Confirmation of the Formation of Colloidal Particles in Aqueous Cobalt Salt Solution by Radiotracer Electrodialysis

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(Received October 16, 1958)

It has been pointed out by a series of our experiments[1] as well as of others[1], that polyvalent metallic ions such as aluminum, iron, copper and thorium exhibit remarkable effects in regard to surface-chemical properties, for instance, wettability of paraffin by water and the nature of monomolecular films of fatty acids. Such effects were explained by the assumption that these ions when dissolved in water mainly exist as hydrated polynuclear ions in a region of suitable pH, rather than as simple monomeric ions, as in the case of alkali and alkaline earth metal ions which show no remarkable effects in regard to the surface-chemical properties. Such an assumption of the existence of aggregated ions has also been proposed by Haissinsky[2] to explain a large fluctuation in the published data on the solubility product of one and the same insoluble compound. McGee, Kraus, Milburn and Kohlschütter[3] also offered similar opinions. Thus the existence of the polynuclear structure becomes increasingly convincing. However, all of these experimental evidences are rather indirect in nature. As a more direct evidence of the existence of such polynulear ions, we can also refer to a number of studies upon radiocolloid formation which proved the existence of colloidal particles in extremely dilute solutions of polonium, bismuth, lead, thorium, yttrium, etc.[4] In more concentrated solutions, the formation of aggregated particles were also observed in cobalt salt solution, for instance, by a self-diffusion method[5].

The present authors have also carried out the experiment of radiotracer electrodialysis[6], coupled with an ordinary filtration, to obtain a direct evidence of the formation of colloidal particles in an aqueous cobalt salt solution.

Experimental

(1) Radiotracer Electrodialysis.—The apparatus employed in the experiment was shown in Fig. 1. In this figure, A is a glass U-tube with one end somewhat wider than the other.

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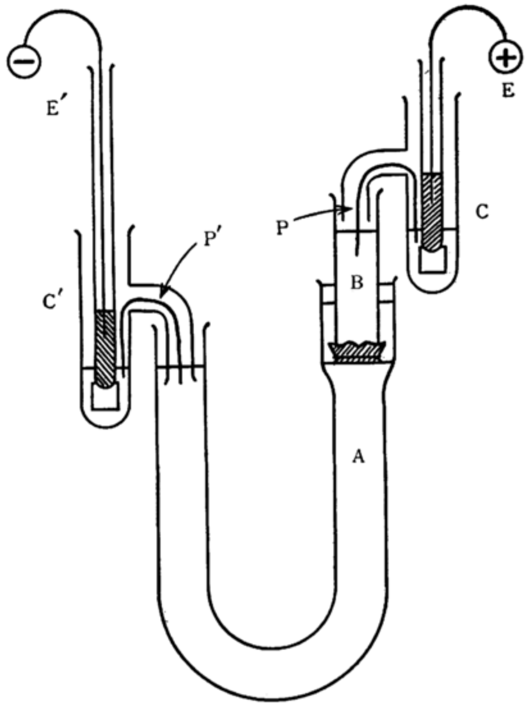

Fig. 1. Electrodialysis cell.

B is a glass cylinder, to the bottom of which a semipermeable cellophane membrane is tightly attached as shown in the figure, with the aid of a rubber ring. The electrode cells C and C′ consist of two platinum electrodes E, E′ and filter paper bridges P, P′. To carry out an experiment, the tubes A, B and cells C, C′ are all filled with the same solution to be studied, that is 10^{-3} mol./l. aqueous solution of cobaltous chloride, with the exception that the solution in B alone is especially tagged with a suitable amount of radioisotope cobalt-60 as a tracer. Hereby, care should be taken that the lower end of the tube B is so placed that it just touches the surface of the solution in A. Now, when we apply D. C. voltage to the electrodes as indicated in Fig. 1, the cobalt ions will move from C to C′. So they will pass through the cellophane membrane downwards, if they are in a state of single ions or relatively small aggregates, while they will not be able to pass through the membrane if they exist as colloidal particles or even larger particles. Thus we can confirm the formation of particles larger than a colloidal size, when we trace the change in concentration of the solution in A.

