

DIFFUSION MEASUREMENTS IN THE STUDY OF THE STRUCTURE OF SOAP SOLUTIONS

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INTRODUCTION

THE importance of soaps in the preparation of pharmaceuticals is widely realised, yet even to-day uncertainty exists as to the detailed structure of a soap in solution. This arises out of the fact that a soap can exist in the same solution in two forms which are in equilibrium, a simple ionic form and a colloiddally dispersed micellar form. Experimental methods for investigating this association of soaps into micelles have varied widely; conductivity, solubilisation studies, light scattering, viscosity and other physical properties have frequently been reported. Many of these measurements involve the application of an external force, or additive to the soap solution. Such application of an external agent is liable to vitiate the results as far as calculation of the size, shape, number or other structure of the particles in the pure soap solution.

In the present studies, anionic soaps and other association colloids have been investigated by means of the recently revived Gouy interference method for studying diffusion^{1,2,3}. This is a free boundary method, briefly described below. Other diffusion measurements using soap solutions have involved tagging with dyes⁴, diffusion through porous discs^{5,6} or the use of the Lamm scale-line method^{7,8}. The Gouy interference method provides a sensitive, accurate means of determining diffusion coefficients without extraneous additives and without the limitations imposed by the use of glass discs or porous plates. Sodium dodecyl sulphate (NaDS) has been used here as an example of the type of investigation that has been attempted.

EXPERIMENTAL METHODS

Materials. Sodium dodecyl sulphate was prepared according to the method described by Dreger *et al.*⁹, as modified by Burick¹⁰. The sulphur content of the pure material (two samples) after three re-crystallisations from water at 5° C. was 11.07 and 11.15 per cent. (theoretical 11.12). The sulphur content was determined by hydrolysis with 50 per cent. hydrochloric acid, ether extraction and precipitation with barium chloride. Potassium laurate was prepared by the neutralisation with carbonate-free standard alkali of pure lauric acid (Eastman Kodak) which had an equivalent weight of 200.5, determined potentiometrically, and a melting point of 42 to 43° C. Water used was double distilled from potassium permanganate. All sols were allowed to age for 24 hours before use.

Diffusion coefficients. The apparatus (see Fig. 1) consists of a two metre optical bench mounted on a steel beam supported on concrete pillars embedded in earth beneath a basement laboratory floor. A water cooled

STRUCTURE OF SOAP SOLUTIONS

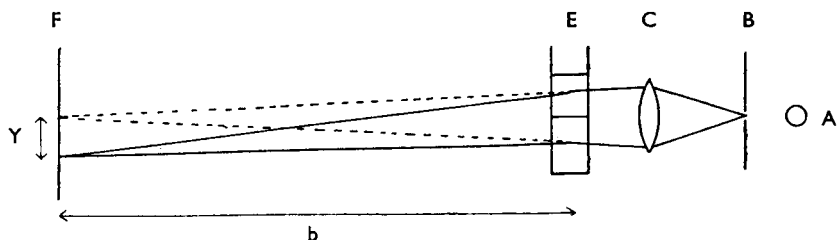


FIG. 1. The optical system of the Gouy interference diffusiometer.

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|---|---|
| <p>A. Mercury vapour lamp fitted with filters (5461 Å°).</p> <p>B. Spectrometer slit.</p> <p>C. Lens.</p> <p>E. Cell.</p> <p>F. Photographic plate.</p> | <p>Y. Displacement of the Gouy minima below the optic axis.</p> <p>b. Optical distance between the centre of the cell and the photographic plate.</p> |
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mercury vapour lamp, A, fitted with suitable filters to isolate monochromatic light (5461 Å) illuminates a horizontal spectrometer slit, B. A precision camera lens, C (Ross Express $f2.9$) of 13.5 cm. focal length focusses an image of the slit through the thermostat fitted with circular optically flat ($\lambda/2$) windows, on to a photographic plate, F, at the far end of the bench. The thermostat is supplied with constant temperature water from a larger tank, the supply being so arranged as to avoid any vibration of the thermostat.

