On The Stability and Electrokinetic Potential of Ferric Hydroxide Sol

Nirmalendu Maitra

A fairly pure and stable ferric oxide sol has been prepared by a slight modification of Graham's method, with a view to ascertaining the existence of any relation between the stability and electrokinetic potential. The true zeta potential found for rapid rate of coagulation is 30.7 m.v. and that for ferric oxide gels is 46.5 m.v.

A systematic investigation has been undertaken to ascertain if a relation between the true zeta potential and rate of coagulation, as suggested by Ghosh,[1],[2] holds in the case of ferric hydroxide sol. With this object in view, use has been made of the following equations, which permitted the evaluation of true zeta potential of ferric hydroxide sol for the rapid rate of coagulation and that for ferric oxide gel.

(1) For Electroosmosis: Ghosh[1] suggested the equation,

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} \times m.\frac{1}{S} \qquad .. \qquad .. \qquad .. \qquad (1)$$

where, ζ_a = the apparent zeta potential,

ζ = the true zeta potential,

S = the specific bulk conductance of the supernatant solution

and $m = \dfrac{3x}{a\zeta r}$, ('a' represents the phase volume ratio of the liquid to solid form-

ing the diaphragm, 'x' is the specific surface conductance and 'r' is the radius of the particles.)

(2) For Microcataphoresis, the expression given by Ghosh et al.[2] is

$$\frac{1}{U_a} = \frac{1}{U} \times m'.\frac{1}{S} \qquad .. \qquad .. \qquad (2)$$

where U_a = The apparent mobility of the particles,

U = the true mobility of the particles,

$m' = \dfrac{x}{UR}$ where 'x' is the specific surface conductance and 'R', the radius of the particles.

EXPERIMENTAL

Preparation of the sol: Ferric Hydroxide sols can be obtained both in the positively and negatively charged states. Positively charged sols are generally prepared either by peptisation of a freshly formed gel or by the hydrolysis of ferric salts of univalent anions.

1. Ghosh, B. N., *Trans. Farad. Soc.*, 1953, **49**, 1977.

2. Ghosh, B.N., *Nature*, 1955, **176**, 1061.

A slight modification of the method of Graham[1], however, furnished a hydrosol of the desired quality.

To a $FeCl_3$ solution (80 gm. in 500 c.c. conductivity water) is added a saturated solution of $(NH_4)_2CO_3$, drop by drop with vigorous stirring until permanent precipitate is obtained. The precipitate is peptised with a dilute solution of $FeCl_3$ (1%). The volume of the sol thus prepared is made upto one litre by conductivity water. By repeating the above procedure, four litres of the sol are prepared and the whole lot is subjected to continuous hot-dialysis (45-55°) for 20 days. It is collected in a Jena flask and allowed to age for 20 days before use. The sol is positively charged. Its pH is 4.41 and the specific conductance at 25° is 2.90×10^{-4} mhO/cm.

Equicoagulating concentration of electrolytes. Coagulating concentration of different electrolytes which are just sufficient to bring about coagulation of a definite volume of the Ferric Hydroxide sol in equal times are termed equicoagulating concentrations and are determined in the following manner.

2 c.c. of the sol and 2 c.c. of the electrolyte solution are taken in separate clean and dry test tubes. The electrolyte (equal volume) is first added to the colloid and the mixture poured back again into the first tube so that the mixing is thorough. Any unnecessary jerking is avoided and the mixture left to itself for 15 minutes. If the colloid coagulated, there would be formed a sharp boundary, below which would be the coagula and above which the transparent liquid. The minimum concentration of the electrolyte which just causes complete flocculation of the sol, with separation of a clear meniscus is taken as the equicoagulating concentration. Trying with different concentrations of the same electrolyte and repeating the process for other electrolytes as well, the exact values of equicoagulating concentrations are found out. The following coagulants are used, KCl, K_2SO_4, $K_3Fe(CN)_6$ and mixtures of KCl and K_2SO_4, and K_2SO_4 and $K_3Fe(CN)_6$.

