

Physico-chemical Investigations on Micelles of Potassium Myristate and Laurate

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Following Mc Bain's¹ positive evidence that soaps in water solution form colloidal systems, intensive investigation has been directed toward the elucidation of the structure of these colloids. The ability of soap aggregates — the micelles — to bring water insoluble substances into solution, as well as their rôle as primary reaction loci in emulsion polymerization, has further increased the interest in their structure.

It is now certain that the association of soap into colloidal micelles occurs in steps²⁻⁴. Below a limiting concentration the solutions behave as ordinary electrolytes. Above this critical concentration (the concentration is reduced with increasing chain-length) lies a region of small, truly spherical, micelles. At still higher concentrations there are large roentgenographic micelles⁵⁻⁷, which are aggregates of a lamellar structure, with water intercalated between sheets of polar groups.

The exact size and shape of the micelles existing above the critical concentration are still in question. Furthermore it has not been ascertained whether two different kinds of micelles really exist, or whether possibly only the degree of association is increased with increased concentration⁸⁻¹⁰.

This paper reports an investigation of the molecular weights and shapes of the micelles of potassium myristate and laurate in salt solutions of various ionic strengths, as determined by sedimentation, diffusion and viscosity measurements.

DETERMINATION OF DEGREE OF SOLVATION

When using sedimentation and diffusion measurements to determine the degree of association of soaps it is quite necessary to have information about the density of the soap micelles. Soap dissolved in salt solution is always

more or less solvated and in order to calculate a correct molecular weight one has to know the partial specific volume of the complex, soap-water. The degree of solvation, k , was determined by the method of McBain and Jenkins¹¹, which is based on the assumption that the water of solvation is free of salt. In this method the soap solution is slowly pressed through an ultrafilter (viscose membrane) and the amount of salt in the filtrate measured. At any time during the filtration the concentration of salt in the filtrate is equal to the concentration of salt in the original solution exclusive of the amount of soap and solvation water; that is

$$c' = \frac{c}{1 - a(1 + k)} \quad (1)$$

where

c' = concentration of salt in filtrate in g/g of solution.

c = » » » » original solution in g/g of solution.

a = amount of soap in g/g of solution.

k = degree of solvation in g/g of soap.

Solving equation (1) for k gives

$$k = \frac{c' - c}{a \cdot c'} - 1 \quad (2)$$

At the high salt concentrations used here the amount of unassociated soap passing into the filtrate has been disregarded. The salt concentrations were determined gravimetrically. The following salt solutions were used:

Molar composition	Ionic strength
0.4 <i>M</i> KBr + 0.1 <i>M</i> K ₂ CO ₃	0.7
0.8 <i>M</i> » + 0.1 <i>M</i> »	0.9
1.0 <i>M</i> » + 0.1 <i>M</i> »	1.1
1.6 <i>M</i> » + 0.1 <i>M</i> »	1.9

The soaps were prepared by neutralizing the corresponding acids (Schering-Kahlbaum "reinst") with fresh alcoholic potassium hydroxide and recrystallized from acetone. The results of these measurements are given in Table 1. The values are averages of several determinations and refer to a soap concentration of 1.0 per cent by weight. The limits of the experimental errors have been calculated assuming that c and c' can be determined with an accuracy of 0.1 per cent and a with an accuracy of 0.2 per cent. The solvation shows a dependence on soap concentration, which is especially pronounced

Table 1. Degree of solvation of K-myristate and K-laurate at different ionic strengths.

Soap	μ	k g/g soap
K-myristate	0.7	1.7 ± 0.4
»	1.1	0.9 ± 0.2
»	1.3	0.8 ± 0.2
K-laurate	1.1	1.1 ± 0.2
»	1.9	0.7 ± 0.15

at low soap concentrations when the amount of salt is high, the k -values decreasing rapidly. Measurements in this region, however, are very unreliable.

PARTIAL SPECIFIC VOLUME

The calculation of the size and shape of the micelles requires knowledge of the partial specific volume of the components in the solution. The centrifugal force acting on an unsolvated particle is given by

$$M_1 (1 - \bar{V}_1 \rho) \omega^2 x \quad (4)$$

where M_1 is the molecular weight of the particle, \bar{V}_1 is the partial specific volume, ρ the density of the solution, ω the angular velocity of the centrifuge rotor and x the distance from the centre of rotation. Kraemer¹² has shown that in a case where the sedimenting particle is solvated, the centrifugal force is

$$M_c (1 - \bar{V}_c \rho) \omega^2 x \quad (5)$$

where M_c and \bar{V}_c respectively denote the molecular weight and the partial specific volume of the solvated particle. These two quantities are given by

$$M_c = M_1 (1 + \Sigma k_i) \quad (6)$$

$$\bar{V}_c = \frac{\bar{V}_1 + \Sigma k_i \bar{V}_i}{1 + \Sigma k_i} \quad (7)$$

k_i is the degree of solvation of component i expressed in g/g of substance. \bar{V}_i is the partial specific volume of component i . If the partial specific volume of the unsolvated particle, \bar{V}_1 , is used in molecular weight calculations, the

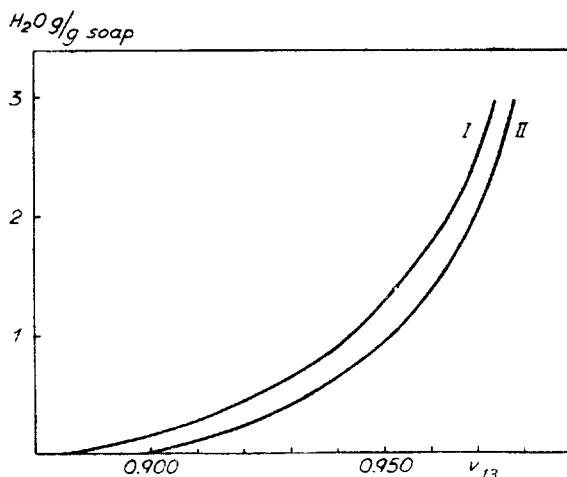


Fig. 1. Specific volume (v_{13}) vs. degree of solvation, according to formula (8).

I: K-myristate
II: K-laurate

error introduced in the molecular weight is eliminated by extrapolation to infinite dilution only in case of binary solutions (Kraemer¹³). Thus for all multicomponent systems the partial specific volume of the solvated particle must be used in the calculations. This is especially important for concentrated salt solutions, and when \bar{V}_ρ is near to unity.

The conditions under which the sedimentation of soap micelles can be performed are limited. A concentrated salt solution must be used in order to increase the numerical value of the Archimedian factor, $1 - \bar{V}_\rho$, and because \bar{V} for solvated micelles is near to unity. In this case especially an accurate calculation of the degree of association is impossible without information about the partial specific volume of the solvated micelles.

