Macromolecules **1992,** *25,* 3125–3128

Micellization of a Polystyrene-*block*-poly(ethylene/propylene) Copolymer in *n*-Alkanes. 1. Thermodynamic Study

José R. Quintana, Manuel Villacampa, Marta Muñoz, Arantza Andrio, and Issa A. Katime*

Grupo de Nuevos Materiales, Departamento de Quimica Fisica, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao, Spain

Received June 19, 1991; Revised Manuscript Received December 19, 1991

ABSTRACT: Light scattering was used to determine the dependence of the critical micelle temperature on concentration for solutions of a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and *n*-dodecane. The results were used to estimate the standard Gibbs energy, $\Delta G°$, the standard enthalpy, $\Delta H°$, and the standard entropy, $\Delta S°$, of micellization. The values of $\Delta H°$ were large and negative and were markedly dependent on the carbon number for the lower *n*-alkanes. The values of $\Delta G°$ are negative for all *n*-alkanes studied. The variation of $\Delta G°$ with the number of carbons in the *n*-alkane chain depends on the temperature, showing a maximum for *n*-octane at 85 °C. At 25 °C, $\Delta G°$ becomes more negative as the *n*-alkane carbon number increases, showing a marked decrease between *n*-heptane and *n*-octane. The different behaviors for the studied *n*-alkanes are explained by taking into account the differences in the polystyrene/*n*-alkane interactions.

Introduction

Block copolymers dissolved in selective solvents, i.e., in solvents that thermodynamically favor one block but at the same time are unfavorable for others, form micelles which consist of a compact core composed of the insoluble block and a shell formed by soluble blocks.[1,2]

Electron micrographs of micellar particles isolated from dilute solutions of polystyrene-*block*-poly(ethylene/propylene) (SEP) in octane,[3] decane,[4] and a base of lubricating oil[5] show that spherical micelles have a narrow size distribution and provide support for the use of the closed association model in treating the thermodynamic data.

For micelles having a narrow size distribution, the standard Gibbs energy of micellization per mole of copolymer chain is given by

$$\Delta G° \approx RT \ln(\mathrm{cmc}) - RTm^{-1} \ln([\mathrm{A_m}]) \qquad (1)$$

where cmc is the critical micelle concentration, m the association number, and $[\mathrm{A_m}]$ the concentration of the micelles.

For copolymer systems with a high association number and a low micelle concentration, the second term of eq 1 is very small and so

$$\Delta G° \approx RT \ln(\mathrm{cmc}) \qquad (2)$$

If the association number is independent of temperature, it follows from eq 2 and the van't Hoff relation that

$$\Delta H° \approx -RT^2 \frac{\delta \ln(\mathrm{cmc})}{\delta T} \qquad (3)$$

If $\Delta H°$ is taken to be independent of the temperature, eq 3 yields on integration

$$\ln(\mathrm{cmc}) \approx \frac{\Delta H°}{RT} + \text{constant} \qquad (4)$$

This equation allows us to estimate the contribution made by the enthalpy term to the standard Gibbs energy of micellization, and from both magnitudes, it is possible to determine the standard entropy of micellization, $\Delta S°$

$$\Delta G° = \Delta H° - T\delta S° \qquad (5)$$

For micromolecular surfactants in aqueous media, a positive standard entropy of micellization is the thermodynamic factor mainly responsible for micelle formation. The standard enthalpy of micellization is generally small and positive or negative depending on the system.[6] On the contrary, for block copolymers in organic solvents, the enthalpy contribution to the Gibbs energy change is solely responsible for micelle formation.[4,7,8] The entropy is negative and therefore unfavorable to micelle formation as would be expected from simple statistical arguments.

The properties of the micelles and the mechanism of micellization are strongly dependent upon the selective solvent. To get a better understanding of this influence, we examine in this paper and in the following one the behavior of a polystyrene-*block*-poly(ethylene/propylene) copolymer in dilute solutions of different *n*-alkanes. *n*-Alkanes are selective solvents for the copolymer; they are good solvents for poly(ethylene/propylene) but precipitants for polystyrene. As the molecular weight of the *n*-alkanes increases, the solvent quality decreases.

