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Properties of a drag reducing micelle system

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Abstract: Rheological properties of a drag-reducing surfactant were investigated with the intention to find out the influence of shear rate and the duration of shear straining on the Shear Induced Structure. The ability of the surfactant to restore the broken drag-reducing network after the decrease of shear stress is well known. This property of reversible change caused by high shear at different flow conditions was compared to a more intensive mechanical straining by means of ultrasound. Observations using electronmicroscope and spectrometer are also presented.

Key words: Surfactant – micelle structure – drag reduction – rheological properties

Introduction

The phenomenon of drag reduction in a turbulent flow in pipes has been studied very thoroughly by a multitude of scientists since it was described for the first time almost 50 years ago. Mainly two types of drag reducing additives were investigated. Polymers were first investigated as effective additives, and later attention was paid also to micelle systems [1–3]. Each additive has specific advantages.

The object of our interest are micelles of some surfactants and their secondary networks which are built up during the flow of such a system in a pipe with respect to the ability of the surfactant to reduce the friction losses in turbulent flow. Cationic surfactants are effective as drag reducers within limited concentration and temperature ranges [4]. This is very important for the possible usage in heating systems [5–6]. It is always emphasized that the surfactants demonstrate "a reversible shear degradation", that is, they suffer a mechanical change of the structure in regions of high shear and regain their drag-reducing effectiveness when the level of shear stress decreases. This behavior is usually ascribed to the breakdown and reformation of the network structure built up from rod-like micelles [7–12]. It is certainly an advantage over the polymeric solutions. The long chain molecules of polymers are subjected to breaking by shear and the degraded polymer has much less ability to decrease the friction than the undegraded one. Moreover, the polymer mechanical degradation is permanent.

Experimental

The following instruments were used for the measurement and observation of the surfactant solutions: rotational rheometers Rotovisco RV 20 and CV 20 N with coaxial cylinder sensors (Haake, FRG), transmission electronmicroscope Geol JEM 100 B (Geol Ltd., Japan), ultrasonic disintegrator and photon correlation spectrometer.

The first component of the used additive was the commercial product Ethoquad T/13-50 (ET) which is produced by Akzo Chemie America. Its composition is as follows: 50% active tenside-tallow tris hydroxyethyl ammonium acetate, 36% isopropanol, and 14% water. Its molecular weight Mw is approximately 454, specific gravity 0.952 g/cm^3 at 20 °C. The second component of the surfactant is natrium salicylate (NA) with $Mw = 160.11$.

Most of our rheological measurements were carried out with the mixture of ratio ET:NA

= 5 mMol/l of active tenside ET:7.5 mMol/l of NA (which was 4.54 g/l:1.20 g/l in total weight).

Results

The evidence of shear-induced structure

There exist several theories explaining the micelle function in drag reduction in the turbulent flow. After Hoffmann et al. [9], the rod-like micelles make up a lattice in which the rods are statistically distributed. Their orientation is arbitrary, but when sheared they become ordered parallel with the stream. Such an oriented structure grows from small clusters to the entire flow field with the increasing rate of shear. This network dampens the turbulence. It is broken up when a certain rate of shear is exceeded and the drag-reducing effect is lost. When the rate of shear is diminished again, the oriented lattice reshapes.

Another theory [11, 12] states that the supermolecular structure is built up from single micelles. The rod-like micelles bounce against one another, join and form long parallel chains in the flow field. A similar hypothesis was expressed in [8], with the presumption that the micelles are flexible and that the velocity fluctuations perpendicular to the flow are dampened by long micelle chains. With high values of rate of shear the chains break, but when the rate of shear is decreased again, they reform.

Orthokinetic aggregation of colloidal particles is well known. For example, the growth of latex particles caused by shearing was studied by Husband and Adams [13]. This effect occurred at rather high shear rates above $10^3\ s^{-1}$. A similar mechanism may take place in aggregation of micelles up to a critical shear rate when the aggregates break. The computer simulation for aggregation of sphere-shaped colloids at low shear rates was made in [14] with the result of steep increase of viscosity (when plotted against shear strain at constant shear rate) at the beginning and achievement of the constant viscosity for higher values of shear strain. Our measurement (not presented here) of time dependence of viscosity at constant low shear rates proved the quick viscosity change at the beginning and no time dependence after a certain time.

