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Diblock Copolymer Micelles in Solvent Binary Mixtures. 2. Selective Solvent/Good Solvent

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ABSTRACT: Solutions of polystyrene-*b*-poly(ethylene/propylene) block copolymer in mixtures of 4-methyl-2-pentanone (a selective solvent of the polystyrene block) and 2-chlorobutane (a good solvent of both copolymer blocks) were studied by static and dynamic light scattering and viscometry. Micelle structural parameters and micellization thermodynamics have been analyzed as a function of the solvent composition. The micelle molar mass decreased as the 2-chlorobutane percentage in the binary mixture increased. However the apparent radius of gyration, the second virial coefficient, and the hydrodynamic radius hardly showed variations. Static light scattering was used to establish the dependencies of the critical micelle temperature on concentration. The standard Gibbs energies, enthalpies, and entropies of micellization have been calculated for the different solvent mixtures from these relationships. The three thermodynamic magnitudes became less negative as the good solvent percentage increased.

Introduction

The effect of solvent selectivity on the behavior of block copolymer solutions has been studied for a long time.[1−9] However, a full comprehension of the solvent influence on the micellization process has not been achieved yet. We have undertaken a study on the influence of the selectivity degree of the solvent in the micellar structure and in the micellization thermodynamics. Whereas in the previous paper[10] solvent selectivity has been decreased by adding a precipitant of both copolymer blocks, in this one, solvent selectivity has been decreased by adding a good solvent for both blocks. The micellization process of polystyrene-*b*-poly(ethylene/propylene) block copolymer in the 5-methyl-2-hexanone/2-pentanol solvent mixtures was studied as a function of the solvent composition in the previous paper. By variation of the solvent composition, the solvent quality of the medium was changed with respect to the copolymer blocks which form the micelle shell. However, the solvent quality of the medium with respect to the block copolymer which forms the micelle core hardly varied since both solvents are precipitants of these blocks.

The addition of a precipitant to a selective solvent leads to a decrease in the apparent radius of gyration, in the second virial coefficient, and in the solvation degree and to a slight increase in the molar mass. The hydrodynamic radius remains constant. The micellization thermodynamics hardly depends on the precipitant percentage in the solvent mixtures.

In the present paper the micelle structure and the micellization thermodynamics for a polystyrene-*b*-poly(ethylene/propylene) diblock copolymer in binary mixtures of 4-methyl-2-pentanone and 2-chlorobutane have been analyzed as a function of the solvent mixture composition. 4-Methyl-2-pentanone is a selective solvent of the polystyrene block, and 2-chlorobutane is a good solvent for both copolymer blocks. Both solvents have similar refractive indices, and consequently, the eventual contributions of selective adsorption to light scattering can be disregarded. By addition of 2-chlorobutane to 4-methyl-2-pentanone the solvent selectivity is continuously decreased, increasing the goodness of the binary solvent especially for the poly(ethylene/propylene) blocks, that form the micelle core. Analogously to the previous paper, light scattering, viscometry, and photon correlation spectroscopy have been used in this study.

Experimental Section

The molecular characteristics of polystyrene-*b*-poly(ethylene/propylene), SEP2, are reported in the previous paper.[10]

Different composition mixtures of 4-methyl-2-pentanone (a PS selective solvent) and 2-chlorobutane (good solvent for PS and PEP blocks) have been used as solvents. Solvent mixtures were made up by volume and contain 0, 10, 20, 30, 40, and 50% 2-chlorobutane. Both solvents (analytical purity grade) were used without further purification.

The preparation of the copolymer solutions and the experimental techniques used are described in the previous paper.[10]

Results

Structure and Hydrodynamic Behavior. The first part of this study dealt with the characterization of the structure of the micelles formed in different 4-methyl-2-pentanone/2-chlorobutane mixtures at 25 °C. In order to do that, static light scattering, SLS, viscometry, and dynamic light scattering, DLS, techniques were used. SLS was mainly performed on solutions whose concentrations ranged between 1×10^{-3} and 5×10^{-3} g·cm^{-3} at 25 °C. Zimm plots were obtained from the dependencies of scattering light intensity on angle and concentration at 25 °C. The plots were linear and had a normal shape for the systems with 0, 10, 20, and 30% 2-chlorobutane. These plots led to very high values of molar masses (Table 1). This fact and the shape of the Zimm plots evidenced the existence of micelles in the solutions and that the equilibrium overwhelmingly favored micelle formation.

