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VISCOMETRIC RESEARCH OF CONCENTRATION REGIMES FOR POLYVINYL ALCOHOL SOLUTIONS

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Experimental researches are carried out for the concentration and temperature dependences of the kinematic viscosity and the density of diluted and semidiluted solutions of polyvinyl alcohols (PVAs) with hydrolysis degrees of 85.2 ± 1.0 mol.% and 98.4 ± 0.4 mol.% in dimethyl sulfoxide and water. Critical concentrations of the transition from the diluted solution to more concentrated regimes are calculated. The results of calculations show that the critical crossover concentrations for PVA solutions in dimethyl sulfoxide are lower than that for PVA aqueous solutions. The obtained temperature dependences of the effective hydrodynamic radii of macromolecules in the diluted PVA solutions testify that this parameter decreases, as the temperature grows.

Keywords: polyvinyl alcohol, viscometry, crossover concentration, solution.

1. Introduction

Researches of the physical properties of polyvinyl alcohol (PVA) solutions are very challenging owing to the application of those solutions in various branches of industry [1], agriculture [1, 2], pharmacology, and medicine. In particular, PVA solutions are used in medicine for the controlled delivery of medicines and proteins [3]; the detoxification of organism [4]; as hydrogels, thickeners, and nutrient media [5]; as film formers for the coating of tablets and pills, as well as in tissue transfer [6, 7]; and as prolongators in eye drops and in ophthalmology [8, 9]; they also enter the composition of membranes for dialysis [10, 11]. The use of PVA for biomedical needs results from its capability of biodegradation (microbial or enzymatic) to simpler compounds and its subsequent removal from organism [4, 11].

On the other hand, researches of the behavior of liquid systems, when hydrogen bonds play a crucial role in the interaction between molecules, is an important task for the physics of condensed state [12–14]. As the PVA concentration grows, the solutions change from diluted through semidiluted to concentrated ones (i.e. we have different concentration regimes), and the structure of solutions also changes, by transforming from isolated macromolecules to aggregates and, finally, to the formation of spatial in-

termolecular networks in the solution. Therefore, regular researches of the physical properties of aqueous and non-aqueous PVA solutions, in particular, the concentration regimes, in a wide range of concentrations and temperatures are actual for the solution of technological projects, finding ways for the target delivery of drugs, and creating the compositions with prescribed characteristics.

2. Materials and Methods of Researches

Polyvinyl alcohols Mowiol 3-85 (Kuraray) with a hydrolysis degree of 85.2 ± 1.0 mol.% and Mowiol 4-98 (Kuraray) with a hydrolysis degree of 98.4 ± 0.4 mol.%, both without additional purification, were used. As solvents, we used twice-distilled water and dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$) of pharma grade. The latter was held on NaOH and distilled at a low pressure of 3–5 mm Hg, with the middle fraction being collected, in accordance with work [15].

The kinematic viscosity and the density of PVA solutions in water and dimethyl sulfoxide with concentrations from 0.2 to 20 wt.% were experimentally studied in a temperature interval of 293–363 K with the use of standard techniques. Solutions were prepared gravimetrically. The kinematic viscosity ν was studied on capillary viscometers with capillaries of various diameters. The error of viscosity measurements did not exceed 2%. The density ρ was determined using the picnometer method with an error of 0.05%.

3. Experimental Results and Their Model Interpretation

Polyvinyl alcohol belongs to flexible-chain polymers of the aliphatic series. In its macromolecular chain, it contains hydroxyl groups, which are responsible for intra- and intermolecular interactions by means of hydrogen bonds. As the polymer concentration in the solution grows, the average distance between macromolecules becomes shorter, and the motion of segments becomes hindered, which gives rise to the emergence of aggregates and spatial molecular networks. In addition, the viscosity of concentrated PVA aqueous solutions grows in time owing to the irreversible gelation process [16, 17], which is similar to the crystallization [18–20]. Therefore, experimental researches were carried out right after the dissolution of polymer followed by cooling the solution down to measurement temperatures [21].

The temperature-concentration dependences of the density, $\rho = \rho(T, C)$, and the kinematic viscosity, $\nu = \nu(T, C)$, were obtained experimentally for PVA solutions in water or dimethyl sulfoxide. The shear viscosity was calculated, by using the known formula

$$\eta = \rho\nu. \quad (1)$$

The obtained experimental data testify that the temperature dependences of the density of PVA solutions in dimethyl sulfoxide have a linear character in the examined temperature interval, unlike their counterparts for the PVA aqueous solutions. For the latter, the temperature dependences of the density become more and more similar to those for water, as the concentration decreases (Fig. 1). It should be noted that the increase of the PVA concentration in water results in that the curvature radius in the temperature dependences of a PVA aqueous solution density grows. The densities of all solutions grow linearly (within experiment errors) with the PVA concentration in the whole temperature interval.

