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Mechanism of anomalous high adsorption activity of surfactant–polyelectrolyte complexes between tetradecyltrimethylammonium bromide and (carboxymethyl)chitin

Valery G. Babak,*[a] Galina A. Vikhoreva[b] and Mikhail A. Anchipolovsky[a]

[a] *Institute of Food Substances, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: babak@ipv.ineos.ac.ru*
[b] *Moscow State Textile Academy, 117918 Moscow, Russian Federation.*

A mechanism explaining the anomalously high synergistic effect of oppositely charged surfactants and polyelectrolytes on the surface tension of their mixed solutions is suggested.

It is known that oppositely charged ionic surfactants and polyelectrolytes form addition complexes resulting from strong electrostatic forces and that complexation begins at a very low surfactant concentration.[1–7] It has been found that complexes with a 1:1 stoichiometry with respect to the charges precipitate from aqueous solution.[1,8] With increasing surfactant concentration micelle-like clusters bound to a polyelectrolyte (PE) backbone begin to form; this process is characterized by a highly cooperative zipper mechanism and the concentration at which it commences is known as the critical aggregation concentration (CAC). Usually the CAC is 1–3 orders of magnitude smaller than the critical micelle concentration, CMC (in the absence of polyelectrolyte). The surfactant clusters (aggregates) are generally smaller than the polymer-free micelles,[9–11] and it is more than likely that the polyelectrolyte is predominantly coiled around the exterior of the bound surfactant micelles, as described by the so-called 'necklace model'.[11,12]

Hydrosoluble, weakly-hydrophobic polyelectrolytes, in the absence of neutral electrolyte and with a relatively high degree of ionization, are known to possess rather poor adsorption activity at both air–water and oil–water interfaces.[13,14] In contrast, hydrosoluble surfactant–polyelectrolyte complexes (SPECs) manifest very high adsorption activity at both air–water and oil–water interfaces, as well as increased emulsifying and foaming capacities.[15–18] A high synergistic action on the surface and interfacial tensions of mixed aqueous solution has been found for different oppositely-charged pairs of ionic surfactants and polyelectrolytes forming SPECs; for example, dodecyl sulfate (DDS) – *N*,*N*′-dimethylaminoethylmethacrylate,[15] tetraalkylammonium (TAA)–carboxymethyl cellulose,[16] TAA–(carboxymethyl)chitin[17] and DDS–chitozan.[18]

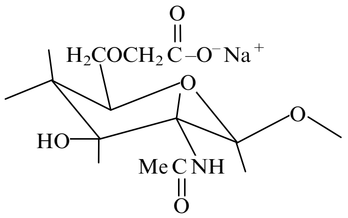

Figure 1 Repeating unit of the CMCh macromolecule.

As part of our investigations into the problem of the steric stabilization of dispersions by adsorption layers of PE, we have studied the surface properties of SPECs formed between different derivatives of chitin and ionic micelle-forming surfactants.[17–19] In this paper we present the results of our experimental study on the surface activity at the air–water interface of the SPEC between the anionic PE (carboxymethyl)chitin (CMCh) and the cationic surfactant tetradecyltrimethylammonium bromide (TDTMABr). The anionic surfactant sodium dodecyl sulfate (DDSNa) was taken as a surfactant which is believed not to form a SPEC with CMCh.

The sample of CMCh [DP = 600; the DS of carboxylic and *N*-acetyl groups are equal to 1.1 and 0.85, respectively; $pK_{\alpha=0.5} = 3.4$ relative to carboxylic groups (Figure 1)] was synthesized and characterized according to ref. 20. Both TDTMABr and DDSNa were obtained from Fluka.

We have found[17] that CMCh at pH = 6 ± 0.2 does not reduce the surface tension σ of its aqueous solutions even for concentrations (C) up to 0.01 mol dm^{-3} (curve 1, Figure 2) testifying to the zero surface adsorption activity at the air–water interface. Cationic TDTMABr and anionic DDSNa surfactants also manifest low surface activity below a concentration of 2×10^{-4} mol dm^{-3} while they reduce σ by less than 3 mN mol^{-1} (curves 2 and 3, Figure 2). But in mixed solutions of CMCh and TDTMABr in the molar ratio Z = [surfactant]/[CMCh] equal to 0.001–1 with [TDTMABr] equal to 2×10^{-4} mol dm^{-3}, the surface tension σ is reduced by more than 30 mN m^{-1} (curves 4–7, Figure 2)

