Dynamic surface tension and viscoelastic properties of adsorption layers of amphiphilic chitosan derivatives systems.

J. Desbrières*, V.G. Babak, C. Bousquet

Laboratoire de Physico-Chimie des Polymères (UMR CNRS/UPPA 5067, IPREM FR CNRS 2606),

Helioparc Pau Pyrenees, 2 Avenue President Angot, 64053 PAU cedex 9, France.

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 SDS-chitosan complexes) have been studied by the tensiometric method based on the axisymmetric rising bubble shape analysis in function of the bulk concentration of polymers and the ageing time of their adsorption layers. The kinetics of the adsorption of chitosan (Ch), alkylated chitosans (ChC_3, ChC_8, ChC_{12}) and surfactant-polyelectrolyte complexes (SPECs) 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. The post-lag stage of the formation of the adsorption layer is characterized by the remarkable rate of increase of the surface pressure π that corresponds to the conformational rearrangement of polyelectrolytes inside the adsorption layer by increasing the number of hydrophobic groups (adsorbing centers) in contact with the non polar phase at the interface. It has been confirmed that at equal content of alkyl groups in the system, the surface activity of the SPECs is much higher with regard to that of polysoaps. These phenomena allow the use of such amphiphilic systems based on natural polymers for a wide variety of applications.

Introduction.

It is well known that the hydrophobic modification of polyelectrolytes (PE) by the covalent binding of alkyl groups or by the formation of non stoichiometric dynamic associates with the oppositely charged surfactants (surfactant-polyelectrolyte complexes, SPECs) in the mixed aqueous solutions, leads to the remarkable increase of the adsorption of PEs at the interfaces. [1-9] The driving force of adsorption of hydrophobically modified polyelectrolytes (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 non polar phase (air or oil). In the case of polysoaps, the increase of 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 meaning, the interfacial behavior of the alkylated polyelectrolytes 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 one macroion either in the solution of a polysoap, or in the mixed surfactant-polyelectrolyte 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 regards 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 SPEC 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 the destruction. [8, 16, 17]. 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 the structure formation inside these adsorption layers. The aim of this work is to study the kinetics of the adsorption and of the structure-formation inside the adsorption layers of the hydrophobically modified chitosans and surfactant-chitosan complexes by dynamic tensiometry and two-dimensional dilational rheology.

Materiel and Methods.

Materiel
The precursor chitosan from Pronova (Norway) with molecular weight 190,000 and degree of acetylation (DA) 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 method [18] known as non destructive for the polymer. [19] Therefore, HM chitosans had the same value of degree of polymerisation as its precursor. The content of hydrophobic side chains in HM chitosans were 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 SDS and chitosan solutions were prepared by stirring in 0.3 M AcOH/0.05 M AcONa buffer during at least 24h

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

Measurement of dilational viscoelasticity of adsorption layers of polymers. Two dimensional complex elasticity modulus $\overline{E}$ 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 sufficiently long time (usually greater than 5.10^4 s) in order to follow the effect of the ageing on the surface tension and on the dilatational rheological properties of the adsorption layers.

