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Dynamic surface tension and dilational viscoelasticity of adsorption layers of alkylated chitosans and surfactant–chitosan complexes

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Abstract The kinetics of the adsorption at the air-water interface and the processes of the structure formation inside the adsorption layers of hydrophobically modified systems [alkylated chitosans and sodium dodecyl sulfate (SDS)–chitosan (Ch) complexes] have been studied by the tensiometric method based on the axisymmetric rising-bubble-shape analysis as a function of the bulk concentration of polymers and the ageing time of their adsorption layers. The kinetics of the adsorption of chitosan, alkylated chitosans (ChC_3, ChC_8, and ChC_{12}), and surfactant–polyelectrolyte (PE) complexes formed by the chitosan and the polysoaps with oppositely charged anionic surfactant SDS is characterized by an induction time (the so-called lag time), τ_{lag}, corresponding to the diffusion stage of the formation of adsorption layers. During this time, the decrease in the surface tension (or the increase in the surface pressure π) does not exceed several millinewtons per meter that corresponds to the “gaseous” state of adsorption layers. The postlag stage of the formation of the adsorption layer is characterized by the remarkable rate of increase in the surface pressure π that corresponds to the conformational rearrangement of PEs inside the adsorption layer by increasing the number of hydrophobic groups (adsorbing centres) in contact with the non-polar phase at the interface. It has been found that during the lag time, the adsorption of alkylated chitosans (cationic polysoaps) increases with increasing alkyl chain length, whereas during the postlag time, the adsorption of the ChC_3 is maximal with regard to other polysoaps. It has been confirmed that at equal content of alkyl groups in the system, the surface activity of the SDS–Ch complexes is much higher with regard to that of the polysoaps. The viscoelasticity of adsorption layers of individual PEs and their complexes continuously increases with the ageing time, giving evidence for the interaction between the polymers inside the adsorption layers. It has been found that the rate of increase in the dilational storage module E' of the adsorption layers of SDS–Ch complexes is much higher than for the polysoaps that correlates with the higher surface activity of the former with regard to the latter. For the mentioned systems, the module E' is much higher than the loss module E'' that confirms the solid-like properties of their adsorption layers. On the other hand, the adsorption layers of the chitosan are liquid-like, while $E' << E''$.

Keywords Chitosan · Alkylated chitosan · Surfactant–polyelectrolyte complexes · Adsorption layers · Adsorption kinetics · Dynamic surface tension · Dilational viscoelasticity · Two-dimensional elasticity module

Introduction

It is well known that the hydrophobic modification of polyelectrolytes (PEs) by the covalent binding of alkyl groups or by the formation of non-stoichiometric dynamic associates with oppositely charged surfactants (surfactant–PE complexes, SPECs) in mixed aqueous solutions leads to a remarkable increase in the adsorption of PEs at the interfaces [1–9]. The driving force of adsorption of hydrophobically modified PEs (polysoaps) and SPECs is the substantial gain in free energy of the system due to the hydrophobic effect accompanying the transfer of covalently or electrostatically bound hydrophobic (alkyl) chains from the aqueous solution into the non-polar phase (air or oil). In the case of polysoaps, the increase in the linear density of alkyl chains along the macromolecular backbone leads to the irreversible adsorption of these polysoaps because of the multiplicity of adsorption contacts with the interface [6, 10]. In this regard, the interfacial behaviour of the alkylated PEs is analogous to that of the proteins, which adsorb irreversibly at the interface undergoing the denaturation (i.e. the transfer from the compact globular to the extended flat conformation) at the interface [11–13].

It has been found [10] that at equal content of alkyl groups per macroion either in the solution of a polysoap or in the mixed surfactant–PE solution [i.e. at equal degree of substitution (DS) for the polysoap and the composition Z=[C_s]/[C_{PE}] of SPEC], the surface activity of the SPEC is much higher with regard to that of polysoaps. This difference is explained by the higher mobility at the interface of the adsorbed surfactant molecules belonging to the SPEC with regard to the alkyl chains of the macroions: the lability of electrostatic bonds between surfactants and PE in the SPECs allows these surfactants to realize wholly their surface activity, unlike the adsorbed alkyl chains of macroions whose mobility is restricted by the stiffness of the macromolecular backbone [10, 12].

Due to the increased local concentration of components in the adsorption layers at the interface, the hydrophobic chains of polysoaps and surfactant molecules of SPECs can form the intermolecular associates leading to the formation of the physical gel structure inside the adsorption layer [14, 15]. This effect may have considerable consequences on 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 [8, 16; Bousquet et al., unpublished data].

Although the structure formation inside the adsorption layers of PEs and particularly of SPECs is obviously important for practical applications, there are no systematic studies devoted to the kinetics of the structure formation inside these adsorption layers. The aim of this work was to study the kinetics of the adsorption and of the structure formation inside the adsorption layers of the hydrophobically modified chitosans (Chs) and surfactant-Ch complexes by dynamic tensiometry and two-dimensional (2-D) dilational rheology.

Experiments

Materials

The precursor chitosan from Pronova (Norway) with molecular weight of 190,000 and degree of acetylation (DA) of 12 mol% 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 random. The hydrophobically modified chitosans (HM chitosans) were prepared by reductive amination of chitosan in homogeneous conditions using *n*-alkyl aldehyde according to a method [18] known to be non-destructive for the polymer [19]. Therefore, HM chitosans had the same degree of polymerization as its precursor. The content of hydrophobic side chains in HM chitosans was 5 mol% for dodecyl-chitosan (designated as ChC_{12}), 21 mol% for the octyl-chitosan ChC_8, and 82 mol% for the propyl-chitosan ChC_3. Individual and mixed sodium dodecyl sulfate (SDS) and chitosan solutions were prepared by stirring in 0.3 M AcOH/0.05 M AcONa buffer for at least 24 h.

