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EXTRACTION OF URANIUM(VI) WITH BINARY MIXTURE OF LIX 984 AND NAPHTHENIC ACID

S. P. Mohanty, S. K. Sahu, I. Mohanty, M. L. P. Reddy* & V. Chakravortty
Department of Chemistry, Utkal University,
Vani Vihar, BHUBANESWAR, ORISSA (INDIA).
*** Regional Research Laboratory, TRIVANDRUM, KERALA (INDIA).**

Extraction studies of uranium(VI) with LIX 984 (HX) (an equivolume mixture of LIX 84 and LIX 860 in kerosene having a resulting mixture of 5-dodecyl salicylaldoxime and 3-nonyl acetophenone oxime in kerosene) and its binary mixture with naphthenic acid (HR) (a mixture of cyclic aliphatic carboxylic acids) have been made. The proposed extracted species are found to be UO_2X_2 and $UO_2X_2(HR)_{2n}/UO_2R_2(HX)_n$/ $UO_2R_2X(HR)_{2n}(HX)_n$ on the basis of slope analysis for individual LIX 984 and its binary mixture, respectively. Effect of various diluents on the extraction with individual extractants and their mixture was studied. Influence of addition of various salts on the extraction has also been carried out.

1. Introduction

Alkaline leach process for uranium ores produces a good grade of mill precipitates. However ,there are few satisfactory extractants for extraction of uranium(VI) in the presence of large salt concentration and at high pH of the aqueous solutions [1]. Commercially marketed chelating extractants under the trade name LIX are a series of 2-hydroxy benzophenone oximes. The use of these extractants for the separation and isolation of metals has been reviewed [1,2]. The mechanism of the synergistic uranium extraction has been studied as a function of the pH using a mixture of LIX 63 and D2EHPA [3], LIX 54 and TBP [4] as extractants. We have carried out the extraction of uranium(VI) with benzoic, cinnamic, enanthic, caprylic, pelargonic, Versatic, naphthenic acids and their binary mixtures [5-8]. However,

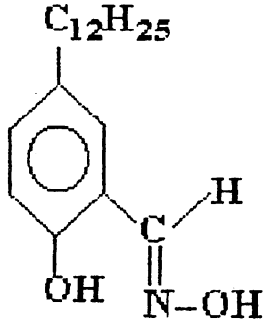
literature dealing with the extraction with the binary mixture of LIX reagents and carboxylic acids are not available. We have initiated a program for carrying out studies on solvent extraction behaviour of uranium(VI) in the acidic range with an equivolume mixture of LIX 84 and LIX 860 in kerosene having a resulting mixture of 5-dodecyl salicylaldoxime and 3-nonyl acetophenone oxime in kerosene (commercially available as LIX 984) and naphthenic acid. This is the continuation of our previous work on the extraction of U(VI) with LIX 26 [9], LIX 54 [10] in various diluents and with the mixture of LIX 860 and Versatic 10 [11].

The reactive components of the extractants are :

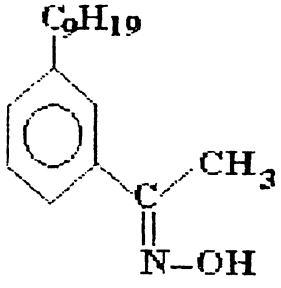
LIX 984 : An equivolume mixture of LIX 84 and LIX 860 in kerosene.

LIX 84: 3-nonyl acetophenone oxime and small amount of 5-dodecyl salicylaldoxime in kerosene.

