322. *Solutions of Metal Soaps in Organic Solvents. Part III.* The Aggregation of Metal Soaps in Toluene,* iso*Butyl Alcohol, and Pyridine.*

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The degree of aggregation of a number of metal soaps in toluene, *iso*butyl alcohol, and pyridine has been investigated by an ebullioscopic method. In toluene, the degree of aggregation is strongly dependent on the length of the hydrocarbon chain and on the polarity of the soap. The more polar soaps form larger micelles or are insoluble, while increase of chain length in soaps of the same metal leads to a decrease in the degree of aggregation. In the polar solvents *iso*butyl alcohol and pyridine the associating effect of the soap dipoles is reduced and unimolecular solutions are obtained at low concentrations. Stability of the soap micelles is due to diple interaction and to the decrease in interfacial energy which occurs on aggregation.

Part I (Martin and Pink, *J.*, 1948, 1750) recorded some measurements of micellar weights of zinc and copper soaps by means of an ebullioscopic method. The present report describes the extension of the method, by aid of an improved apparatus, to a variety of metal soaps. The effect of solvent dielectric constant on the degree of aggregation has also been examined.

Little information is available on the aggregation of metal soaps in organic solvents. Most of the soaps for which data are available appear to form aggregates of micellar weight between 2000 and 10,000 (Kahlenberg, *J. Phys. Chem.*, 1902, **6**, 1; Soyenkoff, *ibid.*, 1930, **34**, 2519; Bhatnagar, Kapur, and Hussain, *Proc. Indian Acad. Sci.*, 1939, **9**, *A*, 143; Martin and Pink, *loc. cit.*). These scattered observations, made in most cases over a limited concentration range, have been insufficient to permit an evaluation of the relative importance of the various factors involved in the aggregation process. The basic aluminium soaps are a special case and have not therefore been included in this study (cf. Gray and Alexander, *J. Phys. Colloid Chem.*, 1949, **53**, 23; Glazer, Schulman, and McRoberts, *J.*, 1950, 2082).

There is some difficulty in obtaining accurate measurements in this micellar weight range. Cryoscopic methods are unsuitable since the metal soaps frequently show critical solution phenomena well above the freezing points of the solvents (Martin and Pink, *loc. cit.*). Osmotic-pressure measurements with cellulose-type membranes are stated to be unsatisfactory for solutes with micellar weights below 10,000 (Weissberger, "Physical Methods of Organic Chemistry," Vol. I, p. 488, Interscience, 1949). Studies of sedimentation equilibrium and sedimentation velocity are also better suited to a higher micellar weight range (Alexander and Johnson, "Colloid Science," Vol. I, p. 188,

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* **Part II, *J.*, 1951, 1804.**

Clarendon Press, 1949). On the other hand, conventional vapour-pressure methods and the ebullioscopic method, used in the present work, require special precautions if accurate measurements are to be obtained with micellar weights above 2000.

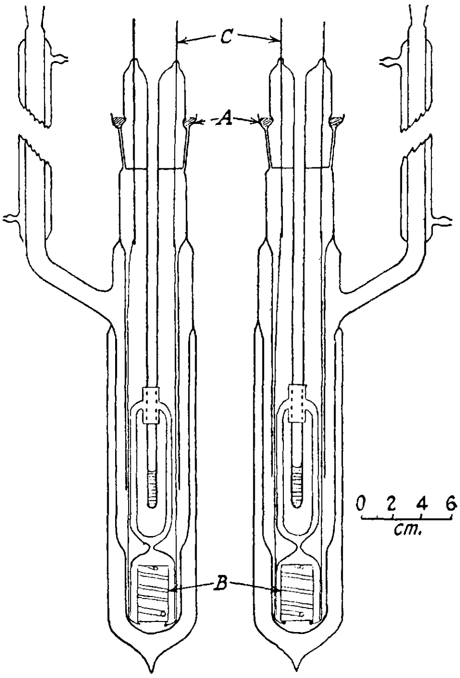
EXPERIMENTAL

Preparation and Purification of Materials.—Lauric, myristic, and oleic acids were pre-war " purissimus grade " samples from Schering–Kahlbaum. The remaining acids were purified, where necessary, by fractional crystallisation from ethanol; their m. p.s were : octanoic, 16·0°; decanoic, 31·1°; lauric, 44·1°; myristic, 57·5°; stearic, 69·2°; oleic, 15·0°.

