INFLUENCE OF STRUCTURE OF AQUEOUS POLYMER SOLUTIONS ON THE TOMS EFFECT

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The influence of the structural characteristics of dilute polymer solutions on the Toms effect has been investigated with reference to the example of aqueous solutions of polyoxyethylene, containing inorganic salts, and polyvinyl alcohol, characterized by the existence of a supermolecular order.

The drag reduction obtainable by adding small amounts of polymer to a turbulent flow (known as the Toms effect) is a well-established fact. However, the phenomenon still lacks a full explanation [1]. This is partly due to a failure to make effective use of the principles of the physical chemistry of polymer solutions, despite the fact that the effect in question must be associated with the nature of the polymeric state of the additives and the structural characteristics of their solutions.

It is known that dilute aqueous solutions of polyoxyethylene (POE) are characterized by the presence of structures associated with the hydration of the oxygen atoms of the polymer's ether groups [2]. The light-diffusion technique has revealed the existence of a strong, highly oriented network of POE and water molecules [3]. A detailed study of aqueous polyvinyl alcohol (PVA) solutions [4] has shown that dilute PVA solutions are also characterized by a supermolecular order. By means of special heat treatment of the PVA solutions the authors of [4, 5] achieved a substantial increase in the number of supermolecular particles.

In order to investigate the influence of the structural characteristics of dilute POE and PVA solutions on the Toms effect, we carried out experiments under conditions that led to the existence of various structures. Thus, the structure of the aqueous POE and PVA solutions was varied by introducing low-molecular-weight electrolytes or by special heat treatment.

Experimental

We used commercial samples of POE and PVA with molecular weights $M = 10^6$ and $7 \cdot 10^4$, respectively. The POE solutions were prepared by directly dissolving weighed amounts of the sample in water and in aqueous solutions of the electrolytes $MgSO_4$, K_2CO_3, K_2SO_4, KOH, KJ, which have cations and anions of different sizes and charge. The PVA solutions were prepared in two ways. In method 1 a weighed amount of polymer was covered with a certain quantity of water and left to swell for 24 h at room temperature. Then the system was heated for an hour at 80°C so that the polymer completely dissolved. In method 2 a weighed amount of polymer was placed in a stainless-steel autoclave, covered with a certain quantity of water and left to swell for 24 h. The autoclave was placed in a glycerin bath, heated for 5 h at a constant temperature of 130°C, and then cooled to room temperature. The solutions subjected to heat treatment in the autoclave had a concentration of 0.5%. Solutions of lower concentrations were obtained by diluting them. The M values were estimated by viscometry using the formulas given in [2, 4]. The intrinsic viscosities η of the solutions were measured with an Ubbelohde viscosimeter with a 70-sec flow time. The drag reduction experiments were performed on an apparatus with two coaxial cylinders, similar to that described in [6], at $Re = 2.7 \cdot 10^5$. When the outside cylinder is made to rotate at a speed that ensures a turbulent-flow regime, the inside cylinder experiences a torque which is measured during the experiment. The drag reduction was calculated from the expression

$$\mathrm{DR} = \frac{P_0 - P}{P} \cdot 100\%,$$

where P_0 are the instrument readings for water and P those for the solution. We measured the drag reduction for POE and PVA solutions on the concentration interval from 0.005 to 0.5%. In the turbulence regime em-

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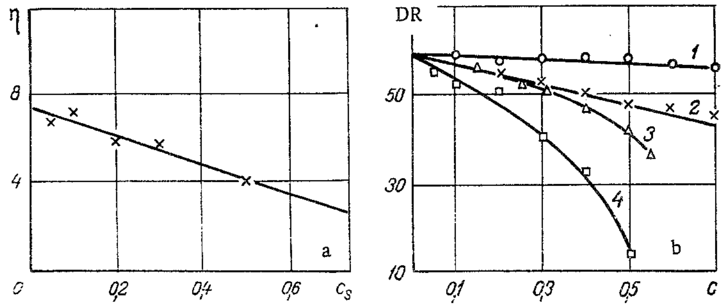

Fig. 1. Effect of K_2CO_3 concentration on η (a) and drag reduction (DR) (b) for POE solutions: 1) KJ; 2) KOH; 3) K_2SO_4; 4) K_2CO_3. c, mole/liter.

