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Spectrophotometric Investigation of the Interaction between Iron(II) and Iron(III) in Hydrochloric Acid Solutions¹BY HARDEN MCCONNELL AND NORMAN DAVIDSON²

This communication describes a study of "optical interaction absorption" in hydrochloric acid solutions containing iron in two oxidation states, iron(II) and iron(III). That is, a 5–12 *F* hydrochloric acid solution containing both iron(II) and iron(III) exhibits a total light absorption in the 550–800 $m\mu$ wave length range which is markedly greater than the sum of the light absorptions of (a) complexes containing only iron(II) and (b) complexes containing only iron(III), present in the solution.

Investigations in this Laboratory of the interaction absorption exhibited by hydrochloric acid solutions of antimony(III) and (V),³ by hydrochloric acid solutions of tin(II) and (IV), and by mixed hydrochloric acid–perchloric acid solutions of copper(I) and (II)⁴ have already been reported.⁵

Experimental

Hydrochloric acid solutions containing iron(III) were prepared by slowly dissolving anhydrous ferric chloride in hydrochloric acid of the desired formality. It was assumed that the change of the hydrochloric acid formality was negligible. The iron(III) concentration was determined by reduction to the ferrous state with amalgamated zinc and titration with standard potassium permanganate solution, using the Zimmerman–Reinhardt procedure. Hydrochloric acid solutions containing both iron(II) and (III) were prepared by washing crystals of $FeCl_3 \cdot 4H_2O$ with hydrochloric acid and then dissolving the crystals in hydrochloric acid solutions containing iron(III). The iron(II) concentration was determined with standard potassium permanganate solution and the total iron concentration was determined as above. Solutions containing manganese(II) and iron(III) were prepared by dissolving weighed samples of crystalline $MnCl_2 \cdot 4H_2O$ in 12 *F* hydrochloric acid solutions containing iron(III). The crystals of $MnCl_2 \cdot 4H_2O$ were analyzed by the method of Lingane and Karplus⁶ to insure that the water of hydration corresponded to this formula. Weighed crystalline samples of $MgCl_2 \cdot 6H_2O$ were dried at 85° (dec. temp. 117°) for a period of thirty minutes. Zinc chloride solutions were prepared from fused zinc chloride. Hydrochloric acid solutions containing only iron(II) were prepared by dissolving powdered iron metal in hydrochloric acid of known formality, and then filtering the solution through a fine sintered glass funnel. The operations of dissolving the iron, filtering the solution and measuring volumetric samples were all performed in the same closed air-free apparatus, which was completely flushed with carbon dioxide. Titrations of iron(II) were performed in a carbon dioxide atmosphere. Hydrochloric acid concentrations

were determined by titration with standard sodium hydroxide solution to the methyl orange end-point.

Absorption spectra were measured with the model DU Beckman spectrophotometer. All the absorption data except as given in Figs. 3, 4 and 7 were obtained with one centimeter light paths. The absorption data of Fig. 3 were determined with 0.10, 0.03 and 0.01 cm. light paths obtained with calibrated quartz spacers placed in a quartz cell of 1.00 ± 0.002 cm. light path. Some of the data of Figs. 4 and 7 were determined with a 10.0 cm. light path.

Results and Discussion

Figure 1 illustrates the effects of added ferrous chloride, manganous chloride, zinc chloride and magnesium chloride on the absorption spectrum (550–725 $m\mu$) of a solution of ferric chloride in 12 *F* hydrochloric acid. All of the above divalent halides are essentially colorless in this wave length range. The data of this figure clearly indicate the marked and specific effect of iron(II) on the absorption spectrum of solutions of iron(III).

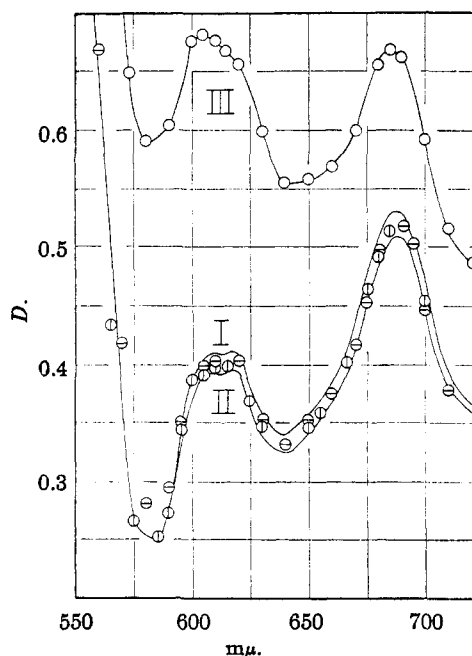


Fig. 1.—Effects of several salts on the absorption spectrum of iron(III) in 12 *F* hydrochloric acid: curve I, 0.88 *F* $FeCl_3$, no added salt; curve II, 0.88 *F* $FeCl_3$, 0.13 *F* $MgCl_2$; ⊙, 0.88 *F* $FeCl_3$, 0.13 *F* $MnCl_2$; ⊗, 0.88 *F* $FeCl_3$, 0.13 *F* $ZnCl_2$; curve III, 0.88 *F* $FeCl_3$, 0.13 *F* $FeCl_2$.

