

Deborah number for the viscoelasticity of adsorption layers of amphiphilic polyelectrolytes

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The fluidity of adsorption layers of amphiphilic polyelectrolytes (chitosan derivatives) is characterised by the Deborah number defined as the ratio of the relaxation frequency of the material and the frequency of the applied deformation.

The Deborah number is a dimensionless parameter introduced by M. Reiner to characterise the rheological properties of materials.^{1,†} Formally, the Deborah number is defined as the ratio of the relaxation time τ_0 , characterizing the intrinsic fluidity of a material, to the characteristic time t of an experiment (or a computer simulation) probing the response of the material:

$$De = \tau_0/t = \omega/\omega_0, \quad (1)$$

where ω_0 and ω are the relaxation and applied frequencies, respectively, defined by $\omega = 2\pi/\tau$. The smaller the Deborah number, the more fluid the material.

Previously,^{2,3} the two-dimensional complex elasticity modulus \bar{E} of adsorption layers was found from the measurement of the surface pressure variations $\pi(t) = \gamma_0 - \gamma(t)$ as the response to sinusoidal dilational variations ΔA of surface area A : $\bar{E}(t) = \varepsilon_a \exp[i\omega t]$, where $\varepsilon = \Delta A/A$ is the relative dilatational deformation of the layer, ε_a is the amplitude of this relative deformation, and γ_0 is the surface tension of the solvent.^{4,5} Representing the variation of the surface pressure as $\bar{\pi}(t) = \pi_a \exp[i\omega t + \varphi]$, where φ is the phase angle, we obtained the frequency dependent complex dilational elasticity modulus: $\bar{E}(\omega) = d\bar{\pi}/d\varepsilon = E'(\omega) + iE''(\omega)$, where the real $E'(\omega)$ and the imaginary $E''(\omega)$ parts could be detected, or that is the same, the general dilational elasticity module $E(\omega) = (E'^2 + E''^2)^{1/2}$ and the effective dilational viscosity $\eta(\omega) = (\omega/2\pi)E''(\omega)/E'(\omega) = (\omega/2\pi) \tan \varphi(\omega)$ may be obtained.

The satisfactory description of the rheological behaviour of adsorption and spread monolayers of polymers in the frequency range 10^{-3} – 10 rad s⁻¹ may be realised by using only several characteristic frequencies to which one attributes a clear physical meaning.² For example, the characteristic relaxation time, $\tau_1 \sim 1$ – 10 s (or $\omega_1 \sim 1$ – 10 rad s⁻¹), is usually attributed to the adsorption–desorption of molecules and segments of macromolecules during dilational perturbations,^{4,6} whereas the second time of the order of $\tau_2 = 10^2$ – 10^3 s and greater (or $\omega_2 \sim 0.01$ – 0.1 rad s⁻¹ and lower) may be attributed to slow reformation of the macromolecules inside the adsorption layer.^{2,3,7} The slow relaxation kinetics is typical of viscoelastic adsorption layers of associative polymers with intense hydrophobic interactions.

When the effective dilational viscosity of adsorption layers of polyelectrolytes η remains constant or varies slowly in a frequency range, one can use a rheological model with only one lowest relaxation frequency (the model of Maxwell) in order to characterise the viscoelastic behaviour of these adsorption layers:²

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

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

where the characteristic relaxation frequency ω_0 and the intrinsic elasticity module E_0 may be obtained experimentally by solving this system of equations. Formally, one can obtain the intrinsic

Table 1 The intrinsic elasticity module E_0 and viscosity η_0 , and the characteristic relaxation frequency ω_0 of adsorption layers of the alkylated chitosan found by fitting the experimental sets of points $E'(\omega)$ and $E''(\omega)$ with the functions (2) and (3).²

$C_p/\text{g dm}^{-3}$	$E_0/\text{mN m}^{-1}$	$\omega_0/\text{rad s}^{-1}$	$\eta_0/\text{N s m}^{-1}$
0.0025	60	0.03	10
0.11	20	0.06	1
0.75	10	0.3	0.2

dilational viscosity η_0 of an adsorption layer from the relationship

$$\eta_0 = E_0 \tau_0, \quad (4)$$

where $\tau_0 = 2\pi/\omega_0$. At $\omega > \omega_0$ where the Deborah number $De > 1$, the adsorption layer behaves as a solid-like two-dimensional rheological body, whereas in the region of $\omega < \omega_0$ ($De < 1$) the adsorption layers manifest fluidity.

