Diblock Copolymer Micelles in Solvent Binary Mixtures. 1. Selective Solvent/Precipitant

José R. Quintana, María D. Jáñez, Manuel Villacampa, and Issa Katime*

Grupo de Nuevos Materiales, Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080-Bilbao, Spain

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ABSTRACT: The association of a block copolymer polystyrene-*b*-poly(ethylene/propylene) in mixtures of 5-methyl-2-hexanone (a selective solvent of polystyrene block) and 2-pentanol (a precipitant of both copolymer blocks) has been studied by static and dynamic light scattering and viscometry. Micelle structural parameters have been analyzed as a function of the solvent composition. As the precipitant percentage increases in the solvent mixture, the molar mass increases, the apparent radius of gyration and the second virial coefficient decrease, and the hydrodynamic radius remains constant. Static light scattering was used to establish the dependence of the critical micelle temperature on concentration. Dynamic light scattering measurements have shown that the micelles have narrow size distributions and micellization can be thermodynamically treated as a closed association. The light scattering results were used to calculate the standard Gibbs energies, enthalpies, and entropies of micellization. As the 2-pentanol percentage increases, the standard Gibbs energy becomes more negative, whereas the standard enthalpy and entropy remain almost constant.

Introduction

Over the last years, many studies have been done on micelle formation by block copolymers into organic and aqueous media.[1,2] Block copolymers can form micelles only if the solvent is selective, i.e. a good solvent for one block and precipitant for the other. In these solutions, block copolymers show an amphiphilic nature and a behavior similar to conventional surfactants. Furthermore, a conception of spherical copolymer micelles has been suggested in analogy to dilute aqueous surfactant solutions. These are formed by a core and an external shell. The core consists of poorly soluble sequences of block copolymer, and the shell consists of solvated sequences which prevent macroscopic flocculation of the copolymer.

Because the solvent sensitivity is one of the main factors which control the micelle formation by block copolymers, we have undertaken an extensive study of the solvent influence on the micellization process as well as on the micelle structure in our laboratory. The considered block copolymer is a polystyrene-*block*-poly(ethylene/propylene) copolymer (SEP). The behavior of this copolymer in different *n*-alkanes[3,4] and in several ketones[5] has been reported in previous papers. Whereas alkanes are good solvents for the poly(ethylene/propylene) block and precipitants for polystyrene blocks, ketones show the opposite solvent capacity. In order to change the solvent selectivity in a continuous way, the micellization process of SEP copolymer in solvent binary mixtures has begun to be analyzed. *p*-Dioxane/*n*-dodecane binary mixtures were considered first.[6,7] Both solvents are inversely selective solvents; i.e. whereas *p*-dioxane is a selective solvent of PS blocks, *n*-dodecane is a selective solvent of PEP blocks. When the solvent composition of the binary mixtures is changed from a pure solvent into the other, the micelles, existing at compositions rich in one of the solvents, disappear at around 50/50 solvent composition. New micelles begin to appear when the solvent mixture becomes rich in the other selective solvent.

The present paper is concerned with experimental results obtained in binary solvents formed of 5-methyl-2-hexanone (a selective solvent of PS blocks) and 2-pentanol (a precipitant of both copolymer blocks). These two solvents present the advantage of having a very similar refractive index and, consequently, allowing the cancelation of eventual contributions of selective adsorption to light scattering. In this way the solvent selectivity is continuously decreased by increasing the precipitant character of the binary solvent. The influence of the solvent selectivity on the structure and hydrodynamic behavior of the micelles and on the thermodynamics of micellization have been elucidated in detail by means of light scattering, viscometry, and photon correlation spectroscopy.

Block copolymers undergo closed association in dilute solution to form micelles that have an appreciable association number.[8] For these systems, the standard Gibbs energy of micellization, $\Delta G°$, can be determined by using the relation

$$\Delta G° \approx RT \ln(\mathrm{CMC}) \tag{1}$$

where CMC is the critical micelle concentration, which is experimentally determined.[9] The critical micelle concentration is defined as the concentration at which the experimental method in use can just detect the presence of micelles in the system when the concentration is increased at a constant temperature. If the association number is temperature independent, the standard enthalpy of micellization, $\Delta H°$, can be determined by measuring the temperature dependence of the critical micelle concentration, since[10]

$$\Delta H° \approx R \frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}T^{-1}} \tag{2}$$