Result and Discussion

Comparative study of the surface activity of surfactant-chitosan complexes and alkylated chitosan.
Figure 1 represents the dynamic surface tension curves γ(t) for the chitosan (curve 1), the SDS (curve 2), the alkylated chitosan ChC_{12} (curve 3) and the mixed chitosan-SDS solution (curve 4). The 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 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 which was chosen lower than the c.a.c. (the critical aggregation concentration) approximately equal to $\sim 5.\,10^{-4}$ mol L^{-1} [23] and much lower than the CMC of SDS equal to 8.10^{-3} mol L^{-1}.[24] So, the free dodecyl group content in individual and mixed chitosan-SDS solutions, on the one hand, and the content on 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 Ch-SDS (curve 4) shows that for the equal length of alkyl groups and their concentration in the solution, or for the equal values of DS for the polysoap and of φ for the mixed solution of surfactant and PE, the decrease of 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, 23] The formation of water soluble electrostatically stabilized dynamic associates (surfactant-polyelectrolyte complexes, SPECs) leads to the mutual hydrophobisation of the components and, consequently, to the increase of 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 surfactants molecules, desorption of macroions and surfactant molecules from the interface, becomes kinetically unfavorable that 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 (Figure 2), 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.
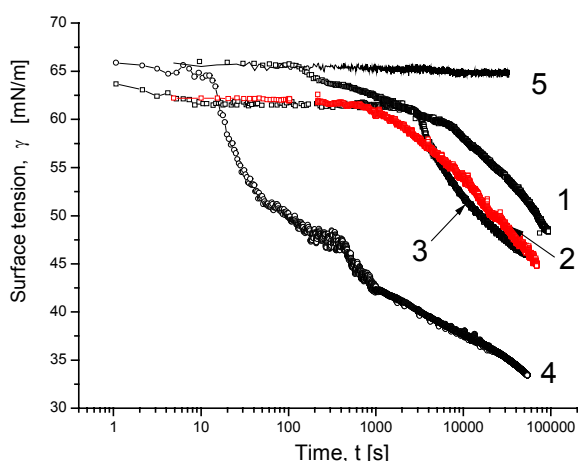
Figure 1 : Dynamic surface tension for the aqueous solutions of chitosan (curve 1), SDS (curve 2), alkylated chitosan ChC$_{12}$ (curve 3), SDS-chitosan complex (curve 4), and acetate buffer (curve 5). Concentrations: SDS (curves 2 and 4 ; $C_s = 5.10^{-5}$ mol L^{-1}) ; chitosan and ChC$_{12}$ (curves 1, 3 and 4 ; $C_p = 10^{-3}$ mono-mol L^{-1})
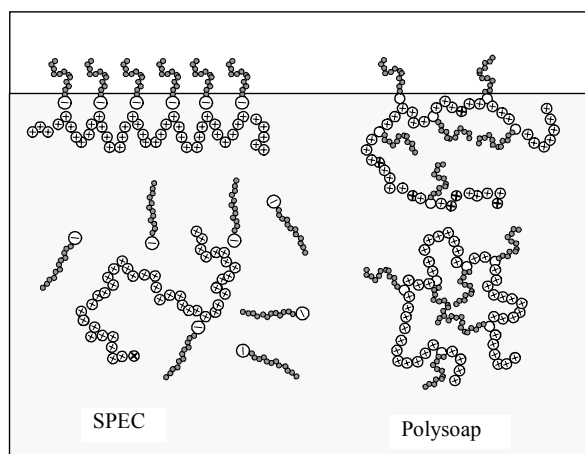
Figure 2 : Schema illustrating why the surfactant-polyelectrolyte complex (SPEC) is much higher surface active than the polysoap

All the compounds studied manifest a monotonic decrease of the surface tension after the lag time which 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

post lag stage and the final stage. [12, 13] The lag period is characterized by very low decrease of 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 two dimensional "liquid" state is formed leading to the remarkable increase of 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 [13]. In the long time, one can observe the final stage of the formation of the adsorption layer which is characterized by the significant decrease of the adsorption rate of the surfactant molecules. For the macromolecular compounds this retardation of the adsorption rate testifies for the formation of the 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 the hydrophobic interactions or the hydrogen bonds formation.

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

For this time, one of the non resolved problems of the theory of adsorption of hydrophobically modified polyelectrolytes (polysoaps) is the role which is played by the degree of substitution of the alkyl groups (DS) and their length on the surface activity of such polysoaps and on their adsorption kinetics. One may expect that in the concentration range below the c.a.c., corresponding to the solubility of the polysoaps, their surface activity will increase with increasing the length of the covalently bound alkyl chains $n(C)=C_nH_{n+1}$ at some constant DS (i.e. at the constant linear density of alkyl chains along the macromolecular backbone) as well with increasing DS at some constant $n(C)$. Really, with increasing the total mass of the alkyl chains which is proportional to both, DS and $n(C)$, increased will be the hydrophobicity of the polysoap that increases 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 $n(C)$. 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 affirmative if all alkyl groups will be able to adsorb at the interface and realise their potential surface activity. But, as it 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. So, with increasing DS, the surface activity will increase only if $l_{Alk} \geq l_K$, but becomes only partially realized with the later decrease of l_{Alk}.

