

Studies on Manganese Ferrocyanide Sol. Part III. Studies on the Conductivity during Slow Coagulation by Electrolytes

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An attempt has been made in the present work to throw some light on the mechanism of the changes in electrical conductance of the manganese ferrocyanide sol during the process of slow coagulation with LiCl, KCl, BaCl₂, SnCl₂, AlCl₃ and Th(NO₃)₄.

Manganese ferrocyanide sol was obtained by mixing potassium ferrocyanide and manganese chloride both B.D.H. Analar as described in our previous communication¹. The intermicellar liquid (Potassium ferrocyanide solution) having the same conductance as that of the sol was prepared by dissolving potassium ferrocyanide in conductivity water. The conductance of the sol and the intermicellar liquid was determined on the lines suggested by Pauli², Chaturvedi and Bhattacharya³. The amount of electrolyte required to coagulate the sol in one hour was at first determined by the visual surface-separation method. After mixing this amount of the electrolyte with the sol the conductivity was determined at different intervals of time. This process was repeated by mixing the intermicellar liquid with the same amount of electrolyte. The sol, the electrolytes and the intermicellar liquid were placed in separate Pyrex tubes in the Gallenkamp thermostat before and after mixing, the temperature was maintained at 20±0.1°. Electrical conductivity was determined by Sarfaas Conductivity Bridge using a dipping type conductivity cell. All these operations were carried out in dark room using red lamp, as dilute aqueous solution of potassium ferrocyanide undergoes the photo-reaction on exposure to sun light⁴.

The results are plotted in Figs. 1 & 2 (curves a to f). From these observations it may be concluded that ion exchange phenomenon like adsorption, is an instantaneous process.

The conductivity of the sol and the coagulating electrolyte is in all cases greater than that of the intermicellar liquid containing the same amount of electrolyte except in case of LiCl, where however not much difference was noted. Black dots indicate value of intermicellar liquid+LiCl. The difference in the conductivity between the sol and the intermicellar liquid system also seems to depend on the nature of the precipitating electrolytes. With higher valency of precipitating ions, the difference in conductance is greater than with monovalent ions except with the quadrivalent Th⁴⁺ ion. This is likely due to the formation of the Th Fe (CN)₆.

1. Joshi and Hari Mohan, *This Journal*.
2. Pauli, *Kolloid Z.*, 1937, 60, 175.
3. Chaturvedi and Bhattacharya, *This Journal*, 1954, 31, 132.
4. Asperger, *Trans. Faraday Soc.*, 1932, 28, 617.

On adding the electrolyte the conductivity instantaneously shoots upto the maximum both in the case of the sol and the intermicellar liquid, but there is an appreciable difference in the conductivities of the coagulating sol and the intermicellar liquid + electrolyte. This difference is obviously connected with the mechanism of coagulation.

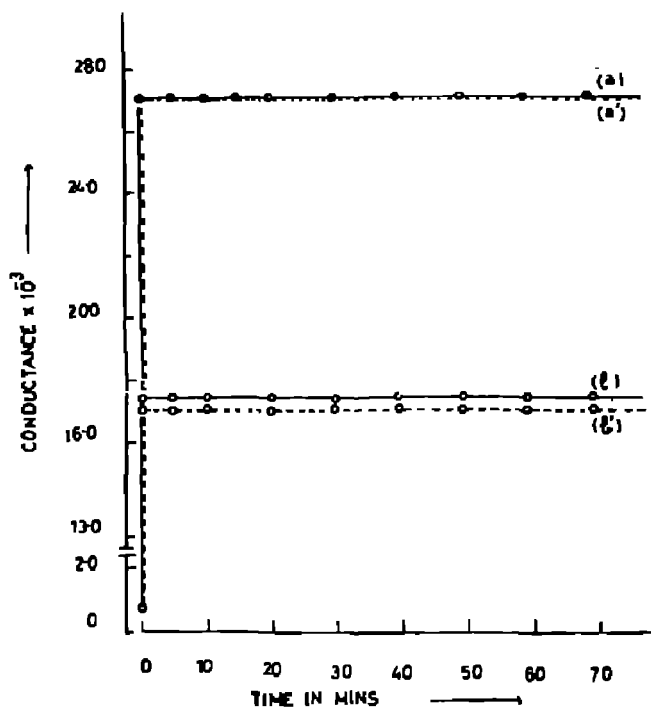


FIG. 1.

FIG. 1 Conductivity variations during slow coagulation of Manganese ferrocyanide sol.

(colloid content of the sol = 3.8 gms/litre)

(a) Sol + LiCl

(a') Intermicellar liquid + LiCl

(b) Sol + KCl

(b') Intermicellar liquid + KCl

In the case of $AlCl_3$, unlike that of KCl, LiCl, and $SrCl_2$, there is a slight lowering of the conductance afterwards, instead of a jump, as in other cases. It is suggested to be due to some surface reaction. Al^{3+} ions being sufficiently hydrolysable, some aluminium hydroxide is formed by surface reaction, and the H^+ ions in the system would thus decrease, thereby the conductance is lowered. These results are in conformity with the conclusions of Chaturvedi and Coworkers^{3,5}.

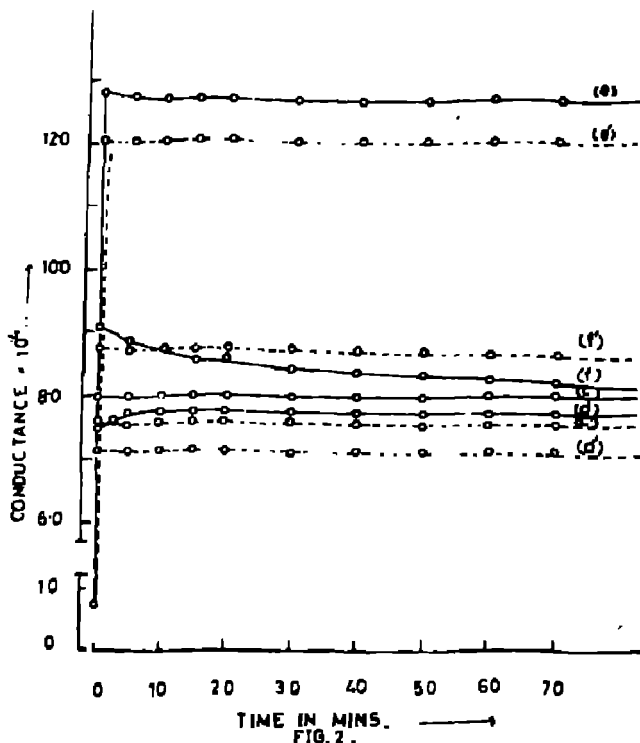


FIG. 2. Conductivity variations during slow coagulation of Manganese ferrocyanide sol.

- (a) Sol + SrCl_2
- (b) Intermicellar liquid + SrCl_2
- (c) Sol + BaCl_2
- (d) Intermicellar liquid + BaCl_2
- (e) Sol + AlCl_3
- (f) Intermicellar liquid + AlCl_3
- (g) Sol + $\text{Th}(\text{NO}_3)_4$
- (h) Intermicellar liquid + $\text{Th}(\text{NO}_3)_4$

These results, however, do not show any relationship between the growing size of the particles and the corresponding conductance of the system as should be expected from the formula given by Smoluchowski⁶.

Further work in this line is in progress.

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⁶ Smoluchowski, *Polymer J.*, 1905, 6, 525.