Adsorption of the Ferric Ion by Weakly Acidic Resins. Preferential Uptake of the Ferric Ion by Alginic Acid

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Weakly acidic ion-exchange resins have strong affinity to the hydrogen ion and it is scarcely exchanged at all for other cations including heavy metal ions. Recently, it has been revealed[1,2] in the course of separation experiments of heavy metal ions that alginic acid adsorbs the ferric ion to a great extent, although it is a weakly dissociated acid.

In this paper, adsorptive properties for ferric ions of weakly acidic ion-exchange resins, Amberlite IRC-50 and alginate resin, are examined and discussed.

Experimental

The exchange resins used are Amberlite IRC-50 (Rohm and Haas Co., Ltd., U. S. A.) and alginic acid*. They were washed thoroughly with pure water and air-dried, after conditioning with acid and alkali.

All the equilibrium experiments were carried out by the batch-method. Resins of acidic form were used unless otherwise stated. About 0.2 g. of the resin and 50 ml. of the external salt solution were taken in a beaker and allowed to stand for a week or more with stirring occasionally, since the rate of exchange is rather low for weakly dissociated resins as shown by the preliminary test (Fig. 1). To prevent the vaporization of the solution, the beaker was covered with polyvinylchloride sheet. The concentrations of metal ions in the added solutions were about 0.03 meq./ml. except these described otherwise. After equilibrating, the metal and hydrogen ions remaining in solution were assayed and the amount of the metal ions adsorbed on the resin was estimated as usual. The iron, aluminum and copper were analyzed colorimetrically.

All reagents are of commercial special-grade and were used without further purification.

Absorption spectra were measured using a Hitachi EPU-2A spectrophotometer.

Results and Discussion

Exchange of the Hydrogen Ion for the Ferric Ion.—Quantitative data on the adsorption of the ferric ion by weakly acidic resins from chloride solutions of varying initial concentrations of

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[1] H. Specker and H. Hartkamp, *Z. anal. Chem.*, **140**, 167; **141** 33 (1953).

[2] T. Takahashi and S. Emura, *Japan Analyst* (*Bunseki Kagaku*), **7**, 568 (1958).

* It was prepared by treating commerical sodium alginate (Kimitsu Chemical Industry, Co., Ltd.) with 10% hydrochloric acid, after it was once dissolved in water and filtered.

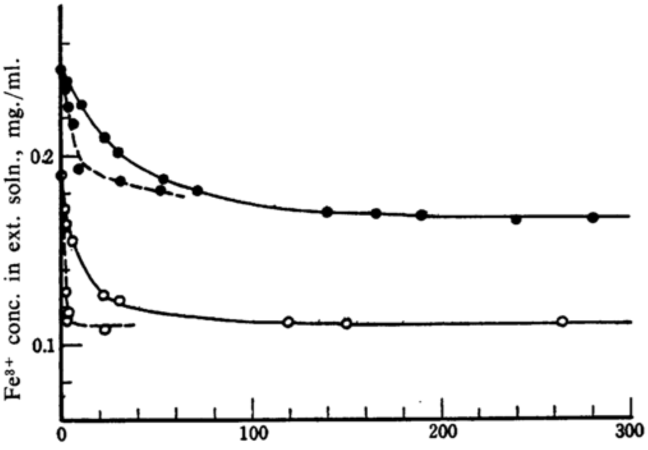

Fig. 1. Rate of exchange
○ Alginate resin, —— in settling
● Amberlite IRC-50, ---- with stirring
Resin, acidic form. Alg. 0.32 g., IRC-50 0.49 g.; Soln., 0.001 N HCl, 150 ml.

