

# Polymer–surfactant interactions: Thermodynamics of some polypropylene glycols in sodium dodecylsulfate aqueous solutions at 298.15 K. Comparison with cationic CTAB aqueous solutions

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Received 28th February 2001, Accepted 22nd May 2001

First published as an Advance Article on the web 20th June 2001

Interactions between poly(propylene) glycols and sodium dodecylsulfate, in aqueous solutions were investigated through thermodynamic analysis. Densities and heat capacities, measured with the corresponding well-known Picker apparatus, were determined as a function of the surfactant concentration at 298.15 K. The apparent and transfer molar volumes and heat capacities of the solutes, surfactant and polymer, were deduced therefrom. From the analysis of their variations as a function of the surfactant concentration, it was shown that mainly strong hydrophobic interactions are involved between solutes, similar to the medium chain ( $C_4$ – $C_6$ ) 1-alcohols in equivalent surfactant systems. However, the large variations of these properties observed close to the critical micellar concentration signify profound structural changes in micelles caused by the presence of the polymer. Comparison with hexadecyltrimethyl ammonium bromide solutions shows a similar pattern of aggregation and complex formation although the strength and nature of the interactions are somewhat different.

## Introduction

Interactions between ionic surfactants and neutral water soluble polymers have been extensively studied on a fundamental level. The polymer–surfactant systems offer numerous potential applications in industrial processes (*e.g.* foaming, floating). The formulation of a variety of systems can be easily obtained in relation to the wide range of surfactants and polymers of different nature and/or structure, yielding a diversity of interactions. Moreover, variations in composition and temperature also induce structural changes, thus offering a large diversity in physical behaviour able to fit the required needs for practical applications.

Most of the studies have dealt with systems formed with anionic surfactants because stronger interactions were generally observed. The sodium dodecylsulfate/poly(ethylene)glycol systems have been widely investigated with different techniques and numerous works can be found in the literature.<sup>1–8</sup> These studies show that with the longer polymers (when the molar masses are greater than 4000), well characterized complexes are formed, resulting in the binding of small micelles onto the polymer chains until saturation is attained. The nature of the interactions leading to such structures is not clearly established. Even though hydrophobic interactions play a major role, polar attractive interactions in the aqueous palisade layer also contribute to the binding.

We have been engaged in the thermodynamic studies of surfactant–polymer solutions to characterize the nature of the different interactions involved in these systems depending on the nature of solutes, surfactants or polymers. Although few studies have been devoted to their thermodynamic properties, these quantities often provide quantitative information;<sup>9,10</sup> more specifically, apparent molar volumes and heat capacities are well suited to exhibit structural changes occurring in the micellar solutions in relation to the different interactions.

In this work, we have focussed our attention on the behaviour of solutions containing sodium dodecylsulfate (SDS) and

poly(propylene)glycols (PPO). These polyethers are more hydrophobic than poly(ethylene)glycols (PEG) and their lower aqueous solubilities limit their study to the low molar mass polymers (up to  $1000 \text{ g mol}^{-1}$ ). Due to the presence of the branched  $\text{CH}_3$  group on the ethoxyl chain, along with the increased number of monomer units, they interact strongly with SDS. It was shown that the aggregation of SDS monomers occurs at lower concentration than the critical micellar concentration (c.m.c.) in water, and that the aggregates contain only a few monomers and are more ionized than normal micelles.<sup>11–15</sup> With an increase in the surfactant concentration, the aggregation number of bound micelles increases while concomitantly free micelles are formed in the aqueous phase. However, due to the limited length of the polymer chains, well-defined complexes SDS/PPO were not as clearly characterized as in the case of PEGs.<sup>5</sup> Even if a pseudo-saturation concentration of the polymer can be obtained by calorimetric titration<sup>10,14</sup> or by conductimetry,<sup>12,15</sup> PPOs still interact with SDS, and the formation of mixed micelles was presumed. The densities and heat capacities obtained at 298 K, in the aqueous SDS systems with the three PPOs (425, 725, 1000) give an insight into the micellization of the surfactant and the role of the chain length of the polymer.

## Experimental

### Materials

Sodium dodecylsulfate (SDS) was a pure grade reagent (greater than 99%) from Merck and was used without further purification after drying at 323 K for several days. The polypropylene glycols (PPO) were purchased from Aldrich and were also used as received. Only the low molecular weight compounds (PPO 425, PPO 725, PPO 1000) were studied. The solubility in water of the polymers of higher masses was too low to allow accurate measurements.

All solutions were prepared by weight with deionized water that was degassed prior to use.

### Equipment

The densities of the solutions ( $\rho$ ) were measured with a vibrating tube densimeter (model SODEV 03D) operating at low flow rate. The calibration constant was regularly checked using water and vacuum. The temperature was maintained constant at 298.15 K within 0.005 K, which ensured in the present experimental conditions a sensitivity better than  $3 \times 10^{-6} \text{ g cm}^{-3}$ .

