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Dilational viscoelasticity of the adsorption layers of hydrophobically modified chitosans

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Two-dimensional dilational rheology has been applied to a comparative study of the kinetics of structure formation in the adsorption layers of cationic polysoaps (alkylated chitosans) and dynamic associates (surfactant-polyelectrolyte complexes, SPECs) formed between a cationic polyelectrolyte (chitosan) and an anionic surfactant (SDS).

It is well known[1,2] that the hydrophobic modification of hydrophilic polyelectrolytes (PEs) by covalent binding with 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 in the surface activity of such polyelectrolytes. The surface activity of PEs is understood as their ability to adsorb at the interface and, consequently, to decrease surface (interfacial) tension σ. The driving force of adsorption of alkylated polyelectrolytes (polysoaps) and SPECs is the gain in free energy of the system due to the immersion of covalently or electrostatically bound hydrophobic (alkyl) chains into a nonpolar phase (air or oil). At equal contents of alkyl groups per one macroion either in the solution of a polysoap or in the mixed surfactant-polyelectrolyte solution {*i.e.*, at equal degrees of substitution (DS) for the polysoap and the composition $Z = [C_s]/[C_{PE}]$ of SPEC in the mixed surfactant-polyelectrolyte solution} the surface activity of the SPEC is much more pronounced with regard to that of polysoaps.[3] This difference is explained by higher mobility at the interface of the adsorbed surfactant molecules belonging to the SPEC with regards to the alkyl chain of the macroions: the lability of electrostatic bonds between surfactants and PE in the SPECs allows these surfactants to exhibit their surface activity unlike the adsorbed alkyl chains of macroions, whose mobility is restricted by the stiffness of the macromolecular backbone.[3,4]

Due to the increased local concentration of components in the adsorption layer at the interface, the hydrophobic groups of polysoaps and the surfactant molecules of SPEC can form intermolecular associates leading to the formation of a physical gel structure inside the adsorption layer.[5,6] This affects the stability of emulsions and foams while the gel-like adsorption layer behaves as the structuro-mechanical barrier preventing the rupture of emulsion and foam films and consequently protecting these disperse structures (emulsion and foams) against destruction.[2,7] In spite of the fact that the structure formation inside the adsorption layers of PE and particularly of SPECs is obviously important for practical applications, there are no systematic studies devoted to the kinetics of structure formation inside these adsorption layers.

The aim of this work was to study the kinetics of structure formation inside the adsorption layers of hydrophobically modified chitosans by the two-dimensional dilational rheology.

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 repeat units along the chains of this polymer was

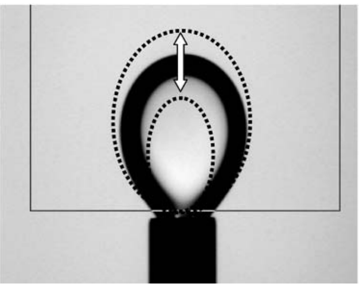

Figure 1 Laplacian profile of an air bubble formed in water. Arrows show the sinusoidal variation of the area of the bubble surface.

random. The hydrophobically modified chitosans (HM chitosans) were prepared by reductive amination of chitosan in homogeneous conditions using *n*-alkyl aldehyde according to a published method[8] known as non-destructive for the polymer.[9] Therefore, HM chitosans had the same degree of polymerisation as the precursor. The content of hydrophobic (dodecyl) side chains (the degree of substitution, DS) in the alkylated chitosan was 5 mol%. Individual and mixed SDS and chitosan solutions were prepared by stirring in a 0.3 M AcOH/0.05 M AcONa buffer during at least 24 h. The water used was of ultrapure grade from a Milli-Q plus system (Millipore, France).

The drop tensiometer (Tracker, IT Concept, France) was used to measure the surface tension by analysing the axial symmetric shape (Laplacian profile) of a rising bubble in the aqueous solutions of surface active species (Figure 1).[10] Two-dimensional complex elasticity modulus E of adsorption layers was found from the measurement of the surface tension variations as the response to sinusoidal dilational variations of surface area.[10–12] By analogy with the 3-D rheology, the real part of this function, the two-dimensional storage modulus E', and the imaginary part, the two-dimensional loss modulus E'', characterise a conservative and a dissipative adsorption layer behaviour, respectively. All the measurements were made during a sufficiently long time (usually, longer than 5×10^4 s) in order to follow the effect of ageing on the surface tension and on the dilatational rheological properties of the adsorption layers.