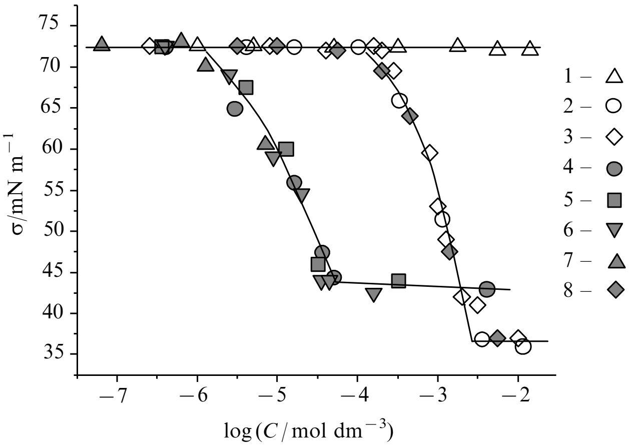

Figure 2 Surface tension (σ) of CMCh, ionic surfactants and their mixed solutions against the concentration of the surfactant at 25 °C (Z = [surfactant] / [CMCh]): 1, CMCh; 2, TDTMABr; 3, DDSNa; 4, TDTMABr + CMCh ($Z = 1$); 5, TDTMABr + CMCh ($Z = 0.1$); 6, TDTMABr + CMCh ($Z = 0.03$); 7, TDTMABr + CMCh ($Z = 0.001$); 8, DDSNa + CMCh ($Z = 1$).

and this effect is independent of Z. In contrast to TDTMABr, the anionic surfactant DDSNa is not affected by the presence of CMCh and the surface tension isotherm for a blend of DDSNa and CMCh (curve 8, Figure 2) coincides with that of pure DDSNa in solution (curve 3, Figure 2).

The adsorption amount Γ of TDTMABr in the presence of CMCh can be evaluated according to the Gibbs' adsorption equation:

$$\Gamma = \frac{1}{nRT}\frac{\mathrm{d}\sigma}{\mathrm{d}\ln C} \qquad (1)$$

(where n = 2 for ionic surfactants dissociating as $AB \rightarrow A^+ + B^-$) and is found to be increased more than 100 times compared to that of pure TDTMABr at the same bulk concentration of 2×10^{-4} mol dm^{-3}. However, Γ for DDSNa at the same concentration is identical to that of TDTMABr but, unlike TDTMABr, it does not depend on the presence of CMCh. Thus, it is obvious that nonstoichiometric SPECs are formed between CMCh and TDTMABr in their mixed solutions, and that such complexes do not form between CMCh and DDSNa.

Moreover, all the adsorbed molecules of TDTMABr at the air–water interface in mixed solutions with CMCh are bound with the negatively charged carboxylic groups of the CMCh macromolecular chain; their adsorption energy is much greater than that of free TDTMABr molecules adsorbed at the same interface in the absence of CMCh. The standard adsorption free energy $\Delta_{ad}G^0{}_{298}$, of one mole of TDTMABr molecules in the presence of CMCh can be evaluated according to the relationship derived and discussed in ref. 21:

$$\Delta_{ad}G^0{}_{298} \;=\; RT\ln(C/\pi)|_{20} \qquad (2)$$

which is defined for the hypothetical standard state $a \cong C = 1$ and $\pi = 1$ (where a and C are bulk surfactant activity and concentration, respectively, π is the surface pressure equal to the difference between the surface tension of pure water (σ_0) and that of the solution (σ) and the index '20' signifies that the corresponding quantities are taken at π = 20 mN m^{-1}), the derived value is −34.0 kJ mol^{-1}, whereas $\Delta_{ad}G^0{}_{298}$ = −24.0 kJ mol^{-1} for a solution of free TDTMABr. To account for the fact that the adsorption amount Γ of TDTMABr molecules, free and bound to SPEC, evaluated according to equation (1), are both equal to 3.4×10^{-6} mol m^{-2}, we can conclude that the difference in $\Delta_{ad}G^0{}_{298}$ (equal to −10.0 kJ mol^{-1}) is due to the qualitatively new adsorption ability of TDTMABr molecules resulting from their binding to CMCh macromolecules. In this connection it is interesting to point out that the increment of $\Delta_{ad}G^0{}_{298}$ per one mole of CH_2 (or CH_3) group of the alkyl radical is equal to −1.8 kJ mol^{-1} for the free surfactant molecule (which is typical of ionic surfactants) and to −2.4 kJ mol^{-1} for the TDTMABr molecules which are part of a SPEC (which is typical of non-ionic oxyethylated surfactants).[22,23]

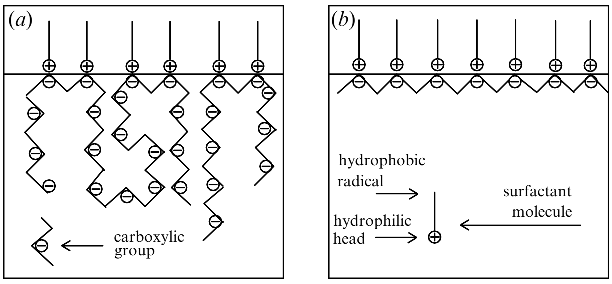

Figure 3 Schematic representation of the adsorption of the SPEC at (*a*) low and (*b*) high composition; φ = [surfactant] / [CMCh].

