

Binding between (Ethylene Oxide)₁₃–(Propylene Oxide)₃₀–(Ethylene Oxide)₁₃ and Sodium Decanoate. Volume, Enthalpy, and Heat Capacity Studies

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Received: February 6, 2002; In Final Form: June 4, 2002

Volume, enthalpy, and heat capacity of transfer (ΔY_t) of (ethylene oxide)₁₃–(propylene oxide)₃₀–(ethylene oxide)₁₃ (L64), at some concentrations, from water to the aqueous sodium decanoate (NaDec) solutions as functions of the surfactant concentration (m_s) were determined at 298 K. The copolymer was studied in both the unassociated and associated forms. For a given L64 concentration (m_c), the ΔY_t vs m_s profiles for the volume and the enthalpy are equal but different from that of the heat capacity because the latter contains also the relaxation terms. The experimental data were analyzed by assuming the distribution of L64 between the aqueous and the micellar phases and the shift of micellization equilibrium induced by the copolymer. A very good fit was obtained at $m_c = 35 \text{ mmol kg}^{-1}$, which provided the L64–micelles binding constant (K_b), the volume of transfer of L64 from water to micelles ($\Delta V_{t,M}$) and the Setchenov constant. By using K_b , $\Delta V_{t,M}$, and the L64-free surfactant interaction parameter (obtained from the study in the pre-micellar region), ΔV_t as a function of m_s at lower m_c was calculated. The simulations resulted unsatisfactory since neither the shape of the ΔV_t vs m_s trend was reproduced. Nevertheless, by adjusting K_b and $\Delta V_{t,M}$, the maximum in the ΔV_t vs m_s curve was generated but the agreement with the experimental points was only qualitative. The data at $m_c < 35 \text{ mmol kg}^{-1}$ below the cmc of NaDec were interpreted in terms of a premicellar association between n mol of NaDec and 1 mol of L64.

Introduction

In the last years, a growing scientific interest to the behavior of the poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) copolymers (commercially available as Pluronic or Poloxamers) in solution has been addressed. The effect of the presence of polar additives,^{1–7} organic compounds,^{4,5,8,9} inorganic salts,^{10,11} surfactants,^{11–22} etc. has been analyzed. The importance of these studies is the ability to design microstructures with different functional properties useful in the applications.

A number of papers on the Pluronic–surfactant–water systems^{11–22} has been reported but the information provided is very far to be exhaustive, as the surfactant–copolymer mechanism of interaction is quite complex. The sodium dodecyl sulfate (NaDS)/(ethylene oxide)₉₇–(propylene oxide)₆₉–(ethylene oxide)₉₇ (F127) system, studied by different points of view, is an example.^{13–16,21} Earl experiments of Hecht et al.^{13,15,21} indicated that the surfactant destroys the F127 micelles because of the surfactant–copolymer aggregation complex formation. Recent thermodynamic and structural studies^{14,15} evidenced two specific modes of binding: (1) the interactions between monomeric F127 and NaDS micelles and (2) the interactions between NaDS and micellar F127 followed by the breakdown of the NaDS/F127 mixed micelles into smaller aggregates upon the addition of NaDS. Further detailed studies¹⁶ showed that at temperatures just below the critical micellar temperature of pure F127, small amounts of NaDS cause the formation of F127 micelles that are broken-down by a further addition of NaDS. A similar mechanism of interaction was invoked for the F127/

tetradecyltrimethylammonium bromide system.¹⁷ A different behavior¹⁸ was exhibited by hexaethylene glycol mono-*n*-dodecyl ether, which forms mixed micelles with F127. This feature seems to be specific of nonionic surfactants as *N,N*-dimethyloctylamine-*N*-oxide forms mixed micelles with L64 and (ethylene oxide)₇₅–(propylene oxide)₃₀–(ethylene oxide)₇₅ (F68).¹⁹

To shed some light to the thermodynamics of the copolymer–surfactant mixtures, we studied the water–sodium decanoate–L64 system as functions of both the copolymer and the surfactant concentrations at 298 K. The simultaneous determination of several thermodynamic properties can provide straightforward information on the interactions controlling these systems and, for this reason, we measured the volume, the enthalpy, and the heat capacity.

Experimental Section

Materials. Sodium decanoate (Sigma) was recrystallized from absolute ethanol and dried in a vacuum oven at 313 K for at least 4 days. Its aqueous solutions gave pH = 9. The standard partial molar volume of the surfactant, evaluated from density measurements, agrees with the value reported elsewhere.²³

Sodium chloride (Aldrich, 99.999%) was dried in an oven at 573 K for 2 days. (Ethylene oxide)₁₃–(propylene oxide)₃₀–(ethylene oxide)₁₃ (Pluronic L64, nominal MW = 2900 g mol^{–1}) was provided by Fluka. It was used as received because no difference in the apparent molar volumes of purified and not purified L64 in water was observed.³

