Stability and Electrokinetic Potential of Aluminium Arsenate Sol

B. N. Ghosh and S. Bandyopadhyay

Aluminium arsenate sol has been prepared with a view to ascertaining whether any relationship exists between the stability and electrokinetic potential of the colloid. A correction for surface conductance effect, appreciable for slow rate of coagulation, has been applied by using an expression:

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

The true zeta-potential for the rapid rate of coagulation is 11.5 mv and that for the slow rate is 17.6 mv, determined electro-osmotically.

From electrophoresis the true zetapotential comes out to be 18.1 mv.

A given rate of coagulation of the sol is characterised by a definite value of true zeta-potential, independent of the valency of the counter-ions used.

Theoretical and experimental work, carried out during the last twenty five years, have led to the conclusion that from electrokinetic measurements the true zeta-potential of colloidal particles can be found only when corrections due to surface conductance[3,4] and relaxation effects[5,7] are properly introduced into the Helmholtz-Smoluchowski equation[1,2]. All previous experimental data on electrokinetic potential of colloidal particles, in which such correction has not been made, are therefore of doubtful validity, especially if the concentration of the added electrolyte to the colloid is very low.

Assuming that in presence of equicoagulating concentrations of electrolytes, the specific surface conductance of the colloidal particles remains constant, Ghosh et al[8]. have derived the following equation for the evaluation of true zeta-potential from electro-osmotic measurements:

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

where ζ_a represents the electrokinetic potential calculated by using the Smoluchowski equation; ζ, the true electrokinetic potential; S, the bulk specific conductance of the electrolyte filling the pores of the diaphragm and $m = 3V_1 \chi / \zeta V_2 R$

1. Smoluchowski, Bull. Acad. Sci. Cracovie, 1903, 182.
2. Smoluchowski, "Graetz," Handbuch der Elektrizitat und des Magnetismus", II, p. 366, 1914.
3. Rutgers, Trans. Faraday Soc., 1940, 36, 69.
4. Bikerman, ibid., p. 154.
5. Henry, Proc. Roy. Soc., 1931, A133, 106.
6. Overbeek, "Advances in Colloid Science", Vol. III.
7. Booth, Proc. Roy. Soc., 1950, A203, 514.
8. Ghosh et al., this Journal, 1955, 32, 69.

V_1 and V_2 are the volumes of the coagula and the solution respectively contained in the diaphragm; R, the radius of the particles and χ, the specific surface conductance.

For electrophoresis they have used[9] a similar expression:

$$\frac{1}{\zeta_n} = \frac{1}{\zeta} + \frac{m'}{N}$$

(where $m' = \chi/\zeta R$) which can be derived directly from equation of Booth[10] or of Henry[11].

In the present communication the results of our experiments on aluminium arsenate sol have been recorded.

EXPERIMENTAL

Preparation of the Sol.—To a normal solution of disodium hydrogen arsenate, taken in a large beaker, a suitable excess of normal aluminium chloride solution was added in a thin stream with constant stirring and the sol was allowed to stand for half an hour. It was then transferred to cellophane bags, dialysed against distilled water for 15 days, and stored in a Jena flask for another two weeks. The positively charged milky white sol with a pH 3.6 had a specific conductance at $25° = 2.46 \times 10^{-4}$ mho. cm^{-1} and a concentration of 0.264 g./100 ml.

Equicoagulating Concentration of Electrolytes.—Chloride, sulphate, and citrate of potassium and mixtures of KCl-K$_2$SO$_4$ and KCl-K-citrate were used as electrolytes. Time allowed for coagulation was 15 mins. for rapid rate and 18 hours for slow rate, followed by centrifuging for 2 minutes at a constant speed in each case. The minimum concentration of an electrolyte, which just produced a clear supernatant solution by the above procedure, when mixed with an equal volume of sol, was taken as the equicoagulating concentration.

Electro-osmotic Experiment at 25°.—The sol (300ml) was mixed with an equal volume of an electrolyte of requisite concentration. After the prescribed time the mixture was centrifuged. The coagula separating were transferred to a U-shaped tube and by centrifuging a compact diaphragm was obtained, the volume of which was kept the same in each experiment. The velocity of electro-osmotic flow of water was measured by the moving-bubble method of Mukherjee *et al*[12].

