Studies on Metal Complex Species Using an Anion Exchange Resin. I. Derivation of Equations and Application to Mercury(II)-Nitrate Complex

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An equation and a method for determining the composition of metal complex species using an anion exchange resin have been developed by Kraus et al.[1,2] These are mostly applicable[3] in the case where a stable negatively-charged complex ion of a metallic element is formed even in a dilute solution and adsorbed in the same form as that in the solution when it is in contact with the resin. On the other hand, it is also often observed that a metallic element may be significantly adsorbed on an anion exchange resin even from a solution in which the presence of any complex anion seems hardly to be considered. In this case it is likely enough that a metal ion or a low complex ion of the metallic element enters the resin phase and then converts itself there into a complex anion or a higher complex ion respectively, because the resin phase may be regarded as a kind of extremely concentrated solution of electrolytes. Accordingly, the complex formation in such a case should rather depend directly on the concentration of an anion as a ligand and on the ionic strength in the resin phase. In this paper an equation for determining the composition of metal complex species, including the cases mentioned above, will be derived by introducing the complex formation equilibrium in the resin phase and applied to mercury-nitrate complex taken up by anion exchange resin.

Derivation of Equations

Since the ion exchange can be theoretically treated as a Donnan equilibrium, the following relationship holds between the ion concentrations in the resin phase [ ] and in the external solution ( ) in the equilibrium state:

$$[\mathrm{M}^{a+}]\,[\mathrm{X}^{b-}]^{a/b}\gamma_{[\mathrm{M}]}\gamma_{[\mathrm{M}]}^{a/b} = (\mathrm{M}^{a+})\,(\mathrm{X}^{b-})^{a/b}\gamma_{(\mathrm{M})}\gamma_{(\mathrm{X})}^{a/b} \qquad (1)$$

where M^{a+} and X^{b-} represent a metal ion and an anion respectively, and γ stands for the activity coefficient of the ion given as subscript. When a complex ion $\mathrm{MX}_m^{(bm-a)-}$ is formed in the external solution, the formation constant is defined by

$$K_m = \frac{(\mathrm{MX}_m^{(bm-a)-})}{(\mathrm{M}^{a+})\,(\mathrm{X}^{b-})^m} \cdot \frac{\gamma_{(\mathrm{MX}_m^{(bm-a)-})}}{\gamma_{(\mathrm{M})}\gamma_{(\mathrm{X})}^m} \qquad (2)$$

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[1] K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, 73, 9 (1951).

[2] K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products" in "Peaceful Uses of Atomic Energy", Proceedings of the International Conference in Geneva, Vol. 7, p. 113 (1955) (United Nations).

[3] S. Misumi and T. Taketatsu, This Bulletin, 32, 876 (1959).

Since the resin phase may be regarded as a concentrated aqueous solution of electrolytes, the formation constant may also be defined by

$$K_n = \frac{[\mathrm{MX}_n^{(bn-a)-}]}{[\mathrm{M}^{a+}]\,[\mathrm{X}^{b-}]^n} \cdot \frac{\gamma_{[\mathrm{MX}_n^{(bn-a)-}]}}{\gamma_{[\mathrm{M}]}\gamma_{[\mathrm{X}]}^n} \tag{3}$$

for a complex ion $\mathrm{MX}_n^{(bn-a)-}$ in the resin phase, in analogy to Eq. 2. For the purpose of the determination of the complex form, the formation equilibria in both phases should be taken into account.

The distribution coefficient may be defined at

$$D = \sum[\mathrm{M}]/\sum(\mathrm{M}) \tag{4}$$

where $\sum[\mathrm{M}]$ and $\sum[\mathrm{M}]$ are the total stoichiometric concentrations of the metallic element in the resin and the solution phase (irrespective of species). If it is assumed for simplicity that the greater part of the metallic element in the resin exists in the form $\mathrm{MX}_n^{(bn-a)-}$ and in the solution in the form $\mathrm{MX}_m^{(bm-a)-}$ (generally n is not equal to m), the coefficient may be written as

$$D \doteqdot \frac{[\mathrm{MX}_n^{(an-a)-}]}{(\mathrm{MX}_m^{(bm-a)-})} \tag{5}$$

