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Analytical Application of Oleophilic Quaternary Ammonium Salts. XV. Extraction of the Uranium(VI)–4-(2-Pyridylazo)resorcinol Complex with Tridodecylethylammonium Bromide

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The uranium(VI)-4-(2-pyridylazo)resorcinol(PAR) chelate anion was extracted with tridodecylethylammonium bromide(TDEABr) into chloroform to form an ion associate. The ternary complex has an absorption maximum at 550 nm in the organic layer. The optimum pH range for the extraction is 6.8—10.7. The distribution ratio and the molar absorptivity are 1.34×10^2 and 4.25×10^4 cm^{-1} mol^{-1} l, respectively. The composition of the ternary complex is estimated to be $UO_2(X)(PAR)(R_3R'N)$. The equation representing the extraction equilibrium would be

$$UO_2(X)(PAR)^- + R_3R'NBr_{(o)} = UO_2(X)(PAR)(R_3R'N)_{(o)} + Br^-.$$

The extraction constant K_{ex} is given by $\log K_{ex}=3.07$.

4-(2-pyridylazo)resorcinol(PAR)[1] is a well-known chelating agent which is useful for the sensitive colorimetric determination of various metal ions. Recently, the ion-pairs of the metal–PAR chelate anions with bulky organic cations have been studied by several workers; the spectrophotometric determination of many metals was made by the extraction method. The PAR chelate anions of cobalt(III),[2,3] chromium,[4] copper,[5] iron(II),[2] iron(III),[6] gallium,[7] niobium,[8] nickel,[2,9] palladium,[10] vanadium(III),[11] vanadium(V),[2,12,13] and zinc[14] were extracted into an organic layer in the presence of zephiramine, tetraphenylarsonium, diphenylguanidine, or Crystal Violet. Uranium(VI) reacts with PAR to form a water-soluble red chelate. The chelate is slightly extractable into butanol, but not extractable into chloroform, carbon tetrachloride, and benzene. From the extraction experiments, it was found that the uranium(VI)–PAR chelate anion was extracted with tridodecylethylammonium bromide(TDEABr) in chloroform to form an ionic associate. The oleophilic quaternary ammonium salts such as TDEABr have been already used for the extraction of metal-Xylenol Oranges,[15]- Eriochrome Cyanine R,[16] and -Pyrocatechol Violet[17] chelate anions. In the present study, the fundamental conditions for the extraction of uranium(VI) as the uranium(VI)–PAR–TDEA ternary complex in chloroform and the composition of the ternary complex will be discussed.

Experimental

Reagent. About 2.5×10^{-3} M uranium(VI) solution was prepared by dissolving a definite amount of uranyl acetate in 0.05 M sulfuric acid. The resulting solution was standardized by the gravimetric method. The solution was diluted as required. A 5×10^{-4} M PAR solution was prepared by dissolving the Dotite PAR in a small amount of 0.2 M NaOH and diluted with deionized water. The TDEABr was prepared by refluxing an ethanolic solution of tridodecylamine and ethyl bromide for 4 h. After the evaporation of the solvent, the salt was recrystallized two times from butyl acetate. A 10^{-3} M TDEABr solution was prepared by dissolving the above TDEABr in the purified chloroform. A 0.05 M sodium borate solution was used as a buffer solution. All the other chemicals used were of guaranteed reagent quality.

Apparatus. A Hitachi 101 spectrophotometer, a Hitachi UV-vis. recording spectrophotometer, and a Hitachi-Horiba F-7 pH meter were employed.

Standard Procedure. Up to 30 µg of uranium(VI), a definite amount of 0.1 M sulfuric acid, and 2 ml of 5×10^{-4} M PAR solution were mixed in a 100 ml polypropylene beaker. The pH of the solution was adjusted to 9 by the addition of 5 ml of 0.05 M sodium borate solution and then the solution was diluted to 25 ml with deionized water. The solution was transferred into a 35 ml test tube and 5 ml of 5×10^{-3} M TDEABr in chloroform was added. The extraction was carried out for 5 min by turning the test tube upside down twice every 5 s. After the phase separation, the organic layer was taken out and centrifuged for 2 min at 3000 rpm. The extract was transferred into an absorption cell and the absorbance at 550 nm was measured aginst the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. The absorption spectra of the ternary complex extracted into chloroform and of

