SPECTROPHOTOMETRIC STUDY OF FERRIC DIMETHYLGLYOXIME COMPLEX

It is well known that dimethylglyoxime forms complexes with various metallic ions.[1–4] The ferrous iron complex[5] with dimethylglyoxime gives in an ammoniacal solution a characteristic pink colour which is measured at maximum absorbancy. The presence of dimethylglyoxime prevents the precipitation of ferric salts as hydroxide even at high pH. This indicates the formation of a ferric complex, which is studied spectrophotometrically using a Beckman DU Spectrophotometer with a matched 1 cm. silica cell. Chemicals used in these experiments are E. Merck Guaranteed or B.D.H. Analar Reagents.

Dimethylglyoxime in alcohol shows a continuous absorption in the ultraviolet region [Fig. 1 (A)]. Ferric chloride in aqueous solution shows an absorption maximum at 335 mμ which shifts to 345 mμ on addition of alcohol [Fig 1 (B, C)]. The colour of the alcoholic solution is deeper and the optical density greater than that of the aqueous solution. The absorption curves obtained with ferric chloride to which different amounts of dimethylglyoxime have been added are identical with the curve for alcoholic solution of ferric chloride.

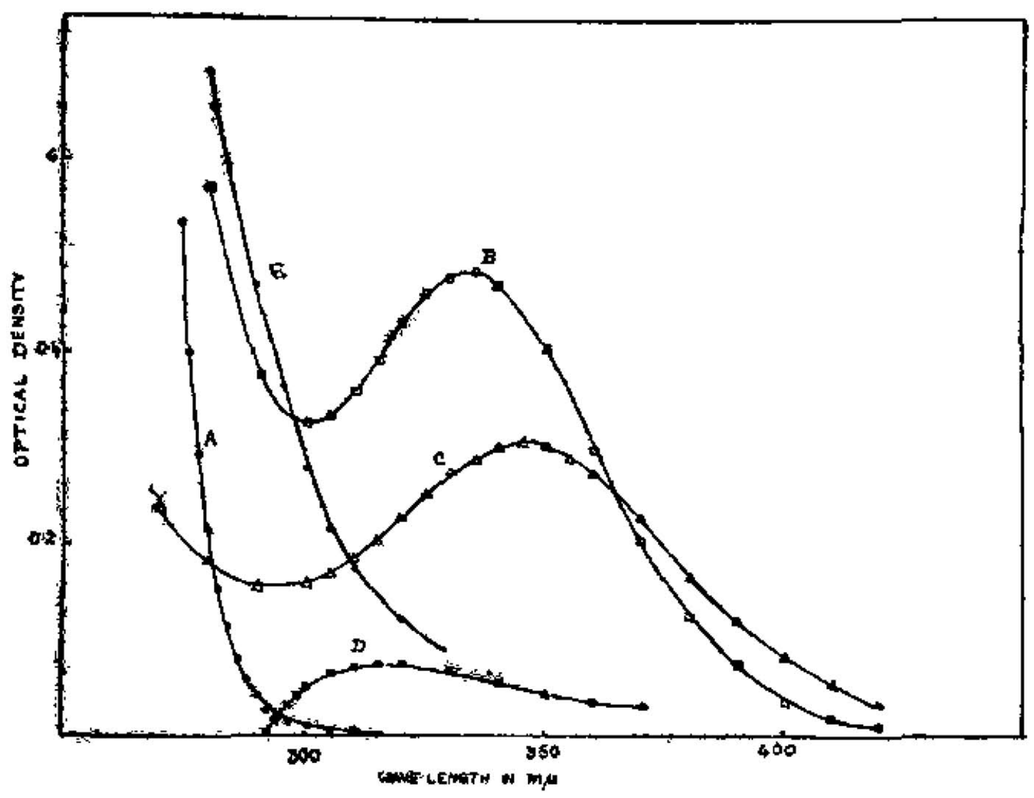

FIG. 1.

A—Dimethylglyoxime in alcohol 0·025% solution.
B—Ferric chloride in water 0·055 mg. of Fe_2O_3/ml.
C—Ferric chloride in alcohol 0·011 mg. of Fe_2O_3/ml.
D—Ferric chloride (0·0022 mg. of Fe_2O_3/ml.) and dimethylglyoxime (4·0 mg./ml.) in alcohol pH 10·4.
E—Ferrous dimethylglyoxime complex in ammonia C_{Fe} 0·0044 mg. Fe_2O_3/ml.

