

## Solvent Extraction of Uranium(VI) with 8-Quinolinol in the Presence of Some Heterocyclic Nitrogen Bases

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Equilibrium distribution studies have been made on the extraction of mixed complexes of uranium(VI) in presence of oxine and some heterocyclic nitrogen donors such as pyridine, 2-picoline, 3-picoline and 4-picoline. The composition of the extraction species is found to be  $UO_2(L)_2HL.B$  where HL is oxine and B is the nitrogen donor. The equilibrium constants of the mixed complexes and the adduct formation constants have been determined. The order of effectiveness of these donors both in forming mixed complexes and adducts is found to be: 4-picoline > 3-picoline > pyridine.

In order to improve the extractability of metal chelates, some or all of the water molecules in the coordination sphere of metal may be replaced by organic ligands<sup>1</sup>. The second ligand is usually, monodentate and forms adduct. The synergic effect of heterocyclic nitrogen bases in solvent extraction of neutral metal chelates has been extensively investigated and the mechanism of the effect well explained on the basis of the formation of the base adducts. It was observed earlier in our laboratories that at low concentrations of oxine the extraction of uranium could not be followed as an insoluble residue resulted as the third phase. The increase in the concentration of oxine facilitated the extraction of uranium(VI) which formed a self adduct of the type  $UO_2(L)_2HL$ . On the other hand, the presence of a nitrogen donor made the extraction possible even at low concentrations of oxine. The addition of pyridine bases also increased the intensity of the colour of the extract and sensitivity. Koppiker and Gajankush<sup>2</sup> reported the beneficial effect of pyridine in the extractive spectrophotometric determination of uranium with oxine, but they did not make a detailed study of the extracting species. In view of this the present authors felt the need of a thorough investigation of the effect of pyridine bases on the formation and extraction of uranium(VI)-oxine complex into benzene. Results of these investigations are presented in this paper.

### Materials and Methods

A Spekol spectrophotometer (CARL ZEISS, DDR) and a digital Eltop pH meter (3030) were used.

A 0.01 M uranium(VI) solution was prepared by dissolving 2.1208 g of uranyl acetate (AR, BDH, England) in 500 ml double distilled water. Solutions of required strengths were obtained by appropriate

dilution of this stock solution.

A 0.1 M oxine solution was prepared by dissolving the required amount of 8-hydroxyquinoline (BDH, AR) in doubly distilled water using a small amount of 1 N sulphuric acid.

Pyridine bases and benzene used in the present study were distilled before use. All the other reagents were of AR grade.

### Extraction procedure

An aliquot of  $2.0 \times 10^{-4}$  M uranium(VI) solution and 3 ml of 0.4 M oxine solution were taken in a separatory funnel, the volume was made up to 20.0 ml, and the pH was adjusted to the required value with dilute sulphuric acid or dilute ammonia. The resulting solution was then equilibrated with 20.0 ml of 10 per cent (v/v) solution of nitrogen base in benzene. The organic phase was separated and dried over anhydrous sodium sulphate and the absorbance was measured at 390 nm against the reagent blank prepared under similar conditions. The optimum equilibrium pH range for the extraction of the mixed complexes is 6-9. A thirty-fold excess of oxine and an equilibration period of 2 min were found quite sufficient for quantitative extraction of uranium and maximum colour development. The colour of the extract was stable for more than 12 hr. The absorption spectra of the extract in all the systems showed maximum absorbance at 390 nm, but the corresponding average molar extinction coefficients per uranium atom differed slightly: 6,800 (pyridine); 6,900 (3-picoline); and 7,100 (4-picoline). However, the uranium(VI)-oxine binary complex showed maximum absorbance at 390 nm and had a molar extinction coefficient of 5,800. The upper limits of uranium/ml for Beer's law to be obeyed were 19  $\mu$ g (pyridine), 14  $\mu$ g (3-picoline), and 14  $\mu$ g (4-picoline).

