LITERATURE CITED

1. Methods of Laser Doppler Diagnostics in Hydroaerodynamics [in Russian], Énergiya, Moscow (1978).
2. V. A. Zverev and A. I. Kalachev, "Sound radiation from the domain of intersection of two sound beams," Akust. Zh., 15, No. 2 (1969).
3. O. V. Rudenko and M. I. Soluyan, Theoretical Principles of Nonlinear Acoustics [in Russian], Nauka, Moscow (1975).
4. L. K. Zarembo and V. A. Krasil'nikov, Introduction to Nonlinear Acoustics [in Russian], Nauka, Moscow (1966).
5. O. V. Rudenko and A. S. Chirkin, "Theory of nonlinear interaction between monochromatic and noise waves in weakly dispersing media," Zh. Eksp. Teor. Fiz., 67, No. 5(11) (1974).
6. A. N. Abdel'khamid, D. T. Harrier, T. G. Pullet, and M. Summerfield, "Noise characteristics of a subsonic jet issuing from a combustion chamber," Raketn. Tekhn. Kosmonav., 12, No. 3 (1974).
7. M. A. Ibragim, A. I. Klimov, and F. V. Shugaev, "Sound wave interaction with a shock," Akust. Zh., 24, No. 4 (1978).

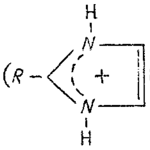
DRAG REDUCTION BY CATION SURFACTANTS: THE RELATION TO PHYSICOCHEMICAL AND MICELLAR CHARACTERISTICS

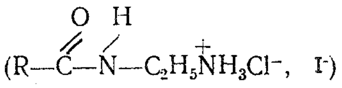
I. L. Povkh, A. I. Serdyuk,
A. V. Naumov, and N. P. Kovalenko

UDC 532.517.4:661.185.23

It is shown that systems containing the cationic surfactant α-naphthol begin to reduce the hydrodynamic resistance at concentrations of 0.02-0.05%, at which solutions contain nonspherical micelles of a particular size.

We have previously shown [1] that the combination of cetylpyridinium chloride (CPCl) with α-naphthol with a 1:1 ratio of the components reduces the drag in the turbulent flow of a liquid (water). Here we consider the drag reduction for water caused by various cationic surfactants in the presence of α-naphthol, and we derive a relationship between the reduction in the drag and the physicochemical parameters of the solutions.

We chose the cationic surfactants cetyl-γ-picolinium bromide (C-γ-PicBr), cetylpyridinium bromide (CPBr), cetylpyridinium iodide (CPI), the hydrochlorides and hydroiodides of alkylamidazolines (Cl^-, I^-), alkylamines ($R\overset{+}{-}NH_3Cl^-$, I^-), and alkylamidoamines



$$(R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-C_2H_5\overset{+}{N}H_3Cl^-,\ I^-)$$

in which the lengths of the alkyl chains R were 12 and 16 carbon atoms.

The drag was measured with a glass tube of length 4 m and diameter 5.45 mm for a Reynolds number of 10,000. The drag reduction ($\Delta\lambda/\lambda$) was calculated from

$$\frac{\Delta\lambda}{\lambda}=1-\frac{\tau_2^2}{\tau_1^2}\frac{\Delta P_2}{\Delta P_1}.$$

The viscosities of the solutions were determined with a BPZh-2 capillary viscometer, while the density was determined by a pycnometer method. The IR spectra of these surfactants dissolved in carbon tetrachloride with and without α-naphthol were recorded with a UR-20 spectrophotometer in the OH stretching region. The optical density of Sudan II (a water insoluble dye solubilized by the surfactants) was measured with an SF-16 spectrophotometer at 550 nm.

The measurements (Fig. 1) show that systems such as C-γ-PicBr–α-naphthol, CPBr–α-naphthol, and CPI–α-naphthol reduce the drag at the very low overall concentration of

---

Donetsk University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 6, pp. 1031-1037, June, 1980. Original article submitted May 4, 1979.

