

MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS: INTERACTION
BETWEEN COLLOIDAL ANTIMONY SULPHIDE AND COLLOIDAL
FERRIC HYDROXIDE AND THE EQUILIBRIUM DIALYSATE
OF COLLOIDAL FERRIC HYDROXIDE

By P. M. BARVE AND A. K. JAMBOTKAR

By a modified process of dialysis, colloidal ferric hydroxide and its "equilibrium dialysate" of nearly the same ionic environments have been compared for their powers as coagulating agents. It is found that in mutual coagulation the colloidal ferric hydroxide particles play a very important part, and in fact, they may be taken to act as polyvalent cations.

Dialysis of a colloidal solution of ferric hydroxide has been a subject of numerous investigations. Ferric hydroxide sol, when prepared by the hydrolysis of ferric chloride at an elevated temperature, contains ferric chloride, which has remained unhydrolysed, and hydrochloric acid formed as a result of hydrolysis. Changes in the composition of the intermicellary liquid are brought about when the colloidal solution is submitted to dialysis. These changes create a marked effect on the properties of the colloidal solution as a whole. Desai and Barve (*Trans. Nat. Inst. Sci. India*, 1939, 2 39) have fully dealt with the changes brought about by dialysis in the case of ferric hydroxide. They have shown therein that the cataphoretic speed of the colloidal particles increases, reaches a maximum, and then decreases; the conductivity, however, decreases continually, and the stability, as determined by flocculation values with electrolytes, also decreases continually with progress of dialysis. Desai and Borkar (*Trans. Faraday Soc.*, 1933, 29, 1269), Dhar and collaborators (*J. Phys. Chem.*, 1920, 26, 700) and Mukherjee and co-workers (this *Journal*, 1931, 8, 373; 1933, 10, 27) have supported the conclusions reached by Desai and Barve (*loc. cit.*).

Among the investigations of the properties of colloidal ferric hydroxide with progressive dialysis, the study of its power to coagulate mutually another colloid, namely antimony sulphide, was specially undertaken. The properties of antimony sulphide remained unchanged as it was not submitted to dialysis or any other treatment. It was prepared by dropping slowly a 0.5% solution of tartar emetic in water, saturated with hydrogen sulphide through which H_2S gas was slowly bubbled, the excess of the gas being driven out by passing hydrogen through the sol so formed.

In case of colloidal ferric hydroxide, the coagulating power is made up of the effect of the pure colloid and the electrolytes present in the intermicellary liquid. The process of dialysis "purifies" the colloid, and hence in the later period of dialysis, the coagulating power is more and more due to the colloid and less and less due to the intermicellary liquid.

EXPERIMENTAL

To ascertain the coagulating effect of the pure colloid alone, the following modified process of dialysis was adopted.

A colloidal ferric hydroxide solution was placed in a parchment paper bag and suspended in conductivity water. The water outside the bag, in which the electrolytes of the intermicellary liquid diffused, became the dialysate and went on increasing in its conductivity till it reached a maximum value at which it remained stationary. This means that an equilibrium has reached between the colloid and the dialysate as regards the diffusion of the electrolytes in the intermicellary liquid. Usually this condition was attained within 48 to 72 hours. At this stage the dialysate was removed, as also a part of the colloid for quantitative analysis. The dialysate was then entirely replaced by conductivity water and the process repeated as indicated above for every stage of dialysis. This dialysate is termed the "equilibrium dialysate".

In the process of dialysis, the dialysing membrane allows a free passage to the electrolytes present in the intermicellary liquid, but not to the colloid particles. By adopting the process of dialysis, as stated above, the distribution of the electrolytes between the colloid and the dialysate at equilibrium is governed by the Donnan equilibrium. On analysis of the colloid and the dialysate Mukherjee and co-workers (*loc. cit.*) have shown that the ultrafiltrate is poorer in chloride ions but richer in hydrogen ions and of a higher specific conductivity than that of the residual sol.

