STUDIES IN IRON OXIDE SOLS

Part I. Electrical Conductivity of Iron Oxide Sol

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In an investigation on the equivalent conductivity of colloidal sulphur sols, Bolam and Trivedi,[1] have shown that the equivalent conductivity of the bound polythionate *increases* with increase in the concentration. Thus the behaviour of sulphur sol is similar to the behaviour of soap solutions and paraffin chain electrolytes, in that at relatively high concentrations, the equivalent conductivity increases with the increase in the concentration. McBain[2] remarks: ".... any colloid which carries electrical charges will in some measure approach the behaviour of a typical colloidal electrolyte." Hartley[3] points out that the micelles may be regarded as highly polyvalent ions and the increase in conductivity is ascribed to the smoothing out of the variations in the distribution of oppositely charged ions. In the present investigation an attempt was made to see whether iron oxide sols show the anomalous increase in conductivity similar to sulphur sol and soap solutions.

Concentrated iron oxide sol was prepared. The conductivity of the sol with dilution as well as the concentrations of the various constituents were determined. Like the sulphur sol, the relative proportions of the colloid and the crystalloid constituents are not likely to change significantly on dilution; hence, the detailed study of sols of this type may throw light on the anomalous conductivity of colloidal electrolytes.

Experimental

Concentrated iron oxide sol was prepared by a modification of Graham's method.[4] Iron hydroxide was freshly precipitated from 500 ml. of a normal solution of ferric chloride by 4 N ammonia. The precipitate was thoroughly washed with water and suspended in 500 ml. of water. 4 N hydrochloric acid was gradually added while stirring. The sol obtained in this way was concentrated to about one-fourth the volume, and subjected to hot intermittent dialysis in a parchment paper bag for a period of one month. The diffusate was changed every day, distilled water at 60°–70° C. being used throughout. The dialysis was continued until the diffusate failed to give turbidity with silver nitrate.

ANALYSIS OF THE SOL

The iron oxide content of the sol was estimated by evaporating the sol to dryness. The total chloride was estimated as follows:—To an aliquot portion of the sol, excess of sodium hydroxide was added and the precipitate obtained was digested for three hours on a water-bath. An equivalent quantity of sulphuric acid was then added and after a further digesting of three hours on a water-bath, the precipitate was filtered. One gram of calcium carbonate was then added to neutralise the acid, and the solution was titrated with N/10 silver nitrate by Mohr's method. Duplicate experiments showed that the method was quite reproducible. Fixed and free hydrogen ions were estimated as follows:—To an aliquot portion of the sol, exactly one gram of sodium sulphate was added. The precipitate obtained was allowed to settle for three hours on a water-bath and kept at room temperature for several hours. The precipitate was then filtered and washed. The filtrate and the washings were titrated with N/10 sodium hydroxide. This method gives the free hydrogen ions in the sol. The results obtained were fairly reproducible.

The determination of the fixed hydrogen ions in the sol had to be done in an indirect manner, by determining the total hydrogen-ion concentration and the free hydrogen-ion concentration in the sol. The difference between the two gives fixed hydrogen-ion concentration in the sol. The method however was not very sensitive. The total hydrogen-ion concentration was estimated as follows:—To an aliquot portion of the sol, a definite quantity of standardised sodium hydroxide was added and the contents were heated on a water-bath to coarsen the particles. An amount of hydrochloric acid equivalent to the previously added sodium hydroxide was then added (this is done to avoid the filtration of the alkaline solution). After a further digestion of one hour iron oxide was filtered off, and the filtrate and the washings were titrated with standard sodium hydroxide. This gives the total hydrogen-ion concentration of the sol. The composition of the sol is given in Table I.

TABLE I

Sol	Concentration				Fixed H per gm. Fe_2O_3	$Fe^{\cdot\cdot\cdot}$ per gm. Fe_2O_3
	Iron oxide gm./l	Free H m.e./l	Fixed H m.e./l	Total Cl m.e./l		
Fe_2O_3	105·0	1·20	7·20	96·0	0·068	0·2781

THE DETERMINATION OF THE CONDUCTIVITY OF THE SOL

The conductivity of the sol was determined by using a Leeds and Northrup Potentiometer. The conductivity cell was specially platinized (Findlay[5]), and it was placed in a thermostat maintained at 34·5° C. An audiofrequency oscillator was used to supply 500 cycle A.C. current. The sol was diluted by mixing with conductivity water. 50 ml. of sol was taken and 50 ml. of conductivity water was added. This was termed 0·5 C. sol. Similarly 0·9 C., 0·8 C., etc., sols were prepared. The conductivity of the diluted sols was determined in two series. In one case, starting from the most concentrated sols, the conductivity was determined by proceeding to the diluted ones. In second case, the conductivity of the most dilute sol was first determined followed by the determination of the conductivity of the more concentrated sols. For every observation, several readings were taken which agreed fairly closely with one another. The specific conductivity of the conductivity water was also determined, but as it was very low ($1{\cdot}5\times10^{-6}$) in comparison with that of the sol, it was neglected. The specific conductivity of the sol is obtained after determining the resistance of N/10 KCl at 34·5° C. The value of the specific conductivity of N/10 KCl at 34·5° C. is obtained graphically by plotting the values of the conductivity of N/10 KCl at different temperatures (Jones and Bradshaw[6]). In Table II are given the relative concentrations of the sol and their resistances.