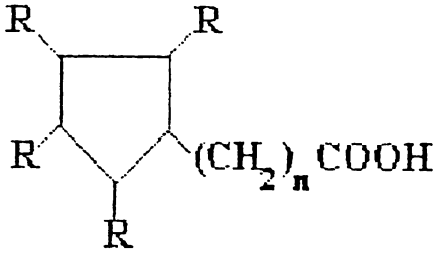
LIX 860: 5-dodecyl salicylaldoxime and a small amount of 3-nonyl acetophenone oxime in kerosene



(5-dodecyl salicylaldoxime)



(3-nonyl acetophenoxime)



(Naphthenic acid)

2. Experimental

The extractants used in the present work were naphthenic acid, and LIX984. LIX 984 and naphthenic acid were supplied by Henkel Corp., Ireland and BDH Chemical Ltd. respectively. Commercially available blue kerosene in Orissa (India) was decolourised by treating with animal charcoal and then used as organic phase diluent. All other organic reagents were used as received, without further purification. Stock solution of uranium(VI) (1.0 x 10^{-4} M) was prepared by dissolving uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$ (LOBA) in distilled water. 1 mL of concentrated HNO_3 was added to 100 mL of the stock solution to suppress hydrolysis. The pH of the aqueous phase was adjusted with pyridine/dil. HCl before extraction, since pyridine alone does not extract uranium(VI).

Aliquots of aqueous feed solution and organic phase, 10 mL each, were introduced into 50 mL separating funnels. The funnels were stoppered and shaken vigorously for 20 minutes at room temperature. After allowing the phases to separate for 20 minutes at the same temperature, the aqueous phase was removed and pH was measured with a combined glass electrode. The concentration of uranium(VI) in the feed solution and raffinate were determined spectrophotometrically with Arsenazo III [12] at λ max = 656 nm .The uranium content in the organic phase was calculated from the difference in the concentration in the aqueous phase before (feed solution) and after (raffinate) extraction.

3. Results & discussion

3.1 Variation of shaking time:

The shaking time for the extraction was varied from 5 minutes to 1hour, keeping all other factors constant. Results showed quantitative extraction was obtained within 20 minutes.

3.2 Effect of equilibrium pH:

Extraction of uranium(VI) was carried out by 2-20%(v/v) of LIX 984 (HX) and 0.5%(v/v) naphthenic acid (HR) in kerosene as a function of equilibrium pH ranging from 3.26-5.48, and 3.88-5.49, respectively. It has been observed for both the cases that the distribution ratio increases regularly with the increase in equilibrium pH (Fig-1). This may be due to less availability of H^+ ion at higher pH facilitating the dissociation of the extractant, which in turn enhances the formation of more extractable complex. Quantitative extraction was obtained at 4.83 and 5.49 equilibrium pH with 20% LIX 984 and 0.5% naphthenic acid, respectively. By plotting the logarithm of the distribution ratios against equilibrium pH for the mixtures consisting of 2 to 20%(v/v) LIX 984 and 0.5% (v/v) naphthenic acid, linear plots

with slopes of 1.5, 1.55, 1.7, 1.8 and 1.69 (Fig-2) were obtained in comparison to the slopes 1.6, 1.7, 1.6, 1.75 and 1.68 respectively found out by the least square analysis methods. This revels the involvement of two H^+ ions in the following extraction mechanisms.

$$UO_2^{2+}{}_{(aq)} + 2HX_{(org)} = UO_2X_{2(org)} + 2H^+ \quad (1)$$

where HX is LIX 984

$$UO_2^{2+}{}_{(aq)} + 2(HR)_{2(org)} = UO_2R_2.2HR_{(org)} + 2H^+{}_{(aq)} \quad (2)$$

where $(HR)_2$ is the dimerised naphthenic acid because carboxylic acids dimerise in organic solvents [13, 14].

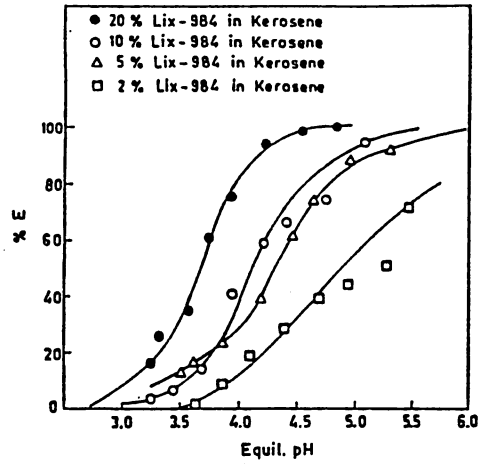


Fig.1. Extraction curves of uranium (VI) with varying concentration of LIX 984 in kerosene