Methods

Dynamic surface tension measurements A drop tensiometer (Tracker, IT Concept, France) was used to measure the surface tension γ by analyzing the axial symmetric shape (Laplacian profile) of the rising bubble in aqueous solutions of low molecular weight surfactants, PEs, and their complexes [20]. All the measurements were performed at controlled temperature (25±0.1°C).

The parameters of the dynamic surface tension $\gamma(t)$ were determined by fitting the experimental curves with a three (or two) times exponential decay function as described in [13]: $\gamma(t) = \gamma_0 + \sum_{i=1}^{3} \pi_i[\exp(-t/t_i) - 1]$, where γ_o is the surface tension of the solvent, π_i are relaxation amplitudes corresponding to the relaxation times t_i. In terms of the surface pressure, $\pi(t)=\gamma_o-\gamma(t)$, produced by the surface-active species at the interface, the above-mentioned expression may be rewritten in the form $\pi(t) = \sum_{i=1}^{3} \pi_i[1 - \exp(-t/t_i)]$.

Measurement of dilational viscoelasticity of adsorption layers of polymers Two-dimensional complex elasticity modulus $\bar{E}$ of adsorption layers was found from the measurement of the surface tension variations as the response to sinusoidal dilational variations of surface area [20–22]. All the measurements were made during a sufficiently long time (usually greater than 5×10^4 s) to follow the effect of the 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 surface-active compounds was performed by applying a small dilational perturbation $\Delta A(t)$ to the bubble area A and simultaneously recording the variation of the surface tension $\gamma(t)$ [or the surface pressure $\pi(t)=\gamma_o-\gamma(t)$]. Periodic variation of the drop area A according to the sinusoidal law $\overline{\varepsilon}(t)=\varepsilon_a \quad \exp(i\omega t)$ (where $\varepsilon=\Delta A/A$ is the relative dilational deformation of the layer, and ε_a is the amplitude of this relative deformation) produces a variation of the surface tension $\overline{\pi}(t)=\pi_a \quad \exp[i(\omega t+\phi)]$, where ϕ is the phase angle (Fig. 1). In the linear deformation domain, the frequency-dependent complex elasticity module may be expressed as

$$\overline{E}(\omega)=\frac{d\overline{\pi}}{d\overline{\varepsilon}}=-\frac{d\overline{\gamma}}{d\overline{\varepsilon}}=E'(\omega)+iE''(\omega),$$

where $E'(\omega)$ and $E''(\omega)$ are the real and the imaginary parts, which depend on the applied frequency ω. By analogy with the 3-D rheology, one attributes to these functions the meaning of 2-D "storage" and "loss" moduli, which characterize a conservative and a dissipative rheological behaviour of adsorption layers, respectively.

The adsorption layer is conventionally considered as solid-like for some applied frequency ω if the elasticity storage modulus E' is much higher than the loss modulus E''. Inversely, in the case $E'<<E''$, the adsorption layer is considered as a liquid-like 2-D rheological body. To characterize the fluidity of adsorption layers, we have suggested to use the Deborah number (De) defined as the ratio of the applied dilational frequency ω to the characteristic relaxation frequency of the monolayer ω_o, i.e. $De=\omega/\omega_o$ [23]. The smaller the De, the more fluid the adsorption layer appears. The results of the frequency dependence of adsorption layers for an alkylated chitosan have been published elsewhere [13]. The systematic study of the frequency dependence of polysoaps and SPEC adsorption layers is prepared for publication.

As has been pointed out previously [23], our familiar understanding of the mechanisms of the 3-D viscoelasticity sometimes fails in the case of the 2-D viscoelasticity of adsorption layers of polymers. The specific properties of interfaces, e.g. the Gibbs elasticity and the Marangony effect, complicate the understanding and interpretation of the 2-D elasticity storage E' and loss E'' modules of the adsorption layers. As an example, it has been found [23] that the intrinsic parameters E_0 and ω_o of adsorption layers of alkylated chitosans are very sensitive to the bulk concentration C_p of the PEs. With increasing C_p, the liquid-like properties of adsorption layers become more pronounced (the characteristic frequency ω_o and the De increase). This finding, concerning the decrease in the 2-D elasticity module E_0 and the viscosity η_0 of adsorption layers of the alkylated chitosan with increasing bulk concentration, may be understood in terms of the structural organization and of the intermolecular lateral interactions inside the adsorption layers of polymers.

Results and discussion

Comparative study of the surface activity of surfactant–chitosan complexes and alkylated chitosan

Figure 2 represents the dynamic surface tension curves $\gamma(t)$ for the chitosan (curve 1), the SDS (curve 2), the alkylated chitosan ChC_{12} (curve 3), and the mixed SDS–Ch solution (curve 4). Curve 5 corresponds to the acetate buffer. The concentrations of the chitosan and the alkylated chitosan were equal to 10^{-3} monomol l^{-1}, whereas the concentration of the SDS was equal to 5×10^{-5} mol l^{-1} in its individual solution and in the mixed SDS–Ch solution. The composition of the mixed SDS–Ch solution ($\varphi=[C_s]/[C_{PE}]=0.05<<1$) was highly non-stoichiometric as shown by the charges of the components that ensured the solubility of the formed

