

Note

Effect of the nature of the counterion on the interaction between cesium and tetraalkylammonium dodecylsulfates and poly(ethylene oxide) or poly(vinylpyrrolidone)

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Abstract

The interaction between poly(ethylene oxide) or poly(vinylpyrrolidone) and cesium and tetraalkylammonium (tetramethyl to tetrabutyl ammonium) dodecylsulfate has been investigated by means of electrical conductivity measurements to determine the critical aggregation concentration (cac) of the surfactants in the presence of polymer. The cac values were compared to the values of the critical micellization concentration (cmc) of the surfactants in the absence of polymer. The value of the cac/cmc ratio increased with the radius of the counterion in the sequence: $\text{Na}^+ < \text{Cs}^+ < \text{tetramethylammonium}^+ < \text{tetraethylammonium}^+ = \text{tetrapropylammonium}^+ = \text{tetrabutylammonium}^+ = 1.0$. This result indicates that the strength of the interaction decreases upon increasing counterion radius. For the last three tetraalkylammonium ions the value $\text{cac}/\text{cmc} = 1$ indicates the absence of interaction. The results are discussed in an attempt to gain a better understanding of the mechanism of formation of surfactant aggregates bound to water-soluble polymers such as poly(ethylene oxide) or poly(vinylpyrrolidone).

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1. Introduction

Surfactants and water-soluble polymers are present together in many formulations and industrial processes to boost the properties of the surfactant by the added polymer or vice versa (synergism) and also for producing properties that neither the surfactant nor the polymer possesses when used alone. The numerous applications and uses of polymer/surfactant systems have been reviewed [1]. Besides, important changes in the properties of both the polymer and surfactant often occur when these two types of compounds are used together. This has greatly stimulated the interest in polymer/surfactant systems and the study of polymer/surfactant interactions is an actual topic in surfactant science. Papers on mixed polymer/surfactant systems are being published in large number and the field has been recently reviewed [2,3]. In most studies as well as in the present

work *interaction* between surfactant and polymer means that the surfactant binds noncovalently to the polymer, i.e., only *associative systems* are considered, when using the terminology introduced by Picullel and Lindman [4].

Among water-soluble polymers, neutral polymers have solution properties that are less complex than charged polymers (polyelectrolytes). Nevertheless, the interaction between neutral polymers and surfactants is less well understood than that between polyelectrolytes and surfactants. Indeed, in the second type of systems electrostatic interactions strongly dominate and determine whether an interaction occurs. In neutral polymer/surfactant systems the electrostatic interactions are much weaker and other mechanisms are responsible for the polymer/surfactant interaction. For these systems it is generally observed that the surfactant self-associates cooperatively, i.e., under the form of aggregates, at the so-called critical aggregation concentration (cac). The cac is usually lower than the critical micellization concentration (cmc) of the surfactant by a factor say between 1 and 10 [2,3,5]. This is in contrast with polyelectrolyte/oppositely charged surfactant systems where the cac may be 10^2 – 10^4 times lower than the cmc [5]. The strength of the interaction

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between a polymer and a surfactant can be characterized by the cac/cmc ratio, even if this quantity gives only a semi-quantitative idea of the interaction [6]. For ionic surfactants the nature of the charged head group and of the counterion has a strong impact in determining the occurrence and the strength of the polymer/surfactant interaction. The same is true for the nature of the surfactant head group in the case of uncharged (nonionic, zwitterionic) surfactants [5].