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

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Equipment. *Density.* The solutions densities were measured at 298 K by using a vibrating tube flow densimeter (Model 03D, Sodev Inc.) sensitive to 3 ppm. The temperature was maintained constant within 0.001 K by using a closed loop temperature controller (Model CT-L, Sodev Inc.). The calibration of the densimeter was made with water ($d = 0.997\,047\text{ g cm}^{-3}$)²⁴ and aqueous sodium chloride solutions the densities of which are reported in the literature.²⁵

Heat Capacity Measurements. The relative differences in the heat capacities per unit volume ($\Delta\sigma/\sigma_0$) were determined with a Picker flow microcalorimeter (Setaram) at 298.426 ± 0.001 K. Using a flow rate of about $0.01\text{ cm}^3\text{ s}^{-1}$ and a basic power of 19.7 mW, the temperature increment was approximately 0.5 K. The reproducibility of the specific heat capacity measurement is $1 \times 10^{-4}\text{ J K}^{-1}\text{ g}^{-1}$.

The specific heat capacity (C_p) of a solution of density d is related to $\Delta\sigma/\sigma_0$ through the equation

$$C_p = C_{p,0}\{1 + \Delta\sigma/\sigma_0\}d_0/d \quad (1)$$

where $C_{p,0}$ and d_0 correspond to the specific heat capacity and density of pure water the values of which were taken from the literature.²⁵

Enthalpy. Enthalpies of mixing experiments were carried out at 298.00 ± 0.01 K by means of a flow LKB 2107 microcalorimeter. The injection of the solutions into the apparatus was made by means of a Gilson peristaltic pump (Minipuls 2).

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

The flows of the solutions were determined by weight.

The final concentration of the surfactant (f_{SMS}) and the copolymer (f_{CMC}) solutions, upon the mixing process, were calculated by using the dilution factors

$$f_s = \Phi_s/(\Phi_s + \Phi_c) \quad (2)$$

$$f_c = \Phi_c/(\Phi_s + \Phi_c) \quad (3)$$

where Φ_c and Φ_s are the flows of water in the copolymer and the surfactant solutions, respectively.

Conductivity. The specific conductivity measurements were carried out at 298.0 ± 0.1 K (digital conductimeter Analytical Control 120) to evaluate the critical micellar concentration of sodium decanoate and the degree of ionization of the micelles (β) in water and in the water+copolymer mixtures. The former was evaluated as the intersection point of the straight lines (in the pre- and postmicellar regions) of the plot of specific conductivity vs surfactant concentration whereas β is given by the ratio of the slopes of these straight lines.²⁶ The calculated values are collected in Table 1.

Apparent Molar Property Calculations. The apparent molar volumes ($V_{\Phi,C}$) and heat capacities ($C_{\Phi,C}$) of L64 in the water–surfactant mixture were calculated by means of the following equations

$$V_{\Phi,C} = \frac{M}{d} - \frac{10^3(d - d_0)}{m_C d d_0} \quad (4)$$

$$C_{\Phi,C} = M C_p + \frac{10^3(C_p - C_{p,0})}{m_C} \quad (5)$$

TABLE 1: Critical Micellar Concentration and Degree of Ionization of Micelles for Sodium Decanoate in Water + L64 Mixtures^a

m_C	cmc_{w+L64}	β
$T = 298\text{ K}$		
0	108	0.52
5.16	96	0.71
15.43	80	0.71
25.54	62	0.78
30.04	59	0.82
34.70	56	0.77
90.01	15	0.95
$T = 318\text{ K}$		
2.50	72	0.72

^a Units: m_C and cmc_{w+L64} , mmol kg^{-1} .

where m_C and M are the molality and the molecular weight of the copolymer, d and C_p are the densities and the specific heat capacities of the water + surfactant + copolymer ternary system, respectively, and d_0 and $C_{p,0}$ are the corresponding properties of the water + surfactant mixed solvent.

The volume and the heat capacity of transfer of L64 from water to the aqueous sodium decanoate solution (ΔV_t) were calculated as difference between $Y_{\Phi,C}$ and the apparent molar property of the copolymer in water.

The enthalpy of transfer (ΔH_t) was evaluated as difference between ΔH^{exp} and the enthalpy of dilution of the copolymer with water (-3.08 kJ mol^{-1}).¹⁹

Thermodynamic Measurements. The volume and the heat capacity measurements were performed by choosing L64 concentrations, which fall in the pre- ($m_C = 15, 25$ and 35 mmol kg^{-1}) and postmicellar (90 mmol kg^{-1}) regions. Remember that the cmc^{11} of L64 in water is 65 mmol kg^{-1} at 298 K. For each copolymer concentration, the experiments were carried out in a wide interval of the surfactant concentration.

