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The Effect of Solvents on the Adduct Formation of Uranyl Thenoyltrifluoroacetonate with Tributyl Phosphate

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Addition compound formation between uranyl bis-thenoyltrifluoroacetonate (UO_2A_2) and tributyl phosphate(S) was studied by a partition method, using uranium-237 as the tracer. The formula of the adduct complex was shown to be $UO_2A_2 \cdot S$. The solvent effect on the adduct formation constant was taken into account in connection with the activity; the activity coefficients of each species in various solutions were calculated from the molar volume and the solubility parameter. The formation constants based on the molar fraction, K_x, in a number of solvents were pre-estimated, employing $\log K_x = 7.08$ in carbon tetrachloride as a reference. They are in agreement with the observed values. The formation constant in terms of activity was found to be constant $\log K_S^\circ = 5.77 \pm 0.30$. A correlation between the formation constants of the two adducts, $UO_2A_2 \cdot S$ and $ZnA_2 \cdot S$, was demonstrated.

An addition of one or more basic molecules to a formally neutral chelate with unsaturated coordination sites has been found in many organic solutions. Most of the synergistic effects in extraction are ascribed to the formation of addition compounds, though various explanations of these effects have been postulated.[1] The adduct formations of uranyl complexes with neutral ligands have received much attention; several authors have investigated the effects of *β*-diketones (*e.g.*, TTA) and/or organophosphorous esters (*e.g.*, TBP).[2-4] However, there have been only a few systematic studies of the solvent properties governing the equilibrium constants in synergistic extraction processes.

In previous papers, the solvent effect on distribution coefficients was elucidated in typical extraction systems.[5-7] Further, the adduct formation constants of the zinc-TTA chelate with TBP in a variety of organic solvents were correlated with the activity coefficients of the substances involved in the reaction.[7]

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[1] Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, London (1969), p. 815.

[2] K. Batzar, D. E. Goldberg, and L. Newman, *J. Inorg. Nucl. Chem.*, **29**, 1511 (1967).

[3] T. V. Healy, *ibid.*, **19**, 314 (1961).

[4] H. Irving and D. N. Edgington, *ibid.*, **15**, 158 (1960).

[5] K. Akiba, N. Suzuki, H. Asano, and T. Kanno, *Radioanal. Chem.*, in press, "Regularities of Extraction of Uranyl Thenoyltrifluoroacetonate into a Number of Solvents."

[6] N. Suzuki and K. Akiba, *J. Inorg. Nucl. Chem.*, in press, "Distribution Regularity of the Divalent Metal Chelate into Various Organic Solvents-Distribution of Beryllium Thenoyltrifluoroacetonate."

[7] K. Akiba, N. Suzuki, and T. Kanno, This Bulletin, **42**, 2537 (1969).

The present study has been undertaken in order to clarify the regularities in the formation of an adduct complex between a coordinatively unsatulated chelate, uranyl bis-thenoyltrifluoroacetonate, and tributyl phosphate. The formation constants are pre-estimated from the calculated activity coefficients and are compared with those observed. The relation between the formation constants of uranyl -and zinc-TTA adducts with TBP is also investigated.

Experimental

Materials. A radioisotope of uranium-237 was produced by irradiating natural uranium with a 60 MeV bremsstrahlung from a linear electron accelerator in the Laboratory of Nuclear Sciences, Tohoku University. The irradiated sample was then treated as before.[5]

Thenoyltrifluoroacetone (TTA) was purified by sublimation under reduced pressure, while tributyl phosphate (TBP) was purified as before.[7]

The organic solvents used were purified in the usual manner.

Procedure. An aqueous (H,Na)ClO_4 solution (ionic strength=0.10) including ^{237}U was shaken for 20 hr with an equal volume of a desired organic solution containing TTA and TBP. The phases were separated by centrifugation, and aliquots of both phases were taken for the measurement of the γ-radioactivity. All the experiments were performed in a room thermostated at 25±1°C.

