철(III)과 인산간의 착물형성에 관한 연구

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Complex Formation Between Ferric Ion and Phosphoric Acid

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요　약. 철(III) 이온과 인산간의 착물형성에 관하여 넓은 인산산성범위(0~40%)에서 가시부 스펙트럼과 용액으로 부터 분리해낸 화합물을 검토함으로써 연구하였다.

철(III)함유 인산용액의 전자흡수 스펙트럼은 19. 2 kK 및 24. 1 kK에서 철(III)-인산 착물형성을 나타내는 두개의 가시부 흡수를 나타내었다. 24. 1 kK 밴드의 인산농도에 따른 흡광도 변화의 측정으로 부터 아마도 [Fe(H_2PO_4)]^{x+} 및 [Fe_2(H_xPO_4)]^{(3+x)+}등 두개의 형태가 틀린 철(III)-인산착물이 존재함을 알 수 있었다. 이들 두화합물중 몰비가 1:1인 착물은 고체상태로 분리하는데 성공하였으며 인산 이온은 염기도 1인 상태로 금속에 배위되어 있음을 알 수 있었으나, 이합체로 생각되는 화합물은 분리해낼 수 없었다.

ABSTRACT. Complex formation between ferric ion and phosphoric acid has been studied in the wide range of the acid concentration (0~40%) by uv-visible spectroscopy and by characterization of the isolated products.

The electronic spectra of Fe(III)-containing phosphoric acid solutions exhibit two visible bands at 19. 2 and 24. 1 kK, which are characterestic of Fe(III)-phosphate complex formation. The measureme nts of acid concentration dependence of the opical density of the 24. 1 kK band indicates the presence of two distinct forms of Fe(III)-phosphate complexes possibly $[Fe(H_xPO_4)]^{x+}$ and $[Fe_2(H_xP-O_4)]^{(3+x)+}$. The 1:1 complex has been isolated for characterization, and the phosphate ion was found to be coordinated to the metal in monobasic state whereas the isolation of the dimeric species was unsuccessful.

INTRODUCTION

The nature of Iron(III)-phospate complex formation has been extensively studied by several workers.[1~6] In dilute acid solutions, the existence of the monomeric forms $FeH_2PO_4^{2+}$ and $FeHPO_4^+$ has been established.[1,2,6] It was claimed from the ion exchange studies by Salmon and his coworkers[3] that a cationic complex $FeHPO_4^+$ was formed in relatively concentrated solutions containing equimolar amounts of ferric chloride and phosphoric acid whereas anionic complexes $Fe(HPO_4)_3^{3-}$ and $Fe(PO_4)_3^{6-}$ were formed in

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solutions of ferric phosphate in phosphoric acid.

Furthermore, evidences[3,4] for the presence of polynuclear phosphatoferric complexes are also available depending on the solution compositions. However, no study has been reported on the system of ferric ion in the concentrated phosphoric acid which simulates the wet process acid containing iron as impurity. In this work the iron(III)-phosphate complex formation has been examined in the wide range of phosphoric acid concentration by spectroscopic means and by characterization of the isolated complexes.

EXPERIMENTAL

As a source of ferric ion Baker's analytical reagent grade ferric chloride hexahydrate or Chamelion reagent grade ferric chloride hexahydrate or Chamelion reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ was used without further purification. Phosphoric acid solutions at various concentrations were prepared by use of reagent grade 85% phosphoric acid(Wako). Ferrocyanide and all other chemicals are also reagent grade unless is specified.

Isolation of Fe(III)-phosphate Complexes. The Fe(III)-containing phosphoric acid solutions were prepared by adding appropriate ferric salts directly to the aqueous or alcoholic (absolute methanol) phosphoric acid solutions at desired concentration varing from 0 to 40%. The ferric ion concentration was fixed at 1.0% (wt/vol) in all cases. To 100 ml of this solution(18 mmole Fe) 19 ml of 20% potassium ferrocyanide solution (9 mmole) was slowly added with stirring. The resultant blue precipitate was separated from the supernatant solution by centrifugation and then washed with water or alcohol more than three times. The ferrocyanide salts of Fe(III)-phosphate thus prepared were dried in the air and then vacuum-dried over P_2O_5.

