*On The Mechanism of the Extraction of Uranyl Nitrate by TBP**
(Partition Study)

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The TBP (tri-*n*-butyl phosphate) extraction has been extensively employed for the uranium refining and the reprocessing of reactor spent fuel. A number of researches on this subject have appeared[1], and the mechanism of the uranium extraction by TBP was already proposed by Moore[2] as follows:

$$UO_2^{2+}(aq.) + 2NO_3^-(aq.) + 2TBP(org.) \rightleftarrows UO_2(NO_3)_2(TBP)_2(org.) \qquad (1)$$

The more rigorous analysis for the mechanism of TBP extraction was made by McKay et al.[3-5] and the mechanism of uranium extraction was confirmed as Eq. 1 proposed by Moore.

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* This study was presented at the 1st Symposium on Atomic Energy, Tokyo, January 13, 1957, and the 1st Symposium on Radiochemistry, Tokyo, December 21, 1957.

[1] For example, R. I. Smith, TID-3502.

[2] R. L. Moore, AECD-3196 (1951).

[3] K. Alcock et al., *Trans. Faraday Soc.*, **52**, 39 (1956).

[4] T. V. Healy and H. A. C. McKay, ibid., **52**, 633 (1956).

[5] E. Hesford and H. A. C. McKay, ibid., **54**, 573 (1958).

The extraction of the nitric acid by TBP was also observed by Moore[2] and the following mechanism was proposed,

$$HNO_3(aq.) + TBP(org.) \rightleftarrows HNO_3 \cdot TBP(org.) \qquad (2)$$

The formation of the complex $HNO_3 \cdot TBP$ was supported by McKay et al.[3] and the behavior of uranium on the TBP extraction from a nitric acid solution was concluded as a result of the competition of uranium and nitric acid[4].

The object of the present work is to propose a method of analysis to confirm the formation of a complex and to apply this analysis to the extractions of uranyl nitrate and nitric acid with TBP. The discussion for the extraction behavior of uranium from nitric acid solution by TBP is the second object of this work and thirdly the thermochemical functions for this kind of complex formation are to be determined.

Experimental

Reagents.—The reagents used in these experiments are as follows:

A) *TBP.*—The TBP (tri-*n*-butyl phosphate) was used after vacuum distillation.

B) *Uranyl nitrate.*—Uranyl nitrate was obtained from British Drug Houses Ltd. and was used after recrystallization.

C) *Diluents.*—As diluents, carbontetrachloride and kerosene were used. Boiling point range of kerosene used in the experiments is 190~260°C, specific gravity (15/4°C) is 0.8094.

Equipment and Method.—The Measurements of the distribution equilibrium were always made at constant temperature using a thermostated water bath. The separatory funnels were specially designed in order to be easily dipped into the water bath. The method for the measurement of distribution coefficients was the following. The necessary volumes of both aqueous and organic phases were put into a separatory funnel, which was dipped in the water bath. After the temperature had reached equilibrium, shaking of about one minute was repeated at intervals of fifteen or twenty minutes. Both phases were separated rapidly after an equilibrium time of about three or four hours. A centrifuge was used in the case where the separation was difficult. The distribution coefficients of both uranium and nitric acid were obtained by analyzing both in the aqueous phase.

The methods of analysis are the following. For uranium, the alkaline peroxide method[6] was adopted and a Hitachi EPU-2 spectrophotometer was used for the determination (at $\lambda = 400$ mμ). For nitric acid, the uranium peroxide precipitation method[7] was taken.

Notation.—C_M and C'_M denote the equilibrium concentrations of a species M in aqueous and organic phases respectively. Kd(M) denotes the distribution coefficient of the species M $(= C'_M/C_M)$. a_M is the activity of the species M in aqueous phase or organic phase, and f_M is its activity coefficient.

Results and Discussion

Distribution Equilibrium.—Prior to a discussion about the extraction mechanism, a general survey of distribution equilibrium of uranium between the aqueous and TBP phase was made. The results of the measurement can be summarized briefly as the following.

(a) In case nitric acid is added, the distribution coefficient of uranium is constant when the uranium concentration is low and the nitric acid concentration is kept constant, on the other hand, when nitric acid is absent, a constant distribution coefficient can not be obtained.

(b) The uranium concentration in organic phase increases with the uranium concentration in aqueous phase and reaches a constant which corresponds to the uranium concentration of $UO_2(NO_3)_2 \cdot (TBP)_2$ in organic phase as pointed out by Moore[2].

(c) The distribution coefficients of uranium increases with the nitric acid concentration in aqueous phase and reaches a maximum value, and then decreases gradually. Fig. 1 shows the influence of nitric acid concentration upon the distribution coefficient of uranium at various uranium concentrations.