The system with 40% 2-chlorobutane shows quite a different Zimm plot at 25 °C (Figure 1). The concentration dependence of $Kc/\Delta R_{\theta=0}$ is not linear. The curvature of the plot is due to the increase of the unimer fraction as the copolymer concentration decreases. This fact suggests that micelle formation in this solvent mixture is not totally favored at this temperature. The

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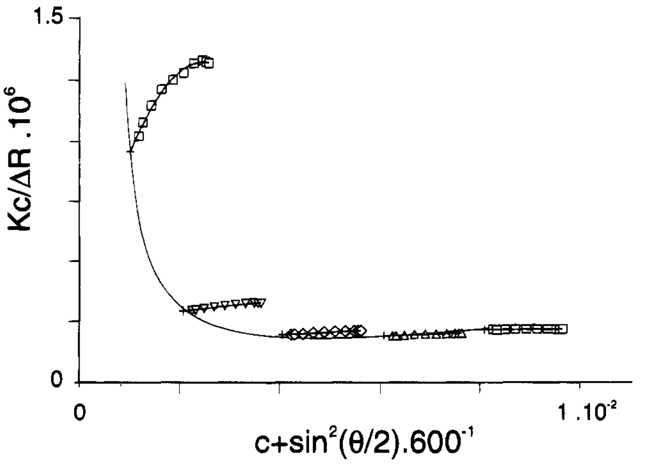

Figure 1. Zimm plot of copolymer SEP2 in the mixture 4-methyl-2-pentanone/2-chlorobutane (60/40) at 25 °C.

Table 1. Molar Mass, M_w, Second Virial Coefficient, A_2, Apparent Mean Square Radius of Gyration, R_G*, Intrinsic Viscosity, [η], and Hydrodynamic Radius, R_h, Obtained for Copolymer SEP2 Micelles in 4-Methyl-2-pentanone and in It Mixtures with 2-Chlorobutane at 25 °C (10, 20, and 30% 2-Chlorobutane) and 20 °C (40% 2-Chlorobutane) and for the Unassociated Copolymer SEP2 in 4-Methyl-2-pentanone/2-Chlorobutane (50/50 at 25 °C

	2-chlorobutane					
	0%	10%	20%	30%	40%	50%
$10^{-6} M_w$/g·mol^{-1}	50	48	35	29	20	0.1
$10^6 A_2$/mol·cm^3·g^{-2}	5.8	6.1	5.9	6.2	5.4	270
R_G*/nm	31.1	30.8	29.9	30.5	34.3	
[η]/cm^3·g^{-1}	14.0	16.5	18.5	22.8	24.0	60.2
R_h/nm	48.0	50.1	46.8	47.2	42.4	10.0

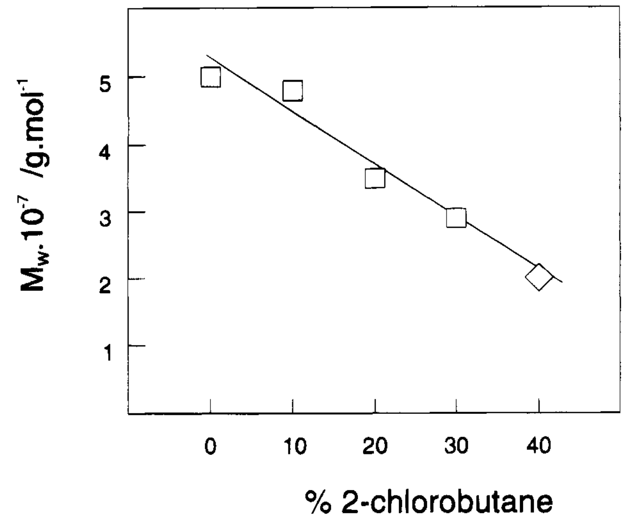

Figure 2. Molar mass of copolymer SEP2 micelles as a function of solvent composition.

curvature of the angle dependence of $Kc/\Delta R$ for the lowest copolymer concentration suggests a high polydispersity due to the fact that both species, micelles and free copolymer chains, coexist in this solution at comparable concentrations. However, the shape of the Zimm plot measured at 20 °C was normal and values of M_w, R_G, and A_2 could be obtained. Previous studies[7,9] have demonstrated that these micellar magnitudes hardly depend on temperature. Therefore, the values of M_w, R_G, and A_2 obtained at 20 °C can be considered as analogous to those corresponding to the micelles at 25 °C.