Results and Discussion

The adduct formation of the neutral chelate in the organic solution is expressed by:

$$UO_2A_2 + m\,S \rightleftarrows UO_2A_2\cdot m\,S \tag{1}$$

$$K_S = \frac{[UO_2A_2\cdot m\,S]}{[UO_2A_2][S]^m} \tag{2}$$

where UO_2A_2 represents the uranyl-TTA chelate; S, tributyl phosphate, and K_S, the molar formation constant of the adduct.

In the extraction of the uranyl complex with a TTA solution containing TBP from an aqueous medium, the distribution ratio of uranium ($D_{M,S}$) is given by:

$$D_{M,S} = \frac{P_M\beta_2[A^-]^2_{aq}\{1+\sum K_S[S]^m\}}{1+\sum\beta_n[A^-]^n_{aq}} \tag{3}$$

where $P_M=[UO_2A_2]_{org}/[UO_2A_2]_{aq}$ and $\beta_n=[UO_2\text{-}A_n^{(2-n)+}]/[UO^{2+}][A^-]^n_{aq}$. At a fixed aqueous concentration of the TTA anion, the next equation is given:

$$\frac{D_{M,S}}{D_M} = 1 + \sum K_S[S]^m \tag{4}$$

where D_M is the distribution ratio in the absence of TBP. When only one adduct is predominant, Eq. (4) may be simplified to:

$$K_S = \frac{D_{M,S}}{D_M}\frac{1}{[S]^m} \tag{5}$$

The formation constant can be obtained by a curve fitting method[8] according to Eq. (4) or by Eq. (5).

Distribution of Uranyl Complexes. The distribution ratios in the presence of TBP are independent of the uranyl concentration in the experimental range of 10^{-7} to 10^{-4} M, as Fig. 1 shows, even for paraffinic solvents such as *n*-hexane where the influence of the uranyl concentration has been found in the absence of TBP, as has been described previously.[5] It seems likely that the addition of organophilic TBP very greatly increases the solubility of the uranyl complex in these solvents and eliminates the change in the activity coefficients with an increase in the concentration.

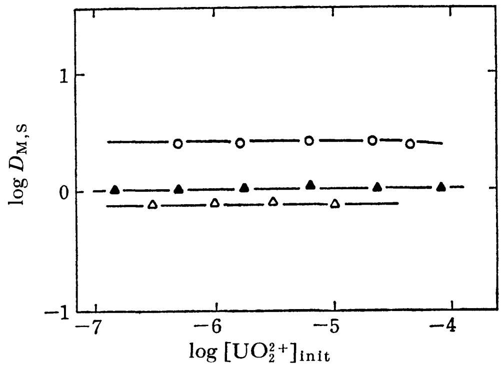

Fig. 1. Distribution ratios of uranyl complexes as a function of uranyl concentration.
$[HA]=10^{-2}$ M; $[S]=3.66\times10^{-3}$ M; ○, *n*-hexane (pH=1.76); ▲, carbon tetrachloride (pH=1.76); △, benzene pH=1.80)

The uranyl concentration was kept at 10^{-5} M in subsequent experiments.

The plots of log $D_{M,S}$ against pA at a fixed concentration of TBP gave a series of straight lines, with a slope of −2, which run parallel with the broken line for benzene at no TBP, as Fig. 2 shows; the addition

