Thermodynamic Properties of Diblock Copolymers of Ethylene Oxide and Styrene Oxide in Aqueous Solution

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Apparent molal volumes and adiabatic compressibilities of aqueous solutions of block copolymers $E_{45}S_{10}$, $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$ (E = oxyethylene, S = oxyphenylethylene, and the subscripts denote block lengths) have been determined by density and ultrasound velocity measurements. Values of the critical micelle concentrations (cmc's) were impossible to evaluate by ultrasound velocity because of their low concentration motivated by the hydrophobicity of the oxyphenylethylene block. Copolymer $E_{45}S_{10}$ was studied in the temperature range of 20−50 °C. Its cmc and the enthalpy of demicellization have been also determined by isothermal titration calorimetry at 30 °C. The low enthalpy values that are obtained are attributed to the hydrophobicity of the S block being tightly coiled in the molecular state in water. The thermodynamic aggregate properties of copolymers $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$ were determined from density and calorimetry at 30 °C.

1. Introduction

Block copoly(oxyalkylene) polymers comprising a hydrophilic poly(oxyethylene) block and a second hydrophobic block have interesting properties, including micellization in dilute solution and the gelation of concentrated micellar solutions.[1,2] Above a critical concentration, copolymer molecules form aggregates, which have been found to be useful in a number of applications as associative thickeners for surface coatings and the solubilization of sparingly soluble substances. Thermodynamic parameters are the key to effective physical and chemical processing. Furthermore, from an understanding of synthetic polymers aggregation, one can possible gain better insight into the more intricate behavior of biopolymers in solution.

A diblock copolymer of ethylene oxide and styrene oxide is denoted E_mS_n, where E denotes the oxyethylene unit, OCH_2CH_2, S denotes the oxyphenylethylene unit, $OCH_2CH(C_6H_5)$, and the subscripts *m* and *n* denote the number-average block lengths in repeat units. Booth et al. in different studies[3−7] of the family of diblock copolymers of ethylene and styrene oxides have shown that temperature changes do not promote micellization and that these copolymers have low values of the cmc and enthalpy of micellization, $\Delta_{mic}H^0$, which is consistent with the high hydrophobicity of the oxyphenylethylene block. They have also shown that the cores of ES copolymers micelles have sufficient mobility at 25 °C to solubilize aromatic drugs readily.[7] Previous work on the micellization and micelle properties of diblock copolymers[8] has involved copolymers $E_{45}S_{10}$, $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$. The results of surface tension, light scattering, and rheometry provided a broad account of the association behavior of the diblock copolymers in aqueous solution and indicated that the sequence of polymerization, indicated by ES or SE, does not significantly affect the measured properties. These techniques have been used to characterize the association aspects of these copolymers in water, where they aggregate as the classical surfactants do. It was demonstrated that these diblock copolymers have at room temperature very low values of the critical micelle concentration (cmc) (i.e., 5.4×10^{-6} mol dm^{-3} for $E_{45}S_{10}$) and that within the experimental error the values of the cmc do not change in the temperature range of 20−40 °C. As far as thermodynamic is concerned, there is scarce data based on direct measurements (density, isentropic compressibility, and enthalpy). All of the properties of micellization have been almost obtained from the dependence of the cmc on temperature. This approach is not very precise and is quite limited because it usually implies that the size and shape of micelles do not change with temperature. To the best of our knowledge, no previous work has been found in the literature reporting the volume and compressibility properties of block copolymers containing E and S blocks. The literature search revealed few studies of this type on pluronics, mainly with triblock structure, that contain oxypropylene units as the hydrophobic core.[9−21]

The sound velocity is one of the properties required to obtain the compressibility coefficient, and it is very sensitive to the onset of aggregation processes induced by changes in temperature or composition. Apparent molal volumes, expansibilities, and adiabatic molal compressibilities of copolymer $E_{45}S_{10}$ were obtained by using density and speed-of-sound measurements in the temperature range of 20−50 °C. Its cmc and the enthalpy of demicellization have also been determined by isothermal titration calorimetry at 30 °C. We have also examined the apparent molal volumes, enthalpies of demicellization, and adiabatic molal compressibilities of copolymers $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$ at 30 °C.