Experimental Section

Materials. The diblock copolymer sample polystyrene-*b*-poly(ethylene/propylene), SEP2, employed in this study was a commercial copolymer synthesized by Shell. The weight average molar mass of SEP2 determined by light scattering in tetrahydrofuran and chloroform at 25 °C was 1.05×10^5 g·mol^{-1}. The difference of molar mass in both solvents was

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smaller than the experimental error. As both solvents have different refractive indices, this copolymer can be considered homogeneous in chemical composition. The ratio of the weight average to number average molar mass of the copolymer—determined by size exclusion chromatography, SEC, at 25 °C using chloroform as solvent and a standard polystyrene calibration—was 1.08. UV spectroscopy in tetrahydrofuran showed that the copolymer contains 35 ± 3% by weight polystyrene.

Mixtures of 5-methyl-2-hexanone (a PS selective solvent) and 2-pentanol (precipitant of both blocks) of different compositions have been used as solvents. Solvent mixtures were made up by volume and contained 0, 5, 10, and 15% 2-pentanol. Copolymer SEP2 was not soluble in a solvent mixture with 20% 2-pentanol. Both solvents (analytical purity grade) were used without further purification. All the solutions were prepared by dissolving the copolymer in the solvent mixtures at temperatures higher than 70 °C. This heating process must be repeated before every measurement to break the potential aggregation of micelles and to get reproducible results. In order to clarify copolymer solutions for light scattering measurements, they were filtered at room temperature directly into the scattering cells using 0.2 μm PTFE Acrodisc CR filters (Gelman Scientific). Then the cells were sealed. Number 3 glass filters were used to clarify the solvents and solutions used in viscosity measurements. Solution concentrations used to determine the CMTs were recalculated at these temperatures. As all the used copolymer solutions were diluted, solutions were assumed to have the same thermal expansion coefficient as that of the solvent mixture.

Static Light Scattering. In order to obtain information on the micellization thermodynamics and structural parameters of the micelles, light scattering techniques have been employed. Static light scattering measurements (SLS) were performed on a modified FICA 42000 light scattering photogoniodiffusometer. Both the light source and optical block of the incident beam were replaced by a Spectra-Physics He–Ne laser, Model 105, which emits vertically polarized light at 632.8 nm with a power of 5 mW. The instrument was calibrated with pure benzene by taking the Rayleigh ratio at 25 °C as 12.55×10^{-6} cm^{-1}.

Investigations of the thermodynamics of micellization of block copolymers in organic solvents[11] have shown that, within experimental error

$$\frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}T^{-1}} = \frac{\mathrm{d}\ln(c)}{\mathrm{d}(\mathrm{CMT})^{-1}} \qquad (3)$$

where CMT is the critical micelle temperature, which is defined as the temperature at which the formation of micelles can just be experimentally detected. Thus, (2) becomes

$$\Delta H^\circ \simeq R\,\frac{\mathrm{d}\ln(c)}{\mathrm{d}(\mathrm{CMT})^{-1}} \qquad (4)$$

To establish critical micelle temperatures, measurements of scattered light intensity were made at series of temperatures within the range 25–90 °C at scattering angles of 45, 90, and 135°. Thus, the variation of the dissymmetry factor Z (i.e. $I_{45^\circ}/I_{135^\circ}$) as a function of the temperature has also been analyzed.

To get classical Zimm plots, light scattering measurements were made at ten angles between 37.5 and 150° for the solvent and for each copolymer solution at 25 °C. The light scattered by a dilute polymer solution may be expressed as[12]

$$\frac{Kc}{\Delta R(\theta)} = \frac{1}{M_\mathrm{w}}\left(1 + \frac{16\pi^2 n_\mathrm{o}^2 R_\mathrm{G}^2}{3\lambda_\mathrm{o}^2}\sin^2(\theta/2) + \ldots\right) + 2A_2c + \ldots \qquad (5)$$

where K is an optical constant, c is the polymer concentration, $\Delta R(\theta)$ is the difference between the Rayleigh ratio of the solution and that of the pure solvent, M_w is the weight average molar mass, R_G^2 is the mean square radius of gyration, n_o is the solvent refractive index, λ_o is the wavelength in vacuum, and A_2 is the second virial coefficient.

