Studies on Metal Complex Species using an Anion Exchange Resin. III. Uranium(VI)-Nitrate Complex and Zinc-Chloride Complex

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Kraus and Nelson[1] reported a method to identify the principal metal complex species in the aqueous phase by using an anion exchange resin. This may be applicable when the complex is very stable and when its form in the resin phase is the same as that in the aqueous phase. However, it is also often observed that the complexes in these two phases have different forms. Recently, Marcus and Coryell[2-4] have developed a method for the evaluation of stability constants by taking into consideration an invasion of electrolytes into the resin phase and by using the available data on activity coefficients in equations.

On the other hand, in the previous papers[5-7] of this series two new methods for the determination of the complex form have been derived which are particularly suitable for a study of the relatively unstable complexes.

It is known that uranium(VI) is adsorbed on an anion exchange resin from nitric acid or nitrate solutions[1], but no investigation of its anionic nitrate complex has be undertaken. It is also known that zinc is strongly adsorbed on the same resin from hydrochloric acid or chloride solutions, and thorough studies of its chloride complex have been made by Horne et al.[8,9] by means of anion exchange.

In the present study, the "indifferent electrolyte-adding" method described in the first papers[5,6] of this series was applied to the uranium(VI)-sodium nitrate system and also to the zinc-sodium chloride system in order to examine the applicability of the method to complex species in the aqueous phase. Sodium perchlorate was selected as an additional electrolyte in the uranium(VI)-nitrate system and sodium nitrate in the zinc-chloride system,

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

[2] Y. Marcus and C. E. Coryell, *Bull. Res. Council Israel*, **8A**, 1 (1959).

[3] Y. Marcus, ibid., **8A**, 17 (1959).

[4] Y. Marcus, *J. Inorg. Nucl. Chem.*, **12**, 287 (1960).

[5] H. Waki, This Bulletin, 33, 1469 (1960).

[6] H. Waki, **34**, ibid., 829 (1961).

[7] H. Waki, **34**, ibid., 1842 (1961).

[8] R. A. Horne, *J. Phys. Chem.*, **61**, 1651 (1957).

[9] R. A. Horne, R. H. Holm and M. D. Meyers, ibid., **61**, 1655 (1957).

because they have no direct effect on the complex formation in each system.

Experimental

a) **Uranium-Nitrate System.**—The sodium nitrate solution was prepared from a guaranteed reagent, and the sodium perchlorate solution from a first class reagent. The uranyl nitrate solution was prepared by dissolving the guaranteed reagent $UO_2(NO_3)_2 \cdot 6H_2O$ in dilute nitric acid. Each mixture of these solutions added to the resin had a volume of 10 ml. and contained 0.0347 mmol. of uranium and a series of sodim nitrate and sodium perchlorate mixed in various ratios, although the total concentration was constant within the individual series.

An anion exchanger "Dowex 1-X8" of a nitrate form (100~200 mesh) was swollen in water and then fitered under suction, after which the adhering water was removed with filter paper. Two grams of this resin was promptly put in a stoppered glass vessel. In order to estimate the exchange capacity of this amount of resin, at the same time another 0.5 g. of the resin was converted to chloride form in a small column. Its exchange capacity was then determined by the desorption of the chloride ions with a sodium nitrate solution and by Mohr's titration of them in the effluent. Resin set in this way tends to have a relatively constant value with respect to the exchange capacity and does not suffer an appreciable change in volume when it comes in contact with a nitrate solution.

The batch experiment was carried out with total concentrations of the solutions at 2, 3.2, 3.5, 4 and 6 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. It was recognized in the preliminary test that a sufficient equilibrium state was attained in about forty minutes. After the equilibrium mixture was filtered through a glass filter under suction without any further washing of the resin, 5 ml. of the filtrate was taken out, and the uranium concentration in the solution phase was determined colorimetrically at 372 mμ by the hydrogen peroxide method, using a Hirama photoelectric colorimeter. The amount of uranium in the resin was estimated from the difference between the total amount given and the amount in the solution phase at equilibrium. The distribution coefficient was calculated as

$$D=\frac{\text{mmol. of U per mequiv. of the resin}}{\text{mmol. of U per ml. of the soln.}}$$

This representation of the ion concentration in the resin phase is suitable in such a system because the density of resin varies with the nitrate-perchlorate exchange. On the other hand, nitrate concentrations were estimated in the following manner: the resin separated from the solution was wrapped in filter paper and pressed in order to remove the solution attached to the surface. About 1 g. of this resin was transferred to 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 a Shimadzu spectrophotometer QB-50. A correction was made for uranyl ion, which had a little absorption at this wavelength, after the exchange capacity of resin in the column had been determined in the same way as before. The nitrate concentration in the resin phase was represented as millimole of the ion per milliequivalent of the resin.