In some cases the specific volume of the solvated particles can be used instead of the partial specific volume. This is true when the specific volume of the solution is a linear function of the specific volumes of the components. In such a case the specific volume, v_{13} of the solvated micelle is given by the following formula according to Adair and Adair¹⁴

$$v_{13} = (v_1 + k/\rho)/(1 + k) \quad (8)$$

v_1 is the specific volume of the unsolvated micelle and ρ is the density of water.

The specific volumes of the solid soaps were measured pycnometrically in toluene. The values 0.833 cm³/g and 0.898 cm³/g were found for potassium myristate and laurate respectively. In Fig. 1 v_{13} from equation (8) is given as a function of the degree of solvation.

However, it is known that soaps in a solid and a dissolved state show remarkable differences in specific gravity. Thus a water solution of cetylpyridinium chloride has a lower density than pure water though this substance in the solid state is heavier than water⁸. Therefore, it is necessary to determine the partial specific volume of the soap in every medium used.

All determinations of partial specific volumes were made in a pycnometer containing about 44 cm³ of solution. The following notations are introduced:

c_1 = concentration of soap in g/g of solution.

c_2 = » » salt » » » »

c_3 = » » water » » » »

x_1 = amount of soap in g.

x_2 = » » salt » ».

x_3 = » » water » »

\bar{V}_1 = partial specific volume of soap in cm³/g.

\bar{V}_2 = » » » » salt » »

\bar{V}_3 = » » » » water » »

V = total volume of mixture in cm³.

v = specific volume of mixture in cm³/g.

Then

$$c_1 = \frac{x_1}{x_1 + x_2 + x_3}; c_2 = \frac{x_2}{x_1 + x_2 + x_3}; c_3 = \frac{x_3}{x_1 + x_2 + x_3}; \quad (9)$$

and consequently

$$c_1 + c_2 + c_3 = 1 \quad (10)$$

Furthermore

$$v = \frac{V}{x_1 + x_2 + x_3} \quad (11)$$

and by definition

$$\bar{V}_1 = \partial V / \partial x_1; \bar{V}_2 = \partial V / \partial x_2; \bar{V}_3 = \partial V / \partial x_3 \quad (12)$$

Introducing v instead of V in equations (12) we obtain

$$\bar{V}_1 = v + (x_1 + x_2 + x_3) \cdot \partial v / \partial x_1 \quad (13 a)$$

$$\bar{V}_2 = v + (x_1 + x_2 + x_3) \cdot \partial v / \partial x_2 \quad (13 b)$$

$$\bar{V}_3 = v + (x_1 + x_2 + x_3) \cdot \partial v / \partial x_3 \quad (13 c)$$

Eliminating x_1 , x_2 and x_3 by means of equations (9) and taking equation (10) into account we finally obtain

$$\bar{V}_1 = v + (1 - c_1) \cdot \partial v / \partial c_1 - c_2 \cdot \partial v / \partial c_2 \quad (14 a)$$

$$\bar{V}_2 = v - c_1 \cdot \partial v / \partial c_1 + (1 - c_2) \cdot \partial v / \partial c_2 \quad (14 b)$$

$$\bar{V}_3 = v - c_1 \cdot \partial v / \partial c_1 - c_2 \cdot \partial v / \partial c_2 \quad (14 c)$$

If we want to determine only \bar{V}_1 , it is advantageous from an experimental point of view to keep the ratio c_2/c_3 constant. Then

$$\bar{V}_1 = v + (1 - c_1) \frac{dv}{dc_1} \quad (15)$$

which is the same formula as for a binary system.

For a ternary system where a complex is formed between components 1 and 3 we are interested in the partial specific volume, \bar{V}_{13} , of the complex. Using the symbols

k = amount in g/g of component 3 bound to component 1.

$y_{13} = x_1(k + 1)$ = amount of complex in g.

$y_2 = x_2$ = amount of component 2 in g.

$y_3 = x_3 - k \cdot x_1$ = amount of component 3 in g.

c'_1, c'_2 and c'_3 = concentrations of components in g/g of solution.

In the same way as before

$$\bar{V}_{13} = \partial V / \partial y_{13} = v + (1 - c'_1) \cdot \partial v / \partial c'_1 - c'_2 \cdot \partial v / \partial c'_2 \quad (16)$$

In this case the ratio y_2/y_3 is obviously not constant even if the x_2/x_3 is constant. Thus the system cannot be treated as a binary one. Using the relations

$$c'_1 = c_1(k + 1); c'_2 = c_2; c'_3 = c_3 - k \cdot c_1 \quad (17)$$

the concentrations c instead of c' can be introduced in equation (16)

$$\bar{V}_{13} = v + [1 - c_1(k + 1)] \frac{\partial v}{\partial c_1} \frac{1}{k + 1} - c_2 \frac{\partial v}{\partial c_2} \quad (18)$$

From equations (14a), (14c) and (18) it is easily seen (Kraemer¹³) that

$$\bar{V}_{13} = \frac{\bar{V}_1 + k \cdot \bar{V}_3}{k + 1} \quad (19)$$

which is a special case of equation (7).

