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Association behaviour of diblock copoly(oxyethylene/oxybutylene) in aqueous solution determined by eluent gel permeation chromatography

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Abstract

The association behaviour of a diblock copolymer of ethylene oxide and 1,2-butylene oxide, $E_{40}B_{10}$ [E denotes oxyethylene, B denotes oxybutylene, and the subscripts denote number-average block length in chain units] in aqueous solution was studied using eluent gel permeation chromatography (EGPC) over the temperature range of 9–50 °C. In the experiment a solution of $E_{40}B_{10}$ (0.5 wt%) was used as an eluent, into which a solution of higher concentration was injected. The critical temperature for micelle formation was approximately 10 °C. With allowance made for adsorption in the EGPC system, the extent of micellisation was determined over the full temperature range and compared with the van't Hoff prediction and with related data for triblock oxyethylene/oxypropylene copolymer F127. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A block copolymer dissolved in water that is a non-solvent for one of its components but a good solvent for its other may form micelles. The application of conventional gel permeation chromatography (GPC) with water as solvent to such a solution is complicated by the molecule/micelle equilibrium [1]. During the elution the injected solution is diluted and the micelles dissociate. A second flaw of conventional GPC applied to such a system is the adsorption of copolymer molecules onto the packing [2].

Eluent gel permeation chromatography (EGPC), which is a form of differential GPC [3], provides a way of studying associating systems. In EGPC, an eluent of block polymer solution is injected with a higher concentration solution of the copolymer. The working mechanism of EGPC is based on following premises:

(i) For a given block copolymer solution at a given temperature, the equilibrium between micelles and molecules is determined by its concentration. The injectant is diluted as it passes through the EGPC system and its concentration approaches that of the eluent. At equilibrium at the point of elution the ratio of micelles to molecules in the injectant is essentially the same as that in the eluent.
(ii) In passing through the EGPC system, the excess of micelles and molecules in the injectant separate because of their different sizes.
(iii) With a refractive index detector, the peak areas in the EGPC signal relate directly to the mass concentrations of micelles and molecules in the eluent.

The injectant is used only to probe the equilibrium state of the eluent. In other words, the information derived describes the eluent and is independent of the injectant concentration, provided the injectant concentration does not greatly exceed that of the eluent [4].

The association behaviours of water soluble copolymers of ethylene oxide and propylene oxide have been studied extensively by many methods [5–7], including EGPC [4,8]. Certain laboratories, particularly our own, have examined corresponding oxyethylene–oxybutylene block copolymers [7,9]. Because the hydrophobicity of an oxybutylene unit is six-times that of an oxypropylene unit, comparable association properties can be achieved at much lower molar masses [7]. Another advantage is that the chain transfer reaction

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which is a source of impurities in copolymers based on propylene oxide is not a problem in the laboratory polymerisation of 1,2-butylene oxide [9,10]. The work presented in this paper was carried out using diblock copolymer $E_{40}B_{10}$, where E denotes an oxyethylene unit, OCH_2CH_2, B denotes an oxybutylene, $OCH_2CH(C_2H_5)$, and the subscripts denote number-average block lengths in chain units.

2. Experimental methods

Two samples of copolymer $E_{40}B_{10}$ were made available from other work [11,12]. Their compositions were identical within the experimental error of determination. Both were prepared by the sequential oxyanionic polymerisation of ethylene oxide followed by 1,2-butylene oxide. All reagents were distilled and dried before use and vacuum line and ampoule techniques were used to minimise initiation by moisture at any stage. The polymerisations were monitored and the copolymers characterised by GPC for distribution width ($M_w/M_n = 1.04$), and by ^{13}C NMR for number-average molar mass ($M_n = 2480$ g mol^{-1}) and composition (71 wt% E) as well as confirmation of block architecture and sample purity. Details can be found elsewhere [11,12].

Two EGPC systems were used in the work, referred to as System A (Shenzhen Group) and System B (Manchester Group). Both systems used two 30 cm columns packed with TSK gel-PW (G4000 and G3000), refractive index detection, eluent pumped at 0.5 cm^3 min^{-1}, and injection of sample solution via 0.1 cm^3 loop. In each case calibration was performed using poly(oxyethylene) standards. Column temperature was controlled either by a stainless-steel block thermostat (System A, ±0.5 °C) or by a stirred-air temperature-controlled oven (System B, ±0.2 °C). The column sets differed somewhat in properties, that in System B having the better resolution. Results were recorded by strip-chart recorder (System A) or by on-line computer (System B).

