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# Spectrophotometric Study of the Zirconium-Pyrocatechol Violet-Tridodecylethylammonium Ternary Complex

Yoshio SHIJO

*Department of Industrial Chemistry, Faculty of Engineering, University of Utsunomiya, Ishii-machi, Utsunomiya 321-21*

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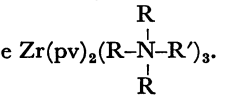
The zirconium-pyrocatechol violet chelate anion is extracted with tridodecylethylammonium bromide in butyl acetate to form a ternary complex. The ternary complex has an absorption maximum at 586 nm in the organic layer. The optimum pH range for the extraction is from 5 to 6. Beer's law holds for 0.4—9 μg of zirconium in 5 ml of the organic phase. The molar absorptivity of the ternary complex is $3.9\times10^4$ cm$^{-1}$ mol$^{-1}$ l at 586 nm. The composition of the ternary complex is estimated to be



$$Zr(pv)_2(R\text{-}\overset{R}{\underset{R}{N}}\text{-}R')_3.$$

The ternary complexes formed by the ionic association of the metal-Pyrocatechol Violet (PV) chelate anions and the bulky organic cations such as diphenylguanidine and quaternary ammonium salt have been studied by many workers. Kohara *et al.*[1] extracted ion pairs such as molybdenum-Pyrocatechol Violet(PV)-dialkylmethylbenzylammonium. Extraction of the indium-PV-hexadecylpyridinium system was reported by Ishito and Tonosaki.[2] The gallium-PV-diphenylguanidine system was studied by Akhmedli *et al.*[3] The gallium-PV-hexadecylpyridinium system was extracted in 1-butanol by Ishito.[4] The iron(III)-PV-diphenylguanidine system was studied by Yuryavichus and Valyukyavichyus.[5] Moreover, studies of the ternary complexes of the aluminum-PV-diphenylguanidine,[6] the bismuth-PV-diphenylguanidine,[7] and the titanium-PV-diphenylguanidine[8] systems have been reported. The water soluble metal-PV-quaternary ammonium ternary complexes in the micelle solution have been applied to the spectrophotometric determination of aluminum,[9] antimony and molybdenum,[10] niobium,[11] and tantalum.[12]

In the process of investigating the extraction of the metal chelate anions with an oleophilic quaternary ammonium salt such as tridodecylethylammonium bromide (TDEA), we reported an extraction spectrophotometric method for scandium[13] and yttrium[14] as Xylenol Orange chelate and for iron[15] as Eriochrome Cyanine R chelate and for copper,[16] tin,[17] and aluminum[18] as Pyrocatechol Violet chelate. In this paper, the fundamental conditions for the extraction of zirconium as the zirconium-PV-TDEA ternary complex with tridodecylethylammonium bromide in butyl acetate and the composition of the ternary complex will be discussed.

## Experimental

*Reagent.* A $2.5\times10^{-3}$ M zirconium solution was prepared by the following procedure. 0.1140 g of zirconium was placed in a platinum crucible and to this was added 6 ml of hydrofluoric acid (1+1). After the zirconium had been dissolved, 2 ml of sulfuric acid was added and evaporated to fuming sufur trioxide on a hot plate. Ater cooling, 137 ml of sulfuric acid was added and diluted to 500 ml with de-ionized water. A working standard solution was prepared as needed by the dilution of the $2.5\times10^{-3}$ M solution with de-ionized water to each desired concentration. A $5\times10^{-4}$ M PV solution was prepared by dissolving the Dotite PV in de-ionized water without any further purification. TDEA was prepared by the reflux to ethanolic solution of tridodecylamine and ethyl bromide for 4 h. After evaporation of the solvent, the salt was recrystallized two times from butyl acetate. A $6\times10^{-4}$ M TDEA solution was prepared by dissolving the above TDEA in butyl acetate. 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, mode 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 9 μg of zirconium were placed in a 50 ml polyethylene beaker to which were added a definite amount of 0.1 M sulfuric acid and 2 ml of $5\times10^{-4}$M PV solution. pH of the solution was adjusted to 5 by the addition of 2 ml of 2 M sodium acetate solution and then the solution was diluted to 25 ml with de-ionized water. The solution was transferred into a 35 ml test tube and 5 ml of $6\times10^{-4}$ M TDEA in butyl acetate was added. The extraction was carried out for 5 min by turning the test tube upside down at two times per 5 s. After the complete 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 586 nm was measured against the reagent blank obtained in the same way.

## Results and Discussion

*Absorption Spectra.* Absorption spectra of the ternary complex extracted into butyl acetate and of the zirconium-PV chelate anion in an aqueous solution are given in Fig. 1, along with that of the reagent blank. The ternary complex and the zirconium-PV chelate anion have an absorption maximum at 586 and 595 nm respectively.