From Eqs. 1, 2, 3 and 5 the following equation is derived:

$$D = \frac{[\mathrm{X}^{b-}]^{n-a/b}}{(\mathrm{X}^{b-})^{m-a/b}} \cdot \frac{K_n}{K_m} \cdot \frac{\gamma_{(\mathrm{MX}_m^{(bm-a)-})}\gamma_{[\mathrm{X}]}^{n-a/b}}{\gamma_{[\mathrm{MX}_n^{(bn-a)-}]}\gamma_{(\mathrm{X})}^{m-a/b}} \tag{6}$$

or

$$\log D = (n-\frac{a}{b})\log[\mathrm{X}^{b-}] - (m-\frac{a}{b})\log(\mathrm{X}^{b-}) + K + G \tag{7}$$

where

$$K = \log\{K_n/K_m\}$$

$$G = \log\frac{\gamma_{(\mathrm{MX}_m^{(bm-a)-})}\gamma_{[\mathrm{X}]}^{n-a/b}}{\gamma_{[\mathrm{MX}_n^{(bn-a)-}]}\gamma_{(\mathrm{X})}^{m-a/b}}$$

And

$$\frac{\mathrm{d}\{\log D + (m-a/b)\log(\mathrm{X}^{b-})\}}{\mathrm{d}\log[\mathrm{X}^{b-}]} = n - \frac{a}{b} \tag{8}$$

$$\frac{\mathrm{d}\{\log D - (n-a/b)\log[\mathrm{X}^{b-}]\}}{\mathrm{d}\log(\mathrm{X}^{b-})} = -(m-\frac{a}{b}) \tag{9}$$

when K and G are constant. When m is known and D, (X^{b-}) and $[\mathrm{X}^{b-}]$ are measurable, n can be determined graphically, and m is also obtained when n is known. Even if both are unknown, one of them can be determined in a case where either (X^{b-}) or (X^{b-}) can be kept constant.

Although it is practically impossible to set a condition in which the activity coefficient term is strictly constant, this condition may be realized roughly when a small quantity of the metallic element is used and the ionic strengths in the two phases are each kept constant by the addition of an indifferent anion, and therefore the complex form may be determined through measurements in the range where the greater part of the anion given is X^{b-}.

In the case of the mercury(II)-nitrate complex in the presence of sodium nitrate and perchlorate, where Hg^{2+} is taken as M^{a+}, $\mathrm{NO_3}^-$ as X^{b-} and $\mathrm{ClO_4}^-$ as an additional anion, Eq. 7 may become as follows:

$$\log D = (n-2)\log[\mathrm{NO_3}^-] - (m-2)\log(\mathrm{NO_3}^-) + K + G \tag{10}$$

Assuming that a mercuric ion does not form any metal-nitrate complex species in a moderately concentrated aqueous solution of nitrates, the following equations may be applicable,

$$\log D - 2\log(\mathrm{NO_3}^-) = (n-2)\log[\mathrm{NO_3}^-] + K + G \tag{11}$$

and

$$\frac{\mathrm{d}\{\log D - 2\log(\mathrm{NO_3}^-)\}}{\mathrm{d}\log[\mathrm{NO_3}^-]} = n-2 \tag{12}$$

where K and G are constant. From the slope of the curve $\log D - 2\log(\mathrm{NO_3}^-)$ vs. $\log[\mathrm{NO_3}^-]$, n can be determined. When n is not in the vicinity of an integer, the coexistence of two complexes may be presumed.

Experimental

Sodium nitrate solution and sodium perchlorate solution were prepared from the guaranteed and the first class reagent, respectively. Mercuric nitrate solution was prepared by dissolving the guaranteed reagent $\mathrm{Hg(NO_3)_2 \cdot 1/2 \sim 1\ H_2O}$ in dilute nitric acid. These solutions were added to the resin so that the mixture of solutions had a volume of 10 ml., and contained 0.1 mmol. of mercury, 0.5 mmol. of nitric acid and a series of $\mathrm{NaNO_3 + NaClO_4}$ of various mixing ratios, providing that its total concentration was constant at individual series.

