

Spectrophotometric Determination of Successive Formation Constants for Chloro-Bromo Mixed Ligands Iron(III) Complexes :

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Introduction

Recent studies have shown that the solutions of the salts of polyvalent metals often contain not only free ions and undissociated molecules, but also diverse intermediate ionic species.¹⁾ For a number of cations, the formation constants of associates have been determined,²⁾ for several, formation constants of successive steps with anion,^{3),4)} but relatively few for mixed ligands complex.^{5),6)} The interrelationship and utilization of many determination methods of the formation constants about successive steps have been described in several excellent papers, some^{7),8)} rely upon the measure of the concentration of either the free ligand, free metal ion or a particular complex ion, the other⁹⁾ described by Newman etc., the measure of the extinction coefficients and ligand ratios. Newman computation technique is an exceedingly attractive approach in that the technique can be applied not only to single ligand complex, but also to mixed ligand complex. In this paper, successive formation constants of chloro-bromo mixed ligands iron(III) complex was calculated, based on different assumptions. There are a number of works about halogeno iron(III) complex.^{10),11),17)} and it is already reported that in aqueous solution, several methods such as solvent^{12),13),14),18)} extraction and ion exchange proved for the highest halogeno iron(III) complex to be FeX_4^- and, that in its ultraviolet and visible spectrum, three maximums are recognized. It was also found that the highest halogeno iron(III) complex was formed only in high concentrated acidic halogenic solution and, with increasing of the concentration of halide and acid, the more of the highest halogeno iron(III) complex was formed. The method employed in this study was in principle the same as in Newman's works, but several determination equations have been rearranged conveniently. We have studied the spectra of iron(III) in chloride bromide mixture in which the total halide concentration was maintained about 10000 times of iron(III), and the concentration of perchloric acid, 7 M. The ionic strength of the solution was adjusted to 8.0 M with sodium chloride, sodium bromide and perchloric acid, which according to other workers were sufficient to maintain practically all the iron in its most complexed state. It also can be seen from the figure that shifts in the spectra take place when chloride replaces bromide or the converse occurs. As chloride and bromide are most like each other, we applied computation equation for mixed similar ligands complex.

Experimental

Materials and apparatus.- The stock solutions of iron(III) were prepared as follow.

Ferric perchlorate was formed by dissolving proper amounts of electrolytic iron in hydrochloric acid, oxidizing by hydrogen peroxide (30%) and evaporating the solution until the crystal appear. After perchloric acid was added to dissolve the deposit, the solution was evaporated again. The procedure was repeated until the solution gave negative test for chloride and iron(II) ion. The concentration of iron(III) stock solution was 0.7×10^{-1} M.

Each stock solution of 5 M sodium chloride and 5 M sodium bromide were prepared with dissolving and filtering Wako special grade reagent materials.

Spectrophotometric measurements were made with Shimadzu Spectrophotometer QR-50 with 1.00 cm, silica transmission cells.

Results and Discussion

General characteristics of the absorption curves. -The absorption spectra of solution containing 10^{-4} M Fe^{3+} at various concentration of halide and perchloric acid were measured against a blank containing each concentration of halide and perchloric acid. It can be seen in Fig. 1, 2, that one or two absorption peaks are present in it. The spectra in high concentra-

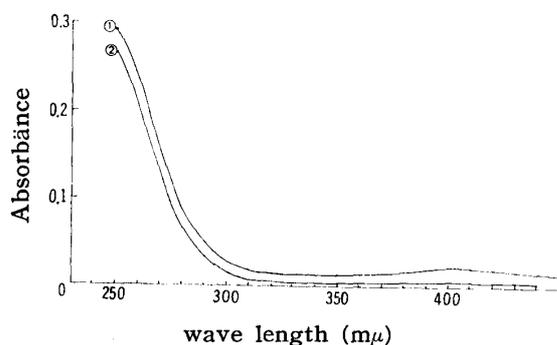
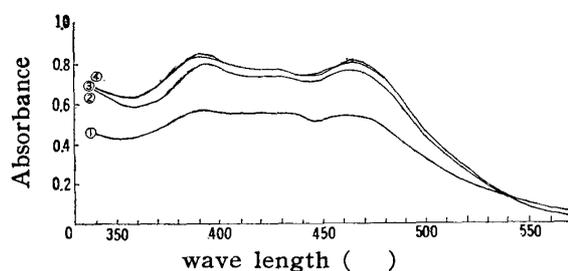