Chemical Analysis and Spectroscopic Mea-surements. The Fe(III)-phosphate complexes were subjected to chemical analysis as in the following. Approximately 0.5 g of the sample was accurately weighed and dissolved in alkaline water at PH=12. The reddish brown hydrous ferric oxide precipitate thus formed was filtered off and used for the determination of the total ferric ion by red-ox titration[7]. Aliquots of the yellow or light yellow filtrate were used for the analyses of ferrocyanide, phosphate and potassium ions. Ferrocyanide ion was determined by spectrophotometry at 3200Å and potassium by atomic absorption spectrophotometry. The gravimetric determination of phosphate was accomplished by AOAC method.[8]

The electronic absprotion spectra of the Fe(III)-containing phosphoric acid solutions were measured at various acid concentrations (0~40%) on the Cary Model 14 Spectrophotometer using 1.0 cm quartz cell. The ferric ion concentration (1.0%) was suitable for the spectral recording in the 9000~4500Å range but must be diluted in the higher energy region by using phosphoric acid at the same concentration.

The infrared spectra of the ferrocyanide salts of the Fe(III)-phosphate complexes were recorded on the Beckman IR-12 Spectrophotometer in KBr waffer.

RESULTS and DISCUSSION

In general ferric ion in aqueous solution undergoes hydrolysis to a great extent even in considerably acidic solution (PH=2~3) to form hydroxo complexes[9] such as $[Fe(H_2O)_5(OH)]^{2+}$. It is also known that such hydroxo-species exhibits yellow color due to the tailing by the charge transfer bands appearing in the UV region. Since the intense charge transfer bands obscure the weak ligand field bands in the visible range, no definite results of the spectral study of Fe(III) complexes were reported. In this paper de-
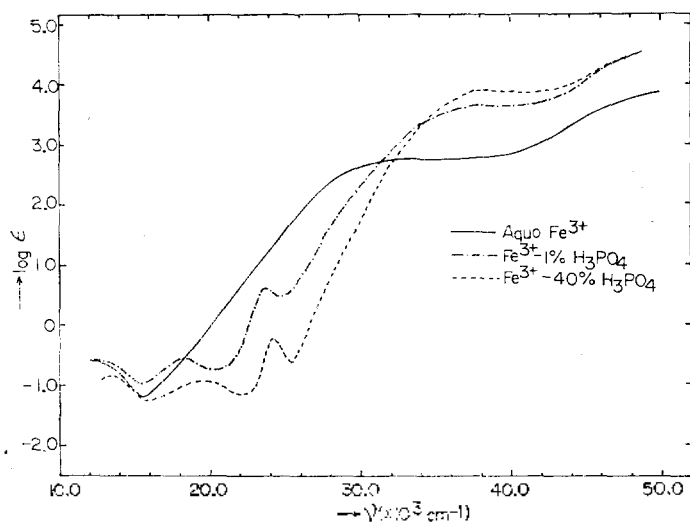
Fig. 1. Electronic spectra of ferric ion in aqueous and phosphoric acid solutions.

Table 1. Spectral data of Fe(III)-phosphoric acid solutions.

Complex	$\nu_{max\,cm^{-1}}$	ϵ
Fe(III)-H$_2$O	33,300(sh)	2,540
	>50,000	>10,000
Fe(III)-1% H$_3$PO$_4$	18,200	0.274
	23,600	4.40
	38,500	4,470
	>50,000	>10,000
Fe(III)-40%H$_3$PO$_4$	19,200	0.120
	24,100	0.642
	38,500	7,570
	>50,000	>10,000

tailed band assignment will neither be attempted but it has been found during this study that the presence of phosphoric acid gives rise a remarkable change in the spectra of ferric aquo-complexes and new bands characterestic of Fe(III)-phosphate complex formation appear in the visible region. The whole electronic spectra of the relevant ferric complexes are given in *Fig.* 1 and the apparent bands are listed in *Table* 1. In the absence of phosphoric acid ferric ion shows only one broad shoulder in the visible region and weak spin-forbidden d-d bands seem to be hidden. However, when phosphoric acid is added, a strikingly different spectral pattern is observed which is not noticeably influenced by the acid concentration up to 40%. Two visible bands appear at 19,200 and 24,100cm^{-1} in the concentrated acid solution, but these bands both suffer bathochromic shift with decreasing acid concentration probably because of their adjacent strong bands (tailing effect). Irrespective of their origins, these two bands must be due to the formation of Fe(III)-phosphate complex, although no exact molecular form can be thereform informed. One may imagine that the spectral change is not ascribed to the complex formation but simply to the acidity change(by phosphoric acid) resulting in depression of the formation of the hydroxo species. However, no such visible bands were observed when other acids were employed instead of phosphoric acid.

