Studies on Metal Complex Species Using an Anion Exchange Resin. II. On the Adsorption of Silver from Nitrate Solution

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In the previous papers[1,2] the author has derived equations for determining the composition of a metal complex by use of an anion exchange resin and applied them to mercury-(II)-nitrate complex species. Silver is, as well as mercury, adsorbed on an anion exchange resin from solutions of various nitrates or nitric acid, though its adsorption is not strong. In this paper the adsorption of silver from nitrate solutions and nitric acid was studied and its form in the resin was determined by the previously reported method[1,2] as well as by a new method.

The adsorption of silver nitrate on an anion exchanger Dowex 1-X8 was examined and compared with that of alkali nitrates. Even alkali nitrates are taken up a little in the resin, but no appreciable difference in the adsorbability between sodium and potassium is evident, as shown in Fig. 1. The apparent adsorption of alkali metals may be considered merely as a permeation of dissociated normal salts. On the other hand, the adsorbed amount of silver nitrate is considerably larger than that of alkali nitrates.

This difference in the adsorbability between silver and alkali metals is remarkable when a small quantity of these elements is used in a nitric acid medium, as shown in Fig. 2. The

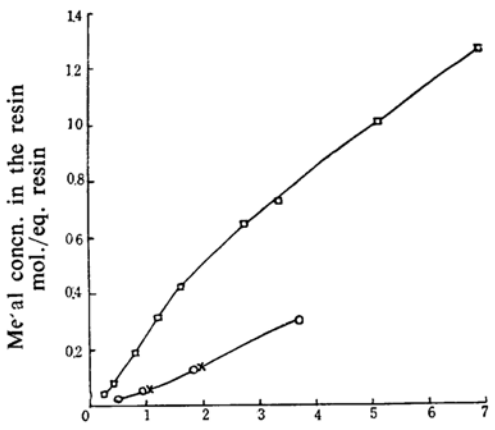

Fig. 1. Adsorption of Ag, Na and K from the solution of its nitrate only.
□ $AgNO_3$ ○ $NaNO_3$ × KNO_3

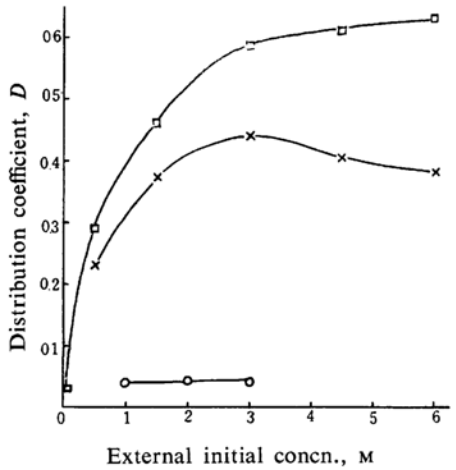

Fig. 2. Adsorption of Ag and Na in small quantity from nitrate solutions.
Metal: 0.1 mmol., Resin: 3 g., Solution: 8 ml.
□ Ag in $NaNO_3$ × Ag in HNO_3
○ Na in HNO_3

1) H. Waki, This Bulletin, 33, 1469 (1960).
2) H. Waki, ibid., 34, 829 (1961).

distribution coefficient of sodium is very small and scarcely increases at all with an increase in nitric acid concentration. On the other hand, the distribution coefficient of silver in nitric acid increases rapidly in the beginning, then gradually to a maximum near 3 M nitric acid and then decreases gradually. In sodium nitrate solution, the coefficient has no maximum and is somewhat greater than that in nitric acid. Although the coefficient is considerably smaller than that of mercury[1,2], it may be reasonable to consider that the adsorption of silver is not a simple permeation of the normal salt but is related to the formation of nitrate complex species.

