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ORIGINAL CONTRIBUTION

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Significance of shear induced structure in surfactants for drag reduction

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Abstract Cationic drag reducing surfactants are suitable means for reducing the energy costs in city district heating and cooling systems. Water used in these systems is usually a treated water, however, the loss of water due to the leakage is often supplied by water from the municipal network and thus the content of ions in the system may increase. That is why the influence of ions present in water and temperature on viscosity curves has been investigated and the effect of both on Shear Induced Structure (SIS) is shown here. We have proved that SIS is not an indispensable condition for the surfactant ability of drag reduction.

Key words Drag reduction – surfactants – viscosity

Introduction

Drag reducing surfactants show a great variety in rheological behavior, however, a particular feature which could be considered as a characteristic of the ability of an additive to reduce the drag is always looked for. Rose and Foster [1] have doubted the importance of the storage and loss modulus data obtained by forced oscillation. It was also shown in [2] that neither the existence of the first normal stress difference does necessarily accompany the drag reduction. But it is generally believed by many investigators that the dynamic viscosity and elongational viscosity are characterstic properties considered to be relevant for drag reduction. The presence of worm-like micelles ordered by the flow causes an anisotropy of dynamic viscosity which might be a good idea for the explanation of the phenomenon.

The viscosity curve of a surfactant containing long micelles is sometimes shown with a pattern which closely resembles the pattern of a polymer viscosity curve, see e.g. [3, 4]. Nevertheless, many authors have shown different results and described a particular behavior of micelle forming surfactants which has been called a Shear Induced Structure (SIS), see e.g. [5–9] where the influence of concentration on the structure can be found. Ohlendorf et al. [10] show also a dependence of SIS on temperature in the system of hexadecyl trimethyl ammonium bromide with sodium salicylate and the same surfactant uses Bewersdorff [11] to show the formation of SIS in detail. Hu et al. [12] report a shear thickening behavior of the system tetradecyl dimethyl aminoxide with sodium dodecylsulfate plus added NaCl with a peak of the viscosity curve around 60 s^{-1} for a fixed concentration ratio of all three components. Cates and Candau [13] suggest that salt concentration and specific counterion effects are important in determining the dependence of average micellar size on concentration, and that the size of micelles influences the viscosity curve. They discuss the cetylpyridinium salt (CPy) system, they show e.g. that NaBr is able to promote a large increase of the size of micelles while NaCl has no noticeable effect. Berret et al. [14] showed a steep increase of viscosity of CPy–sodium salicylate mixture when the concentration increases, however, the measurement was done only at a constant brine concentration. The effect of NaBr concentration on the mixture of cetyl trimethyl ammonium bromide (CTAB) was investigated by Hu et al. [15]. The influence found is rather complex, there appear peaks on the viscosity vs. NaBr concentration curves. However, it seems that the general tendency is a viscosity decrease at high concentrations. Candau et al. [16] show a constant viscosity of a solution of dodecyl methyl ammonium bromide but when NaCl is added, viscosity decreases.

With reference to results of many investigators, the viscosity curve of a drag reducing surfactant can thus be described in general as follows. At very low values of shear rate D the dynamic viscosity η shows a sudden sharp increase from the initial low value to a very high value. This jump occurs at shear rates which are usually of the order of units or utmost tens of reciprocal seconds. This behavior is described as being due to a building of superstructures the effect of which is in opposition of the expected behavior of dispersed micelles or micelle chains, that is their alignment with the flow which should be followed necessarily by a decrease of shear viscosity in the longitudinal direction. From this early peak on the viscosity curve the viscosity decreases to a minimum which is usually attained within several hundred reciprocal seconds. We believe that only at this point the full alignment of long micelles with the flow becomes true. It has been confirmed by flow birefringence experiments, too. Further development of the viscosity curve shows a great variety depending on the structure of the surfactant.

When the measurement of viscosity curve is not performed at very small shear rates, the sudden increase of viscosity is not detected and the curve starts already at high values of viscosity followed by its decrease.

We have described a general shape of the viscosity curve of a drag reducing surfactant based on results of many scientists, however, absolute values of viscosities of all surfactants differ. Of course, concentration, temperature and the salt/surfactant ratio have the greatest impact on viscosity and we have seen [17] that the increase or decrease of the viscosity value depends on the shear history, too. Along with these named categories the viscosity is also influenced by ions present in the solvent (water).

