The Cation Exchange Investigation of Scandium Acetate and Sulfate Systems

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Previously the present author¹⁾ has reported on the adsorption of scandium ions on several adsorbents, showing that the concentrations and kinds of salts contained in the solution have an influence on the ratios of scandium adsorption. The aim of the present investigation is to make quantitative studies of the formation equilibria of the complexes in the scandium acetate and sulfate systems, in order to get some clue as to the mechanism of the influence described above.

A work²⁾ has recently reported on the scandium acetate system, in which, by the cation exchange method, scandium was separated from rare earth elements, using a 0.5 M ammonium acetate-acetic acid solution (pH 4.5) as an eluent. However, there has been no study of the composition of the eluted species.

In the present study, the compositions of the scandium acetate and sulfate complexes will be determined by the cation exchange method according to the procedures of Fronaeus,³⁾ with some simplification to be described below. Judging from the data obtained, species with scandium to ligand ratios of 1 : 1, 1 : 2 and 1 : 3 seem to be formed both in acetate solutions and in sulfate solutions at a constant ionic strength of $\mu=0.5$ and at 25°C. Then overall formation constants of the various complexes will be determined.

Derivation of Equations

An equation for determining the compositions and the formation constants of metal complex species using cation exchange resin has been derived by Schubert.⁴⁾ Fronaeus³⁾ has applied the cation exchange method to the step to step equilibria between a divalent cation and a univalent complexing anion. In this investigation, an equation was derived for the complex systems of the $M^{3+}-A^-$ and $M^{3+}-B^{2-}$ types, and a graphical method developed by Banerjea and Tripathi⁵⁾ was used in evaluating the formation constants. According to the data of Biedermann⁶⁾ concerning the hydrolysis of scandium ions, the mononuclear complexes exist in an acid solution which contains a low concentration of scandium. As a small amount of radioactive scandium was used in these experiments, the formation of only the mononuclear complexes need to be considered.

The following equilibrium is obtained between a cation exchanger in the sodium form and a solution containing scandium ions, Sc^{3+}, and complex ions, ScA_j^{3-j}:

$$(3-j)\,Na_R^+ + ScA_j^{3-j} = (3-j)\,Na^+ + ScA_{jR}^{3-j};\ (j=0,\ 1,\ 2)$$

If the law of mass action is applied to this exchange equilibrium,

$$[ScA_j^{3-j}]_R/[ScA_j^{3-j}] = k_j[Na^+]_R^{3-j}/[Na^+]^{3-j}=l_j;\ (j=0,\ 1,\ 2) \tag{1}$$

where [ ] indicates the molar concentration and the subscript R indicates the resin phase.

In this experiment, the total concentration of the scandium ions is very low and the load of metal ions in the resin phase is very low compared with the total exchange capacity. Moreover, the ionic strengths of both the resin and the aqueous phase have been nearly constant. Under these conditions, k_j and l_j in Eq. 1 may be considered to be constant. The total concentration of scandium ions in the

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1) J. Yoshimura and A. Tateda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 1018 (1962).

2) J. Yoshimura, Y. Takashima and H. Waki, ibid., **79**, 1169 (1958).

3) S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951); **6**, 1200 (1952).

4) J. Schubert, *J. Colloid. Chem.*, **52**, 340 (1948); *J. Phys. Chem.*, **56**, 113 (1952).

5) D. Banerjea and K. K. Tripathi, *J. Inorg. Nucl. Chem.*, **18**, 199 (1961).

6) G. Biedermann, M. Kilpatrick, L. Pokras and L. G. Sillén, *Acta Chem. Scand.*, **10**, 1327 (1956).

resin phase, C_{MR}, and in solution, C_M, are considered to be as follows:

$$C_{MR}=[Sc^{3+}]_R+[ScA^{2+}]_R+[ScA_2{}^+]_R \qquad (2)$$

and

$$C_M=[Sc^{3+}]+[ScA^{2+}]+\cdots\cdots+[ScA_N{}^{3-N}]$$
$$=[Sc^{3+}](1+\sum_{j=1}^{N}\beta_j[A^-]^j) \qquad (3)$$

where a N indicates a maximum ligand number bound to a scandium ion, and β_j is the overall formation constant of jth complex, $ScA_j{}^{3-j}$, i. e. $\beta_j=[ScA_j{}^{3-j}]/[Sc^{3+}][A^-]^j$.

