

## On the Interaction of Sodium Dodecyl Sulfate with Oligomers of Poly(Ethylene Glycol) in Aqueous Solution

Luca Bernazzani,<sup>†</sup> Silvia Borsacchi,<sup>†</sup> Donata Catalano,<sup>†</sup> Paolo Gianni,<sup>\*,†</sup> Vincenzo Mollica,<sup>†</sup> Matteo Vitelli,<sup>†</sup> Fioretta Asaro,<sup>‡</sup> and Luigi Feruglio<sup>‡</sup>

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35 – I-56126 Pisa, Italy, and Dipartimento di Chimica, Università di Trieste, Via L. Giorgeri 1-I-34127 Trieste, Italy

Received: January 22, 2004; In Final Form: April 26, 2004

Isothermal calorimetric titrations of aqueous solutions of poly(ethylene glycol) (PEG) with sodium dodecyl sulfate (SDS) are known to exhibit a peculiar trend consisting of endothermic and exothermic effects. This behavior was explained with the formation of two different mixed micellar aggregates, one characterized by hydrophobic interactions and the second by ion–dipole association. Present NMR measurements on <sup>13</sup>C, <sup>1</sup>H, and <sup>23</sup>Na nuclei do not support the formation of a number of PEG–SDS aggregates characterized by interactions of different nature. Our data are rather in accordance with the initial formation, at low surfactant concentration, of a polymer–surfactant aggregate in which the polymeric chain assumes a strained conformation in order to bind a small micellar cluster. The subsequent growing of the aggregate with increasing surfactant concentration allows the polymer to relax to a more expanded, energetically favored, conformation. Further calorimetric titrations with a set of PEG samples of different molecular weight (200 to 20000 Daltons) allowed to establish a few points so far unclear. The minimum molecular weights necessary for observing the onset and the settling, respectively, of polymer–surfactant interaction were identified and the characteristic multiple peak curve of the titration of the polymer with molecular weight of 8000 Dalton was found related to the discrete binding of two successive SDS micellar clusters on the same polymeric chain.

### Introduction

In the past forty years the interaction between synthetic nonionic hydrophilic polymers and ionic surfactants dissolved in water has been extensively studied.<sup>1–4</sup> The poly(ethylene glycol)/sodium dodecyl sulfate/water (PEG or PEO/SDS/H<sub>2</sub>O) is a typically important system and has been investigated through many different techniques. The pertinent bibliography has been recently summarized in refs 5 and 6. Additional thermodynamic measurements (*H*, *V*, *C<sub>p</sub>*) can be found in refs 7 to 10. For this system it has been found that there is a minimum polymer molecular weight for the existence of an observable polymer–surfactant interaction and different values of this minimum weight have been proposed. For polymers of about 4000 Daltons a significant interaction exists and, at higher weights, this interaction becomes independent of the molecular weight itself. In the following we will indicate PEG of *x* molecular weight as PEG<sub>*x*</sub>.

A technique that has proved very sensitive to the interactions between surfactants and polymers in water is isothermal titration calorimetry (ITC), accurately described and rationalized by Blandamer et al.<sup>11,12</sup> Originally applied to the system under investigation by Olofsson et al.,<sup>13,14</sup> the ITC technique was used recently by Dai and Tam<sup>5</sup> to investigate the nature of PEG–SDS aggregates formed by short polymers of different molecular weight (MW). By adding an SDS aqueous solution (containing concentrated micelles) to solutions of different PEGs, they

observed various unexpected effects, dependent on the polymer MW. In particular, two different kinds of interaction were found between SDS and polymers of MW ≥ 1500 Dalton: an endothermic one at low SDS concentrations and an exothermic one (with respect to the dilution in water) at higher SDS concentrations. Following these authors, the above effects should be ascribed to a dehydration–hydration process of the PEG chains that would be involved in two different types of micellar aggregates.

NMR spectroscopy of <sup>1</sup>H and <sup>13</sup>C has been intensively and fruitfully employed in the wide field of the aggregation of amphiphilic molecules.<sup>15,16</sup> The data are usually interpreted on the basis of either a mass-action model or a pseudo-phase model. The former is better suited for surfactants with high critical micelle concentration (cmc) and low aggregation number, while the latter is used profitably for surfactants with lower cmc. Due to its simplicity, the latter is the framework of choice for the discussion of NMR data.<sup>17</sup>

NMR spectroscopy of the counterions, owing to the fundamental role they play in the aggregation processes of ionic surfactants, has been extensively applied as well.<sup>15,18–20</sup> Most of the counterions have nuclear spin quantum number *I* > 1/2, and therefore they possess a quadrupole moment. The interaction of the latter with the electric field gradients generated by distortions in the hydration shell induced by the charged micellar surface leads to a very efficient relaxation of the nuclear magnetization. Thus it is common to determine the relaxation times of quadrupolar nuclei, in addition to their chemical shifts. The <sup>23</sup>Na nucleus has *I* = 3/2 and its chemical shift and relaxation rate have been employed to determine the critical

\* Corresponding author. Phone: +39 050 2219263; Fax: +39 050 2219260; E-mail: gianni@dcc.unipi.it.

<sup>†</sup> Università di Pisa.

<sup>‡</sup> Università di Trieste.

aggregation concentration of many anionic surfactants and dissociation constants of their aggregates.

The present system PEG/SDS/H<sub>2</sub>O has already been investigated through NMR techniques.<sup>21–24</sup> A study based on the <sup>13</sup>C chemical shift of surfactant and polymer by Cabane<sup>21</sup> concluded that the long polymeric chains of PEG20000 do not penetrate into the surfactant micellar core. On the contrary, other authors argue, for instance from NOESY measurements,<sup>22</sup> that PEG20000 penetrates into micellar aggregates, interacting with the whole SDS chain.<sup>23,24</sup>

The aim of this work is to investigate the peculiarities of the aggregates of PEG oligomers with SDS in water by further ITC measurements and NMR experiments. As far as ITC is concerned, direct and reverse calorimetric titrations of PEG solutions with SDS were performed with several PEG polymers with molecular weights in the range  $200 \leq \text{MW} \leq 20000$ . A few samples with a certified low dispersity molar mass were also employed to look for possible effects related to the distribution of molecular weights in commercial products. <sup>1</sup>H, <sup>13</sup>C, and <sup>23</sup>Na NMR spectroscopy was here applied to aqueous solutions of SDS with a few PEG polymers (MW = 3400, 8000, 20000 Daltons) in the range of SDS concentration investigated by means of the isothermal titration calorimetry. Some NOESY experiments were also performed, as suggested by Gjerde et al.<sup>22</sup>

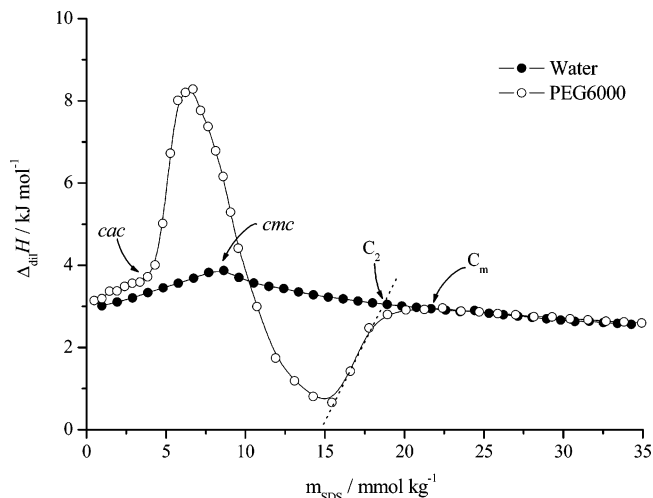
Our investigation leads to better determination of the molecular weights which prove critical to observe the arising and settling of PEG-SDS interactions, provides new clues for comparing micellar aggregates formed by SDS at various concentrations and PEGs of different molecular weight, and allows to propose a simple model for these aggregates.

## Experimental Section

**Materials.** Poly(ethylene glycol) (PEG) samples with nominal molecular weight of 200, 600, 900, 1500, 2000, 3400, 4600, 8000, 10000, and 20000 Dalton were obtained from Aldrich. Standard samples of PEG of certified molecular weight, characterized by a low polydispersity index ( $D = M_w/M_n$ ) were Fluka products. For these samples the effective molecular weight was chosen as the average between  $M_w$  and  $M_n$ : PEG6000 ( $D = 1.03$ ), PEG8300 ( $D = 1.02$ ), and PEG11200 ( $D = 1.07$ ). Sodium dodecyl sulfate (SDS) was from Fluka, purity > 99%. Doubly deionized water was used as the solvent. Deuterated water was from Aldrich, purity 99.9%. All solutions were prepared by weight. PEG solutions were allowed to stand overnight before use.

