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SHORT COMMUNICATION

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A comparison of some rheophysical properties of cetyltrimethylammonium bromide/H_2O and cetyltrimethylammonium bromide/D_2O solutions

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Abstract In this paper, we report the results of rheological and optical experiments performed on two solutions of cetyltrimethylammonium bromide in D_2O and H_2O. The molar concentration of surfactant is the same in both solvents, with the solvents only differing in their atomic number. Important differences in the behaviour of the shear stress and of the birefringence intensity with the shear rate are found. We try to interpret these results by referring to the difference in solubility of ionic salts in D_2O and H_2O.

Introduction

Aqueous solutions of various surfactants are known to exhibit birefringence when submitted to the orientating action of a shear flow. This crystal-like behaviour indicates that the particles, called micelles, have an important shape dissymmetry and when the concentration of surfactant becomes large enough, their length can be so large that we call them "wormlike micelles". The action of a simple shear flow can then trigger a phase transition from an isotropic state to a nematic or hexagonal phase. This phenomenon has been observed with many surfactants [cetyltrimethylammonium bromide (CTAB) [1], cetyltrimethylammonium chloride (CTAC) [2], cetylpyridinium chloride (CPCl) [3], cetylpyridinium chlorate ($CPClO_3$) [4]] and is the reason for the emergence of a shear-banding flow in a Couette device, for example.

When a transition to a liquid-crystalline phase is expected, flow birefringence (FB) and small-angle neutron scattering (SANS) are two very useful techniques for characterizing the alignment of the particles in the flow. The first one allows the direct observation of the shear-banding structure, while the second provides information on the nature of the transition and on the size of the micelles.

However, when different methods of investigation are used, care must be taken to operate under exactly the same conditions and, since SANS experiments require D_2O, the same solvent must be used for the study of other physical properties. In this paper we compare some physical properties of two solutions of CTAB at the same concentration (0.54 M) in H_2O and D_2O. This particular value of the concentration of the surfactant is close to the concentration which gives a nematic liquid-crystalline phase at rest ($\simeq 0.63$ M at 32 °C) in H_2O. The phase transition which occurs in the 0.54 M solution in D_2O is triggered by a weak shear flow in a Couette device. The nature of the two solvents, which differ only in their atomic number, is of critical importance in the process of micelle formation with this surfactant. We shall first make a qualitative comparison of the phase diagram of the ztwo samples and see that they are different. Then quantitative measurements of FB and viscosity will be presented. Previous SANS experiments have confirmed that a phase transition occurs in the CTAB/D_2O solution [5].

Phase diagram of CTAB/H_2O and CTAB/D_2O

The static phase diagrams of a solution of CTAB in H_2O and D_2O are shown in Fig. 1. They are simply derived by direct observation of the sample between crossed polarizers. The points representing the different states of the

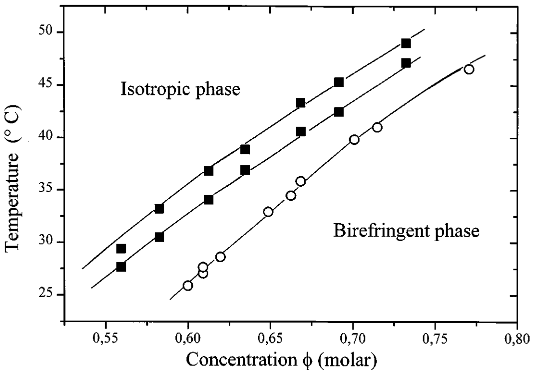

Fig. 1 Static phase diagram of the cetyltrimethylammonium bromide (*CTAB*)/D_2O (■) and CTAB/H_2O (○) solutions. The temperature of the transition is drawn as a function of the concentration, ϕ, of the surfactant

solution are placed on a (T, ϕ) co-ordinate system. At first glance, it can be seen that the phase diagrams are different: this particular behaviour has not been seen in the system $CPClO_3/NaClO_3/H_2O$ or D_2O [4], where the phase diagrams are found to be the same in both solvents.

