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INSTABILITY OF AQUEOUS SOLUTIONS OF POLYACRYLAMIDE IN A HYDRODYNAMIC FIELD

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This article discusses findings obtained regarding the effect of a hydrodynamic field on the reduced viscosity, effect of turbulent friction reduction, light scattering, double refraction, and optical density of aqueous solutions of hydrolyzed polyacrylamide.

The instability of polymer solutions during flow in a turbulent regime is an extremely undesirable phenomenon in regard to practical use of the solutions and is thus constantly a focus of investigators. To alleviate instability, it is necessary to determine the nature of the mechanisms responsible for it.

Several studies have examined the effect of different factors on lessening of the phenomenon of a reduction in hydrodynamic resistance as a function of the number of runs of a

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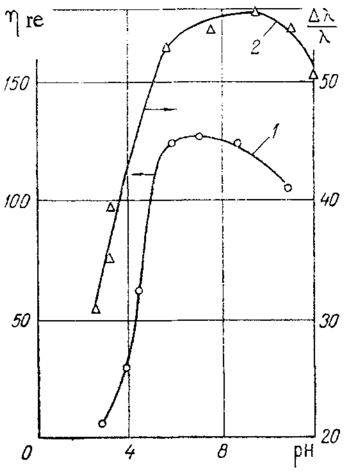

Fig. 1

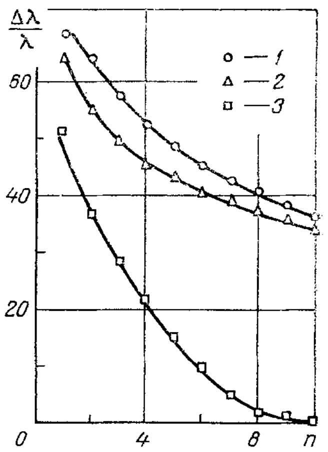

Fig. 2

Fig. 1. Effect of the pH of the medium on the reduced viscosity n_{re} (dl/g) (curve 1, $C_p = 0.001\%$) and hydrodynamic efficiency $\Delta\lambda/\lambda$ (%) (curve 2, $C_p = 0.0002\%$) of aqueous solutions of PAA. T = 293°K.

Fig. 2. Dependence of the hydrodynamic efficiency $\Delta\lambda/\lambda$ (%) of PAA solutions on the number of runs n through the channel ($C_p = 0.0005\%$, T = 293°K, $\tau_w = 33$ N/m²: 1) pH ≈ 7; 2) pH ≈ 12; 3) pH ≈ 3.

solution through a channel [1-4]. The observed instability of the solutions has been attributed to degradation of the molecules, since a decrease in molecular weight leads to a decrease in the hydrodynamic efficiency of molecules, other conditions being equal. At the same time, it is known that the phenomenon of resistance reduction may also be affected by a change in the conformational state of the macromolecules for a constant molecular weight [5-8].

The studies [9-13] investigated the instability of polymer solutions by the methods of viscometry and partition chromatography (PTC). The observed reduction in the viscosity characteristic and the shift of the PTC curve led the authors to conclude that polymer molecules had ruptured under the influence of hydrodynamic forces. However, these results can also be explained by a change in the conformation of the macromolecules and their association, since viscometry and PTC give information on the effective hydrodynamic volumes rather than on molecular weight. Such changes in the flow are possible in accordance with the equivalence of the effect of chemical and mechanical energy on the conformation of macromolecules [14]. The hydrodynamic field shifts the phase diagram of the polymer solution in the direction of a decrease in thermodynamic stability [15]. Here, the polymer–solvent type of interaction is weakened and the polymer–polymer interactions are reinforced, which promotes the formation of intra- and intermolecular bonds. In view of this, it becomes understandable that the instability of polymer solutions can increase with a deterioration in the quality of the solvent, as was seen experimentally in [12, 13, 16]. Meanwhile, the same results cannot be attributed to degradation, which presumes an increase in the probability of rupture with an increase in the size of the macromolecules.

It is apparent from the foregoing that direct methods of measuring molecular weight have not been used to study the instability of polymer solutions under the influence of turbulent flows, so there is no convincing proof of degradation. At the same time, other physicochemical transformations besides degradation may occur up to phase separation in polymer solutions under the influence of a hydrodynamic field [17, 18].

