Formation and Aging of Precipitates. VI. Morphology of Crystals in Various Vanadium Pentoxide Sols by Electron Microscopy

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Since the report of Biltz[1], the formation and aging of vanadium pentoxide sol has been investigated by many scholars. Recently, as the fibrous shape of the crystals contained in the sol which was confirmed distinctly with the electron microscope has attracted the attention of many investigators, morphological and crystallographic investigations have become popular. The crystals in Biltz sol were small fibrils at the outset and they grew like long fibers upon aging. Huber and Zbinden[2], watson, Heller and Wojtowicz[3] and Tamamushi[4] observed the growth of the crystals in Biltz sol with an electron microscope and they found that the fibrous crystals were nearly monodisperse at first, but they became polydisperse upon aging. The present author prepared vanadium pentoxide sols by Biltz', Müller's, and ion exchange method and studied the crystals in these sols by means of the electron microscopy to make a research on the aging process.

Experimental and Results

Formation of Sols.—*Biltz sol.* Two g. of ammonium metavanadate was mixed thoroughly with 6 ml. of 3 N hydrochloric acid in an agate mortar. The brownish red precipitate produced was washed in a glass filter and all the precipitate was dispersed completely in 200 ml. of water, giving a clear reddish brown sol.

Müller sol. Five g. of ammonium metavanadate was fused in a porcelain crucible for about half an hour and the melt was poured into 500 ml. of cold water. The sol formed in this way was dark reddish brown in color.

Ion exchange sol. Ammonium metavanadate solution (0.5%) was passed through a column of hydrogen ion exchange resin (Amberlite IR-120) and the yellow vanadic acid produced was decomposed in boiling water for about half an hour, and a reddish brown sol was formed.

Concentration of Sols and Quantity of Impurities.—The concentration of sols and the quantity of electrolytes in sols were determined as stated below.

Concentration of sols. The total quantity of vanadium pentoxide contained in the sols was determined as follows: a certain quantity of a sol was mixed with a small amount of 6 N sodium hydroxide solution, and the mixture was warmed until the vanadium pentoxide was completely dissolved. After the addition of sulfuric acid, the vanadic acid was titrated potentiometrically with 0.01 N standard ferrous ammonium sulfate.

Dissolved vanadium pentoxide in sols. A certain quantity of the sol was mixed with a suitable amount of potassium chloride solution to coagulate the disperse phase, and the coagulum was filtered and washed with potassium chloride solution. Vanadium pentoxide in the filtrate was determined as described above.

Ammonia in sols. The quantity of ammonia contained in the sol was determined by Kjeldahl's method.

Chloride in sols. The disperse phase of the sol was coagulated with potassium nitrate solution and the coagulum was filtered and washed. The filtrate was titrated with standard silver nitrate solution by potentiometry.

Results of the measurements. The results obtained by the above-mentioned methods are listed in Table I.

TABLE I

CONCENTRATION OF SOLS AND IMPURITIES

No.	Sol	Time of aging	Concn. of sol g./l.	Concn. of dissolved V_2O_5 g./l.	Concn. of NH_3 mg./l.
1	Biltz sol	0	7.083	1.052	—
2	〃	2 day	7.057	0.526	218.8
3	〃	6 months	7.120	0.281	—
4	〃	18 months	7.184	0.285	214.5
5	Müller sol	0	6.990	1.090	0.2
6	〃	10 days	6.420	0.325	—
7	Ion excange sol	0	6.094	0.400	0
8	〃	0	6.370	0.298	0

The concentration of every sol was about 7 g. V_2O_5 per liter. The amount of the dissolved vanadium pentoxide in Biltz and Müller sols was about 1 g. per liter (about 15% of the total vanadium pentoxide) in those fresh sols, but it decreased to about 0.28 g. per liter (about 4% of the total vanadium pentoxide) upon aging. In

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[1] W. Biltz, *Ber.*, **37**, 1095 (1904).

[2] H. Huber and H. Zbinden, *Z. anorg. Chem.*, **258**, 188 (1949).

[3] J. H. Watson, W. Heller and W. Wojtowicz, *Science*, **109**, 274 (1949).

[4] B. Tamamushi, *J. Electron-Microscopy*, **1**, 35 (1950).

