PHYSICOCHEMICAL PROPERTIES OF AN AQUEOUS SOLUTION OF METAUPON AND HYDRODYNAMIC-RESISTANCE REDUCTION

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It is shown that a surfactant efficiently reduces the hydrodynamic resistance of a liquid when the solution contains aspheric micellar structures.

The solutions of some micelle-forming surfactants SA reduce the hydrodynamic resistance HR [1, 2]. The use of SA to reduce HR has a certain advantage over the use of linear macromolecular polymers. The micellar structures formed in SA solutions are destroyed in a flow but recover their hydrodynamic performance rapidly. The destruction of polymer macromolecules under a velocity gradient is irreversible because of chain breakage. An SA such as metaupon retains its performance on prolonged use in closed circulation systems.

However, to produce solutions that efficiently reduce HR it is necessary to have relatively high SA concentrations (0.1-1%), while certain inorganic and organic additives are also necessary. It is therefore important to search for new and effective SA. For this purpose it is necessary to establish a relationship between the extent and mode of reduction in the HR by SA and the physicochemical properties of the solutions. This relationship can then be used to forecast the capacity of SA to reduce HR.

We have correlated the reduction of HR by metaupon with the micellar characteristics. Metaupon is a detergent, whose main surfactant is the sodium salt of β-(N-methyl-N-olenoyl)-ethylsulfonic acid. We have examined the effects of various water-soluble organic compounds on the physicochemical properties of metaupon with regard to the capacity to reduce HR.

The reduction in HR was determined in a glass tube of diameter 5.45 mm at a Reynolds number for water of 9000. The formula is [3]

$$\frac{\lambda_W - \lambda_s}{\lambda_W} = \frac{\Delta\lambda}{\lambda} = \left[1 - \left(\frac{t_s}{t_W}\right)^2 \frac{\Delta P_s}{\Delta P_W}\right] \cdot 100\%. \tag{1}$$

We used physicochemical methods that enable one to characterize the bulk properties of the SA solution: viscosity measurement, solubilization of water-insoluble dye, turbidity spectra, and Craft point.

The viscosities of the aqueous solutions were determined with an Ubbelhode glass capillary viscometer with a flow time for the solvent (water) of 80-150 sec. The flow time of the liquid was measured with a manual timer with an accuracy of 0.1 sec.

The dye was azoazoxy BN and was used with aqueous solutions of metaupon in a thermostatic chamber for periods of 8-10 h. It has previously been established that this time is sufficient to produce equilibrium in the SA-dye system. The remaining unsolubilized dye was filtered off, and the optical density of the SA solution was measured at 490 nm with an SF-16 spectrophotometer. The dependence of the optical density on the SA concentration indicates the structure of the micelle and the critical SA concentrations at which changes occur [4-6] (Fig. 1).

The turbidity spectra were recorded with an FÉK-N-57 photoelectric colorimeter—nephelometer. To eliminate dust, the metaupon solutions were filtered 4-5 times through a Shott filter with a pore diameter of 1.6×10^{-5} m, which is considerably larger than the micelles in the SA solution (not more than 10^{-7} m) [4]. The resulting solutions were placed in working glass cells of appropriate thickness l in centimeters and the optical density was measured at various wavelengths. The turbidity τ, cm^{-1}, was calculated from

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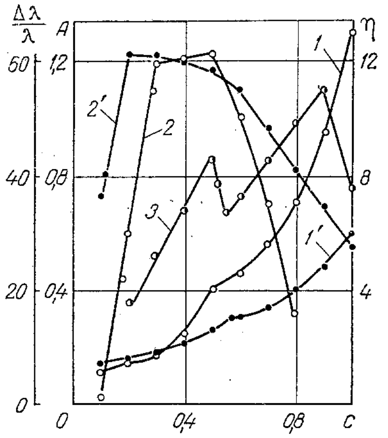

Fig. 1

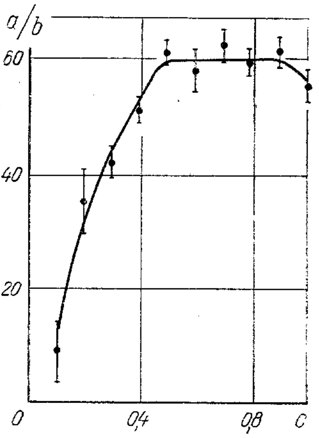

Fig. 2

Fig. 1. Effects of metaupon concentration in 8% sodium chloride on the relative viscosity η, reduction in HR (Δλ/λ, %), and optical density of solubilized dye A (curves 1-3, respectively) with the addition of 1% butanol (1' and 2') and without it (1-3).

