A Study by the Gouy Interference Method of the Diffusion in Water of Potassium Laurate.

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The rate of diffusion of potassium laurate in salt-free aqueous solutions at various concentrations has been measured by means of the Gouy interference method. The mean diffusion coefficient falls rapidly with increasing concentration above the critical concentration for micelle formation, to a minimum value. The diffusion coefficient then rises again to an almost constant value in concentrated solutions. Anomalous interference patterns were obtained above the critical concentration.

A method for determining weight-average diffusion coefficients for heterogeneous solutions has been applied to the anomalous patterns. Theoretical diffusion coefficients have been calculated, based on a simple mass-law interpretation and fair agreement with the experimental results has been found. The obscuration of the minimum in the diffusion coefficient–concentration curve by the addition of electrolytes is discussed.

Diffusion measurements were used in the investigation of the structure of aqueous solutions (or sols) of potassium laurate by McBain and Liu (*J. Amer. Chem. Soc.*, 1931, **53**, 59). Laing-McBain (*ibid.*, 1933, **55**, 545) used sodium oleate as the association colloid and concluded that the primary particles of this paraffin-chain salt were not much larger than those of potassium laurate. The earliest intensive diffusion measurements with the anionic soaps were made by Jander and Weitendorf (*Angew. Chem.*, 1934, **47**, 197) who, using sodium laurate and sodium decanoate, postulated the formation of bimolecular aggregates before the formation of micelles in these solutions. Hartley and Runnicles (*Proc. Roy. Soc.*, 1938, *A*, **168**, 420) measured the diffusion of cetylpyridinium chloride in the presence of a swamping excess of simple electrolyte with a sintered-disc cell, but found that the diffusion of anionic soaps in this type of apparatus led to erroneous results owing to the build-up of a structure in the glass disc. They suggested the use of a free-boundary method in the determination of diffusion constants for the normal paraffin-chain soaps. Such a method was applied to lauric acid salts in the absence of added electrolyte (Lamm and Högberg, *Kolloid Z.*, 1940, **91**, 10) and in a salt-containing medium (Lamm, *ibid.*, 1942, **98**, 45; Granath, *Acta Chem. Scand.*, 1950, **4**, 103). The diffusion of potassium laurate by tagging it with dyes has been studied by Hoyer and Mysels (*J. Phys. Colloid Chem.*, 1950, **54**, 966) in the presence of excess of alkali.

In the present work, Gouy's interference method (Longsworth, *J. Amer. Chem. Soc.*, 1947, **69**, 2510; Saunders, *J.*, 1953, 519) has been used to examine the diffusion of potassium laurate in a salt-free medium.

