

Association of cationic surfactants to humic acid Effect on the surface activity

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Abstract

Surface properties of aqueous solutions of mixtures of humic acid, HA, and a series of cationic surfactants, C_n TAB, have been studied. For a fixed amount of HA, the concentration of surfactant at which micelle-like aggregates are formed, cac , were determined. The $\log(cac)$ varies with the number of carbon atoms in the surfactant alkyl chain in a way similar to that shown by the $\log(cmc)$ of the pure surfactants. The addition of small amounts of C_n TAB to an aqueous solution of HA has a huge effect on the surface tension decrease of water. This enhancement of the surface activity exhibited by mixtures of HA and C_n TAB is explained in terms of the efficiency and effectiveness of surface adsorption. These parameters were determined by measuring the values of pC_{20} , and the excess surface concentration Γ , respectively. The values of the standard free energy of adsorption, ΔG_{ad}° , were also determined as a function of the surfactant chain length, and from this relation the contribution by methylene group was determined.

Keywords: Humic acid; Cationic surfactants; Surface activity; Critical aggregate concentration

1. Introduction

Humic acids HA are natural polyelectrolytes, formed by enzymatic degradation of plant polymers. In this process carboxylic acid groups are formed at one or more ends of polymer segments [1–4]. The unaltered segments of the polymer will be relatively more hydrophobic than the carboxylated segments. Therefore, the resulting polymer has both hydrophilic and hydrophobic moieties in their structure, giving to the HA characteristics of an amphiphile [5–7]. Thus, HA exhibit surface activity in aqueous solution and form micelle-like aggregates at high concentration [8]. Recently, the effect of pH on the surface activity of HA has been reported [9]. The results indicate that both the surface activity and the aggregation are enhanced at low pH. These surface activities generate important effects on the physical and chemical properties of soils and sediments, such as transport, and solubility of hydrophobic organic pollutants [10–15]. In addition of pH, and in analogy to

the behavior of synthetic polyelectrolytes, the surface activity of HA should be a function of the degree of charge neutralization of the negative charged segments by opposite charged species.

Interaction between polyelectrolyte and ionic surfactants in aqueous solutions has been the subject of a number of studies and reviews mainly because of the fundamental and technological importance of these mixtures [16–23]. The binding of ionic surfactant to oppositely charged polyelectrolyte is a cooperative process [24,25]. Because of the strong electrostatic attraction between the two species, the interaction starts at very low concentrations forming hydrophobic domains [26]. These mixtures show a synergistic effect on the surface tension and stabilization of emulsions and foams. Indeed, the addition of very small amounts of cationic surfactant to aqueous solutions of anionic polyelectrolyte produces an abrupt decrease of surface tension [27,28].

Humic acids behave like weak-acid polyelectrolyte and exhibit the ability to associate with different molecules by electrostatic and/or hydrophobic interactions. On the other hand surfactants from detergents are often present in wastewaters and enter the environment through wastewater discharge. In this work the association of alkyltrimethylammonium bromides

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(C_n TAB) to HA, and the influence of this interaction on the surface activity of HA are studied.

2. Experimental

2.1. Materials

2.1.1. Surfactants

The cationic surfactants, hexadecyltrimethylammonium bromide C_{16} TAB was from Sigma; tetradecyltrimethyl ammonium bromide C_{14} TAB and dodecyltrimethylammonium bromide C_{12} TAB were from Aldrich; and decyltrimethylammonium bromide C_{10} TAB was from Eastman, were purified by successive recrystallizations from acetone.

2.1.2. Humic acid

Sodium salt of humic acid from Aldrich was used as received. To characterize this humic substance it was converted to the acid form HA following the method described by Fukushima et al. The results of the elemental analysis were: C 49.65%, H 4.49%, N 0.96%, S 0.33%, ash content 2.46%. The content of acidic groups of HA (C_A , meq g^{-1}) was determined by titration of a HA solution in NaOH with HCl. The C_A value was found to be 3.23 meq g^{-1} of HA, which is similar to other values previously reported [9,29]. All aqueous solutions were prepared in bidistilled and deionized water.