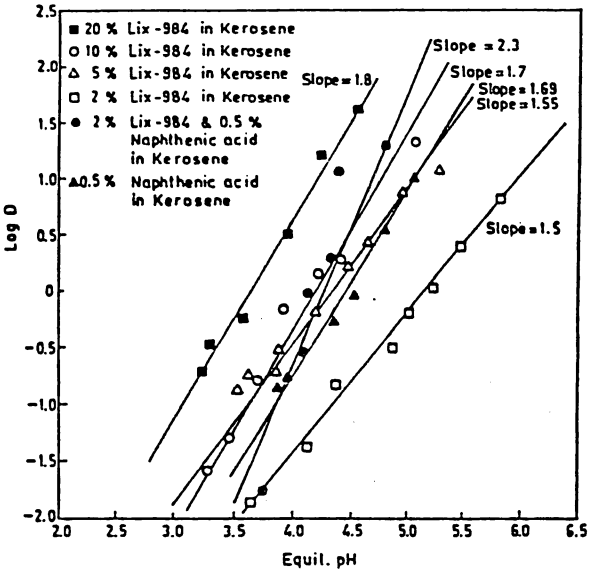


Fig.2. Plot of logD vs. equil. pH for the extraction of uranium(VI) with varying concentration of LIX 984 and its mixture with 0.5% (v/v) Naphthenic acid in kerosene.

3.3 Variation of extractant concentration:

The concentrations of LIX 984 and naphthenic acid were varied from 1-8% (v/v) at pH 5.0 and 0.1-0.8% (v/v) at pH 5.0 respectively. A regular increase in the percentage of extraction was obtained with the increase in the concentration of the extractants. A linear relationship between logD and log[extractant] with slopes ~2 (Fig.3 & 4) for the extraction of uranium (VI) with 1-8% (v/v) LIX 984 and 0.1-0.8% (v/v) naphthenic acid was obtained in comparison to the slopes of 1.92 and 1.91 found by the least square analysis method. This confirms the involvement of two extractant molecules in the reaction mechanism given in equation 1 and 2.

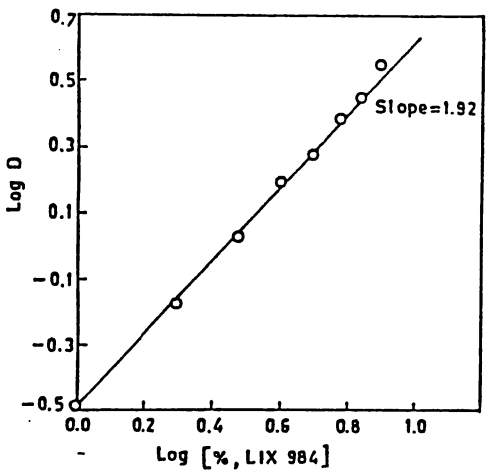


Fig.3. Plot of logD vs log[%, LIX 984] for the extraction of uranium(VI).

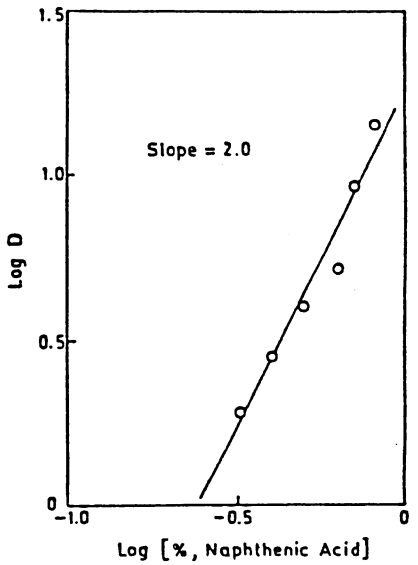


Fig.4. Plot of logD vs log[%, Naphthenic acid] for the extraction of uranium(VI).

