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Dilational rheology and relaxation properties of the adsorption layers of electrostatic complexes between Eudragit RS and chitosan sulfate at the methylene chloride–water interface

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The electrostatic interpolyelectrolyte complex formation between the hydrophobic cationic polyelectrolyte Eudragit RS and the anionic hydrophilic polyelectrolyte chitosan sulfate at the methylene chloride–water interface has been studied by dilational rheometry.

Dilational rheology of interfacial polymer layers plays a determinant role in nano- and microtechnologies dealing with polymer solutions: production of nanofibers and nanocapsules by evaporation of volatile organic solvents,[1–3] micro- and nanofluidics, submicron dispersion of liquid jets, *etc*. This role is explained by the prevailing influence of capillary effects on the hydrodynamic flow of thin liquid jets,[4] which is formally expressed by the Weber number $We = v^2/\rho d\gamma$ (v is the velocity, d is the jet diameter, ρ is the density of the liquid and γ is the interfacial tension). On the other hand, the adsorption layers of polymers exhibit viscoelastic properties due to physical gel formation as a result of hydrophobic and electrostatic interactions between active functional groups of polymers[5–7] to make the interfacial tension γ dependent on the deformation rate. Such layers behave as two-dimensional non-Newtonian liquids manifesting dilational rheological properties that complicate the hydrodynamic description of thin jets.

The viscoelastic properties of adsorption polymer layers at a given rate of dilational deformations (deformation frequency f/s^{-1}, or radial frequency $\omega = 2\pi f/\text{rad s}^{-1}$) are unequivocally characterised by the frequency dependent dilational complex elasticity modulus $\bar{E}(\omega) = E'(\omega) + iE''(\omega)$, where $E'(\omega)$ and $E''(\omega)$ are dilation storage and loss moduli, respectively. The measurement of this modulus $\bar{E}$ was described elsewhere.[5,6,8,9] The experimental functions $E'(\omega)$ and $E''(\omega)$ serve to determine the so-called 'crossing' frequency $f_c = \omega_c/2\pi$, *i.e.,* the characteristic relaxation frequency of an adsorption layer relating to the intersection (equality) of frequency dependent elasticity moduli: $E'(\omega_c) = E''(\omega_c)$.[5,6] At $f < f_c$, the polymeric adsorption layer behaves as a liquid-like rheological body ($E' < E''$), whereas this layer is solid-like at $f > f_c$.

Reiner[10] has introduced the dimensionless Deborah number $De = f/f_{rel}$ defined as the ratio of applied deformation frequency (or deformation rate) to characteristic relaxation frequency f_{rel} of the material. The smaller the Deborah number, the more fluid is the material. For polymeric interfacial layers, the Deborah number is[8] $De = f/f_c$. Particularly, the inequality $De < 1$ corresponds to the liquid-like behaviour of the interfacial layer, whereas at $De > 1$ the layer behaves as a two-dimensional solid-like rheological body.

