Mass Action Model Applied to the Thermodynamic Properties of Transfer of Nonionic Copolymers from Water to the Aqueous Surfactant Solutions

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A thermodynamic model which enables the properties of aqueous copolymer/surfactant mixtures to be fit quantitatively was proposed. Namely, a relationship between the properties of transfer of the unassociated copolymer from water to the aqueous surfactant solutions (ΔY_t) and the surfactant concentration was derived. The model was based on the idea that ΔY_t can be expressed in terms of the following contributions: (1) interaction between monomers of copolymer and surfactant, (2) displacement of the monomer-micelle equilibrium induced by the copolymer, (3) formation of the surfactant-copolymer aggregation complex, and (4) formation of the mixed micelles. Such a model was applied to most literature data relative to the systems formed by (ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (L64) or (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (F68) copolymers and hydrogenated surfactants, i.e., sodium octanoate, sodium decanoate (NaDec), *N*-octylpyridinium chloride, and *N,N*-dimethyloctylamine-*N*-oxide. New enthalpy data of both L64 and F68 in decyltrimethylammonium bromide were analyzed, as well. The appropriate comparison among the parameters generated by the fitting processes gave physical insights on the mechanisms of binding between the copolymer and the surfactant according to the quantitative model. The quantities obtained from the minimizing procedure were used to predict ΔY_t of the L64/NaDec system in conditions not yet investigated. The agreement between the calculated values and the new experimental points was satisfactory.

Introduction

Poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), PEO−PPO−PEO, are tri-block copolymers forming a new class of peculiar surfactants. They are nonionic compounds capable of decreasing the interfacial tension and of self-assembling.[1−3] In the resulting aggregates, the PPO block is located in the core and the PEO segments form the hydrophilic shell. This behavior makes them very promising and interesting macromolecules, and then, several studies are being addressed to their characterization in the presence of additives such as surfactants. Light scattering,[4−6] small-angle neutron scattering (SANS),[4] and electric birefringence[5] give structural details. The thermodynamic properties supply information on the copolymer−surfactant affinity provided that they are treated by suitable models. Despite the large number of papers published in the last years,[1,4−9] efforts of modeling thermodynamic properties are scarce,[8,9] and furthermore, they have not reproduced straightforwardly the experimental data.

In last fifteen years, thermodynamic functions of the surfactant/polar additive systems[10−12] were determined and modeled by two methodologies which enabled fundamental parameters to be extracted, and consequently, the gained knowledge is satisfactory. Based on this experience, we thought it would be significant to dedicate our endeavors to the modeling of the volume and the enthalpy of transfer of PEO−PPO−PEO from water to the aqueous surfactant solutions. Specifically, the copolymer is unassociated and the surfactant is in both the monomeric and micellized states. Such a model was applied to most literature[8,9] data relative to the systems formed by (ethylene

oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (L64) or (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (F68) copolymers and hydrogenated surfactants, like sodium octanoate, sodium decanoate (NaDec), *N*-octylpyridinium chloride, and *N,N*-dimethyloctylamine-*N*-oxide. New enthalpy data of both L64 and F68 in decyltrimethylammonium bromide were analyzed, as well.

Experimental Section

Materials. Sodium decanoate (Sigma) and decyltrimethyl-ammonium bromide (Kodak) were recrystallized from absolute ethanol and ethanol-ethyl acetate (10/70 v/v), respectively. Both of the products were dried in a vacuum oven at 313 K for at least 4 days. *N*-Octylpyridium chloride was synthesized according to the literature procedure.[13] (Ethylene oxide)$_{13}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{13}$ (Pluronic L64, nominal $M_w = 2900$ g mol^{-1}) and (ethylene oxide)$_{75}$−(propylene oxide)$_{30}$−(ethylene oxide)$_{75}$ (Pluronic F68, nominal $M_w = 8350$ g mol^{-1}) were gifts from BASF. Density measurements on some dilute aqueous solutions of F68 and L64 gave apparent molar volume values in good agreement with the literature ones.[1,14] Therefore, they were used as received.

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

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

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(model CT-L, Sodev Inc.). The densimeter was calibrated by using the procedure reported elsewhere.[8]

The apparent molar volume (V_Φ) of L64 in the water−sodium decanoate mixtures (0.06976 and 0.1032 mol kg^{-1}) was calculated as

$$V_\Phi = \frac{M}{d} - \frac{10^3 (d - d_0)}{m_R d d_0} \qquad (1)$$

where m_R and M are the molality and the molecular weight of the copolymer, d is the density of the water + surfactant + copolymer ternary system, and d_0 is the corresponding property of the water + surfactant mixed solvent. The volume of transfer of L64 from water to the aqueous sodium decanoate solution (ΔY_t) was calculated as difference between V_Φ and the apparent molar property of the copolymer in water.

Enthalpy. Enthalpies of mixing between the surfactant and the copolymer solutions were measured at 298.00 ± 0.01 K by means of a flow LKB 2107 microcalorimeter. The procedure to evaluate the experimental enthalpy (ΔH^{exp}) is reported elsewhere.[15] The solutions were injected into the equipment by means of a Gilson peristaltic pump (Minipuls 2) and their flows were determined by weight.

The final concentration of the surfactant (m_S) and the copolymer (m_R) solutions, upon the mixing process, were calculated by using the dilution factors

$$f_S = \Phi_S/(\Phi_S + \Phi_R) \qquad f_R = \Phi_R/(\Phi_S + \Phi_R) \qquad (2)$$

where Φ_R and Φ_S are the flows of water in the copolymer and the surfactant solutions, respectively.

The enthalpies of transfer (ΔH_t), evaluated as difference between ΔH^{exp} and the enthalpies of dilution of the copolymer with water,[9] were determined at fixed m_R (1 and 5 mmol kg^{-1} for F68 and L64, respectively) as functions of m_S for DeTAB/F68 and DeTAB/L64. Additional points were measured for OPC/L64 and OPC/F68.