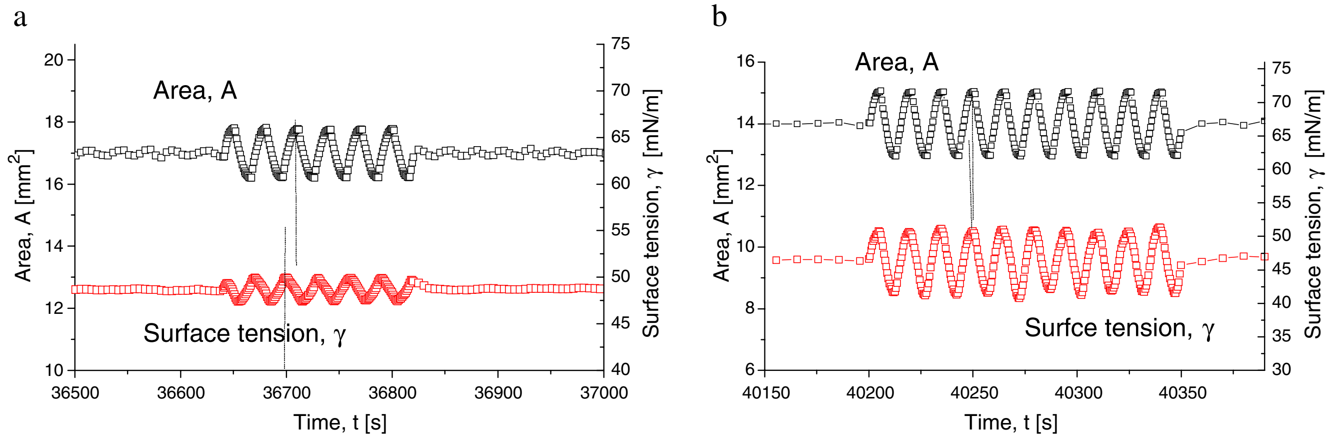

Fig. 1 Sinusoidal variations of area $A(t)$ and surface tension $\gamma(t)$ for precursor chitosan (**a**) and an alkylated chitosan (**b**)

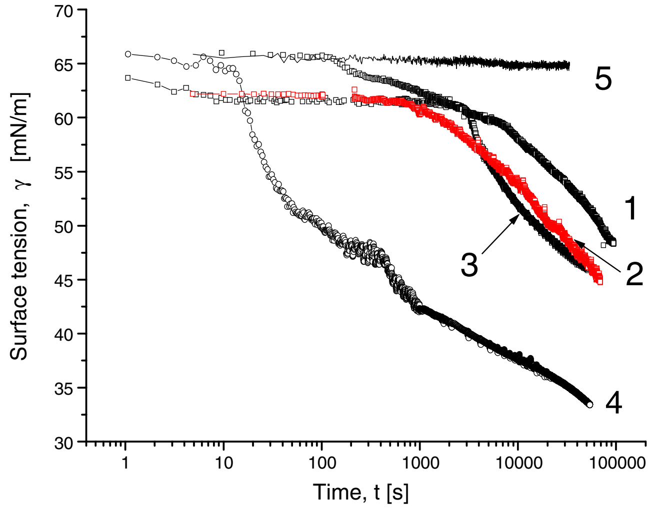

Fig. 2 Dynamic surface tension for the aqueous solutions of chitosan (*curve 1*), SDS (*curve 2*), alkylated chitosan ChC_{12} (*curve 3*), SDS–chitosan complex (*curve 4*), and acetate buffer (*curve 5*). Concentrations: SDS (*curves 2* and *4*; C_S=5×10^{-5} mol l^{-1}); chitosan and ChC12 (*curves 1*, *3*, and *4*; C_p=10^{-3} monomol l^{-1})

dynamic associates (SPEC) in the acetate buffer for the SDS concentration, which was chosen lower than the critical aggregation concentration (CAC), approximately equal to 5×10^{-4} mol l^{-1} [24], and much lower than the critical micelle concentration (CMC) of SDS, equal to 8.10^{-3} mol l^{-1} [25]. Therefore, the content of the free dodecyl group in individual and mixed SDS–Ch solutions, on the one hand, and the content of covalently bound dodecyl chains in the case of the alkylated chitosan, on the other hand, was approximately equal. This allows us to compare the surface properties of alkylated chitosan and of SPEC containing the same number of alkyl groups of the same nature. The comparison between the surface activity of the polysoap ChC_{12} (curve 3) and the complex SDS–Ch (curve 4) shows that for an equal length of alkyl groups and their concentration in the solution, or for equal values of degree of substitution for the polysoap and of φ for the mixed solution of surfactant and PE, the decrease in the surface tension γ in the case of SPEC is more significant than in the case of the polysoap. The origin of the anomalous high adsorption capacity of the SPECs lies in the cooperative adsorption of surfactants and PE at the interfaces [4, 24]. The formation of water-soluble electrostatically stabilized dynamic associates (SPECs) leads to the mutual hydrophobization of the components and, consequently, to the 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, desorption of macroions and surfactant molecules from the interface becomes kinetically unfavorable and leads to the practically irreversible adsorption of SPECs. 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 the contact with the interface (Fig. 3), the SPECs are characterized by higher mobility: the lability of the bonds between surfactants and PE in these dynamic associates makes it possible for these bound surfactants to realize wholly their surface activity.

All the compounds studied manifest a monotonic decrease in the surface tension after the lag time whose value depends on the type of the system and on the bulk concentrations of components. Different characteristic periods of the adsorption may be mentioned: the lag time, the postlag stage, and the final stage [12, 13]. The lag period is characterized by a very low decrease in the surface tension, while the adsorption layer in this period remains in the “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 the molecules from the bulk of the solution to the interface, and the 2-D “liquid” state is formed, leading to the remarkable increase in the surface pressure. In this postlag period, the adsorption layer becomes denser, and the decrease in 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 run, one can observe the final stage of the formation of the adsorption layer, which is characterized by the significant decrease in the adsorption rate of the surfactant molecules. For the macromolecular compounds, this retardation of the adsorption rate gives evidence for the formation of the steric barrier to the diffusion of new-arrival molecules to the interface. Another factor that is able to contribute to the retardation of the adsorption may be the possible structure (gel) formation inside these layers by the mechanism of the hydrophobic interactions or the hydrogen bond formation.

