

## HYDROGEL COMPOSITION BASED ON CARBOXY-METHYLCELLULOSE AND AGAR-AGAR

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*The results are given of a study of the rheological properties of concentrated solutions of CNC and agar-agar and the influence of their quantitative ratio on the anomalous flow behavior of their solutions. A hypothesis is put forward of the formation of intermolecular associates from CMC and agar-agar which leads to the formation of a stronger structural network of solutions of the initial polysaccharides.*

The structure of concentrated solutions is usually modeled by a labile structural network formed from fluctuating associates. The formation of associates in aqueous solutions of the polysaccharides carboxymethylcellulose (CMC) and agar-agar has been established in a number of studies for various ranges of temperatures and shear stresses [1].

The disturbance in the regularity of the structure of a concentrated solution of a polysaccharide (CMC, agar-agar) on passing to compositions based on them leads to a change in intermolecular interaction and in the structures of the solutions that is reflected primarily on the viscosity. The study of the rheological properties of solutions of polysaccharides under various conditions of flow will therefore give valuable information on the structures and compositions of solutions of polysaccharides.

The main method of investigating the rheological properties of systems is to determine the dependence of the rate of deformation on the shear stress,  $\log D = f(\log \tau)$ , and the numerical values of these parameters. Here,  $\tau$  is the shear stress, i.e., the force acting tangentially to the laminarly moving layers, referred to unit area, and  $D$  is the velocity gradient (rate of deformation of the shear, characterizing the change in velocity over unit distance measured at right angles to the direction of flow,  $c^{-1}$ .\* The function, shown graphically, is expressed by a flow curve.

Flow curves for 2% solutions of CMC and their compositions (with a ratio of CMC to agar-agar of 0.5:1.6 wt.-%) at various temperatures are shown in Fig. 1 in logarithmic coordinates. These curves characterize Newtonian flow.

For the systems investigated, Newtonian flow was expressed feebly down to 323 K, since, as is known [1], in water at high temperatures (in the region of 323 K) the molecules of polysaccharides are folded into coils, and the intensity of intermolecular interactions is very low. When the temperature was lowered to 313 K, Newtonian flow appeared clearly because of the unfolding of the polysaccharide macromolecules and the formation of double helices. The intensity of intermolecular interactions of the solutions of the polysaccharides investigated then rose substantially as was shown by the higher effective viscosities and shear stresses.

For the CMC solutions, the nature of the curves remained the same when the temperature was lowered to 298 K. The main reason for the anomaly in the viscosity of concentrated polymer solutions is the progressive breakdown of the structure with a rise in the shear stress. Other factors may also make a contribution to the anomaly of the viscosity of polymer systems, including the deformation and orientation of the polymer chains, and the formation of associates of them along the flow under the action of the applied shear stress. These two phenomena play important roles that differ according to the nature and concentration of the polymer, which determine the possibility of interchain contacts in solution.

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\*As in Russian original – Publisher.

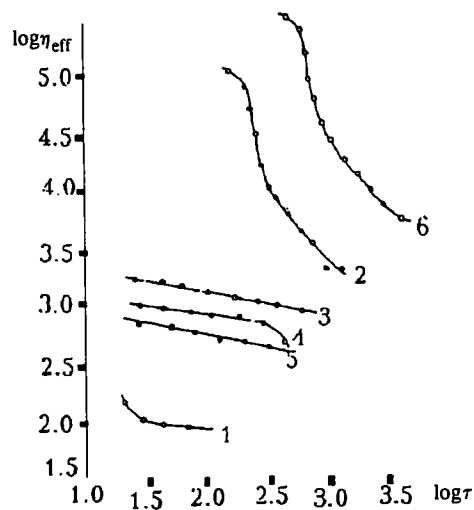


Fig. 1. Flow curves of equiconcentrated solutions of agar-agar at 313 (1) and 303 K (2), of CMC at 303 (3) and 313 K (4), and of the hydrogel composition at 313 (5) and 303 K (6).

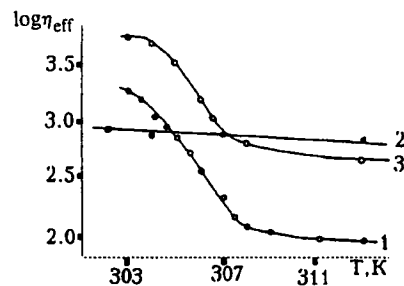


Fig. 2. Dependence of  $\log \eta_{\text{eff}}$  on the temperature for 2% solutions of agar-agar (1), CMC (2), and the hydrogel composition (3).

When the temperature was lowered from 313 to 303 K, a nonlinear increase in the effective viscosity of concentrated solutions of the polysaccharide agar-agar and the agar-agar–CMC composition at the same shear stress,  $\tau = 800$  Pa, was observed, while for CMC there was a smooth linear increase in  $\log \eta_{\text{eff}}$ . At the same time, the composition based on CMC was characterized by higher values of  $\log \eta_{\text{eff}}$  than the additive values (calculated on the basis of the  $\log \eta_{\text{eff}}$  values of equiconcentrated solutions of CMC and agar-agar). This is evidence in favor of the hypothesis of the formation of an intermolecular CMC–agar-agar complex. The maximum rises in  $\eta_{\text{eff}}$  (at  $\tau = 800$  Pa) for solutions of the CMC–agar-agar composition and of agar-agar are found at about 305–306 K and are identical in nature; this also corresponds to the region of the temperature of gelatinization and of the formation of compositions based on these systems.