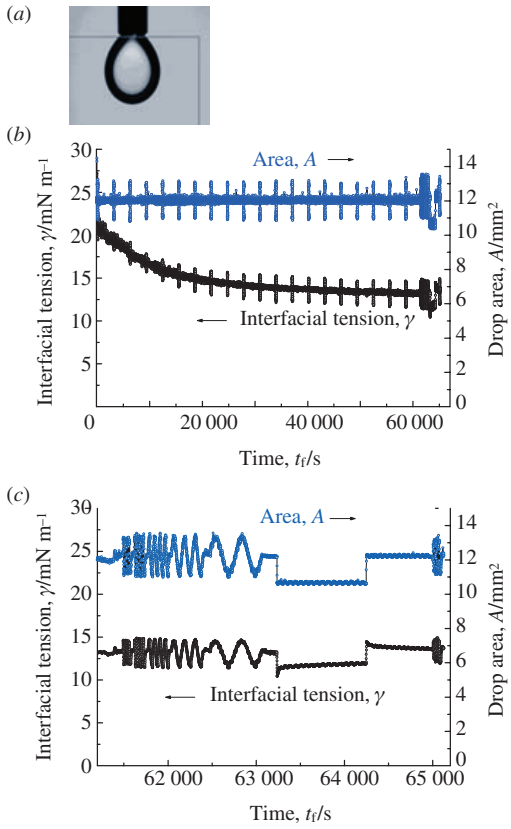

Figure 1 Dilational rheometry applied to the interfacial layers of polymers. The area A of a drop formed from the methylene chloride Eudragit RS solution in water (*a*) is submitted to the periodic dilational sinusoidal deformations with the standard period $T_0 = 10$ s (*b*) and to the frequency scanning with different periods varying from 10 s to ~500 s (*c*).

In this work, we characterised the relaxation properties of adsorption layers of a cationic hydrophobic polyelectrolyte (PE) (Eudragit RS, $Mw = 150000$ Da, Röhm Pharma, Germany) and its interfacial electrostatic complexes with a hydrophilic anionic PE (chitosan sulfate, ChS, $Mw = 300000$ Da) by dilational rheometry.[5,6,8,9]

The two-dimensional complex elasticity modulus $\bar{E}$ of adsorption layers was found from the measurement of interfacial tension variations $\Delta\pi(t) = \gamma_0 - \gamma(t)$ as the response to small dilational deformations $\varepsilon(t) = \Delta A(t)/A$, where γ_0 is the interfacial tension at the methylene chloride–water boundary. The interfacial tension was measured by analysing the axial symmetric shape (Laplacian profile) of a pendent drop of the Eudragit RS methylene chloride solutions in the aqueous solutions of ChS with a drop tensiometer (Tracker, IT Concept, France) [Figure 1(*a*)]. All of the measurements were performed at 20±0.5 °C. In the case of sinusoidal dilational deformations, $\bar{\varepsilon}(t) = \varepsilon_a \exp(i\omega t)$ applied to the drop surface [Figure 1(*b*)] the complex variation $\Delta\bar{\pi}(t)$ of the interfacial pressure was recorded

$$\Delta\bar{\pi}(t) = \Delta\pi_0 \exp[i(\omega t + \varphi)], \quad (1)$$

where ε_a and $\Delta\pi_0$ are the relative deformation and interfacial pressure variation amplitudes, respectively; φ is the phase angle; $\omega = 2\pi/T = 2\pi f$ is the radial frequency; T and f are the period and the linear frequency, respectively. After achieving a quasi-equilibrium interfacial tension γ (when the rate of the relative decrease of γ was lower than 10^{-3}), the procedure of the frequency scanning was used consisting in applying a zug of sinusoidal deformations with the set of frequencies in the range $f \cong 2\times10^{-3}$–0.1 Hz. In the linear deformation region used in this study, the frequency dependent complex dilational elasticity modulus was determined as $\bar{E}(\omega) = \mathrm{d}(\Delta\bar{\pi})/\mathrm{d}\bar{\varepsilon} = E'(\omega) + iE''(\omega)$, where $E'(\omega)$ and $E''(\omega)$ are the dilational storage and loss moduli, respectively. Sometimes, the deformations of a stepwise form were applied to follow the relaxation of interfacial tension during a time of ~10^3 s[11] [Figure 1(c)].

The frequency dependence of dilational storage and loss moduli is described by a model of two relaxation frequencies[6,11]

$$E'(f) = E_{01}\frac{(f/f_{01})^2}{1 + (f/f_{01})^2} + E_{02}\frac{(f/f_{02})^2}{1 + (f/f_{02})^2}; \quad (2)$$

$$E''(f) = E_{01}\frac{f/f_{01}}{1 + (f/f_{01})^2} + E_{02}\frac{f/f_{02}}{1 + (f/f_{02})^2}; \quad (3)$$

where f_{0i} and E_{0i} (i = 1, 2) are the characteristic frequencies and elasticity moduli, respectively, obtained by the fitting of experimental curves $E'(f)$ and $E''(f)$ with the help of equations (2) and (3). Remember that characteristic relaxation times and dilational viscosities of polymeric layers could be obtained from the expressions $\tau_{0i} = 1/f_{0i}$ and $\eta_{0i} = E_{0i}\tau_{0i} = E_{0i}/f_{0i}$, respectively.

