

Polymer–Surfactant Interactions. A Quantitative Approach to the Enthalpy of Transfer of Poly(Ethylene Glycol)s from Water to the Aqueous Sodium Perfluoroalkanoates Solutions

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The enthalpy of transfer (ΔH_t) of nonionic polymers at a fixed concentration from water to aqueous substrate solutions as a function of the substrate concentration (f_{sm}) was determined. The substrates studied are sodium perfluorobutanoate to sodium perfluorooctanoate, and the polymers are poly(ethyleneglycol)s with molecular weights of 400 and 35 000. For the PEG 400–sodium perfluoroheptanoate–water systems, measurements were also performed at some polymer compositions. As a general feature, the enthalpy of transfer steeply changes with f_{sm} , reaching a maximum beyond which it decreases, tending to level off. A qualitative analysis of the enthalpy data assigned the steep increase of ΔH_t to the binding between the polymer and “loose” aggregates of surfactant and the maximum to the critical micellar concentration in the presence of the polymer. Theoretical approaches for the pre- and post-micellar regions were proposed. In the pre-micellar region, the cooperative binding was treated as a simple one-step association process based on the formation of complexes between one mole of polymer and n moles of surfactant. The standard free energy and the enthalpy and entropy for the polymer–surfactant complex formation were determined. As far as the micellar region is concerned, an approach was proposed taking into account the following contributions: (i) the shift of micellization equilibrium induced by the polymer, (ii) the formation of the polymer–surfactant complexes in the aqueous phase, and (iii) the formation of polymer–micelle complexes. The standard free energy, enthalpy, and entropy for the polymer–micelles complex formation are consistent with the micelles being wrapped by the polymer chains.

Introduction

The literature dealing with the polymer–surfactant interaction topic is very extensive, as documented by recent books.^{1–3} Yet this argument is still attracting the interest of many researchers, since the mechanism of interaction needs to be clarified.

Mixtures of nonionic polymers and anionic surfactants have been mostly studied, since they show large affinity to each other. It has been demonstrated that the polymer–surfactant interactions depend on both the polymer and surfactant concentrations. The addition of the surfactant to a given polymer–water mixture induces⁴ (i) the onset of binding between surfactant and polymer at a given surfactant concentration (critical aggregation concentration, cac), leading to the formation of aggregates or clusters bound to the polymer, and (ii) the formation of free micelles whenever the polymer is saturated by the surfactant. It was shown^{4,5} that in some cases the free micelle formation begins long before the polymer is fully saturated.

Generally, the cac ^{4,6} depends on the nature of the polymer but not on its molecular weight, and the polymer saturation concentration⁷ depends on its stoichiometric concentration. Schwuger et al.⁸ showed the existence of a critical polymer molecular weight value to observe surfactant–polymer interactions. Accordingly, poly(ethylene glycol) with a molecular weight of 600 (PEG 600) does not show affinity toward sodium dodecyl sulfate (NaDS), while PEG having a molecular weight larger than 4000 strongly interacts with NaDS. Some studies

have indicated the hydrophobic forces^{9–13} as being responsible for the interactions between surfactants and nonionic polymers in aqueous media, and others have showed that polymers can interact with micelles through electrostatic forces.^{9,14–16}

The thermodynamics of polymer–surfactant systems has been investigated through volume,^{17,18} heat capacity,^{17,18} dialysis equilibrium,^{3,7,12,19–21} emf,^{4,5,21,22} and enthalpy data.^{4–6,21,29–31} In the very recent years, much attention has been focused on the enthalpy of the water–polymer–surfactant ternary systems aimed at studying the effect of the nature of both solutes on the polymer–surfactant interactions. Usually, enthalpy curves of the surfactant in the water–polymer mixture at a fixed composition as functions of the surfactant concentration are determined. Despite the numerous calorimetric data, their analysis has given only qualitative information on the energetics of polymer–surfactant systems. To our knowledge, the only quantitative approach to the enthalpy was proposed by Blandamer et al.^{28,29} On the basis of the Frumkin adsorption isotherm, they developed equations that describe the titration microcalorimetry curves of NaDS and sodium decyl sulfate in the presence of 1% poly(N-vinyl pyrrolidone). It was assumed that the micelles are adsorbed on the polymer and interact with each other. The alkyl chain length of the surfactant strongly influences the standard enthalpy of adsorption, and hardly does the degree of surface coverage of the polymer.

To obtain quantitative information on the surfactant–polymer interactions, we determined the enthalpy of transfer of nonionic polymers, at a fixed concentration and at very low concentrations, from water to the aqueous substrate solutions as a function

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of the substrate concentration. In these conditions, the coil–coil interactions are negligible, and the thermodynamic property reflects the interactions between the polymer and its environment, which changes upon the increase of the substrate concentration. The substrates studied are sodium perfluorobutanoate to sodium perfluorooctanoate, and the polymers are PEG 400 and PEG 35 000. These systems were chosen to give a contribution to the thermodynamics of nonionic polymer–fluorinated compound systems, which is very scarce.³²

Experimental Section

Materials. Sodium perfluorobutanoate (PFBNa), sodium perfluoropentanoate (PFPNa), and sodium perfluoroheptanoate (PFHNa) were obtained by neutralizing their corresponding acids (Aldrich) with sodium hydroxide ethanolic solutions at 323 K. The products were obtained by cooling and recovered by filtration. They were dried in a vacuum oven at 323 K for at least 4 days.