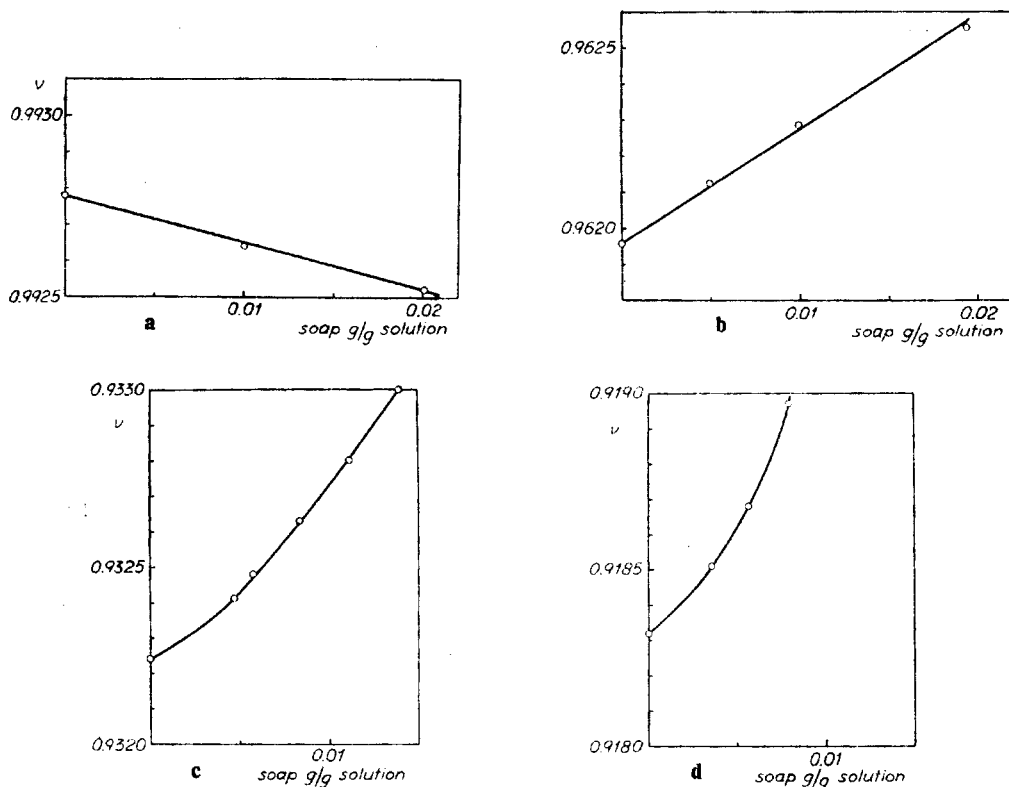


Fig. 2. Specific volume of the soap solution vs. concentration of soap.

- a. *K*-myristate in 0.1 M K_2CO_3
 b. » » 0.4 » *KBr* + 0.1 M K_2CO_3
 c. *K*-myristate in 0.8 M *KBr* + 0.1 M K_2CO_3
 d. » » 1.0 » » + 0.1 » »

Fig. 2 illustrates the change of the specific volume of some solutions as a function of the soap concentration in various media. In these measurements the ratio, salt/water, was kept constant. But as the measurements have been made at different salt concentrations it has been possible to calculate $\partial v/\partial c_2$ and $\partial v/\partial c_1 = dv/dc_1 + c_2/(1 - c'_1) \cdot \partial v/\partial c_2$ at different values of c_2 . Equations (14a), (14c) and (18 or 19) then give the required partial specific volumes. These are given in Table 2.

It is evident from Fig. 2 that v is not always a linear function of the soap concentration, in which case the partial specific volume will also be dependent on concentration. The values given in Table 2 refer to the concentration range 0.005—0.01 g/g of solution.

Table 2. *Partial specific volume of soap solutions of various ionic strengths.*

Soap	μ	$\frac{\partial v}{\partial c_1}$	\bar{V}_1	\bar{V}_3	\bar{V}_{13}
K-myristate	0.3	-0.022 ± 0.001	0.9798 ± 0.0001	1.0021 ± 0.0004	
»	0.7	-0.008 ± 0.001	0.9940 ± 0.0001	1.0020 ± 0.0005	0.999 ± 0.0007
»	0.9	-0.020 ± 0.001	0.9826 ± 0.0001	1.0027 ± 0.0005	0.994 ± 0.0007
»	1.0	-0.011 ± 0.002	0.9916 ± 0.0001	1.0025 ± 0.0006	0.997 ± 0.0009
»	1.1	-0.005 ± 0.005	0.9970 ± 0.0001	1.0020 ± 0.0010	1.000 ± 0.0008
»	1.3	-0.002 ± 0.010	1.0000 ± 0.0002	1.0020 ± 0.0020	1.001 ± 0.0010
K-laurate	1.1	-0.031 ± 0.001	0.9705 ± 0.0001	1.0017 ± 0.0005	0.987 ± 0.0012
»	1.9	-0.030 ± 0.001	0.9713 ± 0.0001	1.0020 ± 0.0010	0.984 ± 0.0014

Instead of the partial specific volume, V , in the expression $1 - \bar{V}_0$ Mc Bain²⁸ used the density of the sedimenting particle, which can be determined from a graph of sedimentation velocity versus the density of the medium by extrapolation to zero sedimentation velocity. As pointed out by Lansing and Kraemer²⁹ this method is reliable only if the change in density of the medium has no influence on the sedimenting substance. From the measurements obtained here it is obvious that the partial specific volume of the solvated particle changes with the density of the medium and hence the method of McBain cannot be used in soap investigations.

SEDIMENTATION MEASUREMENTS

As far as the author knows no valuable sedimentation measurements on soaps have been published. The partial specific volume of the solvated micelles is very near that of water; hence the sedimentation velocity is low and the uncertainty of the measurements is high. Furthermore the light absorption method previously used to follow the sedimentation is in this case unsuitable since the soap solutions do not obey Beer's law.

The introduction of Lamm's scale method¹⁵, however, has made possible a more accurate study of the sedimentation properties of the soap micelles. The use of a medium consisting of low molecular electrolytes at a high concentration facilitates the measurements. Such a medium was used by Lamm¹⁷ in his diffusion measurements on soaps. It has two advantages: firstly the density of the medium will be higher and secondly the critical concentration¹⁸ for micelle formation and probably also the transformation to roentgenographic micelles will be shifted towards lower soap concentrations.

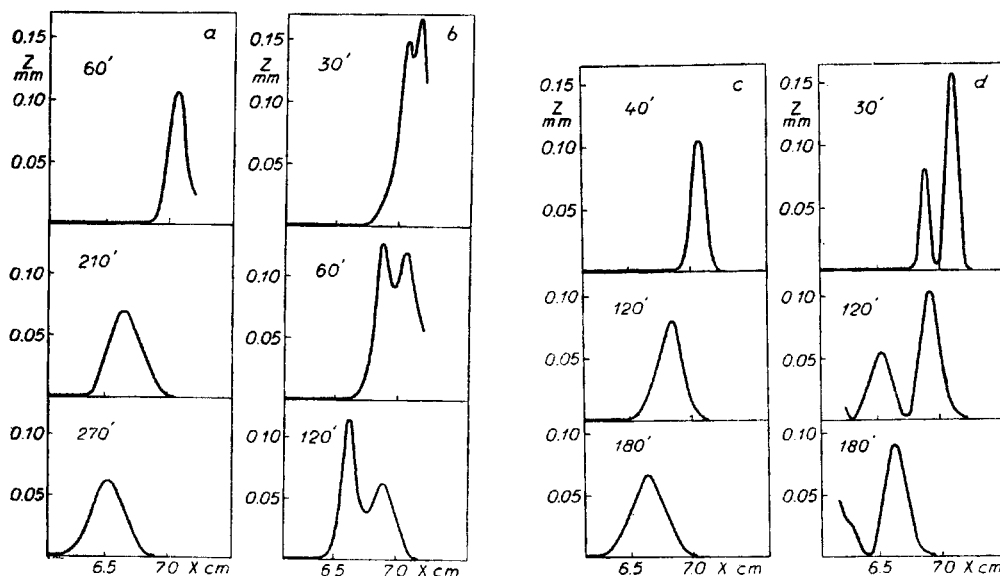


Fig. 3. Sedimentation diagrams of *K-myristate* in various media.