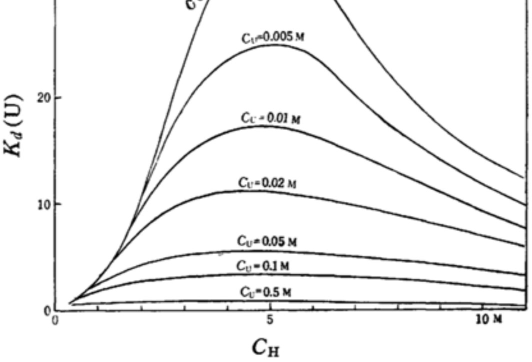

Fig. 1. Influence of nitric acid concentration upon the distribution coefficient of uranium at various concentrations.

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[6] C. J. Rodden and J. C. Warf, "Analytical Chemistry of the Manhattan Project", (National Nuclear Energy Series VIII-1(1950)).

[7] R. E. Connik, MDDC-1245 (1945).

(d) The distribution coefficient of uranium is nearly proportional to the square of the TBP concentration in the organic phase when the concentrations of uranium and nitric acid are low and the nitrate concentration is held constant.

(e) The distribution coefficient of uranium decreases with the increase of temperature.

(f) The distribution coefficient of nitric acid coexisting with uranium decreases gradually with the increase of the uranium concentration in aqueous phase, but in the case where the nitric acid concentration is low the distribution coefficient of uranium reaches a maximum value and then decreases gradually.

(g) The influence of the nitric acid concentration in the aqueous phase on the distribution coefficient of nitric acid is markable when the uranium concentration is low. However, this influence becomes smaller with the increase of the uranium concentration in aqueous phase, and finally the distribution coefficient of nitric acid becomes nearly constant against the concentration of nitric acid in aqueous phase when the uranium concentration is higher than 0.1 M (Fig. 2).

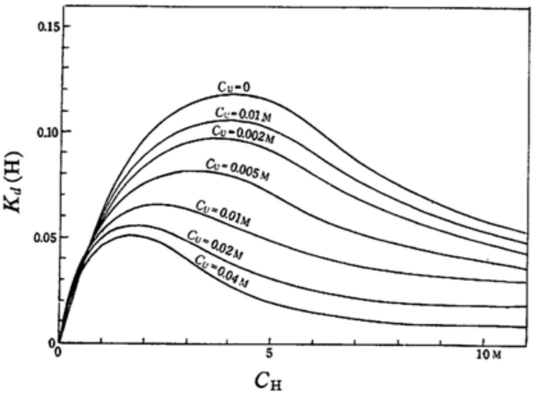

Fig. 2. The distribution coefficient of nitric acid coexisting with uranium.

From the above-mentioned distribution equilibrium of uranium, several pieces of information about the mechanism of the extraction of uranium can be obtained.

Facts b) and d) indicate that formation of the uranium complex with TBP in organic phase is likely. Therefore, it is possible to expect the following complex formation reaction considering the salting-out effect of nitrates on the extraction of uranium,

$$\mu \mathrm{UO_2}^{2+}(\mathrm{aq.}) + 2\mu \mathrm{NO_3}^-(\mathrm{aq.}) + \nu \mathrm{TBP}(\mathrm{org.}) \rightleftarrows [\mathrm{UO_2(NO_3)_2}]_\mu(\mathrm{TBP})_\nu(\mathrm{org.}) \tag{3}$$

where μ and ν are positive integers. The determination of μ and ν will be discussed later.

It is estimated from fact e) that this reaction should be an exothermic reaction.

Facts c) and f) also suggest that nitric acid is extracted together with uranium by TBP and both of these extraction reactions take place competitively.

Method of Analysis for an Extraction Mechanism.—Although there are several types of mechanisms by which a solute in aqueous phase can be extracted by organic solvent, one is the " mass-action " reaction between the solute ions and the organic solvent molecules as shown by Eq. 3.

This kind of extraction mechanism such as Eq. 3 is written as the following general expression,

$$\mu \mathrm{M}^{n+}(\mathrm{aq.}) + (n/m)\mu \mathrm{X}^{m-}(\mathrm{aq.}) + \nu \mathrm{S}(\mathrm{org.}) \rightleftarrows (\mathrm{MX}_{n/m})_\mu \mathrm{S}\nu(\mathrm{org.}) \tag{4}$$

where

M_mX_n=inorganic solute (M^{n+}=cation, X^{m-}=anion)

S=organic solvent (extractant)

μ and ν=positive integers.

The purpose of the analysis is to obtain the value of μ and ν respectively without contradiction. The equilibrium constant (K) for Eq. 4 is given as

$$K=(a_{\mathrm{complex}})/(a_{\mathrm{M}})^{\mu}(a_{\mathrm{X}})^{(n/m)\mu}(a_{\mathrm{S}})^{\nu}, \tag{5}$$

where a is the activity in aqueous phase or in organic phase and $a=fC$.