Since of these two visible bands the higher energy absorption at 24,000cm^{-1} is more sensitive in intensity to the phosphoric acid concentration, its absorbance is plotted versus the acid concentration (as mole ratio of (H$_3$PO$_4$) to (Fe)) as is shown in *Fig.* 2.

The curve in the figure suggests that two distinct Fe(III)-phosphate complexes exist in the range of acid concentration 0~40%. When the acid concentration is increased the absorbance of the 24,000cm^{-1} band gradually increases to reach the maximum at the mole ratio of (H$_3$PO$_4$)/(Fe) =1:2, which indicates that probably a dimeric species (Fe$_2$H$_x$PO$_4$)$^{(3+x)+}$ is formed in the dilute acid solution. As a matter of fact, such an obse-
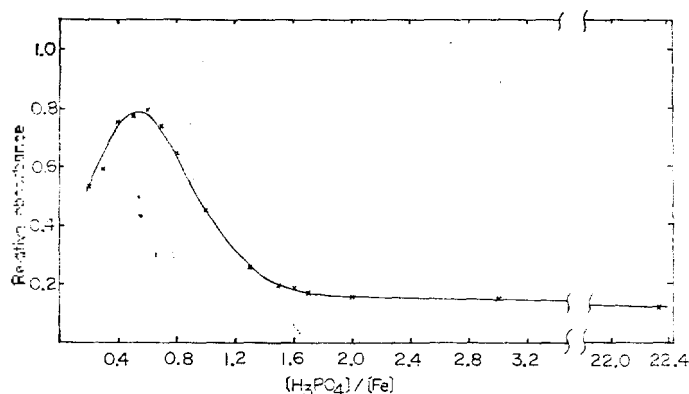
Fig. 2. Relative absorbance of 24.1kK band *v.* phosphoric acid concentration.

rvation is in accord with the results of Salmon's magnetic susceptibility measurements[5] which show lowest magnetic moment for solution of this mole ratio. Salmon proposed as the diamagnetic dimeric species a hydroxo-bridged form, either of $[Fe_2(OH)(HPO_4)]^{3+}$ or $[Fe_2(OH)(PO_4)]^{2+}$ which could not be ascertained.

When however the acid concentration is further increased the absorbance gradually falls off after the maximum until the mole ratio of $[H_3PO_4]/[Fe]$ approaches 1.6, after which it remains almost at constant value. Such a result evidently indicates that another species possibly 1:1 complex $[Fe\ H_xPO_4]^{x+}$ where x may be 1, 2, or 3 is formed.

In order to determine the exact composition of the two abovementioned Fe(III)-phosphate complexes, isolation of these species was attempted using large anions including ferrocyanide and dichromate, the latter being unsuccessful. Addition of the aqueous ferrocyanide solution to the alcoholic solution containing ferric ion and phosphoric acid resulted in rapid precipitation of dark blue salts insoluble or slightly soluble both in alcohol and water. The phosphatocomplexes thus obtained with varied acid concentration were

subjected to chemical analysis and the results are presented in mole ratio in *Table* 2. According to the molecular formulas deduced from the mole ratio and charge balance, iron(III) and phosphoric acid form a 1:1 complex in the concentrated solutions and the phosphate ion is coordinated to the metal as monobasic state in contradiction to the results of ion exchange study by Salmon,[3] which is hardly explicable because of the differences in experimental conditions. Two other possible ways of formulation may be excluded for the following reasons.

