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Calorimetric and Volumetric Investigations of the Effect of the Hydrophobicity of the Surfactant on the Binding between (Ethylene oxide)$_{13}$-(propylene oxide)$_{30}$-(ethylene oxide)$_{13}$ and Sodium Alkanoates in Aqueous Solutions

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ABSTRACT: The enthalpy and the volume of transfer (ΔY_t) of the unassociated (ethylene oxide)$_{13}$-(propylene oxide)$_{30}$-(ethylene oxide)$_{13}$ (L64) from water to the aqueous sodium alkanoate solutions as functions of the surfactant concentrations (m_S) were determined at 298 K. The surfactants studied are sodium hexanoate, sodium heptanoate, sodium octanoate, sodium undecanoate, and sodium dodecanoate. As a general feature, for the short alkyl chain surfactants, ΔY_t describes an S-shaped curve in the range of m_S analyzed whereas for the more hydrophobic surfactants the ΔY_t vs m_S trends exhibit maxima which appear at m_S values very close to the critical micellar concentration in water. The experimental properties were quantitatively treated by means of a thermodynamic model, recently proposed by us, which assumes that the processes of micellization and the formation of both the surfactant−copolymer aggregation complex and the micelle−copolymer mixed aggregate take place simultaneously. The thermodynamics for the surfactant/copolymer aggregation complex formation states that both the compounds release water molecules from their nonpolar moieties which interact through the van der Waals forces generating a hydrophobic microenvironment in the aggregation complex similar to that in the micellar state. Conformational variations of the copolymer produced by the attachment of the surfactant molecules induce the formation of some hydrogen bonds between the ether oxygen of the ethylene oxide units and water. The thermodynamics of transfer of L64 from the aqueous phase to the sodium alkanoate micelles was also determined. The interactions in the mixed micelles and the surfactant−copolymer aggregation complex are similar. However, due to the large size of the micelle, the conformational effects caused by the L64 solubilization in the micelle are quite significant.

Introduction

Several physicochemical studies[1−6] have been carried out in the last years to gain knowledge on the aqueous mixtures formed by poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) and conventional surfactants. Such macromolecules are studied because they are widely used in several fields (pharmaceutics, food, cosmetics, etc.) due to the low toxicity[7] and to the simultaneous polymeric and amphiphilic features making them very attractive in the colloidal science. Accordingly, they adsorb onto the solid/solution and the air/solution interfaces where the structures are controlled by the hydrophobic PPO blocks.[8] Furthermore, they self-assemble into aggregates formed by the PPO core and the hydrated PEO shell.[4,7,9] The combination of the copolymer and the surfactant may allow the microstructures to function for specific purposes such as the solubilization processes of compounds sparingly soluble in water. The nature of the various forces present in such mixtures may be straightforwardly evidenced by applying the same techniques and models to several copolymer/surfactant systems where the nature of both compounds is systematically changed, namely, the surfactant alkyl chain length, the polarity and the charge of the headgroup, the molecular weight of the copolymer, the hydrophobic/hydrophilic balance, and so on. At this stage, the experiments have been done on relatively few systems and, thereby, particular effects have not yet been investigated. Furthermore, the absence of theoretical approaches has prevented the obtaining of information at the molecular level. We recently[10] proposed a thermodynamic model to interpret properties (first derivatives of Gibbs free energy) of transfer of unassociated copolymers from water to the aqueous surfactant solutions as functions of the surfactant concentration. This approach assumes that three processes are simultaneously present: (1) the surfactant−copolymer aggregation complex formation; (2) the micellization; (3) the micelle−copolymer mixed aggregate formation.

To shed some light on this topic, the effect of the hydrophobicity of the surfactant was studied by determining the enthalpy and the volume of transfer of the unassociated (ethylene oxide)$_{13}$-(propylene oxide)$_{30}$-(ethylene oxide)$_{13}$ (5 mmol kg^{-1}) from water to the aqueous sodium alkanoate solutions as functions of the surfactant concentrations at 298 K. The surfactants studied are sodium hexanoate, sodium heptanoate, sodium octanoate, sodium undecanoate, and sodium dodecanoate.

Experimental Section

Materials. Sodium hexanoate (NaHex), sodium octanoate (NaOct), and sodium dodecanoate (NaL), Sigma products, were used as received. Sodium heptanoate (NaHept) and sodium undecanoate (NaU) were obtained by neutralizing their acids (Aldrich), dissolved in absolute ethanol (Merck), with an ethanolic solution of sodium hydroxide (Fluka). The products were crystallized three times from ethanol and dried in a vacuum oven for 1 week at 323 K. The aqueous surfactant solutions gave pH ≈ 9. The standard partial molar volume of

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each surfactant, evaluated from density measurements, agrees with the value obtained by the additivity rule.[11]

(Ethylene oxide)$_{13}$-(propylene oxide)$_{30}$-(ethylene oxide)$_{13}$ (Pluronic L64, nominal $M = 2900$ g mol^{-1}) was obtained as a gift from BASF, Trading Centre, Italia spa. It was employed as received since the apparent molar volumes determined in the dilute region well agree with the literature values.[12,13]

All solutions were prepared by mass, and their concentrations were expressed as molalities.

The copolymer concentration value was kept below the L64 cmc[4] (65 mmol kg^{-1}), and the surfactant concentrations covered both the pre- and the postmicellar regions. Experimental difficulties prevented the performance of calorimetric studies in the NaHex concentrated region, as well.

