Effect of Magnetic Field on Rheological Properties of Cellulose Ether Solutions

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Abstract: Application of a magnetic field is shown to be accompanied by an increase in the viscosity of hydroxyethyl cellulose, ethyl cellulose solutions and sodiumcarboxymethyl cellulose solutions in 2 - 4 times. The concentration dependences of solution viscosity in the presence of a magnetic field are described by curves with maxima.

Keywords: Liquid crystal, phase transition, solution viscosity, cellulose ethers.

INTRODUCTION

In recent years, the rheological study of solutions of rigid chain polymers –biodegradable cellulose ethers – has been continued at the Department of Macromolecular Compounds at the Ural Federal University [1 – 4]. The pioneer investigations of viscosity of rigid chain polymer solutions were described in [5 –7]. The molecules of cellulose and its derivatives occur in rigid helical conformations. Moreover, they are capable of ordering, so that, in concentrated solutions, cholesteric liquid crystals (LC) are formed [8-12]. Owing to additional orientation of such macromolecules induced by a magnetic field, the temperature–concentration region of existence of liquid crystalline phases extends and additional self assembly of macromolecules appears [2, 9, 12-14]. However, little is known about the effect of a magnetic field on the viscosity of polymer solutions [3, 4]. The aim of this study was to investigate the rheological properties and structure of cellulose ethers in the presence and absence of a magnetic field.

MATERIALS AND METHODS

Samples of hydroxyethyl cellulose (HEC) with a degree of substitution of α=2.5 and $M_\eta=6.2\times10^4$ (trademark Natrosol, type HHBR, Aqualon), ethyl cellulose (EC) with α=2.5 and $M_w=1.6\times10^5$ (type N100, Aqualon) and sodiumcarboxymethyl cellulose (trademark Blanose, type 7M, Aqualon) with α=0.7 and $M_\eta=1.2\times10^5$ were studied.

The bidistilled water, DMAA and DMF were used as solvents.

The type of phase transition in a solution was determined on a polarization photoelectric unit [12, 13]. Melting temperatures of gels were determined as follows: ampoules with gels were turned so that gels were located at the top, the system was heated slowly (~1 K/h), and the temperature of flow onset was fixed [1]. The phase states of solutions and gels were studied with an Olympus BX 51 polarization microscope.

The solution viscosity was determined on a Rheotest RN 4.1 modified rheometer with a working unit made from a weakly magnetic material, such as brass. The effect of a magnetic field on the rheological behavior of solutions was studied with the use of two magnets. The first magnet, which induces a magnetic field with an intensity of $H_\perp$=3.7 kOe and field lines directed perpendicularly to the rotational axis of a rotor and the second magnet, with an intensity of $H_{||}$=3.6 kOe and field lines parallel to the axis of rotor rotation. The working unit with the solution was placed in a magnetic field at 298 K and kept for 20 min, and the viscosity in the presence of the magnetic field was measured at an increasing shear rate. The viscosity of liquid η, was determined by the common method [15].

A metallic rotor rotating in a magnetic field can be regarded as a generator closed on itself [16]. During operation of the generator, a braking torque (electromagnetic moment) is induced. As a result, during shear stress measurements for deformed solutions, the measured stress exceeds the true stress by a value related to the electromagnetic moment. To account for the electromagnetic moment, a correction dependence of shear stress on shear rate in the working unit with cylinder surfaces separated by air was determined. The true shear stress for solutions was calculated as the difference between the measured and correction values for the same shear rate. When magnetic field lines are oriented along the rotor rotational axis, the magnetic flux through the vertical cross section of the rotor is zero and the

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electromagnetic moment is likewise zero. The results of calibration experiments showed the absence of electromagnetic retardation when the magnetic field lines are oriented along the rotor rotation axis.

RESULTS

Figures **1** and **2** show the experimental results on phase transitions of studied systems. As can be seen, HEC and EC solutions pass into the LC state at 298 K at a polymer weight fraction of ω_2>0.15. Figure **3** shows the experimental results on phase transitions in the Na-CMC–water system. It is evident that, at 298 K, Na-CMC solutions are isotropic in the composition range 0<ω_2<0.08 and anisotropic in the composition range ω_2>0.08, where ω_2 is the Na-CMC weight fraction in the system. Note that, at room temperature, the concentrations of isotropic phase → anisotropic phase and solution → gel transitions are practically coincident.

