Preparation of N, N'-diacylpiperazine and its extraction property for U(VI)

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Abstract A novel extractant, N, N'-diacylpiperazine (DAPEZ), was synthesized and characterized for the first time. Its extraction property for U(VI) from aqueous nitric acid media has been studied. The effects of concentration of nitric acid and extractant on the distribution ratio were examined and the extraction mechanism were discussed.

Keywords Extractant, Solvent extraction, Diamide, Uranium (VI)

CLC numbers O615, O615.11 A

1 INTRODUCTION

During the last forty years, many literatures about amide have been published. Amide has been reckoned as an alternative to TBP for the reprocessing of spent nuclear fuel.[1~5] They not only can selectively extract U(VI) effectively from nitric acid media, but also has a lot of advantages compared with TBP, such as their complete incinerability, innoxious degradation products, easier preparation and back extraction. However, when the acidity or the content of U(VI) is higher, the third phase usually appears.[6,7] In order to modify the chemical structure of amide and improve their extraction properties, a series of amide N, N'-diacylpiperazine, such as N, N'-dihexanoylpiperazine (DHPEZ), N, N'-dioctanoylpiperazine (DOPEZ), N, N'-didecanoyl piperazine (DDPEZ), and N, N'-dilauroylpiperazine (DLPEZ) were synthesized and characterized. Some physical properties of the four amides were given and some extraction properties for U(VI) were studied.

2 EXPERIMENTAL

2.1 Preparation of N, N'-diacylpiperazine

The synthesis procedure of DAPEZ can be expressed as follows:

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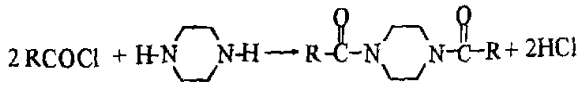
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl \quad (1)$$



$$2\,RCOCl + H\text{-}N\langle\rangle N\text{-}H \longrightarrow R\text{-}C(=O)\text{-}N\langle\rangle N\text{-}C(=O)\text{-}R + 2HCl \quad (2)$$

where R=C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$.

DAPEZ was synthesized by dropwise adding a stoichiometric quantity of chloride into a bottomed flask containing a mixture of piperazine and triethylamine in dichlorethane medium, being cooled to 0°C. After the addition, the mixture was heated under reflux for 10 hours at temperature of 75~80°C. On cooling, the contents in the flask were washed three times with distilled water, two times each with 5% hydrochloric acid and 5% sodium hydroxide and finally with distilled water till free from alkali. The thick brown liquid obtained was dried overnight with an excess of anhydrous sodium sulphate. The solvent was evaporated in vacuum and the rough product was recrystallized in ether and then the colorless (or light yellow) crystal was obtained with higher yield.

2.2 Characterization of DAPEZ

The purity of DAPEZ was checked by IR spectrometry, ^1H NMR spectrometry and elemental analysis, respectively.

The data of elemental analysis for C, H, N are shown in Table 1. They are, for DHPEZ: 68.34% (68.04%), 10.58% (10.71%), 9.90% (9.92%); DOPEZ: 70.86% (70.91%), 11.52% (11.31%), 8.15% (8.27%); DDPEZ: 72.97% (73.04%), 11.47% (11.75%), 7.15% (7.09%); DLPEZ: 74.85% (74.61%), 11.87% (12.08%), 6.16% (6.21%), respectively, where the symbol '( )' refers to the theoretical valves. It indicates that the theoretical valves and experimental ones are well agreeable, It means the products are sufficiently pure.

Table 1 Physical properties and IR, ^1H NMR, elemental analysis data of DAPEZ

Sample name	Melting point/°C	IR($V_{C=O}$) /cm^{-1}	^1H NMR (δ in $CDCl_3$)	Elemental analysis/%
DHPEZ	65-66	1643.3	3.45;3.65(8H,CH_2-N);2.36(4H,CH_2-CO) 1.35;1.62(12H,CH_2);0.90(6H,CH_3)	C:68.34;H:10.58; N:9.90
DOPEZ	71-72	1646.5	3.44.3.63(8H,CH_2-N);2.36(4H,CH_2-CO) 1.33,1.60(28H,CH_2);0.87(6H,CH_3)	C:70.86;H:11.52 N:8.15
DDPEZ	57-59	1644.8	3.45;3.60(8H,CH_2-N);2.35(4H,CH_2-CO) 1.30,1.62(28H,CH_2);0.85(6H,CH_3)	C:72.97;H:11.47; N:7.15
DLPEZ	56-57	1643.1	3.45;3.65(8H,CH_2-N);2.35(4H,CH_2-CO) 1.30,1.62(36H,CH_2);0.85(6H,CH_3)	C:74.85;H:11.87; N:6.16

The data of IR spectra of DAPEZ are shown in Table 1, and it helps us to observe the v (C=O) stretching band. The strongly absorptive peaks are found at 1643.3, 1646.5,

16544.8, 1643.1 cm-1, respectively, in the IR spectra. They are the characteristic peaks of v (C=O) of amide.

The chemical shift of ^1H and the hydrogen number calculated by the area of absorptive peak in ^1H NMR spectra are shown in Table 1. The data of ^1H NMR spectra fit well the structure of diacylpiperazine.

