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Interfacial layer-by-layer interpolyelectrolyte complex formation studied by flow dilational rheometry

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The interpolyelectrolyte complex formation at the air–water interface has been studied by flow dilational rheometry.

The formulation of vectors for controllable drug delivery is an actual task in medicine, and a new class of hollow micro- and nanocapsules produced by interfacial surfactant–polyelectrolyte or interpolyelectrolyte complex formation has been introduced.[1,2] The walls of these capsules are formed *via* the layer-by-layer assembly of oppositely charged species, surfactant-polyelectrolyte (SPEC) or interpolyelectrolyte (IPC) complexes. It has been established by SAXS that the structure of the microcapsule walls made by SPEC is ordered in a nanometric scale[3] and manifests the viscoelastic properties of physical gels.[1] The walls made of IPC possess obvious mechanical strength and viscoelasticity.[4,5]

The mechanism and kinetics of formation of interfacial physical gel structures of SPECs and IPCs remain unclear. Recently,[6] it was found that the adsorption layers of SPEC of a mixed chitosan–SDS system manifest anomalously high two-dimensional viscoelasticity due to the formation of a gel-like network at the interface. The two-dimensional elasticity storage E' and loss E'' moduli of this adsorption layers continuously increased with ageing time manifesting different kinetics: diffusion flow of the complexes from the bulk to the interface, competitive and cooperative adsorption at the interface of oppositely charged components, electrostatic and hydrophobic interaction between these components at the interface leading to the formation of the physical gel structure. One of the drawbacks of this method is that the complexes form in the bulk of solution, and one studies the formation of the gel-like interfacial structures, whose kinetics is screened by the diffusion of complexes already formed in the bulk of the mixed solution. Another inconvenience is that, in this method, one is restricted by only soluble complexes while insoluble ones precipitate from the mixed solution.

We developed a novel flow dilational rheometry method to study the kinetics of interfacial reactions including the surfactant–polyelectrolyte and interpolyelectrolyte complex formation between oppositely charged species. This method is based on the dynamic interfacial tensiometry, gauged by the axisymmetric shape analysis of rising or pendant static drops or bubbles (Tracker, IT Concept, France) (Figure 1).[7] The area of a drop is submitted to periodic small sinusoidal or step-wise deformations that make it possible to measure continuously the inter-

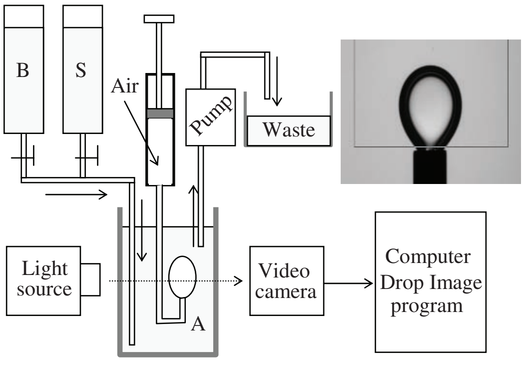

Figure 1 Schematic diagram of the novel controlled flow dilational rheometry method (for explanation, see the text).

facial tension γ and the two-dimensional complex elasticity modulus $\overline{E}$ of adsorption layers during a sufficiently long time (usually, greater than 50000 s to achieve a quasi-equilibrium state).[8,9] The initial aqueous solution containing a surface-active compound (A) after a time t_1 of the formation of adsorption layers may be removed from the measurement cell and replaced by the pure solvent (S) and, afterwards, by the solution of another compound (B), which interacts with the adsorption layer of the compound (A) by forming a complex (SPEC or IPC, depending on the nature of compounds A and B). This operation may be repeated many times in order to form layer-by-layer complexes.

The tensiometric study of the kinetics of enzymatic reactions at the interface by the shape analysis of the Laplace profile of drops was first undertaken by Labourdenne *et al.,*[10] who injected an enzyme solution into an initial solution using a syringe. In our method, we apply a constant or periodic flow of a solvent or surfactant (polymer) solution through the cell, thereby allowing the study of the kinetics of interpolyelectrolyte (IP) or surfactant–polyelectrolyte (SPE) complex formation at the interface avoiding reactions between the components in the bulk of the solution. Note that our flow dilational rheometry method is the development of continuous-flow tensiometry, which was proposed by Svitova *et al.*,[11] differing from this method by the possibility of measuring the kinetics of interfacial complex formation reactions by the dilational rheometry of adsorption layers of complexes.

