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A Study of the Mechanism for the Extraction of Uranium, Water, and Nitric Acid with Trioctylphosphine Oxide Using a Binary Molten Mixture of Biphenyl and Naphthalene as the Solvent

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Liquid-liquid distribution with trioctylphosphine oxide (TOPO) and a binary molten mixture of biphenyl and naphthalene (weight ratio=3:1) has been examined for the extraction of uranium from a 0.1 mol kg^{-1} nitric acid solution. The stoichiometry of the TOPO complex of uranyl nitrate in the molten biphenyl-naphthalene phase was established to be $UO_2(NO_3)_2(TOPO)_2$. The extracted species of water and nitric acid are $H_2O \cdot TOPO$ and $H_3O^+ \cdot TOPO \cdot NO_3^-$ at concentrations of TOPO of less than 0.1 mol kg^{-1}. The thermodynamic quantities ($\Delta H°$, $\Delta G°$, and $\Delta S°$) were obtained for the extraction of uranyl nitrate, nitric acid, and water into TOPO-biphenyl-naphthalene and TOPO-cyclohexane solutions from the temperature dependence of the extraction constants. More exothermic enthalpy and smaller entropy changes were observed for the binary molten mixture; these differences were attributed to the aromatic and viscous properties of the solvent.

Solvent extraction systems with organophosphorus compounds, such as trioctylphosphine oxide (TOPO) and tributylphosphate (TBP), have been reported in many papers[1-5] and have been documented in books.[6-7] Furthermore, to clarify the mechanism of the selective extraction many fundamental investigations have been done: the competitive extraction of uranium complexes and acid,[8-9] the extraction of water and acids,[10-16] and the thermodynamic quantities of the free energy, enthalpy, and entropy changes in the extraction process.[17-21]

A method involving solid-liquid separation after liquid-liquid extraction has been developed by Fujinaga *et al.*[22] The method has been applied to the spectrophotometric determination of micro amounts of metals by using a molten organic compound, such as biphenyl (mp 70 °C)[22] or naphthalene (mp 80 °C),[23-25] combined with appropriate chelating agents such as 8-quinolinol. The extraction method with molten solvents has some advantages: metal ions can be efficiently concentrated, since only an organic/aqueous volume ratio of 1/1000 is available, the phase separation is easily facilitated by cooling without a separatory funnel, and high distribution ratios are obtained.

Recently we have studied the process of capturing uranium from sea water by adsorption on adsorbents made of polyacrylamide and hydrous titanium oxide.[26-27] Although the solvent extraction with TOPO and ordinary liquid solvents such as toluene has been carried out by others,[4-5] we ourselves have efficiently applied solvent extraction with a molten solvent to the concentration of uranium in the eluent in order to determine uranium or zirconium spectrophotometrically.[28-32]

However, the molten-solvent method suffers from two disadvantages: the volatilization of naphthalene and the adhesion of the extractants to the walls of vessels. It is desirable to do extraction at as low a temperature as possible to minimize volatilization. Therefore, the mixed molten solvent of molten biphenyl and naphthalene was chosen because the melting point of the extraction phase become lower, reaching a minimum temperature of 52 °C at a biphenyl-naphthalene weight ratio of 3/1. There have, however, been few reports on the mechanism of the extraction with molten solvents, especially with the binary molten solvent.

The present paper investigates the separation of uranium as the TOPO complex by solvent extraction with a binary molten mixture of biphenyl and naphthalene and elucidates the mechanism of the extraction more thermodynamically than the extraction by cyclohexane. There is an appreciable difference in the enthalpy and entropy changes of extraction between the binary molten-mixture solvent and cyclohexane. The enthalpy and entropy changes for the extraction process indicate that the extracted species, $UO_2(NO_3)_2(TOPO)_2$, is more stable in the binary molten solvent than in cyclohexane.

Experimental

Reagents. TOPO (Doindo Co., Ltd.) of a reagents grade was used without further purification. A standard uranium solution (10^{-2} mol kg^{-1}) was prepared by dissolving 0.502 g of uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$, Yokozawa Chemical Co., Ltd.) in deionized water and then diluting it to 100 cm^3. The binary molten mixture solvent with a melting point of 52 °C was prepared by mixing 100 g of naphthalene (mp 80 °C) and 300 g of biphenyl (mp 70 °C). The other reagents used were of an analytical grade.