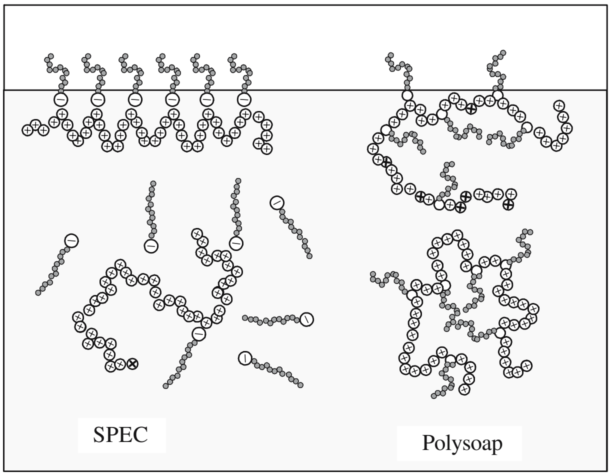

Fig. 3 Schema illustrating why the surfactant–polyelectrolyte complex (*SPEC*) is much highly surface-active than the polysoap

The monotonic decrease in the surface tension for the low molecular weight ionic surfactant SDS (curve 2, Fig. 2) after the lag time of the order of t_{lag}~10^3 s seems surprising, although long relaxation times have been mentioned for the micelle-forming surfactants by many authors [26, 27]. This lag period is quite realistic for the concentration of $C_{\mathrm{s}}=5\times10^{-5}$ mol l^{-1} of the ionic surfactant SDS and may testify for the formation of an adsorption monolayer by the mechanism of diffusion. According to the Ward and Tordai equation [28], the adsorption amount Γ of the surfactant may be approximately expressed as a function of C_{s} and t_{lag} as $\Gamma\left(t_{lag}\right) \cong C_s\sqrt{Dt_{lag}}$, where $D\cong10^{-11}$ m^2 s^{-1} is the coefficient of diffusion of molecules in the bulk of the solution. Believing that at the lag time t_{lag} the surfactant molecules fill the interface by one monolayer, and estimating the monomolecular adsorption amount as $\Gamma(t_{\mathrm{lag}})=1/N_{\mathrm{A}}a_1$~$5\times10^{-6}$ mol m^{-2} (a_1~0.25 nm^2 is the area per one molecule in the saturated monolayer), one finds the abovementioned estimation t_{lag}~10^3 s.

The free energy gain of the hydrophobic interaction per -CH_2 group inside the sparse adsorption layer being approximately 1 kT [29], the adsorption free energy of this surfactant having 12 -CH_2 groups in its alkyl radical may be estimated as $\Delta G_1\cong10$ kT. If one assumes the possibility of the formation of associates inside adsorption layers, the adsorption free energy may increase and become much higher. 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 $\Delta G_2\cong20$ kT. This corresponds to the decrease in the apparent coefficient of diffusion and, consequently, to the decrease in the rate of desorption of the molecules from the interface by a factor of $\exp[(\Delta G_2-\Delta G_1)/\mathrm{kT}]$ ~10^4. In this case, the adsorbed dimers behave as poorly soluble surfactants, such as the succinates (e.g. Aerosol OT, having two long alkyl chains and one sulfate group). Thus, the decrease of the surface tension for the SDS in the post lag period we would like to explain by the further increase of the adsorption amount and by the interaction between the surfactant molecules at the interface.

On the other hand, according to the opinion expressed by Mysels [25] and Elworthy [30], the SDS may be hydrolysed in the acidic solution during the long storage by forming dodecanol, which is known as a very surface active substance. For the time being, we are not able to confirm or reject this assumption. Nevertheless, this feature of the SDS has no impact on the logic of this presentation, which consists in the comparative study of the surface activity of the hydrophobically modified chitosans, if one restricts oneself by 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 beginning of the adsorption layers' formation and ageing. We have verified and confirmed this statement by replacing the SDS in the mixed chitosan–surfactant systems by sodium decyl sulfonate (Bousquet et al., unpublished data), which is known to be perfectly stable to the hydrolysis in the acidic medium [31].

Effect of degree of alkylation and alkyl chain length on the surface activity of polysoaps

At present, one of the unresolved problems of the theory of adsorption of hydrophobically modified PEs (polysoaps) is the role played by the DS of the alkyl groups and by their length on the surface activity of such polysoaps and on their adsorption kinetics. One may expect that in the concentration range below the CAC, corresponding to the solubility of the polysoaps, their surface activity will increase by increasing the length of the covalently bound alkyl chains $n(\mathrm{C})=\mathrm{C}_n\mathrm{H}_{n+1}$ at some constant DS (i.e. at the constant linear density of alkyl chains along the macromolecular backbone) and with increasing DS at some constant n(C). Increasing the total mass of the alkyl chains, which is proportional to both DS and n(C), will increase the hydrophobicity of the polysoap that increases its surface activity.

Nevertheless, this conclusion will not be so obvious for the polysoap samples that have identical hydrophile–lipophile balance (HLB) (i.e. the total mass of alkyl chains) but different alkyl chain lengths n(C). For example, it is impossible to predict beforehand if the surface activity of the polysoaps ChC_{12} (DS=5 mol%), ChC_8 (DS=7.5 mol %), or ChC_3 (DS=20 mol%) having equal mass of alkyl groups will be equal. This conclusion could be affirmed if all alkyl groups will be able to adsorb at the interface and realize their potential surface activity. However, as has been demonstrated [10], 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. Therefore, with increasing DS, the surface activity will increase only if $l_{\mathrm{Alk}}\geq l_{\mathrm{K}}$ but becomes only partially realized with the later decrease in l_{Alk}.