Shear-induced phase transitions were described by several authors [4, 10–12]. The shear-induced structure (SIS) as a result of growing shear strain can also be very well observed by means of rheological measurements. The appearance of SIS in water solutions of Etna with different concentrations is presented in Fig. 1. As can be seen, the viscosity of the solutions decreases at first with the rising rate of shear (pseudoplastic behavior), and at a certain critical value of the rate of shear a sudden increase of viscosity is encountered which is caused by the formation of SIS. We conclude also that the critical value of the rate of shear for the formation of the SIS is smaller with the smaller tenside concentration.

The effect of temperature on SIS is shown in Fig. 2; the critical value of the rate of shear decreases with increasing temperature as well as with decreasing concentration (Fig. 1). In this respect the surfactant Etna differs from some other described micellar systems [4, 15]. Increasing the rate of shear beyond the region of the SIS origin (above about $1100\ s^{-1}$) there appears again a decrease of viscosity. This region can be called the second region of pseudoplastic behavior. Repeated measurements unambiguously showed that the structural changes due to temperature straining are reversible. When measuring the temperature

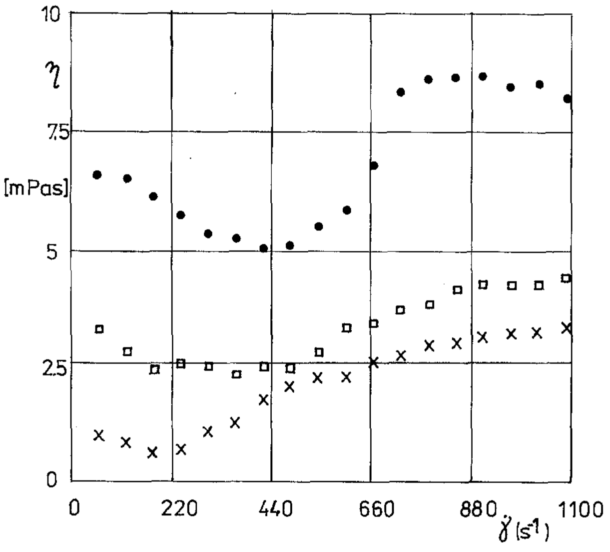


Fig. 1. Viscosity curves of Etna solutions with the total weight ratio ET:NA = 3.78:1 and total weight concentrations: ● 5.74 g/l; □ 4.305 g/l; × 2.153 g/l

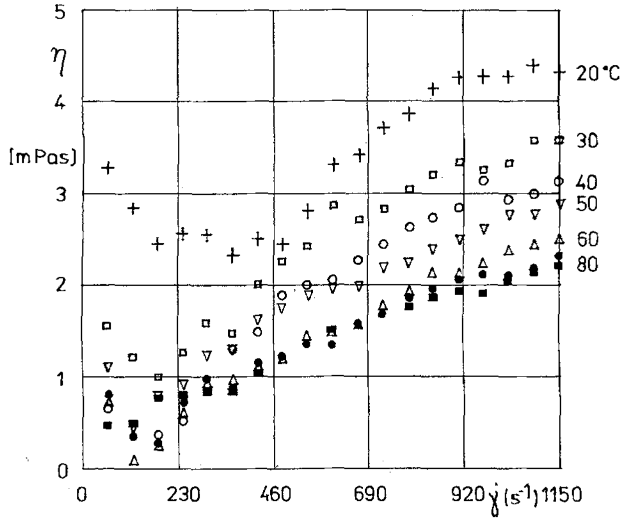


Fig. 2. The temperature dependence of viscosity of Etna solution with total weight concentration 4.305 g/l