An anion exchanger Dowex 1-X8 of nitrate form was swollen in water and then filtered under suction, followed by the removal of the attached water by pressing between filter papers. Two or three grams of this resin was at once put in a stoppered small glass vessel. At the same time another 0.5 g. of this resin was converted into chloride form in a small column and its exchange capacity was determined by the elution of the chloride ion with a sodium nitrate solution and by Mohr's titration of the effluent. The resin set in this way have a relatively constant exchange capacity and does not suffer an appreciable change in volume when it comes in contact with nitrate solution.

The batch experiment was carried out at total concentrations of the solution of 0.5, 1, 2, 3 and 5 M, and each series consisted of 4—6 batches of various nitrate concentrations. The resin and the solution were equilibrated at room temperature by being allowed to stand for an hour with frequent shaking.

After the supernatant liquid was directly taken for the dilute solution or the resin was separated from the solution by filtering with a glass filter under suction without further washing for the concentrated solution, the mercury in the solution was titrated as follows: mercury in 5 ml. of the supernatant or the filtrate was titrated with 0.0100 M EDTA solution after 1 ml. of 0.05 M Mg-EDTA, 1 ml. of NH_4OH-NH_4Cl buffer (pH=10) and a few drops of Eriochrome Black T indicator were added. The amount of mercury in the resin was estimated by subtraction of that in the solution from the total amount. The distribution coefficient was calculated as

$$D=\frac{\left(\begin{array}{c}\text{millimole of Hg adsorbed per}\\ \text{milliequivalent of the resin}\end{array}\right)}{\left(\begin{array}{c}\text{millimole of Hg per milliliter}\\ \text{of the solution}\end{array}\right)}$$

On the other hand, the nitrate in the resin was determined spectrophotometrically as follows: the resin separated from the solution in the way described above was wrapped in a filter paper and pressed to remove the solution attached to the surface. About 1 g. of this resin was transferred into a short column, and then the nitrate ions were desorbed by 25 ml. of 2 M perchloric acid. The effluent was diluted to 50 ml. and its absorbance was measured at 300 mμ using the Shimadzu spectrophotometer QB-50. As shown by the calibration curve in Fig. 1, it may be recognized that the absorption of nitrate ion in the region $\sim 10^{-1}$ M in the presence of 1 M perchloric acid obeys Beer's law. The presence of mercuric, sodium and perchlorate ions has no effect. The exchange capacity of resin in the column was determined in the same way as was done before, for the purpose of estimating the total amount of nitrate in the resin. The amount of nitrate in the solution was estimated by subtraction. The nitrate concentration in the resin phase was represented as millimole of the ion per milliequivalent of the resin as in the calculation of *D*, because the quantity of an ion adsorbed per apparent weight of the resin is not suitable for a representation of concentration in a mixed solution system, since the density of resin varies with the nitrate-perchlorate exchange.

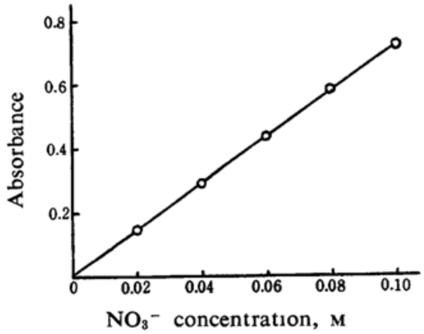

Fig. 1. The calibration curve of nitrate ion in the 1 M perchloric acid by spectrophotometric measurement at 300 mμ.

