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Note

Structural aspects of phase separation in the furcellaran–water system*

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The structure and gel-forming properties of the furcellaran–water system has been investigated by turbidity spectroscopy, viscosimetry, electron microscopy, differential thermal analysis and other methods, and composition *vs.* properties diagram was obtained. Experimental data indicate that gelation in the furcellaran–water system is associated with micro-crystallization of polysaccharide macromolecules and that, under conditions of phase separation, the system itself is a system with incomplete crystallization, according to the Papkov classification. The influence of K^+ and Ca^{2+} cations on the phase separation has been investigated. It was found that potassium ions shifted the phase equilibrium more towards the zone of higher temperatures than did calcium ions.

Furcellaran, a natural anionic polysaccharide, resembles agar, agaroid, and carrageenan in belonging to the class of sulfated galactans contained in red algae. Furcellaran is present in particular in *Furcellaria fastigiata* growing in the Baltic Sea, and is extracted from the seaweed. The unique ability of low concentration aqueous solutions to form gels makes sulfated galactans useful in food production, microbiology, and in other fields. The physical and chemical properties of furcellaran have not been well studied. As yet there is no clear answer as to the type of phase equilibrium involved in the gelling furcellaran–water system. According to the concepts of Rees *et al.*[1] and Smidsrød *et al.*[2], this equilibrium must be classified as of the crystalline type. However, according to Plashina *et al.*[3], the equilibrium in the furcellaran–water system should be considered as a combination of amorphous and crystalline equilibria. Determination of the exact type of equilibrium is a problem not solely of theoretical importance. Practicians must know the system-state diagram to optimize technological processes and generate a product having predetermined properties. To solve this problem it is necessary to perform a range of physical and chemical investigations

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concerning the kinetics of gel network, gel structure, and gel properties. The results of such investigations are presented here.

EXPERIMENTAL

Materials. — The furcellaran used was a commercial product from Nakotno (Latvia); its composition is given in ref. 4. The potassium (K-furcellaran) and calcium (Ca-furcellaran) salts of furcellaran were prepared according to ref. 5. The degree of substitution of SO_3^- groups by the respective cations was 92%. The limiting viscosity of the salt forms of furcellaran was 160 mL/g in 0.1M NaCl solution at 323 K.

Methods. — Turbidity spectra (λ = 400–580 nm) were recorded with a *ΞEK*-56M photocolorimeter. The separation temperature (T_e) was determined from a linear extrapolation plot as $V_0 \rightarrow 0$ of V_0 *vs.* T, were V_0 is the initial velocity of the turbidity rise.

Viscosity measurements were made with a Heppler viscosimeter. T_e was determined from a linear extrapolation plot as $\tau^{-1} \rightarrow 0$ of T^* *vs.*τ^{-1}, where T^* is the lowest temperature at which cooling and heating curves [$\eta = \eta\,(T)$] become indistinguishtable and τ is the time of thermal treatment at a given temperature under conditions of stepped (in 5 K steps) cooling or heating of the system.

The curves for differential thermal analysis of gels were recorded with a modified d.t.a. measuring device at a heating velocity of 1.5 K/min. The value was defined as the temperature at the beginning of deviation of the d.t.a. curve towards the exothermal zone.

Photomicrographs of diluted solutions were obtained with a Tesla-242E electron microscope, according to ref. 6.

A thermal–mechanical study for determination of the glass-transition temperature was performed with the a Kargin dynamometric balance at a constant stress of $8 \cdot 10^4$ N/m^2 and a heating velocity of 1.5 K/min.

The swelling of furcellaran films in saturated water vapour was studied by the balance method. The film thickness was usually 30–50 μm.

RESULTS AND DISCUSSION

Figure 1 shows a composition *vs.* properties diagram of the potassium furcellaran–water system. Curve 1 was obtained by the methods of turbidity spectra, viscosimetry, and differential thermal analysis. All three methods agree well, within experimental error. This curve shows the dependence of the phase separation (T_e) on the polymer fraction (ω_2), namely it is the phase equilibrium curve.

Curve 2 shows the temperature dependence of the equilibrium extent of K-

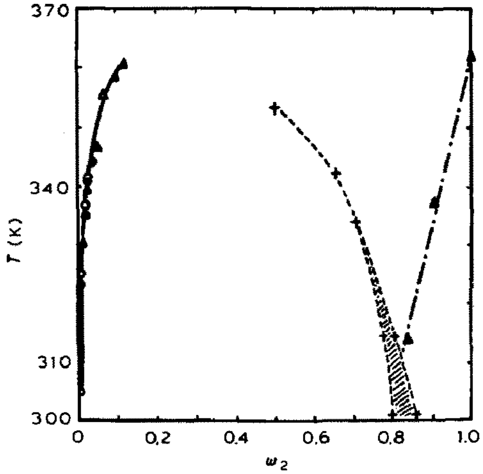

Fig. 1. Composition *vs.* properties diagram of the furcellaran–water system. Curve 1 was obtained by turbidity spectrum method (○), viscosimetry (●), and differential thermal analysis (△).