Fig. 1. (a) Absorption Spectra of Iron (III) in 1N-perchloric acid and various concentration of sodium bromide: 1. 1M NaBr 2. 10^{-1} M NaBr



(b) Absorption Spectra of Iron(III) in 7N-perchloric acid various concentration of sodium bromide. 1. 0.3M NaBr 2. 0.6M NaBr 3. 0.9M NaBr 4. 1.2M NaBr

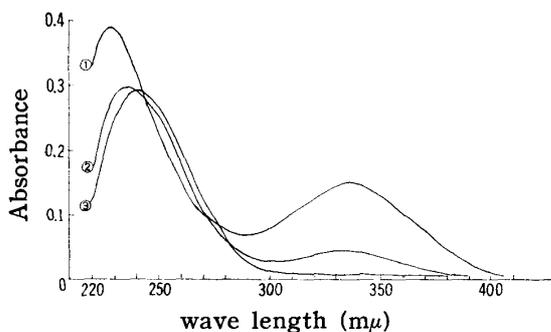
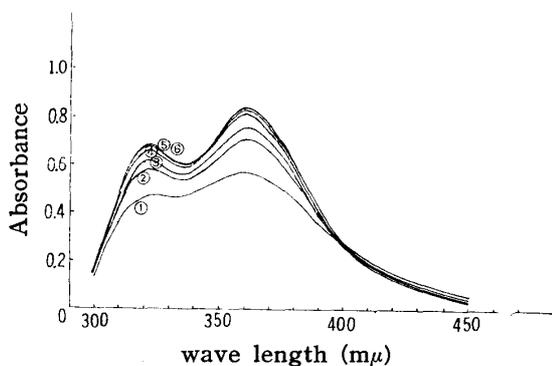


Fig. 2. (a) Absorption Spectra of Iron(III) in 1N-perchloric acid and various concentration of sodium chloride. 1. 1M NaCl 2. 10^{-1} M NaCl 3. 10^{-2} M NaCl.



(b) Absorption Spectra of Iron(III) in 7N-perchloric acid and various concentration of sodium chloride. 1. 0.2M NaCl 2. 0.4M NaCl 3. 0.6M NaCl 4. 0.8M NaCl 5. 0.9M NaCl 6. 1.0M NaCl.

tion of halide and perchloric acid resemble very much to those published by Metzler¹²⁾, Gamlen²⁰⁾ and Ishibashi^{10), 19)}. In Fig. 3 are shown the changes in absorbance at a given wave length against the concentration of halide at 7 N constant acidity. Apparently it would appear that in the atmosphere of 7 M perchloric acid and 1 M halide, most parts of iron is in FeX_4^- . It can be also seen from Fig. 4 that FeCl_4^- converts to $\text{FeCl}_{4-n}\text{Br}_n^-$ and $\text{FeCl}_{4-n-m}\text{Br}_{n+m}^-$ etc, when chloride replaces bromide at constant concentration of halide.

In attempting a study of the bromide complex of iron(III), it was found that bromide was oxidized to bromine in presence of perchloric acid.

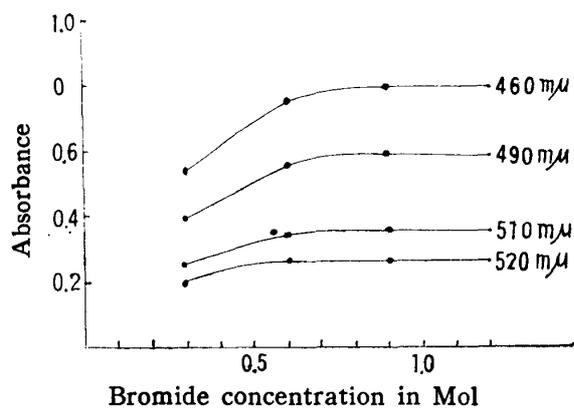


Fig. 3. (a) Correlation of bromide concentration and 7N constant acidity.

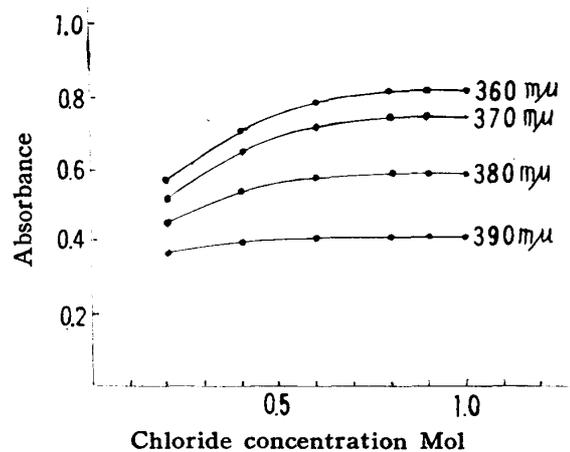


Fig. 3. (b) Correlation of chloride concentration and 7N constant acidity.