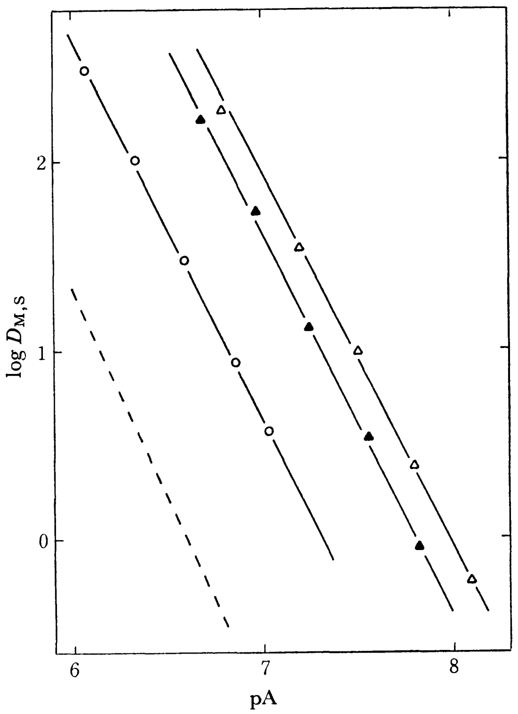

Fig. 2. Distribution ratios of uranyl complexes in the presence of TBP.
$[HA]=10^{-2}$ M; $[S]=3.66\times10^{-3}$ M; ○, *n*-hexane ▲, carbon tetrachloride; △, benzene; broken line: benzene at no TBP.

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[8] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

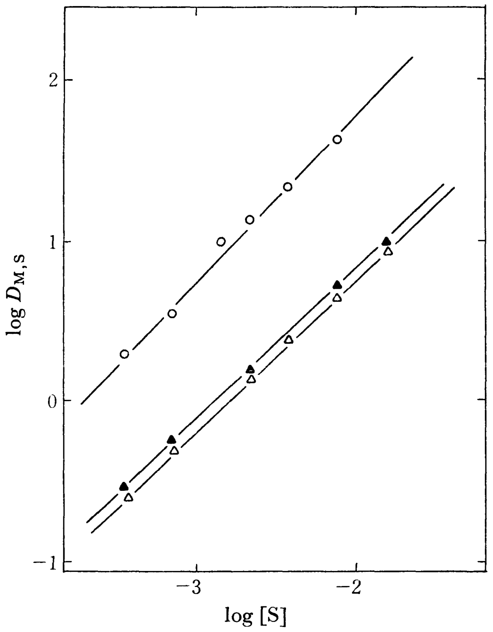

Fig. 3. Distribution ratios of uranyl complexes as a function of TBP concentration.
[HA] = 10^{-2} M; ○, *n*-hexane (pH = 2.24); ▲, carbon tetrachloride (pH = 1.96); △, benzene (pH = 2.03)

of TBP much enhances the distribution ratios, but the uranyl complexes still retain the two molecules of TTA which are bonded with each uranyl ion. It seems that the formally neutral chelate transfers to the organic phase from the aqueous phase and associates with TBP to form a coordinatively saturated adduct, or that, preferably, the water molecules in the complex are replaced by hydrophobic-donor molecules of TBP.

The variation in $\log D_{M,S}$ with log [S] were represented by a family of straight lines with a slope of 1, as Fig. 3 shows; this indicates that only one molecule of TBP is associated with the chelate and that there is no higher adduct, $UO_2A_2\cdot m$S ($m>1$), under the experimental conditions here adopted. The extraction of the uranyl complex with TBP alone, free from any chelating agent, is negligibly small at these low concentrations of TBP and acid. Accordingly, only one adduct, $UO_2A_2\cdot S$, is taken up in this study.

Estimation of Adduct Formation Constants. An equilibrium constant will be strongly influenced by the nature of the medium, though the stoichiometry of the adduct remains unaltered. For a comparison of reactions in different media, the formation constant should be considered in connection with the activity, because the activity coefficient of the solute is very sensitive to the properties of the medium and the concentration is not always directly proportional to the activity. In a previous paper, an approach to the problem of the role of solvents in the adduct formation of the zinc-TTA chelate with TBP was made from this point of view; the regularity of equilibrium constants in various organic solutions was fairly well established.[7] Such a treatment seems to be valid for the uranyl adduct in this work.