When the concentration of the solute is low, the ratio of the number of bonded solvent molecules to that of free solvent molecules is very small, so that Eq. 5 becomes

$$K=(f_{\mathrm{complex}})(C_{\mathrm{complex}})/(f_{\mathrm{M}}C_{\mathrm{M}})^{\mu}(a_{\mathrm{X}})^{(n/m)\mu}(a_{\mathrm{S}}^0)^{\nu} \tag{6}$$

where a_S^0 is the activity of the extractant solvent which corresponds to the initial concentration of extractant solvent in organic phase. In Eq. 6, f_{complex} is determined by the concentration of solvent in organic phase so that both f_{complex} and a_S^0 are constant at constant concentration of solvent.

If it is assumed that all M ions in organic phase are related to the formation of the complex, the following relation is obtained:

$$C_{\text{complex}}=C_{\text{M}}'/\mu \tag{7}$$

Then from Eqs. 6 and 7, considering the relation: $C_{\text{complex}}/C_{\text{M}}=Kd(\text{M})$

$$Kd(\text{M})=\text{const.}\ (f_{\text{M}}{}^{\mu}/f_{\text{complex}})\cdot (C_{\text{M}})^{\mu-1}(a_{\text{X}})^{(n/m)\mu}(a_{\text{S}}{}^0)^{\nu} \tag{8}$$

From Eq. 8, the integers in Eq. 4 are determined experimentally as follows.

(1) Determination of μ.—In the case where the salting-out agent is absent, the activity a_{X} can be replaced with the concentration C_{X}, and f_{M} becomes unity, and C_{X} is determined uniquely by C_{M} as $(n/m)C_{\text{M}}$. When the distribution coefficient of M is measured at constant solvent concentration, f_{complex} and $a_{\text{S}}{}^0$ are constant, as has been stated, so that Eq. 8 becomes

$$Kd(\text{M})\cong\text{const.}\ (C_{\text{M}})^{(1+n/m)\mu-1} \tag{9}$$

Thus by plotting $\log Kd(\text{M})$ against $\log C_{\text{M}}$ the slope of the line indicates the value of $(1+n/m)\mu-1$, from which μ can be determined.

In the case where the salting-out agent exists, C_{X} is determined by both C_{M} and the concentration of the salting-out agent. If one adds a large amount of salting-out agent compared with C_{M} (which is low), both C_{X} and the ionic strength of the aqueous solution are mainly determined by the concentrationof the salting-out agent. Thus, when the distribution coefficient of M is measured at constant solvent concentration keeping the concentration of salting-out agent constant, Eq. 8 becomes

$$Kd(\text{M})\cong\text{const.}\ (C_{\text{M}})^{\mu-1} \tag{10}$$

because f_{M} and a_{X} are constant at costant ionic strength of the aqueous phase and f_{complex} and $a_{\text{S}}{}^0$ are constant at constant solvent concentration. Thus, by plotting $\log Kd(\text{M})$ against $\log C_{\text{M}}$ one can determine μ from the slope of the line.

(2) Determination of ν.—When the distribution coefficient of M is measured, keeping the aqueous phase concentration of M constant, and also keeping the concentration of the salting-out agent constant (if the salting-out agent exists), Eq. 8 becomes

$$Kd(\text{M})\cong\text{const.}\ ((f_{\text{S}}{}^0)^{\nu}/f_{\text{complex}})(C_{\text{S}}{}^0)^{\nu} \tag{11}$$

where $f_{\text{S}}{}^0$ is the activity coefficient for $C_{\text{S}}{}^0$. Unfortunately both $f_{\text{S}}{}^0$ and f_{complex} are the function of the solvent concentration $C_{\text{S}}{}^0$, and the determination of these activity coefficints for various solvent concentrations is not easy. However, if the measurement is made at low solvent concentration, the slope which is obtained by plotting $\log Kd(\text{M})$ against $\log C_{\text{S}}{}^0$ roughly indicates the value of ν, because the deviation from the ideal solution becomes smaller according to the dilution of the solution.

The above-mentioned method is applicable to any reaction of the type of Eq. 4; however, it should be noticed that this method stands upon the assumption that all M ions in organic phase are combined with the solvent molecules. If this assumption does not exist, the method of analysis will become more complicated. On the other hand, when one can determine the integers μ and ν without contradiction under this assumption, one recognizes the validity of this assumption. An attention should be given to the case in which the successive complex formation by anion takes place according to the increase of the anion concentration, for example,

$$\text{UO}_2{}^{2+}+\text{NO}_3{}^- \rightleftarrows \text{UO}_2(\text{NO}_3)^+,$$

$$\text{UO}_2(\text{NO}_3)^+ + \text{NO}_3{}^- \rightleftarrows \text{UO}_2(\text{NO}_3)_2$$

Since the above-mentioned method of analysis is adopted for a low concentration region of the solute, this method can be applied without correction in case the salting-out agent is absent. In the case salting-out agent is added, the successive formation of the complex by anion will be expected, but the method is still applicable without correction, because the ionic strength of the solution is kept nearly constant. However, if an anionic complex such as $\text{UO}_2(\text{NO}_3)_3{}^-$, $\text{UO}_2(\text{NO}_3)_4{}^{2-}$, etc., is formed, the treatment must be changed.

