

Studies in Chromium Arsenate Sol. Part III. Changes in Extinction, pH and Electrical Conductance of the Sol During Coagulation at Different Stages of Dialysis

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A study of the influence of K_2SO_4 on the colloidal solution of chromium arsenate by light extinction method reveals that coagulation is accelerated with increasing amount of electrolyte until at a certain concentration it is maximum. Higher concentrations than this give rise to loose aggregation. The pH of the sol increases with increasing amounts of K_2SO_4 . This is not limited up to the coagulation point but goes on even beyond it. The electrical conductance of the sol itself decreases continuously with addition of the electrolyte.

The structure of the sol particles and the changes taking place during their coagulation have been discussed on the basis of the observations of extinction, pH and electrical conductivity.

The constitution of the particle in many sols, especially of the hydrous oxides of iron, aluminium, chromium and several other colloidal systems has been the subject of many enquiries. Thus, Wyrouboff and Verneuil (*Bull. Soc. chim.*, 1899, **21**, 137) in their studies of coagulation of a ferric oxide sol with an electrolyte, suggested that the various preparations contained basic salts or chlorides of condensed hydroxides. Weiser (*J. Phys. Chem.*, 1920, **227**, 328) criticised this view of a definite formula because the composition of the dialysed colloid depends on the mode of its formation. Thomas *et al* ("Colloid Chemistry", 1934, Chap. VIII) state that the dispersed phase in the hydrous oxide sols consists of olated and possibly oxalated compounds of Werner type. Ghosh *et al* (*Kolloid Z.*, 1951, **124**, 69, 1952, **127**, 27; 1953, **130**, 167; 1955, **142**, 104; *Proc. Nat. Acad. Sci. India*, 1954, **23**, 489, 142; 1956, **25**, 190) have emphasised the role of exchange adsorption in the precipitation phenomenon and have opined that the formation of a basic salt is a remote possibility. Ghosh and Aditya (this *Journal*, 1952, **29**, 296) came to a similar conclusion for stannic oxide sol. In a preceding paper (*ibid.*, 1959, **36**, 323) we have dealt with the changes in pH of chromium tungstate sol. The increase in pH with the addition of K_2SO_4 has been explained there as due to adsorption of H_3O^+ ions on the partly neutralised surface of the sol particle, causing thereby an increase in the OH^- ion concentration of the medium.

In the present communication we have studied the changes in extinction, pH , and electrical conductance of chromium arsenate sol during coagulation at various stages of dialysis.

EXPERIMENTAL

The extinction measurements were made with a photoelectric colorimeter (Lichtelektrisches Kolorimeter, Modell-VI) using red filter and 5 c.c. cuvette. As difference in the method of mixing of electrolyte with the sol causes a difference in the coagulation behaviour, care was taken to maintain uniformity in the process of mixing as far as possible. The procedure followed was to arrange a series of eleven beakers containing the electrolyte solution in which its concentration was systematically varied keeping the total volume constant (20 c.c.). These solutions were then added and thoroughly mixed in the same number of beakers each containing 20 c.c. of the sol. Everytime extinction readings were taken after 3 minutes of mixing. The results of such measurements are represented in Fig. 1.

pH measurements were taken with a Beckman pH-meter (Model-M) using glass and calomel (saturated) electrodes. The instrument was standardised with a standard buffer solution. Fig. 2. shows the changes in the pH of sol with the addition of varying amounts of electrolyte.

Conductance measurements were made with a Doran oscillator and a Mullard conductivity bridge. Specific conductances of the mixture of sol plus electrolyte (K_m) and that of the electrolyte alone (K_e) were determined. The latter was subtracted from the former so as to provide the changes in conductance of the sol itself effected by the addition of the electrolyte. Fig. 3 shows such changes in the sol conductance.

Table 1 records the percentage composition of the sol and the concentration of K_2SO_4 used for coagulation of the sol under various stages of dialysis.