Solutions of copolymer SEP2 in the binary mixture 4-methyl-2-pentanone/2-chlorobutane (50/50) show a linear Zimm plot with no angular dependence. The molar mass obtained corresponds to the unassociated copolymer. The micelle formation is not favored under these experimental conditions ($c \leq 5 \times 10^{-3}$ g·cm^{-3} and $T = 25$ °C).

The micelle molar mass values found are high and they range between 20×10^6 and 50×10^6 g·mol^{-1}. These high values have been found for other copolymer/solvent systems in which the insoluble block is relatively large.[8,11] The variation of the micelle molar mass is plotted in Figure 2 as a function of the 2-chlorobutane percentage in the solvent binary mixture. M_w decreases as the percentage of the good solvent increases. There seems to exist a relationship between the core solvation and the micelle molar mass. The variation of the micelle molar mass that we have found agrees with that reported in the previous paper[10] where, for the micelle system SEP/5-methyl-2-hexanone/2-pentanol, the micelle molar mass increases slightly as the 2-pentanol percentage becomes higher. Taking into account that 2-pentanol is a stronger precipitant for the poly(ethylene/propylene) blocks than 5-methyl-2-pentanone, we can say that the molar mass increases as the micelle core becomes less solvated. Thus, the micelle association number does not depend on the selectivity character of the solvent but on the solvent quality in relation to the copolymer blocks which form the micelle core.

The system with 50% 2-chlorobutane has a relatively high A_2 value (2.7×10^{-4} mol·cm^3·g^{-1}) that corresponds to a system with unassociated chains. All the micellar systems show positive and very low values (ranging between 5×10^{-6} and 6×10^{-6} mol·cm^3·g^{-1}), that can be explained by taking into account the fact that the micelle structure avoids insoluble copolymer block/selective solvent contacts. No solvent composition dependence of the second virial coefficient has been found in these micellar systems (Table 1). This fact can be explained by considering that the main contribution to the A_2 value is that corresponding to the micelle shell, and all solvent mixtures studied show a similar solvent goodness for the micelle shell.

The apparent mean square radius of gyration, R_G*, remains constant as the percentage of the good solvent increases (Table 1). This behavior suggests that the addition of a good solvent does not affect the micelle shell, which is mainly responsible for the R_G value.

The viscometry technique was used to obtain more structural information. The concentration dependencies of η_{sp}/c (Huggins equation) and $\ln(\eta_r/c)$ (Kraemer equation) were linear for 4-methyl-2-pentanone and the binary solvent mixtures with 10, 20, 30, and 50% 2-chlorobutane at 25 °C. Both straight lines led to the same value of the intrinsic viscosity, [η], in the mentioned systems (Table 1). Whereas the copolymer SEP2 is not associated in the solvent mixture 4-methyl-2-pentanone/2-chlorobutane (50/50), practically only micelles exist in the solvent mixtures with a 2-chlorobutane percentage equal to or lower than 30%. The predominance of one type of particle explains the existence of a linear plot. Both kinds of particles exist with significant concentrations in the solvent mixture with 40% 2-chlorobutane at 25 °C, showing in the viscosity plots a strong curvature (Figure 3). As the copolymer concentration decreases, the unassociated copolymer chains become superior in number, leading to higher viscosity values. When the temperature is

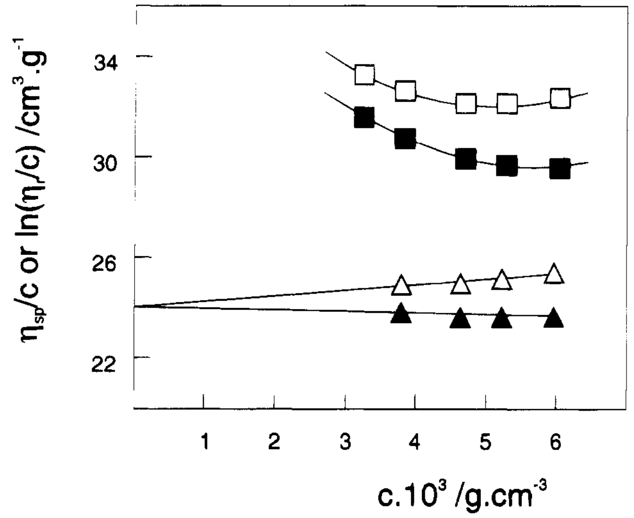

Figure 3. Concentration dependencies of η_{sp}/c (open symbols) and $\ln(\eta_r/c)$ (filled symbols) for copolymer SEP2 in the solvent mixture 4-methyl-2-pentanone/2-chlorobutane (60/40) at 25 (□) and 20 °C (△).

