The Solvent Extraction of the Copper-Pyrocatechol Violet Chelate with Tridodecylethylammonium Bromide

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The solvent extraction of the copper–Pyrocatechol Violet chelate with tridodecylethylammonium bromide (abbreviated TDEA) in benzene as an ion-association system has been investigated by the spectrophotometric method. The copper–PV–TDEA complex can be extracted into such aromatic hydrocarbons as benzene, toluene, and xylene, but not into such polar solvents as *n*-butanol, ethyl acetate, methylisobutylketone, and nitrobenzene. When a sample solution containing copper and PV, the pH of which has been adjusted to 7.5—8.5, is shaken with TDEA in benzene for 10 s, the maximum extraction of the ternary complex is obtained. The extractability of the complex from 50 ml of an aqueous solution into 10 ml of benzene is 98.3% under the optimum conditions. The absorbance and stability of the complex increase upon the addition of a small amount of ethanol to the extracted layer. Beer's law is obeyed up to 6.5 μg copper per 10 ml of benzene, and the molar absorptivity of the complex is 7.9×10^4 cm^{-1}·mol^{-1}·l at 663 nm. The composition of the complex is confirmed to be Cu: PV: TDEA=1: 2: 2 by the continuous variation method. A structure for the complex is proposed.

Pyrocatechol Violet (abbreviated as PV) forms water-soluble chelates with many metal ions and has been used as a metallochromic indicator or as a colorimetric reagent for several metal ions. The PV metal chelate anions react with quaternary ammonium salts as cetylpyridinium to form a water-soluble or a water-insoluble ion-association complex. The solvent extraction of the ion pair formed by the interaction of PV metal chelate anions with cations of 1,3-diphenylguanidinium, cetylpyridinium, *etc.* has been applied to the spectrophotometric determination of molybdenum(VI),[1] indium,[2] gallium,[3] and iron(III).[4] Recently, Přibil and Vesely[5] used a chloroform solution of Aliquat 336-S (methyltricaprylammonium chloride) in the solvent extraction of the Xylenol Orange metal cheletes. Because of its superior extraction efficiency, the oleophilic quaternary ammonium salt as Aliquat 336-S has been used for the extraction of many inorganic or organic anions[6-10] and also used as an ion exchanger for a liquid-membrane ion-selective electrode.[11,12] In this paper, the fundamental conditions for the solvent extraction of the copper–PV chelate anion with a benzene solution of tridodecylethylammonium bromide which has been synthesized in our laboratory and the composition of the ternary complex extracted into benzene are discussed in terms of the spectrophotometric method.

Experimental

Reagent. About a 2.5×10^{-3} M copper solution was prepared by dissolving a definite amount of cupric chloride in 1 M hydrochloric acid and by subsequent dilutions with deionized water. The resulting solution was standardized by EDTA titration. A working standard solution was prepared as needed by the dilution of the 2.5×10^{-3} M solution with deionized water to the desired concentration. A 5.0×10^{-4} M PV solution was prepared by dissolving the Dotite PV in deionized water without any further purification. The TDEA was prepared by the reaction[13] of tridodecylamine with ethylbromide in an alcoholic solution. The salt was recrystallized from petroleum benzine. A 6.0×10^{-4} M TDEA solution was prepared by dissolving the above TDEA in benzene.

All the other chemicals used were of a guaranteed reagent quality.

Apparatus. All the absorption spectra were obtained on a JASCO automatic recording spectrophotometer, model ORD-UV5. On the other hand, at a fixed wavelength measurements were made on a Hitachi manual spectrophotometer, model 101. Matched 1 cm absorption cells were used in all instances. The pH measurements were made with a Hitachi-Horiba model M-5 glass electrode pH meter.

Standard Procedure. Place up to 6.5 μg of copper in a 100 ml separatory funnel and add a definite amount of 0.2 M hydrochloric acid. Adjust the pH to 7.6 with a sodium acetate-sodium phosphate buffer solution. Add 4.0 ml of a 5.0×10^{-4} M PV solution and dilute to 50 ml with deionized water. Add 10 ml of 6.0×10^{-4} M TDEA in benzene and extract for 10 s with vigorous shaking. After the phases have separated, draw off the aqueous layer and centrifuge the extract for 5 min at 6000 rpm. Transfer 3.0 ml of the extract into a absorption cell and add 0.2 ml of ethanol. Measure the absorbance at 663 nm against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. The absorption spectra of the ternary complex extracted into benzene and the copper–PV chelate in an aqueous solution are given in Fig. 1, along with that of the reagent blank. The absorption curves of the ternary complex and the copper–PV chelate all have their maximum at 663 and 632 nm respectively. In the former, however, the absorbance is about three times greater than that of the latter. The bathochromic effect and the increase in the absorbance in the former are probably due to the combination with TDEA. By the addition of 0.2 ml of ethanol to 3.0 ml of the extract, the absorbance and stability of the ternary complex increase, but the absorbance of the reagent blank decreases. By the addition of ethanol into the initial organic phase, however, the extraction of the ternary complex is decreased extremely. PV is extracted into the organic layer under the conditions used in the standard procedure.