Dialysis Stages.	Duration.	TABLE I Percentages of			Conc. of K_2SO_4 soln.
		Cr^{3+} .	AsO_4^{3-} .	Cl^- .	
I	1	0.4465	0.4662	0.4731	2M/3
II	2	0.3456	0.4078	0.3154	M/10
III	3	[0.3029	0.3713	0.1912	M/25
IV	4	0.2772	0.3545	0.1005	M/50
V	5	0.2581	0.3420	0.0602	M/75
VI	6	0.2485	0.3375	0.0200	M/100

DISCUSSION

Fig. 1 shows the extinction-concentration curves, which indicate that to start with there seems to be no change in extinction by the addition of K_2SO_4 . With increasing

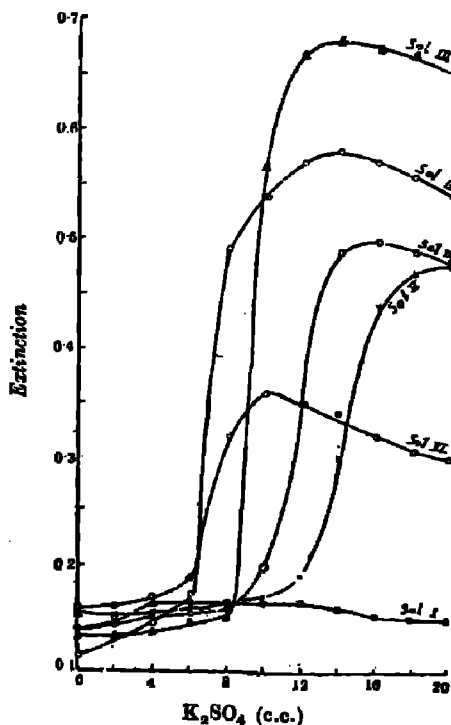


FIG. 1. Variation of extinction by the addition of K_2SO_4 to chromium arsenate sol at different stages of purity.

amounts of the electrolyte, coagulation is accelerated until rapid coagulation sets in and there is a sudden rise in the extinction curves. It is further observed that at higher concentrations of the electrolyte, there is a fall in the extinction curves. This is due to the formation of loose flocs which scatter relatively little light than those formed at lower concentrations. In the latter case, the aggregates obtained are comparatively dense as the repulsive action of the double layer is not completely removed. In the absence of repulsive action, attained with the addition of excess of the coagulating electrolyte, the rate of formation of flocs is large; irregular, and rather loose flocs scatter less light, giving thereby lower extinction values (sol IV and sol V). It has been observed that highly purified sols tend to gel formation with the addition of electrolyte, which is not sufficient to lead to a normal flocculation. In such cases the partly discharged particles are evidently attached to each other at very few spots and give rise to the formation of a lace-like structure in which the included intermicellar liquid is immobilised and consequently the extinction values are much lower (sol VI). Similar behaviour has been noted by us in the case of chromium tungstate sol (*loc. cit.*).

Fig. 2 shows that the pH increases with the purity of the sol. This phenomenon is ascribed to the removal of stabilising agent, acidic chromium chloride, from the intermicellar liquid.

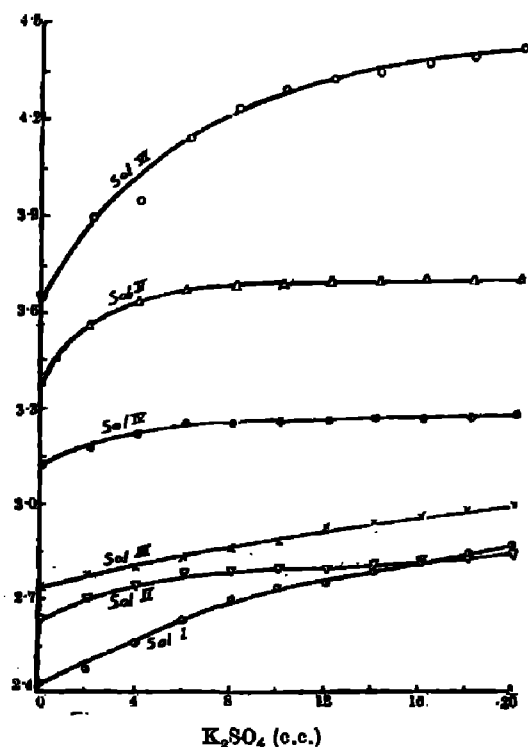


FIG. 2. Variation of pH by addition of K_2SO_4 to chromium arsenate sol at different stages of purity.