It was not possible to perform heat capacity measurements of water + L64 mixtures at compositions larger than 90 mmol kg^{-1} because the baseline was noised due to the solutions viscosity. The $C_{\Phi,C}$ value in water at 90 mmol kg^{-1} ($18.4\text{ kJ K}^{-1}\text{ mol}^{-1}$) is higher than that at infinite dilution ($10.0\text{ kJ K}^{-1}\text{ mol}^{-1}$), which is in very good agreement with the literature value.²⁷ This result is not surprising although negative heat capacity of micellization is expected. In fact, in the $C_{\Phi,C}$ vs m_C curve the pseudo phase transition model predicts²⁸ for the relaxation term of the micellization equilibrium a hump of $72\text{ kJ K}^{-1}\text{ mol}^{-1}$ at the cmc and a value of $52\text{ kJ K}^{-1}\text{ mol}^{-1}$ at $m_C = 90\text{ mmol kg}^{-1}$, as calculated by using eq 18 in ref 28 and the value of 230 kJ mol^{-1} for the enthalpy of micellization.²⁹ Therefore, the relaxation contribution is expected to be minimized at high m_C and, consequently, the $C_{\Phi,C}$ value at 90 mmol kg^{-1} does not correspond to the property of L64 in the micellar phase.

Experimental difficulties did allow determining the enthalpy of transfer to 5 mmol kg^{-1} .

The standard (infinite dilution) partial molar properties were evaluated as an intercept of the property of L64 against its concentration plot, at a given surfactant concentration. As well, heat capacity data at $m_C = 2.5$ and 5 mmol kg^{-1} were interpolated.

Results and Discussion

Qualitative Analysis of the Properties of Transfer. (a) *Unassociated L64.* Figure 1 illustrates the plots of the volume of transfer (ΔV_t) of L64 from water to the aqueous NaDec solutions as a function of m_s at the copolymer concentrations

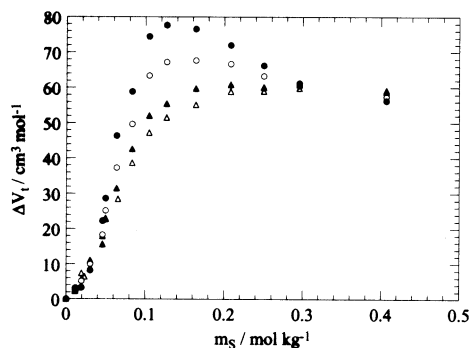


Figure 1. Volume of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration: (●) $m_C = 0$; (○) $m_C = 15 \text{ mmol kg}^{-1}$; (▲) $m_C = 25 \text{ mmol kg}^{-1}$; (Δ) $m_C = 35 \text{ mmol kg}^{-1}$.

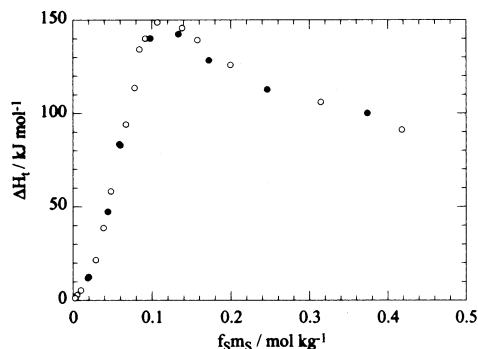


Figure 2. Enthalpy of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration: (○) $f_{cmC} = 2.5 \text{ mmol kg}^{-1}$; (●) $f_{cmC} = 5 \text{ mmol kg}^{-1}$.

studied. The standard partial molar volume of transfer vs m_S trend is also reported, and it exhibits a sigmoid shaped curve to 0.11 mol kg^{-1} ; thereafter it decreases, tending to a constant value. A similar trend with a smoother maximum is observed at $m_C = 15 \text{ mmol kg}^{-1}$. When m_C is increased, the maximum tends to disappear and the ΔV_t vs m_S curves are S-shaped in the range of m_S analyzed. Regardless of the copolymer concentration, the ΔV_t vs m_S trends tend to the same value at high m_S .

Figure 2 shows the plot of the enthalpy of transfer (ΔH_t) of L64 5 mmol kg^{-1} as a function of the surfactant concentration (fsm_S). The data¹⁹ at 2.5 mmol kg^{-1} are also plotted. The experimental points are independent of the copolymer concentration and define a single ΔH_t vs fsm_S curve showing the same shape as the volume. The region below the maximum of the ΔH_t vs fsm_S trend at $f_{cmC} = 2.5 \text{ mmol kg}^{-1}$ was consistent¹⁹ with the premicellar aggregation involving n mol of surfactant and 1 mol of copolymer, leading to the formation of the surfactant–copolymer aggregation complex. Contrary to classic nonionic polymers, L64 possesses hydrophilic and hydrophobic blocks, which are responsible for the copolymer micellization. Upon the NaDec addition, the PPO block as well as the surfactant chain may undergo the dehydration process and interact with each other, forming the NaDec–L64 aggregation complex, a schematic representation of which is shown in Figure 3. Such complexes are likely precursors of mixed micelles, the composition of which is expected being dependent on the copolymer concentration.

The profiles of the ΔH_t and ΔV_t vs surfactant concentration curves are reminiscent of those dealing with the hydrophobic solutes in the aqueous surfactant solutions, which were interpreted in terms of the shift of the micellization equilibrium induced by the solute and the distribution of the solute between

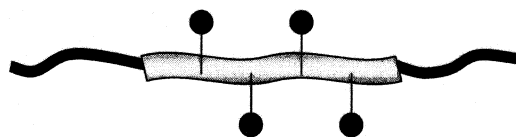


Figure 3. Schematic representation of a surfactant–copolymer aggregation complex formed by 4 surfactant molecules and 1 copolymer molecule.

