TURBULENT-FRICTION REDUCTION IN SURFACTANT-POLYMER AQUEOUS SOLUTIONS

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A study is made on the effects of anionic surfactants on the hydrodynamic performance and stability for polyethylene oxide (PEO) and for hydrolyzed and unhydrolyzed polyacrylamide (PAA).

Aqueous solutions containing mixture of polymers and surfactants have various uses, including in fire extinguishers [1, 2]. Surfactants can affect the capacity of PEO and PAA to reduce turbulent friction in water [3-6]. The hydrodynamic performance from a polymer in a surfactant solution is sometimes increased and sometimes decreased.

We have examined the effects of anionic-surfactant concentration on the reduction in hydrodynamic resistance in aqueous PEO and PAA solutions, as well as the stability of these polymers in turbulent flows.

Laboratory specimens were used, the characteristics being given in Table 1: commercial "Progress" surfactant grade 20 containing 20% of the sodium salts of secondary alkyl sulfates [1], sodium dodecyl sulfate (SDDS) of pure grade, which was additionally purified by recrystallization, and pure-grade sodium chloride. The solutions were made up in distilled water. The viscosities were measured with a VPZh-2 capillary viscometer, capillary diameter $0.56 \cdot 10^{-3}$ m. The molecular masses of the PEO and PAA were calculated from the characteristic viscosities via $[\eta] = 12.5 \cdot 10^{-5} \cdot M^{0.78}$ [7] and $[\eta] = 9.8 \cdot 10^{-5} \cdot M^{0.76}$ [8], correspondingly. The degrees of hydrolysis were determined by potentiometric titration. The dynamic-resistance coefficients were measured with an open-loop system providing automatic flow-time recording [9]. The sodium-ion activity for the SDDS was determined conductometrically by means of an ESL-51-07 selective electrode with an EV-74 universal ionometer, while the ζ potential for the micelles was calculated from the electrophoretic mobility as determined by microelectrophoresis with a Keen instrument.

With 3% "Progress" surfactant, which corresponds to the level used in foam fire extinguishers, the hydrodynamic performance from the PEO was increased throughout the range in Reynolds number Re up to the critical value (Fig. 1). The critical Re was reduced. Improved PEO performance in "Progress" solution is indicated by the concentration dependence for the effect shifting to lower concentrations (Fig. 2). Figure 3 shows that the effect increases in the region where the spherical micelles are formed (CCM_1), which for SDDS is $8.11 \cdot 10^{-3}$ M and for "Progress" 0.02% [1]. These surfactants of themselves do not reduce the hydrodynamic resistance in this concentration range.

The characteristic viscosity is proportional to the specific macromolecule volume and for PEO in 3% "Progress" was larger than in water (Table 1). The increased molecular size for PEO in anionic surfactant solutions is due to polycomplexes being formed, as has been shown by various methods [10]. The molecules may aggregate with individual ions or with surfactant micelles. Hydrophobic interactions give rise to charged parts in the polymer chain, and repulsion between these enlarges the macromolecule [11]. The charges and correspondingly the repulsive forces are proportional to the surfactant ionization and the micelle ζ potential. Therefore, any changes in these should affect the hydrodynamic resistance reduction. Figure 3 shows that SDDS below the micelle structure level does not affect the PEO hydrodynamic performance, in spite of the reduced degree of ionization, while in the CCM_1 and critical-concentration region for spherical micelle reconstruction (CCM_2), which is $7 \cdot 10^{-2}$ M for SDDS [1], the increases in the degree of ionization and the ζ potential are corre-

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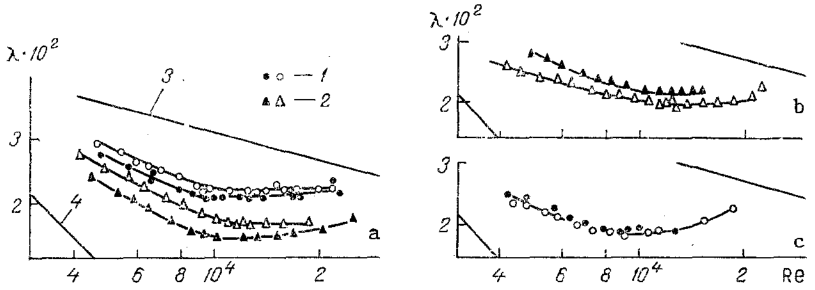

Fig. 1. Dependence of hydrodynamic-resistance coefficient λ on Re for PEO (a), PAA-16 (b), and PAA-0 (c) in water (dashed lines) and in 3% "Progress" solution (solid lines): 1) C_p = 0.0001%; 2) 0.0002% in water; 3) turbulent state; 4) laminar state; T = 293 K (in a and b, the lines bearing the open symbols are to be taken as dashed).