0022-0841/80/3806-0639$07.50

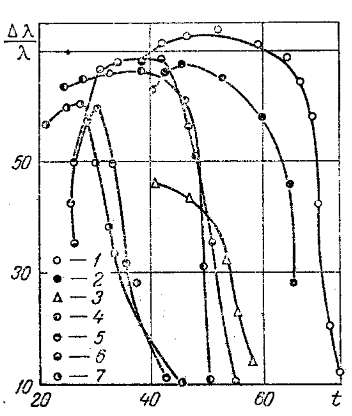


Fig. 1

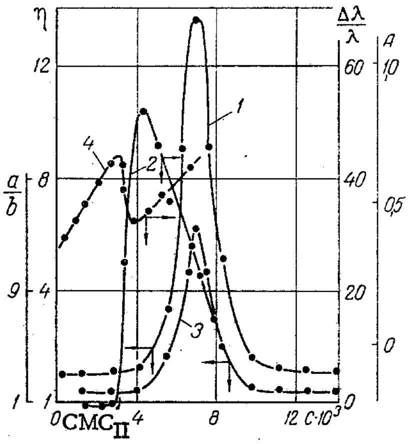


Fig. 2

Fig. 1. Drag reduction ($\Delta\lambda/\lambda$, %) for cationic surfactants with α-naphthol at various concentrations (C, %) in relation to temperature (t, °C). CPI—α-naphthol: 1) $C_1 = 0.075$, $C_2 = 0.016$; 2) $C_1 = 0.037$, $C_2 = 0.008$; 3) $C_1 = 0.018$; $C_2 = 0.004$; CPBr—α-naphthol; 4) $C_3 = 0.060$, $C_2 = 0.022$; 5) $C_3 = 0.030$, $C_2 = 0.011$; C-γ-PicBr—α-naphthol: 6) $C_4 = 0.100$, $C_2 = 0.048$; 7) $C_4 = 0.050$, $C_2 = 0.024$.

Fig. 2. Effects of α-naphthol concentration on the physicochemical parameters of CPCl—α-naphthol at $C_5 = 0.007$ M and t = 25°C: 1) relative viscosity η_{rel}; 2) drag reduction ($\Delta\lambda/\lambda$, %); 3) ratio of semiaxes (a/b); 4) optical density A of solutions in this system containing Sudan II.

0.02-0.05%. This is well below the levels of all surfactants reported in the literature as reducing hydrodynamic resistance in liquids [2-4]. The structures of the surfactant solutions were examined by reference to the physicochemical parameters (Fig. 2). The viscosities of surfactant solutions containing α-naphthol were plotted as a function of the α-naphthol concentration; there is a kink showing a sharp increase in viscosity at a particular α-naphthol level. This indicates [1] that the micellar structures at that point go over from spherical to aspheric. The concentration is called the second critical micelle concentration (CMC_{II}); the first critical micelle concentration (CMC_I) is the surfactant concentration at which spherical micelles are formed.

This aspheric transition gives rods, which involves compression and compaction of the micelles [5]. This reduces the solubilizing action of the micelles by comparison with the spherical case. There is a marked reduction in the solubilizing capacity for Sudan II in surfactants combined with α-naphthol (Fig. 2) at a particular concentration of the latter, which also indicates that aspheric micelles are formed. The drag reduction occurs approximately at the concentration CMC_{II} (Fig. 3), i.e., the published data for CMC_{II} for various surfactants serve to characterize not only the physicochemical properties but also the drag performance. These values constitute the minimum surfactant concentration necessary to reduce the frictional loss in the turbulent flow of water.

The considerable increase in viscosity in surfactant—α-naphthol solutions at concentrations above CMC_{II} indicates [1] that aspheric micelles occur. Coombe's equation [5] describes the relative viscosity of a surfactant solution as a function of the semiaxes of the micelles, which are considered as flattened ellipsoids of rotation, and Guth and Simha [6] transformed this to the form

$$a/b = 1 + 0.663\exp(3.46\varphi),$$

where φ is found from the observed relative viscosity;

$$\eta = 1 + 2.5\varphi + 14.1\varphi^2.$$

These equations have been widely used in the literature to estimate the shapes of micelles [7,8]. The ratio of the semiaxes at which the drag drop occurs is in the range from 2 to 14 for various surfactants. The minimum ratio at which the effect originates corresponds to a concentration of surfactant close to the concentration of CMC_{II}.