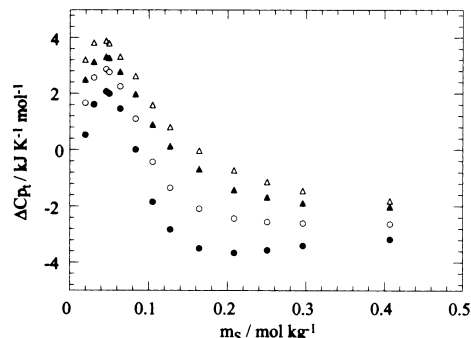


Figure 4. Heat capacity of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration: (●) $m_C = 0$; (○) $m_C = 15 \text{ mmol kg}^{-1}$; (▲) $m_C = 25 \text{ mmol kg}^{-1}$; (Δ) $m_C = 35 \text{ mmol kg}^{-1}$.

the aqueous and the micellar phases.^{31–34} Based on these findings, both the mass action model for the mixed micelles formation and the copolymer–surfactant aggregation complex formation could explain our results.

For a given m_C , the heat capacity of transfer ($\Delta C_{p,t}$) as a function of m_S shows a maximum around at ca. 0.05 mol kg^{-1} ; thereafter it decreases, tending to a constant value at high m_S (Figure 4). An inflection point is displayed by the standard property around at ca. 0.2 mol kg^{-1} . As well, the $\Delta C_{p,t}$ vs m_S curve is shifted toward larger values upon the copolymer addition.

The distinctive characteristics of the heat capacity can be due to the fact that volume and enthalpy are first derivatives of Gibbs free energy whereas heat capacity is a second derivative. Consequently, the latter contains the relaxation contributions and, only when they are negligible, all the thermodynamic properties are expected to show the same features.

The L64 concentration effect is not clear. One may assume that still at high m_C values, the adsorption of the surfactant onto the copolymer occurs or, alternatively, that L64 and NaDec form mixed micelles. The latter hypothesis is supported by the evidence of mixed micelles formation between Pluronics and surfactants.^{11,18,20} To shed some light on this aspect, cmc of NaDec in the water + L64 mixtures (cmc_{w+L64}) were determined (Table 1). When m_C is increased, cmc_{w+L64} decreases in a nonlinear manner, indicating that L64 behaves like an hydrophobic compound (Figure 5). This result apparently disagrees with the volume data: if the maximum of the property of transfer against m_S curve evidences the cmc_{w+L64} , then it should be located at lower surfactant concentration by increasing m_C . Indeed, because the L64 concentration smoothes the maximum and does not essentially influence the property at high m_S values, it may occur that cmc_{w+L64} is buried.

By combining the enthalpy of transfer at $f_{cmC} = 2.5 \text{ mol kg}^{-1}$ with the corresponding heat capacity, ΔH_t as a function of temperature was calculated. The ΔH_t vs m_S plots (not shown) display maxima that are located at lower m_S by increasing temperature. For instance, at 318 K the maximum is present at 0.08 mol kg^{-1} , which is close to cmc_{w+L64} determined by conductivity (Table 1).

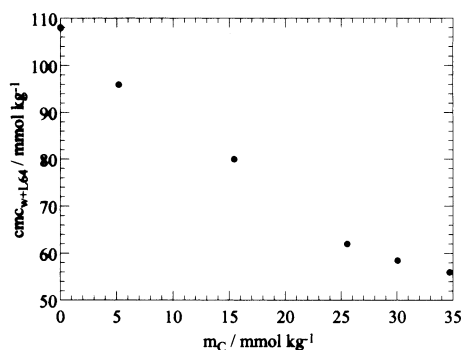


Figure 5. Dependence of the critical micellar concentration of sodium decanoate from the L64 concentration.

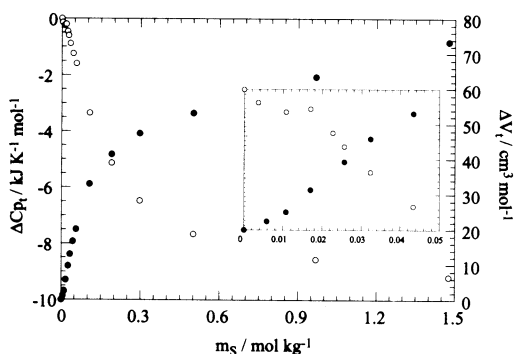


Figure 6. Volume (●) and heat capacity (○) of transfer of micellar L64 ca. 0.09 mol kg⁻¹ from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration.

