RHEOLOGICAL PROPERTIES OF THE MIXTURES OF SEMIDILUTED AND CONCENTRATED SOLUTIONS OF POLYVINYL ALCOHOL AND CARBOXYMETHYL CELLULOSE

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A study has been made of the rheological properties of semidiluted and concentrated aqueous solutions of polyvinyl alcohol and carboxymethyl cellulose and their mixtures with different ratios of the components at temperatures of 0 to 80°C.

One promising way of producing new polymer materials with optimum physicochemical, mechanical, and other service properties is mixing of polymers with each other [1, 2]. The interactions of the solutions of polymers of different compositions, chemical properties, and molecular weight provide vast possibilities for producing polymer materials with new properties.

Investigation of polymer–polymer interactions is of both scientific and practical importance. The products of these reactions, i.e., intermolecular complexes (one can consider them as new individual compounds), possess unique properties which are significantly different from the properties of the initial components. However, realization of these possibilities necessitates data on the mechanism of interaction of polymeric solutions; rheological methods, as the most sensitive to a change in the size and shape of macromolecules in formation of a polycomplex, represent an acceptable and indicative means of realizing these possibilities [3].

Among the different types of polymer–polymer interaction, of special interest is the formation of interpolymer complexes (IPCs) due to the formation of hydrogen bonds between variously composed macromolecules. There are a number of hydrogen-bond-stabilized IPCs based on water-soluble ethers of cellulose and polycarboxylic acids [4], polyvinyl alcohol and polymethyl methacrylic acid or polyacrylic acid [5, 6], and citric pectin with polyvinyl alcohol or polyvinyl pyrrolidone [7].

The field of application of water-soluble polymers and IPCs based on them is being continuously extended. In this connection, it is of undeniable interest to study intermolecular interactions on a wider set of natural and synthetic macromolecules and to produce new types of IPCs.

In the present work, we have investigated the rheological properties of interaction of polymers of different nature: of a rigid-chain sodium salt of carboxymethyl cellulose and a flexible-chain nonionic polyvinyl alcohol due to the intermolecular interaction, which is the determining factor of the process of structure formation. Of certain practical interest is modification (not related to chemical synthesis) of the properties of carboxymethyl cellulose and polyvinyl alcohol, since they are rather widely used in various fields (thickeners, plasticizers, glues).

The employment of capillary rotational viscosimetry and of a low-frequency vibrational method enabled us to evaluate, in the first approximation, the change in macromolecular associates.

Experimental. In the work, we employed commercial samples of polyvinyl alcohol and carboxymethyl cellulose and measured the kinematic viscosity of the aqueous polymeric solutions at 20°C using a Ubbelohde capillary viscometer. The molecular mass of the samples was calculated from the value of the characteristic viscosity of the solutions according to the Mark–Kuhn–Houwink equations. It was $3.62 \cdot 10^6$ for carboxymethyl cellulose with $[\eta] = 0.233 \cdot 10^{-3} M^{1.28}$ in a 2% NaCl at 20°C; for polyvinyl alcohol at $[\eta] = 8.86 \cdot 10^{-4} M^{0.72}$ and 20°C the molecular mass was equal to $2 \cdot 10^5$ [8]. Distilled water was used as the solvent. The discharge time of the solvent was 137 sec.

TABLE 1. Dynamic Viscosity (Pa·sec) and Shear Stress (Pa) of the Aqueous Solutions of Polyvinyl Alcohol and Carboxymethyl Cellulose

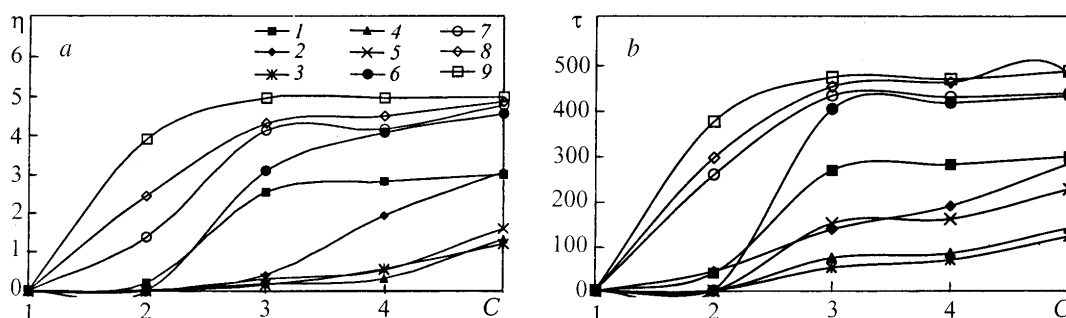| C, %	Polyvinyl alcohol		Carboxymethyl cellulose	
	τ	η	τ	η
1	0.652	0.004	3.7	0.029
2	0.815	0.006	18.3	0.156
3	1.46	0.011	80.8	0.661
4	4.7	0.037	173.2	1.411
5	6.84	0.051	334.9	2.800
6	12.7	0.100	–	–
7	13.5	0.106	–	–
8	13.8	0.112	–	–

