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Mechanism of steric stabilization of microscopic foam films by adsorption surfactant layers of surfactant–polyelectrolyte complexes of oppositely charged tetradecyltrimethylammonium bromide and carboxymethylchitin

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The mechanism of steric stabilization of microscopic foam films is discussed from the viewpoint of the anomalously high adsorption activity of the complexes formed by oppositely charged surfactants and polyelectrolytes in mixtures of their aqueous solutions.

It has been shown previously[1–3] that the surfactant–polyelectrolyte complexes (SPEC) formed between the oppositely charged cationic surfactant tetradecyltrimethylammonium bromide (TDTMABr) and the anionic polyelectrolyte carboxymethylchitin (CMCh) exhibit an anomalously high adsorption activity at the water–air interface. We found that the value of the standard free energy of adsorption $\Delta_{\mathrm{ad}}G^0_{298}$ of surfactant molecules bound to SPEC considerably exceeds the corresponding value of the adsorption energy for free (unbound in complex) surfactant molecules. We explained this fact by the influence of two factors: (i) neutralization of the electric charge of the surface-active cation bound with SPEC and (ii) possible adsorption of hydrophobic fragments of the anionic PE at the water–air interface. A mechanism suggested for the adsorption of SPEC explains why the value of the standard free energy of adsorption $\Delta_{\mathrm{ad}}G^0_{298}$ is almost independent of the composition of the complex $\varphi = [\mathrm{TDTMABr}]_\mathrm{b}/[\mathrm{CMCh}]$ which was varied within a rather wide range (from 0.001 to 1), where $[\mathrm{TDTMABr}]_\mathrm{b}$ is the concentration of surfactant molecules bound in the complex.

In terms of our studies on the problem of the steric stabilization of dispersions by adsorption PE layers, we studied the ability of SPEC, formed by the oppositely charged species TDTMABr and CMCh in mixed aqueous solutions, to stabilize microscopic foam films (MFF) and foams.[4–5]

The sample of CMCh [DP ≈ 600; DC with respect to carboxyl and *N*-acetyl groups is 1.10 and 0.85, respectively; $\mathrm{p}K_{\alpha=0.5}$ is equal to 3.4 when the ionic strength of the solvent (NaCl) is 0.5 mol dm^{-3}] (Figure 1) was synthesized and characterized according to ref. 6. TDTMABr is commercially available (Fluka).

Microscopic foam films (MFF) with a rigidly controlled surface area were obtained by the method of contact interactions between fluid drops in a liquid medium as described in refs. 7 and 8. This method is based on the achievement of mutual contact between two air bubbles in a mixed aqueous solution of a surfactant and a PE. Air bubbles 1 mm in diameter are fixed at the ends of two glass pipes, one of which is motionless and the second pipe is rigidly fixed to the holder of a dynamometer of a magnetoelectric system (MES) graduated by the current strength. The lifetime τ before coalescence of these air bubbles (or, which is the same, the lifetime before the rupture of MFF formed between the bubbles) was measured. The MFF surface area A was maintained constant (equal to 1.2×10^4 μm^2) in all experiments by application of a constant compressive force f_p using the MES dynamometer. The characteristic lifetime of MFF (τ^*) corresponding to the probability of their destruction (which is

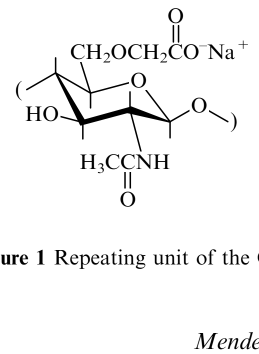

Figure 1 Repeating unit of the CMCh macromolecule.

equal to 63%[7,8]) was determined from the experimental histograms of the film distribution over their lifetimes, which were plotted on the basis of 10 to 20 independent measurements of τ. The controlled parameters were the concentrations of PE (C_p) and the surfactant (C_s) in mixed aqueous solutions, pH and the concentration of the neutral electrolyte (C_{NaCl}), time of formation (ageing) of adsorption layers of the surfactant and PE (t_f), temperature T, *etc.*

Typical isotherms of stability of MFF (*i.e.*, the dependences of the characteristic lifetime τ^* on the PE concentration C_p) are presented in Figure 2. The characteristic feature of these isotherms is a drastic increase in the τ^* value from several seconds to 10^3 s and more in a narrow range of the change in PE concentration beginning from some critical concentration C^*, which is unambiguously determined by the type of the surfactant or PE as well as by the combination of the physicochemical parameters characterizing the conditions of formation of MFF (for example, $Z = C_s/C_p$, pH, C_{NaCl}, t_f, T, *etc.*). The drastic increase in the stability of MFF is caused by the formation of protecting adsorption layers on their surface, which prevent a fast thinning and rupture of MFF.