In order to estimate M_w and R_G, the refractive index increments, dn/dc, and the solvent refractive index, n_o, must be determined. The refractive index increments of the copolymer solutions were measured using a Brice-Phoenix differential refractometer equipped with a He–Ne laser as the light source (Spectra-Physics, Model 156, 632.8 nm and 1 mW). The differential refractometer was calibrated with solutions of highly purified NaCl. The refractive indices of solvents were measured in an Abbè refractometer.

Dynamic Light Scattering. Dynamic light scattering measurements, DLS, have been carried out in a PL-LSP-700 instrument (Polymer Laboratories) working in the dynamic homodyne mode. The autocorrelation functions $g^{(2)}(\tau)$, where τ is the delay time, were obtained and analyzed in a personal computer by means of the software PL-LSP. These $g^{(2)}(\tau)$ functions are transformed into the electric field autocorrelation functions, $g^{(1)}(\tau)$. The translational diffusion coefficient and the hydrodynamic radius of the micelles have been obtained by two different methods of analysis.

(1) The second-order cumulant method gives the translational diffusion coefficient, D, the average line width, $\bar{\Gamma}$, and the variance of the size distribution function $\mu_2/\bar{\Gamma}^2$. To get this information, the cumulant expansion method[13] is applied

$$\log[g^{(1)}(\tau)] = -\bar{\Gamma}\tau + \frac{1}{2!}\mu_2\tau^2 \qquad (6)$$

(2) The histogram method[14] consists of the decomposition of $g^{(1)}(\tau)$ in a sum of single exponential functions,

$$g^{(1)}(\tau) = \sum_{i=1}^{N} G_i \exp(-\bar{\Gamma}_i\tau) \qquad (7)$$

where N is the number of steps in the histogram, G_i is the total integrated intensity scattered by all the species i that contribute to the amplitude of the Γ_i increment from $\Gamma_i - \Delta\Gamma/2$ to $\Gamma_i + \Delta\Gamma/2$ ($\Delta\Gamma = (\Gamma_\mathrm{max} - \Gamma_\mathrm{min})/N$ being the width of each step), and $\bar{\Gamma}_i$ is the average value of Γ in the Γ_i increment. This process allows us to determine the Γ size distribution function of the particles and, thus, the weight and number size distribution functions. A non-negative least squares algorithm has been selected to fit the experimental correlation function in order to get a possible multimodal size distribution function. The lower limit of the fitting has been selected close to the value of the hydrodynamic radius of an unassociated chain (≈10 nm), whereas the higher limit (60 nm) has been selected far above the one corresponding to the micelles.

The translational diffusion coefficient, D, and the hydrodynamic radius (the average value obtained with the cumulant method or each fraction value obtained with the histogram one) can be obtained from Γ by using the equation

$$\Gamma = DK^2 = D\left(\frac{4\pi n_\mathrm{o}}{\lambda_\mathrm{o}}\sin\left(\frac{\theta}{2}\right)\right)^2 \qquad (8)$$

and the Stokes–Einstein relation

$$D_\mathrm{o} = \frac{k_\mathrm{B}T}{6\pi\eta_\mathrm{o}R_\mathrm{h}} \qquad (9)$$

where D_o is the translational diffusion coefficient extrapolated to nil concentration, K is the scattering vector, θ is the angle of scattering, λ_o is the vacuum wavelength, n_o is the refractive index of the medium, k_B is Boltzmann's constant, T is the absolute temperature, η_o is the viscosity of the solvent, and R_h is the particle hydrodynamic radius.

Measurements were carried out for solutions of 1×10^{-3} g·cm^{-3} at 25 °C, at an observation angle of 90° and averaging 500 measurements achieved during a delay time of 1024 μs using either 128 or 1024 channels. The spherical shape, small size, and high density of the micelles lead to very low values

Table 1. Intrinsic Viscosity, Translational Diffusion Coefficient, D, Hydrodynamic Radius, R_h, Variance, μ_2/Γ^2, and Polydispersity Index, I, Determined by DLS (Cumulant and Histogram Methods) for Solutions of Copolymer SEP2 in 5-Methyl-2-hexanone/2-Pentanol Binary Mixtures ($c = 1 \times 10^{-3}$ g·cm^{-3})

