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研究論文

176. *Solvent Extraction of Metals by Organophosphorus Compounds, (I)*

General study

有機リン化合物による金属の溶媒抽出, (I)

総 論

By Keichi OSHIMA*

A systematic study of the basic chemistry of solvent extraction of metals by organophosphorus compounds carried out in JAERI is reported. As for the general study, thermodynamic and structural chemical approaches were employed.

The thermodynamical treatment of the distribution equilibrium measurement was carried out rather precisely to analyse the mechanism of solvent extraction. This was applied to determine the compositions of the complexes formed and the chemical reactions underlying.

Further, it was shown the competition of metal and proton acid could clearly explain the extraction behaviors in these systems.

The spectroscopic measurements of the solvents were conducted. Especially, in the infra-red region, the shift of the $P=O$ vibrational spectra of the solvent and the splitting of the NO_3 vibrational spectra of the nitrate ions gave very powerful measures to study the microscopic mechanism of complex formation between the solvent and the species extracted.

The thermodynamic and structural chemical approaches carried out were turned out to be in good accord and complementary.

I. INTRODUCTION

As a part of the study on reprocessing of

irradiated nuclear fuel, a systematic study on the basic chemistry of solvent extraction of

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metals by organophosphorus compounds have been carried out in Japan Atomic Energy Research Institute since 1956. Some of the results have been published already, and during this period there came out reports on this subject from various other groups. However, the accumulation of the results from our research has come to the point that we feel it is adequate to present here the whole study in an unified form.

In Part I of this paper, the general study of solvent extraction conducted in this research is reported, and its extension to several specific extraction systems is treated in Part II.

One of the main subjects of the study was to find out the mechanism of solvent extraction by organophosphorus compounds. The methods of approach employed for this purpose is to be roughly divided into two lines. One is thermodynamics, and the other is structural chemistry.

As for the former, the distribution equilibrium of the metal was treated from the standpoint of thermodynamics to obtain basic information of the mechanism. And for the latter, the spectroscopy of the solvents was employed for the main.

II. MEASUREMENTS OF THE DISTRIBUTION EQUILIBRIUM

The measurement of distribution equilibrium is one of the most fundamental procedures for the study of solvent extraction.

Though somewhat inexact in the treatment, Moore⁽¹⁾ was the first to argue the mechanism of solvent extraction of uranium by TBP from the thermodynamic analysis of the distribution equilibrium.

In order to obtain the idea of the basic chemical equilibrium underlying the extraction, this analysis was carried ahead more precisely by our group⁽³⁾. This turned out to be a similar treatment as carried out independently by McKay⁽²⁾, but is still different to some extent in the details.

The distribution equilibrium of a metal ion between the aqueous and organic phases can be expressed, in general, by the following

equation.

Where $M_n X_n$: inorganic solute (M^{n+} =cation, X^{m-} =anion)

S : organic solvent (extractant)

μ and ν : positive integers

Then, in case the concentration of the solute in the organic phase is low and it is to be assumed that all the M ions in the organic phase take part in the formation of the complex, the following equation for the distribution ratio, K_d , can be derived.

$$K_d(M) = \text{const.} \left[\frac{(f_{\pm})^{(1+n/m)\mu} (f_S^0)^{\nu}}{(f_{\text{complex}})} \right] \left[\frac{(C_M)^{\mu-1} (C_X)^{(n/m)\mu} (C_S^0)^{\nu}}{1} \right] \quad (2)$$

Where, f_{complex} : activity coefficient of the complex compound formed

$f_{\pm}$: mean activity coefficient of M^{n+} and X^{m-} ions

f_S^0 : activity coefficient of the solvent at its initial concentration

C_{complex} : concentration of the complex compound in the organic phase

C_M : concentration of M^{n+} ion in the aqueous phase (stoichiometric)

C_X : concentration of X^{m-} ion in the aqueous phase (stoichiometric)

C_S^0 : initial concentration of the solvent in the organic phase

The experimental determination of the values of μ , ν , in this equation will give an important information about the mechanism of extraction.

