Thermodynamics of Aqueous Poly(ethylene oxide)−Poly(propylene oxide)−Poly(ethylene oxide)/Surfactant Mixtures. Effect of the Copolymer Molecular Weight and the Surfactant Alkyl Chain Length

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A calorimetric study was performed to focus attention on the interactions between copolymers and anionic surfactants in aqueous solutions. Three aspects were analyzed: (1) the hydrophobicity of the surfactant, (2) the change of the copolymer molecular weight, and (3) the nature of the hydrophilicity of the copolymer. To this purpose, the family of sodium alkanoates (sodium octanoate through sodium dodecanoate) and the tri-block copolymers $EO_{76}PO_{29}EO_{76}$ (F68), $EO_{103}PO_{39}EO_{103}$ and $EO_{132}PO_{50}EO_{132}$ were investigated. Comparing F68 and $EO_{13}PO_{30}EO_{13}$ (L64), previously studied by us, provided information on the effect of the copolymer hydrophilicity. The experimental data were analyzed by means of a thermodynamic model which assumes that in the surfactant dilute region monomers of surfactant interact with unimeric copolymer leading to the formation of surfactant-copolymer aggregation complexes; when micelles do form, they can solubilize the copolymer, and then, the copolymer−micelle aggregates formation takes place. Data modeling provided useful parameters which allowed us to discriminate the various effects contributing to the formation of such aggregates. The thermodynamic properties for the formation of both the surfactant−copolymer aggregation complexes and copolymer−micelle aggregates were not consistent with the expectation; despite the more hydrophilic sites available in F68, the enthalpy and entropy for F68 were larger and the free energy more negative than those of L64. Moreover, the role of the copolymer molecular weight was important although the ratio between the number of the hydrophilic and the hydrophobic sites of binding is constant. An effort was done to verify whether these findings are representative of the physical interactions between copolymer and surfactant or reflect the large difference in the molecular masses. Therefore, the thermodynamic properties were normalized for the number of EO and PO units. They straightforwardly showed that L64 has a larger hydrophobic character than F68 and the copolymer molecular weight plays a small role.

Introduction

Poly(ethylene oxides)−poly(propylene oxides)−poly(ethylene oxides), commercially available under the trade name of Pluronics, are tri-block copolymers ($EO_aPO_bEO_a$ where a and b are the numbers of repetitive EO and PO units, respectively) exhibiting an amphiphilic character. Therefore, they can self-assemble at the interfaces[1] and in the bulk phase.[2,3] These features can allow us to modify the liquid/air or solid/liquid interfaces as well as to improve the solubilization capability of additives sparingly soluble in water. Moreover, they are advantageous because of their low toxicity.[4,5] By adding a third component to the water−copolymer mixture, an additional degree of freedom in tuning nano-aggregates systems for specific applications is provided. Recently,[4] Pluronics were chosen to prepare oil-in-water microemulsions in order to powerfully scavenge compounds from bulk media. It was demonstrated that they may be efficient tools to treat cardiotoxicity caused by bupivacaine or other lipophilic drugs. Accordingly, Pluronic-based microemulsions were administered[4] to human patients in large amounts without evidence of ill effect. Pluronics were used to incorporate drugs and transport them into the cell and within the body,[6] as well.

Their aqueous mixtures with conventional surfactants may possess features that can be employed to design and create

functional nanostructures. Understanding the modality of interactions between copolymer and surfactant is a fundamental step to achieve this objective. During the last years, several physicochemical studies were carried out on aqueous copolymer−surfactant mixtures. Structural[7−9] and thermodynamic[7,10−14] investigations were performed by changing the copolymer and the surfactant concentration simultaneously or one at a time. The complexity of these systems justifies the absence of unambiguous indications on the mechanism of interaction so that only qualitative or semiquantitative information has been drawn from the experimental data. Our recent efforts were addressed to thermodynamic studies[10,11,15,16] of aqueous EO_a-PO_bEO_a−surfactant mixtures, and we proposed[16] a mass action model which successfully fitted the experimental data. At this stage, the effect of the surfactant hydrophobicity was examined by studying $EO_{13}PO_{30}EO_{13}$ (L64) in the presence of sodium alkanoates,[15] whereas the variation of the surfactant headgroup as well as the copolymer hydrophobic/hydrophilic balance were partially investigated.[10,16] The present study is an effort to extend our knowledge on the changes of the surfactant−copolymer interactions produced by varying the hydrophobicity of the surfactant and the copolymer molecular weight, by keeping constant the hydrophobic/hydrophilic ratio, and finally the hydrophilicity of the copolymer. To this aim, the family of sodium alkanoates (sodium octanoate through sodium dode-

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TABLE 1: Thermodynamic Properties of Sodium Alkanoates and Copolymers Aggregation in Water at 298 K[a]

	NaN	NaDec[b]	NaU[c]	NaL	F68	F88	F108
K_M	$(6 \pm 9)10^{9\ d}$	0.76×10^{16}	$(1.0 \pm 1.3)10^{19}$	$(4 \pm 3)10^{25\ c}$			
N	18 ± 2^d	20	20 ± 4	20 ± 3^c			
$-\Delta G^o_{m,S}{}^e$	3.1 ± 0.5	4.5	5.4 ± 1.0	7.3 ± 1.0			
B_L	4.2 ± 0.5^f	13.51	18.9 ± 1.2	-16 ± 3^g			
C_L	10.4 ± 1.3^f			300 ± 18^g			
$\Delta H^o_{m,S}{}^e$	12.3 ± 0.4^f	10.0	10 ± 3	9.67^g			
$\Delta S^o_{m,S}$	51 ± 3	49.0	50 ± 13	57 ± 3			
$cmc_P{}^h$					35 ± 2	19 ± 3	6 ± 2
$-\Delta G^o_{m,P}{}^e$					8.3 ± 0.1	9.8 ± 0.4	12.7 ± 0.8
$\Delta H^o_{m,P}{}^i$					215	169	266
$\Delta S^o_{m,P}$					748	600	936

[a] Units are K_M, $kg^{N-1}\ mol^{1-N}$; B_L, $kJ\ kg\ mol^{-2}$; C_L, $kJ\ kg^{3/2}\ mol^{-5/2}$; free energy and enthalpy, $kJ\ mol^{-1}$; entropy, $J\ mol^{-1}\ K^{-1}$. cmc_P, $mmol\ kg^{-1}$. [b] From ref 26. [c] From ref 15. [d] Calculated by applying a mass action model (ref 24) to the enthalpy data in ref 22. [e] From ref 29. [f] From ref 22. [g] From ref 23. [h] From ref 21. [i] From ref 28.

canoate) and $EO_{76}PO_{29}EO_{76}$ (F68), $EO_{103}PO_{39}EO_{103}$, and EO_{132}-$PO_{50}EO_{132}$ were analyzed. The examination of the effect of increasing hydrophilic character of the copolymer was performed by comparing F68 to L64.

