January, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., **56**, 105—107 (1983)* 105

Extractive Spectrophotometric Determination of Antimony(III), Bismuth, Indium, and Gallium with Pyrocatechol Violet and Tridodecylethylammonium Bromide

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(Received April 28, 1982)

The spectrophotometric method for the determination of trace amounts of antimony(III), bismuth, indium, and gallium based on the solvent extraction of the ion associate formed between anionic metal–Pyrocatechol Violet complexes and tridodecylethylammonium bromide is proposed. The maximum absorbance of the extracted species occur at 530, 564, 600, and 595 nm for antimony(III), bismuth, indium, and gallium. The molar absorptivities for antimony(III), bismuth, indium, and gallium are 3.32×10^4, 3.31×10^4, 8.20×10^4, and 8.00×10^4 dm^3 mol^{-1} cm^{-1}. The optimum pH ranges for the extraction of antimony(III), bismuth, indium, and gallium are from 3.7 to 4.8, from 5.8 to 6.7, from 5.3 to 5.4, and from 5.5 to 6.2 respectively. The composition of the extracted complexes (metal:PV:TDEA) are estimated to be 1:2:3 for antimony(III) and 1:2:2 for the other metals. The interference of foreign ions is described.

The extraction of the anionic metal complexes with lipophilic quaternaryammonium salts has been utilized for various analytical purposes, such as the separation of metal ions,[1] and the extractive spectrophotometric,[2] fluorometric,[3] polarographic,[4] and atomic-absorption spectrophotometric[5,6] determination of metals. Trioctylmethylammonium chloride (Aliquat 336 or Capriquat) has been in common use as an extracting reagent in this field. Iodide of antimony and 17 other elements,[6] anionic complexes with EDTA of bismuth and 14 other elements,[7] iodide of bismuth and six other elements,[8] indium in a hydrochloric–sulfuric system,[9] chloride of indium,[10,11] thiocyanate of indium,[12] and chloride of indium and gallium[13] were extracted with the foregoing reagent.

Tridodecylethylammonium bromide (TDEABr), which is more lipophilic than trioctylmethylammonium chloride, is also useful for the extraction of the anionic metal complexes. The Pyrocatechol Violet (abbreviated to PV hereafter) complexes of aluminium,[14] tungsten,[15] vanadium,[16] *etc.* were extracted with TDEABr in organic solvents. The anionic PV complexes of antimony(III), bismuth, indium, and gallium can also be extracted with TDEABr in several nonpolar solvents. The fundamental conditions for the extractive spectrophotometric determination of antimony(III), bismuth, indium, and gallium with PV and TDEABr are studied in this paper.

Experimental

Reagent. A 2.50×10^{-3} mol dm^{-3} antimony(III) solution was prepared by dissolving 0.4174 g of antimony potassium tartrate in 500 cm^3 of 3 mol dm^{-3} hydrochloric acid. A 2.50×10^{-3} mol dm^{-3} bismuth solution was prepared by dissolving 0.2612 g of bismuth metal in 71.4 cm^3 of 7 mol dm^{-3} nitric acid and then diluting the mixture to 500 cm^3. A 2.50×10^{-3} mol dm^{-3} indium solution was prepared by dissolving 0.1435 g of indium metal in 37.2 cm^3 of nitric acid and then diluting the mixture to 500 cm^3. A 2.50×10^{-2} mol dm^{-3} gallium solution was prepared by dissolving 0.1743 g of gallium metal in 53.6 cm^3 of hydrochloric acid and then diluting the mixture to 100 cm^3. Working solutions of the metals were prepared as needed by the dilution of the stock solutions with the corresponding acid. A 1×10^{-3} mol dm^{-3} PV solution was prepared by dissolving 0.0966 g of the Dotite PV in 250 cm^3 of de-ionized water. TDEABr was prepared by the method described in a previous work.[17] The 2×10^{-3} mol dm^{-3} TDEABr solutions were prepared by dissolving 0.3155 g of TDEABr in 250 cm^3 of carbon tetrachloride for antimony(III) and in xylene for bismuth, indium, and gallium. The acetate buffer solutions were used for these metals. All the other chemicals used were of a guaranteed reagent quality.