The goal of the present work is to study the nature of the instability of aqueous solutions of hydrolyzed polyacrylamide in a hydrodynamic field.

The object chosen for study was a commercial sample of linear polyacrylamide (PAA) with a molecular weight $M_{SD} = 4.5 \cdot 10^6$ as determined by sedimentation and a degree of hydrolysis of 26%. The solutions were prepared in distilled water, while the hydrogen ion index of the medium pH was changed by adding hydrochloric acid and caustic soda. Here, the ionic strength was not kept constant. The hydrodynamic resistance coefficient was determined on an open-

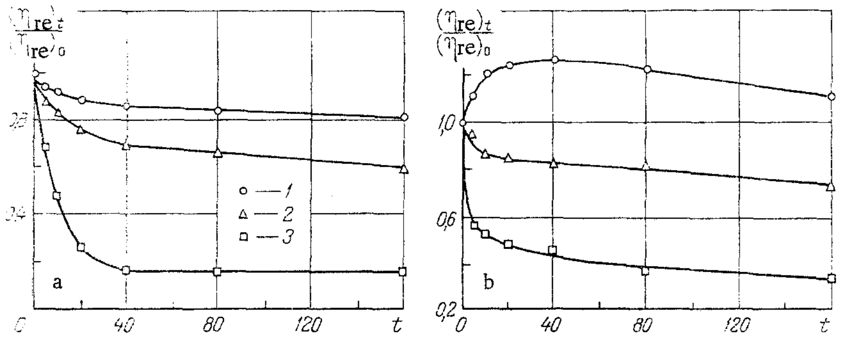

Fig. 3. Dependence of the ratio of the reduced viscosities $(\eta_{re})_t/(\eta_{re})_0$ of solutions of PAA on mixing time t (min) (a – $C_p = 0.005\%$; b – 0.01%, T = 303°K): 1) pH ≈ 7; 2) ≈ 12; 3) ≈ 3.

type unit with an automatic system to record discharge time [16]. The PAA solutions were subjected to high-speed mixing in a thermostatted chamber at 30°C by means of a four-paddle mixer of $50 \cdot 10^{-3}$ m diameter rotating at a speed of 2100 rpm. The viscosity of the solutions was measured on a VPZh-1 viscometer with a capillary-tube diameter of $0.34 \cdot 10^{-3}$ m.

Hydrolyzed PAA is a polyelectrolyte, which allowed us to change the conformation of the macromolecules by varying the pH of the medium. The relative change in the dimensions of the macromolecules was judged from the reduced viscosity η_{re} of a dilute solution, since the characteristic viscosity could not be determined due to polyelectrolytic effects with nonisoionic dilution. It is apparent from Fig. 1 that the smallest molecules of the investigated PAA were present in the acid medium. An increase in pH was accompanied by an increase in the number of ionized carboxyl groups, and the macromolecules increased in size as a result of electrostatic interactions. At large pH, charged carboxyl groups were shielded by counterions of sodium, and the macromolecules decreased somewhat in size. The hydrodynamic efficiency of hydrolyzed PAA correlates qualitatively well with the sizes of the macromolecules. The instability of aqueous solutions of PAA with different pH was manifest in a change in their hydrodynamic efficiency during repeated runs through the channel. It is apparent from Fig. 2 that all of the solutions lost their efficiency, but the rate of change in efficiency depended heavily on the pH. The phenomenon of a reduction in hydrodynamic resistance diminished most rapidly at low pH and most slowly at pH close to neutral. The empirical data obtained conflicts with the assumption of degradation of the polymer molecules. Such degradation should be manifest to a greater degree, the larger the macromolecules.

The investigated solutions had a concentration of 0.0005%, i.e., they were extremely dilute. This prevented us from using other methods of study that would have allowed us to determine the presence or absence of degradation.

Concentration was subsequently increased, and instead of multiple runs through the channel the solutions were subjected to high-speed mixing. Figure 3a shows the dependence of reduced viscosity, numbered according to the reduced viscosity of the initial solution, on mixing time for solutions with different pH. The dependences agree with the dependences of hydrodynamic efficiency on the number of runs through the channel shown in Fig. 2 at a PAA concentration of 0.005%. The most stable solutions were also those with a pH close to neutral, in which the macromolecules were of maximum size. Acid solutions with a pH on the order of 3, where the macromolecules were of minimum size, proved to be the least stable.