By analogy with other investigations of interaction absorption,^{3,4} it is anticipated that the total optical density, $D(\lambda, c_{II}, c_{III})$, of a hydro-

(1) Presented in part at the San Francisco Meeting of the American Chemical Society, April 1, 1949.

(2) To whom inquiries concerning this article should be addressed.

(3) J. E. Whitney and N. Davidson, *THIS JOURNAL*, **69**, 2076 (1947); **71**, 3809 (1949).

(4) H. McConnell and N. Davidson, *ibid.*, **73**, 3168 (1950).

(5) Dr. Harvey Diehl and collaborators at Iowa State College, Ames, have independently studied the iron(II), (III) system (private communication).

(6) J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

chloric acid solution containing iron(II) and (III) can be expressed by the equation

$$D(\lambda, c_{\text{II}}, c_{\text{III}}) = (c_{\text{II}} - c_{\text{D}})\bar{\epsilon}_{\text{II}} + (c_{\text{III}} - c_{\text{D}})\bar{\epsilon}_{\text{III}} + (c_{\text{II}} - c_{\text{D}})(c_{\text{III}} - c_{\text{D}})k \quad (1)$$

The three terms on the right hand side of (1) represent the optical densities of iron(II) complexes, iron(III) complexes and "interaction complexes," each interaction complex containing one atom of iron(III), one atom of iron(II), and a number of coordinating chloride ligands. In eq. (1), c_{II} and c_{III} are the formal concentrations of iron(II) and (III), c_{D} is the concentration of the interaction dimer, $\bar{\epsilon}_{\text{II}}$ and $\bar{\epsilon}_{\text{III}}$ are the formal extinction coefficients of iron(II) and iron(III). The interaction constant, k , is a function of the formation constants and extinction coefficients of the various interaction complexes. By analogy, with previous studies, it is further anticipated that the interaction dimer is strongly colored and is present at sufficiently low concentration so that equation (2) holds.

$$D(\lambda, c_{\text{II}}, c_{\text{III}}) = c_{\text{II}}\bar{\epsilon}_{\text{II}} + c_{\text{III}}\bar{\epsilon}_{\text{III}} + c_{\text{II}}c_{\text{III}}k \quad (2)$$

To evaluate the interaction function, k , we assume that there is a small non-specific effect of ferrous chloride on the $c_{\text{III}}\bar{\epsilon}_{\text{III}}$ term of (2) which may be estimated from the effect of manganous chloride or magnesium chloride on the $c_{\text{III}}\bar{\epsilon}_{\text{III}}$ term.

Figure 2 exhibits the values of the interaction function, k , calculated from the data of Fig. 1 using equation (2) and also values of k calculated from a series of measurements on 12 *F* hydrochloric acid solutions containing one-half the concentrations of iron(III), iron(II), manganese-

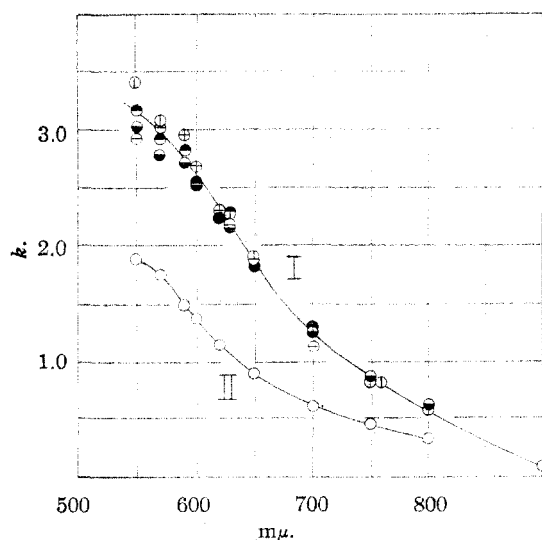


Fig. 2.—Dependence of k on wave length and hydrochloric acid concentration: I, 12 *F* HCl solutions. Points \circ and \ominus of this figure calculated from the data of Fig. 1, using magnesium and manganese corrections, respectively; points \bullet and \bullet , solutions of Fig. 1, diluted by a factor of two, magnesium and manganese corrections, respectively. II, 5.0 *F* HCl solutions, data of Fig. 5 (ordinates, $k \times 10$).