Results and Discussion

Data of the measurement and the calculation are tabulated in Table I. $[NO_3]^*$ from spectrophotometric measurement means the total nitrate concentration in the resin phase i. e., the sum of concentrations of the free nitrate ion and the nitrate ion bound to the mercuric ion. Accordingly, the free nitrate ion concentration is represented by

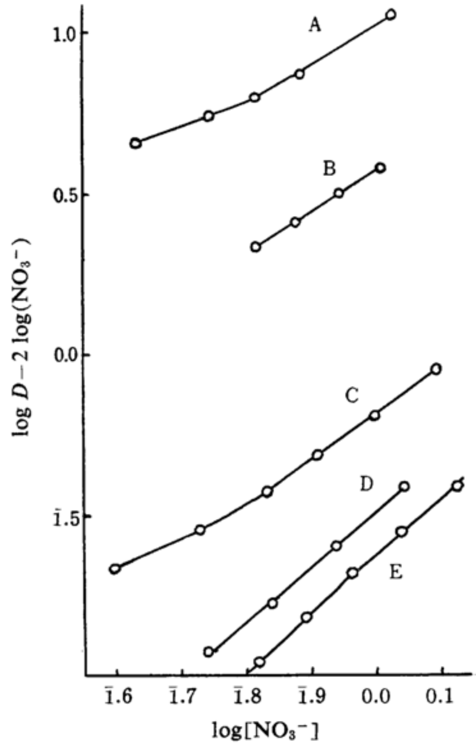

Fig. 2. Determination of *n* at various total concentrations of the external solution in the nitrate-rich range. The rightest point in each curve is one in the absence of perchlorate.
Total external concentration : A: 0.5 M, B: 1 M, C: 2 M, D: 3 M and E: 5 M.

$$[NO_3^-] = [NO_3]^* - n[Hg]$$

assuming that almost all mercury in the resin exists as $Hg(NO_3)_n^{(n-2)-}$. Since n is still unknown, $[NO_3^-]$ is practically estimated by

$$[NO_3^-] = [NO_3]^* - n^*[Hg]$$

where n^* represents an approximate value of n, which may be obtained by $\log D - 2\log(NO_3^-)$ vs. $\log[NO_3]^*$ plot. A little deviation of n^* from n may hardly affect $[NO_3^-]$ and therefore the value of n.

In Fig. 2, $\log D - 2\log(NO_3^-)$ is plotted

TABLE I

A. 0.5 M series

Resin: 4.68 meq.
Solution: 10 ml.

Batch No.	1	2	3	4	5
$NaNO_3$ given, mmol.	1.80	2.40	3.00	3.60	4.80
$NaClO_4$ 〃, 〃	3.00	2.40	1.80	1.20	0.00
HNO_3 〃, 〃	0.50	0.50	0.50	0.50	0.50
$Hg(NO_3)_2$ 〃, 〃	0.105	0.105	0.105	0.105	0.105
(Hg), mmol./ml.	0.00678	0.00632	0.00584	0.00538	0.00448
[Hg], mmol./meq.	0.00795	0.00893	0.00996	0.01094	0.01286
D, ml./meq.	1.17	1.41	1.71	2.04	2.87
$[NO_3]^*$, mmol./meq.	0.452	0.582	0.686	0.804	1.107
(NO_3^-), mmol./ml.	0.507	0.507	0.518	0.523	0.500
$\log D - 2\log(NO_3^-)$	0.659	0.740	0.803	0.872	1.060
$n^*[Hg]$, mmol./meq. ($n^*=3.2$)	0.026	0.029	0.032	0.036	0.041
$[NO_3^-]$, mmol./meq.	0.426	0.553	0.654	0.767	1.065
$\log[NO_3^-]$	$\bar{1}.629$	$\bar{1}.743$	$\bar{1}.815$	$\bar{1}.885$	0.027

B. 1 M series

Resin: 4.72 meq.
Solution: 10 ml.

Batch No.	1	2	3	4
$NaNO_3$ given	7.60	8.40	9.20	10.00
$NaClO_4$ 〃	2.40	1.60	0.80	0.00
HNO_3 〃	0.50	0.50	0.50	0.50
$Hg(NO_3)_2$ 〃	0.105	0.105	0.105	0.105
(Hg)	0.00544	0.00484	0.00418	0.00370
[Hg]	0.01072	0.01199	0.01338	0.01440
D	1.97	2.48	3.20	3.89
$[NO_3]^*$	0.687	0.794	0.922	1.068
(NO_3^-)	0.954	0.983	1.003	1.014
$\log D - 2\log(NO_3^-)$	0.336	0.409	0.502	0.578
$n^*[Hg]$ ($n^*=3.3$)	0.035	0.039	0.043	0.047
$[NO_3^-]$	0.652	0.755	0.879	1.021
$\log[NO_3^-]$	$\bar{1}.814$	$\bar{1}.878$	$\bar{1}.944$	0.009

C. 2 M series

Resin: 6.90 meq.
Solution: 10 ml.