From Eqs. 1, 2 and 3, putting $l_1\beta_1/l_0=L_1$ and $l_2\beta_2/l_0=L_2$, the distribution coefficients of the scandium between the resin and the solution, K_d, can be represented by:

$$K_d=C_{MR}/C_M=l_0(1+L_1[A^-]+L_2[A^-]^2)/X \qquad (4)$$

where

$$X=1+\sum_{j=1}^{N}\beta_j[A^-]^j$$

For determining the value of L_1, the following function, f_1, is introduced:

$$f_1=(K_d{}^{-1}-l_0{}^{-1})/[A^-] \qquad (5)$$

The relation, Eq. 6, is derived by introducing the expression of K_d from Eq. 4 into Eq. 5 and by extrapolating it to $[A^-]=0$;

$$\lim_{[A]\to 0} f_1=f_1{}^0=(\beta_1-L_1)/l_0 \qquad (6)$$

When the ligand concentration, $[A^-]$ in Eq. 4, is very small, it may be assumed that the L_1 and L_2 terms can be disregarded. Then an approximate value of β_1 can be determined graphically by extrapolation to $[A^-]=0$, according to the following equation:

$$(l_0/K_d-1)/[A^-]=\beta_1+\beta_2[A^-]+\cdots\cdots$$
$$+\beta_N[A^-]^{N-1} \qquad (7)$$

As l_0 is measurable or calculable, L_1 can be estimated from Eq. 6. L_2 can be determined in the same way. Another function, f_2, is also introduced as follows:

$$f_2=[f_1-(\beta_1-L_1)l_0]/[A^-] \qquad (8)$$

Now the values of $f_1{}^0$, L_1 and l_0 and an approximate value of β_2 being known or calculated, the value of L_2 can be calculated from Eq. 9, obtained by extrapolating the f_2 function to $[A^-]=0$:

$$\lim_{[A^-]\to 0} f_2=f_2{}^0=[(\beta_2-L_2)-f_1{}^0l_0L_1]/l_0 \qquad (9)$$

When L_1 and L_2 have been determined in this way, the function X in Eq. 4 can be calculated, and from the corresponding values of X_j and $[A^-]$ the formation constant can be computed from the relations:

$$X_1=(X-1)/[A^-]=\beta_1+\beta_2[A^-]$$
$$+\beta_3[A^-]^2+\cdots\cdots+\beta_N[A^-]^{N-1} \qquad (10)$$
$$X_2=(X_1-\beta_1)/[A^-]=\beta_2+\beta_3[A^-]$$
$$+\beta_4[A^-]^2+\cdots\cdots+\beta_N[A^-]^{N-2} \qquad (11)$$

This process is continued till the X_N function independent of $[A^-]$ is obtained, where:

$$X_N=\beta_N$$

Hence a plot of X_N versus $[A^-]$ will be a straight line parallel to the $[A^-]$ axis, indicating that the highest complex formed in the system is $ScA_N{}^{3-N}$.

In the case of a divalent complexing anion B^{2-} such as the sulfate ion, it has only to be considered that the complex ions in the resin phase are Sc^{3+} and ScB^+. Therefore, Eq. 4 can be rewritten as:

$$K_d=l_0(1+L_1[B^{2-}])/X \qquad (12)$$

Since L_1 can be determined as has been described above, the function X can be calculated and β_j can be estimated.

Experimental

Reagents. — Radioactive ^{46}Sc ($T_{1/2}=85$ days) in dilute hydrochloric acid, obtained from N. V. Philip-Duphar (Holland), was employed as a stock solution of scandium ($\sim 5\times 10^{-4}$ M). In these experiments, a portion of the above solution was dried in a glass dish and then dissolved in dilute perchloric acid. When the solution was converted into a 0.5 M sodium perchlorate solution, the radioactivity corresponded to about one microcurie per ml. of solution.

The resin used in all the experiments was the sodium form of the cation exchanger, Amberlite IR-120, with a particle size of 60 to 100 mesh and with a capacity of 3.69 meq. per g. in hydrogen form.

The sodium acetate solution and the sodium sulfate solution used as sources of complexing anions were prepared from guaranteed reagents.