The aforesaid statement is illustrated by the kinetic surface tension $\gamma(t)$ curves for the polysoaps ChC_{12} (5 mol%), ChC_8 (21 mol%), or ChC_3 (82 mol%), corresponding to their limit degrees of alkylation, ensuring yet the solubility of these HM chitosans in the acetate buffer at 10^{-3} monomol l^{-1} (Fig. 4). Comparing the $\gamma(t)$ curves of chitosan and polysoaps during the lag stage of the adsorption ($t<t_{\mathrm{lag}}$), one finds that the surface activity of compounds (the surface pressure π for some equal time) increases with increasing alkyl chain length in the order Ch < ChC_3 < ChC_8 < ChC_{12}. This is comprehensible and well expected because for equal concentrations of PEs in the solution, the diffusion fluxes of the macroions from the bulk of solution to the interface are equal for each species, on one hand, and the factor of

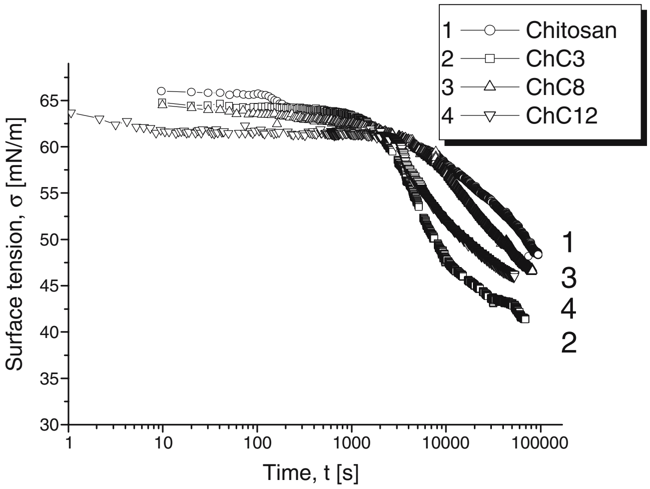

Fig. 4 Dynamic surface tension for solutions of chitosan (*curve 1*) and alkylated chitosans ChC_3 (*curve 2*), ChC_8 (*curve 3*), and ChC_{12} (*curve 4*). The concentration of all polymers is equal to $C_p=10^{-3}$ monomol l^{-1}

irreversibility of the adsorption increases with increasing alkyl chain length, on the other hand. One can imagine that the polysoap ChC_{12} having long alkyl chains will more easily acquire a flat conformation at the interface than the polysoap ChC_3, whose short alkyl chains do not have sufficient adsorption energy to change the coil conformation into extended ones of this polysoap in contact with the interface.

Comparing the $\gamma(t)$ curves corresponding to ChC_{12} and ChC_8, one finds that after the induction period of the adsorption, the sample ChC_{12} manifests remarkably higher surface activity with regard to the sample ChC_8 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. The mean distance between the dodecyl groups C_{12} in the sample ChC_{12}, being equal to l_{C12}~10 nm is of the same order of magnitude as the persistence length $l_K \cong 10$ nm [32]. Therefore, one may conclude that for this sample, the flexibility of the macroion is still sufficiently high to not hinder the adsorption of all the C_{12} groups at the interface. However, for the sample ChC_8, which has the mean distance between the C_8 groups equal to l_{C8}~2.5 nm, the persistence length l_K becomes considerably higher than l_{C8}. In this case, not all of the C_8 groups could be adsorbed at the interface, which explains the considerably lower surface activity of the ChC_8 with regard to the ChC_{12}.

On the other hand, comparison of the kinetic curves $\gamma(t)$ for the samples ChC_3 and ChC_8 shows that the surface activity of the former is much higher than that of the latter. At first sight, this may be explained by the fact that the total mass of alkyl chains of the sample ChC_3 is 1.4-fold higher than that of the sample ChC_8. However, as has been shown, the surface activity of the sample ChC_{12} is almost the same as that of ChC_3, although the total mass of alkyl chains of the sample ChC_3 is fourfold higher than that of ChC_{12}. Consequently, this is not the total alkyl chain mass (or the HLB), which is the main factor determining their surface activity, although the repartition of these substituents along the macromolecular chain is also an important parameter. In spite of the fact that the mean distance between the short propyl groups (C_3) of the water-soluble sample ChC_3 is equal to l_{C3}~0.6 nm (which is much lower than l_K), nevertheless, the majority of them are able to realize their surface activity, while practically each segment of the macroion contains such groups (Fig. 5).

Another factor that may influence the adsorption activity of polysoaps is the ability of alkyl chains to form the intra- and interpolymer micelle-like aggregates via hydrophobic interaction between the alkyl chains. When the intrapolymer 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 approximately 1 kT [29], one can assume that relatively short propyl groups (C_3) are not able to form aggregates or at least stable associates unlike longer alkyl chains in the samples ChC_8 and ChC_{12}, with the energy of hydrophobic interaction of the order of approximately 10 kT. This may explain why the apparent hydrophobicity and, consequently, the surface activity of the ChC_3 sample are higher than that of the ChC_8. On the other hand, the higher surface activity of the ChC_{12} with regard to the sample ChC_8 may be explained by the fact that the former sample does not form intramacromolecular aggregates in spite of its longer alkyl chains, while the density of these chains corresponding to DS=5 mol% is lower than the critical DS, which is of the order of 10 mol% for the groups C_{12} [33]. In contrast, the DS=21 mol% of the ChC_8 sample exceeds this critical DS, which leads to intramacromolecular aggregation in the case of low bulk concentration and to the decrease in the surface activity of this polysoap. With

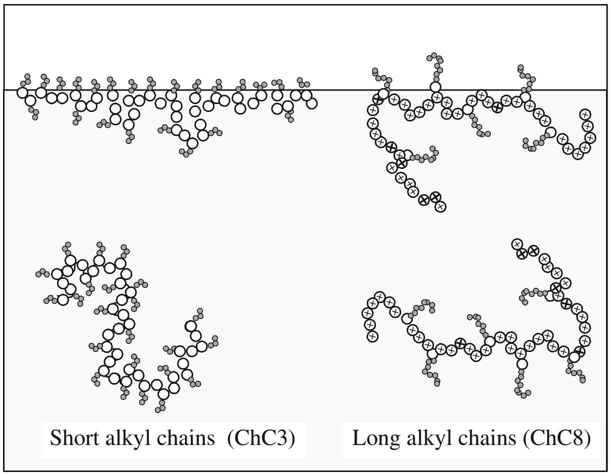

Fig. 5 Schema illustrating why the polysoap with short alkyl chains adsorbs better than that with long alkyl chains

increasing bulk concentration, intermacromolecular aggregates could be formed that also decreases their kinetics of adsorption.