Batch No.	1	2	3	4	5	6
$NaNO_3$ given	14.0	15.2	16.4	17.6	18.8	20.0
$NaClO_4$ 〃	6.0	4.8	3.6	2.4	1.2	0.0
HNO_3 〃	0.50	0.50	0.50	0.50	0.50	0.50
$Hg(NO_3)_2$ 〃	0.102	0.102	0.102	0.102	0.102	0.102
(Hg)	0.00670	0.00598	0.00524	0.00450	0.00384	0.00320
[Hg]	0.00507	0.00612	0.00719	0.00826	0.00922	0.01014
D	0.76	1.02	1.37	1.84	2.40	3.17
$[NO_3]^*$	0.414	0.555	0.706	0.841	1.030	1.287
(NO_3^-)	1.88	1.90	1.91	1.94	1.93	1.87
$\log D - 2\log(NO_3^-)$	$\bar{1}.333$	$\bar{1}.454$	$\bar{1}.574$	$\bar{1}.688$	$\bar{1}.810$	$\bar{1}.957$
$n^*[Hg]$ ($n^*=3.5$)	0.018	0.021	0.025	0.029	0.032	0.035
$[NO_3^-]$	0.396	0.534	0.681	0.812	0.998	1.252
$\log[NO_3^-]$	$\bar{1}.598$	$\bar{1}.728$	$\bar{1}.833$	$\bar{1}.910$	$\bar{1}.999$	0.097

TABLE I (Continued)

D. 3 M series

Resin: 4.96 meq.
Solution: 10 ml.

Batch No.	1	2	3	4
$NaNO_3$ given	26.4	27.6	28.8	30.0
$NaClO_4$ 〃	3.6	2.4	1.2	0.0
HNO_3 〃	0.50	0.50	0.50	0.50
$Hg(NO_3)_2$ 〃	0.104	0.104	0.104	0.104
(Hg)	0.00688	0.00596	0.00484	0.00380
[Hg]	0.00701	0.00887	0.01112	0.01322
D	1.02	1.49	2.30	3.48
$[NO_3]^*$	0.579	0.728	0.912	1.156
(NO_3^-)	2.92	2.97	3.00	3.00
$\log D - 2\log(NO_3^-)$	$\bar{1}.073$	$\bar{1}.227$	$\bar{1}.407$	1.588
$n^*[Hg]$ ($n^*=3.8$)	0.027	0.034	0.042	0.051
$[NO_3^-]$	0.552	0.694	0.869	1.105
$\log[NO_3^-]$	$\bar{1}.742$	$\bar{1}.841$	$\bar{1}.939$	0.043

E. 5 M series

Resin: 4.84 meq.
Solution: 10 ml.

Batch No.	1	2	3	4	5
$NaNO_3$ given	45.2	46.4	47.6	48.8	50.0
$NaClO_4$ 〃	4.8	3.6	2.4	1.2	0.0
HNO_3 〃	0.50	0.50	0.50	0.50	0.50
$Hg(NO_3)_2$ 〃	0.103	0.103	0.103	0.103	0.103
(Hg)	0.00470	0.00382	0.00304	0.00242	0.00190
[Hg]	0.01161	0.01342	0.01504	0.01632	0.01740
D	2.47	3.51	4.94	6.74	9.16
$[NO_3]^*$	0.706	0.829	0.981	1.155	1.429
(NO_3^-)	4.73	4.79	4.84	4.87	4.86
$\log D - 2\log(NO_3^-)$	$\bar{1}.043$	$\bar{1}.185$	$\bar{1}.326$	$\bar{1}.454$	$\bar{1}.588$
$n^*[Hg]$ ($n^*=3.8$)	0.045	0.052	0.058	0.063	0.079
$[NO_3^-]$	0.661	0.777	0.923	1.092	1.350
$\log[NO_3^-]$	$\bar{1}.820$	$\bar{1}.890$	$\bar{1}.965$	0.038	0.130