In this paper we report on the thermodynamic investigation carried out on the micelle formation by a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and *n*-dodecane. Light scattering was used to study the dependence of the micelle/free chain equilibrium on temperature and concentration.

Experimental Section

The polystyrene-*block*-poly(ethylene/propylene) (SEP1) was synthesized by Shell Research plc. It was prepared by hydrogenating the polyisoprene block of an anionically synthesized polystyrene-*block*-polyisoprene copolymer. UV spectroscopy of the copolymer in tetrahydrofuran showed the copolymer contained 34 ± 3% by weight polystyrene. The weight-average molar mass of the copolymer determined by light scattering in tetrahydrofuran and 1-chloroform at 25 °C was 1.05×10^5 g·mol^{-1}. Values of dn/dc of the SEP1 solutions were measured in a Brice-Phoenix differential refractometer. The values obtained in THF and chloroform were 0.116 and 0.066 mL·g^{-1}, respectively. The difference of molecular weight in both solvents was smaller than the experimental error; therefore this copolymer can be considered homogeneous in chemical composition. The ratio of the weight-average to number-average molar mass of the copolymer determined gel permeation chromatography (GPC) at 25 °C using chloroform as solvent was 1.08.

n-Alkanes (Merck, analytical purity grade) were used without further purification. Solutions were prepared by dissolving the copolymer in the *n*-alkanes at 90–100 °C. Frequent agitation of

0024-9297/92/2225-3125$03.00/0

the solutions was required for periods up to 6 h to ensure that all the copolymer was dissolved. The copolymer solutions were filtered at room temperature directly into the scattering cells, which were sealed.

Measurements were made using a modified FICA 42000 equipped with a He–Ne laser (Spectra Physics, Model 105-1), which emits at 632.8 nm, with a power of 5 mW. To establish critical micelle temperatures in the n-alkanes, measurements were made at a series of temperatures within the temperature range 25–90 °C at three scattering angles (θ = 45, 90, and 135°).

Results and Discussion

Instead of keeping the temperature constant and varying the concentration to find the critical micelle concentration, it is far better experimentally to carry out investigations in which the concentration is kept constant and the scattered light intensity is monitored over a range of temperature so as to find the critical micelle temperature (cmt). The critical micelle temperature of a solution of a given concentration is the temperature at which the formation of micelles can just be detected experimentally. In investigations of the thermodynamics of micellization of block copolymers in organic solvents,[2] it has been shown that within experimental error

$$\frac{\delta \ln (\mathrm{cmc})}{\delta T^{-1}} = \frac{\delta \ln (c)}{\delta (\mathrm{cmt})^{-1}} \tag{6}$$

Therefore eq 4 becomes

$$\ln (c) \approx \frac{\Delta H^\circ}{R(\mathrm{cmt})} + \text{constant} \tag{7}$$

In this way, once the cmt for different concentrations has been found, we can calculate all thermodynamic magnitudes of the micelle formation from the plot of ln (c) against (cmt)$^{-1}$.

We have determined the relationship of concentration and cmt for the copolymer SEP in five different n-alkanes (n-hexane, n-heptane, n-octane, n-decane, and n-dodecane). It was not possible to find this relationship for n-hexadecane because the cmt's are higher than the maximum temperature that our experimental device allows us to reach. To find cmt's lower than this temperature, it is necessary to use solutions of so low concentration that the light scattering technique cannot be used. Taking into account that the cmt corresponding to a solution of concentration 2.56×10^{-6} g·cm^{-3} is higher than 85 °C, we can say that the cmc at 85 °C is lower than this concentration. Therefore the standard Gibbs energy of micellization at 85 °C is more negative than −52 kJ·mol^{-1}.