- a. 0.27 % *K-myristate* in 0.6 M *KBr* + 0.1 M K_2CO_3
 b. 0.9 » » » 0.6 » » + 0.1 » »
 c. 0.11 » » » 0.8 » » + 0.1 » »
 d. 1.07 » » » 0.8 » » + 0.1 » »

In the sedimentation runs (Svedberg and Pedersen¹⁶) a rotor speed of 65 000 r.p.m. and a cell distance of 6.5 cm from the axis were used in all measurements.

Since an alkaline medium increases the solubility of potassium soaps¹⁷, measurements were made in a mixture of 0.1 M K_2CO_3 and 0.4–1.6 M *KBr*, under which conditions a sufficient range of soap concentrations was possible even at high salt concentrations. The temperature was 28° C. Reference scales were always taken on the pure medium.

The data about the sedimentation experiments are given in Figs. 3–4. The *s*-values are expressed in S-units and refer to the actual medium at 20° C. Reference to pure water can hardly be made because of the difficulties encountered in determining the partial specific volume of the complex soap-water in a salt-free medium. Correction has been made for the viscosity of the medium. A negative sign indicates that the sedimentation occurs towards the centre of rotation. It has been possible to extrapolate the sedimentation constants to zero concentration with a fairly high accuracy. This procedure is an attempt to correct for the interaction between the

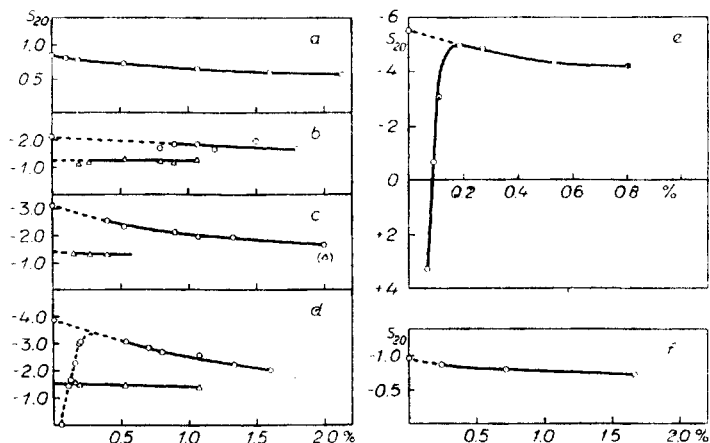


Fig. 4. Sedimentation constant s_{20} vs. soap concentration.

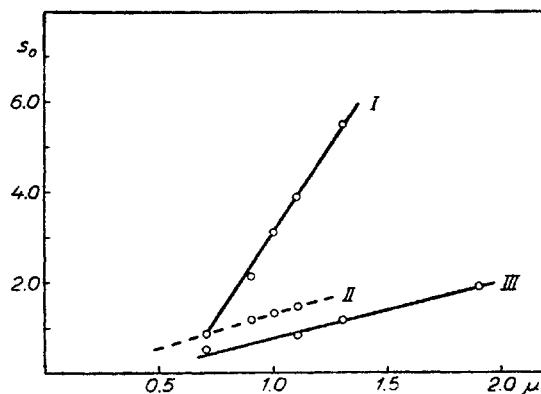
- a. *K*-myristate at $\mu = 0.7$
 b. » » » = 0.9
 c. » » » = 1.0
 d. » » » = 1.1
 e. » » » = 1.3
 f. *K*-laurate » » = 1.1

micelles under the assumption that the micelles do not change with variations in concentration. The extrapolated values then give the sedimentation constant which the micelles would have at any soap concentration if there were no interaction between them. In Fig. 4 s_{20} is plotted as a function of the soap concentration.

The sedimentation behaviour of the soap micelles is as follows. At the ionic strength $\mu = 0.7$ the sedimentation constant of potassium myristate increases with dilution within the whole concentration interval investigated. At $\mu = 0.9$ anomalies occur and two components appear within the interval $c = 0.8$ —1.1 per cent. Below $c = 0.8$ per cent only the slower component is present. Its concentration dependence is very small. Whether both components exist above $c = 1.1$ per cent is uncertain. Due to the limited resolving power of the centrifuge, the small difference in the s -values and unfavourable density conditions a separation of the peaks may not be possible. At $\mu = 1.0$ the concentration dependence seems to increase slightly. A slower moving component appears at $c = 0.4$ per cent, and this is the only one present at lower concentrations. Whether this slower component also exists at higher concentrations cannot be judged because of the reasons given above. At $\mu = 1.1$ the two components are still present even at low concentrations.

Fig. 5. Sedimentation constant vs. ionic strength.

I: *K*-myristate, faster component
 II: » slower component
 III: *K*-laurate (80,7 %)



That component which originally had the higher sedimentation constant has, however, at $c < 0.3$ per cent, an s -value which decreases rapidly with dilution, and at a very low concentration the sedimentation seems to change direction. The slower component is still present at $c = 1.1$ per cent and may persist even at higher values. Its concentration dependence is very low. At $\mu = 1.3$ only one peak seems to exist. A tendency to separate can be observed but the s -values were not reproducible. At high concentrations salting out effects made the measurements very difficult. The sedimentation constant starts to decrease at $c = 0.2$ per cent and is zero at $c = 0.1$ per cent. Then it increases again and the direction of sedimentation changes. This behaviour can only be explained as a change in the structure and partial spec. volume of the micelles.

The concentration dependence of potassium laurate is very small (Fig. 4 f). No separation into two peaks has been observed.

It is evident from Fig. 4 that the concentration dependence increases as the amount of electrolyte in the medium increases. Using Gralén's relation ²¹

$$s(c) = s_0 / (1 + k_s \cdot c) \quad (20)$$

where s_0 is the sedimentation constant at infinite dilution, the following k_s -values can be obtained

	μ	k_s
Potassium myristate	0.7	0.29
	1.0	0.44
	1.3	0.53
Potassium laurate	1.1	0.19

The change of s_0 with the ionic strength is given in Fig. 5. Curves I and II refer to potassium myristate (fast and slow component respectively), curve III refers to potassium laurate. The relationships are evidently linear but they are very difficult to interpret because the partial specific volume and also the density of the solution change with the ionic strength.

Evidently the increase in the s_0 -values of the faster component of potassium myristate with increasing ionic strength indicates a pronounced enlargement of the micelles. This property of micelles has been shown earlier by Mattoon, Stearns and Harkins¹⁹ and by Debye²⁰. The degree of association of the slower component in potassium myristate seems to be almost independent of the amount of low molecular electrolytes present. The same is true for potassium laurate; here also s_0 changes very little with the ionic strength.