All the metal soaps were prepared by metathesis of the corresponding sodium soaps in aqueous ethanol (Pink, *J.*, 1938, 1252). The precipitated soaps were washed with water and ethanol to remove excess of precipitant and free fatty acid and dried by various methods, depending on the properties of the soaps. The soaps prepared from saturated acids were dried in an air-oven at temperatures ranging between 60° and 95°, the magnesium, nickel, and manganese soaps having been first dehydrated in boiling toluene. Zinc oleate, which is susceptible to oxidation, was dried at room temperature *in vacuo* over phosphoric oxide. For analysis, the soaps were hydrolysed with 7N-sulphuric acid, and the metal contents of the hydrolysates determined by standard procedures, after the free fatty acid had been removed by filtration. The calcium and cadmium soaps were analysed in the monohydrated form. The results of the analyses, shown above, indicate that the materials obtained were the neutral soaps with, in most cases, a slight excess of metal.

	Metal content, % :	
	Found	Calc.
Zinc octanoate	19·11	18·58
Zinc decanoate	16·10	16·03
Zinc laurate	14·66	14·09
Zinc myristate	13·28	12·57
Zinc stearate	10·52	10·34
Zinc oleate	10·73	10·40
Magnesium laurate	5·85	5·75
Calcium laurate	8·83	8·78
Manganese laurate	12·07	12·11
Nickel laurate	13·28	12·82
Copper laurate	13·79	13·76
Cadmium laurate	20·80	21·24
Mercuric laurate	32·72	33·48
Silver laurate	34·72	35·13
Lead laurate	34·84	34·20

FIG. 1. *Micellar-weight apparatus.*



Solvents. Rigorous drying was found to be the most important aspect of purification for satisfactory operation of the ebullioscopic apparatus. Thiophen-free toluene was dried over sodium metal, from which it was distilled in an all-glass apparatus, b. p. 110·2—110·6°; *iso*butyl alcohol was dried over baryta and distilled from calcium metal, b. p. 107·7—108·1°; " AnalaR " pyridine was stored over potassium hydroxide and distilled from the freshly fused alkali through a fractionating column immediately before use, b. p. 115·2—115·6°.

Micellar-weight Apparatus.—The ebullioscopic apparatus was essentially a modified version of that employed by Mair (*J. Res. Nat. Bur. Stand.*, 1935, **14**, 345). A scale drawing of the apparatus, the dimensions of which are important, is shown in Fig. 1. Mercury sealing (*A*) was used to prevent loss of solvent from the twin boiling tubes, and solute was added directly through the condenser openings. The heating units (*B*), which were 24·3 and 24·8 Ω severally, were of 36-gauge Brightray resistance wire jointed by 26-gauge nichrome leads to tungsten rods (*C*) sealed through the B.40 ground-glass joint. The mains voltage, controlled by a Variac transformer, was used for heating. With 47·0 ml. of toluene in each of the boiling-tubes satisfactory ebullition was obtained with a current of 1·55 amp. The actual value of the current for each solvent was found to be critical, a small variation in heater current from the selected value leading to marked temperature instability.

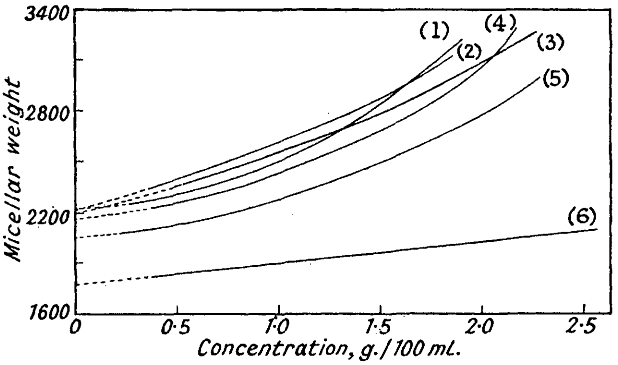


FIG. 2. *Micellar weights of zinc soaps in toluene. (Formula weights in parentheses.)*

(1) *Octanoate* (351·8).
(2) *Decanoate* (407·9).
(3) *Laurate* (464·0).
(4) *Myristate* (520·1).
(5) *Stearate* (632·3).
(6) *Oleate* (628·3).

