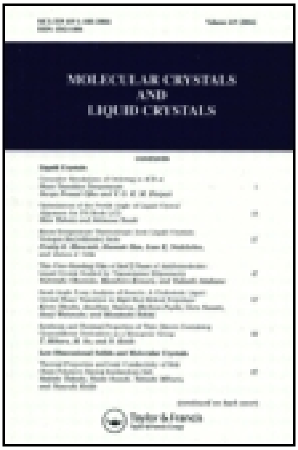

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VISCOSITY INVESTIGATION OF DBS MICELLES

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Abstract: We have investigated the shape of the DBS micelles with regard to the concentration We have determinated the shape factor a and the effective specific micellar volume V_0 as a function of the surfactant concentration.

The present paper describes our research on the dodecylbenzene sulfonate(DBS) micellar phase. The shape of the micelles which depends on the concentration of the surfactant has been investigated. We used the viscosity methods.

It is well known from viscosity theory that the viscosity of a micellar solution is given by:

$$\eta = \eta_0 (1 + aV) \qquad [1]$$

where η is the intrinsic viscosity related to micellar properties, η_0 is the viscosity of the solvent (in our case η_0 is the viscosity of the solution at the critical micellar concentration, i.e., $\eta_0 = \eta_{CMC}$) a is the shape factor, which for spherical micelles has the value 2,5 , while for rodlike micelles a increases since its exact value depends on the parameters of the micelles, V is the volume concentration of the micelles in the sample. This expression is valid for a sufficiently diluted solution, i.e., one with non-interacting particles. The micelles considered are electrically charged, and they can be treated as not interacting only when the average distance l between them exceeds the thickness of the surrounded ionic atmosphere $1/\varkappa$. One estimation of these values (1a) is for concentrations of DBS 1 % $1/\varkappa = 18 Å$ $l = 78 Å$ and 3 % $1/\varkappa = 10 Å$ $l = 44 Å$, under the assumption that the only ions in the medium are dissociated Na-ions. When we add to the solution 5 % by weight NaCl, $1/\varkappa$ decreases by about 3 Å. In this case we accept formula [1] .

In our experiment the solutions were characterized by the weight concentration C of the surfactant. V is proportional to C with a coefficient V_0 effective specific micellar volume

$$V = V_0 C$$

$$\eta = \eta_0 (1 + a V_0 C) \qquad [2]$$

The electric double layer, which is involved in the movement of the micelle, has been included in the volume of the micelles and determines their hydrodynamic behaviour.

From a series of studies to the present (1) it is known that the thickness of the electric double layer strongly depends on the concentration of the ions in the solution. It is a decreasing function of the ion concentration and tends to zero at high concentrations From this it follows that the dependence of V_0 on the concentration will also be a decreasing function. Such is in reality the curve obtained on the basis of our experimental data. V_0' and V_0'' are respectively the values of the specific micellar volume at low and at high ion concentrations.

It is known also (2) (3) (4) (5) that at a low concentration, under 1 % of the surfactant, the micelles are spherical while at higher concentrations they become rodlike. The shape factor a will be an increasing function of the surfactant concentration. The form of this function for the DBS obtained from our experimental results is shown in figure 2. After transformation of [2] we obtain:

$$a V_0 = \frac{\eta - \eta_0}{\eta_0 (C_{TOT} - C_{CMC})}$$

C_{TOT} is the general concentration of the surfactant in the sample, C_{CMC} is the critical concentration of the micellar formation and it characterizes the molecular solution of the surfactant around the micelles. We used $C_{CMC} = 0{,}041\%$ obtained by Lundlum (6) (7) (8) for DBS in the temperature interval from 25°C to 35°C.

By using the proportionality of the viscosity from the flow time t we get:

$$a V_0 = \frac{t - t_0}{t_0 (C_{TOT} - C_{CMC})}$$

The dependence of $a V_0$ on C was experimentally obtained by measuring the viscosity of the DBS water solution at concentrations from CMC to 3 %, (in steps of 0,5 %) and at a temperature of 30°C ± 0,05°C (table 1). The Eigner viscosimeter we used had a capillary length of 1 m and a capillary diameter of 1 mm. Such a viscosimeter produces a small speed gradient which does not permit the deformation of the micelles studied by us. For every concentration the flow time value was determined by more than 20 measurements. The mean square error in determining the flow mean time for the critical concentration is F = 0,04 sec and for all other concentrations F = 0,08 sec . The graphical form of this dependence is shown in figure 3. Its character can be explained by taking into account the concentration dependence on the two factors separately $V_0 = V_0(C)$ figure 1 and $a = a(C)$ figure 2.

