Formation Constants of Some Metal Formate Complexes, and the Use of Formate Buffer Solution as an Elutriant for Cation-exchange Chromatography

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(Received August 19, 1961)

Many studies of the elutriants for the ion-exchange separation of mixed fission products have been made over the part several years. Ammonium citrate(1), ammonium butyrate(2) and ammonium α-hydroxy isobutyrate(3) are used as elutriants for the separation of fission products and for the purification of rare earth elements. They have good separability, but some difficulties are encountered in the preparation and preservation of the elutriants and in further treatment of the eluates for analysis.

Honda has shown that ammonium acetate(4,5) or ethylenediaminetetraacetic acid(6) could be effectively used for separating alkaline earth elements and other elements. He has pointed out that ammonium acetate is easily sublimed. Tsubota and Kitano have shown that a new

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* A part of this work was done at Kobe University, Kobe. The new elutriant, the formate buffer solution, was first reported on by the present author at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

1) E. R. Tompkins, J. X. Khym and W. E. Cohn, *J. Am. Chem. Soc.*, **69**, 2769 (1954).

2) J. G. Cuninghame, M. L. Sigeland, H. H. Willis, J. Eakins and E. R. Mercer, *J. Inorg. Nuclear Chem.*, **1**, 163 (1955).

3) G. R. Choppin and R. J. Silva, ibid., **3**, 153 (1956).

4) M. Honda, *Japan Analyst* (*Bunseki Kagaku*), **3**, 132 (1954).

5) E. Minami, M. Honda and Y. Sasaki, This Bulletin, **31**, 372 (1958).

6) M. Honda, *Japan Analyst* (*Bunseki Kagaku*), **4**, 240 (1955).

elutriant, a mixture of ammonium formate and formic acid, is a good elutriant for analyzing fission products[7] and alkali or alkaline earth elements[8].

A good elutriant will have the following characteristics: 1) To separate various metal ions with cation-exchange resin, it is desirable that the formation constants between the anion of the elutriant and the metal ions to be separated should differ considerably from each other.

2) It is necessary that the reagent used as the elutriant does not interfere with the later procedures of the analysis. For this purpose, it is desirable that the formation constants should not be too large, or that the reagent should be easily removable from the eluates, e. g., by heating.

3) As the separation is done by changing the concentration of the complexing ion in the elutriant, it is desirable that the concentration of the complexing ion be capable of being varied by varying the pH and by keeping the total concentration of the elutriant constant. Therefore, the reagent used as the elutriant should have a buffer action. The reagent used as the elutriant of high quality must be obtainable at low cost, and one must be able to make solutions of various concentrations and pH's without difficulty. As ammonium formate can be vaporized most easily and completely, a formate solution would be the best elutriant if the formation constants of the metal ions to be separated are suitable.

Therefore, determination of the formation constants of these systems was undertaken as follows.

The Formation Constants of Some Metal Formate Complexes

Except for the system of alkaline earth elements[9], the formation constants of the formate complex systems have not yet been measured. In this work, the formation constants of formate are measured for iron, aluminium, rare earth (Ce) and manganese. These elements are essential portions of an analysis of natural waters, rocks and mixed fission products*.

The determination was done by the ion-exchange method[10,11].

Chemicals used.—

Resin: Dowex 50-X8, 60∼80 mesh, Na^+-form, air-dried.

Fe^{3+}-solution: perchlorate prepared from $FeCl_3 \cdot 6H_2O$, reagent grade of Merck.

Al^{3+}-solution: perchlorate prepared from pure aluminum plate (99.99%).

Ce^{3+}-solution: perchlorate prepared from $Ce(SO_4)_2 \cdot 4H_2O$, reagent grade of Merck.

Mn^{2+}-solution: perchlorate prepared from $MnCl_2 \cdot 4H_2O$, reagent grade of Wako-Junyaku.

All other chemicals used were of reagent grade.

Analysical Methods.—Ferric ion was titrated with EDTA, using variamine blue B as an indicator. The Al^{3+} was determined by colorimetry of aluminum oxinate in chloroform at a wavelength of 390 mμ. The determination of Ce^{3+} was made both by colorimetry of Ce^{4+} after oxidizing it with ammonium persulfate and by employing the β-counting method with ^{144}Ce; a good coincidence was obtained. Mn^{2+} was colorimetrically analyzed as potassium permanganate after oxidizing it with potassium periodate.