3.4. Extraction with the mixture of LIX-984 and naphthenic acid:

The extraction of uranium(VI) with a binary mixture of 2%(v/v) LIX 984 and 0.5%(v/v) naphthenic acid (HR) in kerosene has been studied in the equilibrium pH range 3.5-5.5. The extraction increases with the increase in equilibrium pH and becomes quantitative at equilibrium pH = 4.79 (Fig.6). The plot of $\log D_{max}$ (distribution coefficient of the mixture) vs equilibrium pH results in a straight line with a slope 2.3 (Fig.2) against 2.2 (slope calculated by least square analysis method). Hence the mechanism for the synergistic extraction can be suggested as follows:

$$UO_2^{2+}{}_{(aq)} + 2HX_{(org)} + n(HR)_{2(org)} = UO_2X_2(HR)_{2n(org)} + 2H^+_{(aq)} \quad (3)$$

$$UO_2^{2+}{}_{(aq)} + (HR)_{2(org)} + n\,HX_{(org)} = UO_2R_2(HX)_{n(org)} + 2H^+_{(aq)} \quad (4)$$

$$UO_2^{2+}{}_{(aq)} + (n+1)(HR)_{2(org)} + (n+1)HX_{(org)} = UO_2R_2X(HR)_{2n}(HX)_{n(org)} + 2H^+_{(aq)} \quad (5)$$

The extraction has also been studied with the mixture of 0.1%(v/v) naphthenic acid and varying concentrations of LIX 984 (1, 2, 3, 4, 5, 6, 7 & 8%) and also 1% (v/v) LIX 984 and varying concentrations of naphthenic acid (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 & 0.8%) in kerosene at equilibrium pH 4.68 as shown in Table-I, enhancement in the extraction was observed and the synergism increases with increase in LIX 984 concentration, with the mixtures consisting of 0.1%(v/v) naphthenic acid and 1 to 8 % LIX 984 as shown in Table II, but in the extraction with the mixtures consisting of 1%(v/v) LIX 984 and (0.1to 0.8)% naphthenic acid, synergism increases upto 0.3% and then decreases.

3.5. *Effect of diluents:*

The extraction behaviour with 2%(v/v) LIX 984 in kerosene, benzene, toluene, xylene, chloroform, carbontetrachloride amyl alcohol and methyl isobutyl ketone (MIBK) have been investigated in the equilibrium pH range 2.8 to 6.2. Very low distribution ratio values are obtained with MIBK and benzene. 76% uranium was extracted with amyl alcohol. Kerosene was found to be the best among all the diluent used (Fig.5). Since kerosene is cheap and commercially available, it can be used in the industrial scale.

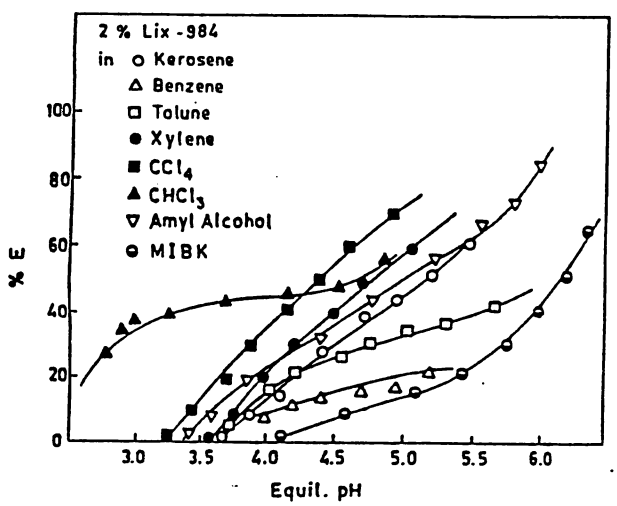


Fig.5 Extraction curves of uranium(VI) with 2%(v/v) LIX 984 with different diluents

