

# STUDIES IN IRON OXIDE SOLS

## Part II. Membrane Equilibrium in Iron Oxide Sol

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Received December 13, 1951

(Communicated by Dr. R. D. Desai, F.A.Sc.)

If a colloid like iron oxide sol is kept in a collodion bag and is allowed to come to an equilibrium with the diffusate outside the bag, then, there will be an unequal distribution of free electrolyte like hydrochloric acid across the membrane due to the following reasons:—The amount of free hydrogen ion per unit volume will be less within the bag than that without the bag, due to (a) the establishment of Donnan Membrane equilibrium effect (Donnan<sup>1</sup>) and (b) the volume occupied by the colloidal micelles ( $\text{Fe}_2\text{O}_3$  plus the water of hydration). On the other hand, adsorption of the hydrogen ions by the micelles will lead to the increase of the free hydrogen ions inside the bag as compared to that outside. In the case of iron oxide sol of Graham type, as in sulphur sol, the free hydrogen ions are not likely to be adsorbed (Bolam and Trivedi<sup>2</sup>). If the composition of the sol is determined and if further it is assumed that ten per cent. of the fixed hydrogen ions contribute to the membrane equilibrium effect, it will be possible to determine the extent of hydration in iron oxide sol (see discussion). Iron oxide sols are known to be hydrated (Freundlich<sup>3</sup>) but as far as we are aware few, if any, attempts have been made to estimate the extent of hydration.

### EXPERIMENTAL

In the present work, partially dialysed sols of Graham type were kept in collodion bags, suspended in water for three weeks until equilibrium was undoubtedly established. Care was taken to avoid evaporation and to protect the sol from light. The apparatus was kept at room temperature. Some difficulty was experienced in obtaining collodion prepared in a mixture of alcohol and ether. Most of the samples available in the market are prepared in methylated spirit instead of ethyl alcohol, and the bags obtained from such a sample of collodion were impermeable. Ultimately collodion prepared by Mallinckrodt Co. (U.S.A.) was obtained. The collodion bags were prepared by coating internal surface of pyrex glass tubes 1" × 8" in

a manner described by Hatschek.<sup>4</sup> Although the liquid was allowed to drain off very slowly from the test tube, so as to give an almost uniformly thick walled bag, it was not possible to obtain a membrane which retained the whole of the iron oxide sol. However, the concentration of the colloidal sol inside the bag was always much greater than that outside the bag. No attempt was made to measure the osmotic pressure that was developed. When equilibrium was attained, the sols inside and outside the bag were analysed for free hydrogen-ion concentration, bound hydrogen-ion concentration and the iron oxide content. For the purpose in view, the most important measurement was the determination of the free hydrogen-ion concentration inside and outside the bag. Hence, 25 ml. of the sol inside and outside the bag, were taken for the determination of the free hydrogen-ion concentration and 10 ml. of the sol inside and outside the bag, for the determination of the iron oxide content. The method of preparation of the sol and methods of chemical analysis have been given in a previous paper ("Studies in Iron Oxide Sols, I, Vol. 36, p. 530). In this case, however, as the quantity of sol was limited, the coagulum obtained by addition of sodium sulphate to the sol, was utilised for the determination of the fixed hydrogen-ion concentration. In Table I are given the data obtained in different experiments. The values in gm./l. ( $\text{Fe}_2\text{O}_3$ ) are obtained on multiplying the corresponding value of 10 ml. by 100, and the values of hydrogen-ion concentration, both fixed and free, in m.e./l. are obtained on multiplying the corresponding value by two. Hence a separate table is not given for the above quantities.

TABLE I

Sol No.	Gm. of iron oxide in 10 ml. of sol		Ml. of N/20 NaOH required by 25 ml. of sol for free H		Ml. of N/20 NaOH required by 25 ml. of sol for fixed H	
	"I"	"O"	"I"	"O"	"I"	"O"
1	0.269	0.008	5.7	7.0	3.1	0.3
2	0.241	0.004	6.4	8.7	5.0	0.2
3	0.253	0.009	6.7	8.4	5.9	0.5
4	0.251	0.019	6.9	8.7	6.5	0.4
5	0.258	0.012	7.3	9.0	4.7	0.3
6	0.263	0.006	6.9	9.4	3.3	0.2
7	0.248	0.013	7.3	9.2	6.6	0.3
8	0.240	0.008	6.4	7.9	4.0	0.3
9	0.242	0.014	6.5	8.1	4.2	0.3
10	0.261	0.004	6.7	9.1	4.6	0.3