In H_2O, the curve $T(\phi)$ (open circles) separates the space into two regions. In the left part, which corresponds to low concentrations of salt, the solution forms an isotropic phase while on the right of the curve, the solution is highly birefringent and is identified as a nematic phase. It must be emphasized here that isotropic simply means that the contour plot of the measured scattered intensity under flow in experiments of neutron diffusion has circular symmetry; these samples are optically anisotropic and often exhibit strong birefringence even under weak shearing conditions.

When D_2O is used as a solvent, a biphasic region appears between the isotropic and the birefringent phase as in the case of the $CPClO_3/NaClO_3/H_2O$ system investigated by Schmitt et al. [4]. The two curves (black squares), which are the loci of the different equilibrium states of the biphasic system, are shifted to the left of the broken line, which represents the states of the CTAB/H_2O solution. At a given temperature, the transition occurs at a lower surfactant concentration than in D_2O. This result is an indication that the characteristics of the micelles are different in these solutions.

Rheology of the solutions

The linear and nonlinear viscoelastic properties of the CTAB solutions were studied with a Carrimed CSL 100 rheometer working in constant shear-stress mode. A cone–plane device (radius 4 cm, angle 0.5°) was used to shear the sample; this can sustain shearing rates up to $3000\,s^{-1}$ without being expelled from the cell. Measurements were carried out at 32 °C.

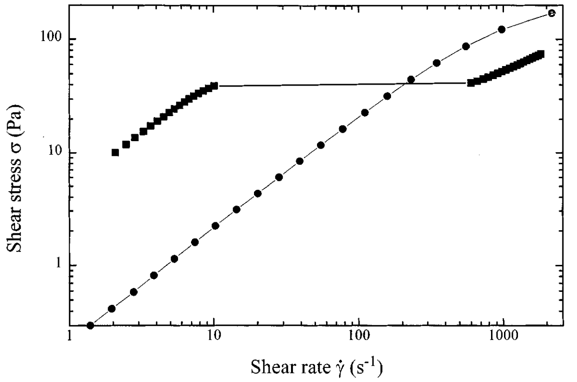

Fig. 2 Shear stress, σ, for the CTAB/D_2O (■) and CTAB/H_2O solutions (○) versus the shear rate, $\dot{\gamma}$

Figure 2 displays the shear stress as a function of the shear rate, $\dot{\gamma}$, for the solutions CTAB/D_2O (solution 1) and CTAB/H_2O (solution 2) in a log-log representation. It can be seen that the behaviour of the two solutions is completely different in the range of shear rates investigated (1–$300\,s^{-1}$). The curve $\sigma(\dot{\gamma})$ of solution 1 shows three different parts characteristic of a solution undergoing a phase transition under shear. This phase transition is quite easy to trigger and occurs in several systems: CTAB/D_2O, CTAB/KBr/H_2O, $CPClO_3$/$NaClO_3$ and CPCl/sodium salicylate [NaSal].

The first part, the low branch, represents the evolution of a Newtonian liquid and finishes when $\dot{\gamma}$ reaches a first critical value $\dot{\gamma}_{1c}$. When $\dot{\gamma}$ is further increased beyond $\dot{\gamma}_{1c}$ the shear stress suddenly jumps to the third part, the higher branch, which starts at $\dot{\gamma}_{2c}$ and σ increases again with $\dot{\gamma}$. The middle region, which extends between the two critical values, is the plateau region which corresponds to the coexistence of the two phases.

The solution CTAB/H_2O behaves in a completely different way: the shear stress varies linearly with $\dot{\gamma}$ over the entire range of shear rates, the viscosity of the solution is constant and the micellar solution behaves like a Newtonian liquid. Let η_0 be the viscosity when $\dot{\gamma} \rightarrow 0$, then the ratio $\frac{\eta_0[\mathrm{CTAB/D_2O}]}{\eta_0[\mathrm{CTAB/H_2O}]} \simeq 20$; this important difference in the zero-shear viscosity indicates that the geometrical characteristics of the micelles must be quite different in the two solutions. This result is confirmed by FB experiments.