TABLE I. EXCHANGE OF THE HYDROGEN ION FOR THE FERRIC ION

	Fe^{3+} exchanged, meq./g. resin (eq./eq. resin)			
HCl concn., N	0	0.001	0.01	0.1
Amberlite IRC-50	4.57(0.44)	2.53(0.24)	1.06(0.10)	0.93(0.09)
Alginate resin	6.67(1.17)	3.88(0.68)	3.54(0.62)	2.12(0.37)
Amberlite IR-120	5.90(1.26)	5.54(1.18)	5.13(1.09)	3.42(0.73)

Resins, acid form 0.1∼0.2 g.
Ferric chloride soln., 0.5 mg. Fe^{3+}/ml., 50 ml.

TABLE II. AMOUNTS OF IONS REMAINING IN SOLUTION PHASE BEFORE AND AFTER EQUILIBRIUM

	Amounts, meq./ml.					
	Orig. ext. soln.			Equil. ext. soln.		
	H^+	Fe^{3+}	Cl^-	H^+	Fe^{3+}	Cl^-
Alginate resin (0.21 g.)	0.0010	0	0.0012	0.0011	0	0.0012
	0.0010	0.0141	0.0152	0.0059	0.0082	0.0153
	0.0010	0.0282	0.0302	0.0056	0.0223	0.0303
Amberlite IRC-50 (0.16 g.)	0.0010	0	0.0012	0.0011	0	0.0012
	0.0010	0.0141	0.0152	0.0019	0.0135	0.0152
	0.0010	0.0282	0.0302	0.0042	0.0250	0.0298

hydrochloric acid were given in Table I. Alginate resin adsorbs the ferric ion more strongly than Amberlite IRC-50. Amounts of ferric ions adsorbed were markedly dependent on pH of the external solution. For comparison, the data on exchange by a strongly acidic ion-exchange resin, Amberlite IR-120, were also shown in the table.

It is interesting to note that the adsorption capacity for the ferric ion is larger than the total exchange capacity**, which is obtained

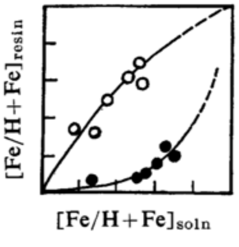

Fig. 2. Exchange diagram between hydrogen and ferric ions.
○ Alginate resin
● Amberlite IRC-50

** The total exchange cepacities are 10 for Amberlite IRC-50, 5.6 for alginate and 4.5 (meq./g. resin) for Amberlite IR-120, respectively.

from a titration curve by alkali, in the case of alginic acid and Amberlite IR–120.

In Fig. 2, the equilibrium diagram of the ferric ion against the hydrogen ion was shown. It is noteworthy that the ferric ion is adsorbed by alginate resin to almost the same extent as the hydrogen ion.

In Table II, the amounts of all ions remaining in external solution before and after equilibrium of the exchange reaction were described. As seen in the table, the adsorption of the ferric ion is intrinsically an exchange reaction of counter-ions of the resins.

Preferential Adsorption of the Ferric Ion.—In Table III and Fig. 3, the results of exchange equilibria of other heavy metal ions, Fe^{2+}, Al^{3+} and Cu^{2+}, for the hydrogen ion were given. As shown already by other investigators[1], who tried successfully to separate the ferric ion from other metal ions by columns of alginic acid powder, alginate resin combines very strongly with the ferric ion compared with other heavy metal ions. This behavior is a remarkable character of alginate resin, in contrast with Amberlite IR–120 and IR C–50; the former adsorbs well all metal ions and the latter has a very strong affinity to the hydrogen ion and, therefore, metal cations replace the hydrogen ion with difficulty.

This result is valid, independently of the acidity of the external solution as seen in Table IV. Of course, as the acidity of a solution becomes very high, these resins can not combine with other cations except in the case of the hydrogen ion.