Moreover, as is it well known, the equilibrium constant, K , can be related to the change of thermodynamic functions of free energy, ΔF^0 , enthalpy, ΔH^0 and entropy, ΔS^0 .

In this study, ΔH^0 , was determined from the distribution ratio, K_d , by the following relation.

$$\ln K_d(M) = \text{const.} - (1/RT) \{ \Delta H^0 + \sum (\delta H)_i \} \quad (3)$$

Where, $(\delta H)_i$ is the deviation of the partial molar enthalpy of species i , from that of the ideal solution. For example, in case of the extraction of uranyl nitrate by TBP,

$$\sum (\delta H)_i = (\delta H)_{\text{complex}} - 3(\delta H)_{\text{UO}_2(\text{NO}_3)_2} - 2(\delta H)_{\text{TBP}} \quad (4)$$

The enthalpy change, ΔH^0 , was obtained by measuring the temperature dependence of $K_d(M)$ under the condition of minimizing $\sum(\delta H)_i$.

As for the F^0 and S^0 , the measurement of dilute solutions was extrapolated to concentration of zero in order to eliminate the effect of activity coefficient in $K(M)$.

1. Determination of μ

In case where there is no salting-out agent present in the solution, and if C_s^0 is constant, Eq. (2), becomes

$$K_d(M)/f_{\pm} = \text{const.} (f_{\pm} C_M)^{(1+n/m)\mu-1} \quad (7)$$

This means the slope of the plot, $\log K_d(M)/f_{\pm}$ vs. $\log f_{\pm} C_M$, gives $(1+n/m)\mu-1$. In case when there exists a salting-out agent, and if $C_M \ll C_X = \text{const.}$ and $C_s^0 = \text{const.}$, Eq. (2) becomes

$$K_d(M) \cong \text{const.} (C_M)^{\mu-1} \quad (8)$$

As an example, this result applied to the analysis of the extraction mechanism of nitric acid by TBP is shown in Figs. 1 and 2; Fig. 1 is a plot of $\log K_d(H)$ vs. $\log C_H$ in case where no salting-out agent exists. Since the slope is unity and $n, m=1$, it is to be derived from Eq. (1) that $\mu=1$ in this case. Fig. 2 is a plot of $\log K_d(H)$ vs. $\log C_H$ in case where the salting-out agent exists. Since K_d is independent of C_H , it is to be derived that

Fig. 1 Determination of μ in case the salting-out agent is absent (TBP-kerosene system) for the extraction of nitric acid

Fig. 2 Determination of μ in the case salting-out agent is added, TBP- CCl_4 - HNO_3 (diluted)- $\text{NaNO}_3(1M)$.

$\mu-1=0$, i.e. $\mu=1$. This is in agreement with the result for the case of no salting-out agent.

2. Determination of ν

If the measurements of $K_d(M)$ are made under various solvent concentrations, keeping the aqueous phase concentrations of the metal and the salting-agent constant, Eq. (2) becomes

$$K_d(M) = \text{const.} [(f_s^0)^{\nu}/f_{\text{complex}}] (C_s^0)^{\nu} \quad (9)$$

In case the measurement is made at low solvent concentration, the slope obtained plotting $\log K_d(M)$ against $\log C_s^0$ gives roughly the value of ν . As an example, Fig. 3 is the plot of $\log K_d(H)$ vs. $\log C_s^0$ for the system of HNO_3 -TBP (diluted with CCl_4).

The curves give the results of $\nu=1$ at the dilute region of TBP. However, at the higher concentration region of TBP, the slope of the curves in Fig. 3 changes from 1 to 2. This fact could be interpreted either by the change of activity coefficient, $(f_s^0)^{\nu}/f_{\text{complex}}$, or the formation of a complex $\text{HNO}_3(\text{TBP})_2$.

