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The Extraction Spectrophotometric Determination of Iron(III) with Eriochrome Cyanine R and Tridodecylethylammonium Bromide

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A sensitive spectrophotometric procedure for the determination of iron(III) has been developed, utilizing the ternary complex system of iron–Eriochrome Cyanin R–Tridodecylethylammonium. The iron–Eriochrome Cyanin R chelate anion was extracted with tridodecylethylammonium bromide in xylene. The extracted species had an absorption maximum at 613 nm in the organic layer. The optimum pH range for the extraction was 5.8—6.5. Beer's law held for 0.2—2 μg of iron(III) in 5 ml of the organic layer. The molar absorptivity of the extracted species was $1.73\times10^5\ \mathrm{cm^{-1}\cdot mol^{-1}\cdot l}$ at 613 nm. The composition of the ternary complex was assumed to be $\{[\mathrm{Fe(HR)_3}]^{6-}\}\cdot\{(\mathrm{R'}-\overset{\mathrm{R''}}{\underset{\mathrm{R''}}{\mathrm{N}^+}}-\mathrm{R''})_6\}$. Lead, mercury, tin, chromium, beryllium, thorium, uranium, nitrate, iodide, thiocyanate, and perchlorate interfered with the determination of iron(III).

In the process of investigating the extraction of the metal chelate anion with tridodecylethylammonium bromide (abbreviated as TDEA) in the organic layer, we have recently described an extraction spectrophotometric method for scandium[1)] and yttrium[2)] as metal–Xylenol Orange chelate anions and for copper,[3)] tin,[4)] and aluminum[5)] as metal–Pyrocatechol Violet chelate anions. These studies showed that the extracted ternary complex systems of [Metal–Ligand–TDEA] were very sensitive in their colour reactions. Eriochrome Cyanin R (abbreviated as ECR) forms water-soluble chelate anions with metal ions and has been used as a metallochromic indicator or as a colorimetric reagent for several metal ions. The interaction of metal–ECR chelate anions with quaternary ammonium salts such as cetyltrimethylammonium chloride had been applied to the spectrophotometric determination of aluminum,[6,8)] beryllium,[7)] iron,[8)] and uranium[9)]. The extraction of the metal–ECR chelate anions, however, had not been yet reported. In this paper, the fundamental conditions for the extraction spectrophotometric determination of iron (III) as the iron–ECR–TDEA ternary complex and the composition of the ternary complex extracted into xylene will be discussed. Further, the relation between highly sensitive colour reaction of the iron–ECR–CTMA complex in a micelle solution of CTMA and the extracted ternary complex of the iron–ECR–TDEA system will be described somewhat.

Experimental

Reagent. A 2.5×10^{-3} M iron(III) solution was prepared by dissolving a definite amount of ferric ammonium sulfate in 1 M hydrochloric acid. 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. Tokyo Kasei Eriochrome Cyanin R was purified following the purification method Chromazurol S.[10)] 4 g of ECR were dissolved in 20 ml of deionized water, and the tetrabasic acid was precipitated by adding 20 ml of concentrated hydrochloric acid. The precipitate was filtered in a glass filter crucible, washed with a 1 : 1 hydrochloric acid solution, and dried in a vacuum over solid potassium hydroxide. The acid was reprecipitated from the solution, filtered, washed, and dried as has been described above. Further, the final product was dried to a constant weight over phosphorus pentoxide. Drying loss at 150 °C; 1.8%. Sulfur found by means of the combustion flask method; S, 6.63%, Calculated for $C_{23}H_{18}O_9S$; S, 6.81%. A 5×10^{-4} M ECR solution was prepared by dissolving the purified ECR in 0.001 M HNO_3 and by then adding 0.02% of urea. The TDEA was prepared by the reaction[11)] of tridodecylamine with ethylbromide in an alcoholic solution. The salt was recrystallized from petroleum benzine. A 8×10^{-4} M TDEA solution was subsequently prepared by dissolving the above TDEA in xylene.

Apparatus. All the measurements of the absorbance were made with a Hitachi manual spectrophotometer, model Epu-2A. Matched 10-mm, 5-mm, and 2-mm absorption cells were used. The pH measurements were made with a Hitachi-Horiba model M-5 glass electrode pH meter.

