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The Synergistic Extraction of Uranium with Mixtures of Cyanex-272 and Cyanex-923, TPBD, TNBD, TOPO from Thiocyanate Medium

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ABSTRACT

The extraction of uranium (VI) from thiocyanate solutions using Cyanex 272, Cyanex 923, TPBD, and TNBD in xylene as extractants has been investigated. Analysis of the extraction data by both graphical and theoretical methods by taking into account complexation of the metal ion in the aqueous phase with organic ligands and all plausible complexes extracted into the organic phase has been done. The metal ion is extracted into xylene as $UO_2(HA_2)_2$. The plot of log D vs pH has a slope of 2. Mixed species of the type $UO_2(HA_2)_2.S$ (where S= TPBD/TNBD) and $UO_2(HA_2)SCN.S$ (where S = cyanex 923/TOPO) obtained may be responsible for the synergism.

***Key words**: Synergistic extraction, Cyanex 272, Cyanex 923, TPBD, TNBD, Uranium*

1. INTRODUCTION

The separation of uranium from its ores has been the subject of a considerable amount of research effort since the inception of nuclear power generation. A large body of work exists on separation techniques for uranium which largely relies on liquid-liquid extraction techniques; commonly known as solvent extraction (SX) [1]. Thiocyanate has been utilized as a selective complexing agent in the spectrophoto- metric determination of metals and as a selective extraction agent for the separation of metals [2]. The extraction from aqueous solutions containing potassium thiocyanate of divalent metals, thorium(IV), and titanium(IV), vanadium (IV) and uranium(VI) by trioctyl methyl ammonium chloride (TOMAC) has been investigated [3-6].

Organophosphorus SX reagents have been widely studied in the past two decades, earlier work concentrated extensively on the di-alkylphosphoric acid, D2EHPA (di-(2-ethylhehyl)-phosphoric acid), resulting in a number of patents, and the commercial implementation of several processes employing this extractant [7-9]. The subsequent development of phosphoric acid and phosphoric acid extractants, in particular 2-ethylhexyl phophonic acid mono-2-ethylhexyl ester, and bis-(2,4,4-tris-methylpentyl)-phosphinic acid (cyanex 272), led to dramatic improvement in extraction of metal separation factors in the order: phosphoric<phosphonic<phosphinic acid. Excellent comparisons on the extraction characteristics of these reagents for uranium and rhenium are given [10,11].

Cyanex-272 is bis(2,4,4-trimethylpentyl)phosphinic acid. Since the active component of cyanex-272 extractant is a phosphinic acid, metals are extracted through a cation exchange mechanism [12-14]. The extractant is totally miscible with common aromatic and aliphatic diluents, and is extremely stable to both heat and hydrolysis. The present work describes the extraction of uranium (VI) from thiocyanate solutions with mixtures of cyanex-272 and TOPO, cyanex 923, TPBD, TNBD and their mixtures in xylene.

2. EXPERIMENTAL

2.1. Materials

Cyanex 923 (mixture of four Trialkyl phosphine oxides $R_3P(O)$, $R_2R'P(O)$, $RR'_2P(O)$, $R'_3P(0)$, where R = $[CH_3(CH_2)_7]$ - normal octyl R'= $[CH_3(CH_2)_7]$- normal hexyl), cyanex 272, supplied by Cytec, Canada were used after purification. Trioctylphosphine oxide (TOPO), 4,4,4-trifluoro-1-pheny-1,3-butadione (TPBD), 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butane dionepheny-1,3-butadione (TNBD) was obtained from E. Merck (India) Limited. Xylene of analytical reagent quality was

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used as a diluent in the present work. All the other chemicals used were of analytical reagent grade.

2.2 Preparation of Stock Solutions

Stock solutions of uranium (VI) were prepared by dissolving appropriate amounts of $UO_2(NO_3)_2$ $6H_2O$ in distilled water. 1 ml of concentrated nitric acid was added to 100 ml of solution to suppress hydrolysis. The initial metal ion concentration was maintained at $1X10^{-4}$ mol/dm^3 for uranium (VI) for all extraction studies.

2.3. The Extraction Conditions

Solvent extraction studies were made on solutions of 0.1-1.0 mol/dm^3 NH_4SCN at 30 ^oC. The initial pH of the aqueous phase was generally maintained at 3 by adding hydrochloric acid. The initial metal concentration was never exceeded $1X10^{-6}$ mol/dm^3. Solutions of Cyanex 272(0-0005 mol/dm^3) TPBD (0-0.5 mol/dm^3), TNBD (0-0.4 mol/dm^3), TRPO (0-0.6 mol/dm^3) were used. The temperature was maintained at 30 ^oC.

