SOME PHYSICO-CHEMICAL STUDIES ON SALTS OF LONG CHAIN DICARBOXYLIC ACIDS

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Conductimetric studies on the dipotassium salts of acids of the type $HOOC(CH_2)_nCOOH$ have been made on sebacic acid (K_2, $n = 8$), dodecanedicarboxylic acid (K_2, $n = 12$), and hexadecane dicarboxylic acid (K_2, $n = 16$). The equivalent conductance-concentration curve for K_2, $n = 16$ showed breaks at 11 and at about 33 mM l.$^{-1}$; diffusion studies indicated that the formation of small aggregates occurred at 10 mM l.$^{-1}$, the aggregates containing two molecules. The second concentration limit was believed to represent either a change in the electrical properties of the solute, or an increase in the amount of aggregate present. Certain tentative deductions about the length of the molecule in solution were made from the diffusion results.

VERY few studies have been made on the salts of dicarboxylic acids of long chain length in solution. Danielsson[1] has studied conductivity, solubilisation, and pH of the dipotassium salts of sebacic, brassylic ($K_2,n = 11$), tetradecane dicarboxylic ($K_2,n = 14$,) and hexadecane dicarboxylic acids. Breaks in the conductivity-concentration curves were observed for the salts of the last two acids, and were believed to correspond to micelle formation. Solubilisation of decanol by $K_2,n = 14$ began at 0·35 M l.$^{-1}$ at 40°, and at 0·027 M l.$^{-1}$ for $K_2,n = 16$ at 60°. The final values assigned to the critical micelle concentrations (CMC) were: $K_2,n = 16$, − 0·04 M l.$^{-1}$ at 60°; $K_2,n = 14$, − 0·32 − 0·4 M l.$^{-1}$ at 40°, and 0·4 − 0·5 M l.$^{-1}$ at 60°.

No direct determination of micelle size was made; this is of interest in view of the introduction of a second polar group into the structure of normal soaps. In this paper conductance studies on solutions of the dipotassium salts of $n = 8$, $n = 12$, and $n = 16$ are reported, and also diffusion measurements on $K_2,n = 16$ to determine the micelle size. (For brevity all dipotassium salts are referred to as $K_2,n = \ldots$.)

EXPERIMENTAL

Materials. The methyl esters of dodecane and hexadecane dicarboxylic acids were converted to the potassium salts by refluxing for 4 hours with 20 per cent potassium hydroxide in 50 per cent aqueous ethanol. On cooling the potassium salts crystallised; the crystals were washed with ethanol, extracted continuously with ether for 48 hours to remove traces of the ester, recrystallised three times from ethanol containing the minimum amount of water, dried in a vacuum oven and stored under vacuum. $K_2,n = 8$ was prepared from recrystallised sebacic acid by boiling with a five times excess of 20 per cent potassium hydroxide in 50 per cent aqueous ethanol for 4 hours, allowing to crystallise, and

purifying in the same manner as the salts of the other acids. A portion of the free acid was prepared from each potassium salt.

Analysis figures were: $n = 8$, free acid molecular weight $= 202 \cdot 7$ $(202 \cdot 2)$; $K_2, n = 8$, $K = 28 \cdot 04$ per cent $(28 \cdot 09$ per cent$)$. $n = 12$, free acid molecular weight $= 258 \cdot 7$ $(259 \cdot 3)$; $K_2, n = 12$, $K = 23 \cdot 35$ per cent $(23 \cdot 38$ per cent$)$. $n = 16$, free acid molecular weight $= 314 \cdot 7$ $(314 \cdot 5)$; $K_2, n = 16$, $K = 20 \cdot 03$ per cent $(20 \cdot 02$ per cent$)$. Theoretical figures are given in brackets.

Density of K_2,n = 16 was determined using a displacement technique in dry benzene in a stoppered specific gravity bottle. Finely powdered solid was used, and was freed from included air by repeated evacuations under dry benzene. Repeat measurements gave $1 \cdot 280$ and $1 \cdot 280$ g.ml.$^{-1}$ at $25°$.

Conductivities. These were determined with a Cambridge Instrument Co. conductivity bridge, the final reading being made by the method of Ward and Chitale[2], using an external resistance. All solutions were made in demineralised water to provide a small solvent correction, and to minimise any effect of carbon dioxide on the long chain salts. Both conductivity and diffusion experiments were performed at $25 \pm 0 \cdot 05°$.

