# Influence of solvents on extraction of U(VI) by N,N'-didecanoylpiperazine

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## **1 INTRODUCTION**

Generally, the solvent plays an important role in solvent extraction system.<sup>[1,2]</sup> In order to well understand how the solvent interacts with N, N'-didecanoylpiperazine (DDPEZ), which was synthesized for the first time, and further extend our research, the effects of some solvents, such as benzene, toluene, dimethylbenzene(DMB), chloroform(CF), and carbon tetrachloride(CT), on the extraction of U(VI) from nitric acid media were studied.

## **2 EXPERIMENTAL**

DDPEZ was prepared in our laboratory. All solvents used here were treated by distillation and the other chemical regents are of analytic purity. The processes of extraction was described in our previous paper.<sup>[3]</sup>

## **3 RESULTS AND DISCUSSION**

#### 3.1 Influence of nitric acid concentration

The variation of distribution ratio of U(VI) with HNO<sub>3</sub> concentration was shown in Fig.1. It is obvious that the change tendencies of distribution ratios with HNO<sub>3</sub> concentration are alike in all solvents. The distribution ratios first increase with the increasing of nitric acid concentration and then decrease after reaching a maximum. However, the acidity at the maximum distribution ratios and the values of D to the same HNO<sub>3</sub> concentration are different. In the case of chloroform, its distribution ratio

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is the smallest owing to the formation of hydrogen bond  $(=C=O\cdots H-CCl_3)$  between DDPEZ and chloroform, restricting U(VI) to coordinate with DDPEZ molecule. But for benzene, the larger distribution ratios result from the increasing of solubility of DDPEZ and their complex in organic phase is attributed to the conjugation effects. In other solvents, the differences of distribution ratios are relatively larger although their dielectric constants are approximative (shown in Table 1). No obvious regulation is found between distribution ratio and physical parameters of solvents. Hence the solvent influence on extracting ability of DDPEZ is very complex.

Solvent	CF	CT	DMB	Toluene	Benzene
$Kex_1$	0.06		0.48	0.62	1.07
$Kex_2$	0.06	2.28	1.51	1.25	1.16
ε	4.90	2.21	2.26	2.24	2.28
δ	9.30	8.60	8.80	8.90	9.20
$E_{\mathrm{T}}$	39.1	32.5	33.3	33.9	34.5

Table 1 Equilibrium constants of U(VI) and some physical properties of solvents

 $[UO_2^{2+}]=5.0\times10^{-3} \text{ mol/L}, [HNO_3]=3.0 \text{ mol/L}, [DDPEZ]=0.5 \text{ mol/L}, T=298 \text{ K}$ 

 $\epsilon$ : dielectric constant at 293K<sup>[4]</sup>,  $\delta$ : solubility parameter<sup>[5]</sup>,  $E_{\rm T}$ : energy parameter<sup>[4]</sup>

Fig.1 also denotes that at higher acidity the extraction competition between  $HNO_3$ and U(VI) is intense which leads to a decreasing of distribution ratio, and the interaction between DDPEZ and  $HNO_3$  is stronger than that between DDPEZ and solvent. Especially when chloroform is used as solvent, the lowest distribution ratios may be owing to the formation of hydrogen bond.

### **3.2 Influence of DDPEZ concentration**

The dependence of distribution ratio on DDPEZ concentration, at  $5.0 \times 10^{-3}$  mol/L U(VI) and 3.0 mol/L HNO<sub>3</sub>, is shown in Fig.2. It can be seen that all the plots of lgD versus lg[DDPEZ]<sub>(o)</sub> are straight lines, but their slopes are quite different, viz. 1.63(CF), 2.04(CT), 1.69(DMB), 1.53(toluene), 1.46(benzene), respectively. Only for carbon tetrachloride, the slope is close to integer 2, which implies that the stoichiometry of the extracted species is UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (DDPEZ)<sub>2</sub> and the extraction reaction is written as equation (2). For other solvents, the slopes are not integer and near to 1.5, which means that there are properly two kinds of extracted species: UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DDPEZ)<sub>2</sub> and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>DDPEZ, and the extraction reaction is given by equations:

$$UO_2^{2+} + 2NO_3^{-} + DDPEZ_{(\circ)} = UO_2(NO_3)_2DDPEZ(\circ)$$
(1)

$$UO_{2}^{2+} + 2NO_{3}^{-} + 2DDPEZ_{(o)} = UO_{2}(NO_{3})_{2}(DDPEZ)_{2(o)}$$
(2)

where the subscript (o) refers to the species in the organic phase.