Distribution ratios were determined by shaking equal volumes of aqueous and organic phase for 30 min in a glass Stoppard vial with the help of a mechanical shaker at 30±0.5 ^oC. The solutions were allowed to settle, centrifuged, separated and assayed spectrophotometrically using a Hitachi 220 double beam microprocessor based spectrophotometer. Uranium (VI) was determined spectrophotometrically as its Arsenazo III complexes in 1 mol/dm^3 HCl solution at 660 nm. The absorbance of the complexes was measured within 5 min of mixing. The metal concentrations in the aqueous phase were computed from the respective calibration graphs. The concentration of the metal ion in the organic phase was then obtained by a material balance. These concentrations were used to obtain the distribution ratio, *D*. The experiments were conducted in duplicate and the extraction coefficient, D, is given by

$$\boldsymbol{D} = \frac{C.P.M.With\ 1\ or\ 2\ ml\ of\ the\ organic\ phase}{C.P.M.With\ 1\ or\ 2\ ml\ of\ the\ aqueous\ phase}$$

All the computer programs were written in FORTRAN 77 and executed on a 32 bit mini-computer (HCL HORIZON III).

3. RESULT AND DISCUSSION

3.1. Extraction of UO_2^{2+} with cyanex-272

The extraction of UO_2^{2+} from 1 mol/dm^3 NH_4SCN solutions by cyanex-272 in xylene was studied. The extraction equilibrium may be expressed as

$$UO_{2\ aq}{}^{2+} + 2(HA)_{2(org)} \overset{K2}{\rightarrow} UO_2(HA_2)_{2(org)} + 2H^+_{(aq)} \quad (1)$$

Where $(HA)_2$ represents dimeric species of cyanex-272.

The equilibrium constant K_2 and the distribution ratio D_2 can be written as

$$K_2 = \frac{[UO_2(HA_2)_2]_{(org)}[H^+]^2}{[UO_2{}^{2+}]_{aq}\ [(HA)_2]^2{}_{org}} \quad (2)$$

$$D_2 = \frac{[UO_2.(HA_2)_2]_{(org)}}{[UO_2{}^{2+}]_{(aq)}\ [1+\sum_{i=1}^{2}\beta i[SCN^-]_{(aq)}} \quad (3)$$

3.2. Effect of pH

The plot of log D vs log [H^+] has a slope of -2., in conjunction with the slope of 2 observed with extractant concentration variation at constant pH value(figure 1).

3.3. Effect of extractant concentration

The effect of cyanex 272 concentration ($5X10^{-4}$ mol/dm^3 to $4X10^{-3}$ mol/dm^3) on the extraction of uranium (VI) has been investigated at 1M NH_4SCN. From figure 2 it can be seenthat the extraction of uranium (VI) increases with increase in cyanex-272 concentration in the organic phase. From the slope of the plot it is inferred that two molecules of cyanex-272 are involved in the extracted complexes of uranium (VI).

3.4. Extraction by mixtures

Synergetic extraction of UO_2^{2+} from 1 mol/dm^3 NH_4SCN aqueous phase was studied with the mixtures of cyanex-272 and TPBD/TNBD/TRPO/TOPO in xylene. Considerable synergetic enhancement in the extraction of UO_2^{2+} was observed. The extraction of UO_2^{2+} with mixtures of cyanex-272 and TPBD/TNBD/TRPO/TOPO may be represented as

$$UO_2{}^{2+}{}_{(aq)} + 2(HA)_{2(org)} + yS = UO_2(HA_2)_2 .y(S)_{(org)} + 2H^+{}_{(aq)} \quad (4)$$

Distribution ratio D_{12} is written as

$$D_{12} = [UO_2(HA_2)_2 .y(S)]_{(org)} / [UO_2{}^{2+}]_{(aq)} \quad (5)$$

$$K_{12} = [UO_2(HA_2)_2\ y(S)]_{(org)}[H^+]_{(aq)} / [UO_2{}^{2}]^+{}_{(aq)}[(HA)_2]^2{}_{(org)}[S]^y{}_{(org)} \quad (6)$$

$$K_{12} = D_{12}[H^+]^2{}_{(aq)} / [(HA)_2]^2{}_{(org)}[TRPO]^y{}_{(org)} \quad (7)$$