	2-pentanol			
	0%	5%	10%	15%
$[\eta]$/cm^3·g^{-1}	16.2	15.5	13.6	12.9
$10^7 D$/cm^2·s^{-1}	7.031	7.097	6.961	6.727
R_h/nm (cumulant)	43.4	43.4	43.0	43.1
μ_2/Γ^2	0.005	0.021	0.013	0.008
R_h/nm (histogram)	43.5	44.3	43.5	43.4
I	1.00	1.06	1.03	1.01

Table 2. Thermodynamic Data for the Micellization Process of Copolymer SEP2 in 5-Methyl-2-hexanone/2-pentanol Binary Mixtures

	2-pentanol			
	0%	5%	10%	15%
$\Delta H°$/kJ·mol^{-1}	−292	−293	−268	−312
$\Delta S°$/kJ·mol^{01}·K^{-1}	−0.78	−0.78	−0.70	−0.82
$\Delta G°_{25}$/kJ·mol^{-1}	−58.5	−61.0	−61.1	−68.9
CMC$_{25}$/g·cm^{-3}	5.7×10^{-9}	2.1×10^{-9}	2.0×10^{-9}	8.5×10^{-11}

of friction coefficients, and no extrapolation at nil concentration or nil angle is required.[15]

Viscometry. Viscosity measurements were made in a Lauda automatic Ubbelohde viscometer model Viscoboy 2, which was placed in a thermostatically controlled bath with a precision of ±0.01 °C. Measurements of copolymer solutions were carried out within the polymer concentration range $2 \times 10^{-3} \leq c \leq 6 \times 10^{-3}$ g·cm^{-3}. The data were evaluated according to the Huggins and Kraemer equations.[16]

Results and Discussion

Structure and Hydrodynamic Behavior. Classic light scattering yields the weight average molar mass, M_w, of all particles present in the solution, the radius of gyration, R_G, and the second virial coefficient, A_2, for micellar systems SEP/5-methyl-2-hexanone/2-pentanol. These parameters are determined by means of Zimm plots obtained from measurements of scattering intensities at different angles and concentrations.

All Zimm plots showed a linear variation of $Kc/\Delta R_\theta$ with copolymer concentration, as it was expected for experimental copolymer concentrations much higher than the critical micelle concentration (Table 2). The M_w obtained from the double extrapolation at nil angle and concentration can be considered as the micelle molar mass since the free chain concentration is negligible compared to the micelle one, the copolymer is chemically homogeneous and eventual contributions of selective absorption to light scattering are nil. Second virial coefficients were determined from the concentration dependence of $Kc/\Delta R_\theta$ at nil angle.

The variations of M_w and A_2 are plotted in Figure 1 as a function of the 2-pentanol percentage in the solvent binary mixture. The micelle molar mass increases slightly with the 2-pentanol content. This behavior suggests that a decrease in the solvent goodness leads to an increase in the association number of the micelles. This result agrees with that found by Quintana et al.[4] for a similar SEP copolymer in n-alkanes, where the association number increased with the carbon number in the n-alkane.

The second virial coefficient is positive and small and decreases as the 2-pentanol content in the binary mixture increases. If a segregated model with no contact between PS and PEP segments is assumed, A_2 is a weighted average between $A_{2,PS}$ and $A_{2,PEP}$. The decrease of $A_{2,PS}$, due to the diminution of the quality of the solvent, leads to the decrease of A_2. It has to be taken into account that both solvents (5-methyl-2-hexanone and 2-pentanol) are precipitants for PEP blocks.

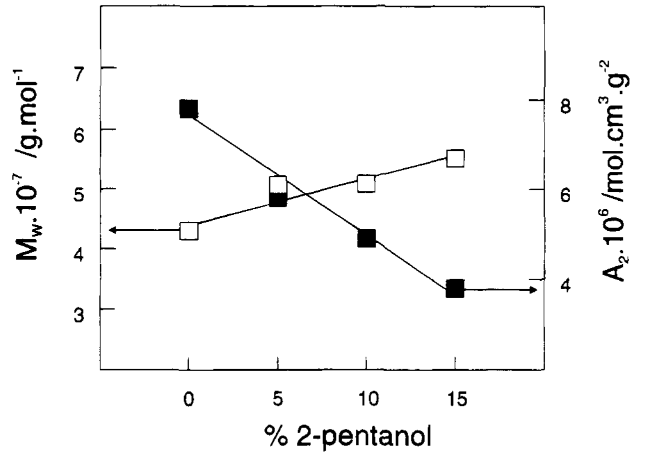

Figure 1. Variation of molar mass (□) and second virial coefficient (■) as a function of 2-pentanol percentage for copolymer SEP2 in 5-methyl-2-hexanone/2-pentanol mixtures at 25 °C.