Apart from these results, indirect proof that degradation is not responsible for instability of polymer solutions in a hydrodynamic field is the data shown in Fig. 3b. In a PAA solution with $C_p = 0.01\%$ and neutral pH, the reduced viscosity first increases and then passes through a maximum after mixing for 30 min. It then gradually decreases. The value of η_{re} decreases continuously in the acid and alkali solutions but it decreases more slowly than in the solution with $C_p = 0.005\%$.

To confirm that the increase in viscosity was not due to final dissolution of the polymer after the beginning of the treatment, we recorded the dependence of viscosity on time of

TABLE 1. Values of Molecular Weight and Rms Radius of Gyration Obtained from Data on Light Scattering in Initial Solutions and Solutions Subjected to High-Speed Mixing for 160 min

Solutions	Series of measurements			
	1st		2nd	
	$M_w \cdot 10^{-6}$	$(\overline{R^2})^{1/2}$, Å	$M_w \cdot 10^{-6}$	$(\overline{R^2})^{1/2}$, Å
Initial	3,7±0,5	620±100	3,3±0,5	550±100
Treated (mixed)	6,5±0,7	1100±150	25,0±3,0	1550±150
Ratios of values of M_W and $(\overline{R^2})^{1/2}$ in treated solutions to their values in the initial solutions	1,8	1,8	7,6	2,8

storage of the initial solution and of solutions treated for 10 and 160 min. The constancy of the viscosity of the initial solution over 15 days provided evidence of the complete dissolution of the polymer. The viscosity of the treated solutions decreased somewhat over the first three days and then remained nearly constant and greater than the viscosity of the initial solution. It follows from this that the change in molecular parameters achieved during high-speed mixing was sufficiently stable, and the solution did not relax back to the initial state.

Solutions of PAA with concentrations equal to and less than 0.01% remained optically transparent after mixing for 160 min. At the same time, treatment of acid solutions of a higher concentration (C_p = 0.1%, pH = 3.2) caused a small amount of polymer to come out of solution. This was also seen in [17]. The process was irreversible, and the supermolecular particles formed did not dissolve after cessation of the action, dilution with alkali, or an increase in temperature. Thus, the solubility of the polymer deteriorated under the influence of the hydrodynamic field rather than improving, which should occur with a decrease in the molecular weight as a result of degradation.

The use of such absolute methods of determining molecular weight as sedimentation, along with diffusion or light scattering, are associated with serious empirical difficulties when used to study the effect of a hydrodynamic field on molecular parameters: Low concentrations of the initial solutions, the formation of aggregates, etc. Nevertheless, it proved useful to conduct a comparative study of light scattering by solutions before and after action by the hydrodynamic field.

Light scattering was measured on a Sofica photogoniodiffusiometer at a wavelength of 546 nm (calibration on benzene $R^{ve} = 2.32$ cm^{-1}) in the angle range 40-150° by a standard method [19]. The initial concentrations of the initial solutions were 0.01%, with pH = 3.05. We also studied solutions with a change in η_{re} (curve 3 in Fig. 3b). In determining the rms radius of gyration of the macromolecules $(\overline{R^2})^{1/2}$, due to the large value of the argument of the function $P(\theta)$ we introduced a 3/2 correction for the ratio of the initial inclination to the asymptotic value. However, it must be kept in mind that the actual form of the molecular weight distribution of the investigated sample was not determined.

The empirical data for the initial solution was analyzed by the Zimm method, and we obtained values of M_W and $(\overline{R^2})^{1/2}$ which agreed well with the values of these quantities obtained by hydrodynamic methods (see Table 1). The scattering function of the solution subjected to a hydrodynamic field was also analyzed by the Zimm method. It differed little from the function of the initial solution for scattering angles of 90° or more (scattering intensity increased by 10-20%), while in the range of angles less than 60° scattering intensity increased quite substantially (on the order of 60-70%). Such a change was typical of the molecular solutions when most of the polymer had not altered its molecular characteristics but a small quantity of coarse particles (aggregates) had formed in the solution and distorted the form of the scattering function at low angles [20, 21]. Averaged values of M_W are shown in Table 1 to emphasize the presence of processes involving the formation of new particles in the solution. The light scattering data cannot be used to make any conclusion regarding the degradation of the polymer in a hydrodynamic field.