(where S= TPBD/TNBD/TRPO/TOPO)

The effect of extraction by mixtures is studied by taking cyanex-272, NH_4SCN concentrations as constant and varying the other extractant at once; and keeping the concentration of other extractant and NH_4SCN as constant and cyanex-272 as varying one (Tables 1-4). The log-log plots for the extraction of uranium (VI) from 1 mol/dm^3 thiocyante solutions by mixtures of cyanex-272-TPBD (0.5-1-.75 mole/dm^3 cyanex-272 at constant TPBD (0.003 mol/dm^3) in xylene); (0.003-0.015

mol/dm^3 TPBD at constant cyanex-272 (0.0075 mol/dm^3) in xylene) are given figures 3 and 4.

The log-log plots for the extraction of uranium (VI) from 1 mol/dm^3 thiocyante solutions by mixtures of cyanex-272-TNBD (0.5-1-.75 mole/dm^3 cyanex-272 at constant TNBD (0.003 mole/dm^3) in xylene); (0.003-0.015 mol/dm^3 TNBD at constant cyanex-272 (0.0075 mole/dm^3) in xylene) are given in figures 5 and 6. The log-log plots for the extraction of uranium (VI) from 1 mol/dm^3 thiocyante solutions by mixtures of cyanex-272-TRPO (0.5-1-.75 mole/dm^3 cyanex-272 at constant TRPO (0.003 mole/dm^3) in xylene); (0.005-0.0175 mol/dm^3 TRPO at constant cyanex-272 (0.0075 mole/dm^3) in xylene) are shown in and figures 7 and 8. The log-log plots for the extraction of uranium (VI) from 1 mol/dm^3 thiocyante solutions by mixtures of cyanex-272-TOPO (0.5-1-.75 mole/dm^3 cyanex-272 at constant TOPO (0.003 mole/dm^3) in xylene); (0.005-0.0175 mol/dm^3 TOPO at constant cyanex-272 (0.0075 mole/dm^3) in xylene) are given in and figure 9 and 10.

Mixed species of the $UO_2(HA_2)_2$.S are obtained with mixtures of cyanex-272 and TPBD/TNBD (S= TPBD/TNBD). On the other hand species of the type $UO_2(HA_2)$.SCN.S are obtained with mixtures of cyanex-272 and TRPO/TOPO (S= TRPO/TOPO). The slope of the plot, log D-log cyanex-272 concentration at constant S concentration (figures 3and5) is ~2 indicating that the number of extractant molecules participating in the complex formation are unaltered by the presence of the second extractant (TPBD/TNBD) concentration. On the other hand the log D - log (TPBD/TNBD) concentration plot at fixed second extractant (cyanex-272) concentration has a slope value ~1 showing that it involves the participation 1 molecule of TPBD/TNBD(figures 4and6). The slope of the plot, log D-log cyanex-272 concentration at constant S (S=TRPO/TOPO) concentration (figures 7 and 9) is ~1 indicating that only one molecule of extractant is involved in the species formation. Also plots of log D-Log S (S=TRPO/TOPO) at constant (cyanex-272) concentration (figures 8 and 10) are having the slopes of ~1. Species of the type $UO_2HA_2.SCN^-$.S may be responsible for the synergistic enhancement.

4. CONCLUSIONS

The synergistic enhancement is more pronounced at higher concentrations of the extractant. The slope of the log D-log [extractant] concentration plot decreases progressively with increase in the concentration of the second extractant. Mixed ligand metal formation is responsible for the enhanced extraction.

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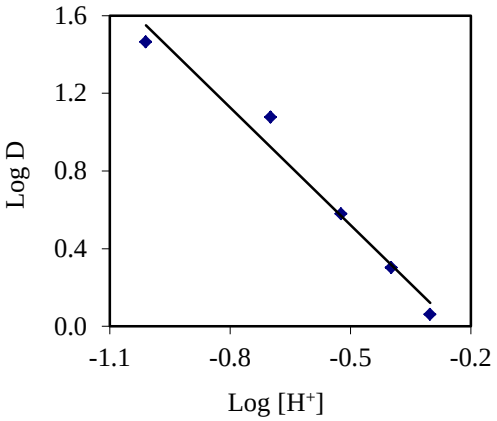

Figure 1: Effect of hydrogen ion concentration.

