SPECTROPHOTOMETRIC INVESTIGATIONS ON THE IRON (III)-MORELLIN COMPLEX

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Abstract

1. Spectrophotometric investigations have been carried out on solutions of ferric chloride and iron (III)-morellin complex in an absolute alcohol medium.

2. It is noticed that there is a continuous shift in the absorption maximum of ferric chloride from 410 mμ to 490 mμ as the concentration is raised from $2 \cdot 24 \times 10^{-4}$ M to $2 \cdot 30 \times 10^{-1}$ M of ferric chloride in alcohol.

3. When ferric chloride is mixed with morellin, only one complex, having the molar composition Fe_2R_3 (R = morellin constituent) with an absorption maximum at 550 mμ, is formed. The advantage of the complex formation can be taken to estimate iron (III) in the range 0·5 to 19 p.p.m.

4. The iron (III)-morellin complex dissociates in the absolute alcohol medium and the equilibrium constant K determined spectrophotometrically averages $4 \cdot 95 \times 10^{-17}$ at 25° C. The free energy of formation of the complex is $-22 \cdot 15$ Kcal./mole.

Morellin,[1] an orange-yellow plant pigment, is isolated from the pericarp of the seeds of a tree, *Garcinia morella*. The molecule[2] of morellin contains the chelating group C, C, C–O, OH[3] which can form with metals inner complexes, having characteristic spiran-type structure. While studying the influence of foreign ions on the estimation of thorium and uranium with morellin, Rao and Patel[4] observed that the ferric iron interfered in all proportions. The present authors have studied the behaviour of ferric iron on morellin and noticed the production of a greenish-black complex in aqueous alcoholic medium. It was found that the complex got hydrolysed in this medium on keeping. The investigation on the complex had, therefore, to be conducted in absolute alcohol medium. The colour formation with morellin in absolute alcohol is almost instantaneous. The maximum intensity of the colour is attained within a few minutes. The colour does not diminish even on keeping the solution for several days in the dark. The complex is found to be stable in alcohol but is destroyed in acid or alkaline alcoholic solutions. The present investigation was undertaken with a view to determining the composition of the complex formed between ferric iron and morellin in alcohol medium. The molar composition of the iron-morellin complex has been determined by the

Job's method of continuous variation[5] and verified by the slope ratio method.[6] The molar ratio method[7] could not be used for the same purpose, since the complex suffered dissociation in solution, as is evident from the plots in Fig. 3. This method was, however, employed to determine the equilibrium constant and the free energy of formation of the iron-morellin complex.

APPARATUS AND REAGENTS

Instrument.—Spectrophotometric measurements were made with Coleman Universal Spectrophotometer, Model 14, with purple filter 14–214, using cuvettes (optical path = 1·58 cm.) of special glass and at constant band-width of 35 mμ in the visible region of the spectrum from 400 to 650 mμ. The wavelength could be altered by means of the diffraction grating.

Reagent Solutions.—(1) Pure morellin (m.p. 156° C.) used in this study was obtained through the courtesy of Dr. P. L. N. Rao and his colleagues of this Institute. The strength of the stock solution of morellin in absolute alcohol was $1 \cdot 352 \times 10^{-3}$ M.

(2) Anhydrous ferric chloride, prepared by the direct chlorination of pure iron filings with dry chlorine and purified by sublimation,[8] was dissolved in absolute alcohol and the solution preserved in an amber-coloured glass-stoppered bottle. Iron content of the stock solution was found to be $1 \cdot 650 \times 10^{-2}$ M by analysis.

(3) Absolute alcohol prepared by the method of Noyes[9] was used for the preparation of solutions. Care was taken to avoid, as far as possible, the absorption of water by the alcohol solutions.

Photochemical Reaction of Ferric Chloride in Alcohol.—It has been reported in literature by numerous workers[10-12] that ferric chloride is photometrically reduced by alcohol. Benrath,[10] however, classifies the photoreduction of ferric chloride as a 'true' photochemical reaction. Experiments were, therefore, conducted to see whether any change in spectral-transmittance curves occurred when the solutions of ferric chloride were preserved in amber-coloured glass-stoppered bottles, kept in dark for several weeks. These experiments did not show any change in the curves and the spot-test analysis also indicated the absence of ferrous iron, indicating that the above method of storage was quite satisfactory.

