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NONSTATIONARY FLOW OF SOLUTIONS OF FLEXIBLE-CHAIN POLYMERS IN A POROUS MEDIUM

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Aqueous solutions of polyethylene oxide have been studied under the conditions of nonstationary longitudinal flow. The investigations have confirmed the deviations from Darcy's law according to the mechanism the basis for which is provided by the concepts of a strong strain action of the hydrodynamic field on coiled macromolecules.

Experiments were conducted with the aim of elucidating the nature of the mechanism of an "abnormally" high degree of coverage of a porous bed with a polymer solution. The most contradictory opinions as to the nonlinearity of filtration flow of polymer solutions are being stated; most researchers believe that the nonlinearity is caused by the adsorption of macromolecules onto the porous-medium walls [1, 2]. There is an opinion that the deviations from Darcy's law are due to the elastic-strain effects manifesting themselves in the case of flow of solutions of flexible-chain polymers in a porous medium [3, 4]. Below, we will be dealing with experiments on checking the mechanism of an "abnormally" high degree of coverage of a porous bed with polymer solutions; the basis for this mechanism is provided by the concepts of a strong strain action of the hydrodynamic field on coiled macromolecules in filtration flow [5].

The mechanism of deviations from Darcy's law lies in the self-oscillating regime of reversible processes of unrolling of macromolecules under the action of the longitudinal velocity gradients quasiregularly arising in the porous medium and in the influence of unrolling macromolecules at both the molecular and supermolecular levels on the structure of the filtration flow. The oscillation of the strains of macromolecules and dynamic supermolecular formations arising under the action of stretching flows results in the higher-than-average energy dissipation and the flow nonlinearity. The latter ensures the equalization of the front of advance and filling of inhomogeneous laminar beds with polymer fluid and hence a wider coverage of the bed.

From the above mechanism of nonlinearity of the filtration of polymer solutions and from the theory of elastic-strain effects in the case of flow with extension of polymer solutions [3], it follows that the higher degree of coverage of a porous medium must be attained in nonstationary injection of a polymer solution into it. To substantiate this prediction we studied the aqueous solutions of polyethylene oxide (PEO) under the conditions of nonstationary longitudinal flow.

Results and Their Discussion. In realizing the model regime of injection of a solution into a porous medium (bed), the solution under study was forced through a flow chamber (module) under the action of a constant pressure difference (see Fig. 1). This is an unusual kind of viscosimeter in which the hydroresistors are short capillaries.

In the stationary regime, flow through the hydroresistors was carried out by creation of a pressure difference at the viscosimeter inlet and outlet, whereas in the nonstationary regime, it was carried out by superposition of a constant pressure difference and the pulsating pressure arising in the vessel between the capillaries due to the vibrations of the membrane of an electromagnetic vibrator. The amplitude of membrane vibrations was monitored by a special device. It was constant at different frequencies in each run of experiments and was selected such that the rate of flow (caused by the membrane vibrations) of the polymer solution through the capillaries was lower than the flow rate due to the constant pressure difference. The nonstationary component of the flow velocity in the capillaries that was caused by the pressure pulsations in the intercapillary volume was smaller than the flow velocity in the capillary due to the

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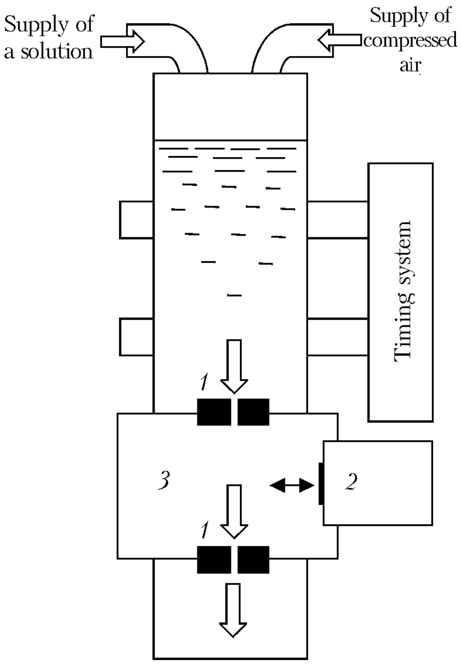

Fig. 1. Diagram of a viscosimetric unit: 1) short capillary; 2) electromagnetic vibrator; 3) zone of action of the vibrator.

constant pressure difference in the viscosimeter. The flow-rate velocity of the polymer solution through the capillaries was higher than the critical value [5]. The diameter of the capillaries was $0.2 \cdot 10^{-3}$ m.