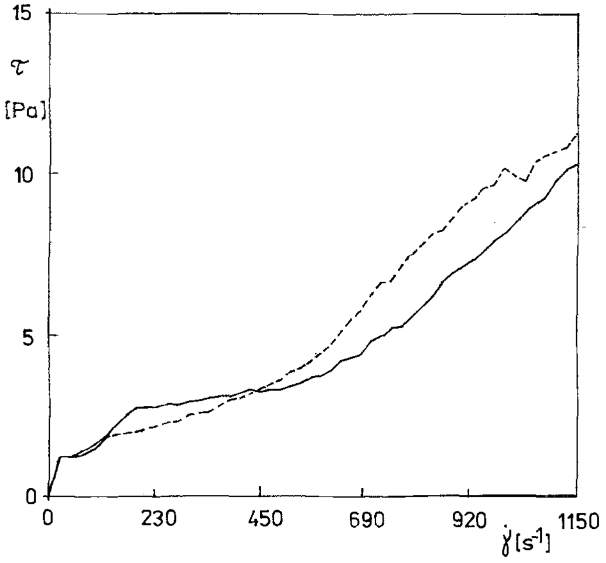


Fig. 3. The flow curves of Etna solution (5.74 g/l) at 20 °C. Solid line: fresh sample; dashed line: after 60 min shearing at $\dot{\gamma} = 200\ s^{-1}$

dependence of the flow curves, control measurements at 20 °C were performed after each temperature step. No changes in the flow curves at 20 °C were observed, thus indicating the good stability of the surfactant with respect to temperature history (within the range 20–80 °C).

Not only the magnitude of the rate of shear influences the rheological properties of the surfactant, but also the duration of application of the shear rate reveals similar effect. To prove this two flow curves measured with Rotovisco RV 20 are drawn in Fig. 3, the one of fresh sample and the second flow curve measured after straining the sample for 60 min by constant rate of shear $\dot{\gamma} = 200\ s^{-1}$. As can be seen, the flow curve of the strained surfactant reaches higher shear stresses than those of unstrained surfactant. However, repeated measurements of flow curves showed that the structural changes due either to small shear straining or its short duration are reversible as no permanent changes in the flow curves were observed.

Breaking of the secondary micellar structure

As we mentioned above, there is a generally accepted idea that the secondary micelle network system breaks at a certain level of shear strain but that it reshapes again when the strain loaded on the solution decreases. The system is able to regain the drag-reducing properties. However, this concept does not apply to any mechanical strain which we proved by measurement of the influence of ultrasound application [16] on the rheological properties of water solution of Etna.

The solution (of 0.574% weight concentration) was strained by ultrasound in a 100 ml beaker for 2 or 8 min. The steady shear viscosity curves were measured before and directly after the exposure to ultrasound and again after 3 days of rest. All measurements were done at the same temperature 20 °C and the results are shown in Fig. 4. The influence of ultrasound is easily seen there; the viscosities of solutions after the straining are lower than those before straining. Figure 4 proves that the secondary micellar structure changes due to ultrasound load. This change is not reversible because the flow curve measured 3 days after straining is almost the same as the one measured immediately after straining. The flow curves of the strained sample at different temperatures are shown in Fig. 5. In comparison with the temperature influence on the flow curves of the unstrained surfactant, the strained sample viscosities are always lower.

The acoustic power at the top of the concentrator of the ultrasound generator was 40 to 50 W and the energy input to the solution during 2 min