In a previous work [5], the CTAB/D_2O sample was studied with two different devices (stress-controlled and shear-rate-controlled rheometers) and the two curves were perfectly superimposed, showing that the results are the same with both devices.

A difference of the same order of magnitude has been seen in the system CTAB/NaSal/D_2O or H_2O. This solution also shows the particular phenomenon of shear-thickening which happens at a critical shear rate, the value of which is completely different in the two solvents: about 210 s^{-1} in D_2O and nearly 3000 s^{-1} in H_2O at 28 °C. (See, for example, Fig. 3 taken from Ref. [6], where $\frac{\eta_0[CTAB/D_2O]}{\eta_0[CTAB/H_2O]} \simeq 20$).

FB experiments

FB measurements were performed on the same solutions and the behaviour of χ and Δn is quite different for the two solutions as could be expected from the rheological experiments. The apparatus and the method for performing a birefringence experiment have been described in detail in earlier papers [7]. We shall just give a brief description of the two physical quantities of interest, i.e. the angle of extinction, χ, and the retardation ϕ, related to the birefringence, Δn. χ is defined as the acute angle between a neutral line of the medium and the tangent to the line of flow in the annular gap of a Couette cell. χ is only related to the orientation of the medium. Its variation with the shear rate, $\dot{\gamma}$, gives information on the size of the micelles in the solution. In the case of semidilute solutions, the information is mainly qualitative, but there is no doubt that when looking at the evolution of χ with $\dot{\gamma}$ (Fig. 4 open and filled black squares for the $CTAB/D_2O$ solution and open and filled black circles for $CTAB/H_2O$) the average length of the micelles must be quite different in the two solutions. $\chi(\dot{\gamma})$ (solution 1) shows the typical behaviour of a liquid undergoing a phase transition under shear (Fig. 4): the curve is formed by two linear segments which join at the point the abscissa of which is the critical shear rate $\dot{\gamma}_{1c}$. In the first part of the curve, χ decreases quickly by several degrees over a narrow range of shear rates ($\approx$ 6–7 s^{-1}) while, for solution 2 the decrease in χ is insignificant and reaches only about 4° when $\dot{\gamma} \simeq 100\ s^{-1}$. This result is in perfect agreement with the results of the rheological experiments which show that $CTAB/H_2O$ behaves like a Newtonian liquid: χ should be constant (45°) or at least vary little with $\dot{\gamma}$.

At about 7–8 s^{-1} (which is roughly the limit of the linear regime), the birefringence intensity, Δn, of the $CTAB/D_2O$ solution reaches approximately the very high value of 70×10^{-7}, while for the $CTAB/H_2O$ solution, Δn is only 3×10^{-7}. The ratio of these two quantities is of the order of 22, a value that should be compared to the ratio of the zero-shear viscosities of the solutions.

The stress optical law (reported in Fig. 5), $\Delta n \sin 2\chi = 2C\sigma$, holds with a fairly good approximation over the entire range of shear rates for the $CTAB/H_2O$ solution and, as concerns the $CTAB/D_2O$ solution up to about 7 s^{-1}, a value which corresponds to the emergence of the shear-banding structure. This result indicates that the main contribution to the birefringence of the solution arises from the intrinsic anisotropy of the micelles.

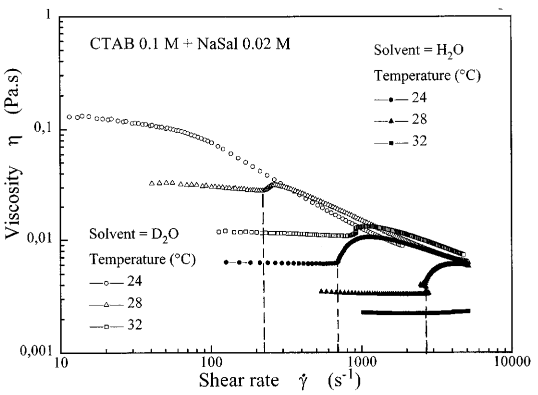

Fig. 3 Shear-thickening phenomenon in a CTAB/■ (*NaSal*) solution: *filled symbols* in H_2O, *open symbols* in D_2O

