16. M. L. Aizenbud and V. V. Dil'man, "Topics in hydraulics of chemical reactors for gas-liquid systems," Khim. Promysh., No. 3, 51 (1961).
17. A. S. Vasil'ev, V. S. Talachev, V. P. Pavlov, and A. N. Planovskii, "Laws of the discharge of a gas jet into a liquid," Teor. Osn. Khim. Tekhnol., No. 5, 727 (1970).
18. Yu. A. Buevich and V. V. Butkov, "Mechanism of bubble formation in discharge of a gas into a liquid from a circular aperture," Teor. Osn. Khim. Tekhnol., No. 1, 74 (1971).
19. P. Patel, "Form und Grosse von Gasblasen in Wasser, Quecksilber und flussigen Eisen," Arch. Eisenhuttenwesen, 44, No. 6, 435-461 (1973).
20. G. Wallis, One-Dimensional Two-Phase Flow, McGraw-Hill (1969).
21. A. E. Wraight, "Two-stage bubble growth at a submerged plate orifice," Chem. Eng. Sci., 26, No. 10, 1659 (1971).
22. K. Mori, M. Sano, and T. Sato, "The size of bubbles formed at a single nozzle immersed in molten iron," Trans. JISI Jpn., 19, No. 9, 553 (1979).
23. M. Sano. K. Mori, and Y. Fujita, "Dispersion of gas injected into liquid metal," JISI Jpn., 65, No. 8, 1140 (1979).
24. L. Davidson and E. H. Amick, "Formation of gas bubbles at horizontal orifices," AIChE J., 2, No. 3, 337 (1956).
25. V. B. Okhotskii, K. S. Prosvirin, A. N. Kovzik, et al., "Parameters of the zone of interaction of gas jets with a metal with base blowing," Izv. Vyssh. Uchebn. Zaved., Chern. Metall., No. 3, 34 (1982).

EFFECT OF THE TEMPERATURE ON THE HYDRODYNAMIC EFFICIENCY AND STABILITY OF POLYETHYLENE OXIDE AND POLYACRYL AMIDE

B. P. Makogon, M. M. Pavelko,
I. L. Povkh, and A. I. Toryanik

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The article describes a comparative study of the effect of the temperature on the hydrodynamic efficiency and stability of polyethylene oxide (PEO) and polyacryl amide (PAA).

A number of authors [1-7] studied the effect of the temperature on the ability of polymers to reduce the hydrodynamic drag of turbulent flow. In the review [1] it was stated that a change of temperature from 4 to 37°C does not affect the ability of polyethylene oxide, polyacryl amide, and guarana resin to reduce hydrodynamic drag. Later, aqueous solutions of polyethylene oxide were investigated most thoroughly. It was experimentally demonstrated that increasing temperature leads to reduced hydrodynamic efficiency of PEO [2, 3] and increased threshold frictional stress on the wall [4]. The authors brought that into connection with the change of the temperature parameters of the solubility of PEO in water [2] and with the reduced anisotropy of viscosity upon reduced size of the macromolecules [4].

It must be noted that a change of temperature of aqueous solutions of PEO leads to a noticeable change of their molecular characteristics. When the temperature increases from 20 to 90°C, the hydration numbers of PEO decrease; that indicates weakened interaction between the polymer and water. At the same time the virial coefficient, the characteristic viscosity, and the size of the molecular agglomerations also decrease [8]. The model of diluted aqueous solution of PEO, worked out by Toryanik [9], explains these changes by the destruction of the structure of water under the effect of the temperature.

The effect of the temperature on the hydrodynamic efficiency of polyacryl amide has been studied less thoroughly. The authors of [5-7] observed a drop of the effect of hydrodynamic drag reduction when the temperature rose.