Technically, the study of the structure formation kinetics inside the adsorption layers of hydrophobically modified chitosans was performed by applying a controlled dilational perturbation $\Delta A(t)$ to the bubble area A and recording simultaneously the variation of the surface tension $\sigma(t)$ (or the surface pressure $\pi(t) = \sigma_0 - \sigma(t)$, where σ_0 is the surface tension of an acetate buffer) (Figure 2). The simplest Maxwell rheological model with only one characteristic relaxation time τ_0 (or one characteristic relaxation frequency $\omega_0 = 2\pi/\tau_0$) is sufficient for the quantitative description of the viscoelastic properties of adsorption layers. Formally, one can express the relaxation time τ_0 by the ratio

$$\tau_0 = \eta/E, \tag{1}$$

where η and E are effective two-dimensional dilational viscosity and elasticity modulus, respectively.

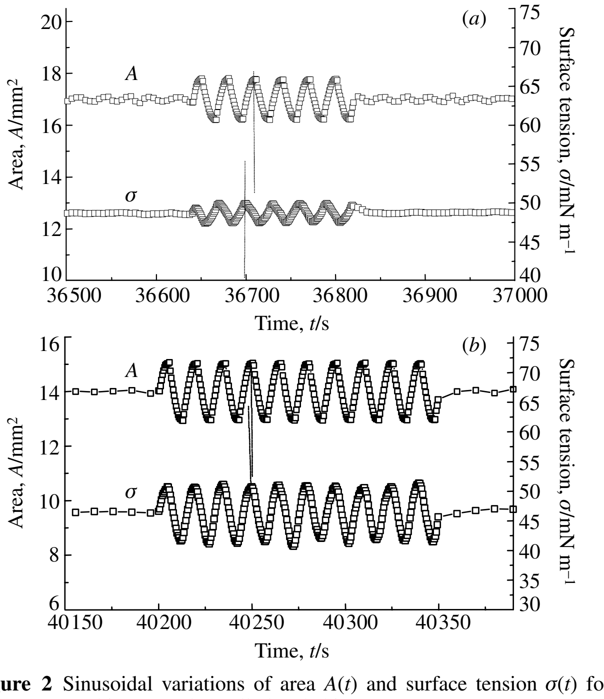

Figure 2 Sinusoidal variations of area $A(t)$ and surface tension $\sigma(t)$ for (*a*) precursor chitosan and (*b*) alkylated chitosan.

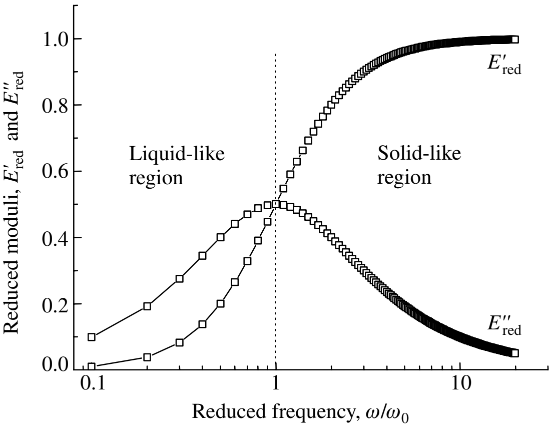

Figure 3 Effect of frequency ω on reduced two-dimensional storage $E'_{\rm red}$ and loss $E''_{\rm red}$ modules for the one-frequency Maxwell rheological model.

Periodic variation of the drop area A according to the sinusoidal law $\bar\varepsilon(t) = \varepsilon_{\rm a}\exp({\rm i}\omega t)$ (where $\varepsilon = \Delta A/A$ is the relative dilatational deformation of the layer, and $\varepsilon_{\rm a}$ is the amplitude of this relative deformation) produces a variation of the surface tension $\bar\pi(t) = \pi_{\rm a}\exp[{\rm i}(\omega t + \varphi)]$, where φ is the phase angle (Figure 2). In the linear deformation domain, the frequency dependent complex elasticity modulus is defined as

$$\bar E(\omega) = \frac{{\rm d}\bar\pi}{{\rm d}\bar\varepsilon} = -\frac{{\rm d}\bar\sigma}{{\rm d}\bar\varepsilon} = E'(\omega) + {\rm i}E''(\omega), \tag{2}$$

where the real $E'(\omega)$ and the imaginary $E''(\omega)$ parts are expressed as

$$E'(\omega) = E_0\frac{(\omega/\omega_0)^2}{1 + (\omega/\omega_0)^2}, \tag{3}$$

$$E''(\omega) = E_0\frac{\omega/\omega_0}{1 + (\omega/\omega_0)^2}, \tag{4}$$

respectively.

