



Phase diagrams and rheological properties of cellulose ether solutions in magnetic field

S.A. Vshivkov, E.V. Rusinova*, A.G. Galyas

Department of Chemistry, Ural Federal University, 19 Mira street, Ekaterinburg 620002, Russia

ARTICLE INFO

Article history:

Received 4 May 2014
Received in revised form 20 July 2014
Accepted 30 July 2014
Available online 14 August 2014

Keywords:

Phase diagram
Rheology
Magnetic field
Liquid crystal
Cellulose ethers

ABSTRACT

The phase transitions and rheological properties of the hydroxyethyl cellulose–water, hydroxyethyl cellulose–DMAA, hydroxyethyl cellulose–DMF, hydroxypropyl cellulose–water, hydroxypropyl cellulose–DMF and ethyl cellulose–DMAA systems were studied. The regions of existence of the isotropic and anisotropic phases were determined. Application of a magnetic field is shown to be accompanied by a change in the relative viscosity by a factor of 1.3–4. The concentration dependences of viscosity in the presence of a magnetic field are described by curves with an extremum.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Phase diagrams of multicomponent systems provide full information on the thermodynamic compatibility of components in wide concentration and temperature ranges. One of the first phase diagrams of polymer–solvent systems was published by Papkov, Kargin, Rogovin in 1937–1939 [1–3]. From the end of the 1940s, systematic research into the thermodynamic properties and construction of phase diagrams of polymer solutions have been performed at the Chair of Macromolecular Compounds, Ural State University (since 2011 Ural Federal University). Over the course of sixty years, phase diagrams have been constructed for hundreds of polymer systems with amorphous and crystalline phase separations. Many of these data were included in textbooks, monographs and reviews [4–11].

In 1956–58 Robinson [12,13] discovered, that poly(γ -benzyl-L-glutamate) (PBG) can form liquid crystals in concentrated solutions in chloroform, methylene chloride, trichloroethane, dioxane, *m*-cresol. In 1956 Flory [14] suggested the phase diagram for a polymer–solvent system with the liquid crystalline (LC) transition. At a later date such diagrams were built for the systems: PBG–DMF [15], polycarbonyloxyline–DMF [16,17], poly-*p*-benzamide–DMA [18], poly-*p*-benzamide–DMA, LiCl [19], poly(*p*-phenyleneterephthalamide)–H₂SO₄ [4,20].

The LC state in solutions and melts of cellulose derivatives was characterized later in 1970–1980s [21–26]. Molecules of cellulose and cellulose derivatives are characterized by a rigid helical conformation and, hence, they are capable of ordering and formation of cholesteric liquid crystals in concentrated solutions. Many studies were devoted to phase equilibrium in the HPC–water system, and the low critical solution temperature values were reported in a number of papers [27–39]. Investigation of the LC state in polymer solutions is of evident practical importance because, owing to the ability to orient under the action of external fields, such solutions are used for the preparation of high-modulus fibers. The influence of

* Corresponding author. Address: Department of chemistry, Ural Federal University, 51 Lenin avenue, Ekaterinburg 620083, Russia. Tel.: +7 (343)261 60 46.

E-mail addresses: Sergey.Vshivkov@urfu.ru (S.A. Vshivkov), elena.rusinova@urfu.ru, monomer2000@mail.ru (E.V. Rusinova), andreiga-galyas@mail.ru (A.G. Galyas).

a magnetic field on the liquid crystal structure was studied by Meuer [40], de Gennes [41]. The authors considered such a field distortion of the cholesteric structure and found out that the transition to complete nematic order occurred at the critical field strength. The theory has been verified for lyotropic liquid crystals of PBG in a number of different solvents [42–45]. Molecules of liquid crystals orient themselves in the magnetic field so that their long chains are oriented parallel to the magnetic field lines [46]. This orientation is associated with the molecular anisotropy of macromolecules rather than with the existence of permanent magnetic moments. 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 [11,39,47–50]. However, little is known about the effect of a magnetic field on the viscosity of polymer solutions [51,52]. The aim of this study was to investigate the phase transitions and rheological properties of the cellulose derivative solutions in the presence and absence of a magnetic field.