Equipment. Density. The solutions densities were measured at 298 K by using a vibrating tube flow densimeter (model 03D, Sodev Inc.) sensitive to 3 ppm. The temperature was maintained constant within 0.001 K by using a closed-loop temperature controller (model CT-L, Sodev Inc.). The densimeter was calibrated according to the procedure reported elsewhere.[3]

The apparent molar volume ($V_{\Phi,P}$) of L64, at a fixed concentration (5 mmol kg^{-1}), in the water–surfactant mixture was calculated by means of the following equation

$$V_{\Phi,P} = \frac{M}{d} - \frac{10^3(d - d_o)}{m_P d d_o} \qquad (1)$$

Here m_P and M are the molality and the molecular weight of the copolymer, respectively, d is the density of the water–surfactant–copolymer ternary mixture, and d_o is the density of the water–surfactant mixed solvent.

The volume of transfer of L64 from water to the aqueous surfactant solutions (ΔV_t) was calculated as the difference between $V_{\Phi,P}$ in the water–surfactant mixture and in water.

Enthalpy. A flow LKB 2107 microcalorimeter was used to carry out enthalpy measurements at 298.15 ± 0.01 K. The injection of the solutions into the apparatus was done by means of a Gilson peristaltic pump (Minipuls 2).

The experimental enthalpy (ΔH^{exp}) was calculated as difference between the thermal effect due to the mixing process of the copolymer solution with the surfactant solution and that due to the dilution process of the same surfactant solution with water.

The final concentration of the surfactant (m_S) and the copolymer (m_P) solutions, upon the mixing process, were calculated as

$$m_S = \frac{m_{S,i}\Phi_S}{(\Phi_S + \Phi_P)} \qquad m_P = \frac{m_{P,i}\Phi_P}{(\Phi_S + \Phi_P)} \qquad (2)$$

Here $m_{S,i}$ and $m_{P,i}$ are the initial concentrations of the surfactant and the copolymer, respectively, whereas Φ_P and Φ_S are the flows of water in the copolymer and the surfactant solutions, respectively.

The enthalpy of transfer (ΔH_t) at $m_P = 5$ mmol kg^{-1} was evaluated as the difference between ΔH^{exp} and the enthalpy of dilution of the copolymer with water.[5]

Results

Figures 1–5 illustrate the plots of the property of transfer (ΔY_t) of L64 from water to the aqueous sodium alkanoate solutions as functions of the surfactant concentration (m_S). For the sake of comparison, the ΔH_t data[5] of NaOct/L64 are also plotted in Figure 3. For short alkyl chains, ΔV_t describes an S-shaped curve in the range of m_S analyzed; namely, ΔV_t slightly increases with m_S to ca. 0.6 and 0.4 mol kg^{-1} for NaHex and NaHept, respectively. Thereafter it sharply increases reaching a constant value at high concentration (Figures 1 and 2). In the case of the enthalpy, the curves exhibit a sharper increase even at low m_S values. Moreover, the ΔH_t vs m_S trend of NaHex is not well defined whereas that for NaHept displays a smooth maximum. The ΔV_t vs m_S curve for the NaOct/L64 mixture is sigmoid to ca. 0.4 mol kg^{-1} beyond which it slowly decreases (Figure 3). The corresponding curve for the enthalpy shows a quite reduced maximum. The data for L64 in sodium decanoate (NaDec),[3] NaU (Figure 4), and NaL (Figure 5) show that by increasing the surfactant alkyl chain both the volume and the enthalpy exhibit pronounced maxima which appear at lower m_S. It is to be

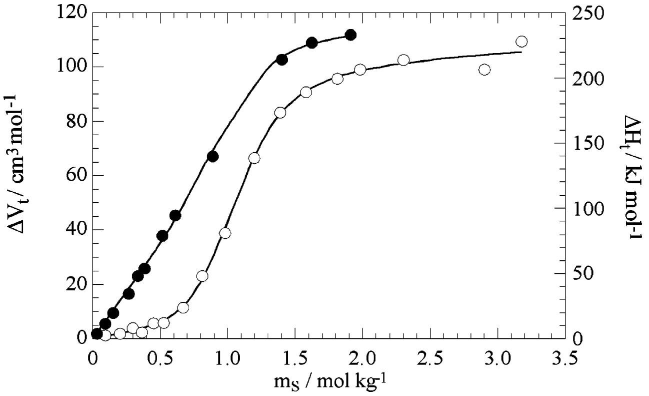

Figure 1. Enthalpy (filled symbols) and volume (open symbols) of transfer of L64 from water to the aqueous sodium hexanoate solutions as functions of the surfactant concentration. Lines are best fits according to eq 5.

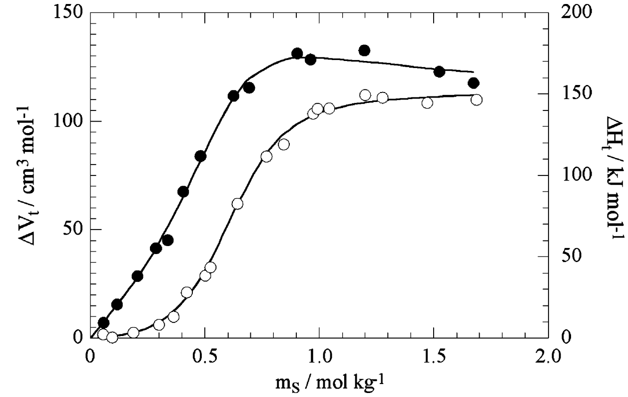

Figure 2. Enthalpy (filled symbols) and volume (open symbols) of transfer of L64 from water to the aqueous sodium heptanoate solutions as functions of the surfactant concentration. Lines are best fits according to eq 5.