It is noteworthy that the lifetime of MFF in the case of mixed solutions of the surfactant and PE is considerably greater than the corresponding lifetime of films stabilized by pure CMCh in the absence of surfactant. For example, the characteristic concentration of PE, C_p^*, corresponding to the lifetime of MFF $\tau^* = 10^3$ s (chosen as standard[7]) decreases from 4×10^{-4} base-mol dm^{-3} corresponding to pure CMCh (curve *1* in Figure 2) to 2×10^{-5} base-mol dm^{-3} corresponding to a mixed solution of the composition $Z = 0.1$ (curve *4* in Figure 2).

The ability of surfactants and PE to stabilize MFF in mixed solutions is characterized by a strong synergetic effect and considerably exceeds the stabilizing effect of individual surfactants or PE at the same concentration. In fact, in the example considered above, the lifetime of MFF, τ^*, is greater than 10^3 s for a mixed solution of composition $Z = 0.1$ at concentrations of TDTMABr and CMCh equal to 2×10^{-6} mol dm^{-3} and 2×10^{-5} base-mol dm^{-3}, respectively (curve *4* in Figure 2). At the same time, the stability of MFF stabilized by individual TDTMABr and CMCh does not exceed several seconds (curves *1* and *7* in Figure 2).

In the case considered of oppositely charged surfactant (TDTMABr) and anionic PE (CMCh), the synergetic effect on the film stability toward rupture can only be reasonably explained by the formation of adsorption layers of SPEC at the water–air interface and mutual repulsion of these layers inside MFF. It is likely that the higher stabilizing effect of SPEC compared to that of pure PE can be explained by the higher surface activity of the complex in which bound hydrophobic alkyl radicals of surfactant molecules act as 'anchors' preventing desorption of the complexes and their removal with the liquid medium flowing away upon thinning of the film (Figures 3*a* and 3*b*).

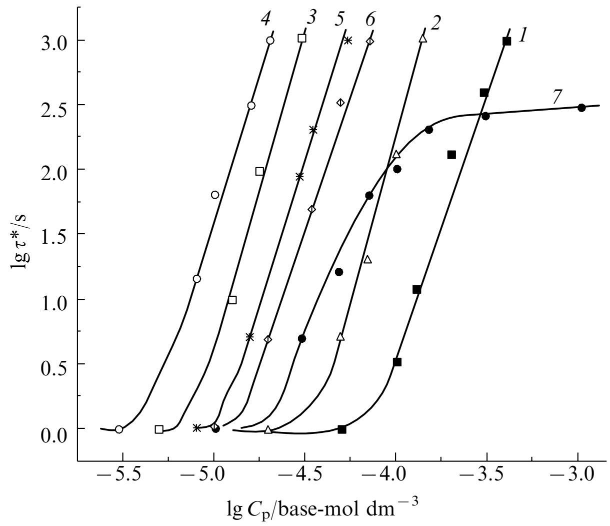

Figure 2 Isotherms of the stability (the lifetime before rupture τ^*) of microscopic foam films (MFF) prepared from mixed TDTMABr–CMCh solutions of different composition Z = [TDTMABr]/[CMCh] against the CMCh concentration C_p (base-mol dm^{-3}) at 25 °C. ($C_{NaCl} = 3\times10^{-3}$ mol dm^{-3}, $t_f = 200$ s). Curve *1* CMCh (Z = 0); *2* TDTMABr + CMCh (Z = 0.01); *3* TDTMABr + CMCh (Z = 0.05) ; *4* TDTMABr + CMCh (Z = 0.1) ; 5 TDTMABr + CMCh (Z = 0.3) ; *6* TDTMABr + CMCh (Z = 1) ; *7* TDTMABr (concentration expressed in mol dm^{-3}).