The coagulating power of the colloidal solution and of the "equilibrium dialysate" was measured by finding out the volume of the respective solutions required for the coagulation of 2 c.c. of the antimony sulphide sol (the total volume of the mixture being kept constant at 10 c.c.). The flocculation of this negatively charged antimony sulphide sol by the colloidal ferric hydroxide, dialysed to different extents, is a case of mutual coagulation, whereas the coagulation of the same antimony sulphide sol by the "equilibrium dialysate" is a case of simple electrolytic coagulation brought about by the positive ions of the electrolyte present in the "equilibrium dialysate". Mutual coagulation, as stated by Weiser and Chapman (*J. Phys. Chem.*, 1931, 35, 543, 1932, 36, 714), is governed by (1) electrical neutralisation of the charge, (2) mutual adsorption of the colloidal particles, (3) interaction between stabilising ions and (4) presence of the excess of free electrolytes in the sol.

The various results obtained by adopting the above process of dialysis gave a better insight into the mechanism of mutual coagulation.

TABLE I
Conductivity.

Stage of dialysis.	Days from the start.	Sp. conductance	
		Colloid.	Eq. dialysate.
1	0	37.80×10^{-3}	...
2	5	17.30	17.37×10^{-3}
3	10	10.00	10.00
4	13	7.20	7.20
5	16	4.95	4.65
6	19	3.33	2.91
7	21	2.70	2.30
8	26	2.65	2.10

TABLE II
Free iron and chloride content.

Stage of dialysis.	Free iron content		Chloride content	
	Colloid.	Eq. dialysate.	Colloid.	Eq. dialysate.
1	4.20 g./litre	...	9.55 g./litre	...
2	2.24	1.12 g./litre	4.40	3.50 g./litre
3	0.84	0.78	2.20	1.32
4	0.36	0.34	1.42	0.90
5	0.164	0.112	0.99	0.46
6	0.075	0.060	0.166	0.099
7	0.011	0.008	0.036	0.027
8	0.020	0.010

TABLE III

Stage of dialysis.	Charge on colloid particles	Coagulation values	
		Colloid.	Eq. dialysate.
1	$27.6 \times 10^{-6} \text{ cm} / \text{volt/cm./sec.}$	0.20 c.c.	...
2	40.1	0.40	0.55 c.c.
3	55.3	0.55	0.75
4	75.0	0.75	1.85
5	82.8	0.85	5.90
6	51.5	1.15	...
7	42.1	1.25	...
8	30.1	1.45	...

DISCUSSION

The dialysis has been carried out in eight stages covering 26 days.

The conductivity (Table I, Fig. 1), it will be observed, decreases continually in both the cases. The conductivity of the colloid, however, does not differ much from that of the "equilibrium dialysate".

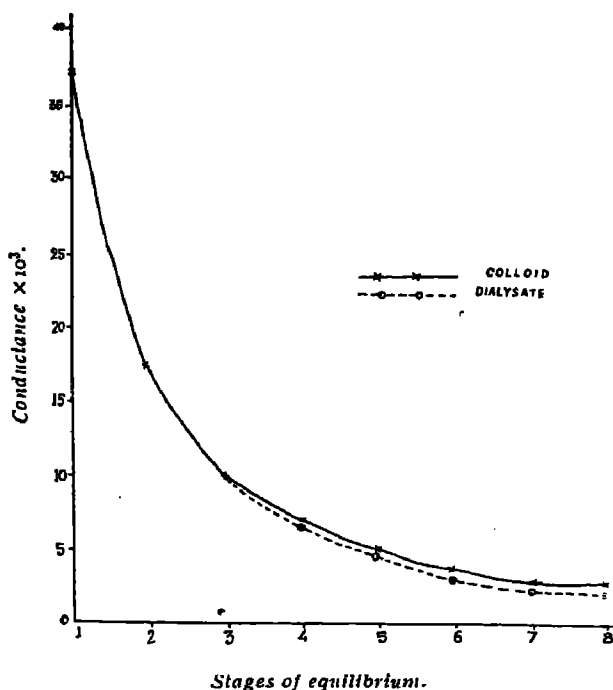
The free iron content of the colloid and that of the "equilibrium dialysate" are given in Table II and Fig 2. It will be observed that the concentration of the free iron in both of them is very nearly equal, showing thereby that the ionic environment of both the colloid and the "equilibrium dialysate", as far as the ferric ions are concerned, is nearly the same.