Experimental Properties of Transfer of Nonionic Unassociated Copolymers and Their Modeling. One of the approaches employed to study the thermodynamics of the aqueous copolymer/surfactant mixtures is based on the determination of the property of transfer of the copolymer, at fixed concentration, from water to the aqueous surfactant solutions (ΔY_t) as a function of the surfactant concentration (m_S). The literature data[8,9] show that the shape of ΔY_t vs m_S trends depends on some factors. Namely, both L64 and F68 in sodium alkanoates[8,9] at low m_R (1 ÷ 2.5 mmol kg^{-1}) exhibit sigmoid curves with maxima followed by small variations. The extrema are usually localized at $m_S \approx$ cmc$_w$ (critical micellar concentration in water) and are more pronounced by lengthening the alkyl chain. By increasing m_R, the maximum disappears and the trends become S-shaped like in the entire range of m_S studied. At low m_R (1 ÷ 5 mmol kg^{-1}), monotonic are also the ΔY_t vs m_S curves for both L64 and F68 in ODAO[9] and OPC[9] as well as in DeTAB. Examples of such trends are represented in Figures 1−4. The efforts to interpret these data by means of an unique model were unsuccessful. For the functions of transfer showing extrema, the experimental points in the surfactant region below cmc$_w$ were fitted[8,9] by using the model[16] for the formation of the surfactant−copolymer aggregation complexes mainly controlled by hydrophobic interactions. For $m_S >$ cmc$_w$, the model was judged inapplicable because of the relatively smooth change of the properties of transfer with m_S. An alternative analysis was suggested by the similarity with the transfer functions of small hydrophobic molecules which distribute between the
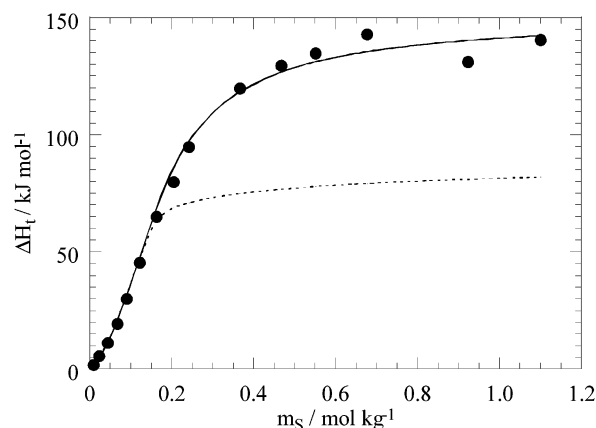

Figure 1. Enthalpy of transfer of L64 5 mmol kg^{-1} from water to the aqueous *N,N*-dimethyloctylamine-*N*-oxide solutions as a function of the surfactant concentration. Dotted line, calculated values by means of eq 19; solid line, best fit of the experimental points according to eq 16.

Figure 2. Enthalpy of transfer of F68 1 mmol kg^{-1} from water to the aqueous solutions of sodium octanoate (●) and N-octylpyridinium chloride (○) as functions of the surfactant concentration. Dotted line, calculated values by means of eq 19; solid line, best fit of the experimental points according to eq 16.
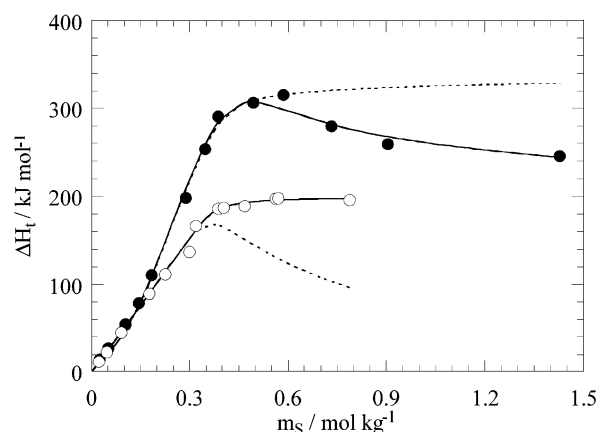