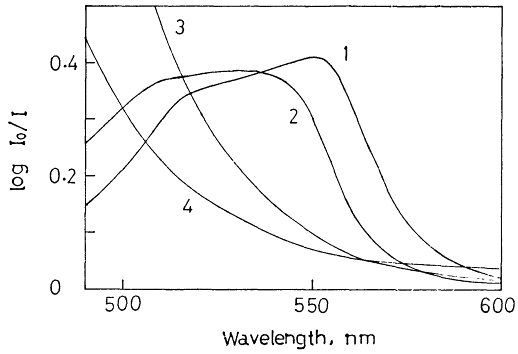

Fig. 1. Absorption spectra of the U–PAR–TDEA complex in chlorohorm and the U–PAR chelate in aqueous solution.
pH=9, V_{aq}=25 ml, V_o=5 ml, $[TDEABr]_o=5\times10^{-3}$ M.
(1): U–PAR–TDEA in chloroform, $[U]_{aq}=2\times10^{-6}$ M,
(2): U–PAR in aq soln, $[U]_{aq}=1\times10^{-5}$ M,
(3): PAR–TDEA in chloroform, $[PAR]_{aq}=4\times10^{-5}$ M,
(4): PAR in aq soln, $[PAR]_{aq}=2\times10^{-4}$M.

the uranium(VI)–PAR chelate anion in an aqueous solution, and also the absorption spectra of the respective blank solutions, are shown in Fig. 1. The ternary complex and the uranium(VI)–PAR chelate anion have an absorption maximum at 550 nm and 530 nm respectively. As compared with the corresponding absorption maximum of the chelate anion, that of the ternary complex is shifted toward the longer wavelengths by 20 nm.

Effect of pH. The aqueous solution containing uranium(VI) and PAR was adjusted to various pH values with the sodium acetate or sodiun borate buffer solution and the extraction was carried out by the above procedure. The results are shown in Fig. 2. The extraction of the ternary complex starts at pH>3, reaches a maximum at pH 6.8, and thereafter remains constant over a wide range (pH 7—10.7). The chloroform extract was stable for at least 1 h. PAR itself is readily extracted from aqueous solution.

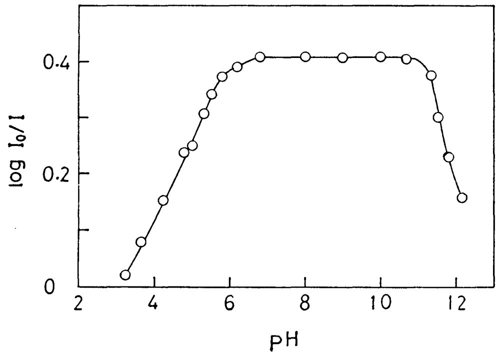

Fig. 2. Effect of pH on the extraction of the U-PAR-TDEA complex.
$[U]_{aq}=2\times10^{-6}$ M, $[PAR]_{aq}=4\times10^{-5}$ M, $[TDEABr]_o=5\times10^{-3}$ M, 550 nm.

Organic Solvents. Several kind of organic solvents which dissolved TDEABr were tested in order to achieve a quantitative extraction of the uranium(VI)–PAR chelate anion. The ternary complex is extracted in such solvents as chloroform, carbon tetrachloride, 1-butanol, butyl acetate, isobutyl methyl ketone, nitrobenzene, and benzene. Molar absorptivities of the ternary complex are much the same in these solvents. Chloroform was used throughout these experiments as the common solvent.

The Effect of the PAR Concentration. The extraction of uranium(VI) from an aqueous solution containing PAR of various concentrations was examined. The absorbance of the extract was found to be constant in the concentration range from 1×10^{-5} M to 1×10^{-4} M. The extraction of the ternary complex is depressed by use of a large excess of the PAR over the TDEABr.

The Effect of the TDEABr Concentration. The concentration of TDEABr in chloroform was varied. The absorbance of the extract was found to be constant in the concentration range from 1×10^{-3} to 5×10^{-3} M.

Effect of the Mixing Time. The mixing time was varied from 30 s to 10 min. The absorbance of the extract was constant for the mixing times from 3 to 10 min.

Extractability and Molar Absorptivity. An aqueous solution of 25 ml containing 29.8 μg of uranium(VI) and PAR was shaken with 5 ml of 5×10^{-3} M TDEABr in chloroform under the optimum conditions. Extraction was repeated for the remaining aqueous phase after the separation of the extract. The extractability of uranium was calculated from the absorbances of the extracts. It was found that 96.4% of uranium(VI) was extracted by one extraction. The distribution ratio and the molar absorptivity are 1.34×10^2 and 4.25×10^4 cm^{-1} mol^{-1} l respectively.

