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THE VARIATION IN THE PHYSICAL PROPERTIES OF PRECIPITATED AND COLLOIDAL MANGANESE DIOXIDE FROM THE POINT OF VIEW OF PHYSICAL CHEMICAL EQUILIBRIUM.

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The preparation and some striking transformations of colloidal manganese dioxide were described in a previous paper.[1] The present paper is an attempt to explain, somewhat more fully, the changes previously observed on the basis of known facts, in the hope of thereby getting a somewhat more intimate insight into the nature of certain colloidal phenomena and the equilibria involved.

In the earlier paper the history of colloidal manganese dioxide was given and the preparation and transformations were described in detail. It was found, if a glucose solution is incompletely oxidized in the cold with potassium permanganate in the presence of a little alkali, that the colloidal manganese dioxide formed under these conditions at first increases in viscosity to give a viscous or gel stage which subsequently is transformed into a limpid liquid colloidal solution. The properties of the first stage correspond well with those of an emulsoid, while the latter stage seems more characteristically a suspensoid. It was shown that the transformations of the emulsoid stage are typical and would be normal in every way if it were not for the simultaneous transformation of the emulsoid into a suspensoid. It was noticed that the latter transformation takes place more rapidly the more alkali there is present. Since A. Mayer, G. Schaeffer and E. Terroine[2] had observed that particles of negatively charged colloids tend to diminish in size in the presence of alkali and to increase in size in the presence of acid, and since colloidal manganese dioxide is a negative colloid[3] it was natural to assume that the enormous drop in viscosity here was likewise due to a great diminution in the size of the emulsoid particles on passing into the suspensoid particles under the influence of alkali. But these changes as noted by Mayer, *et al.*, were relatively small as compared with those obtained with manganese dioxide. The only experiments in which a comparable transformation was observed that could be found in the literature, were those of Scarpa,[4] in which gum arabic and gelatin emulsoids in water were transformed into typical suspensoids by the addition of definite small

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[1] THIS JOURNAL, 35, 1079–91 (1915).

[2] *Compt. rend.*, 145, 918 (1907); 146, 484 (1908).

[3] Bredig and Marck, J. M. van Bemmelen, *Gedenkboek*, 342 (1910); for abstracts, cf. *Kolloid-Ztg.*, 8, 333 (1911); *Chem. Abs.*, 5, 2470.

[4] *Rend. soc. chim. ital.*, [2] 5, 375–9 (1913); *Kolloid-Ztg.*, 15, 8 (1914); *Chem. Abs.*, 8, 3522.

amounts of ethyl alcohol to the cold emulsoids. It was previously known that the addition of ethyl alcohol to these solutions would cause the gum or gelatin to separate as a precipitate,[1] but Scarpa found that by using smaller amounts of alcohol the suspensoid could be obtained. That a true suspensoid was formed was indicated by the enormous fall in viscosity, by its electrophoric properties and by the difference in its behavior toward inorganic ions. Scarpa explained the transformation as follows:

> "The addition of alcohol, the dehydrating properties of which are known (and which probably depend on the formation of the alcohol hydrates, which were discovered by measurements of the viscosity of its aqueous solutions), causes the removal of water from the emulsoid particles; this emulsoid must be conceived as formed of very small globules which are filled with water or a dilute solution of the substance (while their walls are composed of more concentrated solutions), or as possibly of ultramicroscopic droplets of the concentrated solution of the substance, which are suspended in the dilute solution of the same substance. In each case the result would be a contraction of the globules or droplets which finally leads to the appearance of suspensoid particles; the phenomenon would accordingly constitute a preliminary step toward the condition which according to P. P. v. Weimarn leads to the formation of the solid phase."

It is to be noted that Scarpa's transformation took place as the result of the addition of another substance to the system, while our own transformation of manganese dioxide took place as the result of compounds already present in the mixture, *i. e.*, represented the establishment of an equilibrium between the compounds that took part in the reaction. It will be shown below that this difference is not so significant as it at first seems.

