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EFFECTIVE RADII OF MACROMOLECULES IN DILUTE POLYVINYL ALCOHOL SOLUTIONS

The temperature and concentration dependences of the effective radii of polyvinyl alcohol (PVA) macromolecules have been studied on the basis of experimental data on the viscosity of dilute PVA solutions in dimethyl sulfoxide (DMSO) and water, as well as using the Malomuzh–Orlov theory of shear viscosity in polymer solutions. The temperature dependences of the effective radii of PVA macromolecules in DMSO are shown to be linear in the temperature interval 293÷353 K. At the same time, those dependences are more complicated for aqueous PVA solutions. Namely, the effective radii of macromolecules remain unchanged at relatively low temperatures and PVA concentrations, but they decrease nonlinearly at higher temperatures and concentrations. The concentration dependences of the effective radii of PVA macromolecules in both solvents are found to decrease nonlinearly in the concentration interval 0.3–3 wt.%.

K e y w o r d s: polyvinyl alcohol solution, effective radius of macromolecule, dimethyl sulfoxide, Malomuzh–Orlov theory.

1. Introduction

In dilute solutions of polymers with linear flexible macromolecules, the latter are in the coil conformation [1]. The radii of macromolecular coils in dilute polymer solutions decrease with the polymer concentration growth, which is explained by a deformation of flexible macromolecules as a result of the mutual repulsion between the coils and their mutual penetration [2].

The temperature dependence of the radius of macromolecular coils in polymer solutions is not universal. For example, in works [3,4], it was shown that the radii of macromolecules in a solution increase with the temperature, whereas, in works [5,6], they were found to decrease with the temperature growth. There is no agreement on the temperature dependence of the macromolecular radii even for the same liquid system: a nonlinear reduction of the hydrodynamic radius of dextran in aqueous solutions with increasing the temperature was demonstrated in work [7], whereas those dependences turned out linear in work [8]. We may assume that the behavior of the macromolecular radii depends on a number of important factors such as the concentration, temperature, the nature of a polymer and a solvent, and so forth.

Therefore, this work is aimed at elucidating the specific features in the temperature and concentration dependences of the effective radii of polyvinyl alcohol (PVA) macromolecules in aqueous and dimethyl sulfoxide solutions on the basis of viscometric data. Rather dilute PVA solutions are considered, for which the Malomuzh–Orlov formula is applicable (see the discussion in work [2]).

2. Experimental Part

Experimental researches of the temperature dependences of the kinematic viscosity and density of PVA solutions in dimethyl sulfoxide ($(CH_3)_2SO$, DMSO) and water were carried out. The experiments were performed in the temperature interval 293–353 K and for PVA concentrations of 0.3, 0.5, 0.7, 1, 1.65, 2.32, and 3 wt.%.

The density was measured with an error of 0.05% with the help of the pycnometric method. The kinematic viscosity was determined on capillary viscosimeters of the Ubbelohde type with an error of 2%, by using standard techniques.

In the researches, PVA Mowiol 6-98 (Kuraray) with a hydrolysis degree of 98.4 ± 0.4 mol.% and without extra purification was used. Double-distilled water and pharmaceutical-grade DMSO were used as solvents. DMSO was held on NaOH, then distilled at

a low pressure of 3–5 mm Hg, and the middle fraction was collected. The solutions were prepared gravimetrically. The solution concentration was calculated by the formula

$$C = \frac{m_{\mathrm{PVA}}}{m_{\mathrm{PVA}} + m_{\mathrm{S}}} \cdot 100\%, \qquad (1)$$

where m_{PVA} and m_{S} are the masses of the dissolved substance and the solvent, respectively.

3. Theoretical Part

With certain reservations, macromolecular coils can be approximately considered as spherical particles consisting of a relatively hard core and a rarefied periphery ("fur") [10]. Such distribution of the material in a macromolecule directly manifests itself in the shear viscosity of macromolecular solutions. In particular, in work [2], it was shown that the concentration dependence of the shear viscosity for the polymer solution can be put in agreement with the Malomuzh–Orlov formula, if the effective radius of macromolecule, R_{eff}, which coincides with the core size, is assumed to be significantly smaller than the quantity

$$R = R_0 \sqrt{N}, \qquad (2)$$

where $R_0 = 2.5$ Å is the size of the PVA monomer, and N is the number of monomers in a macromolecule.

