

THERMODYNAMIC STUDY OF POLYETHYLENE-GLYCOLS IN MICELLAR SOLUTIONS WATER+SODIUM DODECYLSULFATE

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Abstract

Interactions of a series of polyethyleneglycols (PEG) in aqueous micellar solutions of sodium dodecylsulfate (SDS) were investigated through thermodynamic properties. Volumes, heat capacities and enthalpies of dilution were measured at 25°C. The resulting transfer properties of PEG are reflecting hydrophobic interactions which increase with the polymer length and the hydrophilic interactions occurring in the aqueous polar layer of the micelles. Typically heat capacities clearly evidence various structural changes taking place in the micellar solutions.

Keywords: enthalpies, heat capacities, polyethyleneglycols, sodium dodecylsulfate, surfactant-polymer interactions, volumes

Introduction

Aqueous micellar solutions containing hydrosoluble polymers offer interesting properties in relation with the resulting viscosity increase of solutions and with cosurfactant character of such polymers. In many applications or industrial processes polymers are used as additives: emulsifiers for treatment of hydrocarbon pollution, oil enhanced recovery, lubricant formulations, vehicles in cosmetics and pharmacology are typical examples. In such complex systems the variations of parameters, as temperature, pressure and composition, modify the relative influence of molecular interactions and induce structural changes leading to changes in the mechanical or physical properties. To improve the efficiency of these systems, much attention must be paid to the nature of the interactions between surfactants and polymers. Investigation of thermodynamic properties is useful to provide quantitative information on the perturbation of interactions; in this respect, volumes, heat capacities and enthalpies are properties sensitive to structural rearrangements.

In order to investigate surfactant – polymer interactions, the systems water – SDS (sodium dodecylsulfate) – PEG (polyethyleneglycols) were selected. The

properties of SDS aqueous solutions had been investigated and structural changes were evidenced [1–4]. PEG,s are non ionic hydrosoluble polymers which can be obtained rather pure. Moreover they are available on a large range of molar masses allowing the study of the influence of chain length when the weak hydrophobicity of ether groups are competing with the strong hydrophilic character of terminal OH groups.

Aqueous solutions of SDS + PEG have been the subject of extensive investigations by different techniques [5] essentially in the vicinity of the CMC and at low polymer concentrations [6]. However, no satisfactory model has been proposed to describe the interactions between SDS and PEG [7].

We present here results at 25°C on volumes, heat capacities and enthalpies of transfer of a series of PEG, from water to micellar solutions, over a range of SDS concentrations, the aim is to evidence specific interactions and induced structural changes in the medium.

Experimental

Materials

SDS was provided by Merck Lab with a purity superior to 99%. The different PEG,s 300, 400, 600, 1 000, 2 000, 3 400 and 10 000 were purchased from Aldrich. A given PEG is identified by the number corresponding to its mean molar mass. The chemicals were used without further purification. Solutions were prepared by weight with deionized, distilled water degassed prior to use.

Densities, ρ , were measured with a Picker vibrating tube densimeter and heat capacities, c_p , were determined in the same conditions with a Setaram Picker flow microcalorimeter. For both apparatuses, procedures and accuracies are well documented in the literature [8, 9]. Enthalpies of dilution were obtained with a LKB differential flow calorimeter (type 2107–121), equipped with Gilson HPLC pumps, according to the procedures described previously [10]. For all the techniques, operational procedures, data collection and data treatment are computer controlled.

Methods

The thermodynamic properties of transfer (ΔY_i) of a solute i from water to aqueous micellar solutions are defined from apparent molar quantities ($Y_{\phi,i}$) using the relation:

$$\Delta Y_i(\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{SDS}) = Y_{\phi,i}(\text{H}_2\text{O} + \text{SDS}) - Y_{\phi,i}(\text{H}_2\text{O}) \quad (1)$$

where the solute concentration of i (PEG in our case) is kept low and constant in both water and mixed solvent.

The apparent molar volumes and heat capacities of PEG,s are calculated from densities ρ and heat capacities c_p , using the well known relations:

$$V_{\phi, \text{PEG}} = \frac{M_{\text{PEG}}}{\rho} - \frac{10^3(\rho - \rho_o)}{m_{\text{PEG}}\rho\rho_o} \quad (2)$$

$$C_{p\phi, \text{PEG}} = M_{\text{PEG}}c_p + \frac{10^3(c_p - c_{p_o})}{m_{\text{PEG}}} \quad (3)$$

where M_{PEG} is the mean molar mass and m_{PEG} the molality of PEG in the solution, ρ_o and c_{p_o} refer respectively to density and specific heat capacity of the solvent (water or binary water+SDS).