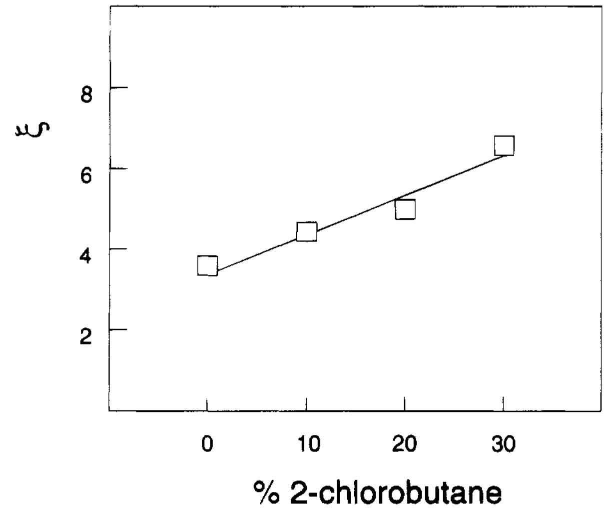

Figure 4. Dependence of the solvation degree, ξ, of copolymer SEP2 micelles on solvent composition at 25 °C.

lowered from 25 to 20 °C the critical micelle concentration is decreased, overwhelmingly favoring the micelle formation in all the experimental solutions. Thus, the viscosity plots become linear (Figure 3). The $[\eta]$ values found for the four micellar systems are very low, suggesting that micelles are very compact.

Intrinsic viscosity becomes higher as the good solvent percentage increases. This tendency may be related to a progressive core solvation that leads to a lower density and molar mass of the micelles. Micelles do not exist in the mixture 4-methyl-2-pentanone/2-chlorobutane (50/50). So, the higher value of the intrinsic viscosity suggests that the unassociated chains have a very much lower density than micelles, as was expected by taking into account their structures.

The values of the solvation degree,[12] ξ, found at 25 °C for the different micellar systems as a function of solvent composition are shown in Figure 4. These values are very low, confirming the fact that micelles have a high density. The increase of the solvation degree as the good solvent percentage increases provides new evidence of the progressive core solvation as the good solvent is added. The value of ξ found for the solvent mixture with 50% 2-chlorobutane (18.9) is very much higher than those corresponding to micelles, as can be expected for an unassociated polymer without an ordered structure.

Table 2. 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 4-Methyl-2-pentanone/2-Chlorobutane Mixtures ($c = 1 \times 10^{-3}$ g·cm^{-3})

	2-chlorobutane				
	0%	10%	20%	30%	40%
10^7D/cm^2·s^{-1}	1.005	0.999	1.040	1.094	1.086
R_h/nm (cumulant)	39.8	42.3	42.2	41.5	43.0
μ_2/Γ^2	0.023	0.022	0.004	0.012	0.050
$R_{h,micelles}$/nm (histogram)	40.7	43.2	42.3	41.9	45.1
$I_{micelles}$	1.06	1.07	1.01	1.00	1.06
$R_{h,unimers}$/nm (histograms)					10.5
$I_{unimers}$					1.01
I_{total}	1.06	1.07	1.01	1.00	1.97
$W_{unimers}/W_{total}$	0.0	0.0	0.0	0.0	0.7

The Einstein relationship allows us to calculate the hydrodynamic radius of the particles in the system, R_h, when the intrinsic viscosity and the molar mass are known.