Perfluorooctanoic acid (Fluka) was crystallized from carbon tetrachloride and dried at room temperature. To obtain the sodium salt (PFONa), we neutralized the acid with an aqueous sodium hydroxide solution. The product was recovered by filtration after the solution was cooled. The aqueous salt solutions gave a pH of ~ 8.5 .

The agreement between the present standard partial molar volumes and those reported elsewhere³³ confirmed the purity of the salts. Poly(ethylene glycol) 400 (PEG 400) and poly(ethylene glycol) 35 000 (PEG 35 000), Fluka products, were used as received.

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

Equipment. The calorimetric measurements were carried out at 298 ± 0.01 K with a flow LKB 2107 microcalorimeter. The injection of the solutions into the microcalorimeter was made by means of a Gilson peristaltic pump (Minipuls 2).

The experimental enthalpy (ΔH^{exp}) corresponds to the difference between the thermal effect due to the mixing of the polymer solution with the substrate solution and that for the dilution process of the same substrate solution with water ($\Delta H_{\text{id},\text{S}}$).

The measurements were carried out at a fixed polymer concentration (0.30% w/w initial composition) in a wide range of substrate concentrations. For the PFHNa–water–PEG 400 system, the experiments were also performed as functions of the polymer concentration (0.30–2.0% w/w).

The flows of the solutions were determined by weight.

Since the mixing process involves the dilution of both the substrate and polymer solutions, the final concentrations of the polymer ($f_{\text{p}}m_{\text{p}}$) and the substrate ($f_{\text{s}}m_{\text{s}}$) were calculated as the product between the initial concentration and the dilution factor given by

$$f_{\text{s}} = \phi_{\text{S}}/(\phi_{\text{S}} + \phi_{\text{P}}) \quad f_{\text{P}} = \phi_{\text{P}}/(\phi_{\text{S}} + \phi_{\text{P}}) \quad (1)$$

Here ϕ_{P} and ϕ_{S} represent the flows of water in the polymer and substrate solutions, respectively.

The enthalpy of transfer (ΔH_{t}) of the polymer from water to the aqueous substrate solution was calculated as the difference between ΔH^{exp} and the enthalpy of dilution ($\Delta H_{\text{id},\text{P}}$) of the aqueous polymer solution with water. The dilution of the polymer solution from 0.30% to 0.15% did involve a null thermal effect for both PEG 400 and PEG 35 000. For the dilution of PEG 400 solutions from 0.80 to 0.39 and from 2.0

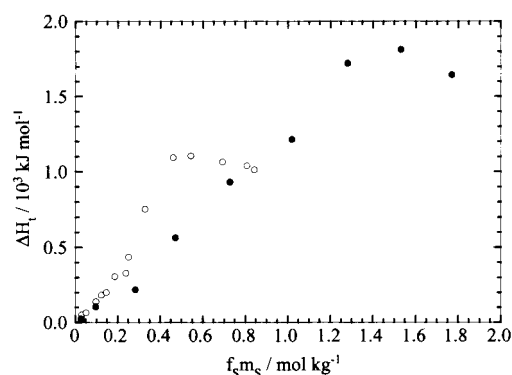


Figure 1. Enthalpy of transfer of 0.15% PEG 35 000 from water to aqueous solutions of sodium perfluorobutanoate (●) and sodium perfluoropentanoate (○) as a function of the surfactant concentration.

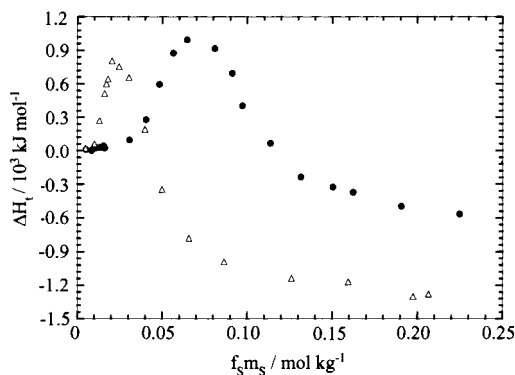


Figure 2. Enthalpy of transfer of 0.15% PEG 35 000 from water to aqueous solutions of sodium perfluoroheptanoate (●) and sodium perfluorooctanoate (Δ) as a function of the surfactant concentration.

to 1.0%, the $\Delta H_{\text{id},\text{P}}$ values are -0.080 ± 0.004 and -0.30 ± 0.02 kJ mol⁻¹, respectively.

The substrate solutions with concentrations larger than those reported here were not studied because of experimental difficulties.

The enthalpies of dilution of the aqueous sodium perfluoroheptanoate solutions with water were determined as functions of the surfactant concentration. From these experimental quantities, the apparent molar relative enthalpies were calculated.³⁴ On the basis of procedure reported elsewhere,³⁴ the micellization enthalpy value of 10 kJ mol⁻¹ was obtained.