The apparent molar relative enthalpies of dilution (L_{ϕ}) cannot be deduced directly from experiments since the measured enthalpies of dilution refer always to the difference between an initial and a final state where the molality of solute varies from m_i to m_f . Thus, L_{ϕ} is defined through the following equation

$$\Delta H_{\text{dil}}(m_i \rightarrow m_f) = L_{\phi, \text{PEG}}(m_f) - L_{\phi, \text{PEG}}(m_i) \quad (4)$$

where the variation of $L_{\phi}(m)$ is represented by a McMillan Meyer development, L_{ϕ}^0 , the value at infinite dilution being conventionally equal to 0. Treatment of experimental results has been presented elsewhere [10].

Results and discussion

Transfer molar volumes

Volumes of transfer of the different PEG,s studied are given in Fig. 1. They are positive and increase regularly with the SDS concentration and no peculiar variation showing a possible structural rearrangement of the medium is observed. Furthermore, transfer volumes become more positive with the augmentation of the number of ethoxy groups in the PEG chain. Interactions of PEG with SDS micelles are favored when the hydrophobic character of the polymer is increased. This behavior is similar to that observed with 1-alkanols of increasing chain length when transferred from water to SDS solutions [11].

Transfer molar heat capacities

Apparent molar heat capacities, as a second derivative of G , are properties by far more sensitive than volumes to structural changes occurring in solutions.

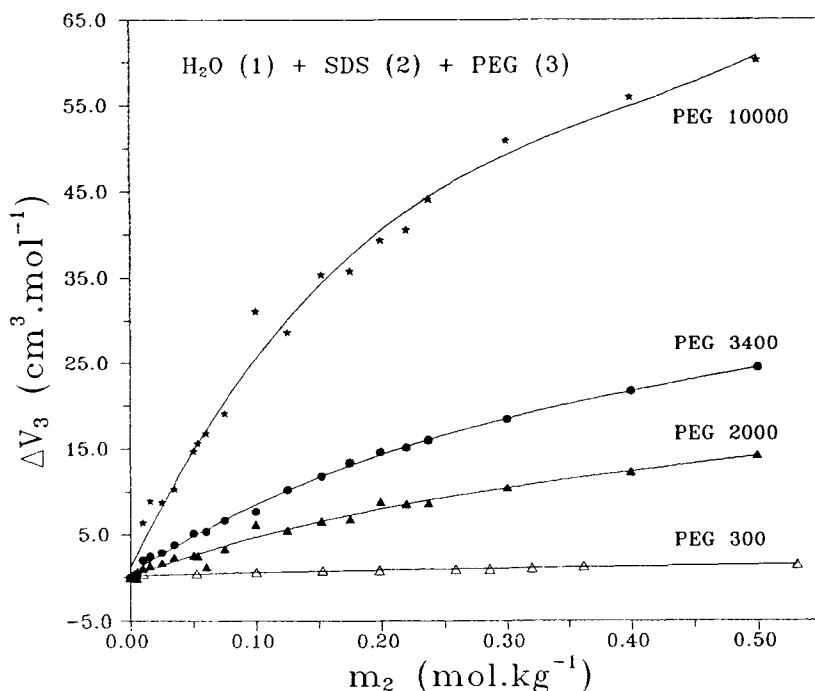


Fig. 1 Variation of the molar volumes of transfer of several PEG,s vs. the SDS concentration

Thus, the variations of the transfer heat capacities of the same series of PEG in SDS solutions, shown in Fig. 2 for short chain PEG,s and in Fig. 3 for the long chain PEG,s appear more complex.

In the case of PEG,s 300, 600, 1 000, at the molality of 0.05 *m* (Fig. 2), the variations of transfer heat capacities of such oligomers are similar to those obtained with alcohols [11]. After the CMC (0.008 *m*), the initial decrease is related to the distribution of solute between micelles and aqueous phase. The maximum which exists around 0.2 *m* has been generally observed with heat capacities when transferring ionic [12] as well as non electrolytes solutes [11]. It has been attributed to a micellar shape transition from spherical to cylindrical micelles. Thus, it appears that PEG,s are also sensitive to this structural change of SDS micellar solutions. However, some differences are observed in comparison with alcohols. In the domain comprised between the CMC and the (0.2 *m*)-transition, the ΔC_p for the different PEG,s are practically identical, as well as the magnitude of the hump. The long chain alcohols are solubilized in the micellar interior leading to larger variations of ΔC_p , while the PEG,s, more hydrophilic and longer molecules, remain essentially adsorbed in the aqueous polar phase of micelles and so are less affected by structural modifications of

micelles. In addition, beyond the transition the $\Delta C_{p,s}$ are more negative, the longer the PEG,s. This might be explained by the existence of more favorable interactions of PEG with micelles due to an increase of surface adsorption when micelles are cylindrical.