2. Experimental Section

2.1. Copolymers. Copolymers were prepared by the oxianionic polymerization of styrene oxide followed by ethylene oxide. The synthesis was described in detail by Crothers et al.[8] Table 1 shows the molecular characteristics of the copolymers. Water was double distilled and degassed before use.

2.2. Equipment. *Density and Ultrasound Velocity.* Measurements were carried out using a commercial density and

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TABLE 1: Molecular Characteristics of the Copolymers[a]

	M_n/g mol^{-1} (NMR)	wt % S (NMR)	M_w/M_n (GPC)	M_w/g mol^{-1}
$E_{45}S_{10}$	3180	37.7	1.04	3310
$S_{15}E_{63}$	4600	39.7	1.04	4780
$S_{17}E_{65}$	4940	42.1	1.04	5140
$S_{20}E_{67}$	5300	44.4	1.05	5570

[a] Estimated uncertainty: M_n to ±3%; wt % S to ±1%, M_n/M_w to ±0.01. M_w was calculated from M_n and M_w/M_n.

ultrasound velocity measurement apparatus (Anton Paar DSA 5000 densimeter and sound velocity analyzer) equipped with a new-generation stainless steel cell. Temperature control was maintained by the Peltier effect with a resolution of 0.001 °C, giving rise to uncertainties in density of ca. ±1 × 10^{-6} g cm^{-3}. Errors in ultrasound velocity measurements arise mainly from variations in temperature, and in this study the resolution was ±10^{-2} m s^{-1}. Solutions were prepared with double-distilled water by weighing the components to ±0.001 mg using a Mettler AT20 balance. The density and ultrasound velocities of dilute aqueous solutions were measured at 20, 30, 40, and 50 °C. The densimeter was calibrated with water. The density values[22] that were used are 0.998202 g cm^{-3} at 20 °C, 0.995645 g cm^{-3} at 30 °C, 0.992214 g cm^{-3} at 40 °C, and 0.988030 g cm^{-3} at 50 °C.

Calorimetry. Heats of dilution were measured using a VP-ITC titration microcalorimeter from MicroCal Inc. of Northampton, MA. Small aliquots of a stock solution of copolymer at a concentration well above the cmc were injected into a known volume of water (ca. 1 cm^3) held in the cell of the calorimeter, initially to produce a solution below the cmc. Repeated additions of the stock solution gave the heat evolved (Q) as a function of copolymer concentration. In the experiment, a stock solution of concentration 10 g dm^{-3} was added at intervals of 400 s using 6 injections each of 0.5 mm^3 followed by 85 injections each of 3 mm^3.

2.3. Calculations. The apparent molal volume, V_ϕ, of the copolymer in water was calculated by means of the following equation[23]

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \tag{1}$$

where m and M are the molality and molecular weight, respectively, of the copolymer (Table 1), ρ is the density of the solution, and and ρ_0 is the density of water.

The apparent molal expansibility, E_ϕ^i, was calculated using the following equation

$$E_\phi^i = \left(\frac{\partial V_\phi^i}{\partial T}\right)_p \tag{2}$$

where $i = 0$ for monomers and m for aggregates.

Density and ultrasound velocity, u, measurements were combined to calculate isentropic compressibilities, k_S, using the Laplace equation[23]

$$k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \frac{10^6}{\rho u^2} \tag{3}$$

where V, p, and S refer to volume, pressure, and entropy, respectively. The isentropic compressibility coefficient is expressed in bar^{-1} when u is expressed in cm s^{-1} and ρ is expressed in g cm^{-3}.