Procedure. — The adsorbability of the scandium ions was measured by a batch method as follows; To the solution which contained a known quantity of a 0.5 M ligand solution and 1.0 ml. of the scandium solution, 0.5 M sodium perchlorate solution was added until the volume of the solution reached 10 ml. in a small stoppered glass vessel. The ionic strength of the resultant solution was then made up to 0.5. Since a 0.5 M acetic acid - sodium acetate buffer solution (pH 4.5) was used as the ligand solution in the case of the acetate system, pH of the solution prepared above could be adjusted easily. In the case of the sulfate system, the pH of the solution was adjusted with a dilute perchloric acid. Each of these solutions was shaken with 0.2 g. of the resin for 24 hr. at 25°C. A portion of the supernatant solution was then taken with a pipet and dried in a glass dish. The radioactivity of the residue was measured, and the distribution coefficient was calculated from the difference in the scandium activity before and after the achievement of equilibrium. The measurements of the radioactivity were carried out with a Toshiba Scintillation Detector, DDS-14301 type (NaI: $1''\phi\times1''l$), attached to a Flow Counter Scaler, UDS-24204 type.

Results and Discussion

On the Formation of Scandium Acetate and Sulfate Complexes.—In Fig. 1 the distribution coefficients, K_d, are plotted against pH values of scandium-perchlorate, -acetate and -sulfate solutions. The ionic strength of each solution was kept constant at 0.5 and, since the radioactive scandium used in this experiment was considered to form radiocollid or to precipitate hydroxide in an alkaline solution,[7,8] these experiments were carried out over the range of pH values from 1.0 to 7.0.

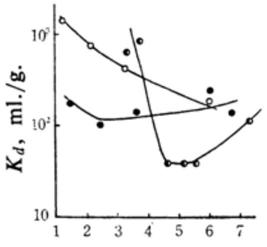

Fig. 1. Relation between the distribution coefficient and pH of the solutions.
Ionic strength: 0.5, Temp.: 25°C
—○— $NaClO_4$
—◐— $CH_3COONa + CH_3COOH$
—●— Na_2SO_4

It may be observed from Fig. 1 that K_d values in the acetate solution in the pH range from 4.5 to 6.0 are smaller than that in the perchlorate solution and that K_d values in the sulfate solution are also smaller than that in the perchlorate solution over a broad range of the acidic side of pH values. In the curve obtained with a perchlorate solution, K_d decreases with an increase in the pH values. This phenomenon may be considered to be due to the hydrolysis of scandium ions. Since the concentrations of scandium ion used in these experiments are below 10^{-5} mol./l., there is little or no tendency to precipitate scandium hydroxide below pH 5, according to the data of the solubility product.[8] $K_{so}=[Sc^{3+}][OH^-]^3 =10^{-27-30.1}$.

Moreover, the formation of the hydroxo complex ions, $Sc(OH)^{2+}$, $Sc(OH)_2{}^+$ and $Sc_2(OH)_2{}^{4+}$, were considered. From the values of the formation constants of these complex ions obtained by Biedermann et at.,*[,6] it has been found that only the scandium ion, Sc^{3+}, is a predominant species in the sulfate solution with pH=2.7 and that the hydroxo complex ions, $Sc(OH)^{2+}$ and $Sc(OH)_2{}^+$, form 26% and 7% of the total scandium concentration respectively in the acetate solution with pH=4.5. The polymerization of scandium ions is negligibly small in both cases.

On the other hand, the K_d value without a ligand obtained by the graphical extrapolation of the relation between $1/K_d$ and $[A]^2$ to $[A]=0$ in the acetate or the sulfate system, agreed with the value K_d obtained experimentally in the perchlorate solution with the same pH. In the case of acetate system, the numerical values of 204 ml./g. and 225 ml./g. respectively were obtained for the extrapolated and the experimental values at pH=4.5, while as regards the sulfate system, 545 ml./g. and 520 ml./g. respectively were obtained. Therefore, it has been proved, as has been shown by Feldman et al.,[9] that the species of the metal ion in the complexes are the same as that in the uncomplexed metal.

On the basis of these facts, it seems reasonable to assume that the decrease in the K_d value in both the acetate and sulfate solutions as compared with the K_d value of the perchlorate solution shows the occurrence of a considerable complex formation, since, although the resin adsorbs not only Sc^{3+} ions but also the cationic complexes, the adsorption of the latter for the resin is small because of the lower charge on the cationic complex and its low concentration in each system.