A plot of scattered light intensity at 45, 90, and 135° against temperature for the SEP1 copolymer at a concentration of 4.9×10^{-5} g·cm^{-3} in n-octane is shown in Figure 1. As the temperature increases, a smooth increase of the scattered light intensity is found followed by a sharp decrease and finally a small increase. The increments of light intensity are due to the increment of the intermolecular interactions as the temperature increases. On the other hand, the sharp decrease is due to the reduction of the micelle concentration as the temperature increases to the temperature at which the copolymer is unassociated. On moving immediately to lower temperatures, a sharp increase of the scattered light intensity is observed as a consequence of the appearance of micelles. The temperature at which the intensity starts to increase is considered as the critical micelle temperature. $I = f(T)$ curves for both increasing and decreasing temperature are coincident. This fact suggests that the micelles behave as spheres as shown by Price et al.[9]

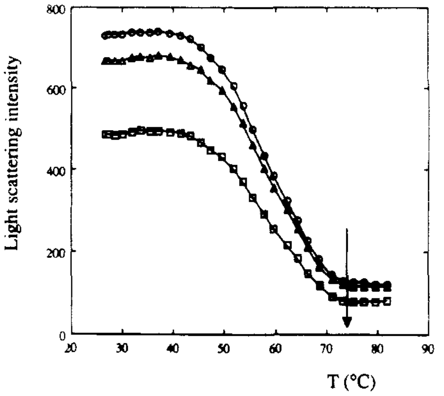

Figure 1. Plot of scattering intensity against temperature for the SEP1 copolymer in n-octane. The concentration of the solution was 4.9×10^{-5} g·cm^{-3} and the scattered angles were 45 (○), 90 (□), and 135° (△). The arrow indicates the critical micelle temperature.

In a similar way the cmt was determined for other solutions of the copolymer in n-octane covering a range of concentrations and also for solutions of the copolymer in the other n-alkanes. All the plots were similar to the one shown in Figure 1.

Plots of ln (c) as a function of (cmt)$^{-1}$, which are equivalent to plots of ln (cmc) against T^{-1}, for the different n-alkanes are shown in Figure 2. All these plots were linear within the experimental error over the dilute solution range studied.

The dissymmetry factor Z, i.e., the ratio of the scattering intensities at 45° and 135°, can give a general idea of the scattering profile. This value is related to the size and shape of the scattering particles. The unassociated copolymer molecules are small and give no angular dissymmetry (Z = 1). For all the studied solutions the dissymmetry factor presented values close to unity at temperatures both higher and lower than the cmt. The low values of Z at temperatures lower than cmt suggest that the micelles have small size and therefore, taking into account their high molecular weight,[10] we can say that micelles show a high compactness. Besides, these values close to unity are in accordance with the spherical shape that the micelles of SEP copolymers have in n-octane and n-decane as shown by electron micrographs of micellar particles isolated from dilute solutions.[3,4]

Values of the standard Gibbs energy, ΔG°, the standard enthalpy, ΔH°, and the standard entropy, ΔS°, of micellization calculated from the experimental result using eqs 2, 7, and 5 with temperatures of 25 and 85 °C are given in Table I. The values listed are per mole of copolymer chain. The standard states for micelles and free chains[11] are states with ideally dilute solution behavior and concentration 1 mol·dm^{-3}. The results show that for the polystyrene-*block*-poly(ethylene/propylene) copolymer in all the n-alkanes studied the standard Gibbs energy of micellization shows negative values, as was expected. The standard entropy of micellization is negative in all the systems studied and, therefore, unfavorable to micellization. The thermodynamic behavior underlying micelle formation by the SEP copolymer in n-alkanes is different from that observed for micromolecular surfactants in aqueous media,[12,13] where entropy is largely responsible for micelle formation. The negative standard entropy of micellization of the copolymer arises from the loss in combinatorial entropy due to the fact that the copolymer chains are less swollen in the micelles than in the unassociated state.[10] The results show that for the SEP block copolymer in n-alkanes it is the enthalpy that is solely responsible