Effect of pH. The effect of the pH of the aqueous phase on the extraction was examined. The results are shown in Fig. 2. The maximum extraction of the

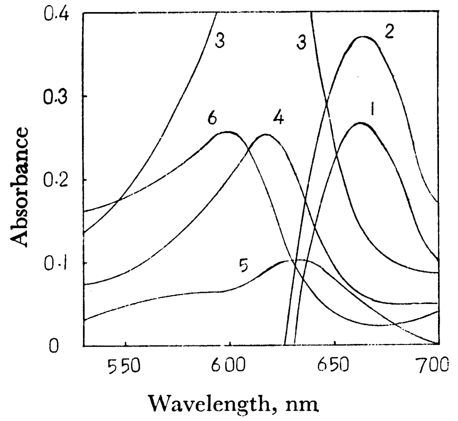

Fig. 1. Absorption spectra of the Cu–PV–TDEA complex in benzene and the Cu–PV chelate in aqueous solution. pH: 7.6, Volume of aq. layer $V_\mathrm{w}=50$ ml, $[\mathrm{acetate}]_\mathrm{w}=0.16$ M; Volume of org. layer $V_\mathrm{O}=10$ ml, $[\mathrm{secondary\ phosphate}]_\mathrm{w}=0.08$ M

(1): Cu–PV–TDEA in benzene	$[\mathrm{Cu}]_\mathrm{O}=5.0\times10^{-6}$ M,
(2): (1)+ethanol 6 vol%	$[\mathrm{Cu}]_\mathrm{O}=4.7\times10^{-6}$ M,
(3): PV–TDEA in benzene	$[\mathrm{PV}]_\mathrm{w}=4.0\times10^{-6}$ M,
(4): (3)+ethanol 6 vol%	$[\mathrm{PV}]_\mathrm{w}=4.0\times10^{-6}$ M,
(5): Cu–PV in aq. solution	$[\mathrm{Cu}]_\mathrm{w}=5.0\times10^{-6}$ M,
(6): PV in aq. solution	$[\mathrm{PV}]_\mathrm{w}=2.0\times10^{-5}$ M.

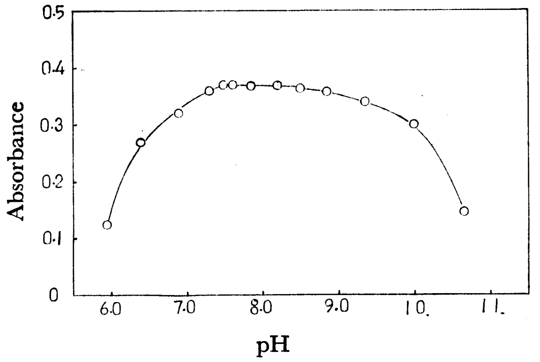

Fig. 2. Effect of pH on the extraction of the Cu–PV–TDEA complex.
pH: 7.6 $V_\mathrm{w}=50$ ml, $V_\mathrm{O}=10$ ml; Cu: 3.2 μg, $[\mathrm{PV}]_\mathrm{w}=4.0\times10^{-5}$ M, $[\mathrm{TDEA}]_\mathrm{O}=6.0\times10^{-4}$ M, $[\mathrm{ethanol}]_\mathrm{O}=6$ vol%, $[\mathrm{acetate}]_\mathrm{w}=0.16$ M, $[\mathrm{secondary\ phosphate}]_\mathrm{w}=00.8$ M.

ternary complex is reached at pH values from 7.5 to 8.5. This pH range is extended to lower pH values by increasing the concentration of TDEA in benzene. The absorbance of the reagent blank in the organic layer increases extremely with an increase in the pH value.

Organic Solvents. Several kinds of organic solvents were tested in order to achieve a quantitative extraction of copper. The ternary complex can be extracted into such aromatic hydrocarbons as benzene, toluene, and xylene, but not into such polar solvents as *n*-butanol, ethyl acetate, methylisobutylketone, and nitrobenzene. Benzene was chosen as the solvent which gave the highest absorbance.

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 was constant when the PV in the initial aqueous phase was in the concentration range from 4.0×10^{-5} M to 8.0×10^{-5} M, as is shown in Fig. 3. The absorbance of the extract gradually decreased upon the further addition of PV. The absorbance of the reagent blank in the organic layer increased extremely with the increase in the PV concentration because the bulk of the PV was extracted into the organic layer. Therefore, the PV concentration was kept at 4.0×10^{-5} M.

