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The Analytical Application of Oleophilic Quaternary Ammonium Salts. XI.[1] The Extraction of the Iron(III)-Pyrocatechol Violet-Tridodecylethylammonium Ternary Complex

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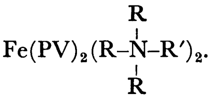
Synopsis. The ionic associate of the iron(III)-Pyrocatechol Violet chelate anion with tridodecylethylammonium bromide is extracted into methyl isobutyl ketone. The ternary complex has an absorption maximum at 623 nm. The optimum pH for the extraction is 5.7—6.4 The molar absorptivity of the complex is 7.76×10^4 cm$^{-1}\cdot$mol$^{-1}\cdot$l. Its composition is estimated to be  $\mathrm{Fe(PV)_2(R{-}\overset{R}{\underset{R}{N}}{-}R')_2}$.

Pyrocatechol Violet (PV) reacts with many metal ions to form water-soluble chelates. The utility of its extraction-photometric variant in ionic-association systems has been reported by many workers.[2–5] Ishito and Ichinohe[6] studied the formation of the iron(III)–PV chelate in an aqueous solution. The extraction of the iron(III)–PV chelate anion in the presence of diphenylguanidine was studied by Jurevicius and Valiukevicius.[7] The author has found that the iron(III)–PV chelate anion is extracted with tridodecylethylammonium bromide (TDEA) in methyl isobutyl ketone to form an ionic associate and that the molar absorptivity is greater than that of the iron(III)–PV–diphenlyguanidine system. The sensitivity of the present method is higher than those of the bathophenanthroline, 4-(2-pyridylazo)-resorcinol, and chromazurol S methods. In this paper, the fundamental conditions for the extraction of iron(III) as the iron(III)–PV–TDEA ternary complex in methyl isobutyl ketone and the composition of the ternary complex will be discussed.

Experimental

Reagent. A 2.5×10^{-3} M iron(III) solution was prepared by dissolving a definite ammount of ferric ammonium sulfate in 0.5 M sulfuric acid. The iron(III) concentration in the solution was determined by EDTA titration. A working standard solution was prepared as needed by the dilution of the 2.5×10^{-3} M solution to the desired concentration with de-ionized water. A 5×10^{-4} M PV solution was prepared by dissolving the Dotite PV in de-ionized water without further purification. The TDEA was prepared by the refluxing of 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 TDEA solution was prepared by dissolving the above TDEA in methyl isobutyl ketone. All the other chemicals used were of a guaranteed reagent quality.

Apparatus. All the measurements of the absorbance were made with a Hitachi mannual 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. To 2 ml of the 2.5×10^{-5} M iron(III) solution in a 50-ml polyethylene beaker, a definite amount of 0.1 M sulfuric acid and 2 ml of the 5×10^{-4} M PV solution were added. The pH of the solution was then adjusted to 5.8 by the addition of 2 ml of the 2 M sodium acetate solution and 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 methyl isobutyl ketone was added. The extraction was carried out for 5 min by turning the test tube upside down two times per 5 s. After the complete phase separation, the organic layer was taken out and centrifuged for 3 min at 3000 rpm. The extract was then transferred into an absorption cell, and the absorbance was measured at 623 nm against the reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of an aqueous solution of the iron(III)–PV chelate and of a solution of the iron(III)–PV–TDEA ternary complex in methyl isobutyl ketone, and also the absorption spectra of the respective blanks, are shown in Fig. 1. The ternary complex and the iron(III)–PV chelate anion have their absorption maxima at 623 and 604 nm respectively. The absorption maxima of the ternary complex shifted toward wavelengths longer by 20 nm compared with that of the iron(III)–PV chelate.

Effect of pH. The effect of the pH of the aqueous phase on the extraction was also examined. The maximum extraction was obtained at pH values from 5.7 to 6.4. PV itself is readily extracted with TDEA in methyl isobutyl ketone.

Organic Solvents. Of the solvents examined,

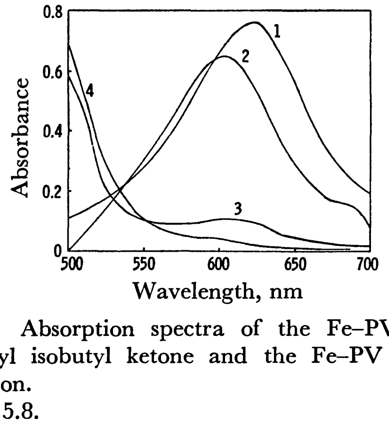


Fig. 1. Absorption spectra of the Fe–PV–TDEA in methyl isobutyl ketone and the Fe–PV in aqueous solution.
pH=5.8.
(1): Fe–PV–TDEA in MIBK, $[\mathrm{Fe}]_w=2\times10^{-6}$ M, (2): Fe–PV in aq soln $[\mathrm{Fe}]_w=10^{-5}$ M, (3): PV–TDEA in MIBK, $[\mathrm{PV}]_w=4\times10^{-5}$ M, (4): PV in aq soln $[\mathrm{PV}]_w=1\times10^{-4}$ M.

methyl isobutyl ketone, butyl acetate, carbon tetrachloride, carbon disulfide, and benzene were suitable for the quantitative extraction of the ternary complex. The organic layers separated out rapidly, and the molar absorptivity was maximal, when the methyl isobutyl ketone was used.