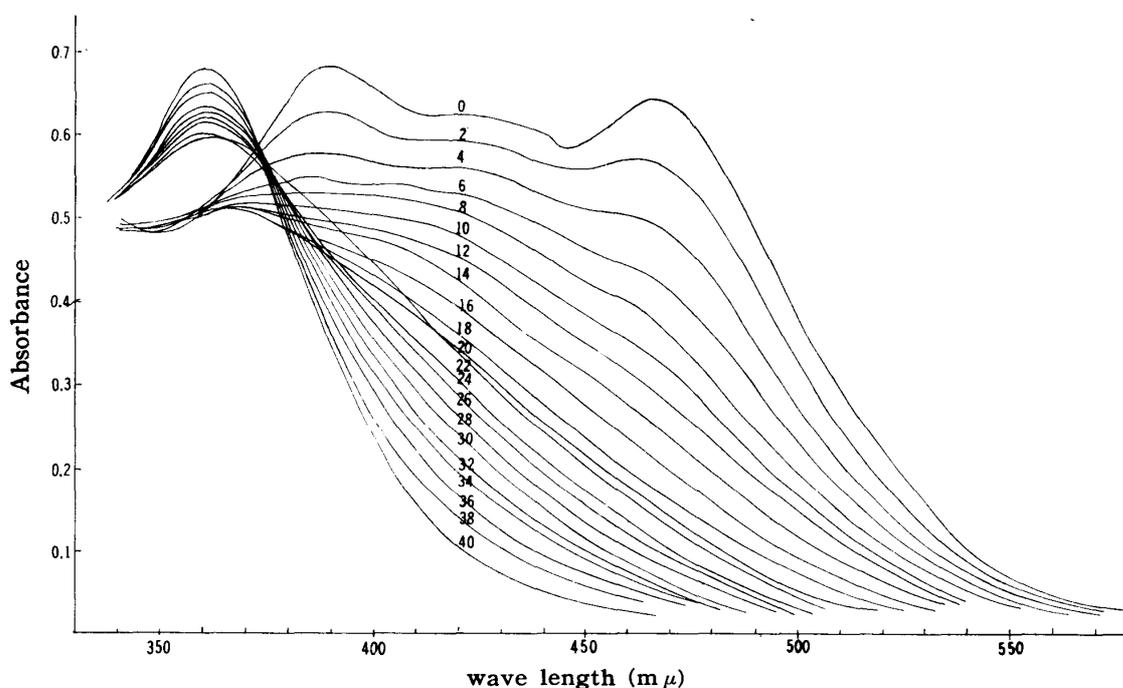
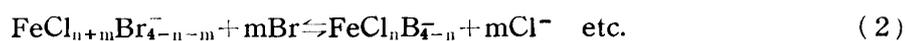
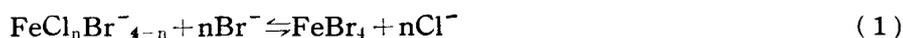


Fig. 4. Absorption spectra of 1.2×10^{-4} M solutions of iron(III) at ionic strength of 8 M, each solution being 7 N in perchloric acid and 1 M in halide (Sodium Bromide plus Sodium Chloride). Bromide per Chloride ratio corresponding to the individual curves, 2:19, 4:9.0, 6:5.6, 8:4.0, 10:3.0, 12:2.3, 14:1.8, 16:1.5, 18:1.2, 20:1.0, 22:0.81, 24:0.66, 26:0.53, 28:0.42, 30:0.25, 32:0.25, 34:0.19, 36:0.11, 38:0.05,

Its effect is not always negligible at relatively high temperature. Particularly, when bromide was low ratio to chloride, is it inevitable. Therefore, the formation constants of the first and the second steps are not so precise as the third and the fourth steps.