Fig. 2. Ratio of the semiaxes of anisodiametric micelles for various metaupon concentrations in 8% sodium chloride solution.

$$\tau = 2.303A/l. \tag{2}$$

These turbidity spectra were used to estimate the sizes of the micelles by the method of [7, 8] (Fig. 2).

In every case, these micelle-forming SA solutions have a definite temperature above which micelles begin to form, i.e., a true solution goes over to a micellar one [4]. This temperature is known as the Craft point. This point for metaupon was determined for a concentration 2-3 times the critical concentration for the formation of spherical micelles CCM_I. The solution was heated at 0.5 deg/min or cooled with constant stirring. During heating we recorded the temperature at which there was complete clearing, and during cooling the temperature of onset of turbidity. The Craft point was taken as the mean of the two values. The temperature was determined with an error of 0.1°C.

The viscosity and solubilization measurements were made at 25 ± 0.1°C, and that point was also used in recording the turbidity spectra and reduction in HR.

Figures 1 and 3 show the effects of metaupon concentration in 8% sodium chloride solution on the viscosity, optical density, and HR reduction. The viscosity and optical-density curves show two concentrations at which there are step changes (0.09 and 0.50%). Published data [5, 6, 9] indicate that these SA points correspond to transition of the micelles from one structure to another. At 0.09% metaupon there is a marked increase in the viscosity and a discontinuity in the solubilization isotherm (Fig. 3), which is due to change in the shape of the particles, which become unsymmetrical, i.e., rod-shaped micelles are formed. The SA concentration corresponding to these micelles is usually called the second critical concentration for micelle formation CCM_{II}. This is 0.09% for metaupon. Confirmation of these

TABLE 1. Reduction in Hydrodynamic Resistance and Ratio of Semiaxes of Anisodiametric Micelles in Metaupon Solutions in the Presence of 8% Sodium Chloride

Parameters determined	Metaupon concentration, %									
	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
Reduction in hydrodynamic resistance Δλ/λ, %	0	30	58	60	61	50	35	16	0	0
Ratio of semiaxes a/b	9	35	42	51	61	58	63	59	62	56

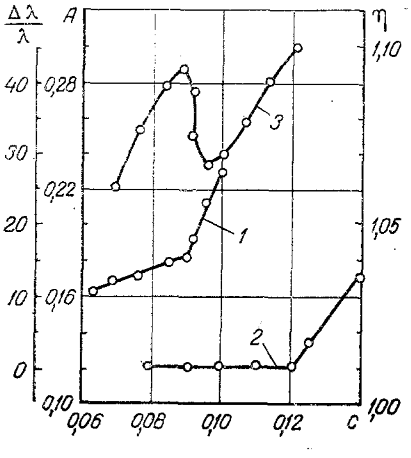

Fig. 3

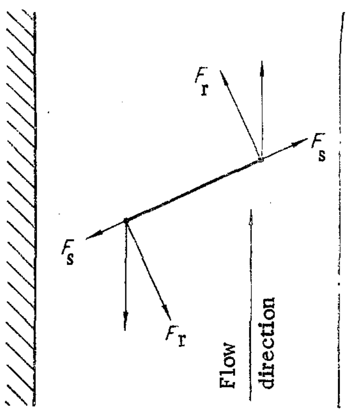

Fig. 4

Fig. 3. Effects of metaupon concentration in 8% sodium chloride solution on the relative viscosity η, reduction in HR ($\Delta\lambda/\lambda$, %), and the optical density A (curves 1-3, respectively).