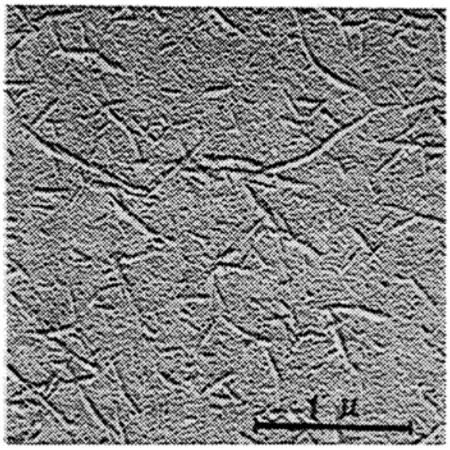


Fig. 1. Crystals in 2 days old Biltz sol. (Cr shadowing) × 20,000

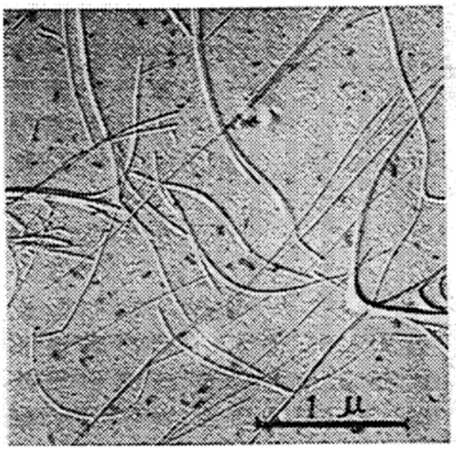
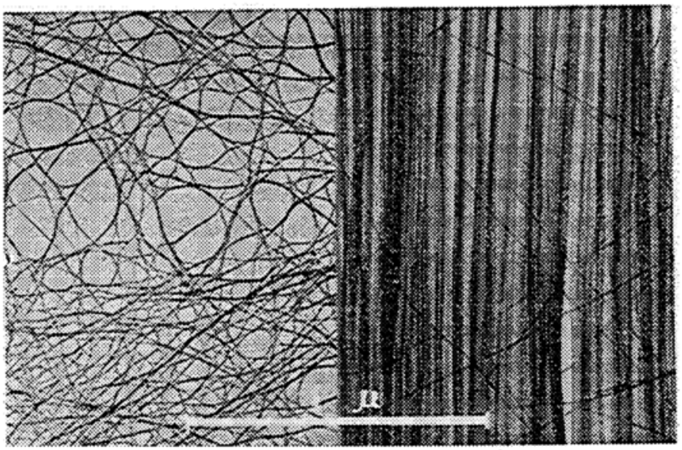


Fig. 2. Crystals in 2 weeks old Biltz sol. (Cr shadowing) × 20,000



a b

Fig. 3. Crystals in 1 year old Biltz sol. × 40,000

the case of ion exchange sol the amount of the dissolved vanadium pentoxide was less than that in Biltz and Müller sols even in the incipient stage of standing. About 0.2 g. ammonia existed in one liter of Biltz sol, (about 0.013 mole NH_3/l.; $V_2O_5 : NH_3 = 3 : 1$), but only a trace of it was found in Müller sol, and it was not detected at all in the ion exchange sol. Chloride ion was not detected in any of the sols. pH of the sols was 2.5 to 3.0.

Morphology of Crystals in Sols by Electron Microscopy.—Morphological characteristics of crystals in the three kinds of sol described above were observed by means of electron microscopy.

Biltz sol. The crystals in Biltz sol were small fibrils, a few score mμ long and 14 mμ thick, at the outset as shown in Fig. 1, but they grew like long fibers on standing. They grew to about 1 μ in size after a week, about 2 μ after 2 weeks (Fig. 2) and over a few μ after a month, then fibrous crystals got intertwined with one another and their length could not be measured. But a few weeks old Biltz sol contained small fibrils also as seen in Fig. 2. The thickness was, however, about 14 mμ and almost constant. An electron micrograph obtained from a specimen of a year old sol mounted on a specimen holder without supporting film showed a network structure as in Fig. 3 a. The fibrous crystals of various lengths clung together, forming a network structure. Thin films of crystals were formed on the surface of the sol which was aged over a few months. They were floated on the water and were scooped up with specimen holders without supporting films. The electron micrographs of these specimens showed the orientation of fibrous crystals with their long axes parallel to one another as in Fig. 3 b. When a small amount of the old Biltz sol was allowed to flow on the surface of still water and was scooped up with a specimen holder, an electron micrograph similar to that described above was also obtained. This figure was formed by the orientation of fibrous crystals to the direction of the flow. The fibrous crystals in Biltz sol grew markedly extended along their long axes on standing, but the fibrils in the sol dialyzed

