Extraction of U(VI) with the binary mixtures of high molecular mass Versatic acids

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Extraction of U(VI) with high molecular mass carboxylic acids, viz., Versatic 10 and Versatic 911 (RH₂ in benzene as diluent has been carried out as a function of equilibrium pH. The extracted species is found to be UO₂R₂(RH₂). A comparison of pHₐₗₗ values for both the extractants shows that they are of comparable extraction efficiency. Synergism was obtained with the binary mixture of the extractants. Diluent effect on the extraction has also been carried out.

High molecular mass carboxylic acids, despite their high solubility in aqueous phase in alkaline conditions, have found considerable use as extractants in industry and atomic energy programme, because of their low cost, easy availability and high metal loading capacities. The general structures of Versatic 10 and Versatic 911 are given below:

Versatic 10
\[ R_1\text{C}(-CH_3)\text{COOH (R}_1, R_2 = C_6) \]

Versatic 911
\[ R_1\text{C}(-COOH (R}_1, R_2 = C_4 - C_5) \]

Versatic 10 has been used for the extraction of di-, tri- and tetra-valent metals. The composition of the extracted species of various metals using Versatic 911 were investigated by several workers. Preliminary work with Versatic 9, Versatic 10, Versatic 911 has been reported for the extraction of Ce(IV), Th(IV) & U(VI). This paper deals with an investigation of liquid-liquid extraction of U(VI) with Versatic 10 and Versatic 911 and their binary mixture.

Experimental procedure—The aqueous feed solution was prepared by dissolving uranyl nitrate hexahydrate, UO₂(NO₃)₂·6H₂O in distilled water. 5 mL of 10 M nitric acid was added to 100 mL of the solution in order to suppress hydrolysis. The pH was adjusted with pyridine and aq HCl.

The ratio of volumes of the aqueous phase and the organic phase was maintained at 1:1. For all the experiments, the contact time was 10 min. The aqueous phase was separated and the equilibrium pH was measured using a calibrated electrode. The U(VI) was stripped from the organic phase with different acids. The stripping time was 10 min for all the experiments. U(VI) concentration in the organic phase gives the distribution ratio, D, from which %E was calculated.

Results and discussion

Effect of equilibrium pH—Percentage of extraction of U(VI) with pyridine alone was found to be nil. Hence pyridine can be used for pH adjustment. Results in Fig. 1 for the extraction of U(VI) with Versatic 10 and Versatic 911 as a function of pH show that the extraction increased with the increase in equil. pH and was quantitative at ~ 4.15 equil. pH for both 10% Versatic 10 and Versatic 911. The slope of plot of log D versus

![Fig. 1—Plot of %E versus equil. pH for the extraction of U(VI) with Versatic 10 and Versatic 911 in benzene](image-url)
equil. pH was 2, which shows the involvement of two Versatic acid molecules per uranyl ion. This confirms the extracted species to be $\text{UO}_2\text{R}_2(\text{RH})_2$.

**Stripping**—Hydrochloric, nitric, sulphuric and perchloric acids were used as the stripping agents for both Versatic 10 and Versatic 911 at ~ 5.0 equil. pH. For both the cases sulphuric acid was found to be the best among all the acids. At 0.1 M $\text{H}_2\text{SO}_4$, 100% U(VI) was back extracted. Back extraction was quantitative for 0.2 M HCl and 0.2 M HClO$_4$. But for nitric acid quantitative back extraction was obtained at 0.6 M.

**Variation of extractant concentration**—The effect of extractant concentration on extraction was studied by varying the concentration of Versatic acids from 1 to 5%. Value of log $D$ increases linearly with the extractant concentrations. The plots of log $D$ versus log [extractant] give slopes 1.6 and 1.7 for Versatic 10 and Versatic 911, against the theoretical slope 2. Percentage of extraction increases with the increase in extractant concentration. The $\text{pH}_{0.5}$ (pH at which 50% extraction is obtained) values are compared for all the cases. A comparison of $\text{pH}_{0.5}$ values for both Versatic 10 and Versatic 911 shows that they are of comparable extraction efficiency.

**Synergism**—Synergic extraction of U(VI) with the binary mixture of Versatic 10 and Versatic 911 has been carried out. Synergism is obtained with both the mixture of 1% Versatic 10 + (1,2,3,4,5,6,7,8)% Versatic 911 and 1% Versatic 911 + (1,2,3,4,5,6,7,8)% Versatic 10. The synergic enhancement may be attributed to adect formation in the organic phase. With the mixture of the Versatic 10 + (1,2,3,4,5,6,7,8)% Versatic 911, the synergism increases with the increase in percentage of Versatic 911. But with the mixture of 1% Versatic 911 + (1,2,3,4,5,6,7,8)% Versatic 10, the synergism increases up to 4% and then decreases.

**Diluent effect**—Extraction experiments were carried out under optimum conditions using different diluents of high and low dielectric constants for both Versatic 10 and Versatic 911. Basing on the $\text{pH}_{0.5}$ values, the increasing order of extraction efficiency of the extractants are: benzene < toluene < chloroform = kerosene < amyl alcohol < xylene for Versatic 911 and benzene < carbon tetrachloride < CCl$_4$ < xylene = kerosene < chloroform < amyl alcohol = toluene for Versatic 10, respectively.

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**References**