Volumetric heat capacities ( $\sigma$ ) were determined using a Picker flow microcalorimeter (Setaram) based on the thermal balance principle, operating at a flow rate of  $0.01 \text{ cm}^3 \text{ s}^{-1}$ . The average temperature of 298.15 K was maintained constant within 0.005 K. At these conditions the sensitivity was  $10^{-4} \text{ J K}^{-1} \text{ cm}^{-3}$ . The procedures and calibrations are well documented in the literature.<sup>16–17</sup> The specific heat capacities ( $c_p$ ) were determined from the differences in volumetric heat capacities using the corresponding densities of the solution and the reference solvent through the relation:

$$c_p = c_{p,r} \left( 1 + \frac{\sigma - \sigma_r}{\sigma_r} \right) \frac{\rho_r}{\rho} \quad (1)$$

where subscript r denotes the property of the reference solvent.

Properties of ternary solutions were always measured against the corresponding binary solution. For binary solutions, the reference solvent was water, while for ternary solutions, the reference binary solution could be either the polymer solution or the surfactant solution at the corresponding fixed concentration.

### Thermodynamic properties

The apparent molar volumes ( $V_{\phi,i}$ ) and heat capacities ( $C_{\phi,i}$ ) of the selected solute in the binary or ternary solutions were calculated from experimental densities ( $\rho$ ) and specific heat capacities ( $c_p$ ) using the following relations:

$$V_{\phi,i} = \frac{M_i}{\rho} - \frac{1000(\rho - \rho_r)}{m_i \rho \rho_r} \quad (2)$$

$$C_{\phi,i} = M_i c_p + \frac{1000(c_p - c_{pr})}{m_i} \quad (3)$$

where  $M_i$  and  $m_i$  are respectively the molar mass and the molality of the solute in the binary solution (water + the other solute).

In ternary solutions, the measurements were carried out following different procedures. When the polymer is taken as the solute, its molality is kept constant and small, while the concentration of SDS in the binary reference solution is varied. In this case the variations of apparent properties of the PPOs as a function of the concentration of surfactant are found. Conversely, when the surfactant is considered as the solute, the apparent properties of SDS are determined as a function of its concentration in binary aqueous polymer solutions at a fixed concentration of PPO. The deduced transfer quantities ( $\Delta Y_i$ ) from water to binary solutions, relative to a solute taken at the same concentration in both solutions, clearly show the effect of the solute on the structure of the solution:

$$\Delta Y_i = Y_{\phi,i}(\text{bin sol}) - Y_{\phi,i}(\text{water}) \quad (4)$$

When the PPO is taken at a sufficiently low molality (the minimum allowing sufficient accuracy and precision for the determination in the case of differential measurements), the solute–solute interactions could be neglected and the solute–solvent interactions characterize the distribution of the solute between the micelles and the aqueous phase. Therefore the

evolution of the structure on a wide domain of surfactant concentration is found. When SDS is transferred from water to a polymer solution, the transfer properties of SDS clearly show the effect of the PPO on the micellar structure, especially when a transition occurs, like micellization.

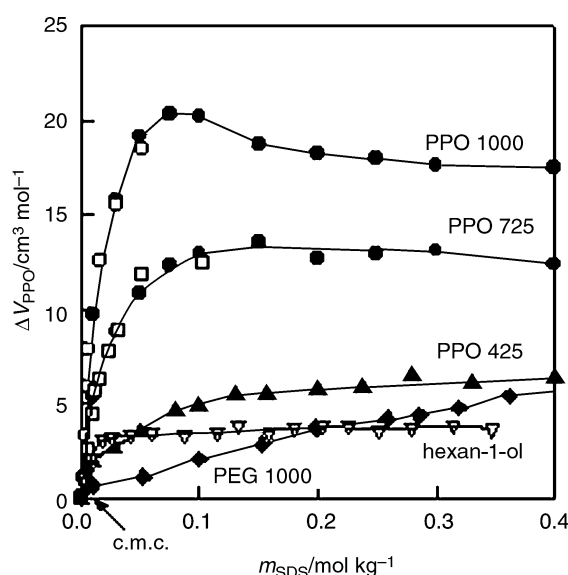
## Results and discussion

The apparent properties of SDS were determined directly in polymer solutions at fixed composition (2% by weight), in the dilute domain close to the c.m.c. of SDS. In parallel, the apparent properties of the different PPO were determined at 2% by weight in micellar solutions of SDS over a large range of surfactant concentration. An equivalent concentration expressed in weight for the different PPOs corresponds to a nearly constant molality in repeated unit monomers for all the solutions. Naturally, whatever the experimental procedure, for a given ternary solution the apparent molar properties ( $V_{\phi,i}$  and  $C_{\phi,i}$ ) of the two solutes can be calculated together, using the same relations but taking into account the change of molalities of the solutes as imposed by the change of the reference solvent. Depending on the concentration of SDS, the accuracy on the transfer properties is related to the measurement procedure.<sup>18</sup>