Composition of the extracting species

In all the three systems, the experiments based on the graphical method of Coleman *et al.*<sup>3</sup> revealed that the extracting species contained a single absorbing species. A constant excess of sodium sulphate was maintained in all the experiments so that the hydrolysis of uranium(VI) under the pH conditions of the present investigation was largely suppressed owing to the formation of anionic sulphato complex of uranium. This assumption in the present investigation, under the conditions of equilibrium studies, appears to be quite reasonable when the orders of values for the formation of  $UO_2(SO_4)_2^{2-}$  and  $UO_2(OH)_2$  reported by Busev *et al.*<sup>4</sup> and Lurie<sup>5</sup> are taken into account.

The conditional extraction constant ( $K_{ex}$ ) at constant  $[SO_4^{2-}]$  may be deduced from Eq. (1),

$$\log K_{ex} = (\log C_{u,o} + 2j \log [H^+] - j \log C_{u,w} - (2+x)j \log [HL] - yj \log [B]) \dots (1)$$

where  $J$  is the polymerization number, HL and B represent oxine and base respectively, and subscripts w and o represent the water and organic phases. At constant [HL] and [B] (maintained by taking large excess of oxine and pyridine base in the organic phase).  $[\log C_{u,o}]$  is linearly related to  $[\log C_{u,w} + 2pH]$ . The slope of such a linear plot gives the number of metal atoms in the extracted molecular species. In the present study the plots of  $[\log C_{u,o}]$  vs  $[\log C_{u,w} + 2pH]$  are

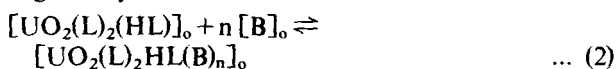
Table 1—Experimental Data for the Determination of Composition of the Extracting Species

Conc. range of variable (mole l <sup>-1</sup> )	Conc. of other reactants (mole l <sup>-1</sup> )	Ionic strength	Type of plot y vs x	Slope of the curve (linear)	Inference
Uranium(VI)-oxine-pyridine system					
[Uranium] = $3.0 \times 10^{-5}$ to $7.0 \times 10^{-5}$	[H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$ , [HL] = $7.5 \times 10^{-3}$	0.2	$\log C_{u,o}$ vs $[\log C_{u,w} + 2pH]$	1.03	$J=1$
[H <sup>+</sup> ] = $2.63 \times 10^{-6}$ to $1.17 \times 10^{-6}$	[Uranium] = $5.0 \times 10^{-5}$ , [HL] = $7.5 \times 10^{-3}$	0.2	pH vs $[\log C_{u,o} - \log C_{u,w}]$	2.0	$2J=2$
[Oxine] = $1.51 \times 10^{-3}$ to $3.47 \times 10^{-3}$	[Uranium] = $5.0 \times 10^{-5}$ , [H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$	0.2	$\log [HL]_{total}$ vs $[\log C_{u,o} - (\log C_{u,w} + 2pH)]$	2.91	$(2+x)J=3$
Uranium (VI)-oxine-3-picoline system					
[Uranium] = $3.0 \times 10^{-5}$ to $7.0 \times 10^{-5}$	[H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$ , [HL] = $7.5 \times 10^{-3}$	0.2	$\log C_{u,o}$ vs $[\log C_{u,w} + 2pH]$	1.02	$J=1$
[H <sup>+</sup> ] = $4.63 \times 10^{-6}$ to $1.17 \times 10^{-6}$	[Uranium] = $5.0 \times 10^{-5}$ , [HL] = $7.5 \times 10^{-3}$	0.2	pH vs $[\log C_{u,o} - \log C_{u,w}]$	1.99	$2J=2$
[Oxine] = $1.51 \times 10^{-3}$ to $3.47 \times 10^{-3}$	[Uranium] = $5.0 \times 10^{-5}$ , [H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$	0.2	$\log [HL]_{total}$ vs $[\log C_{u,o} - (\log C_{u,w} + 2pH)]$	2.96	$(2+x)J=3$
Uranium(VI)-oxine-4-picoline system					
[Uranium] = $3.0 \times 10^{-5}$ to $7.0 \times 10^{-5}$	[H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$ , [HL] = $7.5 \times 10^{-3}$	0.2	$\log C_{u,o}$ vs $[\log C_{u,w} + 2pH]$	1.06	$J=1$
[H <sup>+</sup> ] = $2.75 \times 10^{-6}$ to $1.38 \times 10^{-6}$	[Uranium] = $5.0 \times 10^{-5}$ , [HL] = $7.5 \times 10^{-3}$	0.2	pH vs $[\log C_{u,o} - \log C_{u,w}]$	2.01	$2J=2$
[Oxine] = $1.51 \times 10^{-3}$ to $3.47 \times 10^{-3}$	[Uranium] = $5.0 \times 10^{-5}$ , [H <sup>+</sup> ] $\sim 1.58 \times 10^{-6}$	0.2	$\log [HL]_{total}$ vs $[\log C_{u,o} - (\log C_{u,w} + 2pH)]$	2.93	$(2+x)J=3$