To determine the effective radius of a macromolecule, the following algorithm was applied:

1) the effective radius of a macromolecule is determined by the formula

$$R_{\mathrm{eff}} = \left(\frac{3M_w}{4\pi\rho C N_{\mathrm{A}}} \varphi_{\mathrm{eff}} \right)^{1/3}, \qquad (3)$$

where M_w is the average molecular mass (for PVA Mowiol 6-98, $M_w = 47000$ g/mol [9]), ρ and C are the density and mass concentration of the solution, respectively, and N_{A} is the Avogadro number;

2) the effective concentration of macromolecules in the solution bulk, φ_{eff}, is determined as a fitting parameter in the Malomuzha–Orlov formula $\eta_{\mathrm{MO}}[\varphi_{\mathrm{eff}}]$ [11–13]. So that

$$\eta_{\mathrm{sol}} = \eta_{\mathrm{MO}}[\varphi_{\mathrm{eff}}], \qquad (4)$$

where η_{sol} is the experimental value of shear viscosity for the solution.

Note that the magnitude of φ_{eff} is considerably smaller than that of the quantity $\varphi = (4\pi R^3 \rho C N_{\mathrm{A}}/3M_w)$ calculated according to the standard method. For instance, the effective radius of macromolecules for the aqueous PVA solution with a concentration of 0.3 wt.% and at a temperature of 293 K equals $R_{\mathrm{eff}} = 65$ Å, whereas formula (2) gives 79 Å. Those estimates are in qualitative agreement with the results of work [10].

The Malomuzh–Orlov formula allows the behavior of the viscosity of PVA solutions to be described in the macromolecule bulk concentration interval $\varphi \leq 0.5$. The latter value, in essence, corresponds to the solution density, at which all macromolecules form contacts with one another [2, 12, 13].

4. Discussion of Results

The Malomuzh–Orlov formula for the shear viscosity was applied to treat experimental data following the algorithm described in the previous section. As a result, the concentration dependences of the effective radius R of PVA macromolecules in their aqueous and DMSO solutions along the isotherms were obtained (see Figs. 1 and 2).

In the case of PVA macromolecules in DMSO, the concentration, C, dependences of R constitute a family of nonlinearly decreasing curves with the derivative $\partial R/\partial C$ growing with the temperature (Fig. 1, *a*). From Fig. 2, *a*, one can see that the temperature dependences of the effective radii of PVA macromolecules in DMSO are linear within the experimental error limits, with the slope of the plots decreasing, as the concentration grows. Figure 3, *a* demonstrates the temperature-concentration dependence $R = f(T, C)$ for the effective radius of macromolecular coils in dilute PVA solutions in DMSO.

Another picture is observed for aqueous PVA solutions (Figs. 1, *b* and 2, *b*). In the solutions with concentrations of 0.3–0.7 wt.%, the effective radius of macromolecules remains unchanged up to about 330 K within the experimental error limits. In the aqueous PVA solutions with concentrations of 1.65–3.0 wt.%, the effective radius of macromolecules decreases nonlinearly, as the temperature grows. A "plateau" in the dependence of the effective macromolecular radius is observed at relatively low temperatures and concentrations. Let us try to explain this behavior.
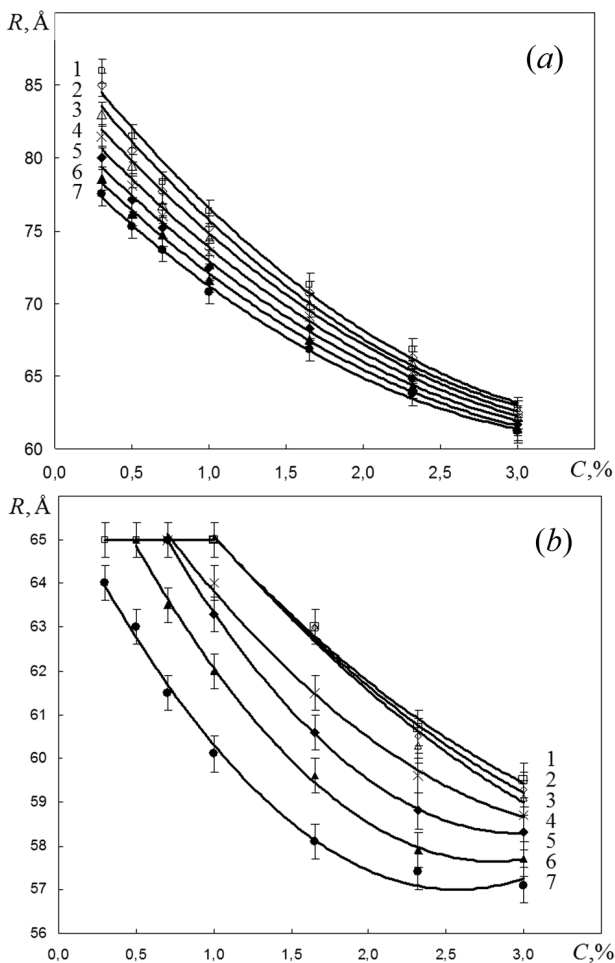
Fig. 1. Concentration dependences of the effective radius of polyvinyl alcohol (PVA) macromolecules in dimethyl sulfoxide (DMSO) (*a*) and water (*b*) at various temperatures: 293 (*1*), 303 (*2*), 313 (*3*), 323 (*4*), 333 (*5*), 343 (*6*), and 353 K (*7*)