Figure 2 shows the dilational storage $E'(f)$ and $E''(f)$ moduli as a function of frequency applied to the adsorption layers of Eudragit RS formed from its methylene chloride solutions at the boundary with (*a*) pure water and (*b*), (*c*) aqueous solutions of chitosan sulfate. Insoluble in water hydrophobic PE Eudragit RS [polymethylmethacrylate with ~2.5 mol% covalently grafted trimethylammonium (TMA) groups] adsorbs practically irreversibly at the methylene chloride–water interface by decreasing the interfacial tension down to 5 mN m^{-1} at C ~ 1%.[12] The adsorption layers of this polymer exhibit strongly pronounced solid-like properties in the whole accessible frequency range $f = 2\times10^{-3}$–0.1 Hz that is proved by the inequality $E' >> E''$ [Figure 2(*a*)].

The estimation of the 'crossing' frequency f_c by the extrapolation of the theoretical curves $E'(f)$ and $E''(f)$ [constructed on the basis of equations (2) and (3)] to low frequencies gives the value of $f_c \sim 8\times10^{-5}$ Hz. This corresponds to the characteristic relaxation time $\tau_c = 1/f_c \sim 10^4$ s for the adsorption layer of Eudragit RS. At the same time, the characteristic relaxation frequencies for two harmonics are estimated as $f_{01} \cong 3.3\times10^{-2}$ Hz and $f_{02} \cong 8\times10^{-5}$ Hz, respectively. The corresponding components $E_{01} \cong 2$ mN m^{-1} and $E_{02} \cong 17$ mN m^{-1} characterise the relative