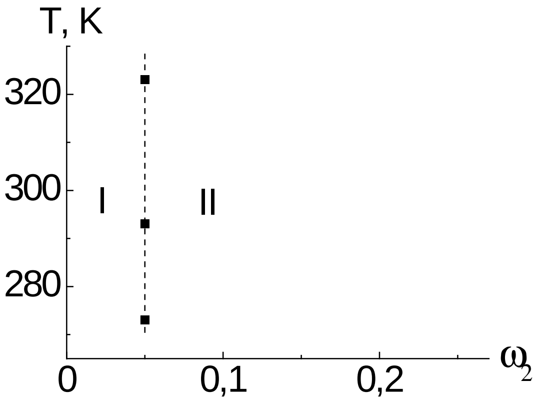


Figure 1: Phase state regions of HEC – DMF system. I and II are the isotropic region and the anisotropic region, respectively.

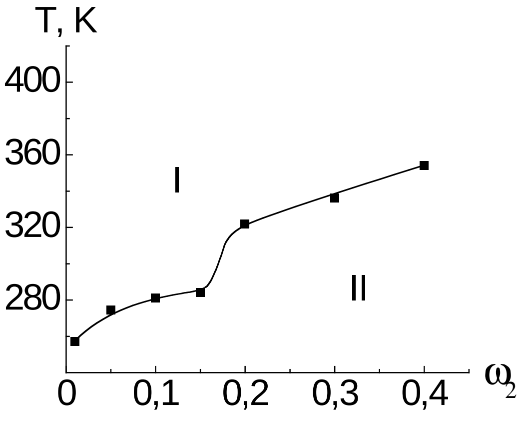


Figure 2: Phase diagram of EC – DMAA system. I and II are the isotropic region and the anisotropic region, respectively.

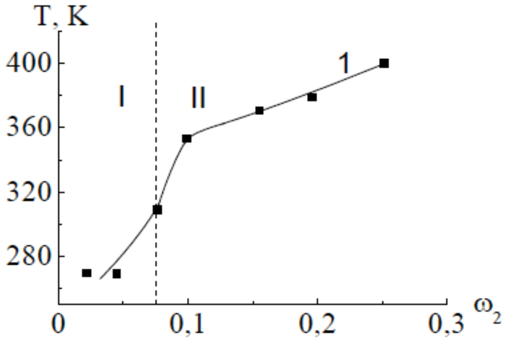


Figure 3: Phase state and gel points for the CMC–water system: I and II are the isotropic region and the anisotropic region, respectively; (1) gelation curve; ω_2 is the weight fraction of CMC in the system. Dash line corresponds to the concentration of the isotropic → anisotropic solution transition.

Figures **4** - **6** demonstrate the data on the rheological behavior of HEC, EC and Na-CMC solutions in the presence and absence of a magnetic field. It is evident that the solutions are non Newtonian fluids. This finding correlates with the literature data available for other LC systems [1-7, 17, 18] and suggests that the initial structure of polymer solutions is broken and that the macromolecules are oriented along the flow direction during deformation.

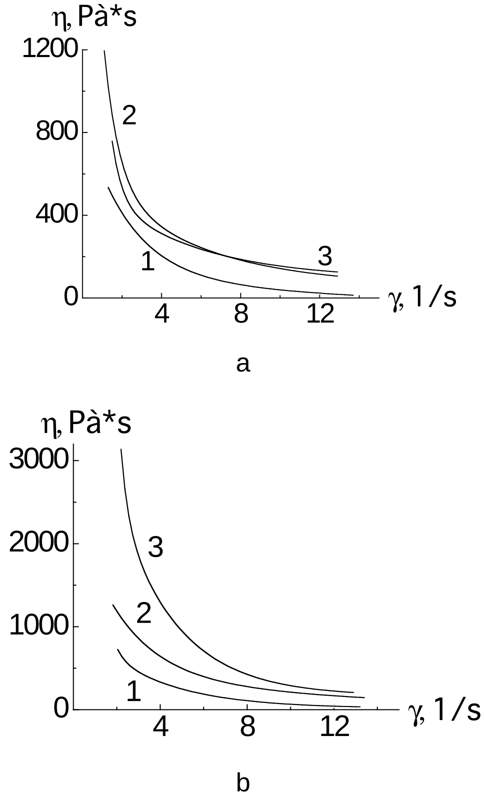


Figure 4: Viscosity vs. shear rate for HEC solutions in DMF: ω_2=0.10 (a) and 0.15 (b) at H=0 (1), $H_{||}$=3.6 (2) and $H_{\perp}$=3.7 kOe (3). T=298 K.