However, in many other cases of extraction by TBP diluted with CCl_4 , the plotting of $\log K_d(M)$ vs. $\log C_s^0$ is linear up to relatively high TBP concentration of about 60%. Therefore, it is fairly reasonable to assume

Fig. 3 Determination of ν (TBP-CCl₄ system) for the extraction of nitric acid

that $(f_s^0)/f_{\text{complex}}$ does not change remarkably with the TBP concentration in this region and conclude the existence of, $\text{HNO}_3(\text{TBP})_2$, in the higher concentration region, here.

The analysis of these facts comes to the conclusion that the mechanism of extraction in the system HNO_3 -TBP is as

And at the region of high concentration of TBP,

It is to be pointed out that with this analysis there is no need to assume the existence of any neutral molecule as HNO_3 in the aqueous phase, which was proposed by Moore⁽¹⁾ by the following equation.

The mechanism of the extraction can be well explained by a chemical equilibrium reaction between the ions in the aqueous phase and the solvent molecules forming complex compounds in the organic phase.

3. Competition of metal and proton acid

The reasoning described can be extended to explain the behavior of the metal and the acid in case of the extraction of metals by a solvent such as TBP from acidic solution.

For example, in case of the extraction of uranium by TBP from nitric acid solution, if the distribution of nitric acid and uranium between aqueous and organic phases occurs simultaneously, the following simultaneous equations should be valid for low TBP concentration,

Then,

$$\left\{ \begin{aligned} K(\text{U}) &= \{f_{\text{complex}}(\text{U}) / (f_{\pm}(\text{U}))^3\} \\ &\quad \{K_d(\text{U}) / (\text{CNO}_3)^2 (a_{\text{TBP}})^2\} \end{aligned} \right. \quad (14)$$

$$\left\{ \begin{aligned} K(\text{H}) &= \{f_{\text{complex}}(\text{H}) / (f_{\pm}(\text{H}))^2\} \\ &\quad \{K_d(\text{H}) / (\text{CNO}_3) (a_{\text{TBP}})\} \end{aligned} \right. \quad (15)$$

Where a_{TBP} denotes the activity of uncombined TBP in the organic phase. Then, if CNO_3 and C_U are small, and ionic strength of the solution is constant, the following equation can be derived.

$$\log K_d(\text{H}) \approx (1/2) \log K_d(\text{U}) + \text{const.} \quad (16)$$

The plot of $\log K_d(\text{H})$ vs. $\log K_d(\text{U})$ in case of the extraction of uranyl nitrate by 20% TBP, is shown in Fig. 4.

$\text{C}_\text{U} : 0.005 \sim 0.05\text{M}$ TBP 20%, 25°C
 $\text{C}_\text{H} : 0.1 \sim 1\text{M}$

Conditions: C_U and $\text{C}_\text{H} \ll$, and ionic strength of solution is const.

Fig. 4 Simultaneous partition of uranium and nitric acid

This is in good agreement with the prediction of Eq.(16), and suggests that the extraction of uranium and nitric acid can be explained by simultaneous extraction of the

both species expressed by Eqs. (12) and (13) respectively.

Accordingly, the maximum in $K_d(U)$ of uranyl nitrate with the change of nitric acid concentration, C_H , can be derived from the Eqs. (14) and (15). In case where the concentrations are low, if the activity coefficients are assumed to be unity in order to make the discussion simple, the following equation can be deduced.

$$K_d(U) = K(U) [C_H C_{TBP}^0 / (1 + K(H)(C_H)^2)]^2 \quad (17)$$

From Eq. (17), the following expression can be given for $K_d(U)_{max}$,

$$K_d(U)_{max} = K(U) (C_{TBP}^0)^2 / 4 K(H) \\ \text{at } C_H = 1 / \sqrt{K(H)}$$

The comparison between the experimental and calculated results for 20% TBP at 20°C is as the following; The calculated value is $K_d(U)_{max} = 45$ at $C_H = 3.5M$ (in this calculation the value of $K(H)$ is taken as 0.08), and the observed value is $K_d(U)_{max} = 34$ at $C_H = 5M$. The agreement is satisfactory.

III. SPECTROSCOPIC MEASUREMENTS

An approach from the standpoint of structural chemistry becomes essential in order to go into more detailed arguments on the extraction mechanism.