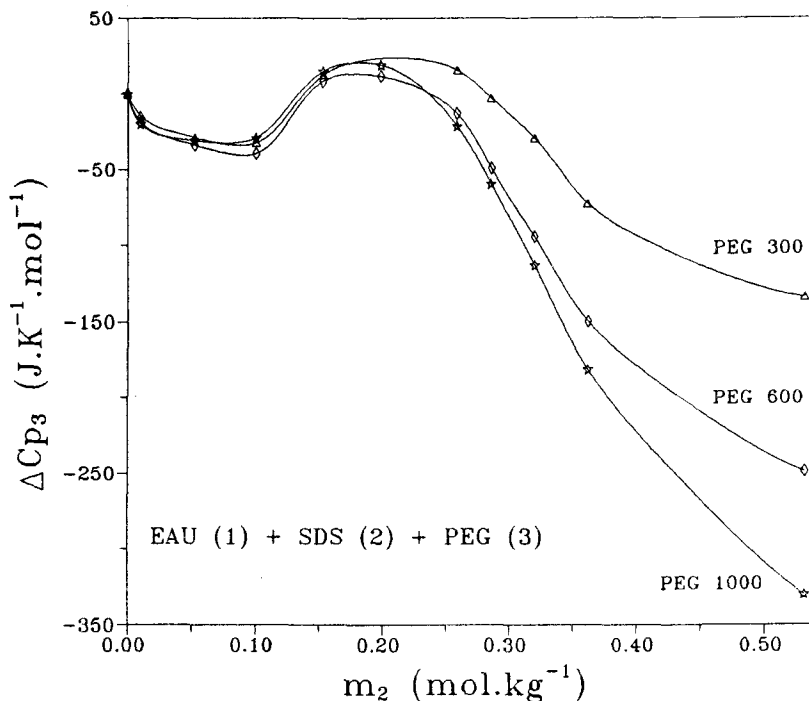


Fig. 2 Variation of the molar heat capacities of transfer of the small PEG,s (300, 600, 1 000) vs. the SDS concentration

For the longest PEG,s (2 000, 3 400 and 10 000), considered as polymers, (at the transferred concentration of about 5% in mass), the general tendencies observed in Fig. 3 are similar but effects are more marked especially after the micellar (0.2 m)-transition. The ΔC_p decreases are very important accounting for stronger interactions between micelles and polymer chains. Effectively, the relative increase of the hydrophobic character of the polymer with chain lengthening, in connection with the cylindrical micellar shape, leads to a larger area of adsorption for PEG. In the dilute domain, before 0.2 m in SDS, the $\Delta C_{p,s}$ for these polymers vary in a non regular manner as it is pointed out in the enlargement in Fig. 3. The maximum related to the shape transition is shifted toward lower SDS concentrations with increasing PEG molar masses. It means that the longer polymer chains would favor the formation of cylindrical micelles. Moreover, a minimum appears near the CMC (more marked with PEG 10000) fol-

lowed by an other one at 0.04 *m* and a maximum near 0.08 *m* in SDS. These extrema are more pronounced with the longest PEG. They can certainly be connected with small changes undergone by micelles. As a matter of fact, previous works have shown the existence of structural modifications beyond the CMC: for example the results of Yasunaga *et al.* [2] based on conductivity, viscosity and speed of sound are referred to a '2nd CMC' around 0.04–0.07 *m*. Also Kim *et al.* [3] using fluorescence measurements have proposed the existence of a transition at 0.07 *m*. Likewise, both Roux-Desgranges *et al.* [12] from the study of salt transfer and Oh *et al.* [4] from measurements of bubble sizes have suggested the existence of a micellar change close to 0.05 *m*. Nevertheless, the different authors agree to relate these changes to variations of the micelle ionicity. As micelles are adsorbed on polymer chains, in the aqueous polar layer, the counterions (Na^+) can interact with negative polar heads of the surfactant but also with oxygens of ethoxy groups of the polymer. Heat capacity being a sensitive property to the variation of the number of bound counterions [13], ΔC_p of PEG would reflect ionicity changes of micelles, the longer is the polymer, the stronger are the interactions SDS-PEG in the aqueous polar micellar layers.