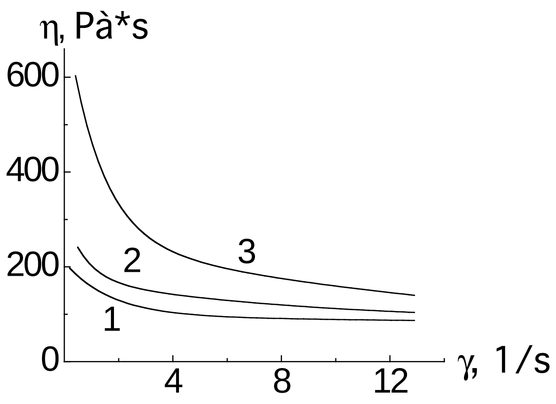


Figure 5: Viscosity vs. shear rate for EC solutions in DMAA: ω_2=0.30 at H=0 (1), $H_{||}$=3.6 (2) and $H_{\perp}$=3.7 kOe (3). T=298 K.

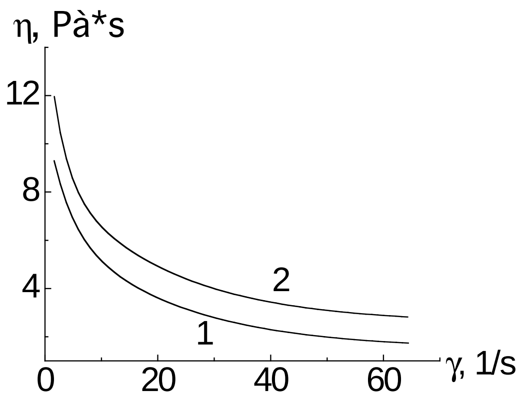
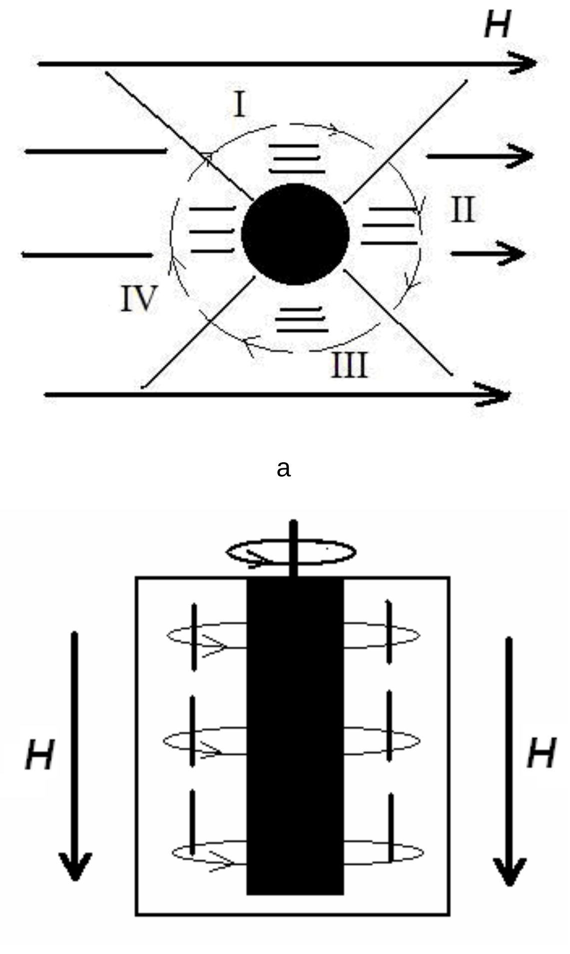


Figure 6: Viscosity of the Na-CMC aqueous solution *vs*. shear rate: (1) in the absence and (2) in the presence of the magnetic field; ω_2=0.04. $H_{\perp}$=3.7 kOe. T=298 K.

The application of a magnetic field leads to an increase in the viscosities of EC solutions in DMAA, HEC solutions in DMF and Na-CMC in water. Similar data were obtained for EC, HEC and Na-CMC solutions of different concentrations. During the analysis of the above dependences, it should be taken into consideration that the magnetic field is responsible for the additional organization of macromolecules. The additional self assembly of macromolecules is related to their ability to undergo orientation in a magnetic field. In the presence of a magnetic field, the long chains of macromolecules are oriented in parallel with field lines [19]. This effect should appear as an increase in viscosity [3, 4].