Measurements.—The complex solutions were prepared by mixing the following two solutions in various proportions:

Solution-1

$$a \text{ mol. } M^{n+}(ClO_4)_n$$

$$(1-na) \text{ mol. } NaClO_4$$

where M^{n+} is a metal ion, and a is kept constant, $1\sim5\times10^{-3}$ mol., in each series of experiments.

Solution-2

$$(1-b) \text{ mol. } HCOOH$$

$$b \text{ mol. } HCOONa$$

where b is kept constant, 0.2∼0.5 mol., in the series of experiments on each metal ion.

Twenty-five milliliters of the mixed solutions were shaken for 24 hr. with 1.000 g. of the dried ion-exchange resin in a thermostat at 25°C. After an exchange equilibrium had been reached, the solution was rapidly separated from resin with glass filter and the metal concentration of the solution phase was measured.

The relative volume decrease of the solution caused by the swelling of the ion exchanger was estimated by the quotient between the initial and equilibrium ion concentrations of the solution. A cation exchanger column in the hydrogen form was used to convert all cations in the solution to H^+. The H^+ was titrated with a 0.1 N sodium hydroxide standard solution, using phenolphthalein as an indicator, to give the initial and equilibrium ion concentrations. The values of these quotients, constant within each series of experiments, were between 0.99 and 0.97.

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[9] G. H. Nancollas, *J. Chem. Soc.*, **1956**, 744.

* Titanium was not measured because titanium is hydrolyzed in such a solution.

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Calculations.—The following notations are used.

$(M)_T$, $(A)_T$= initial total concentrations of metal ion and anion in the outer solution respectively [mol./l.].

(M), (A)=total concentrations in the outer solution at ion-exchange equilibrium [mol./l.].

$(M)_r$=equilibrium total concentrations of the metal ion in the resin phase [mol./g.].

k_d=distribution coefficient of the total metal ion between the outer solution and the resin phase [l./g.].

$k_d{}^0=k_d$ at $(A)_T=0$.

K=formation constant.

δ=relative volume decrease of solutions caused by the swelling of the ion exchanger, or $=v/v_i\ =C_i/C$

When the eqilibrium

$$M+nA \rightleftarrows MA_n \tag{1}$$

exists in the solution, the formation constant can be expressed as

$$K=(MA_n)/(M)(A)^n \tag{2}$$

To obtain the value of the formation constant from the distribution constant k_d and anion concentration (A), the equation derived by Schubert can be used. From the equation

$$\log(k_d{}^0/k_d-1)=n\log(A)+\log K \tag{3}$$

the formation constant K can be obtained.

The k_d-values are calculated from the relation

$$k_d=(M)_r/(M) \tag{4}$$

The total metal concentration in the resin phase at equilibrium, $(M)_r$, can be calculated from the relation

$$(M)_r=\{(M)_T-(M)/\delta\}\times 25/1000 \tag{5}$$

As the $(M)_T$ was always kept very low, the formate ion concentration of the outer solution was influenced only by the swelling of the resin, not appreciably by the sorption of the complexes. Therefore, (A) was obtained from the relation

$$(A)\cdot\delta=(A)_T \tag{6}$$

Since the values of k_d vary with the $(M)_r$, 3 different values of k_d for 3 different values of $(M)_r$ were estimated for each metal ion, and the corresponding k_d-values were obtained as a function of (A) by interpolation or extrapolation.

Results and Discussions.—The measured data are rearranged and shown in Fig. 1 in order to calculate the formation constants from Eq. 3. As is seen in the figure, the straight lines, the solpes of which are nearly equal to 1, are obtained for Al^{3+}-, Ce^{3+}- and Mn^{2+}-formate ion systems. For Fe^{3+}-formate ion systems, not a straight line, but rather a curve is observed. The straight lines indicate that Al^{3+}, Ce^{3+} and Mn^{2+} mostly form a first order complex with formate ion; even if there were the higher orders, they would exist only slightly. But from the curve for the Fe^{3+}-formate system, it can be concluded that the complex ions between Fe^{3+} and formate ion include the complex ions of higher orders.