Experimental Section

Materials. Sodium octanoate (NaOct), sodium decanoate (NaDec), and sodium dodecanoate (NaL), Sigma products, were used as received. Sodium nonanoate (NaN) and sodium undecanoate (NaU) were obtained as follows. Ethanolic solutions of nonanoic and undecanoic acids (Aldrich) were neutralized with NaOH (Fluka) dissolved in absolute ethanol (Merck). The surfactants were crystallized three times from ethanol and dried in a vacuum oven for a week at 323 K. Carbon tetrachloride 99.5% (Aldrich) were used as received. The aqueous surfactant solutions gave pH ≈ 9. The purity of each product for the thermodynamic purpose was verified by using the procedure reported elsewhere.[17] $EO_{76}PO_{29}EO_{76}$ (F68, nominal M = 8350 g mol^{-1}), $EO_{103}PO_{39}EO_{103}$ (F88, nominal M=11400 g mol^{-1}), and $EO_{132}PO_{50}EO_{132}$ (F108, nominal M=14600 g mol^{-1}) were obtained as gifts from BASF. F68 was purified according to the literature procedure[18] where carbon tetrachloride was used instead of methylene chloride. However, its volumes in water are equal to those determined by using not-purified F68 corroborating previous findings[19] relative to $EO_{13}PO_{30}EO_{13}$ (L64). On this basis, the other copolymers were used as received by considering also that, whenever possible to make comparisons, a good agreement between the present and the literature[20] volumes was observed.

The water content of the copolymers determined by thermogravimetry (Mettler TA 3000) was low being 0.84, 0.38, and 0.89% w/w for F68, F88, and F108, respectively; however, it was considered in the calculation of the copolymer concentration.

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

Calorimetric Equipment. A flow LKB 2107 microcalorimeter was used to perform the mixing enthalpy measurements at 298.15 ± 0.01 K. The solutions were pushed into the calorimeter through a Gilson peristaltic pump (Minipuls 2). The experimental enthalpy (ΔH^{exp}) was evaluated as the difference between the thermal effect due to the mixing process of the solutions of copolymer and surfactant and that due to the dilution process of the same surfactant solution with water. The enthalpy of transfer (ΔH_t) corresponds to the difference between ΔH^{exp} and the enthalpy of dilution of the copolymer with water (ΔH_d). For F68, ΔH_d was taken from the literature.[10] The dilution with

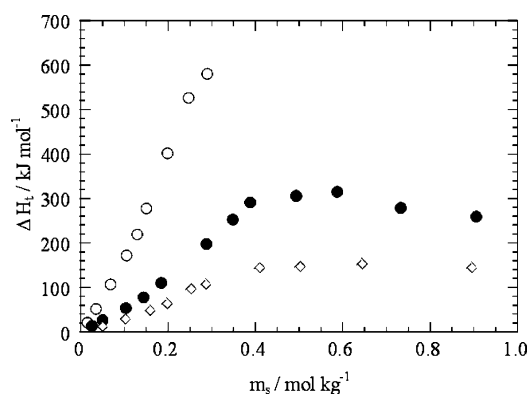**Figure 1.** Enthalpies of transfer of L64 (◇), F68 (●), and F108 (○) from water to the aqueous sodium octanoate solutions as functions of the surfactant concentration. Data of L64 and F68 were taken from ref 10.

water of the F108 solution (from 0.5 to 0.25 mmol kg^{-1}) involved a null thermal effect whereas for F88 the dilution process (from 1 to 0.5 mmol kg^{-1}) gave the ΔH_d value of -2.43 kJ mol^{-1}.

The concentrations of the surfactant (m_S) and the copolymer (m_P) solutions after the mixing process were calculated as

$$m_S = \frac{m_{S,i}\Phi_S}{(\Phi_S + \Phi_P)} \qquad m_P = \frac{m_{P,i}\Phi_P}{(\Phi_S + \Phi_P)} \tag{1}$$

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

The concentration value of each copolymer solution was kept below its critical micellar concentration in water, cmc_P,[21] (values are in Table 1) as the m_P values are 1 mmol kg^{-1} for F68, 0.5 mmol kg^{-1} for F88, and 0.25 mmol kg^{-1} for F108. The surfactant concentration was varied to investigate the effect of the surfactant in both the monomeric and the micellized states.

Experimental difficulties allowed to analyze a quite narrow range of the surfactant concentration of the F108/NaOct system.

Results

The enthalpy of transfer of each copolymer from water to the aqueous sodium alkanoate solutions as a function of m_S for NaOct through NaL are represented in Figures 1–5. For comparison purposes, the enthalpy trends[10,15] for the aqueous sodium alkanoate-L64 systems are also shown. The copolymers studied exhibit the same EO/PO ratio (ca. 5) and different
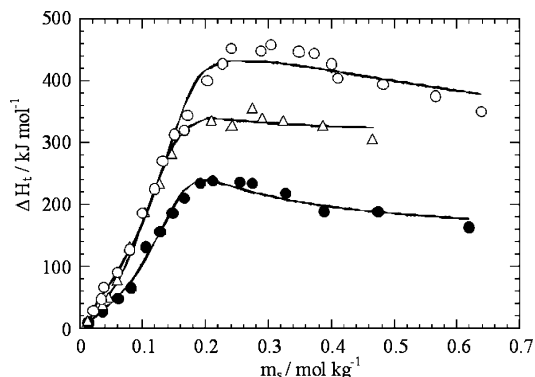
Figure 2. Enthalpies of transfer of F68 (●), F88 (△), and F108 (○) from water to the aqueous sodium nonanoate solutions as functions of the surfactant concentration. Lines are the best fits according to eq 2.
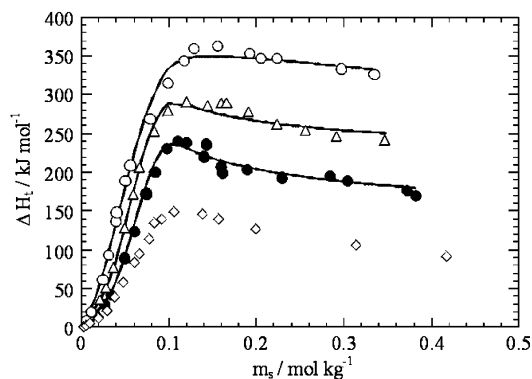

Figure 3. Enthalpies of transfer of L64 (◇), F68 (●), F88 (△), and F108 (○) from water to the aqueous sodium decanoate solutions as functions of the surfactant concentration. Lines are the best fits according to eq 2. Data of L64 were taken from ref 10.

