Dynamic surface tension of hydrophobically modified chitosans

Valery G. Babak*[a,b] and Jacques Desbrières[b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: babak@ineos.ac.ru*
[b] *CERMAV–CNRS, affiliated with Joseph Fourier University, BP53, 38041 Grenoble cedex 9, France*

Dynamic tensiometry has been applied to a comparative study of the kinetics of adsorption of cationic polysoaps (alkylated chitosans) and dynamic associates (surfactant–polyelectrolyte complexes, SPECs) between chitosan and the anionic surfactant SDS at the air–water interface.

It is well known that the hydrophobic modification of hydrophilic polyelectrolytes (PE) by the covalent binding of alkyl groups or by the formation of non-stoichiometric dynamic associates with oppositely charged surfactants (surfactant–polyelectrolyte complexes, SPECs) in mixed aqueous solutions leads to a remarkable increase of the adsorption of polyelectrolytes at interfaces.[1–9]

The moving force of the adsorption of alkylated polyelectrolytes (so-called polysoaps) is a substantial gain in the free energy of the system due to the transfer of alkyl groups of the macroions from the bulk of the solution into the non-polar (air or oil) phase.[1,3] If the density of alkyl groups [related to the degree of substitution (DS) by the alkyl groups] increases, the adsorption of polysoaps becomes irreversible because of the multiplicity of adsorption contacts with the interface.[3,10] In this meaning, the interfacial behaviour of alkylated polyelectrolytes is analogous to that of proteins, which adsorb irreversibly undergoing denaturation (*i.e.*, the transfer from the compact globular to the extended flat conformation) at the interface.[11,12]

The aim of this work was to study the dynamic surface tension of hydrophobically modified chitosans obtained by covalent alkylation and the formation of SPEC with the anionic surfactant SDS.

The precursor chitosan from Pronova (Norway) with a molecular weight of 190000 and the degree of acetylation (DA) of 12 mol%, as determined by ^{1}H NMR, was used after purification. According to NMR data, the distribution of *N*-acetyl-D-glucosamine units along the chains of this polymer was random. The hydrophobically modified chitosans (HM chitosans) were prepared by the reductive amination of chitosan in homogeneous conditions using an *n*-alkyl aldehyde according to a published method,[13] which is non-destructive for the polymer.[14] Therefore, HM chitosans had the same degree of polymerisation as the precursor. The content of hydrophobic side chains in

HM chitosans were 5 mol% (for dodecyl-chitosan designated as ChC12), 21 mol% for the octyl-chitosan ChC8 and 82 mol% for the propyl-chitosan ChC3. Individual and mixed SDS and chitosan solutions were prepared by stirring in 0.3 M AcOH/0.05 M AcONa buffer for 24 h or longer.

A drop tensiometer (Tracker, IT Concept, France) was used to measure the surface tension by analysing the axial symmetric shape (Laplacian profile) of the rising air bubble in the aqueous solutions of surface-active species.[15] All the measurements were made for a sufficiently long time (usually longer than 5×10^4 s) in order to follow the effect of ageing on the surface tension of the adsorption layers.

Figure 1 represents the dynamic surface tension curves $\sigma(t)$ for chitosan (curve *1*), SDS (curve *2*), alkylated chitosan ChC12 (curve *3*) and a mixed chitosan–SDS solution (curve *4*). Curve *5* corresponds to an acetate buffer. The concentrations of chitosan and the alkylated chitosan were equal to 10^{-3} monomol dm^{-3}, whereas the concentration of SDS was 5×10^{-5} mol dm^{-3} in its individual solution and in the mixed chitosan–SDS solution. The composition of the mixed SDS–chitosan solution ($\varphi = [C_s]/[C_{PE}] = 0.05 \ll 1$) was highly non-stoichiometric by the charges of the components that ensured the solubility of the formed dynamic associates (SPEC) in the acetate buffer for the SDS concentration lower than the critical aggregation concentration (c.a.c.) approximately equal to $\sim 5 \times 10^{-4}$ mol dm^{-3},[2] and much lower than the CMC of SDS equal to 8×10^{-3} mol dm^{-3}.[16] Thus, the free dodecyl group content of individual and mixed chitosan–SDS solutions, on the one hand, and the content of covalently bound dodecyl chains in the case of the alkylated chitosan, on the other hand, were approximately equal. This allows us to compare the surface properties of alkylated chitosan and SPEC containing the same number of alkyl groups.