The isentropic apparent molal compressibility, $K_{\phi(S)}$, can be calculated from ultrasound measurements[24]

$$K_{\phi(S)} = \frac{10^3(k_S - k_S^0)}{m\rho_0} + k_S V_\phi \tag{4}$$

where k_S and k_S^0 are the isentropic coefficients of compressibility of the solution and solvent, respectively.

The change in the partial molal isentropic compressibility of aggregation, $\Delta K_{\phi(S)}$, can be evaluated by

$$\Delta K_{\phi(S)} = K_{\phi(S)}^m - K_{\phi(S)}^0 \tag{5}$$

where $K_{\phi(S)}^m$ is the apparent molal adiabatic compressibility of the aggregate and $K_{\phi(S)}^0$ is the isentropic apparent molal compressibility at infinite dilution.

3. Results and Discussion

In the present work, two sets of experiments were carried out in order to describe thermodynamic properties of aqueous oxyphenylethylene/oxypolyethylene diblock copolymers. For the first set, densities and ultrasound measurements for copolymer $E_{45}S_{10}$ at different concentrations were made at 20, 30, 40, and 50 °C to study the variation in apparent molal volumes, compressibilities, and expansibilities with temperature. The enthalpy of demicellization has also been determined by isothermal titration calorimetry (ITC) at 30 °C. For the second set of experiments, density, ultrasound, and ITC measurements at 30 °C were carried out for copolymers $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$ to analyze the effect of the hydrophobic oxyphenylethylene block length on the association behavior of this set of copolymers. Comparison is also made with copolymer $E_{45}S_{10}$. To obtain reliable volume data, it is necessary to measure densities with great precision. By differentiating eq 1 with respect to m at constant ρ, one obtains a probable error in V_ϕ of $(M_2/\rho - V_\phi)(\delta m/m)_p$ that gives a maximum error of ±0.008 cm^3 mol^{-1} for diblock copolymer $S_{20}E_{67}$. If eq 1 is now differentiated with respect to ρ at constant m, we obtain a probable error in V_ϕ of $(1000/m\rho_0 + V_\phi)(\delta\rho/\rho)_m$ that will cause a maximum error of about ±0.02 cm^3 mol^{-1} in the range of data measured for the four diblock copolymers.

Solutions observed during the tube inversion tests (concentration range 0−80 wt %) for the four copolymers remained clear to the eye throughout the temperature range investigated in the present work (20−50 °C).[8]

Apparent Molal Volume. Three regions are usually observed in a plot of V_ϕ against c for aqueous solutions of an amphiphilic substance: (i) in a very dilute solution at concentrations below the cmc, the amphiphile property is nearly independent of concentration until the critical concentration, (ii) after the cmc, there is a steep rise in V_ϕ that increases with c up to the upper limit of measurement, where (iii) V_ϕ becomes essentially independent of concentration if the aggregate is monodisperse. The first and third regions are characteristic of monomeric and micellar states, respectively; meanwhile, the second region represents the change from a monomeric to micellar state. In the present representations, only the second and third regions are displayed. The first region has not been detected because its extremely low concentrations affect the calculations of the apparent molal volume by a large error. In copolymer solutions, the cooperativity of aggregation is much less important than in surfactant solutions, and self-aggregation extends over a wide concentration. However, in ES copolymer solutions, the greater hydrophobicity of the oxyphenylethylene block if compared with
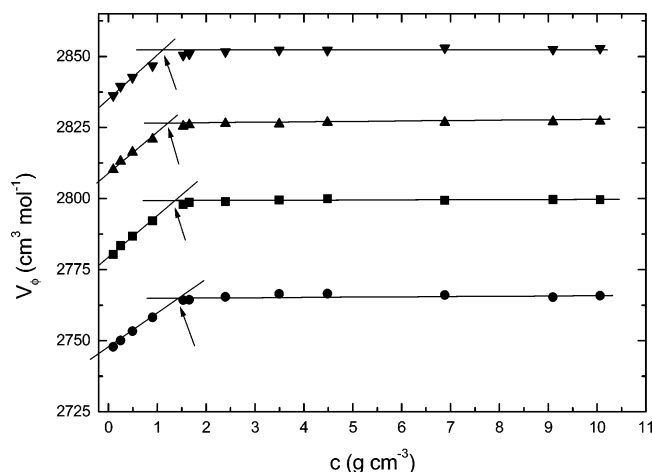
Figure 1. Apparent molal volume, V_ϕ, as a function of concentration c for aqueous solutions of copolymer $E_{45}S_{10}$ at (●) 20, (■) 30, (▲) 40, and (▼) 50 °C. Arrows denote the concentration of stable aggregate formation, c_1.