Figure 4. Enthalpies of transfer of L64 (◇), F68 (●), F88 (△), and F108 (○) from water to the aqueous sodium undecanoate solutions as functions of the surfactant concentration. Lines are the best fits according to eq 2. Data of L64 were taken from ref 15.
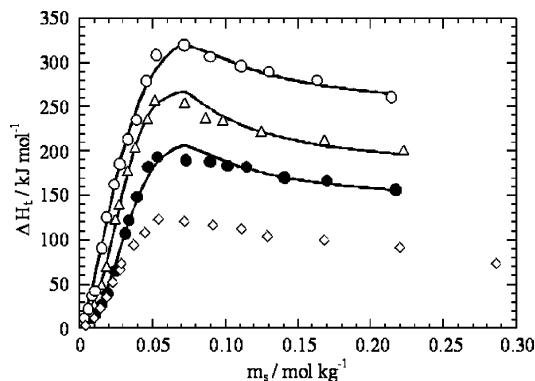
molecular weight which increases in the order F68 < F88 < F108. The L64 and F68 copolymers have the same length of the polypropylene oxide block but with varying the number of EO units. This information may assist in the qualitative understanding of the plots shown in Figures 1−5. For a given surfactant, ΔH_t sharply increases with m_S reaching a maximum and then decreases with further addition of surfactant amount, finally tending to a constant value. The location of the maximum is nearly independent of the nature of the macromolecule since it appears at a m_S value close to the critical micellar concentration in water (cmc$_S$).[11,15,22,23] The larger the copolymer molecular weight is, the more endothermic ΔH_t is. The comparison between L64 and F68 indicates that with increasing the copolymer hydrophobicity the maximum is broader and ΔH_t is
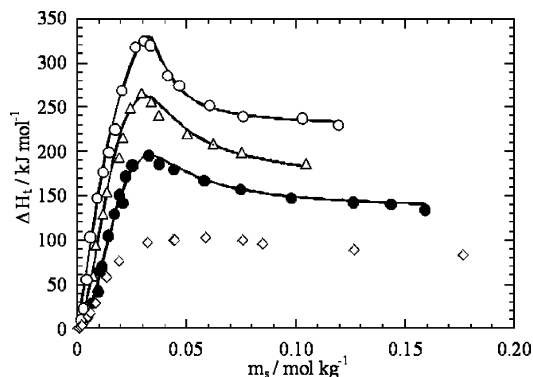

Figure 5. Enthalpies of transfer of L64 (◇), F68 (●), F88 (△), and F108 (○) from water to the aqueous sodium dodecanoate solutions as functions of the surfactant concentration. Lines are the best fits according to eq 2. Data of L64 were taken from ref 15.

less endothermic. The surfactant hydrophobicity enhances the extrema in the ΔH_t vs m_S curves and decreases ΔH_t. The analysis of these data evidences that the enthalpy of transfer increases with the copolymer size, at a fixed EO/PO ratio, and with the number of EO units at fixed PO size. It appears anomalous that F68 exhibits enthalpies more endothermic than L64 if one reminds that positive enthalpy values are generated by the loss of hydrophobic hydration. Nevertheless, our results are in line with literature reports. Recently, Li et al.[14] determined the isothermal titration calorimetry thermograms (ΔH_{obs}) of gemini surfactants in aqueous solutions of F108 and EO$_{17}$PO$_{56}$-EO$_{17}$ (P103). Both copolymers have nearly the same PO block size and different EO units so that F108 is the more hydrophilic. For comparable copolymer concentrations far below the cmc$_P$, the ΔH_{obs} endothermic values are larger for F108. As concerns the copolymer molecular weight effect, to the best of our knowledge, no enthalpy data are available.

Modeling Enthalpy Data

The enthalpies of transfer were analyzed on the basis of a thermodynamic model[16] which assumes that, even in the dilute surfactant region, z monomers of surfactant and 1 copolymer molecule interact forming the surfactant−copolymer aggregation complexes (C), and when micelles do form, they can solubilize the copolymer generating the copolymer-micelle aggregates (D). The following equation was reported[16]

$$\Delta H_t = 2B_{H,PS}\, x_P[m] + x_C\, \Delta H_C + \frac{[m_0] - [m] - zx_C\, m_P}{m_P}\, \Delta H_{m,S} + x_D\, \Delta H_D \quad (2)$$

The first term at the right-hand side of eq 2 takes into account the no-specific interactions between monomers of the surfactant and copolymer; namely, $B_{H,PS}$ is the interaction parameter, $[m]$ is the monomeric surfactant concentration in the presence of the copolymer, and x_P is the fraction of the free copolymer. The $x_C\Delta H_C$ term represents the contribution of formation of the surfactant-copolymer aggregation complex the fraction of which is x_C and ΔH_C is the variation of the property

$$x_C = K_C x_P[m]^z \quad (3)$$

where K_C is the equilibrium constant.

The third term of eq 2 stands for the shift of the micellization equilibrium induced by the copolymer where $[m_0]$ is the monomer surfactant concentration in the water + surfactant binary system and $\Delta H_{m,S}$ is the enthalpy of micellization of the

Thermodynamics of Aqueous EO-PO-EO Mixtures

J. Phys. Chem. B, Vol. 108, No. 47, 2004 **18217**

surfactant. Such quantities were evaluated according to a mass action model following which[24]

$$K_M = \frac{m_S - [m_0]}{N[m_0]^N} \quad (4)$$

where K_M is the equilibrium constant of micellization and N is the aggregation number of the micelles

$$\Delta H_{m,S} = L_{M,S} - L_{D-H}[m_0]^{1/2} - B_L[m_0] - C_L[m_0]^{3/2} \quad (5)$$

here B_L and C_L are the interaction parameters and L_{D-H} is the Debye−Hückel limiting slope coefficient (1973 J mol$^{-3/2}$ kg$^{1/2}$).[25] $L_{M,S}$ is the partial molar relative enthalpy of the surfactant in the micellar state. The values[15,22,26] of these parameters are collected in Table 1. Finally, $x_D \Delta H_D$ is the contribution for the copolymer−micelle aggregates formation where ΔH_D is the change in the property and x_D is the fraction of the aggregate correlated to the equilibrium constant (K_D) as

$$x_D = \frac{(x_P m_P)^w m_M K_D}{m_P} \quad (6)$$

where m_M is the micelles concentration in the water+surfactant + copolymer ternary system and w is the number of copolymer molecules interacting with 1 micelle.