### Transfer properties of PPO in SDS aqueous solutions

The experimental differences in densities and volumetric heat capacities between the ternary and the corresponding binary (water + SDS) solutions and the deduced apparent molar volumes and heat capacities of the three PPOs (425, 725, 1000) as functions of the concentration of SDS, are given in Table 1. The resulting transfer quantities of the PPOs between water and the SDS solutions are shown, respectively, in Fig. 1 for volumes and in Fig. 2 for heat capacities. The values represented by the filled symbols are obtained for solutions with (water + SDS) as solvent, and the open symbols are from measurements of the properties of SDS in PPO solutions. These yield a more precise analysis in the very dilute region. A fairly good agreement is observed between the two series.

As usual, with small organic molecules where the predominant interactions are governed by the hydrophobic–hydrophilic balance, positive transfer volumes and negative transfer heat capacities are observed above the c.m.c. Initially,  $\Delta V_{\text{PPO}}$  increases rapidly close to the c.m.c. and then tends to a

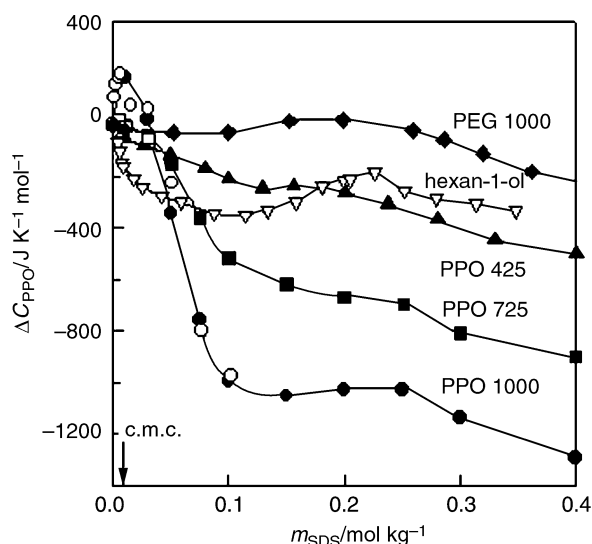


**Fig. 1** Transfer molar volumes of PPO 425, 725 and 1000 at 2% w/w from water to SDS aqueous solutions, as a function of the surfactant concentration. Comparison with hexan-1-ol<sup>19</sup> (0.05 mol kg<sup>-1</sup>) and PEG1000<sup>20</sup> (0.05 mol kg<sup>-1</sup>).

**Table 1** Apparent molar volumes and heat capacities of PPO (425, 725, 1000) in SDS aqueous solutions at 298.15 K

$m_{\text{SDS}}/\text{mol kg}^{-1}$	$m_{\text{PPO}}/\text{mol kg}^{-1}$	$10^6 \Delta\rho/\text{g cm}^{-3}$	$V_{\phi, \text{PPO}}/\text{cm}^3 \text{mol}^{-1}$	$10^3 \Delta\sigma/\sigma$	$C_{\phi, \text{PPO}}/\text{J K}^{-1} \text{mol}^{-1}$
<b>PPO 425</b>					
0	0.050 02	1707	391.26	-0.541	1584.3
0.005 02	0.050 10	1671	391.85	-0.766	1567.8
0.010 01	0.050 00	1604	393.18	-1.28	1529.1
0.027 35	0.050 61	1572	393.97	-1.59	1504.4
0.050 04	0.050 01	1497	394.81	-2.00	1467.0
0.079 97	0.049 88	1423	395.83	-2.60	1415.1
0.099 99	0.049 33	1380	396.13	-3.02	1374.9
0.1299	0.050 00	1347	396.76	-3.49	1336.6
0.1559	0.049 41	1315	396.75	-3.26	1348.2
0.1999	0.049 96	1290	396.97	-3.53	1322.2
0.2380	0.050 04	1259	397.15	-4.05	1275.5
0.2801	0.049 98	1199	397.79	-4.72	1218.1
0.3298	0.049 98	1187	397.42	-5.62	1138.2
0.4000	0.049 67	1127	397.63	-6.14	1087.2
<b>PPO 725</b>					
0	0.029 97	1834	664.37	-0.500	2697.3
0.009 99	0.030 00	1668	669.80	-0.676	2694.5
0.029 97	0.030 00	1555	673.17	-1.01	2654.7
0.049 99	0.030 00	1480	675.25	-1.79	2547.2
0.075 08	0.029 99	1420	676.68	-3.26	2337.5
0.1000	0.030 00	1386	677.25	-4.35	2180.1
0.1500	0.029 99	1331	677.95	-5.01	2077.8
0.1997	0.030 00	1324	677.09	-5.28	2026.2
0.2503	0.029 97	1283	677.31	-5.40	1999.9
0.2999	0.029 98	1246	677.49	-6.17	1887.2
0.3994	0.029 93	1205	676.76	-6.69	1796.9
<b>PPO 1000</b>					
0	0.019 80	1696	915.24	-0.130	3785.8
0.009 99	0.020 00	1515	924.94	0.544	3969.2
0.029 97	0.020 00	1384	930.97	-0.290	3807.2
0.049 99	0.019 99	1303	934.40	-2.04	3442.7
0.075 08	0.019 99	1263	935.62	-3.97	3029.6
0.1000	0.019 96	1249	935.42	-5.06	2789.9
0.1500	0.019 99	1247	934.02	-5.23	2733.9
0.1997	0.020 00	1228	933.48	-5.04	2757.7
0.2503	0.019 99	1201	933.28	-4.97	2755.8
0.2999	0.020 00	1180	932.88	-5.43	2648.5
0.3994	0.020 00	1127	932.73	-6.10	2491.4