In solutions of agar-agar and of the CMC–agar-agar composition, with a fall in the temperature from 313 to 303 K the macromolecules combine into associates, and supermolecular structures are formed, a consequence of which is a sharp rise in the effective viscosity of gelatinizing systems subjected to a shear stress of  $\tau = 800$  Pa. The kinetic unit moving in the flow of these polysaccharides is neither the chain nor segments but macromolecular associates the size of which depends on the temperature, the concentration, and the nature of the polymer.

In equiconcentrated solutions of the polysaccharides investigated, apparently, the maximum size of the macromolecular associates was found in solutions of the CMC–agar-agar compositions, followed by the agar-agar macromolecular associates, and the smallest macromolecular associates were characteristic for the CMC solutions. The packing of the macromolecules in the macromolecular associates depended on their chemical structure. In the formation of a macromolecular associate from the

TABLE 1. Activation Energies of Viscous Flow and Degrees of Structuration for 2% Solutions of CMC, Agar-Agar, and the Hydrogel Composition

Solutions investigated	Activation energy, kJ/mole	Degree of structuration
CMC solution	38.30	1.20
Agar-agar solution	311.68	1.97
Solution of the composition	428.60	2.22

\*Calculations were performed at 303°C.

CMC–agar-agar composition, in all probability, the optimum conditions were created for the spatial packing of the macromolecules in supermolecular formations.

An investigation of the temperature dependence of the viscosity of the polysaccharide solutions investigated in the temperature range of 298–323 K also provided evidence in favor of the formation of associates of the CMC–agar-agar composition. Up to some limiting ratio of the components, the temperature dependence of the viscosity of the solutions in the range of temperatures investigated was described by the Arrhenius–Frenkel equation

$$\eta = A \cdot e^{\Delta E/RT},$$

where  $\Delta E$  is the activation energy of viscous flow.

The physical sense of this equation is that the viscous motion of the molecules, segments, or associates of macromolecules is effected by jumps from one equilibrium state to another, and for this it is necessary to overcome a potential rotation barrier the magnitude of which is determined by the activation energy  $\Delta E$ . The apparent activation energy of viscous flow is determined from the slope of the curve plotted in the coordinates  $\log \eta = f(1/T)$ , which follows from the equation

$$\lg \eta = \lg A + \Delta E n / 2.303RT.$$

The apparent activation energies of viscous flow,  $\Delta E n$ , which are a measure of the intensity of intermolecular interaction of the macromolecules in polysaccharide solutions, are as follows: for CMC – 38.3; for agar-agar – 311.68; and for the CMC–agar-agar composition – 428.6 kJ/mole.

The results obtained can apparently be explained on the basis of the hypothesis of the existence in concentrated polymer solutions of two types of structural formations, stronger and weaker, forming a fluctuating network.  $\eta$  and  $\Delta E$  apparently characterize interrelated but, nevertheless, different phenomena.

The heat of activation of viscous flow is determined by the intensity of intermolecular interaction and the strength of the structural formations in the solutions. In view of this, the formation of stronger sections of the structure in a solution of the CMC–agar-agar composition exerts a greater influence on the rise in the activation energy than the formation of a fluctuating network and of "strong" sections in individual solutions of CMC and agar-agar. Thus, a rise in the temperature of the polysaccharide solutions to 313–323 K led to the formation of a more labile structural network of equiconcentrated solutions of agar-agar than of the CMC–agar-agar composition, and the strongest structural network for CMC solutions. With a fall in the temperature below 309 K, the intensity of intermolecular interactions was smaller in solutions of agar-agar and the CMC–agar-agar compositions, which led to smaller values of  $\eta$  for CMC over the whole range of changes in  $\tau$ , lower values of  $\Delta E n$  and of the degree of structuration of equiconcentrated solutions  $n$  (Table 1), to characterize which use was made of the well-known equation

$$D = k\tau^n.$$

It can be seen from the table that the greatest degree of structuration at temperatures below 309 K characterized solutions of the CNC–agar-agar composition and then came agar-agar, while the CMC solutions had the lowest degree of structuration. The appearance of an intermolecular network in concentrated solutions of polysaccharides is considered as the result of the appearance of bonds of the Van-der-Waals type between the individual atom groups of closely adjacent macromolecules, and of hydrogen bonds of the type of  $\text{OH} \cdots \text{OH}$ ,  $-\text{COOH}$ , and  $\text{SO}_4 - \text{PO}_4$  [sic].

These bonds migrate from place to place. With a rise in the temperature the number of migrations decreases, and with a lowering of the temperature the rate of migration diminishes.

Thus, while in some sections the molecules of agar-agar and CMC have similar geometric structures, at points of contact they may form stronger bonds than in homopolysaccharides, and this explains the formation of nonthixotropic compositions at temperatures below 309 K.

## EXPERIMENTAL

To prepare the hydrogel composition, we took 0.8-2.6 wt-% of agar-agar solution and 1.2-3.2 wt-% of carboxymethylcellulose (CMC) and mixed them at 353-373 K. Then the mixture was cooled to 293-298 K and was milled to give a soft gel of homogeneous consistency.

Solutions (2 wt.-% in water) of CMC and agar-agar were prepared at 353-373 K.

The rheological properties of the solutions of the hydrogel composition, CMC, and agar-agar so obtained were investigated by a standard method [2] with the aid of a Rheotest rotational viscometer in a range of working temperatures of 293-473 K and at shear stresses of up to  $\tau = 3 \cdot 10^3 \text{ N/m}^2$ .

## REFERENCES

1. N. M. Bikales and L. Segal, Cellulose and Its Derivatives, Wiley-Interscience, New York (1971).
2. State Pharmacopeia, XIth ed., No. 1 [in Russian], Meditsina, Moscow (1987).