Kinetics of diffusionally induced gelation and ordered nanostructure formation in surfactant–polyelectrolyte complexes formed at water/water emulsion type interfaces

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A kinetic approach to study the physical gel formation from insoluble surfactant–polyelectrolyte complexes has been developed in connection with the problem of microencapsulation.

Ionic surfactants in mixed aqueous solutions with oppositely charged polyelectrolytes may form insoluble surfactant–polyelectrolyte complexes (SPECs) and self-organise in micelle-like clusters bound to polyelectrolyte chains at a concentration referred to as a critical aggregation concentration (c.a.c.). This c.a.c. is about two orders of magnitude smaller than the critical micelle concentration (c.m.c.) of the surfactants in their individual solutions. The binding of ionic surfactants to oppositely charged polyelectrolytes has been reported as cooperative,[1] whereas the SPECs are believed to be stoichiometric relative to ionic functional groups of polyelectrolyte macroions. At a relatively high surfactant concentration C_s and ratio $\varphi = C_s/C_{PE}$ in a mixed solution, the hydrophobic interactions between surfactant molecules may produce the over-stoichiometric binding of surfactants to the complexes and the inversion of the electric charge of these complexes.[2] The SPECs condense as colloidal or microscopic disperse-phase particles which precipitate in more or less dense sediments depending on the parameters C_s, C_{PE}, φ, electric charge density and rigidity of polyelectrolyte chains, as well as on the mechanical power applied to stir or sonicate the mixed solution.

Small angle X-ray scattering (SAXS) measurements have evidenced an ordered nanostructure in the SPECs sediments, which was attributed to the side-by-side hydrophobic interactions between bound surfactants.[2–5] The more pronounced ordering of clusters and even the formation of regular and crystalline nanostructures with cubic or hexagonal symmetries have been found by SAXS in the complexes of covalently cross-linked polyelectrolyte gels and oppositely charged surfactants.[6–14] The formation of SPECs by mixing two aqueous solutions seems to be improbable. The diffusion of surfactant molecules from the outside solution into the macroscopic samples of these gels makes possible and enhances the formation of these super-regular nanostructures on the macroscopic level. On the other hand, a high cross-linker density of the polyelectrolyte network chains could hinder the formation of a highly ordered structure of surfactant molecules in the complexes.[10] The degree of order in the complexes also decreases with increasing electrolyte concentration in the solution.[14]

The aims of this work were (i) to study the kinetics of the physical gel formation in the production of microcapsules from SPECs by the frontal diffusion of components [oppositely charged cationic polyelectrolyte chitosan and anionic surfactant sodium dodecyl sulfate (SDS)] through water/water emulsion type interfaces and (ii) to estimate the structure-mechanical properties of these physical gels.

The physical gelation of polyelectrolyte solutions by the action of surfactants can find practical applications in the production of pH-, electrolyte- and thermosensitive hydrogel beads and microbeads for medicine, cosmetics, food industry, *etc*.[15] Naturally occurring polyelectrolytes (such as polysaccharides and proteins) and surfactants (fatty acids and phospholipids) may be used for this purpose. Avoiding cross-linking reagents in the formulation reduces the toxicity of carriers made on the basis of these physical gels.

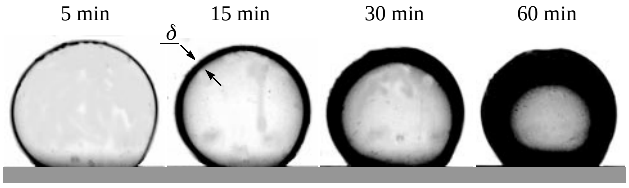

Figure 1 The thickness δ of the gel bead wall visibly grows in time. C_{Ch} = 0.1 base-mol dm^{-3}; C_{SDS} = 0.05 mol dm^{-3}.

Chitosan (Ch), *MW* = 550.000, DA=0.12;[16,17] and the anionic surfactant SDS (Fluka) were used. All solutions were prepared in an acetate buffer with pH 3.6 and ionic strength 0.05 M.

Capsules with a diameter of ~1 mm were formed by the dropwise addition of a chitosan solution to an SDS solution. The capsule membranes were formed *via* the formation of insoluble SPECs as a result of the frontal diffusion of surfactant molecules through the water/water emulsion type interface inside the chitosan solution in the drop.