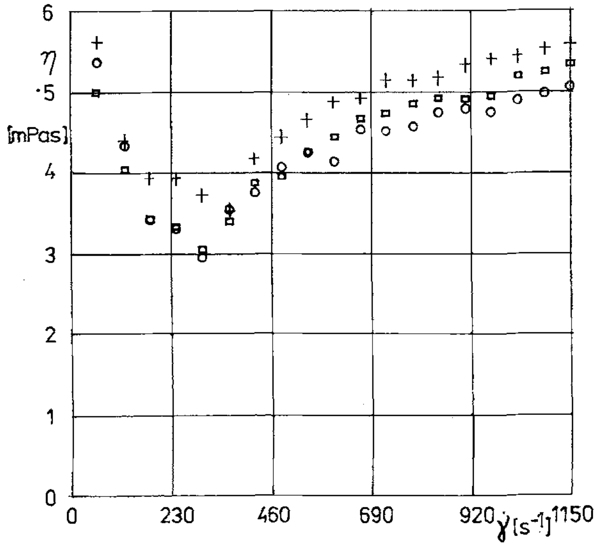


Fig. 4. The viscosity curves of Etna solution (5.74 g/l) at 20 °C. + fresh sample; □ after 2 min straining by ultrasound; ○ after 8 min straining by ultrasound

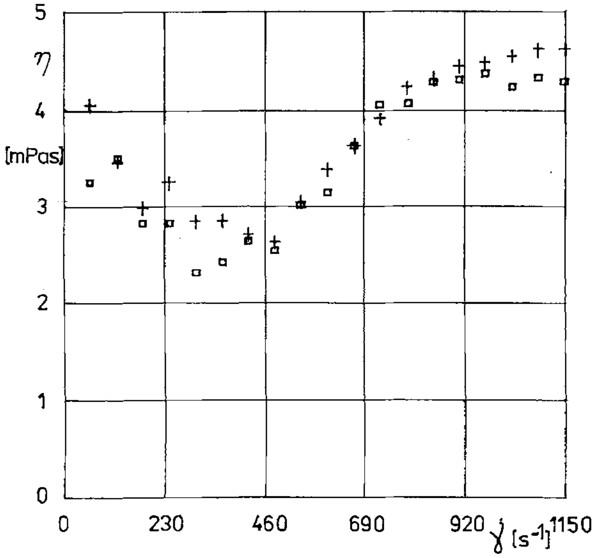


Fig. 6. The viscosity curves of Etna solution (4.305 g/l) at 20 °C. – fresh sample; □ after 2 min straining by ultrasound

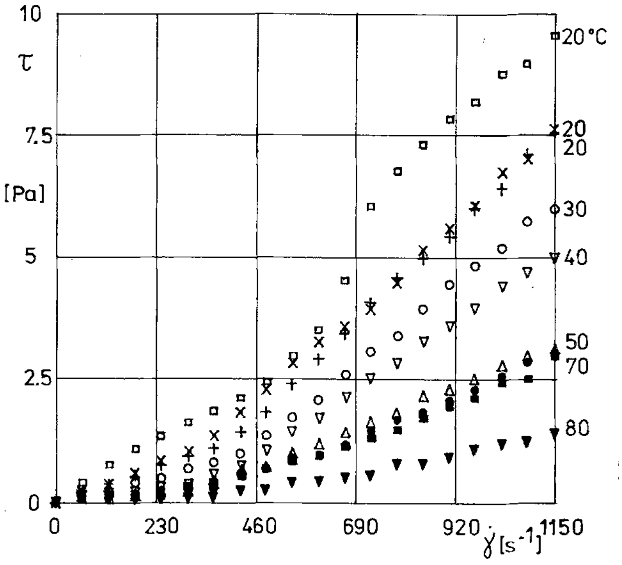


Fig. 5. The flow curves of Etna solution (5.74 g/l). □ fresh sample; + sample measured immediately after straining by ultrasound; all other symbols are temperature-dependent flow curves of the strained sample measured after 3 days' rest

