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RELAXATION TIME OF ELASTIC STRESSES IN LIQUIDS WITH SMALL ADDITIONS OF SOLUBLE POLYMERS OF HIGH MOLECULAR WEIGHTS

V. N. Kalashnikov, A. N. Askarov

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Measurements have been made of the characteristic times of dilute solutions of polyethylene oxide in water and of polyisobutylene in kerosene. Considerable deviations are observed between the experimental data and the predictions of the theories assuming complete distribution of the macromolecules in the solution.

Solutions of polymers of high molecular weights possess distinct viscoelastic properties even at extremely small concentrations of the dissolved material. These properties lead to a number of dramatic hydrodynamic effects, many of which are of practical value. In this connection, the reduction of the hydrodynamic resistance and heat transfer during flow in tubes and in external flows around solids and the increase in the filtrational resistance in porous media are quite well known.

Investigators of this area of hydromechanics have found considerable difficulties in the way of obtaining generalizations of the behavior which arise from the absence of quantitative methods of measuring the elasticities of polymer solutions of low concentrations. The known methods for the experimental determination of the elastic characteristics based on the linear response of the medium are not sufficiently sensitive. The minimum concentration of solutions whose elasticities can be investigated by these methods is 0.1%.

The difficulties can be surmounted to a certain extent if nonlinear effects are used. Among these methods there has been developed [1, 2] a relative method for determining characteristic times (the times of relaxation of the elastic stresses at small perturbation frequencies) which is applicable to solutions with polymer concentrations starting at a few parts per million. It is based on the transition from the laminar flow regime to the regime of elastic turbulence in channels of varying cross section.

In the present work measurements have been carried out by this method of the characteristic times of aqueous solutions of polyethylene oxide (PEO) and of solutions of polyisobutylene (PIB) in kerosene. The investigation of the elastic properties of the PEO solutions has been carried out in particular detail. In this case, the concentration and temperature of the solution and the molecular weight of the polymer have been varied. Industrial samples of PEO of domestic manufacture have been used, as well as samples manufactured by the firms Union Carbide (USA) and Meisei (Japan). Dissolution was carried out in distilled water. The molecular weight of the polymer was not varied in the investigations of the PIB solutions. The domestic industrial polymer P-200 was used, with technical-grade kerosene as the solvent.

The characteristic time was measured by using a collection of geometrically similar channels previously investigated in [1] which had square cross sections which varied peri-

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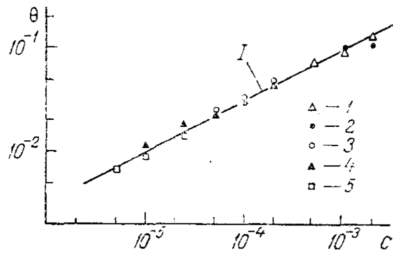

Fig. 1

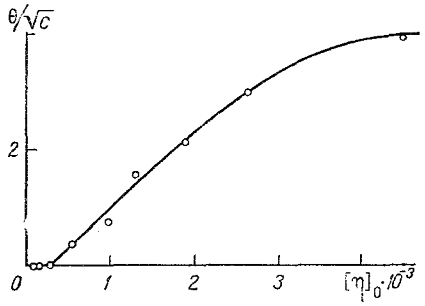

Fig. 2

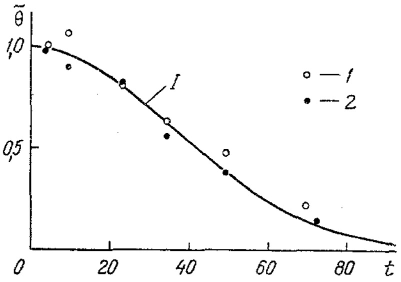

Fig. 3

Fig. 1. Concentration dependence of the characteristic time of aqueous solutions of PEO of $[\eta]_0$ = 2650 at 23.9°C for the following channels: 1) a = 2.8 mm; 2) a = 2.0 mm; 3) a = 0.97 mm; 4) a= 0.58 mm; 5) a= 0.42 mm. The curve I is expressed by $\theta/\sqrt{c} = 3.1$, with θ in seconds; c is dimensionless.

