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Physico-chemical Investigations on Soap Micelles

II. Sodium lauryl sulfate, potassium oleate, and cetyl trimethylammonium bromide

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The present investigation is a continuation of a previously published study [1] on the degree of association of potassium laurate and myristate micelles in the presence of salts. There it was shown that the micelles grow larger as the ionic strength of the medium increases. The effect is more pronounced with the longer hydrocarbon chain of potassium myristate (14 C atoms) than with potassium laurate (12 C atoms).

In the present study these investigations have been extended to include, besides potassium oleate, also soaps of other types, such as lauryl sulfate and cetyl trimethylammonium bromide, which latter is a cation active soap.

The same methods of investigation as in the study quoted above, namely sedimentation, diffusion, and viscosity measurements, were used for characterizing the size and shape of the soap micelles. All results refer to 30° C. For experimental details, the previous publication should be consulted. The sedimentation constants are expressed in S units ($1\ S = 10^{-13}$ c.g.s.). The diffusion constants have the unit 10^{-7} c.g.s. The limits of error of the molecular weights are estimated, as earlier, to $\pm$ 12 %.

Since the micelles are solvated, the partial specific volume in Svedberg's formula for calculating the molecular weight from sedimentation and diffusion data must refer to the solvated particle ($\overline{V}_{13}$). The following relation holds:

$$\overline{V}_{13} = \frac{\overline{V}_1 + k\ \overline{V}_3}{k+1};\ \text{where}$$

k = amount of H_2O in g/g soap.

$\overline{V}_1$ = pycnometrically determined partial specific volume for the non-solvated particle,

$\overline{V}_3$ = the partial specific volume of the water of solvation. The solvation was determined by ultrafiltration (*cf.* Granath [1]).

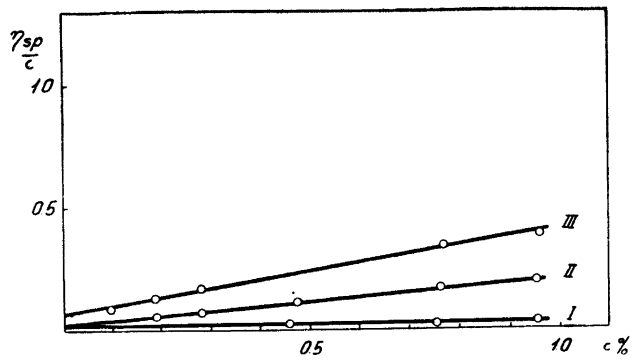

Fig. 1. Specific viscosity as a function of the soap concentration.

I Na-lauryl sulfate in 0.5 M Na_2CO_3
II » » » » 0.8 M NaBr
III Na-myristyl sulfate in 0.8 M NaBr (40° C)

RESULTS

Sodium lauryl sulfate

The Na-lauryl sulfate was prepared from pure dodecyl alcohol (Procter and Gamble) according to a method described by Shedlowsky [2].

The results of the viscosity measurements are seen in Fig. 1, where $\eta_{sp/c}$ is plotted *versus* c (g/100 g solution). The intrinsic viscosity $[\eta]$ is 0.02 in both media (0.5 *M* Na_2CO_3 and 0.8 *M* NaBr). For comparison, a series of measurements were made with Na-tetradecyl sulfate in 0.8 *M* NaBr. The value of $[\eta]$ for this compound was determined as 0.07.

Sedimentation constants of Na-lauryl sulfate were determined in 0.1 *M* and 0.2 *M* Na_2CO_3, and in 0.6 *M* NaBr. The results are given in Table 1.

Table 1. Na-lauryl sulfate. The sedimentation constant as a function of soap concentration.

Medium	c g/100 ml	S_{30}
Na_2CO_3, 0.1 *M*	0.6	1.0
» »	0.4	1.1
» »	0	1.4
Na_2CO_3, 0.2 *M*	0.8	1.0
» »	0.4	1.1
» »	0	1.3
NaBr, 0.6 *M*	1.2	1.1
» »	0.6	1.2
» »	0	1.3

Table 2. Na-lauryl sulfate. The diffusion constant as a function of the salt content at 30° C.

Medium	D_A
NaBr, 0.2 *M*	13.7
» 0.4 »	10.6
» 0.6 »	7.6
» 1.0 »	2.0
Na_2CO_3, 0.05 *M*	9.2
» 0.2 »	7.6
» 0.3 »	7.3
» 0·7 »	3.2

The diffusion constants as functions of the amount of salt (Na_2CO_3 and NaBr, respectively) present are given in Table 2. The diffusion constants changed with concentration within the error limits of these measurements.