On the Composition and Formation Constants of Scandium Acetate Complexes.—In the formation reaction between the scandium ion and the acetate ion, it must be taken into consideration that the scandium ion has been hydrolyzed in the solution with pH=4.5, as has been described above. Therefore, the following equilibria are considered in solution, assuming that: 1) the species of the scandium ions reacting with the acetate ion, A^-, are Sc^{3+} and $Sc(OH)^{2+}$; 2) since only a few dihydroxo complex ions, $Sc(OH)_2{}^+$, are present in the solution under the experimental conditions, they can be disregarded as central metal ions; 3) the monohydroxo complex ion, $Sc(OH)^{2+}$, forms complexes with acetate ions. The formation of the hydroxo acetato complex ion, $Sc(OH)A_n{}^{2-n}$,

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[7] J. D. Gile, W. M. Garrison and J. G. Hamilton, *J. Chem. Phys.*, **18**, 1685 (1950).

[8] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal-ion Complexes, Part II: Inorganic Ligands," The Chemical Society, London (1958).

* These values are used: $^*K_1=[Sc(OH)^{2+}][H^+]/[Sc^{3+}] =10^{-4.90}$, $^*K_2=[Sc(OH_2)^+][H^+]/[Sc(OH)^{3+}]=10^{-5.1}$ and $\beta_{22}=[Sc_2(OH_2)^{4+}][H^+]^2/[Sc^{3+}]^2=10^{-5.9}$ (cf. Biedermann et al.[6]).

[9] L. Feldman, T. V. Toribara, J. R. Havill and W. F. Neuman, *J. Am. Chem. Soc.*, **77**, 878 (1955).

may be supported by the finding[10] that Sc(OH)A_2 was precipitated from a hot and concentrated solution with pH=4.76 and 4.93.

$$\mathrm{Sc}^{3+}+j\mathrm{A}^-=\mathrm{ScA}_j{}^{3-j}$$
$$\beta_j=[\mathrm{ScA}_j{}^{3-j}]/[\mathrm{Sc}^{3+}][\mathrm{A}^-]^j$$
$$\mathrm{Sc}^{3+}+\mathrm{H_2O}=\mathrm{Sc(OH)}^{2+}+\mathrm{H}^+$$
$$^*K_1=[\mathrm{Sc(OH)}^{2+}][\mathrm{H}^+]/[\mathrm{Sc}^{3+}]$$
$$\mathrm{Sc(OH)}^{2+}+n\mathrm{A}^-=\mathrm{Sc(OH)A}_n{}^{2-n}$$
$$\beta_n'=[\mathrm{Sc(OH)A}_n{}^{2-n}]/[\mathrm{Sc(OH)}^{2+}][\mathrm{A}^-]^n$$

The exchange equilibrium in the resin phase is considered, along with that of Eq. 1, as follows:

$$(2-n)\mathrm{Na_R}^++\mathrm{Sc(OH)A}_n{}^{2-n}$$
$$=(2-n)\mathrm{Na}^++\mathrm{Sc(OH)A}_{n\mathrm{R}}{}^{2-n}$$
$$[\mathrm{Sc(OH)A}_n{}^{2-n}]_\mathrm{R}/[\mathrm{Sc(OH)A}_n{}^{2-n}]$$
$$=k_n'[\mathrm{Na}^+]_\mathrm{R}{}^{2-n}/[\mathrm{Na}^+]^{2-n}=l_n'\,;\ (n=0,1) \tag{13}$$

From these equations, K_d is represented as follows, by the same treatment from Eq. 1 to Eq. 4:

$$K_d=\frac{\begin{pmatrix} l_0+l_0'{}^*K_1[\mathrm{H}^+]^{-1}+l_1\beta_1[\mathrm{A}^-]+ \\ l_1'\beta_1'{}^*K_1[\mathrm{H}^+]^{-1}[\mathrm{A}^-]+l_2\beta_2[\mathrm{A}^-]^2\end{pmatrix}}{\left(\begin{array}{c}(1+\sum\limits_{j=1}^{N}\beta_j[\mathrm{A}^-]^j)+ \\ ^*K_1[\mathrm{H}^+]^{-1}(1+\sum\limits_{n=1}^{M}\beta_n'[\mathrm{A}^-]^n\end{array}\right)}$$

