

흡착법에 의한 금속이온과 유기산간의 친밀 생성계수의 측정법

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Determination of the Formation Constants of Metal Complexes with Organic Acids by Adsorption Method

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Abstract The adsorption method for the determination of the formation constants of the metal complexes with organic acids was developed by using membrane filters. The adsorption method involved the measurements of radioactivities of the adsorbed metal on membrane filters and the filtrate solution after the radioactive metal ion were filtered through membrane filters in the presence of organic ions of varying concentration. Comparing the adsorption method with the ion exchange method, it was seen that the adsorption method was simpler and faster than the ion exchange method. As an example of the metal complex with organic acid yttrium citrate complex was chosen, and the formation constant of the complex obtained by the adsorption method showed $K_f=2.0 \times 10^{-4}$ ($1. \text{mole}^{-1}$) at a pH of 7. Also the present study revealed that the carrierfree state of yttrium in aqueous solution was present in the completely ionized state.

Introduction

Formation of the metal complexes with organic acids was intensively studied by Schubert^{1,2}, Sang Up Choi^{3,4}, and their coworkers with applying the methods of ion exchange, and it was known that the methods were convenient and useful to determine the formation constants of metal complexes.

In present investigation it was intended to develop the adsorption method for the determination of the formation constants of metal complexes. The adsorption method include simply the determination of the activity of radioisotopes adsorbed on membrane filters

during filtration.

By the adsorption method it is expected that the formation constants of metal complexes can be determined rapidly and simply compared to the ion exchange method and also it helps to understand the state of microquantities of the radioisotopes.

For metal complex of organic acid, yttrium citrate complex was chosen, because the isotope is readily available and easy to manipulate by the short half-life of 64 hours.

The Theoretical Considerations of Adsorption Method

The adsorption of radioisotopes on membrane

filters was satisfactorily explained by the theory of the transient state of adsorbed ions, and the result for the case of carrier-free yttrium-90 was described in the previous paper.⁵ As the result yttrium concentration in the adsorbed $\text{Yttrium}(Ad)$ was expressed in the form

$$Ad = kAs^{\frac{1}{n}} \left\{ \frac{K_{h_1} K_{h_2} K_{h_3}}{(\text{H}^+)^3} + \frac{K_{h_1} K_{h_2}}{(\text{H}^+)^2} \right. \\ \left. + \frac{K_{h_1}}{(\text{H}^+)} + 1 \right\} \quad (1)$$

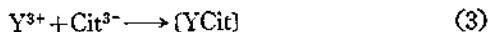
where k and n represent constants of Freundlich adsorption isotherm and K_{h_i} and As represent proportional values of successive hydrolysis constants of yttrium and yttrium concentration of filtrate respectively.

In general

$$Ad = kAs^{\frac{1}{n}} K'((\text{H}^+)) \quad (2)$$

where $K'((\text{H}^+))$ is a function of hydrogen ion concentration and it would be constant for a given hydrogen ion concentration.

When citrate ion is introduced in the solution, yttrium ion would form the citrate complex



Then the formation constant K_f of yttrium citrate can be expressed as follows.

$$K_f = \frac{[\text{YCit}]}{[\text{Y}^{3+}] [\text{Cit}^{3-}]} \quad (4)$$

Total concentration of yttrium in the solution should be sum of yttrium ion concentration and the citrate complex.

$$As = [\text{Y}^{3+}] + [\text{YCit}] \quad (5)$$

Here the higher order of citrate complex such as (Y Cit^{3-}) , (Y Cit^{3-}) is not necessary to be considered because it was known already in the previous reports that the only one to one complexes of metal ions were formed in aqueous solution.