A comparison between the surface activity of the polysoap ChC12 (curve *3*) and the SPEC (curve *4*) shows that for the equal lengths of alkyl groups and their concentration in the solution or for the equal values of DS for the polysoaps and of φ for the mixed solution of surfactant and PE, the decrease of the surface tension σ in the case of SPEC is more significant than in the case of the polysoaps. The origin of the anomalously
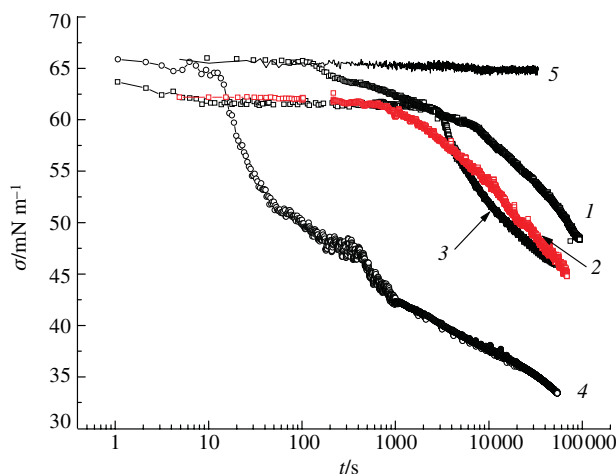
Figure 1 Dynamic surface tension for the solutions of chitosan (curve *1*), SDS (curve *2*), alkylated chitosan ChC12 (curve *3*), SDS–chitosan complex (curve *4*), and the buffer (curve *5*). Concentrations: SDS (curves *2* and *4*; $C_s = 5 \times 10^{-5}$ mol dm^{-3}); chitosan and ChC12 (curves *1*, *3* and *4*; $C_p = 10^{-3}$ monomol dm^{-3}).
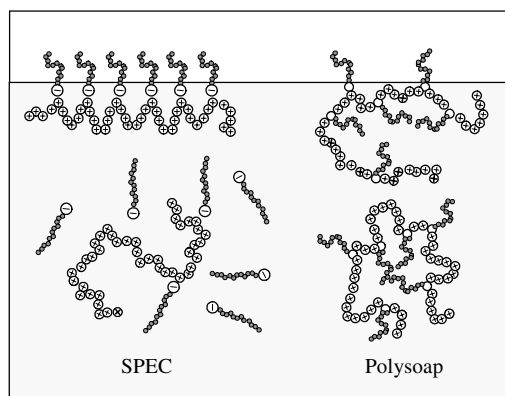
Figure 2 Schematic diagram illustrating why the surfactant-polyelectrolyte complex (SPEC) is much more surface active than the polysoap.
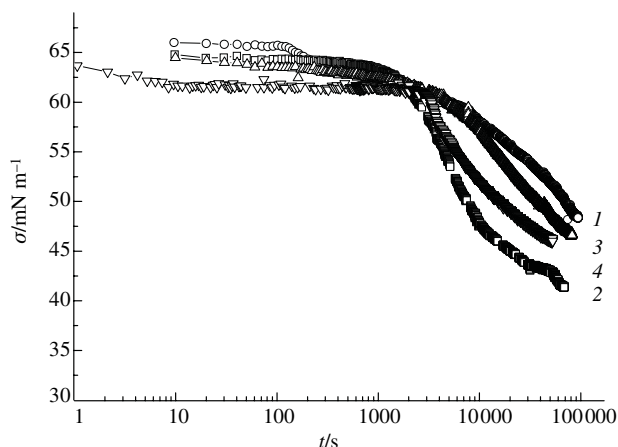
Figure 3 Dynamic surface tension for the solutions of chitosan (curve *1*) and alkylated chitosans ChC3 (curve *2*), ChC8 (curve *3*) and ChC12 (curve *4*). The concentrations of all polymers are equal to $C_p = 10^{-3}$ monomol dm^{-3}.