$[\mathrm{H}^+]$ is determined by the pH value in solution and a constant value in this experiment, while $^*K_1$ is a known value.* Putting $l_0+l_0'{}^*K_1[\mathrm{H}^+]^{-1}=K_{d_0}$, $l_1\beta_1/{}^*K_{d_0}=L_1$, $l_1'\beta_1'{}^*K_1\cdot[\mathrm{H}^+]^{-1}/{}^*K_{d_0}=L_1'$ and $l_2\beta_2/{}^*K_{d_0}=L_2$, K_d can be represented by:

$$K_d={}^*K_{d_0}[1+(L_1+L_1')[\mathrm{A}^-]+L_2[\mathrm{A}^-]^2]/X'$$
$$X'=1+{}^*K_1[\mathrm{H}^+]^{-1}+B_1[\mathrm{A}^-]+B_2[\mathrm{A}^-]^2+\cdots\cdots \tag{14}$$

where B represents $\beta_j+\beta_j'{}^*K_1[\mathrm{H}^+]^{-1}$ and gives a constant value when $[\mathrm{H}^+]$ is kept constant. Since the distribution coefficients of Sc^{3+} and $\mathrm{Sc(OH)}^{2+}$ ions in the absence of an acetate ion, K_{d_0}, are obtained by the graphical extrapolation of K_d to $[\mathrm{A}^-]=0$, $^*K_{d_0}$ can be calculated from the following equation:

$$K_{d_0}={}^*K_{d_0}/(1+{}^*K_1[\mathrm{H}^+]^{-1})$$
$$\text{or}\quad {}^*K_{d_0}=K_{d_0}(1+{}^*K_1[\mathrm{H}^+]^{-1}) \tag{15}$$

Equation 14 can be made analogous to Eq. 4 by substituting L_1 and β_j for (L_1+L_1') and B_j respectively. Similarly, the following equations are obtained instead of Eqs. 5, 6, 7, 8 and 9 respectively:

$$f_1=(K_d{}^{-1}-K_{d_0}{}^{-1})/[\mathrm{A}^-] \tag{16}$$
$$\lim_{[\mathrm{A}]\to 0} f_1=f_1{}^0=[B_1-(L_1+L_1')$$
$$\times(1+{}^*K_1[\mathrm{H}^+]^{-1})]/{}^*K_{d_0} \tag{17}$$
$$[{}^*K_{d_0}/K_d-(1+{}^*K_1[\mathrm{H}^+]^{-1})]/[\mathrm{A}^-]$$
$$=B_1+B_2[\mathrm{A}^-]+\cdots\cdots \tag{18}$$
$$f_2=(f_1-f_1{}^0)/[\mathrm{A}^-] \tag{19}$$
$$\lim_{[\mathrm{A}]\to 0} f_2=f_2{}^0$$
$$=[B_2-L_2-(L_1+L_1')f_1{}^0{}^*K_{d_0}]/{}^*K_{d_0} \tag{20}$$

In the case of an acetate system, the ratios of ligands to scandium can be determined, but the chemical formulae and the formation constants for the corresponding complex ions can not be estimated unless either β_j or β_j' are estimated.

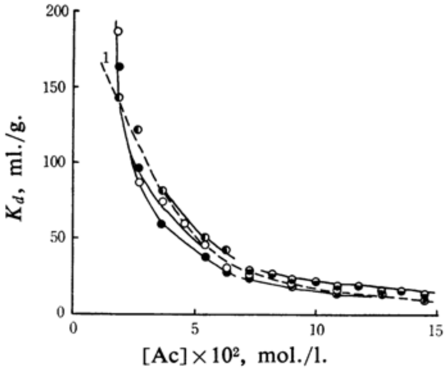

Fig. 2. K_d as a function of acetate ion concentrations at different Sc(III) concentrations.
Ionic strength: 0.5, Temp.: 25°C, pH: 4.5
—⊙— Total concentration of Sc(III) added, $C_\mathrm{M}'=1.17\times10^{-4}$ mol./l.
—●— $C_\mathrm{M}'=8.1\times10^{-5}$ mol./l.
—○— $C_\mathrm{M}'=5.0\times10^{-5}$ mol./l.
—◒— $C_\mathrm{M}'=3.6\times10^{-5}$ mol./l.
—◐— $C_\mathrm{M}'=2.9\times10^{-5}$ mol./l.
Broken line curve: Total concentration of Sc(III) in resin phase, $C_\mathrm{MR}=1\times10^{-4}$ mol./l.

Figure 2 shows the dependence of K_d on the acetate ion concentrations and the scandium concentrations, when the ionic strength is kept constant at 0.5 in a sodium perchlorate solution and at pH 4.5. The acetate ion concentration of the solution was calculated from the added acetate concentration, the pH of the solution and the dissociation constant of acetic acid.** In all of the above equations, $[\mathrm{A}^-]$ represents the concentration of free acetate ions. However, since the total acetate ion concentration is very much larger than the total scandium

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[10] J. S. Sterba-Bohm and M. Melichar, *Collection Czechoslov. Chem. Commun.*, 7, 56 (1935).