Figure 3. Enthalpy of transfer of L64 (●) and F68 (○) from water to the aqueous decyltrimethylammonium bromide as functions of the surfactant concentration. Dotted line, calculated values by means of eq 19; solid line, best fit of the experimental points according to eq 16.
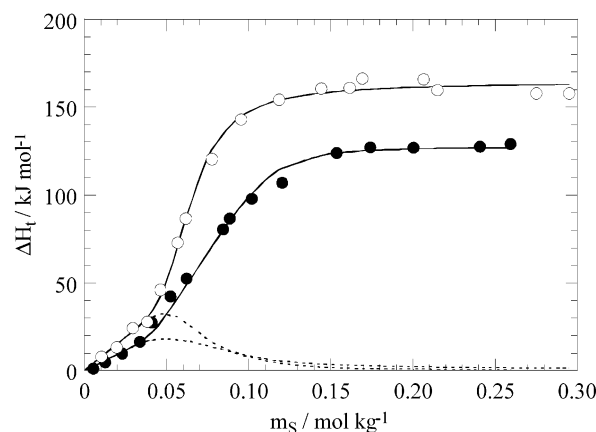
aqueous and the micellar phases.[11,12,17] It is well documented for the latter systems that the extremum in the properties of transfer is due to the shift of the micellization equilibrium induced by the solute and appears only when the solute hydrophobicity is greater than that of the surfactant, namely,
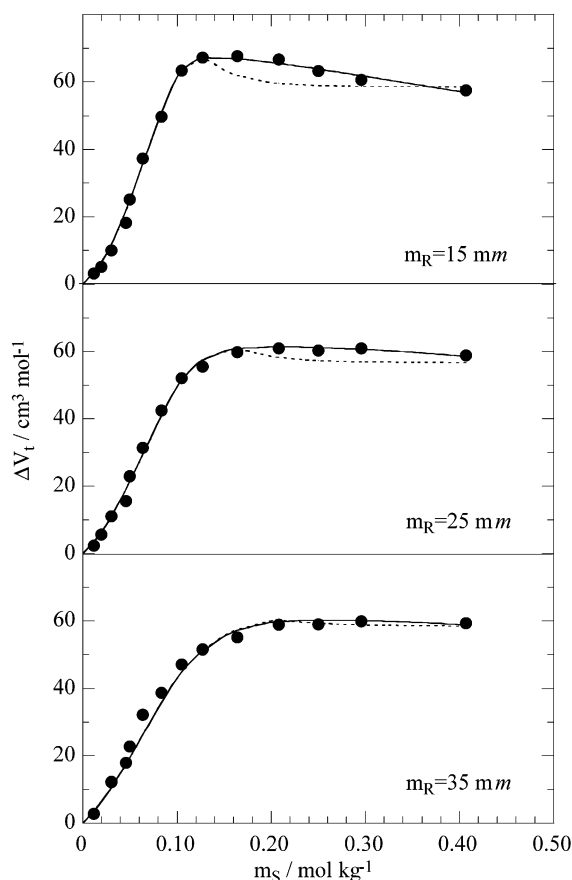
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Figure 4. Volume of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration. Dotted line, calculated values by means of eq 19; solid line, best fit of the experimental points according to eq 16.

for short-chain surfactants[11,12,17] and long-chain solutes.[18] By increasing the solute concentration, the magnitude of the shift of the micellization equilibrium decreases, and consequently, the extrema in the property of transfer reduce in magnitude. The volume data of L64/NaDec systems[8] determined at $m_R =$ 15, 25, and 35 mmol kg^{-1} (Figure 4) seemed consistent with such equilibria. Contrary to the expectations, the model well described only the data at $m_R = 35$ mmol kg^{-1}.

At this stage, the property of transfer profiles are not straight connected to the mechanisms of binding in spite the involved interactions are expected to be similar (ion−dipole, dipole−dipole, hydrophobic forces) whatever is the architecture of the nonionic copolymer and the nature of the surfactant.

Mass Action Model for the Thermodynamics of the Surfactant−Water Binary Systems. To rationalize the experimental data of the water−surfactant−copolymer ternary systems, a model for the micellization process is needed. The pseudo-phase transition approach[19] has been mostly used for long alkyl chain surfactants whereas the mass action model has been employed to represent in a more realistic manner the behavior of any surfactant. It was documented[20] that a mass action model based on a 1 step aggregation process successfully fitted the thermodynamic functions of nonionic surfactants in water providing the properties of the surfactant in the monomeric and micellized states, the equilibrium constant (K_M) and the aggregation number (N)

$$NS \rightleftarrows M \qquad (3)$$

here S and M stand for the monomeric surfactant and the

micelle, respectively. The equilibrium constant is given by

$$K_M = \frac{m_{M,0}}{[m_0]^N} \qquad (4)$$

where $[m_0]$ is the monomer surfactant concentration and $m_{M,0}$ is the concentration of the micelles

$$m_{M,0} = \frac{m_S - [m_0]}{N} \qquad (5)$$

here m_S is the stoichiometric surfactant concentration. By combining eqs 4 and 5, $[m_0]$ can be evaluated by means of the Netwon-Raphson method provided that K_M and N are known.

Because the model gave reliable thermodynamic properties of micellization of ionic surfactants,[12] it was applied to the apparent molar volumes of OPC,[21] NaOct,[22] and DeTAB[23] in water to evaluate K_M and N. These values along with those for ODAO[20] and NaDec[17] are collected in Table 1 where the data of L64 determined by applying the model to the volumes[1] are also reported.

The property of micellization (ΔY_m) was calculated[12] as ($Y_M/N - Y_m$) being the property of the dispersed surfactant given by

$$Y_m = Y_S^0 + Y_{D-H}[m_0]^{1/2} + B_Y[m_0] + C_Y[m_0]^{3/2}$$
$$Y_m = Y_S^0 + B_Y[m_0] + C_Y[m_0]^2 \qquad (6)$$

The expressions on the left and right-hand sides of eq 6 are valid for ionic and nonionic surfactants, respectively. Y_S^0 and Y are the partial molar properties of the micelle and the surfactant in the standard state, respectively; Y_{D-H} is the Debye−Hückel limiting law coefficient (1.865 cm^3 mol$^{3/2}$ kg$^{1/2}$ for the volume[24] and 1973 J mol$^{3/2}$ kg$^{1/2}$ for the enthalpy[24]), whereas B_Y and C_Y are the pair and triplet interaction parameters, respectively. Their values[17,20−25] are collected in Table 1.

