

REVIEW ARTICLE

THE STRUCTURE AND PROPERTIES OF AQUEOUS SOLUTIONS OF SOAP

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THE sodium and potassium salts of the higher members of the homologous series of saturated fatty acids have different properties from those of the lower members. For example, there is no reason to suspect the existence of colloidal particles in solutions of sodium acetate, but it is impossible to deny their existence in solutions of sodium stearate or palmitate¹. McBain and Taylor² found that the equivalent conductivity curve of potassium palmitate shows a pronounced minimum at 0.2N and a maximum at 0.5N. Such a phenomenon had not previously been met in aqueous solutions. Similar maxima and minima were found by McBain, Cornish and Bowden³ in the equivalent conductivity curves of sodium myristate and sodium laurate. An examination by McBain, Laing and Titley⁴ of the whole range of potassium soaps from the acetate to the stearate showed that the equivalent conductivity-concentration curves are smooth in form for the soaps below the laurate, whereas the laurate, myristate, palmitate and stearate all exhibit pronounced maxima and minima.

Experiments^{5,6} showed that the equivalent conductivity of solutions of soap cannot be attributed to the presence of free hydroxyl ions produced by hydrolysis. The latter could only account for a few per cent. of the observed conductivity, which is nearly as great for solutions of ammonium soaps as it is for the corresponding potassium soaps⁷. The belief that hydrolysis could account for the conductivity was finally disposed of by Reychler⁸ who found that solutions of cetyltriethylammonium iodide behaved similarly.

MCBAIN'S MICELLE THEORY

McBain believed that the discrepancy between the conductivity and osmotic properties of the sodium and potassium salts of the higher members of the homologous series of fatty acids, must be due to the colloidal matter that such solutions undoubtedly contain. He postulated that groups of fatty ions or "ionic micelles" developed in the solutions⁹, and that they are responsible for the colloidal character of the solutions. Their formation would, he thought, also explain the minima which are observed in the equivalent conductivity-concentration curves of aqueous solutions of soap because, according to Stokes' Law, the micelles would be more mobile, and therefore, more highly conducting than the simple

ions from which they are formed. That is, the micelles would produce a rise of equivalent conductivity.

Hartley¹⁰ maintained that the comparison of osmotic activity and equivalent conductivity led McBain to the correct conclusion that the discrepancy could be accounted for by the formation of micelles, but did not agree with McBain that micelles begin to be formed at the soap concentration at which the equivalent conductivity is a minimum. He explained that the aggregation of fatty ions produces a considerable local concentration of negative charge in the solutions, as a result of which there must be a corresponding local increase of cations. The cations cease to play their normal part in conduction and, instead, carry positive charges towards the anode, resulting in a lower mobility and a *fall* in the equivalent conductivity of the solution.

Hartley sought to prove his point by determining the "Wien Effect"^{11,12} of a long-chain salt in aqueous solution. He subjected solutions of cetylpyridinium bromide to electric fields of such high intensity that the effect of the bromide ions on the micelles, composed of cetylpyridinium ions, was completely annulled¹³. The result was a rise in equivalent conductivity, indicating that the formation of micelles can only be accompanied by a rise in equivalent conductivity when the atmosphere of "gegenions" is sufficiently removed from the micelles. Hartley obtained further evidence that the micelles begin to form at the soap concentration at which the total conductivity falls, by calculating the equivalent conductivity of the paraffin radical alone¹⁴. He showed that when the total equivalent conductivity falls, that of the paraffin radical rises steeply. The fall of total equivalent conductivity is due to the atmosphere of oppositely charged "gegenions" around the micelles, and the rise of equivalent conductivity of the paraffin radicals due to their aggregation as micelles, with a resulting Stokes' Law-like effect. The concentration of soap at which the transition from simple ions or molecules to micelles takes place is known as the "critical concentration for micelles"^{15,16}.