(b) *Micellized L64.* The trends of the volume and the heat capacity of transfer of L64 0.09 mol kg⁻¹ as functions of m_S are illustrated in Figure 6. The aqueous L64 solution 0.09 mol kg⁻¹ exists as an equilibrium mixture of micelles with large amounts of monomers because its cmc is 0.065 mol kg⁻¹.¹¹ ΔV_t and $\Delta C_{p,t}$ increase and decrease, respectively, in the whole range of m_S showing a change in the slope around at ca. 0.015 mol kg⁻¹ (see insert in Figure 6). Literature $V_{\Phi,C}$ data at 301 K in the presence of NaDec 0.015 mol kg⁻¹ and sodium decyl sulfate (NaDeS) at several concentrations¹¹ agree with the present ΔV_t . For a given L64 micellar solution, the shape of the ΔV_t vs NaDec concentration curve is monotonic. For $0 \leq m_S \leq 0.015$ mol kg⁻¹, NaDec likely solubilizes in the preexistent L64 aggregates. Because of the synergic interactions between the surfactant and L64, experienced by the decrease of the NaDec cmc with m_C , the surfactant does aggregate at $m_S = 0.015$ mol kg⁻¹ (Table 1) and the NaDec–L64 mixed micelles become richer in the NaDec content with increasing m_S .

Surfactant–Copolymer Mixed Micelles Formation Model.

As stated previously, the profiles of the properties of transfer seem to be classic of systems where the hydrophobic solute distributes between the aqueous and the micellar phases.^{31–34} The following equation, independently proposed by De Lisi et al.³⁵ and Desnoyers et al.,^{32,36} was used to treat quantitatively the volume of transfer

$$\Delta V_t = 2\nu_{CS}[m]N_f + (1 - N_f)\Delta V_{t,M} + \Delta V_m\{[m_0] - [m]\}/m_C \quad (6)$$

where $\Delta V_{t,M}$ is the volume of transfer of the copolymer from water to the micellar phase. On the basis of the pseudo phase transition model for micellization and a mass action model for the solute distribution between the aqueous and the micellar phases,³⁷ the fraction of the copolymer in the aqueous phase

TABLE 2: Thermodynamic Properties for the Binding between L64 and Sodium Decanoate at 298 K^a

m_C	0	2.5	5.0	15	25	35
ν_{CS}	81 ± 33					154 ± 16
n	3.1 ^b ; 3.9 ^c					
$10^3 K_{cpx}$	3.6 ± 0.4; ^b 44 ± 10 ^c					
ΔH_{cpx}	183 ± 6 ^b	191 ± 2	199 ± 5			
ΔV_{cpx}	81 ± 3			95 ± 4	100 ± 5	
$\Delta C_{p,cpx}$	-20.0 ± 0.9	-21.3 ± 0.7	-19.7 ± 0.9			
h_{CS}	227 ± 36 ^b					
K_b						43 ± 9
K_S						-36 ± 13
$\Delta V_{t,M}$						64 ± 1

^a Units: m_C , mmol kg⁻¹; ν_{CS} , cm³ kg mol⁻²; K_{cpx} , kgⁿ mol⁻ⁿ; ΔH_{cpx} , kJ mol⁻¹; ΔV_{cpx} and $\Delta V_{t,M}$, cm³ mol⁻¹; $\Delta C_{p,cpx}$, kJ K⁻¹ mol⁻¹; h_{CS} , kJ kg mol⁻²; K_b and K_S , kg mol⁻¹. ^b From ref 19. ^c From volume.

(N_f) and the shift of micellization equilibrium term, are given by^{35,37}

$$N_f = 1/\{1 + K_b(m_S - [m])\} \quad (7)$$

$$\Delta V_m\{[m_0] - [m]\}/m_C = \{\Delta V_m[m]/2\}\{2.3K_SN_f + (1 + \beta)K_b/[1 + K_b(m_S - [m]) + K_b m_C]\} \quad (8)$$

where $[m]$ and $[m_0]$ stand for the cmc in the presence and the absence of the copolymer; K_S and K_b represent the Setchenov constant and the copolymer–micelle binding constant, respectively, whereas ΔV_m is the NaDec volume of micellization (9.6 cm³ mol⁻¹).²⁸ ν_{CS} is the parameter for the copolymer–surfactant interaction in the aqueous phase.

Equations 6–8 fitted very well the experimental data at $m_C = 35$ mmol kg⁻¹ providing K_b , $\Delta V_{t,M}$, and K_S . Also, from data in the premicellar region the ν_{CS} parameter was obtained. The results are collected in Table 2.

The corresponding equation for the heat capacity is available,³⁸ but the lack of the enthalpy data prevented its use at $m_C = 35$ mmol kg⁻¹.

Equation 6, combined with eqs 7 and 8, predicts a break at the cmc of a given thermodynamic property of transfer, which is mostly appropriate for surfactants having low cmc's. Therefore, eqs 7 and 8 are not valid to explain the extrema in the properties of transfer (ΔY_t) in the cmc region usually exhibited by short-chain surfactants.^{31–34} The Desnoyers et al.^{32,36} approach, based on a mass action model for the micellization and the pseudo phase transition model for the distribution of the solute between the aqueous and the micellar phases, is able to fit the ΔY_t vs m_S trend, showing a maximum or a minimum in the cmc region. Such peculiarity was ascribed to the shift of micellization equilibrium induced by the solute that becomes more important by decreasing m_C . The behavior of our volume data seem to be consistent with this effect. For this reason, we assumed the Desnoyers et al. model in using eq 6. The surfactant monomer concentration in the absence of the solute, $[m_0]$, was calculated at each m_S value by using the data of the water–NaDec binary system.³³ For fixed m_S , m_C , and K_b values, the surfactant monomer concentration in the presence of the solute, $[m]$, and N_f were evaluated by means of an iterative method.