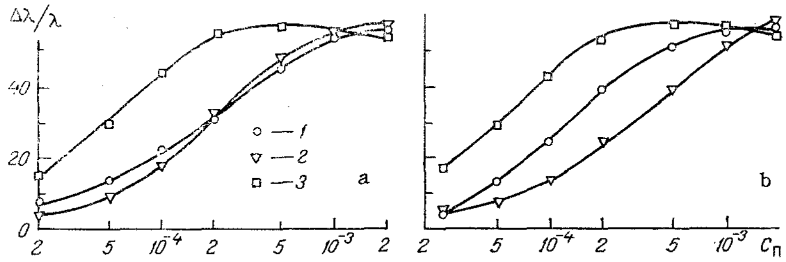

Fig. 2. Hydrodynamic resistance effect Δλ/λ (%) as a function of polymer concentration C_p (%) in water (a) and in 3% "Progress" solution (b): 1) PEO; 2) PAA-16; 3) PAA-0; τ = 13 Pa, T = 293 K.

TABLE 1. Polymer Specimen Characteristics

Specimen	$M\cdot10^{6}$	β, %	[η] (303 K), dℓ/g		
			water	3% "Progress"	10% NaCl
PAA-0	8,3	0	17,3	17,3	17,4
PAA-16	2,4	16	—	13,9	7,3
PEO	0,9	—	8,9	17,6	—

lated with the increased effect, so hydrophobic complexes of PEO with the surfactant micelles have the largest hydrodynamic effect.

The reduction in the critical Re for PEO and surfactant solutions in Fig. 1 may be due to the polycomplexes being disrupted in the turbulent flow.

Hydrolyzed PAA, degree of hydrolysis 16% (PAA-16), with "Progress" gave hydrodynamic resistance coefficients larger than the polymer alone (Fig. 1), while the concentration dependence for the effect shifted to higher concentrations (Fig. 2). The surfactant effect decreased as Re increased, and the fall in the effect when PAA-16 was mixed with these surfactants occurred below the micelle range (Fig. 3).

It has been found [12, 13] that the effect is reduced with hydrolyzed PAA combined with simple electrolytes, and it is therefore of interest to compare the effects of such an electrolyte and those of ionic surfactants on the capacity of hydrolyzed PAA to reduce the turbulent friction. We used PAA-16 and examined the effects of NaCl and SDDS concentrations on the resistance reduction (Fig. 3). Although SDDS is a weaker electrolyte than NaCl, it has more effect on the performance of PAA-16, so there are specific interactions that adversely affect the capacity of the polymer to reduce the friction.

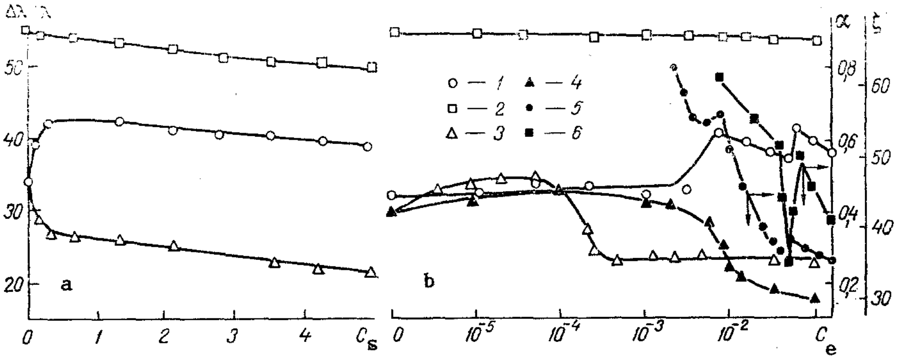

Fig. 3. Dependence of Δλ/λ (%) on "Progress" concentration C_s (%) (a) and SDDS concentration (curves 1-3) and the same for NaCl concentration (curve 4) C_e in M (b): 1) PEO; 2) PAA-0; 3, 4) PAA-16, C_p = 0.0002%; T = 293 K, τ = 13 Pa, and effects on the degree of molecular ionization α (curve 5), the ζ potential for the micelles (ζ, mV) (curve 6) from the SDDS concentration.