quite constant plateau, and the value is more positive as the PPO molar mass increases. For PPO 1000, a slight maximum after the c.m.c. is observed, as in the case of medium chain 1-alcohols in some surfactant solutions.<sup>21,22</sup> The variations of  $\Delta C_{\text{PPO}}$  show a more irregular profile. The classical decrease



**Fig. 2** Transfer molar heat capacities of PPO 425, 725 and 1000 at 2% w/w from water to SDS aqueous solutions, as a function of the surfactant concentration. Comparison with hexan-1-ol<sup>19</sup> (0.05 mol kg<sup>-1</sup>) and PEG1000<sup>20</sup> (0.05 mol kg<sup>-1</sup>).

observed at the c.m.c. is preceded by a small maximum more pronounced with the longer PPO. Also, the large negative values are dependent on the molar mass of the polymer. In the micellar region an almost constant plateau is observed and above 0.2 m  $\Delta C_{\text{PPO}}$  decreases slowly again.

The profiles and magnitudes of the transfer quantities of PPO with changing surfactant concentration can be compared with other parent polymers like polyethylene glycols (PEG)<sup>20</sup> or with 1-alcohols<sup>19</sup> in SDS solutions. Contrary to PEGs, which are soluble in water over a wide range of molecular masses and over a large temperature domain, the PPOs of low molecular masses, like medium chain length 1-alcohols, are only slightly soluble in water. As a consequence the distribution of these solutes between the aqueous phase and the micelles is largely affected by their solubility in water. In Fig. 1 and 2 the transfer properties of hexan-1-ol and PEG 1000 in SDS solutions have been reported to emphasize their differences. The profiles of PPO transfer quantities show similarities with those of alcohols such as hexan-1-ol. This reveals the affinity of PPO for organic media due to the strong hydrophobic interactions between propylene units and the hydrocarbon chain of the surfactant. In contrast, with PEG the variations are more regular with SDS concentration and the values of  $\Delta V_{\text{PEG}}$  or  $\Delta C_{\text{PEG}}$  are much smaller even with the larger polymers, demonstrating that the hydrophilic interactions are predominant.

Structural changes in micellar solutions, as expressed by the variations of the transfer quantities of PPO, are revealed in a magnified way when a transition occurs. The transfer quantities are the result of the various contributions dealing with

the displacements of the different chemical equilibria existing in the solution (*i.e.*, surfactant association and distribution of the solute) with the addition of solute or with temperature change. In the case of micellization, thermodynamic models, like the mass action law and partition model developed by Desnoyers *et al.*,<sup>23–25</sup> have been used to reasonably predict the observed trends in the presence of a solute. The addition of an amphiphilic solute favors the aggregation of the surfactant and is accompanied by an enhancement of the micellar phase that is more pronounced with the hydrophobic character of the solute. It is expressed by a marked increase of the apparent or transfer volume preceding the plateau. In the case of transfer heat capacity the characteristic decrease can be followed by a minimum in the case of the more hydrophobic solutes.<sup>25</sup> With heat capacities near the c.m.c., the shape may be somewhat more varied because the model predicts that a maximum could appear preceding the minimum. In fact, the two equilibria, the micellization of surfactant and the partition of the solute, are also affected by the temperature change, and a supplementary term exists for the equilibrium shifts for second derivatives of free energy, like heat capacities. This maximum, observed at the c.m.c. on  $\Delta C_{\text{PPO}}$  curves, is more pronounced with the more hydrophobic PPO 1000, whereas it has disappeared with PPO 425 where the aqueous solubility is much larger.