Fig. 2. Effect of the value of the characteristic viscosity on the elastic properties of aqueous solutions of PEO at 23.9°C. $[\eta]_0$ is dimensionless.

Fig. 3. Effect of temperature on the elastic properties of aqueous PEO solutions; $\tilde{\theta} = \theta(1.82 \cdot 10^{-3}[\eta]_0 - 2.9 \cdot 10^{-11}[\eta]_0^3 - 0.51)^{-1}\sec^{-1/2}$; $[\eta]_0$ = 550 (points 1), or $[\eta]_0$ = 2650 (points 2); curve I is given by $\tilde{\theta} = \exp(-4 \cdot 10^{-4} t^2)$. $\tilde{\theta}$ is given in seconds and t in °C.

odically over the length of the channel. The sides of the squares at the narrow cross sections of the various channels were a = 0.42, 0.58, 0.97, 2.0, and 2.8 mm. The flow of solution was supplied from a head tank. The reservoir and feed line were fitted with jackets through which a thermostating liquid was circulated. In order to avoid the effects of evaporation the experiments were carried out with only one passage of the solution through the channel. The pressure drop in the channel was determined by means of a piezometer, and the flow rate was determined by the volumetric method.

The transition to the regime of elastic turbulence was determined by the deviation of the resistance curve from the laminar behavior. This made it possible to determine the mean velocity in the narrow cross section corresponding to the transition. The characteristic time was calculated from this velocity and the known dimensions of the channel. In the calculations use was made of the critical value of the Weissenberg number equal to 4.7, which was found in [1].

Measurements were made of the characteristic viscosities of the solutions at small shear rates. For this purpose a viscometer of the Zimm–Crothers type [3] was fabricated with various rates of rotation of the rotor. The attainment of the limiting value was determined from the disappearance of the dependence of the reduced viscosity on the shear rate on moving to slower rotor speeds and on the concentration on moving to more dilute solutions.

The experiments showed that the value of the characteristic time for both the PEO and the PIB solutions increased in proportion to the square root of the concentrations. The $\theta \sim \sqrt{c}$ proportionality occured over quite a wide range of concentrations. As can be seen from Fig. 1, for PEO in water this proportionality exists over a range of almost three orders of magnitude for the concentration.

The dependence of the characteristic time on the molecular weight is of a threshold nature for dilute solutions. At small molecular weights no significant elastic properties are observed in the solutions. The flow of such solutions along channels of variable cross section does not differ from the flow of Newtonian fluids. The elastic properties only appear starting with some critical value of M. With further increase of the molecular weight but otherwise unchanged conditions the characteristic time increases. For aqueous solutions of PEO this is illustrated in Fig. 2, in which the quantity $\theta/\sqrt{c}$ is plotted as a function of the characteristic viscosity $[\eta]_0 = \lim\limits_{c\to 0}(\eta_0 - \eta_S)/c\eta_S$. Elasticity of the solutions whose concentrations satisfy the condition $c[\eta]_0 < 1$ appears when $[\eta]_0 = 280$. The relationship $[\eta]_0 = 1.25\cdot 10^{-2}\ M^{0.78}$, which was found to be valid for solutions of PEO in water [4], gives the possibility of determining the value of the critical molecular weight. This is found to be $3.78\cdot 10^5$.

A strong dependence of the characteristic time on the temperature is observed. As the temperature increases the value of θ decreases noticeably.

The empirical relationship for the characteristic times of aqueous solutions of PEO for $[\eta]_0 > 280$ can be represented in the form

$$\theta = (1{,}82\cdot 10^{-3}[\eta]_0 - 2{,}9\cdot 10^{-11}[\eta]_0^3 - 0{,}51)\exp(-4\cdot 10^{-4}t^2)\sqrt{c}, \tag{1}$$

where t is given in °C, θ is given in seconds, and c and $[\eta]_0$ are dimensionless. The solid lines in Figs. 1 and 2 and also in Fig. 3, which indicate the temperature dependence of θ, correspond to this relationship.