Figure 4 (curve *1*) illustrates the dependence of the characteristic concentration C_p^* on the composition φ of the complexes on the assumption that it coincides with the composition of the mixed solution Z.[1,2] When φ decreases in the range from 0 to 0.1, the characteristic concentration C_p^* decreases by more than an order of magnitude, which testifies to the increasing stabilizing ability of SPEC. Upon a further increase in the composition of the complex (φ), the C_p^* value no longer decreases and even undergoes an increase in the range $\varphi = 0.1$–1. In other words, the composition of SPEC $\varphi = 0.1$, *i.e.* 60 surfactant molecules per macro-ion consisting of 600 monomeric units, is the critical composition for the stabilization of MFF, and a further increase in the amount of hydrophobic radicals per macro-ion does not result in an enhancement of the stabilizing ability of SPEC. Thus, beginning from this critical composition $\varphi^* < 0.1$, the complex gains a qualitatively new ability of stabilization of MFF, which differs from its stabilizing ability in the range of $\varphi < 0.1$.

The aforementioned variation of the stabilizing ability of

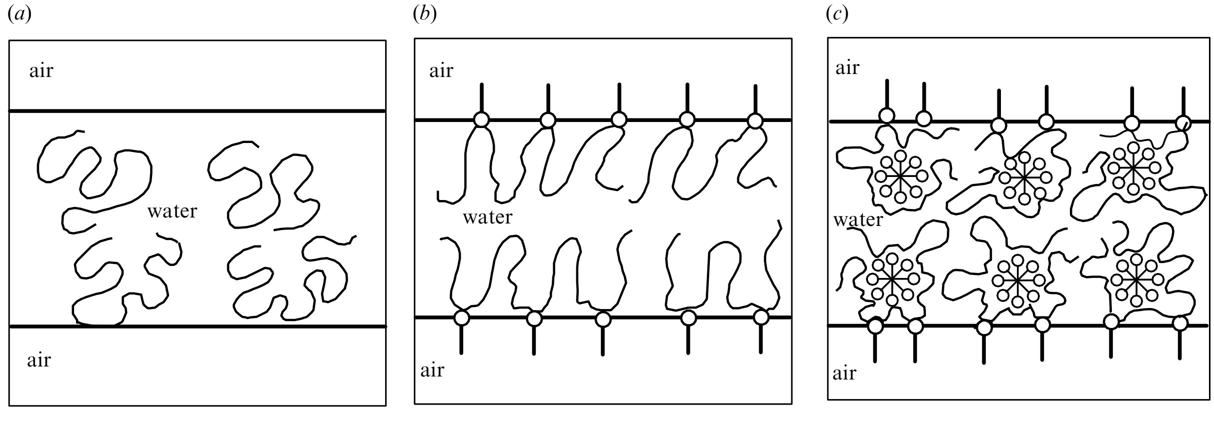

Figure 3 Schematic representation of the steric stabilization of MFFs by pure PE (*a*) and SPEC below (*b*) and above (*c*) the critical aggregation concentration.

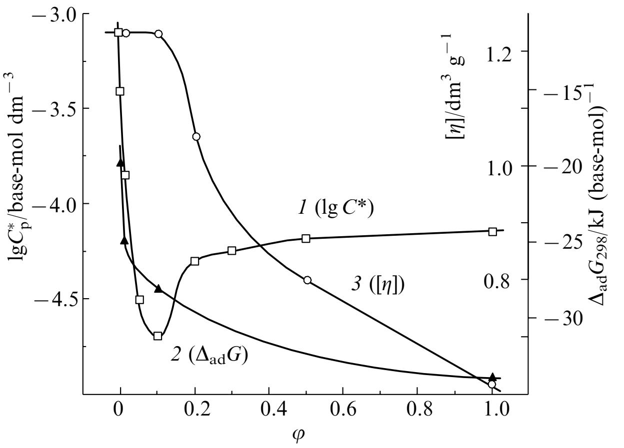

Figure 4 Effect of the composition (φ) of SPEC between TDTMABr and CMCh on the characteristic concentration C^*_p of CMCh (corresponding to the MFF lifetime $\tau^* = 10^3$ s) (*1*), on the standard adsorption free energy ($\Delta_{ad}G^0_{298}$) of SPEC at the air–water interface (*2*), and on the intrinsic viscosity, $[\eta]$, of SPEC solutions (*3*).

