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THE EFFECT OF THE CONFORMATION OF MACROMOLECULES ON THE HYDRODYNAMIC EFFECTIVENESS OF POLYACRYLAMIDE

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It was experimentally discovered that when the dimensions and the asymmetry of macromolecules are increased, their hydrodynamic effectiveness and stability improve.

The search for materials and the necessity of studying the molecular aspects of the phenomenon of reducing turbulent drag by additions of polymers are decisive for the interest in investigations of the effect of the conformation (dimensions and shape) and pliability of macromolecules on their hydrodynamic effectiveness and stability.

For most authors working in this field the objects of investigations were synthetic polyelectrolytes, viz., polyacrylic acid and hydrolyzed polyacrylamide (PAA); the conformation of their macromolecules can be easily changed by changing the hydrogen ion indicator pH of the solution [1-8] and by the quality of the solvent [9, 10]. However, the study of separate specimens of the mentioned polymers did not make it possible to trace the effect of the conformation on the hydrodynamic effectiveness of macromolecules with the same degree of polymerization upon transition from neutral to polyelectrolytic ones. Such an attempt was made in [11] but only in the region of neutral pH values.

Apart from some contradictory data in [1, 3], most authors note that the maximal effect in reducing the resistance is attained in the region of neutral and weakly alkaline pH values where the macromolecules of polyelectrolytes are in a bulking, extended state [2, 4, 5, 7, 8].

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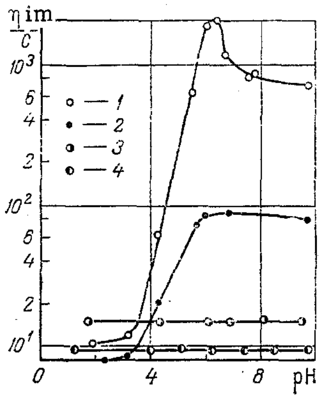

Fig. 1

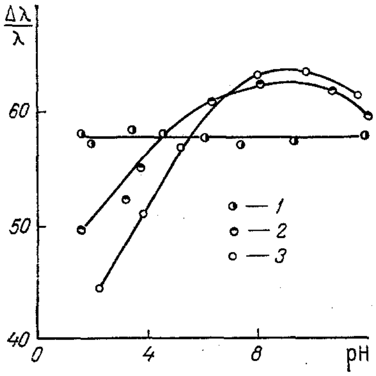

Fig. 2

Fig. 1. Effect of pH on the reduced viscosity η_{im}/C, dl/g, of aqueous solutions of PAA ($C_p = 0.005\%$, $T = 303°K$): 1 and 2) PAA-17; 3 and 4) PAA-0; 1 and 3) $\tau \approx 0$; 2 and 4) $\tau = 2.5$ Pa.

Fig. 2. Dependence of the effect of reduced hydrodynamic resistance $\Delta\lambda/\lambda$, %, on pH ($C_p = 0.0004\%$, $T = 293°K$, $\tau = 33$ Pa): 1) PAA-0; 2) PAA-12; 3) PAA-17.

It is obvious that changes in the conformation of macromolecules are bound to manifest themselves in the stability of their hydrodynamic effectiveness to the action of shear stresses. This was confirmed by data of [7, 8] where it was established that the molecules of hydrolyzed polyacrylamide are stablest in neutral medium. The decrease in size of macromolecules upon lowering of pH was accompanied by more rapid loss of their ability to reduce turbulent drag.

The object of the present work is to study the effect of the conformation of macromolecules of polyacrylamides with different degree of hydrolysis on their ability to reduce turbulent drag on their stability to the action of a hydrodynamic field.

We investigated three laboratory specimens of PAA synthesized at the institute IVS of the Academy of Sciences of the USSR. The initial nonhydrolyzed polyacrylamide PAA-0 had a characteristic viscosity of 15 dl/g; this was determined by a capillary viscometer. The other two specimens were obtained by hydrolysis of PAA-0 in 0.5 M solution of NaOH at 40°C. Henceforth they will be designated PAA-12 and PAA-17 because, according to the data of potentiometric titration, they have a degree of hydrolysis of 12.5 and 16.8%, respectively. The characteristic viscosities of these specimens, found in a solvent containing 0.01 M NaOH and 10% NaCl for suppressing the polyelectrolyic effects, were equal to 14.7 dl/g. Such a negligible difference between this and the characteristic viscosity of PAA-0 indicates that the degree of polymerization did not change during hydrolysis. According to the dependence $[\eta] = 9.8 \cdot 10^{-5} M^{0.76}$ from [12], the investigated PAA had a molecular mass of the order $6 \cdot 10^6$.

The solutions were made with distilled water, and to change the pH, we added hydrochloric acid and sodium hydroxide. The ionic strength was not maintained constant. The pH of the solutions was determined with an instrument pH-121. Viscosity was measured with a viscometer VPZh-2 with $0.56 \cdot 10^{-3}$ m diameter of the capillary and on a Zimm-Krosers viscometer at slip velocities $\gamma < 1$ sec^{-1}. The resistance coefficient was determined on an open-type installation with a system for the automatic recording of the time of discharge of the solution [13]. During the viscometric and hydrodynamic experiments the temperature was maintained constant with an accuracy of ±0.1°C by an ultrathermostat UT-15.