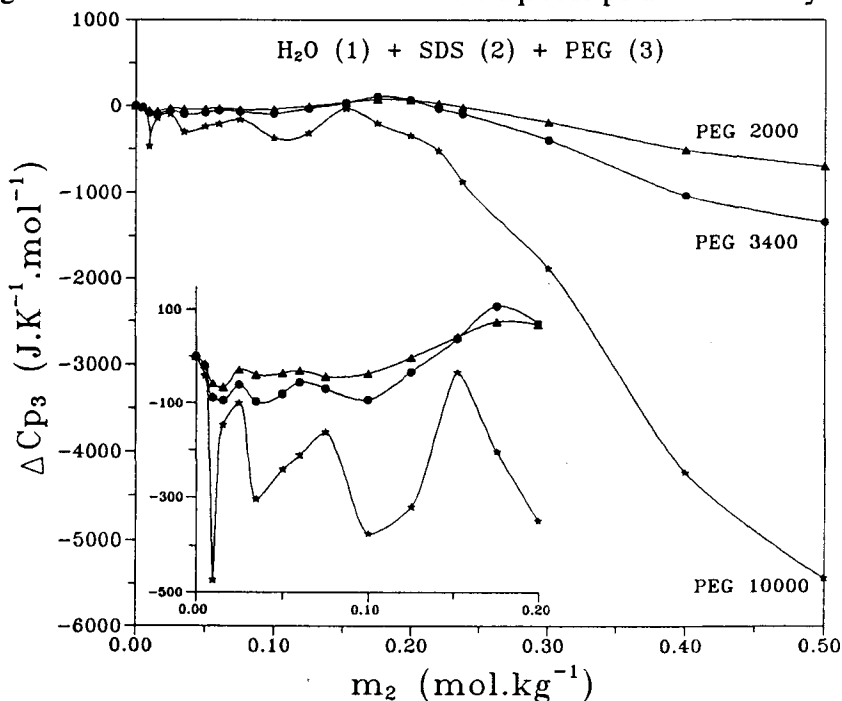


Fig. 3 Variation of the molar heat capacities of transfer of the longest PEGs (2 000, 3 400, 10 000) vs. the SDS concentration

Transfer relative molar enthalpies of dilution

The variations of ΔL , the relative molar dilution enthalpies of transfer, for the series of PEG studied are reported in Fig. 4 vs. the SDS molality. They look relatively complex and dependent on the length of the PEG. For the short PEG,s (300 and 400) ΔL is slightly increasing, whereas with the others, enthalpies decrease initially with a more negative slope and the following minimum is more pronounced, shifted toward higher SDS concentrations, when the PEG chain becomes longer. This behaviour is certainly a consequence of the relative augmentation of the hydrophobic character of PEG with chain lengthening and stronger interactions between micelles and PEG.

