CHAPTER - VIII

Conclusion
CONCLUSION

In the investigations reported in the previous chapters, the equilibrium extraction behaviour of hexavalent uranium ion from different pH with various liquid cation exchangers viz., benzoic, cinnamic, enanthic, caprylic, pelargonic and naphthenic acids; chelating extractant such as acetyl acetone and a variety of neutral donors like, tri-n-octyl phosphine oxide, tri-phenyl phosphine oxide, triphenyl arsonie oxide, tri-n-butyl phosphate, diphenyl sulfoxide, dinonyl sulfoxide, 1,10-phenanthroline, 2,9-dimethyl 1,10-phenanthroline; 4,7-diphenyl 1,10-phenanthroline; 2,2'-bipyridyl and 2,2'-biquinoline was investigated. The enhancement in the extraction with the binary mixtures of the above extractants has been carried out. The composition of the extracted species are obtained from the slope analysis method and pH\(_{0.5}\) values are also obtained. The effect of various parameters such as equilibrium pH, extractant concentration, various diluents on the extraction have been studied. Salting in or out effect due to the presence of various salts like NaCl, Na\(_2\)SO\(_4\), NaSCN, CH\(_3\)COONa and stripping or back extraction with mineral acids like aq. HCl, H\(_2\)SO\(_4\), HNO\(_3\), H\(_3\)PO\(_4\) and HClO\(_4\) have also been carried out. All the experiments were carried out at room temperature.

Quantitative extraction was obtained with 1 M acetyl acetone and 0.1 M benzoic acid at \(\sim 4.6\) and \(\sim 6.5\) equilibrium pH, respectively. Synergism was obtained with the binary mixture of 1 M acetylacetone + (0.001, 0.005, 0.01, 0.05, 0.1 M) benzene acid and 0.005 M benzoic acid + (0.2, 0.4, 0.6, 0.8 M) acetyl acetone. The increase in pH\(_{0.5}\)
values with Na₂SO₄ may be due to the formation of UO₂(SO₄)²⁻. Salting out effect comes into picture at higher salt concentration.

Cinnamic acid is a better extractant than benzoic acid. With 0.1 M cinnamic acid, the extraction was quantitative at ~4.8 equil. pH. Synergism was obtained with the mixtures of 0.01 M benzoic acid + (0.005, 0.01, 0.03, 0.05, 0.1 M) cinnamic acid and 0.03 M cinnamic acid + (0.001, 0.005, 0.01, 0.05, 0.1 M) benzoic acid. The percentage of extraction decreases with the increase in concentration of Na₂SO₄, NaSCN, CH₃COONa.

The percentage of extraction was 100 at ~4.1 equil. pH with 0.315 M caprylic acid. Quite low synergism was observed up to ~3.5 equil. pH and thereafter, antagonism was observed with the mixture of 1 M acetyl acetone + (0.025 M, 0.1 M) caprylic acid. The influence of NaCl on the extraction was nil. Due to the formation of UO₂(SCN)₄²⁻ and UO₂(SO₄)₂⁻, the extraction decreases with the increase in salt concentration. Salting in effect takes place due to the presence of CH₃COONa.

96 % U(VI) was extracted at ~4.65 and ~4.2 equil. pHs with 0.1 M enanthic & pelargonic acid. Benzene was found to be the effective diluent for both 0.1 M enanthic and pelargonic acid. 0.08 M H₂SO₄; 0.2 M HCl, H₂SO₄, HNO₃, HClO₄ and 0.06 M HCl, H₂SO₄, HNO₃, HClO₄ were found to be the effective stripping agents for 0.1 M enanthic; caprylic and pelargonic acid. With the mixture of 0.1 M enanthic acid + (0.025-0.2 M) pelargonic acid, synergism was obtained. Antagonism followed by low synergism was observed with 0.1 M pelargonic acid + (0.025-0.2 M)
enantitic acid. But synergism followed by antagonism was observed with the mixture of 0.1 M caprylic + (0.025-0.2 M) enanthitic, 0.1 M enanthitic + (0.025-0.3 M) caprylic and 0.1 M caprylic + (0.025-0.2 M) pelargonic acid and 0.1 M pelargonic acid + (0.025-0.3 M) caprylic acid.

Quantitative extraction was obtained in the equil. pH range 4.7-5.2 with 2% naphthenic acid. Percentage of extraction was nil with 0.2 M TBP, DPhSO, DNSO, 0.01 % 1,10-Ph;2,9-dimethyl 1,10-Ph; 4,7-diphenyl 1,10-Ph; 0.01 M 2,2' bipyridyl and 2,2'-biquinoline, in the equil. pH range 2.5-5.2. 66.7 % and 25 % U(VI) was extracted with 0.001 M TPAsO and TOPO, respectively. Kerosene, carbontetrachloride and benzene were found to be the effective diluents for the extraction. Hydrochloric acid was suitable for complete stripping. Synergism was obtained with the mixture of 2% naphthenic acid and 0.2 M TBP, DPhSO and DNSO and the increasing order of efficiency is DPhSO < DNSO < TBP.

With the mixture of 2% naphthenic acid + 0.001 M TOPO, + 0.001 M TPAsO, antagonism followed by synergism was obtained. Synergism was also obtained with 0.1 M TPPO + 0.5 % naphthenic acid and 2% naphthenic acid + 0.01 % 1,10-Ph; + 0.01 % 2,9-dimethyl 1,10-Ph; + 0.01 % 4,7-diphenyl 1,10-Ph; + 2,2'-bipyridyl and + 0.05 M 2,2'-biquinoline.

However, studies involving the mathematical modelling of the equilibrium state of a counter-current system made up of a number of discrete stages (in industry) will be more interesting. The following three categories of models will be used for the development of mathematical formulation of the extraction reaction:

(i) Chemical models where the extraction equilibrium data are modelled on the known chemistry of the extraction reactions.
(ii) Semi-empirical models which generally are analogous with gas adsorption or vapour-liquid equilibria.

(iii) Totally empirical models which are generalised mathematical expressions such as polynomials.

The study of the extraction efficiency and various parameters of the extracted phase such as the ultrasonic velocity, viscosity, dielectric properties and computation of thermodynamic parameters of various commercial liquid extractants in different diluents for extraction of uranium(VI) will be studied in future. The different acoustic and thermodynamic properties and their excess parameters of various commercial extractants in different diluents have to be computed in order to correlate the extraction efficiency of the extractants.