

THERMODYNAMIC PROPERTIES OF CTAB IN AQUEOUS SOLUTIONS OF NEUTRAL POLYMERS AT 25°C

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Abstract

Interactions of polyethylene glycols (PEGs) and polypropylene glycols (PPOs) in aqueous solutions of hexadecyltrimethylammonium bromide (CTAB) were investigated through thermodynamic properties at 25°C. The densities and heat capacities of the solutions were measured with a vibrating tube densimeter and a Picker flow microcalorimeter, respectively. The variations in the apparent molar volumes and heat capacities of both solutes, calculated from the densities and heat capacities of the solutions, are unusually large in the vicinity of the CMC, reflecting the existence of very strong interactions between CTAB and PPOs. With the more hydrophilic polymers, PEGs, the apparent properties of CTAB are less affected by the presence of the polymer, indicating that PEGs interact only weakly with CTAB.

Keywords: heat capacities, hexadecyltrimethylammonium bromide, molar volumes, polyethylene glycols, polypropylene glycols, surfactant-polymer interactions

Introduction

Aqueous micellar solutions containing water-soluble polymers have interesting properties, as illustrated by their numerous applications in industrial processes. In such complicated systems, small changes in variables such as composition or temperature (even pressure) would induce deep structural changes in the solution, expressed by large variations in mechanical or physical properties. Depending on the subsequent applications, it is of the greatest importance to select the nature and the composition of the systems appropriately. In particular, in order to improve the efficiency of these systems, much attention must be paid to the nature of the interactions between surfactants and polymers. In this respect, the investigation of thermodynamic properties provides quantitative information on these interactions, together with their dependence on the nature and concentration of the components and on temperature.

Most previous studies have dealt with the systems formed by anionic surfactants and neutral polymers, various techniques being used to investigate these mixtures [1, 2]. It has been well established that strong interactions occur between the surfactant and the polymer, and that complexes are formed in which the polymer wraps around micelles if the polymer chain is long enough, while the formation of aggregates takes place at a concentration lower than the CMC [3–7]. With cationic surfactants, it was assumed that, in part because of their bulky polar heads and unfavorable polar charge, they had only low affinity for polymers, but the subject was not clearly understood [8, 9]. However, much attention has recently been paid to these systems, and significant interactions between hydrophobic polymers and cationic surfactants have been evidenced [10–16]. Investigation of these systems by several techniques has revealed that the polymer lowers the CMC and also decreases both the micellar aggregation number and the degree of counter-ion binding of the micelles adsorbed on the polymer chains [11–16]. These variations are more significant when the micelle to polymer ratio is low (close to the CMC), since the polymer can easily penetrate between the surfactant chains, and it partially screens the polar heads owing to the strong hydrophobic interactions between the alkyl segments of the surfactant and the polymer. With increase of the surfactant concentration, the polymer chains become saturated with larger micelles, requiring simultaneously an increased counter-ion binding. The nature of the surfactant polar head and counter-ion, together with the hydrophobicity of the polymer, plays a major role in determining the micelle–polymer complexation. Systems containing hexadecyltrimethylammonium bromide (CTAB) and polypropylene glycols (PPOs), which undergo strong interactions, are currently under study.

We have undertaken a study of the thermodynamic properties of surfactant–polymer systems, and more specifically the volumes and heat capacities, which are properties sensitive to the structural changes occurring in micellar solutions [17, 18]. In this work we report results on the volumes and heat capacities of systems containing CTAB and different selected polymers, polyethylene glycols (PEGs) and PPOs. The two series of polymers were chosen in order to investigate the influence of their hydrophobicity and their chain length on the interactions between polymer and surfactant and also the subsequent possible induced structural changes in the solutions.

Experimental

CTAB was of puriss. grade from Fluka; it was used without further purification after being dried for several days in vacuum at a temperature below 50°C. The different polymers (PEG 10000, PPO 425 and PPO 1000, where the associate number is representative of the mean molar mass of the polymer), were purchased from Aldrich, and also used as bought. All solutions were prepared by mass with deionized water degassed prior to use.