In the EGPC experiments, the eluent was prepared by dissolving 0.5 wt% $E_{40}B_{10}$ in distilled water. The injectant was prepared by dissolving $E_{40}B_{10}$ in the eluent with an excess concentration of either 0.6 wt% (System A) or 0.2 wt% (System B). The experiments were carried out over a temperature range of 9–50 °C (System A) or 25–50 (System B).

3. Results and discussion

3.1. EGPC curves

Fig. 1 shows EGPC curves obtained using the two systems. We show examples of the curves obtained at low temperature using System A (Fig. 1(a)) and, because of the better resolution, those obtained at high temperature using System B (Fig. 1(b)). The elution volumes (V) and peak widths reflect this difference in resolution, but with due allowance made (by reference to the calibration curves) results for the two systems were seen to be essentially identical.

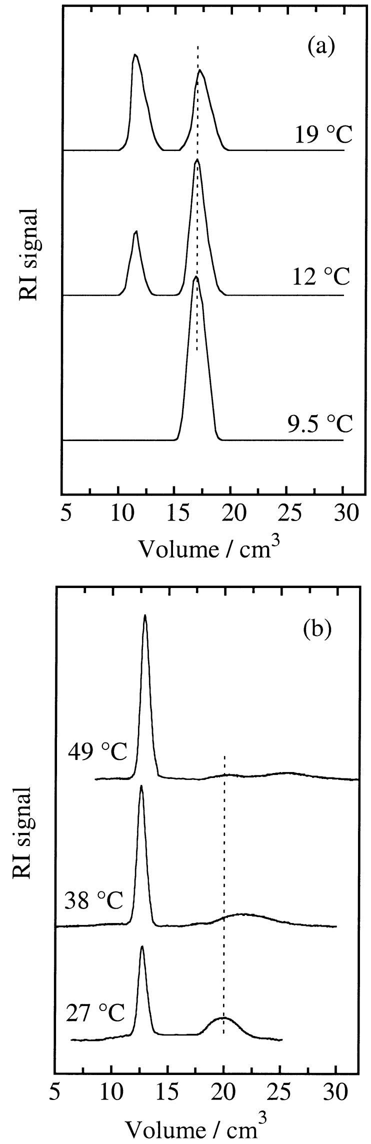

Fig. 1. EGPC curves for 0.5 wt% aqueous solutions of $E_{40}B_{10}$. (a) System A, 0.6 wt% excess concentration in the probe. (b) System B, 0.2 wt% excess concentration in the probe. Temperatures in °C are indicated. The ordinate scales and zeros are arbitrary.

In Fig. 1(a), the single peak at $V = 16.7$ cm^3 in the EGPC curve obtained with the eluent at 9.5 °C is assigned to $E_{40}B_{10}$ molecules. This was confirmed by noting that its elution volume corresponds to a molar mass of approximately 2000 g mol^{-1} on the poly(oxyethylene) calibration for System A. The single molecules peak indicates that 9.5 °C is below the critical micelle temperature (cmt) of $E_{40}B_{10}$ in 0.5 wt% solution. The second peak at $V = 11.8$ cm^3 observed in the EGPC curve obtained with the eluent at 12 °C corresponds to a molar mass of 18 000 g mol^{-1} and is assigned to micelles. The co-existence of micelles and molecules at 12 °C confirms that the cmt has been exceeded.

These and related experiments place the cmt of the 0.5 wt% $E_{40}B_{10}$ solution at approximately 10 °C.

As is well known [7] an increase in temperature favours the formation of micelles in solutions of E_mB_n copolymers. This is clearly seen in the EGPC curves in Fig. 1. As the temperature was increased from 12 to 19 °C (Fig. 1(a)) and further to 49 °C (Fig. 1(b)) the micellar peak became more pronounced. The position of the micelle peak is essentially independent of temperature.