PHYSICAL PROPERTIES AFFECTED BY MICELLE FORMATION

Equivalent conductivity is only one of several factors affected by the formation of micelles. Others include surface tension, interfacial tension, density, transport number, depression of freezing point, osmotic coefficient, diffusion coefficient and capacity to solubilise water-insoluble material. The decrease in surface tension that accompanies an increase in the concentration of aqueous solutions of soap is arrested at the critical concentration, in excess of which there is no further fall. A pronounced dip in surface tension-concentration curves has been noted by several workers^{17,18,19} who show that the soap concentration at which it occurs is influenced by the length of the hydrocarbon chain of the soap, and by the presence of electrolytes, which shift it to a lower concentration. Solutions containing only pure soaps do not exhibit the dip in their surface tension-concentration curves, but the presence of trace quantities of electrolytes²⁰ or carbon dioxide²¹ are sufficient to produce it. Powney and Addison²² and Lottermoser and

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Püschel²³ showed that critical concentrations deduced from surface tension measurements were in good agreement with those deduced from conductivity and interfacial tension measurements. They obtained values of 0·008 molar for C₁₂ compounds and 0·00017 molar for C₁₈ compounds. The relation between the interfacial tension of aqueous solutions of soap and their concentration has been studied by Powney and Addison²² and Alexander and Trim²⁴ who noted a change in the slope of the curves at the critical concentration.

Bury and Parry²⁵ examined the densities of aqueous solutions of potassium laurate and found an abrupt change of slope in the density-concentration curves at about 0·025 molar. This concentration of potassium laurate agrees well with that reported by others as the critical concentration. Transport numbers of the long-chain ions in solutions of soap have been shown by Hartley, Collie and Samis¹⁴ to be affected by the formation of micelles and therefore to change in magnitude at the critical concentration. The variation of osmotic and diffusion coefficients with concentration have also been shown^{26,27} to change sharply at the critical concentration.

FACTORS AFFECTING THE CRITICAL CONCENTRATION

The critical concentration for a particular soap is dependent upon several factors, and the value obtained experimentally appears to vary somewhat with the physical property used to detect micelle formation^{10,28}. Nevertheless, it is apparent that the length of the hydrocarbon chain of a soap molecule influences the concentration of soap at which the transition from ions to micelles takes place. Measurements of conductivity²³, refraction²⁹ and transport number³⁰ have shown that the longer the paraffin-chain the lower the concentration of soap at which the change occurs. Table I shows the critical concentrations for C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈ compounds as determined by different methods.

TABLE I
CRITICAL CONCENTRATION, MOLAR, OF C₁₀, C₁₂, C₁₄, C₁₆ AND C₁₈ COMPOUNDS

		C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈
Equivalent conductivity ²¹	...	—	0·0076	0·0028	0·0011	0·00039
Refraction ²⁹	0·098	0·0255	0·0066	—	—
Transport number ³⁰	0·032	0·013	0·0045	—	—
Interfacial tension ²²	—	0·008	—	—	0·00017

The addition of two —CH₂ groups to a hydrocarbon chain seems to reduce the critical concentration by about 65 per cent. The discrepancies for the critical concentrations for a particular chain length may be, in part, due to the use by different workers of compounds with different hydrophilic groups although the effect of the latter is quite small.

Lottermoser and Püschel were unable to detect any difference between the critical concentrations of potassium and sodium alkyl sulphates.

Klevens²⁹ and Ekwall and Otterstrom³¹ have shown that an increase in temperature decreases the amount of colloid present in the solutions at any concentration. That is, an increase in temperature increases the critical concentration.