In Fig. 2, the temperature dependences of the shear viscosity in PVA solutions in water and dimethyl sulfoxide are shown. Their analysis testifies that, within experiment errors, the shear viscosity in the 5% solution of PVA in dimethyl sulfoxide has the same value and temperature dependence as the 10% solution of PVA in water. The same is observed for the 10% solution of PVA in dimethyl sulfoxide and the 15% solution of PVA in water, as well as for the 15% solution

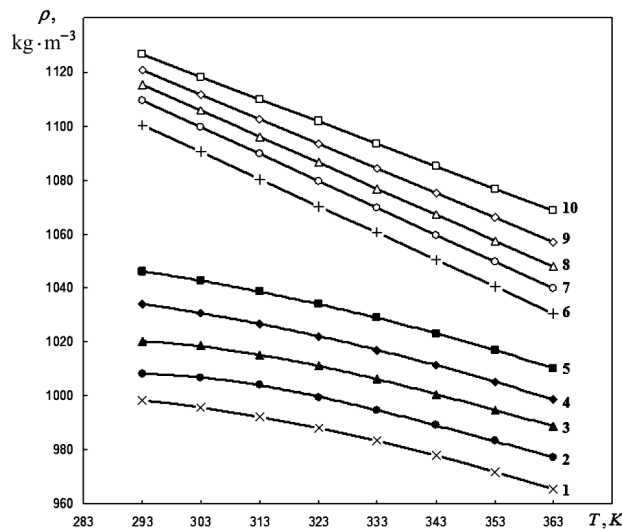


Fig. 1. Temperature dependences of the density of solutions of PVA with a hydrolysis degree of 85.2 ± 1.0 mol.% in water (curves 1 to 5) and dimethyl sulfoxide (curves 6 to 10) for various mass fractions of solute: 0 (curves 1 and 6); 5 (curves 2 and 7), 10 (curves 3 and 8), 15 (curves 4 and 9), and 20% (curves 5 and 10)

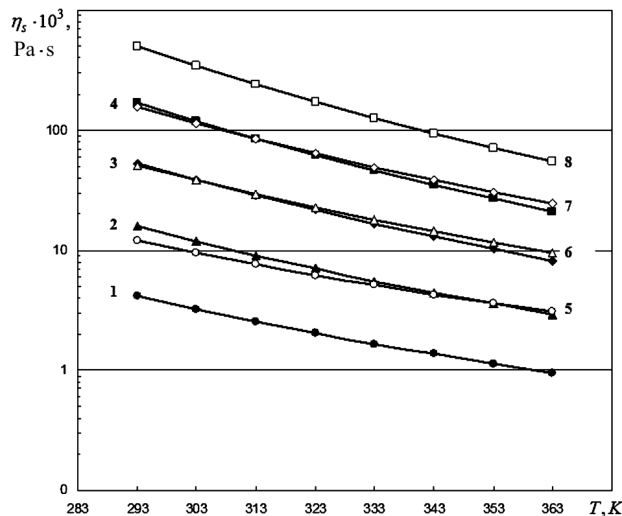


Fig. 2. Temperature dependences of shear viscosity in solutions of PVA with a hydrolysis degree of 85.2 ± 1.0 mol.% in water for concentrations of 5 (1), 10 (2), 15 (3), and 20% (4), and in dimethyl sulfoxide for concentrations of 5 (5), 10 (6), 15 (7), and 20% (8)

of PVA in dimethyl sulfoxide and the 20% solution of PVA in water. The analysis of the shear viscosity dependences on the PVA solution concentration testifies to a reduction of the curvature radius in the con-

centration dependences of the shear viscosity in PVA solutions in dimethyl sulfoxide as compared with similar dependences for the PVA aqueous solutions.

In order to process the experimental data obtained for the PVA solutions in water and dimethyl sulfoxide, the intrinsic viscosities are calculated, which depend only on the polymer origin and do not depend on its concentration. The intrinsic viscosity of the polymer is obtained by extrapolating the concentration dependence of the reduced viscosity to the zero concentration [22]:

$$[\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta - \eta_0}{\eta_0 C} \right), \quad (2)$$

where η is the viscosity of a polymer solution, η_0 the viscosity of a solvent, and C the solution mass concentration.