To confirm this selective uptake of the ferric ion by alginic acid, the exchange equilibria between Fe^{3+} and Al^{3+} or Cu^{2+} were examined under the condition that the concentration of hydrochloric acid in salt solution was kept constant. Also the total concentration of the metal ions in the system was almost kept constant, 0.15 meq./ml. The results were given in Fig. 4. Preferential adsorption of the ferric

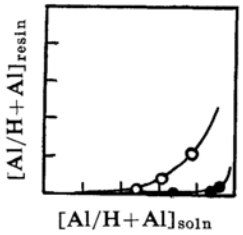

Fig. 3. Exchange diagram between hydrogen and aluminum ions.
○ Alginate resin
● Amberlite IRC–50

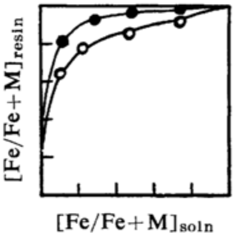

Fig. 4. Exchange equilibria of alginate resin between Fe^{3+} and Al^{3+} or Cu^{2+} at a constant acid concentration, 0.01 N H_2SO_4.
○ Fe^{3+}∼Cu^{2+}, ● Fe^{3+}∼Al^{3+}

TABLE III. EXCHANGE OF THE HYDROGEN ION FOR HEAVY METAL IONS IN SOLUTION OF CONSTANT ACID CONCENTRATION, 0.01 N

	Ions exchanged, meq./g. resin			
Ions	Fe^{3+}	Fe^{2+}	Al^{3+}	Cu^{2+}
Salt form	$FeCl_3$	$FeCl_2$	$Al_2(SO_4)_3$	$CuSO_4$
Amberlite IRC–50	1.06	0	0.20	0
Alginate resin	3.54	0.13	0.50	1.17
Amberlite IR–120	5.13	4.02	4.84	4.36

Resins, acid form 0.1∼0.2 g.
Metal ion soln., ca. 0.03 meq./ml., 50 ml.

TABLE IV. EXCHANGE OF THE HYDROGEN ION FOR THE FERROUS OR THE ALUMINUM ION

	Ions exchanged, meq./g. resin			
Fe^{2+}, $FeCl_2$–HCl (0.60 mg. Fe^{2+}/ml., 50 ml.)				
HCl concn., N	0	0.001	0.01	0.1
Amberlite IRC–50	0.12	0.05	0	0
Alginate resin	0.41	0.23	0.13	0.05
Al^{3+}, $Al_2(SO_4)_3$–H_2SO_4 (0.25 mg. Al^{3+}/ml., 50 ml.)				
H_2SO_4 concn. N	0	0.0001	0.001	0.01
Amberlite IRC–50	0.28	0.22	0.19	0.17
Alginate resin	2.18	2.06	1.49	0.47

Resin, acid form 0.1∼0.2 g.

TABLE V. DESORPTION OF METAL IONS WITH ACID FROM RESINS

		Ions retained, meq./g. resin			
Added soln.		H_2O	0.01 N HCl	0.1 N HCl	1.0 N HCl
Alginate resin	Fe^{3+}	6.98	6.06	1.44	0
	Al^{3+}	4.33	2.75	0.53	0
	Cu^{2+}	4.61	3.18	0.11	0
Amberlite IRC-50	Fe^{3+}	6.00	4.97	0.02	0
	Al^{3+}	5.93	3.78	0.43	0
	Cu^{2+}	6.33	4.00	0	0

Resin, metal salt form 0.3～0.4 g., soln., 100 ml.

TABLE VI. EFFECT OF ANION ON ADSORPTION OF THE FERRIC ION

	Fe^{3+} adsorbed, meq./g. resin			
Salt form	$FeCl_3$	$Fe(NO_3)_3$	$Fe_2(SO_4)_3$	$FeK(SO_4)_2$
HCl concn., N	0.0135_6	0.0100_5	0.0110	0.0111
Amberlite IRC-50	1.07	1.07	0.98	1.05
Alginate resin	3.24	2.96	3.14	3.09

Resin, acid form 0.1～0.2 g.
Ferric ion soln., 0.5 mg./ml., 50 ml.

ion against the aluminum or copper ion is very remarkable and, therefore, it is clear that the ferric ion can easily be separated from these ions by using alginic acid as an ion-exchange resin.