### Apparent and transfer properties of SDS in PPO solutions

The aggregation behaviour of SDS in polymer solutions is revealed through the variations of the transfer molar volumes and heat capacities of SDS from water to aqueous PPO solutions. Experimental values of densities and heat capacities, obtained for aqueous solutions of PPO 725 and PPO 1000 at 2% weight, together with the deduced apparent quantities, are reported in Table 2. The apparent volumes of SDS in solutions of PPOs (open symbols) and water are given *vs.* surfactant concentration in Fig. 3(a) together with those calculated from the first series of Table 1 (filled symbols). The deduced transfer volumes,  $\Delta V_{\text{SDS}}$ , are plotted in Fig. 3(b) as functions of the molality of SDS.

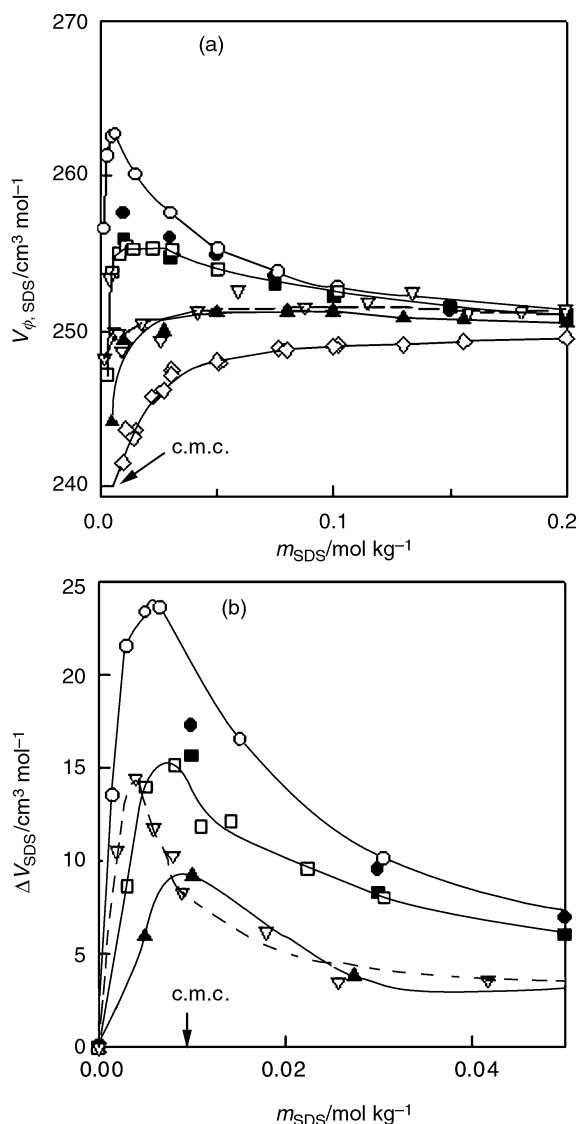
In aqueous solution, the apparent volume of SDS increases sharply at the c.m.c. and tends to an almost constant value in the micellar domain. In polymer aqueous solutions, the appar-

ent volumes go through a more pronounced maximum with the longer PPO chain. Namely, the narrow peak present at the c.m.c. on the transfer volumes curves (Fig. 3(b)), corresponds to an increase in volume of about  $25 \text{ cm}^3 \text{ mol}^{-1}$  in the case of PPO 1000. After this maximum,  $\Delta V_{\text{SDS}}$  decreases and levels off to a slightly positive value of about  $0.8 \text{ cm}^3 \text{ mol}^{-1}$  in the micellar domain with all the PPOs. This value expresses the contribution to the volumes of the hydrophobic SDS–PPO interactions inducing a partial dehydration of the surfactant in micelles. The maximum in transfer volumes is characteristic of the displacements associated with the different equilibria present near a structural transition as mentioned previously. The more hydrophobic PPO 1000 interacts strongly with SDS and thus affects to a large extent the aggregation of the surfactant, while the shorter PPO 425, partially soluble in water, is partitioned between the aqueous and the micellar phase and so is not altering the micelle structure as much. Some comparison is made with pentan-1-ol ( $m = 0.09 \text{ mol kg}^{-1}$ ) in Fig. 3. Although the general behaviour of the alcohol on  $\Delta V_{\text{SDS}}$  is quite similar to PPOs, a narrower peak is observed, located at a lower concentration than PPOs. This trend is related to the more hydrophobic character of the methylene group in the chain of the alcohol compared to the isopropoxyl unit of PPOs.

