Macromolecules **2002,** *35,* 7067−7073

Binding of Short Alkyl Chain Surfactants to the (Ethylene oxide)$_{13}$−(Propylene oxide)$_{30}$−(Ethylene oxide)$_{13}$ and (Ethylene oxide)$_{75}$−(Propylene oxide)$_{30}$−(Ethylene oxide)$_{75}$ Copolymers Studied by Microcalorimetry

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Received December 18, 2001; Revised Manuscript Received May 30, 2002

ABSTRACT: The enthalpy of transfer (ΔH_t) of neutral copolymers, at a fixed and low concentration ca. 10^{-3} mol kg^{-1}, from water to the aqueous surfactant solutions as a function of the surfactant concentration ($f_S m_S$) was determined at 25 °C. The surfactants studied are sodium octanoate, sodium decanoate, *N*-octylpyridinium chloride (OPC), and *N*,*N*-dimethyloctylamine-*N*-oxide (ODAO). The copolymers are (ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (L64) and (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (F68). The two copolymers show different hydrophilic−hydrophobic ratios, the larger being for F68. As a general feature, the shape of the ΔH_t vs $f_S m_S$ curve depends on the nature of the surfactant whereas the magnitude of the enthalpy depends essentially on the nature of both the surfactant and the copolymer. A quantitative analysis of the experimental data of the systems investigated was done. L64 and F68 in ODAO solutions behave like classical hydrophobic nonionic additives. OPC does not exhibit specific interactions toward F68. A cooperative binding between the copolymer and the surfactant is present in the other systems studied. The standard free energy, enthalpy and entropy for the copolymer−surfactant complex formation were obtained. From these data, the isotherm bindings were calculated in the range 20−30 °C; temperature is a crucial parameter in determining the copolymer−surfactant interactions.

Introduction

Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-(poly(ethylene oxide)) (PEO−PPO−PEO) are water-soluble amphiphilic copolymers, which exhibit interesting thermodynamic and structural behaviors in solution.[1−4] The main feature of these macromolecules is the unique ability to self-assemble in water and to modify the interfacial properties. This can be easily achieved, since modulating the PEO/PPO ratio and the molecular weight of each block may change the architecture of the copolymer. The aggregates are core−corona structures where the PPO block is located in the core and the hydrated PEO block in the corona.[1−4] For instance, a recent small-angle neutron scattering[1] study showed that the aggregation number of (ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (L64) micelles increases with temperature leading to the formation of aggregates of larger radius. Also, at temperatures above 50 °C the micelle aggregation number exhibits a stronger increase because the core and the corona become less solvated. Volume studies[2,3] demonstrated a water free core of L64 aggregates in the range 20−28 °C.

Surfactant−copolymer (or polymer) mixtures may associate into different microstructures, which can be designed by simply changing the composition of the species in the system. Using copolymers is more advantageous than polymers as they undergo aggregation processes. It is known that copolymers interact with classical surfactants, although the literature on this topic is not extensive.[2,5−10] The studies were focused on mixtures formed by PEO−PPO−PEO and classical anionic, cationic, and nonionic surfactants. The calorimetry was revealed to be very appropriate in analyzing these systems: isothermal titration calorimetry[5,8−10] and differential scanning calorimetry[8−10] are the most used techniques for this purpose; namely, the systems formed by (ethylene oxide)$_{97}$−(propylene oxide)$_{69}$−(ethylene oxide)$_{97}$ (F127) and sodium dodecyl sulfate,[8] tetradecyltrimethylammonium bromide[10] and hexaethylene glycol mono-*n*-dodecyl ether[9] were studied. It was demonstrated that the mechanism of interaction between copolymer and surfactant is system specific and strongly dependent on temperature. No quantitative information on the thermodynamics of interaction between copolymer and surfactant has been drawn.

To contribute to the understanding of the thermodynamic behavior of the copolymer/surfactant systems, the effect of the surfactant headgroups as well as the copolymer hydrophobic/hydrophilic ratio were analyzed. The surfactants studied are sodium octanoate, sodium decanoate, *N*-octylpyridinium chloride, and *N*,*N*-dimethyloctylamine-*N*-oxide. The copolymers are (ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ and (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (F68), which show different hydrophilic/hydrophobic ratios, the larger being for F68. Since the aim of the paper was to study the behavior of unassociated copolymers, fixed and low concentrations far from the cmc values were chosen (ca. 10^{-3} mol kg^{-1}). The enthalpies of transfer of the copolymer from water to the aqueous surfactant solutions as functions of the surfactant concentrations were determined at 25 °C.

Experimental Section

Materials. Sodium octanoate (NaOct) and sodium decanoate (NaDec), Sigma, were recrystallized from absolute

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10.1021/ma012194o CCC: $22.00

ethanol and dried in a vacuum oven at 40 °C for at least 4 days. *N*-Octylpyridinium chloride (OPC)[11] and *N*,*N*-dimethyloctylamine-*N*-oxide (ODAO)[12] were synthesized according to the literature procedures. The water content of OPC and ODAO was determined by thermogravimetry (Mettler TA 3000). An additional determination of the ODAO water content was done by performing a conductivity titration of a given surfactant mixture by means of a standard HCl 0.1 N solution (Aldrich).