Equations of the mass balance for both the surfactant and the copolymer were expressed in terms of $[m]$, x_P, N, and z and solved through the Newton−Raphson method extended to two dimensions. Then, x_C and x_D were evaluated from eqs 3 and 6, respectively.

In applying eq 2 to the experimental data, the $B_{H,PS}$ parameter was determined from the ΔH_t points in the very dilute surfactant concentration region. The minimizing procedure was performed by means of a program based on a nonlinear least-squares fitting method. The best fits, shown in Figures 2−5, provided the parameters collected in Table 2. For all of the mixtures investigated, $w = 1$ was obtained. The minimizing procedure for the F108/NaOct mixture was not performed because the experimental points are available in a fairly narrow range of m_S. Details on the model and the fitting procedure are reported elsewhere.[16]

For the formation of the surfactant−copolymer complexes (subscript i = C) and copolymer−micelle aggregates (subscript i = D), the standard free energy (ΔG_i^o) and entropy (ΔS_i^o) were evaluated as

$$\Delta G_i^o = -RT \ln K_i \quad \Delta S_i^o = (\Delta H_i - \Delta G_i^o)/T \quad (7)$$

The calculated values are collected in Table 2.

Discussion

Modeling experimental data is a powerful tool providing parameters which allow to discriminate the various effects contributing to the formation of the EO$_a$PO$_b$EO$_a$−surfactant aggregation complexes and the EO$_a$PO$_b$EO$_a$−micelle aggregates. This aspect is relevant if one remembers that, at this stage, the thermodynamic knowledge[7,12,14] is gained from the qualitative or semiquantitative analysis of the experimental data. For instance, very recently Li et al.[14] proposed that possible contributions to the endothermic enthalpies of gemini surfactants in aqueous P103 and F108 solutions are the conformational changes of the copolymer, the dehydration of unimers, and the interactions between the surfactant and the copolymer monomers. Indeed, such contributions were successfully highlighted

TABLE 2: Thermodynamic Properties for the Formation of the Surfactant−Copolymer Aggregation Complexes and the Copolymer−Micelle Aggregates at 298 K^a

F68			
	NaN	NaDec	NaU	NaL
m_P	1	1	1	1
$B_{H,PS}$	393 ± 9	570 ± 50	600 ± 160	1570 ± 280
K_C	(4.1 ± 0.2)10³	(29 ± 13)10³	(39 ± 14)10³	(5.6 ± 0.2)10⁵
z	4.5	4.7	3.2	3.2
$-\Delta G_C^o$	20.61 ± 0.12	25.5 ± 1.1	26.2 ± 0.9	32.8 ± 0.1
ΔH_C	305 ± 4	270 ± 2	228 ± 2	216 ± 2
ΔS_C^o	1093 ± 13	989 ± 10	852 ± 10	835 ± 7
K_D	570 ± 80	(1.8 ± 0.2)10³	(7 ± 2)10³	(23 ± 4)10³
$-\Delta G_D^o$	15.7 ± 0.3	18.6 ± 0.3	21.9 ± 0.7	24.9 ± 0.4
ΔH_D	129 ± 7	130 ± 4	133 ± 6	130 ± 2
ΔS_D^o	486 ± 23	500 ± 13	520 ± 23	520 ± 7

F88			
	NaN	NaDec	NaU	NaL
m_P	0.5	0.5	0.5	0.5
$B_{H,PS}$	533 ± 4	760 ± 50	1350 ± 120	(3.2 ± 0.1)10³
K_C	(3.81 ± 0.06)10³	(5.6 ± 0.2)10⁴	(10 ± 4)10⁴	(1.5 ± 0.4)10⁵
z	4.1	4.1	3.4	2.9
$-\Delta G_C^o$	20.43 ± 0.04	27.09 ± 0.09	29 ± 1	29.5 ± 0.7
ΔH_C	385 ± 2	326.0 ± 1.3	282 ± 2	280 ± 2
ΔS_C^o	1358 ± 7	1184 ± 5	1043 ± 10	1040 ± 10
K_D	930 ± 200	(1.7 ± 0.4)10³	(9 ± 2)10³	(1.6 ± 0.5)10⁴
$-\Delta G_D^o$	16.9 ± 0.5	18.4 ± 0.6	22.6 ± 0.6	24.0 ± 0.8
ΔH_D	304 ± 5	215 ± 10	165 ± 9	155 ± 10
ΔS_D^o	1077 ± 20	781 ± 37	631 ± 34	600 ± 37

F108			
	NaN	NaDec	NaU	NaL
m_P	0.25	0.25	0.25	0.25
$B_{H,PS}$	742 ± 80	926 ± 16	1935 ± 7	(4.0 ± 0.1)10³
K_C	1300 ± 40	359 ± 9	970 ± 25	230 ± 50
z	4.4	2.3	2.1	1.4
$-\Delta G_C^o$	17.76 ± 0.08	14.58 ± 0.06	17.04 ± 0.06	13.5 ± 0.5
ΔH_C	602 ± 5	426 ± 3	337 ± 2	378 ± 4
ΔS_C^o	2079 ± 17	1479 ± 10	1187 ± 7	1311 ± 17
K_D	43.1 ± 0.9	50 ± 12	(2.4 ± 0.9)10³	(29 ± 5)10³
$-\Delta G_D^o$	9.32 ± 0.05	9.7 ± 0.6	19.3 ± 0.9	25.5 ± 0.4
ΔH_D	0.2 ± 0.7	40 ± 70	232 ± 13	226 ± 2
ΔS_D^o	32 ± 3	170 ± 235	842 ± 47	842 ± 7

^{a} Units are m_P, mmol kg^{-1}; $B_{H,PS}$, kJ kg mol^{-2}; K_C, kg^z mol^{-z}; K_D, kg mol^{-1}; standard free energy and enthalpy, kJ mol^{-1}; entropy, J mol^{-1} K^{-1}.

for the L64/sodium alkanoate systems[15] from the properties obtained by applying the above cited thermodynamic model to enthalpy and volume data. Thus, the thermodynamic properties of the present systems may provide straightforward insights into the effect of the molecular weight and the hydrophilicity of the copolymer as well as the hydrophobicity of the surfactant.