Hartley^{32,33} demonstrated by the indicator displacement phenomenon that the addition of electrolytes to an aqueous solution of a soap depresses the critical concentration. His method consisted of buffering methyl red at about pH 3.5, at which it has a red colour, and slowly adding a solution of cetylpyridinium chloride, when the colour changed abruptly to yellow. Dilution with water until the concentration of the cetylpyridinium chloride was below its critical concentration restored the red colour of the indicator. The yellow colour could then be regained by the addition of either more cetylpyridinium chloride or a neutral salt such as potassium or sodium chloride, indicating that the chloride lowers the critical concentration. Hartley found that the addition of sodium chloride to a solution of cetylpyridinium chloride so that the concentration of the former is 0.032M lowers the critical concentration of the cetylpyridinium chloride from about 0.0009M to 0.0001M, or approximately ten-fold.

DETERMINATION OF THE CRITICAL CONCENTRATION

Clearly, any physical property which is affected by the formation of micelles can be used as a means of detecting their formation. The magnitude of the physical property under consideration is plotted on a graph as ordinate and the concentration of the soap in solution as abscissa and the curve examined for the characteristic "break" or change of slope that is associated with the critical concentration. As explained earlier in this Review, the value obtained for a particular soap will depend on the physical property being examined^{10,28}.

THE STRUCTURE OF THE MICELLES

McBain's early belief⁹ was that soap in dilute aqueous solution behaves as a normal electrolyte, molecules of undissociated soap being in equilibrium with paraffin-chain ions and metallic ions, and that at the critical concentration the paraffin-chain ions re-associate to form comparatively simple ionic micelles. Later McBain³⁴ and Lottermoser and Püschel²³ believed that neutral colloid, which makes little or no contribution to the conductivity of soap solutions, is formed simultaneously with the ionic micelles. Ralston³⁵ upheld this view as he thought it was not logical to suppose that ionic micelles can first produce a drop in equivalent conductivity, and later account for an appreciable rise.

Hartley¹⁰ attacked this contention and maintained that the conclusions had been drawn without consideration of the effect of Coulomb forces between the ions and the micelles. He believed that the rise in conductivity in the more concentrated solutions could be explained by the liberation of some of the attached gegenions from the more closely

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packed micelles, and that it in no way suggested the formation of a second type of micelle. He regarded the micelle as being symmetrically spherical and consisting of an aggregate of hydrophobic hydrocarbon chains jumbled together and away from the water, and with their end-groups projecting into the surrounding water, and the whole aggregate surrounded by an atmosphere of the hydrophilic ions of the soap, which he called "gegenions." Figure 1 shows a diagram of Hartley's representation of an ionic micelle.

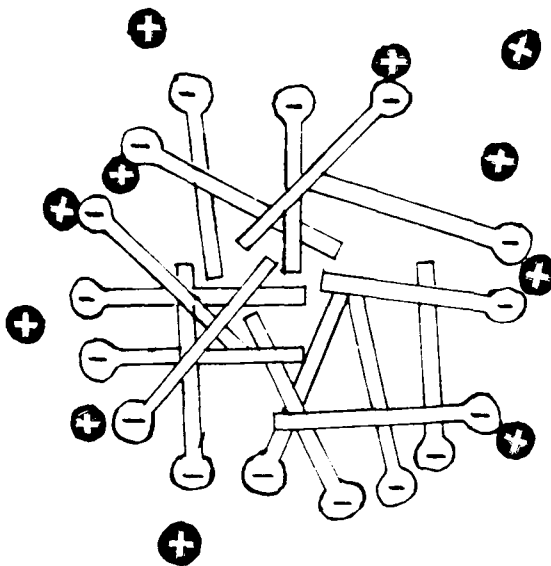


FIG. 1. Diagrammatic Representation of a Spherical Ionic Micelle. (From Hartley.)

Lawrence³⁶ considered that aqueous solutions of soap contain both "primary" and "secondary" micelles, both of which have a liquid structure. His "secondary" micelles are to be regarded as filamentous groups of "primary" micelles rather than as micelles of a different type.

