

THE ELECTRICAL CONDUCTIVITY OF SILICA SOLS

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THE conductivity of silica sols has been investigated by a number of workers. Robinovitsch and Laskin¹ determined the H^+ concentration of silica sol and concluded that the adsorbed silicic acid is dissociated to a greater extent than in true solution. Ghosh and Dhar² observed that ageing of the silica sol is accompanied by an increase in conductivity. In the present investigation, negatively charged silica sols prepared by adding ammonia to purified silica gel are studied by measuring the change in conductivity on ageing as well as on dilution. Results obtained have been discussed to throw light on the nature of the stabilizing electrolyte.

EXPERIMENTAL

Several methods have been employed for the preparation of silica sols.³ In the present investigation, negatively charged silica sols are obtained by the modification of the methods suggested by Farbenind⁴ and Neundlinger.⁵

Sodium silicate solution (20%) was added to hydrochloric acid (3-N approx.) while constant stirring. The resulting mixture was subjected to continuous cold dialysis in a parchment paper bag till the gel was formed. The gel was then peptized with the required quantity of ammonia, the excess of which was removed by heating the sol on a water-bath at about 70° C. till free from ammonia. The sol so obtained was further purified by continuous cold dialysis for the required period. It was found that stable sols of fairly high concentration and purity can be prepared by this method.

Silica content of the sol was determined on evaporating to dryness 10 ml. of the sol in a previously weighed crucible at a temperature 110–20° C. To determine ammonium ion, an aliquot portion of the sol was coagulated, filtered and washed. Ammonia was estimated in the filtrate by treating it with an excess of standard NaOH solution, the excess after the reaction being estimated by titrating with standard HCl solution.⁶ Chloride was found to be absent in all the samples. Table I gives composition of various sols.

TABLE I

Sol	Silica (g./l.) <i>a</i>	NH ₄ ⁺ ion concentration (g./l.) <i>b</i>	NH ₄ ⁺ ion concentration (m.e./l.)	Purity <i>a/b</i>
F	36.7	0.162	9.0	226
G	34.0	0.288	16.0	118
H	45.0	0.1224	6.8	368
I	43.8	0.0864	4.8	507
J	35.8	0.0648	3.6	552
K	43.4	0.1008	5.6	431

CHANGE IN CONDUCTIVITY ON AGEING

The conductivity of silica sol K was measured over a number of days. Double distilled water (sp. conductivity = 2×10^{-8} mhos. at 35° C.) was employed for dilution and its conductivity was neglected. Dilutions were checked by analysis. The conductivity of the sols was measured at 35° C. as shown before.⁷ The data are represented graphically in Fig. 1.

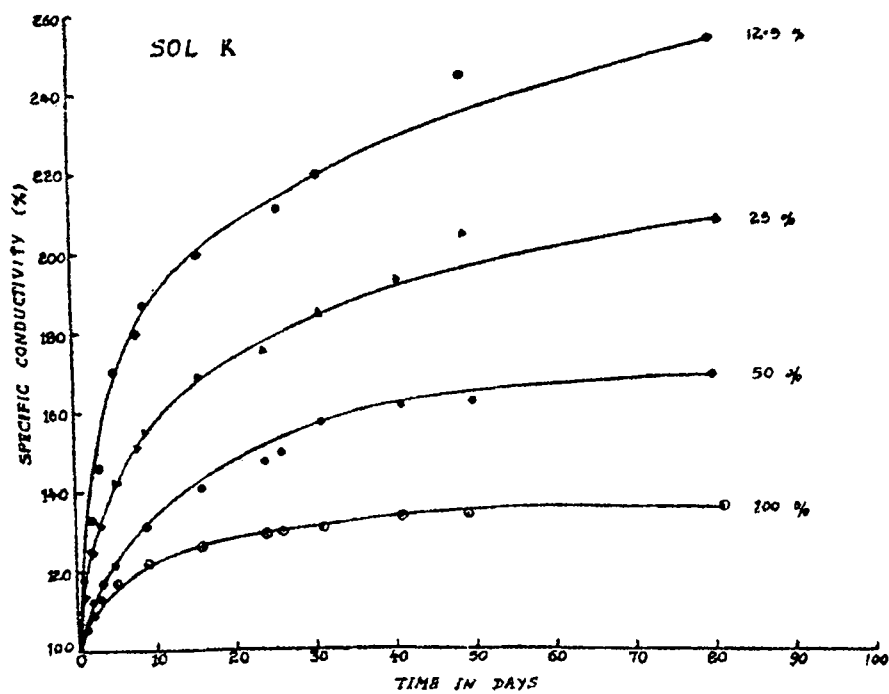


FIG. 1

CHANGE IN CONDUCTIVITY ON DILUTION

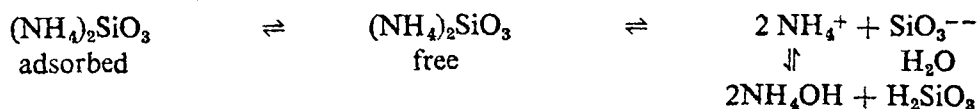
Change in conductivity on dilution was followed in the case of sols, F, G, H, I and J. Table II gives the data regarding the sp. conductivity and eq. conductivity of the micelles in the case of sols I and J.