b) **Zinc-Chloride System.**—The solutions of sodium chloride, sodium nitrate and zinc chloride were prepared from guaranteed reagents. To the zinc chloride solution a small quantity of hydrochloric acid was added to prevent the hydrolysis of the zinc. "Dowex 1-X8" chloride form (100~200 mesh) of 0.5 g. was set, and at the same time the exchange capacity was determined in the same way as described in a). Each mixture of the solutions added to the resin had a volume of 50 ml. and contained 0.0970 mmol. of zinc and a series of sodium chloride+sodium nitrate mixed in various ratios, although the total concentration was always 0.4 M or 3 M.

The resin and the solution were equilibrated at 25°C for an hour and the zinc and the chloride concentrations in the resin determined by EDTA and Mohr's titration respectively, after the two phases had been separated by a procedure similar to that used in a). The concentrations of these ions in the solution were estimated by subtraction. The distribution coefficient was calculated as:

$$D=\frac{\text{mmol. of Zn per mequiv. of the resin}}{\text{mmol. of Zn per ml. of the soln.}}$$

Results and Discussion

Uranium - Nitrate System. — By the same treatment as in the previous papers, the following equation obtained for the uranyl-nitrate complex:

$$\log D=(n-2)\log[NO_3^-] - (m-2)\log(NO_3^-)+K+G \qquad (1)$$

where (NO_3^-) and $[NO_3^-]$ represent the concentrations of nitrate ion not bound to uranyl ion, and m and n are the numbers of nitrate ions bound to each metal ion of the complex, in the solution and the resin phases respectively. K and G indicate the terms containing equilibrium constants and activity coefficients.

Assuming that a uranyl ion does not form any nitrate complex in the solution ($m=0$) and that at a constant ionic strength the activity coefficient term is kept constant, the following equations may be derived from Eq. 1:

$$\log D-2\log(NO_3^-) = (n-2)\log\{[NO_3]^*-n[U]\}+K+G \qquad (2)$$

and

$$\frac{d\{\log D-2\log(\mathrm{NO_3^-})\}}{d\log\{[\mathrm{NO_3}]^*-n[\mathrm{U}]\}}=n-2 \qquad (3)$$

where $[\mathrm{NO_3}]^*$ is the stoichiometric concentration of all the nitrate ions in the resin, obtained directly by spectrophotometric measurement, and [U] is the concentration of the uranyl-nitrate complex in the resin.

Using the approximate n-value obtained from the gradient of the $\log D-2\log(\mathrm{NO_3^-})$ vs. $\log[\mathrm{NO_3}]^*$ curve, $\log D-2\log(\mathrm{NO_3^-})$ was plotted against $\log\{[\mathrm{NO_3}]^*-n[\mathrm{U}]\}$, i. e., $\log[\mathrm{NO_3^-}]$. As shown in Fig. 1, the gradient in the nitrate-rich range was 1.1, 1.4, 1.4, 1.9 and 2.0 for the external concentrations of 2, 3.2, 3.5, 4 and 6 M respectively. The n-values obtained from Eq. 3 in this way are plotted against the external nitrate concentration in Fig. 2. It may be recognized that uranium(VI) exists as $\mathrm{UO_2(NO_3)_3^-}$ for the external nitrate concentration of 2 M, as $\mathrm{UO_2(NO_3)_4^{2-}}$ for 4～6 M, and as a mixture of $\mathrm{UO_2(NO_3)_3^-}$ and $\mathrm{UO_2(NO_3)_4^{2-}}$ for the range between 2 M and 4 M.