The dependences of the reduced viscosity η_{im}/C of the solutions of PAA-0 and PAA-17 on the pH obtained with different shear stresses τ are presented in Fig. 1. The reduced viscosity of nonhydrolyzed PAA-0 remained constant when pH changed from 1.5 to 10.0. With pH > 10.0 viscometric measurements were not carried out because of the hydrolysis of PAA-0 in the process of preparing the solutions and carrying out the experiment. Increasing τ from 0 to 2.5 Pa caused the η_{im}/C of the solution of PAA-0 to decrease from 16.0 to 9.6 dl/g with all pH values.

The reduced viscosity of the solution of PAA-17 with $\tau \approx 0$ in an acid medium is of less importance than the η_{im}/C of the solution of PAA-0. An increase of pH and the attendant decrease of ionic strength lead to an abrupt increase of η_{im}/C (by more than two orders of magnitude) and to the maximal value being attained in distilled water. When sodium hydroxide

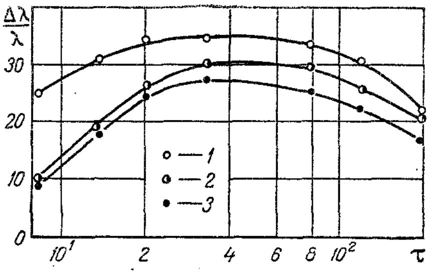

Fig. 3. Dependence of the effect of reduced hydrodynamic resistance $\Delta\lambda/\lambda$, %, on the frictional stress τ, Pa (C_p = 0.0002%, T = 293°K): 1) PAA-17, pH $\approx$ 7 and 12; 2) PAA-0, pH $\approx$ 2, 7, and 12; 3) PAA-17, pH $\approx$ 2.

is added, it causes the reduced viscosity to decrease. An increase of the shear stress to 2.5 Pa greatly reduces the viscosity of the solution of PAA-17, especially in the region of neutral and alkaline pH values. The maximal value of η_{im}/C decreases from 2000 to 90 d*l*/g.

The corresponding dependence of the reduced viscosity of the solution of PAA-12 with the same concentration takes up an intermediate position.

Before we discuss the presented data, we have to recall some information on the effect of conformation and pliability of polyelectrolyte molecules on the viscosity of their solutions. In his monograph Tanford [14] analyzed the theory and the experimental data on viscosmetry and scattering of light that have a bearing on the effect of the degree of ionization of macromolecules of pliable-chain polyelectrolytes on their conformation. He showed that the macromolecules unfold and become more asymmetrical when the number of charges with the same sign on the polymer chain increases. The free electrostatic energy attains its minimal value when the polyion becomes rod-shaped; however, in practice this is not attained.

Tsvetkov et al. [15] established that the transition of molecules from the rigid extended shape to a convolute and much more symmetrical shape is accompanied by a decrease of the absolute viscosity of the solution, and in addition by the practical disappearance of its gradient dependence.

Taking the results of these authors into account and also the fact that the reduced viscosity of dilute solutions is determined by the shape and the dimensions of the macromolecules, we are entitled to the following assumption concerning changes in conformation of the macromolecules of the investigated PAA when the pH of the medium is changed.

The molecules of PAA-0 have the conformation of an extended statistical coil characteristic of molecules of uncharged linear polymers with pliable chains in good solvents [15]. That there is some asymmetry of their shape is indicated by the decrease of η_{im}/C when the shear stress is increased since it is improbable that there will be noticeable deformation with such small values of τ. When pH changes from 1.5 to 10.0, the conformation of macromolecules of PAA-0 does not change.

In distinction to the molecules of nonhydrolyzed PAA-0, the molecules of PAA-17 change their shape and dimensions substantially when the pH changes. In distilled water, which corresponds to pH = 6.1, the carboxyls are in an ionized state, and between the negative charges situated along the chain there act electrostatic repellent forces. This leads to a great increase of the dimensions of the macromolecules, which is indicated by the maximal value of η_{im}/C, and to asymmetry of the shape. This is confirmed by the abrupt decrease of reduced viscosity when the shear strain increases imperceptibly. Increased concentration of NaOH leads to shielding of the charged carboxyls by sodium ions and to reduced dimensions and asymmetry of the macromolecules.