In distinction to PEO, the corresponding molecular characteristics of polyacryl amide are much less subject to the effect of the temperature. An increase of the temperature to

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TABLE 1. Influence of the Temperature on the Optimum Concentration and Maximum Hydrodynamic Efficiency of Aqueous Solutions of PEO and PAA

Temp., °C	Solutions of PEO		Solutions of PAA	
	$(C_p)_{opt}$, %	$(\Delta\lambda/\lambda)_{max}$, %	$(C_p)_{opt}$, %	$(\Delta\lambda/\lambda)_{max}$, %
6	0,0003	64,0	0,0006	62,0
20	0,0014	67,5	0,0008	67,5
50	0,0050	71,0	0,0014	73,5
80	0,0200	—	0,0050	75,5

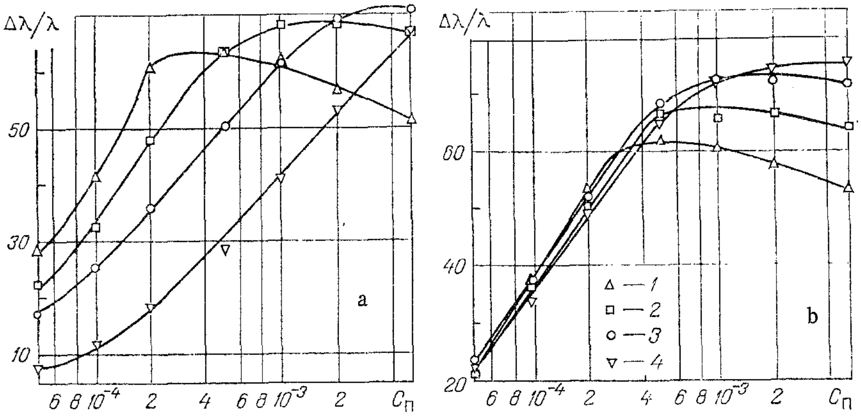

Fig. 1. Influence of the temperature on the dependences of the effect of drag reduction Δλ/λ (%) on the concentration C_p (%) of polyethylene oxide (a) and polyacryl amide (b): 1) t = 6°C; 2) 20; 3) 50; 4) 80°C; τ_w = 33 N/m².

90°C leads to a relatively small change of the hydration numbers of PAA. Klenina et al. [10] showed that in the temperature range 20 to 80°C the second virial coefficient decreases whereas the characteristic viscosity and the radius of inertia of the agglomerations remain practically unchanged. The observed correlation between the sizes of the PEO molecules and their ability to reduce turbulent friction and also the previously presented data on the effect of the temperature on the molecular parameters of PAA permit us to expect that the stability of the hydrodynamic efficiency of PAA under the effect of temperature is greater than that of PEO.

Our work entailed studying the effect of the temperature in the range 6-80°C on the hydrodynamic efficiency and stability of polyethylene oxide and polyacryl amide. As objects of the investigation we chose an industrial sample of PEO Polyox Coagulant and a laboratory sample of linear nonhydrolyzed PAA synthesized at the Institute of MC of the Academy of Sciences of the USSR.* The characteristic viscosities of samples of PEO and PAA, determined at 30°C and zero shear rate q, were equal to 18.3 and 15.0 dl/g, respectively. This indicates that the molecular agglomerations of PAA and PEO at rest have similar dimensions, and it enables us to compare their hydrodynamic properties upon variation of parameters such as concentration, temperature, Reynolds number, shear stress, and shear rate.

The solutions were prepared in distilled water with an addition of potassium iodide which proved to be a good antioxidant. An addition of 0.05% potassium iodide makes it possible to keep the investigated solutions for 10 days at room temperature or for 1 h at 80°C without loss of their efficiency. The viscosity of the solutions was measured with a Simm-Krosers rotational viscometer at a shear rate of less than 1 sec^{-1}, and with a capillary viscometer with 0.56-mm diameter at a shear rate of 1100-2300 sec^{-1}. The hydrodynamic drag coefficient was measured with an open-type pumpless installation with automatic recording of the time of discharge. In its design described in [11] some changes were introduced.