By these preliminary results, we have evidenced 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 and 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 obtained results, we are now performing a more detailed investigation of the effect of the degree of alkylation (DS) and the alkyl chain length n(C) on the kinetics of the adsorption of HM chitosans.

Surface activity of complexes formed between alkylated chitosans and SDS

The interaction between oppositely charged alkylated PEs (polysoaps) and surfactants presents an obvious interest from both fundamental and practical points of view. In our previous publication [10], we have evidenced that the formation of complexes between an anionic polysoap (carboxymethylchitin-C_{12}) and the cationic surfactant tetradecyltrimethylammonium bromide (TDAB) is controlled by both the electrostatic and hydrophobic interactions between oppositely charged carboxy and ammonium groups and the alkyl chains of the polysoap and the surfactant, respectively. At a very small surfactant concentration in the mixed solution, the hydrophobic interaction binds surfactant molecules to the macroion that screens the hydrophobicity of the latter and makes it more hydrophilic. However, with a later increase in the surfactant concentration in the mixed solution, highly surface active complexes are formed whose surface activity considerably overpasses that of the polysoaps.

Figure 6 illustrates the effect of the small quantity of the anionic surfactant SDS on the surface activity of alkylated cationic polysoaps (ChC_3 and ChC_8). It is surprising that the induction times of adsorption are considerably decreased for all the ChC_n–SDS complexes with regard to those of polysoaps ChC_n. This effect is partially related to the interaction between the adsorbed complexes at the interface. In a future publication, we will show that the viscoelasticity of the complexes ChC_n–SDS is much higher than that for the polysoaps ChC_n.

Kinetics of the structure formation inside the adsorption layers of SPEC and polysoaps

The measurement of the structuro-mechanical properties of adsorption layers of hydrophobically modified chitosans (polysoaps) and surfactant–chitosan and surfactant–polysoap complex layers in the course of ageing was carried out during a sufficiently long time (usually greater than 50,000 s) to follow all stages of the formation of adsorption layers. Figure 7 shows how the real E' and the imaginary E'' components of the complex 2-D elasticity module $\bar{E}$ of adsorption layers depend on the time t. First of all, it points out a sharp increase in the storage module E' for the adsorption layers of SDS–Ch complexes (curve 3, Fig. 7a), which tends to be a relatively high constant value exceeding 80 mN m^{-1}. According to the conventional designation of 2-D rheological states, 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

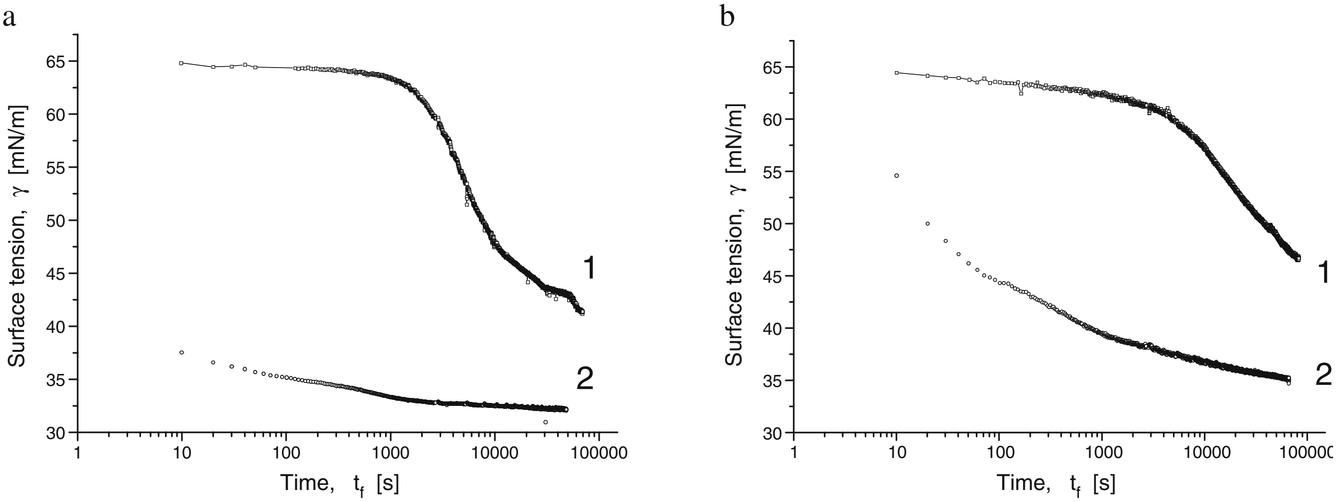

Fig. 6 Kinetic curves $\gamma(t)$ for the solutions of polysoaps (*curve 1*) and SDS–polysoap complexes (*curve 2*) for the ChC_3 (**a**) and ChC_8 (**b**) systems. Concentrations: $[ChC_3]=1.4\times10^{-3}$ monomol l^{-1}; $[SDS]=2.1\times10^{-4}$ mol l^{-1} in ChC_3-SDS solution; $[ChC_8]=1.2\times10^{-3}$ monomol l^{-1}; $[SDS]=2.3\times10^{-4}$ mol l^{-1} in ChC_8–SDS solution

