Extraction of Th(IV) from nitric acid with 4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3- thione*

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Abstract The BMPPT (4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione) was synthesized from BMPP. Its m.p. is 106-108°C. The results of the element analysis are as follows: C, 68.51%, H, 4.51%, N, 9.26%, S, 11.47%, which are in conformity with the theoretical value (C, 69.15%, H, 4.76%, N, 9.52%, S, 10.90%). The solvent extraction of Th^{4+} from nitric acid solution by BMPPT in benzene was studied. The extraction ability of BMPPT is not so high as that of its parent (BMPP). The Th^{4+} distribution ratio (D_{Th}) increases with the increasing pH of the aqueous phase, and $pH_{1/2}$ for Th^{4+} was 3.2 ([BMPPT]=0.10 mol/L). When the pH increases, the distribution ratio of Th^{4+} increases linearly with the slope of 1.59. When the concentration of BMPPT increases, the distribution ratio of Th^{4+} increases rapidly. The $\lg D_{Th}$-lg[BMPPT] is linear with the slope of 1.42 and the extraction mechanism is the cation ion-exchange.

Keywords Solvent extraction, 4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (BMPPT), Th(IV), Distribution ratio of extraction

1 Introduction

The extraction of Actinide (III) and Lanthanide (III) from aqueous solution with BMPPT and TOPO in benzene has been studied by some authors.[1~5] To some extent, BMPPT is a very useful extraction agent for separation of Am(III) and Eu(III). The extraction of Th^{4+} from aqueous solution has not been studied ever, so we here report the extraction behavior of Th^{4+} in nitric acid media with BMPPT in benzene.

2 Experimental

2.1 Synthesis of BMPPT

Compound BMPPT was synthesized from BMPP (4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one). 25 g BMPP and 25 ml $POCl_3$ were refluxed for 4 h at 125°C, and then 100 ml H_2O was added in it. The organic phase was extracted by 100 ml CH_2Cl_2 (dichloromethane), soon CH_2Cl_2 was transferred by vacuum distillation. The product (Cl-BMPP) was re-crystallized in 30 ml ether and 30 ml petroleum benzine solution with the yield about 74%, of which m.p. is 79-81°C. BMPPT was synthesized with a procedure similar to that of Jarvinen[5] by refluxing (6 h) 30 g Cl-BMPP with 38 g $NaSH{\cdot}H_2O$ (4 equivalents) in ethanol (350 ml). The nitrogen-purged reaction mixture was cooled and allowed to settle. The product was isolated by transferring (reduced pressure) the supernatant liquid through a teflon tube and by subsequent reduction of the solvent volume in vacuum. H_2O (400 ml) was added and the solution (pH>11) was extracted with (60 ml) chloroform ($CHCl_3$) to remove neutral materials. The aqueous layer was made acidic (pH 5-6) with 120 ml of 3 M HCl, and extracted 3 times with $CHCl_3$ (50 ml each). The organic fractions were combined, washed with 120 ml water, and dried over anhydrous Na_2SO_4. The solvent was subsequently removed under vacuum and the solid residue dissolved in 60 ml hot ethanol and re-crystallized to yield 27 g of orange crystals, m.p. 106~ 108°C.

2.2 Distribution ratio determination

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The extraction procedure was as follows: 5 ml of the aqueous phase which contains a certain amount of Th^{4+} and HNO_3 was shaken for 15 min with 5 ml of the organic phase containing a given concentration of BMPPT, which had been pre-equilibrated with a suitable nitric acid solution. The diluent was benzene. The concentration of Th^{4+} in aqueous phase was analyzed immediately by the arsenazo-III spectrophotometric method[6,7] after the phase separation, and the distribution ratio was calculated. The pH of aqueous solution was measured after equilibrium. We choose lower concentration of Th^{4+} in aqueous phase, and lower phase ratio (V_o:V_a=1:5), in order to reduce the change of pH in aqueous phase.

3 Results and discussion

3.1 Identification of BMPPT purity

The results of the element analysis are as follows: C, 68.51%, H, 4.51%, N, 9.26%, S, 11.47%, which are in conformity with the theoretical values (C, 69.15%, H, 4.76%, N, 9.52%, S, 10.90%). The mass spectra show that the molecular weight of BMPPT is 294 (theoretical value is 294), and the strong fragment mass of 105 show that the sulfur is not on the-benzoyl (the mass weight is 105). The IR (KBr) is similar to that of Jarvinen.[5]

3.2 Effect of diluent on distribution ratio of Th^{4+}

The BMPPT is not dissolved in the diluents, such as petroleum benzine, kerosene, cyclohexane etc., and is dissolved a little in ether, however, can be easily dissolved in toluene, benzene, dichloromethane, chloroform, etc. as shown in Table 1, where little difference among the distribution ratios of Th^{4+} can be seen.

Table 1 The distribution ratios of Th^{4+} at T=25°C, in different diluents with $[Th^{4+}]$ = 5.68×10^{-4} mol/L, [BMPPT] = 0.15 mol/L, $[NH_4NO_3]$=0.1 mol/L and pH=3.2.