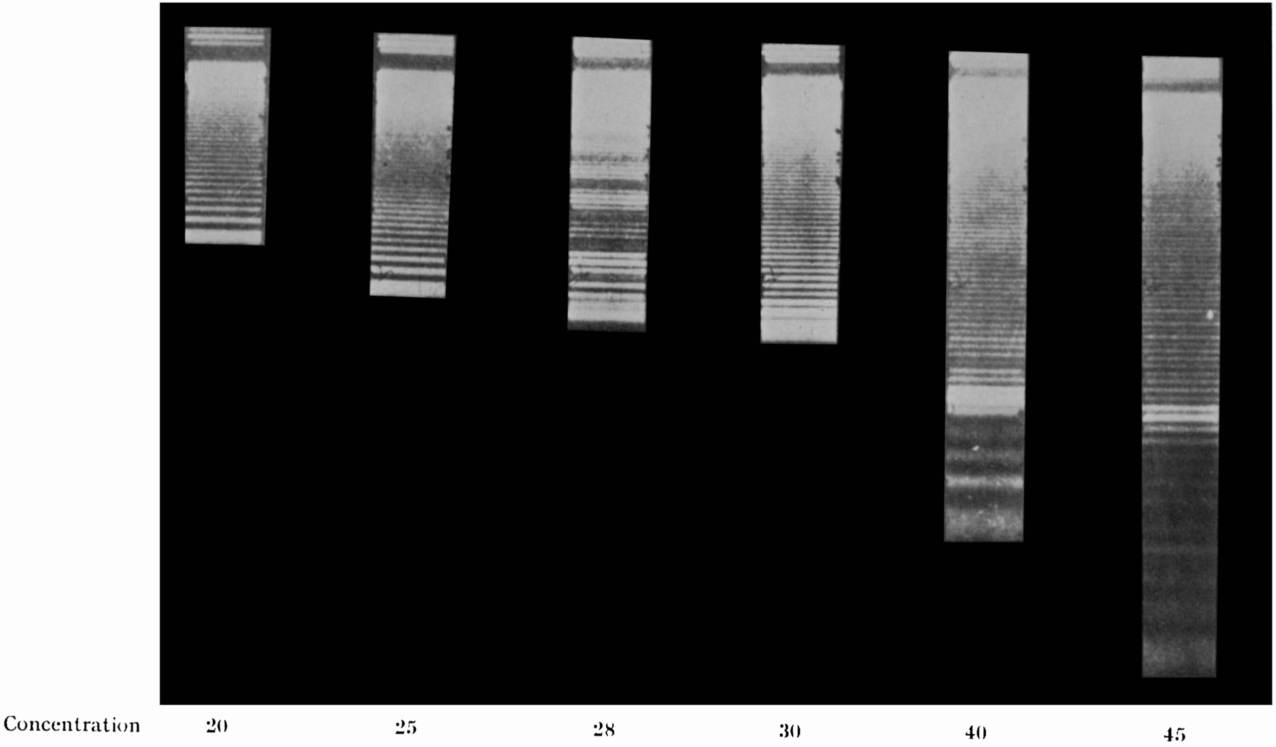
Experimental

Materials.—Lauric acid (Eastman Kodak) had equiv. 200·5, determined potentiometrically, and m. p. 42—43°. The acid was neutralised with a solution of "AnalaR" potassium hydroxide from which traces of carbonate were removed by ion-exchange. Sols were allowed to "age" for at least 24 hr. before use. Little trouble was experienced with hydrolysis, except in solutions containing less than 20 mmoles/l.: to these solutions a small excess of alkali was added.

Diffusion Coefficients.—The sol–water boundary was formed in a metal cell which has replaced the all-glass cell used in the apparatus previously described (Saunders, *loc. cit.*). This metal cell, made in these laboratories, of nickel-coated brass, is fitted with two windows made of half-wavelength optical flats. The 50-micron slit through which the two liquids are drawn is made of two nickel-coated brass blocks spaced with platinum foil. The whole of the interior of the cell is Silicone-coated 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. This method has replaced the pipettes and rubber tubing used in the

Gouy patterns for the diffusion of potassium laurate into water taken 1800 *seconds after diffusion has started.*

Intensity minima are dark



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earlier apparatus and permits easier control of the rate of the inflowing liquids. For more rapidly diffusing materials a very fast photographic plate (Kodak P 2000) has been used to record the Gouy patterns, permitting a reduction of exposure time. Apart from these alterations, the apparatus and calculation of diffusion coefficients are as previously described. Values of average diffusion coefficients for potassium laurate solutions are shown in Table 1 (concentrations in mmoles/l.; diffusion coefficients in cm.^{2}/sec. at 25°).

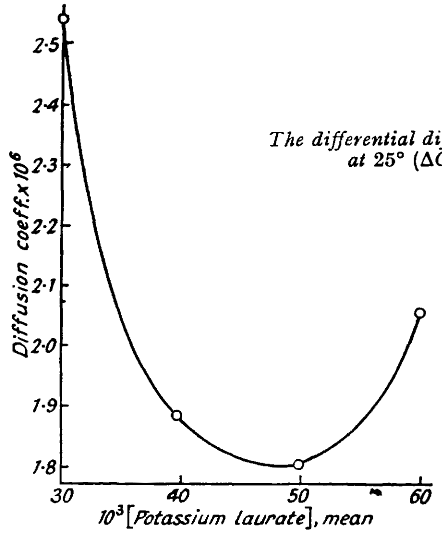
Table 1. *Diffusion of potassium laurate into water.*

(For meaning of symbols, see *J.*, 1953, 519.)