The development of X-ray absorption analysis enabled Stauff³⁷ and Kiessig and Phillipoff³⁸ to show that 0.2M solutions of sodium laurate and 0.1M solutions of sodium tetradecyl sulphate contain much larger particles than had hitherto been believed. Stauff called these large particles "large micelles" to distinguish them from the smaller colloidal aggregates present in the solutions, and regarded them as consisting of double layers of soap *molecules* closely packed side by side and at right angles to the lamellæ. McBain³⁹ coupled Stauff's work with a suggestion from Meyer and van der Wyk⁴⁰ and regarded it as proof that aqueous solutions of soap contain two kinds of colloidal particles. He now believed that ionic micelles begin to form in very dilute solution and steadily increase with concentration, and that the "lamella micelles" arise from ion-pairs and higher aggregates formed at the critical con-

centration for micelles, increasing in size and amount until their development is sufficient to produce an X-ray pattern in the solution."

X-ray studies of soap solutions have been continued by Harkins and his co-workers. In general, they have confirmed the findings of the German workers as regards the structure of the micelles. Unfortunately, X-ray measurements have as yet only been made with fairly concentrated soap solutions (i.e. several times the critical concentration) and hence we are left to infer that the soap lamellæ, the presence and structure of which has been determined in the concentrated solutions, are similar, except perhaps in dimension, to those produced at the critical concentration from ion-pairs and smaller aggregates.

Harkins, Mattoon and Stearns⁴¹ and Harkins, Mattoon and Corrin⁴² examined 5 per cent. to 30 per cent. aqueous solutions of potassium laurate by means of X-ray diffraction, and concluded that the lamella micelles consist of four or more double layers of soap molecules oriented like the ions of the spherical micelles of McBain and Hartley, with their hydrophilic portions projecting into the surrounding water, and the paraffin chains towards one another, forming a liquid structure in the plane of the layer. The double layers of soap molecules are separated by layers of water and are kept apart by repulsion of the positive ions produced by ionisation of the molecules. Harkins' representation of such a soap micelle is shown in Figure 2A.

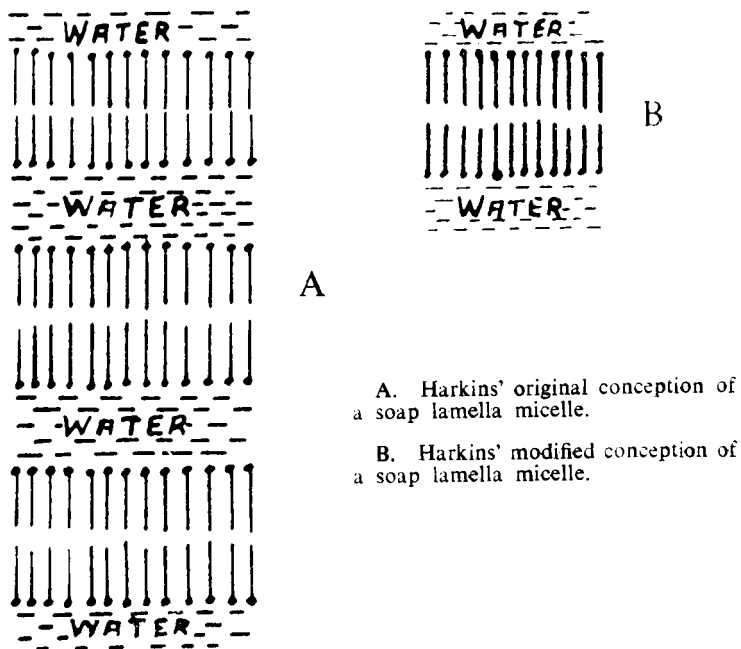


Fig. 2. Diagrammatic Representation of a Lamella Micelle. (From Harkins *et. al.*)

More recent work by Mattoon, Stearns and Harkins⁴³ has led to the recognition of a new X-ray diffraction band, from which the authors conclude that the micelles probably have a somewhat simpler structure

than they originally proposed. They now believe them to consist, as shown in Figure 2B, of only one double layer of soap molecules and to increase in size and number as the concentration increases.