## DISCUSSION

It is easy to see that the free hydrogen-ion concentration outside the membrane is considerably greater than that inside the membrane and that the difference in the free hydrogen-ion concentration is far beyond the experimental error. It may, therefore, be assumed that these differences are real and are due to (a) the membrane equilibrium effect and (b) the hydration effect, as the adsorption of the free hydrogen ions is not possible. If it is further assumed that only ten per cent. of the bound ions contribute to the membrane equilibrium effect (McBain and Thomas<sup>5</sup>), then the hydration of the micelles can be calculated in the following way:—According to Donnan's fundamental relation (T. R. Bolam<sup>6</sup>), and assuming that the activities of the chloride and the hydrogen ions are identical with their relatively low concentrations, we have:

$$(H_B)_I = \frac{[(H_F)_O]^2 - [(H_F)_I]^2}{[(H_F)_I]} \quad (1)$$

where  $(H_B)_I$  = concentration of bound hydrogen ions inside the bag  
 $(H_F)_I$  = the concentration of free hydrogen ions inside the bag and  
 $(H_F)_O$  = the concentration of free hydrogen ions outside the bag; all concentrations are expressed in m.e./l.

As only ten per cent. of the bound hydrogen ions are effective in membrane equilibrium, we can calculate "x", i.e., the concentration of free hydrogen ions outside the bag [the hypothetical value of  $(H_F)_O$ , if the difference between  $(H_F)_O$  and  $(H_F)_I$  is only due to the membrane equilibrium effect]. For calculations, the difference between  $(H_B)_I$  and  $(H_B)_O$  is used instead of  $(H_B)_I$ . In practice it was found that  $(H_F)_O$  was always higher than "x". The volume "V" occupied by the micelles, the apparent density "D" of the micelles and the specific hydrodynamic volume can be calculated by the equations similar to the equations given in the case of sulphur sol (Bolam and Trivedi<sup>2</sup>) and arsenic sulphide sol (Trivedi and Patani: Paper submitted to the *J.I.C.S.*):

$$D = \frac{[(H_F)_O] \times [(Fe_2O_3)_I - (Fe_2O_3)_O]}{1000 [(H_F)_O - "x"]} \quad (2)$$

The value of density D comes out to be much lower than the density of iron oxide (Mellor<sup>7</sup>). S. H. V. is the ratio of the actual and the apparent density of iron oxide. In Table II are given the calculated values of "x", the observed values of  $(H_F)_O$ , the apparent densities and the values of S.H.V. for different experiments.

TABLE II

Sol No.	Calculated value of "x" m.e./l.	Observed value of (H <sub>v</sub> ) <sub>o</sub> m.e./l.	Apparent density "D"	S.H.V.
1	11.7	14.0	0.159	30.93
2	13.3	17.4	0.101	48.87
3	13.9	16.8	0.141	34.85
4	14.4	17.4	0.135	36.40
5	15.0	18.0	0.148	33.29
6	14.1	18.8	0.103	47.79
7	15.2	18.4	0.135	36.40
8	13.2	15.8	0.141	34.85
9	13.4	16.2	0.132	37.26
10	13.8	18.2	0.106	46.23

It is easily seen that in all cases, the apparent density "D" is much lower than the actual density of iron oxide (4.913) and the values of S.H.V. are always greater than one. It therefore follows that the micelles contained water which is not acting as a solvent for hydrogen-ions. The average of S.H.V. is about 40 (it must be admitted that the figure obtained is liable to some error). Thus there are 39 ml. of non-solvent water to one ml. of iron oxide, or 39 gm. of water to 4.913 gm. of Fe<sub>2</sub>O<sub>3</sub> :—

There are  $(39/18) \times (1000/4.913) = 441$  millimoles of water to one gram of Fe<sub>2</sub>O<sub>3</sub>. Multiplying this by the molecular weight (160) of iron oxide:

$(160) \times (441/1000) = 70.56$ . Thus there are about 70 moles of water to one mol of iron oxide in the micelles.

Thus the micelles in the case of iron oxide sol are highly hydrated; the hydration in the case of iron oxide sol being much greater than that in the case of sulphur sol (Bolam and Trivedi<sup>2</sup>) or arsenic sulphide sol (Trivedi and Patani<sup>8</sup>). In Table III are given the millimoles of water per gram of colloid.

TABLE III

Name of the colloid	Millimoles of water/gm. of colloid
Sulphur .. ..	30.00
Arsenic sulphide .. ..	14.33
Iron oxide .. ..	441.00

The micelles in the case of iron oxide sol are highly hydrated, has been assumed by nearly all workers, and is borne out by the present investigation.

#### SUMMARY

The unequal distribution of an electrolyte across a semipermeable membrane, in the presence of iron oxide sol is partly due to the establishment of (a) the membrane equilibrium and (b) hydration of micelles. Assuming that ten per cent. of the bound hydrogen ions are active in membrane equilibrium the hydration in the case of iron oxide micelles is calculated. It has been found that there are about 441 millimoles of water to one gram of iron oxide.

#### ACKNOWLEDGEMENT

Our thanks are due to the Ahmedabad Education Society for generous grant towards chemicals and apparatus.

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