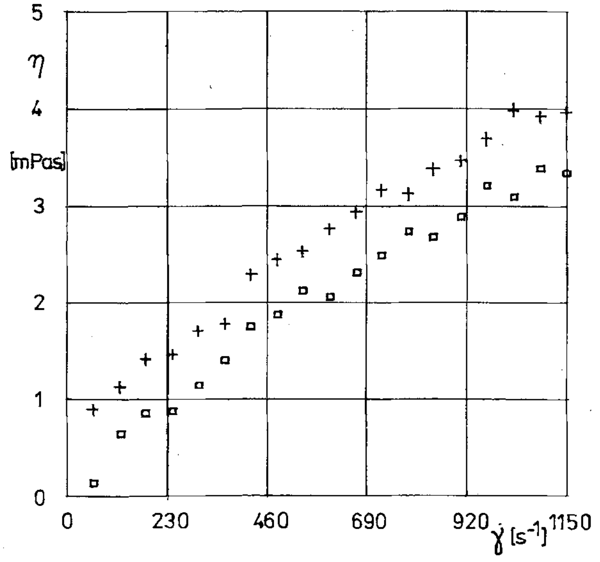


Fig. 7. The viscosity curves of Etna solution (2.87 g/l) at 20 °C. – fresh sample; □ after 2 min straining by ultrasound

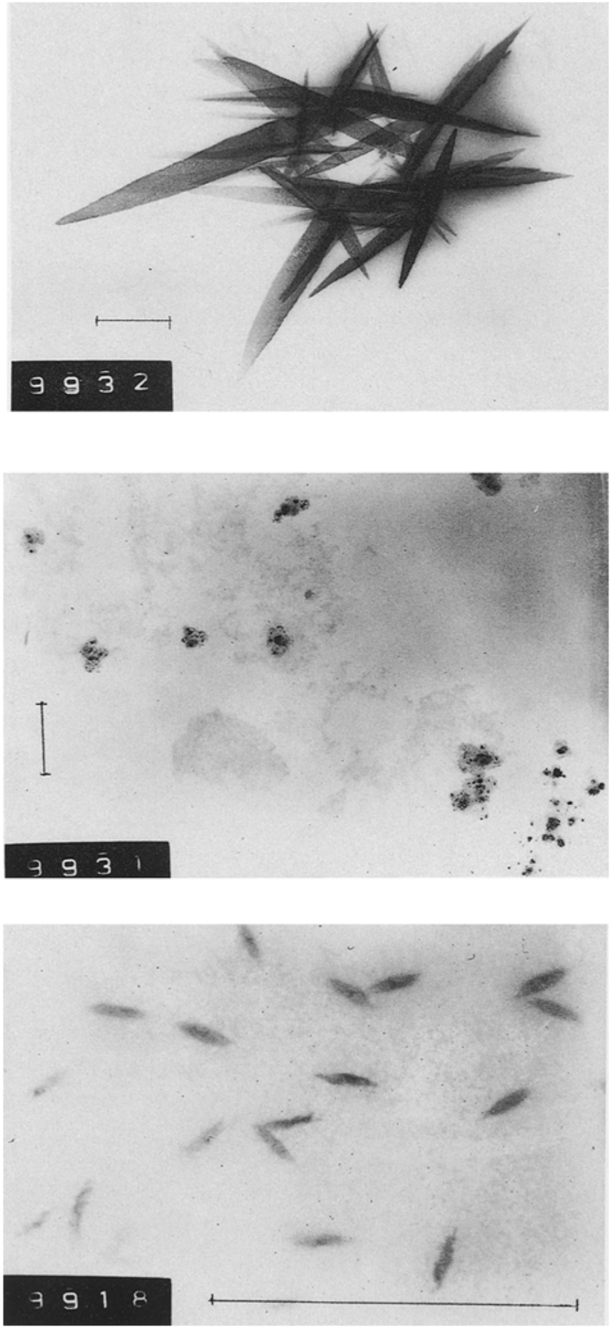
was 4800 Ws, which equals the specific work of 32 Ws/g. Part of energy input is the heat loss.

The viscosity curves are shown also in Figs. 6 and 7. The viscosity after ultrasound application is always smaller than the one before application. Longer application decreases the viscosity even more (see Fig. 4). The flow curves after 3 days' rest do not change. This proves that the partial permanent change of the micelle network by means of very intensive mechanical straining is possible.

The influence of other types of mechanical straining is now being investigated.