Since Scarpa's explanation hinges on the dehydrating effect of ethyl alcohol, the question at once arises as to what agency in our own case produces this effect on the manganese dioxide colloid. Recently G. Poma and A. Patroni[2] studied the influence of neutral salts on the conditions of ions in solution. They used solutions of copper nitrate in the presence of nitrates of Rb, K, Na, Li, Sr, Ca and Mg as well as ethyl alcohol, in order to study the displacement of the equilibrium expressed thus

$$[Cu''] \rightleftarrows K[Cu(H_2O)''_n]$$

due to the presence of these compounds. If $[Cu''_0]$ represents the concentration of the Cu ion in the absence of neutral salts and $[Cu'']$ represents the concentration in the presence of neutral salts, then the addition of nitrates of K, Rb, Na and Li were found to increase the ratio

$$[Cu''_0] : [Cu''],$$

i. e., the concentration of Cu ions is increased by the presence of these salts. It was noted that the nitrates crystallizing with the greatest amount of water of crystallization produce the largest effect, and that the effect of the neutral salt is to displace the equilibrium

$$[Cu(H_2O)''_n] \rightleftarrows Cu'' + nH_2O$$

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[1] P. P. v. Weimarn, "Grundzüge d. Dispersoidchemie," p. 116; *Kolloid-Ztg.*, **2**, 78 (1907).

[2] *Z. physik. Chem.*, **87**, 196–214 (1914); *Chem. Abs.*, **8**, 2094.

to the right. If the above assumption is tenable Poma and Albonico[1] considered that the analogous effect should be observed in the hydrolysis and esterification equilibria of esters in the presence of a strong acid and of a neutral salt of the above type. Without attempting to report their results in full, one of the general conclusions drawn by them from their experiments was that the presence of a neutral salt changes the homogeneous equilibrium of esterification and hydrolysis as if part of the water present in the system were removed from an active role in the immediate equilibrium. This displacement depends on the concentration of the neutral salts used and on the nature of their cations; it increases rapidly with the diminution of the electroaffinity of the latter and thus the effect increases in the order K, Na, Li, Ca and Mg. As a whole the results may be completely explained by assuming that the neutral salts in solution form hydrates, the complexity of which increases with the decrease in the electroaffinity of their ions.

The work cited above shows rather conclusively that the hydration-dehydration phenomena in the case of ionizable crystalloids are true equilibria and are amenable to the laws that have been found to apply to chemical equilibria. If the general results described above are true for crystalloids there is no *a priori* reason why the same general results should not be true for colloids. As a matter of fact Galeotti, in 1904,[2] examined the precipitation of metallic compounds of the proteins and found that the composition of the precipitate depends on the composition of the solution with which it is in contact. From his results he was able to construct the triangular diagram for the ternary system: metallic salt–protein–water. He therefore concluded that this system obeys the thermodynamic laws of chemical equilibrium. From a study of the phase rule diagram for the ternary system: egg albumin–ammonium sulfate–water, the same conclusion was arrived at. Galeotti did not, however, consider the chemical and physical forces involved in these equilibria since he was primarily interested in establishing the application of the phase rule to these phenomena.[3]

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[1] *Atti accad. Lincei*, **24**, I, 747–54, 979–85; II, 43–51 (1915).

[2] "Über die sogenannten Metalverbindungen der Eiweisskörper nach der Theorie der Chemischen Gleichgewichte," *Z. physiol. Chem.*, 40, 492–547 (1904); "Über die Gleichgewichte zwischen Eiweisskörper und Elektrolyten. I. Eieralbumin, $(NH_4)_2SO_4$-H_2O," *Ibid.*, **44**, 461 (1905).

[3] No attempt has been made to determine who first thought of these processes of equilibria. A few instances in which the idea was most clearly stated were finally found and have been selected for a historical basis. The fact that none of the authors cited had found an earlier statement of the principle indicates how little emphasis has been placed on the matter. It seems that our widely accepted theories of osmosis and electrolytic dissociation, which are admittedly only accurately applicable to certain kinds of weak solutions, prevent us from thinking clearly about phenomena in intermediate and concentrated solutions.

In looking for facts that would assist in elucidating these phenomena it is found at once that another group of workers in studying the action of neutral salts and other compounds on emulsoids have found that the viscosity of emulsoids is diminished in many cases by the addition of these compounds. This diminution in viscosity is commonly ascribed to dehydration of the colloid particles and in the case of electronegative colloids the effect increases with the diminishing electroaffinity of the cations, as was noted in the equilibria studied by Poma and Albonico.

Now it seemed a simple matter to assume that the deductions of Galeotti for the three component heterogenous aqueous protein systems are applicable to colloids in general and that one of the factors in what are generally acknowledged to be complex equilibria (cf. Poma, *et al.*) is the hydration ⇄ dehydration equilibrium. It was of interest to apply this conception to the colloidal manganese dioxide system. It was also important to learn whether the existence of other equilibria could be deduced from the experimental observations.

Experiments with Acetone.

