N,N,N',N'-tetrabutylmalonamide as a new extractant for extraction of nitric acid and uranium(VI)*

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Abstract N,N,N',N'-tetrabutylmalonamide (TBMA) is synthesized and used for extraction of uranyl(II) ion from nitric acid media in a diluent composed of 50% 1,2,4-trimethyl benzene (TMB) and 50% kerosene(OK). The effects of nitric acid concentration, extractant concentration, temperature, salting-out agent (LiNO₃) and back extraction on distribution coefficients of uranyl(II) ion have been studied. The extraction of nitric acid is also studied. The main adduct of TBMA and HNO₃ is HNO₃·TBMA, and there are more than two kinds of adducts in 3.0 mol/L nitric acid solutions, such as HNO₃·TBMA, (HNO₃)₂·TBMA and (HNO₃)₃·TBMA. The complex formation of uranyl(II) ion, nitrate ion and TBMA (1:2:1) as extracted species is further confirmed by IR spectra of the saturated extraction of uranyl(II) ion with TBMA, and the values of thermodynamic parameters have also been calculated.

Keywords N,N,N', N'-tetrabutylmalonamide(TBMA), Solvent extraction, Uranium(VI), Saltingout agent, Back extraction

1 Introduction

Diamides as extractants for actinides and lanthanides have been reported in many papers since Siddall III first suggested the substituted alkylamide as a promising extractant for actinides extraction in the early 1960's.^[1~5] The diamides have excellent extractability for tri-, tetra- and hexavalvent actinides such as Am(III), Pu(IV) and U(VI) from high acidic waste solutions, particularly from high level radioactive wastes.^[2,3] We have also done some research work about the diamides for extraction of U(VI) and Th(IV) ions from the nitric acid solutions.^[4,5] The main advantages of these extractants and their innocuous radiolytic products, their easy incinerability, all make them become promising candidates for further investigations in nuclear waste management.

In the present paper, we have discussed systematically the extraction of nitric acid and uranium(VI). The results indicate that TBMA (N,N,N',N'-tetrabutylmalonamide) is better for the extraction of uranyl (II) ion from nitric acid medium than TBP.The extraction mechanism of uranyl (II) ion by TBMA and thermodynamic parameters have been also presented.

2 Experimental

2.1 Preparation of extractant

TBMA was obtained by the reaction of di*n*-butylamine with malonchloride in methylene chloride medium^[6]:

$$CH_2(COCl)_2 + 2HN(C_4H_9)_2 \xrightarrow{CH_2Cl_2} CH_2(CON(C_4H_9)_2)_2$$
(1)

After alkali and acid wash, TBMA was purified by distillation under vacuum. The final distilled TBMA was checked by element analysis, IR spectrometry and NMR spectrometry. The purity of the product was higher than 98%.

2.2 Procedure and apparatus

1 ml aqueous phase containing a certain amount of uranyl (II) ion and HNO_3 was shaken with 2 ml organic phase containing a given concentration of TBMA for 10 min. The diluent was composed of 50% 1,2,4-trimethyl benzene (TMB) and 50% kerosene (OK). Samples

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of both phases were analyzed immediately after the phase separation. The concentration of uranyl (II) ion was determined by UV-240 spectrometer by the arsenazo-III spectrophotometric method.^[7] The distribution coefficients of uranyl (II) ion were calculated.

 $0.1 \sim 1.0 \text{ mol/L}$ TBMA was equilibrated with 1.0 mol/L and 3.0 mol/L HNO₃ respectively for 10 min. After the phase separation, the aqueous phase was titrated with 0.05 mol/LNaOH solution to determine the nitric acid concentration. IR spectra were recorded by a 5DXC Nicolet Fourier transform spectrometer which used KBr window cells. Signals of 96 scans at a resolution of 4 cm^{-1} were averaged before Fourier transformation and the IR spectra covered the range of $400 \sim 4000 \text{ cm}^{-1}$.