ABSORPTION SPECTRA

(1) *Spectral Characteristics of Morellin Solutions.*—The absorption spectra of morellin solutions, studied at various concentrations, showed a simple broad band with absorption maximum at 410 mμ. The spectra also showed that there was negligible absorption between 550 mμ and 650 mμ for the concentrations employed. These findings are in conformity with the earlier observations made by Rao and Patel.[4]

(2) *Spectral Characteristics of Ferric Chloride Solutions.*—An investigation of the spectrum of ferric chloride at different concentrations showed a continuous shift in the absorption band in the visible region of the spectrum.

TABLE I

Variation of Absorption Maximum with Change in Concentration of Ferric Chloride in Alcohol

Concentration of ferric chloride M	Wavelength of maximum absorption mμ
$2 \cdot 30 \times 10^{-1}$	440–490
$5 \cdot 74 \times 10^{-2}$	440–460
$1 \cdot 44 \times 10^{-2}$	445
$7 \cdot 18 \times 10^{-3}$	440
$3 \cdot 59 \times 10^{-3}$	435
$1 \cdot 80 \times 10^{-3}$	427
$8 \cdot 97 \times 10^{-4}$	420
$4 \cdot 49 \times 10^{-4}$	415
$2 \cdot 24 \times 10^{-4}$	410

Table I shows that with the increase of concentration of ferric chloride the wavelength of maximum absorption shifts to higher values. The way in which this shift takes place indicates the existence of several coloured species, which are formed successively. The coloured species may be due to the progressive polymerisation or formation of multi-nuclear compounds of ferric chloride in alcohol. It is also likely that the continuous shift in the absorption bands towards red with the increase in concentration of ferric chloride, may be due to the progressive distortion of the 3*d* electron shell of the ferric ions by the increasing density of the ions in the medium. This reason may also be valid since the absorption is due to the excitation of some of the electrons in the 3*d* shell of the ferric ion. As this problem does not affect our present study in any way, no effort is made here to substantiate the above explanations with adequate experimental evidence.

(3) *Spectral Characteristics of Iron-Morellin Complex.*—The absorption spectra of the mixtures of equimolar solutions of ferric chloride and morellin ($6 \cdot 76 \times 10^{-5}$ M) in the ratios of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 in absolute alcohol showed only one absorption maximum at 550 mμ, indicating thereby that only one type of coloured complex is formed in each case. Beer's law is valid for the complex at this wavelength up to 19 p.p.m. of ferric iron. It indicates that the estimation of iron can be quantitative in dilute solutions up to 19 p.p.m.

It is interesting to note from the absorption curves of morellin and of ferric chloride solutions that there is very little absorption both by morellin solution and by ferric chloride solution, as compared to that of the complex at its absorption maximum, 550 mμ and at higher wavelengths. Hence in the subsequent studies, no correction for absorption due to the unreacted constituents present in the complex solution was applied, when the studies were carried out at 550 mμ and at higher wavelengths.

COMPOSITION OF THE COMPLEX

The composition of the iron-morellin complex was investigated spectrophotometrically by applying two methods for establishing the molar composition of the soluble coloured complexes. The iron complex was found to be insoluble in water but soluble in alcohol. The complex solution in alcohol was found to be free from colloidal particles.

(1) *Job's Method of Continuous Variation.*—The method of continuous variation first proposed by Job[5] and later modified by Vosburgh and co-workers[13,14] was applied to determine the ratio of morellin to iron in the complex at three different concentrations of the mixtures (1-X litre of morellin + X litre of ferric chloride) of equimolar solutions of ferric chloride and morellin (*viz.*, $6 \cdot 76 \times 10^{-4}$ M, $4 \cdot 51 \times 10^{-4}$ M and $3 \cdot 38 \times 10^{-4}$ M). The transmittance measurements with the mixtures were made at four wavelengths 550, 580, 610 and 640 mμ, at which the individual absorption due to the complex-forming constituents is negligible. The Y function, proposed by Job and defined as the difference between the optical density observed and the corresponding optical density calculated for no reaction, is equal in this particular case, to the observed optical density of the complex ($Y = -\log T$). In Fig. 1, the values of Y, at the wavelengths mentioned above, for the mixtures of $3 \cdot 38 \times 10^{-4}$ M ferric chloride and $3 \cdot 38 \times 10^{-4}$ M morellin in various ratios, are plotted against X, the mole-fraction of morellin. The maximum obtained in this figure indicates a formula $FeR_{1 \cdot 5}$ or Fe_2R_3 for the complex, R being morellin. Further, as the maximum in Y occurred at the same value of X for all the wavelengths mentioned or concentrations at which the measurements were made, it is evident that only one coloured complex is formed between ferric ions and morellin.