Calculation Equation of Mixed Similar Ligands Complex.- If mixed halide ligand is added in great excess compared to the central stom, in solution following equilibria are formed,



In each step, the formation constants are defined as

$$K_4 = \frac{[\text{FeBr}_4^-][\text{Cl}^-]^n}{[\text{FeCl}_n\text{Br}_{4-n}^-][\text{Br}^-]^n} \quad (3)$$

$$K_{4-n} = \frac{[\text{FeCl}_n\text{Br}_{4-n}^-][\text{Cl}^-]^m}{[\text{FeCl}_{n+m}\text{Br}_{4-n-m}^-][\text{Br}^-]^m} \quad (4)$$

The most complicated case is for all species to be absorbing then,

$$A = E_4[\text{FeBr}_4^-] + E_{4-n}[\text{FeCl}_n\text{Br}_{4-n}^-] + \dots + E_0[\text{FeCl}_4^-] \quad (5)$$

A is the absorbance for mixture of many species and E is the extinction coefficient for a particular species.

In a given experiment, total concentration of central atom added is

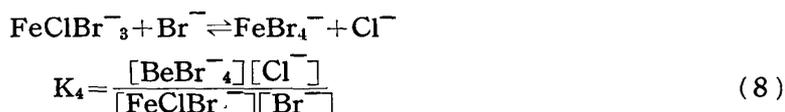
$$F_{\text{et}} = [\text{FeBr}_4^-] + [\text{FeCl}_n\text{Br}_{4-n}^-] + \dots + [\text{FeCl}_4^-] \quad (6)$$

Neglecting unnecessary clause, and combining each formula, we could obtain following used determination equations referring to Newman works.

Determination of Formation Constants.- For high bromide to chloride ratios, only one mixed ligand complex should be formed, if long enough wave length were selected, then, the formula,

$$\log \frac{E_4 F_{\text{et}} - A}{A} = n \log \frac{[\text{Br}^-]}{[\text{Cl}^-]} - \log K_4 \quad (7)$$

for the mixed ligand system of two species present with one absorbing should hold. Application of this equation to the data at 570 m μ gave a straight line plot as indicated in Fig. 5. From the slope, the value of n was found to be unity, and the following reaction must be taken place



where K_4 is 0.29. In Table 1 are presented the value of K_4 at various wave length.

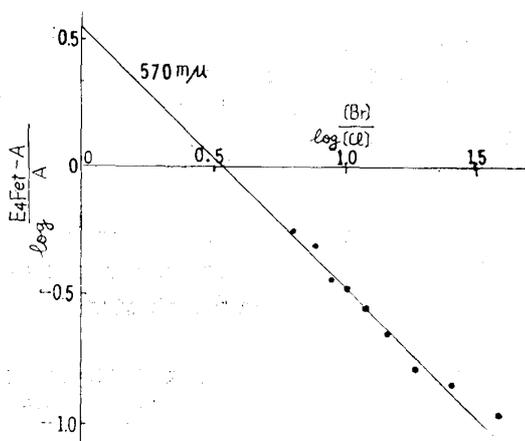


Table 1 The value of k_4 at various wave length: 2species absorbing

wave length (m μ)	k_4
570	0.29
565	0.26
560	0.23
555	0.27
550	0.25

Fig. 5. Determination of formation constant, k_4 for the reaction, $\text{FeBr}_4^- + \text{Cl}^- \rightleftharpoons \text{FeClBr}_3^- + \text{Br}^-$; 2species absorbing

Over all wave length, the equation for two species and both absorbing may be applied.

$$A = K_4 [E_4 \text{Fet} - A] \frac{[\text{Br}^-]^n}{[\text{Cl}^-]^n} + E_3 \text{Fet} \quad (9)$$

Also application of this equation gave a straight line plot as indicated Fig. 6. From the slope we could obtain 0.23 for K_4 . The results are shown in table 2. Further replacing bromide by chloride, forming two species of mixed ligand complex, for three species, we can apply the equations.

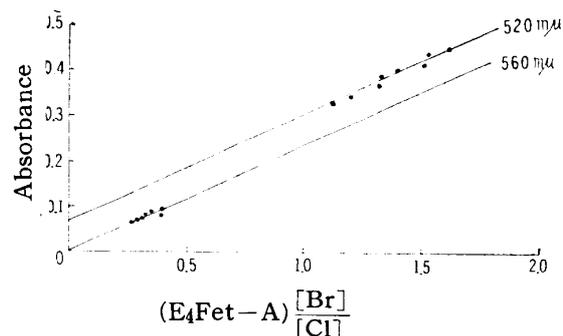


Fig. 6. Determination of formation constant, k_4 at wave length for 2 species 2 absorbing.

Table 2 The value of k_4 at various wave length. ; 2species 2absorbing.