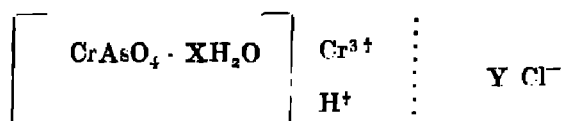
There is increase in pH of the sol with the addition of increasing amounts of K_2SO_4 . This is not limited up to the coagulation point, but goes on even beyond it.

It has already been pointed out that Thomas *et al* (*loc. cit.*) held the view that the in-

crease in pH with the addition of a neutral electrolyte to the hydroxide sols of iron, chromium, aluminium, thorium, and beryllium was due to the replacement of OH^- groups by the anions of the added salts. Iyer (*Proc. Indian Acad. Sci.* 1934, **11**, 372) postulated the presence of OH^- and Cl^- ions in the diffuse portion of the double layer and accounted for the change in the pH value as due to the displacement of OH^- ions.

The above explanations for the increase in alkalinity of the medium observed during coagulation do not appear probable. X-ray studies by Böhm *et al* (*Z. anorg. Chem.*, 1925, **149**, 208; 1923, **132**, 7,) and by Fricke and Havestadt (*ibid*, 1930, **188**, 357; 1931, **196**, 120; *Kolloid Z.*, 1931, **56**, 166) and later on by Weiser and Milligan (*Trans. Faraday Soc.*, 1936, **32**, 358; *J. Phys. Chem.*, 1938, **40**, 40) rule out the formation of basic salts. Rai and Ghosh (*loc. cit.*) ascribed the increase in pH to the adsorption of hydroxonium ions during the process of coagulation.

Taking in view the above considerations and the tendency of a particle to extend its crystal lattice as well as the fact that the concentration of Cr^{3+} ions is relatively large (Table I), the structure of the colloidal units of the chromium arsenate sol may be represented as follows, thus implying that the positive charge and the stability are to be attributed



to chromium ions and the hydrogen ions which are firmly attached to the surface of the colloidal particle, whereas Cl^- ions form the diffuse outer layer in equilibrium with the adsorbed ions.

The chloride ions are mostly held by electrostatic attraction of the adsorbed positive inner layer (the fixed part of the double layer). It may be argued that the chloride ions may function in the same manner as suggested for the chromium and hydrogen ions. A sol is known to be preferably stabilised by an ion, which is present in its own lattice. On the addition of the sulphate ions, the Debye-Hückel atmosphere shrinks and a decrease in its shell thickness occurs. This results in the redistribution of charges within the shell from uniform to non-uniform and in the increase of their density, whereby the probability of encounter between the stabilising and coagulating ions, which is very low in the peptised sol, increases in the coagulating sols. Whereas in the metastable sols, the association-dissociation tendencies are at equilibrium (Tezak, *Archiv. Chem.*, 1950, **22**, 26), when the anions are introduced, the electric charge on the colloidal particle decreases by neutralisation and a partly neutralised surface is formed. It has the tendency to adsorb H_3O^+ from the system. In this way, the surface is continually discharged by the SO_4^{2-} ions and again becomes charged by the hydrogen ions from the medium leaving OH^- ions in the system. Thus the increase in pH is observed (Fig. 2).