(2) *Slope Ratio Method.*—Harvey and Manning[6] proposed a method for determining the molar composition of soluble coloured complexes and applied it to a few complexes of ferric iron. The method serves to establish the ratio of colour-forming radicals to the metal.

In applying the ' Slope Ratio Method ' to this complex, two series of solutions were prepared. In one series, the concentration of iron was varied while that of morellin kept constant; in the other, *vice-versa*. The concentration of the variable component was varied from $1 \cdot 69 \times 10^{-5}$ M to $5 \cdot 0 \times 10^{-5}$ M in the presence of the excess concentration of $27 \cdot 04 \times 10^{-5}$ M of the constant component in both the series of the experiments. The absorption measurements were made at 550 mμ with

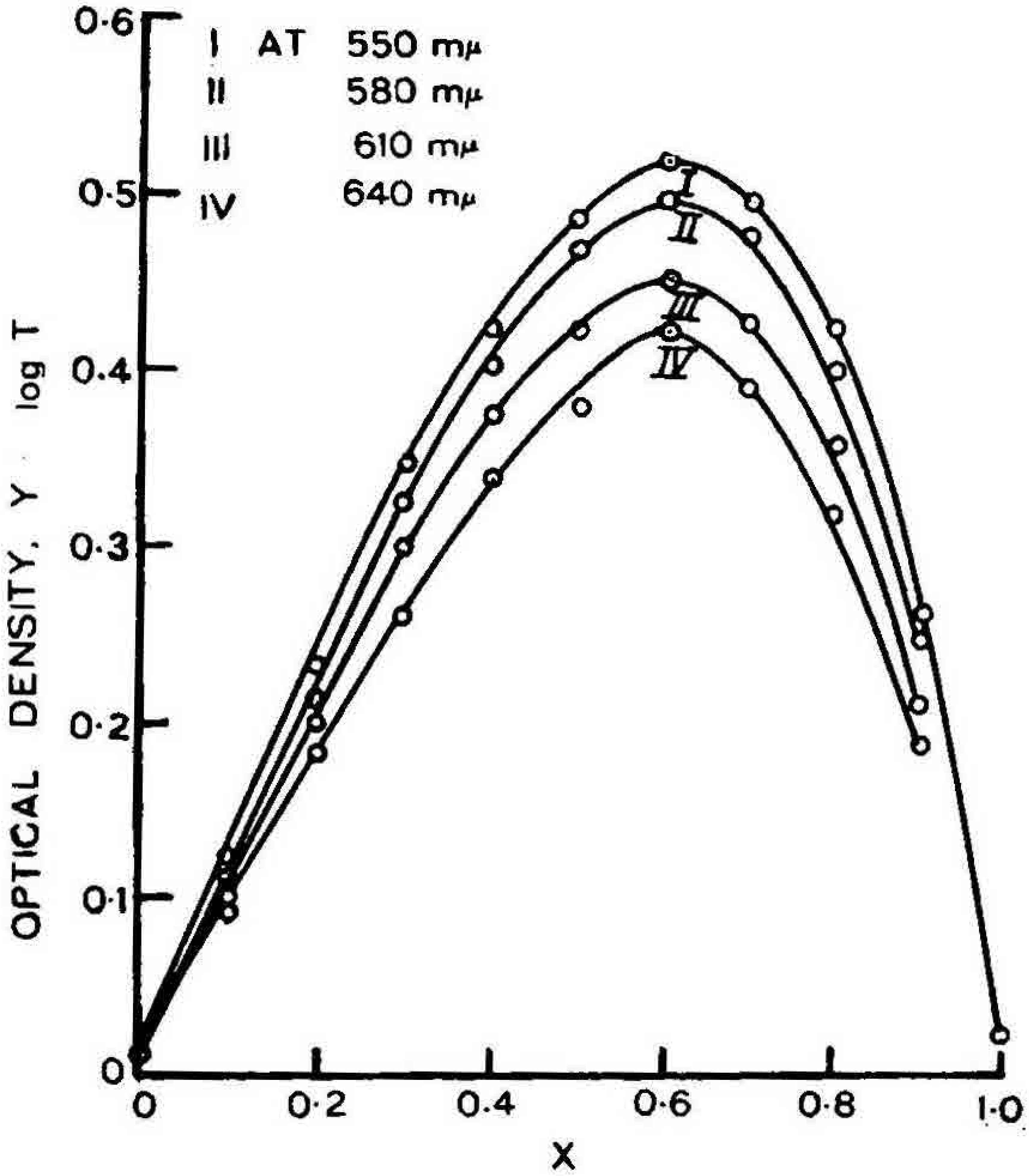

FIG. 1. Curves for Job's Method of Continuous variations. X litres of 3·38 × 10^{-4} M morellin solution added to (1 – X) litres of 3·38 × 10^{-4} M Fe solution.

absolute alcohol as the reference solution. These data gave linear curves (Fig. 2) and the slope ratio of the two curves gave an iron to morellin ratio as 1 : 1·54, which is in good agreement with the ratio obtained by the method of continuous variation.

(3) *Molar Ratio Method.*—When the complex formation was represented by the equation:

Constituent + Reagent → Coloured complex,

Yoe and Jones[7] showed that for a very stable coloured complex, obeying Beer's law, the plot of the optical density of the complex against the molar ratio of the reagent to the constituent (keeping the concentration of the constituent constant) is a straight line, passing through the origin and breaks sharply at the point when the molar ratio of the reagent to the constituent corresponds to the composition of the complex.

For the study of the complex, a series of solutions in which the molar ratio of iron to morellin varied from 1 : 0·25 to 1 : 9·0 was prepared and their absorption