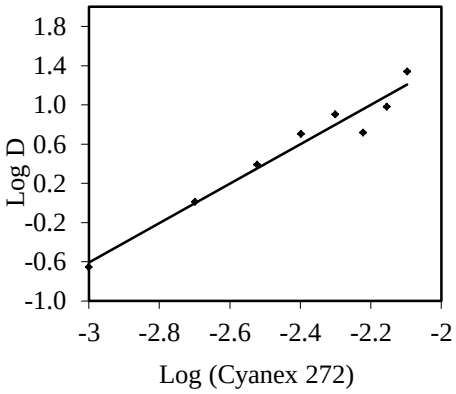

Figure 2: Effect of concentration of cyanex-272.

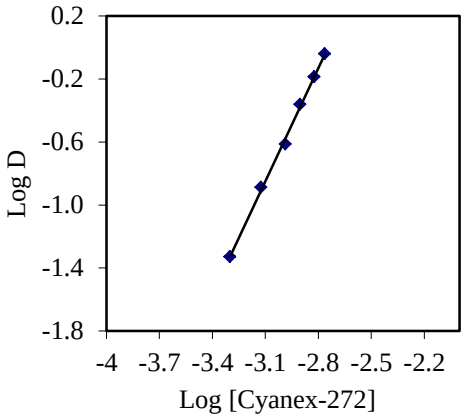

Figure 3: Effect of cyanex-272 in presence of TPBD.

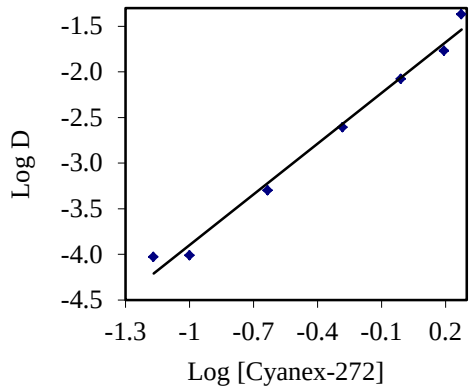

Figure 4: Effect of TPBD in presence of cyanex-272 in xylene.

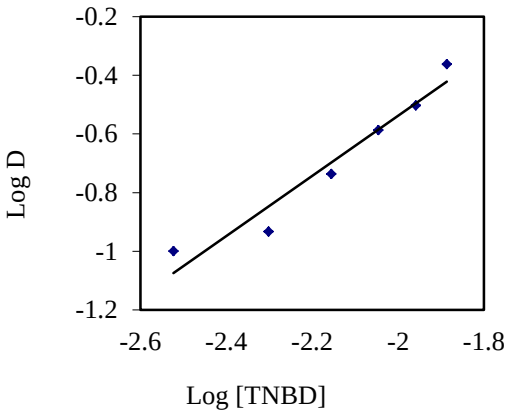

Figure 5: Effect of cyanex-272 in presence of TNBD in xylene.

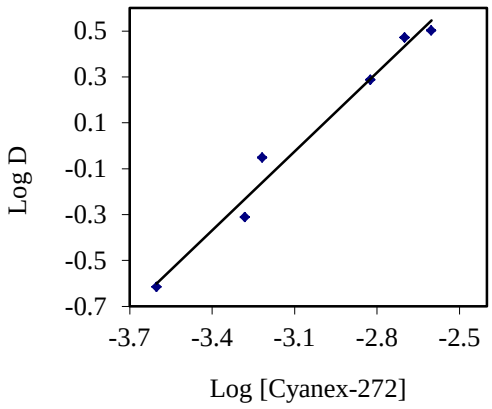

Figure 6: Effect of TNBD in presence of 272 in xylene

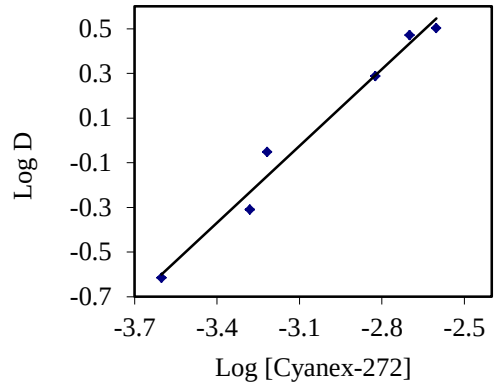

Figure 7: Effect of cyanex-272 in presence of presence of TOPO in xylene .