However, silver ion does not appear to form any nitrate complex anion in an ordinary nitrate solution, since silver nitrate may be regarded as a kind of relatively strong electrolyte, as seen from the fact that the mean activity coefficient[3] of silver nitrate is similar to that of alkali nitrate, especially that of potassium nitrate and rubidium nitrate, and at the utmost the presence of undissociated silver nitrate[4] may be considered only in concentrated nitrate solution. Even if a slight quantity of the complex anion is present in the solution, it may be difficult to consider that the adsorption of silver takes place by a successive permeation of the complex, because it takes only a short time to reach the adsorption equilibrium. Accordingly, the adsorption of silver may be explained by its movement into the resin phase as silver ion Ag^+ and neutral species $AgNO_3^0$, followed by the conversion into a silver-nitrate complex in the resin phase.

For the purpose of determining the composition of a metal complex by use of an anion exchange resin, the distribution coefficient D of a metal element was expressed as follows[1,2]:

$$\log D=\left(n-\frac{a}{b}\right)\log[X^{b-}]-\left(m-\frac{a}{b}\right)\log(X^{b-})+K+G \qquad (1)$$

where ( ) and [ ] indicate the concentrations in the solution phase and the resin phase, m and n represent the numbers of an anion X^{b-} binding to one metal ion M^{a+} in these phases, and K and G represent the terms containing the complex formation constants and the activity coefficients in both phases, respectively. When the metal is present as M^{a+} in the solution, Eq. 1 may be written as follows:

$$\log D=\left(n-\frac{a}{b}\right)\log[X^{b-}]+\frac{a}{b}\log(X^{b-})+K+G \qquad (2)$$

if a similar assumption is made in a silver-nitrate system, the following equation is obtained.

$$\log D-\log(NO_3^-)=(n-1)\log[NO_3^-]+K+G \qquad (3)$$

Experiment by the Addition of an Indifferent Anion.—This experiment was carried out in a way similar to that in the mercury-nitrate system. Two grams of an anion exchanger Dowex 1-X8 (100~200 mesh) of nitrate form was mixed with 10 ml. of a solution containing 0.3 mmol. of silver nitrate and a series of mixtures of sodium nitrate and sodium perchlorate of various mixing ratios (total concentration is 3 M). After equilibrium is reached silver and nitrate in the resin were determined. Silver was analyzed titrimetrically with a potassium thiocyanate and nitrate spectrophotometrically at 300 mμ. The amounts of silver and nitrate in the solution were estimated by subtraction from their total amounts.

The ion concentrations in the resin phase were always represented as millimoles of the ion per milliequivalent of the resin. The distribution coefficient of silver was calculated as

$$D=\frac{\text{mmol. of Ag adsorbed per meq. of the resin}}{\text{mmol. of Ag per ml. of the soln.}}$$

After the nitrate concentration in the resin was corrected as in the case of mercury-nitrate, $\log D-\log(NO_3^-)$ was plotted against the logarithm of the nitrate ion concentration in the resin. As shown in Fig. 3, in the range where nitrate is predominant, the gradient of the curve is 0.9, which corresponds approximately to $n=2$. From this result, it may be recognized that most of the silver-nitrate complex adsorbed from 3 M sodium nitrate solution has the form of $Ag(NO_3)_2^-$.

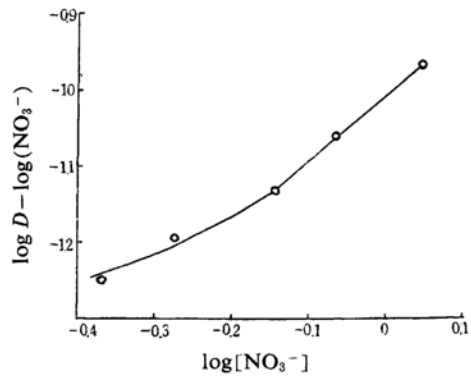

Fig. 3. Distribution coefficient of Ag as a function of the nitrate concentration in the resin phase. The measurements were carried out at the nitrate-rich range. Total concentration of the external solution is 3 M.

3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London (1955).

4) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants. Part II Inorganic Ligands", London (1958).