Fig. 4. Effects of the velocity gradient on an anisodiametric micelle in a flow.

micelles, which reduce HR, is provided by the ratio of the semiaxes deduced from the turbidity spectra (Fig. 2).

Metaupon concentrations above CCM_{II} produce an increase in the ratio of the semiaxes of the rod micelles. There is also an increase in the reduction of the HR in this concentration range (Table 1). Therefore, one assumes that the capacity of the SA to reduce HR is due to these rod micelles. These are oriented by the velocity gradient along the flow and produce anisotropy in the viscosity and reduced resistance [3]. Consequently, the onset of the effect should coincide with CCM_{II}. However, Fig. 3 shows that the reduction begins at 0.12% metaupon, whereas CCM_{II} is 0.09%. Here we note that the velocity gradient makes itself felt not only by orienting the micelles along the flow but also in deforming and destroying the rods. The flow speed varies over the cross section of the tube, and therefore the ends of such a micelle at an angle to the flow direction move with different speeds, i.e., the ends are subject to forces differing in magnitude. These forces may be resolved into perpendicular or orienting ones (which rotate the micelle) and parallel (stretching) ones, which can break the micelle (Fig. 4).

The degrading action of the flow is particularly pronounced in the initial stage of formation of the rod micelles at concentrations at or slightly above CCM_{II}, when the ratio of the semiaxes is still small and the micelles do not have time to recover (Fig. 2). This effect of the velocity gradient can reduce the ratio of the semiaxes and retard the formation of the unsymmetrical structure, which is shifted to higher SA concentrations. These rod micelles are responsible for reducing the turbulent friction, so the reduction occurs at a metaupon concentration of 1.3 times CCM_{II}, at which the effect might be expected (Fig. 3) [10, 11].

At 0.5% metaupon, there is a new change in the micellar structure; the semiaxis ratio remains constant, but the viscosity increases (Fig. 1). This is due to interaction between the micelles at such high concentrations. The reduction in HR is less at and above this concentration (Table 1). We determine the reduction relative to water, not of a liquid having the same viscosity but did not reduce HR, so the marked increase in the viscosity is evidently responsible for the fall in the effect in this concentration range, the more so since the ratio of the semiaxes remains constant.

One way of influencing CCM_{II} and the capacity of the SA solution to reduce HR is to add organic compounds. We therefore examined the effects of butanol on the micelle formation in metaupon solution and the reduction in HR. In the presence of butanol, the viscosity of a metaupon solution with an SA:butanol ratio of 1:3 is raised on account of the existence of larger micelles. The flow has less degrading action on such micelles, and therefore the

TABLE 2. Effects of Organic Additives on the Craft Point of Metaupon in the Presence of 8% Sodium Chloride

Additive	Concn., %	Craft point, °C ±0.1 °C	Dielectric constant of organic additive [12]	Additive	Concn., %	Craft point, °C ±0.1 °C	Dielectric constant of organic additive [12]
Glycerol	1,0	9 2	42,5				
	5,0	10,3	42,5	Propyl	2,0	8,5	19,7
Dioxane	1,0	8,0	2,21		4,0	4,5	19,7
	4,0	10,0	2,21	Butyl	0,25	6,5	17,7
Dimethylformamide	1,0	10,0	37,6		0,5	4,0	17,7
Alcohols:				Amyl	0,12	4,5	14,4
Methyl	4,0	11,5	32,6				

anisodiametric form is acquired earlier, which displaces the start of HR reduction to lower SA concentrations. With an SA:butanol ratio above 1:3 the solution has a viscosity less than that without butanol. The effects of the viscosity on the fall in the hydrodynamic resistance are then less. Therefore, the reduction in the turbulent friction is observed at higher metaupon concentrations (Fig. 1). Therefore, the additional butanol, which influences the physicochemical properties of the solution, expands the concentration range in which the HR is reduced.