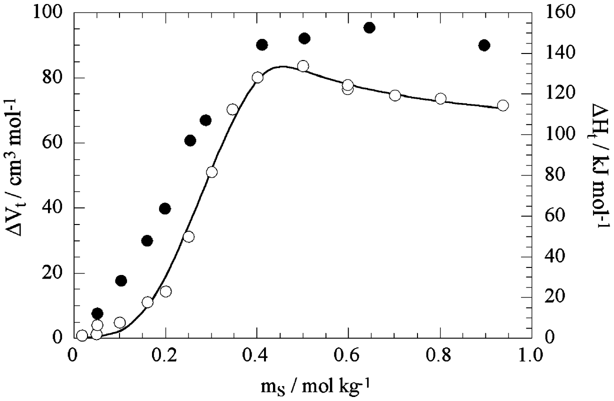

Figure 3. Enthalpy (filled symbols) and volume (open symbols) of transfer of L64 from water to the aqueous sodium octanoate solutions as functions of the surfactant concentration. The line is best fit according to eq 5. Enthalpy data are from ref 5.

Table 1. Thermodynamic Properties of Sodium Alkanoates and L64 in Water at 298 K[a]

	NaHex	NaHept	NaOct	NaDec[b]	NaU	NaL	L64
K_M	$(2.1 \pm 0.3) \times 10^{-3}$	0.11 ± 0.05	$(2.2 \pm 0.9) \times 10^{3}$[c]	7.6×10^{15}	$(1.0 \pm 1.3) \times 10^{19}$	$(4 \pm 3) \times 10^{25}$	$(2 \pm 1) \times 10^{3}$[c]
N	8 ± 1	9 ± 1	18 ± 2[c]	20	20 ± 4	20 ± 3	5.7 ± 0.3[c]
$\Delta G^\circ_{m,S}$	1.9 ± 0.3	0.6 ± 0.3	-1.1 ± 0.2	-4.53	-5.4 ± 1.0	-7 ± 1	-3.3 ± 0.4
B_L	0.68 ± 0.05[d]	1.6 ± 0.1[d]	4.45 ± 0.03[d]	13.51	18.9 ± 1.2	-16 ± 3[e]	
C_L	1.46 ± 0.07[d]	2.9 ± 0.2[d]	2.16 ± 0.08[d]			300 ± 18[e]	
$L_{M,S}$	11.0 ± 0.3[d]	11.5 ± 0.4[d]	11.6 ± 0.2[d]	10	10 ± 3	9.67[e]	
$T\Delta S^\circ_{m,S}$	9.1 ± 0.6	10.9 ± 0.7	12.6 ± 0.4	14.5	15 ± 4	17 ± 1	
V°_S	101.35 ± 0.04	116.14 ± 0.07	132.60 ± 0.02	164.01	178.3 ± 0.4	194.5 ± 0.2	2561.9 ± 0.3[f]
B_V	-0.3 ± 0.1	-0.15 ± 0.2	0.11 ± 0.07	4.64	29 ± 13	110 ± 10	60 ± 6[f]
C_V				0.71			
$V_{M,S}$	116.5 ± 0.7	131 ± 1	144.2 ± 0.3	175.20	192.9 ± 0.7	209.31 ± 0.08	2712.9 ± 0.1[f]

[a] Units are the following: K_M, kg^{N-1} mol^{1-N}; B_L, kJ kg mol^{-2}; C_L, kJ $kg^{3/2}$ $mol^{-5/2}$; $\Delta G^\circ_{m,S}$, $L_{M,S}$, and $T\Delta S^\circ_{m,S}$, kJ mol^{-1}; V°_S, and $V_{M,S}$, cm^3 mol^{-1}; B_V, cm^3 kg mol^{-2}; C_V, cm^3 $kg^{3/2}$ $mol^{-5/2}$. [b] From ref 19. [c] From ref 10. [d] From ref 18. [e] From ref 20. [f] From ref 4. Note that for L64 the subscript S is replaced by P.

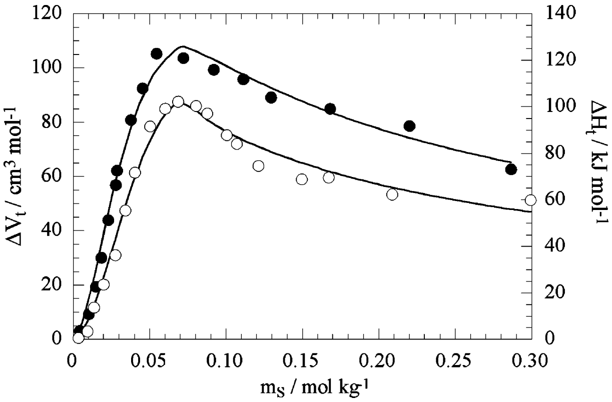

Figure 4. Enthalpy (filled symbols) and volume (open symbols) of transfer of L64 from water to the aqueous sodium undecanoate solutions as functions of the surfactant concentration. Lines are best fits according to eq 5.

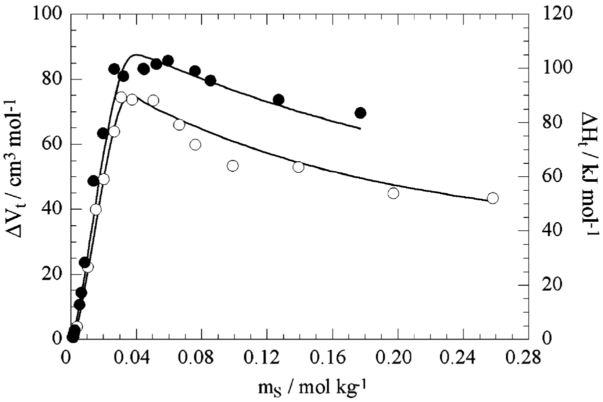

Figure 5. Enthalpy (filled symbols) and volume (open symbols) of transfer of L64 from water to the aqueous sodium dodecanoate solutions as functions of the surfactant concentration. Lines are best fits according to eq 5.

noticed that such extrema are present at m_S values very close to the critical micellar concentrations in water.