The formation constant expressed in activities is:

$$K_S^\circ = \frac{a_{M\cdot S}}{a_M\cdot a_S} \tag{6}$$

where a is the activity, and where the two subscripts, M and M·S, denote the molecules of the chelate and its adduct respectively. When the activity of a pure supercooled-liquid is chosen as the standard state, K_S° can be considered to be constant, regardless of the solvents; the effect of the solvent may be connected with the change in the activity coefficient with the solvent properties. In using the expression based on the molar fraction for thermodynamic convenience, K_S° is represented by:

$$K_S^\circ = \frac{x_{M\cdot S}}{x_M\cdot x_S}\cdot\frac{\gamma_{M\cdot S}}{\gamma_M\cdot\gamma_S} \tag{7}$$

where x is the molar fraction, and γ, the activity coefficient. Eq. (7) is then rewritten as follows:

$$\log K_x = \log K_S^\circ - \log F_\gamma \tag{8}$$

where $K_x = x_{M\cdot S}/x_M\cdot x_S$ and $F_\gamma = \gamma_{M\cdot S}/\gamma_M\cdot\gamma_S$. Therefore, when the quantity related to the activity coefficients is given in the desired solvents, the constant, K_S°, can be derived from the K_x value obtained experimentally in a certain solvent; the K_x values in others can be pre-estimated from the values of K_S° and F_γ.

The activities of TBP have been measured in many solutions,[9,10] but those of the uranyl chelate and the adduct have never been given. It is not always easy to measure the activity, but the activity may be practically evaluated by the aid of the following equation for a regular solution consisting of two components, A and B:[11]

$$\boldsymbol{RT}\ln a_A = \boldsymbol{RT}\left[\ln\varphi_A + \varphi_B\left(1-\frac{V_A}{V_B}\right)\right] + V_A\varphi_B^2(\delta_A-\delta_B)^2 \tag{9}$$

where φ is the volume fraction; V, the molar volume, and δ, the solubility parameter. Taking into account the dilute solution of the solute A in the solvent B, the activity coefficient based on molar fraction can be written as:

$$\boldsymbol{RT}\ln\gamma_A = \boldsymbol{RT}\left[\ln\frac{V_A}{V_B} + \left(1-\frac{V_A}{V_B}\right)\right] + V_A(\delta_A-\delta_B)^2 \tag{10}$$

Accordingly, the activity coefficient can be calculated from the physicochemical properties of a pure liquid, *i.e.*, the molar volumes and the solubility parameters of the solute and of the solvent.

As to the chelate, it is reasonable to postulate that $\delta_M \fallingdotseq \delta_{HA} = 9.9$ (HA denotes the TTA molecule) and $V_M \fallingdotseq 2V_{HA} = 320$ ml as has been described previously.[5] We have no sufficient data to evaluate the V and δ of the uranyl adduct. The solubility parameter of $UO_2A_2\cdot S$ is probably close to that of $ZnA_2\cdot S$, because the molecular forms of the adducts appear to be similar to each other. The $\gamma_{M\cdot S}$ values were calculated on the assumption that $\delta_{UO_2A_2\cdot S} \fallingdotseq \delta_{ZnA_2\cdot S} = 9.4$ and that $V_{M\cdot S} = V_M + V_S = 593$ ml.[7] The γ_S values were ob-

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[9] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

[10] S. Siekierski, *J. Inorg. Nucl. Chem.*, **24**, 205 (1962).

[11] J. H. Hildebrand R. L. Scott, "Solubility of Nonelectrolytes," 3rd Ed., Dover, New York (1964), p. 119.

