Sedimentation and Viscosity Studies on Micelles of the Cesium Salt of Hexadecane-dicarboxylic acid-(1,16)-monomethyl ester

ULV LOHMANDER

Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden

Sedimentation and viscosity measurements on $\text{CH}_3 \cdot \text{OOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOCs}$ in 0.10 *M* CsCl show that this solution has the character of a gel. The constant *k* in Freundlich's formula was determined to be 4.6.

The dibasic soaps $\text{CsOOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOCs}$ and $\text{CsOOC} \cdot (\text{CH}_2)_{12} \cdot \text{COOCs}$ also were investigated, but here no macro aggregates were found.

This paper deals with an investigation of the properties of $\text{CH}_3 \cdot \text{OOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOCs}$ in a salt solution, studied by sedimentation and viscosity measurements.

The reason for choosing the cesium soap was that the sodium and potassium soaps were too insoluble. (The solubility at 20° C for the potassium soap in 0.10 *M* KCl is about 0.1 % by weight; the corresponding value for the cesium soap in 0.10 *M* CsCl is 0.5 %).

The soap was prepared by neutralizing hexadecane-dicarboxylic acid-(1,16)-monomethyl ester with cesium hydroxide. The ester was kindly made available by Professor Einar Stenhagen of the Medico-chemical Institute of the University.

PARTIAL SPECIFIC VOLUME

Notations: $\bar{v}_1$ = the partial specific volume¹ of the soap solution
 v = specific volume of the soap solution
 c_1 = concentration of soap.

For a binary system we have

$$\bar{v}_1 = v + (1 - c_1) \frac{dv}{dc_1} \quad (1)$$

For the system soap + electrolyte + water eq. (1) is valid if the concentration of salt is constant. The specific volume *v* was determined with a 10 ml

Fig. 1. Specific volume of the soap solution vs. concentration of soap.

Fig. 2. Relative viscosity as a function of concentration.

pycnometer at 25° C for different soap concentrations using 0.10 M CsCl as solvent (Fig. 1).

Result: $\bar{V}_1 = 0.668 \pm 0.002$.

VISCOSITY

The viscosities of the soap solutions were studied at a temperature of 25° C in an Ostwald viscometer with an effluent time for water of 28.7 sec. at this temperature. 0.10 M CsCl was used as solvent.

From Fig. 2 it is evident that the relative viscosity, η_r , of the soap solutions increases rapidly with increasing soap concentration.

Fig. 3. Dependence of η_{sp}/c upon concentration.

Fig. 4. $\log x = f(t)$ for r.p.s. = 300.

Fig. 5. Sedimentation diagrams for $r.p.s. = 300$.

Fig. 3 shows that the concentration dependence of the reduced viscosity, η_{sp}/c (in dl/g), is very pronounced.

SEDIMENTATION

In the sedimentation runs² the following equipment was used

- 1) A low-speed ultracentrifuge (< 250 r.p.s.) and a cell distance of 5.2 cm from the axis of rotation,
- 2) A high-speed ultracentrifuge (> 250 r.p.s.) and a cell distance of 6.5 cm from the axis.

0.10 M CsCl was used as solvent. The temperature varied between 20° and $24^\circ C$.

Fig. 6. Concentration of the original 0.10 M CsCl solution vs. the distance from the axis. $r.p.s. = 800$, length of run = 390 min.

Fig. 7. The cell.

The sedimentation constant, s , is given by

$$s = \frac{\frac{dx}{dt}}{\omega^2 x} \quad (2)$$

where

x = the distance of the boundary (solvent/solution) from the axis of rotation

t = time after full speed

ω = angular velocity.

Thus from (2)

$$\log x = \frac{\omega^2 s}{\ln 10} \cdot t + c$$

and $\log x = f(t)$ is represented by a straight line if s is a constant.

Sedimentation runs were made for a soap concentration of 0.29 % (by weight) at rotor speeds of 150, 200, 300, 600 and 800 r.p.s. The boundary (solvent/solution) was very sharp. From Figs. 4 and 5 it is evident that the sedimentation is very much retarded which may mean that the solution has the character of a gel³. Naturally the retarded sedimentation also depends on the sedimentation of the CsCl solvent. From the refractive index gradient, the concentration of the cesium chloride was easily determined in every point of the cell at different times from the start of the run (Fig. 6).