The apparent and transfer heat capacities of SDS in the different PPO solutions are given in Fig. 4(a) and (b) respectively. With PPO 1000, close to the c.m.c., the apparent heat capacity attains very high values, leading to a sharp positive peak for  $\Delta C_{\text{SDS}}$ . Compared to pure water the following decrease with concentration is more rapid and the apparent heat capacities are smaller, reaching a minimum near  $0.1 \text{ mol kg}^{-1}$ . Conversely, with PPO 425, the apparent heat capacities are always less than the values in water and  $\Delta C_{\text{SDS}}$  shows a broad minimum. The equilibrium shift terms cause a positive contribution to the transfer heat capacity. In the case of PPO 1000 they counterbalance to a large extent the negative contribution of the hydrophobic SDS–PPO interactions. With PPO 725, the transfer heat capacity remains close to zero, showing the attenuation of the equilibrium displacement terms. With PPO 425, the hydrophobic interactions prevail over the displacement terms yielding negative transfer heat capacity, even close to the c.m.c. In the micellar domain, beyond the more or less pronounced minimum, the transfer heat capac-

**Table 2** Apparent molar volumes and heat capacities of SDS in PPO (725, 1000) aqueous solutions at 298.15 K

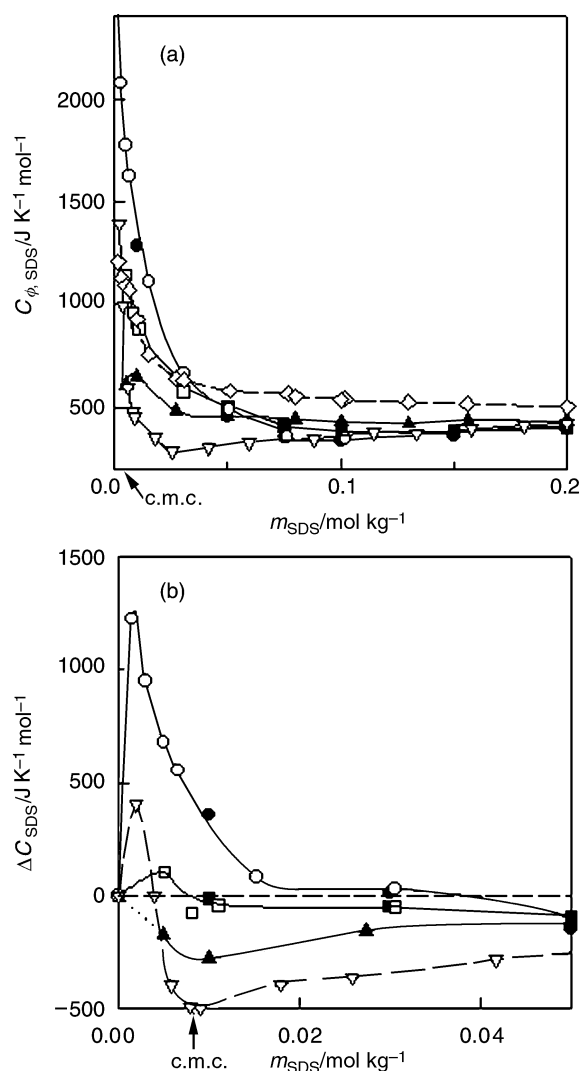
$m_{\text{SDS}}/\text{mol kg}^{-1}$	$10^6 \Delta\rho/\text{g cm}^{-3}$	$\rho/\text{g cm}^{-3}$	$V_{\phi, \text{SDS}}/\text{cm}^3 \text{ mol}^{-1}$	$10^3 \Delta\sigma/\sigma$	$c_p/\text{J K}^{-1} \text{ g}^{-1}$	$C_{\phi, \text{SDS}}/\text{J K}^{-1} \text{ mol}^{-1}$
PPO 1000 ( $m = 0.02000 \text{ mol kg}^{-1}$ )						
0	0	0.998 765		0	4.1710	
0.001 495	48	0.998 813	256.54	0.480	4.1728	2427.4
0.002 996	82	0.998 847	261.28	0.698	4.1736	2074.7
0.004 928	129	0.998 894	262.46	0.792	4.1738	1771.8
0.006 501	169	0.998 934	262.63	0.820	4.1737	1625.1
0.014 96	426	0.999 191	260.08	0.089	4.1696	1112.2
0.030 00	925	0.999 690	257.59	−2.42	4.1550	664.5
0.049 84	1645	1.000 41	255.23	−7.39	4.1358	486.4
0.075 00	2568	1.001 333	253.76	−12.4	4.1087	354.5
0.999 93	3499	1.002 264	252.75	−16.5	4.0878	346.3
0.2000	7113	1.005 883	251.30	−28.8	4.0220	414.8
PPO 725 ( $m = 0.02756 \text{ mol kg}^{-1}$ )						
0	0	0.998 741		0	4.1701	
0.003 018	125	0.998 866	247.17			
0.005 001	174	0.998 915	253.82	0.103	4.1698	1144.5
0.007 999	269	0.999 010	254.96	−0.196	4.1682	959.5
0.010 00	331	0.999 072	255.48	−0.435	4.1669	882.7
0.013 97	465	0.999 206	255.26			
0.021 97	728	0.999 469	255.34			
0.029 99	996	0.999 737	255.19	−3.48	4.1515	574.7
0.049 89	1707	1.000 448	254.01			
0.099 97	3522	1.002 263	252.53			



**Fig. 3** Apparent molar volumes (a) and transfer molar volumes (b) of SDS in different PPO aqueous solutions at 2% w/w, as a function of the SDS concentration;  $\blacktriangle$ , PPO 425;  $\blacksquare$ , PPO 725;  $\bullet$ ,  $\circ$  PPO 1000;  $\nabla$ , pentan-1-ol<sup>19</sup> (0.09 mol kg<sup>-1</sup>);  $\diamond$ , water.