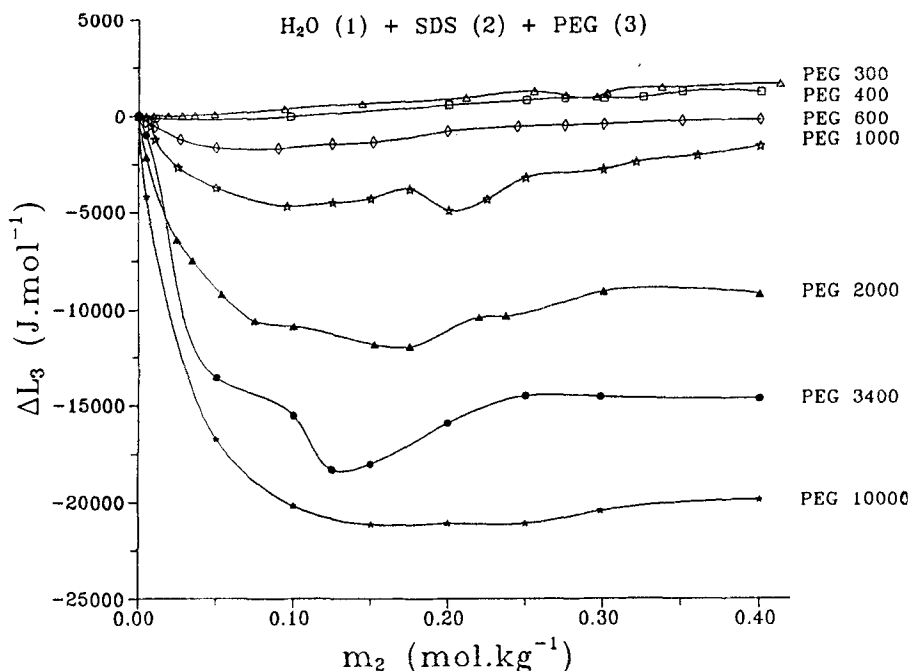


Fig. 4 Variation of the transfer relative molar enthalpies of dilution for the series of PEG,s studied vs. the SDS concentration

The observed small increase of ΔL after the minimum is the result of the compensation of the negative contribution of SDS-PEG hydrophobic interactions and of positive contribution of ionic interactions of counterions with polar heads and of ion dipole interactions with ethoxy groups of the polymer. It can also be noticed on the variation of ΔL the existence of a shallow minimum displaced toward lower SDS molalities with the increased chain length of the PEG. The transition of micellar shape is probably responsible for this perturbation.

But, since enthalpies are mostly sensitive to ionic interactions, the small energetic effect associated to this change is partially masked and then structural changes are not clearly evidenced with enthalpies.

Schematic representation of SDS-PEG interactions

The different results of the thermodynamic investigations of PEG in micellar solutions allow to propose a scheme for the interaction of micelles with long-chain PEG,s as represented in Fig. 5, according to the works of Cabane *et al.* [14] and Xia *et al.* [7]. The flexible long chain of the polymer could wrap around micelles which would adapted their shape to insure a larger surface contact. With the longest PEG,s several micelles could be bound to the polymer chain leading to a 'necklace' structure.

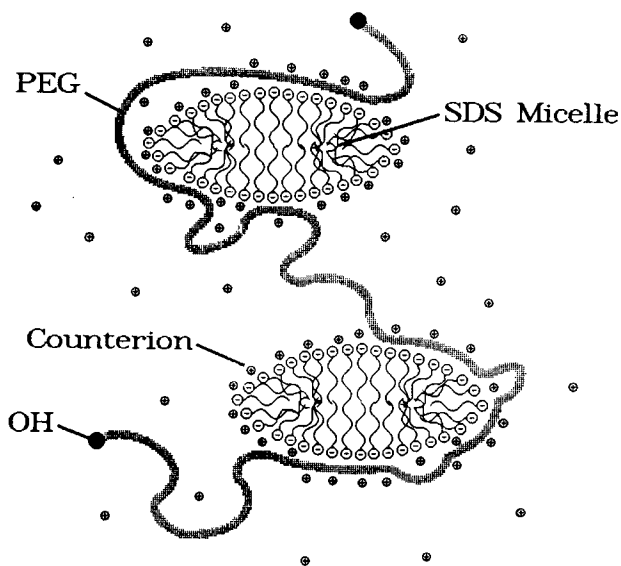


Fig. 5 Schematic representation of PEG macromolecules bound to SDS micelles

Adsorption of PEG on SDS micelles is essentially taking place in the polar micellar aqueous layer. The weak hydrophobic character of PEG associated to the hydrophilic end chain OH-group prevents from a deep penetration of ethoxy groups into the micellar interior, and hydrophobic interactions of the PEG methylene units occur at the organic-aqueous interface in the micelles. Moreover, the electrostatic interactions of polar head groups of SDS with ether oxygen of PEG contribute to the binding of PEG with SDS. As suggested by Dubin *et al.* [15] the counterions present in the aqueous layer play certainly a role in these electrostatic interactions.

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Zusammenfassung — Anhand thermodynamischer Eigenschaften wurden die Wechselwirkungen einer Reihe von Polyethylenglykolen (PEG) in wäßrigen mizellaren Lösungen von Natriumdodecylsulfat (SDS) untersucht. Bei 25°C wurden das Volumen, die Wärmekapazität und die Lösungsenthalpie bestimmt. Die resultierenden Transporteigenschaften von PEG spiegeln hydrophobe Wechselwirkungen wieder, die mit Polymerlänge zunehmen und hydrophile Wechselwirkungen, die in der wäßrigen Schicht der Mizellen stattfinden. Wie üblich zeugen Wärmekapazitäten von verschiedenen Strukturveränderungen, die in mizellaren Lösungen vorstatten gehen.