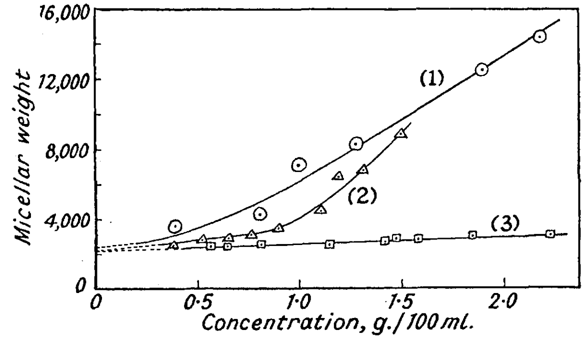
The b. p. elevations were measured with a five-junction copper–constantan thermocouple and a sensitive galvanometer. The absolute values were not calculated; instead, in each run the apparatus was calibrated by addition to the second vessel of a suitable quantity of naphthalene as a reference solute. For micellar weights of the order of 3000 the maximum error with this apparatus was estimated to be ±7%; for lower micellar weights the maximum error was considerably less.

Conductance measurements were made at 1100 c./second with a bridge employing a visual null-point indicator. The conductance cell had bright platinum electrodes.

Micellar-weight Measurements.—Micellar weights at a number of concentrations were obtained by adding successive quantities of solute to one of the twin boiling vessels. At least three such runs were carried out with every metal soap. The results obtained with the zinc soaps are shown in Fig. 2. The effect of different metals in soaps of the same chain length is seen in Fig. 3 which contains data for a number of metal laurates. Calcium and cadmium laurates, although appreciably swollen in boiling toluene, were not completely dispersed. Lead and silver laurates were insufficiently soluble to permit measurements to be made, and nickel and manganese laurates, although soluble, gave galvanometer deflections which were too small for measurement, implying the presence of aggregates of micellar weight >20,000. Anomalous results were obtained with mercuric laurate, the observed molecular weight of which was lower than the formula weight. Analysis showed that decomposition took place in boiling toluene, the recovered soap containing 42·42% of mercury as against 32·75% in the original soap. According to Lawrence (*Trans. Faraday Soc.*, 1938, **34**, 660) the mercury soaps

FIG. 3. *Micellar weights of metal laurates in toluene. (Formula weights in parentheses.)*

(1) *Magnesium laurate* (422·9).
(2) *Copper laurate* (462·2).
(3) *Zinc laurate* (464·0).



decompose suddently on heating, forming metallic mercury and a mixture of anhydride and acid. Mercuric laurate is stated by Lawrence to decompose at 210°.

Measurements in *iso*butyl alcohol and pyridine were made in exactly the same way as in toluene, the same reference solute being employed. Results obtained with zinc and copper laurates in these solvents are shown in Fig. 4.

DISCUSSION

Solutions in Toluene.—Two broad conclusions emerge from the experimental data. First, the number of molecules (N) in the micelle decreases rapidly with increase in the length of the hydrocarbon chain. This is illustrated, for the saturated zinc soaps, in Fig. 5, where the value of N, extrapolated to infinite dilution, is plotted against the number of carbon atoms in the chain. The micellar weight similarly decreases but less rapidly. Secondly, in a series of soaps with the same hydrocarbon chains, the more polar soaps form larger micelles. Dipole moments for the oleates have been published by Banerjee and Palit (*J. Indian Chem. Soc.*, 1950, **27**, 385; cf. Ostwald and Riedel, *Kolloid-Z.*, 1934, **69**, 185) and their data are shown in the following table, together with micellar weights of the laurates of a number of metals at a uniform concentration of 0·02M.