The nickel coated brass cell, E, fitted with two optically flat ($\lambda/2$) windows, fits inside the thermostat. A $50\ \mu$ slit through which the two liquids are drawn to form the boundary is placed such that it lies exactly on the optic axis of the apparatus. The whole of the interior of the cell is coated with silicone by the hydrolysis of methylchlorosilane. The two liquids are introduced into the cell by means of motor driven syringes whose glass needles reach to the top of the cell windows. Mixing of the two solutions during boundary formation is prevented by pre-heating the solutions and by continually withdrawing the liquids through the slit. When sufficient solution has been introduced into the cell, the syringes are removed, the whole allowed to come to temperature equilibrium and a sharp boundary is formed by rapid flowing out through the slit and abruptly stopping flow. That a very sharp boundary is formed initially by this method is confirmed by the fact that the observed diffusion coefficients do not vary with time as has been previously reported in some cases. Longsworth¹ introduced an expression Δt which represented the time which an infinitely sharp boundary would take to reach the state of the boundary existing when flow was stopped. Since no Δt value was obtained in any of the measurements reported here, it is valid to assume that an extremely sharp boundary exists when flow is stopped. The boundary starts to spread by diffusion and the refractive index gradients produced cause a set of interference fringes to appear on the photographic plate. A very fast emulsion plate (Kodak P 2000) has been used to record the interference patterns after timed intervals.

After diffusion has spread beyond the cell windows, the cell is washed

out *in situ* and filled with distilled water. After 30 minutes, when temperature equilibrium is reached, a pair of stops is lowered in front of the cell window and a photograph of the interference pattern produced by the stops is recorded. This record enables the optic axis of the apparatus to be located.

The diffusion coefficient D is calculated by means of the method described by Kegeles and Gosting¹¹ and Gosting and Onsager¹². The calculation is based on the determination of C_t which is obtained from Y , the displacement of each minimum in the Gouy pattern below the optic axis in cm. C_t is the ratio of the observed displacement of a minimum to the theoretical displacement. If the diffusing substance is homogeneous, C_t is constant for the outer minima of a given pattern (see Table I).

TABLE I
EXAMPLE OF THE CALCULATION OF C_t , THE DIFFUSION OF
64 MILLIMOL/L. OF NaDS INTO 50 MILLIMOL/L.
 $t = 1805$ SECONDS

Gouy fringe number* j	Observed displacement below optic axis $Y(\text{cm.})$	Theoretical displacement† $e^{-(z)^2}$	Ratio of observed to theoretical displacement C_t
1	0.4574	0.771	0.593
2	0.4125	0.693	0.595
3	0.3714	0.627	0.592
4	0.3361	0.565	0.595
5	0.3033	0.510	0.595

Mean $C_t = 0.594$.

* Fringe numbers are counted by giving the outermost minimum in the pattern the number zero.

† The theoretical displacement, $e^{-(z)^2}$ is calculated from j and j_m (the difference in optical path length between the two liquids in the cell in wavelengths of light) by the theory of Kegeles and Gosting¹¹. The maximum value of $e^{-(z)^2}$ for any pattern is unity.

D can be found from C_t by the application of Longworth's¹ equation:—

$$D = \frac{b^2 \cdot j_m^2 \cdot \lambda^2}{4\pi \cdot C_t^2 \cdot t}$$

where j_m is the difference in optical path length between the two liquids in the cell in wavelengths of light and is determined from a count of the number of minima in the Gouy pattern. b is a constant for the apparatus and is the optical distance between the centre of the cell and the emulsion of the photographic plate; t is the time in seconds after flow has been stopped, at which the photograph was taken and λ is the wavelength of light in cm. The variation of diffusion coefficient of NaDS with concentration is illustrated in Figure 2 which shows Gouy patterns taken at the same time (1800 seconds) for different mean concentrations (\bar{c}) of NaDS. Δc , the difference between the lower and upper layer concentrations has been kept constant at 14 millimoles/l. The numbers below the Gouy patterns correspond to the numbers used in Table III.