**Isothermal Titration Calorimetry.** The isothermal titration calorimeter was a Thermal Activity Monitor 2277 (TAM) from Thermometric, equipped with a 612 Lund syringe pump. Titrations were performed at  $298.15 \text{ K} \pm 0.02 \text{ K}$  by adding aliquots of a few microliters (5–50) of a concentrated solution of one component into a 20 mL cell containing 15–16 g of the aqueous solution of the other component. Observed heat effects were measured mostly on the 300  $\mu\text{W}$  full-scale detection range, allowing an average uncertainty of  $\pm 1\%$ . All solutions were prepared by weight, and the concentration of SDS was measured as  $\text{mol kg}^{-1}$  ( $m$ ). Direct titrations involved the addition of 0.977  $m$  aqueous SDS to 0.1% w/w PEG solutions and covered an SDS concentration range  $0 < m_{\text{SDS}} < 0.05 \text{ mol kg}^{-1}$ . The concentration of PEG ( $m_{\text{EO}}$ ), intended as molality of the repeat unit ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ), was about  $0.023 \text{ mol kg}^{-1}$ , obviously constant for all polymers. Reverse titrations involved the addition of 0.913  $m$  PEG to a 0.0178  $m$  SDS solution.

**NMR Spectroscopy.** <sup>13</sup>C NMR spectra were recorded from water solutions with a Varian VXR300 spectrometer operating



**Figure 1.** Typical curves of heats of dilution of a concentrated SDS aqueous solution.

at 300 MHz for proton. All experiments were performed at 25 °C, and the temperature of the sample was controlled to within  $\pm 0.1$  °C. A standard single pulse sequence was used at a frequency of 75.43 MHz with a pulse of 12  $\mu\text{s}$  and a number of transients dependent on the solution concentration, from a minimum of about 2000 to a maximum of about 12000. The assignment of the SDS carbon signals was carried out according to ref 21.

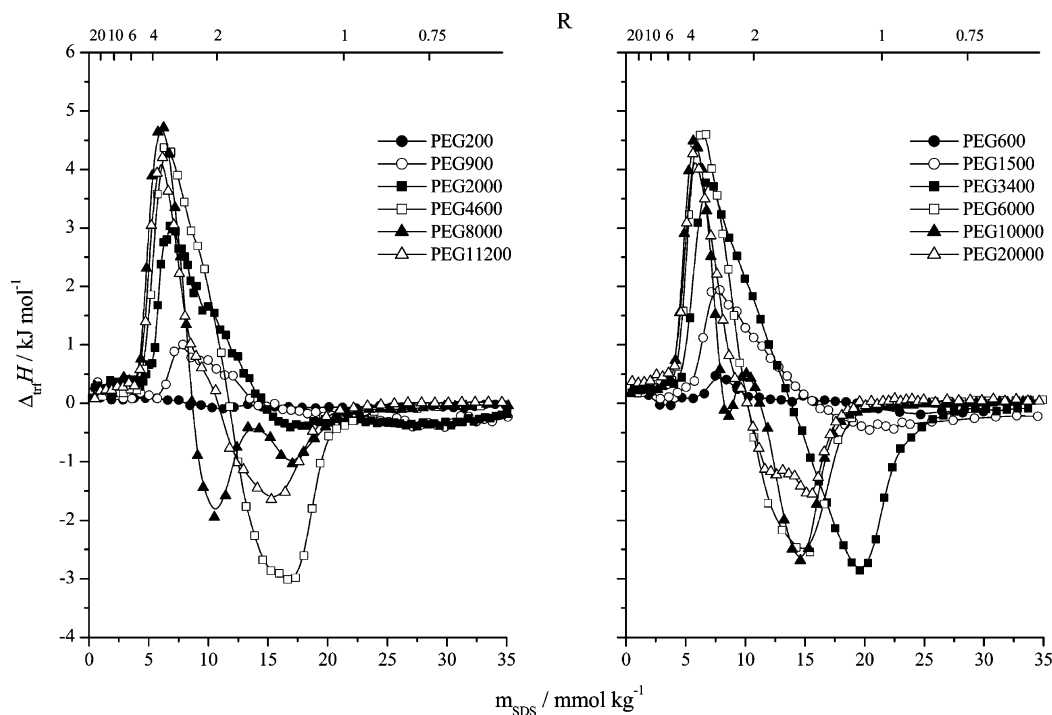
<sup>1</sup>H, <sup>23</sup>Na, and additional <sup>13</sup>C NMR spectra were recorded at 30 °C from D<sub>2</sub>O solutions on a JEOL Eclipse 400 NMR spectrometer operating at 400 MHz for proton, 105.8 MHz for sodium, and 100.5 MHz for carbon. Spectral widths of 2800 Hz over 4096 complex data points for <sup>1</sup>H, of 9000 Hz over 4096 complex data points for <sup>13</sup>C and of 600 Hz over 1024 complex data points for <sup>23</sup>Na were employed. The <sup>1</sup>H and <sup>13</sup>C data were zero filled prior to Fourier transformation. The  $T_1$  of sodium were measured by means of an inversion recovery sequence, using twenty different  $\tau$  intervals.

NOESY spectra were recorded at 25 °C for three D<sub>2</sub>O solutions containing SDS and PEG3400, PEG8000, and PEG20000, respectively. Three spectra were recorded on each sample with 0.5, 1.0, and 1.5 s mixing time, respectively. The FIDs were acquired over 2000 points, with a spectral width of 1500 Hz, 100 scans, and 1 s relaxation delay between transients. 128 experiments were acquired in the second dimension.

In all cases the SDS concentration was chosen such as to sample the range investigated by ITC and the polymer concentration was 0.1% w/w.

## Results

**Isothermal Titration Calorimetry.** Typical enthalpy of dilution ( $\Delta_{\text{dil}}H$ ) curves obtained by adding concentrated aqueous SDS, containing micelles, to water in the presence or absence of some PEG polymer are shown in Figure 1. The figure indicates the critical surfactant concentrations pertinent to polymer-surfactant systems: the critical micellar concentration (cmc) in the absence of the polymer, the critical aggregation concentration (cac or  $T_1$ ), at which the interaction with the polymer begins, and the concentration  $C_2$  (or  $T_2$ ) at which no additional interaction between surfactant and polymer chains is revealed; this condition is often (but not always safely) identified with the saturation concentration where all the polymeric chains have the maximum possible involvement with the surfactant micelles.



**Figure 2.** Enthalpy of transfer ( $\Delta_{\text{tr}}H$ ) of SDS from water to 0.1% PEG (eq 1) as a function of SDS concentration for polymers of different molecular weight. The top abscissa is  $R = m_{\text{EO}}/m_{\text{SDS}}$ .

A further critical concentration,  $C_m$ , might represent the concentration at which free micelles begin to form in the presence of PEG–SDS aggregates. While most experimental techniques can determine the concentrations cmc, cac, and  $C_2$ , an EMF technique was proposed and discussed by Wyn-Jones et al.<sup>25,26</sup> to reveal the possible distinction between  $C_2$  and  $C_m$ . Precise EMF measurements of free SDS concentration in the presence of a hydrophobically modified PEG allowed also to reveal an uncooperative polymer–surfactant interaction well below the cac value.<sup>27,28</sup>

Figure 2 reports the enthalpy of transfer of one mole of SDS from water to 0.1% w/w PEG solutions ( $\Delta_{\text{tr}}H$ ) as a function of SDS concentration, for all polymers examined in this work. The data were obtained by combining dilution enthalpies in water and in water containing PEG:

$$\Delta_{\text{tr}}H(\text{SDS})_{\text{W-PEG}} = \Delta_{\text{dil}}H(\text{SDS})_{\text{PEG}} - \Delta_{\text{dil}}H(\text{SDS})_{\text{W}} \quad (1)$$

The measured enthalpy changes indicate no interaction between SDS and PEG for MW = 200 Dalton. For polymers with MW  $\geq 600$  Dalton, an endothermic effect reveals the well-known polymer–induced micellization process, occurring at a ratio  $R$  of 3 to 4 moles of PEG repeat unit per mole of surfactant ( $R = m_{\text{EO}}/m_{\text{SDS}}$ ). For MW greater than 1500 Dalton the endothermic effect becomes larger and an exothermic effect appears at higher concentrations of SDS ( $R = 1$ –2), before the saturation concentration ( $C_2$ ) is reached. A peculiar effect is noticed for PEG8000, which exhibits clearly two exothermic peaks. Polymers with higher MW also exhibit unusual thermal effects, which range from the two well separated exothermic peaks of PEG10000 to the shoulders of PEG11200 and PEG20000. A few measurements with polymer samples characterized by a very low polydispersity index ( $D < 1.07$ ) did provide results consistent with those of the other samples. Particularly, a standard sample of PEG8300 with  $D = 1.02$  yielded practically the same enthalpy curve as a normally polydispersed sample of PEG8000, thus indicating that the molecular weight distribution has a negligible influence.

