

which corresponds to the formula $\text{Ga}_4(\text{Fe}(\text{CN})_6)_3$ for the precipitate. The precipitate is not of a complex nature and therefore differs from the ferrocyanide of zinc and indium. The determination of this ratio makes it possible to use ferrocyanide solutions, standardized against metallic zinc, for the determination of gallium.

Summary

A method of analyzing gallium chloride solutions by titrating with standard potassium ferrocyanide solution in the presence of ferricyanide and determining the end-point potentiometrically has been described. The accuracy is estimated at two or three tenths of one per cent.

The ferrocyanide precipitate formed under the conditions described has been shown by two independent methods to have the formula $\text{Ga}_4(\text{Fe}(\text{CN})_6)_3$.

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SOAPS AS COLLOIDAL ELECTROLYTES

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It is well known that members of the large class of substances exemplified by the family of soaps exhibit in solution only moderate osmotic effect or activity, whereas their conductivity is excellent. So much is this the case, that often the whole activity seems to be ascribable to the concentration of one simple ion as measured by any of the ordinary methods leaving the carrier of the opposite charges to be explained as highly conducting colloidal particles or ionic micelles.¹ It is clear that this interpretation necessitates a broader interpretation of the electrolytic dissociation theory than that which is currently being attempted for electrolytes in aqueous solution. Linderstrøm-Lang² has tried to fit the data for soap solutions to the Procustes' bed of the 100% ionization theory on the assumption that soap solutions are completely dissociated into ordinary sodium or potassium ions and simple univalent fatty ions. It is the object of this note to point out that this cannot be done without deliberately ignoring too many facts.

It is perfectly possible, by means of *ad hoc* assumptions, to regard almost any substance, whose solution conducts, from the standpoint of 100%

¹ References to previous papers from the Bristol and Stanford Laboratories may be found in the following: McBain and Buckingham, *J. Chem. Soc.*, 1927, 2679-2689; McBain, Willavoys and Heighington, *ibid.*, 1927, 2689-2699; McBain, Chap. 16, pp. 410-429 of "Colloidal Behaviour," Vol. I by Bogue; see also Salmon, *THIS JOURNAL*, 42, 426-460 (1920); other similar references in Linderstrøm-Lang, *ref. 2*.

² Linderstrøm-Lang, *Compt. rend. Lab. Carlsberg*, 16, No. 6, 1-47 (1926).

ionization, provided that one takes into account only osmotic or activity data. This is what is done by Linderstrøm-Lang, apart from a passing qualitative reference to the viscosity of soap solutions. He himself points out that it is going to be difficult to explain the conductivity data but shelves this problem on the ground that conductivity data are no longer thought to be understood.

The picture given by Linderstrøm-Lang² is as follows. In a 1 *N* solution of sodium palmitate the length of each palmitate ion (25 Å.) is more than twice as great as the average distance between the sodium ions (10 Å.) and of course the negative charges are carried only on one end of the long writhing fatty ions. Hence the solution is a tangle something like cotton waste and there will be strong attractive forces between the paraffin chains, minimized only by the sodium ions interspersed amongst them. The tangle might explain a high viscosity³ and its screening action in the "abnormally low" osmotic activity.

Linderstrøm-Lang rightly remarks that osmotic experiments alone cannot prove the presence of micelles or colloidal particles. The converse is equally true, but he prefers not to assume their formation. He is influenced by the observation that soap solutions are "absolutely as clear as water and show no trace of Tyndall effect." However it must be pointed out that there is no optical evidence for the existence of a large number of colloids. It does not appear to be generally appreciated how many colloidal particles are invisible in the ultramicroscope. Further, Dr. H. Harris showed in the Bristol Laboratory that all the colloidal jellies which have been noted in the literature, such as soap, magnesium arsenate, ferric hydroxide, dibenzoylcystine, barium malonate, lithium urate, if prepared with sufficient care, are invisible in the ultramicroscope. Probably no one would care to conclude that these are all in true molecular solution.