(i) Effect of the Molecular Weight and the Hydrophilicity of the Copolymer. Figure 6 illustrates the dependence of ΔG_C^o, ΔH_C, and $T\Delta S_C^o$ on the number of carbon atoms in the surfactant alkyl chain length (n_c) for the present systems and the L64-sodium alkanoate mixtures.[15] Generally, ΔG_C^o decreases with n_c and, for a given surfactant, it depends on the copolymer nature, i.e., on the copolymer molecular weight and the hydrophobic/hydrophilic ratio. Figure 6 shows that, at a fixed n_c, ΔG_C^o for F68 and F88 are very close and more negative than that of F108. Despite F68 larger hydrophilicity, ΔG_C^o(F68) < ΔG_C^o(L64). The ΔH_C and $T\Delta S_C^o$ vs n_c trends are decreasing curves and shifted to larger values by increasing (1) the copolymer molecular weight, at fixed hydrophilic/hydrophobic
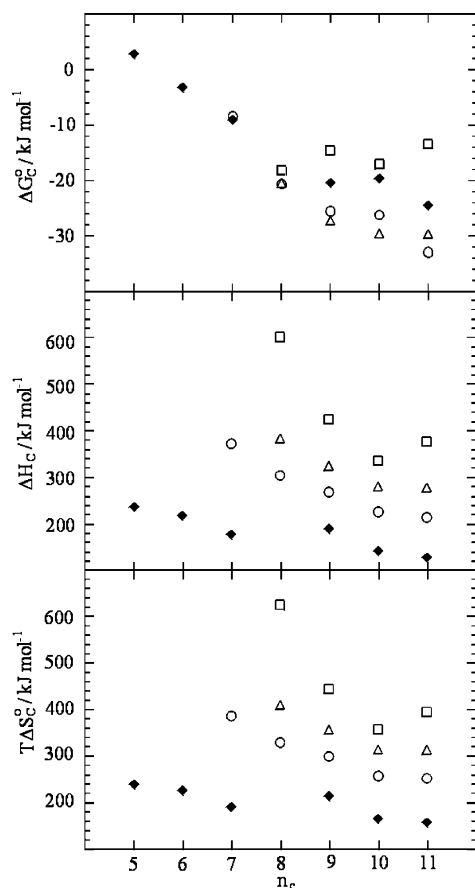
Figure 6. Dependence on the number of carbon atoms in the alkyl chain of the thermodynamic properties for the formation of the aggregation complexes between sodium alkanoates and L64 (◆), F68 (○), F88 (△), and F108 (□) at 298 K.
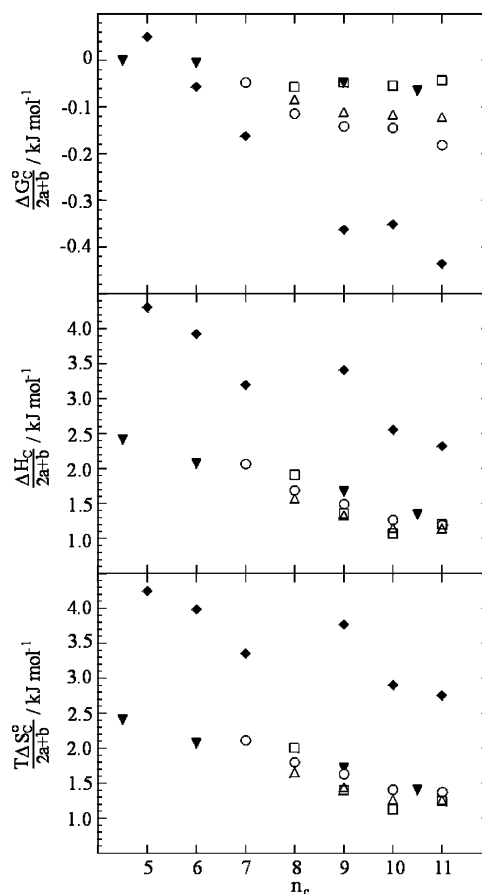
Figure 7. Dependence on the number of carbon atoms in the alkyl chain of the thermodynamic properties, normalized for the number of EO and PO units, for the formation of the aggregation complexes between sodium alkanoates and L64 (◆), F68 (○), F88 (△), and F108 (□) at 298 K. ▼, PEG 35000/sodium perfluoroalkanoates mixtures for which the apparent number of methylene groups was calculated (see text).

ratio, and (2) the length of the ethylene oxide block by keeping constant the number of PO units. These evidences are not consistent with the expectation that as the EO block is lengthening, by fixing the number of PO segments, there would be more hydrophilic sites and less probably the copolymer will be engaged in the hydrophobic-like interactions with the surfactant; consequently, for F68 the enthalpy and the entropy are expected to be smaller and the free energy larger than those of L64. Moreover, as the copolymer molecular weight increases, the ratio between the number of the hydrophilic and the hydrophobic sites of binding remains unchanged, and then, the interactions with the surfactant should generate comparable values of the thermodynamic properties for the copolymer-surfactant aggregation complex formation (ΔY_C).

