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The Analytical Application of Oleophilic Quaternary Ammonium Salts. X.[1-9] The Extraction of the Niobium-Pyrocatechol Violet-Tridodecylethylammonium Ternary Complex

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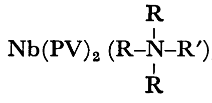
Synopsis. The formation and extraction of the niobium–Pyrocatechol Violet–tridodecylethylammonium ternary complex have been examined. The optimal pH for the extraction is 4—5. The molar absorptivity of the complex is 4.4×10^4 cm^{-1}·mol^{-1}·l at 553 nm. Its composition is estimated to be



$Nb(PV)_2\,(R\text{–}\overset{\displaystyle R}{\underset{\displaystyle R}{N}}\text{–}R')_3$.

Pyrocatechol Violet (PV) reacts with niobium[10] to form a violet chelate which is suitable for photometric determination. The sensitivity of the color reaction increases upon the addition of a long-chain quaternary ammonium salt.[11] Many papers[12–15] have been published on the extraction of Pyrocatechol Violet chelate anions with large organic cations. The lack of information on the extraction of ionic associates in the case of the niobium–Pyrocatechol Violet chelate anion with large organic cations, however, led us to carry out the present investigation. Furthermore, the investigation of the extraction of the metal chelate anions with an oleophilic quaternary ammonium salt such as tridodecylethylammonium bromide (TDEA), its superior extraction efficiency with relation to many chelate anions has been demonstrated. On the extraction of the Pyrocatechol Violet chelate anion with TDEA, we have already reported the spectrophotometric study of copper,[2] tin,[4] aluminum,[5] and zirconium.[8] In this paper, the fundamental conditions for the extraction of niobium as a niobium–PV–TDEA ternary complex with carbon tetrachloride and the composition of the ternary complex will be discussed.

Experimental

Reagent. A 2.5×10^{-3} M niobium solution was prepared by the following procedure. A definite amount of diniobium pentoxide and a small amount of potassium disulfate were placed in a platinum crucible and melted. After cooling, a 104-ml portion of sulfuric acid was added and the solution was diluted to 250 ml with de-ionized water. A working standard solution was prepared as needed by the dilution of the 2.5×10^{-3} M solution with 7.5 M sulfuric acid to each desired concentration. A 5.0×10^{-4} M PV solution was prepared by dissolving the Dotite PV in de-ionized water without further purification. TDEA was prepared, by refluxing for 4 h, to an ethanolic solution of tridodecylamine and ethyl bromide. After the evaporation of the solvent, the salt was recrystallized two times from butyl acetate. The 10^{-3} M TDEA solution was prepared by dissolving the above TDEA in carbon tetrachloride. All the other chemicals used were of a guaranteed-reagent quality.

Apparatus. All the measurements of the absorbance were made with a Hitachi manual spectrophotometer, model Epu-2A. Matched 10-mm absorption cells were used. The pH measurements were made with a Hitachi-Horiba model M-5 glass electrode pH meter.

Standard Procedure. Up to 7 μg of niobium were placed in a 50-ml polyethylene beaker; 0.5 ml of 0.03% hydrogen peroxide, a definite amount of 1 M sulfuric acid, and 3 ml of a 5×10^{-4} M PV solution were then added. The pH of the solution was adjusted to 4.5 by the addition of 2 ml of a 2 M sodium acetate solution and a definite amount of ammonia buffer solution (pH 9). Then the solution was diluted to 25 ml with de-ionized water. The solution was transferred into a 35-ml test tube, and a 5-ml portion of 10^{-3}M TDEA in carbon tetrachloride was added. The extraction was carried out for 5 min by turing the test tube upside down two times per 5 s. After a complete phase separation, the organic layer was taken out and centrifuged for 3 min at 3000 rpm. The extract was transferred into an absorption cell, and the absorbance at 553 nm was measured against the reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of the ternary complex extracted into carbon tetrachloride and of the niobium–PV chelate anion in an aqueous solution are given in Fig. 1, along with that of the reagent blank. The ternary complex and the niobium–PV chelate anion have absorption maximum at 553 nm and 562 nm respectively. The absorbance of the ternary complex increases about two times more than that of the niobium–PV chelate anion.

Effect of pH. The effect of the pH on the extraction of the ternary complex with 2×10^{-6} M niobium, 6×10^{-5} M PV in the aqueous phase, and 10^{-3} M TDEA

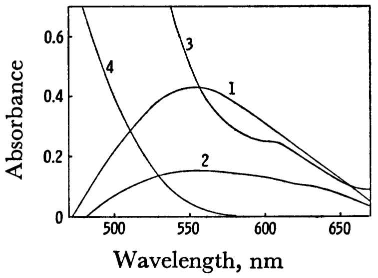


Fig. 1. Absorption spectra of the Nb–PV–TDEA in carbon tetrachloride and the Nb–PV in aqueous solution.
pH=4.5
(1): Nb–PV–TDEA in carbon tetrachloride $[Nb]_w=2\times10^{-6}$ M, (2): Nb–PV in aq soln $[Nb]_w=10^{-5}$ M, (3): PV–TDEA in carbon tetrachloride $[PV]_w=6\times10^{-5}$ M, (4): PV in aq soln $[PV]_w=6\times10^{-5}$ M.

in carbon tetrachloride was examined. The optimum pH range for the extraction is found to be 4—5. The pH dependence of the extraction may change with the change in the reagent concentration. The carbon tetrachloride extract is stable for at least 30 min. The absorbance of the reagent blank in the organic layer increases remarkably with an increase in the pH value.