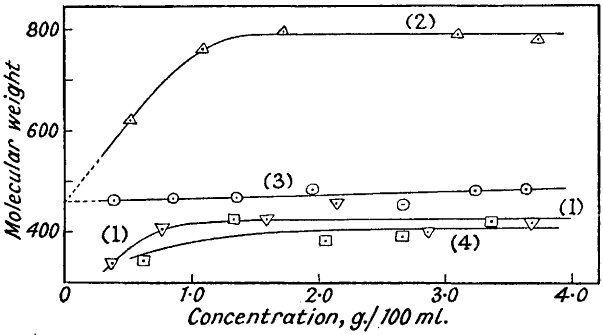


FIG. 4. *Molecular weight of zinc and copper laurates in polar solvents. (Formula weights in parentheses.)*

(1) *Copper laurate in pyridine.*
(2) *Copper laurate* (462·2) *in* iso*butyl alcohol.*
(3) *Zinc laurate* (464·0) *in* iso*butyl alcohol.*
(4) *Zinc laurate in pyridine.*

Metal.	Micellar weight of laurate	μ, D, for oleate
Zinc	2,600	0·29
Copper	3,500	1·20
Magnesium	6,000	1·66
Nickel	>20,000	2·67
Cadmium	Swells in toluene but does not dissolve at b. p.	4·37 *
Calcium	,, ,,	4·49
Lead	Insoluble	4·29

* Datum from Ostwald and Riedel (*loc. cit.*).

Increased polarity in this series corresponds closely with increase in micellar weight, some of the more polar soaps being insoluble at the b. p. of toluene. The zinc soaps differ also from the relatively more polar copper and magnesium soaps in the rapid increase in apparent micelle size of the latter which occurs with increasing concentration (Fig. 3). Although the non-ideal character of the solutions makes it difficult to distinguish sharply between Raoult deviations and real variations in micellar weight, yet the shape of the curves for the copper and magnesium soaps suggests strongly that the apparent increase in micelle size in this case is a real one. The increase in micellar weight with concentration shown by the zinc soaps is much less and could well be explained by departure from ideal behaviour. On the other hand, even with the zinc soaps, very concentrated solutions show a faint opalescence, indicating the presence of some very large micelles. It should be noted that all the quoted micellar weights are number averages and that a low average micellar weight in dilute solution does not, therefore, exclude the existence of some micelles of much larger size. A feature of the results in toluene, in contrast to those of the corresponding aqueous soap solutions, is the presence of aggregates at all observed concentrations. These conclusions, in conjunction, permit the development of a picture of the aggregation process. In a non-polar solvent, aggregation is clearly the result of a balance between the solubilising power of the hydrocarbon chains and the attractive forces between the polar parts of the soap molecules. As is expected on this basis, the soaps with very short chains are insoluble, *e.g.*, the butyrates. On the other hand, with a sufficiently long chain the soap should be molecularly dispersed, unless other factors intervene. Unfortunately, acids with chains longer than 18 carbon atoms were not available to test this hypothesis.

An important factor favouring aggregation is the interaction between the soap dipoles which leads to a decrease in potential energy and a force of attraction, provided the soap molecules are suitably arranged in the micelle. Also favouring aggregation is the decrease in interfacial energy produced by the shielding effect of the hydrocarbon chains on the polar parts of the soap molecules which, in the micelle, are at least partially removed from contact with the non-polar solvent. In opposition to these factors is the kinetic energy of the soap molecules, which will be much reduced in the process of aggregation. Although the change in entropy on micelle formation must also contribute and may account largely for the effect of chain length on micelle size, yet it seems unlikely that it plays the same dominant rôle in aggregation as in aqueous soap solutions (Stainsby and Alexander, *Trans. Faraday Soc.*, 1950, **46**, 587). This is because in non-polar solvents, in contrast to aqueous soap solutions, the environment of the hydrocarbon chains, before and after aggregation, is not greatly different. In the metal soaps studied in this investigation the balance of these various factors in non-polar solvents clearly favours aggregation. Also, different arrangements and different numbers of molecules in the micelle may lead to approximately the same decrease in free energy, when compared to the molecularly dispersed solute, so that various types of micelle may coexist in solution.

