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The effect of alkyl chain length of a polysoap[†] on the surface activity of its complexes with cationic surfactants

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The synergistic effect on the surface activity of the dynamic associations (the surfactant–polyelectrolyte complexes – SPEC) between a polysoap[†] and cationic surfactants is remarkably increased with increasing length of alkyl side chains.

In our previous publications[1–3] we have demonstrated that the dynamic associations [the surfactant–polyelectrolyte complexes (SPEC)] between the oppositely-charged cationic surfactant, tetradecyltrimethylammonium bromide (TDAB), on the one hand, and the non-surface active anionic polyelectrolyte (PE), carboxymethylchitin (CMCh), on the other hand, possess anomalously high adsorption activity at the air–water interface and stabilizing ability for foams.

We have found that the standard adsorption free energy ($\Delta_{ad}G^0_{298}$) of surfactant molecules bound to these SPEC is much greater than that of the free (nonbound) surfactant molecules and is practically independent of the composition $Z = [\text{surfactant}]_b/[\text{CMCh}]$ of SPEC over a large range of Z varying from 0.001 to 1 (where $[\text{surfactant}]_b$ is the concentration of surfactant molecules bound to SPEC).

It has been assumed that the synergistic action of SPECs on the surface tension originates from two factors: neutralization of the electric charges of the surfactant cations bound to PE chains, and also adsorption of the hydrophobic fragments of anionic PE at the air–water interface. In the case of CMCh, its hydrophobic moieties are not very bulky (see Figure 1). Thus, at a rather high degree of ionization of carboxylic groups (*i.e.*, at $\text{pH} \geq 6$) this anionic PE is perfectly soluble in water and manifests no surface activity. Only in its dynamic association with alkyl quaternary ammonium as counterions (usually called SPEC) may its hydrophobic moieties be ‘anchored’ at the air–water interface and contribute to the anomalously high surface activity of SPEC.

It has been assumed[4] that this synergistic action on the surface tension must increase with increasing length of the hydrophobic fragments (the covalently bound alkyl chains to the macromolecule backbone) and the density of alkylation. In the present study we have verified this assumption by tensiometric measurements of the adsorption at the air–water interface of the SPEC formed between covalently alkylated CMCh and cationic surfactants.

CMCh-sodium salt was synthesised by an improved method[5] consisting of treatment of crab chitin with NaOH followed by reaction with monochloracetic acid in water–isopropyl alcohol. The purification and fractionation of CMCh water solution were carried out by ultrafiltration through a selective membrane followed by the freeze drying of CMCh solution. The degrees of substitution (DS) on carboxyl and *N*-acetyl groups were estimated by IR spectrometry of acidic ($\text{pH} \sim 0.7$) CMCh solution in D_2O.[6] Content in carboxyl and *N*-acetyl groups were calculated from the integral intensity of the absorption bands ν(C=O) and ν(amide I) at 1728 cm^{-1} and 1640 cm^{-1}, respectively, assuming molar coefficients of integral intensity as being equal to 50000 and 43000 $\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-2}$, respectively. DS of CMCh in COOH and $NHCOCH_3$ groups were 1.1 and 0.85, respectively. Identical results were observed by using ^{13}C NMR methods. By this method it has been shown that 90% of the carboxymethyl substituents are situated on the C-6 atoms of the elementary units of macromolecules. The molecular weight of the investigated fraction of CMCh was determined by the diffusion–sedimentation method: $M_w = 140000\ \text{g mol}^{-1}$. The carboxylated polymer was then *N*-alkylated with C_{12} or C_{14} aldehyde through a reductive amination.[7] The degree of akylation was $\tau = 0.01$ for the C_{12} chain and $\tau = 0.03$ for the C_{14} chain. This was determined by ^{1}H NMR as previously discussed.[8]

The cationic surfactant tedradecyltrimethylammonium bromide (TDAB) was obtained from Fluka and used without further purification.