found to be linear with slopes around 1 in all the systems indicating that no polynuclear complex is formed in the organic phase in the concentration range studied. The relevant data used to construct the plots are incorporated in Table 1. The inference regarding proton number (2*j*) from the slope of  $[\log C_{u,o}]$  vs  $[\log C_{u,w} + 2pH]$  plot at constant *pH* alone would be misleading. However, it gives the polymerization number correctly and in essence represents the slope of a plot for the variation of  $[\log C_{u,o}]$  against  $[\log C_{u,w}]$ . A separate and independent determination of the number of protons released is, therefore, essential. Under the conditions of constant [oxine] and [pyridine], the plots of  $(\log C_{u,o} - \log C_{u,w})$  vs *pH* gave straight lines with slopes around 2 in all the systems. The data used to construct the plots are presented in Table 1. The ratio of metal to oxine in extracting species was found to be 1:3 by slope analysis technique. The data used for constructing the experimental curves are incorporated in Table 1.

#### Determination of ratio of uranium to pyridine base

The formation and extraction of the mixed complex is given by



where B represents pyridine base and *n* the number of B molecules in the adduct. The distribution of uranium is given by Eq. 3,

$$D = \frac{[\text{UO}_2(\text{L})_2\text{HL}]_o + [\text{UO}_2(\text{L})_2\text{HL B}] + \dots + [\text{UO}_2(\text{L})_2\text{HL nB}]_o}{[\text{UO}_2(\text{SO}_4)_2]^{-2} + [\text{UO}_2(\text{SO}_4)]^{-1} + [\text{UO}_2(\text{L})_2] + [\text{UO}_2(\text{L})_2\text{HL}] + [\text{UO}_2(\text{L})_2\text{HL B}] + \dots + [\text{UO}_2(\text{L})_2\text{HL nB}]} \quad \dots (3)$$

In the lower *pH* range, the simple anionic sulphate complex of uranium is the predominant species in the aqueous phase. Further, it is assumed that the formation of pyridine adducts takes place in the organic phase. Substitution of appropriate equilibrium constants in Eq. (3) gives,

$$D = K_{\text{ex}} \frac{[\text{HL}]_o^3}{[\text{H}^+]^2} (1 + K_{\text{AD}_o} [\text{B}]_o^n) \quad \dots (4)$$

where  $K_{\text{AD}_o}$  is the adduct formation constant in the organic phase of the 1:3 chelate with *n* moles of the adduct forming base, B. Thus a plot of  $\log D$  vs  $\log [\text{B}]_o$  at constant  $[\text{HL}]_o$  and constant *pH* gives two linear portions, viz., one at very low  $[\text{B}]_o$  and the other at high  $[\text{B}]_o$  where the adduct extraction predominates. The slope of the plot gives the number of base molecules *n* involved in the formation, and the value of  $\log K_{\text{AD}_o}$  is obtained from the intersection of these two lines.