Conductivity. The specific conductivity measurements were performed at 298.0 ± 0.1 K (digital conductimeter Analytical Control 120) in order to evaluate the critical micellar concentration of PFHNa and PFONa in the water + PEG 35000 mixture 0.15% w/w according to the literature method.³⁵

Results

(i) Effect of the Alkyl Chain Length of the Substrate. The dependence of the enthalpy of transfer (ΔH_{t}) of 0.15% PEG 35 000 from water to aqueous solutions of sodium perfluoroalkanoates on $f_{\text{s}}m_{\text{s}}$, i.e., the equilibrium substrate concentration, is shown in Figures 1 and 2. In the case of PFBNa, ΔH_{t} increases with $f_{\text{s}}m_{\text{s}}$, showing a smooth change in the slope at ca. 0.6 mol kg⁻¹ while it decreases for $f_{\text{s}}m_{\text{s}} > 1.5$ mol kg⁻¹. For the higher homologues, ΔH_{t} steeply increases with $f_{\text{s}}m_{\text{s}}$ until a maximum is reached beyond which it decreases, tending to level off. The sharp increase of ΔH_{t} and the maximum occurs at smaller $f_{\text{s}}m_{\text{s}}$ values the more hydrophobic the substrate is.

It is reported^{23,28} that when the surfactants bind to nonionic polymers, the enthalpy per injection of surfactant as a function

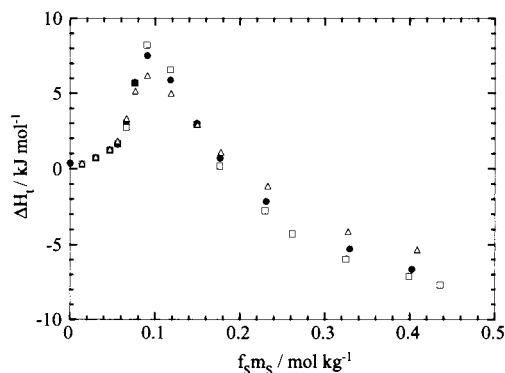


Figure 3. Enthalpy of transfer of PEG 400 from water to aqueous solutions of sodium perfluoroheptanoate as a function of the surfactant concentration at various polymer compositions: □, 0.15%; ●, 0.39%; △, 1.0%.

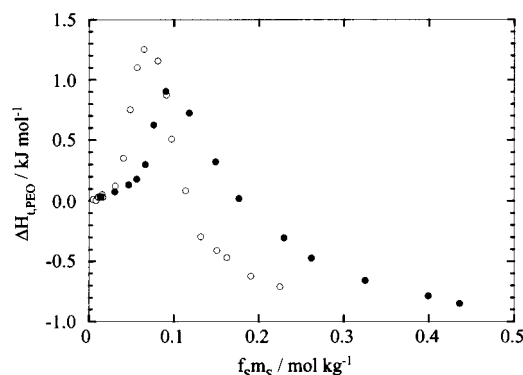


Figure 4. Enthalpy of transfer per mole of PEO units of PEG 400 (●) and PEG 35000 (○) from water to aqueous sodium perfluoroheptanoate solutions as a function of the surfactant concentration.

of its stoichiometric concentration shows a maximum followed by a minimum and a region where it superimposes on that in the absence of polymer. Some authors²⁸ assigned the critical aggregation concentration (cac) to the maximum, while some other authors²³ assigned it to the maximum of the differential enthalpy curve. The two interpretations agree in ascribing the merging point to the saturation of the polymer by the surfactant, above which the polymer no longer interacts with the micelles (so-called “free micelles”). The curves of mixing enthalpy per mole of surfactant, in the presence of polymer at a fixed composition, as functions of $f_s m_s$ show the same shape as those for the present curves whenever surfactant–polymer interactions are present.^{6,30} Recently, Goreishi et al.,^{4,5} on the basis of emf and calorimetric studies, showed that the maximum of the titration enthalpy evidences that the free micelles formation begins at concentrations lower than the cmc in water and long before the polymer becomes saturated with the surfactant. Thus, understanding the calorimetric curves is not straightforward.

(ii) **Effect of the Polymer Concentration and Molecular Weight.** The ΔH_t versus $f_s m_s$ curves of PEG 400 at different

compositions are shown in Figure 3. As can be seen, the localization of the maximum does not depend on the polymer concentration, whereas the steepness of ΔH_t with $f_s m_s$ slightly does.

Comparing the water–PEG 35 000–PFHNa and water–PEG 400–PFHNa systems at the same polymer concentration (4.3×10^{-5} m) evidences the effect of the polymer molecular weight. The ΔH_t values of the former system are 2 orders of magnitude larger from those of the second one. This large difference is strongly reduced if the enthalpy of transfer per mole of poly(ethylene oxide) (PEO) units ($\Delta H_{t,PEO}$) is calculated (Figure 4). The difference in the curves shown in Figure 4 can be ascribed to the different conformational state of the PEO segments in the polymers.

Discussion

Qualitative Analysis of the Enthalpy of Transfer. It was shown in the Results section that the shape of ΔH_t versus $f_s m_s$ curves is independent of the nature of the surfactant, the polymer concentration, and its molecular weight.