From equation (4) and (5), it is obtained that

$$As = [\text{Y}^{3+}] \{1 + K_f (\text{Cit}^{3-})\} \\ [\text{Y}^{3+}] = \frac{As}{\{1 + K_f (\text{Cit}^{3-})\}} \quad (6)$$

When equation (6) is put into equation (2), the result is

$$Ad = k \left\{ \frac{As}{1 + K_f (\text{Cit}^{3-})} \right\}^{\frac{1}{n}} K'((\text{H}^+)) \quad (7)$$

Where k , n , and $K'((\text{H}^+))$ are constants at a given hydrogen ion concentration. Rearranging the equation (7), it is obtained that

$$\frac{As}{Ad^n} = \frac{1}{\{kK'((\text{H}^+))\}^n} \{1 + K_f (\text{Cit}^{3-})\} \quad (8)$$

Let us take $\{kK'((\text{H}^+))\}^n = K$. Then equation (8) can be written in the form

$$\frac{As}{Ad^n} = \frac{1}{K} + \frac{K_f}{K} (\text{Cit}^{3-}) \quad (9)$$

When As/Ad^n is plotted against citrate ion concentration a straight line would be obtained, and the values of intercept and slope of the linear relations between As/Ad^n and citrate ion concentration will give the values of K and K_f .

In the use of adsorption method for calculation of complex formation constants, it always has been tacitly assumed that the complex itself is not taken up by the membrane filter to any appreciable extent. The validity of the

assumption has not been examined experimentally, but in the case of ion exchange resin Schubert and his co-worker² have proved the validity of nonadsorption of complexes on ion exchange resin. Comparing the adsorption on membrane filter with the adsorption on ion exchange resin of a complex, the ion exchange adsorption would be stronger than the membrane adsorption. Therefore, it would be reasonable that the adsorption of citrate complex on membrane filter might be neglected.

Experimental

The details on materials, measurements of radioactivity, Separation of yttrium-90 from strontium-90, and preparation of carbonate-free sodium hydroxide have been fully described in the previous paper.⁵ About 0.2 mc yttrium-90 solution in 0.01N hydrochloric acid was diluted to 60 ml with 0.01N hydrochloric acid. Then the pH of the solution was adjusted to a value of 7 with dilute carbonate-free sodium hydroxide solution, and also pH of 50 ml solution of 0.01N hydrochloric acid free from yttrium-90 was adjusted to a value of 7 similarly. Sodium citrate solution of 0.040 mole/l. was prepared by dissolving citric acid mono hydrate (MERCK'S REAGENZINE) and adding appropriate amount of sodium hydroxide to adjust a pH of 7.0. All the pH measurements were made with a pH meter attached with a combined glass electrode (Analytical Measurements, Summit, New Jersey). In each of six 10 ml pyrex beakers, 6 ml of the stock solution of yttrium-90 was added, and the stock solution of sodium citrate and the solution of a pH of 7 were added into the beakers according to Table. I.

By the procedures mentioned above, the activities of yttrium-90 and pH in each sample solution could be kept at constant values.

Table I. Composition of sample solutions

Beaker No.	Y ³⁺ ml	Cit ³⁻ ml	0.01N NaCl Soln.	Conc. of Cit ³⁻ (10 ⁻³ Mole/l)
1	6	0.050	1.95	0.25
2	6	0.10	1.90	0.50
3	6	0.20	1.80	1.00
4	6	0.40	1.60	2.00
5	6	0.80	1.20	4.00
6	6	1.20	0.80	6.00

Then the solutions were allowed to stand for an hour to reach equilibrium. A 0.100 ml portion of each sample solution was taken with a 0.100 ml micropipette, placed on a 1 inch aluminum planchet and dried under a heat lamp. Its radioactivity was then determined. A membrane filter (HA Type Millipore) was attached to micro-syring filter holder (Cat No. XX 3002500, Millipore), and each sample solution was then filtered, as described in previous report.⁵ The 0.100 ml portion of the each filtrate was taken with 0.100 ml micropipette, and its activity was measured by the same procedure as that described previously.⁵

Results and Discussion

The *n* values of Freundlich adsorption isotherm at various hydrogen ion concentrations were obtained from the previous experiment.⁵ The results are shown in Figure 1. The *n* value at a pH of 7 was found to be 1.35 from Figure 1.

