy correction were made, solution densities being measured using a digital densimeter (Anton Paar, model DMA 58). Temperature was controlled to  $\pm 0.02 \text{ }^\circ\text{C}$ . Each solution was thermally equilibrated for at least 20 min prior to measurement, and average flow times were calculated for four consecutive measurements before being converted to specific viscosities.

### 3. Results and Discussion

**3.1. Critical Micelle Concentration.** Plots of surface tension against logarithm of concentration for aqueous solutions of the two copolymers are shown in Figure 1. For clarity, the data points for 20, 30, and 40  $^\circ\text{C}$  were shifted on the ordinate scale by 6, 4, and 2  $\text{mN m}^{-1}$ , respectively. To emphasize the correspondence of the cmc's for the two systems, the data sets for each temperature were further shifted until they superimposed. The actual values of the surface tension in the plateau region after the cmc ( $\gamma_{\text{cmc}}$ ) are listed in Table 1. Within the error of determination it is clear that the two copolymers have very similar values of the cmc.



**Figure 2.** Concentration dependence of the absorbance (356 nm) of DPH solubilized at  $12 \text{ }^\circ\text{C}$  in aqueous solutions of copolymers (○)  $E_{18}B_{10}H$  and (●)  $E_{18}B_{10}M$ .

Judging from the data points below the cmc, values of  $d\gamma/d\ln(c)$  are consistently lower for  $E_{18}B_{10}M$  (filled symbols) compared with  $E_{18}B_{10}H$  (unfilled symbols), indicating that the surface excess concentration ( $\Gamma$ ) in the Gibbs monolayer is lower for  $E_{18}B_{10}M$ . A lower value of  $\Gamma$  would not be expected for the more polar solute; however, the difference is slight and not outside possible experimental error deriving from minor differences in block lengths between the two samples (see section 2.1).

It was not possible to fit each data set with two straight lines without considerable deviation in the region of the cmc. Such deviation can be attributed to the distribution of block lengths in the copolymer, similar effects being commonly found in the surface tension curves of EB copolymers with short B blocks<sup>3</sup> and for many commercial block copolymers of ethylene oxide and propylene oxide.<sup>12,13</sup> When comparison has been made with other methods which measure directly the presence of micelles, such as light scattering or dye solubilization, it is found that the traditional method of analysis of surface tension data with two straight lines underestimates the cmc.<sup>3,12,13</sup> Fair agreement between methods is obtained if the cmc is equated with concentration at which a constant value of the surface tension is obtained, i.e., a value indicative of a full Gibbs monolayer. Accordingly, the cmc was defined in this way, the values obtained being listed in Table 1. A consistent small dip in the data points for copolymer  $E_{18}B_{10}M$  at concentrations just above the cmc is probably caused by a small residue of impurity left from the methylation process, but the effect is within the scatter of the data.

The cmc at  $12 \text{ }^\circ\text{C}$  was determined by the dye solubilization method. Absorptions at 356 nm (i.e., the wavelength of maximum absorption) were extrapolated to zero absorbance, as shown in Figure 2. The average value of the cmc obtained for the two copolymers is listed in Table 1.

A value of  $\log(\text{cmc}/\text{g dm}^{-3}) = -1.45$  was obtained previously for  $E_{18}B_{10}H$  in aqueous solution at  $25 \text{ }^\circ\text{C}$ .<sup>3</sup> In fact, the raw surface tension data from that experiment are in satisfactory agreement with present results, the lower value of the cmc being derived by drawing two straight lines through the data.<sup>5</sup> The related copolymer,  $E_{24}B_{10}$ , has  $\log(\text{cmc}/\text{g dm}^{-3}) = -1.63 \pm 0.1$  at  $40 \text{ }^\circ\text{C}$ , in agreement with present results.<sup>14</sup> The values of  $\gamma_{\text{cmc}}$  listed in Table 1 are typical of those published for diblock and triblock E/B copolymers with B blocks of similar length, both in their decrease with temperature and in their general level.<sup>5,14,15</sup>

**Table 2. Micelle Association Numbers ( $N_w$ , from Static Light Scattering) and Hydrodynamic Radii ( $r_h$ , from Dynamic Light Scattering) for E<sub>18</sub>B<sub>10</sub> Copolymers in Aqueous Solution<sup>a</sup>**

copolymer	$T/^\circ\text{C}$	$N_w$	$r_h/\text{nm}$
E <sub>18</sub> B <sub>10</sub> H	25	70	6.3
	40	110	6.5
E <sub>18</sub> B <sub>10</sub> M	20	88	6.1
	30	108	5.9
	40	440	13.6

<sup>a</sup> Data from ref 6.