2.2. Methods

2.2.1. Surface tension measurements

The surface tension γ was measured by using the ring method with a Kruss-D8 balance. The aqueous solutions were immersed in a thermostat at 25.0 °C. Sets of measurements were made by adding small aliquots of a concentrated surfactant solution to an aqueous solution of HA (100 mg L^{-1}). Each measurement took 15 min to reach equilibrium. For humic acid solution measurements were done after more than 10 h.

2.2.2. Potentiometric titration

HA (80 mg) dissolved in NaOH 0.01M (10 mL) was titrated under N_2 atmosphere with HCl 0.01M at constant ionic strength (NaCl 0.01 M) The pH was recorded in a potentiometer Orion EA 940 after 2 min of equilibrium at each titration point. The apparent acid dissociation constant of HA was determined by potentiometric titration according to the method proposed by Terashima et al. [9]. The pK_{app} value calculated was 4.25 which is similar to the values found for others HA [9,30], and from a plot of the concentration of the deprotonated form of HA against pH, it is seen that the dissociation of carboxylic groups is almost complete at pH 6.0.

3. Results and discussion

3.1. Interaction between HA and cationic surfactants: critical aggregate concentration

Terashima et al. have recently shown that surface tension γ of HA aqueous solutions decreases with increasing pH, with an

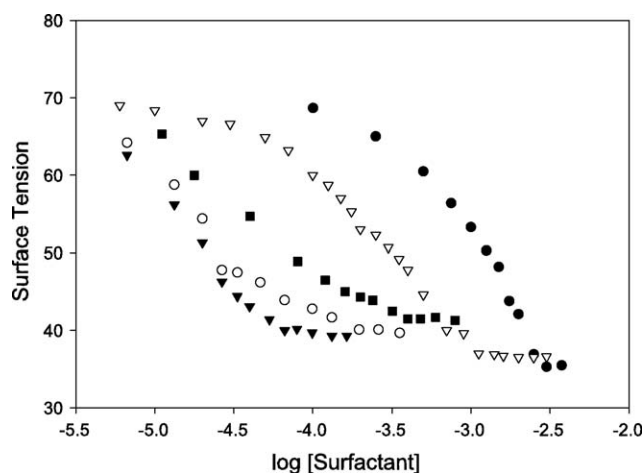


Fig. 1. Surface tension as a function of C_n TAB concentration, in the absence (●) C_{14} TAB, (▽) C_{16} TAB; and in the presence of humic acid (■) C_{12} TAB/HA, (○) C_{14} TAB/HA, (▼) C_{16} TAB/HA.

inflection point at around pH 5.5. Thus, above this pH the surface activity of HA is minimal. Based on these observations we have used pH 6.0 to evaluate the effect of cationic surfactant on the surface activity of HA. At this pH and at very low concentrations of HA the surface tension of water is reduced by no more than 10 mN m^{-1} . However, the addition of very small amounts of cationic surfactants to an aqueous solution of HA (100 mg/L) produces an abrupt decrease of γ . Fig. 1 shows the variation of γ as a function of the logarithm of concentration of cationic surfactant at a fixed concentration of HA (100 mg/L). For comparison the curves obtained for the pure surfactant solutions are also included.

