exact definitions. (Too much have we followed the good old practice, "*Wo ein Idee fehlt steckt man ein Wort hinein.*") We have a stupendous nomenclature, but do substances in the colloidal state have a measurable melting point (or something analogous to it)? We say that nitrocellulose is more soluble in acetone than in amyl acetate; but do colloids have a measurable solubility (or some analogous property)? Of what possible use is the measurement of the viscosity of a colloid if the viscosity is always a function of the particular shearing stress used and therefore not a definite property? When do colloidal solutions pass into true solutions? Gels are elastic, but how elastic? And what is a gel? Dr. Holmes quotes, page 43, with approval the interesting statement, "There is a definite connection between the boiling point, the viscosity and the heat of dilution of a solution of salt and its solvent power for cellulose." How is this solvent power measured, what is this connection and why does it exist? Several experiments in this manual are pretty without teaching much. In other cases the lesson is lost because chemists are in disagreement. It seems obvious to the reviewer that there is great need for more fundamental work on colloidal materials. And perhaps it is not too daring to hope that chemists will be found in agreement when the generalizations are sufficiently broad and far-reaching. Such work should serve not only as a basis for sound theory but offer simple quantitative experiments for instructional purposes of the highest pedagogical value.

EUGENE C. BINGHAM

SPECIAL ARTICLES

PHASE REVERSAL IN PROTOPLASM AND EMULSIONS

THE reversal of phases in oil emulsions by electrolytes was discovered by Clowes.[1] Clowes worked with olive oil emulsions in which the aqueous phase was a soap solution, the soap being added directly or formed through saponification of the oleic acid in the olive oil by an aqueous phase of NaOH. Clowes found that, when the salt of a bivalent cation ($CaCl_2$) is in excess in the aqueous phase, the emulsion is of the water-in-oil type, and when the hydroxide of the monovalent cation Na is in excess, the emulsion is of the oil-in-water type. Clowes came to some very interesting and far reaching conclusions on the basis of his experiments. It does not appear that he worked with emulsions in which the stabilizing agent is some colloid other than soap.

Clowes saw in the behavior of oil and water emulsions (in which soap is the emulsifier) an explanation of changes in protoplasmic permeability. It is now believed (by some biologists) that monovalent cations increase permeability of the plasma membrane, while bivalent cations decrease permeability. The hydroxide of the monovalent cation Na produces in an oil emulsion (with a soap stabilizer) a system in which the continuous phase is water. Such a system would be readily permeable to water soluble substances. Salts of bivalent cations, such as $CaCl_2$, produce an emulsion in which oil is the continuous phase. Such a system would be impermeable to water soluble substances.

On the basis of the similarity of the reactions of oil emulsions and of protoplasm to mono- and bivalent cations, Clowes has conceived of living protoplasm in contact with water as a system which is, within the protoplasmic mass, a dispersion of proteins, lipoids, etc., in water, and, at its surface, a system of the reverse type, in which water is dispersed in an external continuous fatty or lipoid phase. Clowes does not, however, regard the surface layer of protoplasm as a system in which the aqueous phase is wholly discontinuous, but rather as a system in which the continuous lipoid phase is permeated by water channels, *i.e.,* as an emulsion which is near the reversal point.

Clowes has assumed that the stabilizer active in the supposed protoplasmic emulsion is either soap or a substance which is like soap in its reaction to mono- and bivalent electrolytes. While soaps are present in protoplasm it does not seem likely that they are the emulsifier which determines the behavior of the supposed living emulsion when other possible emulsifiers such as proteins and lipoids are present in much greater quantities.

I had the pleasure of discussing phase reversal in emulsions with Mr. Hatschek, of London.

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[1] Clowes, G. H. A., "Protoplasmic equilibrium," *Jour. Phys. Chem.*, 1916, xx, 407-451.

Mr. Hatschek called my attention to the fact that if the emulsifier in an oil emulsion is some colloid other than soap, for example, gum arabic, the emulsion will not reverse when a bivalent electrolyte is added to it. With the kind permission of Mr. Hatschek I have repeated and extended his preliminary experiments.

The manner of making the stabilizers and the emulsions, with also the methods employed in determining the type of system, will all be fully described in a subsequent publication.

Oil emulsions in which sodium oleate or sodium stearate is the emulsifier are of the oil-in-water type and are reversible with $BaCl_2$.

Oil emulsions with casein, gliadin, cholesterin, or cephaelin as the aqueous phase, are of the water-in-oil type and are reversible with NaOH.

Oil emulsions in which saponin (senegin, smilacin), gelatose, gum arabic, albumin, lecithin, or a plant extract is the emulsifier, are oil-in-water systems which are *not* reversible with $BaCl_2$.

It is of interest to note that of three proteins, all present in protoplasm, the most abundant one, albumin, does not permit reversal, while the two others do; and of two lipoids, both constituents of living matter, one, lecithin, does not, and one, chloresterin, does permit reversal. Further, the plant extract (obtained by grinding and pressing fresh spinach), which one might expect to approach somewhat the chemical make-up of protoplasm, does not permit reversal.

Who can tell what the emulsifier in the supposed living emulsion actually is?

Since the hypothesis of Clowes rests on the assumption that the emulsifier in protoplasm is of that type which forms an emulsion which is reversible with $BaCl_2$ or NaOH, and since certain of the substances here experimented with as emulsifiers, are very abundant in protoplasm but form emulsions which are not reversible with $BaCl_2$ or NaOH, one is forced to conclude that, in view of the fact that we are totally ignorant of the actual nature of the active emulsifier in living matter, a theory of the mechanism of permeability changes which is based on the behavior of only one group of emulsions, must be regarded as a purely speculative hypothesis which rests on very uncertain evidence.