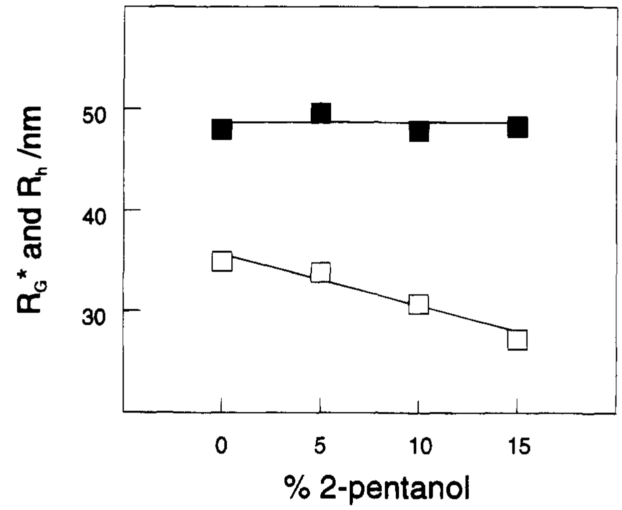

Figure 2. Variation of apparent radius of gyration (□) and hydrodynamic radius (■) as a function of 2-pentanol percentage for copolymer SEP2 in 5-methyl-2-hexanone/2-pentanol mixtures at 25 °C.

The radii of gyration, R_G, are obtained from the angular dependence of $Kc/\Delta R_\theta$ at nil concentration. These values are apparent because the major contribution to the scattering is due to the well-solvated PS sequences (which form the micelles shell) compared to the scattering by PEP sequences (which form the micelle core). The refractive index increment of polystyrene is higher than the one corresponding to poly(ethylene/propylene); therefore the apparent values of the radius of gyration are higher than the real ones.

The variation of the apparent radius of gyration, R_G*, as a function of solvent mixture composition is plotted in Figure 2. R_G* decreases slightly as the 2-pentanol percentage in the solvent mixture increases. 2-Pentanol is a precipitant for PS segments; therefore as the quality of the solvent decreases, the micelle shell becomes less solvated. This fact leads to a diminution of the micelle size.

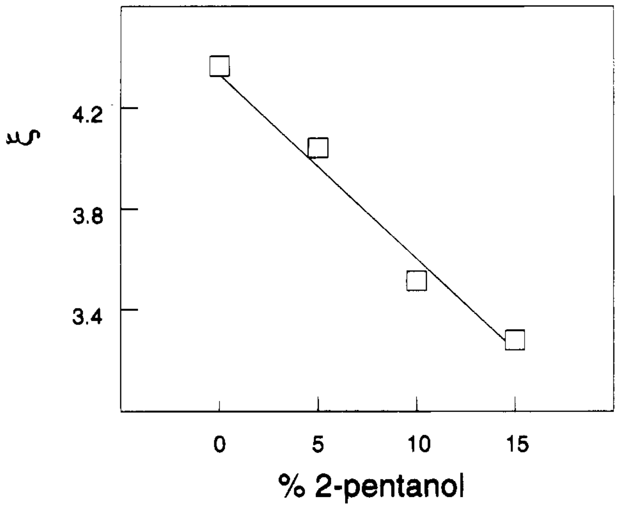

Figure 3. Variation of degree of solvation as a function of 2-pentanol percentage for copolymer SEP2 in 5-methyl-2-hexanone/2-pentanol mixtures at 25 °C.

Viscosity measurements were carried out in order to get complementary information about the solvation and the size of the micelles. The experimental dependencies of the reduced viscosity, η_{sp}/c, and of the inherent viscosity, $\ln(\eta_r/c)$, on the concentration were always linear within the concentration range studied. The intrinsic viscosity decreases as the 2-pentanol percentage increases (Table 1). This fact suggests that a decrease in the solvent quality leads to an increase in the density of the micelle shell.

