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STABILITY OF LYOPHOBIC COLLOIDS

XVII. Role of Adsorption of Ions on the Stability of the Sols of Hydrous Ferric Oxide in the Medium of Varying Dielectric Constant.

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The adsorption of peptising and coagulating ions play an important role in defining the stability of a sol. We have investigated here the extent to which the stability of the sols of hydrous ferric oxide is affected by a change in the dielectric constant of the dispersing medium for H^+ and SO_4^{2-} as stabilising and precipitating ions. It has been concluded that it is not possible to explain the sensitisation or stabilisation of a sol on the views advanced by Weiser, as the adsorption of either of the ions is found to vary according to the dielectric constant values of the dispersing medium.

The stability of a lyophobic sol is mainly defined by the adsorption of ions on the surface of the dispersed colloidal units. Several workers⁵⁾⁹⁾ have emphasized the importance of the adsorption of stabilising and precipitating ions by the sol particles during agglomeration and they¹⁾²⁾ have shown that it is never negligible and even rise to large proportions. Weiser⁸⁾, Ghosh and Dhar⁴⁾ drew attention to the adsorption of similarly charged ions. However, non-electrolytes are also known to affect the adsorption of the stabilising and precipitating ions and hence the stability. Weiser (loc. cit) concluded that the effect of non-electrolytes is due to variation of the adsorption of coagulating or stabilising ions and accordingly the decrease of the adsorption of the coagulating ions by a non-electrolyte will lead to stabilisation, while, a similar effect on the stabilising ion will sensitise the sol. Freundlich³⁾ has suggested that the sensitisation results from the lowering of the charge by the adsorption of non-electrolyte on the surface of the colloidal units, which tends to lower the value of the dielectric constant of the double layer. Thus, in view of these facts, we have studied the adsorption of stabilising and precipitating ions for the sols of hydrous ferric oxide within wide variations of the dielectric constant of the dispersing medium, as the stability of these sols is found to be highly affected by an alternation in the dielectric constants of the dispersing medium⁶⁾.

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- 1) A. C. Chatterjee *et al.*, *J. Ind. Chem. Soc.*, 26, 73 (1949); 29, 132 (1962)
- 2) H. Freundlich, *Kapillarchemie.*, 2nd ed., 637 (1932)
- 3) H. Freundlich, *et al.*, *Kolloid. Z.*, 1, 321 (1907); *Z. physik. Chem.*, 73, 408 (1910); *Kolloid. Z.*, 12, 232 (1913); Gann, *Kolloid-Beihefte*, 8, 73 (1916)
- 4) S. Ghosh and N. R. Dhar, *J. phys. Chem.*, 34, 326 (1930)
- 5) Linder and Picton, *J. Chem. Soc.*, 67, 64 (1895)
- 6) K. C. Nand and S. Ghosh, *Proc. Natl. Acad. Sci. India.*, (Communicated).
- 7) A. I. Vogel, *A text book of quantitative inorganic analysis*, Second Edition page 267.
- 8) H. H. Weiser, *J. phys. Chem.*, 29, 955 (1925), and subsequent papers.
- 9) Whitney and Ober, *J. Am. Chem. Soc.*, 23, 842 (1901)

In the following Tables 1 (a & b) is reproduced the amount of the hydrogen ion adsorbed on the surface of the hydrous ferric oxide. Hydrous ferric oxide was obtained by the interaction of ferric chloride and ammonia at room temperature and it was washed thoroughly till it was free from any trace of soluble electrolyte. The precipitate was made to a suspension (3.63 gm. of Fe^{3+} /litre) with distilled water and 10 ml of it was taken each time in to 100 ml volumetric flasks, to which various amounts of hydrochloric acid (A.R.) were added. A fixed amount of potassium sulphate (A.R.) was added to prevent the colloid formation and volume in each case was made to 100 ml with distilled