The low degree of solvation (< 0.5 g/g) did not enable accurate determinations by ultrafiltration. Therefore, in Table 3 is given the apparent molecular weight M'_A, calculated with $\overline{V}_1$ as the partial spec. volume. In this case M'_A differs only slightly from M_A, the molecular weight of the non-solvated micelle. $M_A = \frac{M_c}{k+1}$, where M_c refers to the solvated particle. In Table 3 the frictional ratio f/f_0 is also given.

Table 3. Molecular constants of Na-lauryl sulfate.

Medium	$\overline{V}_1$	$\overline{V}_{13}$	$1-\overline{V}_1\varrho$	M'_A	f/f_0
Na_2CO_3, 0.1 *M*	0.883	—	0.113	35 000	1.29
» 0.2 *M*	0.883	—	0.103	40 000	1.31
NaBr 0.6 *M*	0.888	—	0.079	54 500	1.29

Potassium oleate.

The potassium oleate was prepared from pure oleic acid and a freshly made up solution of KOH. The product was recrystallized a few times in acetone and dried *in vacuo*.

The viscosity measurements were performed in salt solutions of varying ionic strength. The graphs of $\frac{\eta_{sp}}{c}$ *versus* c are plotted in Fig.2. Extrapolation

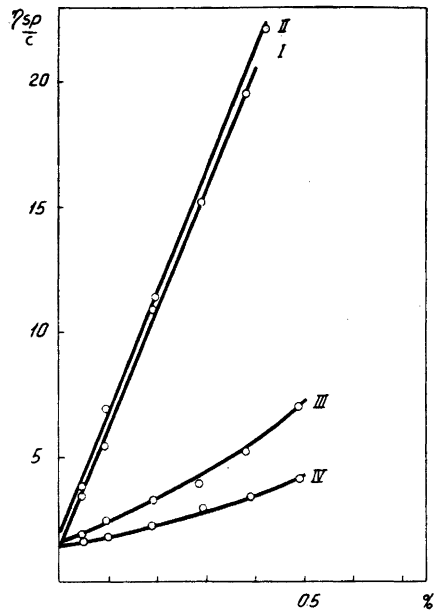

Fig. 2. Specific viscosity as a function of the soap concentration.

I K-oleate + 0.4 *M* KBr + 0.1 *M* K_2CO_3
II » + 0.4 *M* K_2CO_3
III » + 0.2 *M* KBr + 0.1 *M* K_2CO_3
IV » + 0.2 *M* K_2CO_3

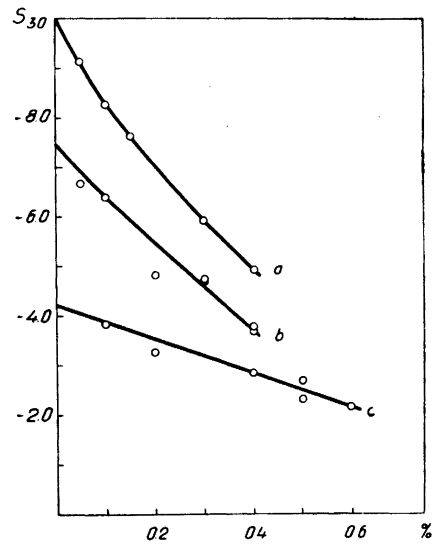

Fig. 3. The sedimentation constant vs. the soap concentration.

a. K-oleate in 0.4 *M* KBr + 0.1 *M* K_2CO_3
b. » » 0.4 *M* K_2CO_3
c. » » 0.2 *M* KBr + 0.1 *M* K_2CO_3

to zero concentration gives notably high values of $[\eta]$ (Table 5) corresponding to very high values of f/f_0. It is apparent that the relative viscosity is a function of the amount of electrolyte present rather than of the ionic strength of the medium.

Fig. 3 illustrates the concentration dependence of the sedimentation constants in a few different media. In all these cases the constants were

Table 4. K-oleate. Diffusion constants in different media.

K-oleate c %	Medium	D_A
0.2/0	0.4 *M* KBr + 0.1 *M* K_2CO_3	0.23
0.2/0	0.2 » » + 0.1 » »	0.52
0.6/0	0.3 » K_2CO_3	1.60
0.6/0	0.1 » »	7.5
0.4/0.1	0.05 » »	9.1

negative, *i.e.* the sedimenting micelles had a lower spec. gravity than the respective media. The diffusion constants in the corresponding media are given in Table 4.

$\overline{V}_1$ of K-oleate was found to be 0.983 in 0.05 *M* K_2CO_3 and 0.996 in 0.4 *M* KBr + 0.1 *M* K_2CO_3. The solvation was determined in the latter medium only and was found to be 1 ± 0.2 g/g soap.