The work of Harkins *et al.*, on the one hand, has done little to settle the dispute over the structure of the micelles in the neighbourhood of the critical concentration. Hartley's postulation of spherical micelles on the other, fails to explain the X-ray diffraction observed in the more concentrated solutions. Vetter⁴⁴ considers that neither theory accounts satisfactorily for all the known properties of solutions of soaps. He believes that a slight modification of the Hartley picture is more acceptable than the present McBain viewpoint, at any rate, for solutions below the concentration at which X-ray diffraction has been observed. He offers no suggestions as to the origin of the lamella micelles in the concentrated solutions.

THE SIZE OF THE MICELLES

It is generally accepted that micelles begin to form at the critical concentration from ions and ion-pairs, and that the transition is not so abrupt that micelles of maximal size are produced over an infinitely small concentration range. Hartley¹⁰ suggests that in aqueous solutions of a 16 carbon atom soap, the micelles which commence to form at about 0.001M (the critical concentration) are probably composed of about 10 ions, and that they simultaneously increase in size and number until at about 0.005M the hydrocarbon ions exist almost entirely of micelles containing about 50 ions each.

The diameter of spherical micelles cannot be less than the length of the paraffin chains unless part of the chain protrudes into the surrounding water, nor can it be greater than twice the length of the chain unless the centre is vacuous. These possibilities are unlikely¹⁰. The diameter, then, will be approximately twice the length of the paraffin chain, and as the homologous series is ascended from C₁₂ to the C₁₈ soap, it will increase. Hartley gives the diameter of micelles formed in solutions of the C₁₆ soap as approximately 36Å.

Measurements by X-ray diffraction of the size of lamella micelles made by Harkins *et al.*⁴², indicate that the thickness of the lamellæ in 15 per cent. aqueous solutions of potassium laurate is about 32.4Å which is similar to the diameter of the Hartley micelles.

SOAP SOLUTIONS AS SOLVENTS FOR WATER-INSOLUBLE SUBSTANCES

The earliest record of the use of soap as a solvent appears to be by Engler and Dieckhoff⁴⁵ in 1892 who prepared clear aqueous solutions of cresol and water by the addition of soap. Their work was quickly followed by British Patent No. 13,201 of 1895 which described the use of soft soap to solubilise water-insoluble materials such as naphthalene.

The explanation usually offered for clear lysol solutions is that the soap lowers the critical solution temperature of cresol and water to such an extent that they become completely miscible at normal temperatures. Some doubt was cast upon this explanation by Angelescu and Popescu⁴⁶ who measured the solubility of *o*-cresol in several soaps of the fatty acid

series and found it greater than in solutions of sodium hydroxide. A number of other organic liquids have been shown to be more soluble in solutions of soap than they are in water^{47,48} and Hartley¹⁰ suggested that they dissolve in the soap micelles. This view has been elaborated somewhat by Lawrence⁴⁹ who proposed that solubilisation of organic substances by aqueous solutions of soap takes place by two different methods. Water-soluble substances have their solubility enhanced by becoming attached to the exterior of the micelles by dipole attraction, and water-insoluble substances form an internal solution in the hydrocarbon interior of the micelles. Most organic substances, though oil-soluble, contain polar groups and thus both mechanisms will operate simultaneously.

X-ray diffraction measurements in aqueous solutions of soap offer practical evidence of the correctness of the suggestions of Hartley and Lawrence. Mattoon, Stearns and Harkins⁴³ demonstrated that the thickness of lamella micelles of potassium myristate is about 40Å, but when oil has been dissolved in the soap solution the micelles are found to have expanded to about 53Å in thickness to incorporate sheets of oil between the hydrocarbon layers of the lamellæ (Fig. 3).