TABLE 1. ADDUCT FORMATION CONSTANTS OF URANYL BIS-THENOYLTRIFLUOROACETONATE WITH TRIBUTYL PHOSPHATE AT 25°C

No.	Solvent	δ	V	$\log F_\gamma$	$\log K_x$			$\log K_S$ Obsd
					Calcd from Eq. (8)	Calcd from Eq. (12)	Obsd	
1	*n*-Hexane	7.3	130	−1.25	7.10	7.69	7.56	6.67
2	*n*-Heptane	7.4	140	−1.38	7.23	7.74	7.32	6.47
3	Cyclohexane	8.2	108	−1.81	7.66	7.61	7.78	6.81
4	Methylene chloride	9.7	64			5.85	5.61	4.42
5	Chloroform	9.3	81	−0.19	6.04	5.50	5.55	4.46
6	Carbon tetrachloride	8.6	96	−1.23	7.08[a]	7.08[a]	7.08	6.06
7	Bromoform	10.5	87	−0.15	6.00	5.53	5.92	4.86
8	Benzene	9.2	89	−1.29	7.14	6.69	6.59	5.54
9	Toluene	8.9	107	−1.13	6.98	6.63	6.67	5.70
10	Isopropylbenzene	8.5	140			6.57	6.24	5.39
11	Chlorobenzene	9.5	102	−0.79	6.64	6.35	6.42	5.43
12	*o*-Dichlorobenzene	10.0	113	−0.52	6.37	6.48	6.57	5.62

a) Observed value employed as reference.

tained from the data on TBP.[9,10]

The constant, $\log K^\circ_S = 5.85$, was given from the calculated F_γ value and $\log K_x = 7.08$ in carbon tetrachloride, which was used as a reference solvent. The adduct formation constants pre-estimated according to Eq. (8) are listed in the sixth column of Table 1. No estimate in methylene chloride or isopropylbenzene is given because of the lack of data on TBP.

The relation between the formation constants for uranyl and zinc adducts with TBP is considered, as the formation constants of $ZnA_2\cdot S$ have been obtained in various organic solutions.[7] The formation constant for $ZnA_2\cdot S$ is also expressed as:

$$K^\circ_{S(Zn)} = \frac{x_{ZnA_2\cdot S}}{x_{ZnA_2}\cdot x_S}\cdot\frac{\gamma_{ZnA_2\cdot S}}{\gamma_{ZnA_2}\cdot\gamma_S} = K_{x(Zn)}\cdot F_{\gamma(Zn)} \tag{11}$$

The activity coefficients of different solutes having the same values of the solubility parameter and of the molar volume should be equal to one another in a given solvent, according to Eq. (10), so long as the specific interaction between the solute and solvent molecules is small enough to be neglected. As the above assumptions for the δ and V of uranyl chelate seem to hold also for the zinc chelate, the activity coefficients of these chelate are taken as equal to each other. Similarly, the γ values for uranyl and zinc adducts may be identical in the same media. These findings lead to the conclusion that $F_{\gamma(U)} \fallingdotseq F_{\gamma(Zn)}$ in a given solvent. Each K°_S value for uranyl and zinc adducts is constant; therefore, the following relation can be given by eliminating the terms of the activity coefficients:

$$\frac{K_{x(U)}}{K_{x(Zn)}} = \frac{K^\circ_{S(U)}}{K^\circ_{S(Zn)}} = h \tag{12}$$

$$\text{or } \log K_{x(U)} = \log K_{x(Zn)} + \log h$$

The formation constants of the uranyl adduct can also be estimated from those of the zinc adduct. The constant, $\log h = 1.63$, was obtained from the observed values for two adducts in carbon tetrachloride. The estimates from Eq. (12) are shown in the seventh column of Table 1.

Regularities in Adduct Formation. The observed adduct formation constants are summarized in Table 1. The molar formation constants ($K_S/K_x = V_B/1000$) are also tabulated. The observed values are in rough accord with the estimates; they are especially consistent with the pre-estimations from Eq. (12). The K_S values in two solvents have been reported. The present datum in cyclohexane agrees with $\log K_S = 6.77$,[12] but that in benzene is larger than the $\log K_S = 5.28$ and 4.74 in the literature.[1]