Although this kind of method of analysis was used at first by Moore[2)], the treatment was not rigorous. Eq. 11 was also derived by McKey et al.[5)] and ν was called the solvation number. It is important, however, to confirm the existence of "mass-action" reaction for the solvent extraction process by applying the above-mentioned analysis.

Mechanisms of the Extraction for Uranium and Nitric Acid.—*(1) Uranyl nitrate extraction by TBP.*—The integers μ and ν in Eq. 3 were determined by applying the above-mentioned method in the following way.

μ is determined easily as $\mu=1$ from fact a) and Eq. 10 in case the salting-out agent exists. However, in case the salting-out agent is absent, no linear relation between $\log Kd(\text{U})$ and $\log C_{\text{U}}$ was observed while a linear relation was expected from Eq. 9. This means that the mechanism of extraction in this case is not consistent with the mechanism postulated in Eq. 3, and uranyl nitrate must be hydrolyzed, especially in the low concentration region and in the case where no acid exists, so that the mechanism of extraction must change.

ν was determined as $\nu=2$ by applying Eq. 11. The linear relation between $\log [Kd(\mathrm{U})/(a_{\mathrm{NO_3}})^2]$ and $\log C^0_{\mathrm{TBP}}$ was observed as $\nu=2$ for the low TBP concentration region.

Accordingly one obtained the same mechanism as that proposed by Moore for uranyl nitrate extraction by TBP. Though the same result was obtained, it should be noticed that the existence of this mechanism was confrimed beyond doubt by this analysis and this mechanism does not exist when the hydrolysis of uranium takes place.

On the extraction of uranium from a nitric acid solution by TBP, it was already observed that nitric acid coexisting with uranium is not only effective as a salting-out agent, also extractable together with uranium by TBP, so that the mechanism of the extraction of nitric acid should also be studied in order to clarify the mechanism of the extraction of the U-HNO_3-TBP system.

(2) Nitric acid extraction by TBP.—One can expect the reaction of nitric acid with TBP molecules as expected in the case of uranyl nitrate extraction, then

$$\mu\mathrm{H}^+(\mathrm{aq.}) + \mu\mathrm{NO_3}^-(\mathrm{aq.}) + \nu\mathrm{TBP(org.)} \rightleftarrows (\mathrm{HNO_3})_\mu(\mathrm{TBP})_\nu(\mathrm{org.}) \qquad (12)$$

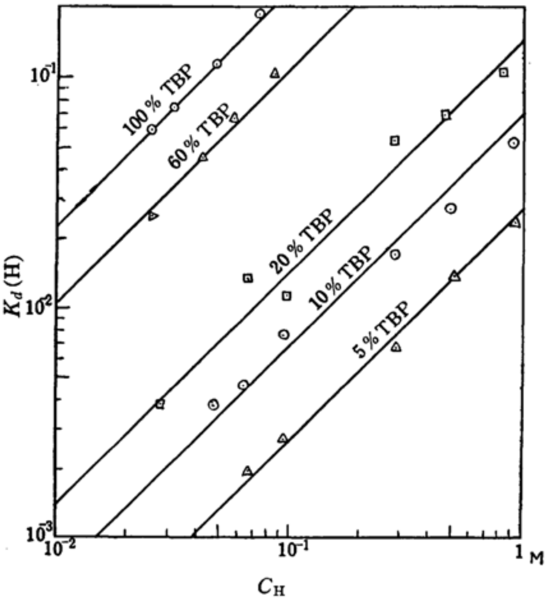

Fig. 3. Determination of μ in case the salting-out agent is absent.

The integers μ and ν in Eq. 12 can be determined as follows.

(a) Determination of μ.—In the case where the salting-out agent exists, μ is determined by Eq. 10. The result of the measurement of Kd(H) for dilute nitric acid when sodium nitrate is added as a salting-out agent shows that Kd(H) is constant independent of C_{H} when the concentration of salting-out agent is kept constant. Then, by applying to Eq. 10, μ is determined as $\mu=1$.

In the case where the salting-out agent is absent, μ is determined by Eq. 9, Fig. 3 was obtained by plotting Kd(H) againts $\log C_{\mathrm{H}}$ at 25°C for TBP-kerosene system. The existence of a linear relation is observed and the slope of this line is 1 independently with TBP concentration. An essentially the same result was obtained when the diluent is carbon tetrachloride. Then, from Eq. 9, μ is determined again as $\mu=1$.