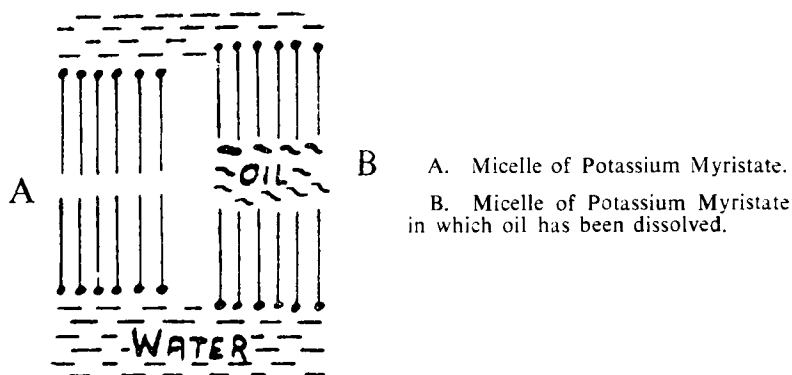


FIG. 3. Cross Section of Highly Idealised Micelle of Potassium Myristate in which Oil has been Dissolved. (From Mattoon, Stearns and Harkins.)

These conclusions are confirmed with an extremely different system by the X-ray work of Palmer⁵⁰ on nerve lipid emulsions containing cephalin. Figure 4 shows the expansion of a lamella of typical lipid material as water is progressively taken up as a layer within the leaflets.

THE RELATION BETWEEN THE SOAP CONCENTRATION AND THE AMOUNT OF WATER-INSOLUBLE MATERIAL SOLUBILISED

If solubilisation of water-insoluble substances by aqueous solutions of soap is due to internal solution within the micelles, it can only occur when the concentration of the soap solution is in excess of the critical concentration. Although, in general, this is borne out by practical experience, McBain, Merrill and Vinograd⁵¹ report that they found that solutions of potassium laurate and laurylsulphonic acid dissolved sufficient of the water-insoluble dye Yellow AB to colour them yellow,

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even though they were below the critical concentration. Similarly Bean and Berry⁵² record that when aqueous solutions of potassium laurate and benzylchlorophenol are diluted with water to below the critical concentration, the amount of benzylchlorophenol remaining in solution

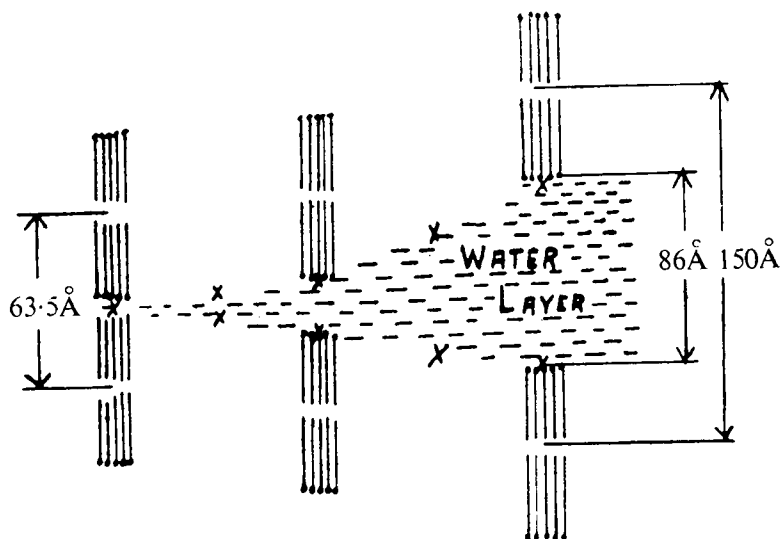


FIG. 4. Expansion of Lamellæ of Nerve Lipides as Water is Taken Up. (From Palmer.)

X^s represent values when water content is 0 (dry), 25, 50, 67 and 75 per cent.

is greater than can be accounted for by its water-solubility. The solvent action shown by aqueous solutions of soap below their critical concentration is attributed by Corrin, Klevens and Harkins⁵³ to the presence in the solution of some elementary organised structures such as the ion-pairs referred to by McBain.