*Effect of pH.* The aqueous solution was adjusted to various pH values with the acetate buffer solution and the extraction was carried out by the above procedure. Although formation of the zirconium-PV chelate should occur at a lower pH, about 2, the optimum pH range for the extraction of the ternary complex is found to be from 5 to 6. It is thought that the extractable higher cordination chelate anion forms at pH values from 5 to 6. The absorbance of the reagent blank

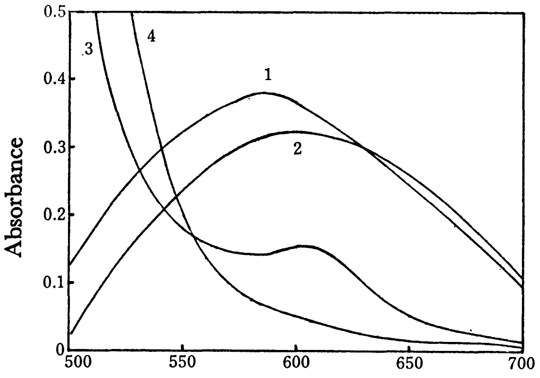


Fig. 1. Absorption spectra of the Zr–PV–TDEA in butyl acetate and the Zr–PV in aqueous solution.
pH=5, $V_w$(volume of aq. layer)=25 ml, $V_o$(volume of org. layer)=5 ml,
(1) Zr–PV–TDEA in butyl acetate $[Zr]_w=2\times10^{-6}$ M.
(2) Zr–PV in aq. soln. $[Zr]_w=10^{-5}$ M.
(3) PV–TDEA in butyl acetate $[PV]_w=4\times10^{-5}$ M
(4) PV in aq. soln. $[PV]_w=2\times10^{-4}$ M.

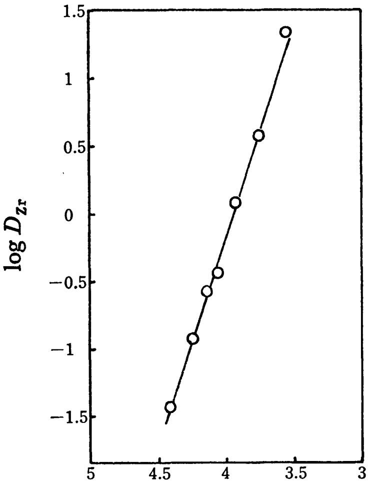


Fig. 2. Equilibrium-shift method applied to the Zr–PV–TDEA system.
$[Zr]_w=2\times10^{-6}$ M, $[PV]_w=2\times10^{-4}$ M, $[Br^-]_w=5\times10^{-4}$ M, pH=5, $V_w$=25 ml, $V_o$=5 ml, 586 nm.

in the organic layer increases very much with an increase in the pH value.

*Organic Solvents.* Several kind of organic solvents were tested in order to achieve a quantitative extraction of zirconium. The ternary complex can be extracted in such solvents as butyl acetate, carbon tetrachloride, benzene, toluene, xylene, and carbon disulfide. Absorbances of the ternary complex are much the same in these solvents. But the lowest absorbance of reagent blank is obtained in butyl acetate. The ternary complex can not be extracted in such solvents as 1-butanol, methyl isobutyl ketone, nitrobenzene, 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 examined by varying the PV concentration while other variables were held constant. The absorbance of the extract is constant when the PV in the initial aqueous phase is in the concentration range from $2\times10^{-5}$—$6\times10^{-5}$ M. The absorbance of the extract gradually decreases upon further addition of PV.

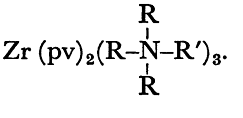
*The Effect of the TDEA Concentration.* The effect of the concentration of TDEA in butyl acetate on the extraction of the ternary complex was examined. The constant and maximum absorbance of the extract is obtained with a concentration higher than $4\times10^{-4}$ M.

*The Effect of the Mixing Time.* The mixing time was varied from 10 sec to 15 min. The absorbance of the extract is constant for the mixing times from 3 to 15 min.

*Extractability and Molar Absorptivity.* The extractability of the ternary complex under the optimum conditions was examined by spectrophotometric determination of zirconium with Xylenol Orange in the extract after evaporating the organic layer. When a 250 ml portion of an aqueous layer containing 45.6 μg of zirconium is mixed with 50 ml of butyl acetate solution of TDEA, 97.8% of the zirconium is extracted by one extraction. The distribution ratio and the molar absorptivity are $2.22\times10^2$ and $3.9\times10^4$ cm$^{-1}$ mol$^{-1}$ l respectively.

*Calibration Curve.* A calibration curve for the determination of zirconium was made under the optimum conditions. A good linear relationship is obtained over the concentration range from 0.45 to 9 μg of zirconium per 5 ml of butyl acetate.

*The Composition of the Ternary Complex.* The molar ratio of PV to zirconium in the ternary complex was estimated to be 1 : 2 by the continuous-variation method. The molar ratio of zirconium to TDEA in the ternary complex was established by the equilibrium-shift method. All the equilibrium concentration and distribution ratios were estimated by measuring the absorbances of the organic or aqueous phase. The plot of log $D_{Zr}$ against log $[TDEA]_o$ gives the number of TDEA which are involved in forming the ternary complex. The number is given by the slope. The slope of the straight line shows that the ratio of zirconium to TDEA is 1 : 3, as is shown in Fig. 2. According to these results, the composition of the ternary complex is estimated to be



$$Zr\,(pv)_2(R\text{-}\overset{\displaystyle R}{\underset{\displaystyle R}{N}}\text{-}R')_3.$$

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