Procedure

Extraction of Uranium(VI). Twenty cm^3 of 10^{-3} mol kg^{-1} uranium in a 0.1 mol kg^{-1} nitric acid solution was transferred to a 50-cm^3 glass-stoppered flask. Then 5 g of the mixture of biphenyl-naphthalene containing TOPO (0.01—0.3 mol kg^{-1}) was added to it, and the flask was heated on a water bath at 60 °C until the TOPO-biphenyl-naphthalene had melted completely. The mixture was stirred for 3 h with a magnetic stirrer (Toyo Kagaku Sangyo Co., Ltd., Model SS-5) and then allowed to stand for 3 h for the phase-separation.

Determinaton of Distribution Ratio of Uranium. The determination of the uranium(VI) remaining in the aqueous phase was carried out spectrophotometrically with 1-(2-pyridylazo)-2-naphthol (PAN).[33] After the phase-separation, an aliquot of the aqueous phase was transferred into a 100-cm^3 separatory funnel by means of a pipet. A 100 mg part in sulphamic acid was then added, followed by appropriate amounts of concentrated nitric acid and water to give 2 mol kg^{-1} nitric acid in a final volume of 20 cm^3. Five cm^3 of the 0.05 mol dm^{-3} TOPO cyclohexane solution was then added, and the funnels were vigorously shaken for 1 min. After phase-separation, the aqueous phase was removed and the organic phase was transferred to a 10-cm^3 volumetric flask containing 1 cm^3 of the 0.1% PAN solution and 2 cm^3 of a 10% triethanolamine ehtanol solution. The solution was adjusted to 10 cm^3 with ethanol. After mixing well, the absorbance of the solution at 555 nm was measured against a reagent blank. The distribution ratio was calculated according to this relation: $D=$ (concentration of uranium(VI) in the organic phase)/(concentration of uranium(VI) in the aqueous phase) × (weight of aqueous phase)/(weight of organic phase).

Determination of Water Content in the Organic Phases. After phase-separation, an aliquot of the molten organic phase (TOPO–biphenyl–naphthalene) was transferred into a 10-cm^3 Erlenmyer flask with a heated pipet, because the molten organic phase is solidified at room temperature. The amount of the organic phase was weighed. Then the solidified organic phase was dissolved in a constant amount of cyclohexane. The water content in the organic phase was measured coulometrically by using a Hiranum AQ-3C aquacounter. In the case of the binary molten solvent, the water content was corrected for the amount of water contained in cyclohexane alone.

Determination of Acid Content in the Organic Phase. The content of acid in the organic phase was determined by back-titration with the standard nitric acid solution (0.1 mol dm^{-3}) after the addition of a constant excess of 0.1 mol dm^{-3} potassium hydroxide solution. Phenolphthalein was used as the indicator.

Results and Discussion

Extraction of Acid and Water. The uranium nitrate and acid are extracted competitively from an aqueous solution.[8–9] It is well known that a trace amount of water is also extracted with an organophosphorus compound.[10–16] Therefore, it is necessary to examine the extraction behavior of acid and water into the binary molten solvent prior to the extraction of uranium(VI). The total concentration of water in the organic phase is written as:

$$[H_2O]_{org} = [H_2O]_{org,blank} + [H_2O]_{org,ext}, \tag{1}$$

where $[H_2O]_{org,\,blank}$ and $[H_2O]_{org,\,ext}$ are the concentrations of the water in the binary molten solvent and of the water extracted with TOPO. The relation of the concentration of extracted water to that of TOPO in the organic phase is shown in Fig. 1. The extraction equilibrium is:

$$m\text{TOPO}_{org} + nH_2O_{aq} \rightleftharpoons m\text{TOPO}\cdot nH_2O_{org}, \tag{2}$$

with the corresponding extraction constant K_{H_2O}:

$$K_{H_2O} = [m\text{TOPO}\cdot nH_2O]_{org}/[\text{TOPO}]^m_{org}[H_2O]^n_{aq}. \tag{3}$$

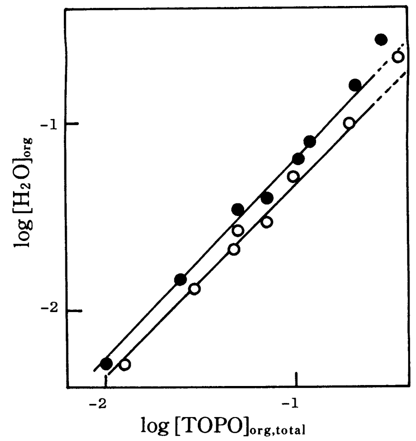

Fig. 1. Variation of water content of the organic phase with total TOPO concentration in cyclohexane or biphenyl–naphthalene, after correction for the dissolved water by the diluent.
Aqueous phase: 10 g, organic phase: 5 g, -●- cyclohexane, at 50 °C, -○- biphenyl–naphthalene, at 55 °C.

In view of the low solubility of the studied TOPO in water and its relatively low initial concentration in the organic phase, the water activity of the aqueous phase may be assumed to be unity; the plot of $\log[H_2O]_{org,\,ext}$ *vs.* $\log[\text{TOPO}]_{org}$ thus reflects the number of water molecules per TOPO molecule. In Fig. 1 the free TOPO concentration is calculated on the basis of its initial concentration in the organic phase and the amount of the water extracted. It can be seen that the log-log plot is linear from 0.01 to 0.1 mol kg^{-1} TOPO, with a slope of 1.0 corresponding to $m=n$. From the dependence of the amount of coextracted water on that of TOPO and from the IR studies,[15] we can say that the 1-1 species TOPO · H_2O is the predominant species in various solvents, such as cyclohexane and carbon tetrachloride.[14] From Eqs. 1 and 3 with $m=n=1$, we get the following relation:

$$[H_2O]_{org,ext} = [K_{H_2O}/(1+K_{H_2O})][\text{TOPO}]_{org}. \tag{4}$$

The K_{H_2O} values at various temperatures were evaluated by using the log-log plot of Eq 4, the results obtained are given in Table 1. The K_{H_2O} value of 3.13 for cyclohexane is comparable with the value reported

Table 1. Extraction constants of water and nitric acid with TOPO at various temperatures

t/°C	Cyclohexane			
	25	30	40	50
K_{H_2O}	2.12	1.80	1.89	1.64
K_{HNO_3}	42.0	38.7	35.0	31.8
t/°C	Biphenyl-naphthalene			
	55	60	65	
K_{H_2O}	0.73	0.70	0.61	
K_{HNO_3}	24.9	12.3	—	

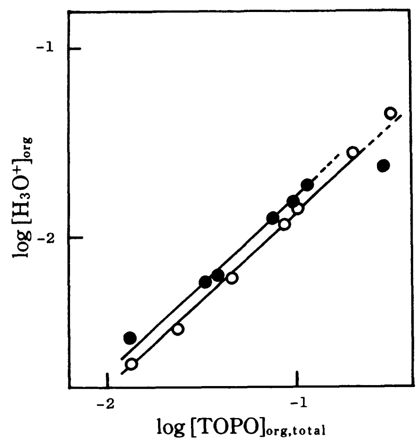

Fig. 2. Variation of organic phase acid with TOPO ncentration in cyclohexane or biphenyl-naphthale.
-●- Cyclohexane, at 50 °C, -O- biphenyl-naphthalene, at 55 °C.

(3.57) at 25 °C[14]: the slightly smaller K_{H_2O} values for TOPO in the binary solvent system have also been reported for carbon tetrachloride (0.85,[10] 0.56,[10] 0.68,[11] at 25 °C). Binary molten biphenyl-naphthalene or cyclohexane containing quantities of TOPO ranging from 0.01 to 0.3 mol kg^{-1} was equilibrated with the 0.1 mol kg^{-1} nitric acid solution. The results are shown in Fig. 2. The amount of nitric acid extracted into the binary molten solvent and cyclohexane without TOPO was confirmed to be negligibly small. The 1:1 stoichiometry for nitric acid-TOPO extraction has been well established,[15] and the above results in the binary solvent are compatible with the 1:1 stoichiometry. Therefore, the extraction equilibrium for nitric acid is written by Eq 5:

$$H^+_{aq} + NO_3^-{}_{aq} + TOPO_{org} \rightleftharpoons HNO_3\cdot TOPO_{org}, \qquad (5)$$

and the extraction constant is:

$$K_{HNO_3} = [HNO_3\cdot TOPO]_{org}/ [H^+]_{aq}[NO_3^-]_{aq}[TOPO]_{org} f_{H^+} f_{NO_3^-}. \qquad (6)$$

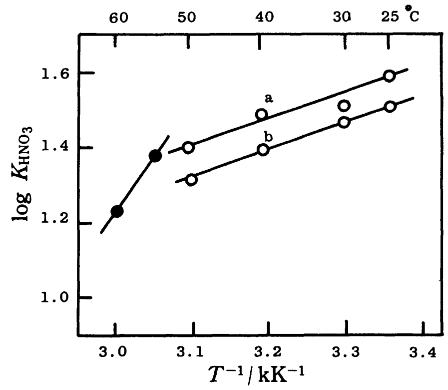

Fig. 3. Effect of varying temperature on extraction of nitric acid by TOPO in cyclohexane or biphenyl-naphthalene.
-●- Biphenyl-naphthalene, TOPO concentration in mol kg^{-1}: 0.013 to 0.3, -O- cyclohexane, TOPO concentration in mol kg^{-1}: a, 0.12; b, 0.09.

In a way similar to that for water extraction, the K_{HNO_3} values were estimated; they are given in Table 1. The mean activity coefficients of nitric acid were estimated by the extrapolation of values at concentrations of more than 0.1 mol kg^{-1} at 25 °C;[34] their temperature dependences were neglected.

Figure 3 shows the temperature dependence of nitric-acid extraction; the thermodynamic quantities ($\Delta H°$, $\Delta G°$, and $\Delta S°$) foı extracton were calculated by means of the following equations:

$$\Delta G° = -2.303\,RT \log K_{ex}, \qquad (7)$$

$$\Delta H° = -2.303\,R(\mathrm{d} \log K_{ex}/\mathrm{d}(1/T)), \qquad (8)$$

$$\Delta S° = (\Delta H° - \Delta G°)/T, \qquad (9)$$

where R is the gas constant and T is the absolute temperature. The results obtained are given, together with those for the water extraction, in Table 4. It should be noted that the enthalpy and entropy changes for the binary system are much larger han those for cyclohexane. The extraordinarily large enthalpy changes accompanying the large entropy loss for nitric acid should be attributed to the solvation of the TOPO nitrate complex by the molten solvent of an aromatic character. Similar aspects were observed for the uranium extraction, as will be described later.

Extraction of Uranium(VI). The distribution ratios of the uranium-TOPO complex at a uranium concentration of 1×10^{-3} mol kg^{-1} from a 0.1 mol kg^{-1} nitric acid solution were determined as a function of the TOPO concentrations, ranging from 0.01 to 0.3 mol kg^{-1}. The results are shown in Fig. 4. The slope of the line in Fig. 4 is 2.1, indicating the composition of the extracted species to be $UO_2(TOPO)_2(NO_3)_2$, just as in cyclohexane.[35]

The distribution ratio for the extraction of uranium(VI) from a 0.1 mol kg^{-1} nitric acid solution was obtained as a function of the TOPO concentration at different temperatures. The results are given in Tables 2 and 3. The D value decreases with an increase in the temperature under all sets of conditions examined. The equilibrium expression for the extrac-

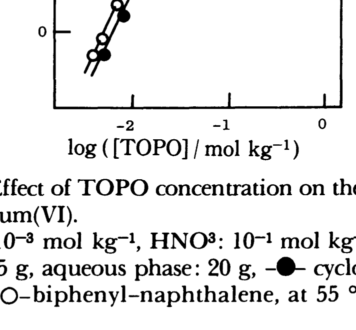

Fig. 4. Effect of TOPO concentration on the extraction of uranium(VI).
U(VI): 10^{-3} mol kg^{-1}, HNO^3: 10^{-1} mol kg^{-1}, Organic phase: 5 g, aqueous phase: 20 g, -●- cyclohexane, at 50 °C, -O-biphenyl-naphthalene, at 55 °C.

TABLE 2. VARIATION IN THE DISTRIBUTION RATIO OF U(VI) FOR CYCLOHEXANE WITH THE TOPO CONCENTRATION AT DIFFERENT TEMPERATURES

TOPO(mol kg^{-1})	0.005	0.007	0.008	0.010	0.013	0.015	0.033	0.067
D, at 20 °C	1.4	—	3.7	7.2	—	18	—	—
25	—	2.9	—	—	11	—	1.2×10^2	8.6×10^2
30	1.2	2.5	2.6	4.7	9.0	11	1.0×10^2	4.9×10^2
40	0.9	—	1.6	3.4	—	8.7	—	—
50	0.6	1.7	1.4	2.9	4.7	8.3	23	1.9×10^2
60	—	—	—	—	2.2	—	14	1.0×10^2

U(VI): 10^{-3} mol kg^{-1}, HNO_3: 10^{-1} mol kg^{-1}, organic phase/aqueous phase: 5/20, solvent: cyclohexane.

TABLE 3. VARIATION IN THE DISTRIBUTION RATIO OF U(VI) FOR MOLTEN BIPHENYL-NAPHTHALENE WITH THE TOPO CONCENTRATION AT DIFFERENT TEMPERATURES

TOPO(mol kg^{-1})	0.010	0.018	0.032	0.054
D, at 55 °C	3.2	12	53	1.8×10^2
60	2.3	7.4	44	1.7×10^2
65	2.0	6.7	32	1.3×10^2

U(VI): 10^{-3} mol kg^{-1}, HNO_3: 10^{-1} mol kg^{-1}, organic phase/aqueous phase: 5/20, solvent: molten biphenyl-napthalene (weight ratio=3:1).

tion of uranium is given by Eq. 10:

$$UO_2{}^{2+}{}_{aq} + 2NO_3{}^{-}{}_{aq} + 2TOPO_{org} \rightleftharpoons UO_2(NO_3)_2(TOPO)_{2\,org}. \tag{10}$$

Thus, the corresponding extraction constant can be expressed by Eq.11:

$$K_{ex} = [UO_2(NO_3)_2(TOPO)_2]_{org}/ [UO_2]_{aq}[NO_3{}^{-}]^2_{aq}\,[TOPO]^2_{org}\,f_{UO_2{}^{2+}}f^2_{NO_3{}^{-}} \tag{11}$$

where the square brackets refer to the concentrations and where f is the activity coefficient of the respective species. The extraction constant was estimated from the distribution ratio D by Eq.12:

$$K_{ex} = D(1+\sum_1^n \beta_n[NO_3{}^{-}]^n_{aq})/ [NO_3{}^{-}]^n_{aq}[TOPO]^2_{org}\,f_{UO_2{}^{2+}}f^2_{NO_3{}^{-}}, \tag{12}$$

where the $(1+\sum_1^n\beta_n[NO_3{}^-]^n_{aq})$ term takes into account the formation of uranyl nitrate complexes with the formation constant for $UO_2(NO_3)_n^{(2-n)+}$ in the aqueous phase. Thus, $D(1+\sum_1^n\beta_n[NO_3{}^-]^n_{aq})$ is equal to the ratio of the concentration of $UO_2(NO_3)_2(TOPO)_2$ in the organic phase (assuming that this is the only species extracted) to that of free UO_2^{2+} in the aqueous phase.

From the temperature dependence of the extractability of 0.1 mol kg^{-1} nitric acid, it was found that, at a TOPO concentation of 0.05 mol kg^{-1} the aqueous nitric acid concentration in mol kg^{-1} varies from 0.0982 at 25 °C to 0.0984 at 50 °C for cyclohexane and from 0.0981 at 55 °C to 0.0982 at 60 °C for the molten mixed solvent.

Therefore, it is reasonable to assume that the equilibrium concentrations of the nitrate ion in the aqueous phase and of free TOPO in the organic phase would remain practically constant over the temperature range studied. A value of 0.02 for $(1+\sum_1^n\beta_n[NO_3{}^-]^n_{aq})$ in a 0.1 mol kg^{-1} nitric acid solution was reported at 25 °C by Patil *et al.*[19] The values of $(1+\sum_1^n\beta_n[NO_3{}^-]^n_{aq})$ for uranium(VI) were estimated by using the method of cation exchange: 1.02 (25 °C) in a 0.1 mol dm^{-3} nitric acid solution,[19] and 2.1 (25 °C) and 2.3 (40 °C) in a 3 mol dm^{-3} nitric acid solution.[36] If the correction term $(1+\sum_1^n\beta_n[NO_3{}^-]^n_{aq})$ and activity coefficients do not change significantly over the temperature range investigated, the enthalpy change, $\Delta H°$, associated with the extraction of uranium can be calculated from Eq. 8.

The logarithms of the distribution ratio at different concentrations of TOPO were plotted against the reciprocal temperature. Some typical plots for the extraction of nitric acid and uranium with cyclohexane and the molten mixture solvent are shown in Figs. 3 and 5 respectively. All the plots were linear. The $\Delta H°$ values obtained from these plots by using a least-square procedure are given in Table 4. It was found that the $\Delta H°$ values are independent of the concentration of TOPO, supporting the above assumptions. The $\Delta H°$ values for uranium in the binary molten solvent are two times higher than that in cyclohexane.

The Gibbs-free-energy and entropy changes for uranium extraction obtained by using Eq. 7 are given in Table 4. A mean activity coefficient of 0.60 for the UO_2^{2+} ions in *ca.* 0.1 mol kg^{-1} nitric acid, which was

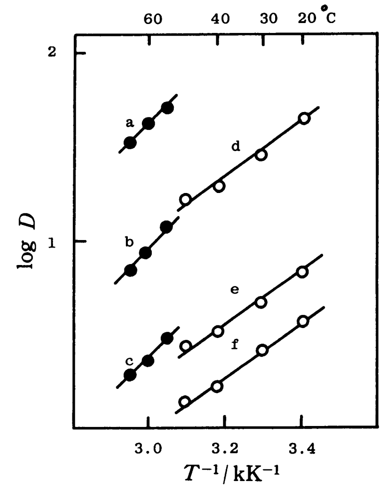

Fig. 5. Effect of varying temperature on extraction of uranium(VI) by TOPO in cyclohexane and biphenyl-naphthalene.

-●- Biphenyl-naphthalene, TOPO concentration in mol kg^{-1}: a, 0.032; b, 0.018; c, 0.009, -O- cyclohexane, TOPO concentration in mol kg^{-1}: d, 0.015; e, 0.010; f, 0.008.

Table 4. Thermodynamic quantities ($\Delta H°$, $\Delta G°$, and $\Delta S°$) associated with the extraction of water, nitric acid, and uranium(VI) into the TOPO-organic phase

		$\Delta H°$/kJ mol^{-1}	$\Delta G°$/kJ mol^{-1}	$\Delta S°$/J K mol^{-1}
H_2O-TOPO in cyclohexane,	at 25 °C	−8.5	−1.9	−22
	at 50 °C	−8.5	−1.3	−22
H_2O-TOPO in the binary molten biphenyl-naphthalene,	at 55 °C	−17	0.9	−53
HNO_3-TOPO in cyclohexane,	at 25 °C	−14	−8.9	−16
		(−16.3)	(−5.4)	(−36.5)
	at 50 °C	−14	−9.2	−14
HNO_3-TOPO in the binary molten biphenyl-naphthalene,	at 55 °C	−63	−8.8	-1.6×10^2
$UO_2(NO_3)_2(TOPO)_2$ in cyclohexane,	at 25 °C	−23	−42	63
		(−24.3)	(−48.1)	(79.8)
	at 50 °C	−23	−42	58
$UO_2(NO_3)_2(TOPO)_2$ in the binary molten biphenyl-naphthalene,	at 55 °C	−44	−45	1.2

The values in paremtheses are quoted from Ref. 35.

calculated by means of the modified Debye-Hückel equation,[34] was used over the temperature range studied.

From Table 3 it may be seen that uranium is a little more extractable in the binary molten solvent, with a more negative enthalpy and smaller entropy changes, than in cyclohexane. As has been stated earlier, a more exothermic enthalpy change is also observed for the nitric acid-molten solvent system; it may be due to the stronger solvation of the extracted TOPO complex by aromatic solvents, with additional interactions of π-electrons, compared with the case for alicylic cyclohexane.

In addition to the strong solvation effect, the viscous characteristics of the binary molten solvent can also be responsible for the smaller entropy changes. However, in the cyclohexane phase the extracted species disperse easily, resulting in larger entropy changes.

In conclusion, the extraction behavior of uranium(VI), water, and nitric acid for the molten biphenyl-naphthalene solvent is similar to that for cyclohexane. However, the metal UO_2^{2+} ion is extracted in the molten solvent with more exothermic enthalpy and smaller entropy changes than those for the cyclohexane system.

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References

1) T. Ishimori, K. Watanabe, and E. Nakamura, *Bull. Chem. Soc. Jpn.*, **33**, 639 (1960).

2) T. Ishimori, K. Watanabe, and L. Kimura, *Nippon Genshiryoku Gakkai Shi*, **2**, 750 (1960).

3) H. Umezawa and R. Hara, *Anal. Chim. Acta*, **25**, 360 (1961).

4) J. C. White and W. J. Ross, NAS-NA 3102 (1961).

5) C. A. Blake, K. B. Brown, and C. F. Coleman, ORNL, 26 (1965).

6) Y. Marcus and A. S. Kerts, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley, New York (1969).

7) M. Tanaka, "Youbai Chyushutsu No Kagaku," Kyoritsu, Tokyo (1979).

8) K. Watanabe, *J. Nucl. Sci. Technol.*, **1**, 155 (1964).

9) T. Sato and T. Nishida, *J. Inorg. Nucl. Chem.*, **36**, 2087 (1974).

10) T. J. Conocchioli, M. I. Tocher, and R. M. Diamond, *J. Phy. Chem.*, **69**; 1106 (1965).

11) J. W. O'Laughlin, J. J. Richard, J. W. Ferguson, and C. V. Banks, *Anal. Chem.*, **40**, 146 (1968).

12) M. Niitsu, N. Iritani, and T. Sekine, *Bull. Chem. Soc. Jpn.*, **52**, 1799 (1979).

13) M. Niitsu and T. Sekine, *Bull. Chem. Soc. Jpn.*, **50**, 1015 (1977).

14) C. Klofyter, S. Palik, M. Sfnegacnik, and B. Jerkovic, *J. Inorg. Nucl. Chem.*, **34**, 3873 (1972).

15) M. Senegacnik, C. Klofuter, S. Paljk, and L. Smrekar, *J. Inorg. Nucl. Chem.*, **32**, 1659 (1970).

16) J. R. Johnson, S. D. Christian, and H. E. Affsprung, *J. Chem. Soc., A*, **1966**, 77.

17) A. Ramanujam, V. V. Ramakrishna, and S. K. Patil, *J. Inorg. Nucl. Chem.*, **40**, 1167 (1978).

18) T. H. Siddall, *J. Am. Chem. Soc.*, **81**, 4176 (1959).

19) S. V. Bagawde, P. R. Vasudava Rao, V. V. Ramakrishna, and S. A. Patil, *J. Inorg. Nucl. Chem.*, **40**, 1913 (1978).

20) S. A. Pai, J. P. Shukla, and M. S. Subramanian, *J. Inorg. Nucl. Chem.*, **43**, 1045 (1981).

21) D. G. Kalina, G. W. Mason, and E. P. Horeitz, *J. Inorg. Nucl. Chem.*, **43**, 159 (1981).

22) T. Fujinaga, T. Kuwamoto, E. Nakayama, and M. Satake, *Bunseki Kagaku*, **18**, 398 (1969).

23) M. Satake, Y. Matsumura, and T. Fujinaga, *Talanta*, **25**, 71, (1978).

24) T. Fujinaga, M. Satake, and T. Yonekubo, *Bull. Chem. Soc. Jpn.*, **46**, 2090 (1976).

25) T. Fujinaga, M. Satake, and M. Shimizu, *Bunseki Kagaku*, **26**, 313 (1976).

26) Y. Shigetomi, T. Kojima, and M. Shinagawa, *J. Nucl. Sci. Technol.*, **14**, 811 (1977).

27) Y. Shigetomi, T. Kojima, and M. Shinagawa, *Bunseki Kagaku*, **26**, 167 (1977).

28) Y. Shigetomi, T. Kojima, H. Kamba, and Y. Yamamoto, *Anal. Chim. Acta*, **116**, 199 (1980).

29) Y. Shigetomi, T. Kojima, and H. Kamba, *J. Nucl. Sci. Technol*, **20**, 120 (1983).

30) T. Kojima, Y. Shigetomi, H. Kamba, H. Iwashiro, T. Sakamoto, and A. Doi, *Analyst*, **107**, 519 (1982).

31) Y. Shigetomi, T. Kojima, and H. Kamba, *Talanta*, **27**,

1079 (1980).
32) Y. Shigetomi and T. Kojima, *Bull. Chem. Soc. Jpn.*, **54**, 1887 (1981).
33) R. J. Baltisberger, *Anal. Chem.*, **36**, 2369 (1964).
34) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth, London (1965).
35) A. H. A. Heyn and Y. D. Soman, *J. Inorg. Nucl. Chem.*, **26**, 287 (1964).
36) S. K. Patil, V. V. Ramakrishna, G. V. N. Avadhny, and M. V. Ramaniah, *J. Inorg. Nucl. Chem.*, **35**, 2537 (1973).