It is of further interest to note that NaCl will not reverse any of the reversible emulsions here studied, yet it is this salt which causes (in the opinion of some investigators) such a pronounced increase in the permeability of protoplasm.

Quite aside from the experimental facts here given, it should be pointed out that the hypothesis of Clowes, like so many other interesting speculations on protoplasmic behavior in general and on permeability changes in particular, rests on two very fundamental assumptions (in addition to the one above discussed) in support of which there is no substantial evidence.

It is assumed by Clowes, and indeed by most biologists as well, that protoplasm is an emulsion in which a reversal of phases is of common occurrence. The emulsion hypothesis of protoplasmic structure is still adhered to by many biologists in spite of the fact that there is in all physical chemistry no *conclusive* evidence that any lyophilic colloid, of which protoplasm is one, is a liquid-liquid system. That the dehydrated lyophilic colloids starch and cellulose are crystalline has been shown to be true by the work in Roentgen ray spectography of Herzog. Although this does not necessarily tell us what the hydrated colloid is like, the consensus of opinion among colloid chemists seems to be that the dispersed particles of the hydrated colloid, in a gelatin sol for example, are solid. In the process of hydration there apparently takes place a breaking down of larger crystalline aggregates into smaller ones, which may even approach the gelatine molecule in size. I believe that I am not misinterpreting the writings of McBain, Freundlich, Proctor[2] and Bachmann when I state they are of this general opinion.

Regardless of the physical nature of the colloidal particles—and after all, as Hatschek has pointed out, the distinction between liquid and solid becomes somewhat vague with particles approaching ultramicroscopic dimensions—there is no evidence that a reversal of phases takes place in the process of gel formation from the sols of lyophilic colloids. On the contrary, the work of Bachmann and Zsigmondy and of Mc-

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[2] Proctor, H. R., The structure of elastic jellies, *Phys. and Chem. of Colloids, Rep. Faraday Soc. and Phys. Soc.*, London, 1921, 40-43.

Bain has shown that in gelatin and in soaps, and therefore probably in many other if not all lyophilic colloids, *there is no reversal of phases in the formation of a gel,* but merely an aggregation of the colloidal particles—the dispersion medium in the sol is still the dispersion medium in the gel. The conception of a reversal of phases in the process of gelation owes its origin to the earlier supposition that the lyophilic colloids are liquid-liquid, "emulsoid" systems, an idea which is not now held by such chemists as Donnan, Freundlich, McBain and Zsigmondy. One wonders, therefore, how far we dare go in our phase reversal speculations on the mechanism of permeability changes and similar vital phenomena.

The full account of the experimental data here briefly reported will include a discussion of the remarkable behavior of the emulsion with a gelatose emulsifier. This is an emulsion of the oil-in-water type and is reversible, in the *same* direction with the hydroxide of either the bivalent cation Ba or the monovalent cation Na, but not with the salt of either cation. There will also be published data on the possible influence of acidity on phase reversal. That pH value is a factor in phase reversal is apparently true in certain cases, but that it is the determining factor in other cases is certainly not true. H-ion concentration must affect the ability of an emulsion to reverse through acting on the emulsifier—possibly the hydration power of the emulsifier—consequently, the effect of pH will differ in emulsions with different emulsifiers, and this the experiments show to be true.

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ACTIVE HYDROGEN BY THE ACTION OF AN ACID ON A METAL

EVIDENCE for the formation of active hydrogen from its positive ion in an acid has been negative. The reports of the latest workers in this field, Wendt and Landauer[1], show that there are certain difficulties to be met. The main one is to eliminate the moisture that accompanies a rapid evolution of hydrogen and at the same time not destroy the active hydrogen if any were formed. If the gas stream were too low a velocity the active component would decay before reaching the sulfur. Then if the velocity were too high the moisture carried over would form a protecting film on the powdered sulfur and prevent the reaction between the two to form hydrogen sulfide.

During the work on the activation of hydrogen by corona discharge it was found by Wendt and Grubb[2] that active hydrogen combines with pure nitrogen to give ammonia. This method of testing for active hydrogen can be used to good advantage where moisture is carried along with the evolved hydrogen, since the spray does not prevent the contact of active hydrogen and the nitrogen.

If hydrochloric acid or sulfuric acid is dropped upon metallic magnesium suspended in such a way that the metal is at no time immersed or partly covered with any large portion of liquid, the drop of acid can react with the metal in the shortest possible time. This gives off hydrogen very rapidly, in fact, almost explosively, and with a minimum quantity of spray. If this evolved hydrogen is brought in contact with pure nitrogen it is found that ammonia is formed readily. The active hydrogen was then passed through a plug of glass wool before coming in contact with the pure nitrogen. The activity of the hydrogen still persisted as shown by the formation of ammonia. Therefore, the activity of the hydrogen cannot be due to ions or atomic gas. But Langmuir[3] has shown that monatomic hydrogen does not react with nitrogen to form ammonia. In view of this fact, if we allow pure nitrogen to escape at the surface of the magnesium where the hydrogen is evolved we find a maximum quantity of ammonia formed. The amount of ammonia formed increases with an increase in the rate at which the acid is dropped upon the metal. This of course means that the amount of the active component varies with the velocity of the gas stream.

If the acid is dropped on the metal very slowly and the evolved hydrogen passed through glass wool before coming in contact with nitrogen, no ammonia is formed. This indicates that

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[1] Wendt and Landauer, *Jour. Am. Chem. Soc.,* xlii, 930, 1920; *Ibid,* xliv, 510, 1922.

[2] Wendt and Grubb, *Ibid,* xlii, 937, 1920.

[3] Langmuir, *Ibid,* xxxiv, 1324, 1912.