Calibration Curve. A calibration curve for the determination of uranium(VI) was made under the optimum conditions. A good linear relationship was obtained over the concentration range from 1 μg to 30 μg of uranium per 5 ml of chloroform.

The Composition of the Ternary Complex. Using the continuous variation method and the equilibrium-shift method, the mole ratio of uranium: PAR was found to be 1:1, as are shown in Figs. 3 and 4. The mole ratio of uranium: TDEA was found to be 1:1, as are shown in Figs. 5 and 6. The same resutls were obtained by applying the mole ratio method. Thus, the composition of the ternary complex was estimated to be $UO_2(X)(PAR)(R_3R'N)$.

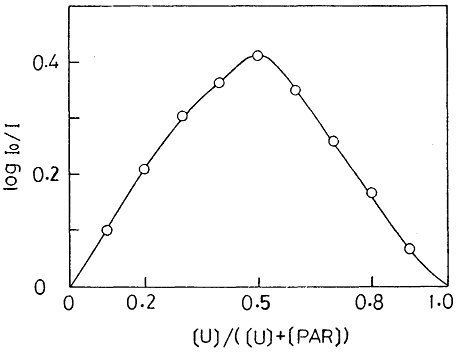

Fig. 3. Continuous variation method applied to the U-PAR-TDEA complex (U : PAR).
$[U]_{aq}+[PAR]_{aq}=2.5\times10^{-5}$ M, $[TDEABr]_o=5\times10^{-3}$ M, pH=9, 550 nm.

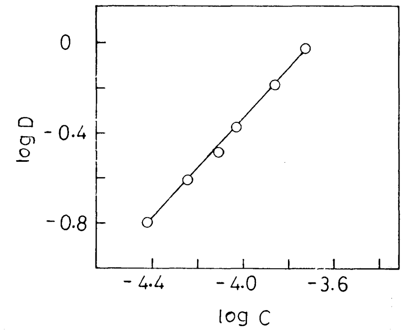

Fig. 4. Equilibrium-shift method applied to the U-PAR-TDEA complex (U:PAR).
$[U]_{aq}=1\times10^{-5}$ M, $[TDEABr]_o=5\times10^{-3}$ M, pH=3.6. *D*: Distribution ratio of U-PAR-TDEA complex between chloroform and water, *C*: concentration of PAR in chloroform.

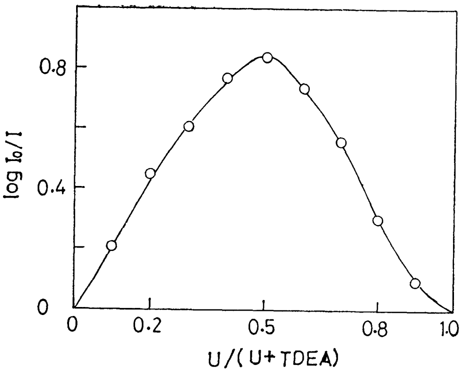

Fig. 5. Continuous variation method applied to the U-PAR-TDEA complex (U:TDEA).
U-PAR+TDEA$=5\times10^{-4}$ mmol, pH=9, 550 nm.

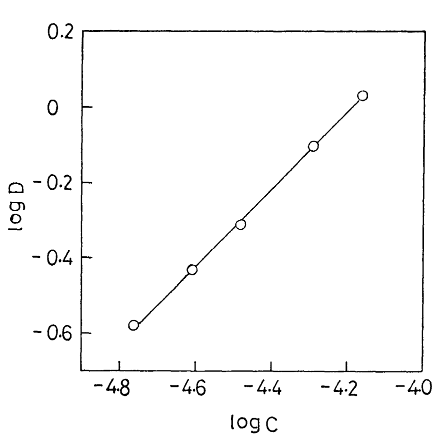

Fig. 6. Equilibrium shift method applied to the U-PAR-TDEA complex (U:TDEA).
$[U]_{aq}=2\times10^{-5}$ M, $[PAR]_{aq}=2\times10^{-5}$ M, pH=9.
D: Distribution ratio of U-PAR-TDEA complex between chloroform and water, C: concentration of TDEABr in chloroform.