2.3 Extraction procedure

Extraction was performed by shaking 1 mL of benzene solution containing DAPEZ, and 1 mL nitric acid solution containing uranyl nitrate, in a stopped tube at 298±1 K for 40 minutes. After centrifugation and phase disengagement, the concentration of U(VI) in aqueous phase was analyzed by the arsenazo-III spectrophotometric method, and that in organic phase was calculated according to the difference between initial and final concentration of U(VI) in aqueous phase. The distribution ratio, D, was then calculated.

3 RESULTS AND DISCUSSION

3.1 Effect of nitric acid concentration

Fig.1 denotes the dependence of distribution ratio on nitric acid concentration in the range of 1~9mol/L. The values of D first increase rapidly with increasing concentration of nitric acid, then decrease gradually at higher acidity after a maximum value at the concentration of HNO_3 about 6.2 mol/L. This is because DAPEZ not only extracts U(VI), but also extracts HNO_3 from aqueous phase especially at higher acidity. Accordingly the concentration of free extractant decreases greatly, which decreases the distribution ratios at higher acidity.

For all the extractants, owing to the similar chemical structures, the variation trends of plots of D versus C_{HNO_3} are similar and the acidities of nitric acid at the maximum values of D are almost same. But the maximum values of distribution ratios are different due to the different length of acyl, that of DLPEZ is the highest and the others are nearly equal. The longer substituted groups not only enhance the solubility of complex in organic phase leading to an increase of extraction ability, but also enlarge steric hindrance resulting in a decrease of extraction ability. The value of D is effected by the both factors at the same time. In the case of DLPEZ, the effect of the former is dominant, and for the others the both effective degrees are nearly equivalent.

3.2 Effect of extractant concentration

The dependence of distribution ratio on extractant concentration is shown in Fig.2. The plots of $\lg D$ versus $\log[\mathrm{DAPEZ}]_{(o)}$ are all straight lines with slopes of 1.46, 1.44,

1.46, 1.35, respectively. Although the substituted groups of DAPEZ are different, but the values of slopes are near, being not integer and close to 1.5, which described that there are properly two kinds of extracted species. The number of NO_3^- in extracted species could be proved to be 2 by IR spectra,[8] viz. $UO_2(NO_3)_2(DAPEZ)_2$. and $UO_2(NO_3)_2DAPEZ$. The extraction reactions were given as follows:

$$UO_2^{2+} + 2NO_3^- + DAPEZ_{(o)} = UO_2(NO_3)_2DAPEZ_{(o)} \quad (3)$$

$$UO_2^{2+} + 2NO_3^- + 2DAPEZ_{(o)} = UO_2(NO_3)_2(DAPEZ)_{2(o)} \quad (4)$$

where the subscript (o) refers to the species in organic phase. For the above reactions, the distribution ratio, D, is

$$D = K_1[NO_3^-]^2[DAPEZ]_{(o)} + K_2[NO_3^-]^2[DAPEZ]_{(o)}^2 \quad (5)$$

The values of K_1 and K_2 were calculated by curve-fitting method,[9,10] for the given values of $[NO_3^-]$ and $[DAPEZ]_{(o)}$, as shown in Table 2. According to the above results, it implies that the length of substituted groups of DAPEZ only influence the values of K_1 and K_2, but not the composition of extracted species under the conditions studied.

Table 2 Equilibrium constants of U(VI) by different extractants in benzene

Extractant	DHPEZ	DOPEZ	DDPEZ	DLPEZ
K_1	0.98	1.07	1.07	0.93
K_2	1.65	1.01	1.16	2.40

$[UO_2^{2+}]=5\times10^{-3}$ mol/L, $[HNO_3]=3.0$ mol/L; $T=298$ K

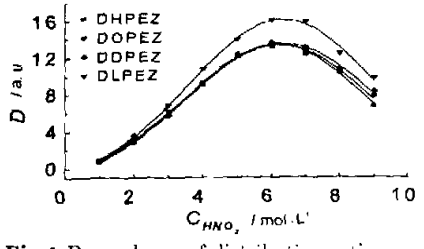


Fig.1 Dependence of distribution ratio on initial aqueous nitric acid concentration for the extraction of U(VI) by DAPEZ in benzene
$[UO_2^{2+}]=5\times10^{-3}$ mol/L,
$[DAPEZ]_{(o)}=0.5$ mol/L, $T=298$ K

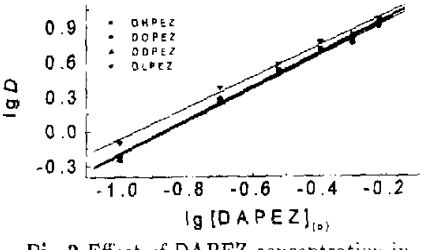


Fig.2 Effect of DAPEZ concentration in benzene on distribution ratio of U(VI)
$[UO_2^{2+}]=5\times10^{-3}$ mol/L, $[HNO_3]=3.0$ mol/L.
$T=298$ K

4 CONCLUSIONS

A series of novel amide extractants have been synthesized, to the best knowledge of the authors, for the first time. The preparing procedures of DAPEZ are reliable. The extraction property of DAPEZ is nice compared with other diamides and the longer acyl benefits the extraction for U(VI).

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