**3.2. Thermodynamics of Micellization.** For closed association of a block copolymer (A) to micelles ( $A_N$ ) with a narrow distribution and average association number  $N$ , the equilibrium expressed per mole of molecules is



and the equilibrium constant is given by<sup>16</sup>

$$K_c = [A_N]^{1/N}/[A] \quad (2)$$

where concentrations are expressed in mol dm<sup>-3</sup>. At the cmc and for large  $N$

$$K_c = 1/\text{cmc} \quad (3)$$

Given that this condition is met, and Hall in his detailed study of associating systems suggests  $N > 50$ ,<sup>17</sup> then the standard Gibbs energy of micellization is obtained without significant error from

$$\Delta_{\text{mic}}G^\circ = -RT \ln K_c = RT \ln(\text{cmc}) \quad (4)$$

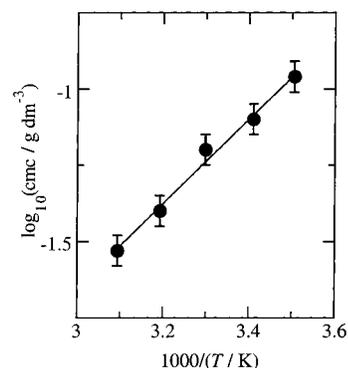
and the standard enthalpy of micellization is obtained by applying the van't Hoff equation as

$$\Delta_{\text{mic}}H^\circ = RT^2 d \ln(\text{cmc})/d(1/T) \quad (5)$$

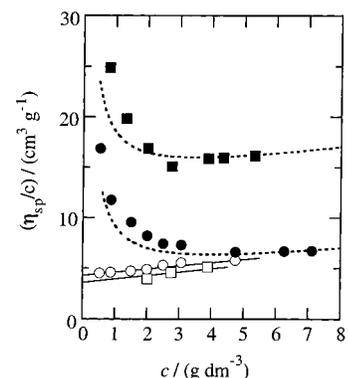
The process referred to is copolymers chains in their standard state of ideally dilute solution at unit concentration (1 mol dm<sup>-3</sup>) going to copolymer chains in the micellar state. (Within the logarithmic terms, dimensionless values are relative to 1 mol dm<sup>-3</sup>.)

The copolymers have been studied previously by static light scattering, and values of the mass-average association number,  $N_w$ , have been determined over the temperature range 25–40 °C, as summarized in Table 2. As required for eq 3 to be valid, the values of  $N_w$  are large, although they do change markedly with temperature, an effect which is discussed further in section 3.3. As expected when  $N_w$  is large, no effect of the variation of  $N_w$  with temperature is seen in the van't Hoff plot shown in Figure 3. The slope of that plot gives  $\Delta_{\text{mic}}H^\circ = 26 \pm 2 \text{ kJ mol}^{-1}$ . This value is in good agreement with  $\Delta_{\text{mic}}H^\circ = 30 \text{ kJ mol}^{-1}$  found for copolymer E<sub>24</sub>B<sub>10</sub><sup>14</sup> and fits well within the pattern established for other diblock E/B copolymers investigated in this way.<sup>2</sup>

**3.3. Micelle Shape and Specific Viscosity.** Small-angle neutron scattering has been used to show that copolymer E<sub>18</sub>B<sub>10</sub>H forms spherical micelles at temperatures below 50 °C and wormlike micelles above.<sup>4</sup> It has also been inferred from light scattering measurements that the sphere-to-worm transition for E<sub>18</sub>B<sub>10</sub>M occurs



**Figure 3.** Van't Hoff plot for micellization in aqueous solutions of copolymer E<sub>18</sub>B<sub>10</sub>. Data points for copolymers E<sub>18</sub>B<sub>10</sub>H and E<sub>18</sub>B<sub>10</sub>M cannot be distinguished.