(II) and magnesium(II) used for Fig. 1. The agreement between the two sets of the data supports equation (2). A test of this relation over a wider range of iron concentrations was precluded by the rather small values of k and by the limited solubility of ferrous chloride in concentrated hydrochloric acid solutions of ferric chloride. There is agreement to within about 10% for the values of k obtained using the magnesium and the manganese corrections.

An attempt was made to determine the interaction absorption at shorter wave lengths, 450–550 *mμ* by employing short light paths. As shown in Fig. 3 the optical density of interaction absorption is small compared to the large optical densities due to the iron(III)–chloro complexes in this wave length range. Furthermore, the difference between the optical densities of an iron(III)–magnesium(II) mixture and an iron(III)–manganese(II) mixture is of the same order of magnitude as the difference between the optical densities of an iron(III)–iron(II) mixture and an iron(III)–manganese(II) mixture. The values of the interaction absorption function, k , are therefore quite different depending on whether mixtures of iron(III) with manganese(II) or with magnesium(II) are used to determine the iron(III) absorption; it is not even possible to say with certainty whether the interaction absorption in this range is greater or less than in the 550–700 *mμ* range.

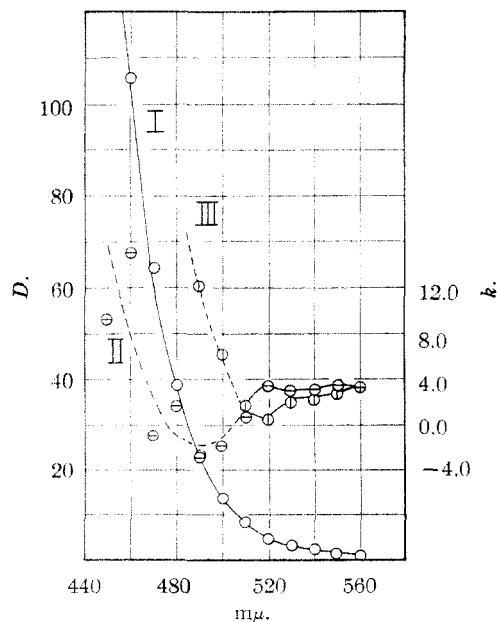


Fig. 3.—Optical interaction in the 460–560 *mμ* range: I, optical density, D (referred to a 1.00 cm. light path), of 0.88 *F* FeCl_3 in 12 *F* HCl and containing 0.13 *F* MgCl_2 . II, III, values of k calculated using magnesium(II) and manganese(II) corrections, respectively. Concentrations identical with those of Fig. 1. (Curves are dashed in regions of large probable error.)

Figure 4 gives the optical densities, $D(\text{II}, \text{III})$, $a_{\text{III}}\epsilon_{\text{III}}$ and $a_{\text{II}}\epsilon_{\text{II}}$, measured with the Beckman spectrophotometer from 720 to 1,000 $m\mu$. As shown in Fig. 2, the interaction absorption is observed to decrease continuously with increasing wave length. At 920 $m\mu$, the optical interaction absorption is equal to zero within the experimental error of 5%. At wave lengths greater than 920 $m\mu$, k was found to be zero within the experimental error; however, the high intensity of scattered light in the spectrophotometer at these wave lengths makes this conclusion uncertain.

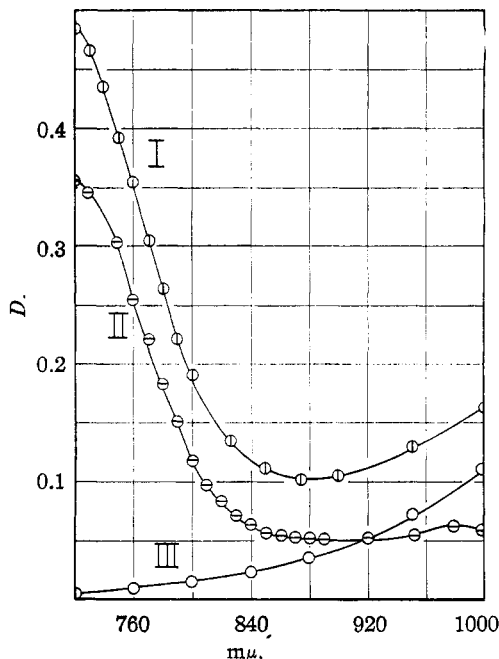


Fig. 4.—Optical densities of 12 F hydrochloric solutions containing I, 0.88 F iron(III) and 0.13 F iron(II); II, 0.88 F iron(III) and 0.13 F magnesium(II); III, 0.13 F iron(II).