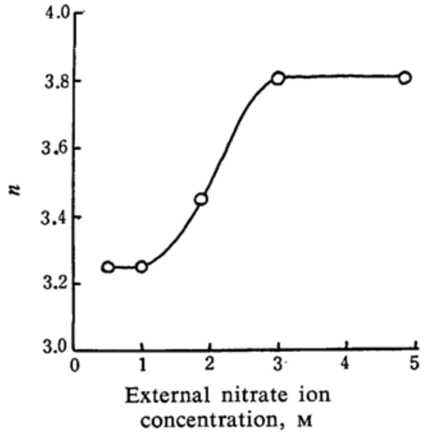

Fig. 3. n-Value of the mercury (II)-nitrate complex adsorbed from sodium nitrate solution of various concentrations.

against log $[NO_3^-]$. Each curve is approximately linear in the range where nitrate is rich compared with perchlorate in the resin. The gradient increases with the external total concentration from 1 M to 3 M, and scarcely varies in a region less than 1 M and from 3 to 5 M.

In Fig. 3, n obtained from the slope is plotted against the concentration of the external solution.

From this curve, it will be recognized that mercury is taken up from a sodium nitrate solution as $Hg(NO_3)_3^-$ in the region from 0.5 to 1 M of the external concentration, as $Hg(NO_3)_4^{2-}$ in the region from 3 to 5 M, and as a mixture of $Hg(NO_3)_3^-$ and $Hg(NO_3)_4^{2-}$ in the region from 1 to 3 M. One might presume that some portions are adsorbed as $Hg(NO_3)_3^-$ in the region from 3 to 5 M solution, since $n=3.8$. However, this possibility may be weakened by considering the fact that n does not rise with an increase of the external nitrate concentration in this region. Furthermore, it may be reasonable to consider that the complex contains no hydrogen ion because the concentration of nitric acid is low.

Although it was assumed that mercury exists only as Hg^{2+} in the solution phase, it may also be possible that a lower complex, such as $Hg(NO_3)^+$ or $Hg(NO_3)_2^0$, exists there when the nitrate concentration is as high as 3 or 5 M. When the presence of these species is assumed in the solution phase, n-value may somewhat deviate from that in the case when the presence of Hg^{2+} only is assumed, through the change of m in Eq. 10. However, these deviations are so small at 3 and 5 M, as estimated from data in Table I, that this uncertainty may hardly affect the conclusion as a whole. The reason why n at the plateau does not take an integer is not clear enough at present.

A number of sources of error are considered. First, failure in realizing the condition where the activity coefficient term is constant for lack of knowledge on activity in a resin and a concentrated solution, must be mentioned. The ideal condition could not be established even by keeping the external ionic strength constant. Besides, there are experimental errors; namely, poor reproducibility of dryness of the resin on weighing, the change in volume on mixing of the resin and the solution, and imperfect removal of the attached solution from the resin. In spite of these difficulties, the present method appears to give some conclusion on a metal complex form.

Though the changes of pH and temperature may have some appreciable effect, they were not studied in this work.

Summary

1) The equations for determining the composition of a metal complex using an anion exchange resin have been derived by considering the complex formation equilibria in both the resin phase and the solution phase.

2) The method based on these equations was successfully applied to the investigation of mercury(II)-nitrate complex at various external nitrate concentrations by means of the sodium nitrate-sodium perchlorate mixed solution.

3) Mercury(II) adsorbed from a sodium nitrate solution exists in the form of $Hg(NO_3)_3^-$ at the external nitrate concentration of 0.5∼1 M, $Hg(NO_3)_4^{2-}$ at 3∼5 M and a mixture of $Hg(NO_3)_3^-$ and $Hg(NO_3)_4^{2-}$ at the middle of these concentrations, though no anionic complex appears to be present in an ordinary nitrate solution.

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