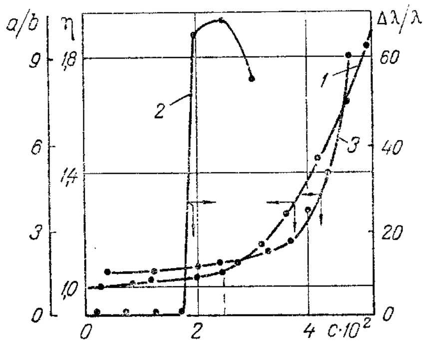


Fig. 3

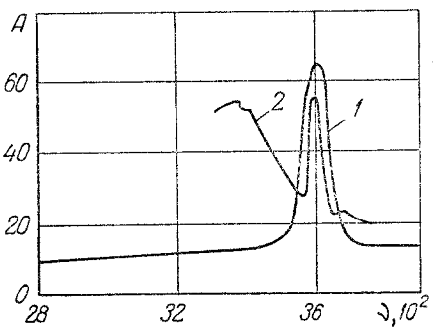


Fig. 4

Fig. 3. Physicochemical parameters of aqueous solutions of CPI in relation to concentration (C, M) at t = 45°C: 1) relative viscosity η_{rel}; 2) drag reduction ($\Delta\lambda/\lambda$, %); 3) ratio of semiaxes, a/b.

Fig. 4. IR spectra: effects of CPCl on the absorption A in the OH-stretching band of α-naphthol: 1) α-naphthol in CCl_4; 2) CPCl + α-naphthol in CCl_4; C_2 = 0.0067 M, C_5 = 0.0033 M.

A detailed discussion of the relationship of the effect to CMC_{II} [1,9] indicates that the reduced drag begins at a surfactant concentration equal to or somewhat less than CMC_{II}; in the system CPCl—α-naphthol the concentration is less than CMC_{II} by a factor 1.1-1.2 (Fig. 2). Figure 3 shows that the reduction in drag occurs at a CPI concentration less than CMC_{II} by a factor 1.6. Spherical micelles exist in solutions with concentrations less than CMC_{II} under static conditions. On the other hand, the micelles are oriented in a flow and are deformed [10]. One consequence of this is that the micelles become aspheric at concentrations lower than those relating to static conditions, because the drag reduction sometimes sets in at surfactant concentrations somewhat less than CMC_{II}.

One result of the orientation may also be that the rod micelles link up into filaments; these resemble the macromolecules of linear polymers as regards behavior in a flow. The surfactants reduce the drag by a mechanism analogous to that applicable to polymers. One of the disadvantages of polymers that reduce the drag is that the performance decreases with time on account of irreversible mechanical destruction of the macromolecules in the flow [11]. Polymer-type filamentary micelles are also undoubtedly damaged mechanically, but micelle formation is reversible [12], so the micelles will recover their properties when the factors causing destruction are eliminated. This itself has disadvantages, because we do not know how to synthesize a micellar structure that reduces the drag. Such structures exist only under particular conditions, which are governed by the temperature, the nature of the material, the concentration, and various other factors. We know of only a few systems that reduce the drag in water. It is therefore necessary to define new additives. The physicochemical parameter characterizing the hydrodynamic effect of a surfactant may be taken as CMC_{II}.

The above surfactants (CPCl, CPBr, CPI, C-γ-PicBr) with α-naphthol reduce the drag, but there are compounds that do not do this in the presence of α-naphthol at any concentration or ratio of the components (Table 1). Examples are substances such as hydrogen halides of alkylimidazolines, alkylamidoamines, and alkylamines.

The viscosity in relation to α-naphthol concentration shows that aspheric micelles are not formed in these solutions; these surfactants have NH groups in the hydrophilic parts of the molecule and low degrees of dissociation of the molecules in micelles [13].