that of oxypropylene (12:1)[1] considerably reduces the extension of the transition range.

The dependence on the concentration, c, and temperature of the apparent molal volume, V_ϕ, is shown in Figure 1 for copolymer $E_{45}S_{10}$. The plots clearly show a region where V_ϕ is dependent on concentration; beyond that region, at a concentration that can be considered to be the concentration of stable aggregate formation, c_1, V_ϕ tends to a constant value according to the transfer of the copolymer molecule from water to a hydrophobic environment ($c_1 \approx$ 1.41, 1.31, 1.20, and 1.06 g cm^{-3} for 20, 30, 40, and 50 °C, respectively). As can be observed in the Figure, V_ϕ and c_1 are dependent on the temperature. This fact arises from the high hydrophobicity of the oxyphenylethylene blocks, attributable to the S blocks being tightly coiled in their dispersed unimer state so that their hydrophobic interaction with water is small.[6] These results are in agreement with the low enthalpy of micellization found, as can be seen in the Calorimetry section. The dependence on temperature of the apparent volume of the aggregate, V_ϕ^m, shows that the size and shape of the aggregates change with temperature. Booth et al.[25] have shown that micelles of copolymer $E_{17}S_8$ in solution at 30 °C are highly elongated and presumably wormlike and that the micelles in solution at 15 °C are elongated, presumably to a spheroidal form. The increase in the volume of copolymer $E_{45}S_{10}$ with temperature is consistent with a change in shape. There is evidence from experimental work on other systems[26] that solubilization is enhanced if the micelles are cylindrical rather spherical. Apparent molal values at infinite dilution, V_ϕ^0, were obtained as an extrapolated value considering a null value for the cmc. This method of calculation does not allow us to be sure that solute/solute interactions have not been entirely eliminated in the extrapolation. Values for V_ϕ^m were obtained from a linear fitting of the apparent volume above the cmc. Table 2 shows values of V_ϕ^0 and V_ϕ^m.

Whereas V_ϕ^0 reflects water-solute interactions, V_ϕ^m provides information about interactions between hydrated solute molecules. The interactions between aggregates, which stabilize the intermolecular structure of water, are sensitive to changes in temperature, as can be observed in Table 2. The influence of polar and nonpolar groups of a solute in aqueous solution is shown by the variations of V_ϕ^0 with temperature. Table 2 shows that by increasing the temperature V_ϕ^0 and V_ϕ^m increase but the increment is shorter for each temperature increment, showing

TABLE 2: Apparent Molal Volumes at Infinite Dilution, V_ϕ^0, Aggregate Apparent Molal Volumes, V_ϕ^m, Changes in Apparent Molal Volumes upon Aggregation, ΔV_m, and $\partial(\Delta H^0)/\partial p$ of Copolymer $E_{45}S_{10}$[a]

$T/°C$	V_ϕ^0	V_ϕ^m	ΔV_m	$\partial(\Delta H^0)/\partial p$
20	2746.3 ± 0.6	2766.3 ± 0.2	20	1896.2
30	2778.8 ± 0.8	2799.0 ± 0.4	20.2	1899.7
40	2808.7 ± 0.5	2825.9 ± 0.3	17.2	1900.6
50	2834.8 ± 0.3	2851.7 ± 0.2	16.9	1897.7