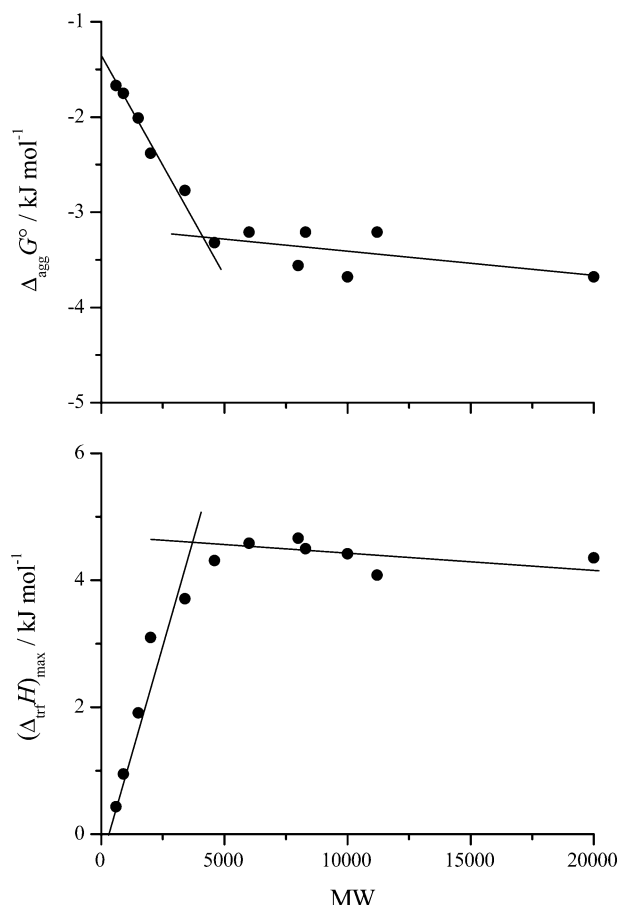
**TABLE 1: Thermodynamic Data Obtained from Calorimetric Titrations of Aqueous PEGs with SDS at 298.15 K**

PEG MW (Dalton)	cac <sup>a</sup> (mmol kg <sup>−1</sup> )	( $\Delta_{\text{tr}}H$ ) <sub>max</sub> <sup>b</sup> (kJ mol <sup>−1</sup> )	$\Delta_{\text{agg}}G^{\text{oc}}$ (kJ mol <sup>−1</sup> )	$C_2^{\text{d}}$ (mmol kg <sup>−1</sup> )	( $\Delta_{\text{agg}}H$ ) <sub>C2</sub> <sup>e</sup> (kJ mol <sup>−1</sup> )
No PEG	8.4 (cmc)				
200	8.4	0	0		
600	6.0	0.43	−1.7		
900	5.9	0.95	−1.8	22	0.18
1500	5.6	1.91	−2.0	42.5	0.19
2000	5.2	3.00	−2.4	41.5	0.16
3400	4.8	3.71	−2.8	23.3	0.11
4600	4.3	4.31	−3.3	20.2	0.00
6000 <sup>f</sup>	4.4	4.58	−3.2	18.4	0.14
8000	4.1	4.66	−3.6	20.8	0.12
8300 <sup>f</sup>	4.3	4.50	−3.3	20.6	0.10
10000	4.0	4.42	−3.7	17.8	0.08
11200 <sup>f</sup>	4.3	4.08	−3.3	19.7	0.16
20000	4.0	4.35	−3.7	17.8	0.34

<sup>a</sup> Uncertainty  $\pm 0.1$  mmol kg<sup>−1</sup>. <sup>b</sup> Calculated from eq 1 in correspondence of the endothermic maximum of the direct ITC titrations.

<sup>c</sup> From eq 2, with  $\alpha = \alpha' = 0$ . <sup>d</sup> Uncertainty  $\pm 0.2$  mmol kg<sup>−1</sup> (except for PEG1500 and PEG2000 where it can be larger). <sup>e</sup> Integral heat of transfer of SDS from micelles to PEG–SDS aggregates at  $C_2$ : obtained from eq 1 using integral dilution heats calculated as the sum of observed heat effects up to  $m_{\text{SDS}} = C_2$ , divided by the total number of SDS moles added at  $C_2$ . <sup>f</sup> Average of  $M_w$  and  $M_n$  values of the low polydispersity commercial samples.

Table 1 lists the values of critical concentrations relevant to the various PEGs, together with an estimate of the enthalpy and free energy of formation of the SDS–PEG aggregates which are first formed at low SDS concentrations. The cmc value of 8.4 mmol kg<sup>−1</sup> is in good agreement with literature values<sup>3</sup>. The cac values are regularly decreasing as the PEG molecular weight is increased, reaching an almost constant value of 4.2 mmol kg<sup>−1</sup> for MWs higher than 4600 Dalton. The enthalpy of transfer of SDS from water to PEG in correspondence of the endothermic maximum ( $\Delta_{\text{tr}}H$ )<sub>max</sub> can be interpreted as a limiting enthalpy of aggregation of SDS micelles on the PEG polymer. On the other hand, according to the pseudo-phase model,<sup>29</sup> the



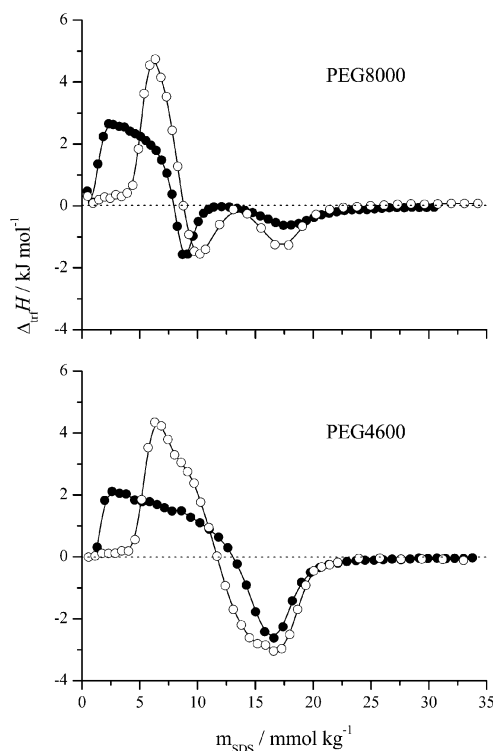
**Figure 3.** Thermodynamic parameters for SDS aggregation on PEG as a function of PEG molecular weight:  $\Delta_{\text{agg}}G^\circ$  and  $(\Delta_{\text{tr}}H)_{\text{max}}$  from Table 1.

free energy of formation of this aggregate, starting from SDS micelles and PEG, can be related to the critical aggregation concentration as

$$\Delta_{\text{agg}}G^\circ(\text{SDS} - \text{PEG}) = RT[(2 - \alpha')\ln \text{cac} - (2 - \alpha)\ln \text{cmc}] \quad (2)$$

where  $\alpha$  and  $\alpha'$  are the ionization degrees of the micelle and the aggregate, respectively. For a simple comparative use among different PEG chains, the  $\Delta_{\text{agg}}G^\circ$  values were calculated under the assumption  $\alpha = \alpha' = 0$ . The values of these thermodynamic properties are plotted in Figure 3 as a function of the molecular weight of the polymers. These curves clearly indicate that at a definite molecular weight the endothermic heat effect as well as the thermodynamic stability of the aggregate reaches its maximum value and then remains nearly constant. These criteria contribute to determine, with a better precision than previously,<sup>5,30–32</sup> the range of PEG chain length that allows SDS-PEG interaction. The trends of the two functions of Figure 3 allow to establish that (i) the minimum MW value at which interaction begins is  $350 \pm 50$  Dalton, i.e., a sequence of about eight repeat units would be the shortest chain capable of generating aggregation of a small micellar cluster; (ii) the endothermic heat effect reaches its maximum value for molecular weights larger than 3800 Dalton, corresponding to a polymeric chain containing almost 90 repeat units.

Values of the integral heats of solution in aqueous PEGs calculated at  $C_2$ , corrected for the solution in pure water, are shown in Table 1. They represent the enthalpies of aggregation per mole of surfactant,  $(\Delta_{\text{agg}}H)_{C_2}$ , of preformed micelles on the



**Figure 4.** Enthalpies of transfer of SDS (eq 1) from water to 0.1% PEG (○) and to 0.1% PEG containing 0.1 M NaCl (●).

PEG chains at the saturation ( $m_{\text{SDS}} = C_2$ ). These data, qualitatively represented by the algebraic sum of the areas of the endo and exo peaks of Figure 2, indicate that the overall interaction enthalpy is small and positive, amounting to about  $0.1$ – $0.2$   $\text{kJ mol}^{-1}$ . This endothermic enthalpy indicates that not only the self-aggregation of surfactant molecules in the presence or absence of PEG but also the aggregation (including possible reorganization) of preformed micelles on the PEG chain is an entropy driven process.