TABLE I. FORMATION CONSTANT OF THE SYSTEM OF FERRIC ION AND FORMATE ION

Formation constant			
$K_1(=\beta_1)$	70 ± 5	M^{-1}	
$K_1(=\beta_2)$	4100 ± 500	M^{-2}	K_2 60
$K_1(=\beta_3)$	9000 ± 3000	M^{-3}	K_3 2.5
$K_4(=\beta_4)$	250000 ± 120000	M^{-4}	K_4 28

where

$\beta_n=[Fe(HCOO)_n{}^{3-n}]/[Fe^{3+}][HCOO^-]^n$

$K_n=\beta/\beta_{n-1}$

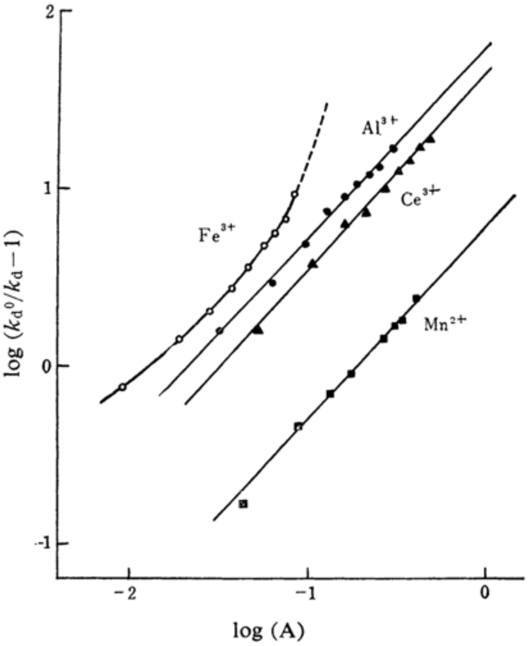

Fig. 1. Relations between log(A) and $\log(k_d{}^0/k_d-1)$ for Fe^{3+}, Al^{3+}, Ce^{3+}, and Mn^{2+}.

The formation constants for the system between Fe^{3+} and formate ion, therefore, were calculated by the Fronæus method[12],*. The results of the calculations gave four possible complex ions, as shown in Table I. Experiments using an anion exchange column were performed to confirm whether the complex anion, the 4th complex ion, exists or not. Thirty milliliters of the mixed solution of 1 M

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* The Fronæus-method was also used to calculate the formation constants for Al, Ce and Mn, but the results were not conclusive because of too small values for the 2nd formation constants compared with the experimental errors.

TABLE II. FORMATION CONSTANT BETWEEN METAL IONS AND FORMATE ION

Metal ion	Codition of measurement (μ=ionic strength)	Method of measurement	Formation constant	Literature
Fe^{3+}	25°C, $\mu=1$	Ion-exchange method	$K_1=70\pm5$	This work
Al^{3+}	25°C, $\mu=1$	Ion-exchange method	61 ± 5	This work
Ce^{3+}	25°C, $\mu=1$	Ion-exchange method	45 ± 5	This work
Mn^{2+}	25°C, $\mu=1$	Ion-exchange method	6.3 ± 0.7	This work
Mg^{2+}	25°C, $\mu=0$	Potentiometry	27.0	10)
Ca^{2+}	25°C, $\mu=0$	Potentiometry	27.0	10)
Sr^{2+}	25°C, $\mu=0$	Potentiometry	24.4	10)
Ba^{2+}	25°C, $\mu=0$	Potentiometry	24.2	10)

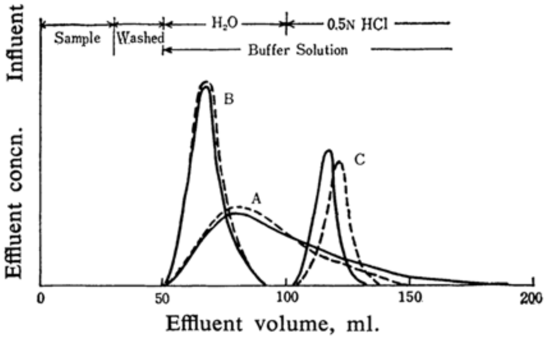

Fig. 2. Adsorption and elution of Fe^{3+} using anion-exchange column.

