SHORT COMMUNICATIONS

Manganese(III) Complexes with Ethylenediaminetetraacetic Acid

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Although there have been some papers[1-3] on the analytical use of maganese(III) complexes with ethylenediaminetetraacetic acid (EDTA), little is known of the nature of the complex compounds. The authors had studied the critical condition of their formation in solution and could isolate the crystalline solid.

Three methods of the preparation of Mn(III)-EDTA complexes from compounds of manganese in higher valency states have been examined. (1) Manganese dioxide suspended in water was mixed with solid ethylenediaminetetraacetic acid (H_4Y) under vigorous stirring. (2) In place of the free acid, a mixture of disodium salt of EDTA ($Na_2H_2Y \cdot 2H_2O$) and acetic acid was added to manganese dioxide. (3) Mn(II)-EDTA complex solution and manganese dioxide were mixed. Of these methods, the first was found to be the most suitable.

The relation between the mole ratio of manganese dioxide to EDTA and that of manganese dioxide to the produced Mn(III)-EDTA was shown in Fig. 1. Through the reaction a little of EDTA was lost and this may be due to its oxidation by manganese dioxide. However the mole ratio of Mn(III) to EDTA in the complex was approximately 1 : 1. Of course permanganate can also be used in place of manganese dioxide in all of these three methods.

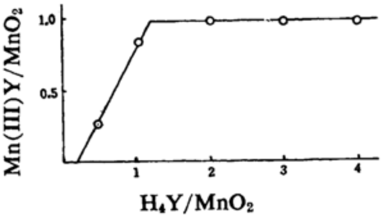

Fig. 1. Relation between the mole ratio of EDTA (H_4Y) : MnO_2 and the mole ratio of Mn(III)-EDTA : MnO_2 (MnO_2: 2.69×10^{-4} mol.).

The general method used to prepare the solid complex was as follows: to manganese dioxide precipitated by reducing potassium permanganate with ethanol, EDTA (in the acid form) was added in a ratio of little less than 1 : 1. On vigorous stirring reaction took place, evolving carbon dioxide, and a deep red solution was obtained. Filtering off the excess manganese dioxide, an equal volume of cold ethanol was added to the filtrate. The solution was allowed to stand for 1~2 hr. Deep red crystals thus obtained were washed with 90% ethanol and then with ethyl ether. Finally it was dried in the air in cold dark place; yield: 45~55%.

The crystal is deep red in color and decomposes easily in the light or on heating, giving carbon dioxide. The decomposition rate seems to be increased by the presence of Mn(II) ion. The oxidation equivalent of the complex was evaluted as 435±3 by iodometric titration. It is very soluble in water but insoluble in most of organic solvents. When a sample was heated with gradual elevation of temperature, 12~13% of weight loss took place at 25~130°C. This value may correspond to the sum of the weight of the water of crystallization and of EDTA partially decomposed. The remaining EDTA was completely

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[1] R. Přibil and J. Horacek, *Collection Czechoslov. Chem. Communs.*, **14**, 626 (1949).

[2] R. Přibil and V. Sumon, ibid., **14**, 454 (1949).

[3] R. Přibil and E. Hornychova, *Chem. Listy*, **40**, 101 (1950).

decomposed at 260～300°C. The solid gave the analysis: K, 9.50; Mn, 12.52; C, 28.56; H, 3.57; N, 6.53%. From these results the formula $K[Mn(EDTA)(OH_2)_2]\cdot H_2O$ was tentatively given as in the case of Cr(III)-EDTA complex[4].

Visible absorption spectra of the complex in acetic acid-sodium acetate buffer solutions of various pH were illustrated in Fig. 2. In the solution of pH 2.5～4.0 the maximum absorption was observed at 500 mμ, while in the higher pH region the color turned yellow and the maximum shifted to 450 mμ. By plotting the extinction against pH of the solution, the p*K* value between the red and the yellow species was evaluated as 5.3. It was also found that the red complex was strongly adsorbed on an anion-exchange resin in the chloride form. On titrating the complex with sodium hydroxide the curve in Fig. 3 was obtained. This curve has a single inflection at a neutralization point with approximately 1 mol. of sodium hydroxide per 1 mol. of the chelate. The pH of the half-neutralized solution is 5.5; which agrees fairly well with the p*K* value obtained from spectral data.

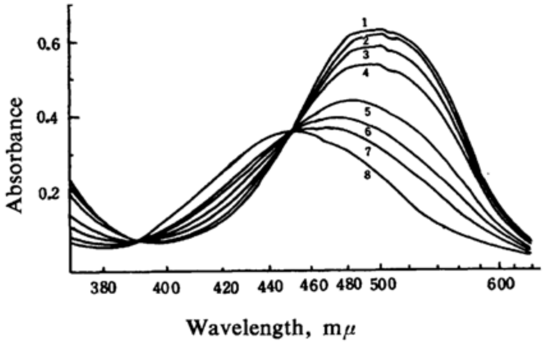

Fig. 2. The absorption spectra of Mn(III)-EDTA in CH_3COOH-CH_3COONa buffer solutions of various pH ($\mu=0.1$) (Mn(III): 9.34×10^{-4} mol./l.).

1: pH=2.50 2: pH=4.09 3: pH=4.54
4: pH=4.98 5: pH=5.40 6: pH=6.00
7: pH=6.28 8: pH=8.70

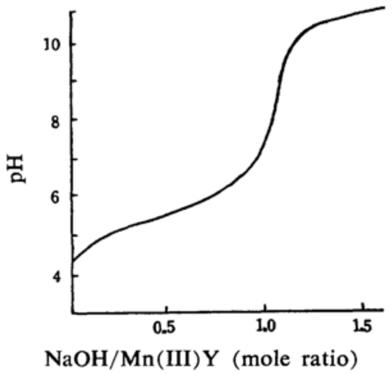

Fig. 3. Potentiometric titration of Mn(III)-EDTA with NaOH. (Concentration of Mn(III): 0.21×10^{-2} mol./50 ml., NaOH: 9.89×10^{-2} mol./l.).

The details of the experiment will be reported elsewhere.

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[4] C. Furlani, G. Morpurgo and C. Sartori, *Z. anorg. u. allgem. Chem.*, 303, 1 (1960).