The activities of the adsorbed yttrium-90 and the filtrate at various citrate concentration are shown in Table II. Then the ratios of the yttrium-90 activities of the filtrate to the *n*th power of activities of the adsorbed state (*As*/*Ad*^{*n*}) can be calculated.

The plots of the values of *As*/*Ad*^{*n*} versus

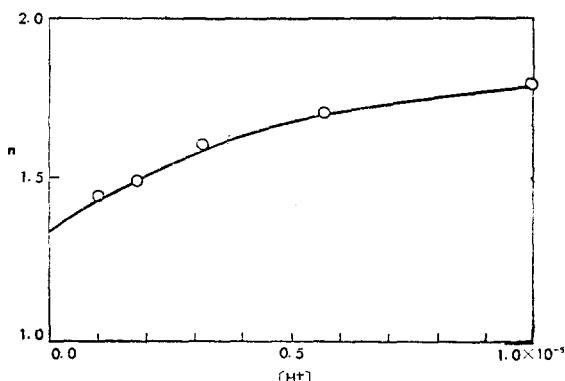


Fig. 1. Plot of n value of Freundlich adsorption isotherm versus hydrogen ion concentration

Table II. Distributions of yttrium ion between filtrate and adsorbed state at various citrate concentrations

sample No.	citrate conc. (10^{-4} mole l ⁻¹)	Activities of adsorbate(Ad^{\ddagger}) (cpm/100 λ)	Activities of filtrate(As^{\ddagger}) (cpm/100 λ)	$As^{\ddagger}/Ad^{\ddagger}$
1	2.5	2.85×10^4	7.89×10^3	0.159
2	5.0	3.19×10^4	4.54×10^3	0.369
3	10.0	3.21×10^4	4.33×10^3	0.396
4	20.0	3.41×10^4	2.34×10^3	0.966
5	40.0	3.50×10^4	1.43×10^3	1.92
6	60.0	3.54×10^4	1.10×10^3	2.90

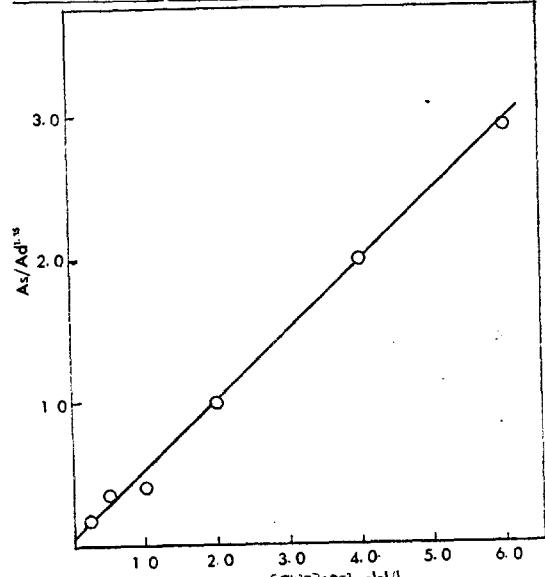
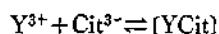


Fig. 2. Plot of $As/Ad^{1.33}$ versus Cit^{3-} for YCit in aqueous solution

molar concentration of citrate ions are shown in Figure 2. From the fact that a good linearity was obtained, it was seen that the one to one complex of yttrium with citrate ions was formed in aqueous solution.



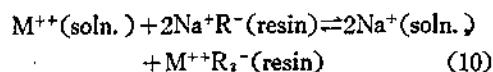
The value of intercept and slope of the straight line were determined, and the values of $1/K$ and K_f of the formation constant of yttrium citrate complex were obtained from equation (9). The results are shown in Table III.

Table III. Formation constants of one to one citrate complex of yttrium in aqueous solution

Complex	1/K	K_f (l. mole ⁻¹)
[Y Cit]	0.025	2.0×10^4

The major difference between the adsorption method and the ion exchange method arises from the fact that metal ions are exchanged stoichiometrically with cation exchange resin but in the adsorption method metal ions are adsorbed on membrane filters according to Freundlich adsorption isotherm.