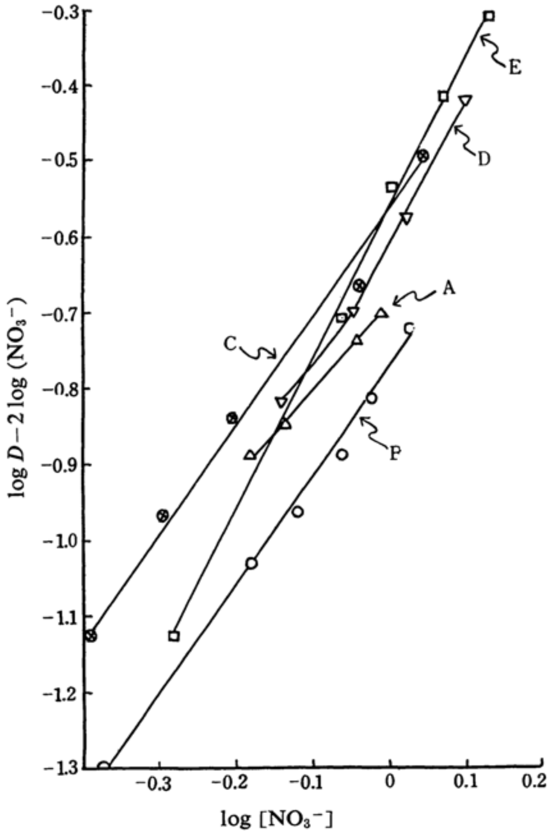
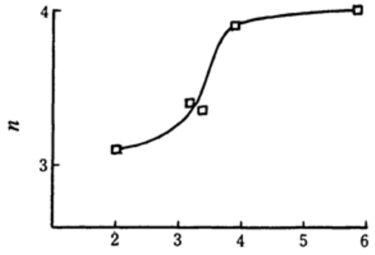


Fig. 1. Determination of n at various total concentration of the external solution in the nitrate-rich range. The rightest point in each curve is one in the absence of perchlorate.

Total external concentration is about; A 2 M, B 3.2 M, C 3.5 M, D 4 M, and E 6 M.



External nitrate concentration, M

Fig. 2. n-Value of the uranyl-nitrate complex adsorbed from sodium nitrate solutions of various concentrations.

Zinc-Chloride System.—In the same way, the following equation was applied to the zinc-chloride complex:

$$\log D=(n-2)\log[\mathrm{Cl^-}] \\ -(m-2)\log(\mathrm{Cl^-})+K+G \qquad (4)$$

where the denotations are the same as those in the uranium-nitrate system. As it is known[9] that zinc is adsorbed as $\mathrm{ZnCl_4^{2-}}$ at a 2～7 M chloride concentration, Eq. 4 becomes as follows by substituting $n=4$:

$$\log D-2\log\{[\mathrm{Cl}]^*-4[\mathrm{Zn}]\} \\ =-(m-2)\log(\mathrm{Cl^-})+K+G \qquad (5)$$

where $[\mathrm{Cl}]^*$ and [Zn] are the stoichiometric concentrations of all the chloride ions and zinc ions in the resin, obtained directly by measurement. $(\mathrm{Cl^-})$ has been estimated, without regard to the chloride ions bound to the zinc ions in the solution. When K and G are constant, the following equation is applicable:

$$\frac{d[\log D-2\log\{[\mathrm{Cl}]^*-4[\mathrm{Zn}]\}]}{d\log(\mathrm{Cl^-})} \\ =-(\overline{m}-2) \qquad (6)$$

where $\overline{m}$ is the mean number of ligands as defined by Bjerrum for the aqueous phase. The $\log D-2\log\{[\mathrm{Cl}]^*-4[\mathrm{Zn}]\}$ vs. $\log(\mathrm{Cl^-})$ plot at the external ionic strength $\mu=3$ is shown in Fig. 3. As can be seen from the curve, no appreciable change in the composition of complex species took place up to the external chloride concentration of 2 M, and from the gradient $\mathrm{ZnCl^+}$ and $\mathrm{ZnCl_2^0}$ were presumed to be the predominant species in this region. At a concentration of more than 2 M, anionic complex species were produced, and at the concentration of 3 M where only chloride ion is present, the coexistence of $\mathrm{ZnCl_3^-}$ and $\mathrm{ZnCl_4^{2-}}$ was presumed from the gradient of about -1.4, i. e., $m=3.4$.

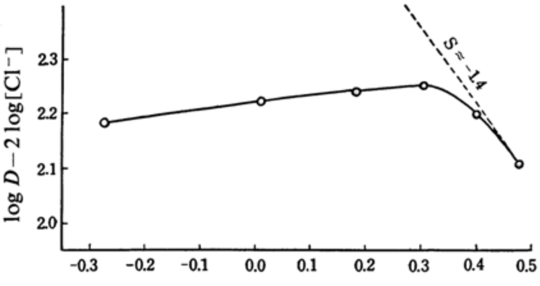


Fig. 3. Variation of distribution coefficient with external chloride concentration at constant ionic strength $\mu=3$.