Diffusion Coefficients. These were measured on a Gouy diffusiometer of a type similar to that of Gosting[3] and Saunders[4]. All components were mounted on a vibration free 2 m. optical bench. The green line (5461 Å) was isolated by interference filters from a mercury vapour lamp and illuminated a slit of $12 \cdot 5 \mu$ width, which was mounted horizontally on the optical bench. The image of the slit was focused through the diffusion cell on to a photographic plate.

The diffusion cell[5], which is of a new type, was fitted with optically flat ($\lambda/2$) windows; it had the general form of a U-tube, the boundary being initially formed in a constricted part of one arm of the U-tube above the cell windows. After formation, the boundary was gently displaced downwards to the middle of the windows, where it was sharpened by flow of liquid through a 50μ slit set in one wall of the cell. An experiment was started by stopping the outflow from the cell, and allowing diffusion to commence. The interference patterns consisted of a series of closely spaced fringes, which were photographed at timed intervals after the start of diffusion. After development, distances on the plates were measured with a Cambridge universal measuring machine to $0 \cdot 0002$ cm.

No correction had to be made for Δt in any experiment; there was a random variation of diffusion coefficient with time. (Δt is the time taken for an infinitely sharp boundary to reach the state of the existing boundary when flow from the cell is stopped.)

RESULTS

The conductivity results are shown graphically in Figure 1 as a plot of the equivalent conductivity (Λ) against (normality)$^{\frac{1}{2}}$. The curves for $K_2, n = 8$ and $K_2, n = 12$ are almost parallel over the concentration range studied, while the $K_2, n = 16$ curve shows two anomalies. The

first, at A, lies between 11 and 12 mM l.$^{-1}$, and is a fairly sharp change of slope of the type usually associated with micelle formation. The second, in the region of B, 32–34 mM l.$^{-1}$, is a gradual change of slope, due either to a second CMC or to some change in the electrical properties of the solute.
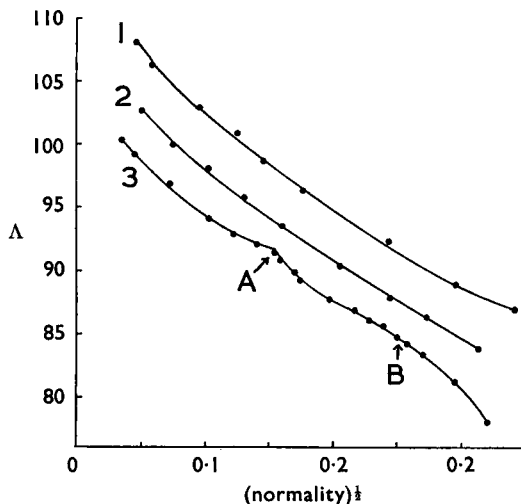

FIG. 1.   Equivalent conductivity (Λ) — (normality)$^{\frac{1}{2}}$ curves for (1) K$_2$, $n = 8$; (2) K$_2$, $n = 12$; (3) K$_2$, $n = 16$.

The integral diffusion coefficients (diffusion from a solution into pure solvent, terminology of Stigter, Williams and Mysels[6]) are shown in Table I and Figure 2 (i).

TABLE I

INTEGRAL DIFFUSION COEFFICIENTS OF K$_2$,$n = 16$ IN WATER

Concn. mM l.$^{-1}$		4·01	5·11	5·75	7·73	10·00	12·00
jm		11·11	14·20	15·01	21·53	27·86	33·35
10^6D, cm.^{2}sec.$^{-1}$		8·62	8·60	8·62	8·63	8·58	8·42
Concn. mM l.$^{-1}$		15·00	19·70	28·08	37·86	44·00	
jm		43·04	52·46	78·21	103·5	123·5	
10^6D, cm.^{2}sec.$^{-1}$		8·35	8·14	8·03	8·00	8·05	