This paper tries to answer a question whether SIS can be considered as a key feature of drag reduction ability. In other words, whether the drag reduction ability of a surfactant can be deduced and predicted from the shape of the viscosity curve.

Utilization of surfactants

About seven large scale field tests with different drag reducing surfactants in five countries in the world have been reported to be done with very good results. In several tests Habon and Habon G of Hoechst, AG, were used, that is with 450 and 200 mm pipes in Germany [18–20] and with 200 mm pipe in Denmark [21] in primary heating circuits, and in secondary heating system of a city district with approximately 330 apartments (40 m^3 water volume) in the Czech Republic [22]. Habon G is thus designated as an effective high temperature drag reducer suitable for use in both primary and secondary city district heating systems.

Ethoquad T/13-50 and Arquad 16-50, products of Akzo Chemie, in mixtures with sodium salicylate were tested in hydronic systems of buildings in the USA [23, 24]. Metaupon was used in 300 mm pipes of a cooling system in mines in Ukraine [25].

At present a large scale field test once more in Denmark is under way.

Experimental

The influence of ions in water was investigated in solutions of Habon G which is hexadecyl-dimethyl-hydroxyethyl ammonium 3-hydroxy-2-naphtoate. Delivered concentrated material contains 53.5% active surfactant, 10.2% isopropanol and 36.5% water, molecular weight is 501. It is easily diluted in water and best drag reducing concentration is reported 2 mM but even less gives excellent results.

Following instruments were used for rheological experiments: Haake rotational rheometers Rotovisco RV 20 with CV 20N and CV 100 (with coaxial cylinder and cone-plate geometry available). The Couette system used was type MV 1 (the ratio of outer to inner radius of cylinders is 1.05), NV (the ratio is 1.02) and ME (Mooney-Ewart) 45 (the ratio is 1.078). Further on, also a set of capillary viscometers was used for simple evaluation of the influence of ions on the solution viscosity. The surfactant solutions were aged at least for several days.

The interval between the onset of shear and the time when the shear stress reaches an equilibrium was measured for a number of different surfactants listed in Fig. 2. This induction time was usually of the order of tens of seconds, however, the time needed for shear stress to increase to a steady value in case of Habon G was of the order of minutes. We chose a uniform initial period of 2 min at each shear rate value before taking the measurement in all tested surfactants. If the same sample is used for measurement of the complete viscosity curve, the received values of the viscosity at low shear rates may be a little underestimated as the sample may not have reached the equilibrium value. Experiments at higher shear rates are more reliable.

Commercial surfactants like other industrial products show some variations in the absolute values of rheological parameters from one batch to an other even though the percentage of the content of the active matter does not change and, which is most important, also its drag reducing ability remains always the same. We have seen that absolute values of dynamic viscosity may differ as high as 20% in different batches but the character and the pattern of the whole viscosity curve remain always the same.

The size of single micelles of several cationic drag reducing surfactants produced by the two above mentioned companies was measured and published in [26]. Micelles of Habon G were found to be far the largest ones and we expect them therefore to show a proneness to the presence of ions in the water.

Rationale

Many laboratory experiments with surfactants and particulary rheological experiments are carried out with solutions of surfactants in distilled water. However, the drag reduction experiments in larger hydraulic facilities are usually done with tap water. The ions present in tap water did not effect the drag reducing ability of surfactants in our experiments and we are not aware of any results reporting a decrease of the effectiveness by use of such a water. Average analysis results of the tap water used in hydraulic experiments in our laboratories is shown in Table 1.

On the contrary to drag reduction results, the ions in water greatly influence viscosity behavior of Habon G solution. The choice and concentration of ions in our experiments covers roughly drinking water analysis shown above.

A decrease of viscosity of cationic Ethoquad T13-50 due to the presence of metal hydroxides in water is described by Hu and Matthys [27]. No other investigation of the effect of ions on drag reducing surfactants has been yet reported.

Water used in heat exchangers is a treated (decarbonated) water. In our field test [22] the initial hardness of this water was claimed to be 0.03 mval/l but the loss of water in the heat system was supplied by water from the municipal network so that the final content of ions in the recirculating water was higher and it was enriched also by ferrum from the piping. Although small concentrations of ions did not affect the drag reduction itself, they certainly influenced the rheological properties.