This is well achieved by spectroscopic measurements of the solvents.

In this study, spectroscopic measurements in visible, ultra-violet and infra-red regions were carried out.

A study in the visible region was already carried out by Kaplan, *et al.*⁽⁴⁾, and the infra-red study was carried out independently by Ferraro⁽⁵⁾ during our study, and he came to a similar conclusion as us.

1. Visible spectra

It is well known that uranyl ions give a fine structure in their absorption spectra in the visible region. The change of the structure has been proposed to be assigned to the change of the species of uranyl compounds existing in the solution⁽⁴⁾. For example, the change of the fine structure in the aqueous solutions of uranyl nitrate with nitric acid is attributed to the formation of mono-, di- and tri- nitrate complexes with the increase in concentration of nitric acid as shown in Fig. 5.

This fact seems to give a measure to identify the species of the uranyl complex in the organic phase. Our study, however, have resulted in a conclusion that these fine structures are not easily attributed to a certain definite species of nitrate-complexes, at least,

Fig. 5 Visible absorption spectra of uranyl nitrate in nitric acid media of different concentration

Fig. 6 Visible absorption spectra of 0.05M uranyl nitrate in various alkyl phosphates

in the organic phase.

For example, Fig. 6 gives the visible spectra of stoichiometric compound of uranyl nitrate dissolved in various alkyl phosphates. These structures are much more complicated (especially with tri-*n*-butyl phosphate and tri-*sec*-butyl phosphate) than what will be expected from di-nitrato complex of aqueous solution, and are strongly dependent on the nature of the organic solvents.

To the present, however, we are not capable to assign the fine structure of the visible spectra to any definite type of a complex formation in the solutions.

2. Infra-red spectra

Most profitable informations were obtained by spectroscopic measurements at the infra-red region. The measurement of the

infra-red spectra of organic phosphate solvents in pure state and dissolving uranyl nitrate was carried out. As an example, the infra-red spectra for tri-*sec*-butyl phosphate are shown in Fig. 7 with full and dotted lines respectively.

This is in good agreement with the measurements and the assignments carried out independently by Ferraro⁽⁵⁾.

One very important precaution to be taken at the measurement is to use windows made of AgCl instead of conventional NaCl.

Because of an exchange reaction of Cl and NO₃ at the NaCl windows, a strong false NO₃⁻ absorption is observed, which does not come out by the measurements with AgCl windows.

The assignment of the lines for UO₂²⁺ and NO₃⁻ are given in Table 1.

Most prominent feature is the shift of the vibrational spectra of P=O, P-O-C and the splitting of the NO₃ vibrational spectra. The shift of the $\nu_{P=O}$ is attributed to the complex formation between the solvent and the UO₂²⁺ ion at the oxygen atom of P=O. The shift of ~ 80 cm⁻¹ in the $\nu_{P=O}$ suggests the binding energy of ~ 10 kcal/mole, which is a reasonable figure.

The splitting of ν_{NO_3} means a deformation of the NO₃ ion from the D_{3h} symmetry. This also suggests the bonding interaction of UO₂²⁺

Fig. 7 Infra-red spectra of phosphate and its nitrate complex

Table 1 Vibrational assignment for UO_2^{2+} and NO_3^- ions

$\text{UO}_2^{2+} (D_{\infty h})$	Infra-red	Raman
ν_a	950 cm^{-1} (v.s)	940 cm^{-1}
ν_s	—	830 cm^{-1}
δ_d	210 cm^{-1} (?)	230 cm^{-1}
$\text{NO}_3^- (D_{3h})$	Infra-red	Raman
ν_d	1380 cm^{-1} (v.s.)	1390 cm^{-1}
ν_s	1030 cm^{-1} (w.)	1030 cm^{-1} (P)
π	815 cm^{-1} (w.)	—
δ_d	720 cm^{-1} (w.)	720 cm^{-1} (D)

with one of the oxygens of NO_3^- in the solution.