SPEC with increasing φ correlates well with the variation of their adsorption activity at the air–water interface as a function of φ. Curve *2* in Figure 4 presents the isotherm of the standard adsorption free energy $\Delta_{ad}G^0_{298}$ as a function of φ, estimated from the isotherms of the surface tension of the mixed TDTMABr–CMCh solutions.[1] In the SPEC compositon range φ = 0–0.1 the value of $\Delta_{ad}G^0_{298}$ decreases sharply by more than 15 kJ base-mol^{-1}, whereas in the range φ = 0.1–1 the corresponding decrease does not exceed 5 kJ base-mol^{-1}. So, the mean rate of decreasing of the adsorption free energy of SPEC with increase of φ diminishes more than 30 times when traversing the critical composition of SPEC is equal to $\varphi^* = 0.1$.

And, finally, the isotherm of the characteristic viscosity $[\eta]$ of mixed surfactant-PE solutions as function of the SPEC composition φ (see curve *3* in Figure 4) manifests a step-wise decrease also at the critical composition of SPEC $\varphi^* = 0.1$. The characteristic viscosity $[\eta]$ remaining practically constant in the SPEC composition region φ = 0–0.1 testifies to the constancy of the size of the statistical macromolecular coil of the SPEC. But decreasing of $[\eta]$ in the region of $\varphi > \varphi^* = 0.1$ may be interpreted as a collapse of the macromolecular coil of SPEC in the bulk of the solution.

The aforementioned dependences of the stabilizing ability (characteristic concentration C^*_p), adsorption activity of SPEC (standard free energy of adsorption $\Delta_{ad}G^0_{298}$), and macromolecular sizes of SPEC (intrinsic viscosity of mixed solutions, $[\eta]$) on the composition of the complexes (φ) (see curve *3* in Figure 4) can be reasonably explained by the formation of micellar-like clusters (associates) of surfactant molecules bound in SPEC.[9] The formation of these associates begins at some critical concentration of the surfactant and is characterized by a highly cooperative character.

Thus, the difference in the stabilizing ability of SPEC (with respect to MFF) with compositions lower and higher than $\varphi^* = 0.1$ is caused by the structure and conformational state of SPEC. At $\varphi < \varphi^* = 0.1$, the SPEC is a statistical ball that is capable of adsorbing at the water–air interface by almost all its alkyl fragments (Figure 3*b*). In this composition range of SPEC, an increase in φ (*i.e.* the number of surfactant molecules bound with the SPEC macromolecule) results in an increase in the free energy of adsorption of the SPEC on the surface and, hence, increases the stability of MFF.

At $\varphi > \varphi^* = 0.1$, the SPEC is an ensemble of micellar-like aggregates bound with the polyelectrolyte chain and it adsorbs on the surface only by its relatively free alkyl fragments, which are not involved in micellar-like aggregates stabilized by hydrophobic bonds (Figure 3*c*). An increase in φ in this range results in an increase in the number of micellar-like aggregates involved in the adsorption process. Therefore, the standard free energy of adsorption of SPEC remains almost unchanged in MFF and exerts no substantial effect on the stability of MFF in the range of a change in the composition of SPEC (φ) from 0.1 to 1. Some decrease in the stability of MFF in the composition range of the complexes from 0.1 to 1 (see curve *1* in Figure 4) can be explained by a substantial decrease in size of the SPEC, *i.e.* by their compacting due to the cooperative hydrophobic interactions between the alkyl radicals of the surfactant molecules forming micellar-like aggregates on the SPEC macromolecules. In this case, a decrease in the adsorption surface of the SPEC macromolecule is compensated by an increase in C^*_p corresponding to the formation of the compact monolayer on the MFF surface.

The stability of MFF toward rupture depends on the composition φ of the SPEC, and this dependence can be predicted, in principle, and described analytically. This provides an opportunity for control and can be of considerable interest in foam technologies.

Another aspect of the problem under study is the possibility of creating (engineering) 'new' macromolecules possessing a finely controlled stabilizing ability with respect to foams *via* the formation of a SPEC between oppositely charged surfactants and PEs. In this case, the low foam-forming ability of CMCh can be substantially enhanced by binding its macromolecules with the number of TDTMABr molecules calculated *via* isotherms of MFF stability (Figure 2).

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