Desorption of Metal Ions from Resins with Acid.—Although in all the experiments mentioned above the acidic form resins were equilibrated with salt solution, here salt form resins were treated with acid to examine the reversibility of these exchange reactions. Resin of Fe^{3+}-, Al^{3+}- or Cu^{2+}- salt form was prepared by treating sodium salt form resin with ferric, aluminum or cupric chloride solution respectively, and washing it several times with pure water.

A definite quantity of each salt resin was immersed in an acid solution of known concentration, and the amount of metal ion desorbed from resin was measured. The results were given in Table V.

The reversibility of the exchange equilibrium does not always hold. It must be pointed out that, in the case of Amberlite IRC-50, the amounts of metal ions retained in this elution experiment are larger than those adsorbed in the adsorption experiment, independently of the variety of ion species. Alginate resin adsorbs ferric ion remarkably and the retained quantity is nearly equal to the adsorbed one shown in Table I.

Metal ions are eluted from resins almost with 0.1 N and completely with 1 N hydrochloric acid.

Effect of Anion.—The effect of anion on adsorption of the ferric ion by resin was examined and the result was given in Table VI.

In both resins the effect of anion is not remarkable.

Mechanism of Ferric Ion Adsorption on Resins.—As mentioned above, alginic acid resin adsorbs the ferric ion more extensively than Amberlite IRC-50 and the ferric ion is more preferentially adsorbed than other heavy metal ions, aluminum and copper ions, by these weakly dissociated resins. Taking into account these facts and the structural character of resins, the mechanism of adsorption of the ferric ion on these resins is examined as follows:

Adsorption of Chloride Complex Ions, $FeCl_n^{+(3-n)}$.—It is well-known[3,4] that the ferric ion combines with the chloride ion to form complex ions, $FeCl_n^{+(3-n)}$, where n becomes four at higher chloride concentration. If these complex ions take a part in the exchange reaction, adsorption of the chloride ion must be observed. However, this is not the case as shown in Table II, probably because the chloride concentration is rather low, less than 0.1 N, and the formation of chloride complexes is not predominant.

Adsorption of Hydroxy Complex Ions, $Fe(OH)_n^{+(3-n)}$. — Since in this experimental condition the hydrogen ion concentration is low in external medium, the ferric ion is hydrolyzed partially and the hydroxy complex ions, $Fe(OH)^{+2}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$, may be formed to a large extent[3,5]. Moreover, the fact that the exchanged quantity of the ferric ion is greater than the total exchange capacity leads to the conclusion that the ferric ion is exchanged not as a trivalent cation but as an ion with less valency on the average.

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3) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

4) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, **1953**, 1435.

5) A. B. Lamb and A. G. Jacques, *J. Am. Chem., Soc.*, **60**, 967, 1215 (1938).

For these reasons, it seems to be a fact that these hydroxy complexes have a part in the exchange reaction. None of the present experiments oppose the above deduction. It supports the probability of this adsorption mechanism that, when alginic acid combines with the ferric ion, it colors to reddish-brown and has a very similar absorption spectrum to that of the ferric hydroxide sol and of $Fe(OH)^{2+}$ given by Rabinowitch et al. (Fig. 5)⁽³⁾.

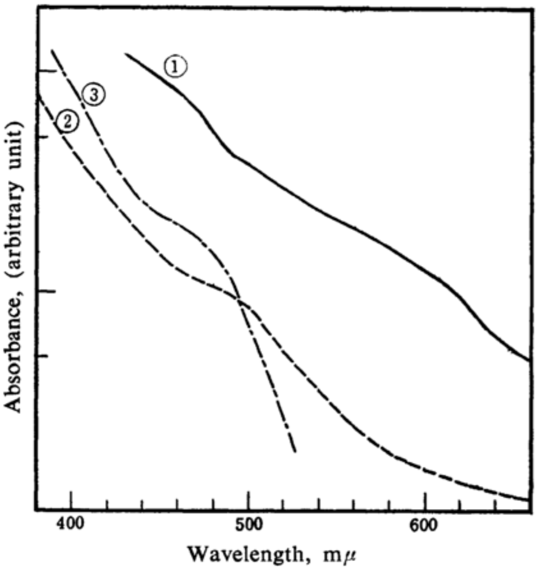


Fig. 5. Absorption spectra of
1. alginate resin membrane adsorbing ferric ion against original alginate membrane,
2. ferric hydroxide sol and
3. $Fe(OH)^{2+}$ given by Rabinowitch et al.⁽³⁾