Fig. 2. Temperature dependences of the effective radius of PVA macromolecules in DMSO (*a*) and water (*b*) at various PVA concentrations: 0.3% (*1*), 0.5% (*2*), 0.7% (*3*), 1% (*4*), 1.65% (*5*), 2.32% (*6*), and 3% (*7*)

In PVA solutions with concentrations up to the overlapping of the cores of macromolecular coils, the role of their rarefied periphery is insignificant. This periphery weakly affects the hydrodynamic interaction between the particles. As the concentration increases, the peripheries of macromolecular coils start to overlap, but they weakly change the interaction between the macromolecules. Such a behavior is also inherent to macromolecules, if the temperature increases. High temperatures activate the motion of periphery segments, but its contribution to the viscosity of PVA solutions remains insignificant in comparison with the contribution of the "hard" core.
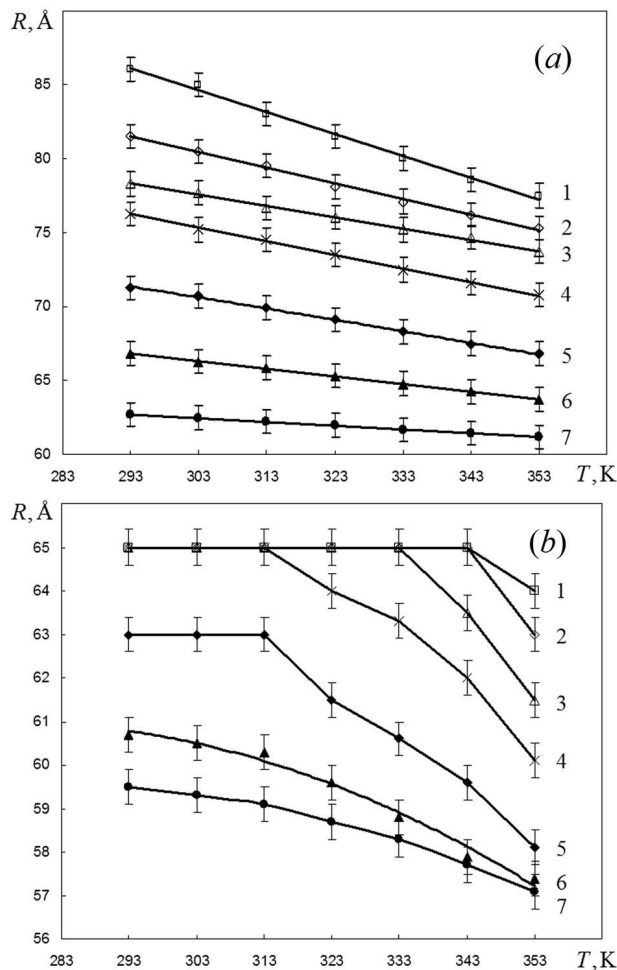
Dimethyl sulfoxide is a better solvent for polyvinyl alcohol than water. This statement is confirmed by the fact that the effective radii of PVA macromolecules in DMSO are larger by 15–20% in comparison with those in the aqueous PVA solutions. In other words, the DMSO solvent favors the increasing in the size of macromolecular coils. Those facts are in good agreement with the conclusions of work [14], where it was shown that the insertion of DMSO to the aqueous PVA solution as the third component gives rise to a weakening of the intermolecular interaction between PVA macromolecules and water, as well as between PVA segments themselves. This fact is ex-
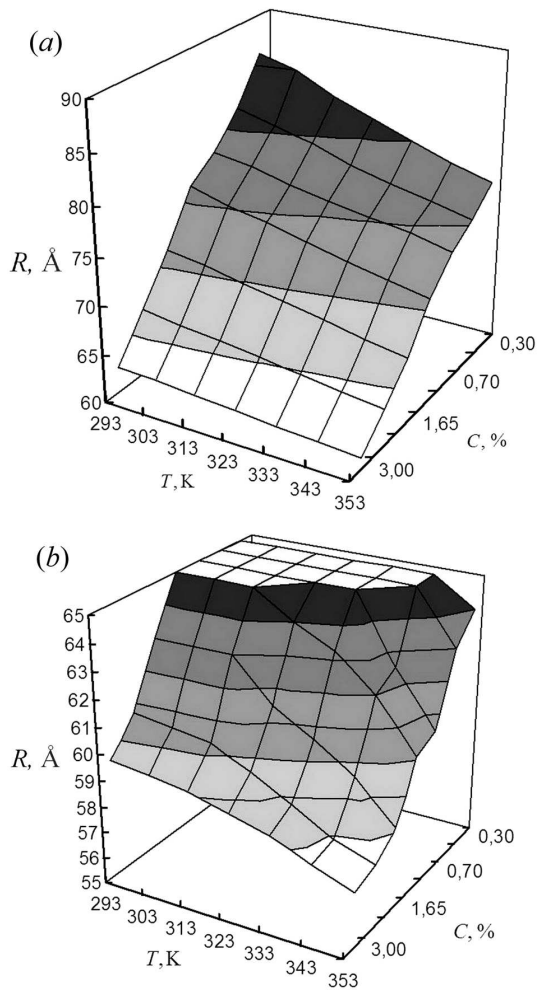
Fig. 3. Effective radii of PVA macromolecules in DMSO (*a*) and water (*b*) as functions of the temperature and concentration