It is noted that the surface activities of both HA and the surfactant are greatly enhanced in the mixtures, and the magnitude of the effect follows the order: C_{12} TAB > C_{14} TAB > C_{16} TAB. In addition, the shape of these curves is almost independent of the added surfactant. All of them show a sharply decrease of γ with increasing surfactant concentration, up to a point where the surface tension remains constant. On the other hand, it has been well established that the binding of ionic surfactants to an oppositely charged polyelectrolyte is a cooperative process due to hydrophobic interactions among the alkyl chains of surfactants. Because of the strong electrostatic attraction between the two species, the interaction starts at very low concentrations forming hydrophobic aggregates at a very low surfactant concentration known as critical aggregate concentration cac , in analogy to the critical micelle concentration observed in pure surfactant solutions [31]. The formation of micelle-like aggregates at the cac has been demonstrated by different techniques, such as viscosity measurements [20], fluorescence probing [22,31,32], and decrease of surface tension [27,28]. Thus, the break points observed in the γ versus $\ln[C_n$ TAB] curves of Fig. 1 correspond to the cac of alkyltrimethylammonium surfactants on HA. The cac values range from 1×10^{-3} to 6×10^{-5} and, decrease with increasing length of the alkyl chain in the surfactant. Surprisingly, the cac are quite similar and show the same chain-length dependence, observed by Chu and Thomas [31] for the aggregation of C_n TAB and poly(methacrylic acid). Fig. 2 shows a

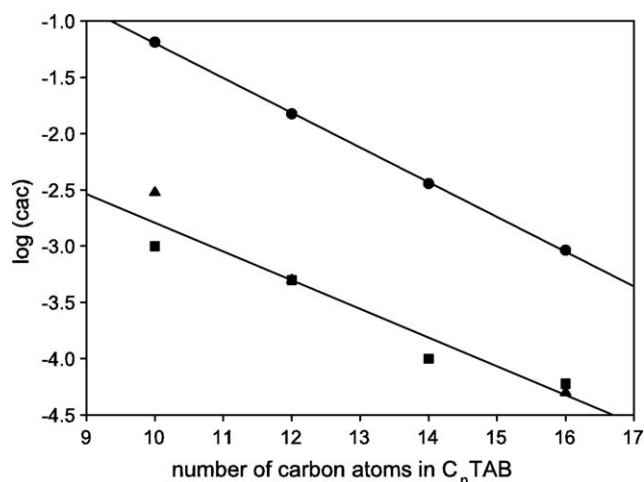


Fig. 2. Plot of the $\log(\text{cac})$ vs. the number of carbon atoms in the alkyl chain of $C_n\text{TAB}$ surfactants. Aqueous solution of: (●) pure $C_n\text{TAB}$, (■) $C_n\text{TAB}/\text{HA}$ mixtures, (▲) $C_n\text{TAB}/\text{PMA}$ mixtures.

plot of $\log(\text{cac})$ versus the number of carbon atoms of $C_n\text{TAB}$, and $\log(\text{cmc})$ is also included for sake of comparison. The figure shows that each cac is one to two orders of magnitude lower than the respective cmc of the pure surfactant, independent of the anionic polyelectrolyte. These results suggest that the aggregation process might be considered as a micellization that occurs at lower surfactant concentrations due to the presence of the polyelectrolyte.

3.2. Thermodynamics of the adsorption at the air–water interface

It is worth to emphasize that most of the surface tension decrease is produced well below the cac. At these concentrations the surface tension decreases almost linearly with $\log[C_n\text{TAB}]$. From the linear part of these curves the surface excess concentration, Γ , can be obtained according to the Gibbs adsorption equation

$$\Gamma = \frac{1}{4.606RT} \left(\frac{d\gamma}{d \log C} \right)$$

The maximum value of the surface excess concentration corresponds to the maximum concentration that a surfactant can attain at the interface, Γ_m , and it has been defined as the effectiveness of adsorption at an interface. On the other hand, the efficiency of adsorption is given by the negative logarithm of the bulk phase concentration of surfactant required to reduce the surface tension of the solvent by 20 mNm^{-1} , pC_{20} [33]. It has also been shown that when the surface tension of pure solvent is reduced by this amount, Γ is close to the saturation value. Thus, the maximum value of Γ can be obtained from the slope of a plot of γ versus $\log C$ at the concentration of surfactant C_{20} . In addition, the area per molecule in a saturated interface, is calculated from the relation

$$a_m^S = \frac{10^{16}}{N\Gamma_m}$$

where N is the Avogadro's number.