Diluent	Toluene	Benzene	Dichloromethane	Chloroform
D_{Th}	2.67	2.65	2.55	2.72

The BMPPT can extract Th^{4+} in ether solution, quantitatively, under the conditions mentioned in Table 1.

3.3 Effect of temperature on the distribution ratio

The effect of temperature on the distribution ratio of Th^{4+} is shown in Table 2. The result shows that temperature has little effect on the distribution ratio of Th^{4+}.

Table 2 The effect of temperature on the distribution ratio of Th^{4+} at $[Th^{4+}]=5.68\times10^{-4}$ mol/L; pH=3.1; [BMPPT]=0.10 mol/L; $[NH_4NO_3]$=0.1 mol/L

T/°C	15	20	25	30	35	40
D_{Th}	1.31	1.28	1.33	1.29	1.32	1.22

3.4 Effect of Th^{4+} concentration on the distribution ratio

The effect of Th^{4+} concentration on the distribution ratio of Th^{4+} is shown in Table 3. The distribution ratio (D_{Th}) of Th^{4+} decreases with the increase of Th^{4+} concentration. It probably results from the increases of pH in aqueous after the ion exchange reaction.

Table 3 The effect of Th^{4+} concentration on the distribution ratio at T=25°C; pH=2.94; [BMPPT]=0.20 mol/L; $[NH_4NO_3]$=0.1 mol/L

$[Th^{4+}]/10^{-4}$ mol·L^{-1}	2.84	5.68	8.52	11.36	14.2
D_{Th}	3.21	3.10	2.48	2.45	2.13

3.5 Effect of acidity of aqueous phase on the distribution ratio

The effect of pH on the distribution ratio of Th^{4+} is shown in Fig.1. The logarithm of distribution ratio of Th^{4+} and pH are in linear relationship. The slope of lgD_{Th}-pH is 1.59.

3.6 Effect of [BMPPT] on the distribution ratio

The effect of [BMPPT] on the distribution ratio of Th^{4+} is shown in Fig.2. The equilibrium pH was measured. The logarithm of distribution ratio of Th^{4+} and lg[BMPPT] are in linear relationship. The slope of lgD_{Th}-lg[BMPPT] is 1.42.

According to the general rule, the extraction reaction between BMPPT and Th^{4+} is cation ion exchange reaction, the slope of lg$D$-pH and lg$D$-lg[BMPPT] is not the whole number, the extraction reaction may be described as follows (HBMPPT=HA):

$$HA \longleftrightarrow A^- + H^+$$

$$Th^{4+} + 2NO_3^- + 2A^- \longleftrightarrow Th(NO_3)_2A_2$$

$$Th^{4+} + 3NO_3^- + A^- \longleftrightarrow Th(NO_3)_3A$$

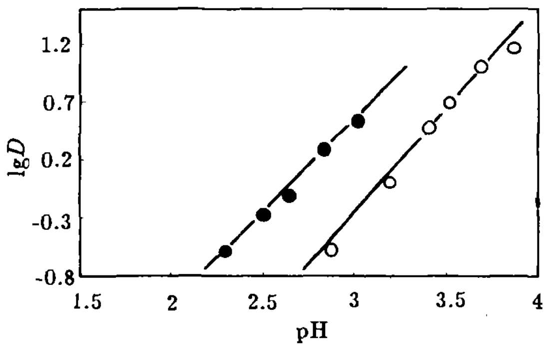

Fig.1 Distribution ratio of Th^{4+} as a function of aqueous acidity at $T = 25°C$; $[Th^{4+}]=5.68\times10^{-4}$ mol/L; [BMPPT]=0.20 (•) and 0.10 mol/L (○); $[NH_4NO_3]$=0.1 mol/L)

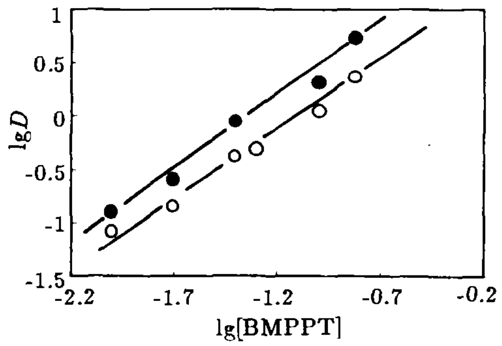

Fig.2 Distribution ratio of Th^{4+} as a function of BMPPT concentration in benzene at $T = 25°C$; $[Th^{4+}]=5.68\times10^{-4}$ mol/L; pH=3.05 (○) and 3.20 (•); $[NH_4NO_3]$=0.1 mol/L)

4 Conclusion

The synthetic product is BMPPT. The extraction ability of BMPPT is not so high as that of its parent (BMPP). The extraction reaction with Th^{4+} is cation ion exchange reaction. The relation of lg$D$-pH is linear with the slope of 1.59. The relation of lg$D$-lg[BMPPT] is linear with the slope of 1.42. The extraction reaction includes two products $Th(NO_3)_2A_2$ and $Th(NO_3)_3A$.

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