[a] V_ϕ^0, V_ϕ^m, ΔV_m, and $\partial(\Delta H^0)/\partial p$ are in cm^3 mol^{-1}.

that the extent of water−hydrophobic interaction decreases with temperature. Micelles of copolymer $E_{45}S_{10}$ may have water in the core associated with the hydroxy end groups of the S blocks; this water is released when the temperature is increased. This result agrees with previous results found by Booth et al.[26] for copolymer $E_{17}S_8$.

The change in the partial molal volume upon aggregate formation when a free monomer−copolymer molecule associates into a micelle can be calculated as $\Delta V_m = V_\phi^m - V_\phi^0$. The results so obtained are shown in Table 2, where it can be observed that the increasing the temperature from 20 to 30 °C has very little effect on ΔV_m; however, the increment from 30 to 50 °C reduces the value of ΔV_m. This effect is due to hydrophobic bonding in the aggregation process.[27,28]

The apparent molal volume increases with temperature; therefore, the apparent molal expansibility is positive ($E_\phi^0 = 2.9$ cm^3 mol^{-1}K^{-1} and $E_\phi^m = 2.8$ cm^3 mol^{-1}K^{-1}). E_ϕ^i ($i = 0$ and m for monomers and aggregates, respectively) values were calculated from linear plots of V_ϕ^i as a function of temperature. Eagland and Crowther[29] suggest that the positive increase in the expansibility agrees with a drop in the hydration of hydrophobic moieties. The main effect on going from free monomers to micelles is the loss of hydrophobic hydration. E_ϕ^i data cannot be interpreted unambiguously because the difference between the premicellar and micellar regions is not very large. Both values are positive, indicating the predominance of the hydrophobic hydration of water molecules around the solute molecules. The slightly higher values for the expansibility of the monomer in solution suggest a little stronger hydration of the monomer when free in solution than when in the aggregate, confirming the volumetric and calorimetric results.

Accurate volume and expansibility data can provide information regarding the effect of pressure on the enthalpy because

$$\frac{\partial H}{\partial p} = V - T\frac{\partial V}{\partial T} \qquad (6)$$

Considering the solution at infinite dilution, if V_ϕ^0 and E_ϕ^0 are inserted into this equation, then the enthalpy term will be the partial heat of solution at infinite dilution, ΔH^0. Table 2 shows $\partial(\Delta H^0)/\partial p$ for the $E_{45}S_{10}$ diblock copolymer. An increment of the pressure, just as an increase in temperature, renders the dilution process more exothermic for the temperature range of 20−40 °C. The effect of pressure is to decrease the intermolecular distances so that the energetic interactions become more favorable. For 50 °C, the process becomes less exothermic, thus the energetic interactions become less favorable (Table 2), confirming previous results of ΔV_m.

The coefficient of cubic expansion α, being the second derivative of the free enthalpy, can also be resolved into enthalpy and entropy contributions. Thus

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$$\alpha = \frac{1}{V} \frac{\partial^2 G}{\partial p \, \partial T}$$

$$= \frac{1}{V}\left[T \frac{\partial^2 S}{\partial p \, \partial T} + \frac{\partial S}{\partial p}\right] \qquad (7)$$

where the last term may provide information about structural changes resulting from the effects of pressure and temperature. The fit, to a linear function, of $\partial(\Delta H^0)/\partial p$ versus the temperature gave a slope of $-7.05 \times 10^{-4} \pm 10^{-5}$ cm^3 mol^{-1} K^{-1} and a correlation coefficient of 0.9997. This result shows that the second-to-last term is much larger than α and that it also possesses a temperature dependence, thus confirming the previous result that the size and shape of the aggregate change with temperature.