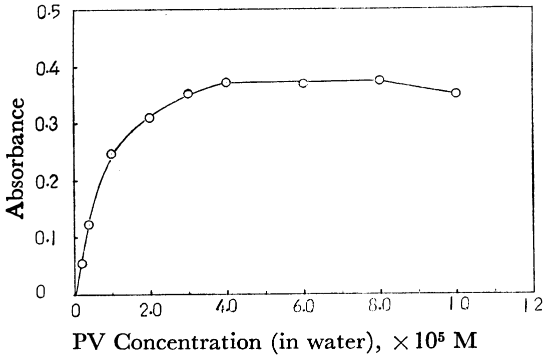

Fig. 3. Effect of the Pyrocatechol Violet concentration in aqueous phase on the extraction of the Cu–PV–TDEA complex.
pH: 7.6, $V_\mathrm{w}=50$ ml, $V_\mathrm{O}=10$ ml; Cu: 3μg, .2 $[\mathrm{TDEA}]_\mathrm{O}=6.0\times10^{-4}$ M, $[\mathrm{ethanol}]_\mathrm{O}=6$ vol%, $[\mathrm{acetate}]_\mathrm{w}=0.16$ M, $[\mathrm{secondary\ phosphate}]_\mathrm{w}=0.08$ M

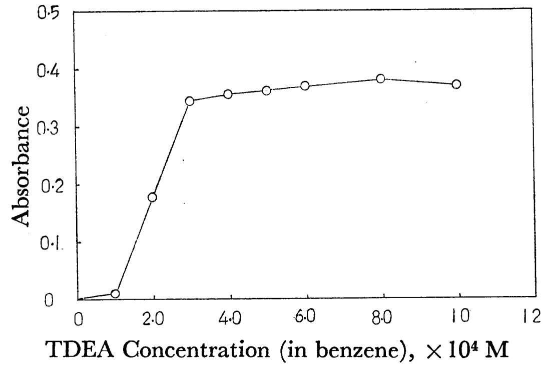

Fig. 4. Effect of tridodecylethylammonium bromide concentration in benzene on the extraction of the Cu–PV–TDEA complex.
pH: 7.6, $V_\mathrm{w}=50$ ml, $V_\mathrm{O}=10$ ml; Cu: 3.2 μg, $[\mathrm{PV}]_\mathrm{w}=4.0\times10^{-5}$ M, $[\mathrm{ethanol}]_\mathrm{O}=6$ vol%, $[\mathrm{acetate}]_\mathrm{w}=0.16$ M, $[\mathrm{secondary\ phosphate}]_\mathrm{w}=0.08$ M

The Effect of the TDEA Concentration. The effect of the concentration of TDEA in benzene on the extraction of the ternary complex was examined. The absorbance of the extract increased gently when the TDEA in benzene was in the concentration range from 3.0×10^{-4} M to 8.0×10^{-4} M, as is shown in Fig. 4. The absorbance of the reagent blank increased with the increase in the TDEA concentration in benzene. Therefore, the TDEA concentration was kept at 6.0×10^{-4} M.

The Effect of the Shaking Time. The shaking time was varied from 5 s to 10 min. The absorbance of the extract was constant for the shaking times from 5 s to 30 s, but upon further shaking it gradually decreased. A shaking time of 10 s was, therefore, selected.

The Effect of the Ethanol. The effect of the addition of ethanol to the extract on the absorbance of the ternary complex was examined. The absorbance became highest when the ethanol concentration in the extract was about 6 vol%. The absorbance of the extract decreased upon the further addition of ethanol. The stability of the ternary complex and the reproducibility of the absorbance increased upon the addition of ethanol to the extract. The absorbance of the reagent blank, however, decreased upon the addition of ethanol.

Extractability, Distribution Ratio, and Molar Absorptivity. The extractability of the ternary complex under the optimum conditions was determined by a repetition of the extraction procedure on the same aqueous layer. When a 50 ml portion of the aqueous layer containing 6.4 μg of copper was shaken with 10 ml of benzene, 98.3% of copper was extracted by one extraction and almost completely by two. The distribution ratio and the molar absorptivity calculated by using the percentage extraction and the absorbance were 3.78×10^2 and 7.9×10^4 $\mathrm{cm^{-1}\cdot mol^{-1}\cdot l}$ respectively.

Calibration Curve. A calibration curve for the determination of copper was made under the optimum conditions. A good linear relationship was obtained over the concentration range from 0 to 6.5 μg of copper per 10 ml of benzene.