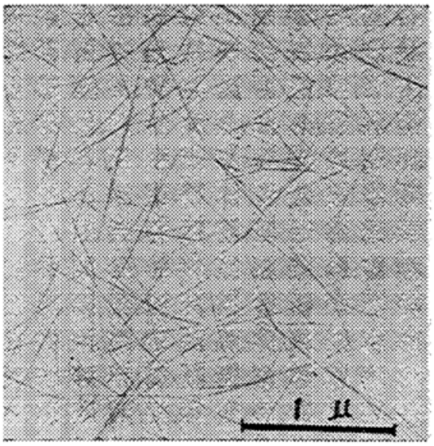


Fig. 4. Crystals in dialyzed Biltz sol. (1 year old sol) × 20,000

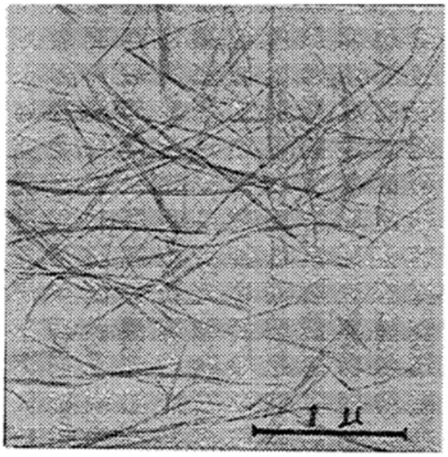


Fig. 5. Crystals in 1 year old Müller sol. × 20,000

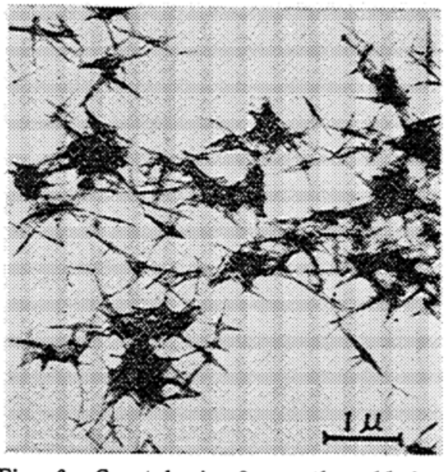


Fig. 6. Crystals in 2 months old ion exchange sol. × 10,000

immediately after preparation hardly grew at all as compared with the original Biltz sol, and an electron micrograph taken for one year old dialyzed sol showed needle crystals, a few μ long, as in Fig. 4.

Müller sol. The crystals in a freshly prepared Müller sol were small fibrils, about 50 mμ long and about 15 mμ thick, similar to those in Biltz sol. After standing for one year, their length was about 400 mμ and after 2 years it was about 1 μ as shown in Fig. 5. That is to say, the fibrous crystals more or less grew like fibers, but the rate of their growth was very small as compared with those of Biltz sol.

Ion exchange sol. The crystals in ion exchange sol were like needles, which were about 1.2 μ long and about 50 mμ thick, as shown in Fig. 6. Many needle crystals crossing at their center are observed in the micrograph. The shape and the size of the crystals are independent of the decomposition time and standing of the sol. A characteristic of the ion exchange sol is that the needle crystals in it do not grow on standing.

The crystals in these three kinds of sol described above were identified as vanadium pentoxide by electron diffraction method, which will de mentioned in the next paper.