Figure 4 shows the relation between the adduct

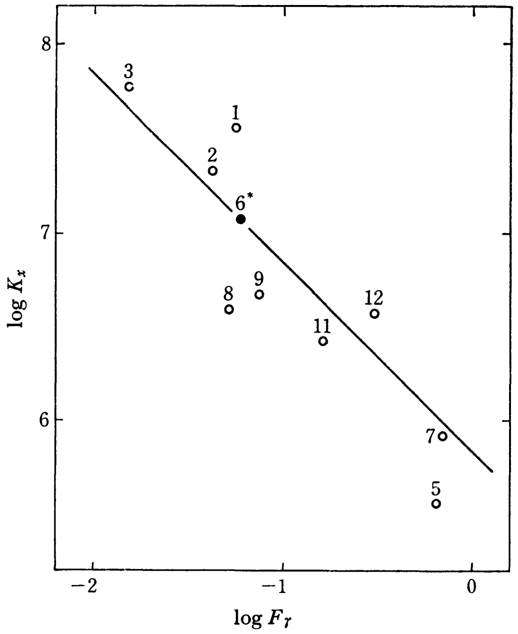

Fig. 4. Relation between the adduct formation constants and the activity coefficients.
The numbers in Figs. 4 and 5 correspond to those in Table 1.
* Employed as reference

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[12] H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **20**, 314 (1961).

formation constants and the activity coefficients. The straight line with a slope of -1 passing through a experimental point in carbon tetrachloride is the estimate. The points observed are close to the line, although negative deviations are found in benzene and chloroform and a positive one in *n*-hexane. This tendency is similar to the case of the zinc adduct.[7] The negative deviation in chloroform appears to be due to the formation of a hydrogen bond between TBP and solvent molecules.[13] The values of log-K_S^0 were found to be 5.77±0.30 by the method of least-squares. Thus, the solvent effect on the equilibrium constant was explained in connection with the activity coefficients evaluated from the properties of pure substances.

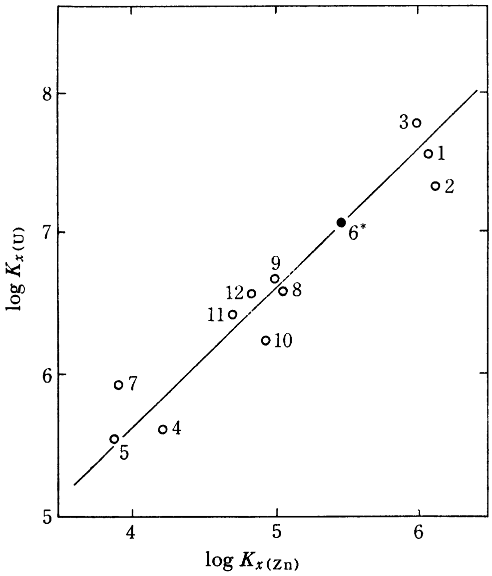

Fig. 5. Relation between the formation constants of $UO_2A_2 \cdot S$ and $ZnA_2 \cdot S$.
The $K_{x(\mathrm{Zn})}$ values were given from Ref. 7.
* Reference

The formation constants of the uranyl adduct are plotted against those of the zinc adduct in Fig. 5. The values thus established are in accord with the estimated line, with a slope of 1, passing through the point in carbon tetrachloride. There are small deviations even in the solvents such as chloroform where some deviations are found in evaluating from the activity coefficients. This shows that the influence of the solvent on the formation of the uranyl adduct is essentially the same as that in the case of the zinc adduct, as was expected. In the estimation by Eq. (12), since there is no need to calculate the γ values, the estimates seems to be free from errors due to the evaluation of such fundamental values as V or δ. This method may be practically useful for the reactions involving components with unknown V or δ values, when we have evidence that these values of the desired substance are equal to those of the reference. For example, the formation constants for the same type of adducts may be estimated in a similar manner. However, it should be remembered that this simple method is based on the similarity of complexes and is not always valid for different types of adducts. In general, the change in the activity coefficients should be taken into account for each species in solution.

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[13] M. F. Pushlenkov, E. V. Komarov, and O. N. Shuvalov, *Radiokhim.*, **2**, 537 (1960).