The Effect of Diverse Ions. The effect of foreign ions on the determination of copper according to the standard procedure was also examined. Thorium, iron(III), cobalt, and nickel interfered at all the concentrations investigated. Up to about 10 μg of vanadium(V), aluminum, beryllium, manganese, zirconium, and uranium(VI) did not interfere with the determination of copper. Of the anions examined, chloride, sulfate, nitrate, and citrate did not interfere. However, thiosulfate and EDTA interfered seriously, giving negative errors.

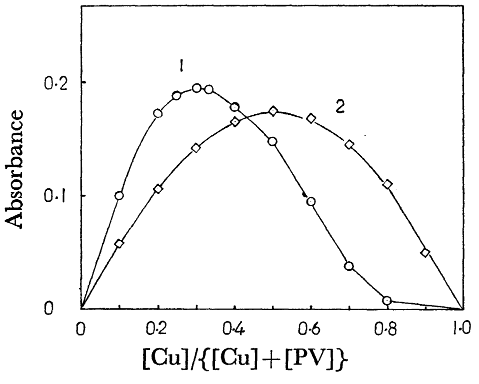

Fig. 5. Continuous variation method applied to the Cu–PV–TDEA complex and the Cu–PV chelate.
pH: 7.6, $V_w=10$ ml, $V_O=10$ ml; $[\text{acetate}]_w=0.16$ M, $[\text{secondary phosphate}]_w=0.08$ M
1 Cu–PV–TDEA complex, $[\text{Cu}]_w+[\text{PV}]_w=2.5\times10^{-5}$ M, $[\text{TDEA}]_O=6.0\times10^{-4}$ M, $[\text{ethanol}]_O=6$ vol%
2 Cu–PV chelate, $[\text{Cu}]_w+[\text{PV}]_w=4.0\times10^{-5}$ M

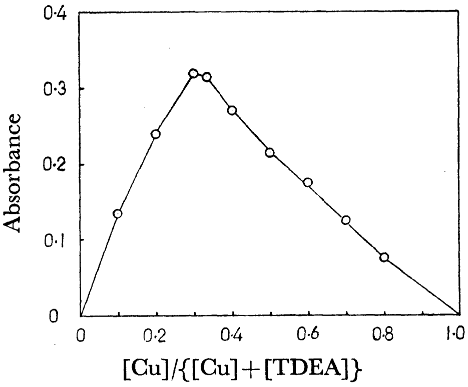

Fig. 6. Continuous variation method applied to the Cu–PV–TDEA complex.
pH: 7.6, $V_w=10$ ml, $V_O=10$ ml; $[\text{Cu}]_w+[\text{TDEA}]_O=5.0\times10^{-5}$ M, $[\text{PV}]_w=2.0\times10^{-4}$ M, $[\text{ethanol}]_O=6$ vol %, $[\text{asetate}]_w=0.16$ M, $[\text{secondary phosphate}]_w=0.08$M

The Composition and Structure of the Ternary Complex. Using the continuous variation method, the molar ratio of copper to PV was found to be 1 : 2, as is shown in Fig. 5. The molar ratio of copper to TDEA was also found to be 1 : 2, as is shown in Fig. 6. Thus, the composition of the ternary complex was estimated to be $\text{Cu(PV)}_2\text{(TDEA)}_2$. Recently, the structures of the ternary complexes of Sn–PV–cetyltrimethylammonium, Al–PV–cetyltrimethylammonium, and Mo–PV–diaklylmonomethylbenzylammonium were proposed by Bailey *et al.*,[14] Chester *et al.*,[15] and Kohara *et al.*[1] respectively. A similar structure, such as is shown in Fig. 7, may be possible for the ternary complex $\text{Cu(PV)}_2\text{(TDEA)}_2$.

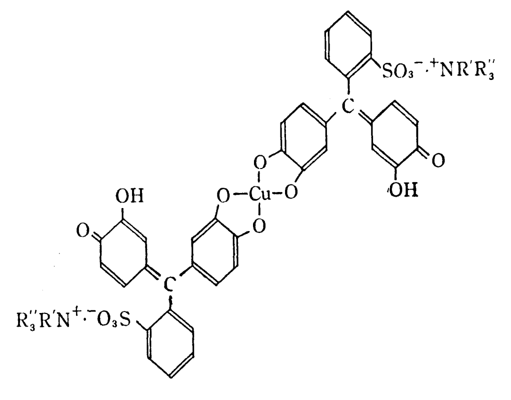

Fig. 7. Structure of the Cu–PV–TDEA complex.
$\text{R'}=\text{C}_2\text{H}_5$, $\text{R''}=\text{C}_{12}\text{H}_{15}$

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