Wave length	k_4	$E_3 \text{Fet}$	Wave length	k_4	$E_3 \text{Fet}$	Wave length	k_4	$E_3 \text{Fet}$
570	0.23	0	530	0.23	0.050	485	0.20	0.230
565	0.24	0	525	0.22	0.060	480	0.22	0.249
560	0.23	0	520	0.23	0.070	475	0.23	0.270
555	0.26	0	515	0.22	0.110	470	0.23	0.355
550	0.22	0.010	510	0.22	0.130	465	0.22	0.480
545	0.20	0.020	500	0.23	0.150	460	0.21	0.650
540	0.20	0.035	495	0.22	0.220	455	0.24	0.725
535	0.20	0.040	490	0.24	0.240	450	0.26	0.955

for 3 species 1 absorbing for long wave length

$$\log \left(\frac{K_4 (E_4 \text{Fet} - A) \frac{[\text{Br}^-]^n}{[\text{Cl}^-]^n} - A}{A} \right) = m \log \frac{[\text{Br}^-]}{[\text{Cl}^-]} - \log K_3 \quad (10)$$

for 3 species 1 absorbing for long wave length

$$\left(\frac{E_4 \text{Fet} - A}{A} \right) \frac{[\text{Br}^-]}{[\text{Cl}^-]} = \frac{1}{K_4 K_3} \frac{[\text{Cl}^-]^m}{[\text{Br}^-]^m} + \frac{1}{K_4} \quad (11)$$

and for 3 species 3 absorbing at wave length FeBr_4^- , FeBr_4Cl^- , and $\text{FeBr}_2\text{Cl}_2^-$ absorbing

$$A = K_3 \left[K_4 (E_4 \text{Fet} - A) \frac{[\text{Br}^-]}{[\text{Cl}^-]} - A + E_3 \text{Fet} \right] \frac{[\text{Br}^-]^m}{[\text{Cl}^-]^m} + E_{4-n-m} \text{Fet} \quad (12)$$

From the slope of a logarithm straight line plot for three species and one absorbing, we can obtain unity for m , Application of three types of equation is shown Fig. 7, 8, and 9, and so 0.5 for K_3 could be obtained.

Table 3, and 4 show these results.

Further more replacing bromide by chloride apparently from Fig. 4, the complex, FeBr_4^- , is not recognized in spectra, then, we can apply the equation of 3 species 3 absorbing for FeBr_3Cl^- , $\text{FeBr}_2\text{Cl}_2^-$ and FeBrCl_3^- , and, shown in Fig. 10, 2.5 for K_2 was obtained for unity complexation. Table 5 shows these values.

Replacement of Chloride by Bromide.- In order to determine the formation constants for

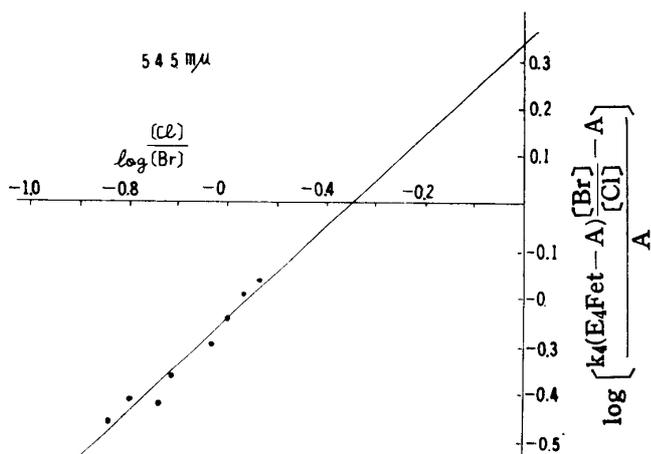


Fig. 7. Determination of formation constant, k_4 for the reaction $\text{FeCl Br}_3^- + \text{Cl}^- \rightleftharpoons \text{FeCl}_2 \text{Br}^- + \text{Br}^-$; 3 species 1 absorbing.