Results and discussion

The influence of temperature

Table 1

Source	Locality	
	Prague (CZ)	Columbus, OH (USA)
Calcium	44–52 mg/l	27 mg/l
Magnesium	9.3 mg/l	10 mg/l
Sodium		9 mg/l
Ferrum	0.1 mg/l	
Chlorides	25 mg/l	23 mg/l
Sulphates	114 mg/l	
pH	6.8–7.1	7.6
Hardness	3.4 mval/l	2.16 mval/l

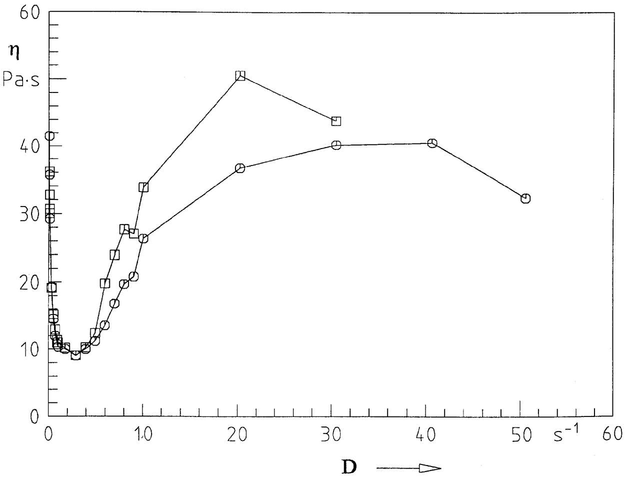


Fig. 1 Viscosity of cationic surfactant Habon G solution with 2 mM concentration at 20 °C and at low shear rates *D*. Squares: first measurement of the unpresheared sample, circles: second measurement of the same sample

Rheometer Haake CV 100 is more sensible than CV 20N, it enables measurement of fluids with low viscosity at smaller shear rates. Figure 1 shows the viscosity curve of Habon G with 2 mM concentration at 20 °C, squares denominate the measurement of a fresh solution, circles the repeated measurement of the same sample. A sudden initial decrease of both curves at the beginning to the minimum at 3 s^{-1} can be seen and only after that a steep increase of the viscosity within two or three decades of shear rate to a maximum, which is followed again by a decrease of the viscosity. The initial pattern with a decrease of the viscosity is a small difference from Bewersdorff's [11] results. However, we see that the viscosity value makes a fivefold jump from the minimum.

Rheometer Haake CV 20N was used for comparision of viscosity curves of Habon G with some other drag reducing cationic surfactants. It is shown in Fig. 2. Concentration of the effective matter of Habon G is 2 mM and all other measured solutions are mixtures of the surfactant with sodium salicylate at a concentration 5:12.5 mM, all

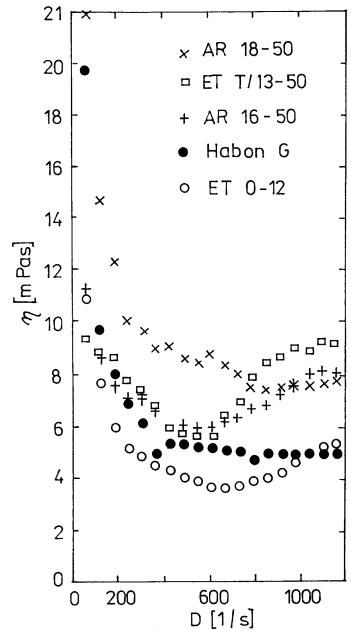


Fig. 2 Viscosity curves of drag reducing surfactants Arquad 18, Arquad 16, Ethoquad O-12 and Ethoquad T/13-50, all with the concentration 5 mM in the mixture with 12.5 mM sodium salicylate, and 2 mM Habon G. Temperature 20 °C and shear rates range $D = 0\text{–}1190\ \mathrm{s}^{-1}$

in distilled water. These concentrations are believed to be most effective in drag reduction.