Table 1 (a) Adsorption of the peptising ion

Amount added of H^+ (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{H}^+ \times 10^4$)					
	Dioxane employed					
	0 %	5 %	10 %	20 %	30 %	40 %
	Dielectric constant values :					
	76.76	71.19	67.98	59.24	50.52	51.71
200	12.84	12.35	12.32	12.29	12.26	12.22
180	12.82	12.34	12.31	12.27	12.24	12.20
160	12.81	12.33	12.29	12.26	12.22	12.17
140	12.79	12.31	12.27	12.24	12.21	12.15
120	12.77	12.29	12.25	12.22	12.19	12.13
100	12.75	12.27	12.23	12.20	12.17	12.11
80	12.74	12.24	12.22	12.19	12.15	11.00
60	12.72	12.22	12.21	12.17	12.13	11.06
40	12.69	12.20	12.18	12.14	12.11	11.03
20	12.66	12.17	12.15	12.10	12.09	11.00

Table 1 (b)

Amount added of H^+ (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{H}^+ \times 10^4$)					
	Formamide employed					
	0 %	5 %	10 %	20 %	30 %	40 %
	Dielectric constant values :					
	76.76	77.32	77.92	79.29	80.88	82.54
200	12.84	13.70	13.75	13.81	13.85	13.92
180	12.82	13.68	13.74	13.80	13.84	13.90
160	12.81	13.67	13.72	13.78	13.83	13.89
140	12.79	13.65	13.70	13.76	13.80	13.87
120	12.77	13.63	13.68	13.74	13.78	13.85
100	12.75	13.61	13.66	13.73	13.76	13.83
80	12.74	13.59	13.63	13.71	13.74	13.81
60	12.72	13.56	13.62	13.68	13.71	13.78
40	12.69	13.53	13.59	13.65	13.69	13.75
20	12.66	13.50	13.56	13.62	13.66	13.72

water. After six hours the supernatant liquid was estimated for hydrogen ion and the amount adsorbed was thus calculated. Such studies were repeated in the medium of the varying dielectric constant affected by dioxane or formamide.

Tables 2 to 4 give the amount of adsorption of the SO_4^{2-} at the varying dielectric constants of the dispersing medium. For these studies a known amount of potassium sulphate (A.R.) sufficient to cause agglomeration in about six hours was added to each of 100 ml flask containing 10 ml of the sol, keeping the total volume to 100 ml. The contents were kept overnight and the supernatant liquid was estimated⁷⁾ for unadsorbed SO_4^{2-} and the amounts adsorbed on the colloidal surface were calculated. Similar studies were repeated at the varying dielectric constant of the dispersing medium for the three samples A, B and C of the sols of hydrous ferric oxide obtained by Graham's methods, containing 3.63 gm. of Fe^{3+} /litre. The pH of these sols were maintained at 2.2, 3.6 and 4.5, while their purities ($\text{Fe}^{3+}/\text{Cl}^-$) were

Table 2 (a) Sol sample (A)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{SO}_4^{2-} \times 10^4$)					
	Dioxane employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	7.41	5.19	5.15	5.11	5.08	5.04
180	7.40	5.17	5.13	5.09	5.06	5.02
160	7.36	5.15	5.11	5.07	5.04	5.01
140	7.32	5.13	5.10	5.05	5.03	4.98
120	7.30	5.10	5.07	5.02	5.01	4.96
100	7.27	5.08	5.04	5.01	4.98	4.95
80	7.24	5.06	5.02	4.98	4.96	4.93
60	7.22	5.05	5.00	4.96	4.94	4.90
40	7.16	5.03	4.98	4.94	4.91	4.87
20	7.13	5.00	4.96	4.91	4.89	4.84

Table 2 (b) Sol sample (A)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{SO}_4^{2-} \times 10^4$)					
	Formamide employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	7.41	9.83	9.88	9.94	10.00	10.05
180	7.40	9.81	9.86	9.92	9.98	10.03
160	7.36	8.79	9.85	9.90	9.95	10.01
140	7.32	8.77	9.84	9.89	9.93	9.98
120	7.30	8.75	9.82	9.87	9.90	9.96
100	7.24	8.73	9.80	9.85	9.89	9.95
80	7.24	8.71	9.78	9.83	9.87	9.93
60	7.22	8.69	9.75	9.80	9.85	9.90
40	7.16	8.66	9.73	9.79	9.83	9.89
20	7.13	8.64	9.71	9.76	9.80	9.87

found to be 3.7642, 11.6348 and 19.6897, respectively.