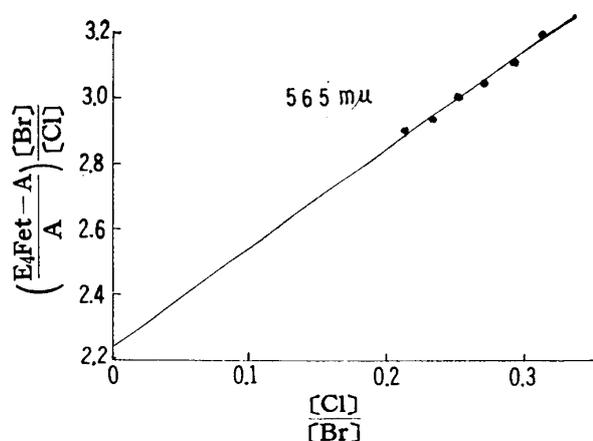


Fig. 8. Determination of k_3 ; 3 species 1 absorbing

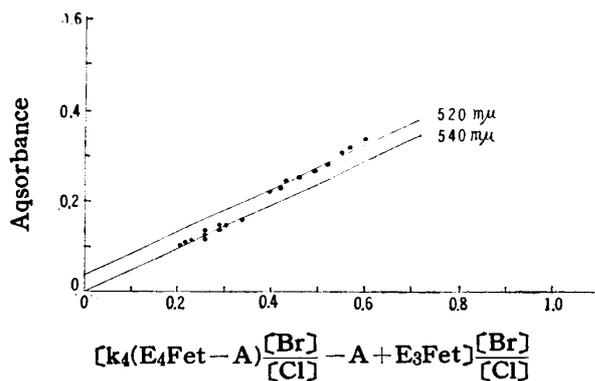


Fig. 9. Determination of k_3 ; 3 species 3 absorbing

Table 3 The value of k_3 at various wave length: 3species laborsing

Wave length ($m\mu$)	K_3
565	0.63
560	0.65
555	0.56
550	0.52
545	0.47
540	0.45

Table 4 The value of k_3 at various wave length: 3species 3absorbing

Wave length ($m\mu$)	k^3	$E_2\text{Fet}$	Wave length ($m\mu$)	k_3	$E_2\text{Fet}$
540	0.47	0	500	0.40	0.088
535	0.45	0.015	495	0.40	0.105
530	0.46	0.016	490	0.40	0.128
525	0.48	0.020	485	0.44	0.165
520	0.50	0.035	480	0.52	0.180
515	0.48	0.035	475	0.64	0.236
510	0.38	0.040	470	0.58	0.335
505	0.40	0.050	465	0.47	0.350

the replacement of chloride by bromide, the data for high chloride to bromide ratios were utilized. When FeCl_4^- converts to FeCl_3Br^- , shifts in spectra are recongnized. Application of the equation for 2 species 2 absorbing gives 2.5 for K_1 , the linearity showed unity for m , as shown Fig. 11a and 11b, table 6 show the results. Samely, replacing bromide by chloride the equilibrium was found to have $K_{n-m} = K_2$ of 1.8, the value was relatively same as the above mentioned value and the summary of these value are showed in table 7.