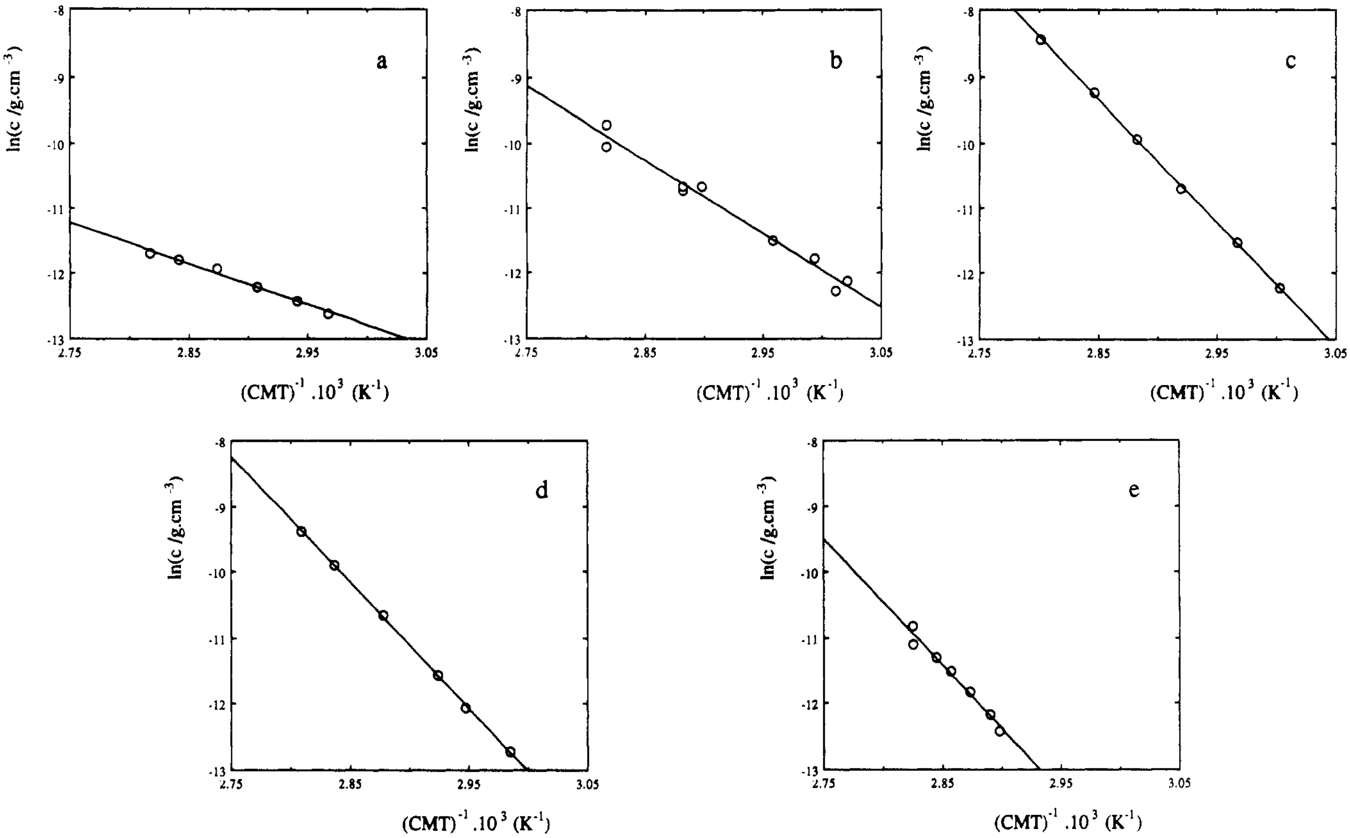

Figure 2. Plots of the logarithm of the solution concentration as a function of the reciprocal of the critical micelle temperature for the SEP1 copolymer in *n*-alkanes: (a) *n*-hexane; (b) *n*-heptane; (c) *n*-octane; (d) *n*-decane; (e) *n*-dodecane.

Table I
Thermodynamic Data for the Micellization of the SEP1 Copolymer in *n*-Alkanes at 25 and 85 °C

solvent	$\Delta G°$(25 °C), kJ·mol^{-1}	$\Delta G°$(85 °C), kJ·mol^{-1}	$\Delta H°$, kJ·mol^{-1}	$\Delta S°$, kJ·mol^{-1}·K^{-1}
n-hexane	-48.7	-48.1	-52.0	-0.011
n-heptane	-51.1	-42.5	-93.9	-0.144
n-octane	-58.3	-38.5	-156.7	-0.330
n-decane	-60.6	-40.8	-158.9	-0.330
n-dodecane	-63.9	-44.6	-160.1	-0.323
n-hexadecane		<-52.0		

for micelle formation. The negative standard enthalpy of micellization results from the exothermic interchange energy accompanying the replacement of polystyrene segment/*n*-alkane interactions by polystyrene segment/polystyrene segment and *n*-alkane/*n*-alkane interactions in formation of the micellar cores.