Equigelating concentrations of electrolytes: Since Ferric Oxide sol sets to gel when a suitable amount of electrolyte is added, concentrations of different electrolytes containing counter ions of different valency, which cause a given amount of the sol to set in a definite time have been determined These concentrations of different electrolytes are called equigelating concentrations and are determined in the following way.

2 c.c. of the sol and 0.5 c.c. of electrolyte are mixed with each other as usual and allowed to stand undisturbed. The concentrations of electrolytes which cause the sol to set in 15 minutes are taken as the equigelating concentrations. The time of gelation is determined by carefully tilting the test tubes, containing the sol electrolyte mixture slightly from time to time. The electrolytes used are KCl, K_2SO_4, $K_3Fe(CN)_6$ and mixtures of KCl and K_2SO_4 and K_2SO_4 and $K_3Fe(CN)_6$.

Electroosmotic Experiments with Ferric Oxide coagula at 25°: A definite volume (25 c.c.) of the Ferric Oxide sol is pipetted into a clean dry bottle and to it is added equal volume of electrolyte of the desired concentration. After allowing the mixture to stand for 15 minutes the coagula are separated from the supernatant solution by centrifuging the mixture at a suitable speed (2500 r.p.m.). The entire coagula are then transferred into the U-tube with a little supernatant solution and a diaphragm is made therein by centrifuging the sys-

3. Graham, *J. Chem. Soc.*, 1862, 15, 149,

tem at a suitable speed (2500 r.p.m.) for 20-30 minutes. For a particular set of experiments, the volume of the diaphragm with the U-tube is maintained the same by adjusting its time of rotation. This ensures the constancy in the value of 'm' assuming that 'x' remained constant at the equicoagulating point. The U-tube containing the diaphragm is filled with the supernatant liquid and electroosmotic velocity is measured by the moving air bubble method of Mukherjee *et al.*[4]

Electroosmotic Experiments with a Ferric Oxide gel at 25°: These have been produced by mixing 6 ml. of the Ferric Oxide sol with 1.5 ml. of the electrolyte solution of the requisite concentration and allowing the mixture to set to a gel in the U-tube. Electroosmotic experiments are now performed with the diaphragm of the Ferric Oxide gel, in contact with the supernatant solution, having the specific conductance of the gel.

Microcataphoretic Experiments with Ferric Oxide particles at 25°: The mobility of the colloidal particles was determined by means of a microcataphoretic apparatus, described by Chakraborty and Ghosh[5]. The microscope with which the particles are observed in the cell carried a micrometer scale in the eye piece. With the help of the scale, particles of the desired size can be selected very easily. The average time taken to cover a given distance for direct and reverse motion is used for calculation.

DISCUSSION

Fig. 1 represents the plot of the reciprocal of the apparent zeta potential against the reciprocal of the bulk specific conductivity, (equation-1) at the equicoagulating concentration of the electrolytes used. It will be observed that the plot provides a straight line in agreement with the equation of Ghosh. For rapid rate of coagulation (time of coagulation-15

ELECTRO OSMOSIS OF FERRIC OXIDE SOL.

FIG. 1
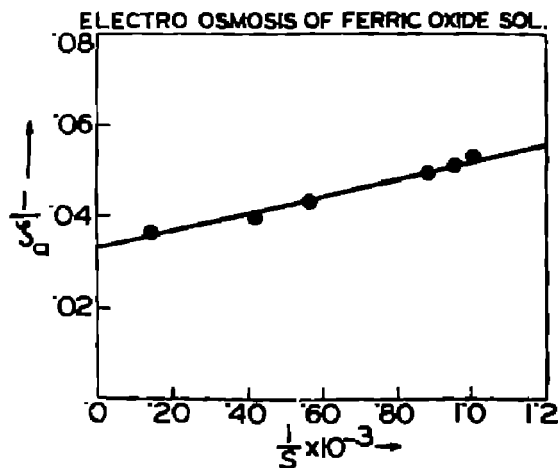
minutes) the value of the apparent zeta potential, obtained from electroosmotic measurements varies from 18.8 to 27.1 m.v. and the true zeta potential obtained from the inter-