Here, we describe the application of flow dilational rheometry to the study of interpolyelectrolyte complex formation at the air–water interface between oppositely charged cationic polyelectrolyte, chitosan, and anionic polyelectrolyte, chitosan sulfate.

Chitosan ($M_w = 225000$, DA = 5%) and its purification and characterization were described previously.[9] Chitosan sulfate ($M_w = 300000$) was kindly provided by Professor G. A. Vikhoreva (Moscow Textile University, Russia). The solutions of chitosan and chitosan sulfate were prepared in a 0.3 M AcOH solution. The methods of measuring the dynamic surface tension γ and the dilational elasticity storage E' and lost E'' moduli were described previously.[6,8] The characteristic relaxation time τ_0 (or the characteristic frequency $\omega_0 = 2\pi/\tau_0$) of adsorption layers was estimated[12] from the frequency dependence of the E' and E'' moduli measured in the range $\omega = 0.01$–0.1 rad s^{-1}.

Figure 2 represents the evolution of the surface tension γ at the air–water interface and real E' and imaginary $\overline{E}''$ components of the dilational complex elasticity modulus $\overline{E}$ *vs.* ageing time t_f of polyelectrolyte adsorption layers. First, the adsorption layer of chitosan has been formed at the air bubble surface from a chitosan solution having a concentration of 0.26 g dm^{-3}.

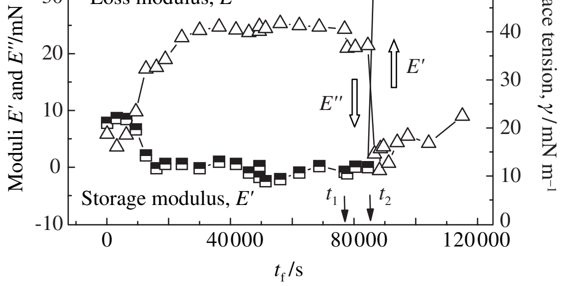

Figure 2 Variation of the surface tension γ, elasticity dilational storage E' and loss E'' moduli of the adsorption layers of polymers in the controlled flow dilational rheology experiment of the interpolyelectrolyte complex formation at the air–water interface between chitosan and chitosan sulfate (for explanation, see the text). $T = 25$ °C; $\omega = 0.63$ rad s^{-1}.

We found that after the ageing time $t_f \sim 20000$ s the loss elasticity modulus achieves its maximum value of $E'' \sim 25$ mN m^{-1}, whereas the storage modulus E' is almost zero. The condition $E'' >> E'$ means that the adsorption layer of chitosan formed from the acidic medium ([AcOH] = 0.3 M) is very fluid without significant association between the macroions at the interface. This corresponds to data[6] according to which electrostatic repulsion between the ionised amino groups of chitosan destroys the network inside the chitosan adsorption layer, which has the tendency to be formed *via* hydrophobic attraction and H-bond formation. The scanning of the elasticity $E'(\omega)$ and $E''(\omega)$ moduli in the frequency range $\omega = 0.02$–0.6 rad s^{-1} confirms this finding (see the curves corresponding to the chitosan adsorption layer recorded at ageing times of 5.0×10^4 and 7.4×10^4 s [Figure 3(*a*)]. The loss modulus E'' is much higher than the storage modulus E', and the corresponding relaxation frequency is located at $\omega_{01} > 1$ rad s^{-1}. The continuous lines correspond to the best fitting of the experimental curves by the functions