Standard Procedure. Place up to 2 μg of iron(III) in a 100-ml separatory funnel and add a definite amount of 0.2 M hydrochloric acid. Add 2 ml of a 5×10^{-4} M ECR solution. Adjust the pH to 6 with a 2 ml portion of a 2 M sodium acetate buffer solution and dilute to 25 ml with deionized water. Add 5 ml of 8×10^{-4} M TDEA in xylene and extract for 2 min with vigorous shaking. After the phase have separated, draw off the aqueous layer and centrifuge the extract for 3 min at 3000 rpm. Transfer the extract into an absorption cell and measure the absorbance at 613 nm against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. The absorption spectra of the ternary complex extracted into xylene, of the iron (III)–ECR–CTMA complex in a micelle solution of CTMA, and of the iron(III)–ECR chelate anion in an aqueous solution are given in Fig. 1, along with that of the reagent blank. The iron(III)–ECR chelate anion had an absorption maximum at 560 nm in an aqueous solution. On the other hand, the absorption maximum of the ternary complex in xylene shifted to a longer wavelength, 613 nm, and the absorbance increased remarkably. The absorption characteristics of the iron(III)–ECR–CTMA complex in a micelle solution of CTMA were similar to those of the ternary complex. These results showed that the

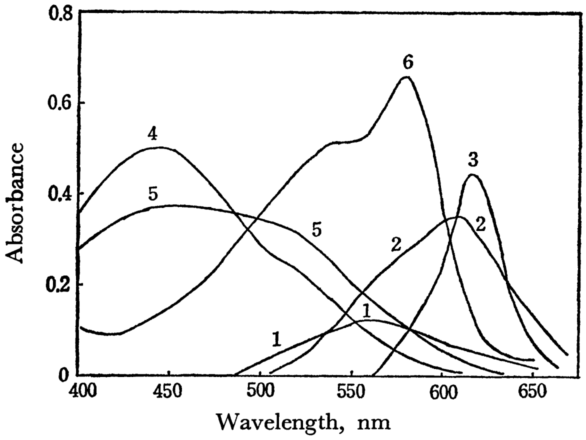

Fig. 1. Absorption spectra of the Fe-ECR-TDEA complex.

pH: 6, Volume of aq. layer $V_w = 25$ ml, $[\text{acetate}]_w = 0.16$ M, Volume of org. layer $V_0 = 5$ ml, 10 mm cell

(1) Fe-ECR in aq. soln. $[\text{Fe}]_w = 2.5 \times 10^{-6}$ M
(2) Fe-ECR-CTMA in micelle soln. of CTMA $[\text{Fe}]_w = 2.5 \times 10^{-6}$ M
(3) Fe-ECR-TDEA in xylene $[\text{Fe}]_o = 2.5 \times 10^{-6}$ M.
(4) ECR in aq. soln. $[\text{ECR}]_w = 3 \times 10^{-5}$ M
(5) ECR in micelle soln. of CTMA $[\text{ECR}]_w = 3 \times 10^{-5}$ M
(6) ECR-TDEA in xylene $[\text{ECR}]_o = 3 \times 10^{-5}$ M.

shift of the absorption maximum and the increase in the absorbance occurred in common with the action of long-chain quaternary ammonium salts to the iron(III)-ECR chelate anion, not only in a micelle solution of them. It was thought that the organic phases in the micelle and the extracted layer were related to the absorption characteristics of the ternary complex. The absorption maximum of ECR extracted with TDEA in xylene shifted to a longer wavelength.

Effect of pH. The effect of the pH of the aqueous phase on the absorbance was examined. The results are shown in Fig. 2. Thc maximum absorbance of the ternary complex was obtained at pH values from 5.8 to 6.5. The complex was extrated at considerably higher pH values, *viz.*, about 8, by the addition of glycine to the initial aqueous phase.

Organic Solvents. Several kinds of organic solvents were tested in order to achieve a quantitative extraction of iron (III). The ternary complex could be extracted into benzene, toluene, xylene, carbon tetrachloride, and *n*-buthyl acetate, but not into such polar solvents as *n*-butanol, methyl isobutyl ketone, and nitrobenzene. Xylene was chosen as the solvent.