Fig. 1. Dynamic viscosity η (a) and shear stress τ (b) of the gels vs. concentration C for the volume ratio of polyvinyl alcohol and carboxymethyl cellulose: 1) 1:1, 2) 2:1, 3) 3:1, 4) 4:1, 5) 5:1, 6) 1:2, 7) 1:3, 8) 1:4, and 9) 1:5. η, Pa·sec; τ, Pa; C, %.

The dependence of the dynamic viscosity and the shear stress of the aqueous solutions of the polymers and their mixtures on the rate of shear was determined on a Rheotest-2 rotational viscosimeter (Germany) with a cylinder–cylinder working unit in the range of rates of shear of 10^{-1}–10^{-3} sec^{-1}.

Results and Their Discussion. A detailed viscosimetric study of the polymeric solutions has been made. The values of the dynamic viscosity of the solutions are given in Table 1. According to the character of the flow curves of the dynamic viscosity and the shear stress as functions of the rate of shear for the aqueous solutions of polyvinyl alcohol and carboxymethyl cellulose, all the solutions possess non-Newtonian flow, except for the solutions of carboxymethyl cellulose with a concentration of 1–3%. The carboxymethyl-cellulose solutions whose viscosity anomalies on the flow curves are more pronounced than in the polyvinyl-alcohol solutions are characterized by the highest viscosity. We have determined the critical concentrations of the crossovers of the two polymers; they were equal to 2% for carboxymethyl cellulose and to 7% for polyvinyl alcohol.

Mixing of the aqueous solutions of polymers leads to the formation of a gel-like composition and the liquid phase of unreacted polymers depending on the concentration and volume ratios of the polymeric solutions.

For the mixtures of polymers with different ratios of the components and with variation of the total concentration we have obtained flow curves of the shear stress and the dynamic viscosity as functions of the concentration (Fig. 1), which show a monotonic growth in the viscosity and the shear stress. The increase in the total concentration and the attainment of the critical concentration of the crossover of at least one polymer leads to substantial changes in the properties of the mixture. Thus, the interaction of 2% aqueous polymeric solutions resulted in an insoluble residue and the liquid phase. The interaction of the aqueous polymeric solutions is the most complete when both polymers attain the concentration of the crossover.

The solvability loss by the mixture of semidiluted or concentrated polymeric solutions can be caused by the deteriorated solvability of the complex formed (since the groups responsible for the dissolution of polymers participate in the formation of an IPC).
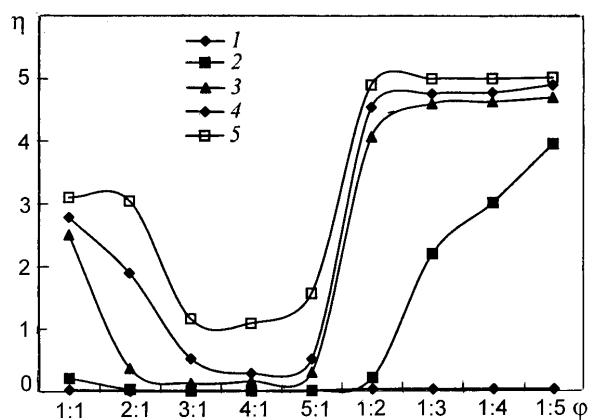
Fig. 2. Dynamic viscosity η of the gels vs. volume ratios φ of the solutions of polyvinyl-alcohol and carboxymethyl-cellulose polymers: 1) $C = 1$, 2) 2, 3) 3, 4) 4, and 5) 5%. η, Pa·sec.
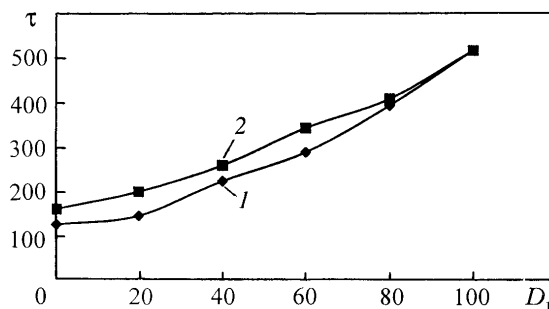
Fig. 3. Shear stress τ of the gels vs. rate of shear D_r with an initial concentration of the polymeric solutions of 5%: 1) loading; 2) unloading. τ, Pa; D_r, sec^{-1}.
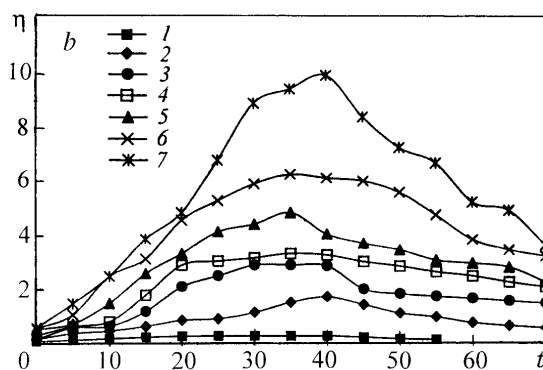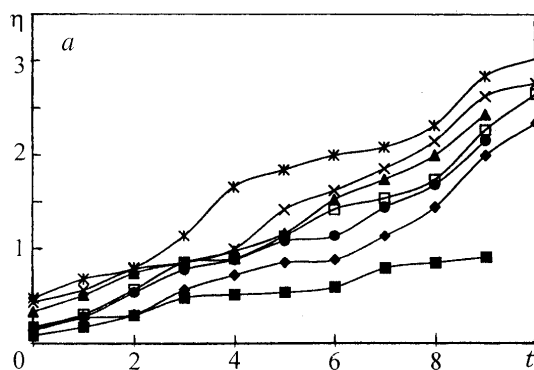

