Separation of Cr(III)-Hexacyanoferrate(II)-Complexes by Sephadex Column Chromatography*1

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The color reaction between chromium(III) ions and potassium hexacyanoferrate(II) has attracted the attention of the several investigators.[1-6] However, reaction products have not been isolated because of their great solubility in water. The chemical compositions of the products remain undetermined after a variety of electroanalytical and spectrophotometric investigations were carried out applying a continuous variation method.[4-6]

In the present work, employing a chromatographic method using Sephadex columns, at least three complex compounds differing with each other in color, chemical composition and molecular size were separated from the reaction mixture. The mixture obtained by reacting potassium hexacyanoferrate(II) with Cr(III) ions (chrome alum) in a molar ratio of 5 : 1 for one hour in an aqueous solution at 47°C, when applied to a Sephadex G-25 column, gave a bluish-green fraction eluting first and a reddish-brown one eluting second, the unreacted hexacyanoferrate(II) and sulfate ions remaining behind in the column. After repeating chromatography a further three times, the second fraction appeared to be pure, not only in paper electrophoresis but in further subjection to chromatography with Sephadex of a smaller pore size. The first fraction, giving two components in paper electrophoresis, was definitely separated when further applied to Sephadex G-75 or G-100 columns, into two fractions, blue and green. Each proved to be a definite constituent in paper electrophoresis and in any further application to a Sephadex column of larger pore size. The three substances separated all consisted of K, Cr, Fe and CN. The reddish-brown and green substances permeated a cellophane film, while the blue substance did not, being confirmed of high molecular size.

The reddish-brown substance was the main product in which more than 90% of the reacted Cr(III) ions were contained, and was the smallest of the three substances in molecular size. It proved on electrophoretic and polarographic examination[3] to include a negatively charged complex ion containing Cr, Fe and CN. The reddish-brown solution described above was evaporated to dryness *in vacuo* in a rotary evaporator at 30°C, and the composition of the resulting solid film was determined by elementary analysis to have the empirical formula $K_5CrFe_2(CN)_{12}\cdot 7H_2O$.

Found: K, 24.2; Cr, 6.5; Fe, 13.8; C, 17.6; N, 20.7; H_2O, 15.1%. Calcd for $K_5CrFe_2(CN)_{12}\cdot 7H_2O$: K. 24.5; Cr, 6.5; Fe, 14.0; C, 18.1; N, 21.1; H_2O, 15.7%.

The same three components separated from reaction mixtures as long as the molar ratio of the reactants, potassium hexacyanoferrate(II) to Cr(III) ions, remaining not below 2.5. The elution diagram in Fig. 1 illustrates the chromatographic separation of the reddish-brown complex on a Sephadex G-25 column from the reaction mixture resulting at a reactant ratio of 2.5.

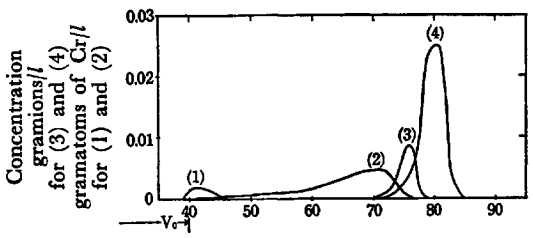

Fig. 1. Separation of the reaction mixture resulting from the mixture containing the reactants in the molar concentrations of 0.076 for $KCr(SO_4)_2$ and 0.19 for $K_4Fe(CN)_6$.
Sephadex G-25, fine (particle size 20—80 microns)
Column dimensions: dia. 2 cm, length 27 cm
Sample volume: 0.8 ml Eluant: Water
Elution velocity: 98 ml/hr Temp: 26°C
(1) Bluish green (In this curve the concentration was exaggerated for distinctness.)
(2) Reddish brown
(3) Hexacyanoferrate(II) ion
(4) Sulfate ion

Details on the products at varying reactant ratios, as well as the results of a structural study, will be presented later.

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