The values of $\Delta G°$, $\Delta H°$, and $-T\delta S°$ calculated from the results of the SEP1 copolymer in *n*-decane at 80 °C are -42.5, -158.9, and 116.6 kJ·mol^{-1}. These values are similar to those found by Price et al.[10] for a series of SEP copolymers in *n*-decane. On the other hand, the values of $\Delta G°$, $\Delta H°$, and $-T\delta S°$ for the SEP copolymer in *n*-heptane at 25 °C are -51.1, -93.9, and 42.8 kJ·mol^{-1}. The $\Delta G°$ value agrees with that reported by Yeung and Frank[14] for a SEP copolymer with a molar mass of 1.35×10^5 g·mol^{-1} and a styrene content of 37% by weight ($\Delta G° = -52$ kJ·mol^{-1}). However, the values of $\Delta H°$ and $-T\delta S°$ are different ($\Delta H° = -136$ kJ·mol^{-1} and $-T\delta S° = 84.3$ kJ·mol^{-1}).

The variation of the standard Gibbs energy of micellization for 25 and 85 °C as a function of the number of carbons in the *n*-alkane is plotted in Figure 3. For T = 25 °C, $\Delta G°$ decreases as the number of carbons increases. However, a sharp decrease appears between *n*-heptane and *n*-octane. On the other hand, for T = 85 °C, the standard Gibbs energy of micellization presents a maximum for *n*-octane. This fact suggests that at this temperature the SEP copolymer has a higher critical micelle concentration in *n*-octane. The different patterns of the curves suggest that the variation of $\Delta G°$ with temperature depends on the *n*-alkane. This fact will be analyzed in detail considering the standard entropy of micellization. To understand the behavior of the Gibbs energy, it is necessary to decompose it into the enthalpy and entropy contributions.

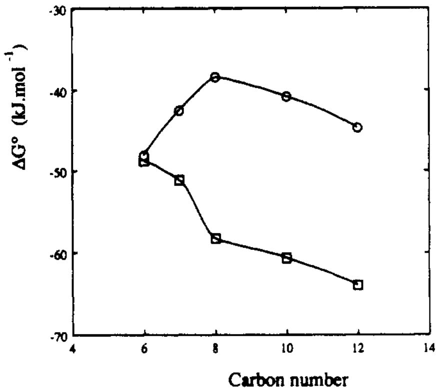

Figure 3. Dependence of the standard Gibbs energy of micellization on the number of carbons in the *n*-alkane chain, T = 25 °C (□) and T = 85 °C (○).

The variations of the standard enthalpy and entropy of micellization as a function of the number of carbons in the *n*-alkane chain are plotted in Figure 4. To explain these it is necessary to take into account the polymer/solvent interactions. Katime et al.[15] have reported that *n*-alkanes become worse solvents for polystyrene as the *n*-alkane carbon number increases. As the carbon number of the *n*-alkane chain increases, the polystyrene segment/*n*-alkane interactions are more repulsive. Thus, when the block copolymer chains form micelles with a compact core composed of a polystyrene block, replacing polystyrene segment/*n*-alkane interactions by polystyrene segment/

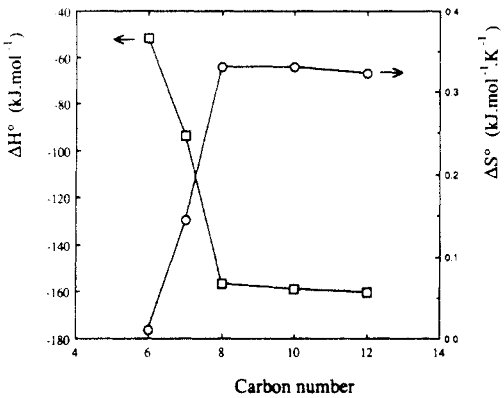

Figure 4. Variation of the standard enthalpy (□) and standard entropy (○) of micellization as a function of the number of carbons in the *n*-alkane chain.