First, the simulation was done for the system at $m_C = 35$ mmol kg⁻¹ being known K_b , $\Delta V_{t,M}$, and ν_{CS} (Table 2). A very good agreement between the calculated and the experimental points was found (Figure 7). The above data were also used to simulate ΔV_t at lower m_C , but the results were unsatisfactory. The example in Figure 7, referring to the standard volume of transfer, shows that neither the shape of the ΔV_t vs m_S trend was reproduced. Nevertheless, by adjusting K_b and $\Delta V_{t,M}$, the

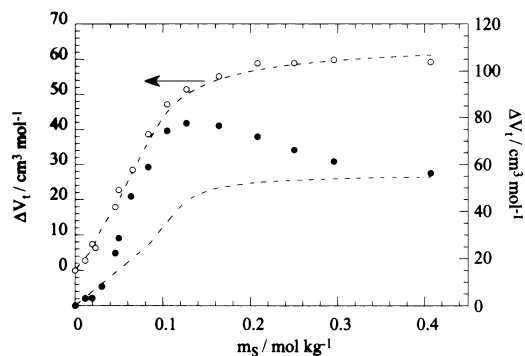


Figure 7. Volume of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration: (○) $m_C = 35 \text{ mmol kg}^{-1}$; (●) $m_C = 0$. Lines, simulations according to eq 6 and the Desnoyers et al. model.

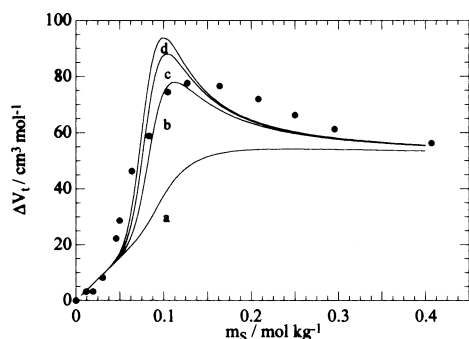


Figure 8. Standard volume of transfer of L64 from water to the aqueous sodium decanoate solutions as a function of the surfactant concentration. Lines, simulations according to eq 6 and the Desnoyers et al. model: (a) $K_b = 50 \text{ kg mol}^{-1}$; (b) $K_b = 500 \text{ kg mol}^{-1}$; (c) $K_b = 1000 \text{ kg mol}^{-1}$; (d) $K_b = 1500 \text{ kg mol}^{-1}$.

maximum in the ΔV_t vs m_S curve was generated but the agreement with the experimental points was only qualitative. This can be seen in Figure 8, which illustrates the simulations of the standard volume of transfer at $\Delta V_{t,M} = 50 \text{ cm}^3 \text{ mol}^{-1}$ and various K_b values. It is surprising that by decreasing m_C , the K_b value must be changed several times in magnitude to explain only qualitatively the experimental data. Desnoyers suggested that one of the assumptions in the model could not be valid, namely, the constancy of the aggregation number of the mixed micelles. In fact, it is probable that the number of sodium decanoate molecules surrounding the L64 molecule is significantly larger than in a normal micelles.

Model for the Surfactant–Copolymer Aggregation Complex Formation. Another hypothesis for the interpretation of the mixtures at $m_C < 35 \text{ mmol kg}^{-1}$ assumes that the large increase of the properties of transfer in the premicellar region reflects the association between a fixed number of surfactant molecules and 1 L64 molecule and, whenever the cmc is reached, mixed micellar aggregates are forming.

(i) *Volume and Enthalpy.* According to the one-step association model based on the formation of aggregation complexes constituted by n mol of surfactant and 1 mol of polymer, the following equation was derived for the property (first derivative of Gibbs free energy) of transfer³⁰

$$\Delta Y_t = \chi_{\text{cpx}} \Delta Y_{\text{cpx}} + 2y_{\text{CS}}(m_S - nm_{\text{cpx}})(1 - \chi_{\text{cpx}}) \quad (9)$$

Here χ_{cpx} is the fraction of the complexed polymer and ΔY_{cpx} is the property change for the aggregation complex formation; m_{cpx} is the molality of the aggregation complex, and y_{CS} assumes the same meaning as above.

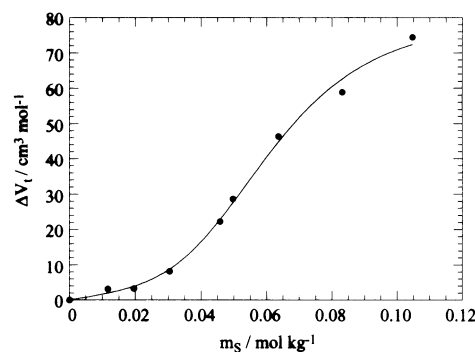


Figure 9. Best fit according to eqs 9 and 10 of the standard partial volume of transfer of L64 from water to the aqueous sodium decanoate solutions.