DIFFUSION MEASUREMENTS

The first diffusion measurements on soaps were published some twenty years ago. McBain and coworkers²² studied the diffusion of potassium laurate, sodium oleate and some sulfonic acids in water. Jander and Weitendorf²³ introduced sodium chloride and sodium hydroxide as low molecular electrolytes in the diffusion of sodium laurate. They showed that the product of the diffusion constant and the viscosity of the medium were independent of the amount of low molecular electrolytes; this was in any case true at high concentrations of such electrolytes. Hartley and Runnicles²⁴ made measurements on cetylpyridinium chloride in the presence of sodium acetate. The low solubility of the soaps at ordinary temperatures made the measurements in a wider range of concentrations difficult. This obstacle was overcome by Lamm¹⁷, who used an alkaline medium in his experiments on potassium salts of fatty acids. He showed that the diffusion constant of potassium myristate was about one tenth that of potassium laurate in the same medium. The measurements performed in this investigation are a continuation of Lamm's work. The main problem here was to study the diffusion constant of these soaps as a function of the ionic strength of the medium.

The experimental method developed by Lamm¹⁵ has been used. From Wiener's equation²⁵, valid for an ideal diffusion, the diffusion constant can be calculated in several ways. Of these the area method (giving D_A) and the moment method (giving D_m) have been used. D_A and D_m have units of 10^{-7} cm²/sec. All the measurements were made by the free diffusion between solutions differing in soap concentration by about 0.4 per cent. The levelling of the solutions was very difficult because of the small difference in density (about 0.0003—0.0005 g/cm³). Some of the first measurements were made in a glass

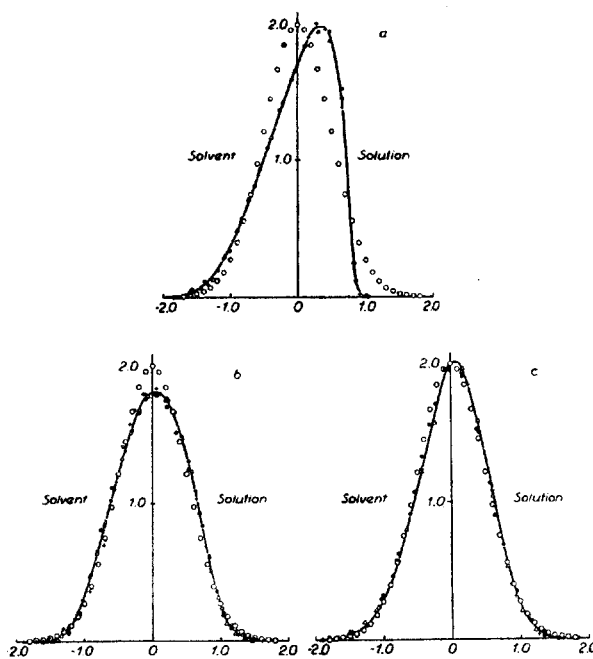


Fig. 6. Normal diffusion curves of soap solutions. Normal ideal curve (—○—○—).

- a. 0.4%|0.1% K-laurate at $\mu = 1.9$
 b. 1.2%|0.8% » » » = 1.9
 c. 0.6%|0.2% K-myristate » » = 0.9

cell of the same type as that used by Lamm in which the boundary is moved in the tube until it has reached its correct position. This often has a blurring effect on the boundary resulting in diffusion diagrams with poorly defined base lines. Furthermore an error in the real starting time is introduced. Later a cell according to Claesson²⁶ was used. This cell gives a sharp boundary and also a correct starting time.

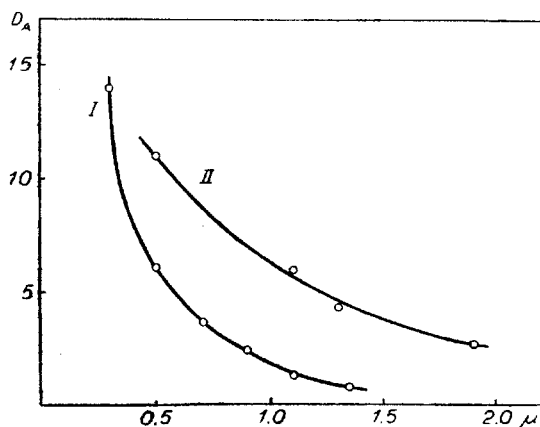
The results of the diffusion measurements are given in Table 3. In Fig. 6 the concentration gradient curves in normal coordinates are given for some of the diffusion experiments performed. A comparison is here made with the ideal (Gaussian) curve. In Fig. 7 the relation between D_A and the ionic strength is given. Table 4 gives the concentration dependence of D_A . All the diffusion constants refer to a temperature of 20° C and are corrected for the viscosity of the medium.

From Fig. 7 and Table 3 it is evident that the diffusion rate decreases with increasing ionic strength. This tendency is more pronounced for potassium

Table 3. Dependence of the diffusion constant on ionic strength.

μ	Medium	K-laurate		K-myristate	
		D_A	D_m	D_A	D_m
0.3	0.1 M K_2CO_3	—	—	14.0	—
0.5	0.2 M KBr + 0.1 M K_2CO_3	11.0	—	6.0	6.0
0.7	0.4 M —»—	—	—	3.6	3.6
0.9	0.6 M —»—	—	—	2.4	2.4
1.1	0.8 M —»—	6.0	5.9	1.3	1.3
1.3	1.0 M —»—	4.3	—	0.80	0.85
1.9	1.6 M —»—	2.7	—	—	—
1.1	1.0 M KCl + 0.1 M KOH	7.9	7.6	—	—
1.7	1.6 M KCl + 0.1 M KOH	5.9	6.4	—	—

myristate than for potassium laurate. Evidently the diffusion rate is also dependent on the particular anion of the electrolyte added. Thus in a medium containing potassium chloride and potassium hydroxide the diffusion constant of potassium laurate is considerably higher than in a medium consisting of potassium bromide and potassium carbonate at the same ionic strength. In regard to the dependence on the soap concentration, the diffusion constant of potassium laurate increases as its concentration decreases. The opposite is true for potassium myristate, except in the lowest concentration, where the diffusion constant rapidly increases. This behaviour seems to be in agreement with the results obtained in the sedimentation measurements; the numerical value of the sedimentation constant decreases at low concentrations. Fig. 6

Fig. 7. Diffusion constant D_A vs. ionic strength.