The Effect of the ECR Concentration. The effect of the ECR concentration in the aqueous phase on the extraction of the ternary complex was examined by varying the ECR concentration, while the other variables were held constant. The absorbance of the extract was constant when the ECR in the initial aqueous phase was in the concentration range from 3.6×10^{-5} M to 4.4×10^{-5} M, as is shown in Fig. 3. The absorbance of the extract decreased suddenly upon the further addition of ECR. It was considered that a large quantity of ECR suppressed the extraction of the ternary complex, consuming the TDEA to form an ion pair with it.

The Effect of the TDEA Concentration. The effect of the concentration of TDEA in xylene on the absorbance of the ternary complex was examined. The absorbance of the extract was constant when the TDEA in xylene was in the concentration range from 7×10^{-4} M to 9×10^{-4} M, as is shown in Fig. 4. The absorbance of the extract gradually decreased upon the further addition of TDEA. However, the extraction of the ternary complex was carried out almost quantitatively in the concentration range of TDEA from 9×10^{-4} M to 1.5×10^{-3} M. The molar absorptivity of the ternary complex decreased when there was a large excess of TDEA in xylene.

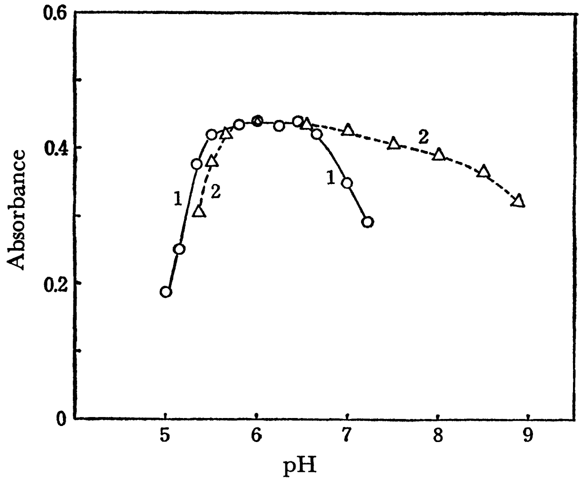

Fig. 2. Effect of pH on the extraction of the Fe-ECR-TDEA complex.

$V_w = 25$ ml, $V_0 = 5$ ml, Fe: 0.7 μg, $[\text{ECR}]_w = 4 \times 10^{-5}$ M, $[\text{TDEA}]_o = 8 \times 10^{-4}$ M, $[\text{acetate}]_w = 0.16$ M, 613 nm, 10 mm cell

(1) $[\text{glycine}]_w = 0$
(2) $[\text{glycine}]_w = 4 \times 10^{-2}$ M.

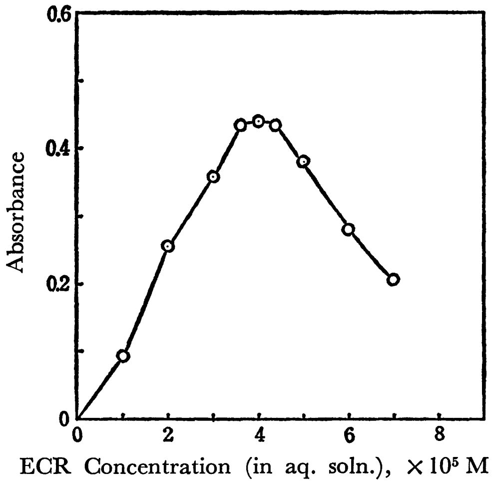

Fig. 3. Effect of the Eriochrome Cyanin R concentration in aqueous phase on the extraction of the Fe-ECR-TDEA complex.

pH: 6, $V_w = 25$ ml, $V_0 = 5$ ml, Fe: 0.7 μg, $[\text{TDEA}]_o = 8 \times 10^{-4}$ M, $[\text{acetate}]_w = 0.16$ M, 613 nm, 10 mm cell.