From the examination of the Figures 1−5, it emerges that the hydrophobicity of the surfactant strongly influences the magnitude of ΔY_t and its dependence on m_S. For instance, the largest ΔH_t values determined for NaHex and NaL are 230 and 100 kJ mol^{-1}, respectively. In addition, for some mixtures, the profiles of the ΔY_t vs m_S trends for the enthalpy and the volume are somewhat different (Figures 1−3). Nevertheless, as it will be demonstrated later, despite their different profiles, these curves can be quantitatively interpreted in terms of the same phenomena.

Thermodynamics of Micellization of Sodium Alkanoates in Water. For the quantitative treatment of the properties of transfer, the knowledge of the thermodynamics of micellization of the surfactants in water is needed. To this purpose, a mass action model[14] was assumed by allowing the correlation between the equilibrium constant of micellization (K_M) and the stoichiometric surfactant concentration (m_S)

$$K_M = \frac{m_S - [m_0]}{N[m_0]^N} \tag{3}$$

Here $[m_0]$ is the monomer surfactant concentration and N stands for the aggregation number of the micelles.

By application of the model to the apparent molar property of the surfactant in water, K_M and N as well as the partial molar property of the surfactant in the standard (Y°_S) and micellar ($Y_{M,S}$) states and the interaction parameters (B_Y and C_Y) can be simultaneously determined. The property of micellization is calculated[14] as

$$\Delta Y_{m,S} = Y_{M,S} - Y^\circ_S - Y_{D-H}[m_0]^{1/2} - B_Y[m_0] - C_Y[m_0]^{3/2} \tag{4}$$

where Y_{D-H} is the Debye−Hückel parameter (1.865 cm^3 $mol^{-3/2}$ $kg^{1/2}$ for the volume[15] and 1973 J $mol^{-3/2}$ $kg^{1/2}$ for the enthalpy[15]). For all the surfactants, the model was applied to the volume data which, whenever possible, were combined with those of literature.[16,17] The fitting parameters are collected in Table 1 where some others for NaOct,[10,18] NaDec,[19] NaL,[20] and L64[4,10] are also reported.

Theoretical Background. The experimental properties of transfer were treated by means of a thermodynamic model[10] which assumes that, upon the addition of the surfactant to a solution of unimers of the copolymer, the binding between 1 copolymer molecule and z surfactant molecules takes place and leads to the formation of the surfactant−copolymer aggregation complexes (C) of z:1 stoichiometry; by further increase of the surfactant concentration, the micellization process occurs, and then mixed micelles (D), composed of 1 micelle and w copolymer molecules, are formed. The following equation was derived[10]

$$\Delta Y_t = 2B_{Y,PS}x_P[m] + x_C\Delta Y_C + \frac{[m_0] - [m] - zx_Cm_P}{m_P}\Delta Y_{m,S} + x_D\Delta Y_D \tag{5}$$

The first term on the right-hand side of eq 5 is the contribution for the interaction between monomers of copolymer and surfactant where $B_{Y,PS}$ is the interaction parameter, $[m]$ is the monomer surfactant concentration in the ternary system, and x_P is the fraction of the free

Table 2. Thermodynamic Properties for L64−Surfactant Binding Equilibria at 298 K[a]

	NaHex	NaHept	NaOct	NaDec[b,c]	NaU	NaL
$B_{V,PS}$	5 ± 1	4 ± 3	3 ± 6	154 ± 16	200 ± 20	220 ± 110
$B_{H,PS}$	72 ± 2	87 ± 4	98 ± 20^{b}	227 ± 36	300 ± 20	710 ± 30
K_C	0.32 ± 0.04^{d}	3.6 ± 0.4^{e}	$39.2 \pm 1.7^{b,e}$	3600 ± 600^{e}	2800 ± 150^{e}	$(1.9 \pm 1.6) \times 10^{4\,e}$
		3.0 ± 1.0^{d}	75 ± 16^{d}	2500 ± 500^{d}	6750 ± 550^{d}	$(1.3 \pm 0.4) \times 10^{4\,d}$
z	5.3^{d}	3.7^{e}	$3.1^{b,e}$	3.1^{e}	2.2^{e}	2.3^{e}
		3.4^{d}	3.7^{d}	3.1^{d}	2.6^{d}	2.4^{d}
$\Delta G^\circ_C/z$	0.53 ± 0.06^{d}	-0.86 ± 0.07^{e}	$-2.93 \pm 0.04^{b,e}$	-6.5 ± 0.1^{e}	-8.90 ± 0.06^{e}	-10.6 ± 0.9^{e}
		-0.80 ± 0.24^{d}	-2.89 ± 0.14^{d}	-6.2 ± 0.1^{d}	-8.40 ± 0.08^{d}	-9.8 ± 0.3^{d}
ΔH_C	241 ± 7	220 ± 12	178.9 ± 1.6^{b}	191 ± 3	143 ± 2	130 ± 1
$T\Delta S^\circ_C$	238 ± 7	223 ± 12	188.9 ± 1.7^{b}	211 ± 3	163 ± 2	154 ± 3
ΔV_C	139 ± 20	108 ± 40	115 ± 10	103 ± 5	105 ± 1	102 ± 1
K_D	22 ± 2^{d}	80 ± 30^{e}	$90 \pm 70^{b,e}$	520 ± 110^{e}	1680 ± 800^{e}	700 ± 90^{e}
		130 ± 60^{d}	380 ± 80^{d}		1910 ± 450^{d}	1660 ± 860^{d}
ΔG°_D	-7.4 ± 0.2^{d}	-10.9 ± 0.9^{e}	$-11 \pm 2^{b,e}$	-15.5 ± 0.5^{e}	-18.4 ± 1.1^{e}	-16.2 ± 0.3^{e}
		-12.1 ± 1.1^{d}	-14.7 ± 0.5^{d}		-18.7 ± 0.6^{d}	-18.4 ± 1.3^{d}
$K_{t,M}$	24 ± 2^{d}	72 ± 27^{e}	$36 \pm 27^{b,e}$	150 ± 30^{e}	440 ± 210^{e}	170 ± 20^{e}
		80 ± 50^{d}	150 ± 30^{d}		500 ± 120^{d}	400 ± 200^{d}
$\Delta G^\circ_{t,M}$	-7.8 ± 0.2^{d}	-10.6 ± 0.9^{e}	$-8.9 \pm 2.3^{b,e}$	-12.4 ± 0.5^{e}	-15.1 ± 1.2^{e}	-12.6 ± 0.3^{e}
		-10.9 ± 1.4^{d}	-12.4 ± 0.5^{d}		-15.4 ± 0.6^{d}	-14.8 ± 1.3^{d}
ΔH_D	257 ± 3	136 ± 12	119 ± 12^{b}	26 ± 14	20 ± 20	-1 ± 4
$T\Delta S^\circ_D$	264 ± 3	147 ± 13	130 ± 14^{b}	42 ± 15	40 ± 20	15 ± 4
ΔV_D	157 ± 9	116 ± 7	58 ± 2	40 ± 2	17 ± 5	18 ± 9