** The dissociation constants of acetic acid used was the value, $K=1.75\times10^{-5}$, given by J. F. J. Dippy [*Chem. Revs.*, 25, 151 (1939)].

TABLE I. K_d, X', X_1', X_2' AND X_3' CORRESPONDING TO THE ACETATE ION CONCENTRATIONS
IONIC STRENGTH : $\mu=0.5$, Temp.: 25°C, pH: 4.5

$[Ac^-]$ 10^{-2} mol. l^{-1}	K_d ml./g.	X'	X_1' mol^{-1} l.	X_2' mol^{-2} l^2	X_3' mol^{-3} l^3
0.00	204	1.40	22	1500	11000
1.81	143	2.32	51	1600	—
2.72	121	3.0	57	1300	—
3.63	80.0	4.8	93	2000	12000
5.44	47.1	9.1	140	2200	12000
6.35	37.1	12.3	172	2300	12000
7.26	29.6	16.4	207	2500	12000
9.07	21.0	24	258	2600	12000
10.90	16.4	35	306	2600	10000
12.70	14.4	42	324	2400	—
14.50	9.9	66	450	3000	10000

ion concentration, $[A^-]$ can be substituted for the total acetate ion concentration, $[Ac^-]$.

The scandium concentration in the resin phase was selected as 1×10^{-4} mmol./g. resin, so that the total concentration in the resin phase might be kept constant. The relation between K_d and the scandium concentration in the resin phase at a constant value of $[Ac^-]$ is presumed to be practically linear when graphically represented. Therefore, it is easy to determine the values of K_d corresponding to a constant and low value of C_{MR} by graphical interpolation. The resultant value of K_d is shown as a broken-line curve in Fig. 2 and in the second column of Table I.

The value of K_{d_0} was determined by graphical extrapolation. Since $1/K_d$ plotted against $[Ac^-]^2$ was shown to be a straight line at a low concentration of $[Ac^-]$, by extrapolation to $[Ac^-]=0$ the value of K_{d_0} was found to be 204 ml./g. Therefore, $^*K_{d_0}$ was calculated from Eq. 15 to be 286 ml./g.

In order to get the values of (L_1+L_1') and L_2, an approximate value of B_1 was calculated according to Eq. 18. The calculated values of approx. $X_1'=[^*K_{d_0}/K_d-(1+{}^*K_1[H^+]^{-1})]/[Ac^-]$ are plotted as a function of $[Ac^-]$ in curve 1 of Fig. 4; by graphical extrapolation to $[Ac^-]=0$, B_1 was found to be 22 ± 10 mol^{-1} l. On the other hand, as is shown in Fig. 3, the relation between f_1 and $[Ac^-]$ is practically linear at $[Ac^-]\leq9.07\times10^{-2}$ mol./l., and f_1^0 was found to be $(30\pm6)\times10^{-3}$ g. ml^{-1} mol^{-1} l. Accordingly, the value of $(I_1+L_1')=9\pm2$ mol^{-1} l. was obtained from Eq. 17.

Therefore, on substituting numerical value for the L_1+L_1' quantity into Eq. 14 the X' function may be shown as:

$$X'={}^*K_{d_0}(1+9[Ac^-])/K_d \qquad (21)$$

The values of f_2 calculated from Eq. 19 are plotted as a function of $[Ac^-]$ in Fig. 3. The f_2^0 value obtained by the extrapolation of f_2 to $[Ac^-]=0$ was 4.93 ± 0.04 g. ml^{-1} mol^{-2} l^2. On the other hand, the approximate value of B_2 at $[Ac^-]\leq9.07\times10^{-2}$ mol./l. was found to be $(15\pm7)\pm10^2$ mol^{-2} l^2 by the extraporation of curve 4 in Fig. 4 plotted from the relation between $X_2'=(X_1'-22)/[Ac^-]$ and $[Ac^-]$. Then the value of L_2 was given as almost zero by calculating from Eq. 20.