In a case when partially hydrolyzed ions, e. g. $Fe(OH)^{2+}$, play a part in the adsorption reaction, reactions of various types may proceed at the same time. For instance, besides the normal exchange reaction 1

$$2HAlg+Fe(OH)^{2+} \rightleftarrows Fe(OH)Alg_2+2H^+ \tag{1}$$

the following reactions including neutralization may occur

$$HAlg+Fe(OH)^{2+} \rightleftarrows Fe(Alg)^{2+}+H_2O$$

$$Fe(Alg)^{2+}+2HAlg \rightleftarrows Fe(Alg)_3+2H^+$$

that is,

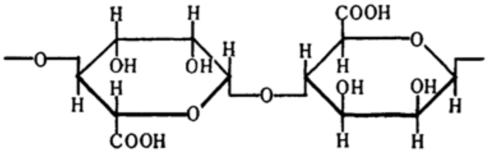
$$3HAlg+Fe(OH)^{2+} \rightleftarrows Fe(Alg)_3+2H^++H_2O \tag{2}$$

where Alg denotes a structural unit of alginate resin. Taking the hydrolysis of ferric alginate into account, reactions 1 and 2 cause the same result.

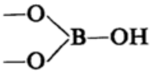
Although the present study can not give any confirmative evidence for the occurrence of these reactions, it is probably true that this mechanism may play an important part in the adsorption of the ferric ion by weakly acidic resin, for neutralization reaction can proceed to a large extent in these weakly dissociated resins.

The detailed discussion of such an exchange reaction including reactions of various types must be made clear in future.

Complex Adsorption.—As alginic acid has the following structure containing two hydroxyl groups and an oxygen linkage, it may be expected to combine with the ferric ion, forming an inner salt complex. To examine the effect



of the hydroxyl groups on the adsorption of the ferric ion by alginic acid, the ferric ion adsorbed on alginate resin was estimated when boric acid was added to the equilibrating system. The result was given in Table VII. The addition of boric acid diminishes the adsorbed quantity of ferric ions. Since it is known⁽⁶⁾ that alginic acid having a *cis*-diol group combines with boric acid to form a chelate compound,


$$\begin{matrix}-O\\ -O\end{matrix}\!\!>B-OH$$

it is confirmed that the presence of the hydroxyl groups influences the adsorption of the ferric ion.

TABLE VII. ADSORPTION OF THE FERRIC ION BY ALGINATE RESIN IN THE PRESENCE OF BORIC ACID

HCl concn., N	0	0.001	0.01	0.1
Fe^{3+} adsorbed, meq./g.	3.28	2.84	2.04	1.99

Boric acid, 1.0 meq. (equiv. to alginate)
Alginate resin, 0.2 g.
Ferric chloride soln., 0.5 mg. Fe^{3+}/ml., 50 ml.

Moreover, to obtain further knowledge concerning the formation of a chelate compound between alginic acid and the ferric ion, absorption spectra of the ferric ion were measured in the presence of glucuronic acid, which is similar structurally to the unit of alginic acid***. As

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6) H. Deuel and M. Neukom, *Makromol. Chem.*, 3, 13 (1949).

*** The structural unit of alginic acid is mannuronic acid and glucuronic acid may be structurally named galacturonic acid. However, it is safely considered that qualitative behaviors toward the ferric ion are similar for both acids.