Surface tension σ was measured at 25 °C using the Wilhelmy plate method with a K-10ST tensiometer (Kruss, Germany) with an accuracy of $\pm 0.3\ \text{mJ m}^{-2}$. The solutions were prepared using twice-distilled and deionized water followed by exposure for 1 day. The surfactants were progressively added to the stoichiometric ratio based on carboxylic groups and expressed as Z. The pH of solutions was *ca.* 6 and the glucosamine units were admitted unprotonated; the carboxymethylchitins are then purely anionic.

Carboxymethylchitin (CMCh) has no tensioactive properties (curve *1* in Figure 2) but the alkyl carboxymethyl chitins, CMCh_{12} (curve *2*) and CMCh_{14} (curve *3*) present some surface activity when the polymer concentration C_p is larger than 10^{-4} monomol dm^{-3} (the subscripts denote the length of the alkyl side chains). A larger effect is observed when the alkyl chain is longer than that illustrated in Figure 2. This is not surprising taking into account that with increasing hydrophobicity of the polysoaps their adsorption at the air–water interface must increase.

An analogous effect on the surface activity of nonalkylated CMCh results in its hydrophobization by the formation of dynamic associations (the surfactant–polyelectrolyte complexes SPEC) with TDAB in their mixed aqueous solutions. With the highly charged anionic polymer (carboxymethylchitin) ion pairs are formed in the presence of TDAB and tensioactive properties occur as previously discussed[1,4] (Figure 2). With increasing stoichiometric ratio Z of the solution in the range

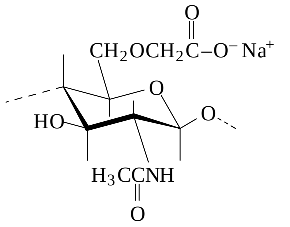

Figure 1 Repeating unit of the nonalkylated CMCh macromolecule.

[†] Polysoap is a covalently alkylated anionic polyelectrolyte carboxymethylchitin.

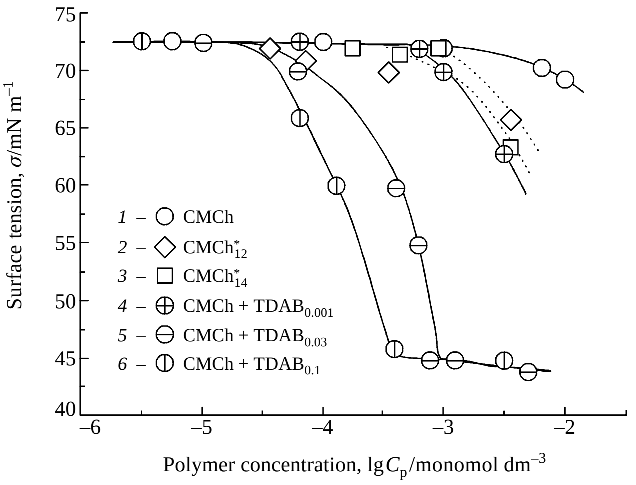

Figure 2 The surface tension isotherms σ as a function of polymer concentration C_p of nonalkylated CMCh (curve *1*), alkylated by C_{12} (curve *2*) and by C_{14} (curve *3*) CMCh, and mixed solutions of nonalkylated CMCh with TDAB at different compositions *Z*: 0.001 (curve *4*), 0.03 (curve *5*) and 0.1 (curve *6*).

0.001–0.1 the surface activity of SPECs increases remarkably (curves *4*–*6* in Figure 2).

It is interesting to point out that from the point of view of their effect on the surface activity the dynamic complexes (SPEC) are revealed to be formally more effective than the alkylated CMCh while the composition $Z \cong 0.001$ of SPECs produces the same effect as the degree of alkylation $\tau = 0.01$ for the C_{12} chain and $\tau = 0.03$ for the C_{14} chain. This is probably related to the impossibility of the adsorbed alkyl side chains of the alkylated CMCh to form a dense packing at the interface because of the steric hindrance originating from the local stiffness of the macromolecule backbone. The nonalkylated sections of the polymeric backbone localized between the neighbouring alkyl side chains 'anchored' at the interface cannot form the 'loops' if their average length *l* is not large enough. So, the average distance between the adsorbed alkyl chains is expected to be determined by this characteristic average length *l* and the stiffness. This explains why the surface activity of the alkylated samples of CMCh are revealed to be relatively low with regard to the nonalkylated CMCh which forms the dynamic SPEC complexes with oppositely charged TDAB molecules.