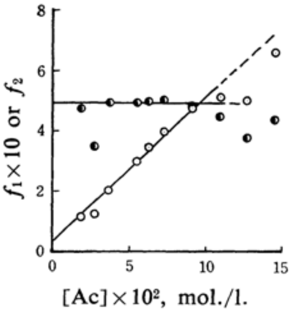

Fig. 3. f_1 and f_2 as a function of acetate ion concentration.
—○— f_1 —◐— f_2

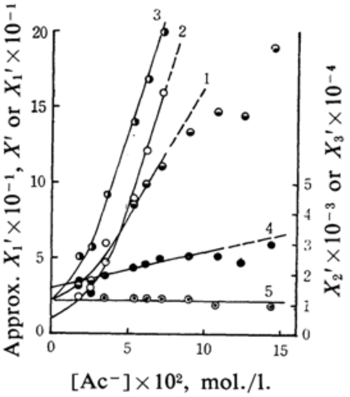

Fig. 4. Approximate X_1' and X_j' as a function of acetate ion concentration.
1: Approx. X_1', 2: X', 3: X_1', 4: X_2', 5: X_3'.

The functions X' calculated are shown in Fig. 4 and in Table I. By the extrapolation of X_1' and X_2' to $[\mathrm{Ac}^-]=0$, B_1 and B_2 agreed, of course, with the values of the first approximation. The function X_3' in curve 5 of Fig. 4 and in the sixth column of Table I has been calculated for such $[\mathrm{Ac}^-]$ values in which the difference $X_2'-B_2$ is not small compared with B_2. By the extraporation of X_3' to $[\mathrm{Ac}^-]=0$, B_3 was determined to be $(11\pm3)\times10^3$ mol.$^{-3}$ l^3. No value of B_4 can be obtained from this experiment.

From the results obtained it appears that the species with scandium to ligand ratios of 1 : 1, 1 : 2 and 1 : 3 are formed in an acetate solution with pH=4.5, while the species with the ratio of 1 : 2, $\mathrm{Sc(Ac)_2}^+$ or $\mathrm{Sc(OH)(Ac)_2}$ or both $\mathrm{Sc(Ac)_2}^+$ and $\mathrm{Sc(OH)(Ac)_2}$, appear to the predominant species in the acetate system under the experimental conditions, judging from the determined values of the formation constants.

On the Compositions and Formation Constants of Scandium Sulfate Complexes. — Figure 5 presents a plot of the K_d value versus the sulfate ion concentration. The experiment was carried out at a constant ionic strength of $\mu=0.5$ and at pH 2.7. The values of f_1 calculated according to Eq. 5 are plotted as a function of $[\mathrm{SO_4}^{2-}]$ in Fig. 6; the extrapolated value of f_1 was found to be $(6.8\pm0.1)\times10^{-2}$ g. ml^{-1} mol^{-1} l. The values of approx. $X_1=(l_0/K_d-1)/[\mathrm{SO_4}^{2-}]$ versus $[\mathrm{SO_4}^{2-}]$ are shown in Fig. 6. The approximate formation constant, $\beta_1=39.2\pm0.3$ mol^{-1} l., was easily found by extrapolating the approx. X_1 to $[\mathrm{SO_4}^{2-}]=0$ at $[\mathrm{SO_4}^{2-}]\leq2.79\times10^{-2}$ mol./l. Then the value $L_1=3\pm1$ mol^{-1} l. was calculated from Eq. 6.

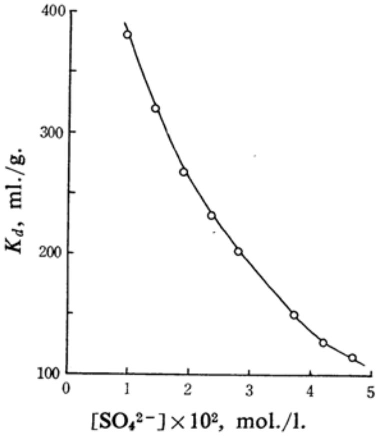

Fig. 5. K_d as a function of sulfate ion concentration.
Ionic strength : 0.5, Temp. : 25°C, pH : 2.7

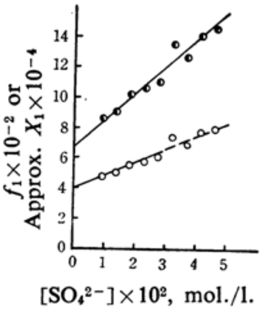

Fig. 6. f_1 and approximate X_1 as a function of sulfate ion concentration.
◐ f_1 ○ Approx. X_1