Viscosity determinations like these of water solution, were also performed on the same surfactant with the addition of NaCl 5 % by weight (0,13 mol per liter) (table 1, figure 4). In these solutions the ion concentration was kept constant independently from the surfactant concentration. With all of them the value of V_0 corresponds to V_0'' , which can be calculated from the experimentally obtained value aV_0 for the smaller concentrations of the surfactant (figure 4), bearing in mind that $a = 2,5$ in this case. We obtained $V_0'' = 1,67$. Under these conditions aV_0 (figure 4, table 1) will depend on C only through a (figure 2 and 4 have an analogous form). We substitute for V_0 here the obtained numerical value for V_0'' and we obtain the concentration dependence of the a (figure 2, table 1). So by substituting the obtained values for $a(C)$ in the function aV_0 shown in figure 3 , table 1 we get $V_0(C)$ (figure 1).

The density of the waterfree DBS is $\rho = 1,05$ (estimated by us). The specific volume of a imaginary micelle formed of only DBS molecules was $V_0^* = 1/\rho = 0{,}95$. The fact that the effective specific volume of the micelles V_0'' at high concentrations of NaCl also exceeds V_0^* shows the essential role of the hydrate binding water molecules to the surface of the micelle. The water molecules increase 1,75 times the effective volume of the micelles.

In the concentration range where $a(C)$ increases, the spherical micelles pass into rodlike ones. In our case this occurs over 2 %.

Simultaneously with the viscosimetric investigations the NMR spectra at longitudinal relaxation time T_1 were recorded to investigate their dependence on the temperature at concentrations 1 %, 2 % and 3 %. The results will be published later. These investigations confirm the conclusions drawn above.

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C %	t_{DBS} [sec]	aV_0 DBS	$t_{DBS+NaCl}$ [sec]	aV_0 DBS+NaCl
0,04	47,66		47,12	
0,5	53,98	8,19	50,43	4,31
1,0	59,6	7,42	53,84	4,19
1,5	64,34	6,82	57,25	4,15
2,0	68,59	6,37	60,81	4,18
2,5	73,51	6,27	65,15	4,39
3,0	79,78	6,47	70,59	4,74
3,5			76,89	5,15
4,0			84,38	5,63