The method of measurement was the same for all solutions. Every sample had been presheared for two hours in the gap between cylinders at maximum shear rate and only afterwards the complete viscosity curve was determined. We can distinguish in all the viscosity curves shown in Fig. 2 only one common feature. It is the attainment of high viscosity values at low shear rates at the room temperature, apparently the formation of SIS. With increasing shear rate D the shear thinning behaviour can be followed down to a point with a minimum viscosity which can be considered as the best alignment of micelles with flow direction. In this conclusion we agree with Wang's [7] statement that the stronger the flow field, the more oriented micelles are in the flow direction. Behind this point we see the viscosity increase in Ethoquad O-12 and Arquad 16 solutions, and a very steep increase in the Ethoquad T-13/50 solution which indicates that a secondary network structure is built up. On the other hand, a quasi plateau viscosity at $D > 800\ \mathrm{s}^{-1}$ is seen in Arquad 18 solution and a Newtonian viscosity in Habon G at $D > 390\ \mathrm{s}^{-1}$. We use this linear plot as it offers a clear view of differences in the pattern of all curves.

Notwithstanding the variety of viscosity curves, these surfactants are capable of reaching the same high drag reducing effectiveness which is marked by the so called maximum drag reduction asymptote in surfactants [28].

Elson and Garside [29] showed a similar viscosity curve pattern to that of Habon G obtained with 0.39 mM hexadecyl-trimethyl ammonium bromide in mixture with 1-naphtol. This surfactant is a very good drag reducer, too. From high values reached at low shear rate the viscosity decreases to a constant value approaching the viscosity of water at shear rates above $300\ \mathrm{s}^{-1}$.

The patterns of viscosity curves shown in Fig. 2 at 20 °C do not change even with the increase of temperature except for SIS formed at low shear rates and only at lower temperatures.

We measured the influence of temperature on Habon G solution and the result is shown in Fig. 3. The viscosity curve changes only at the beginning, the SIS obviously vanishes at high temperatures and the Newtonian like viscosity prevailes in most part of the viscosity curve. Our experiments were done with 2 mM Habon G solution in distilled water. Empty circles are results obtained with an unpresheared sample at 20 °C, all other points are stabilised data obtained with already presheared samples. We noticed in [17] that preshearing or mixing breaks the Habon G micelles but obviously it has no influence on drag reduction. This surfactant is known to keep its effectiveness over 100 °C. It means that drag reduction is caused also by a surfactant which does not exhibit SIS.

The influence of ions in water

Apparent viscosities of Habon G in distilled water with the addition of some ions were measured in capillary viscometers. This procedure was accepted in order to make a choice of ions and their concentration. Always two capillaries with different diameters were used as there appears a difference of obtained data due to the diameter when a non-Newtonian liquid is measured.

Small additions of $FeCl_3$ or $FeSO_4$ do not change the apparent viscosity as can be seen in Fig. 4a and 4b. It means that neither Fe^{++} nor Fe^{+++} affect the character of micelles. Chlorides of calcium or magnesium show a small influence on the viscosity which decreases about 10–20% only when the concentration Cl^- is high enough. It is shown in Fig. 4a and 4c. However, magnesium sulphate in Fig. 4b shows a very strong influence already at small concentration of SO_4^{2-}.

It seems also that Mg^{++} has a greater influence on viscosity decrease than Ca^{++}, see Fig. 5. It also follows from Fig. 6a and b that a considerable influence exhibit NaOH and NaCl, though the second one only at a great concentration. There is no peak in the dependence of

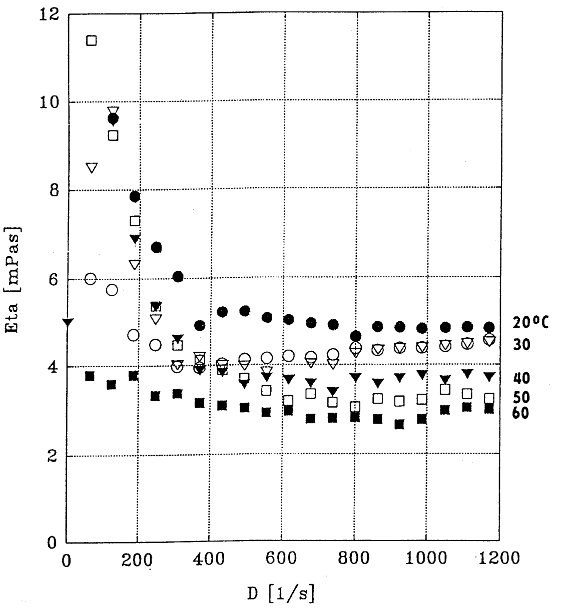


Fig. 3 The influence of temperature on viscosity curves of 2 mM Habon G. Open circles: unpresheared sample at 20 °C, all other symbols apply to presheared samples