The cmc values in water of the surfactants studied are as follows: 0.30 mol kg^{-1} for OPC,[11] 0.15 mol kg^{-1} for ODAO,[13] 0.45 mol kg^{-1} for NaOct,[14] and 0.11 mol kg^{-1} for NaDec.[14]

The purity of the surfactants was confirmed by their standard partial molar volumes, evaluated from density measurements, which agree with those reported elsewhere.[11,13,14]

(Ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (L64) and (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (F68) were obtained from Fluka. L64 (MW = 2900) was used as received since no difference in the apparent molar volume values of purified and not purified L64 was observed.[3] F68 (MW = 8350) was purified according to the literature procedure.[15]

All solutions were prepared by mass using degassed conductivity water and their concentrations were expressed as molalities.

Equipment. (a) Enthalpy Measurements. The calorimetric measurements were carried out at 25 ± 0.01 °C with a flow LKB 2107 microcalorimeter. For the water−surfactant−copolymer ternary systems, the measurements were carried out as follows. A given surfactant solution and water are pushed through two Teflon tubes connected to the cell of mixing (ca. 0.5 cm^3) by means of a Gilson peristaltic pump (Minipuls 2). When the equilibrium is reached, a copolymer solution replaces water. The experimental enthalpy (ΔH^{exp}) corresponds to the difference between the thermal effect due to the mixing of the copolymer solution with the surfactant solution and that for the dilution process of the same surfactant solution with water.

For the copolymer−water systems, it was operated in the following manner: (1) water was taken as baseline, and (2) the copolymer solution replaced water flowing into a tube. The enthalpy of dilution of the copolymer ($\Delta H_{id,P}$) corresponds to the thermal effect recorded upon the mixing of the copolymer solution with water. The dilution of the F68 solution with water (from 2×10^{-3} to 1×10^{-3} mol kg^{-1}) did involve a thermal effect of −3.08 kJ mol^{-1}. The same $\Delta H_{id,P}$ value was obtained for the dilution process of L64 solution from 1×10^{-2} to 5×10^{-3} mol kg^{-1} whereas the value of −1.71 kJ mol^{-1} was derived for the dilution of L64 solution from 5×10^{-3} to 2.5×10^{-3} mol kg^{-1}.

The flow of each solution (ca. 3×10^{-3} g s^{-1}) was determined by weight.

The measurements were carried out at a fixed copolymer concentration in a wide range of the surfactant concentration.

Since the mixing process involves the dilution of both the surfactant and the copolymer solutions, the final concentrations of the copolymer ($f_P m_P$) and the surfactant ($f_S m_S$) were calculated as the product between the initial concentration (m_P or m_S) and the dilution factor given by

$$f_S = \phi_S/(\phi_S + \phi_P) \quad f_P = \phi_P/(\phi_S + \phi_P) \tag{1}$$

Here ϕ_P and ϕ_S represent the flows of water in the copolymer and the surfactant solutions, respectively.

The $f_P m_P$ values are ca. 1 and 5 mmol kg^{-1} for the mixtures containing F68 and L64, respectively; for the L64/NaDec system, $f_P m_P$ is 2.5 mmol kg^{-1}.

The enthalpy of transfer (ΔH_t) of the copolymer from water to the aqueous surfactant solution was calculated as difference between ΔH^{exp} and $\Delta H_{id,P}$.

By excluding the L64−NaDec−water system, experimental difficulties did not permit to extend the measurements to the surfactant concentration values larger than those reported.

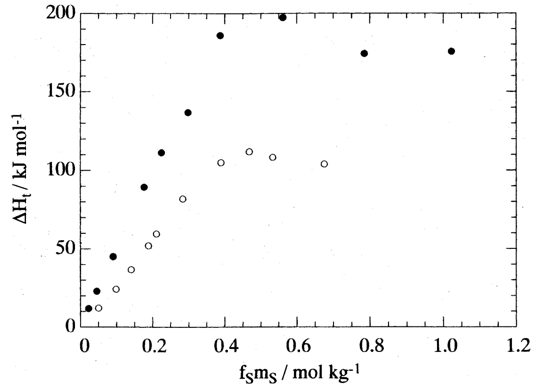

Figure 1. Enthalpy of transfer of L64 (open symbols) and F68 (filled symbols) from water to the aqueous *N*-octylpyridinium chloride solutions as a function of the surfactant concentration.