The total dilatational elasticity modulus E and the phase angle φ are defined as

$$E(\omega) = \sqrt{E'^2(\omega) + E''^2(\omega)} = E_0\frac{\omega/\omega_0}{\sqrt{1 + (\omega/\omega_0)^2}}, \tag{5}$$

$$\mathrm{tg}\,\varphi = \frac{E''(\omega)}{E'(\omega)} = \frac{\omega_0}{\omega}, \tag{6}$$

respectively.

The dependence of reduced real, E'/E_0, and imaginary, E''/E_0, modules on the applied frequency ω is represented in Figure 3. At the characteristic frequency ω_0 of the system the both modules are equal: $E'(\omega_0) = E''(\omega_0)$. In the region $\omega >> \omega_0$, the adsorption layer behaves as a solid-like rheological body; at $\omega \to \infty$, the elasticity storage modulus E' tends to its maximal value E independent of the applied frequency ω. At very low frequencies, $\omega << \omega_0$, the adsorption layer behaves like a liquid while $E' << E''$ and $E'' \sim \omega$.

The one frequency rheological model is valid only for the adsorption layers whose parameters E and η are constant and independent of the applied frequency ω. In the case of gel-like adsorption layers, which are characterised by the two-dimensional yield strength $\pi_{\rm B}$, the parameter E_0 becomes frequency dependent, and the one frequency rheological model of Maxwell becomes insufficient for the quantitative description of rheological properties of such layers. One of the possible ways to avoid this difficulty is to increase the number of characteristic frequencies $\omega_{0i} = 2\pi/\tau_{0i}$ of the rheological model (where $\tau_{0i} = \eta_i/E_{0i}$ are characteristic relaxation times of the system) that allows, by analogy with the 3D rheology,[13,14] to express the modules as the sums

$$E'(\omega) = \sum_i E_{0i}\frac{(\omega/\omega_{0i})^2}{1 + (\omega/\omega_{0i})^2},\quad E''(\omega) = \sum_i E_{0i}\frac{\omega/\omega_{0i}}{1 + (\omega/\omega_{0i})^2},$$

where E_{0i} is the corresponding weight of ith relaxation element in the total elasticity module E. Using this procedure, it is possible, in principle, to describe quantitatively the rheological behaviour of the adsorption layers.

Sometimes, a satisfactory rheological description may be performed by using only several characteristic frequencies having a clear physical meaning. For example, we found that using the rheological model with only two characteristic times, $\tau_1 \sim 10$ s and $\tau_2 \sim 10^3$ s is sufficient to describe the rheological behaviour of adsorption layers of hydrophobically modified chitosans during ageing in the frequency range between 10^{-3} rad s^{-1} and 1 rad s^{-1}. The first characteristic relaxation time, $\tau_1 \sim 10$ s, is usually attributed to the Marangony effect (the adsorption-desorption of molecules during dilatational perturbations),[11,15] whereas the second time, $\tau_2 \sim 10^3$ s we attributed to slower reconformation of the adsorbed macromolecules inside the adsorption layer.[16]

Here, we present preliminary results concerning the rheological behaviour of the adsorption layers of hydrophobically modified chitosans. The measurements of the structuro-mechanical properties of such layers in the course of ageing were carried out on the basis of one frequency rheological model at the constant perturbing frequency $\omega \cong 0.42$ rad s^{-1}, corresponding to the period $T \cong 15$ s. Figure 4 shows the time dependence of the real E' and imaginary E'' parts of the two dimensional elasticity module E of adsorption layer. First, point out the sharp increase of the storage module E' for the adsorption layers of SDS–chitosan complexes [Figure 4(*a*), curve *3*] which tends to a relatively high constant value exceeding 80 mN m^{-1}. We can conclude for the ‘solid-like’ rheological properties of these layers for the used frequency $\omega \cong 0.42$ rad s^{-1} while the value of storage module E' is much higher with regard to the loss module E'' [Figure 4(*b*), curve *3*].

The real module E' of the alkylated chitosan [Figure 4(*a*), curve *2*] increases with storage time and tends to the same value of the order of 80 mN m^{-1} but after some lag time $\tau_{\text{lag}} \sim 2000$ s. This delay of the increase of E' for the alkylated chitosan (polysoap) with regard to the SDS–chitosan complex is likely to delay of increasing of the surface activity of the polysoap comparing to the complex (Figure 5, curves *2* and *3*). In our previous works,[3,4] this effect was explained by the stiffness of the macromolecular backbone of the polysoap, which hinders the adsorption at the interface of covalently bound relatively long alkyl groups. The adsorption of SDS–chitosan complexes occurs much more easily because of the labile character of less strong electrostatic bonds between the components.