An attempt was done to verify whether these findings are representative of the physical interactions between copolymers and surfactants or reflect the large difference of the copolymer molecular masses. In other words, ΔY_C should be normalized for the different amounts of EO and PO units in the copolymer. We thought that the objective could be achieved by calculating the properties for the surfactant−copolymer complex formation as $\Delta Y_C/(2a + b)$, with a and b being the number of repetitive units of EO and PO, respectively. In this procedure, the copolymer nominal molecular weight (M) is replaced by the ratio $M/(2a + b)$ which corresponds to $[X_{EO}M_{EO} + (1 − X_{EO})M_{PO}]$, where M_{EO} and M_{PO} is the molecular mass of the EO and PO unit, respectively, and X_{EO} is the fraction of the EO segments. Consequently, the $M/(2a + b)$ quantity stands for the molecular mass of the smallest unit reflecting the hydrophobic/hydrophilic balance of the copolymer. The three

copolymers under study exhibit equal $M/(2a + b)$ (they possess the same X_{EO} value, i.e., 0.84) which is different from that of L64 having $X_{EO} = 0.46$. $\Delta Y_C/(2a + b)$ were plotted against n_c in Figure 7. From the inspection of the obtained data, it emerges that the increasing copolymer molecular weight moves the $\Delta G_C^o/(2a + b)$ vs n_c trend toward less negative values, whereas an inversion of the standard free energy for L64 and F68 takes place in agreement with the L64 larger hydrophobicity. The enthalpy and the entropy results are interesting (Figure 7). Namely, the very large differences observed for ΔH_C and $T\Delta S_C^o$ for F68, F88, and F108 disappear. By looking at the $\Delta H_C/(2a + b)$ and $T\Delta S_C^o/(2a + b)$ data one may state that, for a given surfactant, the contribution to both properties is nearly constant whatever is the size of the macromolecule featured by the same hydrophilic/hydrophobic ratio. These findings are corroborated by the higher values of L64 data (Figure 7); accordingly, $\Delta H_C^o/(2a + b)$ for L64 are roughly 2-fold as those of F68 like X_{PO} reflecting the larger L64 hydrophobic character.

Based on these evidences, we thought it would be interesting to simulate F108 in NaOct the ΔH_t points of which are available only in the surfactant dilute region. To this purpose, the ΔH_C and ΔG_C^o values of 660 and −12 kJ mol⁻¹ were evaluated from the graphs in Figure 7. Also, the z value of 3.8 was calculated from those of the higher homologues and the $B_{H,PS}$ parameter (813 ± 11 kJ kg mol⁻²) was determined from data in the very dilute region. As Figure 8 shows, the simulation is quite satisfactory and reliable as the computed points using ΔH_C

Thermodynamics of Aqueous EO-PO-EO Mixtures

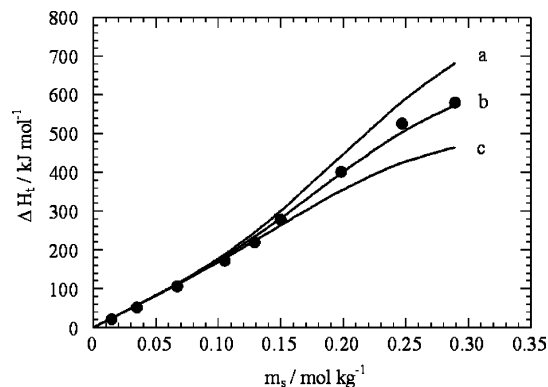*J. Phys. Chem. B, Vol. 108, No. 47, 2004* **18219**

Figure 8. Enthalpy of transfer of F108 from water to the aqueous sodium octanoate solutions as a function of the surfactant concentration. Lines are simulation done by means of eq 2. (a) $\Delta H_C = 860$ kJ mol^{-1}; (b) $\Delta H_C = 660$ kJ mol^{-1}; (c) $\Delta H_C = 460$ kJ mol^{-1}.

values smaller and larger than 660 kJ mol^{-1} deviate from the experimental data.

A better comprehension of such findings can be achieved by inspecting ΔY_C of sodium perfluoroalkanoate−poly(ethylene)-glycol (PEG) 35000 mixtures[27] which, to the best of our knowledge, are the only available data for systems similar to the present ones. Sodium perfluoroalkanoates are surfactants comparable to sodium alkanoates with hydrophobicity that may be evaluated according to the relation $CF_2 = 1.5 \times CH_2$. On this basis, to make these data comparable to the present ones, the number of carbon atoms in the fluorinated chain was multiplied by 1.5 and the *apparent number of methylene groups* was calculated. In addition, ΔY_C was divided by the number of EO units (i.e., 795) and plotted in Figure 7. The standard free energy superimposes to that for F108, which is the copolymer with the highest content in EO, whereas the enthalpies and entropies are very close to those of F68, F88 and F108. These results are not surprising as the latter copolymers have $X_{EO} = 0.84$ and PEG 35000 has $X_{EO} = 1$.

The fate of these copolymer-surfactant aggregation complexes is being transformed into copolymer-micelle aggregates because the copolymer prefers the micellar structures. The K_C and K_D values will establish the importance of this conversion. For a given surfactant, $\Delta G_D^o/(2a + b)$ becomes less negative upon increasing the macromolecule size although the difference in the values is small (Figure 9). The enthalpy and the entropy are very close for F68 and F88, whereas F108 presents smaller values for the shorter alkyl chains. The comparison between F68 and L64 behavior documents the larger hydrophobic character of L64 earlier highlighted by $\Delta Y_C/(2a + b)$. Namely, the standard free energy values are roughly 4-fold more negative as those for F68; moreover, the different enthalpy and entropy, being larger at low n_c and smaller at high n_c, indicates that the reduced macromolecule flexibility[15] is enhanced by the apolar moiety of both the surfactant and the copolymer.

(ii) Effect of the Hydrophobicity of the Surfactant. In the previous paragraph, little attention was paid on the variations of the copolymer−surfactant interactions induced by the surfactant hydrophobicity. This aspect will be carefully analyzed in the following.

It is well accepted that the straight line which correlates a given standard thermodynamic property to n_c provides information on the hydrophilic (intercept) and the hydrophobic (slope) interactions. For the copolymers characterized by the high EO/PO ratio (ca. 5), the hydrophilic contribution to $\Delta G_C^o/(2a + b)$ is nearly null whereas it is positive $(0.42 \pm 0.06$ kJ mol$^{-1})$ for L64 which has a smaller EO/PO ratio (0.87). Increasing the
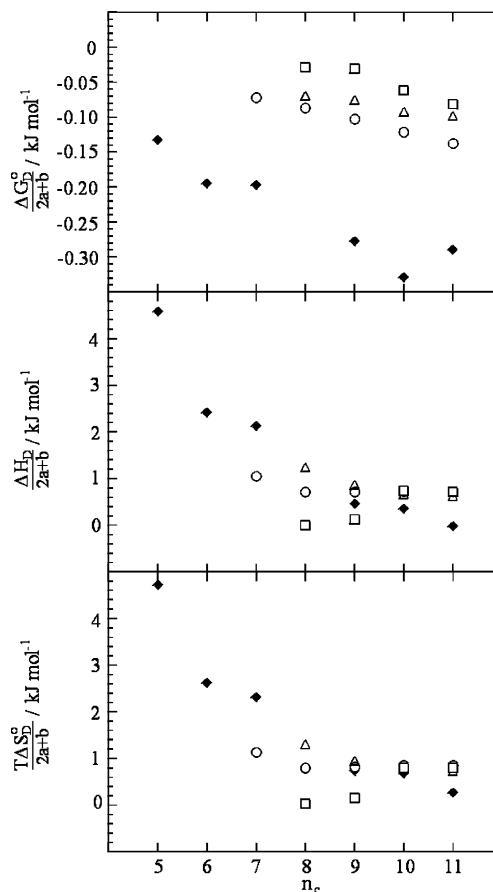