The R_h values calculated for the different solvent compositions are shown in Table 1. As was expected, the mixture 4-methyl-2-pentanone/2-chlorobutane (50/50) has a low value corresponding to the hydrodynamic radius of an unassociated chain. However, the solvent mixtures with lower 2-chlorobutane percentages show higher values of the hydrodynamic radius, providing the existence of other kinds of structures in the solutions. These R_h values are higher than those corresponding to unassociated chains, but they seem very low when the high molar mass of the micelles is considered. The hydrodynamic radii found for these solvent mixtures are similar to those found for other SEP2 micellar systems with similar or lower association numbers.[8-10] Although the R_G values are only apparent, the ratio between the gyration and hydrodynamic radius, ranging between 0.62 and 0.65, suggests that micelles have a spherical shape,[13] as TEM measurements have shown for other micellar systems.[14]

The micelle hydrodynamic radius is not dependent on the solvent mixture composition, as has been reported in the previous paper.[10] In addition the R_h values found for the SEP2/4-methyl-2-pentanone/2-chlorobutane systems are equal to those found for the system SEP/5-methyl-2-hexanone/2-pentanol. This fact confirms the idea, already mentioned in the previous paper, that a given micelle has a unique hydrodynamic volume independent of the quality of the solvent.

Dynamic light scattering has been used to corroborate the previously obtained structural results and to get information on the hydrodynamic size distribution functions of the micelles. Table 2 shows the results obtained by the cumulant and histogram methods for the micellar systems. Unimodal distributions have been obtained in all the favored micellar systems (0, 10, 20, 30% 2-chlorobutane). The hydrodynamic radii obtained by either of the two methods are similar and confirm the constancy of this parameter. However, R_h values are smaller (between 10 and 17%) than those obtained by viscosity and SLS measurements. The variance and the polydispersity indices of the size distributions are very low in all cases ($\mu_2/\Gamma^2 \leq 0.023$, $I \leq 1.07$), pointing out that micelles have very narrow size distribution functions. This confirms the fact that the studied particles follow the close association model.

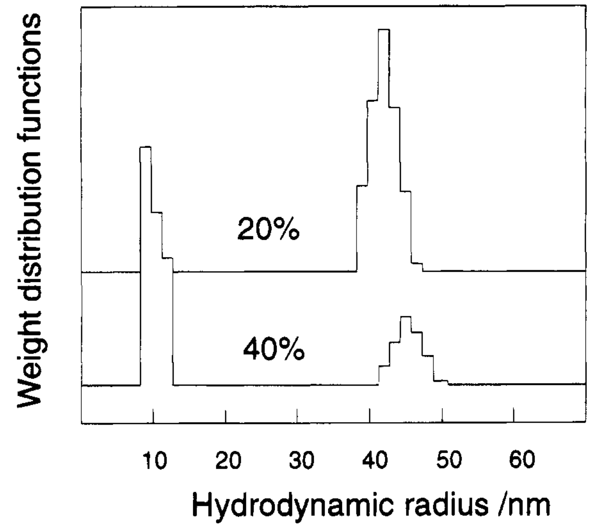

Figure 5. Histograms of the distribution functions obtained for copolymer SEP2 in 4-methyl-2-pentanone/2-chlorobutane mixtures with 20% and 40% 2-chlorobutane at 25 °C and concentration 1×10^{-3} g·cm^{-3}.

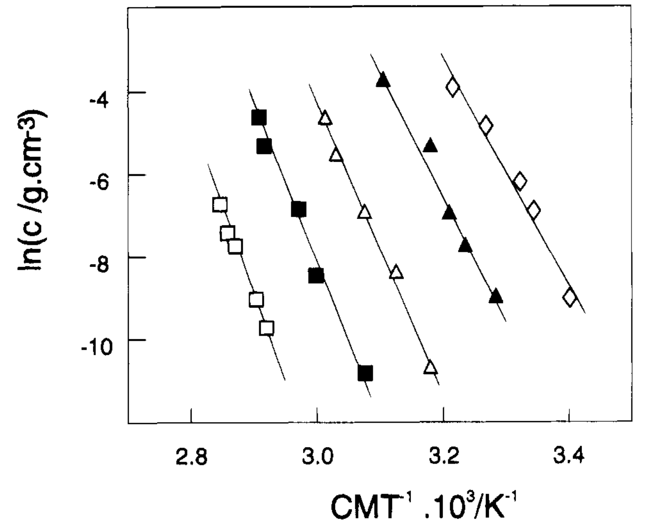

Figure 6. Plots of ln(*c*) as a function of the reciprocal of the critical micellar temperature for solutions of copolymer SEP2 in 4-methyl-2-pentanone/2-chlorobutane mixtures with different 2-chlorobutane percentage: 0% (□), 10% (■), 20% (△), 30% (▲), and 40% (◇).