Figure 4 Schematic diagram illustrating why the polysoap with short alkyl chains adsorbs better than that with long alkyl chains.

high adsorption capacity of the SPECs lies in the cooperative adsorption of surfactants and PE at the interfaces.[1] The formation of water-soluble electrostatically stabilised dynamic associates (SPECs) between the oppositely charged components leads to the mutual hydrophobisation of components and, consequently, to an increase in the free energy of adsorption and the surface activity of both components. Due to the multiplicity of the electrostatic contacts of the macroions with the adsorbed surfactant molecules, the desorption of both the macroion and the surfactant molecules from the interface becomes kinetically unfavourable, which leads to the practically irreversible adsorption of SPECs.[1] Unlike the covalently alkylated chitosan (the polysoap) whose mobility at the interface is restricted by the stiffness of the macromolecular backbone and thereby not all the alkylated chains could be brought into contact with the interface (Figure 2), the SPECs are characterised by a higher mobility: the lability of the bonds between surfactants and PE in these dynamic associates is responsible for the surface activity of bound surfactants.

All the test compounds manifest a monotonic decrease of the surface tension after the lag time which depends on the system and on the bulk concentrations of components. The lag period is characterised by a very low decrease of the surface tension while the adsorption layer in this period is yet in a two-dimensional 'gaseous' state because of the low surface density of the adsorbed species. At the end of this period, the adsorption amount is increased *via* the diffusion transport of molecules from the bulk of the solution to the interface, and the two-dimensional 'liquid' state is formed leading to a remarkable increase in the surface pressure. In this post lag period, the adsorption layer becomes denser, and the decrease of the surface tension is developed *via* the diffusion transport of new molecules from the solution and, simultaneously, by the reconformation of macromolecules inside the already formed adsorption layer by the internal diffusion of surface-active segments and their anchoring at the interface. In the long time, one can observe the final stage of the formation of the adsorption layer, which is characterised by a significant decrease in the adsorption rate of the surfactant molecules. For the macromolecular compounds, this retardation of the adsorption rate testifies the formation of a steric barrier to the diffusion of new arrival molecules to the interface. Another factor, which is able to contribute to the retardation of the adsorption, may be the possible structure (gel) formation inside these layers by the mechanism of hydrophobic interactions or hydrogen bond formation.