Holmberg et al.²⁰ studied by dialysis the interactions between NaDS and cellulose derivatives. At a given polymer composition, the profile of the bound NaDS moles per gram of polymer versus the free surfactant concentration is equal to we found for the enthalpy of transfer. The steepness of the curve was ascribed to a cooperative mechanism of adsorption and the maximum to the formation of “normal” micelles. Goreishi et al.⁵ reported isothermal titration calorimetric curves of surfactants in water–polymer mixtures which are reminiscent of the present ones. They ascribed the steep increase of the enthalpy to the binding between the polymer and highly charged “loose” surfactant aggregates. The latter are considered to be precursors to the “normal” micelles that form at the surfactant concentration corresponding to the maximum in the enthalpy curves. Beyond the maximum, free and bound micelles are present. Similar phenomena can occur in our systems. Thus, we can assign the $f_s m_s$ value where ΔH_t abruptly increases to the cac (their values are collected in Table 1) and at the maximum to the cmc in the presence of the polymer (cmc_{w+p}). As the pseudo-phase transition model for micellization predicts, a linear correlation between the logarithm of the cac and cmc_{w+p} and the number of carbon atoms in the perfluoro alkyl chain (n_c) is observed (Figure 5). This evidence suggests the presence of a cooperative process in our systems. The cmc_{w+p} values are equal to those determined from conductivity and very close to the cmc values in water (cmc_w) (Table 1). On the other hand, the $f_s m_s$ value corresponding the maximum in the ΔH_t versus $f_s m_s$ curve cannot be ascribed to the polymer saturation concentration, since the maximum localization is independent of the polymer concentration. On the basis of this qualitative analysis, in the following section, theoretical approaches for both the pre- and the post-micellar regions will be proposed.

Pre-Micellar Region: Theoretical Approach to the Enthalpy of Transfer. The dependence of ΔH_t on $f_s m_s$ is equal

TABLE 1: Standard Free Energy, Enthalpy, and Entropy for the Surfactant–Polymer Complex Formation at 298 K^a

| | n | K_C | $\Delta G_C^\circ/n$ | $\Delta H_C^\circ/n$ | $T\Delta S_C^\circ/n$ | cac | cmc_w | cmc_{w+p} | h_{PS} |
|------------|-----|-----------------------------|----------------------|----------------------|-----------------------|-------|---------|-----------------|--------------|
| PEG 35 000 | | | | | | | | | |
| PFBNa | 1.8 | 0.80 ± 0.02 | 0.31 ± 0.03 | 1066 ± 31 | 1066 ± 31 | 0.6 | 1.3^b | 1.5 | 198 ± 14 |
| PFPNa | 3.2 | 5.0 ± 1.9 | -1.2 ± 0.3 | 515 ± 140 | 516 ± 140 | 0.25 | 0.50 | 0.5 | 687 ± 11 |
| PFHNa | 5.0 | $(2.9 \pm 0.4) \times 10^6$ | -7.37 ± 0.07 | 266 ± 14 | 273 ± 14 | 0.035 | 0.09 | $0.06; 0.065^c$ | |
| PFONa | 5.0 | $(8.4 \pm 0.8) \times 10^8$ | -10.18 ± 0.05 | 213 ± 9 | 223 ± 9 | 0.01 | 0.03 | $0.02; 0.028^c$ | |
| PEG 400 | | | | | | | | | |
| PFHNa | 5.0 | $(1.5 \pm 0.9) \times 10^5$ | -5.9 ± 0.3 | 3.2 ± 0.8 | 9.1 ± 0.9 | 0.06 | 0.09 | 0.09 | 6 ± 4 |

^a Units: $kg^m mol^{-n}$ for the equilibrium constant, $kJ mol^{-1}$ for the standard properties of the complex formation, $kJ kg mol^{-2}$ for h_{PS} , and $mol kg^{-1}$ for cac, cmc_w , and cmc_{w+p} . ^b Extrapolated from values of longer homologues. ^c Evaluated from conductivity.

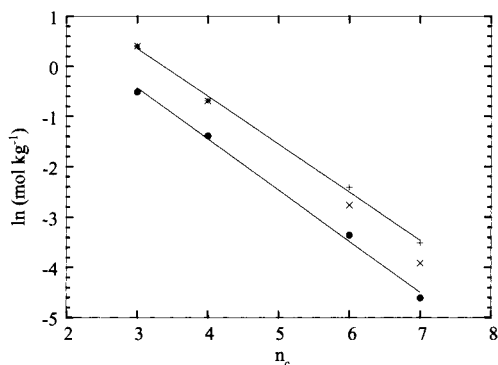
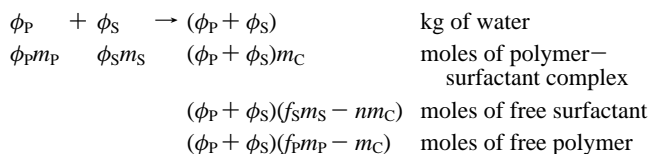


Figure 5. Dependence of the logarithm of cac (●), cmc_w (+), and cmc_{w+p} (x) on the number of carbon atoms in the perfluoro alkyl chain of the surfactant.

to that of the classic adsorption isotherms of surfactants on polymers^{20,31} or inorganic oxide particles³⁶ which have been explained by invoking the cooperative binding. For instance, Monticone and Treiner³⁶ interpreted the adsorption isotherm of surfactants on silica particles surface in terms of the formation of hemimicelles.