The aforementioned increase in the free adsorption energy of TDTMABr molecules binding with CMCh to form a SPEC may be explained, on the one hand, by the neutralization of the electric charges of surfactant ions that reduces to zero the repulsive electrostatic force acting between TDTMABr molecules forming the adsorption layer and favours their deeper immersion in the nonpolar phase. A second reason for this increase may be the adsorption of the hydrophobic fragments of the pyranose cycles of CMCh at the air–water interface which could not be realized before complexation with TDTMABr molecules because of the high solubility of free CMCh macromolecules in the aqueous phase due to their high degree of ionization.

Figure 3 illustrates the suggested mechanism of the adsorption of SPEC molecules at the air–water interface. Particularly, the observed independence of the standard free adsorption energy $\Delta_{ad}G^0{}_{298}$ from the composition Z of the mixed solution may be rationalized by assuming the existence of different conformational states of the SPEC macromolecules near the interface. For example, at low values of Z and, presumably, at low and approximately equal to Z values of [TDTMABr] / [CMCh] (designated φ) of the adsorbed SPEC, the macromolecule of the SPEC is 'anchored' to the interface by only a few alkyl radicals forming the so-called 'loops' and 'tails' in the aqueous phase (Figure 3*a*). The thickness δ of this adsorption layer is of the order of the size of the statistical macromolecular coil in the solution.

But at relatively high values of Z (and presumably at correspondingly high values of φ of SPEC complexes) the

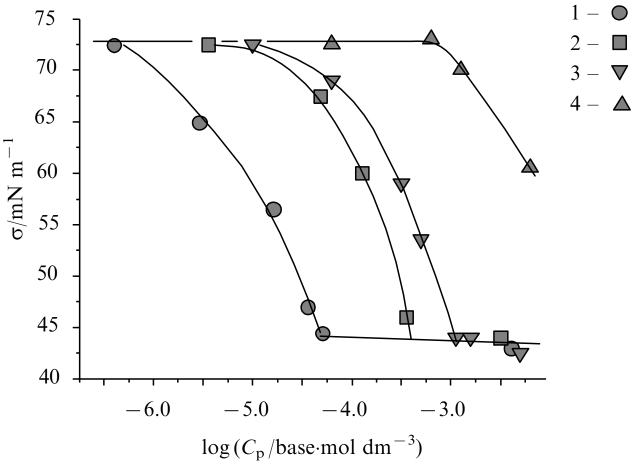

Figure 4 Effect of the value of φ of SPEC between CMCh and TDTMABr on their surface tension isotherms (C_p = concentration of the polysaccharide component in the complexes). 1, φ = 1; 2, φ = 0.1; 3, φ = 0.03; 4, φ = 0.001.

adsorbed SPEC molecules acquire a 'flat' conformation at the interface, and consequently the thickness δ of the adsorption layer is much lower (Figure 3*b*).

Thus, depending on the ratio Z of the mixed solution of the oppositely charged surfactant and PE (or φ of the SPEC) the thickness δ of the adsorption layer is varied. Taking into account that the stability of microscopic emulsion and foam films to rupture increases with increasing thickness of the adsorption layers of polymers and adsorption energy,[24] the possibility of control of this stability by varying the parameter Z may be of great importance for emulsion and foam technology.

Another aspect of the problem considered consists in the possibility of engineering 'new' macromolecules with finely controlled adsorption activity *via* formation of a SPEC between oppositely charged surfactants and PEs. Figure 4 illustrates how the isotherms of surface tension (σ) of a SPEC depend on the value of φ (assumed to be equal to Z). Since the standard free adsorption energy of a SPEC per base.mole of CMCh $\Delta_{ad}G^0{}_{298}$ (kJ base.mol^{-1}) calculated on the basis of equation (2) is given by the relationship

$$\Delta_{ad}G^0{}_{298} \cong -34.0 - RT\ln\varphi \qquad (3)$$

the possibility arises of varying the adsorption energy of a SPEC macromolecule by varying φ of the complex. In our case the zero adsorption ability of CMCh may be highly improved and finely 'corrected' by binding this macromolecule with the exact number of TDTMABr molecules calculated according to equation (3).

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