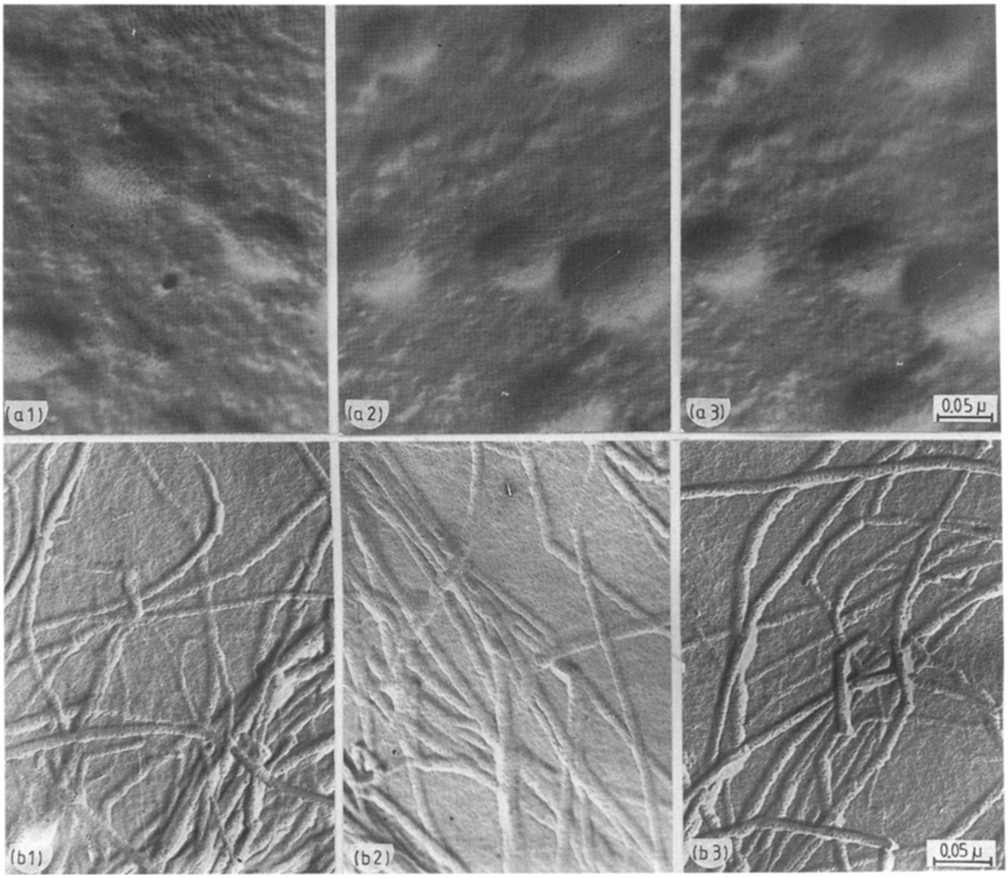

Fig. 2. Photomicrograph investigations of: (*a*) hot and (*b*) cold aqueous solutions, with concentration of K-furcellaran $\omega_2 = 0.001$.

furcellaran film swelling (with ω_2 and T as variables) in saturated water vapour. The cross-hatched region outlines the zone of influence of film formation background on the process of swelling.

Curve 3 was obtained by the thermal deformation method and shows the dependence of the glass-transition temperature on the concentration of the system.

The composition *vs.* properties diagram of the K-furcellaran–water system has a similar shape, but in the concentration range of $\omega_2 < 0.05$ and $\omega_2 > 0.7$, the boundary curves 1–3 lie 10–14 K lower, that is, K^+ ions shift the equilibrium in the furcellaran–water system toward higher temperatures as compared with Ca^{2+}.

Analysis of the system state in the zone above and below the phase equilibrium curve is of especial interest as this zone is significant in practical applications of furcellaran.

Gels are not formed[6] in the solution at polysaccharide concentration of $\omega_2 < 0.003$. Investigations of cold diluted furcellaran solution by electron microscopy show the presence of microgel zones. In addition in the presence of K^+ ions, polysaccharide molecules tend to form elongated fibrils 50–100 Å in diameter crosslinked by Y-shaped nodes (Fig. 2). In the case of Ca-furcellaran solution, these fibrils are not found so frequently, and the microgel network is loose.