**Figure 4.** Concentration dependence of reduced specific viscosity for aqueous solutions of block copolymers E<sub>18</sub>B<sub>10</sub>H (circles) and E<sub>18</sub>B<sub>10</sub>M (squares). Unfilled symbols denote 20 °C, and filled symbols denote 40 °C. The dashed curves are calculated using eq 4.

below 40 °C. This evidence is contained in Table 2, where the values of the association number and the hydrodynamic radius for copolymer E<sub>18</sub>B<sub>10</sub>M are remarkably high at 40 °C. To check that the micelles formed in this work had the same temperature dependence of geometry, specific viscosities were determined over a range of concentrations, and reduced values were extrapolated to zero concentration to obtain the intrinsic viscosity.

Values of the reduced specific viscosity are plotted against concentration in Figure 4. For solutions at 20 °C, values of  $\eta_{sp}/c$  are similar for the two copolymers, and the intercepts of the straight line plots give values of the intrinsic viscosity in the range  $[\eta] = 3\text{--}4 \text{ cm}^3 \text{ g}^{-1}$ . These values are near to those of hard spheres, given by Einstein's equation as  $[\eta] = 2.5/\rho$ , where  $\rho$  is the density of the material of the sphere, which in our case is approximately  $1 \text{ g cm}^{-3}$ . Detailed consideration of the micelle radii obtained from light scattering confirms that these spherical micelles are slightly soft spheres.<sup>6</sup>

The specific viscosities measured at 40 °C show a complicated dependence on concentration. It is possible that values of  $\eta_{sp}/c$  at low concentrations are affected by adsorption of copolymer on the capillary wall. Adsorption will be enhanced at the higher temperature because water becomes a poorer solvent for the copolymer as temperature is increased, the effect being particularly severe for the present samples with 48 wt % B in the copolymer. The same reduction in solubility

with increase in temperature drives the sphere-to-worm transition. The flow time in a capillary viscometer is sensitive to the fourth power of the radius, and for a narrow capillary, adsorption may override the reduction in solution concentration to give a measurable increase in flow time. As pointed out by Ohrn in considering this effect in polymer solutions,<sup>19</sup> the apparent value of the reduced specific viscosity,  $(\eta_{sp}/c)^*$ , is related to the true value by

$$(\eta_{sp}/c)^* = \eta_{sp}/c + \Delta \quad \Delta \approx (\eta_r/c)(4a/r) \quad (6)$$

where  $\eta_r$  is the relative viscosity,  $r$  the capillary radius, and  $a$  the thickness of the adsorbed layer. Given that  $\eta_r \approx 1$  at low concentrations and  $r = 0.315$  mm for the viscometer used, and assuming realistic concentration dependences for the underlying reduced specific viscosities, the data for the copolymers in solution at 40 °C can be fitted approximately (see the dashed curves in Figure 4) assuming that  $a = 0.0004$  mm. Since the contour length of the copolymer is only 10 nm, this value of  $a$  implies multilayer adsorption on glass at this temperature. Values of  $[\eta]$  used in the calculations were  $3.8 \text{ cm}^3 \text{ g}^{-1}$  (E<sub>18</sub>B<sub>10</sub>H) and  $13.1 \text{ cm}^3 \text{ g}^{-1}$  (E<sub>18</sub>B<sub>10</sub>M).

Even if the explanation of the concentration dependence in terms of adsorption is questionable, it is clear from the data at the higher concentrations (see Figure 4) that intrinsic viscosities of the magnitude derived will apply. The value of  $[\eta] = 3.8 \text{ cm}^3 \text{ g}^{-1}$  indicates spherical micelles, and as required, the data points for copolymer E<sub>18</sub>B<sub>10</sub>H in solution at 40 °C converge onto the line established at 20 °C as the concentration is increased. Equivalent hydrodynamic properties at the two temperatures are expected for spherical micelles of this type,<sup>1,2</sup> as can be seen in the values in Table 2 of the hydrodynamic radii obtained previously from dynamic light scattering.<sup>6</sup> The higher value of  $[\eta] \approx 13 \text{ cm}^3 \text{ g}^{-1}$  found for copolymer E<sub>18</sub>B<sub>10</sub>M in solution at 40 °C is consistent with wormlike micelles, in agreement with the light scattering results.

Taking previous (Table 2) and present data together, it is confirmed that the geometry of the micelles of copolymer E<sub>18</sub>B<sub>10</sub>M changes significantly between 30 and 40 °C. Accordingly, for this copolymer the values

of the cmc measured for this copolymer at 40 and 50 °C must relate to wormlike micelles, while those measured in the range 12–30 °C must relate to spherical micelles. The results show that this change in micelle geometry does not change the thermodynamics of micellization.

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