

## ARE LIQUID SODIUM AMALGAMS COLLOIDAL?

A DISCUSSION OF THE PAPER OF PARANYPE AND JOSHI

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A recent issue of This Journal (1) contains an article by Paranype and Joshi which presents arguments purporting to show that sodium amalgams are colloidal in nature and that as such their properties depend on the method of preparation and treatment as well as on the concentration. If the conclusions of these authors are correct, most of the experimental data on sodium amalgams, and by implication the data on all of the alkali metal amalgams, become of doubtful value since in most cases the physical method of handling the amalgams has not been considered a significant factor. It would seem, therefore, worth while to analyze carefully the arguments of Paranype and Joshi and to present further evidence as to the nature of these solutions.

Two questions have been raised by Paranype and Joshi. First, does the method of preparing an amalgam affect the physical properties or is it sufficient to know the concentration, temperature, and pressure? Second, are sodium amalgams colloidal solutions? The answer to the first question does not necessarily answer the second, since it is possible that a reversible colloid might exist. The data and arguments presented by Paranype and Joshi will first be discussed and finally additional data which permit rather definite conclusions will be presented.

### THE REPRODUCIBILITY OF AMALGAMS

Paranype and Joshi enumerate five different types of experimental data in which the results do not seem to be reproducible. They conclude that the different methods used in preparing the amalgams resulted in different colloidal solutions and account in this way for the experimental data. Let us consider these cases in detail. The data on the conductivity of amalgams obtained by Hine (2), Vanstone (3), Bohariwalla (4), and Davies and Evans (5) are described as follows: "Hine finds that the conductance of sodium amalgam passes through a minimum; Vanstone states that the conductivity concentration curve exhibits a maximum corresponding with  $\text{NaHg}_2$ ; Bohariwalla and others obtain two discontinuities, one at 0.079

per cent Na and one at 0.272 per cent Na; while Davies and Evans report only one at 0.272 per cent Na." This treatment does not seem to give a correct picture of the facts. As a matter of fact the first, third, and fourth of these papers agree within the limits of experimental error. The agreement is far from perfect, but seemed to the original investigators satisfactory. Thus, to quote Davies and Evans, "It is difficult to decide with certainty whether these discontinuities in the curves are real, owing to the experimental difficulties;" and again, referring to their work and that of Hine, "It is seen that on the whole the results are in fairly good agreement." Bohariwalla states, "These breaks in the conductivity concentration curves in the case of sodium and potassium amalgams occur at the same composition as have been found by Hine." These data refer to amalgams of from 0 to 5 atom per cent sodium. Vanstone, on the other hand, was working with amalgams containing from 50-100 atom per cent sodium, and therefore his paper is quite irrelevant to the point in question.

The second instance of marked variation in properties has to do with the reactivity of amalgams prepared by Willstätter, Seitz, and Bumm (6) in iron, porcelain, or hessian crucibles. Since Willstätter considered the impurities present sufficient to account for the difference in the behavior of these amalgams, this does not seem to be evidence that pure amalgams have properties which depend on the method of preparation.

The next data to be discussed are those obtained by Vanstone for the phase diagram of sodium amalgams. Paranype and Joshi state, "At all concentrations he observed persistent superfusion and supercooling, which indicates that the freezing point of an amalgam is not definite but extends over a small range of temperature." This conclusion seems to be based on the rather unusual use of the word, "superfusion." The following quotation from Vanstone indicates that the phenomenon observed is nothing more than ordinary supercooling. To quote Vanstone, "The alloy was heated until entirely liquid, then allowed to cool slowly, meanwhile being vigorously stirred. The temperature was read every minute or half minute. In nearly all cases superfusion was observed and the points determined are the maximum temperature reached after overcooling." Nothing is said by Vanstone about heating curves, and we must therefore conclude that he is using the term "superfusion" as synonymous with supercooling. Supercooling is so commonly found for true solutions and pure compounds that it can not be taken to mean that there is any uncertainty regarding the melting point or transition temperature.

The fourth argument has to do with the uncertainty in the composition of the solid phase deduced from the phase diagram. This uncertainty arises chiefly from the fact that the curve is very steep in certain parts and there are many breaks in the curve. For example, in dilute solution Kurnakow states that it is uncertain whether the compound is  $\text{NaHg}_5$  or

$\text{NaHg}_6$ , while Schüller and Vanstone state that the compound is probably  $\text{NaHg}_4$ . It must be emphasized, however, that the disagreement is in the interpretation of the data and not in the data itself. These authors found the break in the temperature concentration curve at 17.95, 18.1, and 17.9 per cent sodium which is quite good agreement. The fact that the experimental data is of such a nature as to make the *authors* of these papers uncertain as to the composition of the solid phase does not indicate that the *solid phase* is of uncertain composition.

The last argument has to do with the change of viscosity of sodium amalgams with the time. The experimental work was carried out in the laboratory of Paranype and Joshi in 1928 but has never been published. In the absence of information regarding the methods of obtaining the data it is difficult to draw conclusions as to its significance. A possible explanation would be that the concentration of the amalgam was changing, owing either to surface oxidation or perhaps to incomplete solution of the solid amalgam, which melts at nearly  $360^\circ\text{C}$ . Since Paranype and Joshi state in another connection that their amalgams exhibit a scum on the surface when left in contact with their purest nitrogen perhaps the first of these explanations is the more probable. At any rate Paranype and Joshi come to the conclusion, in discussing other properties of amalgams, that they are lyophilic colloids. That the viscosity should increase with shaking is certainly not characteristic of lyophilic colloids and would indicate again that some other explanation must be sought for the viscosity data.