(b) Density Measurements. The solutions densities were measured at 25 °C by using a vibrating tube flow densimeter (model 03D, Sodev Inc.) sensitive to 3 ppm. The temperature was maintained constant within 0.001 °C by using a closed loop temperature controller (model CT-L, Sodev Inc.). The calibration of the densimeter was performed with water (d = 0.997047 g cm^{-3})[16] and aqueous sodium chloride solutions whose densities are known.[17]

The apparent molar volume ($V_{\Phi,S}$) of ODAO in the L64+water 5×10^{-3} mol kg^{-1} was calculated as

$$V_{\Phi,S} = \frac{M}{d} - \frac{10^3(d - d_o)}{m_S d d_o} \tag{2}$$

where m_S and M are the molality and the molecular weight of the surfactant; d and d_o are the densities of the solution and solvent, respectively.

The presence of water in the ODAO product modifies the water + L64 mixture composition of the ODAO + water + L64 ternary system. For this reason, the density of the binary solvent was calculated at each surfactant concentration from literature data.[2]

Results

For a given surfactant, the shape of the ΔH_t vs $f_S m_S$ curve is essentially independent of the copolymer nature whereas the magnitude of the enthalpy is larger for F68. Also, for a given copolymer, the profile of the ΔH_t vs $f_S m_S$ curve depends on the nature of the surfactant headgroup.

The enthalpy of transfer of F68 from water to the aqueous OPC solutions changes linearly with $f_S m_S$ up to 0.4 mol kg^{-1}; thereafter, ΔH_t decreases with $f_S m_S$ (Figure 1). For L64, ΔH_t shows a smooth change in the slope around at ca. 0.2 mol kg^{-1} and a maximum at 0.4 mol kg^{-1}. The maxima are localized at $f_S m_S$ values slightly larger than the cmc in water (cmc$_w$).[11]

The copolymer/sodium alkanoate systems exhibit the same behavior as L64/OPC. Namely, for the copolymer/NaOct mixtures, ΔH_t increases with $f_S m_S$ showing a smooth variation in the slope around at ca. 0.3 mol kg^{-1} and a maximum localized at 0.5 mol kg^{-1} (Figure 2). The L64−NaDec system exhibits a stronger variation of ΔH_t with $f_S m_S$ compared to L64/NaOct: ΔH_t sharply increases at ca. 0.03 mol kg^{-1} and exhibits a maximum at ca. 0.1 mol kg^{-1} (Figure 3). For these systems, the maxima appear at $f_S m_S$ values very close to cmc$_w$.[14] By excluding the F68/OPC system, the graphs in Figures 1−3 are reminiscent of those dealing with the poly(ethylene glycol)s (400 and 35000 molecular weight) in aqueous sodium perfluoroalkanoate solutions.[18] It is to

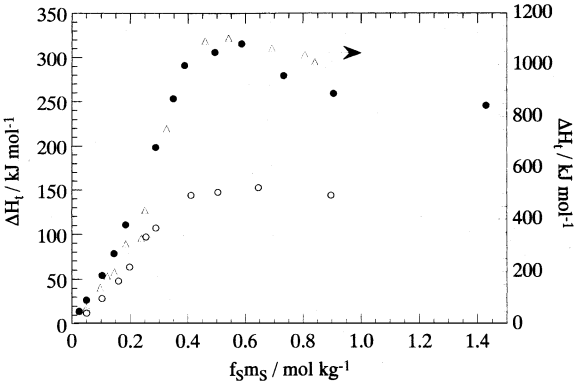

Figure 2. Enthalpy of transfer of L64 (open circles) and F68 (filled circles) from water to the aqueous sodium octanoate solutions as a function of the surfactant concentration. Open triangles show enthalpy of transfer of PEG 35000 from water to the aqueous sodium perfluoropentanoate solutions as a function of the surfactant concentration.

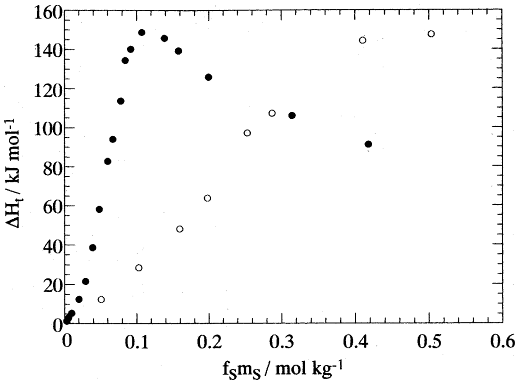

Figure 3. Enthalpy of transfer of L64 from water to the aqueous solutions of sodium octanoate (open symbols) and sodium decanoate (filled symbols) as a function of the surfactant concentration.

be noticed that the profiles of the ΔH_t vs $f_S m_S$ curves of F68 and L64 in NaOct superimpose to that of PEG 35000 in sodium perfluoropentanoate[18] (Figure 2), but the ΔH_t magnitude is quite different. Both surfactants exhibit comparable hydrophobic character according to the accepted idea that the hydrophobicity of the perfluoromethylene group is 1.5 times that of the methylene group;[19,20] the comparable cmc$_w$ values corroborate it.[14,20]