Transition from neutral to acid pH causes suppression of the dissociation of the carboxyls and a reduction of the number of charges with equal sign on the polymer chain. As a result of this the conformation of the macromolecules of hydrolyzed PAA approaches the conformation of nonhydrolyzed PAA. However, with sufficiently low values of pH, the dimensions of the molecules of PAA-17 do not only become equal, but even smaller than those of the molecules of PAA-0. This has to do with the quality of the solvent becoming poorer and with the formation

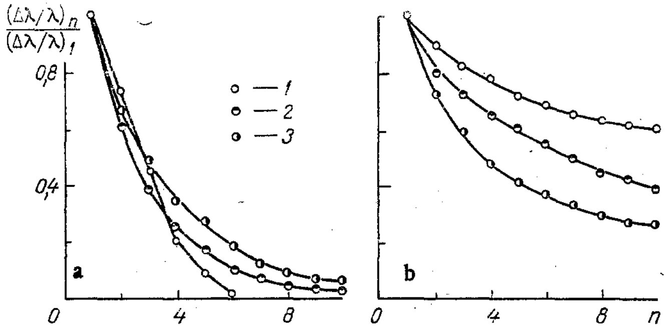

Fig. 4. Dependence of the ratio of hydrodynamic effectiveness in the n-th run to the effectiveness in the 1st run $(\Delta\lambda/\lambda)_n/(\Delta\lambda/\lambda)_1$ on the number of runs ($C_p = 0.0004\%$, $\tau = 33$ Pa, T = 293°K; 1) PAA-17, 2) PAA-12, 3) PAA-0); a) pH $\approx$ 2; b) pH $\approx$ 7.

of intramolecular hydrogen bonds between the amidic and the noncharged carboxyls [16]. With a sufficiently high degree of hydrolysis (more than 25%) such interaction leads to stratification of the solution when $\text{pH} < 2.8$ [17]. It can be seen from Fig. 2 that changes of the conformation of the macromolecules of PAA have an influence on their hydrodynamic effectiveness. Thus the ability of PAA-0 to reduce turbulent drag, as well as the conformation of its macromolecules do not depend on the pH of the solution. With hydrolyzed PAA-17 the dependence of the hydrodynamic effectiveness on pH is satisfactorily correlated with the corresponding dependence of reduced viscosity obtained for $\tau = 2.5$ Pa. The general nature of these dependences is analogous but the maxima of $\Delta\lambda/\lambda$ and η_{im}/C are found with different pH values.

A comparison of the effectiveness of specimens with different degree of hydrolysis enables us to make the following remarks. With equal degree of polymerization, the most effective macromolecules were those with the conformation of an extended asymmetric coil which is assumed by molecules of hydrolyzed PAA in neutral or alkaline media. Somewhat inferior to it is the conformation of the statistical coil which is characteristic of molecules of nonhydrolyzed PAA for all pH values. Least effective are constricted molecules of PAA-17 in an acid medium whose conformation is stabilized by hydrogen bonds.

Intramolecular interactions in the form of electrostatic forces and hydrogen bonds change the dimensions and shape of the macromolecules, and in addition they also change their ability to become deformed under the effect of a hydrodynamic field. Since the reduction of hydrodynamic resistance takes place in turbulent flow with sufficiently large frictional stresses on the wall, where deformation of the macromolecules is possible, we studied the effect of τ on $\Delta\lambda/\lambda$ of molecules with different conformations.

The results presented in Fig. 3 indicate that with all the frictional stresses the constricted and badly deformable molecules of PAA-17 in acid medium have the smallest ability of reducing hydrodynamic resistance. The most effective molecules were the extended asymmetrical molecules of PAA-17 in neutral and alkaline media. With low τ the molecules of PAA-0, having the conformation of a statistical coil, are somewhat more effective than molecules of PAA-17 in an acid medium; however, with increasing τ their effectiveness approaches the effectiveness of extended and asymmetrical molecules of PAA-17. Such behavior can be explained by the fact that with low pH, the molecules of PAA-17 are badly deformable on account of the intramolecular hydrogen bonds, and with high pH on account of electrostatic interaction. The pliable coils of PAA-0 become deformed when the shear strains in a hydrodynamic field increase, and their hydrodynamic effectiveness approaches the effectiveness of asymmetrical molecules of PAA-17 in the ionized state. The decrease of $\Delta\lambda/\lambda$ after some value of τ has been attained is obviously connected with the considerable instability of the solutions of high-molecular polymers with large frictional stresses since in low-molecular specimens of PAA we find increased effectiveness when τ changes from 9 to 200 Pa.

The solutions were regarded as unstable on account of the change of the effect of decreasing hydrodynamic resistance upon repeated runs through the channel. It can be seen from Fig. 4a that in the range of acid pH values the hydrodynamic effectiveness of nonhydrolyzed PAA-0 decreases most slowly although with pH = 2 its macromolecules have larger dimensions than the macromolecules of hydrolyzed PAA. The specimen of PAA-17 whose macromolecules had the smallest dimensions was least stable under these conditions, and PAA-12 occupied an intermediate position. It can be seen from Fig. 4b that in a neutral medium the corresponding dependences for PAA-0 and PAA-17 change in places; however, unchanging is and remains the fact that with equal degree of polymerization, macromolecules with the largest dimensions are stabler in a hydrodynamic field; this was also noted in [11, 13, 18].

NOTATION

$\Delta\lambda/\lambda$, magnitude of the effect of reducing hydrodynamic resistance; τ, shear stress on the wall; pH, hydrogen ion indicator; η_{im}/C, reduced viscosity; γ, slip velocity; n, number of runs of solutions through the channel; C_p, polymer concentration; T, Kelvin temperature.

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