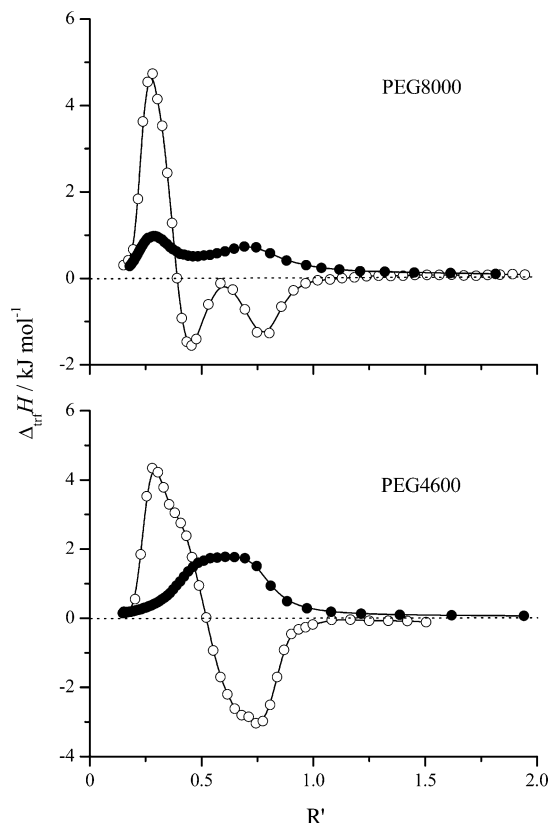
The trend with concentration of the enthalpy of transfer of SDS from water to aqueous PEG observed with polymers with  $\text{MW} > 1500$  (see Figure 2) is probably related to a change of the aggregate structure, attributed by others<sup>5,14</sup> to the dehydration and rehydration of the PEG chain. The peculiar titration curve of PEG8000, however, and those presently obtained for PEG6000, PEG10000, and PEG11200, remain unexplained.

In order to collect more information on PEG-SDS aggregates, we performed different types of titrations, particularly using PEG8000, the polymer exhibiting a double exothermic peak. Titrations performed with increasing concentration of the polymer showed the same trend already noticed for PEG3350,<sup>5</sup> i.e., an almost zero effect on the cac value and a proportional shift toward larger SDS concentrations of the exothermic peaks and the amount of bonded SDS ( $C_2 - \text{cac}$ ).

Figure 4 shows the effect of ionic strength on the enthalpy curves of PEG4600 and PEG8000. Consistent with what was found for larger polymers (see, e.g., ref 1, p 284), the curves obtained in the presence of 0.1 M NaCl indicate a clear decrease of cac and a corresponding shift to lower surfactant concentration of the endothermic peak, while the form of the curve in the exothermic region is practically unchanged.

Figure 5 compares the enthalpies of transfer of SDS from water to aqueous PEG solutions with the corresponding enthalpies of transfer of PEG from water to aqueous SDS solutions. The latter were obtained from reverse titrations in which a concentrated solution of the polymer was added to an SDS

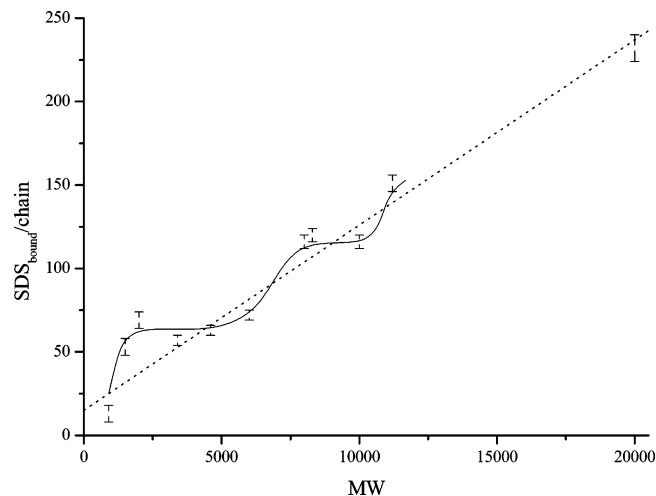




**Figure 5.** Enthalpies of transfer of the titrant from water to the aqueous solution of the other component. Titrant: SDS ( $w \rightarrow 0.1\%$  PEG), direct titration, (○); PEG ( $w \rightarrow 0.0178\text{m}$  SDS), reverse titration (●);  $R' = m_{\text{SDS}}/m_{\text{EO}}$ .

solution containing free micelles. Use of the ratio  $R' = m_{\text{SDS}}/m_{\text{EO}}$  as the common abscissa leads to read the reverse titration from right to left. Titrations of this kind were also extensively performed by Tam et al.<sup>27</sup> for a modified PEG polymer, taking into account also the effect of surfactant concentration. The figure shows that a single endothermic peak is observed with PEG4600. The almost zero effect observed at the beginning of the reverse titration corresponds to the aggregation of preformed micelles on the PEG chains in excess SDS, a process which involves the above-mentioned small average endothermic effect. The curve for PEG8000 presents two endothermic peaks, one falling in the correspondence of the endothermic peak of the direct titration, the second falling between the two exothermic peaks of the latter. This suggests that the latter peaks are in effect the result of the superposition of the exothermic effect following the formation of the first aggregate with a second endothermic–exothermic effect, probably due to the formation of a second aggregate on the same PEG chain. In other words, the peculiar trend of the calorimetric curves exhibited by PEG8000 could be explained by the successive aggregation of two micellar clusters on the same chain. This would be permitted by a chain length about double the one that proved optimal for the aggregation of the first micelle. The formation of multiple micellar aggregates would be also responsible for the peculiar features of the ITC curves of the longer polymers, for instance the second endothermic peak exhibited by the direct enthalpimetric titration of PEG10000 and the small endothermic shoulder exhibited by PEG11200 and PEG20000.

Figure 6 shows the number of SDS molecules bound by a single polymeric chain at saturation as a function of PEG molecular mass. A precise calculation of the amount of surfactant bonded to the polymer would require the direct



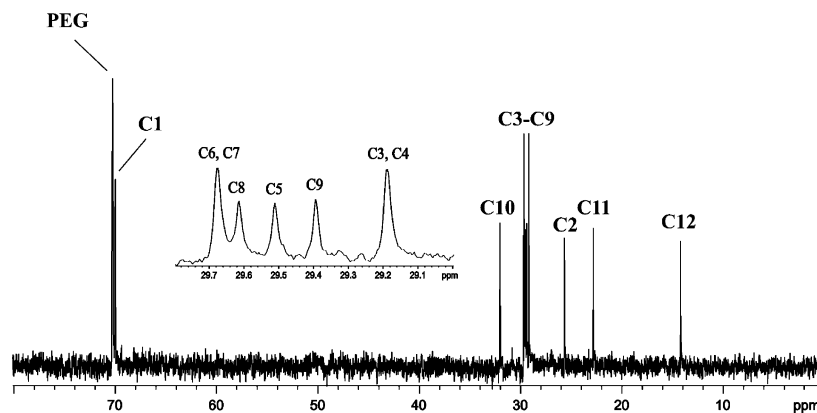
**Figure 6.** Number of SDS molecules bound by a single PEG chain at saturation as a function of PEG molecular weight.  $\text{SDS}_{\text{bound}}/\text{chain} = (C_2 - C^*)/m_p$ , with  $C^* = (\text{cac} + \text{cmc})/2$  and  $m_p$  = molality of the polymer. Vertical bars represent the experimental uncertainties.

determination of free SDS through EMF measurements, as suggested by others.<sup>26,27</sup> Experimental data on the PEG/SDS system indicated that particularly with low molecular weight PEGs the formation of free micelles begins before the saturation of the polymer.<sup>26</sup> The free SDS concentration before  $C_2$  is thus conditioned by the two processes of aggregation on the polymer and micellization: the first one should be accompanied by an increase in the SDS concentration while the second one by a decrease.<sup>26</sup> The result is that in a typical titration the free surfactant concentration changes very slowly from the cac to the cmc value. Data of Figure 6 were calculated assuming for free SDS a value intermediate between the cac and the cmc.