3 Results and discussion

3.1Extraction of nitric acid

TBMA was found to extract nitric acid. The nature of the extracted species and the equilibrium constant $(K_{\rm H^+})$ for^[3]

$$\mathbf{H}_{(\mathbf{a})}^{+} + \mathrm{NO}_{\mathbf{3}(\mathbf{a})}^{-} + n\mathrm{TBMA}_{(\mathbf{o})} \xrightarrow{\mathbf{K}_{\mathrm{H}^{+}}} \mathrm{HNO}_{\mathbf{3}} \cdot n\mathrm{TBMA}_{(\mathbf{o})}$$
(2)

can be written as follows:

$$K_{\rm H^+} = [{\rm HNO}_3 \cdot n{\rm TBMA}]_{(o)} / [{\rm H^+}]_{(a)} [{\rm NO}_3^-]_{(a)} [{\rm TBMA}]^n_{(o)}$$
(3)

$$lg[H^+]_{(o)} - 2lg[H^+]_{(a)} = lgK_{H^+} + nlg[TBMA]_{(o)}$$
(4)

where

$$[H^+]_{(o)} = [HNO_3.nTBMA]_{(o)}$$
 and $[H^+]_{(a)} = [NO_3^-]_{(a)}$

The concentrations of the diamide and HNO_3 were restricted to no more than 1.0 mol/L, molar concentrations instead of activities were employed in all the calculations.

By plotting the left side of Eq.(4) against $lg[TBMA]_{(o)}$, a straight line with slope equal-



Fig.1 Distribution coefficient of HNO_3 as a function of TBMA concentration at 25°C; [HNO₃]=1.0 mol/L

Fig.2 shows the effect of the initial TBMA concentration on the extraction of HNO_3 (the slope is 1.1). The result is similar to the study on N, N'-dimethyl-N, N'-dioctylmalonamide^[8] and N, N, N', N'-tetrabutylglutaramide^[9] re-



ing to n and intercept equaling to $\lg K_{\mathrm{H}^+}$ was



Fig.2 Distribution coefficient of HNO₃ as a function of initial TBMA concentration at 25°C; [HNO₃]=3.0 mol/L

ported by C.Musikas *et al.* In any case, the plots of $\lg D$ vs $\lg[\operatorname{diamide}]$ give a straight line with the slope of 1.1 in the medium of $3\sim 4$ mol/L nitric acid. As a result of detailed IR spectra studies, the formation of TBMA-

HNO₃ adducts, for example, $(TBMA)_2$ · HNO₃ (~1637 cm⁻¹), TBMA·HNO₃ (1595 cm⁻¹), and TBMA·(HNO₃)₂ (1530 cm⁻¹), is responsible for such a phenomenon(the slope is 1.1).

3.2 Extraction of uranyl (II) ion

3.2.1 Distribution coefficients of uranyl (II) ion as functions of aqueous HNO_3 concentration, TBMA concentration and temperature

Fig.3 shows the effect of the HNO₃ concentration on the distribution coefficient of uranyl (II) ion. Accompanied with the increase in the concentration of HNO₃, the distribution coefficient of uranyl (II) ion increased in the region of $1\sim3.5 \text{ mol/L}$ HNO₃. At the point of 3.5 mol/L HNO₃, the curve shows a maximum value of



Fig.3 $D_{UO_2^{2+}}$ as a function of $[HNO_3]_{(a)}$ at 25°C; $[UO_2^{2+}]=5.0\times10^{-3} \text{ mol/L}, [TBMA]=0.5 \text{ mol/L}$

D, which is due to the competition of uranyl (II) ion and HNO_3 for the coordination sites of TBMA.

Fig.4 shows that in the case of 3.0 mol/LHNO₃ and $5.0 \times 10^{-3} \text{ mol/L} \text{ UO}_2^{2+}$, the plot of lgD vs. lg [TBMA] is a straight line with slope 1.1 for uranyl (II) ion. These values indicate that the composition of extracted species is UO_2^{2+} ·TBMA, and the extraction constant calculated is 7.30. These results illustrate that the concentrations of HNO₃ and TBMA are the main factors which can affect the distribution coefficient of uranyl (II) ion, and also indicate that TBMA is a good extractant for extracting uranyl (II) ion from the nitric acid solutions.