The aim of this work was to demonstrate that the dependence of the Deborah number (De), or the lowest characteristic frequency (ω_0) of adsorption layers of polyelectrolytes, on the bulk polyelectrolyte concentration C_p , hydrophobic modification by covalent binding of alkyl groups or by electrostatic complex formation with oppositely charged surfactants, etc., makes it possible to use this parameter to character the effect of these physico-chemical parameters on the viscoelastic properties of adsorption layers of polyelectrolytes.

Chitosan and its hydrophobically modified derivatives with covalently bound dodecyl side chains were the same as described in refs. 2, 3 and 7. The water used for the solutions was of ultrapure grade from a Milli-Q plus system (Millipore, France). The measurements of surface tension were carried out by analysing the axial symmetric shape (Laplacian profile) of a rising bubble in the aqueous solutions of polyelectrolytes with a drop tensiometer (Tracker, IT Concept, France).⁵ The viscoelastic properties of adsorption layers of polyelectrolytes were

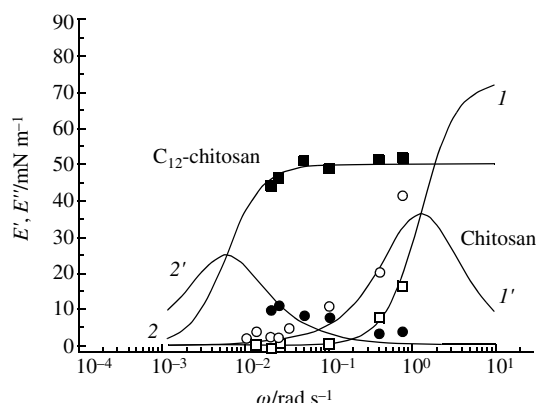


Figure 1 Dependence of the storage E' (squares) and the loss E'' (circles) dilational elasticity modules of adsorption layers of chitosan (open symbols) and C_{12} -chitosan (filled symbols) on the applied frequency ω . The solid lines represent the best fitting of the experimental points by functions (2) and (3). The characteristic relaxation frequency for C_{12} -chitosan $\omega_{02} = 0.006$ rad s⁻¹ is more than 200 times lower than that of chitosan $\omega_{01} = 1.3$ rad s⁻¹.

[†] The origin of the name is the line 'Even the mountains flowed before the Lord' in a song by prothetess Deborah recorded in the Bible. From the song of Deborah after her victory over the Philistines, Judges 5:5 (translated by M. Reiner).¹

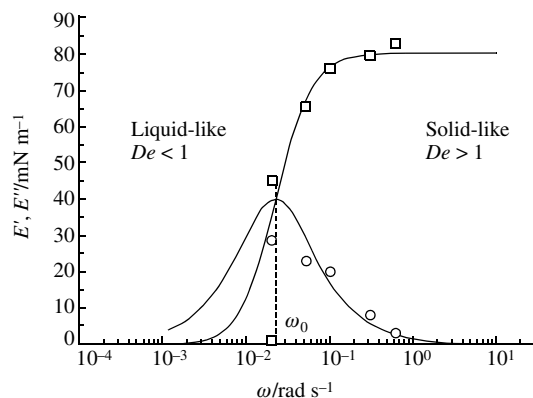


Figure 2 The storage E' (squares) and the loss E'' (circles) dilational elasticity modules of adsorption layers of the surfactant-polyelectrolyte complex (SPEC) formed between SDS and chitosan as a function of the applied frequency ω . The characteristic relaxation frequency ω_0 corresponding to the Deborah number $De = 1$ delineates liquid-like and solid-like rheological behaviours of these adsorption layers.

probed in the frequency range 0.01–1 rad s^{−1} as described previously.^{2,3}

In the adsorption layers of chitosan formed at the surface of an acetate buffer ([AcOH] = 0.3 M; [AcONa] = 0.05 M), the dilational elastic loss module E'' is superior to the storage module E' in the test frequency range (open circles and squares in Figure 1). Fitting the experimental curves $E'(\omega)$ and $E''(\omega)$ by functions (2) and (3) (curves 1 and 1' in Figure 1) leads to the following values: $E_0 = 73$ mN m^{−1} and $\omega_{01} = 1.3$ rad s^{−1}, where E_0 and ω_{01} are the intrinsic elastic module and the characteristic relaxation frequency of chitosan adsorption layers, respectively. The Deborah number is inferior to unity, $De < 1$ in the experimental frequency range, that according to (1) corresponds to the liquid-like behaviour of adsorption layers of chitosan under the considered physicochemical conditions and the frequency range. The alkylated chitosan (C₁₂Ch) containing 5 mol% C₁₂ chains manifests a solid-like behaviour (filled squares and circles in Figure 1) at $De > 1$. The best fitting of experimental points (curves 2 and 2') gives $E_0 = 50$ mN m^{−1} and $\omega_{02} = 0.006$ rad s^{−1} for these adsorption layers. Note that the adsorption layers of a surfactant–polyelectrolyte complex formed between chitosan and SDS with the same quantity of C₁₂ chains in solution as the C₁₂Ch, manifest solid-like properties in the studied frequency range having $E_0 = 78$ mN m^{−1} and $\omega_0 = 0.023$ rad s^{−1} (Figure 2). The dilational viscosity η_0 (N m^{−1} s) of adsorption layers expressed according to relationship (4) is equal to 0.35 or 21 for the adsorption layers of chitosan or alkylated chitosan, respectively, and to 52 for the adsorption layers of SPEC.