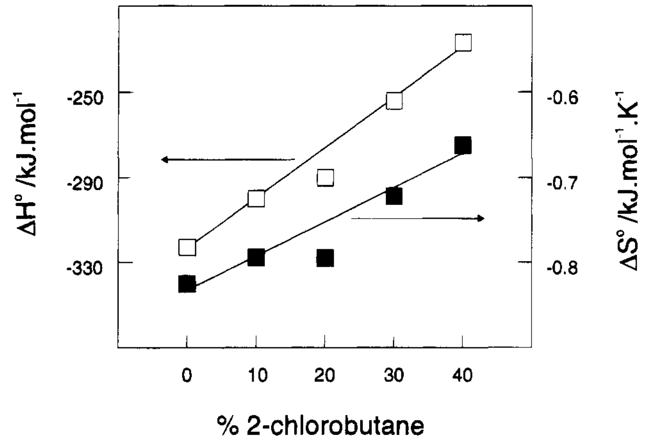

Figure 7. Variations of standard enthalpy (□) and entropy (■) of micellization as a function of solvent composition for systems SEP2/4-methyl-2-pentanone/2-chlorobutane.

A higher variance has been found in the system with 40% 2-chlorobutane where unimers and micelles coexist. A bimodal distribution function has been obtained; i.e. two kinds of particles have been detected (Figure 5). The smallest ones ($R_h \approx 10$ nm) are unassociated chains and the others ($R_h \approx 45$ nm) are micelles. The weight fraction of the former is close to 0.72, suggesting a CMC$_{25 °C}$ close to 7×10^{-4} g·cm^{-3}.

Thermodynamics of Micellization. To establish critical micelle temperatures, CMT, at some given concentrations, measurements of scattered light intensity were made at a series of temperatures within the range 25–90 °C at the scattering angles of 45, 90, and 135°. The relationship between concentration and CMT allows us to obtain the values of the standard enthalpy, the standard entropy, and the standard Gibbs energy of the micellization process.

CMTs were determined for the different solvent compositions covering a range of concentrations. The relationship of ln(*c*) versus CMT^{-1} was linear for all the solvent compositions (Figure 6). Critical micelle concentrations at 25 °C are very low for the solvent mixtures with 0, 10, 20, and 30% 2-chlorobutane (2.5×10^{-12}, 7.6×10^{-10}, 5.9×10^{-8}, and 1.4×10^{-5} g·cm^{-3}, respectively). These results confirm that the values of the different magnitudes obtained from SLS, viscometry, and DLS measurements with concentrations ranging between 1×10^{-3} and 5×10^{-3} g·cm^{-3} correspond to the micelles themselves.

The solvent mixture 4-methyl-2-pentanone/2-chlorobutane (60/40) shows a higher CMC$_{25 °C}$ (6.0×10^{-4} g·cm^{-3}), and thus, the unimer fraction is high enough to affect the shape of the SLS and viscosity plots. This CMC value is in good agreement with the free chain concentration obtained by DLS at 25 °C (7×10^{-4} g·cm^{-3}).

The values of the standard enthalpies and entropies of micellization are plotted in Figure 7 as a function of the solvent composition. For all solvent compositions, the standard enthalpy of micellization, $\Delta H°$, shows negative values and, therefore, is favorable to the micellization process. Its contribution to the Gibbs energy is responsible for the micelle formation. As 2-chlorobutane is added to the solvent mixture, the absolute value of $\Delta H°$ becomes smaller. The enthalpy of micellization is related to the suppression of solvent/insoluble block copolymer interactions that take place when micelles are formed. The decrease in the absolute value of $\Delta H°$ suggests that the number of PEP/4-methyl-2-pentanone interactions substituted for PEP/PEP and 4-methyl-2-pentanone/4-methyl-2-pentanone interactions along the micellization is reduced. The increase of the favorable PEP/2-chlorobutane interactions in the unassociated chains and in the micelle core is responsible for the reduction of the number of substituted unfavorable interactions.

The standard entropy of micellization, $\Delta S°$, also shows negative values and, therefore, is unfavorable to the micellization process. On comparison of different solvent compositions, it can be seen how the absolute value of $\Delta S°$ decreases. This fact can be related to the decrease in the association number and the increase in the micelle solvation degree observed by SLS and viscometry measurements that take place as 2-chlorobutane is added to the solvent mixture.