Discussion of Results

There are two theories for the growth phenomena of the fibrous crystals in Biltz sol. One is the recrystallization theory and the other is the coagulation theory. Nemtsova[5] found the rapid growth of the crystals in Biltz sol when it was enclosed in a collodion bag and was dipped in saturated vanadium pentoxide solution. Tamamushi[6] reported that the aging of Biltz sol depended upon its adsorption of VO_3^- and H^+ ions on the fibrous crystals. These experiments suggested that the crystal growth in Biltz sol was attributed to the recrystallization. Lukjanovich[7] supported the coagulation theory by his studies of a phenomenon of the adsorption of colloidal silver on the ends of fibrous crystals in Biltz sol. Thiele and Kienast[8] also suggested the coagulation theory. The author will discuss the growth phenomenon by his experimental results as stated below.

The small fibrils in the freshly prepared

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[5] V. V. Nemtsova, *Doklady Akad. Nauk, USSR*, **79**, 297 (1951); *Chem. Abst.*, **45**, 6013 (1951).

[6] B. Tamamushi, *Sci. Paper Coll. Gen. Ed. Univ. Tokyo*, **6**, 37 (1956); cf. H. Tanaka and K. Meguro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 49 (1953).

[7] A. V. Bromberg, V. M. Lukjanovich, V. V. Nemtsova, L. V. Radushkevich and K. C. Chemutov, *Doklady Akad. Nauk, USSR*, **79**, 281, 827 (1951); **80**, 615 (1952).

[8] H. Thiele and G. Kienast, *Kolloid-Z.*, **127**, 134 (1952).

Biltz sol increase their length during the aging process, but the fibrils in the dialyzed Biltz sol, Müller sol, and ion exchange sol hardly grow at all on standing. As indicated in Table I, the concentrations of every sol are almost the same. The amount of the dissolved vanadium pentoxide in Biltz and Müller sols is somewhat greater than that in ion exchange sol at the outset of the standing, but it gradually decreased to a constant value, which is almost the same as the solubility of vanadium pentoside, 0.29 g. per liter[9]. The supersaturated vanadium pentoxide is deposited on the crystals during the aging, but this phenomenon seems not to be the origin of the growth of the fibrils to the very long fibrous crystals in Biltz sol, because the fibrils in Müller sol hardly grow at all on standing.

The main difference between the Biltz sol and the other sols is that of the amount of ammonia contained in the sols. Biltz sol contains about 219 mg. of ammonia per liter, but the Müller and the ion exchange sols contain little and no ammonia respectively. As the acidity of various sols is in the range of pH 2.5 to 3.0, it seems that the greater part of ammonia contained in Biltz sol combines with dissolved vanadium pentoxide (about 1 g. V_2O_5/l.) as ammonium vanadate at the initial stage of aging, and a part of ammonia is adsorbed by the crystals. The growth of the fibrous crystals in Biltz sol seems to be promoted by ammonium ion contained in the sol. Huber and Zbinden[2] prepared vanadium pentoxide sols from various alkali vanadates and indicated that alkali ions resulted from the preparation which promoted the growth of the fibrous crystals in sols and the effect increased with the increase of the atomic weight and the concentration of alkali ions. They also observed that the effect of the ammonium ion was almost the same as that of the potassium ion. It seemed that the vanadium pentoxide crystals in Biltz sol were apt to form ammonium vanadiate in the presence of ammonium ion and that the crystals of vanadium pentoxide were in equilibrium with dissolved ammonium vanadate and were liable to recrystallize.

By an electron microscopic observation, the small fibrils are found besides the long fibrous crystals in aged Biltz sol as shown in Fig. 2. The small fibrils were observed even in 2 months old Biltz sol and seemed to be formed by dissolution of small fibrous crystals.

The author considered that the growth of the fibrous crystals in Biltz sol was caused by Ostwald's ripening which was promoted by the increase of the solubility of the crystals owing to the presence of the ammonium ion in the sol.

Summary

Vanadium pentoxide sols were prepared by Biltz', Müller's and ion exchange method, and the crystals in the sols were observed with an electron microscope. The crystals in Biltz sol were small fibrils at first, but they grew into long fibrous crystals upon aging. The crystals in Müller and ion exchange sols were fibrils and needles respectively and hardly grew at all. The growth of the fibrous crystals in Biltz sol is likely to be due to the recrystallization of the fibrils.

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[9] M. Kerker, G. L. Jones, J. B. Reed, N. P. Yang and M. D. Schvenberg, *J. Phys. Chem.*, **58**, 1147 (1954).