On the basis of the pseudo-phase transition model, as mentioned earlier, the $f_S m_S$ value at which the ΔH_t versus $f_S m_S$ profile shows a sharp increase was called cac . This is reminiscent of what occurs at the cmc for the micellization process.³⁷ The latter can be correctly interpreted by assuming a mass action model,³⁸ and in this case, the cmc is an operational definition. A mass action model could also be proposed for the cooperative binding between the polymer and the surfactant. The one-step association model is the simplest way to approach these systems. According to it, one mole of polymer and n moles of surfactant react to form polymer–surfactant complexes. Namely, upon the mixing of $\phi_P m_P$ moles of polymer contained in ϕ_P kg of water and $\phi_S m_S$ moles of dispersed surfactant contained in ϕ_S kg of water, complexes of 1: n stoichiometry are forming



Here m_C indicates the molality of the complex.

By considering that polymer–surfactant interactions different from those leading to the complex formation are present, we can write the partial molar enthalpies of both the surfactant and the polymer in the ternary system in terms of those in water ($H_{P,f}$ and $H_{S,i}$) and of the contributions due to the interactions between the unlike solute molecules.³⁹ If, for the sake of simplicity, only the pair (h_{PS}) interaction parameter is taken, then the initial and final power of the process can be written as

$$W_i = \phi_S(H_w + m_S H_{S,i}) + \phi_P(H_w + m_P H_{P,i}) \quad (2)$$

$$\begin{aligned}
 W_f = & (\phi_P + \phi_S)[H_w + m_C H_C + (f_S m_S - n m_C) H_{S,f} + \\
 & (f_P m_P - m_C) H_{P,f} + 2h_{PS}(f_S m_S - n m_C)(f_P m_P - m_C)] \quad (3)
 \end{aligned}$$

Here H_w indicates the enthalpy of 1 kg of pure water, $H_{S,i}$ and $H_{P,i}$ are the partial molar enthalpies of the substrate and the polymer in the initial state, respectively, and H_C is the partial molar enthalpy of the polymer–surfactant complex.

From eqs 1, 2, and 3, we obtain

$$\begin{aligned}
 \Delta W/(\phi_P + \phi_S) = & m_C(H_C - n H_{S,f} - H_{P,f}) + \\
 & f_S m_S(H_{S,f} - H_{S,i}) + f_P m_P(H_{P,f} - H_{P,i}) + \\
 & 2h_{PS}(f_S m_S - n m_C)(f_P m_P - m_C) \quad (4)
 \end{aligned}$$

Since $(H_C - n H_{S,f} - H_{P,f})$ represents the enthalpy for the complex formation (ΔH_C), $(H_{S,f} - H_{S,i})$ and $(H_{P,f} - H_{P,i})$ correspond to the enthalpies of dilution of the substrate ($\Delta H_{id,S}$) and polymer ($\Delta H_{id,P}$) with water, respectively, from eq 4, we obtain

$$\begin{aligned}
 \Delta W/(\phi_P + \phi_S) = & m_C \Delta H_C + f_S m_S \Delta H_{id,S} + f_P m_P \Delta H_{id,P} + \\
 & 2h_{PS}(f_S m_S - n m_C)(f_P m_P - m_C) \quad (5)
 \end{aligned}$$

Dividing eq 5 by $f_P m_P$ and remembering that $\Delta H_{id,S}$ was taken as baseline for the mixing process, it follows that

$$\begin{aligned}
 \Delta H_t = & \Delta H^{\text{exp}} - \Delta H_{id,P} = \\
 & \chi_C \Delta H_C + 2h_{PS}(f_S m_S - n m_C)(1 - \chi_C) \quad (6)
 \end{aligned}$$

Here χ_C is the mole fraction of the complexed polymer. The interaction contribution is not expected to be negligible if the polymer–surfactant complex formation is not highly cooperative; this can occur for surfactants having high cmc and/or polymers at low molecular weight.

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

$$\chi_C = K_C(f_S m_S)^n / [1 + K_C(f_S m_S)^n] \quad (7)$$

Pre-micellar Region: Standard Thermodynamic Properties for the Polymer–Surfactant Complex Formation. The very low concentration of PEG 35 000 ($4.3 \times 10^{-5} m$) does permit the application of eqs 6 and 7 to the water–PEG 35 000–sodium n -perfluoroalkanoate ternary systems. For PEG 400 in the aqueous PFHNa solutions, the ΔH_t data analyzed refer to $f_P m_P = 4.3 \times 10^{-5} m$.

In the minimizing procedure, the value of n was changed in order to minimize the standard deviation of the ΔH_t versus $f_S m_S$ plot. The results of the best fits are collected in Table 1. In the latter, the h_{PS} for PEG 35 000 in PFHNa and PFONa is not reported because the interaction contribution is negligible.

The standard free energy for the complex formation (ΔG_C°) per mole of surfactant monomer was calculated as³⁶

$$\Delta G_C^\circ/n = -(RT \ln K_C)/n \quad (8)$$

The standard entropy per mole of surfactant monomer was calculated as

$$T \Delta S_C^\circ/n = \Delta H_C^\circ/n - \Delta G_C^\circ/n \quad (9)$$

As Figure 6 shows, $\Delta G_C^\circ/n$ versus n_c is a straight line from which the perfluoromethylene group (slope) and the hydrophilic (intercept) contributions of -2.7 ± 0.2 and 12 ± 1 kJ mol⁻¹ respectively, are obtained. They indicate that the driving force for the complex formation is hydrophobic in nature. Our $\Delta G_C^\circ/n$ value for the CF₂ group compared to that in appropriate solvents could yield information on the state of the surfactant bound to the polymer; i.e., the surfactant molecules are either individually bound or aggregated. Useful to this purpose is the standard free energy of transfer of the CF₂ group from water to