Densities, ρ , were measured with a Picker vibrating tube densimeter, and heat capacities c_p , were determined with a Setaram Picker flow microcalorimeter based on the thermal balance principle. For both apparatuses, the temperature was maintained constant at 25°C within 0.005°C. The experimental procedures and the accuracies of the measurements are well documented in the literature [19, 20].

The apparent molar volumes $V_{\phi,s}$, and heat capacities, $C_{\phi,s}$, of the CTAB in polymer solutions were calculated from the densities and heat capacities of the ternary solutions via the usual relations

$$V_{\phi,s} = \frac{M_s}{\rho} - \frac{10^3(\rho - \rho_0)}{m_s \rho \rho_0} \quad (1)$$

$$C_{\phi,s} = M_s c_p + \frac{10^3(c_p - c_{p0})}{m_s} \quad (2)$$

where M_s is the molar mass and m_s is the molality of the surfactant; ρ_0 and c_{p0} refer, respectively, to the density and specific heat capacity of the reference solvent (water or a binary aqueous polymer solution).

The transfer properties of CTAB from water to polymer solutions are defined as the difference in the apparent quantities $Y_{\phi,s}$ (where Y stands for V or C) of CTAB in water and in polymer solutions for equal concentrations of CTAB in the two solvents:

$$\Delta Y_s = Y_{\phi,s}(\text{water} + \text{polymer}) - Y_{\phi,s}(\text{water}) \quad (3)$$

Results and discussion

Thermodynamic properties of CTAB in polymer solutions

Apparent molar volumes and heat capacities of CTAB were obtained for polymer solutions of PEG 10000, PPO 425 and PPO 1000, kept at fixed concentration (2% in mass), as functions of the concentration of CTAB. Particular attention was paid in the vicinity of the CMC of the surfactant ($9 \cdot 10^{-4} \text{ mol kg}^{-1}$). The curves of transfer volumes (ΔV_s) and transfer heat capacities (ΔC_s), reported in Figs 1 and 2, show that the variations occurring near the CMC are largely dependent on the nature and the chain length of the polymer. As for volumes, in PEG 10000 solutions only a weak variation is observed through a slight minimum near the CMC, and ΔV_s then remains close to zero. In contrast, in PPO solutions a sharp peak is present at the CMC, whose maximum and intensity are widely dependent on the molar mass of the PPO. For PPO 1000, the maximum must appear at a concentration too low to be obtained experimentally. At higher CTAB concentration, ΔV_s decreases progressively, levelling off slowly toward

zero. Similar trends are observed for the heat capacities. For PEG 10000, the slight maximum present near the CMC vanishes subsequently, while for the two PPOs a large maximum is observed around the CMC, preceding the slow decrease in ΔC_s with increasing CTAB concentration.

The variations in the transfer properties of CTAB reveal the major role played by the nature of the polymer in the polymer-surfactant interactions. The presence of PEG 10000 in CTAB solutions does not lead to important variations in

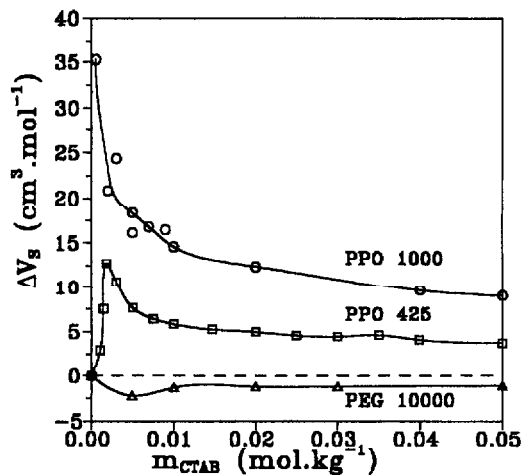


Fig. 1 Variation in molar volumes of transfer of CTAB from water to different polymer solutions at 2% in mass as a function of the concentration in CTAB