Along with the iron content, the chloride content of the colloid and the "equilibrium dialysate" is given in Table II. It is clear, that though the chloride ion concentration in the colloid is considerably higher than that of the "equilibrium dialysate", particularly in the earlier stages of dialysis, both of them tend to zero. This may be due to the adsorption of the chloride ions on the outer surface of the electrical double layer.

The cataphoretic speed of the colloidal particles increases, reaches a maximum in the fifth stage (16 days) and then decreases, with progress of dialysis. This supports the observations of Desai and Barve (*loc. cit.*).

The values obtained for the mutual coagulation of 2 c.c. of the negatively charged antimony sulphide sol, by the colloidal ferric hydroxide and those obtained for the coagulation of an equal amount of the same antimony sulphide sol by the "equilibrium dialysate" are given in Table III. In the case of the coagulation of the antimony sulphide

FIG. 1.

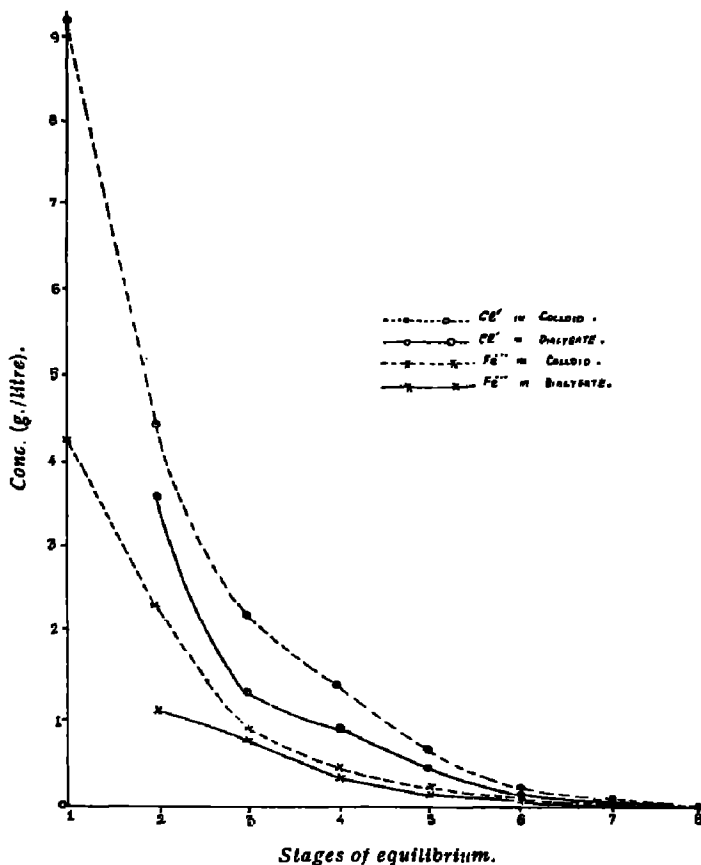
Conductance of colloidal $F(OH)_3$ and eq. dialysate.

by the "equilibrium dialysate", it will be observed that the coagulation values can be obtained up to the fifth stage (16 days) of dialysis only. After this period the coagulating power of the "equilibrium dialysate" is incapable of coagulating the sol. This clearly shows that the concentration of the electrolytes in the "equilibrium" dialysate progressively decreases to such a low value that it cannot coagulate the antimony sulphide sol at all.

The values obtained for the mutual coagulation of the antimony sulphide sol by the colloidal ferric hydroxide go on increasing gradually with its progressive dialysis and no maximum is observed. It may be observed that during this period of dialysis the cataphoretic speed increases, reaches a maximum and then decreases. In the present investigation, allowing for a slight variation in the distribution of the electrolytes between the colloid and the "equilibrium dialysate" due to the influence of the Donnan equilibrium, one can estimate, virtually, the effect of the intermicellar liquid alone and the effect of the same along with the pure colloid particles that are present in the sol. By subtracting one effect from the other, one can get a fairly good idea of the individual coagulating effect of the pure colloidal particles.