I: K-myristate

II: K-laurate

Table 4. Dependence of D_A on concentration.

c per cent	D_A	
	K-laurate 1.6 M KBr + 0.1 M K_2CO_3	K-myristate 0.8 M KBr + 0.1 M K_2CO_3
1.2 / 0.8	2.5	1.5
1.0 / 0.6	—	1.4
0.8 / 0.4	2.6	1.3
0.6 / 0.2	2.7	1.3
0.4 / 0.1	3.6	1.3
0.15/0	3.3	6.4

shows that in this concentration range the concentration gradient curve is skew. Thus the diffusion measurements also indicate a change in the structure of the micelles at low concentrations and high ionic strengths.

VISCOSITY MEASUREMENTS

The viscosities of the soap solutions were studied at a temperature of 30° C in an Ostwald viscometer with an effluent time for water of 206 sec. at this temperature. A correction for the influence of surface tension was applied according to Drucker²⁷

$$\eta_{rel} = \eta_{rel\ obs} \frac{1 + K}{1 + K \cdot h} \quad (21)$$

where K is a constant of the viscometer which accounts for the change in hydrostatic pressure caused by the difference in the radius of the surface of the liquid in the upper and lower part of the viscometer respectively; h is the ratio between the capillary rise of the solution and the medium respectively. The correction factor had a highest value of about 1.006.

The results of the viscosity measurements are given in Figs. 8 and 9. From curves I—IV in Fig. 8 it is evident that the relative viscosity, η_{rel} , of the potassium myristate solutions increases rapidly with increasing ionic strength. The increase for potassium laurate is moderate (curves V and VI). The change in intrinsic viscosity, $\eta_{sp/c}$, is shown in Fig. 9. An almost linear relation between $\eta_{sp/c}$ and c seems to hold for potassium laurate even in a medium of high ionic strength. For potassium myristate the curves are convex toward the c -axis at μ -values lower than 0.9 and concave at higher μ -values. At

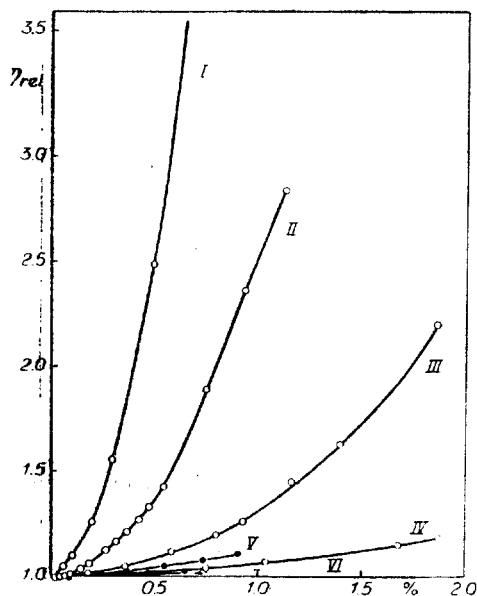


Fig. 8. Relative viscosity as a function of concentration.

I: K-myristate at $\mu = 1.3$
 II: » » » = 1.1
 III: » » » = 0.9
 IV: » » » = 0.7
 V: K-laurate » » = 1.9
 VI: » » » = 1.1

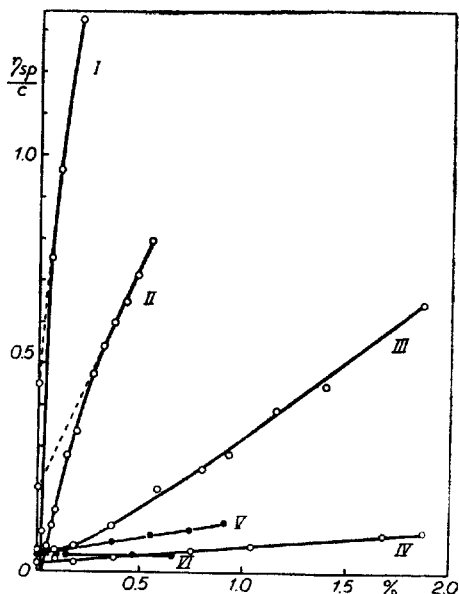


Fig. 9. Dependence of η_{sp}/c upon concentration.

I: K-myristate at $\mu = 1.3$
 II: » » » = 1.1
 III: » » » = 0.9
 IV: » » » = 0.7
 V: K-laurate » » = 1.9
 VI: » » » = 1.1

$\mu = 0.9$ the concentration dependence is rather pronounced, with the slope of the curves increasing rapidly with increasing ionic strength. A constant slope seems to exist above a certain concentration: 0.3 per cent at $\mu = 1.1$ and 0.1 per cent at $\mu = 1.3$. These changes in η_{rel} and η_{sp}/c seem to be in complete agreement with the results obtained in the sedimentation and diffusion measurements. In order to obtain $[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$ of the "stable" micelles extrapolation has been made from the linear part of the curves in Fig. 9. The results are given in Table 5. For potassium myristate there is a considerable increase in $[\eta]$ with increasing ionic strength, whereas the $[\eta]$ -values of potassium laurate seem to be constant.

Table 5. Dependence of intrinsic viscosity $[\eta]$ on ionic strength.

Soap	μ	$[\eta]$
K-myristate	1.3	0.45
»	1.1	0.20
»	0.9	0.05
»	0.7	0.02
K-laurate	1.9	0.04
»	1.1	0.04

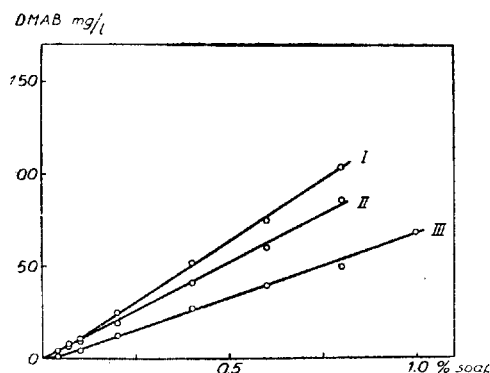
 SOLUBILITY OF *p*-DIMETHYL AMINOAZOBENZENE IN MICELLES

Kolthoff and Stricks³⁰ have shown that the solubility of *p*-dimethyl aminoazobenzene in soap solutions increases considerably above the critical concentration. The solubility is a linear function of the soap concentration. Some measurements were made in order to see the extent to which the two components in potassium myristate solutions could cause an anomalous shape of the solubility curve. The same technique as that of Kolthoff and Stricks was used.

For potassium myristate in a medium with $\mu = 1.1$ a change in the slope of the solubility curve occurred at about 0.1 per cent of soap. At $\mu = 0.7$ the solubility curve is a straight line for all concentrations used. For potassium laurate at $\mu = 1.9$ the solubility increases at 0.04 per cent of soap. This concentration coincides with the critical concentration at this ionic strength. Above 0.04 per cent the solubility curve is a straight line.

 Fig. 10. Solubility of *p*-dimethyl aminoazobenzol (DMAB) mg/l.

