AQUEOUS SOLUTIONS OF PARAFFIN-CHAIN SALTS[1]

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It is well recognized that the behavior of aqueous solutions of paraffin-chain salts is to be explained by the appearance of colloidal aggregates. However, most of the questions relating to the details of the aggregation are still unsettled.

Some of the experimental results are reviewed and their bearing on these questions is discussed.

Aqueous solutions of paraffin-chain salts form an interesting case in which the effects of dissociation and association are clearly evident. At low concentrations these salts behave as ordinary strong electrolytes. As the concentration is increased a point is reached, at a concentration dependent mainly upon the size and shape of the paraffin chain and the magnitude of the electrical charge of the ions, where the paraffin-chain ions more or less suddenly aggregate into particles of colloidal dimensions. This aggregation of the paraffin-chain ions in aqueous solution into colloidal micelles is well known (12, 23). However, the details of the phenomenon are as yet incompletely elucidated. The uncertainty as to the detailed interpretation of the properties of the solutions is due to at least three factors: (*1*) the systems are undoubtedly complex, (*2*) the magnitude of the interionic effects is unknown, and (*3*) the various data which have been reported often disagree considerably.

The questions which are to be answered in the complete description of these solutions are: (*a*) Is there at all concentrations only one type of micelle, or are there several, such as the "ionic micelle", the "lamellar micelle", etc.? (*b*) For a given type of micelle is there a fairly well-defined optimum size, or is there a particle-size distribution with a broad maximum? (*c*) Do the micelles consist solely of paraffin-chain ions, or are some of the simple ions of opposite charge (the "gegen ions" or "counter ions") included in the aggregate? (*d*) How large are the micelles, and how many ions of each type are included in one colloidal particle? (*e*) How are the constituent ions arranged in the micelle? (*f*) What are the concentrations of the free simple ions in equilibrium with the micelles? Obviously, all of these questions cannot be answered by thermodynamic considerations alone but require the application of all types of measurement which may be available.

McBain, who first suggested that the behavior of these solutions could be explained in terms of the formation of colloidal aggregates, has maintained that there are at least two, quite different, types of micelles (23). His "ionic"

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micelle is considered to be a spherical aggregate of not more than ten paraffin-chain ions, retaining its full electrical charge, while the "lamellar" micelle is a much larger particle, having the paraffin-chain ions in an arrangement similar to that in the solid state (3, 42), with a low electrical charge due to the inclusion of a considerable number of gegen ions. Ralston (34), Van Rysselberghe (40) and Stauff (37) have also considered that there must be two types of micelles.

McBain, Ralston, and Van Rysselberghe have based their arguments on the assumption that the interionic forces in the solutions are small, i.e., of the same order as in solutions of ordinary uni-univalent strong electrolytes. McBain has argued that, since the ionic charges on the micelle surface are separated from each other by several atomic diameters, their electrostatic effects will be essentially independent. As experimental evidence supporting this assumption, McBain and Searles (25) and McBain and Brady (24) have measured freezing points and conductivities of solutions containing both paraffin-chain salts and simple salts and have found that the effects are essentially additive. Some doubt may be cast on the interpretation of these data by the fact that the number, size, and electrical charge of the micelles may be changed by the presence of the added salt, which may lead to a set of compensating factors. With this assumption of small interionic effects, it has not been found possible to explain the observed properties of the solutions without the use of several types of micelles.

Hartley, on the other hand, believes that the properties of the solutions are explainable with the assumption of only one type of micelle (12), if one takes into account the large interionic effects due to the high electrical charge of the micelles. As experimental evidence of the existence of large interionic effects, he refers to measurements of electrical conductivity at high frequencies (36) and at high field strengths (19). Both of these investigations, while not conclusive, indicate the existence of large interionic effects. Similarly, Stone (39) has shown that sodium tetradecane-α,ω-disulfonate in aqueous solution gives an ionic strength of a uni-bivalent electrolyte. He has suggested that the bivalent behavior of these ions may be due to a bending of the paraffin chain, bringing the two ionic groups into close proximity. That this is not necessarily true is shown by unpublished data from this laboratory on the effect of sodium 4,4′-biphenyldisulfonate (15) on the solubility of thallous chloride. Although the sulfonate groups are about 11 Å., apart and the ion is rigid, the 4,4′-biphenyldisulfonate ion behaves as a bivalent ion. The recent work of Fuoss and Strauss (9) and Edelson and Fuoss (8) on polyelectrolytes also clearly shows the influence of large interionic effects.

None of the results relating to the magnitude of the interionic effects so far published are conclusive, and it is to be hoped that additional experimental data may appear to resolve the dilemma. Two lines of investigation which may yield significant results are now under way in our Laboratories. First, one can prepare polymers of known molecular weight, containing known numbers and distributions of ionic groups. Studies of the ionic strength effects of salts containing these ions will be of considerable interest. Secondly, to avoid the problem of unknown concentrations arising from the adherence of gegen ions to the micelle, one can attempt to measure the effective ionic strength of solutions of paraffin-chain salts by investigating the rate of a reaction between two ions bearing electrical charges of the same sign as that of the micelles.

Stauff has inferred the presence of two types of micelles, mainly from x-ray diffraction studies (37). At moderate to high concentrations a long-spacing diffraction band appears, which Stauff and others have attributed to the presence of lamellar micelles. As the concentration of paraffin-chain salt is decreased, the spacing increases (interpreted as inclusion of water between the layers of paraffin-chain ions) and the intensity of the band decreases. By plotting the diffraction intensity against the concentration and extrapolating to zero intensity, Stauff concludes that the lamellar micelle exists only at high concentrations and that the colloidal effects observed at lower concentrations are due to a small spherical micelle. Dervichian (6, 7) has suggested, however, that there is only one type of micelle and that the long-spacing diffraction band is due to an intermicelle spacing which only appears after the concentration of micelles reaches a certain limiting value. Mattoon, Stearns, and Harkins (20, 21) agree with Dervichian and present as evidence a newly discovered long-spacing band which they attribute to the single micelles.