Processes occurring during the flow of solutions in the presence of a magnetic field may be represented by the following schemes (Figure **7**). When field lines are perpendicular to the rotor rotation axis, the orientation of macromolecules in quadrants I and III coincides with the flow direction and viscosity may drop. In quadrants II and IV, macromolecules are oriented perpendicularly to the flow direction and viscosity must increase. Supposedly, in this case, viscosity may both increase and decrease. When the field lines are parallel to the rotor rotation axis (Figure **7b**), the long axes of macromolecules are oriented along the axis of rotation, that is, perpendicularly to the flow direction. As a result, viscosity may increase. In general, as was shown experimentally, viscosity increases.

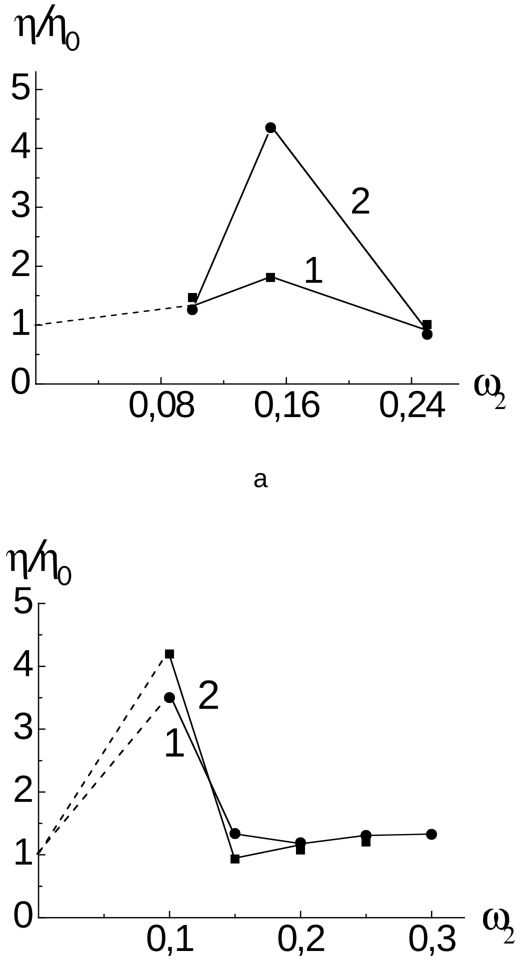


a

b

Figure 7: Scheme of solution flow in the magnetic field with lines of force perpendicular (top view) and parallel (side view) to the rotation axis of the rotor.

The results were used to plot the concentration dependence of η/η_0, where η and η_0 are the viscosities of solutions in the presence and absence of a magnetic field, respectively (Figures **8** and **9**). In this case, the values of viscosity corresponding to low shear rates were chosen because, as was shown in [5–7, 17, 18], the concentration dependence of viscosity at low shear rates is typical for anisotropic systems. In the investigated composition range, the values of η/η_0 are above unity and the concentration dependence of this value is described by a curve with a maximum. In dilute solutions, macromolecules are few and, hence, the field effect is insignificant. The number of macromolecules capable of orientation in the magnetic field increases with the polymer concentration, and the field effect on the system properties becomes stronger. However, at high concentrations, the density of the fluctuation network of entanglements increases, thereby hindering the orientation processes. As was shown experimentally, the maximum increase in viscosity is observed when the magnetic field lines are perpendicular to the rotor rotation axis.



a

b

Figure 8: Concentration dependence of η/η0 for the HEC – DMF (a) and EC – DMAA systems, where η and η0 are the values of system viscosity in the presence and in the absence of the magnetic field, respectively. γ=2.5 s^{-1}. $H_{\parallel}$=3.6 (1) and $H_{\perp}$ = 3.7 kOe (2). T=298 K.

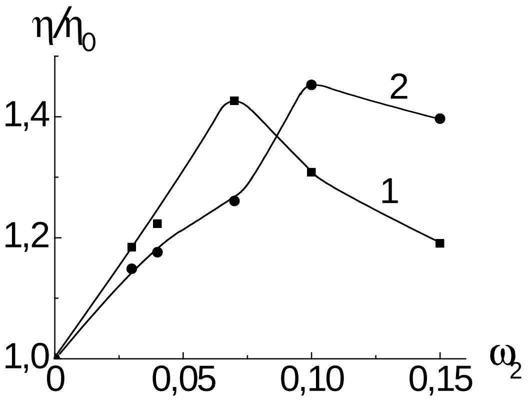


Figure 9: Concentration dependences of η/η0 for the Na-CMC – water system. γ=2.5 s^{-1}. $H_{\parallel}$=3.6 (1) and $H_{\perp}$ =3.7 kOe (2). T=298 K.