Intrinsic viscosity is related to the micelle shape and density by the expression[17]

$$[\eta] = \nu/\varrho_m = \nu(\varrho_c^{-1} + \xi\varrho_s^{-1}) \qquad (10)$$

where ν is the shape factor, ξ is the degree of solvation (solvated solvent mass per gram of polymer), and ϱ_m, ϱ_c, and ϱ_s are the densities of the micelle, copolymer, and solvent, respectively. The degree of solvation for different micellar systems has been calculated by considering the micelles as hard spheres, $\nu = 2.5$. The values found are plotted in Figure 3 as a function of the 2-pentanol percentage in the solvent mixture. The solvation decreases as the content of PS precipitant (2-pentanol) increases. This behavior agrees with the variation of A_2.

If the model of a hydrodynamically equivalent sphere is applied to the spherical micelles, the hydrodynamic radius can be determined from the intrinsic viscosity and the molar mass using the well-known Einstein relation

$$R_h = \left(\frac{3M[\eta]}{10\pi N_A}\right)^{1/3} \qquad (11)$$

where M and R_h are the molar mass and the hydrodynamic radius of the micelles and N_A is the Avogadro number. The dynamic light scattering measurements made on these micellar systems show that the micelles have a very narrow size distribution. Thus, it is correct to use the molar mass determined by classical light scattering in order to calculate the hydrodynamic radius.

The hydrodynamic radii obtained are shown in Figure 2 as a function of the solvent composition. As can be seen in this figure, the hydrodynamic radius of the micelles does not depend on the solvent quality. It seems that the decrease in the micelle solvation is counteracted by the increment in the molar mass.

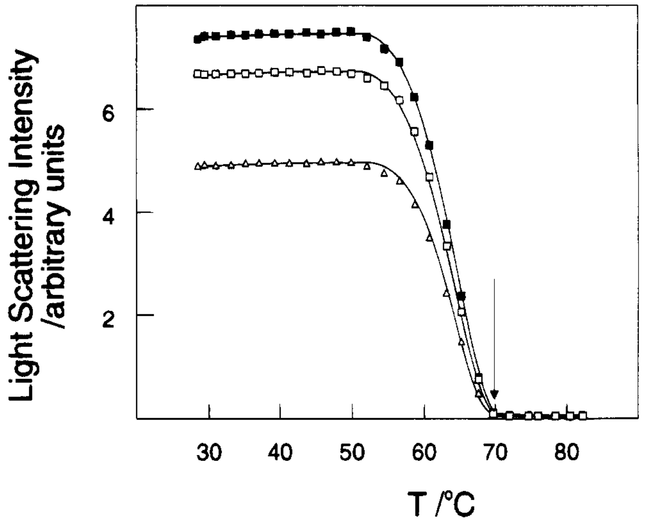

Figure 4. Plots of scattering light intensity against temperature for a solution of the polystyrene-*block*-poly(ethylene/propylene) copolymer in 5-methyl-2-hexanone/2-pentanol (90/10). The concentration of the solution was 2.65 × 10^{-3} g·cm^{-3}, and the scatter angles were 45° (■), 90° (△), and 135° (□).

The hydrodynamic radii have also been determined by dynamic light scattering using the cumulant and histogram methods. The values obtained as well as the variance μ_2/Γ^2 and the polydispersity coefficient, I, are shown in Table 1. The polydispersity indices suggest that the micelles studied have a very narrow size distribution according to other block copolymer micelle systems analyzed by size exclusion chromatography,[18,19] sedimentation analysis,[20] and electron microscopy.[21]

Both methods lead to very similar hydrodynamic radius values, and these are slightly lower than those calculated from viscosity and light scattering measurements. However they confirm the nondependence of the hydrodynamic radius on the solvent quality. This behavior has also been reported for other micellar systems,[4,7] and it seems that a block copolymer forms micelles with a unique hydrodynamic volume independent of the quality of the solvent. This volume only changes when the selective solvent of a block copolymer is substituted by a selective solvent of the other one, giving place to an inverse micelle.[7,22]

Thermodynamics of Micellization. The thermodynamic relationships shown in the Introduction correspond to micellar systems formed by a block copolymer solved in a single solvent. When a copolymer is dissolved in a solvent mixture, the thermodynamic treatment becomes too complex. The expressions of chemical potentials include more terms due to the preferential adsorption of a solvent by micelles. However, we shall use the above equations as a simplified treatment without considering the extra terms. This simplification will be validated by the experimental results.