Concn.	20·0	22·5	25·0	28·0	30·0	35·0	40·0	45·0
j_m	34·5	38·5	42·6	51·9	54·9	61·6	68·1	73·8
10^6D	8·31	8·31	8·24	8·26	7·92 *	6·75 *	5·81 *	5·13 *

* C_t constant over a limited range between the optic axis and the anomalous intensity region, see Plate.

Above the critical concentration for micelle formation (CMC) of 28 mmoles/l., the diffusion coefficient decreased rapidly with increasing concentration. The patterns obtained with solutions below the CMC were quite normal in appearance (see Plate). At the CMC, the pattern appeared diffuse and the intensities of the lines varied throughout the pattern, but with some regularity in the variation. Above the CMC, the pattern was again normal but for two or three very intense maxima, indicating heterogeneity in the diffusing solution. Lamm and Högberg (*loc. cit.*) observed that the calculation of diffusion coefficients when using these solutions above the CMC was very uncertain owing to heterogeneity.



The differential diffusion of potassium laurate at 25° (ΔC = 10 *mmoles/l.*).

To overcome this difficulty, differential diffusion measurements were made (see Table 2 and Figure).

TABLE 2. *Differential diffusion of potassium laurate.*

Concn. of lower sol	Concn. of upper sol or solution	j_m	10^6D_A	$10^6D'$
35·0	25·0	15·39	—	2·545
40·0	0·0	68·17	4·55	5·71
50·0	30·0	31·15	—	2·055
50·0	0·0	85·00	2·90	4·66
50·0	10·0	65·38	2·42	4·11
52·5	47·5	7·18	—	1·61
53·75	46·25	11·23	—	1·72
55·0	45·0	14·76	—	1·80
60·0	40·0	31·09	—	2·13
60·0	20·0	64·45	1·92	2·53
65·0	55·0	14·93	—	2·06
70·0	50·0	31·59	—	2·35
80·0	60·0	31·63	—	2·63
80·0	40·0	62·45	—	2·45
100·0	60·0	62·33	—	2·85
150·0	110·0	61·80	—	3·71
200·0	160·0	61·24	—	4·34
300·0	260·0	60·27	—	4·55
400·0	360·0	60·18	—	4·65

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

Patterns obtained from differential diffusion measurements showed no intensity anomalies, except when the concentration of the upper solution was less than the CMC.

A method for determining diffusion coefficients of heterogeneous solutions by the use of a relative fringe deviation graph (Akeley and Gosting, *J. Amer. Chem. Soc.*, 1953, **75**, 5685) has been applied to these patterns. These authors' symbols being used, the results of an examination of the relative fringe deviation graph for the diffusion of a sol, of 40 mmoles/l., of potassium laurate into water are shown in Table 3.

TABLE 3. *Examination of the relative fringe deviation graph for the diffusion of* 40 *mmoles/l. of potassium laurate into water.*

$f(\zeta)$	$d\Omega/df(\zeta)$	Ω	$1 - \Omega/e^{-\zeta^2}$	$\left[1 + \frac{2}{\sqrt{\pi}}\zeta\left(\frac{d\Omega}{df(\zeta)}\right)\right]^4$	H	$H\left[\frac{2}{\sqrt{\pi}}\zeta\right]^4 e^{-\zeta^2}$
0·01	9·6	0·041	0·957	167·19	0·0057	0·0000285
0·025	0·702	0·064	0·929	2·522	0·368	0·0062
0·05	0·452	0·082	0·902	2·1715	0·415	0·0175
0·075	0·279	0·090	0·886	1·7670	0·501	0·0357
0·10	0·000	0·094	0·874	1·0000	0·874	0·0903
0·15	−0·170	0·086	0·872	0·5968	1·461	0·2529
0·20	−0·176	0·076	0·874	0·5449	1·604	0·3973
0·25	−0·161	0·068	0·875	0·5432	1·611	0·5236
0·30	−0·154	0·060	0·878	0·5304	1·655	0·6671
0·35	−0·145	0·053	0·880	0·5265	1·671	0·8031
0·40	−0·131	0·046	0·883	0·5397	1·636	0·9098
0·45	−0·120	0·039	0·888	0·5493	1·617	1·016
0·50	−0·107	0·034	0·889	0·5695	1·561	1·085
0·55	−0·094	0·028	0·895	0·5935	1·508	1·139
0·60	−0·084	0·025	0·891	0·6134	1·453	1·172
0·65	−0·081	0·021	0·892	0·6076	1·468	1·242
0·70	−0·079	0·017	0·894	0·6000	1·490	1·298
0·75	−0·072	0·013	0·899	0·6096	1·475	1·294
0·80	−0·068	0·009	0·908	0·6082	1·493	1·280
0·85	−0·060	0·006	0·914	0·6263	1·459	1·171
0·90	−0·048	0·004	0·909	0·6685	1·360	0·946
0·925	−0·044	0·0025	0·921	0·6788	1·357	0·831
0·95	−0·037	0·0015	0·928	0·7086	1·305	0·649
0·975	−0·027	0·0005	0·946	0·7613	1·243	0·411
0·99	−0·019	0·0000	1·000	0·8107	1·234	0·211
0·995	approaching zero	zero	1·000	1·0000	1·000	0·1089
0·999	approaching zero	zero	1·000	1·0000	1·000	0·1315