Figure 2 (i) shows that below a concentration of 10 mM l.$^{-1}$ there is only a slight variation of diffusion coefficient with concentration. This is the expected result for the diffusion of single molecules. Above 10 mM l.$^{-1}$ the slope of the curve changes rapidly, probably due to micelle formation. No patterns showing lines of anomalous intensity were observed above the CMC, and all patterns could be analysed for the diffusion of a single solute. This is probably the consequence of there being little refractive index difference per unit concentration between the solutions containing single molecules, and those containing micelles, as a plot of jm against concentration shows only a slight break at the CMC.
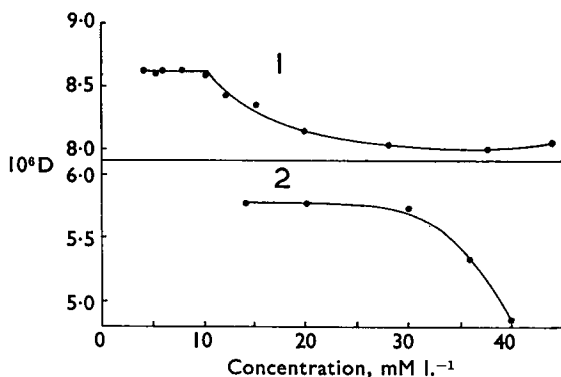
FIG. 2. (1) Plot of diffusion coefficient (D) against concentration for integral diffusions.
(2) Plot of diffusion coefficient (D) against mean concentration ($\bar{c}$) at $\Delta c = 6$ mM l.$^{-1}$ for differential diffusions.

Examples of the analysis of patterns from diffusion experiments at concentrations below and above the CMC are given in Tables II and III.

TABLE II

ANALYSIS OF A PATTERN AT CONCN. $= 5.75$ mML.$^{-1}$ (BELOW CMC)
$jm = 15.01$ $t = 1202$ sec.

j	Y (cm.)	$\exp(-z^2)$	C_t
1	0.2295	0.7202	0.319
2	0.2001	0.6254	0.320
3	0.1739	0.5457	0.319
4	0.1508	0.4740	0.318
5	0.1303	0.4085	0.319
6	0.1112	0.3485	0.319

Mean $C_t = 0.319_0$

TABLE III

ANALYSIS OF PATTERN AT CONCN. $= 19.70$ mM L.$^{-1}$ (ABOVE CMC)
$jm = 52.46$ $t = 1455$ sec.

j	Y (cm.)	$\exp(-z^2)$	C_t
1	0.9123	0.8761	1.041
2	0.8686	0.8334	1.042
3	0.8286	0.7961	1.041
4	0.7942	0.7625	1.042
5	0.7634	0.7310	1.044
6	0.7316	0.7017	1.043
7	0.7027	0.6743	1.042
8	0.6752	0.6472	1.043
9	0.6477	0.6218	1.042
10	0.6224	0.5980	1.041

Mean $C_t = 1.042_1$

In Tables II and III, j is the fringe number, the outermost fringe in a pattern being numbered zero. Y is the observed displacement of a fringe below the undeviated slit image, and $\exp(-z^2)$ is the theoretical displacement calculated from the theory of Kegeles and Gosting[7]. $C_t = Y/\exp(-z^2)$, and should be constant for single component diffusion.

Tables II and III show that the theory for single solute diffusion fits the patterns well for experiments both above and below the CMC.

Each value of the diffusion coefficient quoted is the mean of the results from at least four patterns. D is calculated from Longsworth's[8] equation:

$$D = \frac{jm.^2b.^2\lambda^2}{4\pi.C_t.^2t}$$

where jm is the difference in optical path length between the two liquids used in an experiment in wavelengths of light, b is the optical distance from the centre of the cell to the photographic plate in cm., and λ is the wavelength of light used.

The diffusion of colloidal electrolytes in water is complicated by electrical effects, as the ionic atmosphere around the larger anion is inclined to be in advance of the anion, causing an increase in the latter's diffusion rate. To obtain diffusion coefficients when electrical effects are decreased, differential diffusion experiments were performed by diffusion from a concentrated into a dilute solution. The results are given in Table IV.

TABLE IV

DIFFERENTIAL DIFFUSION COEFFICIENTS OF $K_2, n = 16$

$\bar{c}$	Δc	jm	10^6D, cm.^{2}sec.$^{-1}$
20	10	26·42	7·22
30	10	26·02	7·29
40	10	26·28	5·70
5	8	22·10	7·94
40	8	21·11	5·31
5	6	16·00	7·07
14	6	15·41	5·77
20	6	15·37	5·77
30	6	15·50	5·73
36	6	15·36	5·33
40	6	15·41	4·85
5	5	13·11	6·72
20	5	13·08	5·41
5	4	10·36	6·29
20	4	10·29	4·99
40	4	10·27	4·40

$\bar{c}$ = mean concentration of upper and lower solutions in mM l.$^{-1}$
Δc = concentration difference between solutions in mM l.$^{-1}$