Apparatus. A Hitachi 101 spectrophotometer, a Hitachi 200-20 UV-vis. recording spectrophotometer, and a Hitachi Horiba F-7 pH meter were employed.

General Procedure. Mix a working solution of a metal, a definite amount of 2 or 0.2 mol dm^{-3} hydrochloric acid, and 1 cm^3 of a 1×10^{-3} mol dm^{-3} PV solution in a 100-cm^3 polypropylene beaker. Adjust the pH of the solution to 4.5, 5.9, 5.3, or 5.6 for antimony(III), bismuth, indium, or gallium respectively by the addition of a 2 mol dm^{-3} sodium acetate solution, and then dilute to 20 cm^3 with de-ionized water. Transfer the solution into a 35-cm^3 test tube and extract with 5 cm^3 of 2×10^{-3} mol dm^{-3} TDEABr in an organic solvent for 5 min. Separate the phases and centrifuge the organic phase for 2 min at 3000 min^{-1}. Measure the absorbance of the extract against the reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of the metal–PV–TDEA complexes extracted into the organic phase, and of the anionic metal–PV complexes in the aqueous solutions and also of the respective blank solutions, are shown in Figs. 1 to 4. There is no or only a little bathochromic shift in the absorption spectrum of the metal–PV–TDEA complexes. The absorbance of the extracted complexes for antimony(III) and indium, however, increase remarkably over that in the aqueous phase.

Effect of pH. The effect of the pH on the extraction of the complexes was studied with solutions containing each metal and PV. For the maximum extraction, the optimum pH values for antimony(III), bismuth, indium, and gallium are in the ranges from 3.7 to 4.8, from 5.8 to 6.7, from 5.3 to 5.4, and from 5.5 to 6.2 respectively. The absorbances of extracts are unchanged for indium and gallium, but decrease about 15%, and 20% for antimony(III) and bismuth respectively for 30 min.

Organic Solvents. Several kinds of solvents were

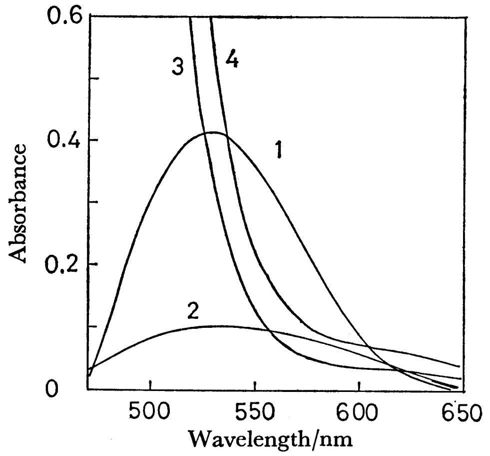

Fig. 1. Absorption spectra of the Sb–PV–TDEA complex in carbon tetrachloride and the Sb–PV complex in aqueous solution.
pH=4.5, $V_{\mathrm{aq}}=20\ \mathrm{cm}^3$, $V_{\mathrm{o}}=5\ \mathrm{cm}^3$, $[\mathrm{TDEABr}]_{\mathrm{o}}=2\times10^{-3}\ \mathrm{mol\ dm}^{-3}$. 1: Sb–PV–TDEA $[\mathrm{Sb}]=3.13\times10^{-6}\ \mathrm{mol\ dm}^{-3}$, 2: Sb–PV $[\mathrm{Sb}]=2.5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 3: PV–TDEA $[\mathrm{PV}]=5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 4: PV $[\mathrm{PV}]=2\times10^{-4}\ \mathrm{mol\ dm}^{-3}$.