Aforesaid is illustrated by the kinetic surface tension curves $\gamma(t)$ 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} mono-mol L^{-1} (Figure 3). Comparing the $\gamma(t)$ curves of chitosan and polysoaps during the lag-stage of the adsorption (t < t_{lag}), one finds that the surface activity of compounds (the surface pressure π for some equal time t) increases with increasing the alkyl chains length in the order $Ch<ChC_3<ChC_8<ChC_{12}$. This is comprehensible and well expected on account that for the equal concentrations of PEs in the solution, the diffusion fluxes of the macroions from the bulk of solution to the interface are equals for each species, on the one hand, and that the factor of irreversibility of the adsorption increases with increasing the alkyl chains 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 have no 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. Really, the mean distance between the dodecyl groups C$_{12}$ in the sample ChC$_{12}$ being equal to $l_{C_{12}} \sim 10$ nm, is of the same order of magnitude that the persistence length $l_K \cong 10$ nm [25]. So, 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 C$_{12}$ groups at the interface. But for the sample ChC$_8$ which has the mean distance between the C$_8$ groups equal to $l_{C8} \sim 2.5$ 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 that explains considerably lower surface activity of the ChC$_8$ with regard to the ChC$_{12}$.

On the other hand, comparison between the kinetic curves $\gamma(t)$ for the samples ChC$_3$ and ChC$_8$ shows that the surface activity of the further is much higher than of the later. At the 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 of the sample ChC$_8$. But, as it has been shown, the surface activity of the sample ChC$_{12}$ is almost the same as the ChC$_3$, although the total mass of alkyl chains of the sample ChC$_3$ is 4 fold higher than of the ChC$_{12}$. 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 substituants along the macromolecular chain being 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 $l_{C3} \sim 0.6$ nm (that is much lower than l_K), nevertheless the majority of them are able to realise their surface activity while practically each segment of the macroion contains such groups (Figure 4).
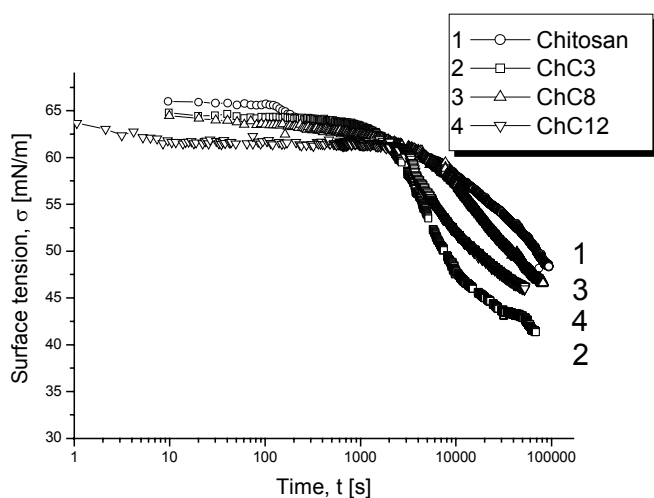
Figure 3 : Dynamic surface tension for solutions of chitosan (curve 1) and alkylated chitosans ChC$_3$ (curve 2), ChC$_8$ (curve 3) and ChC$_{12}$ (curve 4). The concentration of all polymers is equal to 10^{-3} monomol/L.
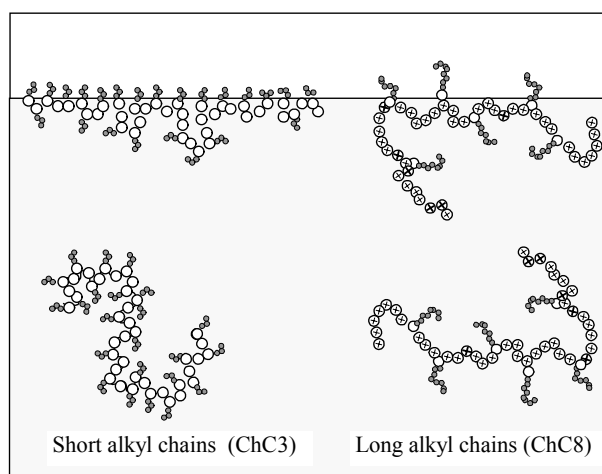
Figure 4 : Schema illustrating why the polysoap with short alkyl chains adsorbs better than with long alkyl

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 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 obtained results we are performing now 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 polyelectrolytes (polysoaps) and surfactants presents an obvious interest from both, fundamental and practical, points of views. In our previous publication [10] we have evidenced that the formation of complexes between an anionic polysoap (carboxymethylchitin-C_{12}) and the cationic surfactant, 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 very small surfactant concentration in the mixed solution, the hydrophobic interaction binds surfactant molecules to the macroion that screens the hydrophobicity of the later and makes it more hydrophilic. But with later increase of the surfactant concentration in the mixed solution, the highly surface active complexes are formed which surface activity overpasses considerably that of the polysoaps.