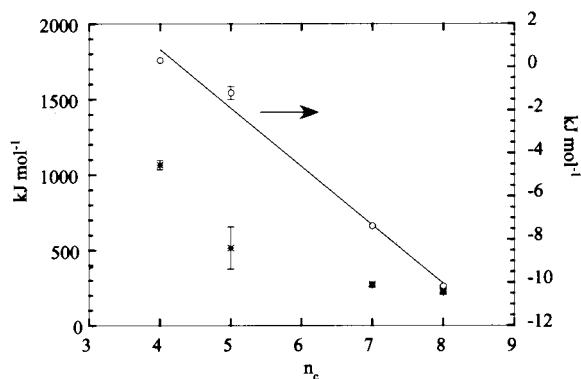


Figure 6. Standard free energy (○), enthalpy (+), and entropy (x) for the formation of PEG 35 000–sodium perfluoroalkanoates complexes as functions of the number of carbon atoms in the perfluoro alkyl chain of the surfactant.

the micelles of sodium perfluorooctanoate (-2.3 kJ mol^{-1})⁴⁰ and poly(ethylene oxide)₁₃–poly(propylene oxide)₃₀–poly(ethylene oxide)₁₃ ($-0.3 \pm 0.3 \text{ kJ mol}^{-1}$).⁴¹ The former micelles well mime aggregates of surfactant while the latter do the environment of the single monomer when interacting with the polymer. From the above data, it can be assessed that the surfactant bound to the polymer is associated. The standard enthalpy and entropy are positive and, consequently, the entropy controls the process. In addition, their values are 2 orders of magnitude larger than $\Delta G^\circ/n$ and their dependence on n_c (Figure 6). These results seem to evidence the enthalpy–entropy compensative effect that occurs in cooperative processes.⁴² Inoue et al.⁴³ checked the validity of this effect in the 1:1 host–guest complexation. They concluded that, for a given series of substrates, the intercept and slope of the linear correlation between the standard entropy and standard enthalpy are quantitative evidences of the degree of desolvation and the conformational changes caused by the complex formation, respectively. The slope of 0.985 ± 0.005 , very close to the unity, obtained from the present data evidences an extensive conformational change of the polymer; only the enthalpy increment of 0.015 contributes to the stability of the complex. The positive value of the intercept ($10 \pm 3 \text{ kJ mol}^{-1}$) is due to the large extent in the desolvation of both the polymer and the surfactant. As suggested by Inoue et al.⁴³ this positive value indicates that the polymer–substrate complex can be formed even if there is not an enthalpic gain, and this occurs whenever the desolvation entropic contribution is the main factor governing the complex formation.

$\Delta G^\circ/n$ for the PFHNa–PEG 35 000 complex formation is comparable to that for PFHNa–PEG 400, while $\Delta H^\circ/n$ and $T\Delta S^\circ/n$ are much larger.

As stated earlier, almost the several calorimetric studies provide qualitative information on the polymer–surfactant interactions. Wang et al.³⁰ reported the enthalpies of aggregation at the cac of poly(ethylene oxide) (similar to the present polymers) and dodecyl sulfates with different monovalent cations; the reported values are not only 2 orders of magnitude smaller from the present ones, but they also differ in the sign.

Critical Micellar Concentration: Effect of the Polymer. The effect of additives on the cmc has been extensively studied. The dependence of the cmc on the additive concentration was interpreted in terms of the surfactant–additive interaction in the aqueous phase and the additive solubilization in the micellar phase.⁴⁴ At low hydrophobic additive concentrations, the latter predominates so that the cmc decreases. The polymer depression effect on the cmc was explained^{4,5,20} by stating that the highly

charged surfactant clusters bound to the polymer increase the local concentration of the free surfactant ions attracted by the unbounded counterions favoring the formation of micelles. The data of PEG 400 in PFHNa indicate that the cmc_{w+p} value is lower than cmc_w but independent of the polymer concentration. According to the above interpretations, we can assume that our experimental cmc_{w+p} is given by the sum of the surfactant concentrations in the dispersed form and bound to the polymer. Since according to eq 7 the concentration of the surfactant bound to the polymer increases with the polymer concentration, the constant cmc_{w+p} value implies that the free surfactant concentration decreases, as observed in the determination of free monomer concentration.^{4,5,20} As far as the effect of the polymer molecular weight is concerned, at a given polymer concentration ($4.3 \times 10^{-5} \text{ mol kg}^{-1}$), the cmc_{w+p} of PFHNa in the water + PEG 400 mixture is larger than that in the water + PEG 35 000 mixture. This difference remains if it is corrected for the surfactant bound to the polymer (calculated by means of eq 7 and the K_C and n values collected in Table 1). This result agrees with findings obtained from emf studies.⁴ According to the current idea of the polar additive effect on the cmc mentioned above, these findings evidence the larger hydrophobicity of PEG 35 000 with respect to that of PEG 400.