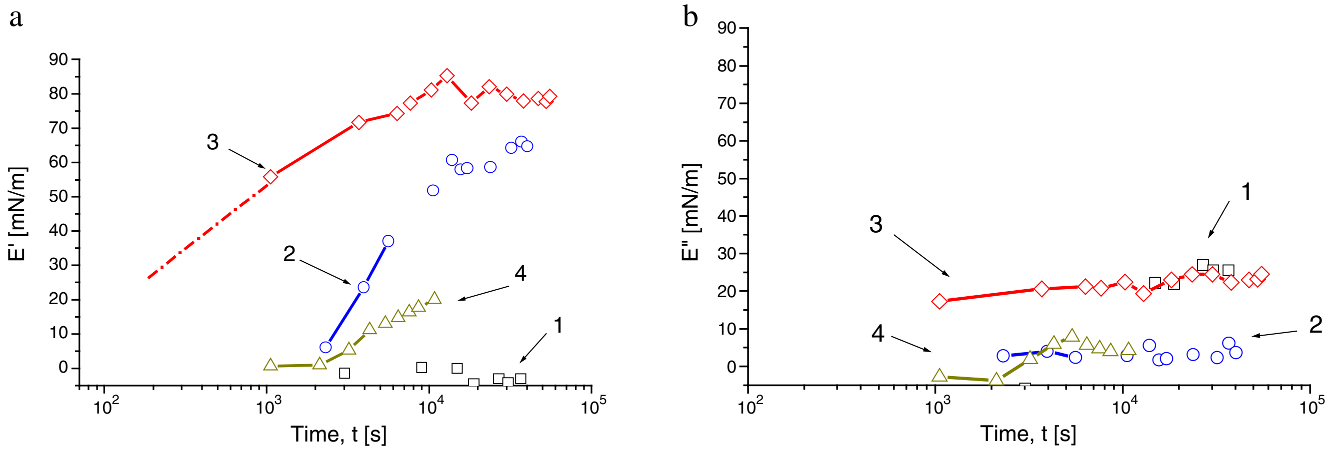

Fig. 7 Increase with the ageing time *t* of 2-D storage *E*′ (**a**) and loss *E*″ (**b**) moduli of adsorption layers of different compounds. *1* Chitosan, *2* alkylated chitosan ChC_{12}, *3* SDS–chitosan complex, *4* SDS. Concentrations: SDS (*curves 3* and *4*; C_s=5×10^{-5} mol l^{-1}); chitosan and ChC_{12} (*curves 1*, *2*, and *3*; C_p=10^{-3} monomol l^{-1})

storage module *E*′ is much higher than the loss module *E*″ (curve 3, Fig. 7b).

The real module *E*′ of the alkylated chitosan ChC_{12} (curve 2, Fig. 7a) increases as well with the storage time and tends to the same value in the order of 80 mN m^{-1}, but after some lag time, τ_{lag}~2,000 s. This delay of the increase in *E*′ for the polysoap with regard to the complex SDS–Ch is likely due to the delay in the increasing of the surface activity of this polysoap compared to the complex (curves 2 and 3, Fig. 2). In our previous works [10, 12], 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–Ch complexes occurs much easily because of the labile character of less strong electrostatic bonds between the components.

A comparison between the corresponding modules *E*′ and *E*″ of the alkylated chitosan (curves 2, Fig. 7) allows us to conclude that after the ageing time *t*≅2,000 s, the adsorption layers of this polysoap acquire solid-like properties (*E*′>*E*″), whereas in the region *t*<2,000 s, these layers are "liquid-like" (*E*′<*E*″). Concerning the chitosan (curve 1, Fig. 7a,b), it is flagrant that its adsorption layers behave as liquid-like (*E*′<*E*″) for the whole ageing time interval (τ≅10^5 s). Unexpected is the solid-like behaviour of adsorption layers of low molecular weight surfactant SDS after the lag time *t*>2,000 s. This feature may be explained by the possible hydrolysis of SDS at the interface, leading to the formation of low water solubility dodecanol [12].

The increase in the 2-D storage module *E*′ in the case of adsorption layers of macroions may be due to two factors: (1) the increase in the energy of interaction (the adsorption energy) of macromolecules with the interface and (2) the increase in the lateral interaction (cohesion) between the macromolecules inside the adsorption layers. In this connection, it seems interesting to discuss the effect of these factors on the dilatational elasticity of different surface-active compounds: polysoap ChC_{12}, SPEC SDS–Ch, and precursor chitosan at some equal bulk concentration (Fig. 8).

The increase in the adsorption energy is manifested by the decrease in the surface tension or the increase in surface pressure $\pi=\gamma-\gamma_o$. From Fig. 2, it follows that in the beginning of the formation of adsorption layers, this increase is most significant for the complex SDS–Ch (curve 4, Fig. 2), whereas the alkylated chitosan $C_{12}Ch$ and the precursor chitosan are characterized by comparatively low adsorption (curves 2 and 1, Fig. 2). This correlates with the high storage module *E*′ for the SDS–Ch and the lowest values of *E*′ for the $C_{12}Ch$ and Ch in the initial stage of adsorption (Fig. 7). This may provide evidence for the influence of the surface pressure π on the storage module *E*′of adsorption layers. The correlation between *E*′ and π values is analogous to the usually observed dependence of the static elasticity modules E_{st}=−dπ/d ln *A* on the surface

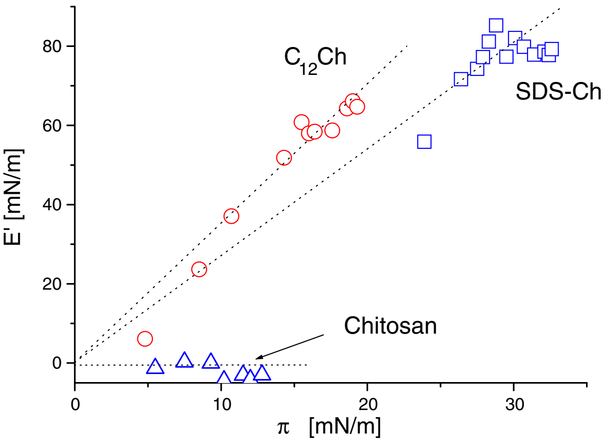

Fig. 8 Dependence of elasticity module *E*′ on the surface pressure π for the chitosan (*Ch*), alkylated chitosan (*C₁₂Ch*) and surfactant–polyelectrolyte complex (*SDS–Ch*)

pressure π for liquid-expanded insoluble Langmuir monolayers. In the latter case, the increase in the module E_{st} is explained by the increase in the interaction energy between the surfactant molecules and the liquid substrate [34].

