Effect of Chloro Substitution in Oxine on Extraction of Uranium(VI)

B SYAMA SUNDAR*, K SREENIVASA MURTHY & E SITA KUMARI

Department of Chemistry, Nagarjuna University, Nagarjunanagar 522 510

Equilibrium distribution ratios have been determined for extraction of uranium(VI) with 5-chlorooxine and 5,7-dichlorooxine into chloroform as a function of pH and reagent concentration at ambient temperature. The extracting species is found to be mononuclear in both the systems. The pH of extraction of uranium(VI) chelates of 5-chlorooxine and 5,7-dichlorooxine shift to lower values as compared to that of uranium(VI)-oxine chelate. Bathochromic shifts in the absorption spectra are observed in uranium(VI)-halooxinate systems.

The work reported in the literature[1-4] on the use of halo substituted oxine derivatives for the extraction of uranium is mainly devoted to analytical rather to equilibrium studies. However, there is no reference for the extraction of uranium by 5-chlorooxine. Since substitution in the oxine is expected to bring about marked changes in the properties of the parent ligand, the present investigation on the extraction of uranium(VI) with 5-chlorooxine and 5,7-dichlorooxine has been undertaken to study the effect of chloro substitution in oxine on the extraction behaviour of the chloro derivatives vis-a-vis the parent ligand.

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

A 0.01 M uranium(VI) solution was prepared by dissolving appropriate amount of uranyl acetate (AnalaR, BDH) in doubly distilled water and standardised using ceric sulphate after reducing U(VI) to U(IV) with Jones' reductor[5]. Solutions of required strengths were obtained by appropriate dilution of this stock solution.

5-Chloro- and 5,7-dichlorooxine solutions (0.05 M) were prepared by dissolving the required amounts of 5-chlorooxine (Koch-Light) and 5,7-dichlorooxine (purim, Fluka) in minimum amount of 4N sulphuric acid. These solutions were diluted as and when required.
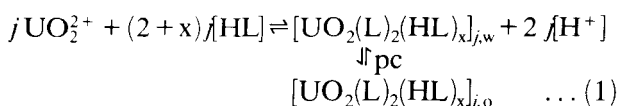
All solvents were distilled before use. The other chemicals used were of AR grade.

General extraction procedure

To an aliquot (5 ml) of 0.0002 M uranium(VI) solution, was added 0.05 M 5-chlorooxine (3 ml) or 0.025 M 5,7-dichlorooxine (2 ml). The total volume was made up to 20 ml, its pH adjusted to the required value (the optimum pH after extraction being in the range of 5.5-7.0) by adding dil. sulphuric acid or dil. ammonia. The solution was equilibrated with chloroform (20 ml) for 2 min, the organic phase separated, dried over anhyd. Na$_2$SO$_4$, filtered and its absorbance measured at 400 nm.

The absorption spectra of uranium(VI)-5-chlorooxine and uranium(VI)-5,7-dichlorooxine systems in chloroform show a plateau region at 390-400 nm while uranium(VI)-oxine complex exhibits absorption maximum at 390 nm. The molar extinction coefficients of U(VI)-5-chlorooxine and U(VI)-5,7-dichlorooxine systems are 6,800 (400 nm) and 7,200 (400 nm), respectively while that of U(VI)-oxine is 5,200 (400 nm). The Beer's law is obeyed up to 16 μg and 12 μg of uranium/ml in the case of 5-chlorooxine and 5,7-dichlorooxine systems respectively.

Experiments based on the graphical method of Coleman et al.[6] reveal that the extracting species contain a single absorbing species in both the systems. The extraction equilibrium in the presence of large excess of sodium sulphate may be given by Eq. (1).

$$j\,UO_2^{2+} + (2+x)j[HL] \rightleftharpoons [UO_2(L)_2(HL)_x]_{j,w} + 2\,j[H^+]$$
$$\downarrow pc$$
$$[UO_2(L)_2(HL)_x]_{j,o} \qquad \ldots (1)$$

Hence expression (2) can be derived for the conditional extraction constant (k_{ex}) as described elsewhere in a similar case[7].

$$\log K_{ex} = \log[C]_{u,o} + 2\,j\log[H^+] - j\log[C]_{u,w} - (2+x)\,j\log[HL]_w \qquad \ldots (2)$$

where j is the polymerization number, HL represents the oxine derivative and subscripts, u, w and o, refer to uranium, water and organic solvent respectively. The data for the construction of several plots which will give polymerization number, hydrogen ion release and the ratio of uranium to the reagent are incorporated in Table 1. The values of slopes recorded in Table 1 indicate that the extracted species has the composition UO$_2$(L)$_2$HL.