By the values of intrinsic viscosity in accordance with the Mark–Kuhn–Hawink equation [22] for diluted PVA solutions, we determined the mean-viscosity molecular mass \bar{M}_η by the viscometric method within the concentration interval (0.2÷0.8) wt. %:

$$[\eta] = K_\eta \bar{M}_\eta^\alpha, \quad (3)$$

where K_η is a constant for the system polymer–solvent, which depends on the temperature, polydispersion, branching, and so forth; and α is a quantity associated with the chain stiffness, macromolecular conformation, and thermodynamic state of the solvent. According to work [22], at a temperature of 303 K, we have $K_\eta = 6.66 \times 10^{-4}$ dl/g and

Characteristic viscosity $[\eta]$, mean-viscosity molecular mass \bar{M}_η , critical crossover concentration C^* , and radius of inertia of polymer coil R_C at the critical crossover concentration

Solution	$[\eta]$, dl/g	\bar{M}_η , kg/mol	C^* , wt. %	R_C , nm
PVA with a hydrolysis degree of 85.2 ± 1.0 mol. % in water	0.27	12.2	3.64	5.10
PVA with a hydrolysis degree of 85.2 ± 1.0 mol. % in dimethyl sulfoxide	0.44	12.2	2.27	5.97
PVA with a hydrolysis degree of 98.4 ± 0.4 mol. % in water	0.34	17.2	2.93	6.15
PVA with a hydrolysis degree of 98.4 ± 0.4 mol. % in dimethyl sulfoxide	0.58	17.2	1.74	7.32

$\alpha = 0.64$ for PVA aqueous solutions, and $K_\eta = 0.26 \times 10^{-4}$ dl/g and $\alpha = 0.70$ for PVA solutions in dimethyl sulfoxide. The sought values are quoted in Table. Hence, the examined specimens are low-molecular polyvinyl alcohols with the average polymerization degrees $\bar{p} \sim 300$ for PVA with a hydrolysis degree of 85.2 ± 1.0 mol. % and $\bar{p} \sim 600$ for PVA with a hydrolysis degree of 98.4 ± 0.4 mol. %, which correlates well with the known regularity $\bar{M}_n < \bar{M}_\eta < \bar{M}_w$ and the values declared by the manufacturer for the used specimens: $\bar{M}_w = 14000$ g/mol for Mowiol 3-85 and $\bar{M}_w = (23000 \div 27000)$ g/mol for Mowiol 4-98. The polymer production technology determines $\bar{M}_w/\bar{M}_n \approx 2$ [23], where \bar{M}_n is the number-average molecular mass, and \bar{M}_w the mass-average molecular mass.

In the theory of diluted polymer solutions, the intrinsic viscosity is used as a criterion for the estimation of a solution concentration regime. Since the size of a macromolecule in the solution determines whether the latter is diluted or moderately concentrated, whereas the intrinsic viscosity is proportional to the macromolecular volume in the solution, the solution is called diluted if its volume occupied by macromolecules is much smaller than the total solution volume. As a rule, isolated macromolecules in diluted solutions of flexible-chain polymers roll up into coil-like conformations [24]. With the growth of the polymer concentration, the solution structure changes, by transforming from isolated macromolecules to aggregates and forming a network of intermolecular links, when achieving a critical concentration of overlapping macromolecular coils, C^* , the beginning of the so-called crossover region. In the case of flexible-chain polymers, the critical crossover concentration C^* can be determined experimentally with the help of the viscometric method [25]:

$$C^* = \frac{1}{[\eta]}. \quad (4)$$

The critical crossover concentration can be calculated according to the equation [26]

$$C^* = \frac{3M}{4\pi N_A R_C^3}, \quad (5)$$

where M is the molecular mass of the polymer, N_A the Avogadro constant, and R_C the radius of inertia of a polymer coil at the critical crossover concentration.

For concentrations below the crossover one, we can use the Einstein model theory, which allows the size of a solute molecule to be determined, by using viscometric methods. In the framework of this theory, the solute molecule is considered as a hard sphere, and the solvent as a continuous medium [27,28]. With certain cautions, the Einstein model theory allows one to estimate the variation of macromolecular sizes in the diluted solution as the temperature changes. For the shear viscosity of a solution, the following formula was obtained [27]:

$$\eta = \eta_0 \left(1 + \frac{5}{2} \frac{4\pi R^3}{3} n \right), \quad (6)$$

where R is the radius of the model sphere or the effective hydrodynamic radius of a molecule, and n the concentration of solute molecules. An example of the temperature dependence of effective hydrodynamic radii of macromolecules in the aqueous PVA solutions with a hydrolysis degree of 85.2 ± 1.0 mol.% and in the solutions of PVA with a hydrolysis degree of 98.4 ± 0.4 mol.% in dimethyl sulfoxide are depicted in Fig. 3.