The sol particles are highly charged, but the total conductance of the pure sol is usually too low due to the smallness of the total number of particles. The electrical conductance of a sol is, in general, due to the conductance of the sol particles as also that of the stabilising electrolytes. The contribution of the former is low unless the behaviour of the colloidal units is like that of a colloidal electrolyte since the colloidal particle may be visualised as a charged unit, which binds up the ions in the double layer so that the oppositely charged ions cannot also contribute substantially to the electrical conductance.

Fig. 3 shows that the conductance of the sol, calculated from $K_m - K_e$ (where K_m is the conductance of the sol plus electrolyte, and K_e that of the electrolyte) at all stages of

dialysis of sol decreases continuously by the addition of increasing amounts of electrolyte and that the decrease in purer sols is of more interest than for impure sols. Onsager and Fuoss (*J. Phys. Soc.*, 1948, 3, 246) have demonstrated that on addition of salts to polyelectrolytes, the observed conductance in an arbitrary mixture of ions is less than the value obtained by adding the individual ionic conductances. Addition of the solution of K_2SO_4 to a solution of sodium arsenate, has been found by us to decrease the conductance though by a small amount as compared to that produced by its addition to the sol especially up to the coagulation point.

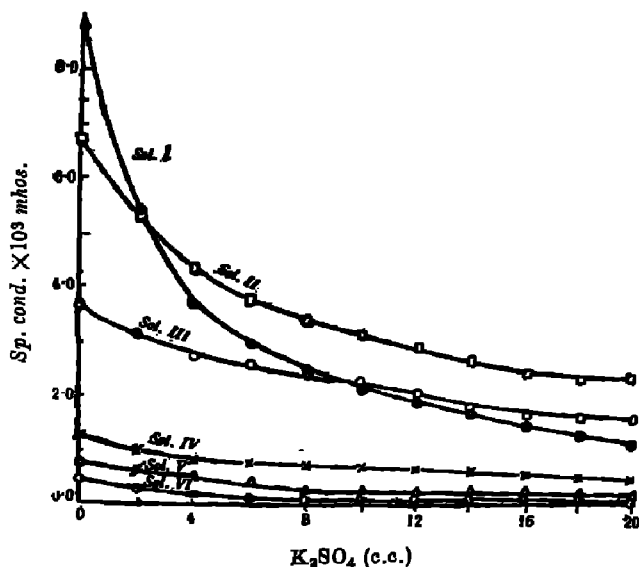


FIG. 3. Changes in electrical conductivity of chromium arsenate sol with the addition of K_2SO_4 .

Rai and Ghosh (*loc. cit.*) observed a decrease in the conductance of hydrous ferric oxide sol with the addition of K_2SO_4 . They explained it as due to the replacement of aquo group from the colloidal micelle. In our opinion the continuous decrease of the conductance of the sol itself ($K_m - K_c$) by the addition of the increasing amount of K_2SO_4 may be due to the following causes:

(i) The thickness of the double layer is decreased whereby the electrostatic attraction between the fixed and diffuse parts of the double layer is increased, resulting in a decrease in the mobility of the micelles.

(ii) The negatively charged sulphate ions are discharged at the surface of the positively charged colloidal particle and hence can no longer contribute to the conductance of the system. In arriving at the true conductance of potassium sulphate from that of the mixture of the sol plus electrolyte, it is assumed that the sulphate ions have the same conductance in the mixture as in its solution, which is not true. This is why the calculated conductivity values of the sols go on decreasing slowly even after coagulation has taken place.

(iii) Adsorption of hydroxonium ions on the partly neutralised surface of the sol particle results in a decrease in the concentration of hydrogen ion (in the form of H_3O^+ ions) which are more conducting than the OH^- ions,

(iv) Due to the salt-effect on the conductivity of polyions, i.e., highly charged colloid particles, there is also a decrease in the conductivity of the sol to a certain extent.

It is expected that there will be a greater fall in conductance of the sol until the stage of rapid coagulation is reached. The slow decrease observed thereafter is mainly due to the effects mentioned above and also to the effect of aggregation when the radius of the micelles increases and their mobility decreases.

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