These two features of the infra-red spectra give a very good measure of the structural chemical approach to the study of the extraction mechanism.

3. Infra-red spectra in the extraction process

A typical example of the infra-red study applied to the study of the extraction mechanism is that of uranyl nitrate by TBP⁽⁶⁾.

From the thermodynamic study described above, it was concluded that the mechanism of the extraction can be explained by simultaneous distribution of proton and uranyl ion between the aqueous and organic phases. The structural chemical study by infra-red spectra gives an information on the detailed mechanism of the extraction, and it becomes possible to follow the formation of complexes of TBP-nitric acid and TBP-uranyl nitrate as well as the competition between the formation of these two.

Fig. 8 gives the infra-red spectra of the

Fig. 8 Replacement of uranyl nitrate with nitric acid

uranyl nitrate-TBP system observed with the change of HNO_3 concentration. Absorptions of 1521, 1275 cm^{-1} are the spectra due to NO_3 group of uranyl nitrate complex and 1187 cm^{-1} is that of $\text{P}=\text{O}-\text{U}$ bonding. These absorptions are, therefore, proportional to the number of uranyl nitrate-TBP complex formed.

On the other hand, the absorptions at 1387, 1305 cm^{-1} , of NO_3 group of nitric acid complex and 1208 cm^{-1} of $\text{P}=\text{O}-\text{H}$ bonding are proportional to the number of nitric acid-TBP complex formed. It is quite interesting that, even though the concentration of $\text{UO}_2(\text{NO}_3)_2$ is kept constant initially, the number of uranyl nitrate-TBP complex increases to the maximum and then decreases with the increase of HNO_3 concentration, while the number of nitric acid-TBP complex increases monotonously.

This is in good agreement with the behavior of $K_d(\text{U})$ of uranyl nitrate extracted by TBP with change in nitric acid concentration. And, since both the nitric acid and uranyl nitrate form complexes with TBP at the same $\text{P}=\text{O}$ position, it can be concluded from this result that first, uranyl nitrate are extracted by complexing with TBP in dilute nitric acid region and then, when the nitric acid concentration is increased, these uranyl nitrate are replaced by nitric acid in competition and this causes the maximum in the value of $K_d(\text{U})$.

IV. DIELECTRIC CONSTANT MEASUREMENT

In order to supplement the spectroscopic measurements, the measurement of dielectric constant was carried out with uranyl nitrate and TBP in CCl_4 solution. The results are shown in Table 2.

It can be seen that the polarization of pure TBP decreases with the addition of uranyl nitrate, and then increases again with the addition of excess TBP. It is to be noted that there is no marked effect of the concentration observed in any case.

The observed values of the polarization

Table 2 Measurement of polarization in CCl_4 solution (at $25 \pm 0.1^\circ\text{C}$)

TBP (wt %)	TBP (cc)	TBP + $\frac{1}{2}$ $\text{UO}_2(\text{NO}_3)_2$ (cc)	$\frac{2}{3}$ TBP + $\frac{1}{2}$ $\text{UO}_2(\text{NO}_3)_2$ (cc)
0.1	0.00117	0.00053	0.00101
0.5	0.00522	0.00285	
1.0	0.01007	0.00422	
1.5	0.01358	0.00667	0.01302
2.0	0.01703	0.00887	
Dipolemoment		3.5 D	3.2 D

shows that there is an interaction between the TBP molecule and uranyl nitrate with a formation of a compound of two TBP molecules and one uranyl nitrate.

The values of the dipolemoment of this assumed compound can be estimated to be 3.2 D from the conventional relation. This is to be compared with the value of 3.5 D of the pure TBP molecule. It can be deduced that the structure of the compound is such that compensates the dipoles of the two solvent molecules partially.

V. CONCLUSION AND DISCUSSION

A general study of the solvent extraction was carried out from two standpoints of thermodynamics and structural chemistry.

As described in Sec. II, the thermodynamic approach is very fruitful in obtaining information of the macroscopic mechanism of the extraction.

The analysis was carried out in a rather general form in order to obtain an idea to what extent such an approach will be useful.