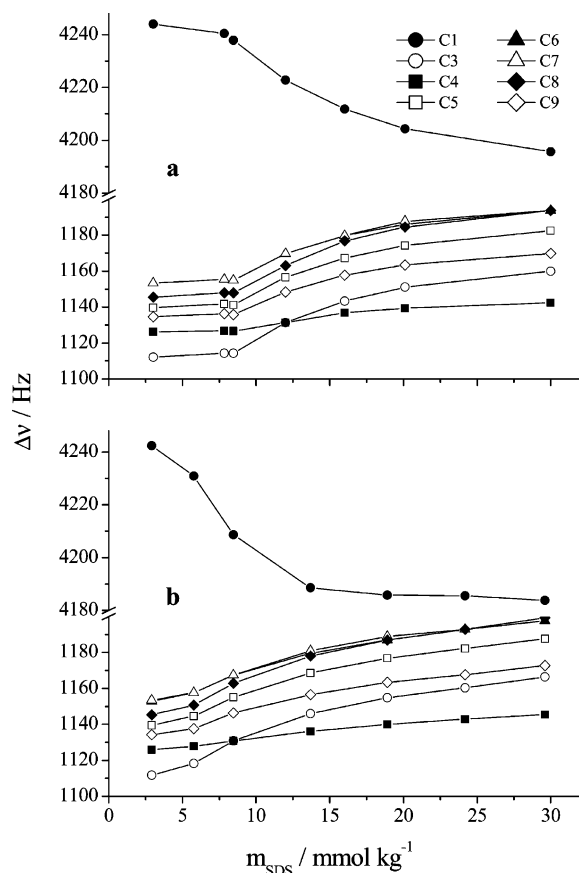
The rate of increase of bound SDS is expected to follow a linear trend for very long polymers, on whose chains the simultaneous aggregation of several micelles at a time takes place. On the contrary, we might expect a smoothed stepwise trend for short polymers, with plateaux occurring when the chain length proves optimal for the aggregation of an integer (small) number of micelles. The data of Figure 6 indicate the departure of the function from a linear trend at low MW values, allowing to identify two plateaux centered in the ranges  $2000 < \text{MW} < 5000$  and  $8000 < \text{MW} < 10000$ , respectively. If one identifies the free SDS concentration with the cac, as is usually assumed, the function of Figure 6 still exhibits these critical plateaux. This observation provides support to the above-postulated stepwise addition of SDS clusters to the PEG chains. The soundness of our choice for the calculation of free SDS is confirmed by the aggregation number of SDS, estimated as 60 molecules per micellar cluster at the polymer saturation ( $\sim 60$  for one micelle at the first plateau,  $\sim 120$  for two of them at the second plateau). A literature survey<sup>33–39</sup> indicates in fact that the aggregates grow from a minimum aggregation number of about 20 up to about 60 at saturation.

**NMR Spectroscopy.** To investigate the structure of the aggregates we pointed our attention to PEG3400, PEG8000, and PEG20000, chosen on the base of the ITC results just presented.

**<sup>13</sup>C Data.** In Figure 7 there is shown as an example the <sup>13</sup>C NMR spectrum of an aqueous SDS solution in the presence of 0.1% PEG3400, with the assignment of the signals to the various surfactant carbons, numbered starting from the carbon nearest to the ionic head. The spectra of the solutions with PEG8000 show a systematically greater line width. The low resolution of these spectra at low SDS concentration prevented us from



**Figure 7.**  $^{13}\text{C}$  NMR spectrum of an aqueous solution of SDS ( $8.5 \text{ mmol kg}^{-1}$ ) and PEG3400 (0.1% w/w). The inset shows the resolution of peaks C3–C9.



**Figure 8.** Frequency shift ( $\Delta\nu = \nu_{\text{Ci}} - \nu_{\text{C12}}$ ) of SDS carbons vs SDS concentration measured at 300 MHz in solution (a) water, (b) 0.1% PEG3400.

resolving all the signals relative to the C3–C9 carbons, which resonate within a narrow range of frequencies, but the signals of carbons C3, C4, C6, and C7 are at the extremes of that range and could always be safely assigned. For both polymers the C12 chemical shift, measured with respect to an instrumental reference, shows practically the same trend as that observed in absence of polymers. For this reason we used the C12 resonance frequency, which is well separated from the other signals, as internal reference.

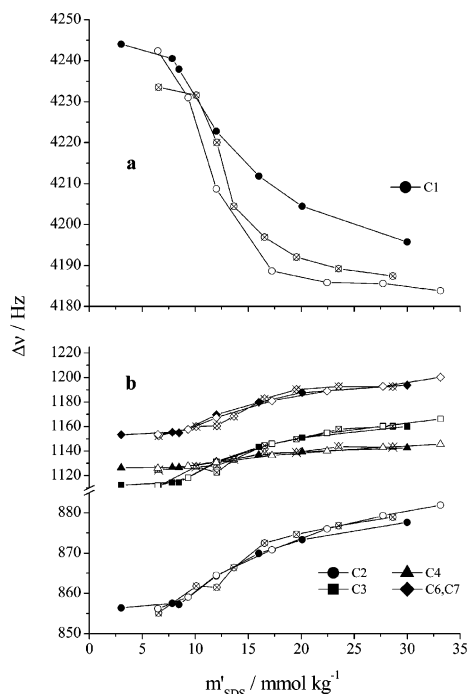
In Figure 8a there are shown the curves of C1 and C3–C9 chemical shifts versus SDS concentration in solutions without polymer. Carbons C2, C10, and C11 show analogous curves. The slope discontinuities of each chemical shift between the third and fourth solution ( $m \sim 8 \text{ mmol kg}^{-1}$ ) are the result of the micellization process. At SDS concentrations exceeding the

cmc, a fraction of surfactant carbon nuclei are inside the micelles where they experience an environment different from that in the aqueous phase. Since the experimental chemical shift of each nucleus is the weighted average of the chemical shifts relative to the different environments experienced, all the carbon chemical shifts steeply change at cmc<sup>21</sup> and continuously vary at higher SDS concentrations. Usually the chemical shift of the carbons of a surfactant tail neatly increase upon micellization both because of the change of the environment from polar to apolar and of the increased amount of trans conformations in the chain.<sup>40</sup> In SDS this happens for all the carbons except C1, the shift of which decreases instead.

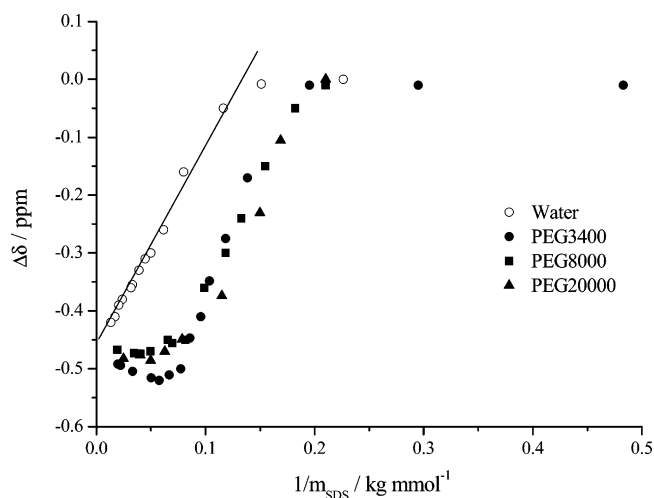
In Figure 8b there are shown the analogous chemical shift curves relative to the SDS solutions containing PEG3400. The presence of the polymer in solution does not modify the trend of the curves, but we can observe that the SDS concentration value for the beginning of the aggregation process can be now located between 3 and 6  $\text{mmol kg}^{-1}$ . The occurrence of the transition in this SDS concentration interval is undoubtedly revealed also by a consistent increase of the line width of the  $^{13}\text{C}$  signal of the polymer. In agreement with the thermograms, this confirms the well-known polymer-induced aggregation of SDS. Like trends with and without polymer seem to reflect a substantial similarity of the aggregation process involving SDS in both solutions.

To facilitate the comparison, in Figure 9 some curves relative to the SDS solutions with PEG3400 and PEG8000 are overlaid to the corresponding ones relative to solutions without polymer. The curves of the PEG3400 solutions were shifted along the concentration axis, to superimpose the data relative to the fourth solution without polymer and the third one with polymer, since they give substantially identical spectra. In this way we obtained a nice matching of all chemical shift trends for the carbons C2–C11 in the two series of solutions (see Figure 9b). Significantly, the applied abscissa shift matches the difference between cmc and cac. An analogous shift was applied to the PEG8000 data.

Figure 9 shows that all carbons of SDS, except C1, exhibit the same chemical shift trend in the three series of solutions. Therefore, all SDS carbon nuclei except C1 substantially experience the same environment in PEG–SDS aggregates as in free SDS micelles. As a matter of fact, if the polymer penetrated into the core of the micelles or if it formed, with SDS, aggregates in which it stayed very near to the hydrocarbon chains, these chains would experience an environment of ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) segments different from that inside the micelles without polymer. Consequently, the experimental chemical shift of the chain carbons should be different in corresponding solutions with and without polymer. Our data



**Figure 9.** Comparison of the frequency shift of some SDS carbons in water (filled symbols), PEG3400 (hollow symbols), and PEG8000 (crossed symbols). The abscissa is defined as  $m'_{\text{SDS}} = m_{\text{SDS}} + k$ , where  $k = 0$  in water and  $k = \text{cmc} - \text{cac}$  in the polymer solutions, to superimpose the values of critical concentrations.



**Figure 10.** Chemical shift change of the SDS C1 carbon measured at 400 MHz in  $\text{D}_2\text{O}$  and 0.1% PEG solutions at 30 °C as a function of reciprocal SDS concentration.

seem to indicate that, at any SDS concentration, the polymers penetrate at most just near C1 and not more deeply into the hydrocarbon core.

The  $^{13}\text{C}$  spectra of SDS/PEG solutions allow to obtain some information from the polymer signals too. The occurrence of the interaction with the surfactant is revealed by a slight decrease of  $^{13}\text{C}$  PEG chemical shift (and an increase of the line width) for small SDS additions, then the shift remains constant, almost independent of SDS concentration. These shifts do not help to discriminate between different models for the PEG–SDS interaction.