The nature of the particle-size distribution curve has been considered theoretically by Meyer and van der Wyk (26), assuming a parallel arrangement of the paraffin chains and neglecting electrostatic effects. They calculate a curve having a very broad, flat maximum which shifts to larger sizes as the concentration increases. On the other hand, Hartley (12) has pointed out the greater likelihood of a spherical micelle with an essentially liquid-like arrangement of the paraffin chains in the interior. The assumption of the spherical micelle leads to a rather sharply defined optimum size, the radius of the sphere being approximately equal to the length of a single, fully extended paraffin-chain ion. Diffusion (1, 10, 14, 41) and ultracentrifuge (28) measurements indicate micellar radii which are in agreement with expectation from the spherical micelle. Thus, the direct experimental evidence as to the size of the micelles indicates, at least at concentrations just above the critical concentration, a micelle radius approximately equal to the length of the paraffin-chain ion. A micelle of this size, having an interior density equal to that of a liquid paraffin hydrocarbon, would contain about 50 ions in the case of a twelve-carbon chain and about 90 for a sixteen-carbon chain.

The sharpness of the change in properties at the critical concentration indicates (29) that the micelles must be fairly large, with a rather small fraction of aggregates of intermediate size.

Direct determination of the mean ionic activity of 1-dodecanesulfonic acid by E.M.F. measurements (30,31,32,43) shows the behavior of an ordinary strong electrolyte at concentrations below the critical concentration (about 0.008 M). Above the critical concentration the mean ionic activity is practically constant, rising only very slowly with increasing concentration.

The evidence for the inclusion of gegen ions in the micelle is considerable.

Aggregation of ions all of one sign would lead to an increase in conductance (22), whereas the equivalent conductance is usually observed to drop above the critical concentration. The transference number of the gegen ion is sometimes negative (13), owing to the transference of attached gegen ions by the micelle in the opposite direction from their motion when free. The yellow color of aqueous solutions of cetylpyridinium iodide (12) can hardly be due to anything but a firm attachment between the ions. The actual fraction of gegen ions attached has not been determined accurately, but estimates range from 50 to 80 per cent.

The evidence concerning the arrangement of the paraffin-chain ions in the micelle is so far inconclusive. Hartley (12) has argued for a random arrangement similar to liquid paraffin both on the basis of probability and from consideration of the lack of specificity in the solubilization of water-insoluble organic molecules by aqueous solutions of paraffin-chain salts. Similarly, Corrin (4) has found that the relationship between the amount of oil dissolved and the increase in x-ray spacing is in somewhat better agreement with a spherical micelle than the cylindrical model. The small-angle x-ray diffraction patterns obtained from solutions containing micelles have been interpreted as evidence for a lamellar micelle with parallel arrangement of the paraffin chains (21, 23, 37), and Brady (2) has discussed the interpretation of the shift of position of the long-spacing band with concentration in terms of the application of the theory of the diffuse ionic double layer to the lamellar micelle. However, Corrin (5) has recently shown that it is possible to account for the observed diffraction effects with the assumption of spherical micelles.

The concentrations of the free ions in equilibrium with the micelles cannot be accurately determined until we are able to take the interionic effects into account by appropriate activity coefficients. The estimates which have been made do not in all cases agree. For example, Hartley's (11) data on the solubilization of *trans*-azobenzene in aqueous solutions of cetylpyridinium sulfate indicate that the concentration of free cetylpyridinium ions decreases above the critical concentration. The data of Stearns, Oppenheimer, Simons, and Harkins (38) on the solubilization of 2-nitrodiphenylamine in aqueous solutions of potassium laurate can be interpreted in the same manner. On the other hand, the solubilization data for dimethylaminoazobenzene in aqueous solutions of potassium laurate (17) have been interpreted by Kolthoff and Stricks to indicate that the concentration of laurate ions does not decrease above the critical concentration. Similarly, the electromotive force data of Kolthoff and Johnson (16) seem to indicate that the activity of laurate ions in potassium laurate solutions is constant above the critical concentration, while the electromotive force measurements of Walton on solutions containing hydrochloric acid and 1-dodecanesulfonic acid (44) or hydrochloric acid and dodecylbenzyldimethylammonium chloride (45) indicate that the activity of the paraffin-chain ion decreases above the critical concentration. In this connection it should be pointed out that any equilibrium constant calculations involving a micelle which contains more paraffin-chain ions than gegen ions leads to a decrease of activity of the paraffin-chain ion above the critical concentration.

One further thermodynamic problem has arisen in the application of the Gibbs adsorption theorem to the surface tensions of aqueous solutions of paraffin-chain salts. Most of the reported data have shown the expected rapid decrease in surface tension with increasing concentration. At the critical concentration, however, the surface tension passes through a minimum and then rises considerably with further increase in concentration (18, 33). This rise would seem to indicate either a negative adsorption or a decrease in activity, both of which are extremely unlikely. Many hypotheses have been proposed to reconcile the anomalies (*cf.* 23), but recently Miles and Shedlovsky (27) and Reichenberg (35) have shown that at least in some cases, and probably in all, the minimum has been caused by traces of impurities (long-chain alcohols, paraffin-chain salts with polyvalent gegen ions, etc.) which are more highly adsorbed than the substance investigated, but which are dissolved in the micelles above the critical concentration. When these impurities are removed, the surface tension becomes practically constant above the critical concentration, as would be expected from the activity data.

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