The following integrals were evaluated by suitable plots :

$$\int_0^1 (H - 1)\,df(\zeta) = 0{\cdot}39$$

$$\int_{\zeta=\infty}^{0} \left(\frac{2}{\sqrt{\pi}}\zeta\right)^4 He^{-\zeta^2} d\left[\frac{d\Omega}{df(\zeta)}\right] = -0{\cdot}086$$

Akeley and Gosting (*loc. cit.*) have shown, taking $s = 1$, that

$$\bar{D}' = D_A'\left\{1 + \int_0^1 (H - 1)\,df(\zeta) + \frac{\pi}{2}\int_\infty^0 \left[\frac{2}{\sqrt{\pi}}\zeta\right]^4 e^{-\zeta^2} H d\left[\frac{d\Omega}{df(\zeta)}\right]\right\}$$

$$\bar{D}' = 4{\cdot}552 \times 10^{-6}\,[1 + 0{\cdot}39 + 1{\cdot}571(-0{\cdot}086)]$$
$$= 5{\cdot}71 \times 10^{-6}$$

The close agreement between this value and the approximate value given in Table 1 is noteworthy. The integrals used in the calculation above, and others like it, were large compared with those of Akeley and Gosting and the possibility of error in their graphical evaluation was therefore increased. The values of Ω were quite large (almost 0·1) and Ω tended to increase with increasing concentration difference between lower and upper solution (Δc). Large values of Ω were thought to be the reason for the failure of an attempt to apply Ogston's method for examination of heterogeneous diffusion patterns (*Proc. Roy. Soc.*, 1949, *A*, **196**, 272) which did not seem to permit evaluations of large deviations from Gaussian form.

From these results and those shown in Table 2 a number of observations can be made. The diffusion coefficient varies with concentration and also with Δc (see Table 4). A plot of Δc against diffusion coefficient at a mean concentration of 50 mmoles/l. (the minimum on the diffusion coefficient–concentration curve, see Fig.), on extrapolation to $\Delta c = 0$, gave $D' = 1{\cdot}43 \times 10^{-6}$. This value has been considered to be the true diffusion coefficient of the micellar form since, as Δc approaches zero, electrical effects are minimised.

TABLE 4. *The variation of diffusion coefficient with* Δc.

Mean concn. of upper and lower soln....	40	40	50	50	50	50	60	60
Δc	40·0	20·0	20·0	10·0	7·5	5·0	40·0	20·0
$10^6D'$	2·53	2·055	2·13	1·80	1·72	1·61	2·45	2·35

Theoretical diffusion coefficients for potassium laurate solutions of concentrations up to 50 mmoles/l. have been calculated, based on the following assumptions :

(i) That the law of mass action without activity coefficients can be applied to the equilibrium between simple laurate ions and micelles; this leads to the equation

$$\log C_2 - n \log C_1 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_2 and C_1 are the concentrations of micelles and simple laurate respectively in any solution and n is the mean aggregation number of the micelle.