The interactions in the polymer/surfactant systems are usually[21] described by two critical concentrations: (1) the critical aggregation concentration (cac), which corresponds to the surfactant concentration where the formation of polymer/surfactant complexes occurs and (2) the concentration at which micelles are forming provided that the polymer becomes saturated with the surfactant clusters. Indeed, for some polymer/surfactant systems,[5,18] before that the polymer is saturated, micelles are forming at m_S values close to cmc$_w$.[18] These different behaviors may be explained on the basis of the literature idea;[22] the polymer/surfactant systems are essentially highlighted by two competitive cooperative processes: the formation of the surfactant–polymer complexes and the micelles. If the equilibrium constant for the first process (K_C) is larger than that for the second process (K_M), free micelles begin to form after the polymer is saturated if the aggregation number of the clusters bounded to the polymer (N_C) is nearly equal to that of the micelles (N_M). This occurs for the sodium dodecyl sulfate (NaDS)–(propylene oxide)$_{19}$–(ethylene oxide)$_{33}$–(propylene oxide)$_{19}$ aqueous system.[5] If K_C is still larger than K_M but $N_M > N_C$, free micelles are forming although the polymer is not yet saturated. This case may be represented by the PEG/sodium perfluoroalkanoate systems;[18] namely, for a given system, ΔH_t increases with $f_S m_S$ in a sigmoidal manner up to the cmc; thereafter, it strongly decreases tending to a constant negative value. The data below the maximum were interpreted by assuming the cooperative binding between polymer and dispersed surfactant whereas those above it were rationalized by invoking the binding of the polymer to the micellar surface.

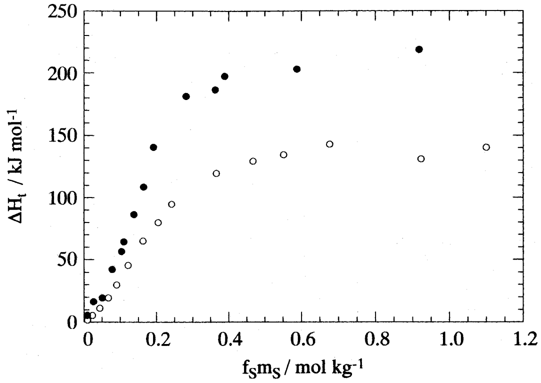

Figure 4. Enthalpy of transfer of L64 (open symbols) and F68 (filled symbols) from water to the aqueous *N*,*N*-dimethyloctylamine-*N*-oxide solutions as a function of the surfactant concentration.

The hypothesis of the copolymer–surfactant complex formation in the premicellar region may be reliable for the systems just discussed with the exception of F68/OPC. The dependence of ΔH_t on $f_S m_S$ in the post-micellar region does not exhibit the characteristics of the micelles/copolymer cooperative binding.

The features of the ΔH_t vs $f_S m_S$ plots for L64 and F68 in ODAO (Figure 4) are different from the others. For a given system, ΔH_t vs $f_S m_S$ is a well-defined S-shaped curve in the wide range of the surfactant concentration analyzed. Thus, in contrast to the above findings, in the surfactant region near the cmc$_w$[13] no peculiarities are present. Two interpretations could take into account the experimental data: (1) the cooperative binding between the copolymer and the surfactant may be present or, in other words, the ODAO micelle formation is excluded and (2) the copolymer–surfactant mixed micelles do form around at ca. 0.1 mol kg^{-1}. The apparent molar volume of ODAO in the water + L64 mixture 5.0×10^{-3} mol kg^{-1} ($V_{\Phi,S}$) as a function of m_S (Figure 5) evidences the cmc at 0.1 mol kg^{-1}. The $V_{\Phi,S}$ vs m_S curve is typical of the micellization process as $V_{\Phi,S}$ slightly changes with m_S up to 0.1 mol kg^{-1} thereafter it increases and it superimposes to the values in water at high concentration. Also, the $V_{\Phi,S}$ points are equal to those in water to 0.1 mol kg^{-1}. The decrease of the cmc upon the addition of L64 is consistent with the hydrophobic behavior of the copolymer, which solubilizes in the ODAO micelles. These results agree with the findings of Courdec et al.[9] who showed that at 20 °C the binding between (ethylene oxide)$_{97}$–(propylene oxide)$_{69}$–(ethylene oxide)$_{97}$ (F127) and the nonionic surfactant hexaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_6$) causes the aggregation of monomeric F127, which forms mixed micelles with $C_{12}E_6$. Also, calorimetric titrations of $C_{12}E_6$ in aqueous solutions of poly(propylene oxide), poly(ethylene oxide) and