Chemical Model for the Surfactant−Water−Copolymer Ternary Systems. (a) Theoretical Approach. The quantitative treatment[8,9] of the thermodynamic properties straightforwardly indicates that a simple model is not suitable to describe the surfactant/copolymer mixtures. Thus, it is quite possible that in the dilute region the surfactant molecules prefer to associate with the copolymer into the surfactant−copolymer aggregation complexes. In the cmc region, once that the surfactant undergoes the micellization process, the copolymer molecules solubilize themselves in the micellar aggregates forming mixed micelles. Then, it may be hypothesized that the addition of surfactant molecules to a solution of unassociated copolymer generates: (1) no-specific surfactant−copolymer interactions in the very dilute surfactant region; (2) the onset of a cooperative binding between z surfactant molecules and 1 copolymer leading to the formation of copolymer-surfactant aggregation complexes; and (3) the formation of mixed micelles. As far we know, no structural evidences of such aggregates are available if one excludes those of similar systems.[4−6] SANS experiments[4] on mixtures of (ethylene oxide)$_{97}$−(propylene oxide)$_{69}$−(ethylene oxide)$_{97}$ (F127) and sodium dodecyl sulfate (NaDS), for instance, were recently performed. The mixing of micellar solutions of both F127 and NaDS allowed micelles with aggregation numbers smaller than micelles in the binary system to be mixed. The combination of micellized F127 and NaDS monomers gave F127/NaDS mixed micelles and NaDS aggregates bound to the monomeric F127. The simultaneous presence of these two kinds of aggregates did not allow the perfect fitting of SANS data[4] confirming the complexity of such

TABLE 1: Thermodynamic Properties of Water−Surfactant and Water−L64 Binary Systems at 298 K[a]

	NaDec[b]	NaOct	ODAO[c]	DeTAB	OPC	L64
K_M	7.6×10^{15}	$(2.2 \pm 0.9) \times 10^3$	4.62×10^6	$(1.0 \pm 0.2) \times 10^{10}$	$(8.7 \pm 0.8) \times 10^9$	$(2 \pm 1) \times 10^3$
N	20	18 ± 2	12.7	11 ± 2	29 ± 2	5.7 ± 0.3
$-\Delta G_m^0$	4.53	1.06 ± 0.06	2.99	5.19 ± 0.05	1.96 ± 0.01	3.3 ± 0.2
B_H	13.51	4.45 ± 0.03^d	11.48		-2.7 ± 0.5^e	
C_H		2.16 ± 0.08^d			14.5 ± 0.9^e	
L_M/N	10.0	11.6 ± 0.2^d	16.70	0.96^f	8.8^e	
V_S^0	164.01					2561.9 ± 0.3^g
B_V	4.64					60 ± 6^g
C_V	0.71					
V_M/N	175.20					2712.9 ± 0.1^g
$V_{\text{(van der Waals)}}$	114.5					1741

[a] Units are K_M, kg^{n-1} mol^{1-n}; ΔG_m^0, kJ mol^{-1}; B_H, kJ kg mol^{-2}; C_H, kJ kg$^{3/2}$ mol$^{-5/2}$; L_M/N, kJ mol^{-1}; V_S^0 and V_M/N, cm^3 mol^{-1}; B_V, cm^3 kg mol^{-2}; C_V, cm^3 kg$^{3/2}$ mol$^{-5/2}$. [b] From ref 17. [c] From ref 20. [d] From ref 25. [e] From ref 21. [f] From ref 24. [g] From ref 1. The standard free energy of micellization per surfactant monomer was calculated as $\Delta G_m^0 = -(RT \ln K_M)/N$.

systems. The information provided by these studies cannot fit quantitatively our systems because the architecture of the copolymer and the nature of the surfactant as well as the copolymer/surfactant ratio are different. However, to the light of these findings, one could assume that the mixed micelles have aggregation numbers and/or shapes different from the pure ones. Taking into account also for these structural effects in the development of the model is quite complicated. In fact, the resulting equation may be multi-parameter and, if on one side, it may fit the experimental data, on the other side, it makes difficult to prove the correctness of the model. On this basis, we stated that the equilibria which can describe the properties of transfer are given in schemes 3, 7, and 8

$$zS + R \rightleftarrows C \quad (7)$$

$$wR + M \rightleftarrows D \quad (8)$$

The process in scheme 7 refers to the association of a fixed number of monomeric surfactant molecules (zS) with 1 copolymer molecule (R) leading to the formation of the surfactant-copolymer aggregation complex of z:1 stoichiometry (C). The equilibrium constant (K_C) is given by

$$K_C = \frac{x_C}{x_R[m]^z} \quad (9)$$

where [m] is the monomer surfactant concentration in the ternary system; x_C and x_R are the fractions of the copolymer-surfactant aggregation complex and the free copolymer, respectively.

According to a mass action model,[26] the equilibrium in scheme 8 assumes that an integer number w of copolymer molecules interact with 1 micelle to form a mixed micelle (D). For this process, the equilibrium constant (K_D) may be written as

$$K_D = \frac{x_D m_R}{(x_R m_R)^w m_M} \quad (10)$$

where x_D is the fraction of the mixed micelles and m_R stands for the stoichiometric copolymer concentration. In addition, m_M is the micelles concentration in the presence of the copolymer

$$m_M = \frac{m_S - [m] - zx_C m_R - Nx_D m_R}{N} \quad (11)$$

The apparent molar property of the copolymer in the water−surfactant mixture is given by

$$Y_{\phi,R} = \frac{Y_T - Y_B}{m_R} \quad (12)$$

where Y_B and Y_T are the properties of the water−surfactant and water−surfactant−copolymer mixtures, respectively. Taking into account the equilibria 3, 7, and 8, one may write

$$Y_B = 55.5Y_w + [m_0]Y_m + m_{M,0}Y_M \quad (13)$$

$$Y_T = 55.5Y_w + [m]Y_m + m_M Y_M + m_R x_R Y_R + \\ m_R x_C Y_C + m_R x_D Y_D \quad (14)$$

where Y_w is the property of pure water, whereas Y_R, Y_C, and Y_D are the partial molar properties of the free copolymer, the copolymer−surfactant aggregation complex, and the mixed micelle, respectively.