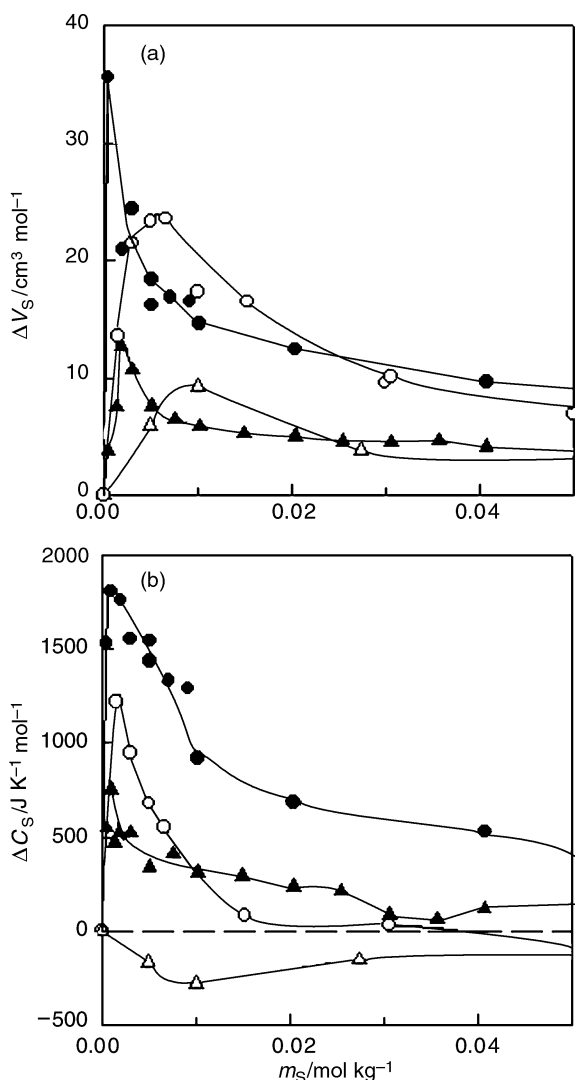
ities tend to an almost constant value of about  $-80 \text{ J K}^{-1} \text{ mol}^{-1}$  independently of the PPO's molecular mass. As for volumes, this value characterizes the intensity of the surfactant-polymer interactions in the micellar region. The comparison of PPO behaviour is made with pentan-1-ol in Fig. 4. Obviously similar variations occur at the c.m.c.: a narrow positive peak is followed by a negative minimum before a slightly negative plateau is progressively attained. This variation is typical of the compromise between the hydrophilic and the hydrophobic character of pentan-1-ol showing the different contributions of equilibrium displacements. In the case of PPO 1000, the prominent positive peak is enlarged to a broader domain of SDS concentration and the minimum is attained at higher SDS molality. In the micellar domain PPO 425 and pentan-1-ol appear to behave similarly.

Although predominant hydrophobic interactions are involved between surfactants and polymers (or other amphiphilic solutes), the association process of the surfactant is dependent on the nature of these solutes. When comparing alcohols and polymers, a different pattern of micellar organization is observed. The amphiphilic alcohols interact with surfactant monomers favouring mixed aggregation: they are inserted into the micelle core within the surfactant hydrocarbon chains, the polar head being preferentially in the aqueous



**Fig. 4** Apparent molar heat capacities (a) and transfer molar heat capacities (b) of SDS in PPO aqueous solutions at 2% w/w, as a function of SDS concentration;  $\blacktriangle$ , PPO 425;  $\blacksquare$ , PPO 725;  $\bullet$ ,  $\circ$  PPO 1000;  $\Delta$ , pentan-1-ol<sup>19</sup> (0.09 mol kg<sup>-1</sup>);  $\diamond$ , water.