Referring now to the system having concentrations of $\omega_2 \geqslant 0.003$, the solution is homogeneous in the zone of states above curve 1. The characteristic feature of the solution is the presence of considerable fluctuation-association processes that are manifested by the turbidity of the system. It should be noted in this connection that the formation of associates having comparably large sized ($F = 0.2\,\mu m$) was found at 348 K in diluted solutions of κ-carrageenan[7]. It is also well known that such associates exist in aqueous solutions of agarose with their lifetimes at temperatures >343K (~0.5 s) rapidly increasing with decrease of temperature[8]. According to data obtained for furcellaran by the turbidity spectrum method[9] the fraction of macromolecules merged into associates at a given period of time is not large, and equals 0.4% of the total mass of the dissolved polymer. As may be seen from Fig. 3, the nature of the cation significantly influences the association of macromolecules: the effective size of associates in K-furcellaran solutions is 1.5–2.0 times as much as that of Ca-furcellaran solutions (Fig. 3a). However N(K-furcellaran) < N(Ca-furcellaran), that is K^+ ions stimulate "deep" penetration of associative processes, whereas Ca^{2+} ions stimulate their "wide" pene-

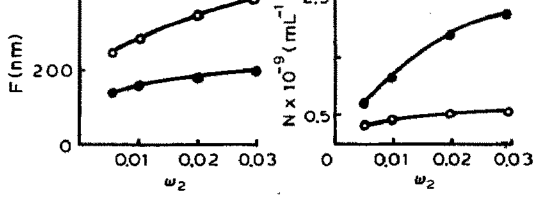

Fig. 3. Concentration dependence of the effective associate radius (*a*) and associate concentration (*b*) in K-furcellaran (*o*) and Ca-furcellaran (●) solutions at 353 K.

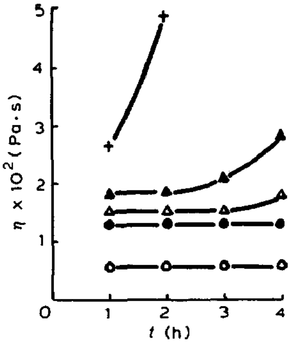

Fig. 4. Viscosity of the K-furcellaran–water system *vs.* time at T = 338K (o), 333K (●), 332K (△), 331K (▲), 330K (+). Polymer concentration $\omega_2 = 0.04$.

tration. The existence of considerable association in furcellaran solutions indicates high statistical correlation between regular segments of macromolecules. It seems that further increase of such correlation with decrease of temperature would lead to microcrystalline ordering.

When the temperature decreases, the system cuts across curve 1 (Fig. 1) and appears in the zone of phase separation where gelation occurs. The gelation kinetics is characterized by the presence of an induction period (Fig. 4) that decreases with decrease in temperature and increase of concentration. Such behaviour of the system is specific for gels whose space network is predetermined by macromolecular microcrystallization.

For systems having amorphous layering, the hysteresis of gel formation and melting temperatures is very small. As a rule, in the furcellaran–water system, it is 10–15 K, and this range can serve as indirect indication of the presence of crystallization processes during gelling[10].

The nature of the cation greatly affects the gelation kinetics. The velocity of gelation of K-furcellaran solution is significantly higher than that for Ca-furcellaran solution. For example a 2% solution of K-furcellaran gelates at room temperature during 1 h, and the gel strength is not significantly changed during several subsequent days. It takes 5–6 h for Ca-furcellaran solution to gelate. The gel strength of K-furcellaran is 6–10 times higher than that of Ca-furcellaran.

The rheological properties of K-furcellaran and Ca-furcellaran solutions in the process of gelation are quite different. In the specific deformation mode that combines mechanical actions upon the system with its relaxation period, a stationary state develops in K-furcellaran that is characterized by an anomalous temperature relation to viscosity. The presence of a zone where the viscosity falls with decrease of temperature is associated with the orientation order developed during the process of deformation of the system fibrillar aggregates. As already mentioned, macromolecules of furcellaran have a tendency for spontaneous formation of these fibrils in the presence of K^+ ions[11].

Data of special interest were obtained by diffractometry of K-furcellaran gels and of films dried from these gels. In the first case, diffractograms show two diffusion maxima in the absence of crystallization peaks. It seems that size and volume of microcrystallites in the gel are so small that they are not visible on diffractograms. In the second case, diffractograms show definite interference peaks of the crystalline phase. The use of powder X-ray photographs and the theory of image identification permitted attribution of the elementary cell to single-wedged syngony and to established[12] the cell sizes: a 18.1; b 22.8; c 12.7Å, and $\gamma = 103°$.

In conclusion, another important fact must be mentioned: gels become paste-like when stored in sealed tubes at room temperature for several months.

The experimental data given here lead to the conclusion that gelation in the furcellaran–water system is associated with microcrystallization of macromolecules of furcellaran, and that in the zone under the phase equilibrium curve, the system itself is a system with incomplete crystallization according to the Papkov classification[13]. The nature of the cations associated with the polysaccharide sulfate groups greatly affects the gelation kinetics and properties of gels. The variation of polymer cation composition is one of the effective means of producing gels having predetermined properties.

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