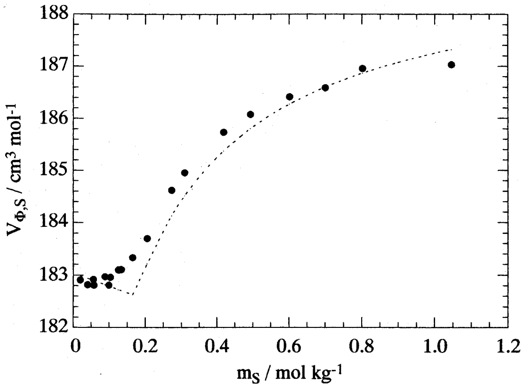

Figure 5. Apparent molar volume of *N*,*N*-dimethyloctylamine-*N*-oxide in water (- - --) and in the aqueous L64 solution 5×10^{-3} mol kg^{-1} (symbols) as a function of the surfactant concentration.

their mixtures demonstrated that the surface activity of F127 is responsible for the promotion of the mixed micelles. Finally, the free $C_{12}E_6$ monomer concentration decreases upon the addition of F127 in agreement with our cmc results.

On the basis of literature data,[23,24] the mixed micelles formation cannot be even excluded for the copolymer/ionic surfactant systems. In fact, water−surfactant−additive ternary systems[23,24] highlighted by the hydrophobicity of the additive being larger than that of the surfactant, exhibited trends of the properties of transfer (ΔY_t) vs m_S similar to those shown in Figures 1−3. The experimental data were interpreted by invoking the shift of the micellization equilibrium induced by the additive and the distribution of the additive between the aqueous and the micellar phases. If the former contribution is predominant, the ΔY_t vs m_S curve displays a maximum in the case of volume and enthalpy and a minimum in the case of heat capacity.

Quantitative Analysis of the Enthalpy of Transfer: Surfactant/Copolymer Complex Formation. The S-shaped curves of ΔH_t vs $f_S m_S$ in the premicellar region can be interpreted according to the one-step association model. It assumes that a constant number of surfactant molecules (n) can complex a copolymer molecule;[18] obviously, *n* is an average value since it likely changes with the surfactant concentration.

$$\Delta H_t = \chi_C \, \Delta H_C + 2h_{PS}(f_S m_S - \mathrm{n} m_C)(1 - \chi_C) \quad (3)$$

Here χ_C is the fraction of the complexed copolymer and ΔH_C is the enthalpy change for the complex formation; m_C is the molality of the complex and h_{PS} is the interaction parameter between the surfactant and the copolymer not involved in the cooperative process.

If the concentration of the polymer is low, as in the present cases, ΔH_C can be stated constant and equal to the standard property (ΔH_C°) and χ_C may be written in terms of the equilibrium constant (K_C) for the polymer−surfactant complex formation as

$$\chi_C = K_C(f_S m_S)^n/[1+ K_C(f_S m_S)^n] \quad (4)$$

In the absence of complexes, ΔH_t changes linearly with $f_S m_S$ according to the interaction contribution ($2h_{PS}f_S m_S$); that is the case for the F68/OPC system. For other copolymer-ionic surfactant systems, both the terms of interaction and complex formation contribute to ΔH_t. It was shown that the interaction contribution is present if the process is not highly cooperative[18] as in the case of short alkyl chain surfactants. For this reason, the experimental curves of ΔH_t vs $f_S m_S$ do not clearly evidence the critical aggregation concentration.

In the minimizing procedure, according to eqs 3 and 4, the value of *n* was changed in order to minimize the standard deviation of the ΔH_t vs $f_S m_S$ plot. The results of the best fits are collected in Table 1 whereas some examples are shown in Figure 6.

The standard free energy (ΔG_C°) and entropy ($T\Delta S_C^\circ$) for the complex formation per mole of surfactant's monomer were calculated as[18]

$$\Delta G_C^\circ/n = -(RT \ln K_C)/n \quad (5)$$

$$T\Delta S_C^\circ/n = \Delta H_C^\circ/n - \Delta G_C^\circ/n \quad (6)$$

Their values are collected in Table 1.

Quantitative Analysis of the Enthalpy of Transfer: Surfactant/Copolymer Mixed Micelles Formation. According to the literature idea,[22] for the copolymer−ODAO system it may occur that $K_M > K_C$ and $N_M \approx N_C$ so that mixed micelles are forming. Thus, the h_{PS} parameter was evaluated from the slope of the ΔH_t vs $f_S m_S$ straight line in the premicellar region.[29] The data in the post-micellar region were analyzed by using the following equation derived on the basis of the additive distribution between the aqueous and the micellar phases and the shift of micellization equilibrium caused by the presence of the additive[28]

$$\Delta H_t = \Delta H_{t,w}^\circ - (\Delta H_{t,a}^\circ - A_{cdc}\Delta H_m)N_f \quad (7)$$

where $\Delta H_{t,a}^\circ$ stands for the standard enthalpy of transfer of the copolymer from the aqueous to the micellar phases and $\Delta H_{t,w}^\circ$ ($=\Delta H_{t,a}^\circ + 2h_{PS}\mathrm{cmc}$) is the standard enthalpy of transfer of the copolymer from water to the micellar phases. The quantities N_f and $A_{cdc}\Delta H_m N_f$ are the fraction of the copolymer in the aqueous phase and the shift of micellization equilibrium term, respectively[28]