The mixture of a mole ratio of $KFe[Fe(CN)_6]$ to $Fe(H_2PO_4)_3 = 2:1$ would lead to the same analytical results, but the former is very soluble in water whereas the isolated is insoluble. Also the same result would arise from the appropriate mixture of potassium phosphate and ferric ferrocyanide. However, this possibility is clearly eliminated if the IR spectra of the relevant salts in *Fig.* 3 are examined. The monobasic potassium phosphate exhibits three broad P—O vibrational bands in the $800 \sim 1400 \mathrm{cm}^{-1}$ region while the phosphato-complex shows only one broad band, from which also the split patterns of dibasic and tribasic potassium phosphates (not shown in the figure) are sharply distinguished. Therefore, it may be concluded that in the 1:1 complex the phosphato ion is coordinated in monobasic state to the ferric ion probably with a chelated structure. It may be commented here that the small amount of potassium in the insoluble Prussian blue $Fe_4[Fe(CN)_6]_3$ indicates coprecipitation of potassium ferrocyanide probably because of its insolubility in alcohol.

The IR spectra of other phosphato-complexes prepared in higher acid concentration showed

Table 2. Results of chemical analysis of the Fe(III)-phosphate complexes prepared in alcoholic medium.

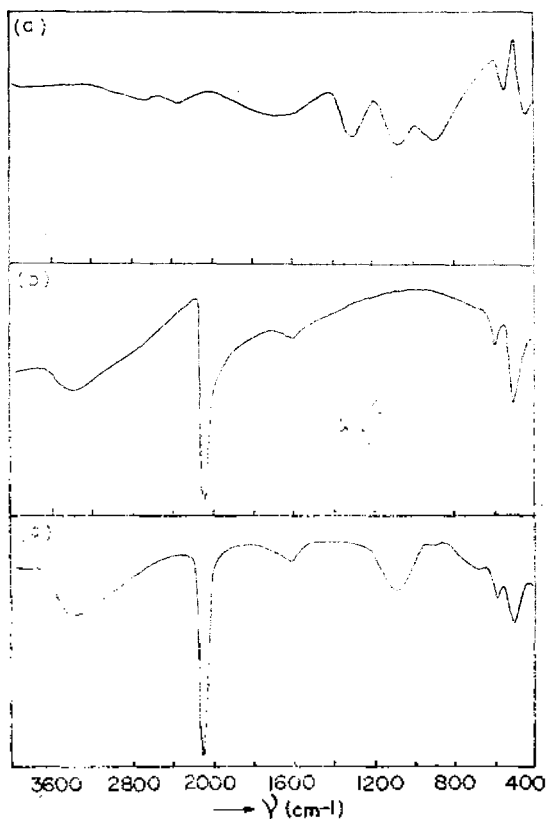| H_3PO_4 concentration(%)	K^+ (mmole)	Fe^{3+} (mmole)	$H_2PO_4^{x-3}$ (mmole)	$Fe(CN)_6^{4-}$	molecular formula
40	1.17	1.56	1.41	1.06	$K_2[Fe(H_2PO_4)]_3[Fe(CN_6)]_2$
30	1.14	1.40	1.46	0.933	$K_2[Fe(H_2PO_4)]_3[Fe(CN)_6]_2$
10	0.889	1.58	1.05	1.09	
4	0.563	1.58	0.826	1.06	
2	0.556	1.53	0.665	1.02	
1	0.735	1.59	0.531	1.22	
0.5	0.671	1.67	0.318	1.33	
0	0.021	2.01	—	1.56	$Fe_4[Fe(CN)_6]_3$

Fig. 3. IR spectra of $KH_2PO_4(a)$, $Fe_4[Fe(CN)_6]$ (b) and Fe (III)-phosphate salt isolated from 10 % H_3PO_4 solution(c).

exactly the same pattern implying that also 1:1 complex of composition $Fe(H_2PO_4)^{2+}$ only is formed in concentrated phosphoric acid solution, which is in agreement with the spectroscopic data. The nonstoichiometric composition of the Fe(III)-phosphate complexes prepared in lower acid concentrations does probably not imply the formation of different type of Fe(III) phosphate complex but of a mixture consisting of simply ferric and $Fe(H_2PO_4)^{2+}$ salts, since the IR spectra of these complexes are also the same. In the dimeric bridged structure, for instance, a different spectral pattern is expected.

It should be reminded that the uv-visible spectroscopic measurements have shown the presence of at least two different Fe(III)-phosphate complexes in the solution. Although the isolation of the 1:1 Fe(III)-phosphate complex has been successful, the 2:1 complex which was also informed from the magnetic susceptibility measurements thus could not be isolated in solid state. The bridged dimer is probably stable only in solution.

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