AFFECTING OF HIGH-SPEED SHIFT ON RHEOLOGICAL BEHAVIOR OF AQUEOUS SOLUTIONS OF MIXES SODIUM CARBOXYMETHYLCELLULOSE AND HYDROXYETYLCELLULOSE

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Properties of diluted and moderate-concentrated aqueous solutions NaCMC and their mixes have been studied by viscosimetry and rheology methods. Last years the attention of researchers has been involved in the self-associated polymeric systems on the basis of natural polysaccharides. Sodium carboxymethylcellulose and hydroxyetylcellulose, widely applied in the capacity of gelling agents, stiffeners, stabilizers and emulsors refer to such polymers. Use of the given cellulose ethers in edible, textile, oil and other industries is in many respects defined by their ability to biodecomposition [1-3]. The mechanochemical activation refers to one of the effective control modes of processes of gelation in solutions of such polysaccharides in the conditions of an act of high-speed shift. However mechanochemical processes in solutions of polymers are not enough studied. It is caused by the fact that at mechanical affecting on solutions of polymers in activators of rotorno-pulsing type is a whole complex of the phenomena, such as a mechanical cracking, a mechanodestruction, phase and conformational transformations of macromolecules, which are rather difficult to divide [4,5]. In the present message agency of machining on structural and rheological behavior of aqueous solutions sodium carboxymethylcellulose, hydroxyetylcellulose and their mixes is observed.

Keywords: self-associated polymeric systems, rheological behavior, viscosity, aqueous solutions.

EXPERIMENTAL PART

In the capacity of subjects of inquiry samples sodium carboxymethylcellulose (NaCMC) and hydroxyetylcellulose (HOEC) with molecular weights 120000 and 350000, have accordingly been used.

The diluted and moderate-concentrated solutions of polymer blends prepared by mixture of equiconcentrated solutions of initial components in distilled water. Viscosity characteristics of dilute solutions with concentration of 0.1 % have been measured on an Ubbelohde viscosimeter at 293 K.

Viscosity of the moderate-concentrated solutions of polymers and their mixes were measured on the rotational viscosimeter «Rheotest 2.1» with the working knot “cylinder-cylinder” over the range of shearing rates from 0.05 to 437.4 c⁻¹ in the temperature intervals 293-318 K.

Parameters of structural heterogeneity of investigated multicomponent systems at 293 K were sized up be the method of the turbidity spectrum on the SF-10 spectrophotometer in the interval of lengths of waves λ =240-450 nanometer with the step of 20 nanometers, using a technique presented in work [6].

Solutions of individual polysaccharides and their mixes were processed in the apparatus of the rotorno-pulsing type within 30 seconds, shearing rate varied in the range of 1831.4 c⁻¹ to 18317.3 c⁻¹, that matched the rotor twirl speed of the activator 200 - 2000 rpm. Before the viscosity measurement, mechanically activated solutions were stood for 4 hours at ambient temperature for deaeration.

The viscometric method [7] is often used for estimation of character of interacting of two polymers in the general dissolvent. This method displays deviations of experimental magnitudes of viscosity of solutions of polymer blends from ideal values which pay off as average weight values of viscosity of two pure components of equal concentrations in the absence of interacting in solutions of mixes. Magnitude of these deviations can be observed as a measure of intermolecular interaction of polymers [8, 9]. In the present work reduced viscosity η_{рд}/C pure components and their mixes of various compositions were defined for registration of intermolecular interaction NaCMC and HOEC in aqueous solutions by the formula:
\[ \frac{\eta}{C} = \left( \frac{\eta}{C} \right)_1 \frac{C_1}{C} + \left( \frac{\eta}{C} \right)_2 \frac{C_2}{C}, \]

Where by index 1 - NaCMC, by index 2 - HOEC; C - the general concentration of polymers blend, \( C_1 \) and \( C_2 \) - concentration of components 1 and 2 accordingly, \( C = C_1 + C_2 \); \( \left( \frac{\eta}{C} \right)_1 \) and \( \left( \frac{\eta}{C} \right)_2 \) reduced viscosity of components 1 and 2 accordingly at concentration \( C = C_1 + C_2 \).

**RESULTS AND THEIR DISCUSSION**

In fig. 1 experimental dependences of reduced viscosity on the mixture ratio NaCMC and HOEC are presented.

For the studied polymers blend the positive deviation of experimental values of reduced viscosity from designed quantities in the whole area of compositions is observed; testifies to interacting of macromolecules of diverse polymers in dilute solutions.

![Graph showing dependence of reduced viscosity on mixture ratio of NaCMC and HOEC](image)

**Fig. 1** Dependence of reduced viscosity \( \frac{\eta}{C} \) mixes diluted with (0,1%) aqueous solutions NaCMC and HOEC on a relationship of components

Besides, the positive deviation can also be connected with formation of the intermolecular structures, whose hydrodynamic volume is larger than hydrodynamic volume of pure components. It was expedient to study intermolecular interactions of NaCMC and HOEC in moderate concentrated solutions. For this purpose 3 % wt. solutions of initial components and their mixes were investigated. Graphs of viscosity of shear stress of the investigated solutions represented incomplete curve currents of non-newtonian liquids. It is necessary to note, that both in solutions of initial polymers, and in solutions of their mixes the curve currents gained in the regimes of raise and reduction of shear stresses, have practically coincided within an error of rheological measurement of viscosity (a bias of 2 %).