TABLE I. EQUILIBRIUM DATA ON THE BATCH EXPERIMENT

A. 2 M Series — Resin: 7.14 meq., Solution: 8 ml.

Batch No.	1	2	3	4	5	6	7
$AgNO_3$ given, mmol.	0.100	1.275	1.985	3.97	5.96	7.94	11.91
$NaNO_3$ given, mmol.	16.00	14.72	14.00	12.00	10.00	8.00	4.00
(Ag) mmol./ml.	0.00813	0.112	0.175	0.361	0.559	0.755	1.175
[Ag] mmol./meq.	0.00490	0.0536	0.0819	0.152	0.209	0.266	0.352
D ml./meq.	0.603	0.481	0.468	0.420	0.373	0.352	0.299
(NO_3^-) mmol./ml.	1.88	1.83	1.80	1.76	1.73	1.66	1.59
$[NO_3]_t$ mmol./meq.	1.15	1.19	1.22	1.27	1.30	1.37	1.45
$\log D - \log(NO_3^-)$	−0.494	−0.581	−0.585	−0.622	−0.666	−0.673	−0.726

B. 3 M Series — Resin: 6.45 meq., Solution: 8 ml.

Batch No.	1	2	3	4	5	6
$AgNO_3$ given, mmol.	0.100	0.985	1.97	3.94	5.91	7.88
$NaNO_3$ given, mmol.	24.07	23.07	22.06	20.06	18.05	16.04
(Ag) mmol./ml.	0.00805	0.0838	0.171	0.349	0.539	0.733
[Ag] mmol./meq.	0.00552	0.0488	0.0938	0.178	0.247	0.313
D ml./meq.	0.686	0.583	0.550	0.551	0.459	0.428
(NO_3^-) mmol./ml.	2.83	2.78	2.75	2.70	2.69	2.62
$[NO_3]_t$ mmol./meq.	1.24	1.28	1.30	1.37	1.38	1.46
$\log D - \log(NO_3^-)$	−0.256	−0.343	−0.374	−0.428	−0.478	−0.533

Experiment by the Loading of the Complex.— In determining the composition of a metal complex, a method in which the ratio of the adsorbed amount of the metal to the exchange capacity of the resin is determined after the resin is saturated with the metal complex anion, has often been employed[5]. This method is simple and reliable when the complex is stable and strongly adsorbed on an anion exchanger. However, it can not be used when the complex is unstable and not strongly adsorbed.

In view of this, a new loading method was studied by the present writer, which is based on Eq. 2. In the proposed method, instead of the addition of the indifferent anion, a greater amount of the same metal element is used to keep the ionic strength in the solution phase constant. The ligand ion concentration in the resin phase is therefore varied by the loading of the metal complex instead of an indifferent anion. Assuming that $MX_n^{(bn-a)-}$ is only one species for the resin phase, this concentration is expressed by

$$[X^{b-}] = [X]_t - n[MX_n^{(bn-a)-}] \quad (4)$$

where $[X]_t$ is the total ligand concentration irrespective of species. From Eq. 2 and Eq. 4 the following equation is obtained.

$$\log D = \left(n - \frac{a}{b}\right)\log([X]_t - n[MX_n^{(bn-a)-}]) + \frac{a}{b}\log(X^{b-}) + K + G \quad (5)$$

When a considerable amount of the metal is adsorbed, for the determination of n, $\log D/(X^{b-})^{a/b}$ can not be plotted against $\log[X^{b-}]$, because the second term in the right side of Eq. 4 can not be neglected and n is unknown. Accordingly, in this case $\log D/(X^{b-})^{a/b}$ is plotted against $[MX_n^{(bn-a)-}]$ and the slope of the curve should be compared with that of the standard curves drawn by substituting 1, 2, 3, ……for n in Eq. 5.

In a system of silver nitrate and sodium nitrate, Eq. 5 is written as follows:

