A Note on the Relative Dissociation Constants of some Metal-oxine Complexes

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The relative dissociation constants of the Mg-, Mn-, and Co-oxine complexes cannot easily be determined in aqueous solution because of their very low solubilities. When 10 ml. of M/1000 oxine in amyl alcohol are equilibrated against 10 ml. of aqueous M/10,000 metal chloride, the concentration of metal complex in the amyl alcohol, and thus its degree of dissociation, may be determined colorimetrically. Because hydrogen ions compete with the metal ions for the oxine, the dissociation of the complex is a function of the pH value of the aqueous phase. Under these conditions, the pH value at which the complexes are half dissociated was found to be pH 5 for cobalt complex and pH 7 for the manganese complex. Taking into account the divalency of the metal, the apparent dissociation constants must, therefore, differ by a factor of about 10^4 , the manganese being more dissociated than the cobalt complex.

The relative value for the magnesium complex could not be determined in this way, because it forms nearly colourless solutions and this only at very alkaline pH values. Because of the pale colour of the solutions of the complex, however, it was possible to use direct competition against manganese. It was found that at pH 10, the manganese complex formed by equilibrating 10 ml. of M/10,000 aqueous manganous chloride against 10 ml. of M/1000 oxine in amyl alcohol was half dissociated by a concentration of M/100 magnesium chloride in the aqueous phase. Thus, the apparent dissociation constants differ by a factor of about 100, the magnesium complex being more dissociated than the manganese complex. The values obtained for the relative apparent dissociation constants in this way do not, of course, represent simple dissociation constants because they involve also the amyl alcohol-water partition coefficient for the oxine and metal complexes. But this should not be any disadvantage from the point of view of the biological material considered in this paper.

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