The hydrodynamic efficiency of the polymer solutions under study was evaluated by the value of the efficient viscosity η_{ef}, which was determined by comparison of the flow-rate velocities of the solution under study and calibration viscous Newtonian fluids at the same pressure difference. The entire unit was placed in a thermostat, where the temperature of the solutions under study was monitored by an electronic heat controller.

The results of the experiment are presented in Fig. 2a, where η_{ef} is the effective viscosity of the solution under the conditions of stationary outflow and $\Delta\eta_{ef}$ is the addition resulting from the nonstationarity that appeared under the oscillating action on the mainstream flow. The curves correspond to different velocities of mainstream flow through the capillaries. It is seen that the critical frequency of action ω'_{cr} on the stationary flow exists; beginning with this frequency, flow becomes more dissipative.

The quantity ω'_{cr} grows with average flow-rate velocity, whereas $\Delta\eta_{ef}$ decreases. With lower concentrations of PEO in the solution and the same flow-rate velocity, the value of the critical frequency is higher.

When polymer systems (PEO solutions in our case) are strained, changes in the strains ε and the stresses σ occur in different phases [6]. The angle δ' characterizing this difference is a composite function of the frequency of actions ω'. Strain in this case is carried out under the action of the stress following the law

$$\sigma(t) = \sigma + \sigma_0 \exp(i\omega' t) . \tag{1}$$

Taking into account that $\sigma(t) = \sigma_0 \cos \omega' t$ and $\varepsilon(t) = \varepsilon_0 \cos(\omega' t - \delta')$ and eliminating the time from these equalities, we obtain the equation

$$\left(\frac{\sigma}{\sigma_0}\right)^2 + \left(\frac{\varepsilon}{\varepsilon_0}\right)^2 = \varepsilon\delta' + \left(\frac{\sigma}{\sigma_0}\right) + \left(\frac{\varepsilon}{\varepsilon_0}\right) \cos\delta' . \tag{2}$$

Expression (2) represents the equation of an ellipse whose area is equal to the work A_0 done in a cycle of harmonic vibrations and irreversibly lost (dissipating) under strain. Then the dissipation function W is computed as the product of A_0 and the number of cycles per unit time:

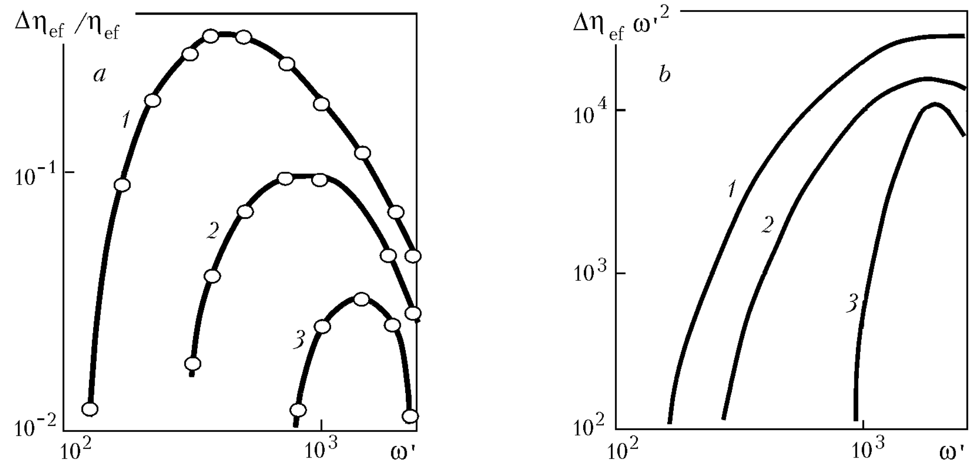

Fig. 2. Influence of the frequency of external action on the change in the effective viscosity (a) and the dissipative function (b) in the case of flow of an aqueous PEO solution ($M_{PEO} = 4.5 \cdot 10^6$ and $C_{PEO} = 0.02\%$) through short capillaries with different average velocities: 1) 0.3; 2) 0.5; 3) 0.7 m/sec. $\Delta\eta_{ef}\omega'^2$, $rad^2 \cdot Pa/sec$; ω', rad/sec.