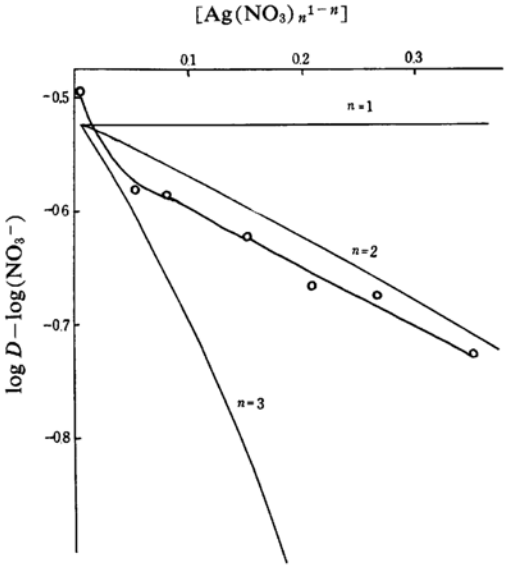

Fig. 4. Comparison with the standard curves in the system where the external initial concentration of $AgNO_3 + NaNO_3$ is 2 M.
The standard curves are drawn in a position in which their gradients may compare with that of experimental curve.
-○- Measured —— Standard

5) For example, R. A. Horne, R. H. Holm and M. D. Meyers, *J. Phys. Chem.*, **61**, 1955 (1957).

$$\log D - \log(NO_3^-) = (n-1)\log([NO_3]_t - n[Ag(NO_3)_n^{(n-1)-}]) + K + G \quad (6)$$

The experiment was carried out by equilibrating 3 g. of an anion exchanger Dowex 1-X8 (100~200 mesh) of nitrate form with 10 ml. of a solution containing a series of mixtures of silver nitrate and sodium nitrate of various mixing ratios (total concentration is 2 M or 3 M), followed by determination of silver and nitrate in the solution phase. The silver concentration in each phase and the distribution coefficient were estimated in the same way as before. The nitrate in the solution was determined by titrating with a sodium hydroxide solution, after it was converted into nitric acid through a cation exchange column of hydrogen form. The amount of total nitrate in the resin was estimated by subtraction.

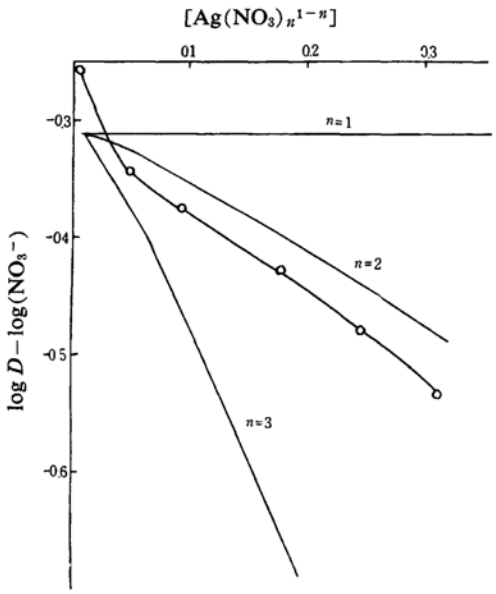

Fig. 5. Comparison with the standard curves in the system where the external initial concentration of $AgNO_3+NaNO_3$ is 3 M.
The standard curves are drawn in a position in which their gradients may compare with that of experimental curve.
-○- Measured —— Standard

The equilibrium data are tabulated in Table I and the curves for analysis are drawn in Fig. 4 and Fig. 5. Each slope of the curve is similar to that of the standard curve for $n=2$ in a wide range of the silver concentration except at a very low concentration. From this fact it may be considered that most silver in the resin phase exist as $Ag(NO_3)_2^-$ at the external nitrate concentration of about 2~3 M. This result is in agreement with that in the former experiment carried out by the addition of an indifferent anion. The high value of the gradient at the low concentration of silver is presumably due not to the presence of higher nitrate complexes, but to the inconstancy of the activity coefficient term in this region.

Summary

1) It was found that silver was to some extent adsorbed on a strong base anion exchange resin from nitrate solutions. Its behavior was significantly different from that of alkali metals.

2) The equations derived in the previous paper were applied to a study of silver-nitrate complex. Starting from the same equation, two methods using either $NaNO_3+NaClO_4$ mixed media or the loading of the complex were employed, and the two results were in good agreement.

3) It was presumed that most silver in the resin exists as $Ag(NO_3)_2^-$ in neutral nitrate media where the external nitrate concentrations were about 2~3 M, although such anionic species may not be considered to exist in an ordinary nitrate solution.

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