It proved impossible to determine the characteristic viscosity for PAA-16 in water because of the polyelectrolyte effect, but in 3% "Progress" that effect vanished, and the reduced viscosity was diminished. Therefore, the PAA-16 molecules in "Progress" micellar solution are smaller than in water.

There are interactions in dilute hydrolyzed PAA solutions that govern the macromolecule size and flexibility. The carboxyl groups are ionized in distilled water, and they show electrostatic repulsion, which causes macromolecule swelling and increases the rigidity [14]. When a simple electrolyte such as NaCl is used at increasing concentrations, the ionic strength increases, while the repulsive forces between the PAA charged groups decrease, so the molecules become more compact and flexible [15, 16]. SDDS differs from NaCl in that on ionization in water it produces anions capable of hydrophobic interaction with the polymer. However, the hydrophobic interaction is opposed by the repulsion between the charged PAA parts and the singly charged SDDS ions, so such interaction can occur only when there is adequate electrolyte, when the electrostatic repulsion is weakened. At a certain SDDS concentration with PAA-16, there may be specific interaction between the surfactant anions and the polymer, which reduces the hydrodynamic effect (Fig. 3).

"Progress" has less effect on the PAA-16 performance as Re increases because of change in macromolecule size caused by the hydrodynamic forces. At small Re, the swollen but rigid PAA-16 molecules are more effective in water than the smaller but flexible ones in "Progress" solution. As Re increases, the flexible molecules are deformed more, so the performance with the mixture approaches that for the pure polymer solution.

PAA-0 in water and aqueous surfactant solutions shows that ionic surfactants have very little effect on the turbulent-friction reduction (Figs. 1-3); the identical characteristic viscosities for PAA-0 in water and 3% "Progress" indicate that the macromolecules are of constant size, and this behavior in anionic surfactants is due to the nonionic character of the polymer and the high hydrophilicity in the amide groups [17].

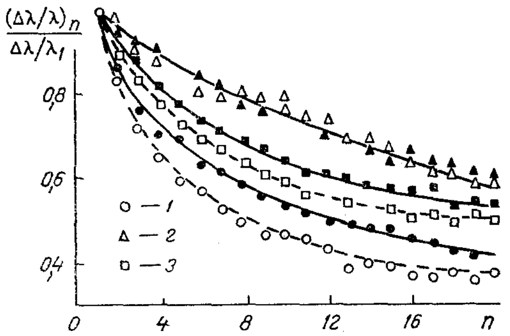

Fig. 4. Ratio of the hydrodynamic performance in pass n to that in the first pass $(\Delta\lambda/\lambda)_n/(\Delta\lambda/\lambda)_1$ as a function of the number of passes in water (dashed lines) and 3% "Progress" (solid lines): 1) PEO; 2) PAA-16; 3) PAA-0; C_p = 0.0002%, τ = 13 Pa, T = 293 K.

We examined the effects of "Progress" on the polymer stability in turbulent flows from the change in the resistance reduction as a function of the number of passes through the hydrodynamic system at a constant pressure difference less than the critical value.

Measurements [9, 12, 18, 19] indicate that the polymer degradation in a turbulent flow decreases as the solvent's thermodynamic quality improves; as [η] for these polymers are altered in 3% "Progress" (Table 1), the micellar solution of this reduces the performance from PAA-16 more rapidly than is the case in water, while that for PEO is less rapid. The loss of hydrodynamic performance from PAA-0 should not be substantially altered in a surfactant solution, but Fig. 4 shows that there is a reduction in the degradation not only for PEO but also for PAA-0 in micellar "Progress" solution. The surfactant hardly altered the degradation for PAA-16. The results show that there is less polymer destruction in the hydrodynamic field when the solution contains a surfactant.

Anionic surfactants at levels equal to or greater than the CCM_1 increase the hydrodynamic performance for PEO but reduce that for hydrolyzed PAA by ~10%. The turbulent-friction reduction for unhydrolyzed PAA is independent of the surfactant concentration.

Anionic surfactants stabilize PEO and unhydrolyzed PAA in turbulent flows and have no effect on the stability for hydrolyzed PAA.

NOTATION

[η], characteristic viscosity; M, polymer molecular mass; β, degree of PAA hydrolysis; T, absolute temperature; τ, wall frictional stress; C_p, polymer concentration; C_e, electrolyte concentration.

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