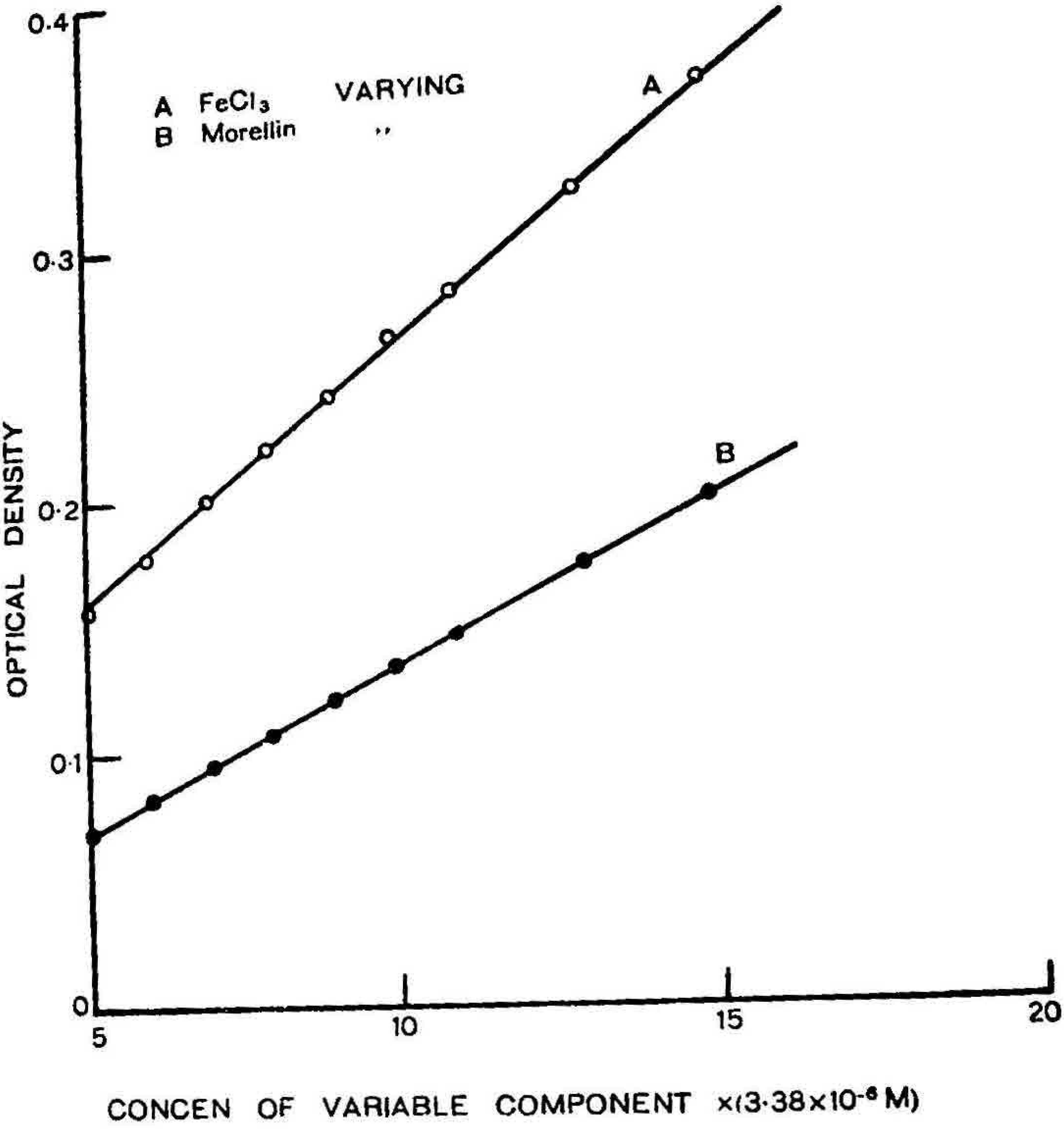

FIG. 2. Curves for Slope Ratio Method.

measured at 550 mμ. Three sets of experiments were carried out, maintaining in each set the concentration of ferric iron constant and within the range for which Beer's law is valid. On plotting the data (Fig. 3), the curves did not show sharp break, owing to the dissociation of the complex in dilute solutions. Hence equilibrium constant of the reaction was calculated by the method suggested by Harvey and Manning.[6]

The dissociation of the complex can be written as

$$\begin{array}{cccc} \mathrm{Fe_m R_n} & \rightleftarrows \; m\mathrm{Fe} & + & n\mathrm{R} \\ (1-\alpha)\,\mathrm{C} & m\alpha\mathrm{C} & & n\alpha\mathrm{C} \end{array}$$

where C represents the total concentration of the complex in moles per litre, and α is the degree of dissociation.