TABLE II

C	(Resistances)	Mean Resistance	R_c	$(1/R_c)\times10^3$
1·0	(133·9, 133·8, 133·7)	133·8	133·8	7·475
0·9	(154·5, 154·5, 154·6)	154·5	139·0	7·194
0·8	(175·6, 175·7, 175·5)	175·6	140·5	7·119
0·7	(202·0, 202·0, 202·0)	202·0	141·4	7·073
0·6	(236·6, 236·7, 237·0)	236·7	142·0	7·042
0·5	(265·7, 265·6, 265·5)	265·6	132·8	7·532
0·4	(311·8, 311·6, 311·3)	311·5	124·6	8·026
0·3	(365·6, 365·6, 365·6)	365·6	109·7	9·110
0·2	(431·2, 430·8, 430·4)	430·8	86·2	11·600

DISCUSSION

The data in Table II show that when the iron oxide sol is diluted, the value of the product R_c (resistance × concentration) increases. The fourth column gives the value of $(1/R_c)\times10^3$ which is therefore proportional to the specific conductivity of the sol. The value of R_c first increases with dilution and then decreases *rapidly* with further dilution. This is shown graphically in Fig. 1.

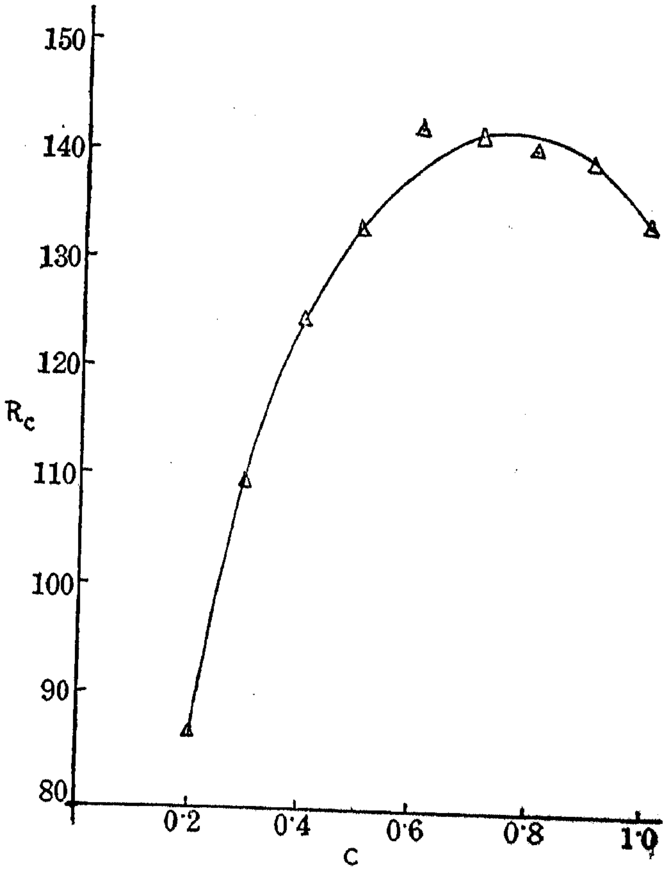

FIG. 1

The conductivity of the sol may be due to (*a*) free hydrochloric acid, (*b*) free ferric chloride, (*c*) fixed hydrochloric acid and (*d*) fixed ferric chloride. The qualitative test indicated that free ferric chloride was absent. Hence the specific conductivity of the sol minus the specific conductivity of the free hydrochloric acid may be taken as the conductivity of the iron oxide sol; *i.e.*, of the colloid with the absorbed gegenions. The specific conductivity of free hydrochloric acid was obtained by assuming the same temperature coefficient for hydrochloric acid as that for potassium chloride solution and obtaining the values of the specific conductivity of hydrochloric acid at 25° C. from the literature (Harned and Owen[7]).

The composition of the micelles can be calculated as follows:—From the total chloride content (m.e./l) the concentration of the hydrogen-ion, both fixed and free, is deducted. The concentration of fixed ferric ions is then equal to the residual chloride divided by three. It is obvious that in the case of dialysed sols, the stabilizing ions consist mostly of ferric ions.

The equivalent conductivity of the micelles is obtained on dividing the specific conductivity of the micelles by its concentration in terms of equivalents per litre. In Table III are given the concentration of chloride in m.e./l, the specific conductivity and the equivalent conductivity of the micelles.