On the other hand, the interface may produce a disproportionating effect on SPECs producing the increase of their composition *Z*. We must account for the effect of high hydrostatic pressure gradients (~10^3 atm) and the electrostatic field (~10^6 V m^{-1}) in the vicinity of the interface on the structure (the composition) of the adsorbed SPECs. In this case, their apparent surface activity may be greater than the expected surface activity of the complexes assumed to have the bulk composition.

In this connection one may anticipate that the effect of the steric stabilization of emulsions and foams by the adsorption layers of alkylated CMCh must be greater compared to SPECs if one takes into account the presumably greater stiffness and stability of the structure which is formed by the former complexes inside the adsorption layer. Investigations of the composition of the dynamic associations (SPECs) adsorbed at the air–water interface and of the stability of the microscopic liquid (emulsion and foam) films are in progress.

The effect of the length of the covalently bound alkyl chains of the carboxymethylchitin derivatives on the surface activity of their complexes with the surfactant TDAB is shown in Figure 3. In this figure the surface tension is plotted as a function of the surfactant concentration ($C_s = C_p \times Z$). The isotherm $\sigma(C_s)$ of the free surfactant (curve *1*) is given as a reference.

Note first that the surfactant molecules TDAB forming SPECs with nonalkylated as well as with alkylated macromolecules CMCh in the mixed solutions are characterized by the much greater surface activity at the air–water interface than in the case of the pure solution (in the absence of CMCh). An analogous effect is described by other investigators working with other pairs of oppositely-charged surfactants and polyelectrolytes[10–14] and is interpreted as an unambiguous demonstration of the formation of dynamic associations (SPECs) in the bulk of mixed solutions.

For example, the same value of the surface pressure $\pi = \Delta\sigma = 20$ mN m^{-1} (which one usually chooses as a characteristic of the surface activity of surfactants[9]) in the case of the mixed solutions is realized at a concentration of surfactant TDAB which is ~10^2 times lower than in the case of the free (nonbound) TDAB in its individual solution. The degree of adsorption Γ of TDAB in the presence of both nonalkylated and alkylated CMCh estimated by the Gibbs' adsorption equation

$$\Gamma = -\frac{1}{nRT}\frac{d\sigma}{d\ln C},$$

(where $n = 2$ for ionic surfactants in the solution dissociating as $AB \rightarrow A^+ + B^-$ and $n = 1$ for SPECs) is found to be increased more than 100 times compared to that of pure TDAB at the same bulk concentration 2×10^{-4} mol dm^{-3}.

An unexpected finding is that all the isotherms $\sigma(C_s)$ corresponding to the complexes almost coincide below their critical aggregation concentrations (CAC), whose values are almost the same for all samples and stoichiometric ratios *Z*. Moreover, the area $A = 1/\Gamma$ per one surfactant molecule in the adsorption layer remains almost constant and equal to ~50 Å^2 for all the values of *Z* varying in the range 0.001–0.1. This feature may be explained rationally by the assumption that the distance between the adsorbed surfactant molecules is controlled by steric factors (*e.g.*, the distance between the ionized carboxylic groups belonging to the pyranose rings of polysaccharides whose value may be estimated as equal to ~2 nm). At low *Z* the macromolecule is 'anchored' at the interface by only a few alkyl chains of TDAB bound to the SPEC, and acquires an extended conformation forming the long 'tails' and 'loops' at the aqueous side of the interface. At high *Z* the macromolecule is 'anchored' at the interface by multiple alkyl radicals of TDAB and acquires a 'flat' conformation near the interface. It will be interesting to confirm this assumption by a direct measurement of the thickness of the adsorption layer, *e.g.* by the method developed in ref. 15.