Four kinds of data will here be cited which are directly at variance with the conception of a 100% dissociation into simple ions; namely, ultrafiltration, migration, viscosity and hydrolysis.

Ultrafiltration experiments by Dr. Jenkins and the writer⁴ and subsequent (unpublished) data have shown that where the comparison between the quantitative data for activity and conductivity indicated the presence of crystalloidal soap only, the whole of the soap solution passed through dense ultrafilters. On the other hand, where such data on our interpreta-

² Linderstrøm-Lang and the writer agree in thinking that the high viscosity observed in certain soap solutions cannot be ascribed to "hydration" but must have a mechanical origin. The writer has developed a general hypothesis for high viscosity on the basis of the immobilization of large tracts of solvent or solution through the chance intermeshing of ramifying aggregates of colloidal particles, *J. Phys. Chem.*, 30, 239-247 (1926); *Nature*, 120, 362 (1927).

⁴ McBain and Jenkins, *J. Chem. Soc.*, 121, 2325-2344 (1922).

tion indicate complete formation of colloid, the whole of the soap may be filtered off by a moderately dense ultrafilter. In intermediate cases where the data showed definite proportions of both crystalloid and colloid, approximately that proportion corresponding to the crystalloid passes through the ultrafilter. It is difficult to avoid the conclusion that the colloid consists of particles and not of the simple ions and molecules to which the ultrafilter is completely permeable. Incidentally it may be mentioned that a very coarse ultrafilter suffices to filter off much of the predicted neutral colloidal particles in a solution of the highest soaps such as sodium oleate. Further it should be pointed out that there is no difference in kind but only in degree in all hitherto observed properties of all soap solutions in the cold and at high temperatures. Colloidal particles persist into much lower concentrations at room temperature. This statement, of course, refers to solutions only and not to systems from which the soap has crystallized out (for example curds).

Migration data have been obtained for various soap solutions by Bowden⁶ and Quick⁸ in the writer's laboratory and a comprehensive study of sodium oleate has been published by Miss Laing.⁷ The salient fact for the present purpose is that in solutions containing colloid the migration number of the fatty radical is greater than unity; that is, the sodium or potassium is moving to the anode—in the opposite direction from that of real sodium and potassium ions. This we explain, quantitatively, as being due to the sodium or potassium carried in the undissociated colloid.

Linderstrøm-Lang casually mentioned viscosity; but it would be almost impossible to explain why the viscosity of the soap solution may vary a thousand-fold with change of temperature alone, if the constituents are only those assumed by him. A further problem would be to try to explain why adding to his tangle a small amount of a salt or base like sodium chloride or hydroxide lowers the viscosity, and still further why a greater addition of almost any soluble salt can thereupon increase the viscosity fifty-fold, and still further addition lowers the viscosity to a small fraction of this again—all in homogeneous solution, and with only simple univalent ions present!

The hydrolysis alkalinity of a simple electrolyte of the type of sodium acetate increases steadily with concentration in accordance with the universal principle of mass action. Not so in soap solutions; here the concentration of hydroxyl ions increases when soap is added to water, passes through a maximum and diminishes again in the more concentrated solution because the hydrolyzable simple fatty ion is being replaced by ionic micelle.

⁶ McBain and Bowden, *J. Chem. Soc.*, **123**, 2417-2430 (1923).

⁸ Quick, *ibid.*, **127**, 1401-1411 (1925).

⁷ Laing, *J. Phys. Chem.*, **28**, 673-705 (1924).

Even conductivity should not be completely ignored, since there is no vast discrepancy between the two extreme oversimplified theories, that of Arrhenius and the 100% hypotheses.