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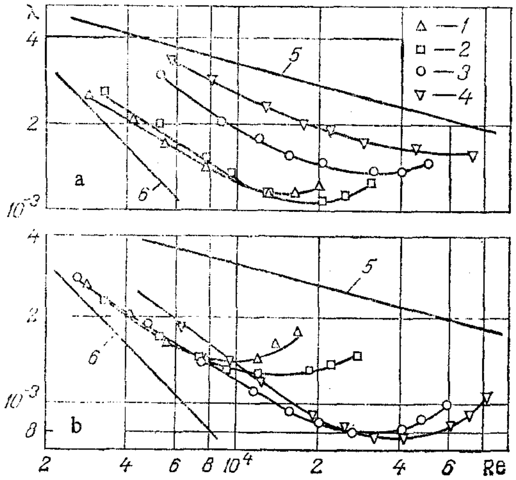

Fig. 2. Dependence of the hydrodynamic drag coefficient λ on the Reynolds number for aqueous solutions of PEO (a) and PAA (b) with a concentration C_p = 0.0005%: 1) t = 6°C; 2) 20; 3) 50; 4) 80°C, and water: 5) turbulent regime; 6) laminar regime.

Instead of electronic heat control, a water thermostat was used, and this made it possible to shorten the time of establishing the temperature. The relatively complex system of automatically recording the time of discharge was simplified by replacing the inductive sensors by hermetic contacts, and the metal ball by a permanent magnet. This improved the reliability of the system without impairing the accuracy of measurement (on the order of 2%).

Viscometer measurements of the aqueous solutions of the investigated polymers showed that it is not only the viscosity of the solutions that depends on the shear rate but the characteristic viscosity as well. For instance, for PEO at zero shear rate it is equal to 18.3 dl/g, and for $q \approx 1100\text{-}2300\ \mathrm{sec}^{-1}$ $[\eta] = 10.6$ dl/g. For PAA these values are 15.0 and 9.0 dl/g, respectively. Such a substantial change of the characteristic viscosity (of the order of 40%) indicates that there occurs deformation and orientation of the polymer molecules in the flow.

In the water channel, the velocity gradient near the wall immediately after the transient flow regime is of the order of magnitude 4000 sec^{-1}, and after that it increases tens of times; this is bound to lead to considerable deformation and orientation of the macromolecules.

The influence of the temperature on the concentration dependences of the effect of reducing turbulent friction for the solutions of PEO and PAA is shown in Fig. 1. All the curves have the typical shape with the maximum of the effect at the optimum concentration of the polymer. Increasing temperature leads to reduced hydrodynamic efficiency of PEO. This is testified to by the decreased effect in the range of low concentrations, where it is most sensitive to changes of the external conditions, and by the increase of optimum concentration by almost two orders of magnitude. It can be seen from Table 1 that this is accompanied by some increase of the maximum effect of drag reduction attained with optimum concentration.

In distinction to PEO, the efficiency of PAA at low concentrations in the solution is practically independent of the temperature. With increasing temperature the optimum concentration increases, but noticeably more slowly than for PEO, and the maximum drag reduction increases more rapidly than for PEO.

The influence of the Reynolds number on the hydrodynamic drag coefficient of aqueous solutions of PEO and PAA at different temperatures is shown in Fig. 2. For aqueous solutions of PEO an increase in temperature leads to a shift of the dependences $\log \lambda = f(\log \mathrm{Re})$ toward larger values of λ and Re. After some Reynolds number characteristic of the given temperature has been reached, the hydrodynamic drag coefficient decreases.

The analogous dependences for aqueous solutions of PAA show substantial differences. In the range of low Reynolds numbers a change in temperature has practically no effect on the hydrodynamic drag coefficient. With large Reynolds numbers the efficiency of PAA increases with increasing temperature of the solutions.