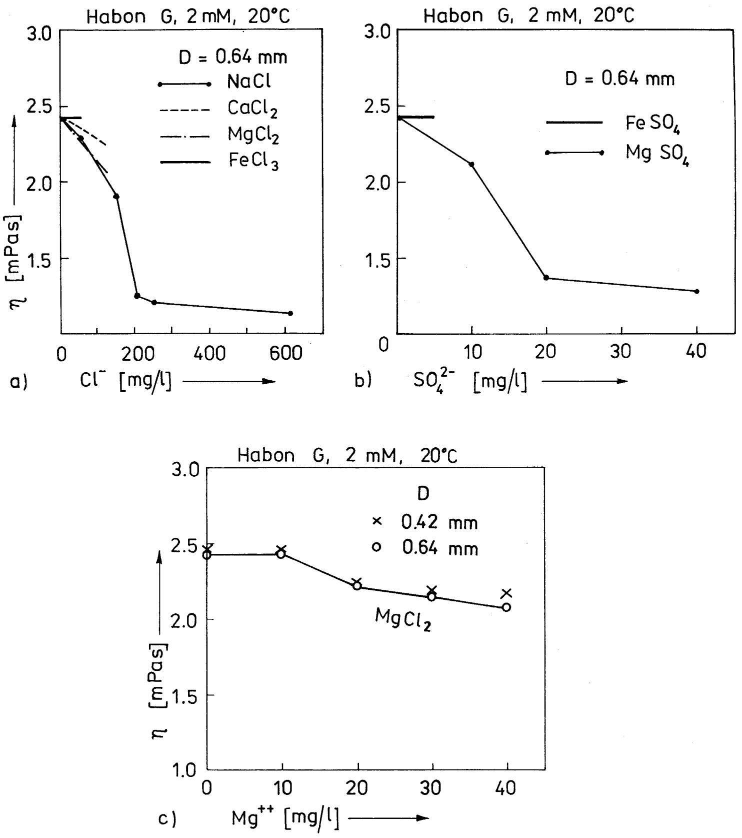
viscosity on NaCl concentration as it occurs in the system salt/Metaupon which was reported by Sedov et al. [30], but we can see only a smooth decrease to the value of viscosity of water. Figure 6a indicates that with 100 mg NaOH/l the solution reaches already the viscosity of water.

Measured pH 5.5–6 of 2 mM Habon G solution decreased with the addition of salts.

Viscosity curves of the surfactant in distilled water (the sample marked HBI) and with the addition of 0.4 mg NaCl (HBII) were measured in the rotational viscometer at shear rates 0–1120 s^{-1} and the results are in Fig. 7a and b. The sample HBI shows a decrease of viscosity with increasing temperature and the Newtonian behavior at all temperatures after the viscosity minimum had been reached. The character of the curves is consistent with results of Habon G of a different batch and different age which is shown in Fig. 3. A quick loss of SIS with the increase of temperature is evident, at 70 °C the viscosity curve exhibits already even a thickening of the solution at low shear rates, and no SIS at all.

The influence of $Ca(NO_3)_2$ and $MgSO_4$ (marked as samples HBIII and HBIV) can be seen in Fig. 8a and b. SIS is completely subdued at all temperatures in the

Fig. 4 The influence of ions in water on apparent viscosity measured in a capillary viscometer (with diameter *D*)



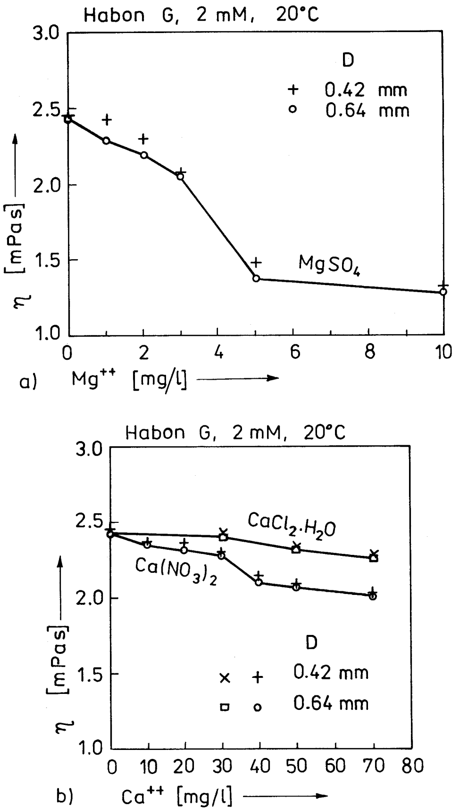


Fig. 5 The influence of ions in water on apparent viscosity measured in a capillary viscometer