The variation of $\Delta H°$ and $\Delta S°$ as a good solvent is added to the system is similar to that found for the micellization of a SEP copolymer in *n*-dodecane/1,4-dioxane mixtures when the inverse selective solvent is added.[15] Taking into account that the addition of an

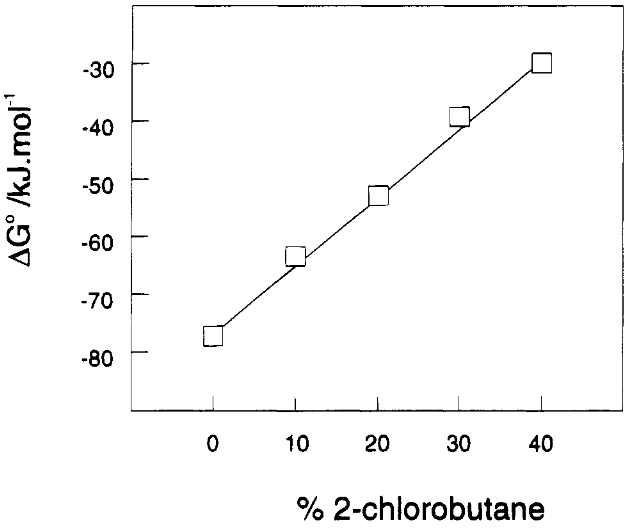

Figure 8. Variation of standard Gibbs energy of micellization at 25 °C as a function of solvent composition for systems SEP2/4-methyl-2-pentanone/2-chlorobutane.

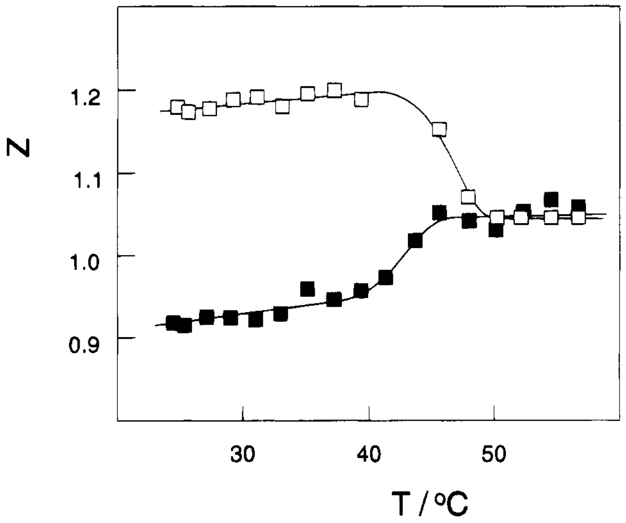

Figure 9. Plots of dissymmetry ratio, Z, against temperature for two SEP2/4-methyl-2-pentanone/2-chlorobutane systems: 20% 2-chlorobutane, $c = 2.32 \times 10^{-4}$ g·cm^{-3} (□) and 30% 2-chlorobutane, $c = 2.45 \times 10^{-2}$ g·cm^{-3} (■).

inverse selective solvent does not improve the solvent quality with respect to the micelle shell, it suggests that core formation is mainly responsible for the micelle stability. This result agrees with that reported in the previous paper for the micellization of copolymer SEP in 5-methyl-2-hexanone/2-pentanol mixtures. The addition of a precipitant did not change significantly the solvent quality of the mixture with respect to the core block, and therefore, $\Delta H°$ and $\Delta S°$ hardly change with the solvent mixture composition.

The variation of the standard Gibbs energy of micellization at 25 °C, $\Delta G°_{25}$, as a function of the solvent composition is plotted in Figure 8. For all the micellar systems, $\Delta G°_{25}$ is negative, as was expected. This value becomes less negative as the good solvent percentage increases, i.e. as solvent goodness increases. So, the stability of the micelles is reduced until no micelle appears at concentrations lower than 5×10^{-3} g·cm^{-3} in the mixture 4-methyl-2-pentanone/2-chlorobutane (50/50) at 25 °C.