$$N_f = 1/[1 + K_b(f_S m_S - \mathrm{cmc})] \quad (8)$$

$$A_{cdc}\Delta H_m = (\Delta H_m \mathrm{cmc})(2.3K_S + K_b) \quad (9)$$

where K_S and K_b represent the Setchenov constant and the copolymer−micelle binding constant, respectively, whereas ΔH_m is the enthalpy of micellization (for ODAO it is 14.6 kJ mol^{-1}).[13] The best fits of the experimental data to eqs 7−9 provided K_b, $\Delta H_{t,a}^\circ$, and K_S, the values of which are collected in Table 1.

The standard free energy and entropy of transfer of the copolymer from the aqueous to the micellar phases were calculated (in the molarity scale) as[28]

$$\Delta G_{t,a}^\circ = -RT \ln(K_b/V_S) \quad (10)$$

$$T\Delta S_{t,a}^\circ = \Delta H_{t,a}^\circ - \Delta G_{t,a}^\circ \quad (11)$$

where V_S is the partial molar volume of the micellized surfactant, which is 188.60 cm^3 mol^{-1} for ODAO.[13]

Equations 7−9 should be used to verify whether the experimental data of the copolymer/ionic surfactant systems are consistent with the mixed micelles formation. These equations were derived by assuming the pseudo-phase transition model for micellization and a mass action model for the additive distribution between the aqueous and the micellar phases.[25] Similar equations, based on the mass action model for the micelli-

Table 1. Thermodynamic Properties for the Binding between Copolymers and Hydrogenated Surfactants at 25 °C[a]

	L64				F68		
	NaOct	NaDec	OPC	ODAO	NaOct	OPC	ODAO
h_{PS}	98 ± 20	227 ± 36	111 ± 4	139 ± 6	200 ± 45	240 ± 3	256 ± 22
K_b				6 ± 1			9 ± 2
K_S				−4 ± 2			−5 ± 2
$\Delta G^\circ_{t,a}$				−8.6 ± 0.4			−9.6 ± 0.6
$\Delta H^\circ_{t,w}$				171 ± 7			247 ± 10
$\Delta H^\circ_{t,a}$				149 ± 7			196 ± 10
$T\Delta S^\circ_{t,a}$				158 ± 7			206 ± 10
n	3.0	3.1	2.9		3.0		
K_C	44 ± 10	3563 ± 444	21 ± 3		32 ± 5		
$\Delta G^\circ_C/n$	−3.1 ± 0.3	−6.5 ± 0.1	−2.6 ± 0.1		−2.9 ± 0.4		
$\Delta H^\circ_C/n$	53 ± 1	59 ± 2	40.3 ± 0.5		113 ± 3		
$T\Delta S^\circ_C/n$	56 ± 1	67 ± 2	42.9 ± 0.5		116 ± 3		

[a] Units are as follows: Free energy, enthalpy and entropy, kJ mol^{-1}; K_b and K_S, kg mol^{-1}. K_C, kg^n mol^{-n}; h_{PS}, kJ kg mol^{-2}.

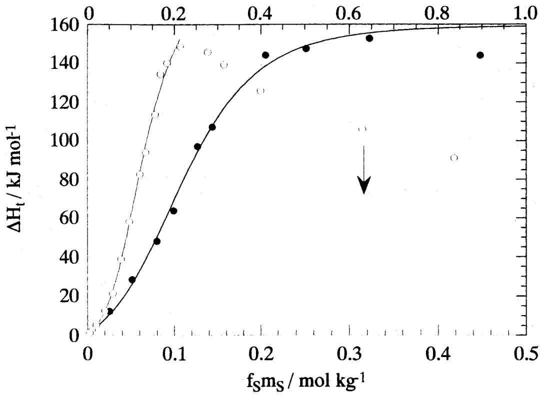

Figure 6. Best fits according to eqs 3 and 4 for L64/sodium octanoate (filled symbols) and L64/sodium decanoate (open symbols) systems.

zation and the pseudo-phase transition model for the additive solubilization in the micellar phase, were proposed by Desnoyers et al.[23,26] The former models predict a discontinuity at the cmc of a given thermodynamic property whereas the Desnoyers et al. models predict a more regular trend in the region near the cmc. Consequently, for surfactants having high cmc the latter approach is preferable. For this reason, we applied the Desnoyers et al. models to the water−L64−NaDec system, which shows a well-defined dependence of ΔH_t on $f_S m_S$. The attempt of minimization failed being impossible to fit all the curve. Other thermodynamic investigations agree with this finding.[27]