$$W = A_0 \frac{\omega'}{2\pi} = \frac{\varepsilon_0 \sigma_0 \omega'}{2} \sin \delta' . \tag{3}$$

From relation (3) it is seen that, under the same conditions of strain, the dissipative function only depends on the polymer characteristics expressed in the value of δ'.

Changing the stresses by the harmonic law, we may track a change in the strain rate $\dot{\varepsilon}$. The latter is related to the strain ε as follows:

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \varepsilon_0 i\omega \exp\left[i\left(\omega' t - \delta'\right)\right] = i\omega' \varepsilon . \tag{4}$$

The value of the ratio $\sigma/\dot{\varepsilon}$ is a complex dynamic viscosity η^*. This quantity may be represented in the form of the real and imaginary components $\eta^* = \eta' - i\eta''$, where $\eta' = (\sigma_0/\varepsilon_0\omega') \sin \delta'$ and $\eta'' = (\sigma_0/\varepsilon_0\omega') \cos \delta'$. Introducing η' into relation (3) and performing transformations, we obtain

$$W = \eta' \frac{\varepsilon_0^2 \omega'^2}{2} . \tag{5}$$

Dynamic viscosity manifests itself in the system under strain, and the increment of the effective viscosity $\Delta\eta_{ef}$ under the conditions of superposition of harmonic actions on mainstream flow is attributable to the appearance of η'. Since the amplitude value of the strain ε_0 remains constant in the experiment, we may use scaling and rewrite (5) in the form

$$W(\omega) = \Delta\eta_{ef} \omega'^2 . \tag{6}$$

For the experimental curves (Fig. 2a), we have obtained dissipative-function curves (Fig. 2b) using expression (6). An analysis of these curves shows that, as the average velocity of flow of the aqueous PEO solution through the capillaries increases, i.e., as the fraction of macromolecules (because of the presence of the molecular-weight distribution) that have experienced unrolling [5] and are unrolled to a higher degree, which causes the induction of rigidity in the macromolecules [3], increases, the dissipation of pulsating-flow energy decreases. The threshold value of the fre-