TABLE III

Concentration of the sol	Concentration of Cl in the micelles (m.e./l)	Specific conductivity of the micelles (···×10^4)	Equivalent conductivity of the micelles
1·0	96·0	9·982	10·40
0·9	86·4	8·440	9·691
0·8	76·8	7·367	9·592
0·7	67·2	6·373	9·482
0·6	57·6	5·420	9·410
0·5	48·0	5·041	10·510
0·4	38·4	4·452	11·630
0·3	28·8	4·039	14·030
0·2	19·2	3·754	19·550

It is obvious that the conductivity of the micelles is only a fraction of the conductivity of the stabilizing ions, if dissolved in pure water. Even if it is assumed that the stabilizing electrolyte is wholly ferric chloride, its equivalent conductivity at the dilution and the temperature used in the experiments will be at least 90 to 100.* Thus the conductivity of the micelles is only of the order of 10%, *i.e.*, the bulk of the stabilizing ions is fixed, because they adhere to the micelles and hence their individuality with respect to charge, osmotic pressure, etc., is considerably reduced. This conclusion is in harmony with the results of McBain and Thomas,[8] who determined the transference numbers of ferric ions and chloride ions in ferric hydroxide sol. They conclude that 89·5 per cent. of the chloride counterions travel towards the cathode. Similar conclusions are reached by Bjerrum[9] in the case of colloidal chromium hydroxide sol; Ghosh[10] in the case of stannic oxide and Bolam and Trivedi[1] in the case of sulphur sols. In Fig. 2 is given the graph of the equivalent conductivity against the square root of the concentration of the bound chloride. The nature of the graph resembles very closely to the nature of the curve obtained in the case of soap

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* According to *International Critical Tables* [p. 233, Vol. VI (1929) McGraw Hill Books] the equivalent conductivity of ferric chloride is 66·5 at 18° C. when the concentration in, *milliformulaweight* is 500. The equivalent conductivity at 34·5° C. for the concentration used in the experiments will be considerably higher.

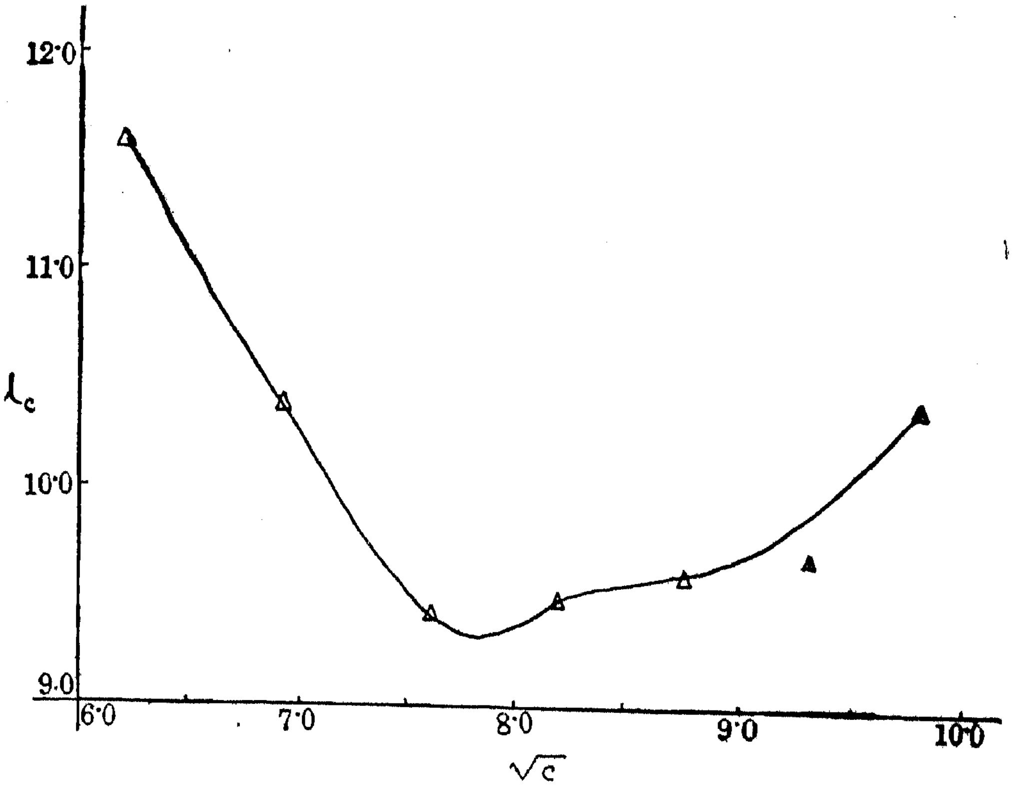

FIG. 2

solutions (McBain and Coworkers[2]). On dilution the equivalent conductivity first decreases and then increases *rapidly* (W. Kopczewski[11]). The curve thus passes through a minimum. It may be remarked that in the case of sulphur sols (Bolam and Trivedi[1]), the rapid increase in conductivity on further dilution was not obtained, as the electrodes adsorbed sulphur in some form or the other, making the measurement of the conductivity of the dilute sol difficult. The behaviour of iron oxide sol, like that of sulphur sol, may therefore be considered to give qualitative support to Hartley's theory.[3]

SUMMARY

Concentrated iron oxide sol of Graham type has been prepared and subjected to hot intermittent dialysis for a period of one month. The composition of the sol as well as the variation of the conductivity with dilution were determined. It has been found that the bulk of the stabilizing ions adhere to the micelles and the variation of the conductivity with dilution shows that the iron oxide sol behaves as a typical colloidal electrolyte.

ACKNOWLEDGEMENT

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