Discussion

The role of the surfactant headgroup has always been fundamental in the studies of surfactant/polymer systems. It is well documented[30] that anionic surfactants show strong affinity toward neutral polymers whereas cationic and nonionic surfactants slightly do or do not. By modulating the hydrophobicity of the polymer, the interaction becomes stronger but it is still weak. It was inferred that ion−dipole interactions are very effective in the case of anionic surfactants whereas they are absent or weaken for large size heads such as trimethylammonium bromide or pyridinium. These literature findings are confirmed by the analysis of the present experimental data, which demonstrated that the mechanism of interaction between the copolymer and the surfactant essentially depends on the nature of the surfactant polar head. Whatever is the binding process (formation of surfactant−copolymer complexes or mixed micelles) the contribution to the enthalpy due to the interactions between dispersed surfactant and free copolymer is always present. The increase of the surfactant hydrophobicity causes a positive contribution, as the h_{PS} values for L64/NaDec and L64/NaOct show. A similar behavior was exhibited by the PEG 35000/sodium perfluoroalkanoate systems.[18] For a given copolymer and a surfactant tail, the h_{PS} parameter is basically independent of the surfactant headgroup suggesting that the main interactions involve dehydrated hydrophobic parts of the copolymer and the surfactant. The h_{PS} values for the F68/surfactant systems are the largest ones. This evidence excludes the ion−dipole interactions (expected to be more favorable for F68, which possesses more EO units) that should involve a negative effect.[5] Nevertheless, a consequence of the interactions between the surfactant and PPO block, the EO units may undergo conformational changes (folding or defolding and eventual consequent coil−coil interactions).

The interaction parameter for the free energy g_{CS} (given by RTK_S/4)[31] is available only for the L64/ODAO and the F68/ODAO systems. Their values are negative according to the favorable interactions between the surfactant and the copolymer. The equal g_{CS} values for both the systems support the above hypothesis and are the result of the enthalpy−entropy compensation. The parameter for the entropy is large and increases with the hydrophilicity of the copolymer.

As concerns the thermodynamics for the copolymer/ODAO mixed micelles formation, $\Delta G^\circ_{t,a}$, within the errors, is independent of the copolymer architecture. This result suggests that the hydrophobic interaction between the micelles and the PPO block is the driving force for the mixed micelles formation. Namely, the PO segments may be solubilized in the palisade layer and the EO units in the aqueous phase. The dehydration of the PO segments and the expulsion of water molecules from the palisade layer alone cannot justify the dependence of the enthalpy and entropy on the copolymer nature. Therefore, the larger $\Delta H^\circ_{t,a}$ and $T\Delta S^\circ_{t,a}$ values for F68/ODAO can be ascribed to the variation of the folding of the PEO blocks induced by the PO segments solubilization in the micellar phases. Our results are consistent with the findings of Li et al.[10] who invoked the interactions between the methyl groups in the PPO segments and the region between the headgroups on the micellar surface to explain the solubilization in the tetradecyltrimethylammonium bromide micelles.

As far as the L64/sodium alkanoate systems are concerned, the $\Delta G^\circ_C/n$ values decrease with the alkyl chain length of the surfactant, providing a methylene group contribution of -1.7 ± 0.2 kJ mol^{-1}. This value is 1.6 times smaller than that evaluated (-2.7 ± 0.2 kJ mol^{-1}) for the perfluoromethylene group in the cooperative binding with PEG 35000;[18] that is consistent with the different hydrophobicity of the two groups. Since it was inferred that the CF_2 group is located in the core of the aggregates bounded to the polymer, the same conclusion may be drawn for the CH_2 group. From the $\Delta G^\circ_C/n$ values, one expects a positive contribution for the interactions between the headgroup and the copolymer. Consequently, hydrophobic forces control the binding process. $\Delta H^\circ_C/n$ and $T\Delta S^\circ_C/n$ are positive and, then, the process is entropy driven. They are consistent with the desolvation of both the surfactant alkyl chain and the hydrophobic block of the copolymer and their interactions. Also, their values, 1 order of magnitude different than $\Delta G^\circ_C/n$, are indications of the enthalpy–entropy compensation present in the cooperative processes.[18,32] PEG 35000/sodium perfluoroalkanoate systems exhibited similar features.[18]

L64/NaOct and F68/NaOct systems show $\Delta G^\circ_C/n$ values that, within the errors, are equal as a compensation effect between different enthalpy and entropy. These results agree with the hypothesis that the methyl groups in the PPO block provide the nucleus for the formation of the surfactant clusters. L64 and F68 differ for the number of EO units so that the different $\Delta H^\circ_C/n$ and $T\Delta S^\circ_C/n$ values may be ascribed to their conformational changes because of the binding process. The effect of the length of the PPO block was studied by determining the isothermal titration calorimetric curves of NaDS in aqueous solutions of (propylene oxide)$_8$–(ethylene oxide)$_{22}$–(propylene oxide)$_8$ and (propylene oxide)$_{14}$–(ethylene oxide)$_{24}$–(propylene oxide)$_{14}$.[5] According to the authors, by increasing the PO units, the NaDS critical aggregation concentration decreases and the corresponding enthalpy (ΔH_{agg}) increases due to the hydrophobic interactions. These findings, indirectly, corroborate our free energy results. Accordingly, the isotherm of binding remains unchanged for L64 and F68 and, therefore, the NaOct cac (50 mmol kg^{-1}) is independent of the copolymer hydrophilicity. Comparing ΔH_{agg} to ΔH°_C for different systems may be useless as the enthalpy is also sensitive to the conformational effects that depend on the architecture of the copolymer.