Now, we have determined a suitable condition for practice from a preliminary experiment. It was evident that the amount dialyzed increased with the increase of applied potential gradient, as well as with the duration of electric current passed, but we performed a 50 volt and 15 minute dialysis*, since prolonged dialysis disturbed the steady condition of the solution to be dialyzed**. After the dialysis, the tube B was removed, 1 cc. of solution in the tube A just below the tube B was taken, heated to dryness in a stainless steel dish, and the radioactivity due to cobalt-60 was measured by a GM counter, as in the usual manner. The permeability was then expressed in c.p.m. Hereby, the GM tube was masked against β-ray and counting was taken only for that due to γ-ray, since the counting due to β-ray fluctuated sensitively for apparently identical geometry of counting arrangement. The cellophane used was a commercial product of a suitable thickness, which was cut in $5\times5\,\text{cm}^2$ pieces, and was kept in distilled water for a long time in order to swell the sheets sufficiently for use.

In the course of experiments we found that the permeability of cellophane fluctuated from one sample to another, and also that one and the same sample gradually lost its permeability when used repeatedly. To overcome these undesirable conditions, we used the same membrane only for a couple of measurements, that is, for the permeability measurement of the reference solution containing 10^{-3} mol./l. cobaltous chloride, kept at pH 1, and for the subsequent measurement of the solution to be studied, which was of the same concentration but varying in pH. The control of pH was made using hydrochloric acid and sodium hydroxide.

From the measured permeability, we calculated the relative permeabilty, by the following formula,

$$P_r = \frac{\text{Permeability at pH}=x}{\text{Permeability at pH}=1}$$

The value P_r was used for further discussion. The change of pH due to the electrodialysis was about 0.5 at most.

Before use, cellophane membrane was also examined against pin holes by measuring a leak of Congo red solution through the membrane into pure water for 24 hours, from which we could confirm the fact that the membrane was free from eventual large pores, and also that the

TABLE I. PERMEABILITY OF AQUEOUS COBALT IONS THROUGH CELLOPHANE MEMBRANE

Permeability P_1 at pH=1	Permeability P' at pH=x		$P_r=P/P'$
		P	
170 cpm	1.0	285 cpm	1.67
173	2.2	92	0.53
146	2.8	52	0.36
163	2.9	97	0.60
188	4.5	104	0.55
169	5.4	119	0.70
136	6.7	50	0.37
148	8.1	44	0.30
144	10.4	0	0

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* The distance between the two electrodes is 22 cm.

** The flow of water due to the hydrostatic pressure of water in the tube B was negligible during the period of experiment.

membrane acted as a sieve for particles at least larger than the Congo red molecule. Stock aqueous solution was kept at pH=1 and made up to a desired pH immediately before use. Permeability at varying pH and corresponding P_r values were listed in Table I.

(2) **Filtration.**—Ordinary filtration was carried out to detect the formation of particles coarser than colloidal ones in aqeous solution of cobalt salt. Radioactive cobalt salt solution of the same origin as used in the electrodialysis was filtered under varying pH using fine pore filter paper (Tôyô 5C) and a cobalt content in the filtrate was analyzed by measuring radioactivity due to the aliquot of the filtrate in the same manner as in the preceding experiment. The results were shown in Table II. In this table we showed the amounts of the cobalt ion in solution before and after the filtration by an arbitrary unit of radioactivity of 1 cc. of respective solution which was considered to be proportional to the concentration of cobalt ion. The degree of permeability of cobalt ion was expressed by the ratio F_r of radioactivities in a solution before and after the filtrations as shown in the last column of Table II.

TABLE II. PERMEABILITY OF AQUEOUS COBALT ION THROUGH FILTER PAPER (TÔYÔ 5 C)

pH	Amount of cobalt (cpm) before filtr. (A)	after filtr. (B)	$F_r=(B)/(A)$
2.5	287*	288*	1
6.6	882	874	0.99
8.4	883	774	0.88
8.9	*873*	*772*	*0.88*
9.4	874	336	0.38
10.1	846	15	0.017

* Geometry of the counting arrangement was accidentally different from the rest of the measurements.