However, an absorption maximum is obtained for the ferric dimethylglyoxime complex in

an ammoniacal medium. The absorption curve is measured with 1 ml. of ferric chloride solution (containing 0·055 mg. Fe_2O_3 per ml.), 10 ml. of 1% solution of dimethylglyoxime, 2 ml. of ammonium hydroxide (pH 11) and ethyl alcohol to make up the volume to 25 ml., and a maximum is obtained at 320 mμ [Fig. 1 (D)]. To confirm that this maximum is not due to the ferrous complex, the absorption curve for ferrous was also taken [Fig. 1 (E)]. It is clear that the maximum at 320 mμ is indicative of the formation of the ferric dimethylglyoxime complex. The necessity of addition of large excess of dimethylglyoxime in order to keep ferric salt in solution in ammoniacal medium is presumably due to the demands of the law of mass action. Without a sufficient excess of dimethylglyoxime the extent of complex formation would not be sufficient to prevent the precipitation of ferric hydroxide. The Beer's Law curve is shown in Fig. 2. The

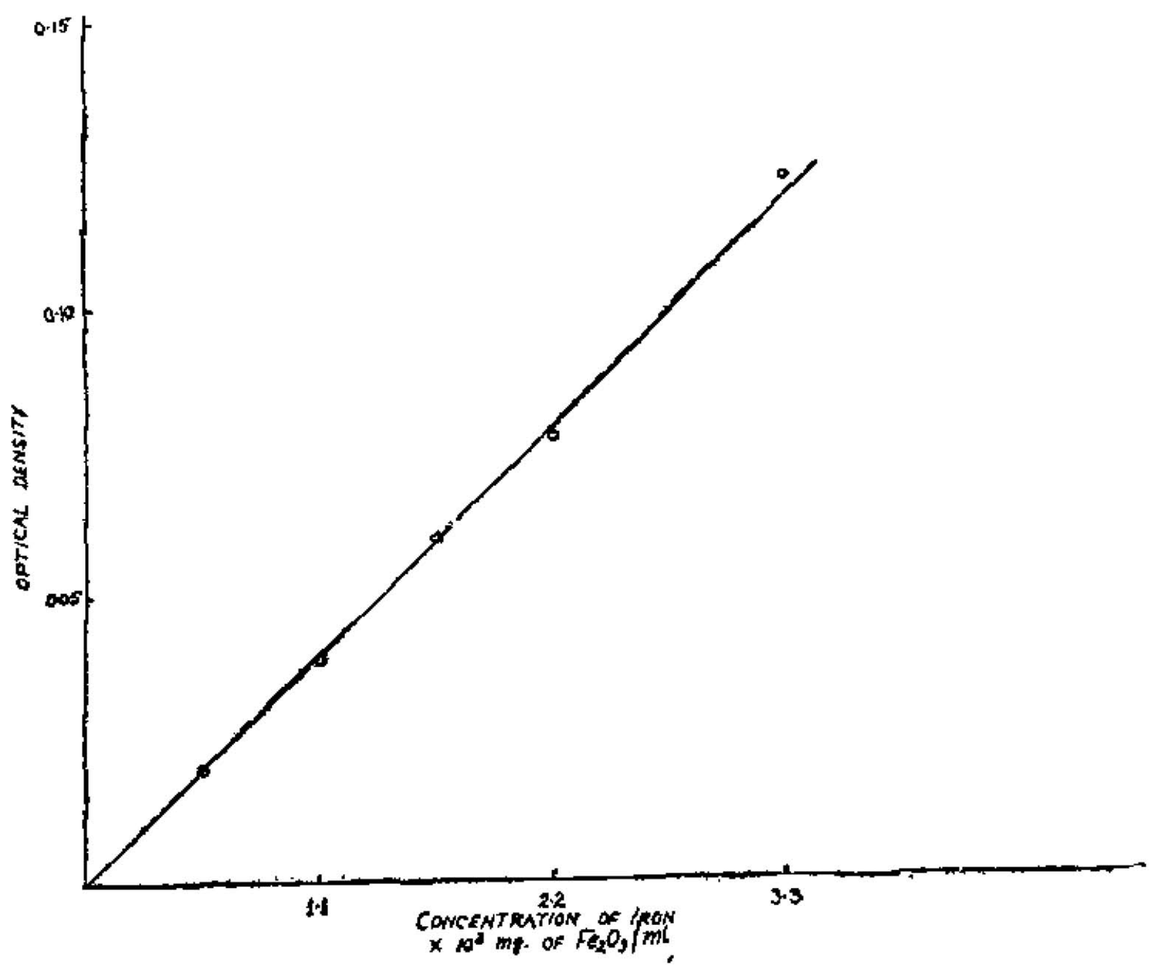

FIG. 2. X mg. of Fe^{+++} added to dimethylglyoxime (4·0 mg./ml.) in alcohol and pH adjusted to 10·4.

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