December, 1980] © *1980 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *53*, *3713—3714 (1980)* 3713

The Ultraviolet Spectrophotometric Determination of Iron with 2-Thenoyltrifluoroacetone in an Aqueous Solution Containing *α*-Hydro-*ω*-dodecyloxynona(oxyethylene)

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(Received April 21, 1980)

Synopsis. 2-Thenoyltrifluoroacetone is used as a spectrophotometric reagent for the iron(III) ion (0—1.5 μg ml^{-1}) in a 0.5% α-hydro-ω-dodecyloxynona(oxyethylene) aqueous solution at pH 3.2—3.8. The molar absorptivities of the iron(III) complex at 338, 388, and 500 nm are 4.75×10^4, 2.30×10^4, and 4.85×10^3 l mol^{-1} cm^{-1} respectively. Many diverse ions do not interfere.

The solvent extraction-spectrophotometric determination of the iron(III) ion with 2-thenoyltrifluoroacetone (TTA) is not practical because the extraction rate of the complex is slow.$^{1)}$ Many investigators have, therefore, examined the effects of trioctylphosphine oxide (TOPO),$^{2)}$ tributyl phosphate,$^{3)}$ the thiocyanate ion,$^{4)}$ pyridine,$^{5)}$ and methyltrioctylammonium chloride$^{6)}$ on the extraction of the iron (III)–TTA complex for the purpose of accelerating the extraction rate.

Recently, we have reported that Eu- and Sm–TTA–TOPO ternary complexes are readily soluble in an aqueous solution containing Triton X-100 and that the strong fluorescence originating from the ternary complexes can be applied to the determination of rare earths.$^{7)}$ In the present paper, it is shown that iron(III) ions can be determined spectrophotometrically with TTA in an aqueous solution containing α-hydro-ω-dodecyloxynona(oxyethylene), $CH_3(CH_2)_{11}-O\!\leftarrow\!CH_2-CH_2-O\!\rightarrow_9\!H$, (BL-9EX). A constant absorption intensity is obtainable within a practical length of time, and the analytical sensitivity is considerably stronger than that of the corresponding extraction method, since the absorption maxima in the ultraviolet region are applicable to the measurement in the present method.

Experimental

Reagent and Apparatus. A standard solution of iron(III) ions was prepared by dissolving the analytical reagent-grade iron(III) chloride in 0.1 mol dm^{-3} hydrochloric acid. The concentration of the metal ions was determined by EDTA titration. A 1×10^{-2} M (1 M = 1 mol dm^{-3}) TTA reagent solution was prepared by dissolving a known amount of the reagent (Dojin Co., Ltd.) in 100 ml of a 5% BL-9EX (Nikko Chemical Co., Ltd.) aqueous solution. An acetate buffer solution (pH 3.6) was prepared by adding 10 ml of a 0.1 M sodium acetate solution to 160 ml of 0.1 M acetic acid. All the other chemicals used were of an analytical reagent grade.

A Hitachi 200-20 automatic recording spectrophotometer and a Hitachi 100-10 manual spectrophotometer were used.

Procedure. A dilute hydrochloric acid solution containing 2—30 μg of iron(III) ions was transferred into a beaker. A 2-ml portion of the buffer solution and 2 ml of the TTA reagent solution were added to the beaker. After the pH of the solution had been adjusted to 3.2—3.8 with a dilute hydrochloric acid solution or a sodium hydroxide solution, the solution was transferred into a 20-ml volumetric flask and made up to volume with water. The absorbance was measured at 338 or 388 nm using 10-ml quartz cells. All experiments were done at 20—25 °C.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectrum of the iron(III)–TTA complex in the 0.5% BL-9EX aqueous solution (pH 3.3). The prominent wavelengths of the maxima of the spectrum are at 338 and 388 nm.

Effects of Reaction Variables. The variation in the absorbances at 338, 388, and 500 nm was investigated as a function of the pH. All the intensities at these wavelengths gave constants over the pH range of 3.0—4.0. The variation in the absorbance at 338 nm was examined as a function of the mole ratio of TTA to the iron(III) ion and as a function of the concentration of BL-9EX. The intensity was almost constant

Table 1. Determination of ferric ion in synthetic samples containing diverse ions

Diverse ions added,	μg	Fe^{3+} found, μg	error, μg	Diverse ions added,	μg	Fe^{3+} found, μg	error, μg
Mg^{2+}	111.0	1.16	+0.04	Cd^{2+}	11.1	1.11	−0.01
Ca^{2+}	111.0	1.09	−0.03	Pb^{2+}	11.9	1.09	−0.03
Mn^{2+}	11.2	1.07	−0.05	UO_2^{2+}	11.3	Serious interference	
Co^{2+}	11.2	1.18	+0.06	UO_2^{2+}	1.1	1.21	+0.09
Co^{2+}	1.1	1.08	−0.04	Al^{3+}	11.6	Serious interference	
Ni^{2+}	11.2	1.26	+0.15	Al^{3+}	1.2	1.78	+0.68
Ni^{2+}	1.1	1.10	−0.02	Al^{3+}	1.2	1.13	+0.01[a)]
Cu^{2+}	11.2	Serious interference		Cr^{3+}	11.3	1.44	+0.33
Cu^{2+}	1.1	1.55	+0.43	Cr^{3+}	1.1	1.14	+0.02
Cu^{2+}	1.1	1.19	−0.07[a)]	NO_3^-	113.3	1.09	−0.03
Zn^{2+}	11.1	1.16	+0.05	SO_4^{2-}	113.0	1.08	−0.04
Zn^{2+}	1.1	1.09	−0.03				

Fe^{3+} taken, 1.12 μg. a) Measured at 388 nm.