If C_t is not constant, then the material diffusing is heterogeneous and another method of calculating D is applied. This method¹³ is based on a measurement of the relative Gouy fringe deviations from Gaussian positions.

STRUCTURE OF SOAP SOLUTIONS

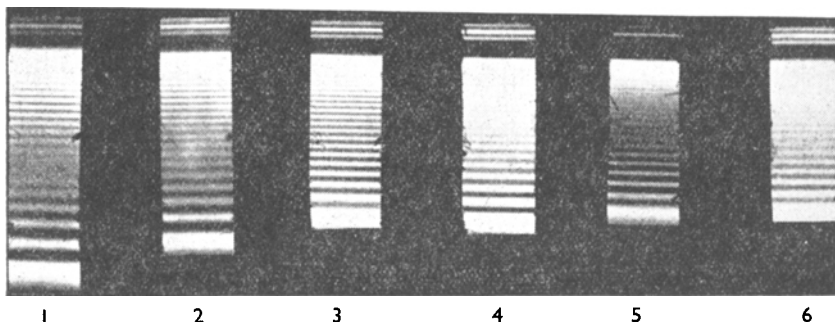


FIG 2. Gouy patterns for the semi-differential diffusion of sodium dodecyl sulphate in water, showing the effect of variation of mean concentration on diffusion coefficient. Numbers correspond to those in Table III. Intensity minima are dark. $t = 1800$ seconds.

RESULTS

The terminology of Stigter *et al.*⁶ has been used throughout this communication, i.e., integral diffusion coefficients are measured by diffusing a solution into water, semi-differential coefficients by diffusing a solution of concentration c_a into c_b (where c_a is greater than c_b and c_b is greater than zero) and differential diffusion coefficient, the value of D when c_a and c_b merge, i.e., when Δc tends to zero. All diffusion coefficients are expressed in cm^2/sec . at 25°C ., concentrations in millimoles/l. Diffusion coefficients are the average values determined from at least three Gouy patterns.

The pattern produced by the diffusion of 10 millimoles/l. of NaDS into water, when calculated gave an anomalous result, D' quoted for this concentration in Table II is derived only from the penultimate minimum and not from several of the outer minima as is the case with the other values of D given. This anomaly is attributed to micelle formation which takes place at about this concentration.

Above the critical micelle concentration (CMC) the diffusion coefficient decreased rapidly with concentration. The intensities of the fringes in patterns obtained with concentrations of 15, 20 and 50 millimoles/l., of NaDS diffusing into water were anomalous. This was due to heterogeneity in the diffusing solution caused by the presence of soap micelles. The values of D given for these solutions in Table II have been calculated by Akeley and Gosting's¹³ method.

Semi-differential diffusion coefficients in which the upper solution was of concentration greater than the CMC gave homogeneous diffusion patterns in which C_t was constant. The results of these measurements are shown in Table III.

TABLE II
INTEGRAL DIFFUSION COEFFICIENTS FOR
SODIUM DODECYL SULPHATE

Concentration	j_m	$10^6 D_a$	$10^6 D'$
5	8.08	—	6.48
7	11.05	—	6.56
8	12.27	—	6.54
9	14.62	—	6.43
10	15.58	—	6.43
15	22.03	1.94	4.58
20	30.49	1.06	3.80
50	79.02	1.59	2.76

D_a = Height-area average diffusion coefficient.
 D' = Weight average diffusion coefficient.

TABLE III
SEMI-DIFFERENTIAL DIFFUSION COEFFICIENTS FOR SODIUM
DODECYL SULPHATE

Number*	Lower layer conc. c_a	Upper layer conc. c_b	Mean conc. c	j_m	$10^6 D$
1	24	10	17	20.94	1.51
2	34	20	27	20.37	2.26
3	54	40	47	20.82	3.21
4	64	50	57	20.80	3.27
5	77	63	70	20.70	3.36
6	100	86	93	20.38	3.46

* These numbers correspond to the number of the Gouy pattern in Fig. 2.