Post-Micellar Region: Theoretical Approach to the Enthalpy of Transfer. A theoretical model able to take into account all the individual contributions (shift of the micellization equilibrium induced by the polymer, dispersed surfactant–polymer interactions, micelle–polymer interactions, changes of the micellar structures and polymer conformations caused by the interactions, etc.) to the enthalpy of transfer is very involved. Thus, we consider that the conformational changes of the polymer and the eventual changes of the aggregation number and/or the structure of the micelles are buried in the polymer–micelles interaction contribution and that in the aqueous phase, only the interactions responsible for the surfactant–polymer complex formation are present. Therefore, the dependence of ΔH_t on $f_S m_S$ can be rationalized by assuming the following equilibria:



Scheme 10 refers to the process dealing with one mole of polymer and q moles of micellized surfactant which form polymer–micelles complexes. Scheme 11 represents the process of interaction between n moles of monomeric surfactant and one mole of polymer in the aqueous phase, i.e., at the cmc_{w+p} , leading to the formation of the surfactant–polymer complex.

By assuming the pseudo-phase transition model for micellization, we can schematize the mixing of an aqueous polymer solution with an aqueous micellar solution as follows:

| | | | | | |
|--------------|---|--|---|---------------------|--|
| ϕ_P | + | ϕ_S | | $(\phi_P + \phi_S)$ | kg of water |
| $\phi_P m_P$ | | $\phi_S(m_S - \text{cmc}_w) \rightarrow$ | $(\phi_P + \phi_S)m_{C,M}$ | | moles of polymer–micelle complex |
| | | $\phi_S \text{cmc}_w$ | $(\phi_P + \phi_S)(f_P m_P - m_{C,M} - m_{C,aq})$ | | moles of free polymer in the aqueous phase |
| | | | $(\phi_P + \phi_S)(f_S m_S - [m] - qm_{C,M} - nm_{C,aq})$ | | moles of uncomplexed micellized surfactant |
| | | | $(\phi_P + \phi_S)[m]$ | | moles of dispersed surfactant |
| | | | $(\phi_P + \phi_S)m_{C,aq}$ | | moles of surfactant–polymer complex in the aqueous phase |

The initial and final power of the process can be written as

$$W_i = \phi_S[H_w + (m_S - \text{cmc}_w)H_{M,i} + \text{cmc}_w H_{m,i}] + \phi_P(H_w + m_P H_{P,i}) \quad (12)$$

$$W_f = (\phi_P + \phi_S)[H_w + m_{C,M}H_{C,M} + [m]H_{m,f} + (f_S m_S - [m] - qm_{C,M} - nm_{C,aq})H_{M,f} + (f_P m_P - m_{C,M} - m_{C,aq})H_{P,f} + m_{C,aq}H_C] \quad (13)$$

Here H_w is the enthalpy of 1 kg of pure water, $H_{M,i}$ is the partial molar enthalpy of the micellized surfactant in the initial state, $H_{M,f}$ is the partial molar enthalpy of the uncomplexed micellized surfactant in the final state, $H_{P,i}$ and $H_{P,f}$ are the partial molar enthalpies of the free polymer in water in the initial and final states, respectively, $H_{m,i}$ and $H_{m,f}$ are the partial molar enthalpies of the dispersed surfactant in the initial and final states, respectively, and $H_{C,M}$ is the partial molar enthalpy of the polymer–micelle complex.

The meaning of the other symbols is the same as above.

From eqs 12 and 13, we obtain

$$(W_f - W_i)/(\phi_P + \phi_S) = m_{C,M}(H_{C,M} - qH_{M,f} - H_{P,f}) - [m]\Delta H_{m,f} + f_P m_P (H_{P,f} - H_{P,i}) + f_S \text{cmc}_w \Delta H_{m,i} + f_S m_S (H_{M,f} - H_{M,i}) + m_{C,aq}(H_C - nH_{M,f} - H_{P,f}) \quad (14)$$

On the basis of the pseudo-phase transition model for micellization, we can write

$$f_S m_S (H_{M,f} - H_{M,i}) = f_S m_S \Delta H_{id,S} - f_S \text{cmc}_w \Delta H_{m,i} + \text{cmc}_w \Delta H_{m,f} \quad (15)$$

In addition, remembering that in our experimental approach the enthalpy of dilution of the surfactant with water was taken as the baseline for the mixing process, by introducing eq 5 in eq 14, and dividing eq 14 by $f_P m_P$, we obtain

$$\Delta H_t = \Delta H^{\text{exp}} - \Delta H_{id,P} = \Delta H_{m,f}(\text{cmc}_w - [m] - nm_{C,aq})/f_P m_P + \chi_{C,M} \Delta H_{C,M} + \chi_{C,aq} \Delta H_C \quad (16)$$

Here $\Delta H_{C,M} = (H_{C,M} - qH_{M,f} - H_{P,f})$ is the enthalpy change for the formation of the polymer–micelle complex, the mole fraction of which is $\chi_{C,M}$.

If the polymer concentration is very low, $\Delta H_{C,M}$ can be assumed to be equal to the standard property ($\Delta H_{C,M}^\circ$), while $\chi_{C,M}$ can be expressed in terms of the equilibrium constant ($K_{C,M}$) by means of eq 7, provided that $f_S m_S$ is replaced by $(f_S m_S - \text{cmc}_w + p)$ and n by q .