Electrophoretic Experiment at 25°.—A modified form of Burton's U-tube apparatus[13] was used. Two reversible Ag/AgCl electrodes were used when the supernatant solution contained Cl ions and platinised platinum electrodes were used when K-citrate was selected

9. Ghosh *et al.*, *Nature*, 1955, **176**, 1080.
10. Booth, *Trans. Faraday Soc.*, 1948, **44**, 955.
11. Henry, *ibid.*, p. 1021.
12. Mukherjee *et al.*, *Nature*, 1922, **110**, 732.
13. Ghosh and co-workers, *Kolloid Z.*, 1948, **158**, 45.

as a coagulant. Equal volumes (40 ml) of the sol and the electrolyte solution of requisite concentration were mixed and after half an hour the mixture was centrifuged at a slow speed to separate the big particles. The supernatant mixture was used in filling the lower part of the U-tube. The upper part of the apparatus was filled with a clear supernatant solution, obtained by centrifuging the equicoagulating mixture of the sol and electrolyte after it had been allowed to stand for 24 hours. The distance moved by the colloid-super-natant liquid boundary under a given current in a given time was measured.

The pH and specific conductance of the supernatant solution in each case were also measured. The pH was found to remain practically the same, viz., 4.0.
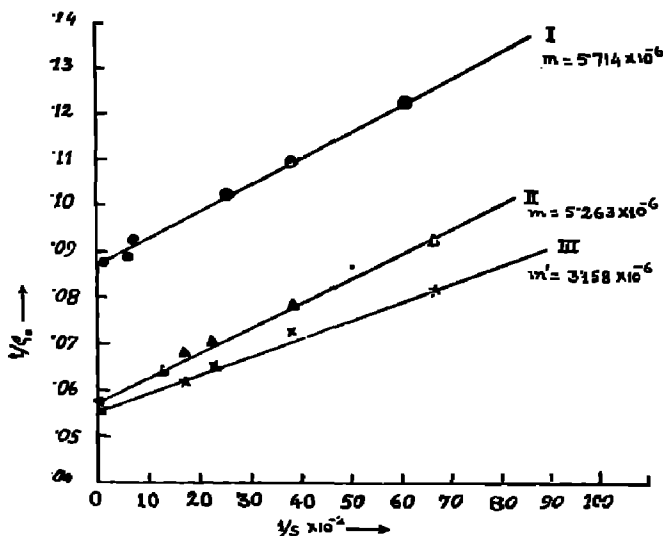

FIG. 1

DISCUSSION

It may be noticed from Fig. (1 curves I and II) that there is a linear relationship between $1/\zeta_a$ and $1/S$. From the intercept and slope of the straight line, the values for ζ and m have been found. The true zeta-potential comes out to be 11.5 mv for the rapid and 17.6 mv for the slow rates of coagulation. The variation of ζ_a, found by using electrolytes containing counter-ions of different valency, is quite small, e.g. 8.20 mv to 11.50 mv for rapid coagulation. The correction for the surface conductance effect is thus small for rapid coagulation. It is, however, quite marked for the slow rate of coagulation where ζ_a, determined by electro-osmotic method, varies from 10.90 mv to 17.30 mv.

For the slow coagulation, the surface-conductance effect is slightly less pronounced in the electrophoretic method than that in the electro-osmotic method. In this region ζ_a is found to vary from 12.4 to 17.9 mv. For slow coagulation also, a linear relationship between $1/\zeta_a$ and $1/S$ has been found. The value of true zeta-potential, found from the interception $1/\zeta_a$-axis is 18.1 mv. (vide Fig 1, curve III).

It may be pointed out that the electrophoretic as well as the electro-osmotic method leads to the same value, namely 17.9 mv (average of 17.6 and 18.1 mv) of true electrokinetic potential in the region of slow coagulation. Thus a given rate of coagulation is characterised by a definite value of true zeta-potential.

From the results we may conclude that a critical zone of zeta-potentials exists for any observable coagulation to occur by the addition of electrolytes to aluminium arsenate sol.

The authors express their grateful thanks to the C. S. I. R. for a research grant.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGES OF SCIENCE & TECHNOLOGY,
CALCUTTA-9.