$$\log K_{\text{AD}_o} = -n \log [\text{B}]_o \quad \dots (5)$$

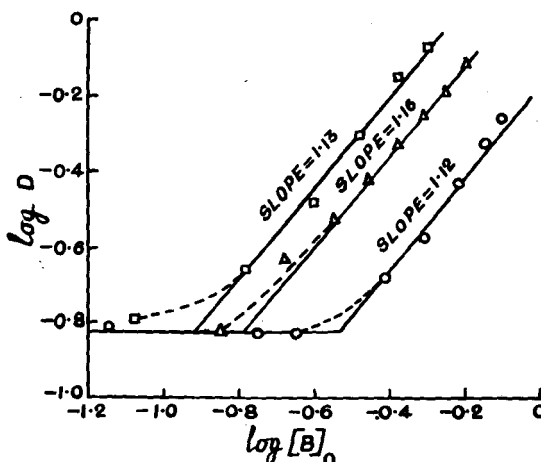


Fig. 1—Plots of  $\log D$  vs  $\log [\text{B}]_o$  [O—O, uranium(VI)-oxine-pyridine system;  $\Delta$ — $\Delta$ , uranium(VI)-oxine-3-pyridine system;  $\square$ — $\square$ , uranium(VI)-oxine-4-picoline system]. Aqueous phase contained 5.0 ml of  $2.0 \times 10^{-4} M$  U(VI) + 1 ml of 0.02 *M* oxine + 4 ml of 1 *M*  $\text{Na}_2\text{SO}_4$ ; *pH* after extraction  $\sim 6.2$ ; total volume 20 ml. The organic phase contained 20 ml of benzene containing various amounts of respective pyridine bases.

This type of determination of the base number has been proposed by several workers<sup>6,7</sup>. The equilibrium concentrations of bases in the organic phase are calculated taking into account the protonation and distribution of ligands<sup>8-10</sup>.

From Fig. 1 it can be inferred that the slopes of all the straight lines are around 1 indicating that one molecule of pyridine base is attached to uranium in the extract. The adduct formation constants are found to be 0.53, 0.78 and 0.93 for pyridine, 3-picoline and 4-picoline systems respectively.

The overall conditional equilibrium constants of these mixed complexes were calculated from the distribution data of uranium(VI) obtained on varying [oxine] in the presence of large excess of base and  $(\text{SO}_4)^{2-}$  at constant *pH* using Eq. 6,

$$\log K_{\text{ex}} = \log D + 2 \log [\text{H}^+] - 3 \log [\text{HL}]_w - \log [\text{B}]_w \quad \dots (6)$$

where  $K_{\text{ex}}$  is the overall conditional extraction constant of the mixed complex.

The  $K_{\text{ex}}$  and  $K_{\text{AD}_o}$  values so obtained are presented in Table 2. It is evident from the results in Table 2 that the effectiveness of the nitrogen bases in forming mixed complexes is in the order: 4-picoline > 3-picoline > pyridine.

The adduct formation constants also follow the same order. The same trend has been reported in several systems with these bases<sup>18</sup>.

The above observations lead to the conclusion that the extracting species is  $\text{UO}_2(\text{L})_2\text{HL B}$ ; it is likely that out of the three oxine molecules one acts as a neutral monodentate ligand while two act as uninegative bidentate ligands; B occupies the eighth coordination

Table 2—Adduct Formation and Overall Extraction Constants

System	Adduct constant $\log K_{AD}$	Overall extraction Constant $\log K_{ex}$
Uranium (VI)-oxine-pyridine	0.53	4.22
Uranium (VI)-oxine-3-picoline	0.78	4.83
Uranium (VI)-oxine-4-picoline	0.93	5.07
Uranium (VI)-oxine*	—	4.06

\*To be published.

