Interaction of carboxymethylchitin with the Langmuir monolayers of cationic surfactants

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The monolayer technique has been used to study the interfacial behaviour of complexes formed between cationic surfactants (insoluble in water: dioctadecyldimethylammonium bromide, DODAB) and anionic polyelectrolyte (carboxymethylchitin, CMCh).

In our previous publications[1–3] we have demonstrated that the adsorption layers of dynamic associates, formed between oppositely-charged surfactants (S) and polyelectrolytes (P) (the so-called nonstoichiometric surfactant–polyelectrolyte complexes, SPEC), are characterised by the high surface density of the bound surfactant molecules and the two-dimensional ordering of their structure (by liquid-crystalline properties).

In particular, we have found that the area per molecule in the adsorption layer of the cationic surfactant (tetradecyltrimethylammonium bromide, TDAB) which forms a SPEC with the anionic polyelectrolyte (carboxymethylchitin, CMCh), is *ca.* 0.5 nm^4 and hardly depends on the composition $Z = C_S/C_P$ of their mixed solutions over the large range of $Z = 10^{-4}$–10^{-1} mol/base-mol. For example, at a concentration of TDAB *ca.* 10^{-5} mol dm^{-3}, corresponding to zero adsorption amount from its individual aqueous solution, the addition to the solution of the surface inactive (non-adsorbing) anionic polyelectrolyte CMCh at $Z < 10^{-1}$ mol/base-mol leads to almost complete transfer of both species, the surfactant and polyelectrolyte.

In the present study we have used the monolayer technique to obtain a more detailed characterization of the parameters of the surface layers of SPEC, formed between oppositely-charged surfactants and polyelectrolytes.

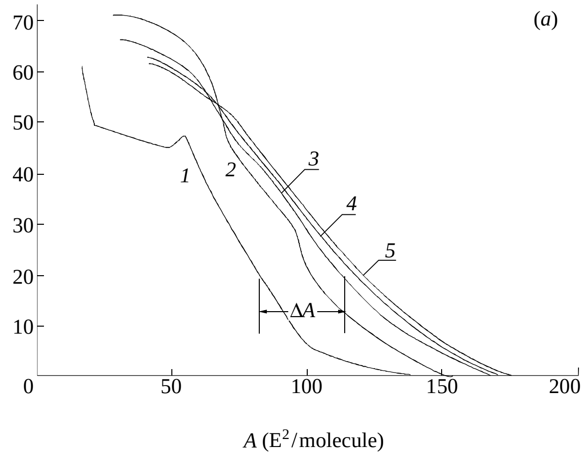
The sample of CMCh (DP = 600; DS on carboxylic, *N*-acetyl and NH$_2$ groups equal to 1.1, 0.85 and 0.1, respectively; p$K_{a = 0.5}$ = 3.4 in 0.5 mol dm^{-3} solution of NaCl) was synthesised and characterised according to ref. 4. The pH of the solutions was *ca.* 6 at which the glucosamine units are therefore confirmed as non-protonated and the carboxymethylchitins are purely anionic.

The water-insoluble dioctadecyldimethylammonium bromide (DODAB) was obtained from ‘Sigma’. Monolayers were studied on a commercial film balance (Lauda, Germany). The solutions of DODAB in chloroform were spread on the air–water interface and CMCh was adsorbed on the surfactant monolayers from the water subphase at a surface pressure value close to zero. The izotherms of surface pressure (p) *versus* area (A) per molecule in insoluble monolayers were recorded during the continuous compression of the monolayers.[5] The rate of compression of the monolayers was 10^{-4} m^2 s^{-1}.

The (p–A) isotherm of DODAB on the air–water interface [see curve *1*, Figure 1(*a*)] is characterised by the collapse at $p = 45$ mN m^{-1}, which is typical for insoluble surfactant monolayers and corresponds to the area A per molecule of DODAB equal to 0.6 nm^2. In the presence of the water-soluble and surface-inactive anionic polyelectrolyte CMCh in the aqueous subphase the corresponding isotherms undergo a pronounced expansion (curves *2*–*5*) testifying to an increase of the *effective* area per molecule in the monolayer.

This increase of the area ΔA occurs simultaneously with increasing the CMCh bulk concentration C_P but only up to the value of 4×10^{-5} base-mole dm^{-3}; after that, ΔA remains constant with further increase in C_P. Figure 1(*b*) illustrates how the area ΔA (conventionally determined at $p = 20$ mN m^{-1}) depends on C_P. The collapse of mixed DODAB–CMCh monolayers occurs at greater values of the surface pressure ($p = 60$ mN m^{-1}) testifying to the increase in the monolayer stability when it is formed in contact with the oppositely-charged macroions of CMCh.