The polymers that have been the most often used in studies of neutral polymer/surfactant interactions are poly(ethylene oxide) and the poly(vinylpyrrolidone) (PEO and PVP, respectively). At room temperature these polymers interact with all anionic surfactants investigated: sodium dodecylsulfate, decylphosphate, dodecylbenzenesulfonate, alkylcarboxylate, di(ethylhexyl)phosphate and perfluorononanoate, lithium perfluorooctanesulfonate, Aerosol OT, potassium 2-alkylmalonates, etc. [5]. In contrast, their interaction with the nonionic surfactants C_mEO_x (poly(ethylene oxide) monoalkyl ethers), with surfactants having a sugar head group (glucoside, thioglucoside), with zwitterionic surfactants such as the dodecyltrimethylammonioethanesulfonate, and with cationic surfactants of the alkyltrimethylammonium bromide type is very weak or not present, at least at room temperature [5]. However, a slight increase of the temperature is sufficient to bring about interactions in the case of the PEO/alkyltrimethylammonium bromide systems owing to the increased hydrophobicity of PEO at high temperature [5]. Likewise, the more hydrophobic poly(propylene oxide) interacts with alkyltrimethylammonium bromides and sugar surfactants, even at room temperature [5].

The PEO/SDS system is probably the one that has been the most investigated. Dubin et al. [7] reviewed the various explanations that have been proposed to explain the binding of SDS to PEO. The authors wrote the following: "It has thus been variously proposed that the PEO/SDS complex is stabilized by hydrophobic interactions between the methylene units of the polymer and those of the surfactant alkyl chain, by interactions between polymeric ether groups and sulfate groups, or by effects more closely related to the nature of the micelle–water interface." They further conclude "that none of the foregoing proposals has been clearly substantiated and that the driving force for the binding of SDS to PEO is open to debate." Dubin et al. [7] investigated the effect of the nature of the surfactant counterion (Li^+ , Na^+ , and NH_4^+) on the PEO/dodecylsulfate micelle interaction. They concluded that the surfactant cation plays a direct role in the stabilization of the PEO/dodecylsulfate complex [7]. The cation would interact simultaneously with the dodecylsulfate micelle surface via electrostatic interaction and with the PEO via coordination complexation. Another way to look at this mechanism is to assume that PEO binds alkali metal ions, thus becoming a polycation that, in turn, binds oppositely charged surfactant anions. This explanation is not always accepted. In a recent study, the interaction between PVP and anionic surfactants (sodium alkylsulfonate

with alkyl = octyl, decyl, undecyl) has been explained in terms of an excluded volume effect of the polymer [8]. In that study the cac was equal to, or only slightly smaller than, the cmc . However, the surfactant alkyl chain was too short to validate the proposed explanation.

This situation and the recent synthesis in our laboratory of tetramethyl, tetraethyl, tetrapropyl, and tetrabutyl ammonium dodecylsulfate (TMADS, TEADS, TPADS, and TBADS, respectively) [9] led us to investigate the interaction between these surfactants and PEO and PVP. Indeed, the tetraalkylammonium ions (TAA^+) are much larger than alkali metal ions and also have rather different properties. In particular, the TPA^+ and TBA^+ ions are hydrophobic enough for self-associating in aqueous solution at high concentration [10]. Obviously, if the polymer/surfactant interaction is mediated by the surfactant counterion, this interaction should be much effected in going from hydrophilic alkali metal ions, such as Li^+ , Na^+ , and NH_4^+ to the much larger and hydrophobic TAA^+ ions. In the present work the polymer/surfactant interaction was characterized by measuring the cac of the surfactant in the presence of the polymer, using the electrical conductivity method [9]. For the sake of completeness measurements have also been performed on the cesium dodecylsulfate (CsDS). Indeed, the Cs^+ ion has a size intermediate between that of Na^+ and TMA^+ . The results presented below show that the strength of the interaction, as characterized by the value of the cac/cmc ratio, decreases rapidly upon increasing counterion size. They lend a strong support to the explanation put forward by Dubin et al. [7].

2. Materials and methods

The cesium and tetraalkylammonium dodecylsulfate have been prepared as described elsewhere [9]. The samples of PEO (Hoechst) and PVP (Aldrich) had molecular weights of about 20,000 and 55,000, respectively.