[a] Units are as follows: $B_{V,PS}$, cm^3 mol^{-2} kg; $B_{H,PS}$, kJ mol^{-2} kg; K_C, kg^z mol^{-z}; free energy, enthalpy, and entropy, kJ mol^{-1}; volume, cm^3 mol^{-1}; K_D, kg mol^{-1}. [b] From ref 10. [c] Volume data at $m_P = 15$ mmol kg^{-1}; enthalpy data at $m_P = 2.5$ mmol kg^{-1}. [d] From volume data. [e] From enthalpy data.

copolymer. $x_C\Delta Y_C$ is the contribution for the surfactant−copolymer aggregation complex formation: ΔY_C is the variation of the property ($\Delta Y_C = Y_C - zY_{m,S} - Y_{m,P}$, Y_C, $Y_{m,S}$, and $Y_{m,P}$ being the partial molar properties of the complex, the free surfactant, and copolymer, respectively), and x_C is the fraction of the copolymer−surfactant aggregation complex given by

$$x_C = K_C x_P [\mathrm{m}]^z \qquad (6)$$

where K_C is the equilibrium constant.

The third term of eq 5 stands for the displacement of the monomer−micelle equilibrium induced by the copolymer. Finally, $x_D\Delta Y_D$ is the contribution for the mixed-micelles formation: ΔY_D is the change in the property ($\Delta Y_D = Y_D - NY_{M,S} - wY_{m,P}$, where Y_D is the partial molar property of the mixed micelle) and x_D stands for the fraction of the mixed micelle correlated to the equilibrium constant (K_D) as

$$x_D = \frac{(x_P m_P)^w m_M K_D}{m_P} \qquad (7)$$

where m_M is the micelles concentration in the presence of the copolymer.

The mass balance for both the surfactant and the copolymer is expressed as

$$m_S = K_D K_M N [\mathrm{m}]^N (x_P m_P)^w + K_C x_P m_P z [\mathrm{m}]^z + K_M N [\mathrm{m}]^N + [\mathrm{m}] \qquad (8)$$

$$m_P = K_D K_M w [\mathrm{m}]^N (x_P m_P)^w + K_C x_P m_P [\mathrm{m}]^z + x_P m_P \qquad (9)$$

By solving the nonlinear system (eqs 8 and 9) through the Newton−Raphson method extended to two dimensions, the [m] and x_P values can be evaluated. Then, x_C and x_D can be obtained from eqs 6 and 7, respectively.

Quantitative Treatment of the Experimental Data. The application of eq 5 to the experimental data may turn out to be difficult, being involved with several parameters. However, the following procedure was pursued. The K_M, N, and $\Delta Y_{m,S}$ values were determined from the data of the water−surfactant binary system (Table 1, eqs 3 and 4) whereas the $B_{Y,PS}$ parameter was evaluated from the ΔY_t points in the very dilute surfactant concentration region. In the absence of the micelles, $x_D\Delta Y_D = 0$ and, hence, eq 5 is a three-unknown parameters (K_C, z, and ΔY_C) equation. Under these conditions, eq 3 provided [m$_0$] whereas eqs 8 and 9 (where the terms with K_D were deleted) gave [m] and x_P at arbitrary values of K_C and z. The minimizing process was carried out through a program based on a nonlinear least-squares fitting method. The parameters provided by the best fits are collected in Table 2. Due to the small K_C value and the quite narrow range of m_S, the minimizing procedure gave very uncertain parameters for the L64/NaHex mixture.

The onset of the deviation of the experimental points from the values calculated through eq 5 where $x_D\Delta Y_D = 0$ starts when $m_M \approx 10^{-4}$ mol kg^{-1} that is indicative of the interactions between the copolymer and the micelles. Therefore, eq 5 in the complete form was applied to the experimental points in the entire range of m_S studied to determine w, K_D, and ΔY_D. Moreover, from the analysis of the volume data of NaHex/L64, the properties for the surfactant/copolymer aggregation complex formation were also derived because the wider range of m_S allowed one to obtain fitting parameters affected by acceptable uncertainties. Then, the enthalpy data, available in a narrower range of m_S, were analyzed by using the equilibrium constants derived from the volumes. The parameters generated by the fits are reported in Table 2. It is to be noticed that for all the systems studied, $w = 1$ was obtained.