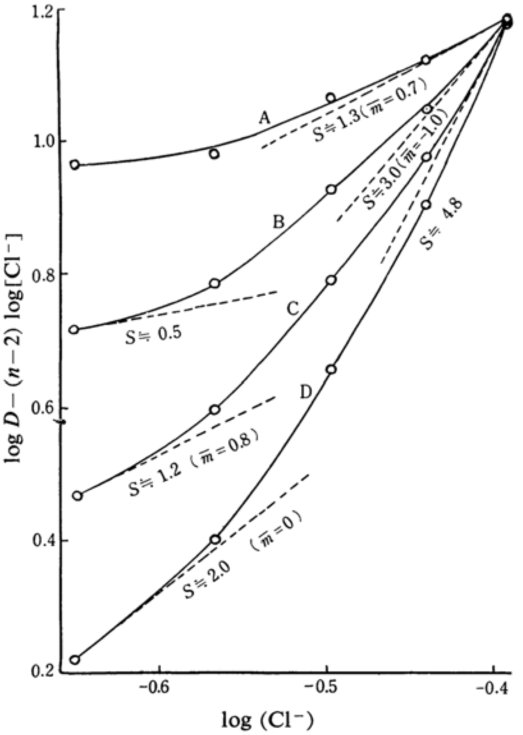


Fig. 4. Distribution coefficient curves when n is arbitrary assumed.

A, $n=4$; B, $n=3.5$; C, $n=3$; D, $n=2.5$

On the other hand, at the ionic strength $\mu=0.4$, the complex in the resin phase does not seem to be limited to one species, this being understood from the fact that the gradient of each curve in Fig. 4 increases with the chloride concentration. Even in such a complicated system, the principal species in the two phases can be identified graphically by introducing a condition $\overline{m}\geqq 0$ and $\overline{n}\leqq 4$. Curves were drawn in Fig. 4 on the assumption that $n=4$, 3.5, 3 and 2.5. At the point designating only the presence of 0.4 M chloride (at the right end of curve), the gradient of the curve was about 1.3 for $n=4$, which corresponded to $\overline{m}=0.7$, and 3.0 for $n=3.5$, which corresponded to $\overline{m}=-1.0$, since the gradient is $-(m-2)$ in Eq. 6. $m=0$ corresponds to $n=3.8$ by interpolation between $n=4.0$ and $n=3.5$. From the fact that $3.8\leqq\overline{n}\leqq 4.0$ corresponds to $0\leqq\overline{m}\leqq 0.7$, it may be considered that $ZnCl_4^{2-}$ is present as a predominant complex in the resin and that Zn^{2+} and $ZnCl^+$ are present in the solution when the aqueous phase is near the 0.4 M chloride solution. For a lower chloride concentration at the same ionic strength, $\overline{m}$ should be less than 0.7. At the chloride concentration of about 0.2 M (at the left end of the curve in Fig. 4), $\overline{m}=0$ corresponded closely to the gradient of the curve D for $n=2.5$ and $\overline{m}=0.7$, nearly to the gradient of the curve C for $n=3.0$ in Fig. 4. Consequently, $ZnCl_3^-$ (more than half) and $ZnCl_2^0$ seemed to be present as principal complexes in the resin phase at this concentration.

Further quantitative relations among the steps of the step-by-step formation of complex species may be estimated only with difficulty unless the stability constants are obtained. The evaluation of these constants requires not only many strict measurements but an extensive knowledge of activity coefficients.

Summary

1) The "indifferent electrolyte-adding" method described in previous papers was applied to the uranyl-nitrate and to the zinc-chloride complexes. A sodium nitrate-sodium perchlorate mixed medium was employed in the former, and a sodium chloride-sodium nitrate mixed medium in the latter.

2) The predominant species of the uranyl-nitrate complex adsorbed from sodium nitrate solutions was $UO_2(NO_3)_3^-$ at the external nitrate concentration of about 2 M and $UO_2(NO_3)_4^{2-}$ at the 4∼6 M concentration. The coexistence of the two species may be presumed at 2∼4 M.

3) The principal zinc-chloride complex adsorbed on the resin from the chloride solution of 0.4∼3 M was simply $ZnCl_4^{2-}$, accompanied by a small quantity of $ZnCl_3^-$ in a low ionic strength. On the other hand, the predominant species in the aqueous phase were $ZnCl_3^-$ and $ZnCl_4^{2-}$ for a sodium chloride concentration of 3 M, and Zn^{2+} and $ZnCl^+$ for a 0.4 M concentration. These results were approximately consistent with those obtained in a hydrochloric acid medium by other investigators.

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