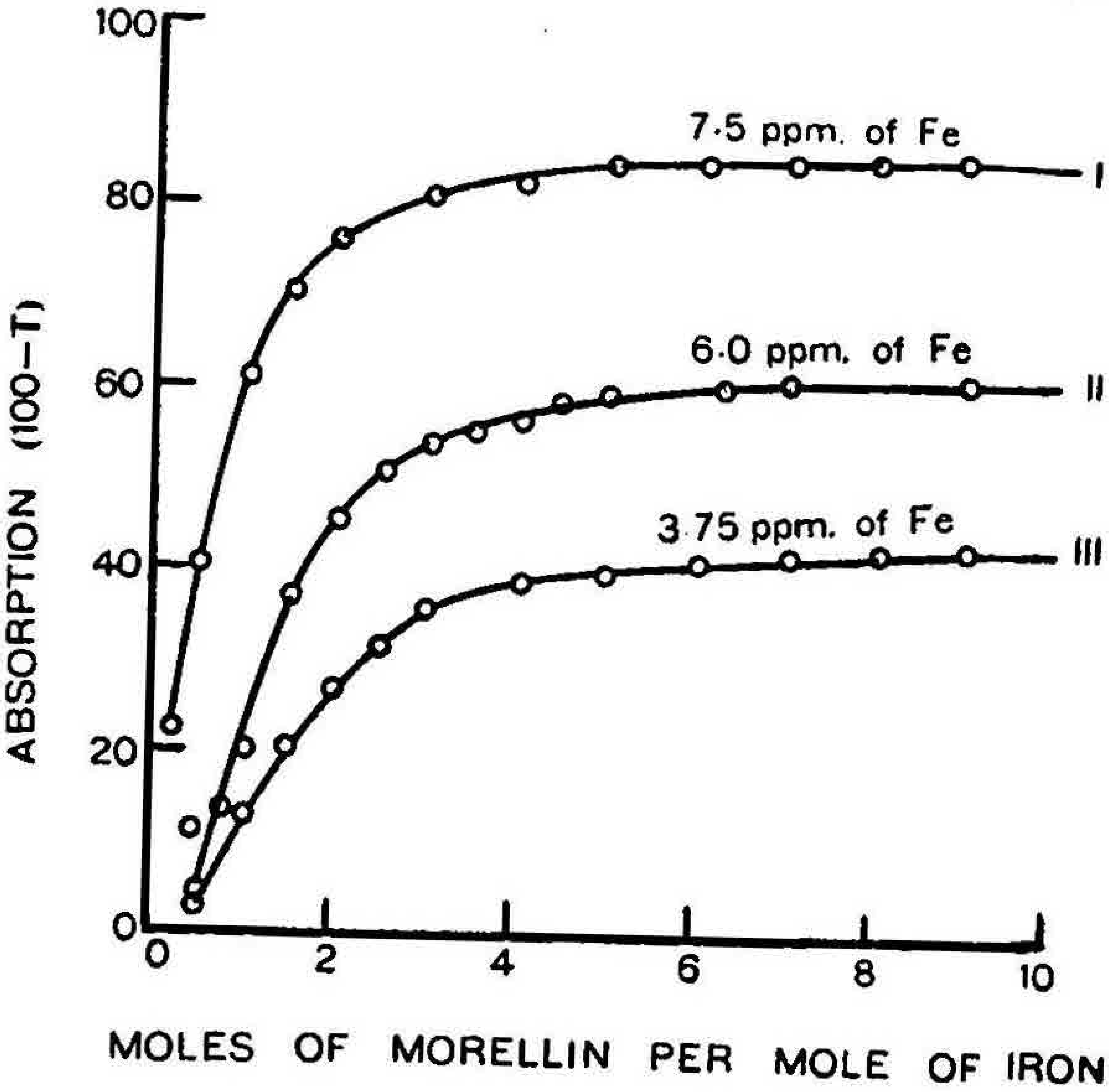

Fig. 3. Curves for Molar Ratio Method.

The equilibrium constant K is given by the equation

$$K = \frac{(m\alpha C)^m \ (n\alpha C)^n}{C(1-\alpha)} \qquad (1)$$

The values of *n* and *m* have been found to be 3 and 2 respectively both by the Job's method and the slope ratio method. The value of α may be obtained from the curves of Fig. 3 by the following relationship:

$$\alpha = \frac{E_{max.} - E_{st.}}{E_{max.}} \qquad (2)$$

where $E_{max.}$ is the maximum optical density calculated from the horizontal portion of the curve, while $E_{st.}$ is the observed optical density at the stoichiometric molar ratio of morellin to iron in the complex. The concentration C of the complex is half of the total concentration of ferric iron employed. The values of K at room temperature (25° C.) are given in Table II.

This yields an average value of $4{\cdot}95 \times 10^{-17}$ for the equilibrium constant K for the dissociation of the complex. The variation in the value of equilibrium constant, noticed in Table II is mostly due to the high powers of α and C involved in the calculations of the equilibrium constant. Another source of error in the dissociation constant is the ambiguity of the nature of the molecular species of ferric