Figure 3 shows the effect on the diffusion coefficient of decreasing the concentration difference (Δc) between the two solutions used in an experiment. In all cases the plots are linear. Results at $\bar{c} = 5$ mM l.$^{-1}$ extrapolate to $D = 4·67 \times 10^{-6}$ cm.^{2}sec.$^{-1}$. Those at $\bar{c} = 14$, 20, and 30 mM l.$^{-1}$ fall on the same line, giving $D = 3·52 \times 10^{-6}$ cm.^{2}sec.$^{-1}$. Although the results at $c = 40$ mM l.$^{-1}$ give a line with a smaller slope than the two preceding sets of results, the extrapolated value of D, 3·50 $\times 10^{-6}$cm.^{2}sec.$^{-1}$, is almost identical with that from $\bar{c} = 14$–30 mM l.$^{-1}$.

DISCUSSION

The first break in the equivalent conductance—(normality)$^{\frac{1}{2}}$ curve occurs between 11 and 12 mM l.$^{-1}$. It is suggested that these concentrations represent a concentration limit, where some discontinuity

occurs in the properties of the solution, e.g., micelle formation. Figure
2 (i) shows a sharp break in the D-concentration curve at 10 mM l.$^{-1}$,
where the diffusion coefficient decreases sharply for a small increase in
concentration. This effect is likely to be due to the formation of micelles,
which would have a smaller diffusion coefficient than the single molecules
which are present below the CMC. The two estimates of the CMC, 10
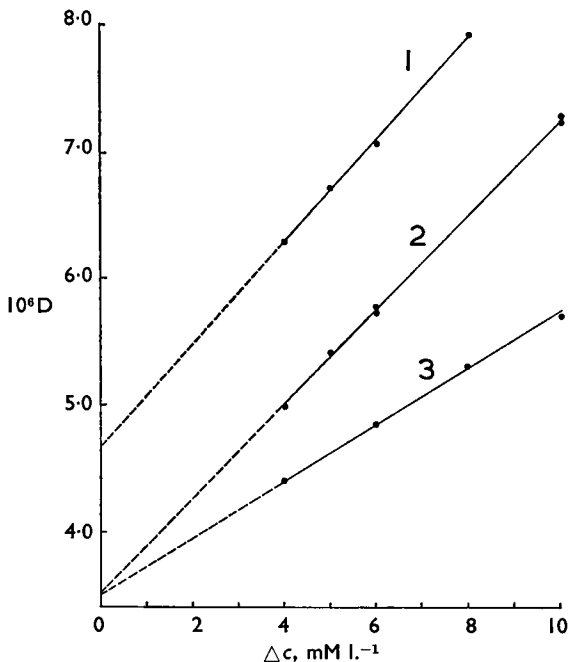and 11–12 mM l.$^{-1}$, obtained from different methods, agree reasonably
well.

FIG. 3. Plots of differential diffusion coefficients (D)
against $\Delta \bar{c}$ for various values of $\bar{c}$.
1, $\bar{c} = 5$; 2, $\bar{c} = 14 - 30$; 3, $\bar{c} = 40$.

The unaggregated solute shows a very large change of D with Δc
(Figure 3, $c = 5$ mM l.$^{-1}$). This indicates that there are large electrical
effects present during diffusion due to the influence of the smaller K^{+}
ions on the rate of diffusion of the long chain anion. By reducing the
concentration difference between two solutions diffusing into each other,
the electrical effects are decreased, and extrapolation to $\Delta c = 0$ should
yield a diffusion coefficient with minimised ionic atmosphere effects.

For differential diffusions where both solutions used in an experiment
have concentrations greater than the CMC, two species are expected to
be present—single molecules and micelles. Generally, aggregation into
micelles is governed by an equation of the mass action type; above the
CMC the concentration of micelles increases more rapidly than that of
single molecules. Two solutions both with concentrations greater than
the CMC will contain roughly equal amounts of single molecules, and

will differ in their content of micelles. As the concentration difference between two such solutions is decreased, the diffusing species consists more and more of the micellar form. An extrapolation to $\Delta c = 0$ gives the diffusion coefficient of the micellar species; this diffusion coefficient is also obtained with minimised electrical effects.