The above discussion leads to the conclusion that experiments cited by Paranype and Joshi do not indicate that the method of preparing pure sodium amalgams is of significance.

#### COLLOIDAL SOLUTION

The second proposition to be discussed is the question whether amalgams are colloidal or true solutions. Even though the method of preparing amalgams is of no significance, these solutions might be colloidal or partly colloidal. If such a solution were in mobile equilibrium it might be colloidal and still give properties determined by only the concentration temperature and pressure. This question cannot be answered with certainty, but one can scrutinize the arguments for and against the colloidal nature of the solution.

The argument of Paranype and Joshi in so far as it is based on the irreproducibility of the properties of amalgams has been discussed in the first part of this paper. They also give as evidence the fact that the transfer of sodium with the electric current is toward the cathode in concentrated amalgams and toward the anode in dilute solutions, thus resembling the behavior of certain colloidal solutions. If the colloid explanation were the

only one possible this would have to be considered an argument. As stated by Paranype and Joshi, however, there are several other possible explanations, so that one cannot consider this by itself as proof.

Several experimental facts are cited (the effect of ultra-violet light on amalgams, the viscosity and surface tension) to prove that the solution cannot be a lyophobic colloid. These are of course of interest after one has concluded that the solutions are colloidal, but do not either prove or disprove this point.

Paranype and Joshi also say that they would expect the solid phase to be crystalline, the heat of solution to be very large, and the vapor pressure of mercury to be less than would be calculated for true solution. These are certainly not attributes of ordinary lyophilic colloids and to say the least do not suggest the colloidal state.

The fact that direct and alternating current measurements give the same value for the conductivity seems to be of no significance, inasmuch as practically all of the conductivity is electronic. Thus it has been shown (7) that the transference number of sodium in these amalgams is less than  $10^{-5}$ . Conductance data would have to be precise to one part in one hundred thousand in order to give much information regarding the behavior of sodium. The data at hand do not begin to approach this degree of precision. If for no other reason than this, the conductance data are not significant in this connection.

In commenting on the work of Richards and Conant (8), Paranype and Joshi state that the deviations from the laws of ideal solution are to be attributed to either colloidal solution or experimental error. Were this true, practically all solutions would have to be considered colloidal, particularly aqueous solutions of strong electrolytes. The object of the experiments of Richards and Conant was to study a solution which gave large deviations from the laws of ideal solution, but they certainly had not the slightest thought that these deviations were due to "experimental error," or that they were due to the colloidal nature of the amalgams.

Finally the suggestion that the formation of scum on the surface of an amalgam is not always due to the formation of oxide but may be due to the disperse phase separating out on the surface, seems to be an argument based on faulty experimental data. Amalgams have frequently been kept for years by the writer in flasks which have been highly evacuated and baked to remove adsorbed water and during such intervals of time showed not the slightest tract of scum.

We may conclude, therefore, that no evidence has been presented which would justify one in concluding that these amalgams are colloidal. This, however, does not prove that amalgams are true solutions. There is some evidence, however, pointing toward true solutions. Perhaps the most convincing is to be found in vapor pressure data. It has been shown (9)

that the vapor pressure curve in dilute solutions is that calculated from Raoult's law, thus indicating that we are dealing with single atoms of sodium as the solute. These atoms of course may be solvated, but this would not constitute a colloidal solution as suggested by Paranype and Joshi. To quote them, ". . . Lewis, Adams, and Lanman formulated a theory and explained the initial decrease in conductivity . . . as due to large aggregates of mercury atoms gathering around a sodium atom . . . This conception of Lewis and coworkers appears to be very similar to the formation of a solutoidal colloid." One might infer from this statement that the hydration of ions in water solution is proof that aqueous solutions of strong electrolytes are colloidal.

The freezing point lowering in dilute amalgams is that calculated from Raoult's law. The calculated value is  $1.9^{\circ}\text{C}$ . per atom per cent and the experimental value is 1.9 (3), increasing in more concentrated solutions. A colloidal solution would give a smaller depression of the freezing point.

The excellent microphotographs of Vanstone, which show several types of crystals corresponding to the compounds indicated by the phase diagram, indicate that the solid phase is not colloidal.

The large heat of solution indicates that we cannot be dealing with a lyophobic colloid in which the disperse phase is sodium. Such a colloid would have a greater amount of energy in the form of surface energy instead of much less energy than the original components.

This leaves the possibility of a lyophilic reversible colloid in rather concentrated liquid amalgams. This is only a possibility, however, and until there is positive evidence one is bound to consider it as only a possibility.

#### SUMMARY

1. Contrary to the conclusion of Paranype and Joshi, there is no proof that the properties of pure sodium amalgams are determined by the method of preparation.

2. The hypothesis that sodium amalgams are colloidal rests upon certain properties which are common to the amalgams and to certain colloidal solutions. Since these properties can be accounted for in other ways, there is no proof at present that sodium amalgams are colloidal.

3. The following facts either prove or constitute strong evidence that sodium amalgams are true solutions.

(a) The freezing point depression of mercury in dilute amalgams is that calculated for an ideal solution.

(b) The vapor pressure lowering is that calculated for an ideal solution. In more concentrated amalgams the lowering is greater than is calculated for an ideal solution. A colloidal solution should show a smaller lowering of the vapor pressure.

(c) The microphotographs of Vanstone of the solid phases indicated by the phase diagram show definite crystalline structure.

(d) The large amount of heat liberated during the formation of an amalgam proves that it cannot be a lyophobic colloid in which the disperse phase is sodium.

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