components are demonstrated which have not vet been identified. The use of countercurrent distribution for separating corticosteroids has previously been described 10 but a more detailed discussion will appear elsewhere 11.

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## On the Hydrolysis of the Bi<sup>3+</sup> Ion — a Preliminary Note

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In 1947, Granér and Sillén <sup>2</sup> studied the hydrolysis of bismuth(III) in 3 M NaClO<sub>4</sub> medium, measuring [H<sup>+</sup>] with quinhydrone and glass electrodes, and [Bi³+] with bismuth amalgam electrodes. A mechanism was proposed which seemed to agree well with their data, which covered the range  $[Bi]_{tot} = 10$  to 50 mM. One of us (A.O.) has now undertaken a

study with similar methods, but with total

Bi concentrations ranging from 0.1 to 50 mM, thus a factor of 1:500 instead of 1:5. The present data can be explained by assuming the presence of only two complexes, the mononuclear BiOH2+ and the hexanuclear Bi<sub>e</sub>(OH)<sub>13</sub> (as usual, plus or minus an unknown amount of water) with the preliminary equilibrium constants:

$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+$$
 $K_{1,1} = 0.026 M$ 
 $6 Bi^{3+} + 12 H_2O \rightleftharpoons Bi_{4}(OH)_{12}^{6+} + 12 H^+$ 
 $K_{12,6} = 2.14 M^7$ 

This result agrees with the findings of Kraus, Holmberg and Johnson in so far as their "equilibrium ultracentrifugations suggest predominance of a low molecular weight polymer (N = ca. 5 or 6)". In a more narrow concentration range Souchay and Peschanski s concluded that there is only one complex present; they ascribed to it the formula, Bi<sub>4</sub>O<sub>4</sub><sup>4+</sup>.

The old data of Granér and Sillén were slightly distorted by the fact, then unknown, that quinone is a base and attracts protons at the highest acidities (Biedermann and Sillén 4). After a correction for this effect, the present data are in general found to agree well with those of Granér and Sillén. This little deviation, however, sufficed (together with the narrowness of the [Bi]total range) to indicate an incorrect mechanism.

Attempts are now being made, in collaboration with Professor Cyrill Brosset, to study the structure of the complex by means of X-ray diffraction on aqueous solutions.

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A detailed paper will be published elsewhere.

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