This was applied, as an example, to the extraction system of HNO_3 by TBP and it turned out to give a consistent and reasonable conclusion regarding the extraction mechanism and complex formation.

It is to be noticed that the mechanism of extraction could be well explained by a direct reaction between the ions in the aqueous phase and the organic solvent, without assuming any formation of neutral species or compounds in the aqueous phase.

Further, this analysis was extended to the system of the extraction of uranyl nitrate

and nitric acid by TBP. It was clearly demonstrated that the mechanism of extraction in this case can be explained by the competition in extraction of uranyl nitrate and nitric acid by the solvent molecules, and the influence of nitric acid concentration on the equilibrium distribution ratio of the uranium, $K_d(\text{U})$, was derived with satisfactory agreement between theory and experiments.

The structural chemical approach, which was carried out mainly by spectroscopy of the solvents, could be concluded to be very useful in obtaining informations of the microscopic mechanism of the extraction.

Especially, the infra-red spectra measurements gave the most profitable results. The shift of the spectra of $\text{P}=\text{O}$ vibration of the solvent, and the splitting of the NO_3 vibrational spectra of the nitrate ions gave measures of the complex formation between the solvent and the species extracted.

The same systems of nitric acid-TBP and uranyl nitrate-TBP as those in the thermodynamic study were treated as examples of the structural chemical approach.

It was deduced that the solvent molecules extract the cation by forming a bonding at the $\text{P}=\text{O}$ oxygen.

In case of uranyl nitrate and nitric acid-TBP system, the competition of uranyl nitrate and nitric acid by extraction was evidently observed as a change in the infra-red absorption spectra which was in good agreement with the thermodynamic conclusion.

The most notable point of this study is that the results of the thermodynamic and structural chemical approaches are in good accord and complement each other. It is essential, therefore, to carry out these two approaches simultaneously in order to come to definite conclusion regarding the mechanism of extraction.

In Part II, the results of the study applied to several particular systems of solvent extraction will be reported.

This study was carried out by the solvent extraction research team in the physical chemistry group. The author wishes to express his gratitude to the members of this team,

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研究論文

177. *The Determination of Isotopic Ratio of $^{235}\text{U}/^{238}\text{U}$ by Neutron Activation*

$^{235}\text{U}/^{238}\text{U}$ の放射化分析

By Tomitaro ISHIMORI* and Takeo FUJINO*

The isotopic ratio of $^{235}\text{U}/^{238}\text{U}$ is determined according to the technique of neutron activation analysis without any tedious chemical separation. Although several works had been carried out along this line, the irradiation of uranium sample was limited to some particular conditions because of high fission cross section value for ^{235}U .

In the present methods, 100 mg of uranium oxide-oxalic acid mixture (1:8000) is irradiated in JRR-1 for 1 hr. After about one day cooling, the γ -activity of the sample is studied spectrometrically.

The dilution of uranium sample with a large amount of oxalic acid gives various advantages in slowing down fast neutrons, in capturing recoil fission products or in taking very small amount of uranium for irradiation.

Two methods are proposed and compared each other. The first method is based on the relative ratio between activities in the energy region containing γ -activity due to ^{239}Np and those in the higher energy region free from the activity of ^{239}Np . In the second method, the strength of γ -activity due to fission products is measured as the amount related closely to the ^{235}U concentration.

Recently, numerous methods have been proposed for determining ^{235}U isotopic abundance under the necessity of checking nuclear fuel elements.

Among these methods, the mass spectrometry^{(1)~(5)} is considered to render the most accurate results. Mass spectrometric method combined with isotopic dilution technique was written by Shirley⁽⁴⁾. Webster, *et al.*⁽⁶⁾ studied the accuracy of this technique recently.

Isotopic line shifts in emission spectrometry were also utilized by many investigators^{(6)~(16)}. The determination of ^{235}U by fission neutron counting has been performed by Voss and other workers^{(17)~(19)}, whereas Echo, *et al.*⁽²⁰⁾ also studied the application of delayed neutron counting for this purpose.

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