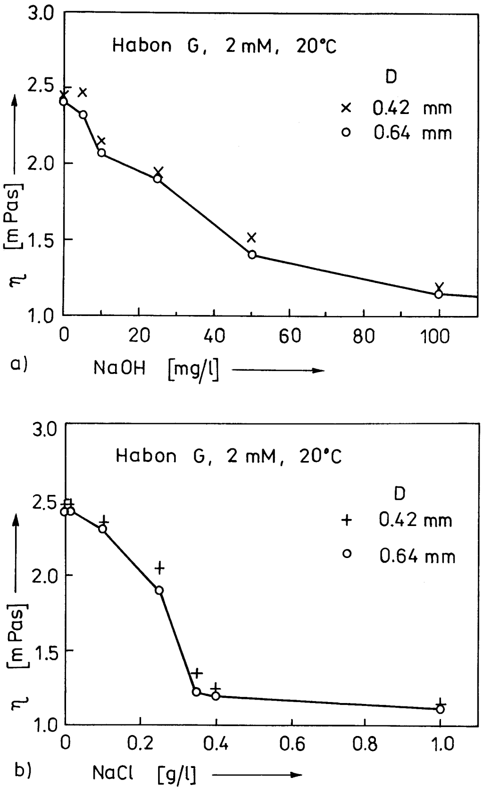


Fig. 6 The influence of NaOH and NaCl on apparent viscosity of the surfactant

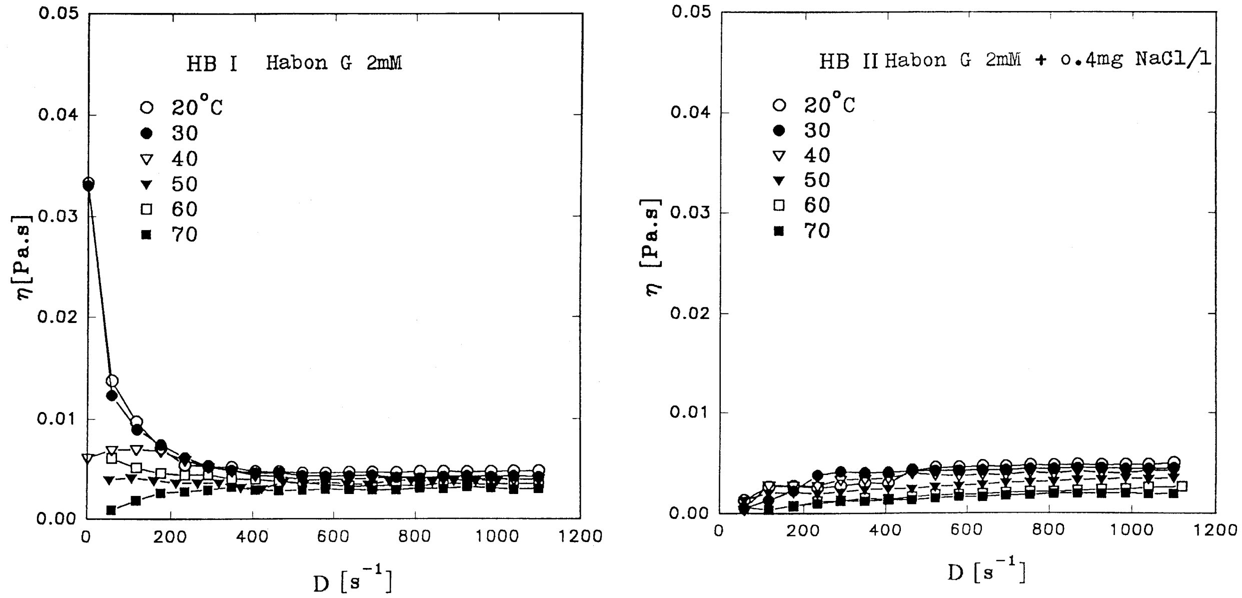


Fig. 7 The influence of temperature and NaCl on viscosity curves measured in the Couette system