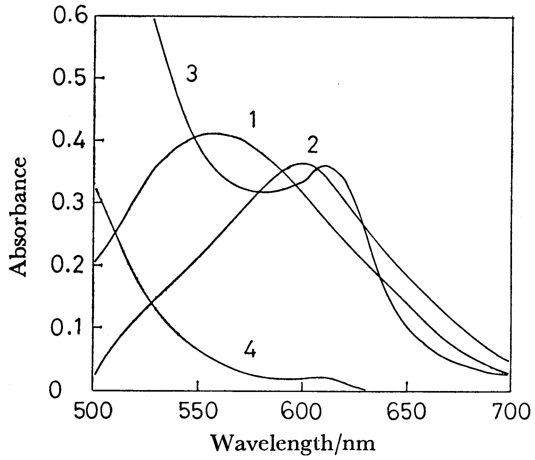

Fig. 2. Absorption spectra of the Bi–PV–TDEA complex in xylene and the Bi–PV complex in aqueous solution.
pH=5.9, $V_{\mathrm{aq}}=20\ \mathrm{cm}^3$, $V_{\mathrm{o}}=5\ \mathrm{cm}^3$, $[\mathrm{TDEABr}]_{\mathrm{o}}=2\times10^{-3}\ \mathrm{mol\ dm}^{-3}$. 1: Bi–PV–TDEA $[\mathrm{Bi}]=3.13\times10^{-6}\ \mathrm{mol\ dm}^{-3}$, 2: Bi–PV $[\mathrm{Bi}]=6.25\times10^{-6}\ \mathrm{mol\ dm}^{-3}$, 3: PV–TDEA $[\mathrm{PV}]=5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 4: PV $[\mathrm{PV}]=5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$.

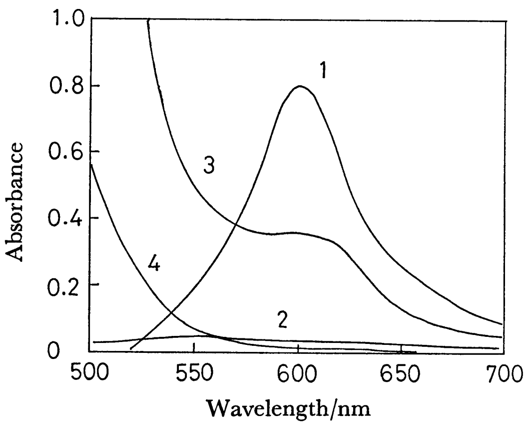

Fig. 3. Absorption spectra of the In–PV–TDEA complex in xylene and the In–PV complex in aqueous solution.
pH=5.3, $V_{\mathrm{aq}}=20\ \mathrm{cm}^3$, $V_{\mathrm{o}}=5\ \mathrm{cm}^3$, $[\mathrm{TDEABr}]_{\mathrm{o}}=2\times10^{-3}\ \mathrm{mol\ dm}^{-3}$. 1: In–PV–TDEA $[\mathrm{In}]=2.5\times10^{-6}\ \mathrm{mol\ dm}^{-3}$, 2: In–PV $[\mathrm{In}]=1\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 3: PV–TDEA $[\mathrm{PV}]=5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 4: PV $[\mathrm{PV}]=8\times10^{-5}\ \mathrm{mol\ dm}^{-3}$.