Equilibrium Constant. When the uranium-PAR chelate anion is extracted with TDEABr into chloroform, the equation representing the extraction equilibrium would be

$$UO_2(X)(PAR)^- + R_3R'NBr_{(o)} = UO_2(X)(PAR)(R_3R'N)_{(o)} + Br^-. \tag{1}$$

The extraction constant K_{ex} is given by

$$K_{ex} = \frac{[UO_2(X)(PAR)(R_3R'N)]_o[Br^-]}{[UO_2(X)(PAR)][R_3R'NBr]_o}, \tag{2}$$

where subscript o denotes the organic layer and X represents an unidentified univalent anion.

Determination of each of the component concentrations in Eq. 1 is a difficult problem, because the complete formation of the uranium-PAR chelate anion occurs in the presence of excess PAR. Under such conditions the equilibrium in Eq. 1 can be represented by the following two steps.

$$PAR^- + R_3R'NBr_{(o)} = R_3R'NPAR_{(o)} + Br^- \tag{3}$$

$$K_{ex1} = \frac{[R_3R'NPAR]_o[Br^-]}{[PAR^-][R_3R'NBr]_o} \tag{4}$$

$$UO_2(X)(PAR)^- + R_3R'NPAR_{(o)} = UO_2(X)(PAR)(R_3R'N)_{(o)} + PAR^- \tag{5}$$

$$K_{ex2} = \frac{[UO_2(X)(PAR)(R_3R'N)]_o[PAR^-]}{[UO_2(X)(PAR)^-][R_3R'NPAR]_o} \tag{6}$$

Thus K_{ex} is given by $K_{ex}=K_{ex1}K_{ex2}$. The concentrations of the $R_3R'NPAR_{(o)}$ species in Eq. 3 and the $UO_2(X)(PAR)(R_3R'N)_{(o)}$ species in Eq. 5 were determined spectrophotometrically as a function of $[Br^-]$ or $[PAR^-]$ respectively. The values of K_{ex1} and K_{ex2} were found to be 52.9 and 22.3 under the conditions shown in Table 1. The value of K_{ex} calculated from K_{ex1} and K_{ex2} is 1180, therefore log $K_{ex}=3.07$. The distribution ratio of the uranium complex between chloroform and water is described by

$$D = \frac{[UO_2(X)(PAR)(R_3R'N)]_o}{[UO_2(X)(PAR)]}. \tag{7}$$

Combining Eqs. 2 and 7, we have

$$D = K_{ex}\frac{[R_3R'NBr]_o}{[Br^-]}. \tag{8}$$

From Eq. 8, one can see that the value of D is a function of $[R_3R'NBr]_o$ and $[Br^-]$. That is, the value of D increases with the TDEABr concentration in chloroform. The larger solubility (about 0.1 M) of TDEABr in chloroform than in other solvents is favorable for the quantitative extraction of the uranium complex. The anions such as perchlorate, thiocyanate and io-

TABLE 1. EQUILIBRIUM EXTRACTION DATA FOR THE PAR-$R_3R'NBr$, THE $UO_2(X)(PAR)$-$R_3R'NPAR$, AND THE $UO_2(X)(PAR)$-$R_3R'NBr$ SYSTEM AT pH 9.0 IN SODIUM BORATE BUFFER (10^{-4} M)

PAR-$R_3R'NBr$		$UO_2(X)(PAR)$-$R_3R'NPAR$		$UO_2(X)(PAR)$-$R_3R'NBr$
$[PAR^-]=5.0\times10^{-6}$ M $[R_3R'NBr]_o=5.0\times10^{-4}$ M		$[UO_2^{2+}]=4.0\times10^{-6}$ M $[R_3R'NPAR]_o=5.0\times10^{-4}$ M		
$[Br^-]$ (M)	K_{ex1}	$[PAR^-]$ (M)	K_{ex2}	$K_{ex}=K_{ex1}K_{ex2}$
5.0×10^{-4}	52.1	2.0×10^{-4}	22.0	
1.0×10^{-3}	52.6	4.0×10^{-4}	21.1	
1.5×10^{-3}	53.7	8.0×10^{-4}	22.7	
2.0×10^{-3}	52.9	1.2×10^{-3}	23.1	
2.5×10^{-3}	53.2	1.6×10^{-3}	22.5	
Average value	52.9		22.3	1180 (log $K_{ex}=3.07$)

All the concentrations in Table 1 are initial concentrations.

dide, which may have large extraction constants, would act as suppressing agents for the extraction.

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