Optical studies (the measurement of capsule volume, contraction and deformation) were performed using a video camera attached to a microscope and recorded with a video printer (Figure 1).

Plane hydrogel layers with the thickness δ = 10–300 μm and the area A = 71 cm^2 for mechanical measurements in an ambient environment were formed by carefully placing a surfactant solution over the chitosan solution (to avoid mixing). Variable parameters were the concentrations C and volumes V of SDS and chitosan solutions.

Scattering measurements were performed on an AMUR-K small-angle X-ray scattering diffractometer (Institute of Crystallography, Russian Academy of Sciences) with a linear position-sensitive detector and a single-crystal monochromator at the wavelength λ = 1.542 Å. The Kratky-type geometry was used with a sample-to-detector distance of 673 mm and a sample slit width of 0.2 mm to cover the range of momentum transfer $0.012 < q < 0.55$ Å^{-1} (here, $q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle). The windows of the sample holder were made from poly(ethylene terephthalate) with a thickness of 0.01 mm; the sample thickness was about 1 mm. The latter varied along the length of the holder window (10 mm) so that the irradiated volume cannot be estimated and no absolute calibration was possible. The data were normalised to the intensity of the incident beam and corrected for the detector response according to standard procedures.[18]

To analyse the structure of the gel–surfactant complexes, mean long-range order dimensions L in the systems were estimated from the Bragg peaks in the SAXS patterns by the Scherrer formula[19] $L = \lambda/\beta_s\cos\theta$ = 19.2 nm, where β_s = 0.33 nm is the full

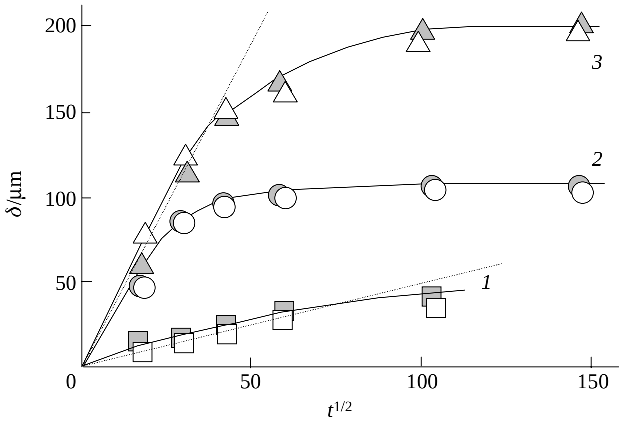

Figure 2 The thickness δ of gel-like layers as a function of time (t) for $C_{SDS} = 0.1$ mol dm^{-3} and $V_{SDS} = 50$ cm^3: (*1*) $C_{Ch} = 0.1$ base-mole dm^{-3}, $V_{Ch} = 10$ cm^3; (*2*) $C_{Ch} = 0.05$ base-mole dm^{-3}, $V_{Ch} = 10$ cm^3; (*3*) $C_{Ch} = 0.05$ base-mole dm^{-3}, $V_{Ch} = 20$ cm^3 (two sets of experimental points illustrate the reproducibility of measurements).

width at a half-maximum intensity of the Bragg peak observed at the mean scattering angle 2θ. From SAXS curves, the radii of interaction $r_m = 0.16\pi^2\lambda/\beta_s = 30.4$ nm and the degrees of disorder in the system $\Delta/\bar{d} = \pi^{-1}(\beta_s\bar{d}/\lambda)^{0.5} = 0.14$ were also calculated (here, $\bar{d} = 2\pi/q_{max}$ is the characteristic size of the ordered elements of the gel–surfactant complex, Δ is the mean-square deviation of distances between the neighbouring molecules).

The elasticity modulus E and the thickness δ of gel-like layers with the thickness 10–300 μm were estimated in the Hertz approximation (a hard sphere of radius 1 mm in contact with an elastic body) using an original device that allowed us to record the force (f)–deformation (Δh) curves with an accuracy of ~1 mN or ~1 μm, respectively.[15] From the f_p–Δh curves, using the Hertz formula $f_p \cong ER^{1/2}\Delta h^{3/2}$,[20] we estimated the elasticity modulus as $E = 10^4$–10^5 Pa.[21]

We found that the kinetics of formation of a gel-like wall in the beginning of the process (the first 30–60 min) is limited by the diffusion of surfactant molecules into the chitosan solution in the drop, and we have $\delta \sim t^{1/2}$ (Figure 2). Later on, the limiting factor is the mass of chitosan (if the surfactant is in an excess).