Table 1

Values of pC_{20} , Γ_m and the area per molecule in the region of surface saturation, for mixtures $C_n\text{TAB}/\text{HA}$

$C_n\text{TAB}$	pC_{20}	Γ_m (mol cm^{-2}) ($\times 10^{10}$)	a_m^S (\AA^2)	cac or cmc (M) ($\times 10^4$)
$C_{10}\text{TAB}/\text{HA}$	3.60	0.9	185	10.0
$C_{12}\text{TAB}/\text{HA}$	4.22	1.4	122	5.0
$C_{14}\text{TAB}/\text{HA}$	4.44	1.9	88	1.0
$C_{16}\text{TAB}/\text{HA}$	4.64	2.3	75	0.6
$C_{10}\text{TAB}$	2.08	1.7	96	650
$C_{12}\text{TAB}$	2.46	2.4	69	150
$C_{14}\text{TAB}$	2.82	3.1	54	36
$C_{16}\text{TAB}$	3.47	2.1	79	8.0
HA	1.46	0.9	190	

The results obtained for all mixtures $C_n\text{TAB}/\text{HA}$ are collected in Table 1. For comparison the corresponding values of aqueous solution of pure surfactant are also given.

The values of Γ_m and a_m^S of an aqueous solution of HA are not affected by the addition of $C_{10}\text{TAB}$. However, the higher $C_n\text{TAB}$ increases the effectiveness of adsorption, reaching a maximum value, which is quite similar to that shown by $C_{16}\text{TAB}$. This parameter is related to the configuration adopted by the surface-active species at the interface. The area occupied per molecule in the mixtures HA/surfactants are larger than those occupied by $C_n\text{TAB}$ in HA-free solutions, and increase from 75 to 185 with decreasing length of the alkyl chain of the surfactant. These results suggest that the HA is somehow involved in the adsorption on the surface, increasing slightly the surface area covered by the ionic group. Similar results have been found for mixtures of $C_n\text{TAB}$ and monoesters of poly(maleic acid-co-styrene), carrying a branched side alkyl chain [27].

On the other hand, the efficiencies of adsorption, reflected by the pC_{20} values, are higher for the mixtures $C_n\text{TAB}/\text{HA}$ than those determined on aqueous solution of each component. These results indicate that the surfactant concentration required to decrease the surface tension of water in 20 mNm^{-1} is almost two orders of magnitude lower in presence of humic acid. The efficiency increases with increasing length of the surfactant aliphatic chain.

In our experiments the polymer concentration C_p was kept constant (100 mg/L) and, therefore the concentration of dissociated carboxylic groups at pH 6.0 is around $3.23 \times 10^{-4} \text{ eq/L}$. This concentration is almost one order of magnitude higher than the concentration of surfactant in the mixture, at which the surface tension has been reduced by 20 mNm^{-1} . Under these conditions it is expected that all surfactant adsorbed on the surface must be associated to the polyelectrolyte. Thus, the interaction between HA and cationic surfactants results in the formation of a very active surface species.

Similar results have been reported for mixtures of $C_n\text{TAB}$ and anionic monoesters of alternating copolymer of maleic acid and styrene. The enhanced surface activity of polymer/surfactant mixture was attributed to the formation of a complex between the charged polyelectrolyte and the surfactant [18].

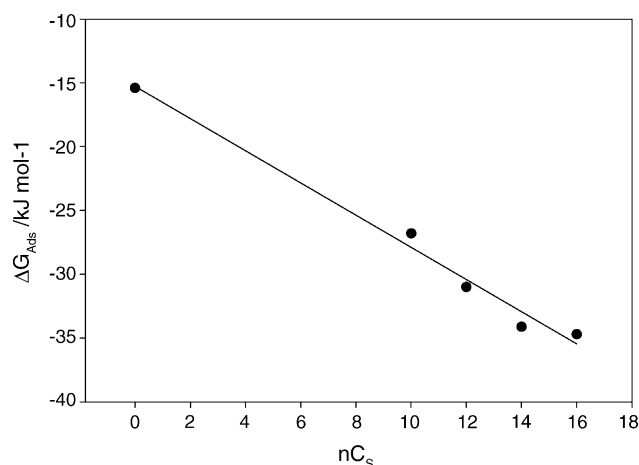


Fig. 3. Standard free energy of adsorption of C_n TAB in presence of HA as a function of the number of methylene group of the surfactant.