As has been mentioned in the introduction, in mutual coagulation any one of the factors or all of them may work simultaneously. The interaction of stabilising ions does not arise here as both the colloids, ferric hydroxide and antimony sulphide, are acidic. The coagulation of the antimony sulphide by the "equilibrium dialysate" is

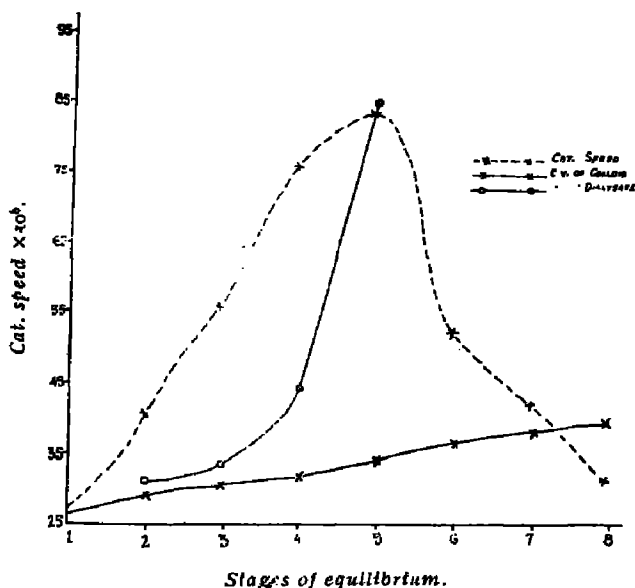
FIG. 2.

Total Fe⁺⁺⁺ and Cl⁻ in the colloid and eq. dialysate.

a case of simple coagulation by electrolytes. As antimony sulphide sol is negatively charged, only the positively charged ions, like the ferric ions, will be effective in coagulation. The concentration of the ferric ions in the colloidal solution and the "equilibrium dialysate" is nearly the same. If only the ferric ions were responsible for coagulation, the values obtained with both of them ought to have been almost the same. The colloidal particles are, however, acting as coagulating ions. Hence, in the case of the colloid, the coagulating power is the combined effect of the ferric ions and the colloidal particles. As the dialysis proceeds, the effect of the ferric ions continually diminishes. The individual effect of the ferric ions alone may be taken to be equal to the effect of the "equilibrium dialysate" as the concentration of the ferric ions in both of them is nearly the same. As the "equilibrium dialysate", obtained after the fifth stage of dialysis, ceases to coagulate the antimony sulphide sol, the values obtained for the colloid after this period may be taken to be the effect of the colloid particles alone. As the size of the colloid particles, as compared with the ferric chloride molecules, is very

FIG. 3

Coagulation value of the colloid of diarsate and cat. speed of colloid.



large, numerous ferric chloride molecules must have undergone hydrolysis to build the colloidal ferric hydroxide particle. The number of colloid particles so formed will naturally be extremely small in comparison with the number of ferric ions which are used up. In spite of small number, colloidal ferric hydroxide particles are highly effective in coagulation. They might therefore be functioning as multivalent coagulating ions with a valency many times more than three. It should, however, be remembered that the process of mutual coagulation is necessarily much more complicated and it is assumed only for the sake of simplicity, that the effect of the colloid and the intermolecular liquid is purely additive.

After the fifth stage of dialysis, it is found that the charge on the colloid decreases and the amount of the colloidal solution required for coagulating the same amount of the antimony sulphide sol increases. This is what one would expect on theoretical grounds, as both the charge and the concentration of the ferric ions are decreasing. The constitution of the antimony sulphide sol remains unchanged as it is not subjected to dialysis, and hence, the effect of the antimony sulphide sol on the colloidal ferric hydroxide may be taken to be constant. It should, however, be emphasized that the process of coagulation being not so simple, the difference between the two values is not necessarily an exact indication of the effect of colloidal particles alone. It is quite sufficient though to give one a clear idea about the influence of colloidal ferric hydroxide particles in mutual coagulation.