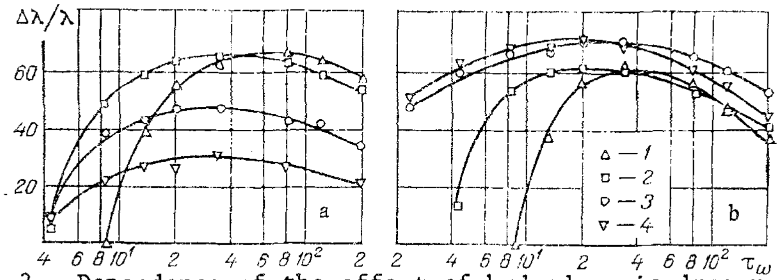

Fig. 3. Dependence of the effect of hydrodynamic drag reduction $\Delta\lambda/\lambda$ (%) in aqueous solutions of PEO (a) and PAA (b) on the frictional stress τ_w (N/m²) on the wall: 1) t = 6°C; 2) 20; 3) 50; 4) 80°C; C_p = 0.0005%.

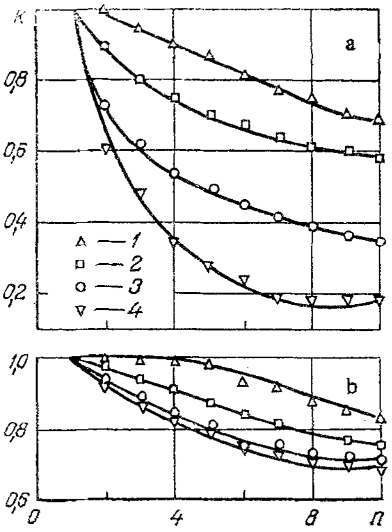

Fig. 4. Change of the relative hydrodynamic efficiency $K = (\Delta\lambda/\lambda)_n/(\Delta\lambda/\lambda)_{n=1}$ of solutions of PEO (a) and of PAA (b) on the number of runs n through the channel: 1) t = 6°C; 2) 20; 3) 50; 4) 80°C; C_p = 0.0005%; τ_w = 20 N/m².

In the examination of the influence of the flow on the polymer molecules, a more physical magnitude than the Reynolds number is the shear stress τ_w on the wall because on it, in particular, is the degree of deformation and orientation of the macromolecules in the viscous sublayer dependent. It is therefore of interest to compare the hydrodynamic efficiency of the solutions when there are equal shear stresses on the wall. Figure 3 shows the dependences of the effect of hydrodynamic drag reduction on the shear stress at different temperatures. In the range of low temperatures, where the size of the PEO and PAA molecules is similar, they have the same ability to reduce turbulent friction. Increasing temperature leads to a certain increase in the efficiency of PAA and a noticeable drop in the efficiency of PEO. The low efficiency of polymers at 6 and 20°C and small shear stresses is due to the fact that the turbulent flow regime at these temperatures begins after shear stresses of 9.0 and 4.0 N/m², respectively, have been attained.

From the dependences presented in Fig. 3 it can be seen that the hydrodynamic efficiency of PAA at all temperatures begins to drop after the shear stresses on the wall have attained the order of 35 N/m². With the solutions of PEO, lower shear stresses correspond to higher temperatures, and then their efficiency drops. In addition, the efficiency of PAA drops more rapidly than the efficiency of PEO.

The degradation of solutions of PEO and PAA, i.e., the drop of their hydrodynamic efficiency, was studied by running them many times through a channel. It can be seen from the graphs in Fig. 4 that with increasing temperature, the degradation of the solutions of PEO, represented in the form of the dependence of the relative efficiency on the number of runs, increases very rapidly. The aqueous solutions of PAA proved to be stabler. Usually the drop in efficiency after numerous runs is ascribed to the rupture of the polymer chains under the effect of the hydrodynamic forces, i.e., destruction [3]. In that case the reduction in size of the macromolecules has to be accompanied by an increase of their resistance to shear stresses. These assumptions contradict the experimental data because increasing temperature leads to a reduction in size of the PEO macromolecules, and degradation at the same time increases. This approach does not explain the dependences of the effect of hydrodynamic drag reduction on the frictional stress on the wall either. In that case an increase in temperature, leading to reduced size of the PEO molecules and of the forces acting on them, is bound to lead to increased frictional stress corresponding to the drop in efficiency, and not to its decrease, as the experimental data (see Fig. 3) show.