Figure 9. Dependence on the number of carbon atoms in the alkyl chain of the thermodynamic properties, normalized for the number of EO and PO units, for the formation of the copolymer-micelle aggregates composed by sodium alkanoates and L64 ($\blacklozenge$), F68 ($\bigcirc$), F88 ($\triangle$), and F108 ($\square$) at 298 K.

surfactant hydrophobicity stabilizes the copolymer-surfactant aggregation complexes according to the copolymer features. In fact, the $-CH_2-$ group contribution to $\Delta G_C^o/(2a+b)$ for L64 $(-0.080 \pm 0.008$ kJ mol$^{-1})$ is more important than those for F68 and F88 $(-0.016 \pm 0.007$ kJ mol$^{-1})$ and F108 $(-0.003 \pm 0.003$ kJ mol$^{-1})$. Therefore, one may assess that the formation of such complexes is driven by the hydrophobic forces which (1) cancel out the unfavorable hydrophilic interactions in the case of L64 and (2) are practically the only present in the case of F68, F88, and F108. The interactions between the copolymer and the surfactant headgroup generate endothermic effects which are basically independent of the copolymer molecular weight and raise with the copolymer hydrophobicity. Exothermic contributions of the methylene group to $\Delta H_C^o/(2a + b)$ were obtained for all of the systems under investigation. According to previous findings,[15] their values reflect the formation of hydrogen binding of the EO units with water induced by the conformational changes of the macromolecule. The larger negative value for L64 shows that such a process is enhanced by the copolymer hydrophobicity.

The nature of the hydrophilic and the hydrophobic forces, which control the formation of the copolymer−surfactant aggregation complexes, can be straightforwardly evidenced by the calculations performed by means of eq 8. Such an equation was derived by assuming that the macromolecule and the surfactant in the complex are surrounded by an environment the features of which are the same as those of the aggregated states. Namely, ΔY_C was correlated[15] to the standard properties of micellization of the surfactant $(\Delta Y_{m,S}^o)$ and the copolymer $(\Delta Y_{m,P}^o)$ as
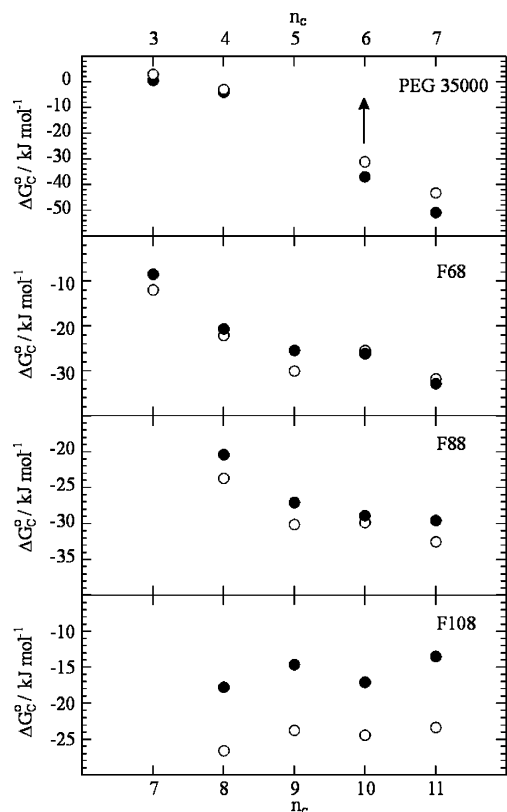
Figure 10. Standard free energy for the surfactant-copolymer aggregation complex formation as a function of the number of carbon atoms in the surfactant alkyl chain calculated by means of eqs 7 (filled symbols) and 8 (open symbols).

$$\Delta Y_C^o = z\Delta Y_{m,S}^o + \Delta Y_{m,P}^o \tag{8}$$

ΔG_C^o was computed by using the $\Delta G_{m,S}^o$ and $\Delta G_{m,P}^o$ values reported in Table 1. As observed for L64,[15] the calculated values for F68 and F88 are in good agreement with the experimental points whereas those for F108 are nearly parallel (Figure 10). Such different behavior is to be ascribed to the large negative $\Delta G_{m,P}^o$ value of F108 which likely does not undergo the same dehydration of the PO occurring in the aggregation process. Equation 8 may be not adequate for the sodium perfluoroalkanoate-PEG 35000 mixtures because the polymer does not form aggregates ($\Delta Y_{m,P}^o$ is absent). Notwithstanding, the ΔG_C^o calculation may facilitate to distinguish the various forces involved in the surfactant−copolymer binding when the copolymer cooperative process is not present. It interestingly turns out that for short tails the calculated values match well with the experimental points, whereas for long tails they are less negative, and this difference likely reflects the variation of the hydration state of the polymer induced by the increased surfactant hydrophobicity (Figure 10).

Equation 8 was not able to reproduce ΔH_C and $T\Delta S_C^o$ (literature data[28] in Table 1 were used for the calculation) confirming the findings for the L64-sodium alkanoate[15] systems that change in the hydration state of the macromolecule, caused by the conformational variations, and hydrophobic effects influence enthalpy and entropy only.

The formation of the copolymer−micelle aggregates is still controlled by both hydrophilic and hydrophobic forces (Figure 9). For a given copolymer, the $\Delta G_D^o/(2a + b)$ vs n_c trend is linear; for L64, the intercept is null and slightly positive for F68, F88, and F108, whereas the slope is 2-fold as that evaluated for the three copolymers, having the same EO/PO ratio, in

agreement with the L64 more hydrophobic character. For F68 and F88, the very close enthalpies allow for endothermic hydrophilic and exothermic hydrophobic contributions, whereas for F108, the opposite is observed reflecting the predominance of hydrophilic forces. The stronger effect of the surfactant hydrophobicity on the L64 enthalpy and entropy, compared to F68, proves that the attachment of the more and more hydrophobic micelles to the hydrophobic copolymer induces significant conformational effects and degree hydration variations of the copolymer. Thus, one may conclude that in the copolymer−micelle aggregates the state of the copolymer (conformation, hydration, etc.) is specific of its size.