The behaviour of the molecules peak is more complex. The dotted lines in Fig. 1 draws attention to two features of the EGPC curves in the region of the molecules peak. In Fig. 1(a) (System A) a small shift of 0.2 cm^3 to a higher value of the elution volume is apparent in the curve for the eluent at 19 °C compared to those at lower temperature. In Fig. 1(b), the shift of peak maximum for eluent at 38 °C compared to 27 °C is seen to be significantly larger (1.5 cm^3), while the curve for the eluent at 49 °C clearly shows two peaks with maxima at $V \approx 20$ cm^3 and $V \approx 25.5$ cm^3. This last observation is emphasised in the enlarged plot of the EGPC curve for the eluent at 49 °C shown in Fig. 2. The shift in the molecules peak (or a part of the molecules peak) with temperature can be assigned as an effect of adsorption at the surface of the column packing which delays the emergence of a proportion of the molecules. The peak at $V \approx 20$ cm^{-3} is not shifted by increase in temperature, and is assigned to a small weight fraction of the copolymer which neither micellises nor adsorbs, possibly poly(oxyethylene) impurity which was not detected by ^{13}C NMR, but more likely copolymer at the extreme of the composition distribution with high wt% E, i.e. with long E blocks and short B blocks.

3.2. Micelle radius

The elution volume of a solute in GPC depends on its hydrodynamic volume, v_h [13,14]. This is equally true for micelles in EGPC. Calibration of the EGPC system with poly(oxyethylene) standards in pure water at 25 °C enables calculation of v_h. For a given value of V, an average molar mass (M) can be read off the calibration curve and used to calculate the corresponding intrinsic viscosity $[\eta]$ of poly (oxyethylene) in water at 25 °C using Ref. [15]

$$[\eta]\ (\mathrm{cm^3\ g^{-1}}) = 0.0125M^{0.78} \tag{1}$$

where M is in g mol^{-1}. The Einstein equation then gives v_h

$$v_h\ \mathrm{cm^3} = [\eta]M/2.5N_A \tag{2}$$

where N_A is Avogadro's constant. The elution volume of 12.6 cm^3 found for the micelles in solution at 25 °C in System B leads to $v_h = 2900$ nm^3, whence a hydrodynamic radius $r_h = 8.8$ nm. This value is in reasonable agreement with those obtained by dynamic light scattering for $E_{40}B_{10}$ in 0.5 wt% solution, i.e. 8.5 and 7.3 nm^3 at 20 and 30 °C, respectively [11].

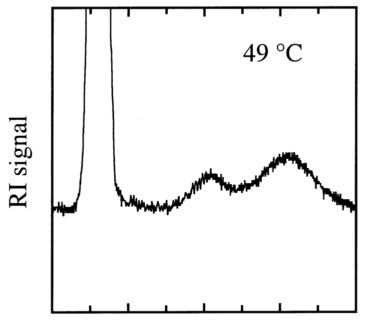

Fig. 2. Expansion of the EGPC curve of an 0.5 wt% aqueous solution of $E_{40}B_{10}$ at 49 °C.

3.3. Extent of micellisation and the standard enthalpy of micellisation

The extent of micellisation can be calculated from the relative areas of the peaks in the EGPC curve provided only that the specific refractive index increments (dn/dc) are equal for the solutes whether they are in molecular or micellar form. This conventional assumption is supported in the present case by the observation that the sum of the peak areas is the same irrespective of the extent of micellisation. The weight fraction of the copolymer in micellar form (w_{mic}) obtained in this way is plotted against temperature in Fig. 3.

A complication is the effect of the equilibrium associated with adsorption. Judged by the shift in elution volume, adsorption is a important factor at eluent temperatures above 25 °C, and increases in importance as temperature is raised. In the present experiments, the adsorption peak was resolved (as in Fig. 2) only using System 2 and at eluent temperatures above 40 °C. For these experiments, carried out with eluent at 43, 46 and 49 °C, the adsorption peak was approximately 15% of the total signal. It was assumed that the adsorbed copolymer reduced the amount available

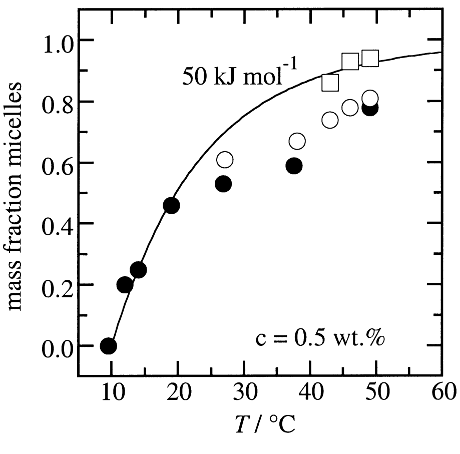

Fig. 3. Temperature dependence of the weight fraction of $E_{40}B_{10}$ in micellar form in 0.5 wt% aqueous solution. (●) System A, (○) System B, (□) System B corrected for adsorption. The curve through the data points is calculated using Eqs. (4) and (5) with $\Delta_{\mathrm{mic}}H^0 = 50$ kJ mol^{-1}.

for micellisation in the same proportion, and appropriately corrected values of w_{mic} are also plotted in Fig. 3.