Fig. 4. Dynamic viscosity η of the gels vs. time t for the volume ratio of polyvinyl alcohol and carboxymethyl cellulose 1:1 at 0°C (a) and at 40°C (b): 1) $C = 1$, 2) 2, 3) 3, 4) 4, 5) 5, 6) 6, and 7) 7. η, Pa·sec; t, days.

At the initial stage of the reaction in diluted polymeric solutions, the gelating system represents isolated coiled macromolecules. As the reaction becomes deeper, the coiled macromolecules are accumulated and they penetrate into each other; their associates occur. The system becomes structurally viscous; next, filling of the medium with coils occurs, which leads to the equalization of the concentration of the polymer and the structure throughout the volume.

Interesting results have been obtained in mixing the polymeric solutions in different volume ratios of carboxymethyl cellulose and polyvinyl alcohol at $T = 20°C$. In Fig. 2, it is seen that with increase in the volume of polyvinyl alcohol we have an insignificant growth in the viscosity of the polymeric mixture, while when carboxymethyl cellulose is in excess the viscosity significantly increases.

Figure 3 shows the hysteresis loop of a rheological curve, which has resulted from the gradual increase and subsequent decrease in the velocity gradient and shows the degree of additional failure of the structure with each subsequent (higher) velocity gradient. The curves of unloading of the gels stay out of the origin of coordinates, which points to the presence of residual deformation that gradually decreases in long storage of the sample.

The viscosity of polymeric solutions and gels is very sensitive to a temperature change. The dynamic viscosity of gels significantly increases as the temperature decreases and the gelation time increases. Figure 4 gives the curves of change of the dynamic viscosity of polymeric mixtures with different total concentrations at 0 and 40°C; as the temperature decreases, the associates of the polymeric mixtures become more viscous and strong. In all probability,
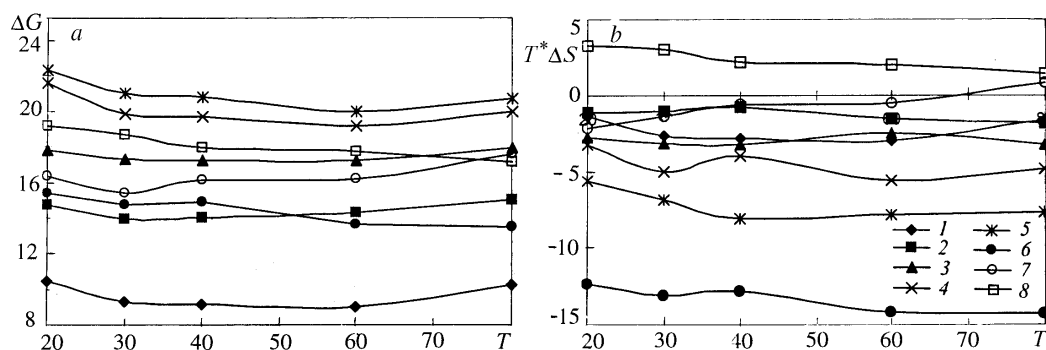
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Fig. 5. Free energy ΔG (a) and entropy of activation of viscous flow $T^{*} \cdot \Delta S$ (calculated from the Gibbs equation) (b) of the gels vs. temperature T: 1) 1% carboxymethyl cellulose + 1% polyvinyl alcohol. 2) 2 + 2, 3) 3 + 3, 4) 4 + 4, 5) 5 + 5, 6) 2 + 6, 7) 3 + 7, and 8) 3 + 8. T, $^{\circ}$C; ΔG and $T^{*}\Delta S$, kJ/mole.