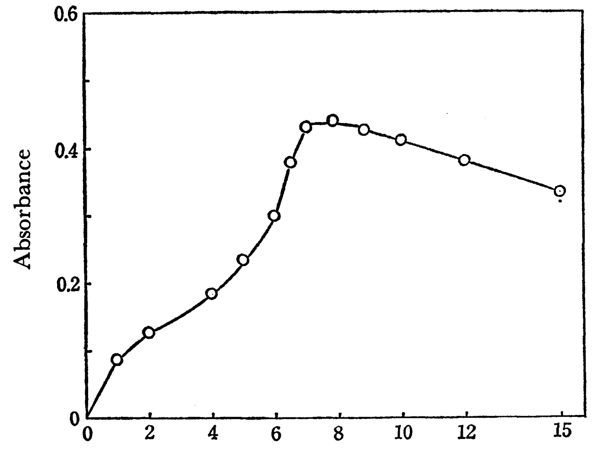

Fig. 4. Effect of tridodecylethylammonium bromide concentration in xylene on the extraction of the Fe-ECR-TDEA complex.
pH: 6, V_w=25 ml, V_0=5 ml, Fe: 0.7 μg, $[\mathrm{ECR}]_w$= 4×10^{-5} M, $[\mathrm{acetate}]_w$=0.16 M, 613 nm, 10 mm cell.

Table 1. Determination of iron(III) in the presence of diverse ions

Ion	Amount added (mg)	Iron(III) found (μg)	Error
None	—	1.4	—
Ni^{2+}	0.1	1.3a)	−0.1
Co^{2+}	0.1	1.3a)	−0.1
Cu^{2+}	0.1	1.3a)	−0.1
Cd^{2+}	0.1	1.4a)	0
Zn^{2+}	0.1	1.4a)	0
Pb^{2+}	0.1	1.1a)	−0.3
Hg^{2+}	0.1	1.1a)	−0.3
Bi^{3+}	0.1	1.4a)	0
Mn^{2+}	0.1	1.4a)	0
Sn(II)	0.1	1.0b)	−0.4
Cr(III)	0.1	1.3b)	−0.1
W(VI)	0.1	1.3b)	−0.1
Mo(VI)	0.1	1.4a)	0
V(V)	0.1	1.4b)	0
Al^{3+}	0.1	1.5b)	+0.1
Be^{2+}	0.1	1.6b)	+0.2
Th^{4+}	0.1	1.1b)	−0.3
Zr^{4+}	0.1	1.3b)	−0.1
Mg^{2+}	0.1	1.4a)	0
La^{3+}	0.1	1.4a)	0
U(VI)	0.1	1.2b)	−0.2
Cl^-	10	1.4a)	0
NO_3^-	10	1.0a)	−0.4
SO_4^-	10	1.5a)	+0.1
I^-	10	−0.6a)	−2.0
SCN^-	10	−1.0a)	−2.4
$C_6H_5O_7^-$	10	0.1a)	−1.3
F^-	10	1.5a)	+0.1
ClO_4^-	10	−1.0a)	−2.4
EDTA	10	−0.1a)	−1.5

a) 1 ml of 1M glycine was added as masking agent.
b) 1 ml of 1 M glycine, 1 ml of 30% hydrogen peroxide, and 1 ml of 1 M potassium fluoride were added as masking agents.

The Effect of the Shaking Time. The shaking time was varied from 10 s to 10 min. The absorbance of the extract was constant for the shaking times from 30 s to 10 min. A shaking time of 2 min was, therefore, selected.

Extractability 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 25-ml portion of an aqueous layer containing 1.4 μg of iron(III) was shaken with 5 ml of xylene, 97% of the iron(III) was extracted by one extraction. The molar absorptivity of the ternary complex calculated by using the percentage extraction and the absorbance was 1.73×10^5 cm^{-1}·mol^{-1}·l.

Calibration Curve. A calibration curve for the determination of iron(III) was made under the optimum conditions. A good linear relationship was obtained over the concentration range from 0.2 to 2 μg of iron(III) per 5 ml of xylene.

The Effect of Diverse Ions. The effect of foreign ions on the determination of iron(III) under the addition of 1 ml of 1 M glycine, 1 ml of 30% hydrogen peroxide, and 1 ml of 1 M potassium fluoride as masking agents to the initial aqueous phase at pH 8 was examined. The results are summarized in Table 1. Lead, mercury, tin, beryllium, thorium, and uranium interfered considerably. Of the anions tested, nitrate, iodide, thiocyanate, and perchlorate interfered seriously, giving a negative error. Chelating agents such as EDTA also interfered.