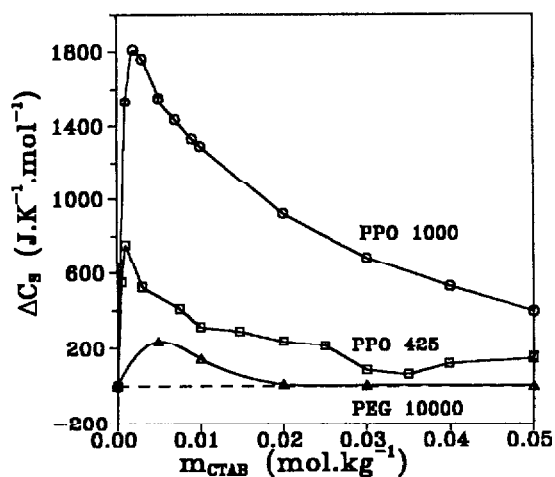


Fig. 2 Variation in molar heat capacities of transfer of CTAB from water to different polymer solutions at 2% in mass as a function of the concentration in CTAB

the properties of CTAB. This means that the micellar structure is only slightly affected by PEG 10000, and thus confirms the lack of interactions between a more hydrophilic polymer and CTAB [5, 8, 9]. In contrast, due to the CH₃ branching, the PPOs are more hydrophobic polymers and their solubility in water is low. The observed large variations in the properties of CTAB demonstrate that the PPOs interact strongly with the surfactant close to the CMC, as previously established from other properties [10–16]. When a transition occurs, the variations in the apparent properties of the solute express the shifts in the equilibrium between two structures [21]. The aggregation of surfactant monomers occurs at a much lower concentration and the effect is the more marked, the longer the polymer chain, when considering the first derivatives of G (V or H). For the second derivatives (heat capacities), additional equilibrium shifts exist, relating to their dependence on temperature. Thus, the spectacular variations observed in the transfer properties of CTAB at the CMC reveal the important structural change undergone by the micelles.

Thermodynamic properties of polymers in CTAB solutions

The apparent molar properties of polymers in CTAB solutions can also be deduced from experimental ρ and c_p data [22]. These quantities were also measured by a direct procedure (the reference solvent now being a CTAB solution) over a larger domain of concentration in CTAB, in order to evidence how other post-micellar transitions, if they occur, are affected by the presence of polymers.

In order to compare the different polymers, the transfer volumes (ΔV_{POL}) and heat capacities (ΔC_{POL}) of the polymers are represented in Figs 3 and 4 as functions of the CTAB concentration. For PPO, two series of values are presented: open symbols relate to values obtained when transferring polymers (water \rightarrow water+CTAB), and closed symbols correspond to the transfer measurements on CTAB (water \rightarrow PPO solutions) for dilute CTAB concentrations. It is important to note the satisfactory consistency of the two series of results. The evolution of the different curves appears somewhat unexpected when only hydrophobic interactions are involved, as observed for alcohols [23] or polymers (PEG or PPO) [17, 24] in anionic surfactant solutions of sodium dodecylsulfate (SDS). The transfer volumes of PEG 10000 are negative ($-5 \text{ cm}^3 \text{ mol}^{-1}$), but very small as compared with its apparent volume in water ($\approx 8400 \text{ cm}^3 \text{ mol}^{-1}$). Moreover, ΔV_{POL} remains almost constant in the studied concentration range of CTAB. In contrast with PPOs, ΔV_{POL} is positive and larger with longer polymer chains, as observed for SDS micellar solutions. In addition, the shape of the curves is different and the values regularly increase with increasing CTAB concentration without levelling-off to a plateau. This might mean that, besides the partition of polymer between aqueous and micellar phases, giving a positive ΔV_{POL} , supplementary effects occur.

As concerns heat capacities, the profiles of ΔC_{POL} are even more unusual, changing in an opposite way to what is expected for the predominantly hydrophobic interactions between polymer and surfactant, as observed in SDS solutions containing the same polymers [17, 24]. For PEG 10000, a narrow positive peak is present in the dilute domain, probably relating to a slight influence of the