(ii) That the value $D_2 = 1{\cdot}43 \times 10^{-6}$ represents the true diffusion coefficient of the micellar form ; this gave n a value of 52·3, by application of the Stokes–Einstein equation.

(iii) In a solution of concentration 25 mmoles/l., all the laurate is present in the simple form.

The value of the constant in equation (1) was determined by using the experimental diffusion coefficient for 35 mmoles/l. diffusing into a 25 mmoles/l. solution ($D' = 2{\cdot}545 \times 10^{-6}$). If D_1 is the diffusion coefficient of simple laurate, determined in measurements on dilute solutions, then

$$D' = \alpha D_2 + (1-\alpha)D_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α is the refractive index fraction of micellar form in the diffusing laurate (*i.e.*, in the laurate between 35 and 25 mmoles/l.). From a knowledge of the refractive index increment per unit concentration of simple and micellar forms, which can be derived from the experimental values of j_m, α was converted into a concentration fraction x; then, by assumption (iii), C_1 and C_2 for the 35 mmoles/l. solution were calculated. From these and similar calculations based on the diffusion of 45 into 35 mmoles/l., and 55 into 45 mmoles/l., and the value of n, the constant for equation (1) was derived. Equation (1) was then used to calculate values of C_2 corresponding to given values of C_1, from which a table of $C_1 + C_2$ and x values was drawn up [$x = C_2/(C_1 + C_2)$]. This Table showed that assumption (iii) was not quite correct, and that a solution of concentration 25 mmoles/l. had a small value of x. Successive approximations were therefore used to give a final value to the constant for equation (1), *viz.*,

$$\log C_2 = 52{\cdot}3 \log C_1 = -73{\cdot}455.$$

Values of C_1, C_2, $(C_1 + C_2)$, and x obtained by using this equation are shown in Table 5; x begins to increase rapidly for total laurate concentrations between 26·5 and 29·5 mmoles/l., which is in agreement with the CMC derived from the diffusion measurements.

TABLE 5. *Relationship of* C_1 *and* C_2 *based on the equation* $\log C_2 - 52{\cdot}3 \log C_1 = -73{\cdot}455$.

C_1	C_2	$C_1 + C_2$	x	C_1	C_2	$C_1 + C_2$	x	C_1	C_2	$C_1 + C_2$	x
24·6	0·19	24·79	0·008	26·0	3·55	29·55	0·121	26·8	17·18	43·98	0·391
24·8	0·30	25·10	0·012	26·2	4·59	30·79	0·149	27·0	25·53	52·53	0·486
25·0	0·45	25·45	0·018	26·4	7·85	34·25	0·229	27·2	37·58	64·78	0·580
25·5	1·01	26·51	0·038	26·6	11·67	38·27	0·305	27·4	55·21	82·61	0·668

By means of this Table, the theoretical diffusion coefficients for the experiments carried out with solutions of less than 50 mmoles/l. were calculated, by the reverse process to that

TABLE 6. *Comparison of experimental and theoretical diffusion coefficients.*

Solution concns.	Diffusion coeff. $\times 10^6$		Solution concns.	Diffusion coeff. $\times 10^6$		Solution concns.	Diffusion coeff. $\times 10^6$	
	theoretical	exptl.		theoretical	exptl.		theoretical	exptl.
52·5/47·5	1·6	1·6	55/45	1·6	1·8	50/30	1·8	2·05
53·75/46·25	1·6	1·7	45/35	1·7	1·9	40/0	6·2	5·7
50/10	4·6	4·1	35/25	2·7	2·55	50/0	5·4	4·7

outlined above for determining the constant of equation (1). In Table 6 these theoretical results are compared with the observed values.