Fig.4 $D_{\text{UO}_2^{2+}}$ as a function of [TBMA]_(o) at 25°C; $[\text{UO}_2^{2+}]=5.0\times10^{-3} \text{ mol/L}$, [HNO₃]=3.0 mol/L

Fig.5 shows that the extraction of uranyl(II) ion from the aqueous phase to the organic phase is an exothermic process, according to the equation

$$\left[\frac{\partial \lg D}{\partial (1/T)}\right]_{p} = -\frac{\Delta H}{2.303R} \tag{5}$$

and the enthalpy of uranyl(II) ion extraction is -19.45 kJ/mol.

3.2.2 IR spectra of the saturated extraction of uranyl(II) ion

In order to gain insight into the structure of TBMA with UO_2^{2+} complex, the IR spectra of saturated extraction of uranyl(II) ion were investigated. The group of C=O stretching vibration is at 1640 cm⁻¹. When the concentration of uranyl (II) ion in organic phase is equal to the concentration of TBMA, the group of C=O stretching vibration vanishes, and the new bands of uranyl (II) ion with TBMA occur at 1627.7 cm⁻¹, 1578.5 cm⁻¹. The feature confirms that TBMA is a bidentate ligands in the extracted complexes.

3.2.3 Effect of salting-out agent on the uranyl (II) ion extraction

Fig.6 shows that the salting-out agent is very strange compared with that in HNO_3 system with the same concentration. A saltingout agent with high water binding capacity will cause the uranyl (II) ion to be less hydrated and render the aqueous solution more deficient in free water. This is why LiNO₃ may improve the extraction of uranyl (II) ion by TBMA.



Fig.5 $D_{\text{UO}_2^{2+}}$ as a function of temperature [UO₂²⁺]=5.0×10⁻³ mol/L, [HNO₃]=3.0 mol/L, [TBMA]=0.5 mol/L



The back extraction of U(VI) with 0.01 mol/L, 0.001 mol/L dilute nitric acid is shown in Table 1. It can be seen that the

Table 1 Stripping of U(VI) from 0.5 mol/L TBMA and 0.5 mol/L TBP in 50%OK-50%TMB

| Metal ion [H | $[NO_3]/mol L^{-1}$ | TBMA | TBP |
|--------------|---------------------|---------------|-----------|
| - | | % Stripping % | Stripping |
| U(VI) | 0.01 | 83.34 | 95.21 |
| | 0.001 | 82.89 | 96.83 |



Fig.6 $D_{\text{UO}_2^{2+}}$ as a function of [LiNO₃] at 25°C [UO₂²⁺]=5.0×10⁻³ mol/L, [HNO₃]=0.01 mol/L, [TBMA]=0.05 mol/L

back extraction of U(VI) from TBMA-50%OK-50%TMB is not easier than from TBP-50%OK-50%TMB.

In these extraction studies, the concentrations of TBMA in organic phase were in a large excess compared with uranyl(II) ion in the aqueous phase. The results suggest that the 1:2:1 complex of UO_2^{2+} , NO_3^- and TBMA was extracted into the organic phase. Thus, the extraction reaction of the present system can be expressed as follows.

$$UO_{2(a)}^{2+} + 2NO_{3(a)}^{-} + TBMA_{(o)} = UO_2(NO_3)_2 \cdot TBMA_{(o)}$$
(6)

4 Conclusions

The extraction of HNO₃ by TBMA dissolved in 50%OK-50%TMB has been studied. At lower acidity (1.0 mol/L HNO₃), the main adduct of TBMA and HNO₃ is TBMA·HNO₃, but at higher acidity, there will be more than two kinds of adducts to be formed, such as TBMA·HNO₃, TBMA·(HNO₃)₂. The extraction of U(VI) from nitric acid solutions by TBMA is better than by TBP, the extraction reaction of U(VI) is exothermic, and the composition of extracted species is $UO_2(NO_3)_2$ ·TBMA. The salting-out agent is very strange compared with that in HNO₃ system. The back-extraction of U(VI) from TBMA-50%OK-50%TMB is not easier than from TBP-50%OK-50%TMB.

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