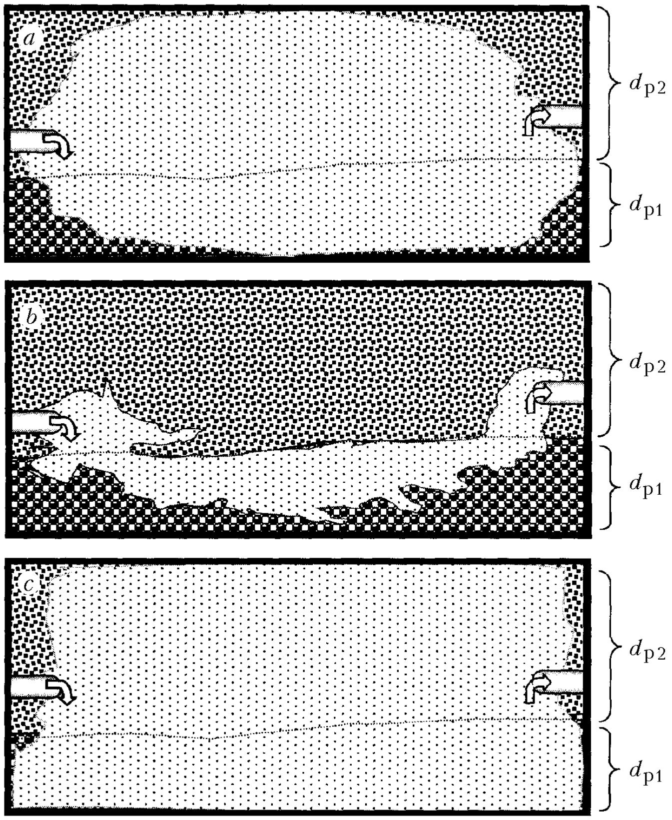

Fig. 3. Patterns of a filling of a porous medium with a laminar inhomogeneity ($d_{p1}/d_{p2} = 4$) with PEO solution: a) stationary regime of filling at supercritical velocities; b) the same, at subcritical velocities; c) supercritical regime of filling in the case of frequency (1000 rad/sec) action on filtration flow.

quency, beginning from which the flow becomes distinctly dissipative, grows for less "flexible" and stretched molecules. As the induced rigidity of macromolecules increases, the dissipative curve acquires a more pronounced extremum character.

From the data obtained it follows that nonstationary filtration flow of polymer solutions must ensure a higher degree of filling and coverage of a porous bed.

Figure 3 shows the patterns of flow of a polymer solution through a model porous bed. The experimental cell represents a layer of quartz compacted in a hermetically sealed space between two glass plates having inlet and outlet pipes. The inlet pipe was connected either directly to a measuring vessel, into which the aqueous polymer solution had been poured in advance, or via a module with a vibrator. In the first version, filling of the pore space with the polymer solution was carried out in the stationary regime, whereas in the second version, it was carried out in the nonstationary (pulsating) regime. The measuring vessel is equipped with a system for recording the flow-rate of the solution injected into the model bed. The solution is injected due to the excess air pressure produced in the measuring vessel; the pressure is monitored by a manometer. The structure of the experimental setup enables us to visualize the process of advance of the front of the polymer solution in the porous bed and to qualitatively evaluate the efficiency of different regimes of its filling by the flow patterns.

Calculation of the injection regimes is based on the use of the De number characterizing the beginning of the development of a higher-than-average hydrodynamic resistance: $\mathrm{De}_{cr} = \theta_c \dot{\varepsilon}$.

The relaxation time may be determined experimentally [3, 7] or from the known molecular characteristics of the polymer [3, 8]:

$$\theta_c = \theta_0 \exp(k)\,, \quad k < 1\,; \quad \theta_c = \theta_0 \,[\exp(k^{2/3})]/k^{1/3}\,, \quad k > 1\,, \quad k = [\eta]_0 C\,.$$

The longitudinal velocity gradient realized in the pore cross sections in flowing of the polymer solution defies an accurate calculation. However, we may evaluate it as a first approximation, solving the problem on flow of a Newtonian fluid in a convergent channel [3] as an element of a pore channel: $\dot{\varepsilon} \approx 2V_f(Kd_p)$. For the ranges of PEO molecular weight and concentrations of practical importance, the Deborah number may be assumed to be equal to unity for $k < 1$ and to 2.5 for $k > 1$ in accordance with experimental data.

Passing from the model to an actual filtration flow and on the basis of the results obtained, we may state that nonstationary filtration flow of polymer solutions ensures a higher degree of filling and coverage of the bed (Fig. 3c) than stationary flow (Fig. 3a); increase in the induced rigidity of polymeric macromolecules (under the same conditions) leads to a decrease in their hydrodynamic activity and hence the degree of coverage of the bed.

CONCLUSIONS

1. The experiments conducted have confirmed the correctness of the prediction of the theory of elastic-strain effects in tensile flow of the higher degree of coverage of a porous bed in the nonstationary regime of its filling with polymer solution and hence the mechanism of deviations from Darcy's law the basis for which is provided by the concepts of a strong strain action of the hydrodynamic field on coiled macromolecules.

2. The effects causing the highly dissipative regime in nonstationary flow of polymer solutions through porous media play an important role in optimization of the process of filling of a porous bed with polymer solutions. Filtration flow of polymer solutions must occur in the nonstationary regime, when elastic strains appear, and the frequency of pulsating action on the filtration flow must correspond to the maximum of the dissipative function $W(\omega) \approx \Delta\eta_{ef}\omega'^2$.