Organic Solvents. The niobium–PV–TDEA ternary complex can be extracted into such substances as carbon tetrachloride, butyl acetate, carbon disulfide, benzene, and nitrobenzene, but not into 1-butanol, methyl isobutyl ketone, and chloroform.

The Effect of the PV Concentration. The effect of the PV concentration in the aqueous phase on the extraction of the ternary complex was also examined. The absorbance of the extract is constant when the initial aqueous phase is in the concentration range $4\times10^{-5}-1\times10^{-4}$ M. The absorbance of the extract gradually decreases, however, upon the further addition of PV.

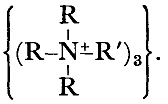
The Effect of the TDEA Concentration. The effect of the concentration of TDEA in carbon tetrachloride on the extraction of the ternary complex was also examined. The constant and maximum absorbance of the extract is obtained when the organic phase is in the concentration range $5\times10^{-4}-2\times10^{-3}$ M.

The Effect of the Mixing Time. The extractability of the ternary complex with 10^{-3} M TDEA in carbon tetrachloride at pH 4.5 is given as a function of the mixing time. The absorbance of the extract is constant for the mixing times from 3 to 10 min.

Extractability and Molar Absorptivity. The extractability of the ternary complex under optimum conditions was examined by the spectrophotometric determination of niobium in the extract with Xylenol Orange after evaporating the organic layer. When a 250-ml portion of an aqueous layer containing 46.5 μg of niobium is mixed with 50 ml of a carbon tetrachloride solution of TDEA, 98.1% of the niobium is extracted by one extraction. The distribution ratio and the molar absorptivity are 2.58×10^2 and 4.3×10^4 cm^{-1}·mol^{-1}·l respectively.

Calibration Curve. A calibration curve was made by extracting different amounts of niobium under optimum conditions. A good linear relationship is obtained over the concentration range from 0.58 to 7 μg of niobium per 5-ml portion of carbon tetrachloride. The variation coefficient of the absorbance is 1.3% for the 7 measurements. The effect of foreign ions was also examined. Copper, bismuth, and tin were masked with 2-mercaptoethanol, but uranium, thorium, molybdenum, tungsten, aluminum, iron, and vanadium interfered seriously. Of the anions tested, nitrate, iodide, thiocyanate, and perchlorate interfered considerably, giving a negative error.

The Composition of the Ternary Complex. The molar ratio of the components in the ternary complex was established by the continuous variation method. The results indicate that the molar ratios of niobium to PV to TDEA are 1 : 2 : 3, as is shown in Figs. 2 and 3. The same results were also obtained by the mole-ratio method. The application of the equilibrium-shift method to this system had not been successfully carried out because the complete formation of the ternary complex occurred in a small excess of reagents. Consequently, it may be assumed that the ternary complex is an ion-association system for $\{[Nb(PV)_2]^{3-}\}\cdot$



$$\left\{(R-\overset{R}{\underset{R}{N^{\pm}}}-R')_3\right\}.$$

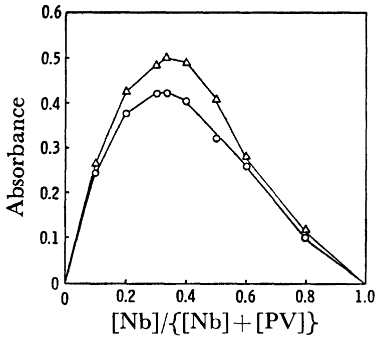


Fig. 2. Continuous variation method applied to the Nb–PV–TDEA system.
$[Nb]_w+[PV]_w=4\times10^{-5}$ M, pH=4.5, —○—: 553 nm, —△—: 590 nm.

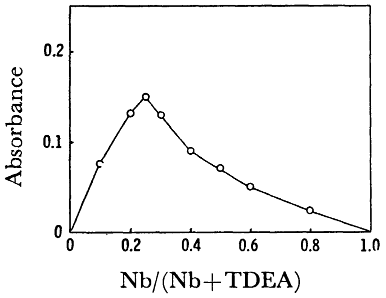


Fig. 3. Continuous variation method applied to the Nb–PV–TDEA system.
Nb+TDEA=2.5×10^{-7} mol, pH=4.5, 553 nm.

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