TABLE II

Sol	Concentration of the sol silica (g./l.)	Concentration of NH_4^+ ion in the micelles (m.e./l.)	Specific conductivity of the micelles $\text{K} \times 10^6$	Equivalent conductivity of the micelles
I	43.8	4.80	13.68	28.49
	39.42	4.32	12.20	28.24
	35.04	3.84	10.50	27.35
	30.66	3.36	9.815	29.21
	26.28	2.88	7.962	27.65
	21.90	2.40	7.252	30.21
	17.52	1.92	5.833	30.38
	13.14	1.44	4.794	33.29
	8.76	0.96	3.512	36.58
	4.38	0.48	2.335	48.65
J	35.8	3.60	7.042	19.64
	32.22	3.24	6.261	19.33
	28.64	2.88	5.624	19.53
	25.06	2.52	4.903	19.45
	21.48	2.16	4.196	19.42
	17.90	1.80	3.660	20.33
	14.32	1.44	2.995	20.80
	10.74	1.08	2.580	23.89
	7.16	0.72	1.973	27.40
	3.58	0.36	1.310	36.39

DISCUSSION

Effect on Ageing.—It is obvious that in all cases the specific conductivity of the sol increases on ageing, the rate of increase being greater, greater the dilution (see Fig. 1). The increase in conductivity on ageing of the silica sol has been observed previously by Ghosh and Dhar.² Sol K used in the present investigation was of a fairly high degree of purity and did not contain any chloride. Since the silica gel was peptized with ammonia, the sol so formed may be stabilized by either the OH ion or the SiO₃ ion with ammonium ion as the gegenion. In other words, the stabilizing electrolyte may be either ammonium hydroxide or ammonium silicate. When the sol is allowed to age, there is a perceptible increase in conductivity owing to the stabilizing electrolyte coming out of the surface of the colloidal particles into the intermicellar liquid. If we assume ammonium hydroxide to be the stabilizing electrolyte, the increase in conductivity on ageing cannot be explained, as ammonium hydroxide which may come out in the intermicellar liquid is a weak electrolyte. Alternatively, we may assume that ammonium silicate is the stabilizing electrolyte and the increase in conductivity is due to its coming out in the intermicellar liquid. However, ammonium silicate is a salt of very weak silicic acid ($K = 1.6 \times 10^{-10}$)⁸ and a weak base, ammonium hydroxide ($K = 1.8 \times 10^{-59}$). Taking the ionic product of water $K_w = 10^{-14}$ and the concentration of ammonium silicate as 0.02 *e* per litre, the hydrolytic constant and the degree of hydrolysis can be easily calculated. The hydrolytic constant and the degree of hydrolysis comes out to be 3.5 and almost 100% respectively. Even sodium silicate is completely hydrolysed in 1/48 N solution.¹⁰ Hence, it appears difficult to explain the increase in conductivity due to the desorption of ammonium silicate. The only explanation appears to be to assume that the hydrolysis of the electrolyte is inhibited as it is adsorbed on the colloidal particle. The state of equilibria may be represented as follows:—



Thus, ammonium silicate may not be completely hydrolysed in the presence of adsorbed ammonium silicate. If the hydrolysis takes place completely, the equilibrium will be entirely shifted on the right hand side and the sol should become immediately unstable on dilution.

Effect on Dilution.—The sols F, G, H, I and J are of fairly high degree of purity and do not contain any free foreign electrolyte. In all cases, the specific

conductivity of the sol decreases with purity (see Fig. 2). This is in agreement with the observation of Chakravarti and Dhar,¹¹ Desai and co-workers¹² and Trivedi, Bhatt and Divatia.¹³