4. Discussion of Results

The analysis of the data presented in Table 1 testifies that the transition from the diluted solution of PVA in dimethyl sulfoxide to the semidiluted one occurs at lower concentrations than those, at which the same transition takes place in the aqueous solution. In our opinion, this behavior stems from the fact that the interaction between PVA macromolecules is less probable than the interaction between PVA and solvent molecules. Those conclusions are confirmed by the results of work [29], where the thermodynamic parameters of a viscous flow in concentrated PVA solutions were analyzed in the framework of the Eyring model theory, and a high quality of dimethyl sulfoxide as a solvent for PVA was pointed out from the thermodynamic viewpoint.

A comparison between the concentration regimes for PVA solutions with PVA hydrolysis degrees of 98.4 ± 0.4 and 85.2 ± 1.0 mol.% (in the latter case, the macromolecular chain contains, besides hydroxyl groups, also acetate ones) shows that the growth of the hydrolysis degree and, hence, the reduction in the number of acetated groups in the polymer chain result in that the critical concentration for the overlapping of macromolecular coils decreases. The effective

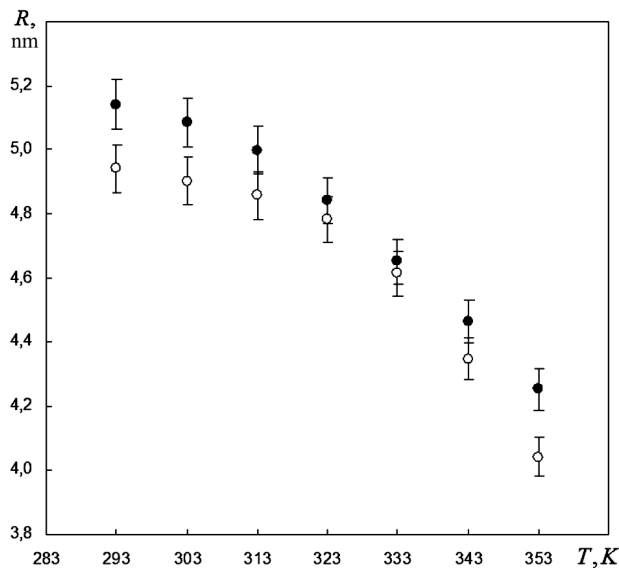


Fig. 3. Temperature dependences of the effective hydrodynamic radii of macromolecules in the aqueous PVA solutions with a hydrolysis degree of 85.2 ± 1.0 mol.% (black circles) and in solutions of PVA with a hydrolysis degree of 98.4 ± 0.4 mol.% in dimethyl sulfoxide (white circles) at concentrations below the critical crossover one C^*

hydrodynamic radii of PVA macromolecules grow in dimethyl sulfoxide, increase with the length of macromolecular chain, and diminish for all solutions, if the temperature grows.

5. Conclusions

Experimental researches of the concentration and temperature dependences of the kinematic viscosity and the density in diluted and semidiluted solutions of low-molecular polyvinyl alcohols with hydrolysis degrees of 85.2 ± 1.0 and 98.4 ± 0.4 mol.% in dimethyl sulfoxide and water are carried out. The critical concentrations of the transition from the diluted solution to more concentrated regimes are calculated.

The results of calculations show that the critical crossover concentrations for PVA solutions in dimethyl sulfoxide are lower than those for PVA aqueous solutions. The results testify that dimethyl sulfoxide is a better solvent in the thermodynamic sense and forms more dispersed molecular solutions of PVA than water does. The increase in the molecular mass or the hydrolysis degree of polymer also results in a reduction of the critical crossover concentrations.

The temperature dependences of the effective hydrodynamic radii of macromolecules in the diluted PVA solutions are obtained. It is shown that the effective hydrodynamic radii of macromolecules decrease with the temperature growth.

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ДОСЛІДЖЕННЯ КОНЦЕНТРАЦІЙНИХ РЕЖИМІВ РОЗЧИНІВ ПОЛІВІНІЛОВОГО СПИРТУ ВІСКОЗИМЕТРИЧНИМ МЕТОДОМ

Резюме

Проведено експериментальні дослідження концентраційних і температурних залежностей кінематичної в'язкості та густини розбавлених і напіврозбавлених розчинів полівінілових спиртів зі ступенями гідролізу $85,2 \pm 1,0$ мол. % і $98,4 \pm 0,4$ мол. % у диметилсульфоксиді та воді. Розраховані критичні концентрації переходу від розбавленого розчину до більш концентрованих режимів. Розрахунки показують, що для розчинів полівінілового спирту в диметилсульфоксиді критичні концентрації кросоверу нижчі, ніж для водних розчинів полівінілового спирту. Отримані температурні залежності ефективних гідродинамічних радіусів макромолекул у розбавлених розчинах полівінілового спирту вказують на те, що зі збільшенням температури ефективні гідродинамічні радіуси макромолекул зменшуються.