The physical meaning and difference between the obtained values of the intrinsic dilational elasticity module E_0 and the relaxation frequency ω_0 (or the intrinsic dilational viscosity η_0) of the adsorption layers of the polyelectrolytes was discussed previously.^{2,8} The obvious 'solidification' of the adsorption layers (the decrease of ω_0) when passing from the cationic polyelectrolyte chitosan to the hydrophobically modified C₁₂-chitosan or to the SDS–chitosan complex (Figures 1 and 2), is due to the considerable hydrophobic interaction between the C₁₂ chains of the polysoap or SPEC. According to Tanford,⁹ the energy of the hydrophobic attraction between these long chains is of the order of ~15 kT, which is much higher than the energy of attraction between the less bulky hydrophobic acetylamine moieties of chitosan interacting with the energy of ~1 kT.

The characteristic relaxation frequency of the polysoap, C₁₂-chitosan, is considerably lower than that of the SDS–chitosan complex (0.006 and 0.023 rad s^{−1}, respectively). By analogy with 3D rheology, one says that the adsorption layer of the SDS–chitosan complex is more 'ductile' with regard to the C₁₂-chitosan in this frequency range. On the other hand, the intrinsic elasticity module E_0 of the C₁₂-chitosan is less than that of the SDS–chitosan complex. The 'ductility' of the complex may be explained by the lability of the electrostatic bonds between the

negatively charged heads of SDS molecules and the positive amino groups of chitosan considering that the energy of the electrostatic attraction between the bulky trimethylammonium ions and sulfate ions is of the order of kT .⁷ In the case of the C₁₂-chitosan, the relatively high energy of the hydrophobic 'bonds' between the C₁₂ chains makes the layer very resistant to the rupture that decreases the dissipative loss of the elastic energy. On the other hand, the weaker electrostatic bonds of the SDS–chitosan complex reversibly destroy under sinusoidal oscillating dilational deformations that lead to the increased dissipative loss of the stored elastic energy and, consequently, to the increased dilational viscosity of the adsorption layers of these complexes ($\eta_0 = 52$ N m^{−1} s) with regard to that of the C₁₂-chitosan ($\eta_0 = 21$ N m^{−1} s).

Note that our 'familiar' understanding of the mechanisms of the 3D-viscoelasticity sometimes fails in the case of the 2D viscoelasticity of adsorption layers of polymers. The specific properties of interfaces such as the Gibbs elasticity and the Marangoni effect complicate the understanding and interpretation of the two-dimensional elasticity storage E' and loss E'' modules of the adsorption layers. For example, the intrinsic parameters E_0 and ω_0 of adsorption layers of alkylated chitosans are very sensitive to the bulk concentration C_p of these polyelectrolytes.² Table 1 shows that, with increasing C_p , the liquid-like properties of adsorption layers become more pronounced (the characteristic frequency ω_0 and the Deborah number De increase). This finding, concerning the decrease of the two-dimensional elasticity module E_0 and the viscosity η_0 of adsorption layers of the alkylated chitosan with increasing bulk concentration C_p , is discussed on the basis of the structural organization and intermolecular lateral interactions inside the adsorption layers of polymers.²

In conclusion, note that the rheological model based on only one characteristic relaxation frequency gives the opportunity to estimate the viscoelastic properties of adsorption layers of polyelectrolytes. The consideration of some main (usually lowest) characteristic frequency, which corresponds to the reformation of polymers inside the adsorption layers during dilational deformation, is useful because this gives a rough characterization of the fluid properties of adsorption layers. In this case, the Deborah number De defined by (1) may be considered as a useful characteristic of the fluidity of these layers submitted to a given dilational strain. Nevertheless, the one-relaxation frequency model does not accurately describe all the rheological features of adsorption layers. When the yield properties of the gel-like structures begin to manifest, the necessity of introducing several characteristic relaxation times becomes obvious in order to describe the elasticity modules, $E'(\omega)$ and $E''(\omega)$ as functions of the applied frequency ω .

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