FIG. 5. *Effect of hydrocarbon chain length on degree of aggregation* (N) *of zinc soaps in toluene.*

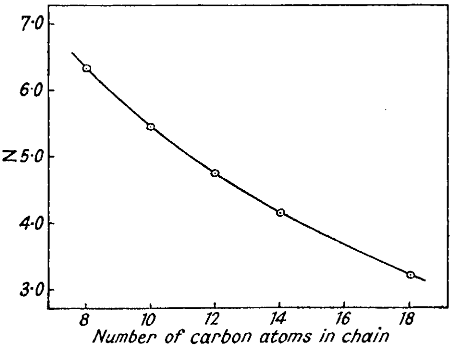
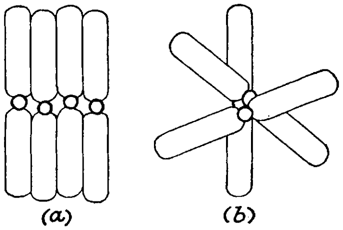


FIG. 6. *Packing of molecules in soap micelle in non-polar solvents.*



The strong dependence of micelle size on the polarity of the soap follows from Keesom's theory (*Physikal. Z.*, 1921, **22**, 126, 643; 1922, **23**, 225) according to which the average attractive potential $\bar{E}$ between two isolated dipoles is

$$\bar{E} = -2\mu_1^2\mu_2^2/3r^6kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ_1 and μ_2 are the dipole moments of the two dipoles, r the distance between their centres, and k the Boltzmann constant. For a number of molecules, the total energy is the sum of all the pair interactions. In a metal soap solution in which the interacting species are identical, $\bar{E}$ is therefore proportional to μ^4; $\bar{E}$ can be calculated if we assign a value to r. Close approach of the dipoles in the aggregate is probably limited, in the first instance, by the hydrocarbon chains, and r, as an aproximation, may be taken as 5·2 Å, the cross-sectional diameter of the hydrocarbon chain, from monolayer measurements. This type of packing is illustrated in Fig. 6(*a*), which also indicates the structural arrangement found in the crystalline soaps as determined by *X*-ray measurements (Vold and Hattiangdi, *Ind. Eng. Chem.*, 1949, **41**, 2311). In the crystal, the chains are slightly inclined to the plane containing the metal–carboxyl groups. For nickel laurate, therefore, with $\mu = 2{\cdot}67$ D (Table 3) and $T = 383°$ (b. p. of toluene), $\bar{E}$ has a value of $-1{\cdot}63 \times 10^{-14}$ erg per molecule. Since the total translational energy of the molecule at this temperature is $7{\cdot}88 \times 10^{-14}$ erg, it is clear that the decrease in potential energy due to dipole interaction alone is insufficient to stabilise the aggregate. This is true also of the less polar soaps of magnesium, copper, and zinc. On this basis, stabilisation of the aggregates must be due partly to the contribution from the interfacial-energy term, which is not so readily evaluated. The calculated value of the dipole interaction energy may, however, be too low for the following reasons. First, equation (1), which is derived on the basis of the simple Boltzmann statistics, is strictly applicable only to a phase in which free rotation is possible. For two dipoles, fixed relatively to one another, the interaction energy is given by

$$E = - \mu_1\mu_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)]/r^3 \quad . \quad . \quad . \quad (2)$$

where θ and ϕ are polar co-ordinates giving the orientation of the dipoles whose moments are μ_1 and μ_2 at a distance r from each other, the polar axis being the line joining their centres. For the most favourable orientation this reduces to

$$E = - \mu_1\mu_2/r_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

With the same assumptions as before this gives for nickel laurate $E = -2{\cdot}53 \times 10^{-14}$ erg per molecule. In view of the marked asymmetry of the soap molecules, hindered rotation of the molecules in the micelle seems not improbable. Secondly, much higher interaction energies would be possible with lower values of r. Such close packing in the aggregate might occur if the molecules were arranged as in Fig. 6(*b*). Lastly, the significance of Banerjee and Palit's dipole-moment data is uncertain. The values of the moments are based on the assumption, common to all dipole-moment evaluations from dielectric-constant measurements on solutions, that the solute is molecularly dispersed. So far as zinc oleate is concerned this is definitely not the case in toluene (Fig. 2). It seems probable, therefore, that the calculated moments are too low, although there is no doubt that the measurements place the soaps in the correct *order* of polarity. The true value of the dipole interaction energy may thus be substantially greater than calculated from (1) above. Although it may be sufficiently large in the case of the more polar soaps to account alone for the aggregate stability, yet it seems likely that in all cases the decrease in interfacial energy also plays a significant part in the aggregation process.