Information on the effect of the surfactant headgroup on the cooperative binding is provided by L64/OPC and L64/sodium nonanoate. The properties of the latter were evaluated from those dealing with L64/sodium alkanoate systems. The less negative $\Delta G^\circ_C/n$ value of L64/OPC system evidences that the hydrophilic interactions are more unfavorable. This confirms the literature results dealing with polymer–surfactant systems.[30] The $\Delta H^\circ_C/n$ and $T\Delta S^\circ_C/n$ values of L64/sodium nonanoate are larger than those of L64/OPC. These results can be ascribed to a different reorganization of the copolymer in showing the hydrophilic segments toward the surfactant polar head.

Prediction of the Binding Isotherms. The determination and the analysis of the binding isotherms are the fundamental characterizations of the polymer/surfactant systems. They are usually obtained by equilibrium dialysis[33,34] and surfactant-selective electrodes.[10,30,36] Several studies are based on isothermal titration calorimetry experiments,[8–10,37] yet as pointed out,[9] methods to evaluate the binding isotherms from the measured enthalpy are not available.

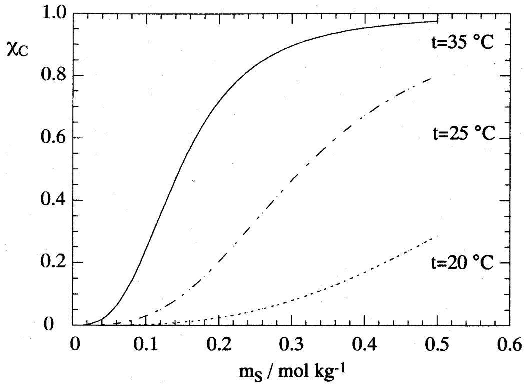

Figure 7. Isotherms of binding between sodium octanoate and F68 as a function of the surfactant concentration.

In the present paper, we derived the standard free energy, enthalpy, and entropy for the surfactant–polymer complex formation from the bulk enthalpies by assuming a theoretical model. These properties are useful tools to predict the behavior of the copolymer/surfactant systems at temperatures far from the experimental one. At 25 °C, the isotherm bindings evidence a cac value of 5 mmol kg^{-1} for NaDec whereas it is 50 mmol kg^{-1} for the other surfactants. Thus, the cac depends on the hydrophobic tail of the surfactant and it does not depend on the EO units of the copolymer.

Because of the lack of heat capacity data, in the calculation of χ_C it was assumed ΔH°_C being temperature independent. For this reason, χ_C was calculated in the restricted range of temperature (20–30 °C) where both copolymers are in the monomeric states. Some examples are shown in Figure 7. For a given surfactant concentration, χ_C increases with temperature because of the positive ΔH°_C values. What is interesting is that relatively small variations in temperature cause strong changes in the copolymer–surfactant binding (Figure 7). On this basis, one may expect that, for temperatures not so far from 25 °C, OPC and F68 undergo the cooperative process. The reliability of this hypothesis is supported by volume data of L64 in aqueous solutions of dispersed decyltrimethylammonium bromide determined at several copolymer concentrations:[2] at 20 °C, volume data superimpose to those in water due to the lack of interactions between the surfactant and the copolymer whereas at 28 °C they are different and tend to the values in water at high copolymer concentration.

Although these calculations are not rigorous, as the heat capacity for the complex formation was assumed to be negligible, it is straightforward that temperature is a crucial parameter in determining the copolymer–surfactant interactions. This intensive variable plays the same role as that on the copolymer aggregates formation. If the copolymer in the presence of the surfactant achieves a critical hydrophilic/hydrophobic ratio, onset of the surfactant–copolymer complex formation occurs.

In conclusion, thermodynamic properties yield direct information on the driving forces governing the copolymer–surfactant binding. A database is necessary to verify whether the thermodynamic behavior of these systems can be predicted under conditions different from the experimental ones.

Acknowledgment. The authors are grateful to the Ministry of University and of Scientific and Technological Research and to the Research National Council (CNR) for financial support.

Supporting Information Available: Tables of the enthalpies of transfer of copolymers from water to the aqueous surfactant solutions at 25 °C (Table A) and the apparent molar volume of *N*,*N*-dimethyloctylamine-*N*-oxide in the water + L64 mixture 5 mmol kg^{-1} at 25 °C (Table B). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA012194O