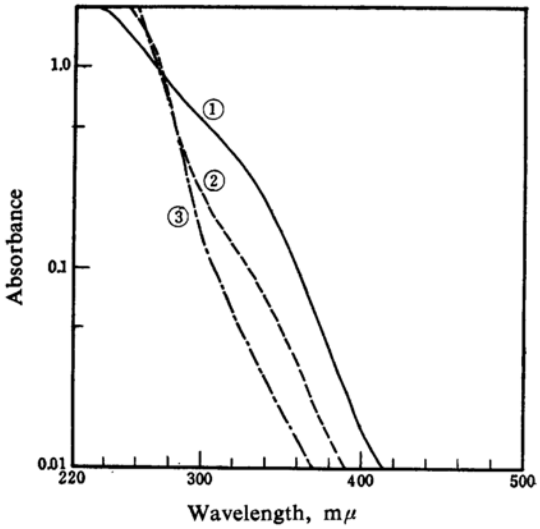

Fig. 6. Absorption spectra of ferric perchlorate $Fe(ClO_4)_3$, 0.0022 meq./ml.; $HClO_4$, 1, 0.007 N; 2, 0.031 N; 3, 0.091 N. Reference, H_2O.

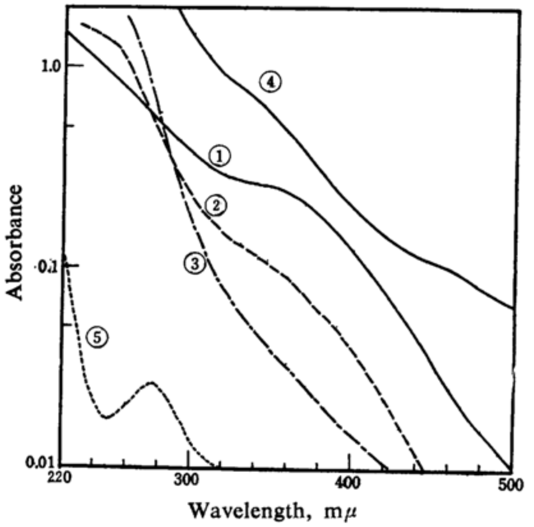

Fig. 7. Absorption spectra of Fe^{3+}~glucuronate.

	$Fe(ClO_4)_3$	$HClO_4$	Na glu.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	〃	0.007	0.022
5	0	0	0.0022

reference, H_2O.

shown in Figs. 6 and 7, it is apparent that there is a shoulder at 320~340 mμ region of the absorption spectrum of the ferric ion in the presence of the glucuronate ion. That is to say, an absorption band appears at about 330 mμ and becomes weaker as the acidity of the solution increases and disappears at 0.1 N of perchloric acid.

When the concentration of the glucuronate ion is high, a weak absorption is observed over the visible wavelength region and the solution becomes weakly reddish-yellow. The absorption at 330 mμ does not become remarkable and a new weak band appears at 470 mμ.

The visible absorption spectrum**** of alginate membrane adsorbing the ferric ion also has a shoulder at 460~470 mμ, as shown in Fig. 5.

The component ions, ferric (aquo), glucuronate and alginate ions, exhibit no absorption peak in these regions⁷⁾. Therefore, although these spectroscopic characters can not be explained completely in the present stage, it may be concluded that there are some interactions between the ferric ion and the glucuronate or alginate ion besides the simple coulombic one. Thus, it is, partly at least, due to the complex formation that alginate resin adsorbes the ferric ion intensively and preferentially.

It must be noticed that a hydroxy complex of the ferric ion has an absorption spectrum over the visible wavelength region and this spectrum has a shoulder at 460~480 mμ, as revealed from the spectrum of the ferric hydroxide sol and the spectrum of $Fe(OH)^{2+}$ obtained by Rabinowitch et al.³⁾ Since the concentration of the hydrogen ion is higher in the resin phase than in the external solution, it can not be expected that these hydroxy complexes exist in a free state, but it may be probable that hydroxy complexes are formed between the ferric ion and the glucuronate or alginate ion.