As Figures 1−5 illustrate, eq 5 is able to take into account for the very dissimilar profiles of the ΔY_t vs m_S curves. Examples are given by NaHex/L64 and NaL/L64, which basically differ for the dependence of x_C on m_S. In fact, Figure 6 shows that when the formation of NaL/L64 mixed micelles takes place, x_C starts to decrease tending to zero at very high m_S whereas the onset of the NaHex/L64 mixed-micelles formation does not lead to the x_C decrease which, indeed, occurs at large m_S values. The dissimilar behavior of the two surfactants is well understood if one is reminded that NaHex is not an effective surfactant allowing the coexistence

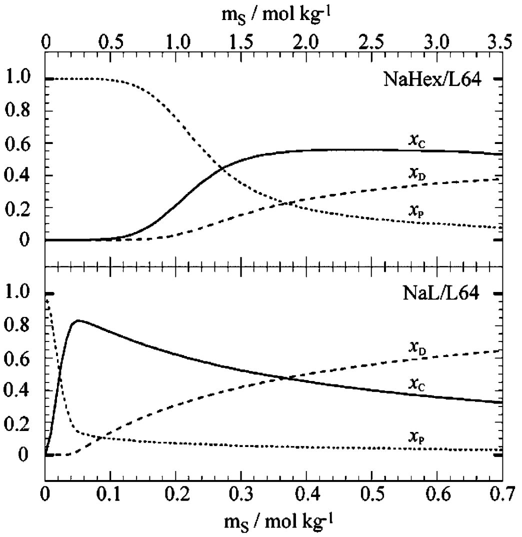

Figure 6. Dependence on the surfactant concentration of the fraction of the free copolymer (x_P), the surfactant/copolymer aggregation complex (x_C), and the mixed micelles (x_D) for L64/sodium hexanoate and L64/sodium dodecanoate.

of both the surfactant/copolymer aggregation complex and the mixed micelles in a wide range of m_S; on the contrary, due to the high NaL hydrophobicity, the NaL/L64 aggregation complexes are precursors of the mixed micelles and, thereby, will be transformed into such mixed aggregates.

For each equilibrium, i.e., micellization (m), surfactant/copolymer complex formation (C), and mixed-micelle formation (D), the standard free energy and entropy were evaluated as

$$\Delta G^\circ = -RT \ln K \qquad T\Delta S^\circ = \Delta H - \Delta G^\circ \quad (10)$$

ΔG°_D can be correlated[21] to the standard free energy of transfer of the copolymer from the aqueous to the micellar phases ($\Delta G^\circ_{t,M}$) which, in the molarity scale, is written as

$$\Delta G^\circ_{t,M} = \Delta G^\circ_D + RT \ln(NV_{M,S}/w) \quad (11)$$

On the basis of the classical thermodynamic equations, from eq 11 the corresponding relationships for the volume and the enthalpy are obtained

$$\Delta V_{t,M} = \Delta V_D - RT\beta_{M,S}/V_{M,S}$$
$$\Delta H_{t,M} = \Delta H_D - RT^2 E_{M,S}/V_{M,S} \quad (12)$$

Here $\beta_{M,S}$ and $E_{M,S}$ represent the partial molar isothermal compressibility and expansibility of the surfactant in the micellar state, respectively. Note that, in the derivation of eqs 12, w was assumed to be independent of the intensive variables. The $\beta_{M,S}$ values were calculated from the corresponding adiabatic data[22] on the basis that $\beta_{M,S}$ is 15% higher[23] than the adiabatic value. To the best of our knowledge, only $E_{M,S}$ for NaDec[23] is available; then, for the other surfactants, $E_{M,S}$ was calculated by means of the additivity rule by using the value[24] of 0.011 cm^3 mol^{-1} K^{-1} for the CH$_2$ group contribution. The computations done through eqs 12 show that the difference between $\Delta Y_{t,M}$ and ΔY_D is even smaller than their errors.

Discussion

The quantitative analysis of the experimental data provided the thermodynamic properties for the formation of both the surfactant/copolymer aggregation complexes and the mixed micelles. These quantities likely reflect the van der Waals forces, the hydrophilic interactions, etc., strictly related to the binding processes and other contributions (changes in hydration, conformation, etc.) which do not necessarily affect the equilibrium constants. For the sake of clarity, the two processes shall be analyzed separately in the following.

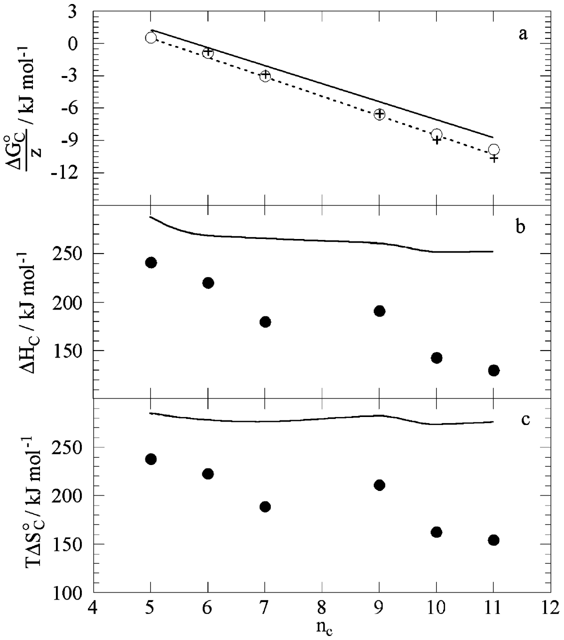

Figure 7. Thermodynamic properties for the surfactant–copolymer aggregation complex formation as functions of the number of carbon atoms in the alkyl chain: (a) standard free energy obtained from the volume (○) and the enthalpy (+); (b) enthalpy; (c) entropy. Lines are calculated properties through eq 13. For the dotted line, the value of −6.77 ± 0.08 kJ mol^{-1} for $\Delta G^\circ_{m,P}$ was used. For the solid line, the value of −3.3 ± 0.4 kJ mol^{-1} for $\Delta G^\circ_{m,P}$ was used. Data at $n_c = 9$ are from ref 10.