We now go on examining in detail the C1 chemical shift trends. Figure 10 reports such shifts against the reciprocal of SDS concentration for data collected at 30 °C, which also include the case of PEG20000. A perfectly analogous trend is

**TABLE 2: Parameters Obtained from  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{23}\text{Na}$  NMR Data on  $\text{D}_2\text{O}$  Solutions Containing SDS and 0.1%w/w PEG at 303 K**

sample	cac (or cmc) <sup>a</sup> (mmol kg <sup>-1</sup> )	$\Delta\delta_{\text{A}}\text{C1}^b$ (ppm)	$\Delta\delta_{\text{A}}\text{C1(H)}^b$ (ppm)	$\Delta\delta_{\text{A}}\text{C2(H)}^b$ (ppm)	$\alpha^c$
SDS	7.6	-0.46	-0.031	0.002	0.37 <sup>d</sup>
SDS + PEG3400	6.1	-0.87	-0.048	-0.011	0.41
SDS + PEG8000	5.2	-0.82	-0.060	-0.012	0.52
SDS + PEG20000	5.2	-0.80	-0.058	-0.013	0.52

<sup>a</sup> Calculated from C1 data using eq 3. <sup>b</sup> Change of chemical shift of the SDS nuclei from monomeric form to aggregate. C1, C1 carbon; C1(H), C1 protons; C2(H), C2 protons. Values obtained by linear regression (eq 3) of the data at low concentration, immediately over the cac. <sup>c</sup> Surfactant ionization degree. <sup>d</sup> Reference 45.

exhibited also by data at 25 °C, collected only for PEG3400 and PEG8000. According to the pseudo-phase model, a linear trend of the function is an indication of an equilibrium between just two species.<sup>41</sup> In effect the value observed for any property  $Y$  averaged between the value in the monomer and that in the aggregate is given by eq 3:

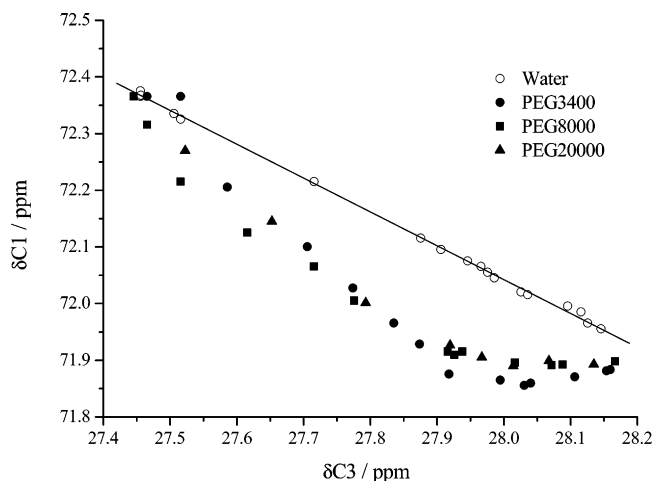
$$\Delta Y_{\text{obs}} = -(\text{cac}/m_{\text{SDS}})\Delta Y_{\text{A}} + \Delta Y_{\text{A}} \quad (3)$$

If the property is the chemical shift,  $\delta$ , here measured relative to a fixed internal reference, then  $\Delta Y_{\text{obs}} = \Delta\delta_{\text{obs}} = \delta_{\text{obs}} - \delta_{\text{monomer}}$  and  $\Delta Y_{\text{A}} = \Delta\delta_{\text{A}}$  is the shift difference between SDS in the aggregate and the monomeric form. This model seems to reasonably fit both the binary SDS/ $\text{D}_2\text{O}$  and the ternary PEG/SDS/ $\text{D}_2\text{O}$  systems at low SDS concentrations and allows to determine the cmc value for the pure SDS, the cac values in the presence of the various PEGs, and the  $\Delta\delta_{\text{A}}$  values. The data reported in Table 2 show that for C1 there is a remarkable difference between the  $\Delta\delta_{\text{A}}$  value of the pure SDS micelles and those of aggregate with various PEGs, the latter on the contrary being almost indistinguishable from one another. The larger negative displacements of the shifts of the C1 carbon in the aggregate could be due to a larger ionic dissociation in the latter (see further) which would allow an enhanced screening effect of this carbon. Values of critical concentrations, cmc and cac, calculated from  $^{13}\text{C}$  NMR spectra can be considered in good agreement with the values from microcalorimetric titrations, since the small differences may be ascribed to the different working temperatures. In effect the two sets of data are very similar, in view of the very small heat of micellization of SDS<sup>42</sup> and of its aggregation on PEG (see above).

The decrease of the C1 chemical shift with increasing SDS concentration above cac is in agreement with the previously mentioned early formation of aggregates (see Figure 10, from right to left). However, upon further increasing  $m_{\text{SDS}}$  in the region of the exothermic effect, the shift of C1 almost remains constant: this indicates that the simple model based on equilibrium between two sites does not fit any longer.

The shift vs shift diagrams<sup>43,44</sup> are further means, very useful for the study of situations in which chemical shift values are the result of an averaging process over various species in equilibrium. They offer the advantage of eliminating the possible error due to concentration uncertainties by relating data pertaining to the same sample. In the case of an equilibrium between only two species, one obtains just a straight line.

For the SDS/ $\text{D}_2\text{O}$  system at concentrations higher than cmc, the plot shift vs shift of any pair of carbon nuclei consists of a straight line, indicating that the SDS exchanges just among two situations: the monomer and the micelle. The plot shift vs shift of the carbon pairs of the hydrocarbon tail (C2–C12) for the PEG/SDS/ $\text{D}_2\text{O}$  systems too give straight lines, which coincide



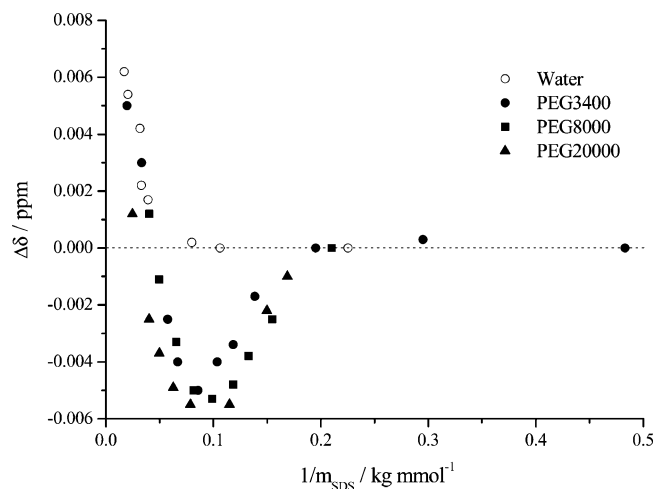
**Figure 11.** Chemical shift of the C1 carbon vs that of the C3 carbon measured at 400 MHz for solutions of SDS in D<sub>2</sub>O and in 0.1% PEG solutions.

with the corresponding ones of the SDS/D<sub>2</sub>O system, again suggesting that the interior of the aggregates with PEG is very similar to the one of the micelles. On the contrary, by plotting the shift of C1 against that of any of the other carbons of the hydrocarbon tail, one obtains a trend that is different from mere micellization. In Figure 11 there are reported the shift diagrams  $\delta C1$  vs  $\delta C3$ , in the absence of polymer and in the presence of 0.1% PEG 3400, 8000, and 20000. The three PEGs exhibit similar trends. Their plots show in the lowest concentration region a descent steeper than for mere micellization, then they become curves, confirming that at higher concentration the aggregation process does not involve just the monomer and a univocally defined structural complex. At still higher surfactant concentration the data points move toward the plot of micellization, in agreement with the formation of pure surfactant micelles after saturation.

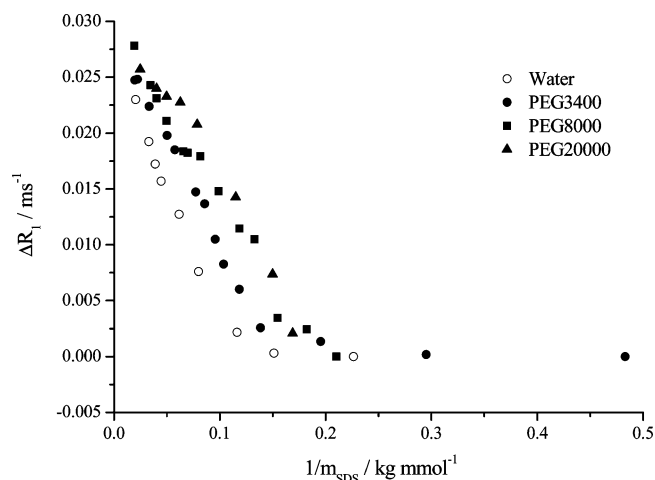
**<sup>1</sup>H Data.** Proton chemical shifts of the surfactant received less attention since they are smaller than <sup>13</sup>C chemical shifts. Moreover, the chain methylenes from C(3)H<sub>2</sub> to C(11)H<sub>2</sub> give rise to an envelope of signals that cannot be resolved. On the other hand, the hydrogens are interesting because, lying on the surface of the molecule, they are suited for monitoring the surroundings.