This conclusion is supported by experiments involving dynamic birefringence in a flow that were performed by a standard method [22]. As was shown earlier [18], a dynamic field affects the optical and hydrodynamic properties of the macromolecules in solution. After the action of a shifted mechanical field (gradients of $3 \cdot 10^3$-10^4 sec^{-1}) for 30-60 min on solutions of hydrolyzed PAA with a concentration of 0.03-0.05% and pH = 3, the corrected viscosity decreased by a factor of 1.5-2.0 and the Maxwell constant [n] increased by a factor of 5-10. The data obtained cannot be explained by degradation of macromolecules, since this would lead to a decrease in [n].

All of the above experimental data is of an averaged character, but it nonetheless shows that degradation is not the determining factor in the instability of solutions of hydrolyzed PAA in a hydrodynamic field.

Proceeding on the basis of [14, 15, 17], it seems more likely that the thermodynamic affinity of a polymer to a solvent decreases under the influence of a hydrodynamic field. The reduction in affinity facilitates the formation of intra- and intermolecular polymer–polymer bonds. This, in turn, leads to freezing of the conformation and a reduction in the size of individual macromolecules, as well as their aggregates. The closer the solution is to the point of phase separation (in the system studied, this corresponds to a decrease in pH), the greater the effect of the hydrodynamic field. In solutions of sufficiently high concentration, these transformations end in the formation of relatively coarse aggregates incapable of being kept in solution, i.e., the transformations end in phase separation.

In contrast to the reversible phase separation which occurs under static conditions, the processes taking place under the influence of the hydrodynamic field are irreversible. This fact is probably connected with important differences in the nature of the interactions. This subject is not addressed here. The complex changes that occur in the parameters of polymer solutions in a hydrodynamic field require further investigation.

NOTATION

η_{re}, reduced viscosity; τ_w, wall shear stress; C_p, polymer concentration; n, number of runs through channel; λ, coefficient of hydrodynamic resistance; t, time of mixing of solution; T, temperature; pH, hydrogen-ion index of medium; M_w, weighted-mean molecular weight; M_{SD}, molecular weight determined from sedimentation; $(\bar{R^2})^{1/2}$, rms radius of gyration; [n], dynamooptical Maxwell constant.

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EQUATIONS OF MOTION OF CONCENTRATED POLYMER SOLUTIONS

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We establish a very simple system of controlling equations to describe the motion of viscoelastic media.

1. The problem of the equations of motion of concentrated polymer solutions to describe the motion of systems exhibiting viscoelastic properties has not been completely solved; there are differences of opinion with regard to the form of the nonlinear controlling equation [1]. Since there is no general form of the rheological relation for all viscoelastic systems, research is necessary based on structural concepts and relating the nonlinear behavior of concentrated solutions to the characteristics of the behavior of macromolecules in the system (deformability, kinetic, rigidity, etc.) taken into account in one form or another. A simple approach to the description of the motion of concentrated solutions based on an analysis of the behavior of dumbbells in a viscous medium is the simplest model of a structural element of the system [2]. When internal viscosity is taken into account, the controlling relations include the stress tensor σ_{ik} expressed in terms of the moments of the distribution function, and a system of equations for the moments [2], which is generally not closed:

$$\sigma_{ik} = -p\delta_{ik} + 2\eta_E \gamma_{ik} + \frac{1}{2} n\zeta \left[\frac{1}{\tau'} \left(\langle \rho_i \rho_k) - \frac{3}{4\mu} \langle e_s e_k \rangle \right) + \frac{1}{\tau_D} \frac{3}{4\mu} \left(\langle e_i e_k \rangle - \frac{1}{3} \delta_{ik} \right) + \frac{2\lambda}{\lambda + \zeta} \langle \rho_i \rho_k e_j e_s \rangle \gamma_{js} \right], \quad (1)$$

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