The absorption spectra of the ferric ion in the presence of acetate and *p*-toluene sulfonate ions were shown in Figs. 8 and 9. These ions are structurally similar to a unit of Amberlite IRC-50 and Amberlite IR-120, respectively. The spectrum of the ferric ion is not affected by the addition of the former⁸⁾ and the addition of the latter does not change in shape, but shifts the spectrum of the ferric ion to a longer wavelength. From these observations it may be concluded that these ions do not combine with the ferric ion to form chelate compounds.

**** It was measured against the original alginate membrane using opal-glass. Measurements in the region of ultraviolet wavelengths are impossible by this method.

7) Ther is a peak at 270~280 mμ in the absorption spectrum of the glucuronate ion. The chloride complexes of the ferric ion have an absorpion peak at 330~340 mμ.

8) W. Reiss et al.⁹⁾ reported that ferric acetate complex exhibits absorption peaks at 337.5 and 465 mμ when the concentration of the acetate ion is high. These peaks were not detected under the present experimental condition.

9) W. Reiss, J. F. Hazel and W. M. McNabb, *Anal. Chem.*, **24**, 1647 (1952).

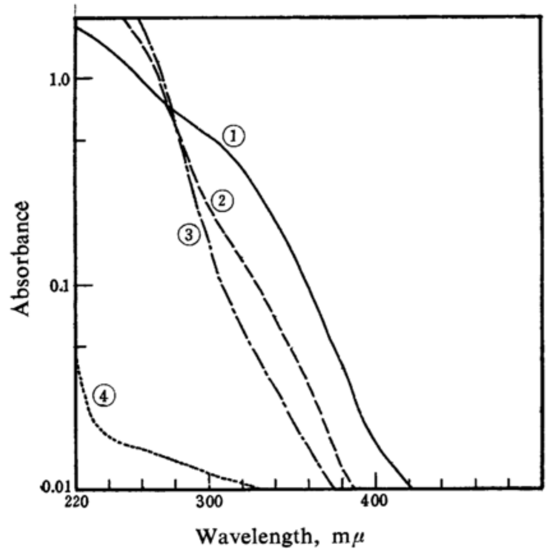

Fig. 8. Absorption spectra of Fe^{3+}∼acetate.

	$Fe(ClO_4)_3$	$HClO_4$	Na acet.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	0	0	〃

reference, H_2O.

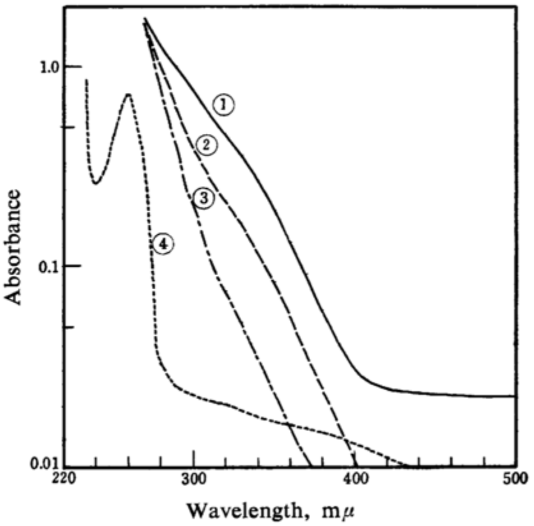

Fig. 9. Absorption spectra of Fe^{3+}∼p-toluene sulfonate.

	$Fe(ClO_4)_3$	$HClO_4$	Na-*p*-TS.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	0	0	〃

reference, H_2O.

Summary

The exchange adsorptions of the ferric ion by the cation-exchange resins of carboxylic acid type, Amberlite IRC-50 and alginate resin, were examined. Equilibration experiments revealed that alginate resin adsorbs metal ions more extensively than Amberlite IRC-50 and the ferric ion is preferentially adsorbed by these resins, especially by alginate resin. The mechanism of adsorption of the ferric ion was discussed and it was concluded that the preferential uptake of the ferric ion by alginate resin was due to the partial hydrolysis of the ferric ion and the complex formation between the ferric ion and alginate resin.

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