A perusal of these tables reveals that the adsorption of the H^+ or SO_4^{2-} tends to decrease according to the decreasing dielectric constant-values of the dispersing medium and it increases for higher dielectric constants. Further, the adsorption of anion is more for the sol samples containing greater free peptising H^+ that is for the sols of lower pH, and the extent of adsorption is found to represent the order $sol\ A > B > C$. In other words a sol which is more stable is found to exhibit greater adsorption of either of the ions. In other words a decrease in the dielectric constant of the dispersing medium tends to lower the adsorption of both the stabilising and precipitating ions and reverse is the case for higher dielectric constant-value. Therefore, it is not possible to explain the degree of sensitisation or stabilisation on the view advanced by Weiser.

Table 3 (a) Sol sample (B)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $SO_4^{2-} \times 10^4$)					
	Dioxane employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	6.52	4.48	4.44	4.40	4.35	4.30
180	6.50	4.46	4.42	4.38	4.32	4.28
160	6.47	4.45	4.40	4.37	4.30	4.26
140	6.45	4.44	4.38	4.35	4.28	4.25
120	6.42	4.42	4.35	4.33	4.26	4.23
100	6.40	4.40	4.37	4.30	4.25	4.20
80	6.37	4.38	4.30	4.28	4.22	4.18
60	6.33	4.37	4.28	4.26	4.20	4.16
40	6.30	4.35	4.26	4.25	4.18	4.14
20	6.26	4.31	4.24	4.23	4.16	4.11

Table 3 (b) Sol sample (B)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $SO_4^{2-} \times 10^4$)					
	Formamide employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	6.52	8.71	8.76	8.81	8.86	8.90
180	6.50	8.70	8.74	8.80	8.84	8.88
160	6.47	8.68	8.72	8.78	8.83	8.86
140	6.45	8.65	8.70	8.76	8.80	8.84
120	6.42	8.63	8.69	8.75	8.78	8.81
100	6.40	8.61	8.67	8.73	8.76	8.79
80	6.37	8.60	8.65	8.70	8.75	8.76
40	6.30	6.76	8.60	8.65	8.70	8.71
20	6.26	6.74	8.57	8.62	8.68	8.69

Table 4 (a) Sol sample (C)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{SO}_4^{2-} \times 10^4$)					
	Dioxane employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	5.61	3.67	3.58	3.54	3.50	3.46
180	5.60	3.60	3.56	3.52	3.48	3.44
160	5.58	3.58	3.54	3.50	3.46	3.42
140	5.54	3.56	3.51	3.48	3.44	3.40
120	5.50	3.54	3.49	3.46	3.41	3.37
100	5.46	3.53	3.47	3.44	3.39	3.35
80	5.43	3.51	3.45	3.42	3.37	3.32
60	5.40	3.49	3.43	3.40	3.35	3.31
40	5.36	3.47	3.40	3.37	3.32	3.29
20	5.32	3.44	3.37	3.33	3.30	3.26

Table 4 (b) Sol sample (C)

Amount added of SO_4^{2-} (gm. eq. $\times 10^4$)	Amount adsorbed (gm. eq. of $\text{SO}_4^{2-} \times 10^4$)					
	Formamide employed					
	0 %	5 %	10 %	20 %	30 %	40 %
200	5.61	7.63	7.67	7.72	7.77	7.83
180	5.60	7.61	7.65	7.70	7.73	7.80
160	5.58	7.60	7.63	7.68	7.70	7.78
140	5.54	7.58	7.60	7.65	7.68	7.76
120	5.50	7.65	7.58	7.63	7.66	7.75
100	5.46	7.54	7.56	7.60	7.65	7.73
80	5.43	7.52	7.54	7.58	7.63	7.70
60	5.40	7.50	7.52	7.55	7.60	7.68
40	5.36	7.47	7.49	7.54	7.58	7.66
20	5.32	7.44	7.47	7.50	7.55	7.63

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