The conductivity measurements were performed using the same setup as in previous investigations [9,11]. The cac was taken as the concentration corresponding to the break in the plot representing the variation of the specific conductivity K with the surfactant concentration. The measurements were performed at 25 °C, unless specified otherwise.

3. Results and discussion

Figure 1 shows the variation of the specific conductivity K of CsDS solutions with the surfactant concentration C in water, water + 0.1 wt% PEO and water + 0.1 wt% PVP. The plot in water shows a break that corresponds to the cmc . The plots in water + 0.1 wt% polymer show two breaks. The low-concentration break corresponds to the cac , concentration at which the surfactant starts associating in the presence of polymer. The second break occurs at a concentration that is often referred to as C_2 and that was until recently assumed

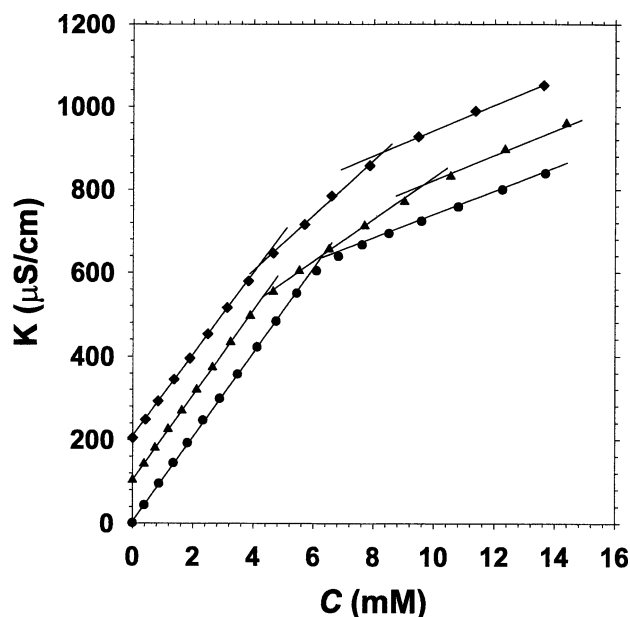


Fig. 1. Variation of the specific conductivity of CsDS solutions at 30 °C in (●) water; water + 0.1 wt% PEO (▲, shifted by +100 $\mu\text{S}/\text{cm}$); and water + 0.1 wt% PVP (◆, shifted by +200 $\mu\text{S}/\text{cm}$).

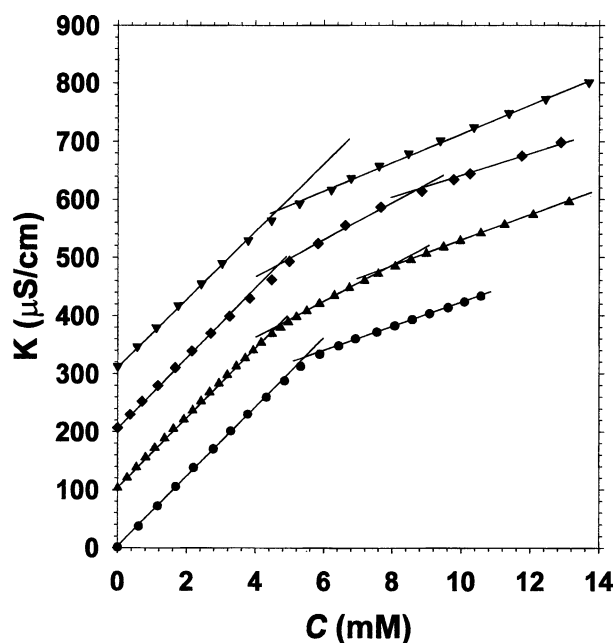


Fig. 2. Variation of the specific conductivity of TMADS solutions at 25 °C in (●) water; (▲) water + 0.1 wt% PEO (shifted by +100 $\mu\text{S}/\text{cm}$); (▼) water + 1 wt% PEO (shifted by +300 $\mu\text{S}/\text{cm}$); and (◆) water + 0.1 wt% PVP (shifted by +200 $\mu\text{S}/\text{cm}$).