- I: K-myristate at $\mu = 1.1$
 II: » » » $\mu = 0.7$
 III: K-laurate » » $\mu = 1.9$



According to Ekwall ² the saturation capacity of the micelles is defined by

$$\frac{\text{mg/l dissolved substance}}{c_{tot} - c_{crit}}$$

where c_{tot} and c_{crit} are the total and critical soap concentrations respectively. From the data in Fig. 10 the following values have been calculated:

Potassium myristate:

Kolthoff and Stricks	2820
$\mu = 0.7$	2650
$\mu = 1.1$ $c < 0.1$ per cent	2900
$c > 0.1$ per cent	3400

Potassium laurate:

Kolthoff and Stricks	1480
$\mu = 1.9$	1750

The saturation capacity does not change greatly in different media. The value for potassium myristate at soap concentrations less than 0.1 per cent at $\mu = 1.1$ is about the same as the value given by Kolthoff and Stricks and the value obtained at $\mu = 0.7$. At soap concentrations above 0.1 per cent the saturation capacity is higher. This may indicate the existence of large micelles within this concentration range. According to Ekwall the saturation capacity increases above the critical concentration for the formation of roentgenographic micelles.

DEGREE OF ASSOCIATION AND SHAPE OF THE MICELLES IN DIFFERENT MEDIA

From sedimentation and diffusion data the molecular weight can be calculated according to Svedberg's formula

$$M = \frac{RTs}{D(1 - V\rho)} \quad (23)$$

Using the values of s , D and \bar{V}_{13} referring to the solvated micelles at 30° C and a soap concentration of 0.4 per cent, the molecular weights of the micelles given in Table 6 were obtained. The molecular weights, M_A , of the unsolvated micelles were then calculated from

$$M_A = M_c/(k + 1) \quad (24)$$

Table 6. "Molecular" weight and degree of association of *K*-myristate and *K*-laurate in various media.

Soap	Medium	μ	$1 - \bar{V}_{13} \cdot \rho$	M_c	M'_A	M_A	Degree of association
<i>K</i> -myristate	0.4 M KBr + 0.1 M K_2CO_3	0.7	- 0.038	130.000 \pm 15.000	150.000	48.000	180
»	0.6 » + 0.1 »	0.9	- 0.049	400.000 \pm 50.000	530.000	181.000	680
»	0.7 » + 0.1 »	1.0	- 0.061	560.000 \pm 65.000	620.000	270.000	1000
»	0.8 » + 0.1 »	1.1	- 0.072	840.000 \pm 95.000	870.000	430.000	1600
»	1.0 » + 0.1 »	1.3	- 0.090	1,550.000 \pm 200.000	1,600.000	860.000	3200
<i>K</i> -laurate	0.8 » + 0.1 »	1.1	- 0.058	60.000 \pm 7.000	83.000	27.000	110
»	1.6 » + 0.1 »	1.9	- 0.119	150.000 \pm 20.000	170.000	87.000	360

where k is the degree of solvation. In Table 6 the degree of association is also given. For the calculation of the correct degree of association, correction for the solvation must be made. This is seen from a comparison of M'_A and M_A in Table 8. M'_A is calculated from (23) using \bar{V}_1 instead of \bar{V}_{13} and differs quite considerably from M_A . The limits of experimental errors given for the molecular weights, M_c , are about ± 12 per cent. The error introduced by s and D has been estimated as ± 10 per cent, the error in \bar{V}_{13} has been calculated to contribute about ± 2 per cent.

As is seen from Fig. 11 the degree of association of the potassium myristate micelles increases very rapidly with the ionic strength as soon as this exceeds about 0.7. For potassium laurate the degree of association is moderately

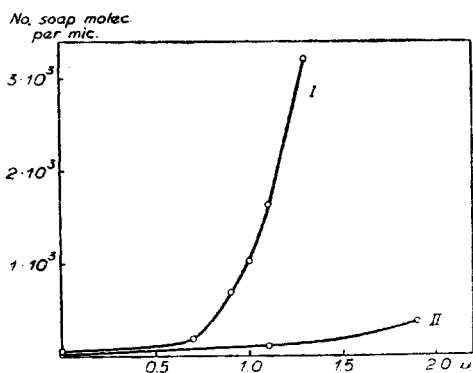
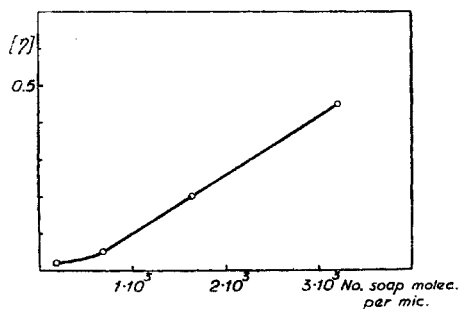


Fig. 11. Degree of association vs. ionic strength.

I: *K*-myristate
 II: *K*-laurate.


 Fig. 12. Intrinsic viscosity $[\eta]$ of *K*-myristate as function of degree of association.

dependent on the ionic strength even at high μ -values. The degree of associations corresponding to pure water ($\mu = 0$) have been taken from Mattoon, Stearn and Harkins¹⁹. Fig. 12 shows that the relation between intrinsic viscosity, $[\eta]$, and the number of soap molecules per micelle is linear except at low values of the degree of association.

The molar frictional coefficient, f_0 , of an unsolvated spherical particle is given by Stokes's law

$$f_0 = 6\pi\eta N \left(\frac{3 MV}{4\pi N} \right)^{1/3} \quad (25)$$

The molar frictional coefficient, f , of the actual molecule is given by

$$f = \frac{RT}{D} = \frac{M_c (1 - \bar{V}_{13} \varrho)}{s} \quad (26)$$

Assuming equation (25) to hold even for a solvated spherical molecule we get from equations (25) and (26):

$$\frac{f}{f_0} = \frac{1}{6\pi\eta} \left(\frac{RT}{DN} \right)^{2/3} \left(\frac{4(1 - \bar{V}_{13} \varrho)}{3\bar{V}_{13}s} \right)^{1/3} \quad (27)$$

The quantity f/f_0 gives a relative measure of the asymmetry of the micelle, the values calculated for potassium myristate and laurate are given in Table 7. Evidently the asymmetry is more pronounced the higher the ionic strength.

Table 7. The asymmetry factor f/f_0 , calculated for *K*-myristate and *K*-laurate in various media.

