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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A generalized equation for determining the composition of metal complex species was derived by introducing the complex formation equilibrium in the resin phase, which has not been considered formerly.

When most part of a metallic element exists in the form of $MX_m{}^{a-bm}$ in the solution phase and $MX_n{}^{a-bn}$ in the resin phase as a result of complex formation between the metal ion M^{a+} and the anion X^{b-}, the following equation may be derived:

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

where D represents the distribution coefficient of the metallic element, ( ) and [ ] indicate the concentrations in the solution phase and the resin phase, respectively, and K and G the terms containing the complex formation constant and the activity coefficient in both phases. Under the condition in which K and G are constant,

$$\frac{d\{\log D+(m-a/b)\log (X^{b-})\}}{d\log [X^{b-}]}=n-a/b \quad (2)$$

$$\frac{d\{\log D-(n-a/b)\log [X^{b-}]\}}{d\log (X^{b-})}=-(m-a/b) \quad (3)$$

Accordingly, when m is known and D, (X^{b-}) and $[X^{b-}]$ 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 when either (X^{b-}) or $[X^{b-}]$ is kept constant. Although it is practically impossible to set a condition in which the activity coefficient term is strictly constant, that may be roughly realized 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 predominant anionic species is X^{b-}.

As an application of these equations, adsorption of mercury(II) from a sodium nitrate solution was studied by means of $NaNO_3+NaClO_4$ mixed medium, where Hg^{2+} was employed as M^{a+}, NO_3^- as X^{b-} and ClO_4^- as an additional anion. Assuming that mercury is present as Hg^{2+} in a sodium nitrate solution acidified by nitric acid, Eq. 1 is obtained simplified as follows:

$$\log D-2\log (NO_3^-) = (n-2)\log [NO_3^-]+K+G \quad (4)$$

The experiment was carried out by equilibrating 2 g. of an anion exchanger "Dowex 1-X8" (100∼200 mesh) of nitrate form with a mixed solution containing 0.1 millimole of mercury(II) nitrate, 0.5 millimole of nitric acid, and a series of mixtures $NaNO_3+NaClO_4$ of various mixing ratios (total concentration is 3 M or 5 M), followed by determination of mercury in the solution and nitrate in the resin. Mercury in the resin and nitrate in the solution were determined by subtraction since their total amounts are known. The distribution coefficient of mercury was calculated as

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

The ion concentrations in the resin phase were always represented as millimole of the ion per milliequivalent of the resin.

$\log D-2\log (NO_3^-)$ was plotted against logarithm of the nitrate ion concentration in the resin, as shown in Fig. 1. The curves show linearity and their slopes correspond to $n=3.8$ for both cases of 3 M and 5 M of the external total concentration. Accordingly, it may be recognized that most mercury(II) is adsorbed in the form of $Hg(NO_3)_4^{2-}$ from the acidified 3∼5 M sodium nitrate solution.

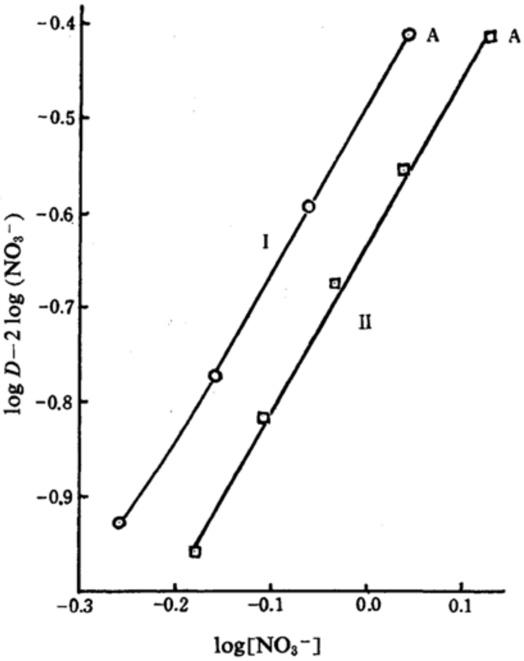

Fig. 1. Distribution coeficient of Hg(II) as a function of the nitrate concentration in the resin phase.
The measurements were carried out at the nitrate-rich range. A is the point in the absence of perchlorate.
I. Total concentration of the external solution is 3 M
II. 〃 5 M

It may also be possible that the lower complex species, such as $Hg(NO_3)^+$ or $Hg(NO_3)_2^0$, exist in the solution. However, since the degree of change in nitrate concentration in the solution phase was much smaller than that in distribution coefficient, the change of the second term on the right side in Eq. 1 may slightly affect the conclusion. Details of this investigation will be reported later.

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