For a rotor speed of 600 r.p.s. and $t = 150$ min. the concentration of the cesium chloride at the meniscus was 0.0866 M , while that at the bottom was 0.1143 M .

For r.p.s. of 300, no sedimentation of CsCl was detected. Thus from the above, it follows that for r.p.s. ≤ 300 , the cause of the retardation is due only to the gel character of the solution.

GEL PRESSURE

The gel pressure was studied by sedimentation measurements.

Notations:

- c_0 = the original concentration of the gel (at start)
 c = " " " " (during run)
 V = partial specific volume " " "
 ζ_s = density of the solvent
 ω = angular velocity.

Notations, illustrated in Fig. 7:

- O = the axis of rotation
 x_0 = the distance of the meniscus from the axis of rotation
 x_n = " " " " bottom " " " " "
 x_1 = " " " " boundary " " " " "
 $x_m = \frac{x_0 + x_n}{2}$
 $x_{m_1} = \frac{x_1 + x_n}{2}$

Fig. 8. $x = f\left(\frac{1}{t}\right)$. ○: r.p.s. = 150, □: r.p.s. = 200, Δ: r.p.s. = 300.

Fig. 9. $\log \frac{\pi}{B} = f(\log c_{m_1})$.

The gravitational force acting on the volume element (base-area = 1, height = dx) is

$$dP = c(1 - V_{\zeta_s})\omega^2 x dx$$

The pressure on any area with the distance x_{m_1} from the axis is

$$P_{m_1} = \int_{x_1}^{x_{m_1}} c(1 - V_{\zeta_s})\omega^2 x dx \quad (3)$$

Let the gel pressure be denoted by π . Then at equilibrium the gel pressure at x_{m_1} is given by $P_{m_1} = \pi$.

The concentration at x_{m_1} is to a good approximation given by

$$c_{m_1} = c_0 \frac{x_{m_2}}{x_{m_1}} \cdot \frac{x_n - x_0}{x_n - x_1}$$

In eq. (3) $c \approx c_{m_1}$ and $1 - V_{\zeta_s} = B = \text{constant}$.

At equilibrium:

$$\frac{\pi}{B} = \frac{c_{m_1}\omega^2}{2} (x_{m_1}^2 - x_1^2)$$

By plotting the position (x) of the gel/solvent boundary vs. $\frac{1}{t}$ (t = time after full speed) the equilibrium position (x_1) was determined by extrapolation to infinite time (Fig. 8).

Thus c_{m_1} and $\frac{\pi}{B}$ could be readily calculated (Table 1).

Freundlich and Posnjak⁴ have shown that

$$\pi = Ac^k$$

where

π = gel pressure

c = gel conc.

A = constant

k = constant ($2 < k < 5$)

$$\text{thus } \frac{\pi}{B} = \frac{A}{B} \cdot c^k$$

whence $\log \frac{\pi}{B} = k \log c + \text{constant}$

and k is easily determined if $\frac{\pi}{B}$ and c are known.

The constant k was found to be 4.6 (Fig. 9).

Table 1.

c_0	ω	x_0	x_n	x_1	$\log c_{m_1}$	$\log \frac{\pi}{B}$
$2.9 \cdot 10^{-3}$	300 π	4.432	5.995	5.677	0.105-2	4.015
$2.9 \cdot 10^{-3}$	400 π	4.368	5.995	5.697	0.147-2	4.280
$2.9 \cdot 10^{-3}$	600 π	5.828	7.276	7.056	0.242-2	4.686

NOTES ON DIBASIC SOAPS

Sedimentation runs were also done with the dicesiumsalts of hexadecane-dicarboxylic-acid-(1,16) and dodecane-dicarboxylic acid-(1,12) in various media:

- 1) H_2O
- 2) $CsBr$ (0.1—0.6 M)
- 3) 0.1 M $CsBr$ + 0.1 M Cs_2CO_3 .

The solubility of the soaps was about 4 % by weight in water and about 2 % in 0.1 M $CsBr$.

The soap concentrations used were 0.4—2.8 % (by weight); the rotor speed was 1 000 r.p.s. and the temperature varied between 21° and 23° C.

No larger aggregates (micelles) were found in these solutions.

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