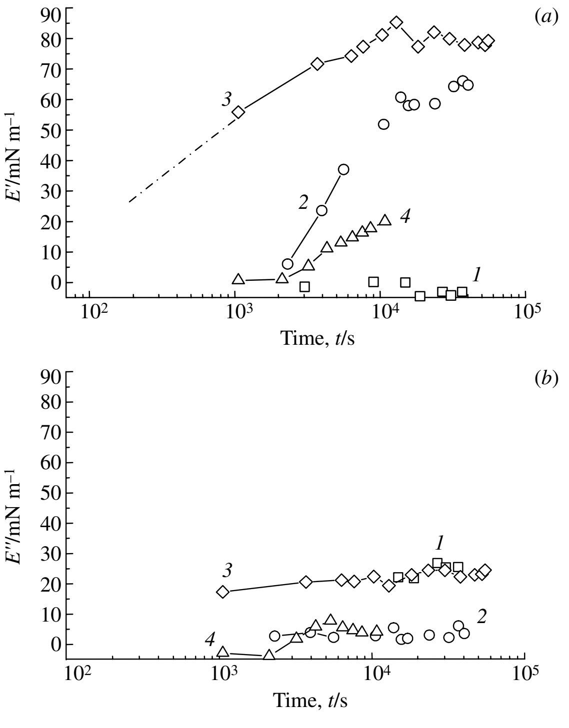

Figure 4 The time dependence of the two-dimensional (*a*) storage E' and (*b*) loss E'' modules of adsorption layers of different components: (*1*) chitosan, (*2*) alkylated chitosan ChC12, (*3*) SDS–chitosan complexes, (*4*) SDS. Concentrations: SDS (curves *3* and *4*; $C_s = 5\times10^{-5}$ mol dm^{-3}); chitosan and ChC12 (curves *1*, *2* and *3*; $C_p = 10^{-3}$ mono-mol dm^{-3}).

Comparison between the corresponding modules E' and E'' of the alkylated chitosan (Figure 4, curve *2*) allows us to conclude that, after the ageing time $t > 2000$ s, the adsorption layers of this polysoap acquire ‘solid-like’ properties ($E' > E''$), whereas in the region $t < 2000$ s, these layers are ‘liquid-like’ ($E' < E''$). As concerned the chitosan [Figures 4(*a*) and 4(*b*), curve *1*], it is flagrant that its adsorption layers behave as liquid-like ($E' < E''$) for the entire ageing time interval ($t \cong 10^5$ s) and the perturbing frequency used. Unexpected is the ‘solid-like’ behaviour of adsorption layers of low molecular surfactant, SDS, after the lag time $t > 2000$ s. This feature may be explained by the possible hydrolysis of SDS at the interface leading to the formation of water insoluble dodecanol.[4]

The increase of the two-dimensional storage module E' in the case of adsorption layers of macroions may be due to two factors: (*a*) an increase in the energy of interaction of macromolecules with the interface (the adsorption energy) and (*b*) an increase in the lateral interaction (cohesion) between the macromolecules inside the adsorption layers. It seems interesting to discuss the effect of these factors on the dilatational elasticity of different surface active compounds: hydrophobically modified chitosans (polysoap and surfactant–PE complex) and precursor chitosan.

Figure 5 represents the kinetic curves $\pi(t) = \sigma_0 - \sigma(t)$ obtained for the chitosan (Ch), alkylated chitosan (C_{12}Ch) and the SDS–chitosan complex (SDS–Ch).[4] Note that the increase of the surface pressure $\pi(t)$ is most significant for the adsorption layers of the complex (SDS–Ch) (Figure 5, curve *3*), which correlates with their high module E' (Figure 4, curve *3*). The lowest modules E' for alkylated (C_{12}Ch) and precursor (Ch) chitosans (Figure 4, curves *1* and *2*) correlate with relatively low surface pressures $\pi(t)$ for these compounds (Figure 5, curves *1* and *2*).[4,17] This may testify for some effect of the surface pressure on the storage module E' of adsorption layers. The correlation between E' and π is analogous to the usually observed dependence of the static elasticity modules $E_{\text{st}} = -\mathrm{d}\pi/\mathrm{d}\ln A$ on the surface pressure π for liquid-extended insoluble Langmuir monolayers. In the latter case, the increase of the module E_{st} is explained by the increase of the interaction energy between the surfactant molecules and the liquid substrate.[18]