The equilibrium constants  $Kex_1$  for Eq.(1) and  $Kex_2$  for Eq.(2) were calculated according to the above reactions, listed in Table 1. From the values of  $Kex_1$  and  $Kex_2$ , it shows that the equation 2 is dominant. In order to look for the relation between Kex $(Kex = Kex_1 + Kex_2)$  and properties of solvent, some given physical parameters such as  $\varepsilon$ ,  $E_{\rm T}$  and  $\delta$ , (listed in Table 1) were correlated with Kex by a linear fit program, and found only  $\varepsilon$  and  $E_{\rm T}$  correlate well, as shown in the relations (3)–(5):

$$Kex = 4.27 - 1.07\varepsilon + 0.05\varepsilon^2 \quad R = 0.96 \tag{3}$$

$$Kex = -49.99 + 3.19E_{\rm T} - 0.05E_{\rm T}^2 \quad R = 0.96 \tag{4}$$

$$Kex = -404.18 + 92.68\delta - 5.28\delta^2 \quad R = 0.53 \tag{5}$$

The above results indicate that solvents not only act as carriers of extractants, but also participate in the chemical reaction themselves, which leads to a series of variation of the mechanism of extraction reaction and the stoichiometry of extracted species.



## Fig.1 Solvent effects on distribution ratio of U(VI) at various HNO<sub>3</sub> concentration $[UO_2^{2+}]=5.0\times10^{-3} \text{ mol/L},$ [DDPEZ]=0.5 mol/L, T=298 K



The difference of stoichiometry of complex may be controlled by the interaction between solvent and extractant or complex, and existing state. In some case, extractants aggregate by the effect of solvent, leading to a variation of the coordinating number. Carbon tetrachloride is regarded as a inert solvent and affects DDPEZ slightly, and allows DDPEZ to coordinate with U(VI) sufficiently and enhances the coordinating number. For benzene and their derivatives, because the effect of conjugation, DDPEZ is solvated and arrested to form coordinating bond, resulting in a lower value of coordinating number.

The variation of  $K_{ex}$  is also because of the different interaction between solvent and DDPEZ. In chloroform, the strong interaction will introduce a greatly solvating effect, so it is difficult to form coordinating bond and shift the extraction reaction to right, which leads to a decrease of  $K_{ex}$ . For benzene and their derivatives, the extraction reactions act easily and completely due to the conjugation effect between solvents and DDPEZ or their complex, which leads to an increase of  $K_{ex}$ .

#### **3.3 Influence of temperature**

Extraction of U(VI) in different solvents was investigated at different temperatures.

as shown in Fig.3. It can be seen that the slopes of lines of  $\lg D$  versus 1/T vary with solvents. The enthalpy changes  $(\Delta H^o)$  listed in the Table 2, being calculated according

to the slopes by means of Van't Hoff equation, are different in various solvents. This results from the difference of interaction between solvent and DDPEZ or their complex, which causes a series of variation of enthalpy change. In chloroform, the strong interaction due to the formation of hydrogen bond will baffle DDPEZ to coordinate with U(VI), so it will consume much more energy to form complex and giving a lower value of  $\Delta H^o$ . For benzene and their derivatives, both DDPEZ and the complex have the conjugate effect and less additional energy to be consumed, so the value of  $\Delta H^o$  is larger.



Fig.3 Solvent effects on distribution ratio of U(VI) at different temperature  $[UO_2^{2+}]=5.0\times10^{-3} \text{ mol/L},$  $[HNO_3]=3.0 \text{ mol/L}, [DDPEZ]=0.5 \text{ mol/L}$ 

Table 2 Enthalpy changes of U(VI) in 3.0 mol/L HNO<sub>3</sub> with DDPEZ in different solvents

Solvent	CF	CT	DMB	Toluene	Benzene
$-\Delta H^o (kJ/mol)$	1.88	17.39	22.90	20.09	16.08

Although the values of  $\Delta H^o$  are different in various solvents, but all the extraction reactions are exothermic and low temperatures are beneficial to them.

#### **4 CONCLUTIONS**

The sequences of DDPEZ extractability for U(VI) is as follows: benzene>toluene> dimethylbenzene>carbon tetrachloride>chloroform.

Solvent itself participates in the chemical reaction and affects the mechanism of reaction and the stoichiometry of extracted species severely. The enthalpy changes and equilibrium constants change with the solvent.

The relationship between extractability of DDPEZ and solvent property is very complex. The internal effective mechanism of solvent needs to be studied further.

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