The relationships of concentration and critical micelle temperature for the copolymer SEP2 in 5-methyl-2-hexanone and 5-methyl-2-hexanone/2-pentanol mixtures of different composition (95/5, 90/10, and 85/15 v/v) were determined. Light scattering intensities measured at the observation angles of 45, 90, and 135° are plotted in Figure 4 as a function of temperature for copolymer SEP2 in 5-methyl-2-hexanone/2-pentanol (90/10) at the concentration of 2.65 × 10^{-3} g·cm^{-3}. The curve shape

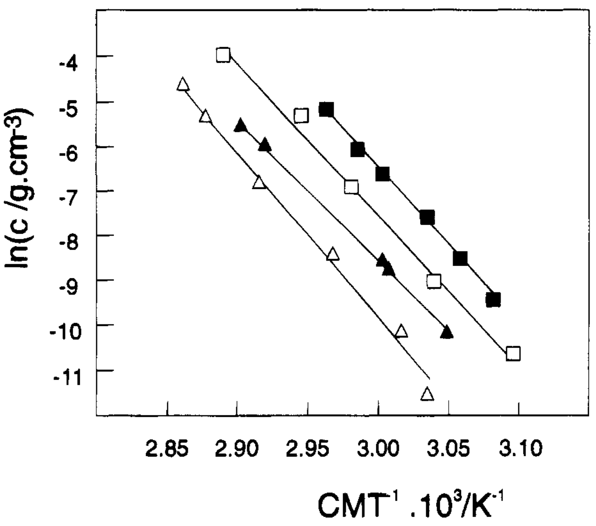

Figure 5. Plots of the logarithm of the solution concentration as a function of the reciprocal of the critical micelle temperature for the polystyrene-*block*-poly(ethylene/propylene) copolymer in 5-methyl-2-hexanone (■) and in 5-methyl-2-hexanone/2-pentanol mixtures: 95/5 (□), 90/10 (▲), and 85/15 (△).

is due to the influence of temperature on the equilibrium between micelles and free copolymer chains. At the upper end of the temperature range studied only free chains exist in the solution, whereas at low temperatures the equilibrium is overwhelmingly in favor of micelle formation. On lowering the temperature from a high value a sharp increase in the scattered intensity is observed due to the appearance of micelles. Simialr curves were found when increasing and decreasing the temperature for all micellar systems studied at different copolymer concentrations.

The variations of the logarithm of copolymer concentration as a function of the reciprocal of the critical micelle temperature are shown in Figure 5 for solutions of copolymer SEP2 in the different solvent mixtures. All these plots were linear within experimental error over the dilute solution range studied.

The values of the standard Gibbs energy, $\Delta G°$, the standard enthalpy, $\Delta H°$, and the standard entropy, $\Delta S°$, of micellization were calculated from the experimental data by means of (1) and (4) and are shown in Table 2. The standard Gibbs energy of micellization shows negative values for the polystyrene-*block*-poly(ethylene/propylene) copolymer in all the micellar systems studied, as expected. The standard entropy of micellization is also negative for all the micellar systems and, therefore, unfavorable to the micellization process. The negative values of the standard entropy of micellization can be explained by simple statistical arguments. The standard enthalpy of micellization also shows negative values, and therefore, it is solely responsible for the micelle formation. These negative values arise from the exothermic energy interchange which accompanies the replacement of core block segment/solvent interactions by core block segment/core block segment and solvent/solvent interactions in the formation of the micelle cores.

The standard Gibbs energy becomes slightly more negative as the 2-pentanol percentage in the solvent mixture increases. This suggests that the decay of the solvent quality leads to more stable micelles. Nevertheless, the standard enthalpy and entropy of micellization hardly depend on the solvent mixture composition. This fact can be explained by taking into account the fact that both solvents are precipitants for PEP blocks and therefore the solvent quality hardly varies with respect to the micelle core. Thus, the exothermic energy interchange which accompanies the formation of the micelle core hardly depends on the 2-pentanol percentage.

Conclusions

The addition of 2-pentanol (a precipitant of both copolymer blocks) to 5-methyl-2-hexanone (a selective solvent of polystyrene blocks) leads to a slight increase in the micelle molar mass and a decrease in the apparent radius of gyration, in the second virial coefficient, and in the degree of solvation, whereas the hydrodynamic radius remains constant. The standard Gibbs energy of micellization also becomes slightly more negative whereas the standard enthalpy and entropy hardly vary with the 2-pentanol percentage.

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