IR spectroscopy in carbon tetrachloride (as a model for undissociated surfactant molecules) has shown that α-naphthol interacts via hydrogen bonds with the hydrophilic part of the surfactant molecule (Fig. 4). The electron-density distributions in the cation and anion [14] indicate that α-naphthol can interact only with the anion molecule not containing NH groups, and it does not interact with the surface-active cation. The α-naphthol interacts with cationic surfactants via the NH groups in the hydrophilic part of the surfactant, i.e., α-naphthol interacts with the undissociated molecules in the micelle in aqueous solution and accumulates in the hydrophilic part of the latter. When α-naphthol is solubilized by a

TABLE 1. Effects of Structure of Cationic Surfactant on the Formation of Aspheric Micelles and Drag Reduction in Aqueous Solutions Containing α-Naphthol

Surfactant	Colloid-chemical properties and hydrodynamic resistance in solutions of surfactant with α-naphthol		
	form of micelles: aspheric(+), spherical (-);	drag: no reduction (-), reduction (+)	constants for ratio of CMC_{II} and α-naphthol concentration ($K=CMC_{II}/C_2$) for various cationic surfactants with α-naphthol at t = 45°
Cetylisoquinolinium bromide	+	+	4,44
Cetylpyridinium chloridee	+	+	2,50
Cetylpyridinium bromide	+	+	1,51
Cetyl-γ-picolinium bromide	+	+	1,05
Cetylimidazolinium chloride	—	—	—
Cetylamidoammonium chloride	—	—	—
Cetylammonium chloride	—	—	—

surfactant having a high degree of dissociation of the molecules in the micelle, most of the compound will appear in the hydrophobic part. Literature data [13] confirm the nonuniform distribution of α-naphthol in the hydrophilic and hydrophobic parts of micelles, where the structure of the surfactant is the relevant feature. The presence of α-naphthol in the hydrophilic part of the micelles interferes with the transition to aspheric form, since this must be accompanied by a reduction in the distance between the hydrophilic parts [15]. Therefore, a surfactant that contains NH groups in the hydrophilic part or has a low degree of dissociation cannot reduce the hydrodynamic resistance of water. This provides a way of selecting surfactants that can reduce the drag in the presence of α-naphthol. This occurs in any surfactant whose hydrophilic part does not contain functional groups that are proton donors (—NH—, —OH—, etc.) and which have a high degree of molecular dissociation in the micelles [13].

It has been shown [13] that the degree of dissociation of a cationic surfactant is directly proportional to the dipole moment; we can therefore list surfactants that will reduce the drag in the presence of α-naphthol. Examples are alkylisoquinolinium and alkyllutidinium halides. The latter are synthesized from coal-tar products and at present have no particular application.

NOTATION

$\Delta\lambda/\lambda$, drag reduction, %; t, temperature, °C; C, concentration, %, mole/liter; C_1, concentration of CPI solution, %, mole/liter; C_3, concentrationof CPBr solution, %; C_4, concentration of C-γ-PicBr solution, %; C_5, concentration of CPCl solution, mole/liter; η, relative viscosity; a/b, micelle semiaxis ratio; τ_1, water efflux time, sec; τ_2, solution efflux times, sec; P_1, water pressure difference, mm water column; P_2, pressure difference in flowing solutions; A, absorption; ν, frequency, cm^{-1}; HR, drag; C_2, concentration of α-naphthol, %, mole/liter; φ, volume fraction of micelles.

LITERATURE CITED

1. I. L. Povkh, I. A. Shevchuk, A. I. Serdyuk, et al., "Solubilizing action of aqueous solutions of cetylpyridinium chloride," Ukr. Khim. Zh., 44, No. 3, 275 (1978).
2. J. L. Zakin, M. B. A. Poreh, and M. Warshavsky, "Exploitation study of friction reduction in slurry flows," Chem. Eng. Progr. Symp. Ser., 67, No. 111, 85-89 (1971).
3. I. L. Povkh, A. B. Stupin, S. N. Maksyutenko, et al., "Laser anemometer study of the turbulent flow of solutions of surfactants," Inzh.-Fiz. Zh., 29, No. 5, 853 (1975).
4. V. M. Dobrychenko, V. G. Lobachev, I. L. Povkh, and A. E. Éidel'man, "Drag reduction by micelle-forming additives of surfactants," Inzh.-Fiz. Zh., 30, No. 2, 240 (1976).
5. V. N. Tsvetkov, V. E. Éskin, and S. Ya. Frenkel', Structures of Macromolecules in Solution [in Russian], Nauka, Moscow (1964), pp. 98-107.
6. E. Guth and R. Simha, "Untersuchungen über die Viskosität von Suspensionen und Lösungen. Über die Viskositet von Kugelsuspensionen," Kolloid. Z., 74, No. 3, 266-275 (1936).