A compilation of the results with K-oleate is found in Table 5.

Table 5. Molecular constants of K-oleate.

Medium	$\overline{V}_1$	$\overline{V}_{13}$	$1-\overline{V}_{13}\varrho$	M	f/f_0	$[\eta]$
0.4 *M* KBr + + 0.1 *M* K_2CO_3	0.996	0.999	− 0.038	29×10^6	5.13	1.6
0.2 *M* KBr + 0.1 *M* K_2CO_3	0.996	0.999	− 0.022	9.4×10^6	3.29	1.6
0.4 *M* K_2CO_3	0.996	0.999	− 0.040	21×10^6	5.22	2.0

Cetyl trimethylammonium bromide

The preparation investigated was an Eastman Kodak product recrystallized in acetone.

Fig. 4 shows the graphs of $\frac{\eta_{sp}}{c}$ *versus* c and Fig. 5 the extrapolation of the sedimentation constants of cetyl trimethylammonium bromide in a number of media.

$\overline{V}_1$ was 0.986 in distilled water and 1.008 in 0.2 *M* KBr. In 0.4 *M* KBr the value of the solvation was $k = 2 \pm 0.2$ g/g soap. $\overline{V}_{13} = 1.004$ was used throughout in calculating the molecular weight of cetyl trimethylammonium bromide in the media used.

Table 6. Molecular constants of cetyl trimethylammonium bromide.

Medium	S°_{30}	D_A	$1-\overline{V}_{13}\varrho$	M_c	f/f_0	$[\eta]$
0.4 *M* KBr	− 8.60	0.94	− 0.034	6.7×10^6	2.11	0.60
0.3 » »	− 4.30	1.10	− 0.026	3.8×10^6	2.16	0.45
0.2 » »	− 3.50	1.43	− 0.017	3.7×10^6	1.68	0.20

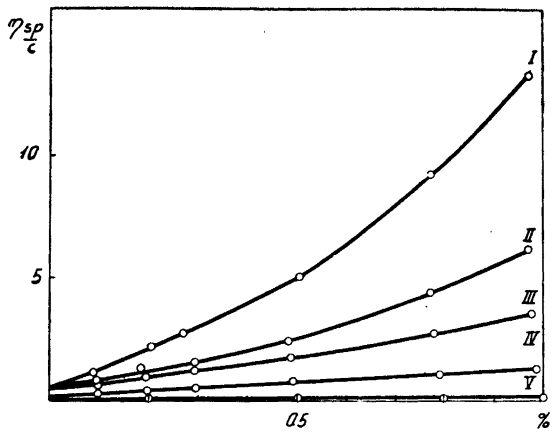

Fig. 4. The specific viscosity vs. the soap concentration.

I Cetyl trimethyl ammonium bromide in 0.5 M KBr
II » » » » » 0.4 M »
III » » » » » 0.3 M »
IV » » » » » 0.2 M »
V » » » » » H_2O

The shape of the micelles

The prevailing opinion concerning the shape of the soap micelles has been that they are cylindrical discs consisting of two parallel layers of molecules oriented with the polar groups out. From light scattering measurements,

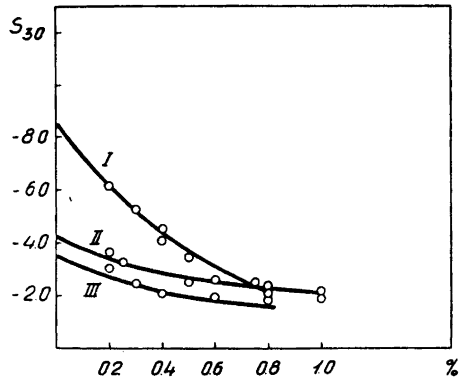

Fig. 5. S_{30} as a function of the soap concentration.

I Cetyl trimethyl ammonium bromide in 0.4 M KBr
II » » » » » 0.3 M »
III » » » » » 0.2 M »

Table 7.