Since the role of glucose as a colloid protector in the preparation of colloidal manganese dioxide was not understood, a series of experiments was carried out in which acetone was used instead of glucose. In this series 2 g. of pure acetone were diluted to 1 liter with water containing potassium hydroxide, as follows:

(1) 0. g. KOH
(2) 1.2 g. KOH
(3) 2.43 g. KOH
(4) 3.63 g. KOH
(5) 4.86 g. KOH
(6) 6.06 g. KOH
(7) 7.29 g. KOH
(8) 8.49 g. KOH
(9) 9.72 g. KOH
(10) 10.92 g. KOH
(11) 12.15 g. KOH
(12) 14.58 g. KOH
(13) 19.55 g. KOH
(14) 38.88 g. KOH
(15) 77.76 g. KOH
(16) 155.52 g. KOH

A small amount (about 0.2 g.) potassium permanganate was added to each bottle and the mixture agitated vigorously for about 15 seconds. The reduction to green potassium permanganate was more prompt the greater the potassium hydroxide concentration. The contents of bottle number (1) showed no reduction at all after standing 18 hours. In all of the others the character of the manganese dioxide precipitate after standing 18 hours showed an interesting variation in the various experiments. The precipitates in numbers (2), (3), (4) and (5) were very voluminous and in the remainder the volume gradually diminished until in the last three or four experiments of the series it was relatively small.

At the end of the second day, after having added the above amount of permanganate three times, the experiments stood as follows: (1) unreduced; (2) and (3) very dark brown flocculent manganese dioxide precipitate one inch deep; the precipitates in the remainder are similar except that the thickness of the precipitate layer is progressively thinner as the concentration of the alkali increases. This progressive diminution in the thickness of the precipitated layer is evident in number (6) and becomes more and more marked on passing gradually to number (16). After agitating the mixtures it was noted that the ones having the higher alkali content settled most quickly. However, in the last four or five experiments of the series only the upper one half of the liquid is quite clear after standing quietly for a few hours, showing that there are some very fine particles present in these cases.

After the addition of potassium permanganate had been continued for 9 days it became increasingly evident that with age the marked differences in the character of the precipitates was gradually diminishing. During the first few days the new portion of manganese dioxide precipitate floated on top of the older portion of the precipitate as a thick flocculent layer, but this difference in the character of the older and new portions of the precipitate diminished as the experiments were continued, owing perhaps to changes in the composition of the solution or to the increasing bulk of the precipitate.

After standing for nine months there was scarcely any perceptible difference in the physical character of the precipitated manganese dioxide. This would indicate that in this case a small amount of alkali acting for a long time has about the same effect as a larger amount acting for a short time.[1]

From the above it is clear that although in this case colloidal manganese dioxide was not obtained in the emulsoid-suspensoid form, the amorphous form, which is truly colloidal according to J. M. van Bemmelen,[2] shows variations in its physical characteristics which are strictly comparable and analogous to the emulsoid-suspensoid stages.

In thinking of the possible explanations of the variations in the physical character of the precipitated or amorphous colloidal manganese dioxide it seems that there are two possibilities: (1) the differences in the precipitate are due to differences in the size of particles; (2) the differences are due to variations in the density of the particles. If (1) is correct then on long standing the fine particles would finally settle down to nearly the same extent as the coarse ones since they would be capable of being packed together even more densely than the larger ones. But on standing many hours the supernatant liquid in the solutions of low alkali content is clear, and the precipitated layer is several times as thick as in the experiments containing more alkali. Since the particles in the more alkaline experiments are obviously finer, these precipitates should be the slowest to settle. The contrary was observed. Thus Explanation 1 does not hold. In considering the second explanation it must be recalled that a chemical

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[1] Observations, on precipitated manganese dioxide, similar to those described above were made in the oxidation of glucose with potassium permanganate, in the presence of variable amounts of alkali (THIS JOURNAL, **36**, 160–6 (1916)).

[2] "Die Absorption," p. 90 (1910).

compound will have the same density whatever the size of its particles, so that *a priori* Explanation 2 only becomes possible if it is assumed that something has combined to a variable extent with the manganese dioxide precipitate. Since the alkali content of the precipitated manganese dioxide seems to be rather constant, whereas the water content is known to be quite variable, it is simple to assume that the amount of water associated with the manganese dioxide is indeed variable. Since water has a much smaller density than manganese dioxide, those precipitates containing the most combined or adsorbed water would settle more and more slowly the more nearly their density approached that of water. At the same time the bulk of the precipitate would be expected, as was observed, to increase owing to the presence of the water. Explanation 2 therefore coincides with the observed facts.