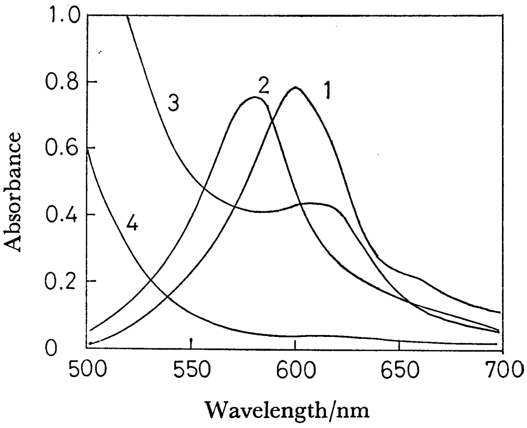

Fig. 4. Absorption spectra of the Ga–PV–TDEA complex in xylene and the Ga–PV complex in aqueous solution.
pH=5.5, $V_{\mathrm{aq}}=20\ \mathrm{cm}^3$, $V_{\mathrm{o}}=5\ \mathrm{cm}^3$, $[\mathrm{TDEABr}]_{\mathrm{o}}=2\times10^{-3}\ \mathrm{mol\ dm}^{-3}$.
1: Ga–PV–TDEA $[\mathrm{Ga}]=2.5\times10^{-6}\ \mathrm{mol\ dm}^{-3}$, 2: Ga–PV $[\mathrm{Ga}]=1\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 3: PV–TDEA $[\mathrm{PV}]=5\times10^{-5}\ \mathrm{mol\ dm}^{-3}$, 4: PV $[\mathrm{PV}]=8\times10^{-5}\ \mathrm{mol\ dm}^{-3}$.

examined from the standpoints of the absorbance and extractability of the complexes. Spectrophotometric studies indicated carbon tetrachloride to be most efficient for antimony(III), and xylene, for the other metals. The other solvents examined include butyl acetate, chloroform, isobutyl methyl ketone, and 1-butanol. Except for butyl acetate, these vary in performance, causing little or no extraction.

Effect of the Reagent Concentration. The variation in the PV concentration in an aqueous phase containing each metal with the optimum pH gives the constant maximum absorbance of the extracts in the PV concentration ranges from 3×10^{-5} to 1×10^{-4}, from 5×10^{-5} to 2×10^{-4}, 5×10^{-5}, and $>2.5\times10^{-5}$ mol dm^{-3} for antimony(III), bismuth, indium, and gallium respectively. The optimum concentrations of TDEABr in the organic phase are in the ranges from 2×10^{-4} to 5×10^{-3}, $>1\times10^{-3}$, and $>1\times10^{-4}$ mol dm^{-3} for antimony(III), bismuth, and indium or gallium respectively.

Extractability and Molar Absorptivity. An aqueous solution of 20 cm^3 containing a definite amount of each metal and PV was shaken with 5 cm^3 of 2×10^{-3} mol dm^{-3} TDEABr in organic solvents under the optimum conditions. Extraction was repeated for the remaining aqueous phase after the separation of the extract. The extractability of each metal was calculated from the absorbance of the extracts. It was found that 99.3, 99.0, 97.6, and 98.2% of antimony(III), bismuth, indium, and gallium respectively were extracted by a single extraction. The distribution ratios for antimony(III), bismuth, indium, and gal-

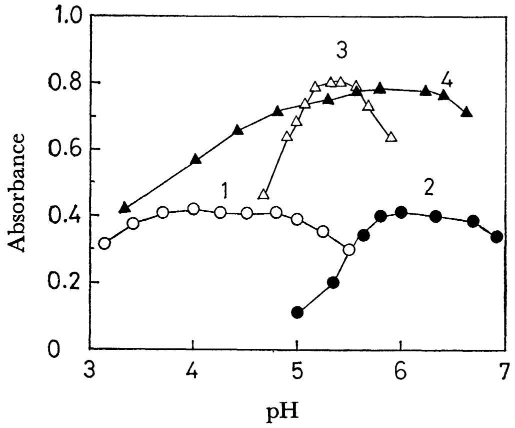

Fig. 5. Effect of pH on the extraction of the metal–PV–TDEA complexes.
$[Sb]=[Bi]=3.13\times10^{-6}$ mol dm^{-3}, $[In]=[Ga]=2.5\times10^{-6}$ mol dm^{-3}, $[TDEABr]_0=2\times10^{-3}$ mol dm^{-3}, $[PV]=5\times10^{-5}$ mol dm^{-3}. 1: Sb, 2: Bi, 3: In, 4: Ga.