The protons on C1 practically behave as the corresponding carbon, displaying an upfield shift with aggregation which is stronger in the PEG aggregate than in micelles (see Table 2). Figure 12 shows the trend of the chemical shift of the C2 protons vs reciprocal concentration. It appears peculiar that for these protons micellization causes an increase of shift, while the formation of aggregates with PEG causes an initial decrease and then an increase. The shift decreases in the SDS concentration region where calorimetry evidences the endothermic effect, while the subsequent increase corresponds to the exothermic effect. Thus these data suggest that the evolution of the PEG-SDS aggregate with increasing SDS concentration, evidenced by ITC titrations, implies a modification of the C2 proton surroundings. For surfactant concentrations larger than saturation, the shift becomes nearer to that of micelles.

NOESY spectra were recorded at 25 °C on three samples containing PEG3400, PEG8000, and PEG20000, respectively, together with SDS at a concentration of about 18 mmol kg<sup>-1</sup>. These experiments aimed at evidencing the proximity of polymer H nuclei to SDS nuclei, on the trace of ref 22, where the <sup>1</sup>H nuclei of PEG20000 are found to give cross-peaks with all the SDS protons. On the contrary, we could not detect any



**Figure 12.** Chemical shift change of the protons on C2 carbon of SDS in D<sub>2</sub>O and in 0.1% PEG solutions.



**Figure 13.** Change of the <sup>23</sup>Na longitudinal relaxation rate of SDS in D<sub>2</sub>O and in 0.1% PEG solutions.

PEG/SDS cross-peak for any polymer. Therefore, our NOESY spectra do not support the hypothesis of aggregates where the polymer CH<sub>2</sub> groups are very near to the SDS hydrocarbon chains.

**<sup>23</sup>Na Data.** Micellization causes a sudden decrease of the chemical shift and longitudinal relaxation time (*T*<sub>1</sub>) of sodium. Figure 13 shows the longitudinal relaxation rate (*R*<sub>1</sub> = 1/*T*<sub>1</sub>) as a function of the reciprocal SDS concentration in solutions containing various PEGs. Applying the pseudo-phase model, the  $\Delta Y_A$  quantity of eq 3 is in this case equal to the product  $(1 - \alpha)\Delta R_{1A}$ , with  $\Delta R_{1A}$  representing the relaxation rate difference between sodium ion in the aggregate (either micelle in the case of pure SDS or mixed aggregates in the presence of PEG) and in the bulk solution and  $\alpha$  the aggregate (or micelle) ionization degree of sodium.

Regression analysis of the nearly linear plots of Figure 13 for both the SDS/D<sub>2</sub>O binary and PEG/SDS/D<sub>2</sub>O ternary systems, in addition to yielding values of cmc and cac close to those of Table 2, indicated that the product  $(1 - \alpha)\Delta R_{1A}$  is smaller in the aggregates with polymers than in the pure micelles. This may be attributed to an increase of the ionization degree,  $\alpha$ , rather than to a decrease of  $\Delta R_{1A}$ . It is indeed reasonable to assume that fast motions, which are the most important as far as the longitudinal relaxation is concerned,<sup>20</sup> change very little in different samples. The values of  $\alpha$  reported in Table 2 for the systems in the presence of PEG were obtained



after determining  $\Delta R_{1A}$  for mere SDS micelles using the value  $\alpha = 0.37$  measured from conductivity studies<sup>45</sup> which showed also that the mixed aggregates with PEG have a higher  $\alpha$  value than SDS micelles. We find, in addition, that  $\alpha$  increases on increasing the PEG molecular weight.

In the PEG/SDS/D<sub>2</sub>O systems, upon increasing SDS concentration up to about 10 mmol·kg<sup>-1</sup> a change of the slope of  $\Delta R_{1,obs}$  vs  $1/m_{SDS}$  is observed (see Figure 13). This effect, evident with PEG20000, recalls what was found in the <sup>13</sup>C spectra and would suggest a change of the structure of the PEG–SDS aggregates. On further decreasing  $1/m_{SDS}$ , the <sup>23</sup>Na relaxation rate approaches that of the pure SDS micelles.

## Discussion

The various types of ITC curves presented before strongly indicate that PEGs of various molecular weights interact with SDS micelles via a stepwise mechanism. This implies the aggregation of just one SDS micelle on one polymeric chain for PEGs of MW = 1500–6000 Daltons, of a maximum of two SDS micelles on one chain for PEGs of 8000–10000 Daltons, and so on for heavier polymers, with a presumably smoothed trend. Such a stepwise mechanism had been already observed with larger PEG polymers through neutron scattering<sup>46,47</sup> and was also postulated in an exhaustive thermodynamic model by Nikas and Blanckstein.<sup>48</sup>

The peculiar endothermic–exothermic effects in the ITC titration curves suggest that the SDS micelle–polymer aggregate exothermally modifies with increasing SDS concentration. Conductivity measurements evidenced for the first time a new step between *cac* and saturation<sup>39</sup> at a concentration  $C_1$  that is slightly dependent on polymer content. The author suggested that this could be related to the saturation of the available sites with isolated molecules or micelles of low aggregation number and that, in the region  $C_1$ – $C_2$ , the added SDS molecules partially contribute to increasing the aggregation number of the micelles. As already mentioned, the existence of two different types of aggregates in the aqueous solutions of PEG was already recognized in ref 5. These aggregates, aggregate I corresponding to the ITC endothermic effect and aggregate II corresponding to the exothermic effect, were explained by an initial dehydration of the PEG chain, which would penetrate the micellar cluster binding the surfactant through purely hydrophobic interactions (endo effect), and the subsequent rehydration of the polymer (exo effect), which would associate with the surfactant through ion–dipole interactions.<sup>5</sup>

Among our data, the only NMR parameters that show differences between the without-polymer and the with-polymer solutions are the chemical shifts of C1 and of the C1 and C2 protons and the relaxation rate of <sup>23</sup>Na, i.e., parameters that reflect the structure and behavior of the outer surface of the micelles. This result is compatible with what is reported in ref 21, where PEG 20000 is found to influence the chemical shifts of the first three carbons of the SDS chain. The other NMR data do not evidence differences in the SDS chains or in their surroundings between micelles and polymer–surfactant aggregates in the whole range of the SDS concentrations here considered and for PEGs of different length. We could not find in our data a clear support to the hypothesis of a strong solubilization of the polymer chain in the micellar core advanced by other authors.<sup>22–24</sup> Our data raise also some doubt about the interpretation of the exothermic peak region as mainly due to ion–dipole interactions: the ITC curves for PEG 4600 and PEG 8000 in solutions containing 0.1 m NaCl (see Figure 4) show a major modification of the endothermic peaks, while the

exothermic ones are just shifted to lower SDS concentrations with no change of their trend. Though the increase of ionic strength may induce a plurality of effects (shielding of the electrostatic interaction between surfactant headgroups, increase of the hydrophobicity of the alkyl groups, alteration of the ion–dipole interactions, with consequent change of the size and number of the aggregated micelles), we would have expected a modification of the exothermic peaks where ion–dipole interactions are assumed to prevail.

Nevertheless, the characteristic trends of the above NMR parameters sensitive to the polymer presence fall in the same SDS concentration range where the opposite heat effects are observed, and this certainly points to some evolution of the PEG–SDS aggregate. Such peculiar evolution is also reflected by other properties. For instance, the viscosity of PEG/SDS aqueous solutions with increasing SDS concentration exhibits an initial decrease, in the region of the endo effect, followed by a steady increase.<sup>39,49,50</sup> Very recently a viscosity and SANS study<sup>51</sup> allowed to explain this fact through a contraction of the coiled conformation of the polymer. A compressed PEG coil at low SDS concentration was also evidenced by Cabane<sup>47</sup> and discussed in two theoretical studies which relevantly mention a collapse of the polymer structure in the neighborhood of *cac*. At larger surfactant concentrations an expanded conformation of the polymer would be more stable, as suggested also by a recent study of the dynamic properties of this system.<sup>6</sup> These observations can be explained by the following model, which is also consistent with our ITC and NMR measurements.

PEGs of various molecular weights endothermically interact with SDS before *cmc*, forming polymer–micelle aggregates. By adding SDS the average aggregation number can grow until a maximum value: if the formation process is less endothermic for large aggregates than for small ones, their growing must be exothermic. The initial endothermic effect might be due to an energetically unstable conformation of the polymer when it surrounds small micelles. A theoretical evaluation of the energy difference between *gauche* and *trans* conformation about a C–C skeletal bond of polyoxyethylene amounts to more than 2 kJ mol<sup>-1</sup>.<sup>52</sup> A number of these *gauche* states in a PEG chain, which is forced in a conformation able to stabilize a small SDS cluster, could be quantitatively compatible with the endothermic effect experimentally observed at low SDS content. The subsequent growing of the micelles would allow the polymer to relax toward a less strained conformation, releasing heat. Therefore, the enthalpic curves could be perfectly consistent with initial and final aggregates which do not differ by the substantial nature of the polymer–surfactant interaction (hydrophobic or ion–dipole), but rather by the different conformation of the PEG polymeric chain induced by different SDS aggregation numbers. In any case, the conformational effect here supposed might be only partly responsible for the total heat effect, and the strong PEG–SDS interaction could be accompanied by a partial dehydration of the PEG chain: a recent study of solvation dynamics<sup>53</sup> indicated in fact a restricted movement of the water molecules squeezed between the polymer chains and the micellar SDS surface.