The value of the characteristic viscosity of the PIB investigated in kerosene was $[\eta]_0 = 930$. For these solutions the value of $\theta/\sqrt{c}$ were 0.92, 0.55, and 0.38 at the temperatures 23.5, 37, and 65.5°C, respectively.

It is interesting to compare the data which have been obtained with the results of the existing theories of the viscoelasticity of polymer solutions. As a rule, if their concentrations are sufficiently small ($c[\eta]_0 < 1$), these solutions are regarded as true molecular solutions in which the polymeric material is broken down into individual isolated macromolecules. It is assumed that as a result of the flexibility of the linear polymeric chains they form macromolecular clusters in the solution. A statistical consideration leads to the concept of an elasticity of the polymer network in the solution. The viscoelastic properties of the solution as a continuum arise as a result of the elasticity of the individual clusters.

Various models of the macromolecules have been considered for calculating the viscoelastic properties of true polymer solutions. The final results differ only slightly from one another both in terms of the structure of the final relationships and also in terms of the order of magnitude of the predicted viscoelastic characteristics.

The bead model has been widely used, in which the macromolecular chain is represented as a succession of spheres connected by springs. According to the assumptions of Kargin and Slonimskii a unit of the necklace of beads is taken to mean a quite long sequence of monomer units (subchain). The viscous resistance during motion of the subchain is replaced by the viscous resistance of the sphere, and the elasticity of the subchain is replaced by the elasticity of the spring. This model was considered in detail by Raus [5] with the assumptions that there were no hydrodynamic interactions between the spheres and that $c[\eta]_0 \ll 1$; he obtained the following relationships for the dynamic viscosity and the modulus of the solution:

$$\begin{gathered}\eta'(\omega) = \eta_s + \frac{c\rho_s RT\tau}{M}\sum_{p=1}^{N}\frac{p^2}{p^4+\omega^2\tau^2},\\ G'(\omega) = \frac{c\rho_s RT\tau^2\omega^2}{M}\sum_{p=1}^{N}\frac{1}{p^4+\omega^2\tau^2}.\end{gathered} \tag{2}$$

Here τ is the maximum time of relaxation for deformation of the chain:

$$\tau = \frac{6\nu_s [\eta]_0 M}{\pi^2 RT}. \tag{3}$$

The characteristic time of the polymer solution can then be found if it is remembered that

$$\theta = \lim_{\omega \to 0} \frac{G'}{\omega^2 \eta'}. \tag{4}$$

Let us now consider two cases: a case where the number of subchains is quite large (large value of N), when it is possible to go to an infinite series in Eq. (2), and the case of an "elastic dumbbell," N = 1.

When $N \to \infty$ and the condition $c[\eta]_0 \ll 1$ is taken into account, it is found that

$$\theta = \frac{\pi^2}{15} c [\eta]_0 \tau = \frac{2}{5} \frac{\nu_s [\eta]_0^2 M}{RT} c. \tag{5}$$

For the "elastic dumbbell,"

$$\theta = \frac{6}{\pi^2} c [\eta]_0 \tau = \frac{36}{\pi^4} \frac{\nu_s [\eta]_0^2 M}{RT} c. \tag{6}$$

From a comparison of the last two relationships it can be concluded that the number of separate subchains has only a small effect on the theoretical value of the characteristic time. The difference between the numerical coefficients in Eqs. (5) and (6) is only ~8%.

A relationship $\theta \sim c[\eta]_0\tau$ with a proportionality constant close to unity can be obtained [6] if the macromolecular cluster is regarded in a simplified way as homogeneous elastic sphere, the modulus of elasticity is determined from statistical considerations, and the theory of Frölich and Sack is used for a suspension of such spheres. An analogous result for θ with a coefficient which is similar in order of magnitude is obtained if the calculation is based on the results of Zimm's theory, in which (in contrast to the theory of Raus) allowance is made for the hydrodynamic interactions in the macromolecules.