Soap	Medium	f/f_0
K-myristate	0.4 M KBr + 0.1 M K ₂ CO ₃	1.49
»	0.6 » + 0.1 »	1.60
»	0.7 » + 0.1 »	1.82
»	0.8 » + 0.1 »	2.22
»	1.0 » + 0.1 »	2.94
K-laurate	0.8 » + 0.1 »	1.18
»	1.6 » + 0.1 »	2.12

DISCUSSION

Among the existing ideas about the structure of the soap micelles, Hartley⁸ represents the opinion that in dilute solutions the micelles are spherical and contain a number of soap molecules proportional to the square of the chain length. Only one type of micelle is present in the soap solution. Hess³¹, Stauff³², Philipoff¹⁰ and Kiessig⁶ discuss two different types of micelles. The small micelles are according to Stauff spherical and contain a comparatively small number of ions, for instance about 120 for a soap with 16 carbon atoms. An increase in concentration diminishes the hydration and dipoles are formed on the surface of the micelle. A further association to large disc-like micelles (Stauff gives dimensions of the order of magnitude of $250 \times 2500 \times 2500 \text{ \AA}$) then eliminates these dipoles with liberation of energy. This arrangement is also favoured by the increasing repulsive forces between micelles in concentrated solutions³³. Kiessig also regarded the large micelles as disc-like, consisting of about 10 double layers of soap molecules. Philipoff considered the small micelles as cylindrical and consisting of two parallel layers of molecules with the ionogenic groups directed outwards. Later Harkins³⁴ accepted this form both for the small and the large micelles. Addition of salt to the solution changes the diameter of the cylinder. According to Debye²⁰ the reason for this is that the coulomb interaction decreases and then the van der Waal forces cause increased association.

The results obtained in this investigation seem to be in agreement with the view of Harkins. At increasing salt concentrations the degree of association increases and judging from the f/f_0 -values the diameter of the micelles also increases. Assuming the micelle to be cylindrical and the volume of a soap molecule to be 445 \AA^3 (Stauff) we find that the diameter of potassium myristate micelles increases linearly from 46 \AA to 194 \AA when the ionic strength is changed from 0.7 to 1.3. The thickness is assumed to be constant 48 \AA . In this model of the micelles the water of solvation forms a mantle around the associated soap molecules. Apparently there is no possibility of obtaining the very large roentgenographic micelles according to Stauff in these low concentrations by increasing the salt content of the solution. The observed anomalies at low concentrations and at high ionic strengths show that the ordered structure of the micelles disappears. The two components observed in the sedimentation of potassium myristate indicate some sort of transition region.

SUMMARY

Physico-chemical measurements have been made on micelles of potassium myristate and laurate in solutions containing potassium bromide and potas-

sium carbonate at various ionic strengths. In these media the degree of solvation, the partial specific volume, the sedimentation and diffusion constants have been determined. The viscosities of the solutions have been studied and also the ability of the micelles to dissolve *p*-dimethyl aminoazobenzene. From the experimental data the degree of association has been calculated. The size of the micelles increases with the ionic strength of the medium; this increase is very pronounced for potassium myristate and rather moderate for potassium laurate. The data obtained corroborate the belief that the micelles are cylindrical discs.

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REFERENCES

1. Mc Bain, J. W., and co-workers *J. Chem. Soc.* **101** (1912) 2042; *J. Chem. Soc.* **113** (1918) 825; *Kolloid-Z.* **12** (1913) 256; *J. Am. Chem. Soc.* **42** (1920) 426.
2. Ekwall, P. *Acta Acad. Aboensis. Math. Physic.* **IV** (1927) 6; *Sjätte nordiska kemistmötet.* Lund (1947) 178.
3. Mc Bain, J. W., Laing, M. E., and Titley, A. F. *J. Chem. Soc.* **115** (1919) 1279.
4. Mc Bain, J. W., Taylor, M., and Laing, M. E. *J. Chem. Soc.* **121** (1922) 627.
5. Kiessig, H., and Philipoff, W. *Naturwissenschaften* **35** (1939) 593.
6. Kiessig, H. *Kolloid-Z.* **96** (1941) 252.
7. Harkins, W. P., Mattoon, R. W., and Corrin, M. L. *J. Coll. Sci.* **1** (1946) 105.
8. Hartley, G. S. *Kolloid-Z.* **88** (1939) 22.
9. Stauff, J. *Kolloid-Z.* **89** (1939) 224.
10. Philipoff, W. *Kolloid-Z.* **96** (1941) 255.
11. Mc Bain, J. W., Jenkins, W. H. *J. Chem. Soc.* **121** (1922) 2325.
12. Kraemer, E. O. *J. Franklin Inst.* **229** (1940) 391, 680.
13. Kraemer, E. O. in Svedberg, T., and Pedersen, K. O. *The ultracentrifuge.* Oxford (1940) p. 62.
14. Adair, G. S., Adair, M. E. *Proc. Roy. Soc. B* **120** (1936) 422.
15. Lamm, O. *Inaugural dissertation.* Uppsala (1937).
16. Svedberg, T., Pedersen, K. O. *The ultracentrifuge.* Oxford (1940).
17. Lamm, O. *Kolloid-Z.* **98** (1942) 45.
18. Corrin, M. L., Harkins, W. P. *J. Am. Chem. Soc.* **69** (1947) 683.
19. Mattoon, R. W., Stearns, R. S., and Harkins, W. P. *J. Chem. Phys.* **16** (1948) 644.
20. Debye, P. *J. Colloid Sci.* **3** (1948) 407.
21. Debye, P. *J. Phys. & Coll. Chem.* **53** (1949) 3.
22. Mc Bain, L., Liu, J. *J. Am. Chem. Soc.* **53** (1931) 59; *J. Am. Chem. Soc.* **55** (1933) 545; *Proc. Roy. Soc. A* **170** (1939) 415.
23. Jander, G., and Weitendorf, K. F. *Angew. Chemie* **47** (1934) 197.

24. Hartley, G. S., and Runnicles, D. F. *Proc. Roy. Soc. A* **168** (1938) 420.
25. Wiener, O. *Ann. Phys. und Chemie* **49** (1893) 105.
26. Claesson, S. *Nature* **158** (1946) 835.
27. Drucker, C. *Arkiv Kemi, Mineral., Geol. A* **22** (1946) no. 20.
28. Mc Bain, J. W. *J. Am. Chem. Soc.* **58** (1936) 315.
29. Lansing, W. D., and Kraemer, E. O. *J. Am. Chem. Soc.* **58** (1936) 1471.
30. Kolthoff, I. M., and Stricks, W. *J. Phys. Coll. Chem.* **52** (1948) 915.
31. Hess, K. *Kolloid-Z.* **88** (1939) 40.
32. Stauff, J. *Kolloid-Z.* **96** (1941) 244.
33. Alexander, A. E., and Johnson, P. *Colloid science*. Oxford (1949) p. 675.
34. Harkins, W. P. *J. Am. Chem. Soc.* **69** (1947) 1428.

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