to correspond to the saturation of the polymer by the bound surfactant. Recent studies, however, demonstrated that the polymer is not always saturated by surfactant when the concentration C_2 is reached [12–16]. The results in Fig. 1 clearly show the difference between the values of the cmc (in water) and of the cac (in water + polymer). The difference is much decreased in going to TMADS as can be seen in Fig. 2, which shows the variations of K with C in water and

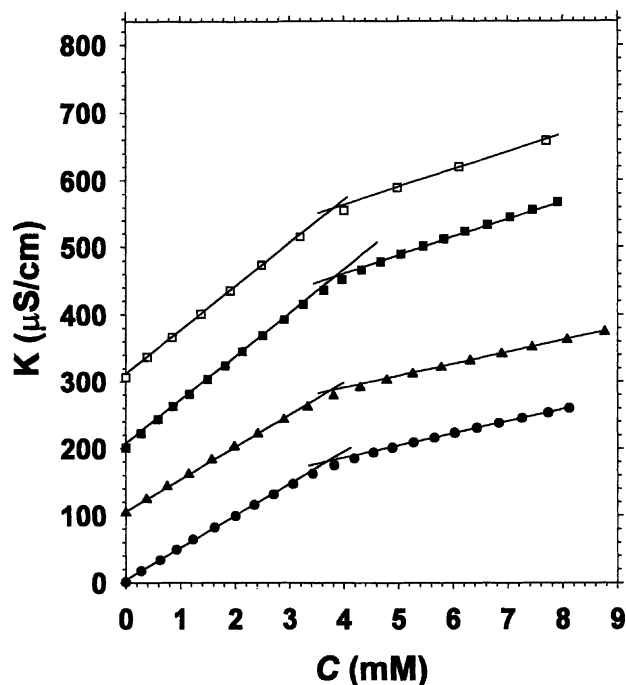


Fig. 3. Variation of the specific conductivity of TEADS solutions at 25 °C in (●) water and in (▲) water + 0.1 wt% PEO (shifted by +100 $\mu\text{S}/\text{cm}$); and at 40 °C in water (■, shifted by 200 $\mu\text{S}/\text{cm}$) and water + 0.1 wt% PEO (□, shifted by +300 $\mu\text{S}/\text{cm}$).

water + polymer. The values of the cmc and of the cac are equal for TEADS (see Fig. 3) and TPADS and TBADS (results not shown) within the experimental error estimated to be about 5% (3–5). Note that the second break is not seen in the plot corresponding to systems in water + 1 wt% PEO or PVP (Fig. 2 and results not shown) because the value of C_2 is outside the investigated concentration range.

Table 1 lists the values of the cmc, cac, ratio cac/cmc, and C_2 , whenever available, of all the investigated systems. Results for SDS extracted from a previous study [17] are also listed. These results demand several remarks.

- (i) For TMADS (Fig. 2) the value of the ratio cac/cmc is independent of the PEO concentration; i.e., the cac is independent of the polymer concentration. A similar result has been reported for SDS [17].
- (ii) The cac/cmc ratio tends toward a value of 1 as the counterion size increases. This value is reached for TEADS, TPADS, and TBADS.
- (iii) The effect of the polymer nature on the cac/cmc ratio is pronounced for SDS, but nearly absent for CsDS and TMADS. This is expected because when the effect of the polymer is smaller, the differences between different polymers must also be smaller.
- (iv) The amount of surfactant that is bound to the polymer at the concentration C_2 can be taken as approximately equal to $C_2 - \text{cac}$. It decreases upon increasing counterion radius since the cac becomes closer to the cmc and vanishes completely for the larger TAA⁺ ions (Figs. 1–3).