Meantime, all the features of the rheological behaviour of the adsorption layers of studied compounds could not be explained by only the effect of the adsorption energy, *i.e.*, by the surface activity. Really, as it follows from the comparison of the modules $E'(t)$ for chitosan and alkylated chitosan (Figure 4, curves *1* and *2*), the E' module of Ch is practically equal to zero in the entire region of the ageing times, whereas for the C_{12}Ch it reaches a high value of about 60 mN m^{-1}. At the same time, the surface tension π of the adsorption layers of Ch (Figure 5) is relatively high (~15 mN m^{-1}), which is only twofold lower than the corresponding values of C_{12}Ch. This means that this is the lateral intermolecular interaction and not the adsorption

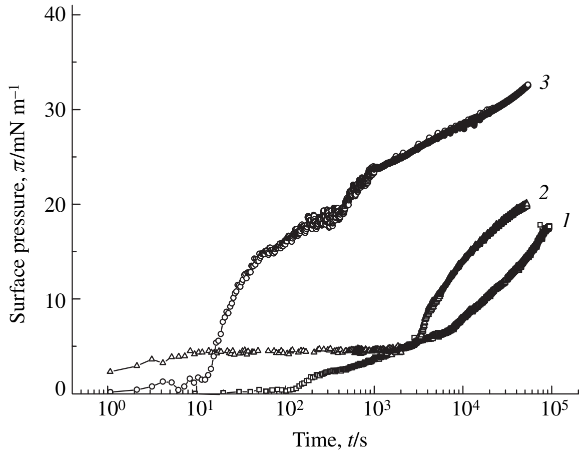

Figure 5 Dynamic surface pressure π as function of time t for the aqueous solutions of (*1*) chitosan, (*2*) alkylated chitosan ChC12 and (*3*) SDS–chitosan complex. Concentrations: SDS ($C_s = 5\times10^{-5}$ mol dm^{-3}); chitosan and alkylated chitosan ChC12 ($C_p = 10^{-3}$ mono-mol dm^{-3}).

energy, which is the main factor influencing the elasticity module E' of adsorption layers. It is likely that the relatively long C_{12} chains of the alkylated chitosan interacting hydrophobically with the energy of the order of ~10kT[19] are responsible for the increased elastic properties of this polysoap. Unlike the polysoap, in the adsorption layers of chitosan, the less bulky residual hydrophobic groups interact with an energy of ~1kT, which is obviously insufficient to obtain a high elasticity module E'.

Comparison between the curves $E'(t)$ and $\pi(t)$ for C_{12}Ch and Ch (Figures 4 and 5) shows that in spite of an obvious correlation between the elasticity module and the surface pressure in the whole ageing time interval, nevertheless, there is a difference between the absolute values of these properties. Really, the maximum values of E' for the polysoap and the complex practically coincide, whereas the surface pressure of the polysoap is approximately twofold lower that that of the complex. The comparatively high module E' for polysoap adsorption layers suggests the effect of the lateral hydrophobic interaction between covalently bound C_{12} groups of the polysoap macromolecules on the elastic properties of their adsorption layers.[20]

Comparison between the absolute values of the storage E' and loss modules E'' of adsorption layers of the test compounds makes it possible to formulate conclusions concerning the mechanism of the interaction between the macromolecules in adsorption layers. Figure 4(*b*) shows that the loss module E'' for the alkylated chitosan (curve *2*) is relatively low and does not exceed ~5 mN m^{-1}, whereas for the SDS–Ch complex this module reaches ~20 mN m^{-1} (curve *1*). This difference may be explained by the difference in the strength of the lateral bonds in the adsorption layers of the polysoap and the complex. A relatively high energy of the hydrophobic 'bonds' between the C_{12} chains of the polysoap makes the layer very resistant to the rupture that decreases the dissipative loss of the elastic energy and makes low the loss module E''. On the other hand, in the case of the SDS–Ch complex, which is also characterised by the lateral hydrophobic interaction between the C_{12} alkyl chains of the SDS molecules, the dilatational deformation leads to the reversible rupture of less strong electrostatic bonds between the oppositely charged components. The periodical destruction and restabilisation of the electrostatic bonds under the sinusoidal dilatational deformation leads to the increased loss of the elastic energy, *i.e.*, to the high loss module E'' for the SDS–Ch complex.

The results show that the formation of adsorption layers by hydrophobically modified chitosans at interfaces is accompanied by structure (gel) formation inside these layers *via* lateral hydrophobic interactions between the covalently bound alkyl chains in the case of alkylated chitosan or between the alkyl chains of surfactants forming SPECs with chitosan.

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