(i) Thermodynamics for the Surfactant/Copolymer Aggregation Complex Formation. Figure 7 shows that $\Delta G^\circ_C/z$ values obtained from both the volume and the enthalpy data agree with each other corroborating the validity of the model; also, they decrease with the number of carbon atoms in the alkyl chain (n_c). Both ΔH_C and $T\Delta S^\circ_C$ are positive and 1 order of magnitude larger than the standard free energy (Figure 7). ΔV_C decreases with increasing the surfactant hydrophobicity (plot not shown). A careful inspection of such properties may evidence the nature of the forces involved in the binding equilibrium. It is expected that the surfactant/copolymer aggregation complex formation is controlled by the hydrophobic effect[25] due to the large positive ΔH_C and $T\Delta S^\circ_C$ values. Likely, the surfactant and the copolymer release the water molecules from their nonpolar surfaces which interact through the van der Waals forces generating a hydrophobic microenvironment similar to that of the micellar state. With this in mind, by assuming that the partial molar properties of the surfactant and the copolymer in the complex are equal to those in the micellized forms in water, i.e., $Y_C = zY_{M,S} + Y_{M,P}$, where $Y_{M,P}$ is the partial molar property of the copolymer in the aggregated form, one may calculate ΔY_C through

$$\Delta Y_C = z\Delta Y_{m,S} + \Delta Y_{m,P} \quad (13)$$

where $\Delta Y_{m,P}$ is the property of the copolymer micellization.

To compute the standard free energies, $\Delta G^\circ_{m,P}$ was evaluated from the K_M and N values[10] (Table 1). As Figure 7 illustrates, the calculated $\Delta G^\circ_C/z$ values are slightly greater than the experimental points (the largest difference is 1 kJ mol^{-1}). Interestingly, the experimental and the calculated points are in a very good agreement by using the $\Delta G^\circ_{m,P}$ value of -6.77 ± 0.08 kJ mol^{-1} obtained on the basis of the pseudophase transition model[26] by employing the cmc value[4] of 65 mmol kg^{-1} (Figure 7). The decrease of ΔG°_C with n_c is due to $\Delta G^\circ_{m,S}$ since the $\Delta G^\circ_{m,P}$ contribution is constant.

ΔH_C and $T\Delta S^\circ_C$ were computed by using the $\Delta H_{m,P}$ value[27] of 230 kJ mol^{-1} which was combined with $\Delta G^\circ_{m,P}$ (-3.3 ± 0.4 kJ mol^{-1}) to obtain the entropy of micellization. Note that the calculated entropy does not change if the other $\Delta G^\circ_{m,P}$ value is used. Compared to the experimental points, the computed values are not only larger but also exhibit a smoother decrease with n_c (Figure 7). The different magnitude suggests that the surrounding of L64 in the complex is different from that in the regular micelles which are highlighted[4,12,13] by a hydrated corona of EO segments and a core of dehydrated PPO blocks. Thereby, the PO units in the complex likely contain some water molecules in agreement with FTIR investigations,[28] which showed that the solvation of the methyl groups of the PPO block in the micelles decreases with increasing the copolymer concentration. The dissimilar dependence on n_c suggests that both enthalpy and entropy are influenced by phenomena which do not contribute to the free energy, which was predicted by eq 13 in a satisfactory manner (Figure 7). On the other hand, the form of enthalpy–entropy compensation is expected[29] for the binding processes involving homologous compounds if the constituent of a series reflects the same phenomenon in an additive way. The increasing hydrophobic character of the copolymer in the complex upon the lengthening of the surfactant alkyl chain cannot explain the experimental findings because it allows for an increase of the properties. The contacts between L64 and the surfactant make the conformation of the copolymer quite rigid whereas the copolymer in the free state may have a higher degree of flexibility. This hypothesis is supported by the report[30] of Nowicki, who correlated the decrease of the conformational entropy of a very long polymer chain, generated by the attachment of a colloidal particle (micelles, protein globules, etc.), to the diameter of the particle. For a given polymer, the increasing particle size causes the entropy decrease because of the larger constraints to which the polymer undergoes. As a consequence of the conformational effects, L64 may change its hydration state allowing to negative enthalpy. For instance, it may take place the formation of hydrogen bonds between the ether oxygen of the EO units and water which causes a change of enthalpy of -17 kJ mol^{-1}.[31] Thus, the significant decrease of ΔH_C and $T\Delta S^\circ_C$ with the surfactant tail is explained. These processes together with the hydrophobic effect do not influence the free energy due to the compensation between enthalpy and entropy proved, according to the statistical test,[29,32] by the straight line obtained by plotting ΔH_C against ΔS°_C which gave the intercept of -61 ± 19 kJ mol^{-1} and the slope of 373 ± 28 K.

Equation 13 was also used to calculate ΔV_C, and to this purpose, the $\Delta V_{m,P}$ value[4] of 143.2 cm^3 mol^{-1} was employed. The results are similar to the enthalpy and entropy findings. The simulated values are larger than the experimental points by a constant quantity (65 cm^3 mol^{-1}) which contains also the negative contribution for the hydrogen bonds formation. Since the latter is relatively small (the value of -1.2 cm^3 mol^{-1} was reported for water[33]), its contribution may be nearly independent of the surfactant tail as the ΔV_C data suggest.