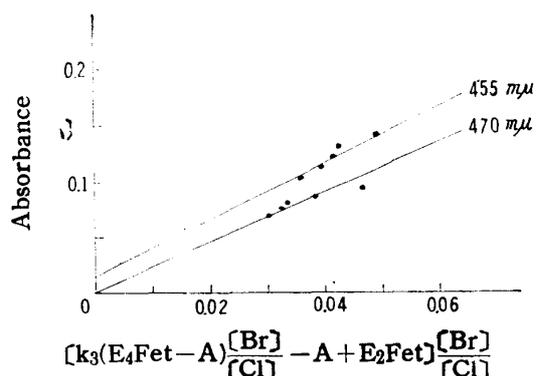


Fig. 10. Determination of k_2 for the reaction

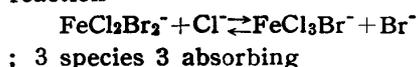


Table 5 The value of k_2 :
3species 3absorbing

Wave length (mμ)	k_2
470	2.3
456	2.6
455	2.7

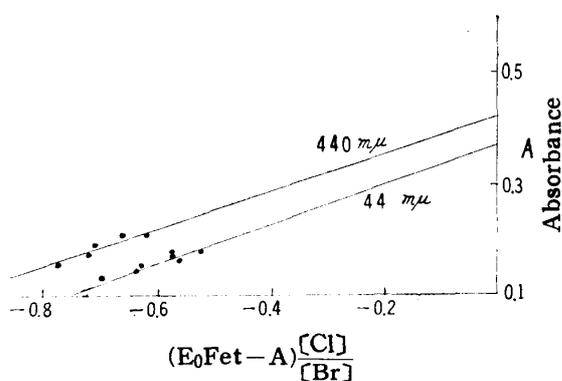
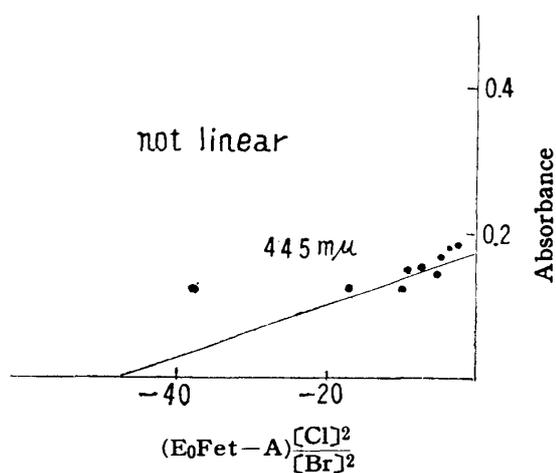
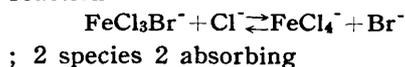


Fig. 11. (a) Determination of k_1 for the reaction



(b) Determination of β_2 for the reaction
 $FeCl_3Br^- + 2Cl^- \rightleftharpoons FeCl_2Br_2^- + 2Br^-$
; 2 species 2 absorbing

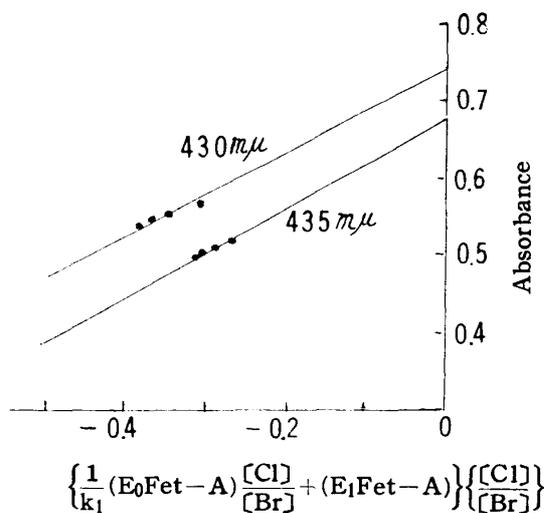


Fig. 12. Determination of k_2 for the reaction
 $FeBr_2Cl_2^- + Cl^- \rightleftharpoons FeBrCl_3^- + Br^-$
; 3 species 3 absorbing

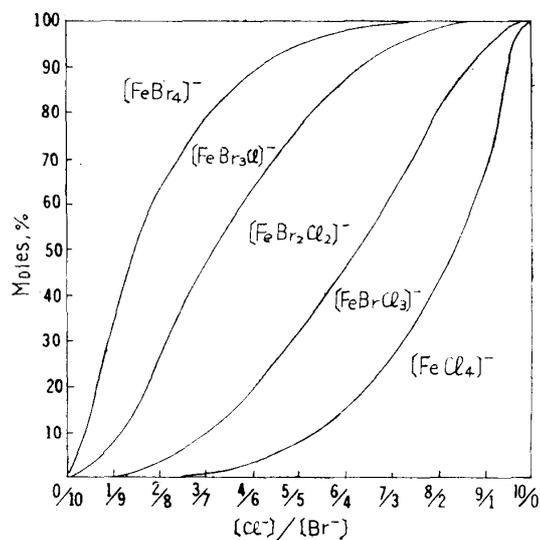


Fig. 13. Distribution of the ferric ion among the Chloro-Bromo mixed ligand complex at various ratio of Chloride per Bromide-ion.

Results.-

It has been shown that when chloride and bromide were added in various ratios to iron solution containing 7 M perchloric acid, three mixed ligands complexes FeBr_3Cl^- , FeBrCl_2^- , FeClBr_2^- are formed in equilibrium with the parent complexes FeBr_4^- and FeCl_4^- .