plained by a better affinity of DMSO with respect to PVA than to water.

Let us append the temperature dependences of the concentration, when the macromolecular coil radius remains unchanged, $C = f(T)|_{R=\text{const}}$ (Fig. 4), to the data obtained above. The corresponding plots are characteristic curves that allow one to distinguish between changes associated either with the overlapping of macromolecular peripheries or with their deformation as a result of the thermal motion. From Fig. 4, *a*, one can see that these dependences have a linearly decreasing character for PVA solutions in DMSO:

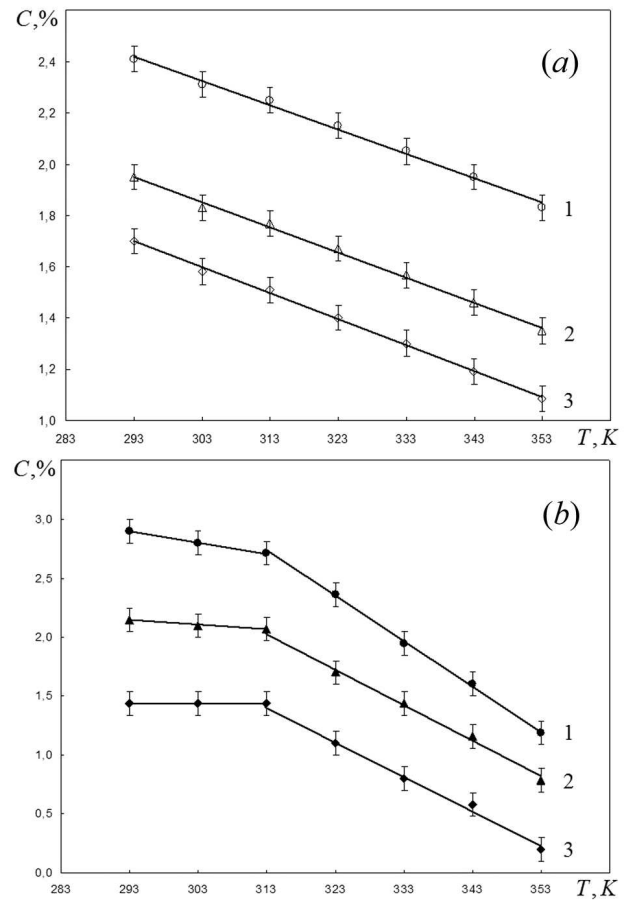$$C = C_0 - \alpha(T - T_0), \tag{5}$$

Fig. 4. Temperature dependences of the concentration (*a*) for the PVA solution in DMSO at various constant radii of the macromolecular coil: 65.75 ± 0.05 (*1*), 68.65 ± 0.05 (*2*), and 70.55 ± 0.05 Å (*3*); (*b*) for the PVA solution in water at various constant radii of the macromolecular coil: 59.65 ± 0.05 (*1*), 61.35 ± 0.05 (*2*), and 63.45 ± 0.05 Å (*3*)

Values of C_0 and α
in Eq. (5) for PVA solutions in DMSO

R, Å	C_0, wt.%	α, K^{-1}
65.75 ± 0.05	5.204	0.009
68.65 ± 0.05	4.819	0.009
70.55 ± 0.05	4.665	0.010

where $T_0 = 293$ K, and the values for C_0 and α are quoted in Table.