Observation in electronmicroscope

One author has observed [17] the shape of particles of a surfactant Sean, which is a mixture of carbo ethoxy pentadecyl trimethyl ammonium bromide with 1-naphthalene. This surfactant proved to be a very effective drag reducer at room temperature [8]. A similar procedure as in [17] was used in the observation of the surfactant Etna presented here.



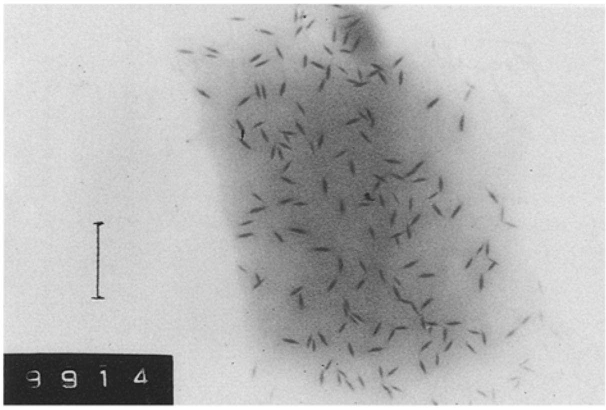


Fig. 8. Electron micrographs of observed dried microparticles of Etna solutions. The line segment equals 1 μm. a) and b) concentration 0.544%; c) and d) concentration 0.1435%.

Observation was done in a transmission electronmicroscope Geol JEM 100 B. The applied voltage was 60 kV. The microscopic preparations for observation were made in such a way that the solution was either dropped or finely sprayed on the underlying collodion film. In Fig. 8 are shown different shapes of observed particles from the dried surfactant Etna. The dried samples do not necessarily correspond to the true wet micellar or network structure. Both shape and size of oberved objects are remarkably similar to the ones from drag-reducing surfactant Sean [17].

Hydrodynamic radius of micelles

The size of micelles at rest was measured by means of quasielastic light scattering. The distributive functions of hydrodynamic radius R_H of micelles were obtained by Laplace transform from autocorrelation functions of intensity of the scattered light. Three different concentrations of Etna were tested as shown in Fig. 9. Only a very small influence of concentration on average values of R_H was determined.

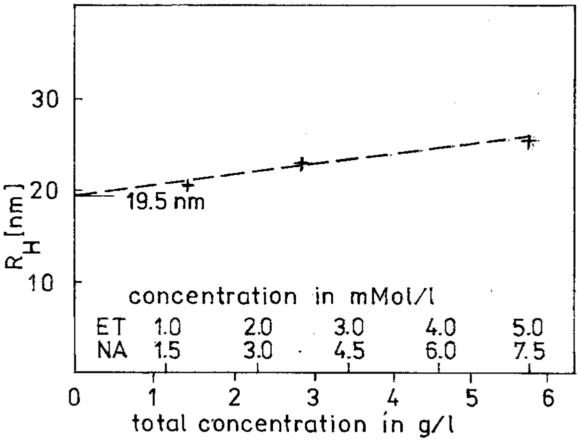


Fig. 9. The hydraulic radius R_H of micelles measured by means of light scattering and its dependence on concentration of Etna solutions.

Conclusion

Cationic surfactants are effective as drag reducers. It had been found that the micelles form the SIS at a certain value of rate of shear. This structure was confirmed by the rheological investigation of the water solution of Ethoquad T 13/50 with natrium salicylate.

It is known that the secondary network structure, which is responsible for the drag reduction, suffers changes in regions of high shear, and the network reshapes again when the level of shear stress decreases, thus demonstrating the ability of reversible change of network. It was proved that this surfactant may also display a permanent change of viscosity curve by ultrasound application.

We have pointed out a remarkable similarity between the shape and the size of observed dried structures of two different surfactants: carbo ethoxy pentadecyl trimethyl ammonium bromide with 1-naphtalene and tallow tris hydroxyethyl ammonium acetate with natrium salicylate. Both surfactants are effective drag reducers. The size of micelles of Etna at rest as measured by light scattering is approximately 0.05 μm.

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