Soap	Buffer	M_c	f/f_0	Rod-shape			Disc-shape		
				a/b	$2b \times 10^8$ cm	$2a \times 10^8$ cm	b/a	$2b \times 10^8$ cm	$2a \times 10^8$ cm
K-laurate	0.8 *M* KBr+ +0.1 *M* K_2CO_3	60 000	1.18	4.0	*36.2*	144	4.3	92	*19.8*
** 35.3 ± 1 Å	1.6 *M* KBr+ +0.1 *M* K_2CO_3	150 000	2.12	23.3	*27.2*	640	35.1	254	*20.0*
K-myristate ** 40.3 ± 1 Å	0.4 *M* KBr+ +0.1 *M* K_2CO_3	130 000	1.49	9.0	*35.8*	320	10.8	164	*15.2*
	0.6 *M* KBr+ +0.1 *M* K_2CO_3	400 000	1.60	11.1	*48.4*	540	13.9	260	*18.8*
	0.7 *M* KBr+ +0.1 *M* K_2CO_3	560 000	1.82	15.8	*48.2*	760	21.9	340	*15.4*
	0.8 *M* KBr+ +0.1 *M* K_2CO_3	840 000	2.22	26.1	*46.8*	1220	40.5	480	*11.8*
	1.0 *M* KBr+ +0.1 *M* K_2CO_3	$1.55 \cdot 10^6$	2.94	49.8	*46.2*	2300	96.6	780	*8.0*
K-oleate	0.2 *M* KBr+ +0.1 *M* K_2CO_3	$9.4 \cdot 10^6$	3.29	63.8	*77.6*	4960	131	1580	*12.0*
	0.4 *M* KBr+ +0.1 *M* K_2CO_3	$29 \cdot 10^6$	5.13	161.4	*83.0*	13400	—	—	—
	0.4 *M* K_2CO_3	$21 \cdot 10^6$	5.22	167.4	*73.0*	12200	—	—	—
Cetyl trimethyl-ammonium bromide	0.2 *M* KBr	$3.7 \cdot 10^6$	1.68	12.7	*97.4*	1240	16.5	580	*35.2*
	0.3 » »	$3.8 \cdot 10^6$	2.16	24.4	*79.0*	1920	37.2	760	*20.6*
	0.4 » »	$6.7 \cdot 10^6$	2.11	23.1	*97.6*	2240	34.5	900	*26.2*
Na-lauryl sulfate ** 37.3 ± Å	0.1 *M* Na_2CO_3	35 000 *	1.29	5.6	*26.0*	146	6.3	85	*13.6*
	0.2 » »	40 000	1.31	5.9	*26.6*	158	6.7	91	*13.6*
	0.6 » NaBr	54 500	1.29	5.6	*30.1*	168	6.3	99	*15.8*

* M'_A values.

** These values are so-called Bragg distances from measurements of electron diffraction [6]. According to these authors, the thickness of the micelle is 10—15 % larger than these values.

Debye [3] has drawn the conclusion that in the presence of salts the micelles of *n*-cetyl trimethylammonium bromide must be rod-shaped. The diameter of the rod should be double the molecular length. The surface of the rod is covered by the polar groups. Debye's values of the molecular weights ($8 \cdot 10^5$ in

0.178 M KBr and $1.86 \cdot 10^6$ in 0.233 M KBr) are in good agreement with the values here obtained ($M_A = 1.23 \cdot 10^6$ in 0.2 M KBr). Thiele [4] in his investigations, among others in the ultramicroscope, arrived at the result that the disc-shaped micelles were converted to positively double refracting rod-micelles in the presence of salts.

The data in this and the previous study have been gathered to throw some light on the question of the shape of the micelles of the soaps investigated under the conditions used. The axial ratio was calculated from the frictional ratio f/f_0 [5], approximating the rod-shape with a prolate ellipsoid of revolution having its major axis $2a$ as the rotational axis, and the disc-shape with an oblate ellipsoid of revolution where the minor axis $2a$ is the rotational axis.

From the relation between f/f_0 and the axial ratio [5], and the equation

$$4/3 \cdot \pi \cdot ab^2 = \frac{M_c \bar{V}_{13}}{N},$$

where N = Avogadro's number, the two half axes, a and b, could be calculated. If the micelles are rod-shaped, the half axis b should be comparable to the length of the corresponding soap molecule. In the other case (disc-shape) the same is true of the half axis a.

From the results in Table 7 it is seen that the assumption of rod-shape of all these soaps in the media investigated gives satisfactory values of the length of the solvated soap molecules. The lengths calculated for the disc-shape are consistently too small.

SUMMARY

This paper reports an investigation of the weights and shapes of the micelles of potassium oleate, sodium lauryl sulfate and cetyl trimethyl ammonium bromide as determined by sedimentation, diffusion and viscosity measurements, in the presence of electrolytes in varying amounts. The degree of association increases strongly with the amount of salt present and with the length of hydrocarbon chain of the respective soaps. The lengths of the shorter half axis of a prolate ellipsoid of revolution, calculated from the frictional ratio, become independent of the medium and are of the same magnitude as the length of the soap molecules. This supports Debye's view that the micelles are rod-shaped. The length of the rod depends on the degree of association, while the diameter is fixed to double the length of the soap molecule.

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