TABLE 2. Heat of Activation of the Solutions and Gels of Carboxymethyl Cellulose and Polyvinyl Alcohol as a Function of the Concentration of Polymers

C, %	ΔH, kJ/mole		
	Polyvinyl alcohol	Carboxymethyl cellulose	Polyvinyl alcohol:Carboxymethyl cellulose = 1:1
1	9.21	9.87	11.95
2	9.61	20.90	16.79
3	10.01	24.90	20.45
4	11.41	27.80	24.80

this is due to the additional structurization of polyvinyl alcohol as a result of cryolitic processes occurring at lower temperatures [9].

The temperature dependences of the viscosity of the solutions and gels investigated in the interval 0–80°C are described by the Frenkel–Eyring relation $\eta = A \exp (\Delta G/RT^{*})$ [10, 11]. From the results of rheological data and their temperature dependences we calculated the thermodynamic parameters of the polymeric solutions and gels, i.e., the Gibbs energy ΔG characterizing the strength of the structures and the enthalpy ΔH and the entropy of activation of viscous flow ΔS that characterize the ordered strength of the structure. Figure 5a shows the dependences of the free energy ΔG on the temperature for polymeric mixtures; they are characterized by positive values (in all probability, the processes of failure of the structure and orientation of macromolecules occur simultaneously in gelation).

The apparent heat of activation of viscous flow ΔH that is the measure of intensity of the intermolecular interaction of macromolecules in polymeric solutions and mixtures is a parameter particularly sensitive to structure formation in the solutions (Table 2). The concentrated aqueous solutions of rigid-chain carboxymethyl cellulose are characterized by higher values of ΔH than the solutions of flexible-chain polyvinyl alcohol and hence the stronger structure. In mixing of the polymeric solutions, the quantity ΔH changes insignificantly in relation to individual polymeric solutions. At lower temperatures (0–10°C), the enthalpy change is much higher, which indicates an ordered and strong structure, unlike the values of ΔH at high temperatures. In all probability, as the temperature increases, the bonds are broken due to the thermal motion and ΔH decreases.

Figure 5b gives the dependences of the entropy of activation of viscous flow on the temperature. The entropy decreases ($\Delta S < 0$) mainly due to the loss in the translational degrees of freedom with increase in the total concentration of the solutions. Exceptional are the polymeric mixtures of 8% polyvinyl alcohol and 3% carboxymethyl cellulose, where the concentration of the solutions exceeds the concentration of the crossover.

In this connection, we can assume that the macromolecular associates of rigid-chain carboxymethyl cellulose and flexible-chain polyvinyl alcohol are rearranged in the solutions of polymeric mixtures, which leads to the formation of structural elements larger in size than in the polymeric solutions. In all probability, this is because the hydrogen bonds between the hydroxyl and carboxyl groups of carboxymethyl cellulose and the hydroxyl groups of polyvinyl alcohol are formed in the polymeric mixture.

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CONCLUSIONS

1. Introduction of flexible-chain polyvinyl alcohol into a more structurized system of the aqueous solutions of rigid-chain Na-carboxymethyl cellulose leads to a significant increase in the dynamic viscosity and the shear stress of a polymeric mixture.

2. Passage from the region of semidiluted solutions to a region of concentrated solutions, increase in the total concentration of the polymers, and decrease in the temperature lead to a decrease in the solvability of the Na-carboxymethyl cellulose–polyvinyl alcohol complex and a monotonic increase in the viscosity with increase in the gelation time.

NOTATION

η, dynamic viscosity, Pa·sec; $[\eta]$, characteristic viscosity; T, temperature, ^{O}C; T^{*}, temperature, K; t, time, sec; D_r, rate of shear, sec^{-1}; τ, shear stress, Pa; C, concentration, %; ΔS, entropy of viscous flow, kJ/(mole·K); ΔG, Gibbs energy, kJ/mole; ΔH, enthalpy of viscous flow, kJ/mole; MM, molecular mass; M, viscosity-average molecular weight; A, preexponential term; R; gas constant, J/(mole·K); φ, volume ratio of the polymers. Subscript: r, rate.

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