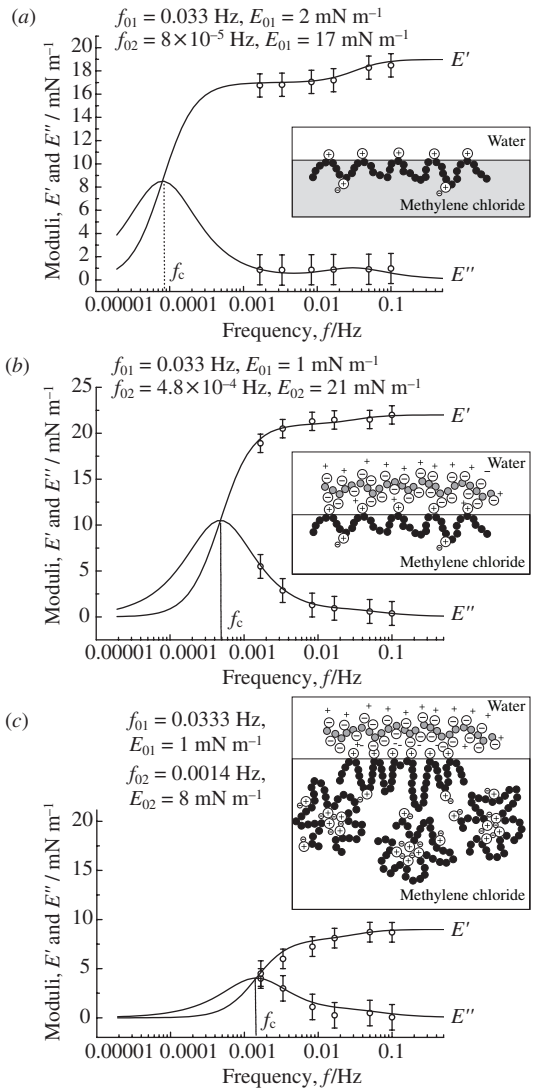

Figure 2 Effect of frequency on the dilational storage $E'(f)$ and loss $E''(f)$ moduli of adsorption layers of polymers formed at the interface between a methylene chloride solution of Eudragit RS (C_{Eud}) and an aqueous solution of chitosan sulfate (C_{ChS}) during $t_f \cong 3\times10^4$ s. (*a*) $C_{Eud} = 4\times10^{-3}$ g dm^{-3} and $C_{ChS} = 0$ (pure water); (*b*) $C_{Eud} = 4\times10^{-3}$ g dm^{-3} and $C_{ChS} = 3\times10^{-2}$ g dm^{-3}; (*c*) $C_{Eud} = 0.1$ g dm^{-3} and $C_{ChS} = 0.1$ g dm^{-3}.

contribution of these harmonics to the whole dilational elasticity modulus. The first high-frequency harmonics with the characteristic relaxation time $\tau_{01} \sim 30$ s corresponds to the liquid-like behaviour of an adsorption layer or to relatively fast diffusion transfer between the interface and the bulk solution of the functional groups with a relatively low adsorption energy [Figure 2(*a*)]. These groups may be the polar carbonyl groups of Eudragit RS, which give a small contribution to the interfacial pressure.[2]

On the other hand, the low-frequency harmonics with the relaxation time $\tau_{02} \sim 10^4$ s may be associated with the adsorption–desorption of ionised hydrophilic TMA groups with a relatively high energy of adsorption. This explains why the probability of desorption of such groups from the surface to the bulk of solution is low, which leads to relatively high relaxation times τ_{02} during the dilational compression of the surface. This property corresponds to the solid-like behaviour of the polymeric adsorption layer. At low bulk concentrations, the Eudragit RS acquires a flat conformation at the interfaces by immersing practically all its TMA groups into an aqueous phase, so the concentration of free (non-adsorbed) TMA groups in the sub-interfacial layer is very low. This explains relatively high relaxation times τ_{02} during dilation cycles of the surface.

The ratio $E_{02}/E_{01} \cong 17/2$ characterises the relative contribution of elasticity and fluidity to the viscoelastic behaviour of an adsorption layer of this polymer in the given frequency range of deformations.

Note that the stepwise deformation tests with the adsorption layers of Eudragit RS [Figure 1(*c*)] lead to the relaxation parameters (the characteristic relaxation frequencies f_{01} and f_{02} and the components of the elasticity moduli E_{01} and E_{02}), which correlate with the oscillatory tests.[11]

Replacing water by an aqueous solution of ChS with the concentration $C_{ChS} = 3\times10^{-2}$ g dm^{-3} [Figure 2(*b*)] leads to a shift of the crossing frequency f_c, as well as of the low-frequency harmonics f_{02}, to the right ($f_c \cong f_{02} \sim 4.8\times10^{-5}$ Hz increased by a factor of ~6 with regard to the previous case). At the same time, the high-frequency harmonics remains at the same level of $f_{01} \cong 3.3\times10^{-2}$ Hz. An increase of the component E_{02} to $\cong 21$ mN m^{-1} should be pointed out, as well as the ratio $E_{02}/E_{01} \cong 21/1$, which is indicative of an increase of the solid-like properties of the layer at $f > f_c$.

Nevertheless, the simultaneous increase of the bulk concentrations of both Eudragit RS and ChS up to 0.1 g dm^{-3} [Figure 2(*c*)] leads to a sharp decrease of the component E_{02} down to 8 mN m^{-1}, and to an increase of the ratio $E_{02}/E_{01} \cong 8/1$, which is reestablished to the corresponding value for pure water [Figure 2(*a*)]. The most spectacular effect is the increase of the 'crossing' frequency f_c and the relaxation frequency f_{02} ($f_c \cong f_{02} \sim 1.4\times10^{-3}$ Hz) by a factor of more than 10 with regard to the case of low PE concentrations. This is indicative of the more intense 'liquefaction' of a polymeric adsorption layer.