Conclusions

The effects of the hydrophobicity of the surfactant, the copolymer molecular weight, at constant hydrophobic/hydrophilic ratio, and the hydrophilicity of the copolymer on the interactions between $EO_aPO_bEO_a$ and sodium alkanoates were investigated by calorimetry at 298 K. The experimental data were modeled by means of a thermodynamic approach which assumes that, even in the pre-micellar region, monomers of surfactant can associate with unimeric copolymer leading to the formation of surfactant−copolymer aggregation complexes, and when the micelles are formed, they interact with the copolymer generating the copolymer-micelle aggregates. A first analysis of the thermodynamic properties for the formation of both the surfactant−copolymer aggregation complexes (ΔY_C) and the copolymer−micelle aggregates (ΔY_D) provided unexpected information. In fact, F68 presented larger enthalpies and entropies and lower free energies than L64 despite its larger number of hydrophilic sites of binding. Moreover, the role of the copolymer molecular weight was important although the ratio between the number of the hydrophilic and the hydrophobic sites of binding was constant. An effort was done to verify whether these findings are representative of the physical interactions between copolymers and surfactants or reflect the difference in the copolymer molecular masses. Therefore, both ΔY_C and ΔY_D were normalized with respect to the number of EO and PO units. They straightforwardly proved that L64 behaves like a solute more hydrophobic than F68 and the copolymer molecular weight play a relatively small effect. Finally, it was demonstrated that the normalized ΔY_C properties are promising tools for predicting behavior of copolymers in sodium alkanoates for a fixed hydrophobic/hydrophilic ratio.

Supporting Information Available: Table of the experimental enthalpies of transfer of F68, F88, and F108 from water to the aqueous sodium alkanoate solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Brandanti, P.; Stroeve, P. *Macromolecules* **2003**, *36*, 9492.
(2) De Lisi, R.; Milioto, S. *Langmuir* **2000**, *16*, 5579.
(3) Wang, R.; Knoll, H.; Rittig, F.; Kärger, J. *Langmuir* **2001**, *17*, 7464.
(4) Varshney, M.; Morey, T. E.; Shah, D. O.; Flint, J. A.; Moudgil, B. M.; Seubert, C. N.; Donn M. Dennis, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 5108.
(5) W. Loh In *Encyclopedia of Surface and Colloid Science*; Hubbard, A. T., Ed.; Marcel Dekker: New York, 2002; p 802.

Thermodynamics of Aqueous EO-PO-EO Mixtures

J. Phys. Chem. B, Vol. 108, No. 47, 2004 **18221**

(6) Batrakova, E. V.; Han, H.-Y.; Miller, D. W.; Kabanov, A. V. *Pharm. Res.* **1998**, *15*, 1525.

(7) Thurn, T.; Courdec, S.; Sidhu, J.; Bloor, D. M.; Penfold, J.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **2002**, *18*, 9267.

(8) Hecht, E.; Hoffmann, H. *Langmuir* **1994**, *10*, 86.

(9) Li, Y.; Xu, R.; Courdec, S.; Bloor, D. M.; Wyn-Jones, E.; Holzwarth, J. F. *Langmuir* **2001**, *17*, 183.

(10) De Lisi, R.; Milioto, S.; Muratore, N. *Macromolecules* **2002**, *35*, 7067.

(11) De Lisi, R.; Milioto S.; Munafò, M.; Muratore, N. *J. Phys. Chem. B* **2003**, *107*, 819.

(12) Da Silva, R. C.; Olofsson, G.; Schillen, K.; Loh, W. *J. Phys. Chem. B* **2002**, *106*, 1239.

(13) Senkow, S.; Roux, A. H.; Roux-Desgranges, G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 822.

(14) Li, X.; Wettig, S. D.; Verrall, R. E. *Langmuir* **2004**, *20*, 579.

(15) De Lisi, R.; Lazzara, G.; Milioto S.; Muratore, N. *Macromolecules* **2004**, *37*, 5423.

(16) De Lisi, R.; Lazzara, G.; Milioto S.; Muratore, N. *J. Phys. Chem. B* **2004**, *108,* 1819.

(17) De Lisi, R.; Lazzara, G.; Milioto, S.; Muratore, N. *J. Phys. Chem. B* **2003**, *107*, 13150.

(18) Michels, B.; Waton, G.; Zana, R. *Langmuir* **1997**, *133*, 3111.

(19) De Lisi, R.; Milioto, S. *Langmuir* **1999**, *15*, 6277.

(20) Senkow, S.; Mehta, S. K.; Douhéret, G.; Roux, A. H.; Roux-Desgranges, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4472.

(21) Lazzara, G.; Lombardo, R.; Milioto, S.; Muratore, N.; Turco Liveri, M. L. (unpublished data).

(22) De Lisi, R.; Milioto, S.; Muratore, N. *Langmuir* **2000**, *16*, 4441.

(23) Milioto, S.; Causi, S.; De Lisi, R. *J. Colloid Interface Sci.* **1993**, *155*, 452.

(24) Desnoyers, J. E.; Caron, G.; De Lisi, R.; Roberts, D.; Roux, A.; Perron, G. *J. Phys. Chem.* **1983**, *87*, 1397.

(25) De Lisi, R.; Ostiguy, C.; Perron, G.; Desnoyers, J. E. *J. Colloid Interface Sci.* **1979**, *71*, 147.

(26) Yamashita, F.; Perron, G.; Desnoyers, J. E.; Kwak, J. C. T. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1986.

(27) De Lisi, R.; De Simone, D.; Milioto, S. *J. Phys. Chem. B* **2000**, *104*, 12130.

(28) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2414.

(29) $\Delta G^{o}_{m,S}$ was calculated as $(-RT \ln K_M)/N$, whereas $\Delta G^{o}_{m,P}$ as $RT \ln \text{cmc}_P$ according to the pseudo-phase transition model (ref 30). Note that $\Delta H^{o}_{m,S} = L_{M,S}$.

(30) Mukerjee, P. *Adv. Colloid Interface Sci.* **1967**, *1*, 241 .