Integral diffusion coefficient measurements therefore show that the diffusion coefficient decreases rapidly with increasing concentration above the CMC. However, semi-differential diffusion coefficient measurements show an increase of diffusion coefficient with increasing concentration to an almost constant value above 60 millimoles/l. There must therefore be a minimum in the overall diffusion coefficient/concentration (D/c) curve. Such a minimum has already been shown to exist in the case of potassium laurate¹⁴. The minimum has been found for NaDS and is very close to the CMC. The minimum was determined by differential diffusion coefficient measurements, these results are given in Table IV together with some differential diffusion coefficients for potassium laurate.

TABLE IV
DIFFERENTIAL DIFFUSION COEFFICIENTS FOR NaDS AND
POTASSIUM LAURATE

Lower layer conc. c_a	Upper layer conc. c_b	Δc	j_m	$10^6 D$
<i>Sodium dodecyl sulphate</i>				
20	10	10	13.39	1.08
15	10	5	8.71	0.97
<i>Potassium laurate</i>				
250	210	40	62.87	4.56
240	220	20	30.34	4.13
235	225	10	14.86	3.55
232.5	227.5	5	7.50	3.26

The differential diffusion coefficient of potassium laurate at the minimum on the D/c curve has previously been reported¹⁴. In the case of NaDS, the differential diffusion coefficient cannot be taken any further than the results quoted in Table IV. This is due to the close proximity of this minimum to the CMC thus preventing any variation of Δc around the constant mean concentration at the minimum.

Theoretical diffusion coefficients have been determined for NaDS in dilute solution by the following calculation. As Δc is decreased, the differential diffusion coefficient of the soap is reached. Taking the lowest value of 9.7×10^{-7} as being the true diffusion coefficient of micelles, a value of n the mean aggregation number has been determined by applying the Stokes-Einstein equation¹⁵:—

$$\text{At } 25^\circ \text{ C., molecular volume of micelle} = \left[\frac{33.06 \times 10^{-6}}{9.7 \times 10^{-7}} \right]^3 \quad (1)$$

STRUCTURE OF SOAP SOLUTIONS

$$\text{then } n = \frac{\text{molecular volume of micelle}}{\text{molecular volume of NaDS}} = 156.5 \quad \dots \quad (2)$$

This equation can be applied since as Δc tends to zero, effects due to any electrical potential difference between the two solutions are eliminated. For a solution containing two components, the weight average diffusion coefficient D' can be defined as follows¹⁶:—

$$D' = \alpha_1 D_1 + \alpha_2 D_2 \quad \dots \quad (3)$$

where D_1, D_2 = the diffusion coefficients of components 1 and 2, α_1, α_2 are the refractive index fractions of components 1 and 2.

$$\text{Then } D^A = (1 - \alpha_2)D_1 + \alpha_2 D_2 \quad \dots \quad (4)$$

Taking the results obtained for D', D_1 as the diffusion coefficient of simple soap and D_2 as the diffusion coefficient of micelles, α_2 can be evaluated. From a knowledge of the refractive index increment per unit concentration of simple and micellar forms, which can be derived from experimental values of j_m , α_2 can be converted to x , a concentration fraction. Assuming that all the NaDS in solution below the CMC is in the simple form, then values of c_1 and c_2 , the concentrations of simple ions and micelles respectively, are found from x .

In this theoretical interpretation, the law of mass action without activity coefficients has been applied to the equilibrium between simple ions and micelles:—

$$\log c_2 - n \log c_1 = \text{constant} \quad \dots \quad (5)$$

This constant can now be determined since all of the other terms in equation (5) are known. From this basic equation, a table of c_1 and c_2 values can be set up as in Table V.