The Composition of the Ternary Complex. The results of the continuous-variation method indicated

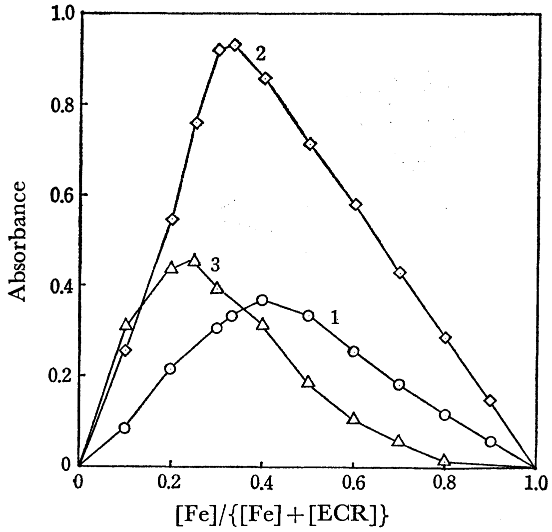

Fig. 5. Continuous variation method applied to the Fe-ECR-TDEA complex, the Fe-ECR-CTMA complex, and the Fe-ECR chelate.
pH: 6, $[\mathrm{acetate}]_w$=0.16 M, 5 mm cell
(1) Fe-ECR chelate in aq. soln. $[\mathrm{Fe}]_w+[\mathrm{ECR}]_w=4\times10^{-6}$ M, 560 nm.
(2) Fe-ECR-CTMA cnmplex in micelle soln. of CTMA $[\mathrm{Fe}]_w+[\mathrm{ECR}]_w=4\times10^{-6}$ M,645 nm.
(3) Fe-ECR-TDEA complex in xylene $[\mathrm{Fe}]_w+[\mathrm{ECR}]_w=4\times10^{-6}$ M, $[\mathrm{TDEA}]_o=8\times10^{-4}$ M, $[\mathrm{Glycine}]_w=4\times10^{-2}$ M, 613 nm.

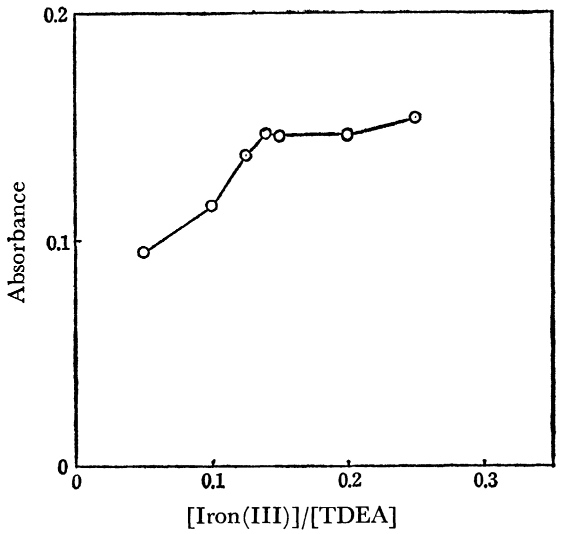

Fig. 6. Mole ratio method applied to the Fe-ECR-TDEA complex.
pH: 6, $[\text{acetate}]_w=0.16$ M, $[\text{ECR}]_w=4\times10^{-5}$ M, $[\text{TDEA}]_o=8\times10^{-4}$ M, 600 nm, 2 mm cell.

that the molar ratios of iron(III) to ECR in the chelates were 1 : 1.5 in an aqueous solution, 1 : 2 in a micelle solution of CTMA, and 1 : 3 in the extracted species, as is shown in Fig. 5. The molar ratios of iron(III) to ECR increased in the micelle solution of CTMA and in the extracted species. It was thought that the increase in the combination ratio of ECR in the extracted species was due to the higher coordinated complex, it was more stable in the organic layer. The results of the mole-ratio method indicated that the molar ratio of iron(III) to TDEA in the extracted species was about 1 : 7, as is shown in Fig. 6. The bulk of ECR, however, existed as HR^{3-} 12) in the aqueous solution about pH 6, and the molar ratio of iron(III) to ECR in the extracted species was estimated to be 1 : 3. Therefore, the extracted species was assumed to be probably the ternary complex $\{[\text{Fe(HR)}_3]^{6-}\}\cdot\{(\text{TDEA}^+)_6\}$.

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