(b) Determination of ν.—The value of ν is determined by using Eq. 11. Fig. 4 was obtained by plotting $\log Kd$(H) against $\log C^0_{\mathrm{TBP}}$ at 25°C, where the diluent is carbon tetrachloride. In this figure, the lines A and A′ are for the case no

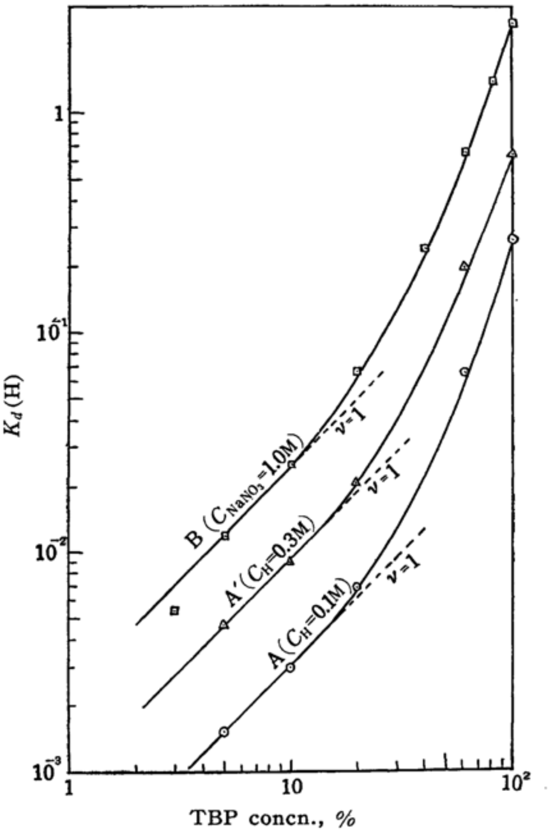

Fig. 4. Determination of ν.

salting-out agent exists and the line B is for the case the salting-out agent exists (1 M $NaNO_3$). It is noteworthy that both A (A′) and B give nearly the same results. For a region where the TBP concentration is low, the linear relations are obtained and slopes are 1 for each case. The essentially the same results are obtained in case the diluent is kerosene. Then, from Eq. 11, ν is determined as $\nu=1$.

However, in a region where the TBP concentration is higher, the slopes are changing from one to two. It is not clear at the present stage whether this is based upon the change of activity coefficients ($f_S{}^0/f_{\text{complex}}$) in Eq. 11 or the formation of a complex $HNO_3(TBP)_2$.

As a result of above-mentioned analysis for the HNO_3–TBP system, the mechanism of the nitric acid extraction by TBP was confirmed as

$$\mathrm{H^+(aq.) + NO_3{}^-(aq.) + TBP(org.)} \rightleftarrows \mathrm{HNO_3 \cdot TBP(org.)} \qquad (13)$$

On the other hand, Moore proposed Eq. 2 as the mechanism of nitric acid extraction by TBP. This mechanism was derived from the fact that $Kd(\mathrm{H})$ is nearly constant, independent of the nitric acid concentration in the case of uranium extraction. However, as shown in fact g) this is true only in case the uranium concentration is higher than about 0.1 M, and his observation was made just in this range ($C_{\mathrm{U}}=0.1\sim0.4$ M). So it is not suitable to discuss the mechanism of nitric acid extraction basing only on this fact. It may be reasonable to interpret this fact as a result of the competition of uranium and nitric acid as will be discussed later.

Competition of Uranium and Nitric Acid.—It has been clarified that both uranium and nitric acid are extracted according to the above-mentioned mechanisms. With these mechanisms, the behavior of both uranium and nitric acid during the extraction process should be interpreted as follows.

(1) Simultaneous partition of uranium and nitric acid.—In case uranium is extracted from a nitric acid solution by TBP, the distribution equilibria of Eqs. 1 and 13 should be established simultaneously. Then, one obtains the following simultaneous equations,

$$K(\mathrm{U}) = [f_{\text{complex}}(\mathrm{U})/(f_{\pm}(\mathrm{U}))^3] \cdot [Kd(\mathrm{U})/C_{\mathrm{NO_3}})^2(a_{\mathrm{TBP}})^2] \qquad (14)$$

$$K(\mathrm{H}) = [f_{\text{complex}}(\mathrm{H})/(f_{\pm}(\mathrm{H}))^2] \cdot [Kd(\mathrm{H})/(C_{\mathrm{NO_3}})(a_{\mathrm{TBP}})] \qquad (15)$$

where $K(\mathrm{U})$ and $K(\mathrm{H})$ are the equilibrium constants of uranium for Eq. 1 and of nitric acid for Eq. 13, $f_{\pm}(\mathrm{U})$ and $f_{\pm}(\mathrm{H})$ are the mean activity coefficients of uranyl nitrate and of nitric acid.