Table 1—Experimental Data for Determination of Composition of Extracting Species, Ionic Strength in all cases 0.2 M

Conc of Ur(VI) M	Conc of H-ion M	Conc of reagent M	Type of plot y vs x	Slope of linear curve	Inference
			Uranium(VI)-5-chlorooxine system		
5.0×10^{-5}	6.31×10^{-6} to 2.95×10^{-6}	7.5×10^{-3}	$\log K_d$ vs pH	2.11	$2j = 2$
3.0×10^{-5} to 7.0×10^{-5}	$\sim 1.0 \times 10^{-5}$	7.5×10^{-3}	$\log C_{u,o}$ vs $[\log C_{u,w} + 2\,p\text{H}]$	1.03	$j = 1$
5.0×10^{-5}	$\sim 7.9 \times 10^{-6}$	5.01×10^{-3} to 1.00×10^{-2}	$[\log C_{u,o} - (\log C_{u,w} + 2\,p\text{H})]$ vs $\log[\text{HL}]_{\text{total}}$	2.99	$(2 + x)j = 3$
			Uranium(VI)-5,7-dichlorooxine system		
5.0×10^{-5}	1.17×10^{-5} to 5.89×10^{-6}	2.5×10^{-3}	$\log K_d$ vs pH	2.17	$2j = 2$
3.0×10^{-5} to 7.0×10^{-5}	$\sim 1.0 \times 10^{-5}$	2.5×10^{-3}	$\log C_{u,o}$ vs $[\log C_{u,w} + 2\,p\text{H}]$	0.95	$j = 1$
5.0×10^{-5}	$\sim 7.9 \times 10^{-6}$	4.79×10^{-3} to 8.50×10^{-3}	$[\log C_{u,o} - (\log C_{u,w} + 2p\text{H})]$ vs $\log[\text{HL}]_{\text{total}}$	2.89	$(2 + x)j = 3$

The overall conditional equilibrium constants for the uranium(VI)-5-chlorooxine and uranium(VI)-5,7-dichlorooxine systems are calculated from the distribution data of uranium(VI) obtained by variation of the concentration of the oxine derivative in the presence of large excess of sulphate ion at constant pH, by substituting the appropriate equilibrium concentrations in Eq. (3).

$$\log K_{ex} = \log D + 2 \log[\text{H}^+] - 3 \log[\text{HL}]_w$$

$$\dots (3)$$

The values of log K_{ex} for 5-chlorooxine and 5,7-dichlorooxine systems are 5.92 and 7.77, respectively at ambient temeprature of 30°, while for the oxine system the value is reported[7] to be 4.06. The values of the conditional extraction constants suggest that the extraction capacities of the ligands are in the order: oxine < 5-chlorooxine < 5,7-dichlorooxine. This increase in the capacity of the ligand to extract U(VI) may be correlated with the increasing Lewis base character of the ligands. Substitution by one or more chlorines in the oxine molecule increases the acidity of the molecule and this permits formation of the complex at a lower pH. Moellor and Jackson[8] have observed that dichlorooxine extracts some rare earth metals almost completely in comparison to that by the parent compound. They attributed this to the higher partition coefficient of dichlorooxine ($P_{\text{HA}} = 3.88$) than that of the oxine ($P_{\text{HA}} = 2.66$). Similar results are found in extraction of lanthanum with oxine and 5,7-dichloroox-

ine[9]. It may be noted that the values of λ_{max} and molar extinction coefficients of the complexes increase with increase in the extent of chloro substitution.

Correlation between the molecular weights of the metal chelates and relative distribution coefficients of the complexes ($K'_{\text{D,c}}$) in the two phases is reported[10]. Hence an attempt has been made in the present investigation to determine $K_{\text{D,c}}$ values from Eq. (4).

$$\log K'_{\text{D,c}} = \log K_{ex} + 3 \log K_{\text{D,r}} \qquad \dots (4)$$

where $K_{\text{D,r}}$ is the distribution ratio of the reagent in both the phases. The values of log $K_{\text{D,c}}$ are found to be 12.03, 15.88 and 19.35 for the oxine, 5-chlorooxine and 5,7-dichlorooxine systems respectively. The log $K'_{\text{D,c}}$ values of the uranyl chelates of oxine and its analogues increase linearly with the molecular weights of the chelates.

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