NOTATION

A_0, strain work done in a cycle of vibrations, J; C, concentration of the polymer in the solution, kg/m^3; De, Debora number; De_{cr}, critical Deborah number; d_p, average pore size, m; d_{p1} and d_{p2}, average pore size in the first and second porous media, m; i, imaginary unit; k, criterion of the degree of concentration of the solution; K, coefficient of porosity of the medium; M, molecular weight of the polymer, amu; t, time, sec; $\bar{U}$, average velocity of flow through a capillary, m/sec; V_f, filtration rate, m/sec; W, dissipative function, rad^2·Pa/sec; δ', phase difference between stress and strain fluctuations, rad; $\Delta\eta_{ef}$, increment of the effective viscosity that arises in nonstationary flow, Pa·sec; ε, relative strain in stationary flow; ε_0, amplitude value of the relative strain in nonstationary flow; $\dot{\varepsilon}$, strain rate, sec^{-1}; η_{ef}, effective viscosity, Pa·sec; η^*, complex dynamic viscosity, Pa·sec; η', dynamic viscosity, Pa·sec; η'', imaginary part of the complex dynamic viscosity, Pa·sec; $[\eta]_0$, characteristic viscosity, m^3/kg; θ_c, relaxation time of the solution, sec; θ_0, relaxation time of weakly strained coiled macromolecules, sec; σ, stress in stationary flow, N/m^2; σ_0, amplitude value of the stress in nonstationary flow, N/m^2; ω', frequency of action on the flow, rad/sec; ω'_{cr}, critical frequency of action on the flow, rad/sec. Subscripts: c, concentration; cr, critical value; 0, amplitude value; p, porous medium; p1 and p2, first and second porous media; f, filtration; ef, efficient.

REFERENCES

1. W. H. Jones and S. P. Ho, The flow of dilute aqueous solutions of macromolecules in various geometries. VII. Mechanisms of resistance in porous media, *J. Phys.*, **12**, No. 3, 383–393 (1979).
2. O. E. Öhrn, Entgengnung zur vorstehnden Publikation von H. Umstätter: Zur Frage der sog. Absorptionsfeler in der Kapillar-Viskosimetrie, *Macromol. Chem.*, **25**, No. 3, 205–209 (1958).
3. V. G. Pogrebnyak and A. A. Shubin, *Physico-Chemical Principles of Polymeric Localization of Toxicants in Lithospheres* [in Russian], DonDUET, Donetsk (2002).
4. Yu. F. Ivanyuta, V. G. Pogrebnyak, N. V. Naumchuk, and S. Ya. Frenkel', Special features of flow of aqueous solutions of polymers through short capillaries and porous media, in: *Proc. 2nd Conf. "Water-Soluble Polymers and Their Application"* [in Russian], SO AN SSSR, Irkutsk (1982), p. 142.

5. V. G. Pogrebnyak and S. Y. Frenkel, The structure of the hydrodynamic field and distortions of the molecular shape of flexible polymers under free-converging flow conditions, *Polymer Sci.*, **34**, No. 3, 270–273 (1992).
6. F. Filippov, Relaxation in polymer solutions, polymeric fluids, and gels, in: W. A. Mason (Ed.), *Properties of Polymers and Nonlinear Acoustics. Physical Acoustics* [Russian translation], Mir, Moscow (1969), pp. 9–109.
7. V. G. Pogrebnyak and A. A. Pisarenko, Polymer solutions under the conditions of near-wall turbulence and the mechanism of drag reduction, *Prikl. Gidromekh.*, **2**(**74**), No. 2, 83–95 (2000).
8. V. G. Pogrebnyak, A. A. Pisarenko, and L. A. Pogrebnyak, Flow of polymer solutions in a porous medium — mechanism of nonlinear filtration, in: *Proc. 18th Int. Symp. on Rheology* [in Russian], A. V. Topchiev INKhS RAN, Moscow–Karacharovo (1996), p. 83.