The monotonic decrease of the surface tension for the low-molecular-weight ionic surfactant SDS (Figure 1, curve *2*) after a lag time of 10^3 s seems surprising although long relaxation times have been mentioned for micelle-forming surfactants.[17,18] This lag period is quite realistic for the concentration of 5×10^{-5} mol dm^{-3} of the ionic surfactant SDS and may testify the formation of an adsorption monolayer by the
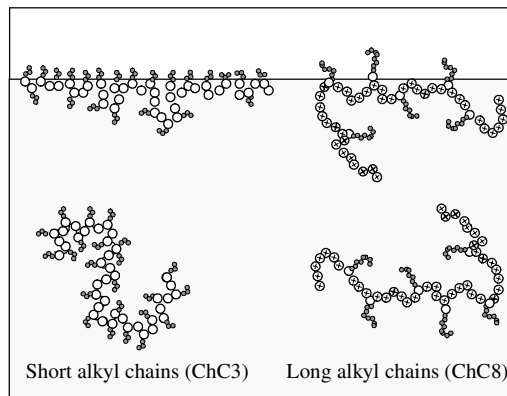
mechanism of diffusion. The free energy gain of the hydrophobic interaction per CH$_2$ group inside the sparse adsorption layer is ~1 kT;[19] the adsorption free energy of this surfactant having twelve CH$_2$ groups in its alkyl radical may be estimated as $\Delta G \cong 10\ kT$. If one assumes the possibility of the formation of associates inside the adsorption layer, the adsorption free energy may increase and become much higher. The above assumption may be justified by the screening of electrostatic repulsion between the ionised groups of SDS in an acetate buffer. For example, in the case of dimers, one expects that the free adsorption energy will increase by a factor of 2 and will be equal to $\Delta G \cong 20\ kT$. This correspond to the decrease of the apparent coefficient of diffusion and, consequently, to the decrease of the rate of desorption of the molecules from the interface by a factor of $\exp(\Delta G/kT) \sim 10^8$. In this case, the adsorbed dimers behave as poorly soluble surfactants, for example, like succinates (*e.g.*, Aerosol OT having two long alkyl chains and one sulfate group). Thus, we can explain the decrease of the surface tension for SDS in the post lag period by a further increase in the adsorption amount and by the interaction between the surfactant molecules at the interface.

On the other hand, according to Mysels *et al.*,[16,20] SDS may be hydrolysed in an acidic solution during long storage to form dodecanol, which is known as a very surface-active substance. We cannot confirm or reject this assumption. Note that octyl and decyl sodium sulfates also decrease the surface tension during the ageing time of the order of 10^5 s. Nevertheless, this feature of SDS has no impact on this comparative study of the surface activity of the hydrophobically modified chitosans, if one restricts oneself to the adsorption layers ageing time of the order of 10^4 s. It is obvious that the surface activity of the SPECs is much higher than that of the polysoap containing the same quantity of the hydrophobic dodecyl chains in the solution.

In the theory of adsorption of HM polyelectrolytes (polysoaps), the role played by the degree of substitution of the alkyl groups (DS) and their length on the surface activity of polysoaps and on their adsorption kinetics remains unknown. One may expect that, at concentrations lower than the c.a.c. corresponding to the solubility of the polysoaps, their surface activity will increase with the length of the covalently bound alkyl chains $n(\text{C})=C_nH_{n+1}$ at a constant DS (*i.e.*, the linear density of the alkyl chains along the macromolecular backbone), as well as with increasing DS at a constant $n(\text{C})$. Really, with increasing the total mass of the alkyl chains, which is proportional to both DS and $n(\text{C})$, the hydrophobicity of the polysoap will be increased to increase its surface activity.

Nevertheless, this conclusion will not be so obvious for the polysoap samples which have identical HLB (*i.e.*, the total mass of alkyl chains) but different alkyl chain lengths $n(\text{C})$. For example, it is impossible to predict the surface activity of the polysoaps ChC12 (DS = 5 mol%), ChC8 (DS = 7.5 mol%) and ChC3 (DS = 20 mol%) having equal masses of alkyl groups. A conclusion can be drawn if all the alkyl groups can adsorb

at the interface and exhibit their potential surface activity. However, it was demonstrated[3] that if the mean distance l_{Alk} between the alkyl groups of the macroion becomes much lesser than the persistence length l_K (half of the Kuhn segment length), the adsorption of all alkyl chains becomes impossible because of the low flexibility of the macromolecular backbone. Thus, with increasing DS, the surface activity will increase only if $l_{Alk} \geq l_K$, but it becomes only partially realised with the later decrease of l_{Alk}.