One of the first studies of the relation between the concentration of a soap solution and its solubilising ability was carried out with cetylpyridinium chloride and *trans*-azobenzene³³, the latter being

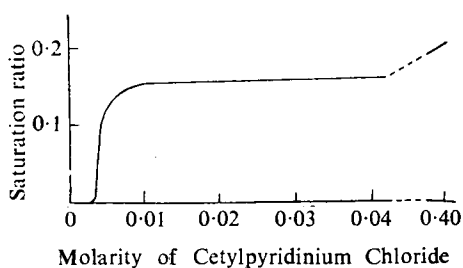


FIG. 5. The Solubility of *trans*-azobenzene in Cetylpyridinium Chloride. (From Hartley.)

chosen because it is not sufficiently water-soluble to modify materially the properties of the micelles. Reference to the solubility curve (Fig. 5) will show that there is no appreciable solvent action when the concentration of the cetylpyridinium chloride is below 0.001M. Above that concentration the solubility of the

trans-azobenzene rises rapidly, and reaches a value more than half that at five hundred times the concentration within the first part of this range.

A curve of very similar shape was obtained for the solubility of Yellow AB in laurylsulphonic acid⁵¹, for chlorophyll and Yellow AB in sodium deoxycholate²⁶, and for benzylchlorophenol in potassium laurate⁵⁴ and it may, therefore, be regarded as typical for water-insoluble materials solubilised by aqueous solutions of soap and other long-chain surface-active compounds.

McBain, Merrill and Vinograd⁵¹ record the interesting fact that solubilisation of water-insoluble materials by aqueous solutions of soap is greater at high temperatures than at room temperature, in spite of there being far less colloid at the higher temperature^{29,31}. The increase in the solubility of the so-called water-insoluble materials in the aqueous phase of soap solutions which is brought about by elevation of the temperature, must therefore be relatively greater than the reduction caused by the smaller number of micelles at the higher temperature.

The very abrupt rise at the critical concentration, of the solubility of dyes and other water-insoluble compounds, provides an extremely simple and sensitive method for the determination of the critical concentration⁵⁵.

THE RELATION BETWEEN THE LENGTH OF THE SOAP MOLECULE AND THE AMOUNT OF MATERIAL SOLUBILISED

The solubilisation of the water-insoluble dye Orange OT by the homologous series of pure potassium fatty acid soaps was examined by McBain and Johnson⁵⁶, who found that the amount of dye solubilised increases as the number of CH₂ groups in the hydrocarbon chain increases. As the homologous series is ascended not only does the dye

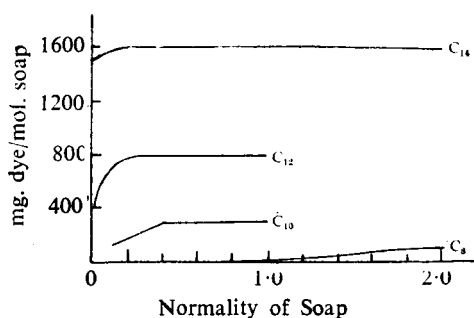


FIG. 6. The Solubility of Orange OT in the Homologous Series of Pure Potassium Fatty-acid Soaps. (From McBain and Johnson.)

commence to go into solution at a lower soap concentration, due to the critical concentration decreasing as the chain length increases, but when the micelles are fully formed the amount of dye necessary to saturate the solution increases considerably (Fig. 6).

McBain and Johnson draw special attention to the fact that for an increase of 50 per cent. in the number of carbon atoms from caprylate to the laurate, solubilisation increases 6.7-fold. The authors maintain that this increase cannot be accounted for if it is assumed that the dye merely dissolves in the hydrocarbon interior of the micelles. The discrepancy is used to lend weight to the argument that soap solutions, in excess of the critical concentration, contain lamella micelles and the authors suggest that solubilisation is probably brought about by packing the spaces between the parallel sheets of hydrocarbon molecules together with adsorption on the exteriors of the micelles.

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