The increase of ΔA observed for mixed DODAB–CMCh monolayers proves that the interaction between oppositely-charged surfactant and polyelectrolyte molecules effectively occurs at the air–water interface. The anionic CMCh, being



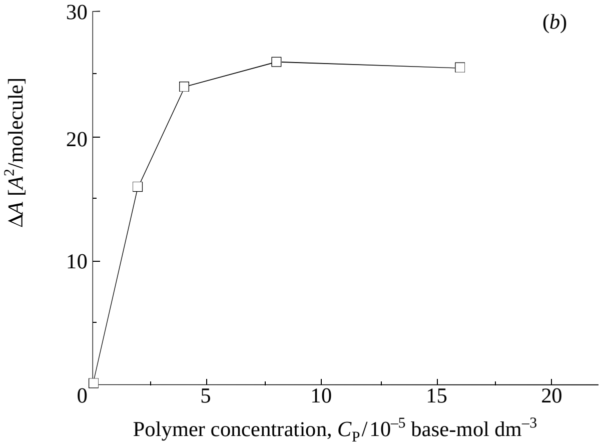


Figure 1 Effect of CMCh in the aqueous subphase on the surface pressure of DODAB monolayers: (*a*) surface pressure p, area A isotherms for different CMCh concentrations, $C_P/10^{-5}$ base-mol dm^{-3}: *1*, 0; *2*, 2; *3*, 4; *4*, 8; *5*, 1.6; (*b*) increase of the area ΔA per one molecule of DODAB as a function of C_P.

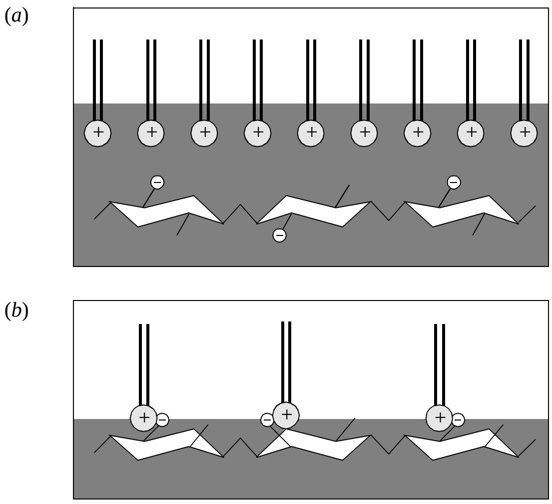


Figure 2 Scheme illustrating the formation of the ordered structures at the interface.

weakly hydrophobic and highly ionized in the aqueous solution, manifests no surface activity within the chosen range of its concentration and one may neglect its contribution to the surface pressure. Consequently, this increase in ΔA may be explained only by the assumption that SPEC effectively form between DODAB and CMCh at the interface.

As regards the increase in ΔA, this may be attributed to different mechanisms. Figure 2 illustrates the difference between the structure of free spread monolayer (*a*) and macroions bound to CMCh (*b*). As has been mentioned in relation to the adsorption layers between TDAB and CMCh, the screening of the electric charge of the DODAB molecule decreases the hydrophilicity of the polar head of this molecule and consequently favours its deeper immersion in the nonpolar phase (air) and thereby increases the area per lipid molecule. The decrease of the free energy of the system (*i.e.*, the increase of the free adsorption energy of surfactant molecules) is also produced similarly to the case of SPECs formed by the water-soluble TDAB.[1–3] On the other hand, one must point out that the observed increase in ΔA seems to be much greater than that which could be produced by partial immersion of the DODAB hydrophilic head in the nonpolar phase. The increase of ΔA contradicts the expected bringing together of ionic surfactant molecules bound to SPEC in the adsorption layer due to the neutralization of their electric charge in contact with the oppositely-charged functional groups of P and consequently to the decrease of the electrostatic repulsion.

We find it very surprising that the area A per one lipid molecule at the interface ceases to vary at some value of the CMCh concentration ($C_\mathrm{P} = 4\times10^{-5}$ base-mole dm^{-3}) and remains constant with subsequent increase in C_P. This fact may be rationalized by the assumption that the area A is determined not by the size of the lipid molecule but essentially by the distance between negatively-charged carboxyl fragments of CMCh macroion in the vicinity of the interface. This distance depends in its turn on the size of the pyranose rings and the flexibility of the polysaccharide macromolecules which determine the possibility for these macromolecules to acquire a ‘flat’ and conveniently oriented conformation near the interface. The alkyl radicals of lipid molecules bound to the negative sites of macromolecules and immersed into the nonpolar phase play the role of ‘anchors’ which stabilize this two-dimensional ordered structure.

The possibility of the hydrophobic fragments of the CMCh macromolecules (*N*-acetyl groups) being adsorbed at the interface and contributing to the increase of A and to the resistance of this structure to collapse under lateral compression must be taken into account. This possibility, which could not be realized at the free air–water interface (in the absence of DODAB monolayer) because of the weak surface activity of CMCh macromolecules, may be realized now when the cooperative (multiple) interaction between the oppositely-charged CMCh and DODAB molecules favours the irreversible adsorption of CMCh macroions at the interface.

Earlier[1] we found that the area A per one lipid molecule in the adsorption layer of water-soluble SPEC formed between TDAB and CMCh does not depend on the bulk concentration of CMCh (more precisely, on the composition Z of the mixed solution). It seems that in the case of insoluble DODAB spreading monolayers the area A is mostly determined by factors influencing the conformation of the macromolecules near the interface (such as the size of the repeating units and the hardness of the macromolecular chain) and the surface density of negatively charged functional groups, and to a lesser extent by the size of the surfactants themselves.

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