All the known data of soap solutions may be interpreted in terms of the writer's theory of colloidal electrolytes, and no other hypothesis has attempted this. On the whole it seems probable, especially from the data on ultrafiltration and migration, that soap solutions contain both neutral colloid and ionic micelle. In an address to the Fourth National Colloid Symposium⁸ the writer advanced the view that reversible colloids such as soap are truly (that is, thermodynamically) stable in the colloid state, inasmuch as the colloidal particles are formed spontaneously from crystals and crystalloidal molecules and ions. It is suggested that this necessitates a structure of the micelle which exposes the active groups of every molecule or ion. Such a stable structure is exemplified by a monomolecular film of palmitic acid on water, or by the conception of the ionic micelle as a radiating ball of ions resembling ten eels tied together by their tails, the charges being on the outside extremities. Likewise a possible structure for the neutral micelle is a double layer of parallel molecules of sodium palmitate with the carboxylate groups and hydration on the outer surfaces. From the standpoint of conductivity, osmotic activity and electrolytic migration, all these can be treated as special cases of a general dissociation theory. The perfect theory would include not only strong and weak electrolytes but even the slightly charged colloids such as ferric hydroxide, gold or the neutral micelles of soap, and it must also embrace the striking phenomena common in non-aqueous solutions.

Finally, the question as to the effect of the presence of ionic micelle upon the observed activity of univalent ions needs to be dealt with. If the ionic micelle is, for example, decavalent, the usual rules of ionic strength might lead us to expect that any monovalent ions in the solution would show abnormally low activity. This might be taken as partly accounting for the low activity of soap solutions, but only after postulating the existence of the polyvalent ionic micelles, the very point in question. Instead of speculating, we may turn to the published facts.^{6,9} For example, when potassium chloride is added to a solution of potassium laurate at 18°, the lowering of vapor pressure or of freezing point is greater than that which the same amount of potassium chloride produces in water, and is thus too large instead of being greatly deficient. The migration data prove that in such mixed solutions the salt has diminished the amount of current carried by the soap (lessened its degree of dissociation) and we conclude that, since the osmotic effect exhibited by the salt is enhanced

⁸ McBain, "Fourth Colloid Symposium Monograph," Chemical Catalog Co., New York, 1926, pp. 7-18.

⁹ McBain, Taylor and Laing, *J. Chem. Soc.*, **121**, 621-633 (1922).

instead of being masked in the presence of ionic micelles, the soap is heavily hydrated, obtaining a value for the hydration in accord with other lines of inference. At 90° the additional lowering of vapor pressure caused in a solution of sodium palmitate on the addition of electrolyte, is between 75 and 80% of that which the electrolyte alone would produce in water, instead of being only the very small fraction expected on the basis of the 100% ionization theory in the presence of a decavalent ion. Soap appears to be far less hydrated at high temperatures and the observed lowering of vapor pressure is almost that which would be expected from the mutual influence of two univalent salts on each other's dissociation.

The data therefore show that the ionic micelle does not in fact conform to the rule of ionic strength, and there is an obvious explanation. In an ordinary polyvalent ion the charges carried by any one ion are necessarily close together, and may be regarded as almost coincident in comparison with the distances separating different ions from each other throughout the solution. An ionic micelle is very different, since the charges are held far apart whether in a protein or a soap micelle. If the ionic micelle of sodium palmitate has the structure indicated above and if the hydrocarbon chains were stretched to their full length, its diameter would be about 50 Å. and the distance between charges on the same ionic micelle would be over 20 Å. That is, the charges on any one such ionic micelle would be twice as far apart as the average distance of chlorine ions from each other in a normal solution of sodium chloride. It is more likely that the hydrocarbon chains do not stretch out so far, but even so the distance between neighboring charges will still be over 10 Å. Hence the ionic micelle does not represent a high local condensation of electric charge and therefore does not exert the expected effect upon activity.

Summary

1. It is shown that the attempt to describe soap solutions on the basis of dissociation into simple monovalent ions only, instead of colloidal micelles, cannot be carried through without ignoring the ascertained facts of ultrafiltration, migration and viscosity as well as conductivity.

2. The ionic micelle is an exception to the rule of ionic strength because of the large distance between the charges carried on a single ionic micelle in contrast to the proximity of the charges on an ordinary polyvalent ion.

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