As was noted above, the character of the precipitates had not assumed a definite form until some hours had elapsed. We are therefore warranted in assuming that the initial state from which the observed state arose was closely similar in each case. That is, if we apply the principle of neutral salt effect as observed by Poma, *et al.*, and started with hydrated manganese dioxide in the presence of variable amounts of alkali, the rate at which it would be dehydrated would in accordance with the law of mass action increase with increase in the concentration of the alkali. This is in accordance with the observed facts. Thus it is evident that so far as alkali concentration is concerned the dehydration of amorphous precipitated manganese dioxide is a true equilibrium.

The difficulty with the conclusion drawn in the preceding paragraph is that it is based on an assumption concerning the conditions in the beginning of the transformation that could not be followed by direct observation. *If we turn now to the observations made with the emulsoid-suspensoid form* of colloidal manganese dioxide (*loc. cit.*) we can follow the early stages of the transformation of the potassium permanganate much more clearly.

In any aqueous colloidal system containing a neutral salt, there are, it seems, besides the ionic equilibria, at least seven types of molecular equilibria: three molecular association $\leftrightarrows$ molecular dissociation and three hydration $\rightleftarrows$ dehydration equilibria and one "adsorption equilibrium" as follows:

(1) $x\text{H}_2\text{O} \rightleftarrows (\text{H}_2\text{O})_x$
(2) $x \text{ salt} \rightleftarrows (\text{salt})_x$
(3) $x \text{ Colloid} \rightleftarrows (\text{Colloid})_x$
(4) $[x \text{ salt} \rightleftarrows (\text{salt})_x] \rightleftarrows [x\text{H}_2\text{O} \rightleftarrows (\text{H}_2\text{O})_x]$
(5) $[x \text{ Colloid} \rightleftarrows (\text{Colloid})_x] \rightleftarrows [v\text{H}_2\text{O} \rightleftarrows (\text{H}_2\text{O})_x]$
(6) $[x \text{ salt} \rightleftarrows (\text{salt})_x] \rightleftarrows [x \text{ Colloid} \rightleftarrows (\text{Colloid})_x]$
(7) Equilibrium 4 $\rightleftarrows$ Equilibrium 5

That is, in (1), (2) and (3) the simple molecules are in equilibrium with their polymers. In (4) the salt equilibrium is in equilibrium with the water equilibrium. The product in this case would be the salt hydrates. In (5) the colloid equilibrium is in equilibrium with the water equilibrium. The product in this case would be the colloid hydrates. In (6) the salt equilibrium is in equilibrium with the colloid equilibrium. The product in this case would be the "absorption compounds." In (7) we have the hydrated form of "Equilibrium 6, *i. e.*, the salt-hydrate Equilibrium 4 in equilibrium with the colloid-hydrate Equilibrium 5. The result in this case is the establishment of equilibrium among the products of Equilibria 4, 5 and 6.[1]

In the case of the emulsoid-suspensoid manganese dioxide we started with prepared solutions of potassium permanganate and glucose containing some alkali. In each solution the water and the solutes (*i. e.*, Equilibria 1, 2 and 3) were presumably in equilibrium. When, however, the potassium permanganate solution was gradually added to the glucose solution in the cold a reaction took place which resulted in the reduction of permanganate to manganese dioxide. We now have the additional association Equilibrium 3, since manganese dioxide is colloidal. Although the strong color of permanganate solutions has been ascribed to complex associated molecules, the polymeric tendencies become relatively enormous in manganese dioxide, so that we can observe the color changes after the permanganate color is all gone and the enormous increase in viscosity during the short interval following the reduction. That this change is due to polymerization is indicated by the corresponding changes in color and viscosity in homogeneous systems such as styrol, isoprene, etc. Since the energy balance is so favorable to this polymerization, as indicated by its great velocity, the reasonable expectation is that the viscosity will continue to increase, as is noted in the case of styrol and isoprene. But this was not the case. The viscosity increases up to a certain maximum and what happens subsequently depends in part on the initial concentration of the alkali. If sufficient or excess alkali was present the gel begins to "melt" more or less quickly, depending on the concentration of the alkali and on the temperature.

At the beginning the potassium permanganate and its ions are in equilibrium with the water in which they exist. The manganese dioxide to which it is reduced in the reaction[2] has a strong affinity for water and no doubt tends to inherit the water of the permanganate from which it is

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[1] The equilibria have all been written in the molecular form. In our own case this seems simpler and so far quite satisfactory. But it seems certain that in many colloids the equilibria for the ions would be very significant. There are a number of other interesting considerations which could have been drawn into the discussion but which have been reserved for the discussion of other experiments.