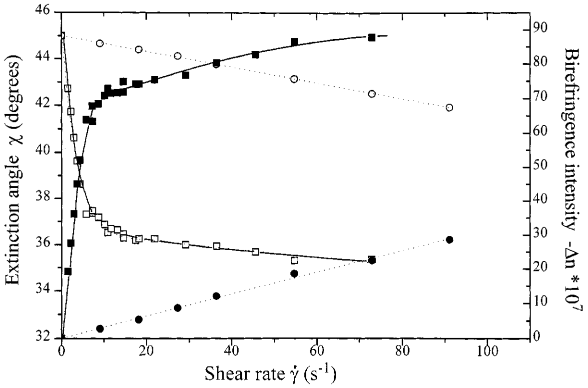

Fig. 4 Extinction angle, χ, (*open symbols*) and birefringence intensity Δn (*filled symbols*) for the two systems in D_2O (*squares*) and H_2O (*circles*)

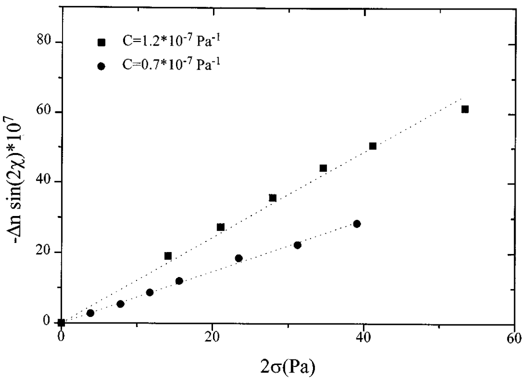

Fig. 5 Stress optical law $\Delta n \sin 2\chi = 2C\sigma$. (■): the solvent is D_2O and $C = 1.210^{-7}\ Pa^{-1}$; (●): the solvent is H_2O and $C = 0.8610^{-7}\ Pa^{-1}$

Conclusion

The phase transition induced by shearing the CTAB/D_2O solution in a Couette device does not happen in the CTAB/H_2O solution at the same temperature, same surfactant concentration and in the same range of shear rates. SANS experiments [5] have shown that the induced phase has all the characteristics of a nematic liquid crystal.

Although the number of individual surfactant molecules is the same in both solutions, the size and shape of the micelles must be quite different as shown by the variation in the angle of extinction, χ, with $\dot{\gamma}$. χ depends on the average orientation only, which is more easily realized with larger particles.

The shear-thickening phenomenon in the CTAB/NaSal system is also dependent on the nature of the solvent; when this phenomenon exists the critical shear rate at which the viscosity starts to increase is lowered towards smaller values of $\dot{\gamma}$. It is also a sign which shows that the size of the micelles is different in the two solvents.

It is a well-known fact that important variations in the solubility of numerous salts have been observed in H_2O and D_2O: the ionic power of D_2O is smaller than that of H_2O. The difference in the solubilities of the salt in the two media can be as high as 36% for $PbCl_2$ [8].

If we admit that ionic surfactants such as CTAB, for example, are also less soluble in D_2O, we can easily assume that the cylindrical micelles will grow longer in D_2O than in H_2O in order to diminish the hydrophobic interaction between the hydrocarbon chain and the solvent molecules. In H_2O, the Br^- ions will be more solvated than in D_2O; consequently the screening of the interaction between the cationic heads of the surfactant will be less efficient in H_2O than in D_2O and the micelles will grow longer in D_2O.

Due to the fact that the zero-point energy of the oscillations of the C–D and C–H groups is quite different, the hydrogen bridging bonds are also quite different in the two solvents and this may explain the difference in size of the micelles. We have no other explanation at the present time for why a single neutron in the nucleus of the deuterium atom changes several rheo-optical properties of the CTAB solutions in such an important way.

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