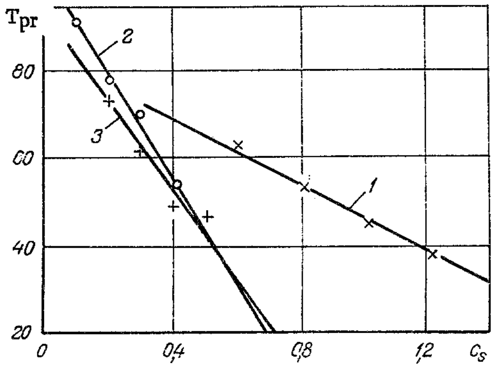

Fig. 2. T_{pr} as a function of salt concentration for POE solutions: 1) 0.1% POE + $MgSO_4$, 2) 0.05% POE + K_2CO_3, 3) 0.1% POE + K_2CO_3. T_{pr}, °C; c_s, mole/liter.

ployed, no drag reduction was recorded for PVA solutions prepared in accordance with method 1. For POE solutions we obtained an extremal dependence of the drag reduction on solution concentration. In the experiments with added salts we used a POE solution having a concentration of 0.2%, which corresponded to a drag reduction effect of 60%.

Results and Discussion

By introducing low-molecular-weight electrolytes into the aqueous POE solutions we substantially modified their structure. It is known [2] that adding electrolytes to aqueous POE solutions reduces the effective concentration of water participating in the formation of hydrogen bonds with the oxygen atoms of the ether groups of the POE chains and that the structural network is destroyed. In this connection, the ability of a salt to destroy the structural network grows as the size of the anion decreases and its charge increases [2], which is reflected in the hydrodynamic behavior of the macromolecules under laminar conditions [2]. The data of Fig. 1 shows that the interaction of the macromolecules with a turbulent flow is also affected. Clearly, the drag reduction decreases with increase in electrolyte concentration and depends on the charge and size of the anion. In order to find the salt concentrations capable of influencing the Toms effect, we constructed the phase diagrams of POE solutions containing various salts. The results for two salts are presented in Fig. 2 in the form of the dependence of the precipitation temperature T_{pr} on salt concentration. Figure 3 shows how the Toms effect depends on the T_{pr} of the POE at different salt concentrations. Clearly, there is a definite relationship between these quantities associated with changes in the conditions of precipitation of the polymer from solution. This explains the contradictory data of a number of authors with regard to the result of adding salts to POE solutions. The lack of influence on the Toms effect reported in [1] is attributable to the accidental choice of a salt concentration insufficient to reduce T_{pr}. In other cases [1] the observed precipitation of the polymer under turbulent conditions can be ascribed to disturbance of phase equilibrium in the POE – H_2O system as a result of the addition of excessive amounts of salt.

The drag reduction data obtained demonstrate the need to study the Toms effect with reference to the concept of the existence, or formation under the influence of powerful shearing forces, of macromolecular structural formations capable of suppressing turbulence. This approach was previously adopted by Kalashnikov

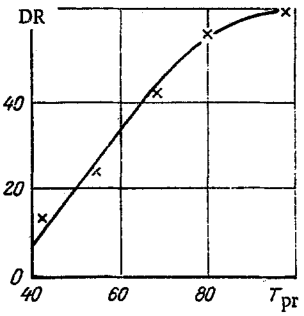

Fig. 3

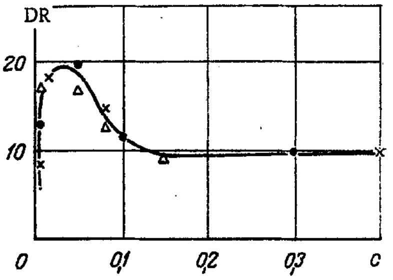

Fig. 4

Fig. 3. Drag reduction as a function of T_{pr} for POE solutions ($c = 0.05\%$) $+K_2CO_3$. DR, %; T_{pr}, °C.

Fig. 4. Concentration dependence of drag reduction for PVA solutions heat-treated at 130°C. DR, %: c, wt. %.

et al., [7] in connection with aqueous solutions of sodium carboxymethylcellulose (CMC). These authors attributed the drag reduction obtained with small amounts of CMC to the presence in the solutions of a certain supermolecular order. Of particular interest are the studies made by the authors of [8] who observed a heightening of the supermolecular order in PVA solutions under turbulent conditions. These data point to the possibility of dynamic structure formation. The formation of crystalline structures built from straightened chains in a solution deformed by turbulence was also observed in [9]. The authors of [9] assumed that this was attributable to uncoiling of the macromolecules under the influence of the hydrodynamic forces. In this connection, the role of the salts we introduced into the POE solutions was evidently to create conditions that prevented the formation of certain structures capable of suppressing turbulence. It is clear from Fig. 2 that when salts are introduced the macromolecules are in a more highly coiled conformation. This results in fewer of the contacts between macromolecules needed for dynamic structure formation, and as the salt concentration increases the drag reduction declines (Fig. 1).