TABLE II

Curve	Concentration of the complex C.	Degree of dissociation a	Equilibrium constant K
I	$6 \cdot 76 \times 10^{-5}$ M	0·416	$4 \cdot 81 \times 10^{-17}$
II	$5 \cdot 408 \times 10^{-5}$ M	0·520	$7 \cdot 31 \times 10^{-17}$
III	$3 \cdot 38 \times 10^{-5}$ M	0·600	$2 \cdot 74 \times 10^{-17}$

iron in solution: it may be either Fe_2^{6+} or $2Fe^{3+}$ or a mixture of the two. If it is Fe_2^{6+}, then the corresponding values for the equilibrium constants will be respectively $4 \cdot 277 \times 10^{-13}$, $6 \cdot 513 \times 10^{-13}$ and $3 \cdot 371 \times 10^{-13}$.

The standard free energy of formation of the complex from ferric chloride and morellin is calculated from the relation $\Delta F^\circ = RT\ln K$, where K denotes the dissociation constant as determined above. Inserting the average value of $4 \cdot 95 \times 10^{-17}$ for K, ΔF° is found to be $-22 \cdot 236$ Kcal./mole at 25° C. It shows, therefore, that the reaction between ferric chloride and morellin is accompanied by a considerable decrease of free energy at room temperature, indicating the spontaneous nature of the reaction.

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