

Stability and Electrokinetic Potential of Nickel Ferrocyanide Sol

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A well-dialysed nickel ferrocyanide sol has been prepared and the electrokinetic potential has been determined by electro-osmotic as well as electrophoretic methods. Correction for surface conductance has been applied by using an equation of the form $1/\zeta_a = 1/\zeta + m/S$. The true ζ -potential for rapid rate of coagulation has been found to be somewhat less than that obtained for the slow rate. The data lead to the conclusion that a given rate of coagulation is characterised by a definite value of true ζ -potential, independent of valency of the coagulating ions used.

All previous experimental evidences in favour of or against Powis' theory¹ of critical coagulation potential and Hardy's theory² of coagulation at the isoelectric point are of doubtful validity owing to the neglect of surface conductance^{3,4} and relaxation⁵⁻⁷ effects. Ghosh *et al.*⁸⁻¹⁰ have shown that the true electrokinetic potential of As_2S_3 , TiO_2 , and AgI sols can be determined in presence of equicoagulating concentrations of electrolytes and have concluded that a given rate of coagulation of a colloid is characterised by a definite value of true zeta-potential, independent of the valency of the counter ions used. For electro-osmosis, Ghosh¹¹ has deduced the expression:

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + \frac{m}{S}$$

where ζ_a represents the apparent electrokinetic potential calculated from the electro-osmotic data, using the Smoluchowski equation; ζ , the true electrokinetic potential; S , the bulk specific conductance of the electrolyte, filling the pores of the diaphragm; m is equal to $2 \alpha \chi / rS$. α represents the specific surface conductance, r , the average radius of a typical pore in the diaphragm, and

$$\alpha = \frac{3}{2} \cdot \frac{V_1}{V_2} \cdot \frac{r}{R}$$

R being the radius of the spherical particles forming the diaphragm. V_1 and V_2 represent the volumes of the solid and liquid respectively in the diaphragm.

1. *Z. physikal. Chem.*, 1915, **89**, 180.
2. *Proc. Roy. Soc.*, 1900, **A66**, 110.
3. Rutgers, *Trans. Faraday Soc.*, 1940, **36**, 89.
4. Bikerman, *ibid.*, 1940, **36**, 154.
5. Henry, *Proc. Roy. Soc.*, 1931, **A133**, 106.
6. Overbeek, "Advances in Colloid Science", Vol. III.
7. Boeth, *Proc. Roy. Soc.*, 1950, **A203**, 514.
8. *Trans. Faraday Soc.*, 1953, **49**, 1477.
9. Ghosh and Rakshit, *Science & Culture*, 1953, **18**, 498.
10. *Trans. Faraday Soc.*, 1954, **50**, 729.
11. *this Journal*, 1955, **32**, 69; *Naturwiss.*, 1955, **42**, 121.

A similar expression :

$$\frac{1}{\zeta_0} = \frac{1}{\zeta} + \frac{m'}{S}$$

has been used by Ghosh and Ray¹² for electrophoresis, where m' represents $\kappa/\zeta R$. The above equation can be derived directly from the equations of Booth¹³ and Henry¹⁴ under conditions in which κR is sufficiently large, κ being the characteristic term of the Debye-Hückel equation.

The present communication records our experimental results on nickel ferrocyanide sol.

EXPERIMENTAL

Nickel ferrocyanide sol was prepared by addition of a decinormal solution of nickel chloride to an excess of a decinormal potassium ferrocyanide solution with constant stirring and dialysing the resulting sol against distilled water for one month. It was then stored in a Jena flask for two weeks. The negatively charged dirty green sol had a pH of 7.32, sp. conductance at 25° = 8.66×10^{-5} mho, and concentration = 0.31 g./100 ml.

Determination of the Equicoagulating Concentration.—KCl, BaCl₂, and AlCl₃ and mixtures of BaCl₂-KCl and AlCl₃-KCl were used as electrolytes for coagulation.

The time allowed for the rapid rate of coagulation was 15 mins. and for the slow rate, 18 hours, followed by centrifuging at a constant speed for 2 mins. in each case. The minimum concentration of an electrolyte, which, when mixed with an equal volume of the sol, produced a clear supernatant liquid in the prescribed time, was taken as the equicoagulating concentration, the exact value of which was determined by trial.