By means of this table, the theoretical diffusion coefficients for experiments carried out with solutions below 24 millimoles/l. were calculated using a reverse process to the one outlined above for finding the constant in equation (5). These theoretical values are compared with the experimental values in Table VI.

TABLE V
THE RELATIONSHIP OF c_1 AND c_2 FOR NaDS
BASED ON THE EQUATION:
 $\log c_2 - 156.5 \log c_1 = -155.801$

c_1	c_2	$c_1 + c_2$	x
9.80	0.208	10.008	0.021
9.90	1.02	10.92	0.094
10.00	5.00	15.00	0.333
10.03	7.98	18.01	0.443
10.04	9.23	19.27	0.479
10.05	10.67	20.72	0.515
10.06	12.76	22.82	0.559
10.07	14.76	24.83	0.594

TABEL VI
COMPARISON OF THEORETICAL AND EXPERIMENTAL DIFFUSION COEFFICIENTS FOR NaDS

Solution concentrations	Theoretical $10^6 D'$	Experimental $10^6 D'$
15/ 0	4.75	4.58
20/ 0	3.87	3.80
20/10	1.12	1.08

DISCUSSION

A minimum in the D/c curve for association colloids has previously been reported for some α -sulphonic acids¹⁷ and for potassium laurate¹⁴. In both of these cases and in the present work, diffusion measurements have been made in the absence of any added electrolyte. Previous measurements of the diffusion coefficient of NaDS in the presence of added electrolyte show no minimum in the D/c curve, e.g., Miller and Anderson¹⁸ in the presence of lithium ions, Hakala¹⁹ in the presence of excess sodium chloride and Granath²⁰ in the presence of sodium carbonate and sodium bromide. The only other reported measurements of the diffusion coefficient of NaDS are those of Stigter *et al.*⁶ who measured micellar self-diffusion both in the presence and absence of added electrolyte. These authors have used a porous glass disc apparatus and measured micellar self-diffusion by tagging the micelles with a dye, Orange OT. In view of the important effect of small additions of both polar and non-polar substances on the structure of soap solutions, we consider that the diffusion coefficients reported by Stigter *et al.*⁶ are not the diffusion coefficients of pure NaDS. It seems difficult to believe that the porous glass discs used by these workers have no effect on the diffusion rate, either by adsorption of the surface active soap or by the modification of boundary potentials. Hartley and Runnicles⁵ have pointed out that a free boundary method is essential for anionic soaps since these substances tend to build up a structure in porous discs.

Hartley and Robinson²¹ were the first authors to suggest that only diffusion coefficient measurements carried out in the presence of a swamping amount of electrolyte were of use in the estimation of micelle size. However, it has been shown by Granath²² that the diffusion coefficient of anionic soaps varies widely with the concentration of added cation, and also with the type of added anion even if the ionic strength is kept constant. Since this variation has such a large effect on D we have completely avoided the addition of electrolytes to the soap solutions and have only measured diffusion coefficients in salt-free media. We consider that the use of differential diffusion measurements in which Δc tends to zero and electrical effects also tend to zero, gives an estimate of the true micellar diffusion rate, and not an artificial rate in the presence of an excess of extraneous additive.

The value of the CMC taken here is between 9 and 10 millimoles/l. The authors are of the opinion that the CMC is not an exact concentration but is a small concentration range. It has often been found in the past that the CMC varies quite considerably with external factors such as temperature, added substances and particularly with the method of determination²³. The value found here for NaDS is in general agreement with previously determined values at this temperature (25° C.), e.g., 9 millimoles/l. from conductivity measurements²⁴ and 8.1 millimoles/l. from conductivity, solubilisation and light scattering measurements²⁵.

Ekwall^{26,27} has shown that the properties of dilute soap sols change abruptly at other concentrations besides the CMC. He terms these points concentration limits. In the case of potassium laurate, the

STRUCTURE OF SOAP SOLUTIONS

minimum in the D/c curve coincides with Ekwall's fourth limit at 50 millimoles/l. A concentration limit for NaDS would seem to occur at approximately 12.5 millimoles/l., where the diffusion coefficient is minimal.