2. Materials and methods

The experiments were performed with the samples of cellulose derivatives (Aqualon/Hercules): hydroxyethyl cellulose (HEC) with a degree of substitution $\alpha = 2.5$ and $M_n = 6.2 \times 10^4$, hydroxypropyl cellulose with $\alpha = 2.25$ and $M_n = 1.6 \times 10^5$ and ethyl cellulose with $\alpha = 2.5$ and $M_w = 1.6 \times 10^5$. Dimethylformamide (DMF), dimethylacetamide (DMA) and twice-distilled water were used as solvents. The solvent purity was studied through refractive index measurements [53]. The polymer solutions were prepared for several weeks at 298 K (water) and 350 K (DMF, DMAA).

Phase-transition temperatures were estimated by the cloud-point method. The phase states of solutions were examined with the help of an “Olympus BX-51” polarization microscope. A polarization photoelectric setup [39,47] was used to determine the type of phase transition in solutions: a sealed ampoule containing the transparent polymer solution was placed in the gap between the crossed polaroids and the temperature of the ampoule was decreased. The polarized light of the GN-2 P He–Ne laser was transmitted through the polaroids in the direction normal to the ampoule containing the solution. When the solution was transparent (isotropic) the intensity of the transmitted light was zero. As the system became turbid upon variation in temperature or increase in the concentration of solution, the transmitted light intensity increased. This indicated formation of the anisotropic phase, that is, the LC phase transition.

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 3.7 kOe and field lines directed perpendicularly to the rotational

axis of a rotor and the second magnet, with an intensity of 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 from 0 to 15 s^{-1} for 5 min.

A metallic rotor rotating in a magnetic field can be regarded as a generator closed on itself [54]. During operation of the generator, a braking torque (electromagnetic moment M_e) 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 [54]. 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. Then the electromagnetic moment is likewise zero. The results of calibration experiments with air, water, and DMF showed the absence of electromagnetic retardation when the magnetic field lines are oriented along the rotor rotational axis.

3. Results

3.1. Phase diagrams of the cellulose ether solutions

The boundary curves delimiting transparent isotropic and opalescent anisotropic solutions for HPC–DMF, HPC–water, HEC–water, HEC–DMF, HEC–DMAA, EC–DMA systems have been determined. Figs. 1 and 2 show the boundary curves delimiting transparent isotropic (I) and opalescent anisotropic (II) solutions for solutions of the cellulose derivatives. It is evident, that at 298 K HEC solutions in DMAA are isotropic in the composition range $\omega_2 < 0.12$ and anisotropic in the composition range $\omega_2 > 0.12$ (ω_2 is the polymer weight fraction in the system), EC solutions in DMAA are isotropic in the composition range $\omega_2 < 0.15$ and anisotropic in the composition range $\omega_2 > 0.15$, HEC solutions in DMF are isotropic in the composition range $\omega_2 < 0.05$ and anisotropic in the composition range $\omega_2 > 0.05$, HEC solutions in water are

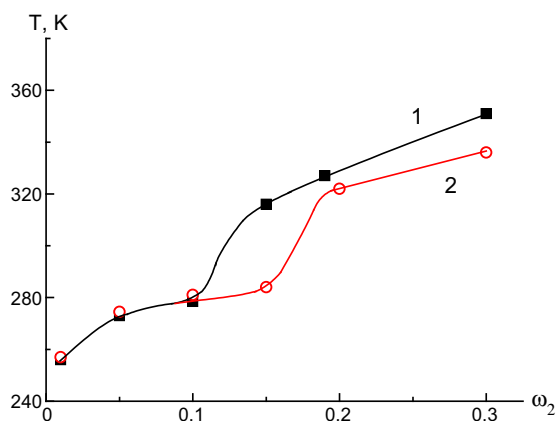


Fig. 1. Phase diagrams for HEC–DMAA (1) and EC–DMAA (2) systems.

Download English Version:

<https://daneshyari.com/en/article/7806113>

Download Persian Version:

<https://daneshyari.com/article/7806113>

[Daneshyari.com](https://daneshyari.com)