The figure 5 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). Surprising is 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 our publication (in preparation) we will show that the viscoelasticity of the complexes ChC_n-SDS is much higher than that for the polysoaps ChC_n.
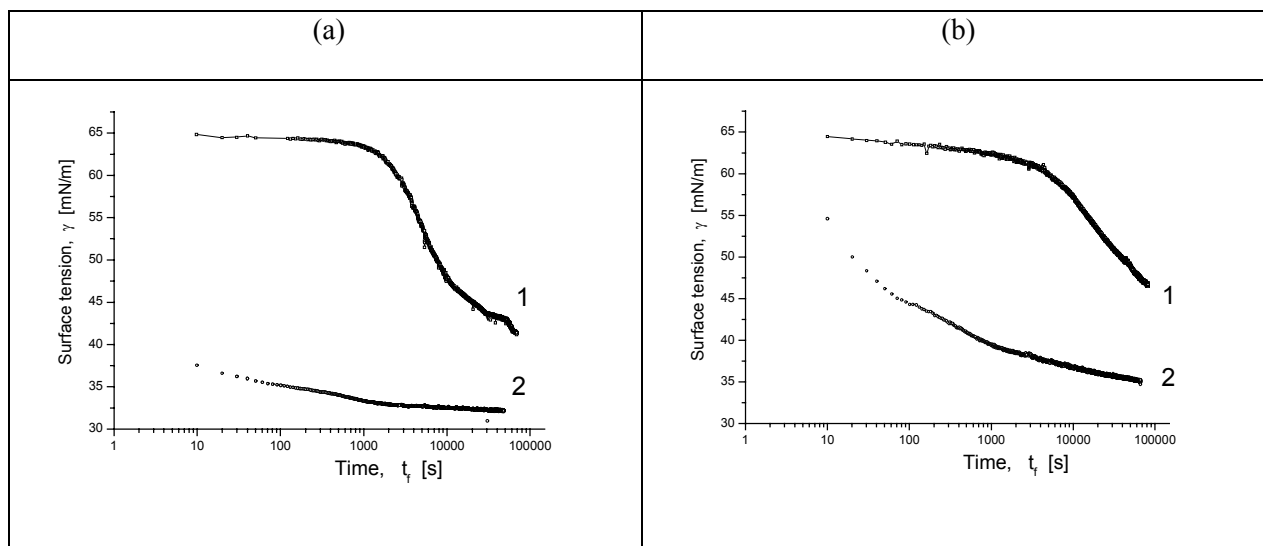
Figure 5 : Kinetic curves $\gamma(t)$ for the solutions of polysoaps (curves 1) and SDS-polysoap complexes (curves 2) for the ChC_3 (a) and ChC_8 (b) systems. Concentrations: $[ChC_3]$=1.4 10^{-3} monomol/L ; [SDS]= 2.1 10^{-4} mol/L in ChC_3-SDS solution ; $[ChC_8]$=1.2 10^{-3} monomol/L ; [SDS]= 2.3 10^{-4} mol/L in ChC_8-SDS solution.