Electro-osmotic Experiment at 25°

Nickel ferrocyanide sol (100 ml) was mixed with an equal volume of an electrolyte of the desired concentration and after the prescribed time (15 mins. or 18 hours) the mixture was centrifuged and the coagula were transferred into a U-shaped tube. The volume of the diaphragm was kept the same in each experiment by regulating the time of centrifuging the U-tube. The supernatant liquid, separated from the coagula, was used for filling the U-tube. Mukherjee's moving-bubble method¹⁵ was followed in measuring the electro-osmotic velocity.

Electrophoretic Experiment at 25°

In this experiment, the sol (20 ml) was mixed with an electrolyte (20 ml) of the desired concentration for slow rate of coagulation. After half an hour, the bigger particles were

12. *Nature*, 1955, **176**, 1080.

13. *Trans. Faraday Soc.*, 1948, **44**, 955.

14. *Ibid.*, 1948, **44**, 1021.

15. Mukherjee *et al.*, *Nature*, 1922, **110**, 732.

separated from the mixture by centrifuging at a suitable speed for two minutes. The sol-electrolyte mixture was then used for filling the lower part of a modified form of Burton's U-tube apparatus¹⁶. Supernatant liquid, prepared by mixing the sol and electrolyte, followed by centrifuging after 24 hours, was used and Ag/AgCl electrodes were introduced into each limb of the U-tube. The movement of the colloid-liquid boundary was noted under a known current and the average value of the upward and downward motion was taken.

Specific conductance and *pH* of the supernatant solutions were measured. The *pH* values of different solutions were found to remain practically the same (4.65).

DISCUSSION

It will be noticed from Fig. 1 (curves I and II) that a linear relationship between $1/\zeta_a$ and $1/S$ exists both for the slow and the rapid rates of coagulation. The extrapolated values of true ζ -potential for rapid and slow rates of coagulation are 17 and 22 mv respectively. For slow coagulation, the slope of the straight line obtained by plotting $1/\zeta_a$, found by electro-osmotic method against $1/S$, is greater than that of the line obtained by plotting $1/\zeta_a$, found by the electrophoretic method. The corresponding values of *m* and *m'* are 3.125×10^{-6} and 2.27×10^{-6} respectively.

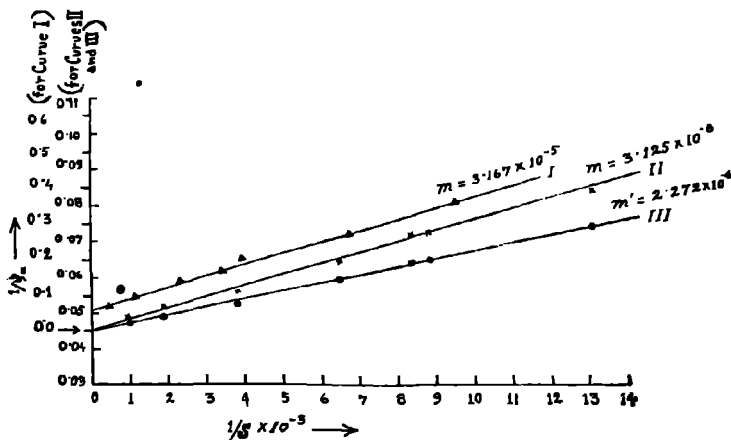


FIG. 1

It may be mentioned that for slow coagulation, the true ζ found by electro-osmotic method is in complete agreement with that found by the electrophoretic method. It may

therefore be concluded that for nickel ferrocyanide sol, a given rate of coagulation is characterised by a definite value of true zeta-potential, independent of the valency of the counter ions used.

It may also be pointed out that for a change in time of coagulation from 15 minutes to 18 hours, the corresponding change in true zeta-potential is quite small (17 to 22 mv).

The authors thank the authorities of the C.S.I.R. for the award of a senior research assistantship to one of them (S.B.).

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Received August 7, 1962.