Table 1
cmc of the investigated surfactants in water and values of the cac in the presence of PEO or PVP

Surfactant	Polymer	<i>T</i> (°C)	cmc or cac (mM)	cac/cmc	<i>C</i> ₂ (mM)
SDS		25	8.0 ^a		
SDS	0.1 wt% PEO	25	4.4 ^a	0.55	
SDS	0.1 wt% PVP	25	2.1 ^a	0.26	
CsDS		30	6.2		
CsDS	0.1 wt% PEO	30	4.2	0.68	9.6
CsDS	0.1 wt% PVP	30	4.1	0.66	8.4
TMADS		25	5.4 ^b		
TMADS	0.1 wt% PEO	25	4.6	0.85	8.0
TMADS	1 wt% PEO	25	4.7	0.87	
TMADS	0.1 wt% PVP	25	4.6	0.85	8.6
TEADS		25	3.7 ^b		
TEADS	0.1 wt% PEO	25	3.7	1.0	
TEADS		40	3.8 ^b		
TEADS	0.1 wt% PEO	40	3.8	1.0	
TPADS		25	2.2 ^b		
TPADS	1 wt% PEO	25	2.2	1.0	
TPADS	0.1 wt% PVP	25	2.25	1.01	
TBADS		25	1.15 ^b		
TBADS	0.1 wt% PEO	25	1.15	1.0	
TBADS	1 wt% PEO	25	1.15	1.0	

^a From Ref. [17].

^b From Ref. [9].

Remarks (ii) and (iii) indicate that the interaction between the polymer, whether PEO or the more hydrophobic PVP, vanishes as the counterion size and hydrophobicity increase. A fairly strong interaction was detected with SDS [17]. An interaction is still detected with CsDS and TMADS at 25 °C (see Figs. 1 and 2), but it is much weaker, with values of the cac/cmc ratio increasing and becoming closer to 1 in going from SDS to CsDS and TMADS. No interaction appears to occur between TEADS, TPADS, and TBADS and PEO since the cac/cmc ratio is equal to 1 at both 25 and 40 °C, within the experimental error. Recall that at 40 °C PEO is less polar than at 25 °C and that at this temperature PEO interacts even with cationic surfactants [18]. Dubin et al. [7] proposed that the interaction between anionic surfactants and PEO is mediated by the surfactant counterion that would form a coordination complex with PEO. This assumption was based on numerous studies that showed that indeed PEO can bind cations in nonaqueous solvents such as methanol [19–21] as well as in water [22]. The reported values of the cac/cmc ratio increased with the counterion radius, for the counterions Li⁺, Na⁺, and NH₄⁺ [7]. Our results can be interpreted similarly. The ability of PEO to bind TAA⁺ ions by coordination complexation decreases as the cation size increases, probably because the polymer cannot form a cavity large enough to accommodate large TAA⁺ cations. One reviewer of this work suggested that the main driving force for the polymer/surfactant interaction in the investigated systems may be of a hydrophobic nature. Polymers such as PEO or PVP would bind to the hydrophobic parts of the micelle surface that are not covered by counterions. Large TAA⁺ counterions would not permit this binding as they cover more or less completely the micelle surface. Our results do not sup-

port this explanation. Indeed, the large TAA⁺ counterions do cover the micelle surface [9]. This makes the outer surface of the shell containing the micelle-bound TAA⁺ counterions hydrophobic or even more hydrophobic than in the absence of such ions. This should therefore not prevent the binding of polymers to this surface via hydrophobic interactions. Unfortunately, the experimental results do not support this expectation.

4. Conclusion

The study of the interaction between cesium and tetraalkylammonium dodecylsulfates and PEO or PVP revealed that the interaction becomes weaker and disappears as the counterion radius is increased. There is essentially no interaction already for the TEADS. Thus, the counterion size provides a new way for tuning polymer/surfactant interaction. It would be interesting to check if the interaction between polyelectrolytes and oppositely charged surfactants is also weakened when the size of the surfactant head group is increased.

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