Figure 2 shows the dependence on concentration, c, of the apparent molal volume of the aggregate, V_ϕ^m, for copolymers $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$ at 303.15 K.

The plots show the aggregate-only domain when it has been reached and the dependence of the apparent molal volume of the aggregate, V_ϕ^m, on the length of the hydrophobic block and the constancy with copolymer concentration that shows that the size and shape of the aggregates do not change with concentration but do change with the hydrophobic block length.

Compressibilities. The variation of sound velocity with concentration was also obtained for copolymers $E_{45}S_{10}$, $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$. Critical micelle concentrations were impossible to evaluate by ultrasound velocity because of the low concentration motivated by the high hydrophobicity of the oxyphenylethylene block. Figure 3 shows plots of the isentropic apparent molal compressibility, $K_{\phi(S)}$, of copolymer $E_{45}S_{10}$ against concentration at different temperatures. Similar plots were found for the other polymers.

Previous studies[30−32] have shown that $K_{\phi(S)}$ is large and negative for ionic compounds in aqueous solutions, positive for hydrophobic solutes, and intermediate, small, and negative for uncharged hydrophilic solutes such as sugars. From a general point of view, the aggregation process of copolymer $E_{45}S_{10}$ is characterized by an increase in $K_{\phi(S)}$, which reveals that monomers trapped in the micellar hydrophobic environment are more compressible than aqueous free-monomer species, and characterizes the progressive dehydration in S blocks that accompanies the aggregation process. This result confirms the previous result that the aggregates of the copolymer have water in the core associated with the hydroxy end groups of the S blocks; this water is released when the temperature is increased. As can be observed in Figure 3, the profiles of the variations of $K_{\phi(S)}$ look like those observed with apparent volumes. When the micellar region is reached, the stable micellar structure is characterized by little or no change with concentration. $K_{\phi(S)}$ usually is small and negative at low concentrations as it correspond to uncharged solutes and increases with concentration up to small, positive values as it corresponds to hydrophobic solutes. The isentropic apparent molal compressibilities of the aggregates increase with temperature because of a decrease in the amount of structured water in the vicinity of the aggregate, which is less compressible than bulk water. As pointed out by Attwood et al.,[33] an increase in temperature will increase the association number but also decrease the swelling of the micelle fringe, both effects being the result of the solvent becoming poorer as temperature is increased.

The isentropic apparent molal compressibilities at infinite dilution, $K_{\phi(S)}^0$, calculated in a similar way to V_ϕ^0, confirm that (Table 3) (a) the negative values of $K_{\phi(S)}^0$ are a consequence of
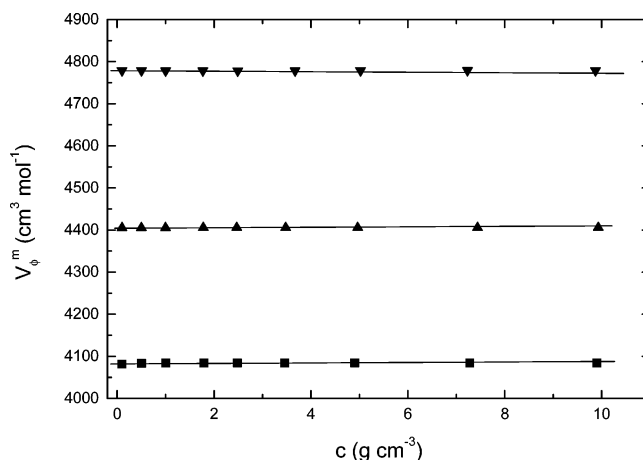