The dissymmetry ratios were determined from the intensity measurements at 45 and 135°. The temperature dependence of the dissymmetry ratio for two micellar systems is shown in Figure 9. For a solution of SEP2 in 4-methyl-2-pentanone/2-chlorobutane (80/20) with a concentration of 2.32×10^{-4} g·cm^{-3} the dissymmetry ratio shows a normal temperature dependence. Three regions can be differentiated in this plot. At lower temperatures, where micelles are favored, Z values are close to 1.2 and hardly depend on temperature. At higher temperatures, where only unimers exist in solution, Z values are close to unity. Between both regions there exists a temperature range in which Z varies from the micelle value to the unimer one. The nondependence of the dissymmetry ratio on temperature at the lower temperatures suggests that micelle size and shape do not depend on temperature, as several studies have demonstrated for other micellar systems.[7,9] The plot of the temperature dependence of the dissymmetry ratio for a solution of copolymer SEP2 in 4-methyl-2-pentanone/2-chlorobutane (70/30) with a concentration of 2.45×10^{-2} g·cm^{-3} also shows three parts but with a different shape. Z values at the lower temperatures are lower than unity. This phenomenon is observed in micellar systems with a high enough copolymer concentration and, according to Price et al.,[16] can be explained by considering that on increasing the concentration, the micelles pack together like hard spheres; i.e. the local packing can be described by radial distribution functions for hard spheres.

Conclusions

The addition of 2-chlorobutane (a good solvent of both copolymer blocks) to 4-methyl-2-pentanone (a selective solvent of polystyrene blocks) leads to a sharp decrease in the micelle molar mass and an increase in the degree of solvation. The second virial coefficient, the apparent radius of gyration, and the hydrodynamic radius remain constant. The standard Gibbs energy, enthalpy, and entropy of micellization become less negative as the 2-chlorobutane percentage in the solvent mixture increases.

The structural and thermodynamic parameters of the micelles show different behaviors depending on the variations in the goodness of the solvent medium with respect to either the copolymer blocks which form the micelle core or the blocks which form the micelle shell. Thus, the micelle molar mass and the thermodynamic magnitudes of micellization depend mainly on the interactions between the solvent and the copolymer blocks which form the micelle core, whereas the apparent radius of gyration and the second virial coefficient depend on the interactions between the solvent and the copolymer blocks which form the micelle shell. The degree of solvation depends on the interactions between the solvent and any of the copolymer blocks. Finally, the hydrodynamic radius of micelles is independent of the solvent quality with respect to any of the copolymer blocks.

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References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Makromol. Chem.* **1972**, *160*, 301.

(2) Mandema, W.; Emeis, C. A.; Zeldenrust, H. *Makromol. Chem.* **1979**, *180*, 2163.

(3) Bednár, B.; Deváty, J.; Koupalová, B.; Králícek, J.; Tuzar, Z. *Polymer* **1984**, *25*, 1178.

(4) Oranli, P.; Bahadur, P.; Riess, G. *Can. J. Chem.* **1985**, *63*, 2691.

(5) Duval, M.; Picot, C. *Polymer* **1987**, *25*, 798.

(6) Quintana, J. R.; Villacampa, M.; Muñoz, M.; Andrío, A.; Katime, I. *Macromolecules* **1992**, *25*, 3125.

(7) Quintana, J. R.; Villacampa, M.; Andrío, A.; Muñoz, M.; Katime, I. *Macromolecules* **1992**, *25*, 3129.

(8) Quintana, J. R.; Villacampa, M.; Katime, I. *Polymer* **1993**, *34*, 2380.

(9) Quintana, J. R.; Villacampa, M.; Katime, I. *Macromolecules* **1993**, *26*, 606.

(10) Quintana, J. R.; Jáñez, M. D.; Villacampa, M.; Katime, I. *Macromolecules* **1995**, *28*, 4139.

(11) Quintana, J. R.; Villacampa, M.; Katime, I. *Makromol. Chem.* **1993**, *194*, 983.

(12) Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley & Sons; New York, 1961.

(13) Katime, I.; Quintana, J. R. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 1, Chapter 5.

(14) Booth, C.; Naylor, T. D.; Price, C.; Rajab, N. S.; Stubbersfield, R. B. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2352.

(15) Quintana, J. R.; Villacampa, M.; Katime, I. *Macromolecules* **1993**, *26*, 601.

(16) Price, C.; Hudd, A. L.; Wright, B. *Polymer* **1982**, *23*, 170.

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