Curve——pH 3.2} 30 ml. of sample solusion and 20 ml. of
Curve----pH 3.6} buffer solution washed

Peak A: eluted with buffer solution
B: washed with water (50 ml.)
C: eluted with 0.5 N HCl after washing with water (Peak B)

formic acid and 1 M ammonium formate containing 3 meq. of Fe^{3+} was passed through a 1.1×10 cm. column of Dowex 1-X4 (50～100 mesh) of formate form and then washed twice with 10 ml. of the mixed solution. Then, the complex ion was eluted with the same mixed solution or water, followed by 0.5 N hydrochloric acid. The results, which are shown in Fig. 2, seem to verify the presence of the anionic, the 4th complex ion.

The values of the formation constants between metal ions and formate ion measured by the author are shown in Table II, together, with the values reported by the other researcher⁹⁾. The elution order from the cation exchanger expected from the table is

$$\text{Fe, Al, R. E. (Ce), Mn,} \tag{7}$$

and

$$\text{R. E., \{Mg, Ca\}, Sr, Ba} \tag{8}$$

To verify the conclusion mentioned above, a sample solution containing 6 meq. of iron(III) and 6 meq. of cerium(III) ions was passed through a 1.1×10 cm. column of Dowex 50-X8 (100～150 mesh) of a hydrogen form. After adsorption and washing, the ferric ion was eluted with 100 ml. of a mixed solution of pH 3.2 prepared from 7 parts of 1 M formic acid and 3 parts of 1 M ammonium formate. The cerous ion was eluted with 100 ml. of another mixed solution of pH 4.0 prepared from 3 parts of 1 M formic acid and 7 parts of 1 M ammonium formate. By this procedure, cerium free from iron was easily obtained, as had been expected.

As an example of separation with anion-exchange resin, the removal of iron(III) from rare earth and alkaline earth elements was carried out. Thirty milliliters of a mixed solution of 1 part of 1 M formic acid and 1 part of 1 M ammonium formate (pH about 3.6) containing 3 meq. of strontium and yttrium (labelled with ^{90}Sr-^{90}Y) was passed through a 1.1×10 cm. column of Dowex 1-X4*(50～100 mesh) of $HCOO^-$ from resin. After the sample solution had passed through, the column was washed twice, with 10 ml. of the buffer solution of the same pH and washed with 20 ml. of water; finally the column was regenerated with 0.5 N hydrochloric acid. The radioactivity of each portion was counted with a GM counter. The results are shown in Table III. It can be seen that only iron was adsorbed on the column, while cerium, yttrium and strontium were not. Thus, it was confirmed that iron could be easily removed from these samples.

As has been previously reported, mixed fission products were completely separated

TABLE III. REMOVAL OF IRON WITH ANION-EXCHANGE RESIN

Influent	Metals in effluent		
	Ce	Sr+Y	Fe
Sample	87.6%	85.7%	0
Washing solution 1	12.3	14.3	0
Washing solution 2	0.03	0.04	0
Washing solution and regenerating hydrochloric acid	0.01	0.01	100

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* It is difficult to elute iron from ion-exchange resin of a high D.V.B. content.

using mixed solutions of formic acid and ammonium formate as elutriants⁷⁾, and alkaline earth elaments were completely separated by a similar solution⁸⁾ of a different pH.

The order of elution of several cations can be predicted by the values of the formation constants between the metal ions to be separated and the anion of the elutriant (cf. (7) and (8)).

However, the other experiments¹²⁾ gave slightly different results from those expected:

Fe, Al, Mn, R. E. (Ce), Mg, Ca, Sr, Ba

The elution of Mn and Mg earlier than expected from the formation constant may be attributed to the very small affinity of Mn^{2+} and Mg^{2+} to the resin¹³⁾.

From the results mentioned above, it was confirmed that the elution order can be predicted mainly on the basis of the values of the formation constants between the metal ions to be separated and the anion of the elutriant. The separation is easily effected when the difference in formation constants is large, but the separation is due both to formation constants and to affinities between the metal ions and the resin when the difference in formation constants is not large.

The author wishes to express his sincere appreciation to Professor Yasuo Miyake of Tokyo University of Education, Professor Hidetake Kakihana of Tokyo Institute of Technology, Dr. Yasushi Kitano of Nagoya University, and Mr. Masami Izawa of the National Institute of Radiological Sciences for their helpful advice and encouragement throughout his work.

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13) O. D. Bonner and L. L. Smith, *J. Phys. Chem.*, **61**, 326 (1957).