It is quite expected that the growth in the solution concentration enhances the interaction between macromolecular coils. This interaction diminishes the
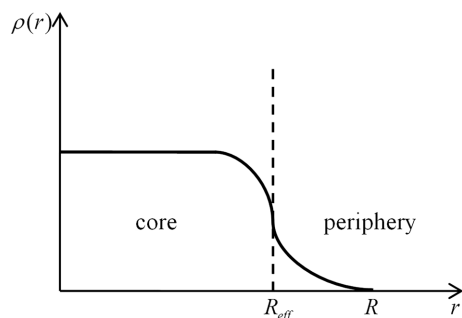
Fig. 5. Schematic diagram of the density distribution in a PVA macromolecule

effective radii of macromolecules. At the same time, the temperature variation at a fixed solution concentration enhances fluctuations of the local density in the macromolecular coil periphery. Therefore, the reduction of the effective macromolecular radius takes place as a result of both the ordinary concentration growth and the growth of the segment density fluctuations in the coil periphery, when the temperature increases.

Furthermore, the thermally induced fluctuations of the segment density in a rarefied periphery (see Fig. 5) are rather substantial. As a result, the periphery "transparency" increases, and its influence on the shear viscosity decreases. The increase in the concentration in the system is associated with a change of the macromolecular chemical potential, i.e. it can be regarded as a reaction of the system to an external force. In a sense, this is an analog of the fluctuation-dissipation theorem [15], which relates a system response to an external force with equilibrium fluctuations of the conjugate quantity. Following the same speculations, an analog of the fluctuation-dissipation theorem can also be formulated for the behavior of macromolecules: fluctuations of segments at the macromolecule periphery are determined by the system response to a change of the macromolecular chemical potential.

The same dependences $C = f(T)|_{R=\mathrm{const}}$, but for aqueous PVA solutions, can be approximated by two straight lines with different slopes, which intersect each other at a temperature of 315 ± 2 K. This implies that the liquid PVA-water system changes its microscopic properties at this temperature. When comparing the concentration dependences on the temperature at a constant macromolecular radius obtained for the PVA-DMSO and PVA-water systems, we may

assume that the indicated changes in the properties of the PVA-water system take place owing to the changes in the properties of the solvent (water). As was shown in work [16, 17], there is a dynamic phase transition in water at a temperature of 42 °C (317 K), at which the character of the thermal motion of water molecules essentially changes, and a redistribution of hydrogen bonds takes place.

5. Conclusions

On the basis of the experimental data obtained for the viscosity of polyvinyl alcohol solutions in dimethyl sulfoxide and water with variuos concentrations ranging from 0.3 to 3 wt.% and in the temperature interval 293÷353 K and the Malomuzh–Orlov theory of the shear viscosity of macromolecular solutions, the temperature and concentration dependences of the effective radii of PVA macromolecules in dilute aqueous and DMSO solutions are calculated. The temperature dependences of the effective radii of PVA macromolecules in DMSO are shown to be linear within the experimental error limits. In aqueous PVA solutions, the temperature dependences of effective macromolecular radii are more complicated: 1) at relatively low temperatures and concentrations, the effective radii of macromolecules remain unchanged; 2) at higher concentrations, the effective radii decrease nonlinearly with the increasing temperature. The concentration dependences of effective macromolecular radii have a nonlinearly decreasing character for both solvents. An important task for further researches is a clear formulation of the fluctuation-dissipation theorem for macromolecules in solutions and a demonstration of its application.

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ЕФЕКТИВНІ РАДІУСИ
МАКРОМОЛЕКУЛ У РОЗБАВЛЕНИХ
РОЗЧИНАХ ПОЛІВІНІЛОВОГО СПИРТУ

Р е з ю м е

На основі експериментальних даних в'язкості розбавлених розчинів полівінілового спирту (ПВС) у диметилсульфоксиді (ДМСО) та воді за допомогою теорії зсувної в'язкості розчинів макромолекул Маломужа–Орлова досліджуються температурні та концентраційні залежності ефективних радіусів макромолекул полівінілового спирту. Показано, що в інтервалі температур 293–353 К температурні залежності ефективних радіусів макромолекул ПВС у ДМСО мають лінійний характер, тоді як у водних розчинах ПВС такі залежності є більш складними: за відносно низьких температур і концентрацій величини ефективних радіусів макромолекул залишаються незмінними, а зростання температури і концентрації призводить до нелінійного зменшення ефективних радіусів макромолекул. Концентраційні залежності ефективних радіусів макромолекул в обох розчинниках для інтервалу концентрацій 0,3–3 мас.% носять нелінійний спадний характер.