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 complexes layers in the course of ageing was carried out during sufficiently long time (usually greater than 50000 s) to follow all stages of the formation of adsorption layers. Figure 6 shows how the real E' and the imaginary E'' components of the complex two dimensional elasticity module $\overline{E}$ of adsorption layers depend on the time t. First of all, point out a sharp increase of the storage module E' for the adsorption layers of SDS-chitosan complexes (curve 3, figure 6(a)) which tends to relatively high constant value exceeding 80 mN/m. According to admitted conventional designation of two dimensional rheological states, we can conclude for the "solid-like" rheological properties of these layers for the used frequency $\omega \cong 0.42$ rad/s while the storage module E' is much higher than the loss module E'' (curve 3, figure 6 (b)).
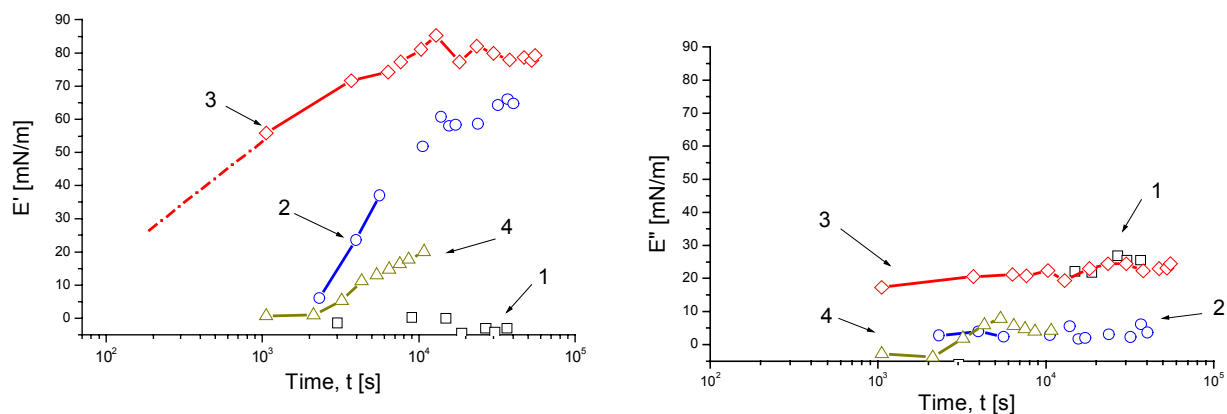
Figure 6 : Increase with the ageing time t of two-dimensional storage E' (a) and loss E" (b) moduli of adsorption layers of different compounds. 1- chitosan, 2 –alkylated chitosan ChC$_{12}$, 3–SDS-chitosan complex, 4 - SDS. Concentrations : SDS (curves 3 and 4 ; C$_s$ = 5.10^{-5} mol L^{-1}) ; chitosan and ChC$_{12}$ (curves 1, 2 and 3 ; C$_p$ = 10^{-3} mono-mol L^{-1}).

The real module E' of the alkylated chitosan ChC$_{12}$ (curve 2, figure 6(a)) increases as well with the storage time and tends to the same value of the order of 80 mN/m but after some lag time τ_{lag} ~2000 s. This delay of the increase of E' for the polysoap with regard to the complex Ch-SDS is likely to the delay of increasing of the surface activity of this polysoap comparing to the complex (curves 2 and 3, figure 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 Ch-SDS complexes occurs much easily because of the labile character of less strong electrostatic bonds between the components.

Comparison between the corresponding modules E' and E" of the alkylated chitosan (curves 2, figure 6) allows us to conclude that after the ageing time t $\cong$ 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 (curves 1, figure 6(a) and figure 6(b)), it is flagrant that its adsorption layers behave as "liquid-like" (E'<E") for a whole ageing time interval ($\tau \cong 10^5$ s). The increase of the two-dimensional storage module E' in the case of adsorption layers of macroions may be due to two factors: (a) the increase of the energy of interaction (the adsorption energy) of macromolecules with the interface, and (b) the increase of the lateral interaction (cohesion) between the macromolecules inside the adsorption layers. Results show that the formation of adsorption layers by hydrophobically modified chitosans at interfaces is accompanied by structure (gel) formation inside thses layers via lateral hydrophobic interactions between the covalently bound alkyl chains in the case of alkylated chitosans or between te lakyl chains of surfactants forming SPECs with chitosan [26].

The influence of the polymer concentration on such behaviours was also studied and related to the internal structure of adsorption layers [13]

Conclusion

The obtained results show that the process of the adsorption at the air-water interface of alkylated chitosans (ChC$_3$, ChC$_8$, ChC$_{12}$) and SDS-chitosan complexes and of the formation of a gel like structure inside the adsorption layers of these compounds develop in the long time with different kinetics. The 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 of the surface tension (or the increase of the surface pressure π) does not exceed several mN/m 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 post-lag time the adsorption of

the ChC$_3$ is maximal with regard to other polysoaps. It has been confirmed that at the 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 post-lag stage of the formation of the adsorption layer is characterized by the remarkable rate of increase of 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-chitosan complexes undergoes a remarkable increase that testifying for the formation of the gel-like structure inside the adsorption layers via the hydrophobic interaction between the alkyl chains of polysoaps and SDS-chitosan complexes.

It has been found that the rate of increase of 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 laters. 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''.

Applications of such systems as emulsion stabilizers or to elaborate capsules was demonstrated [15,17].

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