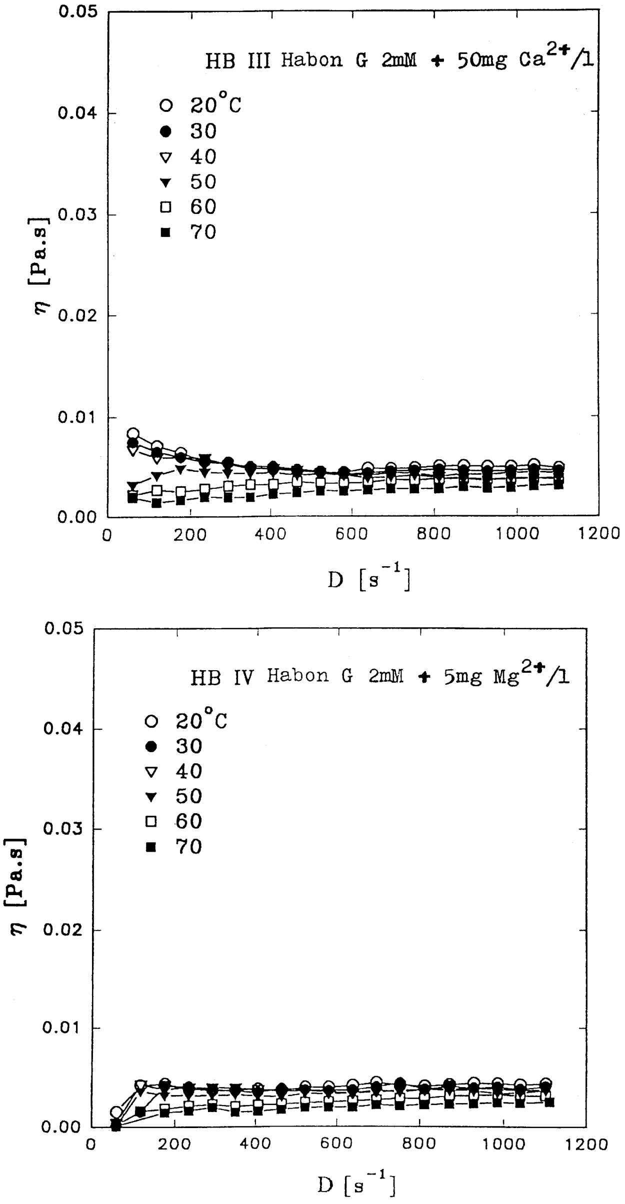


Fig. 8 The influence of calcium and magnesium on viscosity curves of the surfactant at different temperatures

solutions with added ions (HBII, HBIII, HBIV). However, the surfactant diluted in tap water containing ions of similar concentrations did not lose its drag reducing ability [2, 18].

We assume that there must occur a change in the micelle structure when Habon G is solubilized in tap water. The micelles are not able to form the entangled structure at very low shear rates, the solution shows rather a confusing and irregular behavior yielding disarranged data which more or less approach the water viscosity. A reasonable and continuous viscosity curve can be drawn only after a certain shear rate had been passed, approximately above 100 s^{-1}.

At the present state the molecular structure is not clear and the changes which occur during flow cannot be elucidated. We plan to complete our investigation in the future with the measurement of the size of micelles, and also flow birefringence will certainly help to describe the changes in behavior due to presence of ions in water. We assume that some ions cause a rigidity of long micelles, they may lose their flexibility and thus their disposition to intertwine so that SIS is completely subdued.

Summary

1. There exists a great variety in the pattern of viscosity curves of different surfactants but their shapes in no way affect their drag reducing ability.
2. Two categories have been shown which can subdue the formation of Shear Induced Structure in drag reducing cationic surfactant Habon G. They are the temperature of the solution and some ions present in the solvent (water). But neither (of course in certain ranges) decrease the drag reduction effectiveness of the surfactant.
3. We can deduce that SIS is not a key feature characterising the drag reduction ability of a surfactant.

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