DISCUSSION

The results show that the diffusion coefficient–concentration curve for potassium laurate, which is constant in dilute solution, falls off rapidly after the CMC at 28 mmoles/l., to a minimum value at 50 mmoles/l., and then rises again to a constant value at concentrations greater than 200 mmoles/l. (see Tables 1 and 2 and Fig.). This second constant value is approximately half the value of the diffusion coefficient in dilute solution. A similar minimum has been observed in the diffusion coefficient–concentration curves for some sulphonic acids (Laing-McBain, *Proc. Roy. Soc.*, 1939, *A*, **170**, 415). Lamm and Högberg (*loc. cit.*) did not find a minimum in the diffusion coefficient–concentration curve for sodium laurate, but they only used solutions of mean concentrations not greater than 75 mmoles/l. of sodium laurate. The limited solubility of sodium laurate at 20° prevented these authors from using greater concentrations and so only two measurements at mean concentrations greater than 50 mmoles/l. were made. Using the more soluble potassium laurate and a higher temperature, we were able to show this minimum. Other diffusion measurements on anionic soaps, by Lamm, Granath, and McBain (*locc. cit.*), have all been carried out in the presence of a swamping excess of simple electrolyte and excess of alkali, which seems to have obscured the minimum.

The effect of adding electrolytes to soap solutions has been discussed by many authors. Some state that added electrolyte has no effect on the size and aggregation number of association colloids (*e.g.*, Hutchinson, *J. Colloid Sci.*, 1954, **9**, 191; Stainsby and Alexander, *Trans. Faraday Soc.*, 1950, **46**, 587); others (*e.g.*, Debye, *J. Phys. Colloid Chem.*, 1949, **53**, 1, and Yurzhenko and Kucher, *Kolloid. Zhur.*, 1952, **14**, 219) have found that micellar weight increases considerably with the addition of simple electrolyte, indicating either an increase in size, or aggregation number of micelles, or both. Further, addition of different electrolytes of equal ionic strength seems to alter the properties and structure of the sol (Granath, *loc. cit.*). In view of this and the differences of opinion on the effect of salt addition, some doubt must be cast on the value of estimates of micellar size and aggregation number derived from measurements of physical properties in salt-containing media. A further difficulty is the large amount of alkali that must be added to salt-containing soap solutions to keep the soap in solution. Lamm and Högberg (*loc. cit.*) have pointed out the disadvantage of the considerable increase in ionic strength required to maintain solution and the effect that these alien ions have on the micelles.

The results of the present measurements are interpreted as follows. Below the critical concentration, the laurate is present almost entirely in the simple ion form. Between the critical concentration and the concentration at the minimum on the diffusion coefficient–concentration curve, a concentration limit (Ekwall, *J. Colloid Sci.*, 1954, Suppl. 1, 66), there is a considerable increase in the concentration of laurate in micelles (C_2), but little increase in the concentration of simple ions (C_1) (see Table 5). The steady decrease of diffusion coefficient with this increasing concentration of micelles indicates that the micelles are of uniform size, and the data seem consistent with the idea that the micelle is the spherical particle described by Hartley (*Quart. Rev.*, 1948, **2**, 152; *Nature*, 1949, **163**, 767). The results obtained when the concentration limit is exceeded are consistent either with the idea of a break up of the spherical particles to form smaller platelets or discs as has been described by Booij ("Colloid Science," Kruyt, Elsevier Publ. Co. Inc., New York, Vol. II, p. 701) or with Hartley's conception of the single spherical particle, the diffusion coefficient of which varies with concentration, not because of the particle itself, but because of the changing effect of the gegenions upon the micelle (*Trans. Faraday Soc.*, 1939, **35**, 1109)

The general agreement of order between theoretical and experimental values of diffusion coefficients for solutions below the concentration limit seems to confirm that the simple mass-law interpretation in this region is justified as a rough approximation. The larger discrepancy between theoretical and experimental values for diffusion coefficients calculated by means of Akeley and Gosting's method (*loc. cit.*) can be attributed both to the large errors that occur in graphical integration of results showing a large value for the relative fringe deviation (Ω) and to the electrical effects when Δc is large.

The aggregation number used here for the calculation of theoretical diffusion coefficients is 52·3. The theoretical diffusion coefficients were very sensitive to small changes in this aggregation number; a variation of one or two units increased the discrepancies between experimental and theoretical values. This appears to confirm that the correct aggregation number has been used. Other estimates of the aggregation number recorded in the literature vary from 63 ± 8 (Anderson and Carpenter, *J. Amer. Chem. Soc.*, 1953, **75**, 850) to 170 (Hoyer and Mysels, *loc. cit.*), although in both of these cases measurements were made at concentrations much greater than the concentration limit at 50 mmoles/l.

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