On the basis of temperature dependences of viscosity of solutions magnitudes of activation energy of a viscous flow which reflect the strength of the structure of solutions [10] have been counted.

In fig. 2 dependences of the logarithm of the greatest newtonian viscosity \( \lg \eta_{max} \) and a viscous flow activation energy \( (E_a) \) on the mixture ratio of NaCMC and HOEC are presented.
Fig. 2. Dependences of the logarithm of the greatest newton viscosity (A) and a viscous flow activation energy (B) of aqueous solutions of mixes HOEC - NaCMC on their composition at a temperature of 298 K and \( \log \tau = 1.2 \)

Positive deviations \( \eta_{\text{max}} \) and \( E_a \) from the additive values (fig. 2) are characteristic of compatible polymers and can be connected with both formation of new systems of hydrogen bridges, and change of the thermodynamic quality of dissolvent in relation to NaCMC. Dissolvent deterioration is accompanied, as a rule, by increase in viscosity of solutions and their structuring.


In fig. 3 dependences of viscosity of 3 % wt. of solutions of NaCMC and HOEC on the speed of twirl of a rotor-activator at a temperature of 293 K are presented.
For aqueous solutions of polysaccharides nonmonotonic decrease in viscosity with increase of the rotor twirl speed of the activator (W) is observed. Fall of viscosity with increase in the rotor twirl speed of the activator (W) for solutions HOEC is connected with interacting infringement between polymer macromolecules in a solution, which results in a change of their conformation, and also with mechanodestruction [12]. Thus mechanodestruction process is accompanied by a minor alteration of the molecular weight of the polymer (~ 10-15%).

As well as in the case of the initial polymers, dependence of viscosity on the rotor twirl speed of the activator for mixes of cellulose ethers changes nonmonotonously. The positive deviation of viscosity and the activation energy of the viscous flow from the additive magnitudes are observed. And the values of viscosity and the activation energy of a viscous flow of mechanically processed solutions of mixes of polysaccharides are higher than those of the initial polymers.

In fig. 4 dependences of viscosity on the rotor twirl speed of the activator on viscosity of 3 % wt. solutions of polymers blends at a relationship of the components NaCMC: HOEC =50:50 % wt. are presented. It is revealed, that not only the intensity of mechanical affecting is greatly influenced on the value of viscosity of the investigated solutions, but also the design features of the rotor. At decrease of frequency of actions on solutions of polymers a substantial increase of compound viscosity of NaCMC is observed: HOEC at a relationship of the components of 50:50 % of weights. The given phenomenon, according to the authors, is connected with deployment of macromolecular balls in a mechanical field and orientation of chains in the flow direction that results in number of contacts increase between macromolecules [12].

Presence of a stronger grid of hydrogen bridges in mechanically activated solutions of polymers proved to be true values of parameters of heterogeneity (tab.). The table of the value of sizes of the permolecular corpuscles for 3 % wt. of a solution of polymer blends HOEC- NaCMC with a relationship of components 50:50 depending on the rotor twirl speed of the activator.

<table>
<thead>
<tr>
<th>Twirl speed of the rotor-activator (\omega), rpm</th>
<th>(r \cdot 10^8), m</th>
<th>(N, \text{in} \ 1\text{ m}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58</td>
<td>(6.2 \times 10^8)</td>
</tr>
<tr>
<td>200</td>
<td>62</td>
<td>(4.9 \times 10^9)</td>
</tr>
<tr>
<td>500</td>
<td>68</td>
<td>(4.6 \times 10^9)</td>
</tr>
<tr>
<td>1000</td>
<td>65</td>
<td>(4.7 \times 10^9)</td>
</tr>
<tr>
<td>2000</td>
<td>65</td>
<td>(4.7 \times 10^9)</td>
</tr>
</tbody>
</table>
Fig. 4. Influence of the rotor twirl speed of the activator on viscosity of 3 % wt. of an aqueous solution of the mix of HOEC, NaCMC at a relationship of the components (50:50): 1 - 2 blade and 2 - 8 blade rabbles at 293 K.

It follows from the table that with the increase of the rotor twirl speed of the activator to 500 rpm the size of associative formations increases, and their quantity in the unit volume decreases [13]. Deployment and orientation of macromolecules in the conditions of high-speed shift possibly results in an increase of extent of their association. The carried out researches have shown the following:

1. Short-term mechanical actions on aqueous solutions of cellulose ethers and also their mix promote reorganization of the structural organization of solutions and do not result in a significant molecular-chain scission of polymers;

2. Machining of the studied mixes of polysaccharides under the conditions of high-speed shift allows to gain composites with adjustable rheological behavior.

References: