研究简报

正辛烷为稀释剂不对称 *N*-甲基-*N*-辛基烷基酰胺萃取铀(Ⅵ)的研究

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Extraction of U(Ⅵ) with Unsymmetrical *N*-methyl-*N*-octyl alkylamide in *n*-Octane

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Abstract:　The extraction of uranyl nitrate was studied with newly synthesized unsymmetrical alkylamides, *N*-methyl-*N*-octyloctylamide (MOOA), *N*-methyl-*N*-octyldecanamide (MODA), and *N*-methyl-*N*-octyldodecanamide (MODOA), employing *n*-octane as diluent. The effect of the concentrations of nitric acid, sodium nitrate and extractants on the extraction was investigated and the extraction mechanism was suggested. The effect of temperature on the extraction was also studied and the related thermodynamic functions were calculated. The extracted species were characterized by FTIR spectrometry.

Key words: *N*-methyl-*N*-octyl alkylamide; *n*-octane; extraction; uranyl nitrate

0　Introduction

There has been significant interest in recent years in the study of amides as alternative extractants to organophosphorus compounds, e.g., tributylphosphate (TBP) for actinide separation[1~5]. The products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes than those of organophosphorus compounds. In addition, the amide ligands are completely incinerable, which implies that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced[4~6].

The selection of the substitutes on the nitrogen atoms (R and R′) in amides is very important to fa-cilitate metal-ion coordination and to allow the solubility of the amide and its adducts in the organic phase[7]. In order to fulfill both objectives, R and R′ should have different sizes. If R is a small group (typically methyl) and R′ a bigger one, both criteria are satisfied: the stereochemical hindrance around the carbonyl oxygen atoms is kept to minimum and the lipophilic character of the ligands is attained by the presence of a higher chain-alkyl or aryl groups at R′. Cuilerdier[8], Spjuth[9], Mowafy[10] and Nakamura[11] reported the extractability of some unsymmetrical amides for uranium(Ⅵ) and (or) lanthanides(Ⅲ). This paper presents the extraction of U(Ⅵ) from nitric acid

solution with unsymmetrical monoamides in aliphatic diluent, *n*-octane.

1　Experimental

1.1　Reagents

The extractants were obtained by the reaction of N-methyloctylamine with corresponding alkyl chloride in ethylene chloride medium. The unsymmetrical N-methyloctylamine was prepared by reduction of N-methyloctylamide using $NaBH_4$ as reducing agent and acetic acid as catalyst in THF. MOOA, MODA and MODOA were purified by distillation under vacuum and the final products were checked for purity by elemental analysis, IR and ^1H NMR.

N-methyl-*N*-octyloctylamide(MOOA) (yield 69%), colorless oil, b.p. 150~152 ℃/2~4 mmHg; $\nu_{C=O}$(film)/cm^{-1} 1 653.4; δ_H (300 MHz, DMSO), 0.857(6H, C-CH$_3$), 1.247(20H, -CH$_2$-), 1.475 (2H, -CH$_2$-C-N-), 2.233(2H, -CH$_2$-CO), 2.762, 2.906(3H, N-CH$_3$), 3.23 (2H, N-CH$_2$-). Elem. Anal. for $C_{17}H_{35}NO$ (Calcd.): C 75.23% (75.77%), H 12.74% (13.08%), N 4.97% (5.20%).

N-methyl-*N*-octyldecanamide(MODA)(yield 65%), colorless oil, b.p. 154~156 ℃/2~4 mmHg; $\nu_{C=O}$(film)/cm^{-1} 1 651.4; δ_H (300 MHz, DMSO), 0.856(6H, C-CH$_3$), 1.242 (24H, -CH$_2$-), 1.459 (2H, -CH$_2$-C-N-), 2.232(2H, -CH$_2$-CO), 2.762, 2.906(3H, N-CH$_3$), 3.234 (2H, N-CH$_2$-). Elem. Anal. for $C_{19}H_{39}NO$ (Calcd.): C 76.43% (76.70%), H 12.94% (13.21%), N 4.91% (4.71%).

N-methyl-*N*-octyldodecanamide (MODOA) (yield 62%), colorless oil, b.p. 194~200 ℃/2~4 mmHg; $\nu_{C=O}$(film)/cm^{-1} 1 653.2; δ_H (300 MHz, DMSO), 0.855(6H, C-CH$_3$), 1.238 (28H, -CH$_2$-), 1.453 (2H, -CH$_2$-C-N-), 2.231(2H, -CH$_2$-CO), 2.761, 2.905(3H, N-CH$_3$), 3.233 (2H, N-CH$_2$-). Elem. Anal. for $C_{21}H_{43}NO$ (Calcd.): C 77.53% (77.47%), H 13.31% (13.40%), N 4.30% (3.96%).

Other reagents used in this work were all A.R. grades.

1.2　Extraction and analytical procedures

Except otherwise specified, Organic phase was 0.20 mol mol·dm^{-3} extractant in *n*-octane, the aqueous phase was composed of 0.01 mol·dm^{-3} HNO$_3$, 3.00 mol·dm^{-3} NaNO$_3$ and 0.005 mol·dm^{-3} UO$_2$(NO$_3$)$_2$.

Equal volumes of organic and aqueous phases

were agitated for 30 minutes (enough for equilibrium) at 25 ℃ under the desired experimental conditions. The two phases were then centrifuged and assayed by taking known aliquots (0.05~0.1 mL) from the aqueous phases. The concentrations of U(Ⅵ) in the sample were determined by Arsenazo-Ⅲ visible spectrophotometric analysis and that in organic phase were obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of U(Ⅵ). The distribution ratio(D) was calculated as the ratio of the concentration of U(Ⅵ) in organic phase to that in aqueous phase.

1.3　Preparation and characterization of extracted species

The extracted species was prepared by shaking the extractant solutions with a concentrated solution of UO$_2$(NO$_3$)$_2$, centrifuging and the separating organic phase. The organic solvent was removed and FTIR spectra of the residuals were recorded on an FTS-165 Spectrometer in the range 400~4 000 cm^{-1} using Nujol mull technique. The scan times and the resolution were 60 and 2 cm^{-1}, respectively.

2　Results and discussion

2.1　Effect of nitric acid concentration on the extraction of U(Ⅵ)

The effect of nitric acid concentration from 1.00 to 5.00 mol·dm^{-3} on the extraction of U(Ⅵ) with 0.20 mol·dm^{-3} MOOA, MODA or MODOA is shown in Fig.1. The results indicate that the distribution ratio of U(Ⅵ) increases with the increase in the concentration of HNO$_3$, however, it changes slowly when HNO$_3$ concentration is above 4 mol·dm^{-3}, which is attributed to the competition between HNO$_3$ and UO$_2^{2+}$ with the extractants and the salt effect. The higher *D* values in MOOA system may be due to the formation of third phase for more than 4.0 mol·dm^{-3} HNO$_3$ concentration. Comparison of this result with that employing toluene as diluent shows that the extraction efficiency of amides in *n*-octane for uranyl ion is about half of that in toluene[12]. Fig.1 also shows that the length of the alkyl chain adjacent to the carbonyl group affects the extraction ability slightly. Compared with the result of the extraction of *N*,*N*-dibutyldodecanamide[13] one could see that the adoption of unsymmetrical substituted alkyl does not remarkably improve the extractability of monoamides, which indicates that the

two straight long chain alkyls adjacent to nitrogen atom in monoamide extractnats bring only small steric hindrance effect to the formation of the extracted species of uranyl ion.
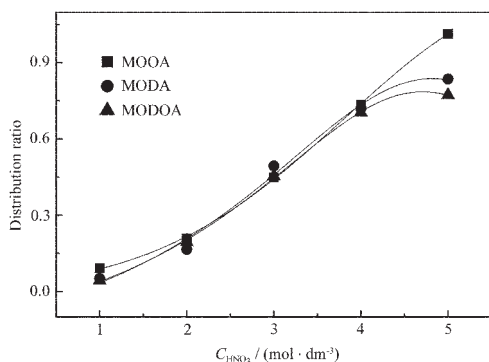

Fig.1　Effect of HNO₃ concentration on the extraction of U(Ⅵ)

2.2　Effect of Sodium nitrate concentration on the extraction of U (Ⅵ)

The effect of sodium nitrate concentration at the presence of 0.01 mol·dm⁻³ HNO₃ on the extraction distribution ratio of U(Ⅵ) is shown in Fig.2. The distribution ratio of U (Ⅵ) increases significantly with increasing NaNO₃ concentration in which the salt effect, especially the co-ion effect plays a crucial role. This is in agreement with the results of Cuillerdier et al.[8].
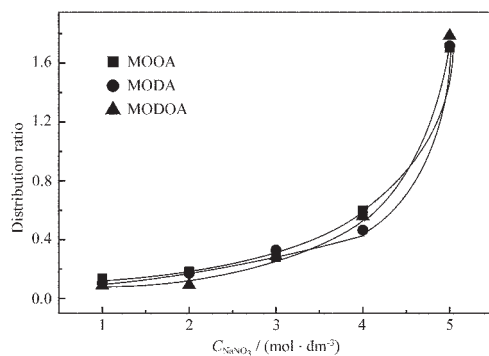

Fig.2　Effect of NaNO₃ concentration on the extraction of U(Ⅵ)

2.3　Effect of the concentration of extractant on the extraction of U(Ⅵ)

The variation in the distribution ratio of U(Ⅵ) with the studied monoamides in *n*-octane is given in Fig.3. The initial HNO₃ concentration was fixed at low level of 0.01 mol·dm⁻³ to minimize the HNO₃ effect on the extraction.

The extraction equilibrium of the uranyl nitrate with monoamide can be written as

$$UO_2^{2+} + 2NO_3^- + nA_{(o)} = UO_2(NO_3)_2 \cdot nA_{(o)} \tag{1}$$
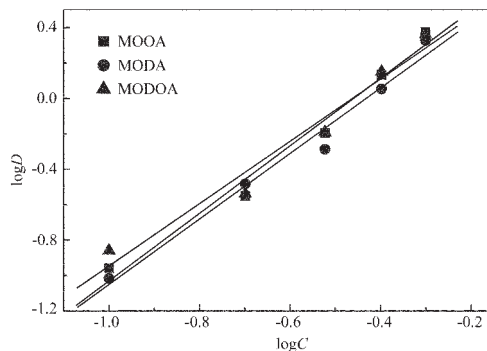
in which A is the employed monoamides, the sub-

Fig.3　Effect of extractant concentration on the extraction of U(Ⅵ)

script (o) denotes the organic phase. The apparent extraction constant, K_{ex}, can be expressed as

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot nA]_{(o)}}{\gamma_{UO_2^{2+}}[UO_2^{2+}] \cdot a_{NO_3^-}^2 \cdot [A]_{(o)}^n} \tag{2}$$

$\gamma_{UO_2^{2+}}$ refers to the activity coefficient of UO_2^{2+} and can be considered as a constant at the given concentrations of sodium nitrate and HNO₃; $a_{NO_3^-}$ represents the activity of NO_3^- and the value is 0.69 in 3.00 mol·dm⁻³ NaNO₃ solution[14]. So we can rewrite the expression for the extraction constant in terms of K_{ex}',

$$K_{ex}' = K_{ex} \cdot \gamma_{UO_2^{2+}} = \frac{[UO_2(NO_3)_2 \cdot nA]_{(o)}}{[UO_2^{2+}] \cdot a_{NO_3^-}^2 \cdot [A]_{(o)}^n} \tag{3}$$

The conditional extraction constant, K, can be written as

$$K = \frac{D}{[NO_3^-]^2[A]_{(o)}^n} \tag{4}$$

Let C_U represents the total uranium present in all the forms in the aqueous phase, then we have

$$D = \frac{[UO_2(NO_3)_2 \cdot nA]_{(o)}}{C_U} = \frac{[UO_2(NO_3)_2 \cdot nA]_{(o)}}{[UO_2^{2+}](1 + \sum \beta_i[NO_3^-]^i)} \tag{5}$$

where $1 + \sum \beta_i[NO_3^-]^i$ is the factor for aqueous phase complexing of UO_2^{2+} ion with NO_3^-. The literature value of β_1 is 0.25 at 25 ℃[15]. Equation (3) can be written as,

$$logD = logK_{ex}' + 2loga_{NO_3^-} - log(1 + \beta_1[NO_3^-]) + nlogC_{A_{(o)}} \tag{6}$$

Here, it is assumed that the activity coefficients of the species involved remain constant at the studied conditions. It is further assumed that the distribution of amides into the aqueous phase and the coordinated ones is negligible. The amide concentration at equilibrium is approximatively equal to the initial concentration before extraction.

The log-log plots of the distribution ratio vs. the initial extractant concentration show that the lines have a slope of nearly 2 (1.91 for MOOA, 1.85 for MODA, 1.80 for MODOA). It implies that the stoichiometry of the extracted species in *n*-octane is $UO_2(NO_3)_2 \cdot 2A$ (A, the used monoamides), which is similar to the result of the extraction of U(Ⅵ) with *N,N*-dibutyldodecanamide[13].

Hence the equilibrium expression, written as a solvating reaction of U(Ⅵ), is given as follows

$$UO_2^{2+}+2NO_3^-+2A_{(o)}=UO_2(NO_3)_2 \cdot 2A_{(o)} \qquad (7)$$
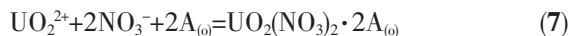
From Fig.3 the values of K_{ex}' and K can be obtained through equations (**3**) and (**4**). The results are shown in Table 1.

Table 1　Values of K and $\log K_{ex}'$ of the extraction of UO_2^{2+} in *n*-octane

Amide	K / (mol$^{-4}\cdot$dm^{12})	$\log K_{ex}$
MOOA	0.96±0.19	1.49±0.08
MODA	0.87±0.17	1.45±0.09
MODOA	1.03±0.30	1.52±0.12

2.4　Influence of temperature on the extraction of U(Ⅵ)

Fig.4 illustrates the influence of temperature on the values of D. The extraction distribution ratio decreases with the incease in the temperature, which shows that the extraction reaction is exothermic. The $\log D$ values increase linearly with the increase of $1/T$. The apparent change in enthalpy, ΔH, associated with reaction (**7**), can be evaluated by means of the Van′t Hoff Equation. The values of ΔH with different monoamides, obtained from Fig.4, are −22.47±3.22, −22.55±1.35 and −22.54±0.27 kJ·mol^{-1} for MOOA, MODA and MODOA, respectively.
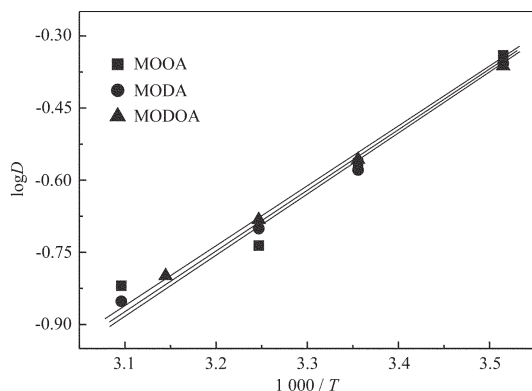

Fig.4　Influence of temperature on the extraction of U(Ⅵ)

2.5　Structure characterization of the extracted species

The IR spectra of the three extracted species are similar. Compared with the IR spectra of free extractants, it shows that the carbonyl group (C=O) stretching vibration of the extracted species shifts from about 1 650 to 1 581 cm^{-1}, which implies that the amide ligand directly coordinates to the uranyl ion through its carbonyl group. The appearance of bands at about 1 030, 1 276 and 1 522 cm^{-1} is attributed to the characteristic bands of the coordinated nitrate ions. An additional band described as the U-O stretching vibration of the uranyl ion is noted at 934 cm^{-1}. Thus, the suggested structure of amide/U(Ⅵ) nitrate complex may be described as that we reported previously[16].

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