4. Mukherjee, *This Journal*, 1927, **4**, 493.
5. Chakraborty and Ghosh, *This Journal*, 1963, **40**, 425.

cept on the reciprocal of the apparent zeta potential axis is 31.3 m.v. From the value of the true electrophoretic mobility U, (Fig. 2) the true zeta potential of the Ferric Oxide sol, in the presence of equicoagulating concentration of different electrolytes is calculated utilizing Smoluchowski's equation for electrophoresis. This is found to be 30.1 m.v. It may
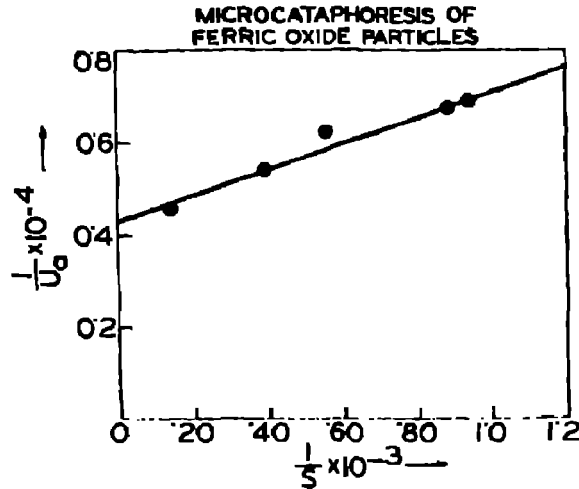

FIG. 2

therefore be concluded that the agreement between the values of true zeta potential obtained by two different methods is quite satisfactory and the mean value 30.7 m.v. may be taken to represent the true zeta potential of Ferric Oxide sol, in the zone of rapid coagulation.

Since microcataphoretic experiments are not possible with Ferric Oxide gels. the zeta potential of the gels have been measured by electroosmotic method only. A plot of the reciprocal of the apparent zeta potential against the reciprocal of the bulk specific conductivity (Fig. 3) yield a good straight line, thereby justifying the application of the equation-2
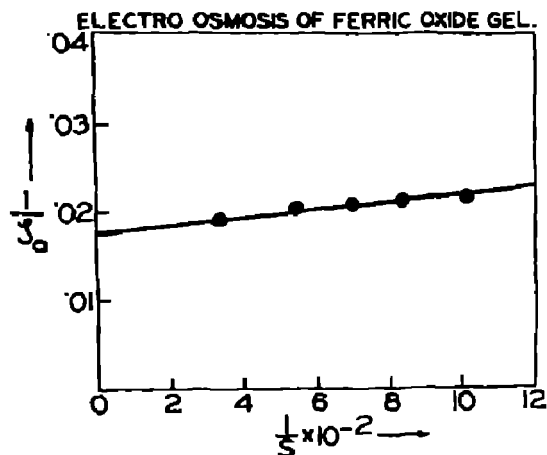

FIG. 3

of Ghosh, to the diaphragm of Ferric Oxide gels. From the intercept, the true zeta potential of Ferric Oxide gel in the presence of equigelating concentrations of different electrolytes is calculated. It is found to be 46.5 m.v. Thus it may be concluded that the zeta potential at which a sol sets to a gel is higher than at which the sol coagulates, the time required for gelation or coagulation being the same in each case.

Thus, a given rate of coagulation of the Ferric Hydroxide sol is characterised by a definite value of true zeta potential, which is independent of the valency of the counter ions used.

The author expresses his grateful thanks to Prof. B. N. Ghosh, D.Sc., F.N.I., Department of Chemistry, University of Calcutta, for the laboratory facilities.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALCUTTA,
CALCUTTA-9.