When the concentrations of both uranium and nitric acid are low, if one keeps the ionic strength of solution constant, the activity coefficient in aqueous phase is kept nearly constant, and the activity coeficients of the complex in organic phase are nearly constant because the concentration is very low. In such a case, the following relation is obtained:

$$\log Kd(\mathrm{H}) \cong (1/2) \log Kd(\mathrm{U}) + \text{const.} \qquad (16)$$

This relation was confirmed by Fig. 5 which was obtained from the measurements under the uranium concentration range: 0.005∼0.05 M, and the nitric acid concentration range: 0.1∼1 M and at TBP 20%, 25°C. Though this measurement was made at various ionic strengths, the linear relationship is still observed in both the TBP–CCl_4 system and the TBP-kerosene system, and the slopes are both 1/2.

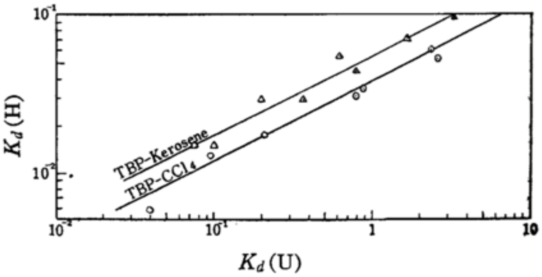

Fig. 5. Existence of simultaneous partition of both uranium and nitric acid.

By this analysis, it was confirmed that when uranium is extracted from a nitric acid solution by TBP, both the extraction reaction of uranium shown by Eq. 1 and the extraction reaction of nitric acid shown by Eq. 13 take place simultaneously.

(2) The influence of the nitric acid concentration upon Kd(U).—In the distribution equilibrium of uranyl nitrate, $Kd(\mathrm{U})$ has its maximum value against the change of C_{H} as shown by fact c). This can be interpreted as a result of the competition of both uranium and nitric acid in the following way.

In the case where the concentration is low, if one replaces the activity by the concentration in order to make the discussion simple, the following simultaneous equations exist approximately,

$$K(\mathrm{U}) \cong Kd(\mathrm{U})/C_{\mathrm{H}}{}^2(C^0{}_{\mathrm{TBP}}-C_{\mathrm{H}}{}')^2 \qquad (17)$$

$$K(\mathrm{H}) \cong C_{\mathrm{H}}'/C_{\mathrm{H}}^2(C^0_{\mathrm{TBP}} - C_{\mathrm{H}}') \qquad (18)$$

where C^0_{TBP} represents the initial concentration of TBP in organic phase. From Eqs. 17 and 18 by eliminating C_{H}',

$$Kd(\mathrm{U}) = K(\mathrm{U})\,[C_{\mathrm{H}}C^0_{\mathrm{TBP}}/(1+K(\mathrm{H})C_{\mathrm{H}}^2)]^2 \qquad (19)$$

Eq. 19 gives the relation between $Kd(\mathrm{U})$ and C_{H} in a region where the uranium concentration is low. It can easily be shown from Eq. 19 that $Kd(\mathrm{U})$ increases with the increase of C_{H}, reaches a maximum value, then decreases gradually. Furthermore, the maximum value of $Kd(\mathrm{U})$ is obtained from Eq. 19 as $K(\mathrm{U})(C^0_{\mathrm{TBP}})^2/4K(\mathrm{H})$ at $C_{\mathrm{H}} = 1/\sqrt{K(\mathrm{H})}$. If one takes $K(\mathrm{U}) = 27$, $K(\mathrm{H}) = 0.08$ as the values of equilibrium constants respectively at 25°C, TBP 20% (these values were obtained tentatively as the equilibrium constants), one obtains as the calculated values: $Kd(\mathrm{U})_{\max} = 45$ at $C_{\mathrm{H}} = 3.5$ M. These correspond to the following experimental values: $Kd(\mathrm{U})_{\max} = 34$ at $C_{\mathrm{H}} = 5$ M. Considering that this calculation was made using the concentration instead of the activity, the agreement seems to be fairly good.

In case the uranium concentration is higher, although the calculation becomes more complicated, one can obtain a similar result.

Accordingly, it was confirmed that fact c) is interpreted as the result of the competition of both uranium and nitric acid as was pointed out by Moore[2)] and McKay[4,8)]. From this point of view, facts f) and g) are also interpreted as the result of the competition of both.

(3) Nitric acid and sodium nitrate as salting-out agent. — On the extraction of uranium from a nitric acid solution, it was clarified that both uranium and nitric acid are extracted by TBP competitively. Accordingly, it is interesting to observe the behavior of the extraction of uranium when the salting-out agent which is not extractable by TBP is added.

Sodium nitrate was chosen as one of those agents that are suitable for this purpose. The salting-out effects of both nitric acid and sodium nitrate for diluted uranyl nitrate are shown in Fig. 6 which was made at 25°C, TBP 20% (in the case of sodium nitrate, 0.5 M nitric acid is added in order to prevent the hydrolysis of uranium).