The obtained results on the degradation of the solutions may be explained by the conformational changes of the polymer agglomerations because impaired effect of hydrodynamic drag reduction may not only be due to the rupture of polymer chains, but also to their reduced size, as was shown above. With rising temperature the system polyethylene oxide—water approaches the point of phase stratification. This entails stronger interaction type polymer—polymer, and the interaction type polymer—water abates [8]. The application of a shear field makes these differences in molecular interaction even greater [12]. Proceeding from this, we may assume that the degradation of diluted solutions is associated with the formation of intramolecular bonds leading to the freezing of invariable agglomerative conformations, and possibly also to an additional convolution of the polyethylene oxide chains.

In aqueous solutions of PAA a rise in temperature does not lead to substantial changes of molecular interactions including interactions type polymer—polymer. With rising temperature additional intramolecular bonds therefore do not form, and the stability of polyacryl amide to the effect of turbulent flow also changes only slightly.

To verify the above assumption, it is necessary to check the molecular mass of the investigated polymers by an independent method (e.g., according to the scattering of light). However, because of the extremely low concentration of the polymer in the solution (0.0005%) this is impossible.

The experimental results obtained in a large temperature range enable us to evaluate two hypotheses on the onset of hydrodynamic drag reduction; one of them is based on the coincidence of time scales, the other on the coincidence of linear scales of polymer molecules and of turbulent pulsations. Berman and George [13] investigated water—glycerine solutions of PEO. Additions of glycerin reduced the size of the macromolecules only slightly whereas viscosity and consequently also the relaxation time increased several times over. The authors believe that the water—glycerin solutions ensure the critical test of the mechanism that is responsible for the onset of drag reduction. If the hypothesis of linear scale is correct, then we would have to encounter a slight decrease of drag reduction. However, an experiment yields increased drag reduction, and the authors conclude that the hypothesis of time scales is correct.

Analogous evaluations were carried out by using the experimental results presented in this article. They showed that the increased size of macromolecules led in all cases to an increase of their hydrodynamic efficiency whereas the criterion of time scales does not always work.

The approach based on comparing the time and linear scales of polymer molecules with the corresponding scales of turbulent pulsations proved to be erroneous. The concept of "suppressing turbulent pulsations" cannot be brought into connection with the reduction of turbulent friction because the creation of pulsations and their subsequent dissipation lead to irreversible energy losses, regardless of what kind of mechanism of suppressing pulsations is involved.

Obviously, the phenomenon of hydrodynamic drag reduction is associated with processes that make the flow of polymer solutions less dissipative. This may occur because of anisotropy of viscosity in the laminar layer whose existence in polymer solutions does not only follow from general physical considerations but was also experimentally proved [14]. The greater the anisotropy of viscosity is, the more laminar is the flow, and the smaller is the hydrodynamic drag. In its turn, the anisotropy of viscosity is determined, on the one hand, by the flow conditions (shear stress, velocity gradient), and on the other hand by the molecular parameters of the polymer solutions (molecular mass and concentration of the polymer, the thermodynamic properties of the solvent, the size of the polymer agglomerations and their flexibility). The results of the experimental investigations presented in this article indicate that with constant molecular mass, the hydrodynamic efficiency of a polymer is determined by the thermodynamic properties of its solution, on which the size of the macromolecules depends. However, in our opinion the mechanism of the phenomenon of reduction of turbulent friction is not based on the interaction of polymer molecules with turbulent pulsations upon coincidence of their linear scales, but on the retarded formation of turbulence thanks to the anisotropy of viscosity in the laminar layer.

The reduced hydrodynamic efficiency of polymer solutions after numerous runs through the channel cannot always be ascribed to the rupture of the polymer molecules. It is obvious that a noticeable contribution to the reduction of efficiency is made by the conformational changes of the macromolecules.