The Effect of the PV Concentration. With other factors kept constant, the PV concentration in the aqueous phase was varied from 2×10^{-6} to 10^{-4} M. The optimum concentration range of PV is from 2×10^{-5} to 6×10^{-5} M. The absorbance of the extract gradually decreases upon the further addition of PV.

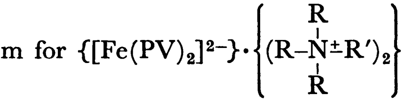
The Effect of the TDEA Concentration. The concentration of TDEA in the organic phase was varied from 1×10^{-4} to 3×10^{-3} M. The optimum concentration range of TDEA is from 4×10^{-4} to 2×10^{-3} M.

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

The Extractability and Molar Absorptivity. 25 ml of an aqueous solution containing 2.8 μg of iron(III) and the reagents of an optimum concentration were mixed with 5 ml of 10^{-3} M TDEA in methyl isobutyl ketone. Extraction was repeated with 5 ml of an organic layer for the remaining aqueous phase, to which 0.2 ml of the 5×10^{-3} M PV solution was added afresh after the separation of the extract. It was found that 97.9% of the iron(III) was extracted by one extraction. The distribution ratio and the molar absorptivity were 2.33×10^{2} and 7.76×10^{4} $cm^{-1}\cdot mol^{-1}\cdot l$ respectively.

Calibration Curve. The plot of the absorbance of the extract *versus* the concentration of iron(III) in the aqueous phase gave a straight line from 2×10^{-7} to 3×10^{-6} M. The variation coefficient of the absorbance was 1.1% for the 8 measurements. The effects of foreign ions were also examined. Copper, bismuth, and tin were masked with 2-mercaptoethanol. Thorium, aluminum, and uranium, also, were masked with hydrogen peroxide and potassium fluoride. However, vanadium, molybdenum, tungsten, chromium, and zirconium interfered seriously. Of the anions tested, nitrate, iodide, thiocyanate, and perchlorate interfered considerably, giving a negative error.

The Composition of the Ternary Complex. The ratio of iron(III) to PV was found to be 1:2 by the continuous-variation method. To find the iron(III) to TDEA ratio, we attempted to apply the continuous-variation, molar-ratio, and equilibrium-shift methods. However, all these experiments were unsuccessful because the complexes precipitated on the aqueous-organic interface in a lower concentration of TDEA when the methyl isobutyl ketone was used as the solvent. When carbon tetrachloride was used as a solvent, no precipitates of the complex appeared on the interface, and the application of the continuous-variation method was successful. The results indicate that the ratio of iron(III) to PV to TDEA is 1:2:2, as is shown in Figs. 2 and 3. Consequently, it may be assumed that the ternary complex in carbon tetrachloride is an ion-association system for



$$\{[Fe(PV)_2]^{2-}\}\cdot\left\{(R\text{-}\overset{\displaystyle R}{\underset{\displaystyle R}{N^{\pm}}}\text{-}R')_2\right\}.$$

The same composition may hold in the methyl isobutyl ketone.

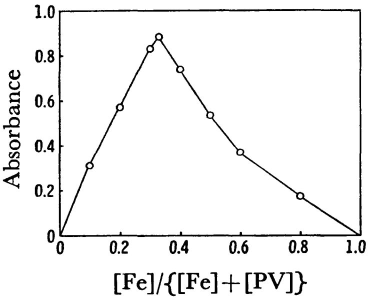


Fig. 2. Continuous variation method applied to the Fe–PV–TDEA system in carbon tetrachloride. $[Fe]_w+[PV]_w=1\times10^{-5}$ M, pH=5.8.

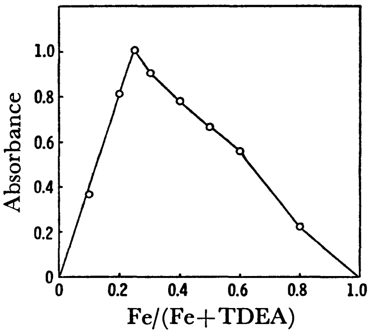


Fig. 3. Continuous variation method applied to the Fe–PV–TDEA system in carbon tetrachloride. Fe+TDEA=5×10^{-7} mol, pH=5.8.

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