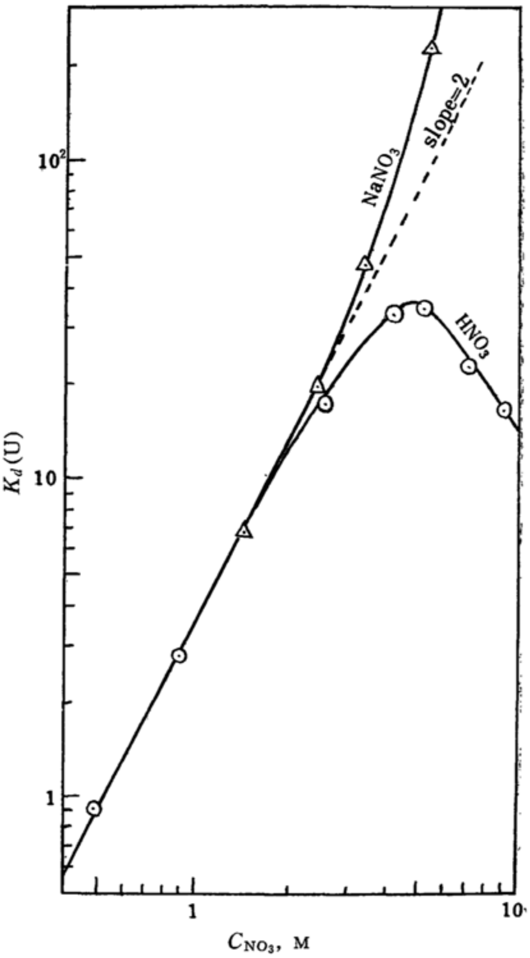

Fig. 6. The salting-out effect of both nitric acid and sodium nitrate for diluted uranyl nitrate.

It is obvious from Fig. 6 that, in the case of nitric acid, $Kd(\mathrm{U})$ has the maximum at $C_{\mathrm{NO_3}}$ of nearly 5 M; and in the case of sodium nitrate, $Kd(\mathrm{U})$ increases monotonously and is nearly proportional to the square of $C_{\mathrm{NO_3}}$.

When the salting-out agent is not extracted by TBP and contributes only to the increase of the concentration of NO_3^-, one obtains the relation: $Kd(\mathrm{U}) = \mathrm{const.} \times (C_{\mathrm{NO_3}})^2$ from Eq. 14 by ignoring the activity coefficient. Then $Kd(\mathrm{U})$ is nearly proportional to $(C_{\mathrm{NO_3}})^2$. It can also be understood from this analysis that little sodium nitrate is extracted by TBP and is effective only as a salting-out agent for the uranium extraction.

However, it is noteworthy that when the concentration of nitric acid is low, nitric acid is also effective mainly as a salting-out agent. This is observed from

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8) H. A. C. McKay, "Int. Conf. Peaceful Uses of Atomic Energy", United Nations, (1955), p./441.

Fig. 6 and is also derived from Eq. 19 as $Kd(\mathrm{U}) = \mathrm{const.}(C_{\mathrm{H}})^2$ by considering C_{H} is small. This relation just corresponds to the relation $Kd(\mathrm{U}) = \mathrm{const.}(C_{\mathrm{NO_3}})^2$, therefore, nitric acid is effective mainly as a salting-out agent when its concentration is low.

Rough Determination of the Thermochemical Functions of the Reaction of Uranyl Nitrate and TBP.—Although the existence of the complex with TBP such as $UO_2(NO_3)_2(TBP)_2$, $HNO_3 \cdot TBP$ was confirmed, the nature of these complexes remains uncertain. At first the measurement of the thermochemical functions was tried.

ΔH^0, ΔF^0 and ΔS^0 are defined as the enthalpy change, the Gibbs' free energy change and the entropy change respectively for Eq. 1 when the activities of each species of Eq. 1 are unity. These thermodynamical functions are determined roughly by using the distribution coefficient as the following.

(1) Enthalpy change. — By applying a thermodynamical relation for the reaction of Eq. 1

$$(\partial \ln K(\mathrm{U})/\partial T)_P = \Delta H^0/\boldsymbol{R}T^2 \qquad (20)$$

The equilibrium constant $K(\mathrm{U})$ is given as Eq. 14. If one keeps both the concentration of salting-out agent and the concentration of TBP constant, the equilibrium constant $K(\mathrm{U})$ becomes

$$K(\mathrm{U}) = \mathrm{const.}\,[f_{\mathrm{complex}}/(f_{\pm}(\mathrm{U}))^3 \times (f_{\mathrm{TBP}})^2]\,Kd(\mathrm{U}) \qquad (21)$$

When the concentration is low, the temperature dependence of the activity coefficient is very small, so that one can obtain the following relation from Eqs. 20 and 21

$$(\partial \ln Kd(\mathrm{U})/\partial T)_P \cong \Delta H^0/\boldsymbol{R}T^2 \qquad (22)$$

If one assumes that ΔH^0 is constant for the integration range, from Eq. 22

$$\ln Kd(\mathrm{U}) \cong \mathrm{const.} - \Delta H^0/\boldsymbol{R}T \qquad (23)$$

Thus by plotting $\log Kd(\mathrm{U})$ vs. $1/T$ the slope of the line indicates the value $-\Delta H^0/\boldsymbol{R}$, from which ΔH^0 can be obtained.