## Conclusions

Isothermal calorimetric data on aqueous SDS solutions in the presence of PEG with increasing chain length allowed to identify MW ~ 350 and MW ~ 3800 as the critical molecular weights of the polymer for the appearance and settling of the interaction with the surfactant, respectively. Evidence was also found for the stepwise aggregation of multiple micelles on PEG polymers with molecular weights larger than about 6000 Daltons.

The variation of  $^{13}\text{C}$  chemical shifts with SDS concentrations recorded for SDS/H<sub>2</sub>O, PEG 3400/SDS/H<sub>2</sub>O, and PEG 8000/SDS/H<sub>2</sub>O did not provide evidence of a change in the environment of the SDS chains due to the presence of polymer, except at the micelle surface. Therefore, any aggregate formed can consist of SDS micelles wrapped by the polymeric chain in accordance with the necklace model.<sup>54</sup> We propose that the endothermic and exothermic effects are due to the formation of aggregates where small clusters of SDS molecules are wrapped by PEG in strained conformation and, respectively, to the release of the strain consequent to the growing of the aggregates. The above explanation seems to be consistent with preliminary ITC measurements performed on the system PEG/cesium perfluorooctanoate/H<sub>2</sub>O.

**Acknowledgment.** The authors are grateful to the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) for financial support (COFIN 2002).

**Note Added in Proof.** After the acceptance of this paper for publication, we came across a paper by Zanette et al. (Zanette, D.; Soldi, V.; Romani, A. P.; Gehlen, M. H. *J. Colloid Interface Sci.* **2002**, *246*, 387) that also attributed the viscosity minimum of PEG solutions at low SDS concentration to a compact structure of the polymeric complex.

## References and Notes

- (1) Goddard, E. D.; *Colloid. Surf.* **1986**, *19*, 255.
- (2) Goddard, E. D.; Ananthapadmanaban, K. P. *Interactions of Surfactants with Polymer and Proteins*; CRC Press: Boca Raton, FL, 1993.
- (3) Jönsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons: New York, 1999.
- (4) Kwak, J. C. T. *Surfactant Science, Series Volume 77: Polymer-Surfactant Systems*; Marcel Dekker: New York, 1998.
- (5) Dai, S.; Tam, K. C. *J. Phys. Chem. B*, **2001**, *105*, 10759.
- (6) Cooper-White, J. J.; Crooks, R. C.; Chockalingam, K.; Boger, D. V. *Ind. Eng. Chem. Res.* **2002**, *41*, 6443.
- (7) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.
- (8) Aucouturier, C.; Roux-Desgranges, G.; Roux, A. H. *J. Therm. Anal.* **1994**, *41*, 1295.
- (9) Ballerat-Busserolles, K.; Roux-Desgranges, G.; Roux, A. H. *Langmuir* **1997**, *13*, 1946.
- (10) Ballerat-Busserolles, K.; Rassinoux, S.; Roux-Desgranges, G.; Roux, A. H. *J. Therm. Anal.* **1998**, *51*, 161.
- (11) Blandamer, M. J.; Cullis, P. M.; Engberts, J. B. F. N. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2261.
- (12) Blandamer, M. J.; Briggs, B.; Cullis, P. M.; Irlam, K. D.; Engberts, J. B. F. N.; Kevelam, J. J. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 259.
- (13) Wang, G.; Olofsson, G. *Pure Appl. Chem.* **1994**, *66*, 527.
- (14) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.
- (15) Du, Y. R.; Zhao, S.; Shen, L. F. *Ann. Reports NMR Spectrosc.* **2002**, *48*, 145.
- (16) Persson, B.-O.; Drakenberg, T.; Lindman, B. *J. Phys. Chem.* **1979**, *83*, 3011.
- (17) Amato, M. E.; Caponetti, E.; Martino Chillura, D.; Pedone, L. *J. Phys. Chem.* **2003**, *107*, 10048.
- (18) Gustavsson, H.; Lindman, B. *J. Am. Chem. Soc.* **1978**, *100*, 4647.
- (19) Gustavsson, H.; Lindman, B. *J. Chem. Soc., Chem. Commun.* **1971**, 93.
- (20) Hedin, N.; Furó, I.; Eriksson, P. O. *J. Phys. Chem. B* **2000**, *104*, 8544.
- (21) Cabane, P. *J. Phys. Chem.* **1977**, *81*, 1639.
- (22) Gjerde, M. I.; Nerdal, W.; Hoiland, H. *J. Colloid Interface Sci.* **1996**, *183*, 288.
- (23) Gao, Z.; Wasylischer, R. E.; Kwak, J. C. T. *J. Phys. Chem.* **1991**, *95*, 462.
- (24) Yuan, H. Z.; Luo, L.; Zhang, L.; Zhao, S.; Mao, S. Z.; Yu, J. Y.; Shen, L. F.; Du, Y. R. *Colloid Polym. Sci.* **2002**, *280*, 479.
- (25) Ghoreishi, S. M.; Li, Y.; Bloor, D. M.; Warr, J.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 4380.
- (26) Ghoreishi, S. M.; Fox, G. A.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 5474.
- (27) Dai, S.; Tam, K. C.; Wyn-Jones, E.; Jenkins, R. D. *J. Phys. Chem. B* **2004**, *108*, 4979.
- (28) Dai, S.; Tam, K. C.; Jenkins, R. D. *J. Phys. Chem. B* **2001**, *105*, 10189.
- (29) Shinoda, K.; Hutchinson, E. *J. Phys. Chem.* **1962**, *66*, 577.
- (30) Schwuger, M. J. *J. Colloid Interface Sci.* **1973**, *43*, 491.
- (31) Tokiwa, F.; Tsujii, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2684.
- (32) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.
- (33) Sasaki, T.; Kushima, K.; Matsuda, K.; Suzuki, H. *Chem. Soc. Jpn.* **1980**, *53*, 1864.
- (34) Zana, R.; Lianos, P.; Long, J. J. *J. Phys. Chem.* **1985**, *89*, 41.
- (35) Van Stam, J.; Almgren, M.; Lindblad, C. *Prog. Colloid Polym. Sci.* **1991**, *84*, 13.
- (36) Painter, D. M.; Bloor, D. M.; Takisawa, N.; Hall, D. G.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2087.
- (37) Zana, R.; Lang, J.; Liamis, P. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1982**, *23*, 39.
- (38) Chary, K. J. *Colloid Interface Sci.* **1992**, *151*, 294.
- (39) Francois, F.; Dayantis, J.; Sabbadin, J. *Eur. Polym. J.* **1985**, *21*, 165.
- (40) Shimizu, S.; Pires, P. A. R.; Fish, H.; Halstead, T. K.; El Seoud, O. A. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3489.
- (41) Douhéret, G.; Viallard, A. J. *Phys. Chim.* **1981**, *78*, 85.
- (42) Woolley, E. M.; Burchfield, T. E. *J. Phys. Chem.* **1984**, *88*, 2155.
- (43) Leibfritz, D.; Haupt, E.; Dubischar, N.; Lachmann, H.; Oekonomopulos, R.; Jung, G. *Tetrahedron*, **1982**, *38*, 2165.
- (44) Polster, J.; Lachmann, H. *Spectrometric Titrations*, VCH: Weinheim, 1989.
- (45) Witte, F. M.; Engberts, J. B. F. N. *J. Org. Chem.* **1987**, *52*, 4767.
- (46) Cabane, B.; Duplessix, R. *J. Physique*, **1982**, *43*, 1529.
- (47) Cabane, B.; Duplessix, R. *Colloids Surf.* **1985**, *13*, 19.
- (48) Nikas, Y. J.; Blankschtein, D. *Langmuir* **1994**, *10*, 3512.
- (49) Prud'homme, R. K.; Uhl, J. T. *Soc. Pet. Eng. J.* **1984**, *24*, 431.
- (50) Mya, K. Y.; Jamieson, A. M.; Sirivat, A. *Langmuir* **2000**, *16*, 6131.
- (51) Chari, K.; Kowalczyk, J.; Lal, J. *J. Phys. Chem. B*, **2004**, *108*, 2857.
- (52) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley & Sons: New York, 1969; p 165.
- (53) Dutta, P.; Sen, S.; Mukherjee, S.; Bhattacharyya, K. *Chem. Phys. Lett.* **2002**, *359*, 15.
- (54) Nagarajan, N.; Kalpakci, B. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1982**, *23*, 41.