Figure 2. Apparent molal volume, V_ϕ^m, as function of concentration, c, of aqueous solutions of copolymers (■) $S_{15}E_{63}$, (▲) $S_{17}E_{65}$, and (▼) $S_{20}E_{67}$ at 30 °C.
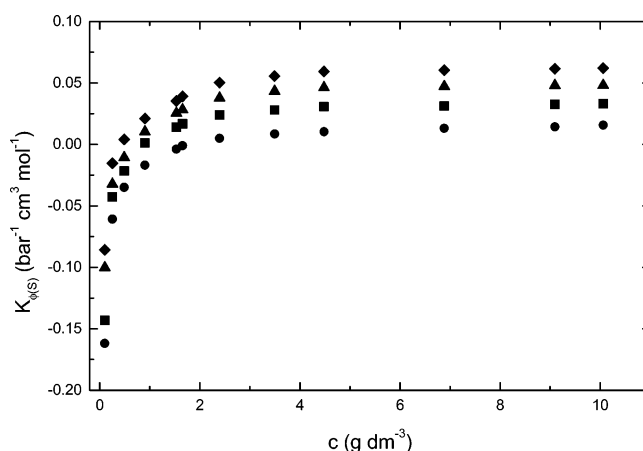

Figure 3. Isentropic apparent molal compressibility, $K_{\phi(S)}$, of copolymer $E_{45}S_{10}$ in aqueous solution as a function of concentration, c, at (●) 20, (■) 30, (▲) 40, and (◆) 50 °C.

TABLE 3: Isentropic Apparent Molal Adiabatic Compressibilities at Infinite Dilution, $K_{\phi(S)}^0$, Isentropic Apparent Molal Adiabatic Compressibilities in the Micellar State, $K_{\phi(S)}^m$, and Change in Adiabatic Molal Compressibility upon the Aggregation of Copolymer $E_{45}S_{10}$, $\Delta K_{\phi(S)}{}^a$

$T/°C$	$K_{\phi(S)}^0$	$K_{\phi(S)}^m$	$\Delta K_{\phi(S)}$
20	-0.17 ± 0.2	0.018 ± 0.002	0.19
30	-0.15 ± 0.4	0.037 ± 0.002	0.19
40	-0.11 ± 0.3	0.053 ± 0.001	0.16
50	-0.09 ± 0.2	0.068 ± 0.005	0.16

^{a} $K_{\phi(S)}^0$, $K_{\phi(S)}^0$, and $\Delta K_{\phi(S)}$ are in cm^3 bar^{-1} mol^{-1}.

the higher resistance to pressure of the structured water around the monomer compared to that of bulk water and (b) the hydrophobic character of the aggregates of the copolymer is indicated by the positive values of $K_{\phi(S)}$ upon aggregation, which are explained in terms of van der Waals solute−solvent interactions and imply that the micellar interior resembles a bulk liquid phase.[35] The low compressibility of the copolymer aggregates is an expected characteristic of the aggregate that does not possess the looseness in structure associated with the micelles of typical surfactants.

Table 3 shows a comparison between the values obtained for the partial molal isentropic compressibility of the aggregate, $K_{\phi(S)}^m$, and the isentropic apparent molal compressibility at infinite dilution, $K_{\phi(S)}^0$, for each temperature. The change in the partial molal isentropic compressibility of aggregation is positive
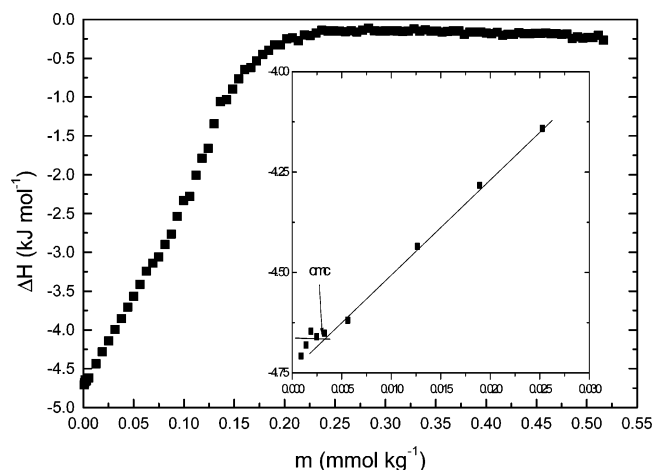
Figure 4. ITC determination of the enthalpy of demicellization of copolymer $E_{45}S_{10}$ at 30 °C. (Inset) See the text for an explanation of the straight lines governing the extrapolation to zero concentration and the calculation of the cmc. The arrow denotes the cmc.

for all temperatures, indicating the predominant role of the decrease of hydrophobic hydration in the association process.