polystyrene segment and *n*-alkane/*n*-alkane interactions, the enthalpy of the process becomes more negative. This behavior is remarkable for *n*-hexane, *n*-heptane, and *n*-octane, but less significant from a given length of the *n*-alkane chain. It can be observed that the variation of ΔH° with the carbon number is very small from *n*-octane. This fact agrees with the results reported by Katime et al.,[15] which suggested that *n*-hexane and *n*-heptane showed remarkably less repulsive polystyrene/solvent interactions than higher *n*-alkanes.

As can be seen in Figure 4, the standard entropy of micellization is almost constant for *n*-alkanes higher than *n*-octane. However, *n*-hexane shows a markedly less negative entropy of micellization. To understand this behavior, it is necessary to take into account that, contrary to what happens for micromolecular surfactants in aqueous media, the cores of the block copolymer micelles contain solvent molecules. The existence of solvent molecules in the micelle core will give rise to a certain disorder in the micelles. As Katime et al.[15] have reported for polystyrene/benzene/*n*-alkane systems, polystyrene can adsorb preferentially molecules of *n*-hexane and *n*-heptane under certain system conditions. However, this does not happen with higher *n*-alkanes. Therefore, it can be supposed that the number of solvent molecules in the micelle core is higher for *n*-hexane and *n*-heptane than for higher *n*-alkanes, and so the standard entropy of micellization will be less negative for the lower *n*-alkanes.

Acknowledgment. We thank Prof. Dr. Colin Price for the copolymer sample, and the Vicerrectorado de Investigación de la Universidad del País Vasco and the Departamento de Educación, Universidades e Investigación del Gobierno Vasco for financial support. M. V. thanks the Departamento de Educación, Universidades e Investigación of the Gobierno Vasco, for the award of a research fellowship.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(2) Price, C. *Pure Appl. Chem.* **1983**, *55*, 10, 1563.
(3) Candau, F.; Heatley, F.; Price, C.; Stubbersfield, R. B. *Eur. Polym. J.* **1984**, *20*, 685.
(4) Price, C.; Kendall, K. D.; Stubbersfield, R. B.; Wright, B. *Polym. Commun.* **1983**, *24*, 326.
(5) Price, C.; Hudd, A. L.; Stubbersfield, R. B. *Polymer* **1980**, *21*, 9.
(6) Jones, M. N.; Pilcher, G.; Espada L. *J. Chem. Thermodyn.* **1970**, *2*, 333.
(7) Price, C.; Chan, E. K. M.; Pilcher, G.; Stubbersfield, R. B. *Eur. Polym. J.* **1987**, *25*, 170.
(8) Price, C.; Booth, C.; Canham, P. A.; de V. Naylor, T.; Stubbersfield, R. B. *Br. Polym. J.* **1984**, *16*, 311.
(9) Price, C.; Chan, E. K. M.; Hudd, A. L.; Stubbersfield, R. B. *Polym. Commun.* **1986**, *27*, 196.
(10) Price, C.; Stubbersfield, R. B.; El-Kafrawy, S.; Kendall, K. D. *Br. Polym. J.* **1989**, *21*, 391.
(11) Price, C.; Chan, E. K. M.; Mobbs, R. H.; Stubbersfield, R. B. *Eur. Polym. J.* **1985**, *21*, 355.
(12) Corkill, J. M.; Goodman, J. F.; Tate, J. R. *Trans. Faraday Soc.* **1964**, *60*, 996.
(13) Teo, H. H.; Yeates, S. G.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1787.
(14) Yeung, A. S.; Frank, C. W. *Polymer* **1990**, *31*, 2101.
(15) Katime, I.; Quintana, J. R.; Cesteros, L. C. *Eur. Polym. J.* **1990**, *26*, 1121.

Registry No. Polystyrene, 9003-53-6; poly(ethylene/propylene) (block copolymer), 106565-43-9.