3.2.1. Standard free energy of adsorption

The adsorption process can be considered as a distribution between the bulk and surface phases. The standard free energy of adsorption, associated with this equilibrium, has been calculated by using the following equation [34]

$$\Delta G_{ad}^{\circ} = RT \ln \left(\frac{C}{\pi} \right)_{20}$$

where C is the bulk molar concentration of the surfactant, π is the surface pressure and the index indicates that these quantities are measured at $\pi = 20 \text{ mNm}^{-1}$.

This equation can be rewritten in terms of pC_{20} as:

$$\Delta G_{ad}^{\circ} = -2.303RT(pC_{20} + 1.30)$$

Using this equation and the values of pC_{20} given in Table 1, the values of ΔG_{ad}° for the mixtures HA/ C_n TAB and for the individual components were calculated. The values of ΔG_{ad}° of the mixtures are more negative than those of the individual components. They are in the range -19 to -27 kJ mol^{-1} , and increase with growing of the surfactant alkyl chain. These results indicate that in the presence of HA the surfactant molecules are pulled up to the interface much more easily.

In analogy to the distribution of hydrophobic molecules between the aqueous and the micellar phases, the standard free energy of adsorption can be broken into additive contributions from different groups [35–38]. Plot of the change of the standard free energy of adsorption as a function of the number of methylene groups in the alkyl chain of the cationic surfactant is presented in Fig. 3.

The slope represents the contribution of each methylene group to the free energy of adsorption, while the intercept is a measure of the contribution of the parent group to ΔG_{ad}° . Clearly, the slopes of both curves are quite similar, -1.18 and $-1.29 \text{ kJ mol}^{-1}$, while the intercepts differ considerably, -16.0 and -6.1 kJ mol^{-1} for the surfactant in presence and absence of HA, respectively. Thus, in mixtures HA/surfactants the contribution to ΔG_{ad}° of the trimethylammonium group associated to the polymer chain of HA is equal to the contribution of the complete surfactant alkyl chain. Therefore, the main driving force for the

surface adsorption of C_n TAB in presence of HA is the neutralization of the dissociated carboxylic acid by the cationic surfactant. These results are on line with values previously found in aqueous solution of C_n TAB in the presence of anionic monoesters of alternating copolymer of maleic acid and styrene. In these systems the formation of a complex has been invoked to explain the enhanced surface activity observed at very low surfactant concentration [27].

4. Conclusions

The addition of very low concentrations of cationic surfactants to an aqueous solution of HA induces a large change on the surface properties of this natural polyelectrolyte. The formation of micelle-like structures occurs at concentrations of HA and surfactants well below the respective critical micelle concentrations. From the dependence of the cac values with the number of carbon atoms in the C_n TAB surfactants it is concluded that this aggregation process might be considered as a micellization induced by the humic acid. On the other hand, the decrease of the surface tension of water is much higher in an aqueous solution of a HA/ C_n TAB mixture than in the solutions of the pure components. The surface area occupied per molecule in the mixtures HA/surfactants are larger than those occupied by C_n TAB in HA-free solutions, and increase from 75 to 185 with decreasing length of the alkyl chain of the surfactant. In addition, the efficiency of adsorption, reflected by the pC_{20} values, is also enhanced in the mixtures C_n TAB/HA, as compared to the aqueous solution of each component. This enhancement effects are attributed mainly to the formation of a very active surface species. This species is formed by the neutralization of dissociated carboxylic groups by the cationic head group of the surfactant. The magnitude of the effect on the efficiency of adsorption is larger than the effect observed in the effectiveness of adsorption. Thus, we suggest that the main driving force for the surface adsorption of C_n TAB in presence of HA is the neutralization of the dissociated carboxylic acid by the cationic surfactant

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