Calorimetry. Isothermal titration calorimetry (ITC) of copolymer $E_{45}S_{10}$ is shown in Figure 4. As seen in the inset, within the uncertainty of the data points, Q is constant at concentrations below the cmc ($\sim 0.010 \pm 0.002$ g dm^{-3}), which is consistent with an ideal dilute solution.

The relatively regions of Q below and above the cmc were extrapolated to the cmc, and the difference was taken as the enthalpy of demicellization, $\Delta_{demic}H \approx -4.5 \pm 1$ kJ mol^{-1}, which is low if we compare it with the enthalpy of micellization of a nonionic surfactant[34] (e.g., Titron X-100 (octylphenol-(ethylene oxide)$_{9.5}$ ether, of 9 kJ mol^{-1}). Booth et al.[35] have calculated the standard enthalpy of micellization of diblock copolymers $E_{50}S_{3.5}$, $E_{50}S_{5.1}$, and $E_{51}S_{6.5}$ using a van't Hoff plot and have obtained 29, 18, and 12 kJ mol^{-1}, respectively. The result that we have obtained in the present work agrees quite well with their results.

The enthalpogram shows the typical behavior of the hydrophobic solutes. For micelles in water, the process of aggregates formation is generally explained in terms of water hydrophobic interactions between water and the nonionic polymer. Hydrophobic interaction is a convenient term that is used to describe an entire array of inter- and intramolecular interactions involved in the aggregation.[36] The formation of aggregates in water is believed to take place via the association of the hydrophobic parts of the polymer and the repulsion of water molecules from their water environment. The overall process of aggregation involves a decrease in the free enthalpy of the system. For aqueous solution, this is generally regarded as an entropy-directed process, the preponderant contribution of the entropy term being explained by the disordering of the water structure by the polymer molecules. It is a well-known fact that near room temperature, for these kinds of solutes, entropy effects dominate the micelle-formation process. $\Delta_{demic}H$ values for the other copolymers have been determined by isothermal titration calorimetry at 30 °C. The value of $\Delta_{demic}H$ obtained for copolymer $S_{15}E_{63}$ was -0.9 kJ mol^{-1}, and for the other two, the values were practically null. These results confirm the small interaction with water that decreases as the hydrophobic chain length of the diblock copolymer increases. The effect has been ascribed to the hydrophobic S block being tightly coiled in its dispersed unimer state so that its hydrophobic interaction with water is small.[6,37,38] Micelle stability across a wide temperature

range is consistent with the low values of the standard enthalpy of micellization found in the present work and previous work on ES systems.[4,6,8]

4. Conclusions

The volumes, isentropic compressibilities of diblock copolymers $E_{45}S_{10}$, $S_{15}E_{63}$, $S_{17}E_{65}$, and $S_{20}E_{67}$, and enthalpy of demicellization extracted from heat dilution data has led to the following observations: (i) The size and shape of the aggregates change with temperature and with the hydrophobic block length. (ii) There is a little stronger hydration of the monomer when it is free in solution than when it is in the aggregate. (iii) Micelles of copolymer $E_{45}S_{10}$ have water in the core associated with the hydroxy end groups of the S blocks; this water is released when the temperature is increased. (iv) The low values of the enthalpy of micellization that are obtained are assigned to the hydrophobicity of the S block being tightly coiled in the molecular state in water. This result confirms the small interaction with water, which decreases as the hydrophobic chain length of the copolymer increases.

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