The above is illustrated by the kinetic surface tension curves $\sigma(t)$ for the polysoaps ChC12 (5 mol%), ChC8 (21 mol%) and ChC3 (82 mol%), corresponding to their limiting degrees of alkylation ensuring yet the solubility of these HM chitosans in the acetate buffer at 10^{-3} monomol dm^{-3} (Figure 3). Comparing the $\sigma(t)$ curves corresponding to ChC12 and ChC8, we found that the first sample manifests a remarkably higher surface activity with regard to the sample of ChC8, in spite of the 2.5 times lower total mass of the alkyl groups per macroion. This may be explained by the effect of the flexibility of the macroion on its adsorption activity. Really, the mean distance between dodecyl groups in the sample of ChC12, which is equal to $l_{C12} \sim 10$ nm, is of the same order of magnitude that the persistence length $l_K \cong 10$ nm.[21] Thus, one may conclude that for this sample the flexibility of the macroion is yet sufficiently high to do not hinder the adsorption of all the C12 groups at the interface. But for the sample ChC8, which has the mean distance between the C8 groups equal to $l_{C8} \sim 2.5$ nm, the persistence length l_K becomes considerably greater than l_{C8}. In this case, not all the C8 groups could be adsorbed at the interface to explain a considerably lower surface activity of the ChC8 with regard to ChC12.

On the other hand, a comparison between the kinetic curves $\sigma(t)$ for samples ChC3 and ChC8 shows that the surface activity of the former is much higher than that of the latter. At the first sight, this may be explained by the fact that the total mass of alkyl chains of sample ChC3 is 1.4 times higher than that of sample ChC8. However, the surface activity of sample ChC12 is almost the same as that of ChC3, although the total mass of alkyl chains is the sample of ChC3 is four fold higher than that of ChC12. Consequently, this is not the total alkyl chain mass (or the HLB), which is the main factor determining their surface activity: the repartition of these substituents along the macro-molecular chain is also an important parameter. In spite of the fact that the mean distance between the short propyl groups C3 of the water-soluble sample of ChC3 is equal to $l_{C3} \sim 0.6$ nm (that is much lower than l_K), the majority of them are able to exhibit their surface activity while practically each segment of the macroion contains such groups (Figure 4).

Another factor, which may influence the adsorption activity of polysoaps, is the ability of alkyl chains to form the intra- and inter-polymer micelle-like aggregates *via* hydrophobic interactions between alkyl chains. When the intra-polymer aggregates are formed, the alkyl chains are hidden from the exterior aqueous phase by more hydrophilic segments, and the macroion becomes less hydrophobic and less surface active. Taking into account that the free energy gain of the hydrophobic interaction per CH$_2$ group in the micelles is $\sim 1\ kT$,[19] one can assume that relatively short propyl groups C3 are not able to form aggregates or at least stable associates unlike longer alkyl chains in the samples of ChC8 and ChC12 with the energy of the hydro-phobic interaction of $\sim 10\ kT$. This may explain why the apparent hydrophobicity and, consequently, the surface activity of ChC3 is higher than that of ChC8. On the other hand, the higher surface activity of ChC12 with regard to the sample of ChC8 may be explained by the fact that the latter sample does not form intra-macromolecular aggregates in spite of its longer alkyl chains, while the density of these chains corresponding to DS = 5 mol%, is yet lower than the critical DS*, which is about 10 mol% for the groups C12.[1] Unlike this, the DS = 21 mol% of the ChC8 sample exceeds this critical DS that leads to the intra-macromolecular aggregation in the case of low bulk con-centration and to a decrease of the surface activity of this poly-soap. With increasing bulk concentration, the inter-macromole-cular aggregates could form that also decreases their kinetics of adsorption.

Thus, we found that the surface activity and the adsorption kinetics of polysoaps depend non-monotonically on the DS and the alkyl chain length. It seems that the conformational state of the macroions, as well as the hydrophobic interaction between the alkyl chains in the bulk of solution and at the interface, could influence remarkably the interfacial behaviour of these polysoaps. To give a more valuable explanation of the results, we are performing a more detailed study of the effect of DS and the alkyl chain length n(C) on the kinetics of adsorption of HM chitosans.

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