NOTATION

q, shear rate; [n], characteristic viscosity; λ, hydrodynamic drag coefficient; Re, Reynolds number; τ_w, shear stress on the wall; $\Delta\lambda/\lambda$, effect of hydrodynamic drag reduction; C_p, concentration of the polymer; t, temperature; K, relative hydrodynamic efficiency; n, number of runs; $(C_p)_{opt}$, optimum concentration of the polymer; $(\Delta\lambda/\lambda)_{max}$, maximum hydrodynamic efficiency.

LITERATURE CITED

1. G. Hoyt, "The effect of additions on drag in liquids," Theoretical Foundations of Engineering Calculations, Trans. ASME, 94, Series D, No. 2, 1-31 (1972).
2. P. Peyser and R. C. Little, "The drag reduction of dilute polymer solution as a function of solvent power, viscosity, and temperature," J. Appl. Polym. Sci., 15, 2623-2637 (1971).
3. N. G. Vasetskaya, V. A. Ioselevich, and V. N. Pilipenko, "Mechanical destruction of polymer molecules in turbulent flow," in: Some Problems of the Mechanical Continuum, Moscow State University (1978), pp. 55-69.
4. I. L. Povkh, A. I. Toryanik, B. P. Makogon, and V. M. Abrosimov, "The influence of temperature on the effect of hydrodynamic drag reduction," Inzh.-Fiz. Zh., 37, No. 6, 1012-1014 (1979).
5. A. N. Shabrin, "Investigation of the influence of the temperature and of salinity on the effect of drag reduction in a pipe with the aid of polymer additives," in: Hydromechanics. Interscience Collection of the Republic [in Russian], Issue 21, Naukova Dumka, Kiev (1972), pp. 80-83.
6. I. P. Chaschin and O. N. Martynenko, The Effect of Organic Additives on the Heat Exchange and Drag in Liquid Flow [in Russian], Deposited at VINITI January 11, 1974, Reg. No. 55-74 Dep., 7 pp.
7. I. P. Chashchin, L. F. Shigina, and N. S. Shvab, The Effect of a Number of Organic Additives on the Heat Exchange and Drag of Flow [in Russian], Deposited at VINITI January 22, 1975, Reg. No. 215-75 Dep., 6 pp.
8. A. A. Tager, S. A. Vshivkov, V. M. Andreeva, and T. V. Sekacheva, "Investigation of the structure of polyethylene oxide solutions with lower critical mixing temperatures," VMS, 16A, No. 1, 9-14 (1974).
9. A. I. Toryanik, Structural Model of Aqueous Solution of Polyethylene Oxide [in Russian], Deposited at ONIITÉKhIM March 9, 1983, Reg. No. 279-83 Dep., 24 pp.
10. O. V. Klenina, M. Yu. Prozorova, V. I. Klenin, and G. Z. Aksel'rod, "The thermodynamic properties of aqueous solutions of polyacryl amide," VMS, 22A, No. 2, 292-295 (1980).
11. I. L. Povkh, V. G. Pogrebnyak, and A. I. Toryanik, "Correlation between the molecular structure of polyethylene solutions and the effect of hydrodynamic drag reduction," Inzh.-Fiz. Zh., 37, No. 4, 581-588 (1979).
12. S. A. Vshivkov, A. A. Tager, and A. D. Ben'kovskii, "Phase equilibrium of polymer solutions in a hydrodynamic field," VMS, 20B, No. 8, 603-606 (1978).
13. N. S. Berman and W. K. George, "Onset of drag reduction in dilute polymer solutions," Phys. Fluids, 17, 250-251 (1974).
14. A. Ya. Malkin, N. V. Vasil'eva, T. A. Belousova, and V. G. Kulichikhin, "Anisotropy of viscosity in lyotropic liquid crystals of poly-n-benzamide," Kolloidn. Zh., 41, No. 1, 200-201 (1979).