ACKNOWLEDGEMENTS

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REFERENCES

[1] Vshivkov SA, Rusinova EV. Liquid crystal phase transitions and rheological properties of cellulose ethers. Russian Journal of Applied Chemistry 2011; 84(10): 1830-1835. http://dx.doi.org/10.1134/S1070427211100260

[2] Vshivkov SA. Phase transitions of polymer systems in external fields. St Petersburg: Lan 2013 [in Russian].

[3] Vshivkov SA, Rusinova EV, Galyas AG. Effect of a magnetic field on the rheological properties of cellulose ether solutions. Polymer Sci 2012; 54(11 Ser A): 827-832.

[4] Vshivkov SA, Byzov AA. Phase equilibrium, structure, and rheological properties of the carboxymethyl cellulose-water system. Polymer Sci 2013; 55(2 Ser A): 102-106.

[5] Yang JT. Non-newtonian viscosity of poly-γ-benzyl-L-glutamate solutions. J Am Chem Soc 1958; 80(8): 1783-1788. http://dx.doi.org/10.1021/ja01541a002

[6] Yang JT. Factors affecting the non-newtonian viscosity of rigid particles. J Am Chem Soc 1959; 81(15): 3902-3907. http://dx.doi.org/10.1021/ja01524a024

[7] Hermans JJr. The viscosity of concentrated solutions of rigid rodlike molecules (poly-γ-benzyl-l-glutamate in m-cresol). J Colloid Sci 1962; 17(7): 638-648. http://dx.doi.org/10.1016/0095-8522(62)90028-4

[8] Kulichikhin VG, Golova LK. Liquid crystal state of cellulose and its derivatives. Khim Drev 1985; (3): 9-27.

[9] Vshivkov SA, Rusinova EV. Effect of magnetic field on phase transitions in solutions of cellulose derivatives. Polymer Sci 2008; 50(7 Ser A): 725-732.

[10] Vshivkov SA, Galyas AG, Kutsenko LI, Tyukova IS, Terziyan TV, Shepetun AV. Self-Organization of Macromolecules and Liquid-Crystalline Phase Transitions in Solutions of Cellulose Esters. Polymer Sci 2011; 53(1 Ser A): 1-5.

[11] Vshivkov SA, Galyas AG. Mechanism of Self-Assembly of Rigid-Chain Macromolecules of Cellulose Ethers in Solutions. Polymer Sci 2011; 53(11 Ser A): 1032-1039.

[12] Vshivkov SA. Effect of magnetic and mechanical fields on phase liquid crystalline transitions in solutions of cellulose derivatives. In: Moreno-Piraján JK, Ed. Thermodynamics. Physical chemistry of aqueous systems. Croatia: In Tech 2011; pp. 407-434.

[13] Vshivkov SA, Rusinova EV, Kudrevatykh NV, Galyas AG, Alekseeva MS, Kuznetsov DK. Phase transitions of hydroxypropylcellulose liquid-crystalline solutions in magnetic field. Polymer Sci 2006; 48(10 Ser A): 1115-1119.

[14] Vshivkov SA, Rusinova EV, Kutsenko LI, Galyas AG. Phase transitions in liquid-crystalline cyanoethyl cellulose solutions in magnetic field. Polymer Sci 2007; 49(7-8 Ser B): 200-202.

[15] Malkin AYa, Isaev AI. Rheology: conceptions, methods, applications. St Petersburg: Professiya 2007 [in Russian].

[16] Kitaev EV, Grevtsev NF. Course of general electric engineering. Moscow: Sovetskaya Nauka 1945 [in Russian].

[17] Kulichikhin VG, Platonov VA, Kogan EG, Mil'kova LP, Andreeva IN, Lukasheva NV, et al. Transitions in anisotropic solutions of poly-p-phenyleneterephthalamide. Vysokomol Soedin 1978; 20(10 Ser A): 2224-2231.

[18] Papkov SP, Kulichihin VG, Kalmykova VD, Malkin AYa. Rheological properties of anisotropic poly(para-benzamide) solutions. J Polym Sci Polym Phys Ed 1974; 12: 1753-1770. http://dx.doi.org/10.1002/pol.1974.180120903

[19] Miller WG, Wu CC, Wee EL, Santee GL, Rai JH, Goebel KD. Thermodynamics and dynamics of polypeptide liquid crystals. Pure Appl Chem 1974; 38(1): 37-58.

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