The differences between the predictions of the molecular theories and the results of the experiments are obvious. As the experiments have shown, the value of θ is proportional to $\sqrt{c}$, and not to c. The dependence of θ on the temperature and the characteristic viscosity is also different. The theory does not give a threshold-type dependence of the characteristic time on the molecular weight (characteristic viscosity) which is observed in the experiments. The discrepancy occurs in the concentration range in which the condition of diluteness, $c[\eta]_0 \ll 1$, is known to be satisfied. It is precisely in this range that the difference between the theoretical and experimental values of θ is most striking. Thus, for a PEO solution with $[\eta]_0 = 2650$, a concentration of $c = 5 \cdot 10^{-6}$, and a temperature of 23.9°C, the measured value of θ is $6.8 \cdot 10^{-3}$ sec, while according to Eq. (5) a value of $3.5 \cdot 10^{-5}$ sec is obtained.

The absence of agreement between the conclusions of the theory and the results of the experiments indicates that the model of a true molecular solution is inapplicable in the present case. It is necessary to assume that interactions occur between the macromolecules in solution, which in view of the smallness of the concentration cannot be of a hydrodynamic nature or be based on the simple tangling of the macromolecular chains. The set of experimental data provides a basis for assuming that equilibrium supermolecular structures arise in the solutions being investigated as a result of physical attraction forces.

A supermolecular organization of the solutions, and in particular, their network structure, has been discussed more than once in connection with the considerable hydrodynamic activity of small quantities of polymer additives. A network of fibrils of the polymer material has been observed by many investigators during the microscopic study of samples taken from the dilute solutions [7-11]. Some of the data on light scattering [12] indicates the existence of networks of interacting clusters in solutions of polymers of high molecular weights at very small concentrations.

It can be assumed that as long as their molecular weight exceeds the critical value, the macromolecules of the polymer acquire as a result of intermolecular attraction the ability to form fibrils in the solution of chains lined up in parallel. From these fibrils a three-dimensional network is built up in the solution which extends over the entire volume. It is clear that the linkages between the macromolecules in the fibrils and between the fibrils in the network are quite weak, since they break down under the action of the small stresses generated by thermal fluctuations or shear, but then are formed anew between other partners. Such reversible aggregation of the macromolecules of the polymer obviously occurs at concentrations which are often regarded as being too small for this, in particular, at concentrations which satisfy the condition $c[\eta]_0 \approx 10^{-2}$, and possibly at even smaller concentrations. The fluctuating fibrillar network leads to elastic properties of the solution which significantly exceed the elastic properties predicted on the basis of models with discrete macromolecular clusters.

In conclusion it should be noted that our inference with respect to the inapplicability of theories based on the concepts of disconnected macromolecules in solutions of polymers of high molecular weights at considerable dilutions is not in agreement with the conclusions of the work carried out by Ferry, Schrag, and their coworkers [13, 14]. In the papers of these authors use was made of a compound multifrequency Birnbaum–Schrag resonator for investigating the viscoelastic properties of polymer solutions in the linear zone of behavior. Comparison of the data from the experiments with theory was carried out by extrapolation of the results obtained at relatively high polymer concentrations in the solution ($c[\eta]_0 > 1$) to the zone of low concentrations. As a rule, in doing this use is made of an extrapolation which is linear in concentration, based on the theory of true molecular solutions. Our own experiments have shown that such extrapolation is incorrect in the general use.

NOTATION

θ, characteristic time; a, side of square cross section of narrow parts of channel; c, mass concentration; M, molecular weight; η_s, dynamic viscosity of solvent; ν_s, kinematic viscosity of solvent; ρ_s, density of solvent; η_0, first Newtonian viscosity of solution; $[\eta]_0$, characteristic viscosity; T, absolute temperature; t, temperature, °C; R, universal gas constant; τ, maximum relaxation time for deformation of macromolecular chain; ω, angular frequency; N, number of subchains; η', real part of complex viscosity; G', real part of complex shear modulus.

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