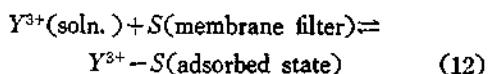
In the case of ion exchange, metal ions exchange with ion exchange resin.³



When a large excess of NaCl is present in solution $[M^{++}R_2^-]/[M^{++}]$ shows constant value.

$$K_d = \frac{[M^{++}R_2^-]}{[M^{++}]} = \frac{\text{Activity in Resin}}{\text{Activity in Solution}} \quad (11)$$

In the adsorption method, the adsorption equilibrium of metal ions on membrane filters can be expressed in the form⁶



Then by Freundlich adsorption isotherm

$$\frac{(Y^{3+}-S)}{(Y^{3+})^{\frac{1}{n}}} = \frac{\text{Activity in Adsorbed State}}{\text{Activity in Filtrate}}^{\frac{1}{n}}$$

$$\times s^{1-\frac{1}{n}} = k' \times s^{1-1/n} = k \quad (13)$$

Where s represents the conversion factor of mole/liter to cpm/unit volume. At a given pH, n is a constant value, than $k' \times s^{1-\frac{1}{n}} = k$ also represents a constant value. Comparing equation (11) with equation (13) the difference between the exchange reaction and the adsorption of metal ions is due to n value of Freundlich isotherm. For the ion exchange, the n value of Freundlich isotherm corresponds to one, and for the adsorption, $n>1$.

As/Ad^n versus citrate concentration at various n values are shown in Figure 3. The curves for n values except $n=1.35$ do not show straight line but concave or convex curve, and the results prove the validity of the adsorption method indirectly.

In the above discussion it is assumed that ultramicro quantity of yttrium is present in completely ionized form in solution.

The validity of the completely ionized state have been proved in the previous paper and the results of present investigation also support

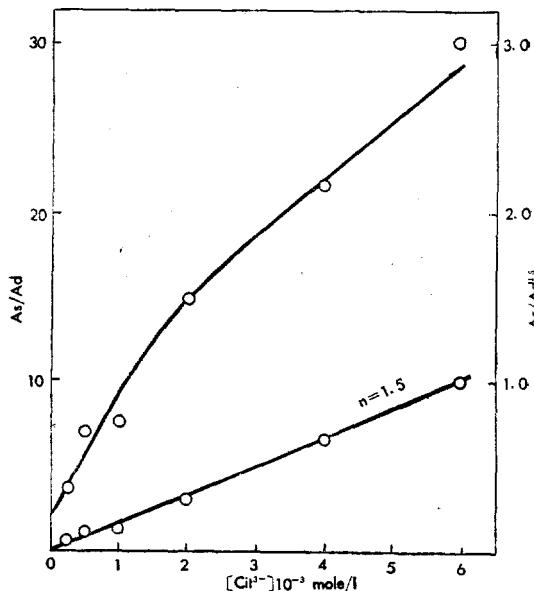


Fig. 3. Plot of As/Ad^n versus Cit^{3-} for $n=1.0$ and $n=1.35$

the view of the ionized state.

As a result of the above discussion for the adsorption method it can be seen that the adsorption method is simple, convenient, and time-saving for the measurements of the formation constants of metal complexes.

References

- (1) J. Schubert, D. R. Russel and L. S. Myers, Jr., *J. Bio. Chem.*, 135, 387 (1950).
- (2) N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White and J. Schubert, *J. Amer. Chem. Soc.*, 79, 5864 (1957).
- (3) Sang Up Choi, Young Il Pae and Won Mok Jae, *This Journal*, 14(1), 65 (1970).
- (4) Sang Up Choi and Dong Hwan Park, *ibid* 14 (1), 91 (1970).
- (5) Won Mok Jae, *ibid*, 14(4), 347(1970).