If the polymer is in the standard state or approaches it, ΔY_{cpx} corresponds to the standard property and χ_{cpx} may be written in terms of the equilibrium constant (K_{cpx}) for the copolymer–surfactant aggregation complex formation as

$$\chi_{\text{cpx}} = K_{\text{cpx}} m_S^n / [1 + K_{\text{cpx}} m_S^n] \quad (10)$$

Equations 9 and 10 were applied to the standard volume of transfer. In the fitting procedure, the value of n was changed to minimize the standard deviation of the ΔV_t vs m_S plot. The best fit of the experimental data is shown in Figure 9 whereas the parameters are reported in Table 2. Note that v_{CS} , within errors, is very close to that obtained from the data at $m_C = 35 \text{ mmol kg}^{-1}$ although it is expected to be the same value.

The shape of the ΔV_t vs m_S trend at $m_C = 15 \text{ mmol kg}^{-1}$ is consistent with the surfactant–copolymer aggregation complex, which is not straightforwardly evidenced at higher m_C values. To a first approximation, we assume that the different shape of the ΔV_t vs m_S curves is due to χ_{cpx} , which is expected to be dependent on m_C . With this in mind, we calculated χ_{cpx} at some m_C values, by using K_{cpx} and n in Table 2 and solving the mass equilibrium equation by the iterative method. The profile of χ_{cpx} vs m_S (not shown) depends on the copolymer concentration; for a fixed m_S , χ_{cpx} decreases with m_C . These results may explain the smoother ΔV_t dependence on m_S with increasing m_C .

The linearity predicted by eq 9 for the plot of ΔV_t , corrected for the interaction contribution, against χ_{cpx} was observed to ca. 0.08 mol kg^{-1} for $m_C = 15$ and 25 mmol kg^{-1} , which is nearly close to the $\text{cmc}_{\text{w+L64}}$ values obtained from conductivity (Table 1). The evaluated ΔV_{cpx} are collected in Table 2.

As concerns the enthalpy, the negligible effect of the copolymer concentration on the ΔH_t values does not imply that the energetics of the copolymer–surfactant aggregation complex formation is not affected. The K_{cpx} , n , and ΔH_{cpx} values reported elsewhere¹⁹ were obtained by applying eqs 9 and 10 to the enthalpy data at $f_{\text{cmc}} = 2.5 \text{ mmol kg}^{-1}$, and they can be assumed by referring to the standard state, as m_C does not influence ΔH_t . For each m_C value, ΔH_t was corrected for the second term at the right-hand side of eq 9 (calculated by using the data in Table 2) and plotted against χ_{cpx} . The obtained ΔH_{cpx} values are collected in Table 2.

(ii) *Heat Capacity.* To fit the heat capacity data, eq 9 was applied to the enthalpy and derived with respect to temperature

$$\begin{aligned} \Delta C_{p,t} = & \chi_{\text{cpx}} \Delta C_{p,\text{cpx}} + 2C_{p,\text{CS}}(m_S - nm_{\text{cpx}})(1 - \chi_{\text{cpx}}) + \\ & (\delta\chi_{\text{cpx}}/\delta T)\Delta H_{\text{cpx}} + 2h_{\text{CS}}(\delta\chi_{\text{cpx}}/\delta T)[nm_C(2\chi_{\text{cpx}} - 1) - m_S] \end{aligned} \quad (11)$$

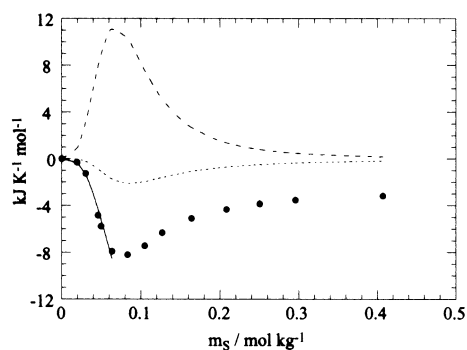


Figure 10. Standard heat capacity of transfer (●) corrected for the relaxation terms of the cooperative binding (---) and the interaction contribution (···) as a function of the surfactant concentration. Best fit (—) according to eqs 10 and 11.

The first two terms are formally equal to those in eq 9. The third and fourth terms represent the relaxation contributions of the surfactant–copolymer aggregation complex process and the interaction equilibrium, respectively. Their presence can explain the peculiar profile of $\Delta C_{p,t}$ vs m_s . The relaxation contribution for $0 \leq m_C \leq 5 \text{ mmol kg}^{-1}$ can be evaluated by using the data in Table 2. Note that in calculating the dependence of χ_{cpx} on temperature, ΔH_{cpx} was assumed to be constant.