By combining eqs 11−14, remembering that Y_R is correlated to the partial molar property in water ($Y_{R,w}$) through the surfactant-copolymer interaction parameter ($B_{Y,RS}$)

$$Y_R = Y_{R,w} + 2B_{Y,RS}\, x_R [m] \quad (15)$$

and by adding and subtracting the $x_C Y_R$, $wx_D Y_D$, and $x_D Y_M$ quantities, the following is obtained

$$\Delta Y_t = 2B_{Y,RS}\, x_R[m] + x_C\,\Delta Y_C + \\ \frac{[m_0] - [m] - zx_C m_R}{m_R}\,\Delta Y_m + x_D\,\Delta Y_D \quad (16)$$

where ΔY_D ($Y_D - wY_R - Y_M$) is the property change for the mixed micelles formation and ΔY_C ($Y_C - Y_R - zY_m$) is the property associated to the copolymer-surfactant aggregation complex formation. The third term on the right-hand side of eq 16 is the displacement of the monomer-micelle equilibrium induced by the copolymer which, hereinafter, will be indicated as E_{shift}.

The mass balance for both the surfactant and the copolymer is expressed as a function of [m]

$$m_S = K_D K_M N[m]^N (x_R m_R)^w + K_C x_R m_R z[m]^z + \\ K_M N[m]^N + [m] \quad (17)$$

$$m_R = K_D K_M w[m]^N (x_R m_R)^w + K_C x_R m_R [m]^z + x_R m_R \quad (18)$$

If the equilibrium constants as well as the stoichiometries of the processes are known, the nonlinear system (eqs 17 and 18) can be solved by using the Newton−Raphson method extended to two dimensions to evaluate [m] and x_R. The x_C and x_D values can be calculated by means of eqs 9 and 10, respectively.

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(b) Property of Transfer in the Absence of the Copolymer−Micelle Interaction Contribution. To a first approximation, one may state that the $x_D \Delta Y_D$ term does not contribute to ΔY_t. This is correct if either the micelles are absent or the copolymer does not associate with the micelles. Therefore, eq 16 assumes the following form

$$\Delta Y_t = 2B_{Y,RS} x_R [m] + \frac{[m_0] - [m] - z\, x_C m_R}{m_R} \Delta Y_m + x_C \Delta Y_C \tag{19}$$

By introducing arbitrary K_C and z values in eqs 17 and 18 (where the terms related to K_D were taken off), [m] and x_C were evaluated through the Newton−Raphson method. In addition, $[m_0]$ was calculated from eqs 4 and 5 where the K_M and N values were introduced. The $B_{Y,RS}$ values for the copolymers in DeTAB and ODAO were evaluated from the data in the very dilute surfactant region whereas those of the other systems are available.[8,9] ΔY_m was calculated as previously described. The minimizing procedure was carried out through a program written by us in the Pascal language based on a nonlinear least-squares fitting method. The best fit gave z, K_C, and ΔY_C (Table 2).

With the exception of the ΔV_t data at $m_R = 35$ mmol kg^{-1} for NaDec/L64, eq 19 fitted the experimental points in the surfactant region where the micelles are absent. Moreover, the analysis of the ΔH_t data for OPC/F68, DeTAB/F68, and DeTAB/L64 did not evidence the surfactant-copolymer aggregation complexes.

Figures 1−4 illustrate the properties of transfer calculated by means of eq 19 for some systems. As can be seen, the ΔY_t points to $m_S \approx cmc_w$ are well matched by the calculated values indicating that regardless of the ΔY_t vs m_S profile, the dispersed surfactant region is highlighted by the same phenomenon. Remind that the calculated ΔH_t values for OPC/F68 (Figure 2), DeTAB/F68, and DeTAB/L64 (Figure 3) do not include the $X_C \Delta Y_C$ term being null. As concerns the copolymer concentration effect, it is evident that by increasing m_R the difference between the experimental points and the calculated values (Figure 4) reduces.

In conclusion, eq 19 is not able to describe quantitatively the experimental data in the wide range of m_S analyzed. Its ability to reproduce the volume data of NaDec/L64 at $m_R = 35$ mmol kg^{-1} also in the micellar region may be fortuitous.

(c) Property of Transfer in the Presence of the Copolymer−Micelle Interaction Contribution. The onset of the divergence between the ΔY_t experimental points and the calculated values takes place when the amount of the micelles becomes appreciable. Therefore, eq 16 is expected to fit successfully the experimental data. To this purpose, the parameters dealing with the water+surfactant binary system (K_M, N, and ΔY_m) and the surfactant/copolymer ($B_{Y,RS}$, K_C, z, and ΔY_C) were taken. The fitting procedure was carried out through the program previously employed which provided K_D, w, and ΔY_D (Table 2). For all systems analyzed, it was obtained $w = 1$. For NaDec/L64, the analysis of volume data available at some copolymer concentrations provided K_D values independent of m_R and in agreement with that evaluated from the enthalpy. However, they were affected by large errors because in the fitting interval the variation of x_D was smooth. Then, K_D obtained from the enthalpy was used to fit the volume data.

As a general result, the best fits matched very well the experimental points as examples in Figures 1−4 show.

A careful inspection of the various terms that contribute to ΔY_t according to eq 16 permits to understand the very different profiles of the ΔY_t vs m_S trends observed for some systems.