Discussion

From Tables I and II, we prepared a diagram showing a pH dependence of permeability of cobalt ions through cellophane membrane and filter paper as shown in Fig. 2. In constructing this diagram, we first plotted P_r against pH, excluding the value at pH 1 which showed an extreme deviation, and obtained a curve which as a whole gave a plateau in the region of pH from 2 to 6. Next, we plotted F_r against pH and a similar curve was obtained. Then we adjusted the units of P_r and F_r axes so that both curves coincided at their plateau portions, assuming that there the complete passage of solute took place for both operations.

Now, in Fig. 2, we can readily recognize that the cobalt ions in the region A pass through both cellophane membrane and filter paper, while those belonging to the region B pass through the filter paper but are retained by the cellophane membrane, and those belonging to the region C are retained both by cellophane membrane and filter paper. Therefore, when we draw an ordinate at a certain pH, a portion *a* of the ordinate belonging to the region A represents a fraction of an amount of cobalt in the state of A region (simple ionic state), and so on. Thus, in the region of pH from 6 to 10, we confirm the formation of colloidal cobalt particles as those permeable to filter paper but not to cellophane membrane. We can also see the initiation of macroscopic agglomerate formation at pH 8 and precipitation of practically all cobalt ions at pH larger than 10, in the aqueous cobalt salt solution.

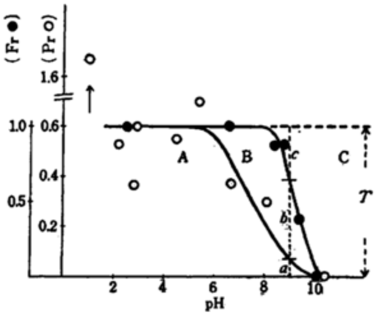

Fig. 2. State of dispersion of aqueous cobalt ion.
A, simple ionic dispersion
B, colloidal dispersion
C, macroscopic aggregation
T, total amount of cobalt in water

Now, from the published data of the solubility product⁷⁾, we calculated the minimum pH required to initiate cobaltous hydroxide precipitate in 10^{-3} molar aqueous cobalt salt solution. It was about 6.8, which happened to be situated between pH values of the initiation of colloidal particle formation and macroscopic agglomerate formation. We can conclude from these facts that in the solution studied, there exists a pH region of colloidal particle formation somewhere near the pH, beyond which solubility is exceeded. This conclusion is consistent with the results of a series of our former investigations already mentioned¹⁾.

It must be added that the dissolved state of cobalt ion in aqueous solution changes gradually in the course of time, in a higher pH region as seen from the

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7) Landolt-Börnstein, "Physikalisch-chemische Tabellen". I. Erg., Verlag J. Springer, Berlin, (1927), p. 662.

change of color of the solution. So we may expect that the boundary between the A regions and B of Fig. 2 will gradually shift presumably to the left in the course of time. The boundary may also shift according to the nature of the semipermeable membrane used.

Summary

(1) Dissolved state of cobalt ions in 10^{-3} molar aqueous solution of cobaltous chloride, varying in pH, was studied by a radiotracer electrodialysis coupled with an ordinary filtration.

(2) Formation of colloidal particles permeable to filter paper but not permeable to cellophane membrane were confirmed in the solution, in the region of pH from 6 to 10.

(3) Macroscopic precipitates of cobaltous hydroxide began to form at about pH 8 and practically all cobalt ions were precipitated at a pH greater than 10.

(4) The value of pH of insoluble cobaltous hydroxide formation in aqueous 10^{-3} molar cobalt salt solution calculated from the solubility product of cobaltous hydroxide was found to be situated between the pH of the initiation of colloidal particle formation and the pH of the initiation of macroscopic agglomerate formation.

The authors express their hearty thanks to the Deparment of Education for the Scientific Research Expenditure given to T. Sasaki.

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