Figure 10 illustrates the dependence on m_s of the two relaxation terms and the standard heat capacity of transfer corrected for them. The large relaxation contribution of the equilibrium aggregation complex formation is responsible for the $\Delta C_{p,t}$ positive values and the maximum present at ca. 0.05 mol kg^{-1} in the $\Delta C_{p,t}$ vs m_s trend. The other contribution is relatively small. The shape of the obtained trend is equal to that observed for the enthalpy and the volume, as it is a sigmoid curve up to ca. 0.08 mol kg^{-1} ; thereafter it increases, tending to a constant value. It seems that the heat capacity with respect to other properties detects a lower cmc.

Equation 11, applied to the data in the pre-micellar region, provided $\Delta C_{p,cpx}$ being used the K_{cpx} and n values obtained from the enthalpy. The $C_{p,CS}$ parameter resulted negligible. The best fit is shown in Figure 10. The large value of $\Delta C_{p,cpx}$ (Table 2) may question the calculated dependence of χ_{cpx} on temperature because ΔH_{cpx} was assumed to be temperature independent. Nevertheless, the uncertainties on ΔH_{cpx} and K_{cpx} make reliable the calculations done. The $\Delta C_{p,cpx}$ values were also obtained at $m_C = 2.5$ and 5 mmol kg^{-1} (Table 2).

Thermodynamics of Interaction between Sodium Decanoate and L64. The parameter reflecting the unspecific interactions between the free surfactant and free L64 is positive for the enthalpy and the volume and null for the heat capacity. Also, the interaction parameter for the free energy (calculated³⁹ as $RTK_S/4$) indicates that the surfactant–copolymer interactions are favorable. The L64/*N,N*-dimethyloctylamine *N*-oxide system displayed a similar behavior.¹⁹

The K_{cpx} and n values provided by the analysis of the volume and the enthalpy data give comparable χ_{cpx} values. As well, the standard heat capacity data indirectly confirm these results. The ΔV_{cpx} and ΔH_{cpx} values are positive as the properties of L64 micellization ($143.2 \text{ cm}^3 \text{ mol}^{-1}$ and 230 kJ mol^{-1} for the volume¹¹ and the enthalpy,²⁹ respectively). To the best of our knowledge, no heat capacity of L64 micellization ($\Delta C_{p,m}$) is known. Notwithstanding, from the specific heat capacity of some Pluronics⁴⁰ in water one expects that $\Delta C_{p,m}$ is negative like $\Delta C_{p,cpx}$.

As concerns the copolymer concentration effect, ΔV_{cpx} increases with m_C (Table 2) tending to the L64 ΔV_m value. The

$\Delta C_{p,cpx}$ and ΔH_{cpx} values, within the errors, are independent of m_C in the range $0\text{--}5 \text{ mmol kg}^{-1}$. Dai and Tam¹² showed that for the NaDS/(propylene oxide)₁₉–(ethylene oxide)₃₃–(propylene oxide)₁₉ system, the enthalpy for the polymer–surfactant aggregation complex formation at the critical aggregation concentration increases with the copolymer concentration in the interval $0.15\text{--}1.3 \text{ mmol kg}^{-1}$.

By increasing m_C , larger proportions of L64 segments may dehydrate and interact with NaDec clusters bound to the polymer. Consequently, the L64–NaDec aggregation complex likely tends to assume a character more and more similar to the L64 aggregates.

The solubilization of L64 35 mmol kg^{-1} in the NaDec micelles involves a change in the volume comparable to the ΔV_t value (ca. $70 \text{ cm}^3 \text{ mol}^{-1}$) at $m_C = 90 \text{ mmol kg}^{-1}$, taken at very high m_s , which may be a measure of the volume of transfer of micellar L64 from water to the NaDec micellar phase. These volume variations together with the degree of ionization of micelles (β) are consistent with highly charged NaDec–L64 mixed aggregates, due to the screening of the copolymer segments. The L64–NaDec mixed micelles¹¹ at 301 K behave similarly although β is more strongly affected.

Conclusions

The present study is a part of a project aimed to characterize the water–surfactant–copolymer ternary systems through thermodynamic experiments and modelization of the data. To this purpose, volume, enthalpy, and heat capacity of transfer of L64, at some concentrations, from water to the aqueous sodium decanoate solutions as functions of the surfactant concentration were determined. The mechanism of interaction is not easily understandable as the models used to quantitatively treat the experimental results do not straightforwardly define all the systems under study. Nevertheless, the information drawn is an important basis for the improvement of the models. On the other hand, as far as we know, no quantitative approaches to the thermodynamics of interaction between surfactants and copolymers are known. For instance, Li et al.¹⁴ reported only a quite detailed qualitative description of the interactions in the NaDS–F127–water mixture, which is one of the most investigated systems.

Acknowledgment. We are grateful to the Ministry of University and of Scientific and Technological Research and to the Research National Council (CNR) for the financial support. We thank also prof. J. E. Desnoyers for the stimulating discussion on the topic of the models and for providing us the program for the property of transfer simulation.

Supporting Information Available: Table of the experimental enthalpies of transfer of L64 from water to the aqueous sodium decanoate solution. Tables of the apparent molar volume and heat capacity for L64 in the aqueous surfactant solutions. Table of specific conductivity of sodium decanoate in water + L64 mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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