palisade layer. The repulsive interactions between ionic charges of the surfactant polar heads are screened, promoting the aggregation of nearly normal micelles. The longer the alcohol chain, the lower the c.m.c. When increasing surfactant concentration, the aggregation number is slightly increased and mixed micelles are formed.<sup>26</sup> With polymers, the hydrophobic character and the length of the polymer chain lead to different structures of the polymer-surfactant complex. The more hydrophilic PEGs of low molar masses are only adsorbed in the aqueous micelle layer, slightly affecting micellar size as do most of the small polar solutes.<sup>20</sup> Conversely, longer PEG polymers start binding to SDS at a common critical aggregation concentration below the c.m.c.: small micelles are adsorbed on the polymer chains until saturation to give stable stoichiometric surfactant-polymer complexes well characterized by different techniques; when SDS is in excess then free normal micelles are present.<sup>3-8</sup> With PPO polymers, the branched  $-\text{CH}_3$  groups on the repeated ether units which induce a more compact structure in water as disk coils,<sup>27</sup> enhance the hydrophobic character of the chain and yield a lower water solubility. Strong interactions exist between PPO chains and SDS monomers and compete with SDS-SDS interactions. So even well below the c.m.c., the aggregation of SDS starts as ionized entities of a few monomers tightly bind on the PPO chains.<sup>11,13</sup> With the increase of SDS concentration these small bound aggregates grow until a critical



**Fig. 5** Comparison of transfer volumes (a) and heat capacities (b) of SDS and CTAB, from water to PPO aqueous solutions, as a function of the surfactant concentration. CTAB: ▲, PPO 425; ●, PPO 1000; SDS: △, PPO 425; ○, PPO 1000.

concentration is reached, characteristic of the saturation of the polymer,<sup>14</sup> as suggested by Rodenas and Sierra using conductometric and fluorescence analysis.<sup>15</sup> Owing to the few PO units in PPO chains, the considered structural model is that between these two critical concentrations, two competitive aggregation processes occur simultaneously: the formation of aggregates of SDS on PPO chains, and the formation of free micelles in solution. Above the concentration of the polymer saturation, the free micelles with normal aggregation numbers are able to incorporate PPO molecules. The hydrophobic chains are inserted between the hydrocarbon chains of SDS while the terminal hydrophilic groups remain at the aqueous interface, characteristic of the formation of mixed micelles.<sup>15,28</sup> In the case of PPO 1000, which is long enough to partially wrap around micelles, it is proposed that, when the polymer chains are saturated, the SDS-PPO complexes are formed with about three polymer chains bound to a micelle.<sup>13-15</sup> The shorter PPO 425, more soluble in water, does not alter the micellar structure to a large extent, and then behaves more like a medium chain alcohol.

The transfer volumes and heat capacities of SDS in aqueous solutions of the different PPOs show the extent of the PPO-SDS interactions. The maximum observed around the c.m.c. is enlarged on a wide domain of SDS concentration, expressing not only the displacement of micellization and partition equilibria as in the case of alcohol, but also the changes

in micellar structure along with the formation of small aggregates of SDS on PPO chains varying in size with the SDS concentration until mixed micelles are formed.

### Comparison with the cationic surfactant CTAB

In a previous work,<sup>29</sup> we presented some results concerning the interactions of PPOs with a cationic surfactant—hexadecyltrimethyl ammonium bromide (CTAB). To show the role of the nature of the polar head, the transfer volumes and heat capacities of SDS and CTAB from water to the same PPO solutions are reported in Fig. 5(a) and (b), respectively. In spite of the difference in c.m.c. between these two surfactants ( $8 \times 10^{-3}$  and  $9 \times 10^{-4}$  mol kg<sup>-1</sup> respectively for SDS and CTAB), the similar typical large variations are observed close to their c.m.c., pointing out the important structural changes occurring in micellar structure when a hydrophobic polymer is present. Moreover, it emphasizes that interactions involving the ionic polar heads seem not to be significant and are masked by the strong hydrophobic interactions between surfactant hydrocarbon chains and the hydrophobic parts of the PPO chains. They are promoting simultaneously the aggregation of the surfactant and the formation of a complex between surfactant and polymer. Similar conclusions have been drawn using conductometric measurements<sup>30</sup> and fluorescence analysis.<sup>31</sup> A more refined inspection of the  $\Delta V$  or  $\Delta C$  variations of surfactants in PPO solutions suggests that stronger interactions may occur with CTAB: the positive peaks are much more pronounced and the decrease toward a constant value, characteristic of a stable micellar domain, is enlarged over a broader surfactant concentration. Even with PPO 425, a relatively prominent positive contribution in  $\Delta C$  is noticed with CTAB, while it is absent in SDS solutions.

Generally it was assumed that no or only weak interactions occurred in cationic surfactant solutions in the presence of neutral water soluble polymers, in contrast to the case of anionic surfactants, in part due to the bulky polar heads and unfavorable ionic charge of CTAB.<sup>32</sup> However, with the more hydrophobic PPO polymers, significant structural changes also occur in cationic micellar solutions. On the whole, it can be concluded that similar patterns of aggregation and complex formation of CTAB and SDS with polymers occur; major differences are essentially in aggregation numbers, critical concentrations of association or polymer saturation.

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