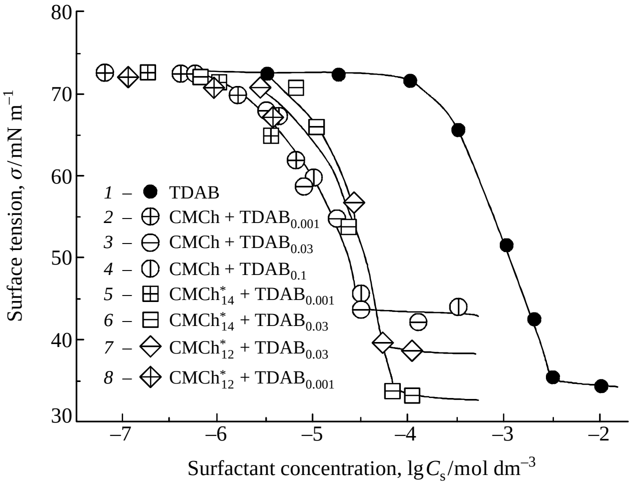

Figure 3 The surface tension isotherms σ as a function of surfactant concentration C_s of an individual TDAB solution (curve *1*) and of mixed solutions of TDAB with nonalkylated (curves *2*–*4*) and alkylated by C_{12} (curves *5*,*6*) and by C_{14} (curves *7*,*8*) samples of CMCh. The stoichiometric ratios and alkyl chain length of alkylated CMCh are indicated as subscripts in the labels of the Figure.

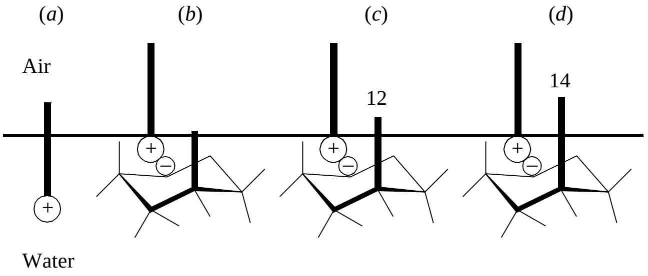

Figure 4 Schematic illustrating the effect of the alkyl chain length on the surface activity of surfactant–polyelectrolyte complexes formed between oppositely-charged surfactants and polysoaps.

In spite of the approximate constancy of CAC in mixed TDAB–carboxymethylchitin solutions, which has been verified for nonalkylated and alkylated CMCh for all alkyl chain lengths, the minimum surface tension $\sigma_{\rm min}$ corresponding to the region $C_{\rm s} > {\rm CAC}$ gradually decreases with increasing length of alkyl side chains (see Figure 3). For example, for nonalkylated CMCh $\sigma_{\rm min} \cong 44$ mN m^{-1} (curves *3*,*4*), whereas for alkylated CMCh with 12 and 14 chains $\sigma_{\rm min}$ acquire the values ~39 mN m^{-1} (curves *5*,*6*) and ~33 mN m^{-1} (curves *7*,*8*), respectively.

Figure 4 explains qualitatively how the alkyl side chains may contribute to an increase in the surface pressure π (*i.e.*, to a decrease of $\sigma_{\rm min}$) of SPEC. In the case of nonalkylated CMCh the synergistic effect on the surface activity is explained by the neutralization of the alkyl counterion TDAB bound to SPEC [Figure 4(*a*)]. This produces a greater immersion in the nonpolar medium (air) [Figure 4(*b*)] and a gain in the free surface energy. An additional contribution to the surface activity is provided by the possible immersion in the air of small hydrophobic fragments peculiar to CMCh [Figure 4(*b*)].

In the case of alkylated CMChs the alkyl side chains are immersed in the air, and the gain in the free surface energy, which characterized the synergistic effect of SPECs on the surface activity, must increase with increasing hydrophobicity of the alkyl chains [Figures 4(*c*) and 4(*d*)]. This explains why the minimum surface tension $\sigma_{\rm min}$ gradually increases with increasing alkyl chain length.

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