TABLE 2: Thermodynamic Properties for the Copolymer−Surfactant Binding Equilibria at 298 K[a]

| | NaDec | | | | NaOct | | ODAO | | OPC | | | DeTAB | |
	L64				F68	L64	F68	L64	F68	L64		F68	L64
m_R	2.5	15	25	35	1.0	5.0	1.0	5.0	1.0	5.0		1.0	5.0
$B_{V,RS}$[b]		154 ± 16	154 ± 16	154 ± 16									
$B_{H,RS}$	227 ± 36[c]				200 ± 45[c]	98 ± 20[c]	164 ± 60	82 ± 8	240 ± 3[c]	111 ± 4[c]		378 ± 14	229 ± 14
K_C	$(36 \pm 6)10^2$	$(24 \pm 5)10^2$	$(42 \pm 17)10^2$	$(18 \pm 13)10^2$	30 ± 1	39.2 ± 1.7	69 ± 10	12 ± 3		9.8 ± 1.8			
z	3.1	3.1	3.3	3.1	3.2	3.1	2.7	2.2		2.8			
ΔG_C^0	−20.3 ± 0.4	−19.3 ± 0.5	−20.7 ± 1.0	−18.6 ± 1.8	−8.43 ± 0.08	−9.09 ± 0.11	−10.2 ± 0.4	−6.2 ± 0.6		−5.7 ± 0.5			
ΔH_C^0	191 ± 3				374 ± 3	179.8 ± 1.6	240 ± 20	270 ± 50		161 ± 11			
$T\Delta S_C^0$	211 ± 3				382 ± 3	188.9 ± 1.7	250 ± 20	280 ± 50		167 ± 11			
ΔV_C		103 ± 5	98 ± 8	101 ± 10									
K_D	520 ± 110				190 ± 20	90 ± 70	179 ± 9	71 ± 5	290 ± 40	350 ± 80		2860 ± 140	9600 ± 1300
ΔG_D^0	−15.5 ± 0.5				−13.0 ± 0.3	−11.1 ± 1.9	−12.85 ± 0.12	−10.56 ± 0.17	−14.1 ± 0.3	−14.5 ± 0.6		−19.72 ± 0.12	−22.7 ± 0.3
ΔH_D^0	26 ± 14				191 ± 8	119 ± 12	227 ± 2	149.5 ± 1.9	193 ± 2	108 ± 2		164.5 ± 1.0	128.1 ± 0.9
$T\Delta S_D^0$	42 ± 15				204 ± 8	130 ± 14	240 ± 2	160 ± 2	207 ± 2	123 ± 3		184.2 ± 1.1	150.8 ± 1.2
ΔV_D		40 ± 2	46 ± 3	41 ± 3									

[a] Units are m_R, mmol kg^{-1}; $B_{V,RS}$, cm^3 mol^{-2} kg; $B_{H,RS}$, kJ mol^{-2} kg; K_C, kg^z mol^{-z}; ΔH_C, $T\Delta S_C^0$, ΔH_D and $T\Delta S_D^0$, kJ mol^{-1}; ΔV_C and ΔV_D, cm^3 mol^{-1}; K_D, kg mol^{-1}. [b] From ref 9. The standard free energy and entropy were calculated as $\Delta G° = - RT \ln K$ and $T\Delta S^0 = \Delta H - \Delta G°$, respectively. [c] From ref 8. [c] From ref 9.
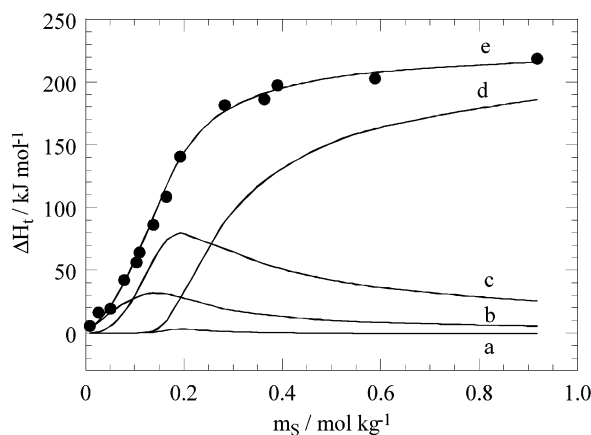
Figure 5. Enthalpy of transfer of F68 1 mmol kg^{-1} from water to the aqueous *N,N*-dimethyloctylamine-*N*-oxide solutions as a function of the surfactant concentration. Lines represent the contributions due to: (a) the shift of the micellization equilibrium; (b) the interactions between monomers of copolymer and surfactant; (c) the surfactant-copolymer aggregation complex formation; (d) the mixed micelles formation; (e) enthalpy of transfer given by the sum of the a–d contributions.
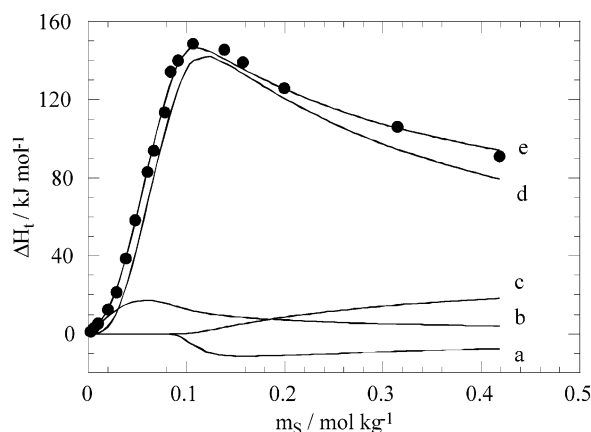

Figure 6. Enthalpy of transfer of L64 2.5 mmol kg^{-1} from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration. Lines represent the contributions due to: (a) the shift of the micellization equilibrium; (b) the interactions between monomers of copolymer and surfactant; (c) the mixed micelles formation; (d) the surfactant-copolymer aggregation complex formation; (e) enthalpy of transfer given by the sum of the a–d contributions.

For this purpose, enthalpy data of L64/NaDec and F68/ODAO were analyzed. Figures 5 and 6 illustrate that the dependence of the various contributions on m_S is equal for both the systems with the exception of E_{shift} which presents a minimum for L64/NaDec and a maximum for F68/ODAO; these peculiarities are not detectable in the graphs because of the E_{shift} small magnitude. The contribution due to the interaction between monomers of copolymer and surfactant reaches the maximum at ca. 0.05 mol kg^{-1} for L64/NaDec and at ca. 0.15 mol kg^{-1} for ODAO/F68. The different location of such extrema reflects the variation of x_R with m_S which is sharper for the former system. For NaDec/L64, the decreasing of $x_C \Delta Y_C$ and the increasing of $x_D \Delta Y_D$ occurs simultaneously whereas for F68/ODAO $x_C \Delta Y_C$ starts to decrease when an appreciable amount of mixed micelles is formed. Then, one may infer that if the contribution for the decomplexation is small, the property of transfer is a S-shaped curve with m_S (Figure 5), whereas if it is large a pronounced maximum is generated in the ΔY_t vs m_S trend (Figure 6).