The first term at the right-hand side of eq 16 represents the shift of the micellization equilibrium induced by the polymer where the quantity $[m] + nm_{C,aq}$ corresponds to $\text{cmc}_w + p$. At $f_S m_S = \text{cmc}_w + p$, this contribution and the contribution for the polymer–micelle complex formation disappear, and ΔH_t is given by the term for the surfactant–polymer complex formation. The absence of the latter equilibrium should involve a discontinuity of ΔH_t at the $\text{cmc}_w + p$, but that is not the case here.

Post-Micellar Region: Standard Thermodynamic Properties for the Polymer–Micelle Complex Formation. Equation 16 is a three-parameter equation ($K_{C,M}$, $\Delta H_{C,M}^\circ$, and q) if the shift of the micellization equilibrium term is known. Due to the impossibility of evaluating it, we treated eq 16 as a four-parameter equation. Changing the q value in order to minimize the standard deviation of the ΔH_t versus $f_S m_S$ plot executed the minimization. It turned out that the shift of the micellization

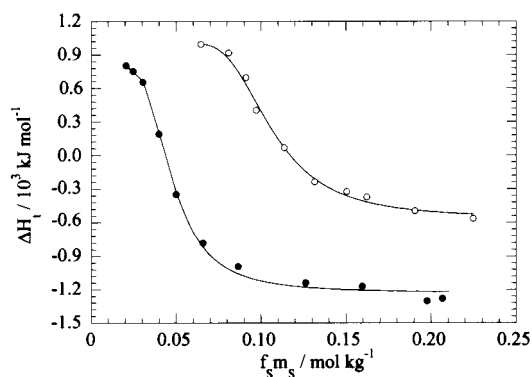


Figure 7. Best fits according to eq 16 for PEG 35 000 in sodium perfluoroheptanoate (○) and sodium perfluorooctanoate (●) micellar solutions.

TABLE 2: Standard Free Energy, Enthalpy, and Entropy for the Polymer–Micelle Complex Formation at 298 K^a

| q | $K_{C,M}$ | $\Delta G_{C,M}^\circ/q$ | $\Delta H_{C,M}^\circ/q$ | $T\Delta S_{C,M}^\circ/q$ |
|------------|-----------------------------|--------------------------|--------------------------|---------------------------|
| PEG 35 000 | | | | |
| PFHNa 2.9 | $(7.1 \pm 0.6) \times 10^3$ | -7.58 ± 0.07 | -540 ± 10 | -532 ± 10 |
| PFONa 2.7 | $(1.6 \pm 0.1) \times 10^4$ | -8.88 ± 0.06 | -752 ± 9 | -743 ± 9 |
| PEG 400 | | | | |
| PFHNa 1.8 | 67 ± 5 | -5.8 ± 0.1 | -9.5 ± 0.2 | -3.7 ± 0.2 |

^a Units: $\text{kg}^q \text{mol}^{-q}$ for the equilibrium constant and kJ mol^{-1} for the standard properties of the polymer–micelle complex formation.

equilibrium term was small and affected by an uncertainty on the same order of magnitude as that of its value. Therefore, it was neglected. Examples of the best fits are shown in Figure 7, whereas their results are collected in Table 2.

The standard free energy for the polymer–micelle complex formation ($\Delta G_{C,M}^\circ$) per mole of micellized surfactant was calculated by means of eq 8, where K_C and n were replaced by $K_{C,M}$ and q , respectively. The corresponding entropy ($T\Delta S_{C,M}^\circ/q$) was calculated by means of eq 9 using the $\Delta H_{C,M}^\circ/q$ and $\Delta G_{C,M}^\circ/q$ values. They are collected in Table 2.

Although the systems analyzed are a very few, some information on the interactions between the polymer and perfluoroalkanoate micelles can be drawn. The decrease of the standard free energy for the micelle–PEG 35 000 complex formation with increasing perfluoro alkyl chains would suggest that interactions between the polymer and the micellar core are present. This disagrees with findings of Segre et al.,³² who showed that the PVP segments do not penetrate the core of lithium perfluorononanoate micelles and suggested that the polymer wraps the micelles, forming dressed micelles. The free energy data can reflect the more hydrophobic character of the micelles with increasing polymer molecular weight. Accordingly, the micelles expel water molecules from their hydrophilic shells likely due to the linkings between the carboxylate groups and the ether oxygen of the polymer. According to Shirahama and Ide,¹⁹ this process involves the reduction of the water/micellar core interface that stabilizes the micellar aggregate. This explanation is supported by the negative values of enthalpy and entropy. In fact, it can be hypothesized that to these properties contribute the hydrophilic desolvation of both the micelles and the polymer units and the coiling of the polymer chains around the micelles. The latter process is expected to involve enthalpy and entropy negative values, which become very large with increasing polymer molecular weight. In addition, these properties do not contribute to the stability of the polymer–micelle complex, as the slope value (0.9960 ± 0.0006) of the $T\Delta S_{C,M}^\circ/q$ versus $\Delta H_{C,M}^\circ/q$ plot for the three systems analyzed indicate.

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Supporting Information Available: Tables of the enthalpies of dilution of sodium perfluoroheptanoate solutions with water, the experimental enthalpies of PEG 35000–water–sodium perfluoroalkanoate ternary systems, the experimental enthalpies of PEG 400–water–sodium perfluoroheptanoate ternary systems at some polymer compositions, and the conductivity of sodium perfluoroheptanoate and sodium perfluorooctanoate in water–PEG 35000 mixture (0.15% w/w).

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