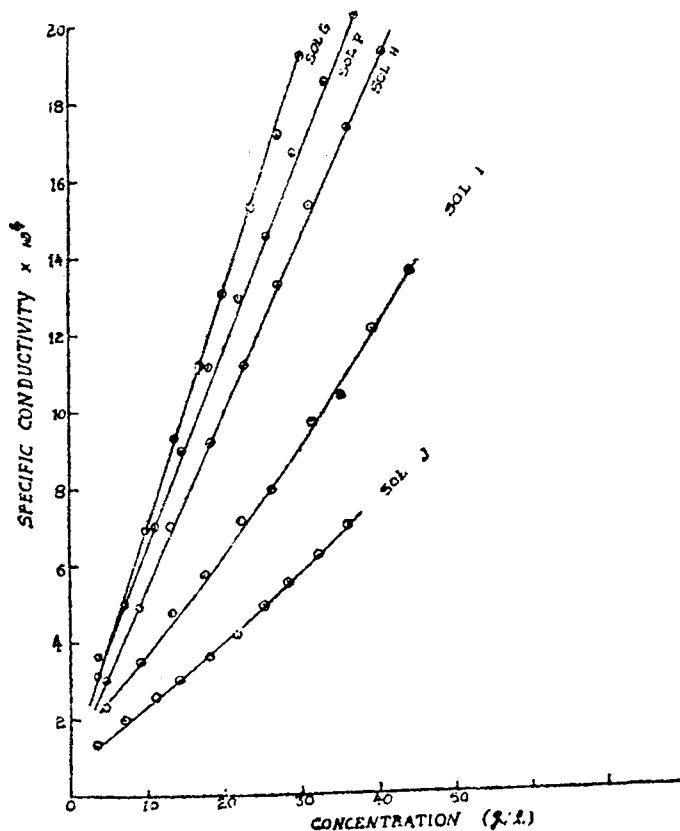


FIG. 2

Table II contains the equivalent conductivity of the micelles in the case of sols I and J. The equivalent conductivity of free ammonium silicate will be about 150 mhos approximately (calculated indirectly). Hence, the equivalent conductivity of the adsorbed ammonium silicate is a fraction of its value in the free condition. The behaviour of the sols F, G and H is also found similar (data not given). It may be further observed that in the case of sols I and J, the equivalent conductivity of the micelles decreases on dilution and then increases on further dilution. The data are graphically shown in the case of sol J (see Fig. 3).

The behaviour of silica sol is in harmony with that of sulphur sol,¹⁴ iron oxide sol,⁷ chromium oxide sol¹³ and aluminium oxide sol.¹⁵ The decrease

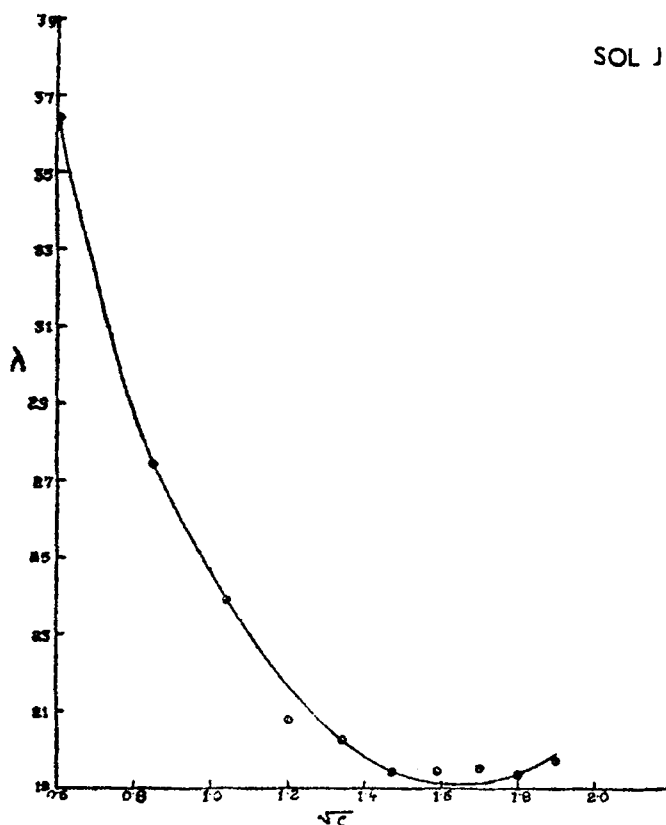


FIG. 3

in the equivalent conductivity on dilution followed by increase in conductivity on further dilution is similar to the behaviour shown by the soap solution. To that extent all the systems mentioned above may be classified as colloidal electrolytes. It may be remarked that the behaviour as a colloidal electrolyte becomes prominent only with sols of very high degree of purity.

SUMMARY

In the case of silica sols prepared by peptizing silica gel with ammonia, ammonium silicate is the stabilizing electrolyte. When the sols are allowed to age, the specific conductivity of the sol increases due to the deadsorption of ammonium silicate. Although ammonium silicate is a salt of a weak base and a very weak acid, it is not completely hydrolysed under the conditions of the experiments. The adsorbed ammonium silicate behaves as a colloidal electrolyte and its equivalent conductivity is a fraction of its value in the free condition.

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