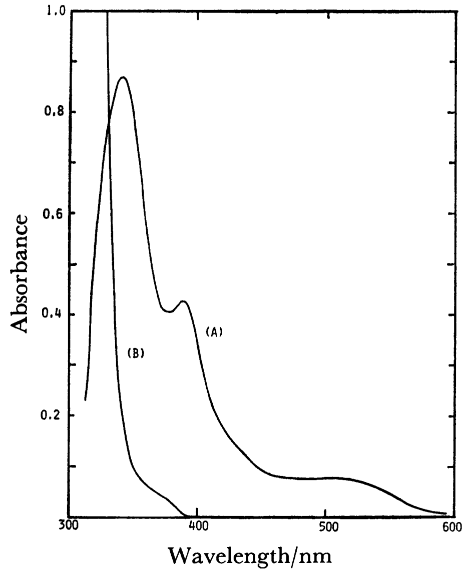

Fig. 1. Absorption spectrum of Fe(III)-TTA complex. (A) Fe(III)-TTA complex: Fe^{3+} 2×10^{-5} M, TTA 1×10^{-3} M, BL-9EX 0.5%, pH 3.3. (B) Reagent blank.

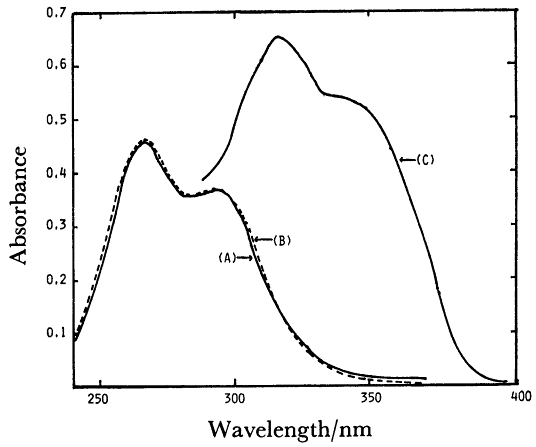

Fig. 2. Absorption spectra of TTA in aqueous solution containing BL-9EX, water, and organic solvents. (A) 0.5% BL-9EX, (B) water (pH 3.4), (C) *n*-heptane or carbon tetrachloride: TTA 5×10^{-5} M.

over the mole-ratio range of 20—100 for TTA to the iron(III) ion and also in the range of 0.2—1% of BL-9EX. With less than about 0.01%, the aqueous solution became turbid because of the precipitating of the complex. The intensity of the absorbance remained constant for 24 h after the preparation of the complex at 25 °C.

Calibration Curve. The absorbances at 338, 388, and 500 nm were linear functions of the concentration in the range of 0—1.5 μg ml^{-1} for the iron(III) ion. The molar absorptivities at the maximum wavelengths of 338, 388, and 500 nm are 4.75×10^4, 2.30×10^4, and 4.85×10^3 l mol^{-1} cm^{-1} respectively.

Effects of Diverse Ions. The effects of diverse ions on the absorbance (Fe^{3+}, 1.12 μg ml^{-1}) were investigated under the optimum conditions. Table 1 shows that 100-fold amounts of magnesium, calcium, nitrate, and sulfate ions, 10-fold amounts of manganese, cobalt, zinc, cadmium, lead, and cerium(III) ions, and equiamounts of nickel and chromium ions do not interfere with measuring the absorbance at 338 nm. However, equiamounts of copper, uranyl, and aluminum ions interfere seriously. The interference of the copper and aluminum ions can, though, be eliminated by measuring the absorbance at 388 nm.

Usually, 0.1—0.2 M TTA solutions in organic solvents are used for the extraction of the iron(III) complex, and so the ultraviolet absorption maxima (at 338 or 388 nm) adopted in the present method are inapplicable to the solvent-extraction method because the concentration of TTA in the reference solution is too high for the ultraviolet spectrum to be drawn. Therefore, the analytical sensitivity obtained by the present method is about ten times larger than that by the corresponding solvent-extraction method. Also, it is a convenience of the present method that the intensity of the absorption spectrum in the range of 320 to 390 nm of the TTA aqueous solution containing BL-9EX is considerably weak in comparison with that in the organic solvents, as is shown in Fig. 2. Also, the figure shows that the pattern of the absorption spectrum of TTA in an aqueous solution (pH 3.4) is scarcely affected by the exsistence of BL-9EX; on the other hand, the pattern of the spectra of these aqueous solutions is quite different from that in heptane or carbon tetrachloride. These facts indicate that most of the TTA exists outside the micelles, *i.e.*, in the bulk phase. After the complexation of the iron(III) ion with TTA, the metal complex can be easily taken in the micellar phase through the large micellar surface.

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