Like the coulombic force between ions, the attractive force due to the dipoles is exerted indiscriminately on all other polar molecules depending only on the distance of separation. The tendency to form clusters through this effect is therefore of the same order of magnitude as that to form pairs provided that the distance of closest approach r does not vary with the size of the aggregate (cf. Hildebrand and Scott, "The Solubility of Non-Electrolytes," p. 56, 1950, Reinhold Publishing Corp.). From (1), $\bar{E}$ is obviously extremely sensitive to variation in this distance of closest approach of the dipoles. Once a metal soap micelle is formed, access of further molecules to the polar interior of the micelle may be hindered by the hydrocarbon chains, so that r may increase rapidly with increase in the size of the aggregate. This inability of the molecules to pack in the micelle in such a way that the maximum decrease in potential energy occurs probably represents a powerful limiting factor on the growth of the micelles in dilute solution. The steric factor is evident in the case of ferric laurate, which has three hydrocarbon chains. In solutions of this soap, aggregation stops at the dimer, partly because of the increased solubilising effect of three hydrocarbon chains as against two in the bivalent soaps, but also because of the steric hindrance to further aggregation provided by the six hydrocarbon chains of the dimer (Nelson and Pink, in the press). The low micellar weight of zinc oleate compared with that of the corresponding saturated soaps (Fig. 2) can probably be accounted for in the same way, the rigidity imparted to the chain by the centrally placed double bond in the oleate preventing close packing in the micelle. Zinc oleate and oleic acid itself have much lower m. p.s than the corresponding saturated compounds for analogous reasons. This difficulty in packing in the most favourable way in the micelle is accentuated by the fact that, at the temperatures at which the soaps dissolve, the *hydrocarbon chains* are above their m. p. and the soaps themselves are often above well-marked mesomorphic transitions in the solid, akin to pre-melting phenomena (Vold, Grandine, and Vold, *J. Colloid Sci.*, 1948, **3**, 339; Hattiangdi, Vold, and Vold, *Ind. Eng. Chem.*, 1949, **41**, 2320; Martin and Pink, *loc. cit.*).

There is no reason to believe that the small micelles found in dilute solutions in toluene are other than roughly spherical in shape. Although some of the soaps separate from solution as a paste or pseudo-gel of very fine crystallites, dilute solutions exhibit none of the viscosity anomalies or gelling properties characteristic of systems containing strongly aniso-dimensional particles. Less can be said about the much larger micelles which appear to exist at higher concentrations in solutions of all the metal soaps; these may be analogous to the neutral lamellar micelles found in concentrated aqueous soap solutions, but much more evidence of a different kind is necessary to elucidate the problem of their structure.

Solutions in Polar Solvents.—Support is given to the theory outlined above by the results obtained in pyridine ($\varepsilon = 12{\cdot}5$) and *iso*butyl alcohol ($\varepsilon = 18{\cdot}7$). In these polar solvents a marked reduction in the aggregating effect of the soap dipoles is to be expected. As shown in Fig. 4, zinc laurate is molecularly dispersed over a wide range of concentration in *iso*butyl alcohol, as is copper laurate in dilute solution. In more concentrated solutions in *iso*butyl alcohol, however, the copper soap appears to aggregate to the dimer, a difference in accord with the more polar character of the copper soaps. In pyridine, the micellar-weight evidence suggests that both the zinc and the copper soaps are not only molecularly dispersed but partly dissociated into ions, the observed molecular weights being lower than the formula weights. Support for this view is provided by conductance data on pyridine solutions of copper laurate. A 0·063M-solution of this soap has a specific conductance of $2{\cdot}140 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ as against $0{\cdot}1625 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ for the pyridine itself. The increase in conductance, however, may be due partly to traces of fatty acid or copper sulphate in the soap.

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