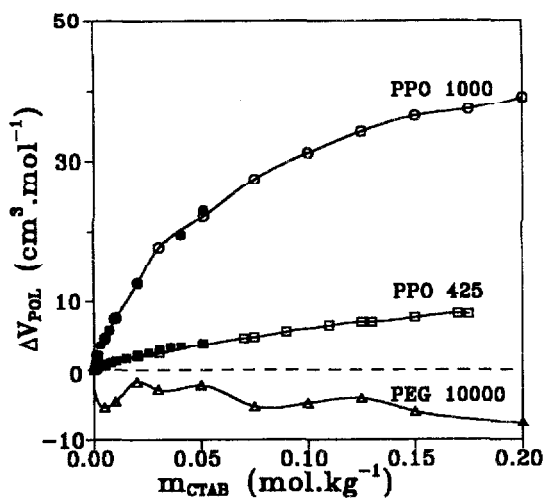


Fig. 3 Variation in molar transfer volumes of the different polymers at 2% in mass from water to CTAB solutions as a function of the CTAB concentration at 25°C

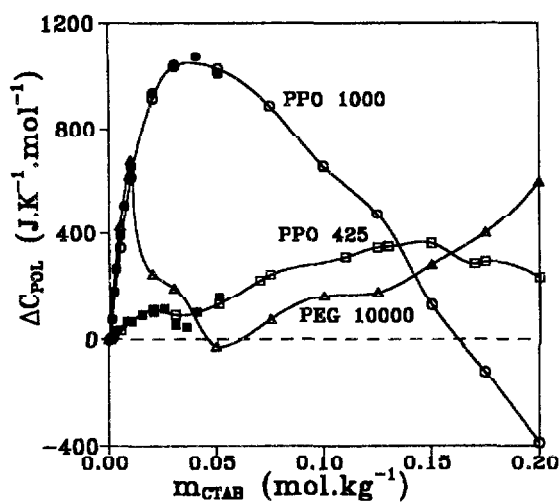


Fig. 4 Variation in molar transfer heat capacities of the different polymers at 2% in mass from water to CTAB solutions as a function of the CTAB concentration at 25°C

long PEG on the equilibrium of micellization; in more concentrated solutions, ΔC_{POL} decreases to zero before slowly increasing again. This should be related to the presence of the second transition of CTAB, generally observed at around 0.15 mol kg^{-1} in aqueous solution and characterizing a change in the shape of the micelles [25]. This transition may occur since the micellar structure is poorly affected by the presence of PEG. When small organic molecules are solubilized in CTAB solutions, this transition is expressed in apparent heat capacity variations by the presence of a hump, the width of which depends on the polar character of the solute [26, 27]. The transfer heat capacities of PPO 425 or 1000 are mostly positive in the CTAB domain investigated. They go through a more pronounced maximum and shift to lower concentration as the PPO chains become longer. These unexpected variations reflect the profound modifications undergone by the micellar structures in the presence of PPO. In the dilute domain around the CMC, when the polymer is in excess, the micellar equilibria are largely disturbed since micelles are formed with much lower aggregation numbers and an increased micellar ionization degree [11–13]. This therefore allows solubilization of segments of the polymer chains inside micelles, due to hydrophobic interactions and reinforced by the screening of the polar head charges. The negative contribution to the apparent heat capacities resulting from these hydrophobic interactions is certainly completely masked by the large positive contribution relative to the equilibrium shifts, as predicted by the mass action model and the partition of the solute developed by Hetu *et al.* [21]. When the concentration of CTAB is increased, the aggregation number and the counter-ion binding of the bound micelles increase so that normal size is attained at saturation [15]. ΔC_{POL} decreases and then becomes negative, thus expressing the weakening of the perturbation terms at equilibrium, compared with the contribution of hydrophobic interactions.

Conclusions

The different variations in the transfer properties of CTAB from water to polymer solutions, or conversely those of polymers in CTAB solutions, evidence certain aspects of the specificity of the interactions involving polymers in cationic micellar solutions, for the induction of or upsetting of structures in solution. It was observed that the PEGs, rather hydrophilic polymers, interact only weakly with CTAB micelles. Accordingly, the PEGs, which remain mainly in the aqueous phase, do not greatly affect the micellar structure. As a consequence, the post-micellar transition persists for concentrations above 0.15 mol kg^{-1} .