The measurement of the distribution coefficient of uranium was made at 10, 25 and 50°C, respectively. The concentration of uranium in this measurement is low enough to neglect the temperature dependence of the activity coefficient and to keep the concentration of TBP constant.

The linearity between $\log Kd(\mathrm{U})$ and $1/T$ was observed obviously in both the TBP-CCl_4 system and the TBP-kerosene system, and the slopes in both systems were exactly the same. Then, the enthalpy change ΔH^0 was obtained by measuring the slope of the line as

$$\Delta H^0 = -4.3\,\mathrm{kcal.}\ (10\sim 50^\circ\mathrm{C})$$

This value has nearly the same order of the bonding energy of the hydrogen bond, so that it can be estimated that the bond strength or stability of this complex should be of nearly the same order as those of the hydrogen bond.

(2) Gibbs' free energy change. — Gibbs' free energy change ΔF^0 for the reaction of Eq. 1 is given as

$$\Delta F^0 = -\boldsymbol{R}T \ln K(\mathrm{U}) \qquad (24)$$

The equilibrium constant $K(\mathrm{U})$ is given as Eq. 14 and it is necessary to know the value of the activity coefficient of each species in order to calculate the $Kd(\mathrm{U})$. Unfortunately the activity coefficient of the organic phase is not clear though the activity coefficient of the aqueous phase is available. However, in organic phase, the activity coefficients of each species can be considered as nearly unity so far as the concentration is very low.

It is necessary to make the solution acidic in order to prevent the hydrolysis of uranium, otherwise the mechanism of extraction will change as has been stated already. Therfore, the measurement of the distribution equilibrium of uranium must be made under slightly acidic condition.

The equilibrium constant was calculated by using activity coefficients of uranyl nitrate and nitric acid in aqueous phase and by assuming the activity coefficients of the complex and TBP in organic phase as unity.

The results obtained are the following: $Kd(\mathrm{U})$ are 25.6, 25.2, 21.6 and 20.2 when the initial concentrations of nitric acid are 0.05, 0.1, 0.2 and 0.3 M, respectively. So one can observe that the equilibrium constant of uranium decreases gradually according to the increase of the concentration of nitric acid. This is considered as the result of the extraction of nitric acid into organic phase which causes the deviation of the activity coefficient in organic phase from unity.

Accordingly the following value is obtained as the rough value of $Kd(\mathrm{U})$ at 25°C by extrapolating to the zero nitric acid concentration: $K(\mathrm{U}) = 27$ (25°C). From this $K(\mathrm{U})$ value, one obtains Gibbs' free energy change of Eq. 1 by using Eq. 24 as

$$\varDelta F^0 \cong -2.0\ \text{kcal.}\ (25^\circ\text{C})$$

This small change of $\varDelta F^0$ suggests that uranium can be transferred easily between aqueous and TBP phases by changing the concentration of salting-out agent.

(3) Entropy change.—The entropy change $\varDelta S^0$ for Eq. 1 is given as

$$\varDelta S^0 = (\varDelta H^0 - \varDelta F^0)/T \qquad (25)$$

If $\varDelta H^0 \cong -4.3$ kcal. which was obtained as the average value for 10～50°C is used as the value at 25°C, the entropy change at 25°C is obtained as

$$\varDelta S^0 = -7.7\ \text{e. u.}\ (25^\circ\text{C})$$

Summary

The method of analysis using the distribution coefficient to confirm the mechanism of extraction was proposed and the formation of the complex $UO_2(NO_3)_2 \cdot (TBP)_2$ and $HNO_3 \cdot TBP$ was confirmed. The extraction behavior of uranium from a nitric acid solution was concluded as a result of the competition of uranium and nitric acid. The thermochemical functions $\varDelta H^0$, $\varDelta F^0$ and $\varDelta S^0$ for the complex formation reaction:

$$UO_2^{+2}(\text{aq.}) + 2NO_3^-(\text{aq.}) + 2TBP(\text{org.})$$
$$= UO_2(NO_3)_2(TBP)_2(\text{org.})$$

were determined roughly from the measurement of the distribution coefficient as follows: $\varDelta H^0(25^\circ\text{C}) \cong -4.3$ kcal., $\varDelta F^0 (25^\circ\text{C}) \cong -2.0$ kcal., $\varDelta S^0(\sim 25^\circ\text{C}) \cong -7.7$ e.u.

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