A rational explanation of these findings may be given on the basis of the known interfacial behaviour of PEs and surfactant–PE complexes.[5–7] The hydrophilic anionic PE ChS with a high linear density of negative charges is characterised by a very low adsorption activity.[6] This PE can be adsorbed at the interface, which is filled by the positively charged TMA groups belonging to the adsorption layer of Eudragit RS. Previously,[2] it has been shown that, in saturated Eudragit RS adsorption layers, the ionised TMA groups are tightly packed occupying the area $a_{TMA} \cong 1$ nm^2. This corresponds to the surface potential $\Delta\varphi \cong 0.8$–0.9 V. Consequently, the ChS macroions can be attracted by the double layer formed by the adsorption layer of Eudragit RS to form interfacial interpolyelectrolyte complexes.

The increase of the 'crossing' frequency f_c and the frequency f_{02} of 'low-frequency' harmonics upon increasing the bulk concentration of ChS in water may be explained by the decrease of the energy of adsorption of hydrophilic TMA groups as the result of the neutralization of their positive charges by negatively charged sulfate groups. This increases the probability of adsorption–desorption events of these complexes that decreases the characteristic relaxation time and leads to the 'liquefaction' of adsorption layers (to the shift of the relaxation frequencies f_c and f_{02} to the right). We could anticipate that the sulfate groups of ChS are carried away from the water inside the subinterfacial layer of the methylene chloride solution by the bound TMA groups. This seems possible from the energetic point of view while the Bjerrum length in the organic solvent (methylene chloride) with the permittivity $\varepsilon_{MCl} = 9.1$ is of the order of $l_B \cong 2$ nm and the energy of electrostatic attraction between the ions exceeds $10kT$. Thus, with increasing the density of ion pairs forming electrostatic complexes, the probability of adsorption–desorption of these complexes increased during the dilation deformation of the interface, and the characteristic relaxation time also decreased.

As concerned the increase of the component E_{02} of the elasticity module from 17 to 21 mN m^{-1} upon replacing water by an aqueous ChS solution with a relatively low concentration of PEs [Figure 2(*b*)], this effect may be due to the increase of the rigidity of adsorbed electrostatic ChS–Eudragit RS complexes (the rigid chitosan sulfate macroion as having a superior linear charge density with regard to Eudrgagit RS determines the overall rigidity of the complex). However, a substantial increase in the concentration of Eudragit RS in methylene chloride up to 0.1 g dm^{-3} [Figure 2(*c*)] leads to the formation of relatively thick adsorption layers at the interface. This increases the concentration of free TMA groups in the sub-interfacial layer that increases the probability of adsorption–desorption process and, consequently, decreases the E_{02}. The fact of decreasing dilational elasticity modulus with increasing the bulk concentration of polymers or surfactants is well known.[9,13]

In conclusion, note that the dilational rheometry method used in this work to study the viscoelasticity of adsorption layers of the hydrophobic cationic PE Eudragit RS formed from its solutions in methylene chloride at a boundary with water and an aqueous solution of the anionic PE ChS is successfully employed to study the dilational and relaxation properties of surfactant–PE complexes (chitosan–SDS[5]), interpolyelectrolyte complexes (chitosan–ChS[7]), and hydrophobically modified (alkylated) chitosan.[10,14,15] An advantage of this method is the opportunity of studying the relaxation properties of polymeric layers in the frequency range ~10^{-3}–0.1 Hz, where a change from liquid-like to solid-like properties of these layers often occurs. The practical significance of the results consists in the control of the stability of spinning and electrospinning processes in the production of nanofibers from the solutions of hydrophobic polymers in volatile organic solvents by controlling the dilational viscoelastic and relaxation properties of polymeric interfacial layers.[3] Another important application is the production of nanocapsules by emulsification–solvent evaporation.[2,16,17]

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