TABLE 1

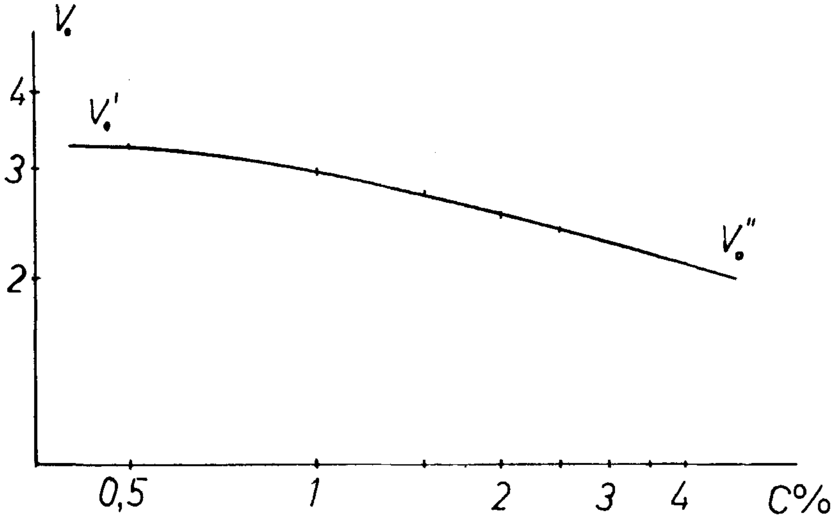

FIGURE 1

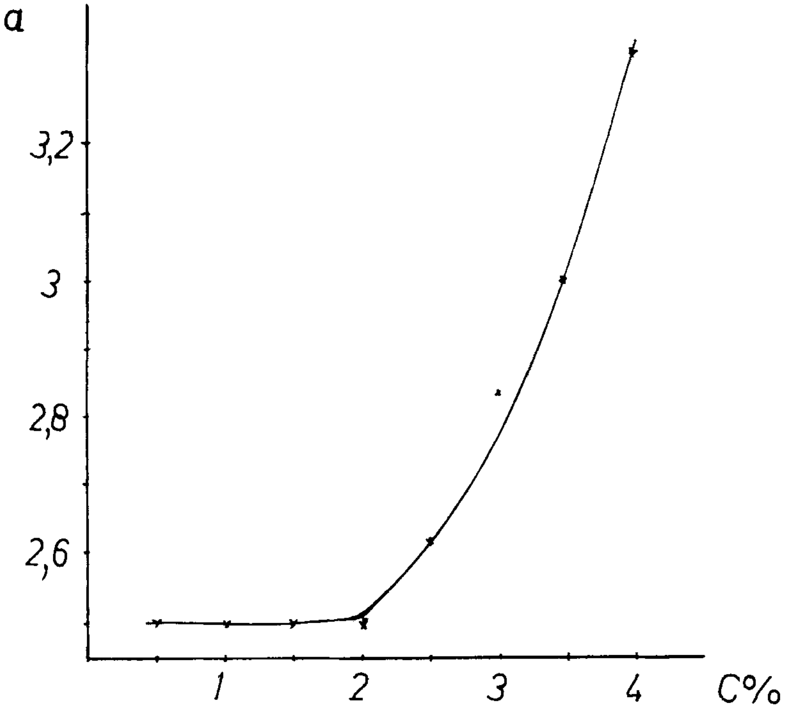

FIGURE 2

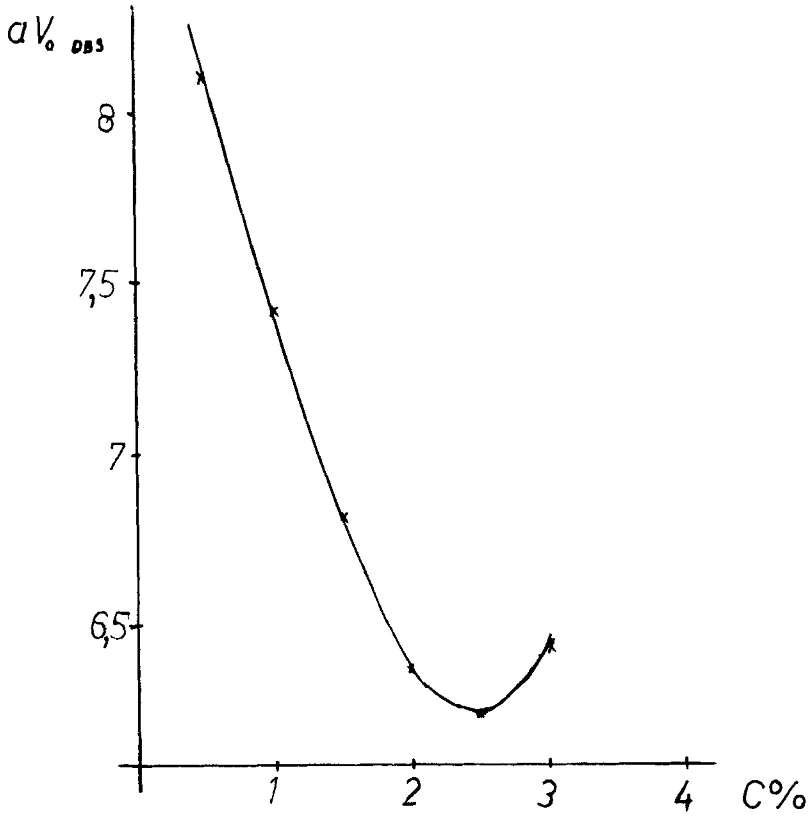

FIGURE 3

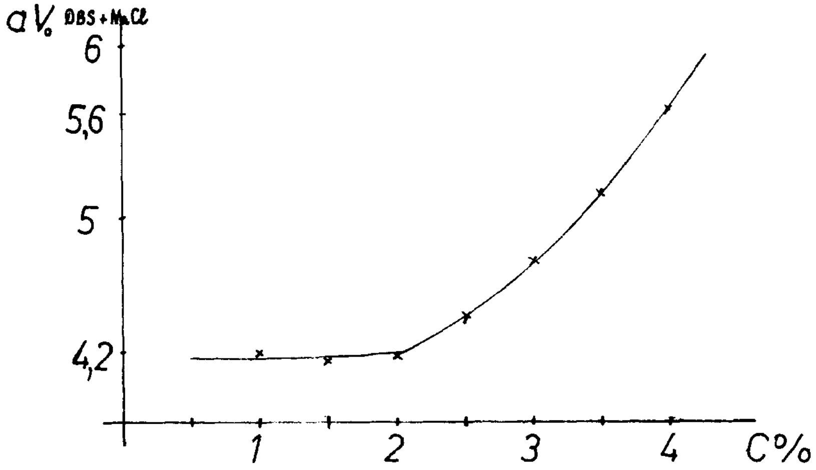

FIGURE 4