A second concentration limit appears in the $K_2, n = 16$ curve of Figure 1 at 32–34 mM l.$^{-1}$. A plot of D against $\bar{c}$ at $\Delta c = 6$ mM l.$^{-1}$ also shows a break at about 33 mM l.$^{-1}$ (Fig. 2 (ii)), while no break is shown on the integral diffusion coefficient-concentration curve (Fig. 2 (i)). The size of the micelles above the second concentration limit is unchanged, as shown by the plot of D against Δc at $\bar{c} = 40$ mM l.$^{-1}$, which gives the same extrapolated diffusion coefficient within experimental error ($3 \cdot 50 \times 10^{-6}$cm.^{2}sec.$^{-1}$) as found for the 14–30 mM l.$^{-1}$ region ($3 \cdot 52 \times 10^{-6}$cm.^{2}sec.$^{-1}$). The second concentration limit is due either to an increase in the amount of solute aggregated, or to a change in the electrical properties of the micelle. It is impossible to decide between the two possibilities on the present evidence.

Size of Micelles. By comparison with diffusion coefficients of other soap micelles obtained by the same procedure, for example, potassium laurate[9], $D = 1 \cdot 43 \times 10^{-6}$cm.^{2}sec.$^{-1}$, containing 52 monomers; sodium dodecyl sulphate[10], $D = 0 \cdot 97 \times 10^{-6}$cm.^{2}sec.$^{-1}$ containing 157 monomers; the diffusion coefficients reported here for $K_2, n = 16$ indicate the micelles are small. The introduction of a second polar group, remote from the first, into the structure of normal soaps, appears to decrease the size of the micelles.

The Stokes-Einstein relationship can be used to calculate the diffusion coefficient of a sphere from its molecular weight:

$$D = \frac{RT}{6\eta \ \pi \ N(3M\bar{v}/4\pi N)^{\frac{1}{3}}}$$

where η is the viscosity of the solvent, M is the molecular weight, $\bar{v}$ is the partial specific volume of the solute, and the remaining symbols have their usual significance.

To interpret the observed diffusion coefficient in terms of particle size, two limiting cases are examined. Firstly, the particles are considered as spheres and their diffusion coefficients are calculated for aggregates containing one, two, and three monomers. Secondly, the particles are considered as ellipsoids. For particles which are larger than the solvent molecules, Perrin's[11] relationships may be applied to relate the ratio of the frictional coefficient of an ellipsoid to that of a sphere of the same molecular weight (f_e/f_o) to the ratio of the semi-axes of an ellipsoid. In this case the extended long chain anion approximates to a prolate ellipsoid, where a in the major semi-axis, and b is the minor semi-axis. The frictional ratio may be related to the ratio of the diffusion coefficient of a sphere, D_o, to that of an ellipsoid of the same molecular weight, D_e,

$$\frac{D_o}{D_e} = \frac{f_e}{f_o}$$

From measurements on molecular models of $K_2, n = 16$ values of a/b can be found, and the diffusion coefficients of the ellipsoids calculated. The results of the calculations are given in Table V.

TABLE V

CALCULATED VALUES OF THE DIFFUSION COEFFICIENT FOR PARTICLES OF DIFFERENT SHAPES

Number of monomers in particle	1	2	3
$10^6 D_O$ (sphere) cm.^{2}sec.$^{-1}$	4·91	3·90	3·41
$10^6 D_e$, fully extended, cm.^{2}sec.$^{-1}$	3·59	3·12	—
10^6 D observed, cm.^{2}sec.$^{-1}$	4·67	3·51	—

D_o for three monomers is lower than the observed diffusion coefficient for the micelles, which falls between the limiting values for a micelle of two monomers. Due to the long hydrocarbon chain, the particles are unlikely to be spherical. The diffusion coefficient of the monomeric form also falls between the two limiting values.

Degree of extension of hydrocarbon chains. A very rough idea of the degree of extension of the hydrocarbon chain in the molecule in solution may be gained by using the observed diffusion coefficient to calculate the frictional ratio, and interpreting this in terms of a/b. For monomers $a/b = 2·12$, for double molecules $a/b = 3·00$. The volume of an ellipsoid will be given by

$$V = 4\pi ab^2/3$$

V can be calculated from the density of the solid, so both a and b can be found.

For monomers, $a = 8·2$ Å and $b = 3·9$ Å, while for double molecules, which are assumed to lie side by side, $a = 13·0$ Å and $b = 4·3$ Å. These results are in the correct order, as the hydrocarbon chain of the monomer would be expected to be contracted to the maximum extent, to minimise the area in contact with water; the double molecule has a smaller amount of hydrocarbon chain/molecule exposed to the water, if the two molecules lie side by side. It should therefore be able to lengthen more, as "bundling up" will cause a strain on the chain. These calculations are tentative, no account being taken of hydration.

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