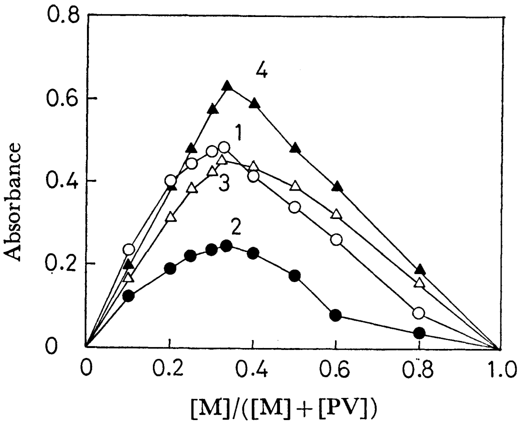

Fig. 6. Continuous variation method applied to the metal–PV–TDEA complexes (metal:PV).
1: Sb–PV–TDEA $[Sb]+[PV]=6.25\times10^{-5}$ mol dm^{-3}, 2: Bi–PV–TDEA $[Bi]+[PV]=1\times10^{-4}$ mol dm^{-3}, 3: In–PV–TDEA $[In]+[PV]=1\times10^{-4}$ mol dm^{-3}, 4:Ga–PV–TDEA $[Ga]+[PV]=1\times10^{-4}$ mol dm^{-3}.

lium are 5.59×10^2, 3.96×10^2, 1.63×10^2, and 2.18×10^2 respectively. The molar absorptivity of the complexes are 3.32×10^4, 3.31×10^4, 8.20×10^4, and 8.00×10^4 dm^3 mol^{-1} cm^{-1} for antimony(III), bismuth, indium, and gallium respectively. A calibration curve for the determination of each metal was made under the optimum conditions. A good linear relationship was obtained over the concentration range from 1 to 20, from 2 to 30, from 0.4 to 7.2, and from 0.3 to 4.3 μg of antimony(III), bismuth, indium, and gallium per 5 cm^3 of the organic phase.

The Composition of the Complexes. A continuous-variation method as described in a previous paper[16] was carried out for the metal–PV–TDEA complexes system. The results are shown in Fig. 6 and Fig. 7. The reacting ratios of metal to PV to TDEA balance well at 1:2:3 and 1:2:2 for antimony(III) and for the other metals respectively. Thus, the composition of the complexes are estimated to be $Sb(PV)_2(R_3R'N)_3$, $Bi(PV)_2(R_3R'N)_2$, $In(PV)_2(R_3R'N)_2$, and $Ga(PV)_2(R_3R'N)_2$ respectively.

Effect of Foreign Ions. The effect of foreign ions

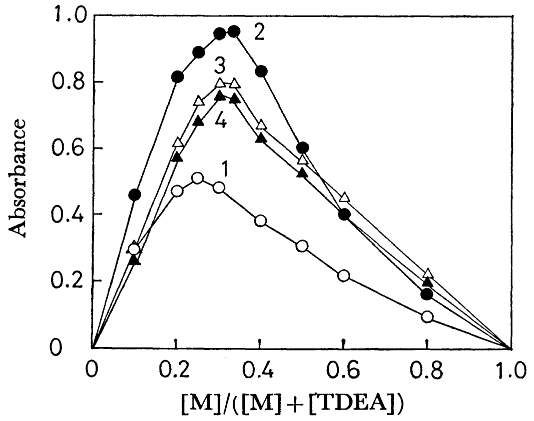

Fig. 7. Continuous variation method applied to the metal–PV–TDEA complexes (metal: TDEA).
1: Sb–PV–TDEA $Sb+TDEA=2\times10^{-6}$ mol, 2: Bi–PV–TDEA $Bi+TDEA=2\times10^{-6}$ mol, 3: In–PV–TDEA $In+TDEA=2\times10^{-6}$ mol, 4: Ga–PV–TDEA $Ga+TDEA=1\times10^{-6}$ mol.

on the determination of antimony(III), bismuth, indium, and gallium was examined under optimum conditions. The anionic PV complexes of many metals, such as beryllium, aluminium, titanium(IV), vanadium(V), iron(III), copper, molybdenum(VI), tin(IV), tungsten(VI), thorium, and uranium(VI) can be extracted with TDEABr and interfere with the determination of the foregoing metals. GEDTA for the determination of antimony(III), 1,10-phenanthroline and fluoride for bismuth, and thiourea or hydrogen peroxide for indium and gallium are useful as masking reagents in this system, but the masking power of these reagents is insufficient. Of the anions tested, iodide, thiocyanate, and perchlorate interfere most seriously, giving a negative error.

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