On substituting the value L_1 into Eq. 12, the function X can be calculated; by the extrapolation of X_1 to $[\mathrm{SO_4}^{2-}]=0$, the more accurate value of β_1 was found, 46 ± 5 mol^{-1} l. Then the value $L_1=8\pm1$ mol^{-1} l. was estimated. For the next approximation, the same procedure was repeated; the β_1 value obtained was practically the constant value. The function X may, then, be shown as follows:

$$X=l_0(1+8[\mathrm{SO_4}^{2-}])/K_d \qquad (22)$$

The functions X calculated from Eq. 22 are shown in Table II and in Fig. 7. The β_1, β_2 and β_3 formation constants were found to be 46 ± 5 mol^{-1} l., $(11\pm6)\times10^2$ mol^{-2} l^2 and $(10\pm7)\times10^3$ mol^{-3} l^3 respectively.

TABLE II. K_d, X, X_1, X_2 AND X_3 CORRESPONDING TO THE SULFATE ION CONCENTRATIONS
Ionic strength : $\mu=0.5$, Temp. : 25°C, pH : 2.7

$[\mathrm{SO_4}^{2-}]$ 10^{-2} mol. l^{-1}	K_d ml./g.	X'	X_1 mol^{-1} l.	X_2 mol^{-2} l^2	X_3 mol^{-3} l^3
0.00	545	1.00	46	1100	10000
0.93	380	1.54	58.0	—	—
1.40	322	1.88	62.9	1200	7000
1.86	268	2.33	72	1400	16000
2.33	233	2.78	76	1300	9000
2.79	203	3.28	82	1300	7000
3.26	159	4.32	102	1700	15000
3.72	152	4.65	98	1400	8000
4.19	129	5.64	111	1600	10000
4.64	116	6.45	117	1500	9000

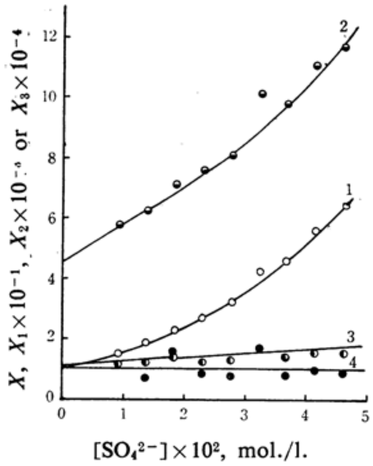

Fig. 7. X_j as a function of sulfate ion concentration.
1: X, 2: X_1, 3: X_2, 4: X_3

Summary

Ion exchange equilibria between the cation exchange resin, Amberlite IR-120, and an aqueous solution containing a small concentration of scandium ions and a relatively large concentration of acetate or sulfate ions have been measured at a constant ionic strength of $\mu=0.5$ and at 25°C. The values of the formation constants of the complexes in solution have been calculated by the application of the Fronaeus method[3)] and by the graphical method.[5)]

In the case of the acetate system, at an acetate ion concentration $[Ac]\leq 14.5\times10^{-2}$ mol./l. and pH 4.5, species with scandium to ligand ratios of 1 : 1, 1 : 2 and 1 : 3 seem to be formed. However, since scandium exists mainly in two ionic species, Sc^{3+} and $Sc(OH)^{2+}$, in the solution, the chemical formulae can not be determined; therefore, the formation constants have been estimated for the addition of each formation constant of two complexes with the same ligand ratio, $Sc(Ac)_j{}^{3-j}$ and $Sc(OH)(Ac)_j{}^{2-j}$. The values of $\boldsymbol{B}_j=(\beta_j+\beta_j'{}^*K_1[H^+]^{-1})$ were $\boldsymbol{B}_1=22\pm10$ mol^{-1} l., $\boldsymbol{B}_2=(15\pm7)\times10^2$ mol^{-2} l^2 and $\boldsymbol{B}_3=(11\pm3)\times10^3$ mol^{-3} l^3 at pH 4.5. In the case of the sulfate system, three complex ions were formed at a sulfate ion concentration of $[SO_4{}^{2-}]\leq 4.65\times10^{-2}$ mol./l. and pH 2.7 : $Sc(SO_4{}^{2-})^+$, $Sc(SO_4{}^{2-})_2{}^-$ and $Sc(SO_4{}^{2-})_3{}^{3-}$. The formation constants were $\beta_1=46\pm5$ mol^{-1} l., $\beta_2=(11\pm6)\times10^2$ mol^{-2} l^2 and $\beta_3=(10\pm7)\times10^3$ mol^{-3} l^3.

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