(ii) Thermodynamics of Mixed-Micelles Formation. The thermodynamic properties for the mixed-micelles formation may be predicted by using an approach similar to that employed for the surfactant/copolymer aggregation complex formation. For this purpose, Y_D may be expressed as $(NY'_{M,S} + wY_{M,P})$, where $Y'_{M,S}$ is the partial molar property of the surfactant in the mixed micelles which can be evaluated if it is stated equal to the value in water ($Y_{M,S}$). On this basis, one obtains $\Delta Y_D = w\Delta Y_{m,P}$, which means that ΔY_D is independent of n_c; that is contrary to the experimental findings. The hypothesis that in the mixed micelles the state of the surfactant and/or L64 is equal to that in their corresponding pure micelles is, thereby, unreliable.

From the analysis of ΔY_D and ΔY_C one may infer that the interactions controlling the mixed micelles and the surfactant–copolymer aggregation complexes are quite similar. The ΔY_D (enthalpy, entropy, and volume) values generally smaller than ΔY_C are due to the absence of the contributions for the hydrophobic desolvation of the surfactant which accompany the micelles formation. In fact, the binding between N surfactant molecules and w copolymer molecules leading to the formation of mixed micelles causes properties changes ($\Delta Y_D'$) which are largely positive and greater than ΔY_C. For NaL/L64, for instance, $\Delta H_D'$ is 192 ± 6 kJ mol^{-1} and $\Delta V_D'$ is 294 ± 15 cm^3 mol^{-1}.

The ΔY_D significant decrease cannot be due to the electrostatic contribution, generated by the release of the counterions of the micelles upon the L64 solubilization, which is expected to be small and positive. Accordingly, it is reported[34] that the enthalpy change for the binding between the sodium ions and the dodecyl sulfate micelles is -4.6 kJ mol^{-1}. Such a strong variation can be explained by analyzing the entropy. The decrease of ΔS°_D with n_c is 2-fold that of ΔS°_C (2.1 ± 0.2), which is nearly equal to the value of 2.3 evaluated from the Nowicki[30] equation for the conformational entropy by assuming that the diameter of the micelle in the mixed aggregates is twice that of the surfactant in the complex. Consequently, the change of the copolymer hydration becomes more significant and strongly affects both the enthalpy and the volume.

Finally, the effect of the hydrophobicity of the surfactant on the mixed-micelles formation can be straightforwardly evidenced through the properties of transfer of the copolymer from the aqueous to the sodium alkanoate micellar phases ($\Delta Y_{t,M}$) (eqs 11 and 12). As Figure 8 shows, the $\Delta G^\circ_{t,M}$ values obtained from the volume and the enthalpy are in a good agreement. Also, they change linearly with n_c providing negative intercept (-4.7 ± 2.0 kJ mol^{-1}) and slope (-0.91 ± 0.24 kJ mol^{-1}). The intercept value is consistent with the favorable interactions between L64 and the shell of the micelle. The slope value, which represents the L64 transferring from the aqueous phase to the CH_2 group in the micelle, is consistent with the increased hydrophobicity of the micellar aggregates. The examination

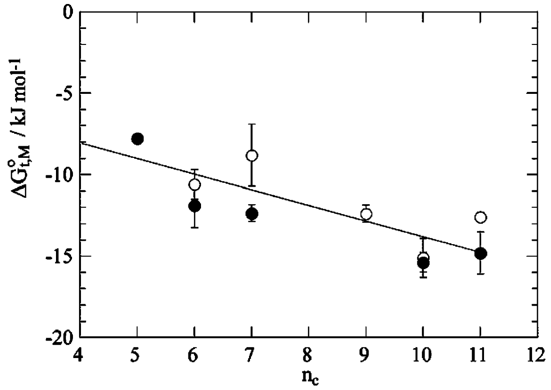

Figure 8. Standard free energy of transfer of L64 from the aqueous to the micellar phases as functions of the number of carbon atoms in the alkyl chain. Filled symbols are from volume values. Open symbols are from enthalpy values. The value at $n_c = 9$ was calculated from data in ref 10.

of the literature dealing with the additive/surfactant mixed micelles may not help for a better understanding of the present mixtures because of the dissimilarity between L64 and the additive usually studied (primary[35] and secondary[35,36] alcohols, nitriles,[37] nitroderivatives,[38] alkoxyethanols,[39] etc.). As a general feature, the wide literature[40,41] shows that the sign of the hydrophilic contribution to $\Delta G^\circ_{t,M}$ depends on the nature of the headgroup of both the additive and the surfactant whereas the hydrophobic contribution is a function of the nature of the tail (hydrogenated or fluorinated). Such a transferring process is entropy controlled, as well.

Conclusions

The effect of the hydrophobicity of the surfactant on the binding between L64 and sodium alkanoates was studied by enthalpy and volume at 298 K. The experimental data, quantitatively treated by means of a thermodynamic model, provided the properties for the formation of both the surfactant−copolymer aggregation complex and the mixed micelles. Upon the formation of the surfactant/copolymer aggregation complex, both compounds release water molecules from their nonpolar moieties which interact through the van der Waals forces generating a hydrophobic microenvironment similar to that in the micellar state. Also, conformational variations of the copolymer produced by the attachment of the surfactant molecules take place. The thermodynamics of transfer of L64 from the aqueous to the sodium alkanoate micellar phases evidences conformational effects which are more significant than those for the surfactant−L64 aggregation complex formation.

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Supporting Information Available: A table of the experimental enthalpies of transfer of L64 from water to the aqueous solutions of sodium hexanoate, sodium heptanoate, sodium undecanoate, and sodium dodecanoate and a table of the apparent molar volume of L64 in the aqueous solutions ofsodium hexanoate, sodium heptanoate, sodium octanoate, sodium undecanoate, and sodium dodecanoate. This material is available free of charge via the Internet at http://pubs.acs.org.

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