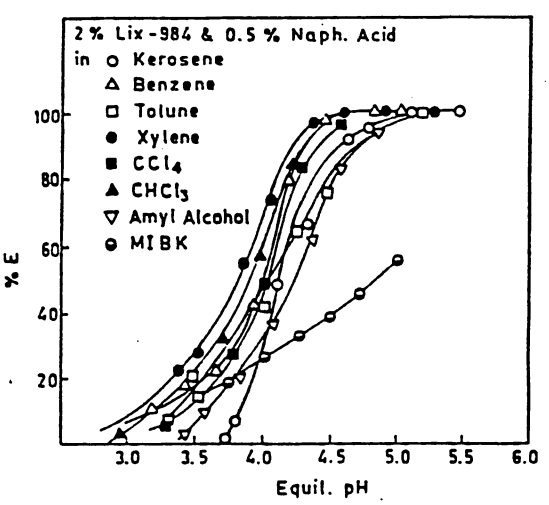


Fig.6.Extraction curves of uranium(VI) with the binary mixture of 2% (v/v) LIX 984 + 0.5%(v/v)Napthenic acid in different diluents

Table - I

Extraction of U(VI) by binary mixture of 0.1% (v/v) naphthenic acid and LIX 984 in kerosene

[LIX 984],%	D_1	D_2	D_{mix}	ΔD	S.C.
1	1.54	0.33	2.81	0.94	0.18
2	1.54	0.46	3.0	1.04	0.18
3	1.54	0.70	3.44	1.20	0.19
4	1.54	1.61	3.71	0.56	0.07
5	1.54	1.92	4.71	1.25	0.13
6	1.54	2.81	7.89	4.17	0.33
7	1.54	2.84	9.0	4.62	0.31
8	1.54	3.56	19.0	13.9	0.57

where D_1 , D_2 and D_{mix} are the distribution ratios of U(VI) for naphthenic acid , LIX 984 and their binary mixture, respectively and $\Delta D = D_{mix} - (D_1 + D_2)$, S.C. = $\log D_{mix}/(D_1 + D_2)$

Table II

Extraction of U(VI) with mixture of 1% (v/v) LIX 984 and naphthenic acid in kerosene

[Naphthenic acid],%	D_1	D_2	D_{mix}	ΔD	S.C.
0.1	0.33	1.54	2.91	1.04	0.19
0.2	0.33	1.77	3.16	1.06	0.20
0.3	0.33	1.90	3.32	1.09	0.17
0.4	0.33	2.81	3.56	0.42	0.05
0.5	0.33	4.08	5.31	0.90	0.08
0.6	0.33	5.10	5.83	0.40	0.03
0.7	0.33	9.17	9.75	0.25	0.01
0.8	0.33	14.25	19.50	4.92	0.13

where D_1 , D_2 and D_{mix} are the distribution ratios of U(VI) for LIX 984, naphthenic acid and their binary mixtures , respectively and $\Delta D = D_{mix} - (D_1 + D_2)$ and S.C. = $\log D_{mix}/(D_1 + D_2)$

Effect of the diluents on the synergistic extraction has also been studied at equilibrium pH range 2.9 to 5.5 (Fig 6). In all the cases the extraction is enhanced as compared to that with 2%(v/v) LIX 984 alone shown in Fig.5. This confirms the dependence of the synergistic effect on the nature of the diluents. The decreasing order can be given as xylene > chloroform > benzene > carbontetrachloride > kerosene > toluene > amyl alcohol > MIBK. For all the cases quantitative extraction was obtained at equilibrium. pH > 4.8 except for MIBK.

3.6. *Effect of Salts :*

The effect of various salts such as NaCl, Na_2SO_4 ,NaSCN and CH_3COONa in the concentration range 0.05 to 1 M on the extraction behaviour of U(VI) from solutions containing 10^{-4} M U(VI), using binary mixture of 2% (v/v) LIX 984 and 0.5% (v/v) naphthenic acid in kerosene was studied as shown in Fig.7. The percentage extraction decreases from 57% to 4 and 2% with increasing salt concentration for CH_3COONa and Na_2SO_4, respectively. For NaCl, the extraction percentage decreases only slightly with increasing salt concentration. All these may be due to the onset of salting in effect [15]. But for NaSCN, the percentage extraction decreases through a maxima at 0.2M.