7. V. A. Ryzhov and L. L. Erokhina, "The structure of micellar solutions of sodium monodecylsuccinate," Kolloidn. Zh., 39, No. 5, 987 (1977).
8. O. M. Aivazyan, "Physicochemical studieson structuring in sodium pentadecylsulfinate accompanying the dissolution of various oleophilic substances," Candidate's Dissertation, IÉB Akad. Nauk Arm. SSR, Erevan (1978).
9. I. L. Povkh, R. V. Kucher, I. A. Shevchuk, et al., "A study of critical micelle concentrations for solutions of surfactants," Zh. Prikl. Khim., 51, No. 5, 1045 (1978).
10. V. N. Tsvetkov, "Birefringence in flowing solutions of semirigid chain molecules," Vysokomol. Soedin., 7, No. 8, 1468 (1965).
11. I. L. Povkh and A. B. Stupin, "Effects of polyacrylamide on the drag reduction in aqueous flows containing solid particles," Inzh.-Fiz. Zh., 22, No. 5, 919 (1972).
12. K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, Colloidal Surfactants: Some Physicochemical Properties [Russian translation], Mir, Moscow (1966), p. 38.
13. R. V. Kucher, A. I. Serdyuk, A. V. Naumov, and V. P. Marshtupa, "Effects of structure of cationic surfactants on the formation of micelles," Kolloidn. Zh., 41, No. 4, 791 (1979).
14. A. K. Sheinkman, "Structures and reactions of pyridinium and benzopyridinium cations," Author's Abstract of Doctoral Dissertation, Donetsk University (1972).
15. M. Kodama and M. Masaji, "The second CMC of the aqueous solution of sodium dodecyl sulphate. II. Viscosity and density," Bull. Chem. Soc. Jpn., 45, No. 8, 2265-2269 (1972).

EXPERIMENTAL STUDY OF TRANSVERSE MASS EXCHANGE IN THE FLOW OF POLYOXYETHYLENE SOLUTIONS IN A ROUND PIPE

A. I. Zhernovoi, Yu. F. Ivanyuta,
and I. I. Takhistova

UDC 532.529.5

A method is proposed for investigating the transverse mass exchange in the turbulent flow of polyoxyethylene solutions in a pipe using the phenomenon of nuclear magnetic resonance.

Investigations of the influence of polymer admixtures on the reduction of hydrodynamic resistance in the turbulent flow of polyoxyethylene solutions in pipes by traditional methods are described in [1].

However, these methods introduce a disturbance into the investigated medium, which can lead to considerable errors when measuring in pipes of small diameter. As for methods based on recording particle tracks [2], they also are not free of important drawbacks, especially when investigating flows of polymer solutions, since polymers, while effectively reducing resistance, are strong flocculants, distorting the behavior of individual particles in the flow. For example, pulsation velocity components in the boundary region in the turbulent flow of water and polymer solutions in a channel were obtained in [2] which differ considerably from those given in [3], where the intensity of turbulence near the wall was studied using photography of small air bubbles included in the liquid and it was established that under the conditions of a decrease in resistance there is a decrease in the intensity of the axial components of turbulent pulsations in comparison with pulsations in a Newtonian liquid, whereas no noticeable changes take place in the radial component.

In this connection it seems appropriate to develop new methods of investigation of the flow structure of turbulent streams. This is also underlined by the fact that, despite the numerous investigations, none of the existing theories ultimately satisfy the requirements of the practical use of small admixtures of polymers for the reduction of hydrodynamic resistance [4].

To study phenomena of transverse diffusion (transverse mass exchange) in the flow of polyoxyethylene solutions in a round pipe we developed a method based on the use of phenomena of nuclear magnetic resonance [5,6].

Lensovet Leningrad Technological Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 6, pp. 1038-1043, June, 1980. Original article submitted January 15, 1979.

0022-0841/80/3806-0643$07.50