For example, in the case of an insoluble surfactant that forms a gaseous-like 2-D Langmuir monolayer, its Gibbs elasticity E_{st} is strictly equal to the surface pressure π. Effectively, for these monolayers, the following relationship holds: $\pi A = RT$, where A is the area of the monolayer, and consequently, $E_{st} = -A\ d(RT/A)/dA = \pi$. The physical meaning of the Gibbs elasticity E_{st} is the storage module E' at the applied frequency equal to zero. Because we are using a constant frequency (0.42 rad s^{-1}), we have to compare the experimental dependencies $E'(\omega)$ at this frequency, with a reference ("standard") state that is the insoluble surfactant gaseous monolayer at $\omega = 0$ rad s^{-1}.

As it follows from the comparison between the modules $E'(t)$ for the chitosan and the polysoap (Fig. 8 and curves 1 and 2, Fig. 7), the E' module of Ch is practically zero in the whole region of the ageing time, whereas it increases linearly for ChC_{12}, with the surface pressure π reaching a rather high value of the order of 60 mN m^{-1}, although the slope E'/π is 2.5-fold greater than the usually observed slope corresponding to the static elastic module E_{st}.

In the meantime, not all the features of the rheological behaviour of the adsorption layers of studied compounds could be wholly explained by only the effect of the adsorption energy, i.e. by the increase in the surface pressure of adsorption layers. This means that this is the lateral intermolecular interaction and not the adsorption energy, which is the main factor influencing the elasticity module E' of adsorption layers. It is more than likely that the relatively long C_{12} chains of the alkylated chitosan interacting hydrophobically with the energy of the order of ~10 kT [29] are responsible for the increased elastic properties of this polysoap. Unlike the polysoap, the less bulky residual hydrophobic group diacetylamide inside the adsorption layers of chitosan interact with the energy of the order of only ~1 kT, which is obviously insufficient to obtain high elasticity module E'.

A comparison between the curves $E'(\pi)$ for ChC_{12} and Ch (Fig. 8) shows that in spite of an obvious correlation between the elasticity module E' and the surface pressure π in the whole ageing time interval, nevertheless, there is a difference between the absolute values of these properties. The maximal values of E' for the polysoap and the complex practically coincide, whereas the surface pressure of the polysoap ChC_{12} is approximately twofold lesser than that of the SDS–Ch. The comparatively high value of the module E' for the polysoap adsorption layers gives evidence for 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.

A comparison between the absolute values of the storage E' and loss modules E'' of adsorption layers of investigated compounds makes it possible to formulate some conclusions concerning the mechanism of the interaction between the macromolecules in adsorption layers. Figure 7 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 the value ~20 mN m^{-1}. Unexpected is the relatively high loss module E'' for the chitosan. This difference may be explained by the difference in the strength of the lateral bonds inside the adsorption layers of the polysoap and the complex. The 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 lowers the value of the loss module E''. On the other hand, in the case of the SDS–Ch complex, which is also characterized by the lateral hydrophobic interaction between the C_{12} alkyl chains of the SDS molecules, the dilational deformation leads to the reversible rupture of the less strong electrostatic bonds between the oppositely charged components. This is also valid for the chitosan adsorption layer. The periodical destruction and reestablishment of the electrostatic bonds under the sinusoidal dilatational deformation lead to the increased loss of the elastic energy, i.e. to the high loss module E'' for the chitosan and the SDS–Ch complex.

Conclusion

The obtained results show that the process of the adsorption at the air–water interface of alkylated chitosans (ChC_3, ChC_8, and ChC_{12}) and SDS–Ch complexes and of the formation of a gel-like structure inside the adsorption layers of these compounds develop in the long run with different kinetics. Both kinetics are characterized by an induction time (the so-called lag time) τ_{lag} corresponding to the diffusion stage of the formation of adsorption layers. During this time, the decrease in the surface tension (or the increase in the surface pressure π) does not exceed several millinewtons per meter that corresponds to the "gaseous" state of adsorption layers.

It has been found that during the lag time, the adsorption of alkylated chitosans (cationic polysoaps) increases with increasing the alkyl chain length, whereas during the postlag time, the adsorption of the ChC_3 is maximal with regard to other polysoaps. It has been confirmed that at equal content of alkyl groups in the system, the surface activity of the SDS–Ch complexes is much higher with regard to that of the polysoaps.

The postlag stage of the formation of the adsorption layer is characterized by the remarkable rate of increase in the surface pressure π that corresponds to the conformational rearrangement of polyelectrolytes inside the adsorption layer by increasing the number of hydrophobic groups (adsorbing centres) in contact with the non-polar phase at the interface. At the same time, the elasticity storage module E' of alkylated chitosans and SDS–Ch complexes undergoes a remarkable increase that gives evidence for the formation of the gel-like structure inside the adsorption layers via the hydrophobic interaction between the alkyl chains of polysoaps and SDS–Ch complexes.

It has been found that the rate of increase in the dilational storage module E' of the adsorption layers of SDS–Ch complexes is much higher than for the polysoaps, which correlates with the higher surface activity of the former with regard to the latter. For the mentioned systems, the module E' is much higher than the loss module E'' that confirms the solid-like properties of their adsorption layers. On the other hand, the adsorption layers of the chitosan are liquid-like, while $E \ll E''$.

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