The agreement between theoretical and experimental diffusion coefficients as shown in Table VI would appear to justify the simple mass law interpretation that has been applied to these dilute solutions. The extremely rapid increase in the concentration of micellar form (c_2) with very small increase in simple form (c_1), see Table V, would account for the rapid falling off of diffusion coefficient with increasing concentration after the CMC, to a minimum value. The rise of diffusion coefficient after the CMC to a constant value above 60 millimoles/l. (see Table III) is a property of soap solutions that has until recently been seldom observed or commented upon. McBain¹⁷ in an attempt to explain the minimum in the D/c curve for α -sulphonic acids which she obtained, has applied McBain's theory of the structure of association colloid solutions. Thus "neutral colloid" is supposed to predominate in the transition region where the diffusion coefficient decreases rapidly with increasing concentration, and "ionic micelle" in the higher concentrations where its mobility in the potential gradient accounts for the subsequent rise of diffusion coefficient. Hartley²⁸ has on the other hand stated that the minimum in the D/c curve can be explained on the basis of a single spherical ionic micelle. Thus, if the one kind of charged micelle is present, it will not contribute as much in the transition region where it exists in excess of simple electrolyte (i.e., c_2 is less than c_1) as it will when it exists in much higher concentration than the simple ions from which it is formed (i.e., c_2 greater than c_1). Hartley therefore considers that the minimum in the D/c curve is not due to a change in the nature of the micelles in solution, but is due to a change in the electrical effect upon the micelles. We consider that the results obtained for potassium laurate shown in Table IV are corroboratory evidence for Hartley's theory. In these measurements the mean concentration (\bar{c}) of the two solutions has been kept constant while the small difference in concentration (Δc) between them has been varied. Consequently the same types of particles are present in all the solutions and the only variation is in the electrical potential differences between the pairs of solutions. The results shown in Table IV for potassium laurate indicate that D varies with Δc , but tends towards a constant value above 20 millimoles/l.

SUMMARY

1. Diffusion coefficients at 25° C. for pure sodium dodecyl sulphate have been measured by the Gouy interference method.
2. A minimum in the overall diffusion coefficient/concentration curve, occurring at a concentration limit close to the critical micelle concentration has been found.
3. An estimate of micellar size from the differential diffusion of pure sodium dodecyl sulphate has been obtained. A table of the relative concentrations of simple soap and micelles in dilute solutions is given.
4. Theoretical diffusion coefficients, showing general agreement with

experimental values, have been determined by application of the law of mass action.

5. Differential diffusion rates for potassium laurate in concentrated solution are reported and these indicate that the increase of D after the minimum point is due to electrical effects.

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DISCUSSION

The paper was presented by MR. N. BRUDNEY.

MR. P. ELWORTHY (Romford) referred to the authors' statement that previous measurements of the diffusion coefficients of NaDS in the presence of added electrolyte showed no minimum in the D/c curve. Those values were not quoted in the paper, and it would be interesting to know how they compared with the present measurements. Had the authors any information on the bactericidal activity of the solution?

MR. H. D. C. RAPSON (Dorking) asked whether the critical micelle size referred to agreed with the measurements made by conductivity methods. It would be very interesting to follow up the work by using

STRUCTURE OF SOAP SOLUTIONS

radio-active tracer techniques as had been done in the study of diffusion in molten metals.

MR. N. BRUDNEY, in reply, said that the values of previous measurements were not given because the main point for consideration was the fact that no minimum in the diffusion coefficient curve had been found, but the values generally obtained were close to the results shown. No endeavour had been made to correlate results with bactericidal activity. It might be considered in the future. Measurements agreed generally with previous measurements of micelle size of potassium laurate. The tracer technique had not been attempted as yet.