It is noteworthy that in our experiments the PVA solutions that were not heat-treated at 130°C did not give a drag reduction effect. This was evidently the result of inadequate structure formation. The additional structure formation produced by heat treatment favors the development of macromolecular formations capable of suppressing turbulence. This is reflected in Fig. 4, where we have plotted the experimental points from three independent series of measurements. Clearly, the concentration dependence is an extremal one, in conformity with previous observations [1]. The characteristics of the supermolecular particles formed are described in detail in [4].

Thus our results show that the structural characteristics of polymer solutions play a definite part in the Toms effect. However, we consider that this approach to the study of the Toms effect requires the support of further research. In particular, it would be interesting to investigate the relationship between the length, structure, conformation, and other characteristics of the macromolecule chain and the properties of the supermolecular structure of dilute polymer solutions.

NOTATION

η, intrinsic viscosity; c_s, salt concentration; DR, drag reduction; T, temperature, °C; f, a function; η_0, solvent viscosity; η_r, specific viscosity of solution; Re, Reynolds number; τ, shear stress; t_r, relaxation time.

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EFFECT OF SURFACTANT ON BUBBLE MOTION CLOSE TO A SOLID WALL

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Numerical analysis is used to study the effect of surfactants on the parameters of gas-bubble motion close to a solid wall under the influence of abrupt pressure change at infinity.

The study of gas-bubble motion close to a solid wall in liquids containing dissolved surfactant is of great interest for the design of chemical-engineering apparatus for a number of important liquid-extraction processes and also in connection with the production technology for various solvents.

The present work gives the results of a numerical investigation of gas-bubble motion close to a solid wall in an incompressible liquid containing surfactant, under the influence of an abrupt pressure change at infinity.

Consider a bubble of radius R situated a distance x from the wall; the bubble pulsates and moves toward the wall with velocity $\dot{x}$. This bubble motion may be described by Lagrange equations [1]

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{x}} - \frac{\partial T}{\partial x} = F_x, \quad \frac{d}{dt}\frac{\partial T}{\partial \dot{R}} - \frac{\partial T}{\partial R} = F_R, \tag{1}$$

where T is the kinetic energy of the liquids, calculated from the potential and its derivatives at the boundary surfaces by the formula

$$T = -\frac{\rho}{2}\iint\limits_S \varphi \frac{\partial \varphi}{\partial n}\, dS.$$

The velocity-field potential φ satisfies the Laplace equation with the following boundary conditions

$$-\left.\frac{\partial \varphi}{\partial n}\right|_{r=R} = \dot{R} - \dot{x}\cos\theta, \quad -\frac{\partial \varphi}{\partial n} = 0 \text{ at the wall, } (\operatorname{grad}\varphi)_\infty = 0. \tag{2}$$

Using the method outlined in [2-4] to find the function φ satisfying the boundary conditions in Eq. (2), the liquid kinetic energy for the bubble close to the solid wall is given, retaining terms of order up to ε^3, by the expression

$$T = 2\pi\rho R^3 [(1/3 - 1/8\,\varepsilon^3)\,\dot{x}^2 + (2+\varepsilon)\,\dot{R}^2 - 1/2\varepsilon^2\dot{x}\dot{R}]. \tag{3}$$

The system in Eq. (1) may be used in the case when the velocity field of the real liquid deviates slightly from the corresponding velocity field of an ideal liquid. It was shown in [5] that this condition is satisfied for a liquid with Re≫1. Assume that the surfactant does not have a great effect on the hydrodynamics close to the bubble surface; then, according to [6], the generalized force F_x is given by the expression

$$F_x = 12\pi\mu R\dot{x} - 1.15\lambda R^* T_1 R\Gamma_0. \tag{4}$$

When the surfactant concentration is small and adsorption is far from saturation [7]

$$\lambda = \frac{\Gamma_0}{RC_0}\left(\frac{|\dot{x}|R}{D}\right)^{1/2}. \tag{5}$$

Substituting Eq. (5) into Eq. (4) gives

$$F_x = 12\pi\mu R\dot{x} - 1.15R^* T_1 \Gamma_0^2 C_0^{-1}\left(\frac{|\dot{x}|R}{D}\right)^{1/2}. \tag{6}$$

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