Validity of the Model. The successful fitting of the ΔY_t data of the copolymer/surfactant systems is satisfactory even if it does not prove the validity of the model. A quite great number

of systems, where the nature of both the surfactant and the copolymer are systematically changed, need to be investigated by means of different thermodynamic techniques to verify the reliability of the proposed model. The small number of the surfactant/copolymer mixtures here analyzed does not permit to obtain detailed information on various effects (architecture of the copolymer, surfactant alkyl chain and headgroup of the surfactant). Notwithstanding, insights which support the validity of the model are given. As concerns the energetics of the processes, it is straightforward that dispersed cationic and nonionic surfactants slightly interact with the copolymer forming weak surfactant/copolymer aggregation complexes or not at all. On the contrary, anionic dispersed surfactants strongly associate with the copolymer. These features have been already established for the binding between surfactants and nonionic polymers such as PEO and PPO.[27] The interaction between the copolymer and the surfactant micelle leads to the formation of mixed micelles whatever is the copolymer architecture and the nature of the surfactant. The K_D values indicate that F68 stabilizes more effectively the NaOct and ODAO micelles whereas L64 does those of OPC and DeTAB; as well, they increase with the surfactant alkyl chain length. Thus, hydrophilic and hydrophobic interactions are involved in the mixed micelles formation. Another general aspect which emerges from the data analysis is the largely positive enthalpy and entropy of the binding processes of both the copolymers. These findings suggest that both the formation of the surfactant/copolymer aggregation complex and the mixed micelles are mainly controlled by the loss of hydrophobic hydration. However, these great effects essentially compensate with each other and, hence, do not contribute to the stability of the formed aggregates. The larger values of the enthalpy and the entropy for F68 compared to L64 appear anomalous on the basis of the PPO/PEO ratio bigger for L64. Indeed, according to the literature,[28] the hydrogen bonding between the ether oxygen and three water molecules favors the increase of the structure of water around the hydrophobic ethyl groups. Therefore, the loss of hydrophobic hydration of the PEO blocks may be invoked to justify such findings.

It is to be pointed out that ΔY_C and ΔY_D cannot provide information on the affinity of the copolymer toward the surfactant in the monomeric state (surfactant/copolymer aggregation complex formation) and micellized state (mixed micelles formation) because they do not refer to the transferring process of the copolymer from the aqueous phase to the mixed aggregates. Consequently, extracting information from these properties on various effects (nature of the copolymer and the surfactant) can be misleading since the initial and the final states are system specific. Therefore, to discriminate the interactions involved in the formation of the two kinds of aggregates, the properties of the surfactant/copolymer aggregation complex (Y_C) and the mixed micelles (Y_D) were compared to the properties of the pure micelles (Y_M) and the copolymer aggregate (Y_M^R). These quantities were possible to be calculated only for the volume. Also, they were corrected for the geometric term, evaluated from the van der Waals volume,[29] to obtain only the interaction contribution. The following sequence was observed: $V_C < V_M \ll V_D \ll V_M^R$. This order is consistent with the idea that the surfactant/copolymer aggregation complex does not exhibit the features of a typical micellar aggregate and may be considered a precursor of mixed micelles which, in turn, display characteristics quite different from the pure copolymer aggregate containing the extended PPO block in the core and the PEO segments into the hydrophilic shell.[1,2]
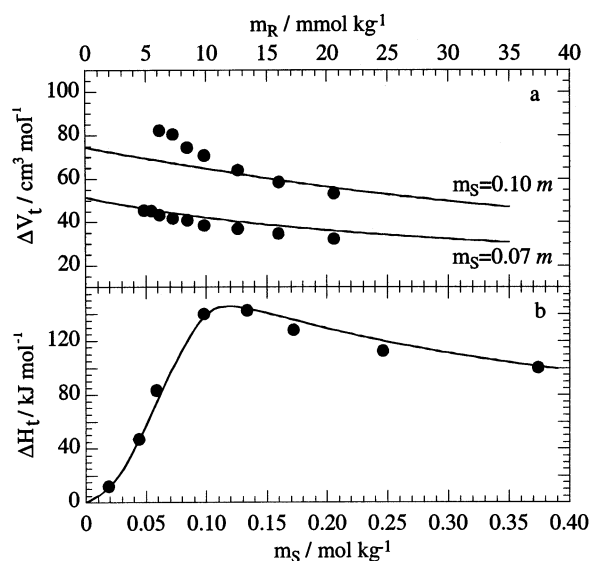
Mass Action Model Applied to Copolymer Transfer

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Figure 7. Water-L64-sodium decanoate ternary system: (a) volume of transfer of L64 as a function of the copolymer concentration in the water−surfactant mixtures; (b) enthalpy of transfer of L64, 5 mmol kg^{-1}, as a function of the surfactant concentration. Lines, calculated values by means of eq 19.