Table 6 The value of k_1 : 2 species 2 absorbing

Wave length ($m\mu$)	k_1	$E_1\text{Fet}$	Wave length ($m\mu$)	k_1	$E_1\text{Fet}$
460	2.6	0.260	425	2.7	0.575
455	2.5	0.295	420	2.8	0.650
450	2.3	0.340	415	2.9	0.710
445	2.7	0.375	410	3.0	0.765
440	2.9	0.420	405	2.8	0.810
435	2.7	0.464	400	3.1	0.362
430	2.9	0.500			

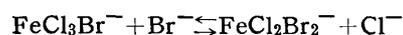
Table 7 The value of k_2 : 3 species 3 absorbing

Wave length ($m\mu$)	k_2	$E_2\text{Fet}$	Wave length ($m\mu$)	k_2	$E_2\text{Fet}$
455	1.8	0.457	425	1.6	0.800
450	2.0	0.530	420	1.6	0.840
445	2.0	0.575	415	1.6	0.895
440	1.6	0.650	410	1.6	0.942
435	1.8	0.675	405	1.8	0.980
430	1.8	0.743	400	1.8	1.280

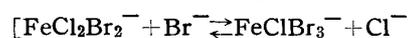
We obtained next values for stepwise formation constants of chloro bromo mixed ligand iron (III) complex as a results.



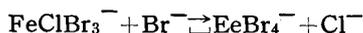
$$K_1 = \frac{[\text{FeCl}_3\text{Br}^-][\text{Cl}^-]}{[\text{FeCl}_4^-][\text{Br}^-]} = 3 \pm 0.5$$



$$K_2 = \frac{[\text{FeCl}_2\text{Br}_2^-][\text{Cl}^-]}{[\text{FeCl}_3\text{Br}^-][\text{Br}^-]} = 2.5 \pm 0.5$$



$$K_3 = \frac{[\text{FeClBr}_3^-][\text{Cl}^-]}{[\text{FeCl}_2\text{Br}_2^-][\text{Br}^-]} = 0.5 \pm 0.1$$



$$K_4 = \frac{[\text{FeBr}_4^-][\text{Cl}^-]}{[\text{FeClBr}_3^-][\text{Br}^-]} = 0.3 \pm 0.1$$

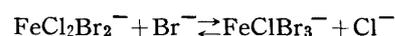
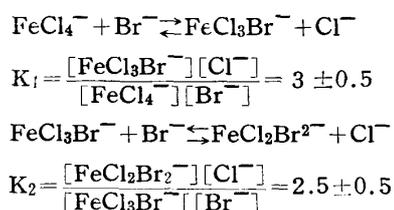
The author wishes to express his appreciation to prof. Dr. yuroku yamamoto of the Hisoshima University for his kind guidance and to Miss. Yasuyo Shintaku for her earnest assistance throughout the investigation.

総 括

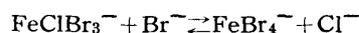
鉄は過塩素酸溶液中において紫外部に1つの吸収帯を示す。また鉄の溶液に塩酸、臭化水素酸を添加

するとその濃度の増加と共に $[\text{FeCl}]^{2+}$, $[\text{FeCl}_2]^+$, $[\text{FeCl}_3]^0$, $[\text{FeCl}_4]^-$ 等の会合錯体を臭化水素酸の

場合も同様の型の会合錯体を形成し吸収スペクトルがレッドシフトする。また鉄の過塩素酸溶液に塩化ナトリウム、臭化ナトリウムを加えても同様のシフトが起こるが鉄の Cl^- , Br^- 配位に対する酸性度の影響は大きく一定濃度のハロゲン溶液中においては酸性度の増加と共に高次ハロゲン配位錯体が生成する。これらの結果から酸性度を過塩素酸 7N, 塩化ナトリウム, 臭化ナトリウムの含量濃度を 1M に保ちつつ Cl^- 対 Br^- の濃度比をかえた吸収スペクトルを詳細に測定し、クロロブromo混合配位錯体の生成定数を計算し次の結果を得た。



$$K_3 = \frac{[\text{FeClBr}_3^-][\text{Cl}^-]}{[\text{FeCl}_2\text{Br}_2^-][\text{Br}^-]} = 0.5 \pm 0.1$$



$$K_4 = \frac{[\text{FeBr}_4^-][\text{Cl}^-]}{[\text{FeClBr}_3^-][\text{Br}^-]} = 0.3 \pm 0.1$$

またこの結果から Cl^- および Br^- が種々の濃度において存在する溶液中の $[\text{FeCl}_4^-]$, $[\text{FeCl}_3\text{Br}^-]$, $[\text{FeCl}_2\text{Br}_2^-]$, $[\text{FeClBr}_3^-]$, $[\text{FeBr}_4^-]$ 錯体の存在%を計算した結果を図13に示す。この結果デクロロチブロモ鉄(III)錯体, $[\text{FeCl}_2\text{Br}_2^-]$ が比較的安定に存在する結論を得た。これは Cl^- および Br^- がお互にトランスに配置した混合配位錯体が立体的に安定であるため比較的生成しやすいのではないかと考えられる。

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