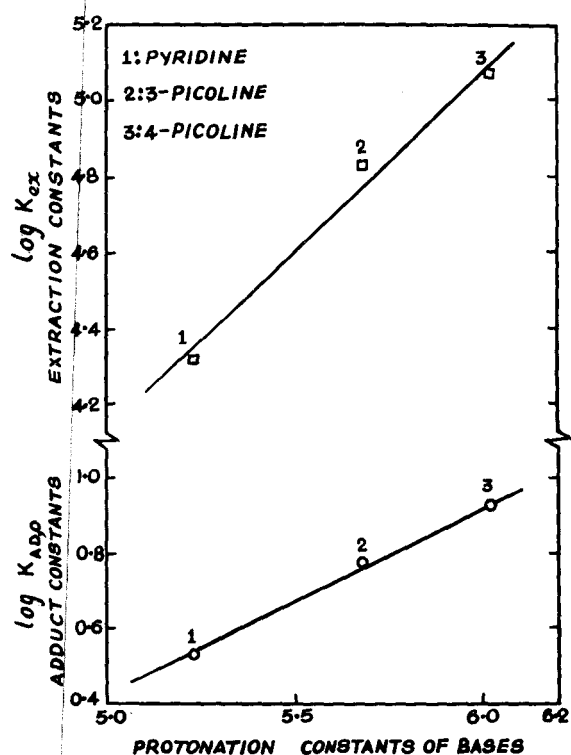


Fig. 2—Correlation between adduct formation constants or extraction constants and the basicities of nitrogen bases.

position by replacing water or by raising coordination number of uranium from seven to eight. This sort of enhancement in coordination number of metals has been reported in literature<sup>9,11-15</sup> in the case of other metal complexes where the donors are pyridine and triphenylphosphine. The existing studies on the nature of synergistic enhancement published so far seem to favour the 'addition mechanism'.

Attempts have been made<sup>16,17</sup> to establish correlation between the stability constants and  $pK$

values of ligands i.e., correlation between basicities towards a metal ion and basicities towards a proton. The relationship between the stability constants of uranium complexes with oxine in presence of pyridine and its derivatives (as well as base adduct constants) and their protonation constants has been investigated; the results are presented graphically in Fig. 2. It can be seen that in both the cases the relationship is found to be linear or nearly linear.

The ESR spectral studies reveal that there is no reduction in the oxidation state of uranium i.e., it remains +6 in the uranium-oxine complex on the addition of pyridine base in contrast to the behaviour observed in vanadium-oxine-pyridine base complex<sup>18</sup>.

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**References**

- Alimarin I P & Zolotov Y A, *Talanta*, **9** (1962) 891.
- Koppiker K S & Gajenkush K B, *Report of the Indian At. Energy Comm, At Energy Estab, Trombay AEET-225*, (1965).
- Coleman J S, Varga L P & Mastin S H, *Inorg Chem*, **9** (1970) 1915.
- Busev A I, Tiptsova V G & Ivanov V M, *Analytical chemistry of rare elements* (Mir Publishers, Moscow) 1981, 124.
- Lurie Ju, *Handbook of analytical chemistry* (Mir Publishers, Moscow) 1975, 285 and 290.
- Akaiwa H, Kawamoto H & Saito N, *Nippon Kagaku Zasshi*, **92** (1971) 1156.
- Bhatki K S, Rane A T & Freiser H, *Inorg Chem*, **17** (1978) 2215.
- Irving H M N H & Al-Niami N S, *J inorg nucl Chem*, **27** (1965) 1671, 2231.
- Irving H & Edgington D N, *J inorg nucl Chem*, **20** (1961) 321.
- Raju A M S & Pandu Ranga Rao V, *Indian J Chem*, **15A** (1977) 1005.
- Carlin R L & Walker F A, *J Am chem Soc*, **87** (1965) 2128.
- Cotton F A & Wilkinson G, *Advanced inorganic chemistry* (Wiley Eastern, New Delhi) 1972, 815.
- Irving H, in *Solvent extraction chemistry*, edited by D Dyrssen, J O Liljensin & J Rydberg (North-Holland, Amsterdam) 1967, 91 and references cited therein.
- Irving H & Edgington D N, *Chem Ind* (London), **77** (1961).
- Liem D H & Dyrssen D, *Acta chem Scand*, **20** (1966) 272; Liem D H in *Solvent extraction chemistry*, edited by D Dyrssen, J O Liljensin & J Rydberg (North-Holland, Amsterdam) 1967, 264.
- Jones J G, Poole J B, Tomkinson J C & Williams R J P, *J chem Soc* (1958) 2001.
- Clarke K, Cowen R A, Gray G W & Osborne E H, *J chem Soc* (1963) 245.
- Syama Sundar B, Sarma B S R & Pandu Ranga Rao V, *J inorg nucl Chem*, **43** (1981) 404 and references cited therein.