Finally, the quantities generated by the minimizing procedure are good tools to predict functions of transfer in conditions different from those experimental and, hence, the comparison between the calculated values and the new experimental points can corroborate the validity of the model. As stated previously, the analysis of ΔV_t for NaDec/L64 at $m_R = 15$, 25, and 35 mmol kg^{-1} gave the equilibrium constants and the related property changes values independent of m_R. This is reasonable because the m_R values are close and relatively small. On this basis, ΔV_t in the L64 region to 35 mmol kg^{-1} was calculated through eq 19 at two m_S values (0.06976 and 0.1032 mol kg^{-1}) and new experimental points were determined (Figure 7). Moreover, the enthalpy of transfer of L64, 5 mmol kg^{-1}, was calculated as a function of m_S and compared with the experimental data reported elsewhere[8] (Figure 7). By considering the errors of both the parameters used in the computations and the experimental data, a satisfactory agreement was observed between the predicted values and the experimental points.

Conclusions

The present article shows that the thermodynamic properties of transfer of unassociated nonionic copolymers, at fixed concentration, from water to the aqueous surfactant solutions can be fitted quantitatively with a chemical equilibrium model based on four contributions: (1) interaction between monomers of copolymer and surfactant, (2) displacement of the monomer-micelle equilibrium induced by the copolymer, (3) formation of the surfactant-copolymer aggregation complex, and (4) formation of the mixed micelles. The generated fitting parameters provided information which support the validity of the proposed model. The satisfactory agreement between the predicted values, calculated by using such parameters, and new experimental points corroborates the reliability of the model, as well.

Supporting Information Available: Table of the enthalpies of transfer of copolymers from water to the aqueous surfactant solutions at 298 K. Table of the apparent molar volume of L64 in aqueous sodium decanoate solutions at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

Appendix

As stated earlier, the Newton−Raphson method extended to two dimensions was used to solve the nonlinear system formed by eqs 17 and 18. In the following, it is briefly described.

For a generic nonlinear system containing the x_1 and x_2 unknown parameters, one can write

$$f_1(x_1, x_2) = 0 \tag{A1}$$

$$f_2(x_1, x_2) = 0 \tag{A2}$$

The Jacobian matrix for the system is defined as

$$J(x_1, x_2) = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} \tag{A3}$$

where $\partial f_i/\partial x_i$ is the partial derivative of the function f_i with respect to x_i.

For initial values of x_1 and x_2, namely x_1^0 and x_2^0, the vector "d" is calculated by solving the linear system

$$\begin{bmatrix} \dfrac{\partial f_1}{\partial x_1}\Big|_{x_1=x_1^0} & \dfrac{\partial f_1}{\partial x_2}\Big|_{x_2=x_2^0} \\ \dfrac{\partial f_2}{\partial x_1}\Big|_{x_1=x_1^0} & \dfrac{\partial f_2}{\partial x_2}\Big|_{x_2=x_2^0} \end{bmatrix} \cdot \begin{bmatrix} d_1^0 \\ d_2^0 \end{bmatrix} = \begin{bmatrix} f_1(x_1^0,x_2^0) \\ f_2(x_1^0,x_2^0) \end{bmatrix} \tag{A4}$$

Then, the new pair of x_1 and x_2 values, namely x_1^1 and x_2^1, are calculated as

$$\begin{bmatrix} x_1^1 \\ x_2^1 \end{bmatrix} = \begin{bmatrix} x_1^0 \\ x_2^0 \end{bmatrix} + \begin{bmatrix} d_1^0 \\ d_2^0 \end{bmatrix} \tag{A5}$$

These x_1^1 and x_2^1 values were used to start the iteration method which stopped when the following condition was satisfied

$$\max[x_1^k - x_1^{k+1}, x_2^k - x_2^{k+1}] < \epsilon \tag{A6}$$

where the superscript k represents the kth iteration and ϵ is the tolerance. In our case, it was set $\epsilon = 10^{-10}$.

The application of the above procedure to the system formed by eqs 17 and 18 gives

$$f_1(x_R, [m]) = K_D K_M N[m]^N (x_R m_R)^w +$$
$$K_C x_R m_R z[m]^z + K_M N[m]^N + [m] - m_S = 0 \tag{A7}$$

$$f_2(x_R, [m]) = K_D K_M w[m]^N (x_R m_R)^w +$$
$$K_C x_R m_R[m]^z + x_R m_R - m_R = 0 \tag{A8}$$

Their derivatives with respect to $[m]$ and x_R are

$$\partial f_1/\partial[m] = K_D K_M N^2[m]^{(N-1)}(x_R m_R)^w +$$
$$K_C x_R m_R z^2[m]^{(z-1)} + K_M N^2[m]^{(N-1)} + 1 \tag{A9}$$

$$\partial f_1/\partial x_R = K_D K_M w N[m]^N (x_R m_R)^w/x_R + K_C m_R z[m]^z \tag{A10}$$

$$\partial f_2/\partial[\mathrm{m}] = K_\mathrm{D}K_\mathrm{M}wN[\mathrm{m}]^{(N-1)}(x_\mathrm{R}m_\mathrm{R})^w + K_\mathrm{C}x_\mathrm{R}m_\mathrm{R}z[\mathrm{m}]^{(z-1)} \tag{A11}$$

$$\partial f_2/\partial x_\mathrm{R} = K_\mathrm{D}K_\mathrm{M}w^2[\mathrm{m}]^N(x_\mathrm{R}m_\mathrm{R})^w/x_\mathrm{R} + K_\mathrm{C}m_\mathrm{R}[\mathrm{m}]^z + m_\mathrm{R} \tag{A12}$$

To optimize the iteration procedure, the initial value of x_R was set equal to the unity for the surfactant mixture having the lowest value of m_S. The x_R value obtained by solving eqs A7 and A8 was used as initial value for the surfactant mixture at the successive concentration and so on. As concerns [m], its initial value is coincident with the stoichiometric surfactant concentration for the dispersed surfactant mixtures whereas it is equal to the critical micellar concentration in the case of micellar solutions. Obviously, these statements are operational definitions since the model assumed for the micellization is based on a mass action law.

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