[2] van Bemmelen, *Die Absorption*, p. 90 (1910).

derived. The potassium salts have a strong affinity for water likewise. We have thus set up a new equilibrium. An examination of our seven equilibria shows that the one that is most significant in this latter stage is the salt-hydrate $\rightleftarrows$ colloid-hydrate Equilibrium 7. Since the experimental result in this case is the transformation of the emulsoid into the suspensoid it is clear that the equilibrium is in favor of the salt-hydrate side and we again have the dehydration discussed above for the amorphous colloidal manganese dioxide taking place.

In the earlier paper it was stated that "All the properties of colloidal manganese dioxide may therefore be explained by the simultaneous action of two forces: the one tending to condense and precipitate the colloid and the other tending to disperse the colloid. The former is a very rapid-acting process and is hastened by increase in temperature and absence of alkali. The latter is a slow-acting process in any case, but can be accelerated greatly by relatively small increases in the alkali concentration and less markedly by increase in temperature up to a certain rather low maximum." From the above it would seem that the first force mentioned is the mutual affinity of the manganese dioxide molecules tending to polymerize the manganese dioxide up to a highly complex molecular aggregate and therefore involves Equilibrium 3. The second force mentioned is a much feebler, therefore more slow-acting force, which controls the equilibria of the dehydration of the manganese dioxide aggregates, *i. e.*, Equilibrium 7. The relative greatness of the first force, as compared with what is observed in other colloids ordinarily, explains why manganese dioxide is so frequently found in the amorphous colloidal form described above instead of the emulsoid-suspensoid form. Moreover, it seems simple to assume that the colloid protecting action of glucose consists in preventing the association Equilibrium 3 from completing the polymerization by virtue possibly simply of mechanical interference. Thus if glucose is substituted for salt in Equilibrium 6 its protective action may consist in the formation of an "adsorption compound." At the same time the free glucose by virtue of its dehydrating power favors the result obtained from Equilibrium 7. Thus if we conceive of the energies involved in these changes as composed of an intensity and a capacity factor it is clear that the intensity factor of the first force involved is very favorable, while it is the capacity factor that is most significant in the second force.

Summary.

It has been previously found that colloidal manganese dioxide prepared from aqueous solutions of glucose and potassium permangante in the presence of some alkali underwent colloidal transformations which varied strikingly with the conditions and which seemed to be definitely dependent on equilibria, the nature of which was not known. It has now been shown

that the amorphous colloidal manganese dioxide obtained by reducing permanganate with acetone in the presence of variable amounts of alkali undergoes changes comparable with those of the emulsoid-suspensoid type of manganese dioxide. On the basis of certain results of other workers the attempt was made to interpret the experimental data for both types of colloids on the basis of two types of dynamic equilibria: (1) molecular association $\rightleftarrows$ molecular dissociation; (2) hydration $\leftrightarrows$ dehydration. It was found that the experimental observations readily fit into such an interpretation.

It is thought that the point of view developed here will be of much interest in the elucidation of a number of other chemical and biological phenomena and further work along these lines is under way.

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NONAQUEOUS SOLUTIONS.

I. CHEMICAL REACTIONS IN ISOAMYL ALCOHOL SOLUTIONS.

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Not many investigations have been made of reactions between inorganic salts in solvents other than water. The most extensive study in this field is that of A. Naumann[1] and his students, who have determined the solubilities of a number of salts and their reactions in acetone, ethyl acetate, methyl acetate, pyridine and acetonitrile. Aside from these investigations, there may be gleaned from chemical literature a considerable number of isolated observations in this field.

The solubility of anhydrous inorganic salts in organic solvents has received considerable attention, but there is much uncertainty as to the dependability of some of the earlier measurements. Values obtained by different investigators are often widely different, and there have been found some cases in which the effect of temperature on solubility is wrongly stated.

The following paper records observations of reactions between anhydrous inorganic salts dissolved in dry isoamyl alcohol. Such salts were used as dissolve readily in the solvent.

Experimental Details.

All glassware used in this work was first carefully cleaned and dried in the usual way. Just previous to use each piece was further dried by passing dry air through it for at least half an hour, the air for this purpose being dried with sulfuric acid and phosphorus pentoxide.

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[1] *Ber.*, **37**, 3600, 4328, 4609 (1904); **42**, 3789 (1909); **43**, 313 (1910); **47**, 247, 1369 (1914).