The Craft point is one of the basic characteristics of an SA solution. The solution reduces HR only above the Craft point, because micelles do not exist below this temperature. The craft point for metaupon is 9.5°C, and we examined the effects of various organic compounds (Table 2). Aliphatic alcohols reduce the Craft point most markedly. The longer the hydrocarbon chain lengths in the alcohol, the more marked the effect on the Craft point. Other organic compounds (glycerol, dioxane, dimethylformamide) have little effect. At relatively low contents (about 1%) they reduce the Craft point slightly, while at higher contents they raise it somewhat. Distinctive features of compounds that reduce the Craft point markedly are low dielectric constant and the presence of OH groups. Butanol is one of these compounds. Therefore, butanol not only expands the concentration range but also reduces the temperature limit for the HR reduction.

We have thus shown that SA solutions show reduced resistance when they contain anisodiametric micelles, which are formed at concentrations equal to or higher than CCM_{II}. The extent of the reduction increases with the asymmetry of the micelles.

Various additives such as butanol and sodium chloride influence CCM_{II} and the Craft point, and therefore one can alter the concentration and temperature ranges in which the HR is reduced.

NOTATION

λ, drag; t_s, time of solution flow; t_w, time of water flow; ΔP_s, pressure drop for solution; ΔP_w, pressure drop for water; τ, turbidity; l, cuvette length; F_r, rotation force; F_s, stretching force; A, optical density.

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FLOW DISTRIBUTION IN PERFORATED CHANNELS WITH A PERMEABLE END FACE

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The distribution of average velocity vs distance along a channel is given by a one-dimensional model based on the energy equation. An estimate is given of the suitability of the model in the presence of a developed turbulent velocity profile at the channel entrance.

An energy principle has previously been used to describe the average flow velocity distribution along the length of a channel with perforated walls [1, 2]. In a one-dimensional model, the differential equation describing the average parallel velocity distribution along the length of a perforated channel takes the form [2]

$$W''W' + aW'W + bW^2 = 0, \tag{1}$$

where

$$a = 2\frac{3-\varepsilon^2}{1+\xi}\left(\frac{\varphi L}{R}\right)^2;\; b = \frac{\lambda\varphi^2}{1+\xi}\left(\frac{L}{R}\right)^3.$$

The solution under the boundary conditions

$$X = 0,\; W = 1;\; X = 1,\; W = 0 \tag{2}$$

is given in [1] and corresponds to the case of a sealed end channel.

If the end face is not sealed but has many perforations and is permeable to liquid or gas, the boundary conditions will be as follows:

$$X = 0,\; W = 1;\; X = 1,\; W = W_{\text{т}}. \tag{3}$$

The solution of (1) with the boundary conditions (3) may be presented in parametric form as a system of three equations [3]

$$\ln W = \eta X + \frac{1}{2}\ln\frac{\theta_0^2 + \theta_0\eta + \eta^2 + a}{\theta^2 + \theta\eta + \eta^2 + a} + \frac{\eta}{2m}\left(\operatorname{arctg}\frac{2\theta + \eta}{2m} - \operatorname{arctg}\frac{2\theta_0 + \eta}{2m}\right),$$

$$X = -\frac{\eta}{2(3\eta^2 + a)}\left[\ln\left(\frac{\theta - \eta}{\theta_0 - \eta}\right)^2\frac{\theta_0^2 + \theta_0\eta + \eta^2 + a}{\theta^2 + \theta\eta + \eta^2 + a}\right] + \frac{3\eta^2 + 2a}{2m(3\eta^2 + a)}\left(\operatorname{arctg}\frac{2\theta_0 + \eta}{2m} - \operatorname{arctg}\frac{2\theta + \eta}{2m}\right), \tag{4}$$

$$1 = -\frac{\eta}{2(3\eta^2 + a)}\left[\ln\left(\frac{\theta_{\text{т}} - \eta}{\theta_0 - \eta}\right)^2\frac{\theta_0^2 + \theta_0\eta + \eta^2 + a}{\theta_{\text{т}}^2 + \theta_{\text{т}}\eta + \eta^2 + a}\right] + \frac{3\eta^2 + 2a}{2m(3\eta^2 + a)}\left(\operatorname{arctg}\frac{2\theta_0 + \eta}{2m} - \operatorname{arctg}\frac{2\theta_{\text{т}} + \eta}{2m}\right),$$

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