From the expression for the frontal diffusion of surfactant molecules $\delta \cong (2D_s t)^{1/2}$, we obtained $D_s \cong 10^{-12}$ m^2 s^{-1} for curves *2* and *3* in Figure 2. Obviously, the final thickness δ of the gel-like layer is proportional to the chitosan mass in the solution. A twofold increase in the bulk chitosan concentration (curve *1*) gave $D_s \cong 10^{-13}$ m^2 s^{-1}, which was consistent with a ~10-fold increase in the viscosity of the chitosan solution ($\eta \cong 0.5$ or 7 Pa s for $C_{Ch} = 0.05$ or 0.1 base-mol dm^{-1}, respectively).[21]

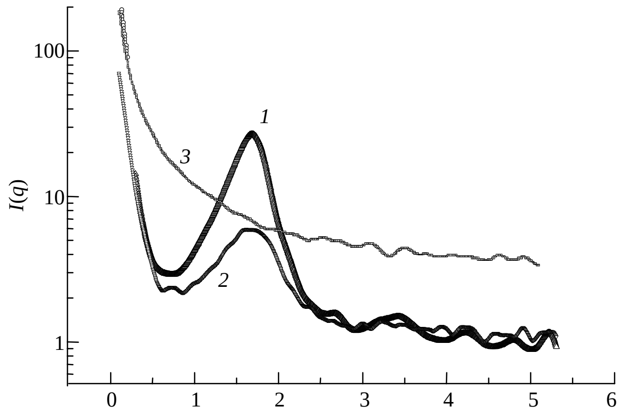

Figure 3 X-ray intensity profiles for chitosan–SDS complexes: (*1*) chitosan gel beads in SDS solutions; (*2*) sedimented chitosan–SDS complex; (*3*) chitosan gel beads in NaOH solutions. $C_{Ch} = 0.1$ base-mol dm^{-3}, $C_{SDS} = 0.1$ mol dm^{-3} (curve *1*) and $C_{SDS} = 10^{-3}$ mol dm^{-3} (curve *2*).

Elemental analysis showed that the ratio $Z = C_{SDS}/C_{Ch}$ [mol/base-mol] in the SPECs is close to unity,[21] *i.e.*, the complexes are stoichiometric in terms of the electric charge of the polycations. From Figure 2, one can estimate the volume fraction of the solid phase in the gel as

$$\varphi = \frac{C_{Ch}M_{Ch}}{DS\rho_{gel}}\frac{V_{Ch}}{V_{gel}}\left(1 + ZDS\frac{M_{SDS}}{M_{Ch}}\right),$$

where $M_{Ch} = 165$ g base-mol^{-1}, $M_{SDS} = 249$ g mol^{-1}, $\rho_{gel} \cong 1.1\times10^3$ kg m^{-3}, $V_{gel} = A\delta$. We found that $\varphi \cong 0.3$, which corresponds to a ~30% solution.

The SAXS measurements (Figure 3) show the existence of an ordered nanostructure in these gels, which is manifested by the appearance of characteristic peaks with the d-spacing at 1.84 and 3.80 nm^{-1} (curves *1* and *2* in Figure 3 and Table 1). The relative positions of the main and secondary peaks are indicative of the formation of fragments with a lamellar structure. The SPEC sediment (curve *3*) also exhibited the formation of an ordered structure; however, the maximum is rather weekly pronounced. Chitosan physical gel beads obtained by dropping the polysaccharide solution into the NaOH solutions without a surfactant (Figure 3, curve *3*) display practically no central scattering (which would indicate the presence of clusters, particles or micelles) and no characteristic peaks (which would appear because of ordering the gel structure). Thus, the formation of an ordered nanostructure is typical of SPEC gels formed by the frontal diffusion of surfactant molecules in the polyelectrolyte solution.

This study demonstrates the possibility to control the preparation of capsules and microcapsules from the physical gel of chitosan–surfactant complexes.

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