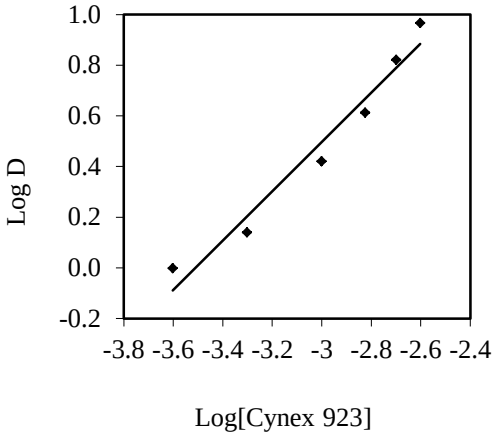

Figure 8: Effect of cyanex-923 in presence of cyanex-923 in xylene.

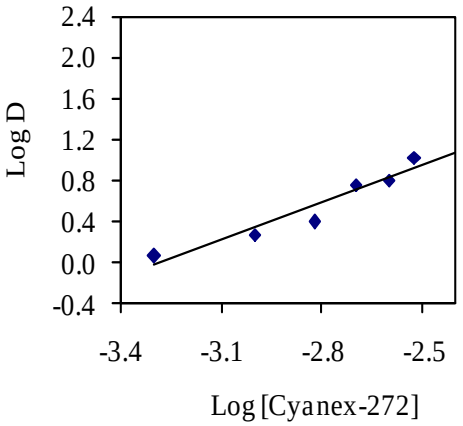

Figure 9: Effect of cyanex-272 in presence of TOPO in xylene.

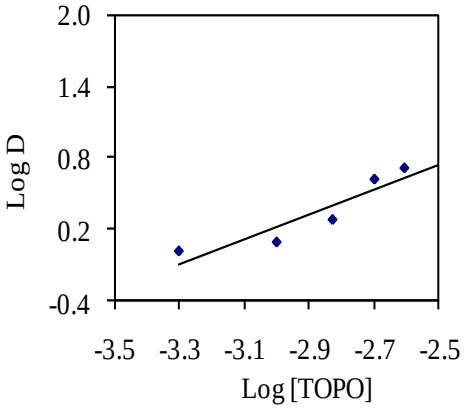

Fig. 10: Effect of TOPO in presence of cyanex-272

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Table 1. Synergistic extraction of uranium(VI) from thiocyanate solution at pH 3 by the mixture of cyanex-272 and TPBD in xylene.

S.No	M Cyanex272	M TNBD	D_1+D_2	D_{SYN}
1	7.50×10^{-4}	3.00×10^{-3}	0.1045	0.1083
2	1.25×10^{-3}	3.00×10^{-3}	0.3192	0.5041
3	1.75×10^{-3}	3.00×10^{-3}	0.7119	1.9728
4	7.50×10^{-4}	7.00×10^{-3}	0.1091	0.174

Table 2. Synergistic extraction of uranium(VI) from thiocyanate solution at pH 3 by the mixture of cyanex-272 and TNBD in xylene.

S.No	M Cyanex272	M TPBD	D_1+D_2	D_{SYN}
1	7.50×10^{-4}	3.00×10^{-3}	0.1033	0.1208
2	7.50×10^{-4}	7.00×10^{-3}	0.10544	0.1694
3	1.25×10^{-3}	3.00×10^{-3}	0.318	0.4348
4	1.75×10^{-3}	3.00×10^{-3}	0.7107	0.9866

Table 3. Synergistic extraction of uranium(VI) from thiocyanate solution at pH-3.0 by the mixture of cyanex-272 and Cyanex-923 in xylene.

S.No	M Cyanex-272	M TOPO	D_1+D_2	D_{SYN}
1	7.50×10^{-4}	7.50×10^{-4}	0.4011	0.8995
2	1.00×10^{-3}	7.50×10^{-4}	0.5236	1.243
3	1.25×10^{-3}	7.50×10^{-4}	0.6158	1.4969
4	7.50×10^{-4}	1.00×10^{-3}	0.5123	1.1459
5	7.50×10^{-4}	1.25×10^{-3}	0.63827	1.4812

Table 4. Synergistic extraction of uranium(VI) from thiocyanate solution at pH-3.0 by the mixture of cyanex-272 TOPO in xylene.

S.No	M Cyanex-272	M Cyanex-923	D_1+D_2	D_{SYN}
1	1.00×10^{-3}	1.00×10^{-3}	0.5782	2.0938
2	1.00×10^{-3}	1.50×10^{-3}	1.033	3.243
3	1.00×10^{-3}	2.00×10^{-3}	1.7389	6.615
4	1.00×10^{-3}	2.50×10^{-3}	2.382	11.379

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