Assuming micelles with fairly high association numbers (and noting that static light scattering measurements indicate values of $N_{\text{w}} = 20\text{–}50$ in the temperature range 20–45 °C [11]), the standard enthalpy of micellisation ($\Delta_{\text{mic}}H^0$) can be used in the van't Hoff equation to calculate the temperature dependence of the critical micelle concentration [5–7]: i.e.

$$\Delta_{\text{mic}}H^0 = R[\text{d}\ \ln(\text{cmc})/\text{d}(1/T)] \tag{3}$$

or in integrated form

$$\ln[\text{cmc}(T)/0.5] = (\Delta_{\text{mic}}H^0/R)[(1/T) - (1/283)] \tag{4}$$

where we use our experimental result that cmc = 0.5 wt% at 10 °C to enable calculation of cmc(T). If the copolymer were uniform, i.e. a single molecular species, then

$$w_{\text{mic}} = 1 - w_{\text{mol}} = 1 - [\text{cmc}(T_1)/0.5] \tag{5}$$

The curve in Fig. 3 shows that this approximation gives a reasonable fit to the EGPC data at low eluent temperatures if $\Delta_{\text{mic}}H^0 = 50\ \text{kJ mol}^{-1}$. Deviation from the calculated curve is seen at 27 °C and above, i.e. in the temperature range where significant effects of adsorption were detected. Correction for the effect of adsorption, as described earlier, brings the points onto the curve. Of course, the calculation based on Eq. (5) ignores the composition and chain-length distributions in the copolymer, and the value of $\Delta_{\text{mic}}H^0$ can be questioned on that account. However, values of $\Delta_{\text{mic}}H^0$ of that order have been found for other diblock and triblock E/B copolymers [7].

3.4. Comparison with other copolymers

EGPC curves and derived values of w_{mic} have been reported for other copolymers, including diblock and triblock oxyethylene/oxypropylene copolymers [4,8,16–19]. In Fig. 4 comparison is made of present results with values of w_{mic} obtained for a 0.06 wt% solution of commercial copolymer F127 [$E_{93}P_{44}E_{93}$, P denotes oxypropylene, $OCH_2CH(CH_3)$] using System A [4]. The wide temperature range seen for the micellisation of $E_{40}B_{10}$ contrasts markedly with the much narrower range for copolymer F127. The curve fitting the data for F127 was calculated as described in Section 3.3 but with $\Delta_{\text{mic}}H^0 = 150\ \text{kJ mol}^{-1}$. A value twice that of, $\Delta_{\text{mic}}H^0 \approx 300\ \text{kJ mol}^{-1}$, was obtained for the same sample by a conventional van't Hoff plot of data from light scattering and surface tension [20]. In part this difference arises because the EGPC data are uncorrected for adsorption [4]. Another consideration is the known inhomogeneity of the F127 sample [20]. Even so, the data in Fig. 4 provides a good illustration of the different temperature sensitivities of the association properties of E/B and E/P block copolymers in water.

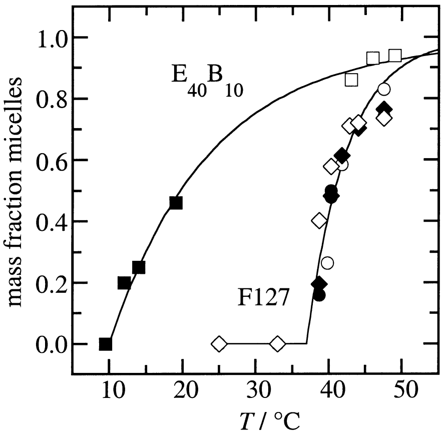

Fig. 4. Comparison of the temperature dependences of weight fraction of micelles for 0.5 wt% $E_{40}B_{10}$ solution and 0.06 wt% F127 solution. The data points are for the $E_{40}B_{10}$ solution in (■) System A and (□) System B (corrected for adsorption) from present work, and for the F127 solution in System A probed with various excess concentrations in the range 0.1–1 wt% (see Ref. [4] for details). The curves through the data points are calculated using Eqs. (4) and (5) with $\Delta_{\text{mic}}H^0 = 50\ \text{kJ mol}^{-1}$ ($E_{40}B_{10}$) and $150\ \text{kJ mol}^{-1}$ 9F127).

Acknowledgements

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