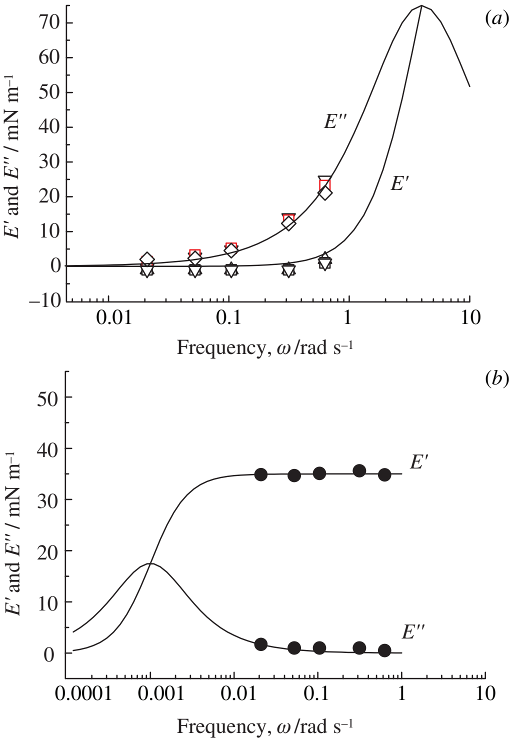

Figure 3 The frequency dependence of dilational storage E' and loss E'' moduli of the adsorption layer of (*a*) chitosan and (*b*) interpolyelectrolyte (chitosan–chitosan sulfate) layers. The adsorption layer formation time t_f was equal to (*a*) 50000 (▽), 74000 (△) and 80000 s (◇) or (*b*) to 137000 s (●). The continuous lines indicate the best fitting of the experimental curves by theoretical functions (1).

$$E'(\omega) = E_0\frac{(\omega/\omega_0)^2}{1 + (\omega/\omega_0)^2} \text{ and } E''(\omega) = E_0\frac{\omega/\omega_0}{1 + (\omega/\omega_0)^2} \qquad (1)$$

corresponding to the Maxwell model,[6,12] where E_0 is the standard (intrinsic) elasticity modulus of the adsorption layer. Note that the adsorption layers of chitosan sulfate manifest a similar liquid-like behaviour: the sulfate groups of this anionic polyelectrolyte are completely ionised at pH ~4.1 in a 0.3 M AcOH solution.

The next step was the replacement of a chitosan solution in the cell by a pure 0.3 M AcOH solution at the time $t_1 = 78000$ s. Suddenly, the surface tension underwent a slight increase and continued to grow during a time of ~8000 s with a slow rate of ~2×10^{-4} mN m^{-1} s^{-1} (Figure 2). This means that the partial desorption of surface-active groups occurred during this time but no remarkable desorption was observed because the values of γ did not remarkably change. Simultaneously, the loss modulus E'' was slightly decreased in this period and the storage modulus E' had a tendency to increase that testifies for some ‘solidification’ of the adsorption layer, which continued to be liquid-like [see the curves corresponding to an ageing time of 8.0×10^4 s, Figure 3(*a*)].

However, a drastic change in the viscoelastic behaviour of the adsorption layer occurred after replacing a 0.3 M AcOH solution by a solution of chitosan sulfate at the time $t_2 = 86000$ s

(Figure 2), although the surface tension γ underwent a negligible decrease and continued to decrease at a rate of ~1×10^{-4} mN m^{-1} s^{-1}. The storage modulus E', which was almost equal to zero, becomes suddenly very high achieving a value of 35 mN m^{-1}, whereas the loss modulus E'' becomes almost zero. This indicates that the adsorption layer became solid-like because $E' >> E''$. The solid-like behaviour of the adsorption layer is confirmed by the frequency dependence of E' and E'' [see the curves corresponding to an ageing time of 1.37×10^5 s, Figure 3(*b*)]: the characteristic relaxation frequency is displaced now in the region $\omega_{02} \sim 10^{-3}$ rad s^{-1}.

This abrupt change in the viscoelastic properties of the adsorption layer of a cationic polyelectrolyte (chitosan), in contact to the solution of an anionic polyelectrolyte (chitosan sulfate), testifies the formation of an elastic solid-like double layer *via* the reaction of interpolyelectrolyte complex formation between the oppositely charged polyelectrolytes at the interface. Note that, unlike the two-dimensional elasticity moduli E' and E'', the surface tension γ is practically insensitive to this drastic change in the rheological state of the adsorption layer.

The variation of both storage E' and loss E'' dilational elasticity moduli of adsorption layers may be considered as a tool to quantify the kinetics of the interpolyelectrolyte complex formation reaction at the interface.

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