Figure 5 gives the data used in the determination of optical interaction absorption in 5 F hydrochloric acid solutions. The optical interaction absorption in 5 F hydrochloric acid solutions is not sufficiently intense to allow an experimental verification of eq. (2). Assuming eq. (2) to hold for these solutions, values of k have been calculated from the data of Fig. 5 and are plotted in Fig. 2. It may be seen that k decreases (by a factor of approximately 20) when the hydrochloric acid concentration is decreased from 12 to 5 F .

Figure 6 shows the absorption spectra of solutions containing $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ in 4 F perchloric acid.⁷ In these solutions the values of k (eq. (5)) are calculated to be 0 ± 0.05 and we may infer that the interaction absorption between $\text{Fe}(\text{H}_2\text{O})_6^{++}$ and $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ is much less than that between the chloro complexes of these ions.

(7) The data of Fig. 6 were taken by Mr. Wendell Miller.

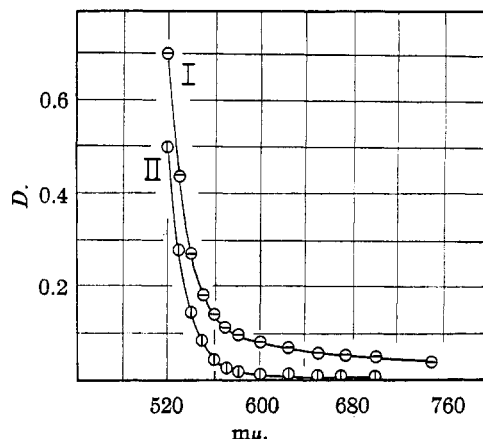


Fig. 5.—Optical densities of 5 F hydrochloric acid solutions containing I, 0.68 F iron(III), 0.71 F iron(II); II, 0.68 F iron(II), 0.71 F magnesium(II). (The light absorption by iron(II), not shown in the figure, is important at wave lengths above 625 $m\mu$ and has been taken into account in calculating k for these wave lengths.)

It is known that iron(III) forms chloro complexes in hydrochloric acid solutions. Rabinowitch and Stockmayer⁸ have determined the formation constants and the absorption spectra of the complexes, FeCl_i^{3-i} , for $i = 1, 2, 3$ in dilute hydrochloric acid solutions. Metzler and Myers⁹ have suggested that FeCl_4^- is the predominant

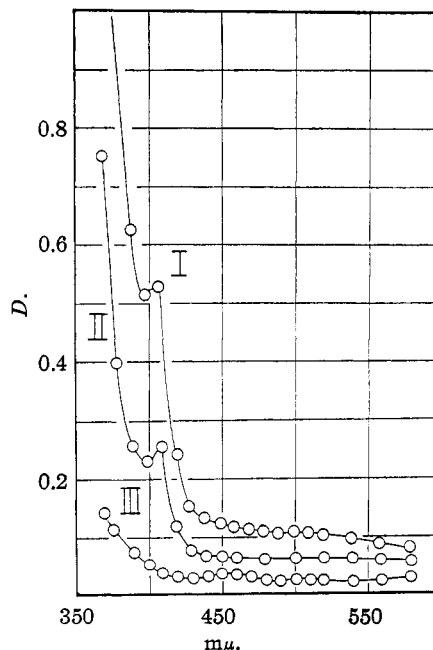


Fig. 6.—Optical densities of 4.0 F perchloric acid containing: I, 1.08 F $\text{Fe}(\text{ClO}_4)_3$, II, 0.54 F $\text{Fe}(\text{ClO}_4)_3$, 0.54 F $\text{Fe}(\text{ClO}_4)_2$; III, 1.08 F $\text{Fe}(\text{ClO}_4)_2$.

(8) E. Rabinowitch and W. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

(9) D. E. Metzler and R. J. Myers, *ibid.*, **72**, 3776 (1950).

complex species of iron(III) in 12 *F* hydrochloric acid.