In contrast, the PPOs, more hydrophobic polymers, interact strongly with CTAB monomers or micelles. The depression of CMC and the perturbation of the micellar structures are such that apparently unusual variations of transfer quantities are observed, though mainly hydrophobic interactions are involved

between neutral polymers and cationic surfactants. For anionic surfactants, the smaller and negative head groups act in a favorable way to promote interactions with any non-ionic polymers, whereas for cationic surfactants, because of the bulky positive head groups preventing polymer penetration into the micelles, the hydrophobic nature of the polymers is of greatest importance as concerns the establishment of interactions.

References

- 1 D. Robb, *Anionic Surfactants*, E. H. Lucassen-Reynders Ed., Dekker, New York 1981, p. 109.
- 2 E. D. Goddard, *Colloids Surf.*, 19 (1986) 255.
- 3 J. Cabane and R. Duplessix, *Colloids Surf.*, 13 (1985) 19.
- 4 J. François, J. Dayantis and J. Sabbadin, *Eur. Polym. J.*, 21 (1985) 165.
- 5 R. Zana, J. Lang and P. Lianos, *Microdomains in Polymer Solutions*, P. Dubin Ed., Plenum, New York 1985, p. 357.
- 6 C. Tondre, *J. Phys. Chem.*, 89 (1985) 5101.
- 7 G. Olafsson and G. Wang, *Pure Appl Chem*, 66 (1994) 527
- 8 K. Hayakawa and J. C. T. Kwak, *Cationic Surfactants: Physical Chemistry*, D. N. Rubingh, P. M. Holland, Eds, Dekker, New York 1991, p. 189.
- 9 R. Nagarajan and B. Kalpakci, *Microdomains in Polymer solutions*, Dubin P. Ed., Plenum Press, New York 1985, p. 369.
- 10 K. Shirahama, A. Himuro and N. Takisawa, *Colloid & Polymer Sci.*, 265 (1987) 96.
- 11 F. M. Witte and J. B. F. N. Engberts, *Colloids Surf.*, 36 (1989) 417.
- 12 J. C. Brackman and J. B. F. N. Engberts, *Langmuir*, 7 (1991) 2097.
- 13 M. L. Sierra and E. Rodenas, *J. Phys. Chem.*, 97 (1993) 12387.
- 14 S. Reekmans, M. Gehlen, F. C. de Schryver, N. Boens and M. Van der Auweraer, *Macromolecules*, 26 (1993) 687.
- 15 O. Anthony and R. Zana, *Langmuir*, 10 (1994) 4048.
- 16 D. M. Bloor, H. K. O. Mwakibete and E. Wyn-Jones, *J. Colloid Interface Sci.*, 178 (1996) 334.
- 17 C. Aucouturier, G. Roux-Desgranges and A. H. Roux, *J. Thermal Anal.*, 41 (1994) 1295.
- 18 K. Busserolles, G. Roux-Desgranges and A. H. Roux, *Langmuir*, 13 (1997) 1946.
- 19 P. Picker, E. Tremblay and C. Jolicœur, *J. Solution Chem.*, 3 (1974) 377.
- 20 P. Picker, P. A. Leduc, R. P. Philip and J. E. Desnoyers, *J. Chem. Thermodyn.*, 3 (1971) 631.
- 21 D. Héту, A. H. Roux and J. E. Desnoyers, *J. Solution Chem.*, 16 (1987) 529; *J. Colloid Interface Sci.*, 122 (1988) 418.
- 22 G. Roux-Desgranges, S. Bordere and A. H. Roux, *J. Colloid Interface Sci.*, 162 (1994) 284.
- 23 G. Roux-Desgranges, A. H. Roux and A. Viillard, *J. Chim. Phys.*, 82 (1985) 441.
- 24 K. Busserolles, G. Roux-Desgranges and A. H. Roux, *Cal. Anal. Therm.*, 26 (1995) 76.
- 25 F. Quirion and J. E. Desnoyers, *J. Colloid Interface Sci.*, 112 (1986) 565.
- 26 F. Quirion and J. E. Desnoyers, *J. Colloid Interface Sci.*, 115 (1987) 176
- 27 K. Busserolles, G. Roux-Desgranges and A. H. Roux, *Thermochim. Acta*, 259 (1995) 49.