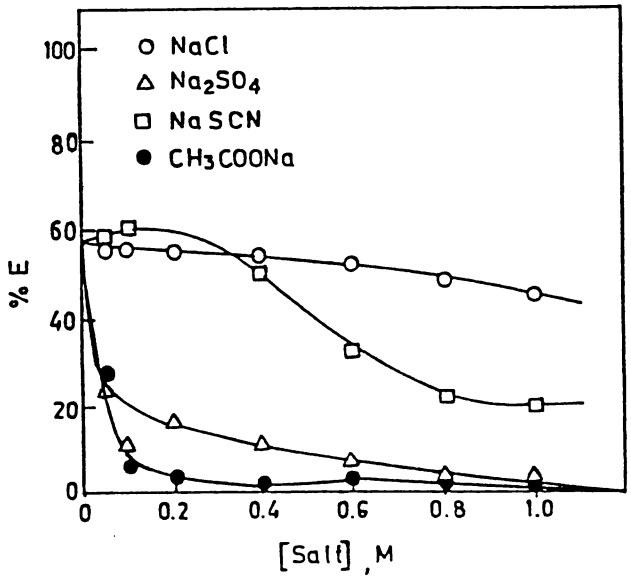


Fig.7. Plot of percentage extraction vs. equilibrium pH for the influence of addition of various salts.

4. Conclusion

Enhancement in the extraction was observed with the binary mixture of LIX 984 and naphthenic acid in kerosene. Extraction efficiency of the mixture is always greater in comparison to the individual LIX 984 in various diluents. Salting in effect comes into picture in presence of NaCl, Na_2SO_4 and CH_3COONa.

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REFERENCES

1. G.M. Ritcey, & A.W. Ashbrook, : Solvent Extraction Principles and Applications to Process Metallurgy, **Vol .I** , p. 115 (Elsevier, Amsterdam) (1979).
2. A.W. Ashbrook, : Coord. Chem. Rev. , **16**, 285 (1975).
3. N. Petrescu, C.S. Gon, L. Ganovici : Revue Roumaine de Chimie, **37(3)**, 359 (1992).
4. K. Akiba, J. Horie, H.Hashimoto: Solv. Extr. Res. Dev. , Japan, **2**, 138 (1995).
5. I. Mohanty, V. Chakravortty : Ind. J. Chem. Technol., **3**, 282(1996).
6. I. Mohanty, S. P. Mohanty, S. K. Gogia, and V. Chakravortty, : Radiochim. Acta., 75, 193(1996).
7. I. Mohanty, J. Muralidhar, V. Chakravortty : J. Radioanal. Nucl. Chem., (in print).
8. S. P. Mohanty, I. Mohanty, P. V. R. Bhaskar Sarma. V. Chakravortty, : Ind. J. Chem.Tech. **4**, 117, (1997).
9. S. Singh, C.R. Panda, V. Chakravortty,K.C. Dash : J. Radioanal. Nucl. Chem., **120 (1)**, 65 (1988)..
10. S. Singh, V. Chakravortty, K.C. Dash : J. Radioanal. Nucl. Chem., **122 (1)**, 137 (1988).
11. S.P. Mohanty, I. Mohanty, S. Mishra, V. Chakravortty : J.Radioanal. Nucl. Chem. (Articles) (in print).
12. A. I. Busev, V. G. Tiptsova, V. M. Ivanov : Analytical Chemistry of Rare Elements, MIR Publication, Moscow, 131 (1981).
13. L. Pauling & L. O. Brockway, : Proc. Natl. Acad. Sci, USA, **20**, 336, (1934).
14. M. M. Davis, G. B. B. M Sutherland, : J. Chem. Phys.,**6**, 775, (1938).
15. Y. Marcus, A. S. Kertes, : Ion Exchange and Solvent Extraction of Metal Complexes, Wiley Inter Science, London,74, (1969).