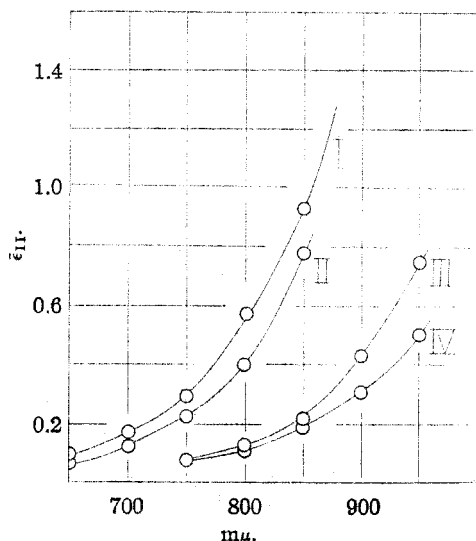


Fig. 7.—Dependence of the formal extinction coefficient of iron(II), $\bar{\epsilon}_{II}$, on hydrochloric acid concentration: I 4.1 *F* HCl, 0.31 *F* FeCl₃; II, 5.0 *F* HCl, 1.42 *F* FeCl₂; III, 10.4 *F* HCl, 0.29 *F* FeCl₂; IV, 12 *F* HCl, 0.08 *F* FeCl₂.

Figure 7 shows that the formal extinction coefficient of iron(II), $\bar{\epsilon}_{II}$, decreases as the hydrochloric acid concentration is increased. It is likely that this is due to the formation of iron(II)-chloro complexes. (It is highly improbable that there is sufficient $\text{Fe}(\text{OH})^+$ at the acidities used to account for the light absorption by the solutions.) Thus it is seen that a strongly colored interaction dimer can be formed in solutions containing chloro complexes of both iron(II) and iron(III). The species $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ and $\text{Fe}(\text{H}_2\text{O})_6^{++}$ do not interact. Mr. J. A. Ibers, in this Laboratory, has observed that there is no interaction absorption in mixed solutions of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. There appears to be interaction absorption in the solid ferroferrocyanides, in Fe_3O_4 , in freshly precipitated mixtures of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, and in numerous minerals containing iron(II) and (III), *e. g.*, biotite and tourmaline.¹⁰ It is possible that direct chemical bridging of a ligand between the two iron atoms is important for the occurrence of interaction absorption. Thus the bridged structure, $\text{Fe}-\text{C}\equiv\text{N}:\text{Fe}$, occurs in the ferri-ferrocyanides, and Fe_3O_4 has O^{2-} bridges between the two kinds of iron atoms. The interaction dimer in the hydrochloric acid solutions may contain a halogen bridge between the iron(II) and the iron(III) atom. This theory leads to the sugges-

tion that interaction absorption due to hydroxyl bridging may occur in mixed solutions of $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ which are less acid than the ones studied here.¹¹

The increase in the interaction constant, k , with increasing hydrochloric acid concentration that has been observed for all the cases of interaction absorption studied in this Laboratory, *viz.*, Sb(III, V), Sn(II, IV), Cu(I, II) and Fe(II, III) may be due to one or both of the following factors. Due to both mass action and activity effects, the concentrations of the interaction dimers may be increased by increasing the hydrochloric acid concentration. Furthermore it is to be expected that of the various interaction complexes formed, those having a larger number of chloride ligands will be the more strongly colored in the long wave length part of the absorption spectrum. This is similar to the shift of the "electron transfer" spectra of complexes containing a single cation to longer wave lengths as the number of chloride ligands is increased.^{8,12}

Acknowledgments.—This research has been supported by the Office of Naval Research. We are indebted to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer. It is a special pleasure to acknowledge that Mr. Rollie Myers, formerly of this Laboratory, made the original observation of the occurrence of interaction absorption for mixtures of iron(II) and (III) in concentrated hydrochloric acid solutions.

Summary

The light absorption in the 450–900 *mμ* wave length range by mixed solutions of iron(II) and iron(III) in hydrochloric acid is interpreted as evidence for the formation of unstable but strongly absorbing interaction complexes, each interaction complex containing one atom of iron(II), one atom of iron(III) and a number of coordinating chloride ligands. The light absorption by interaction complexes decreases with decreasing hydrochloric acid concentration and there is no interaction absorption by solutions containing $\text{Fe}(\text{H}_2\text{O})_6^{++}$, $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ and no chloride ion.

Absorption spectra of iron(II) in solutions of varying hydrochloric acid concentration observed in the 700–900 *mμ* wave length range are used to show the presence of iron(II)-chloro complexes.

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(11) The one known case where there is not a direct bridge of the type discussed above is for the intensely black salts of the type Cs_3SbCl_6 , in which each antimony ion is surrounded by an octahedron of chlorides and each chloride is coordinated to only one antimony ion (L. A. Jensen, *Z. anorg. Chem.*, **252**, 317 (1944)).

(12) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

(10) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).