

Spectrophotometric Determination of Scandium(III) with Eriochrome Cyanine R in the Presence of Cetyltrimethylammonium bromide

Ki-Won Cha[†], Chan-il Park and Jong-Whon Kim*

Department of Chemistry, Inha University, Incheon 402-751, Korea

**Department of Chemistry, Chonju University, Chonju 560-759, Korea*

(Received Mar. 8, 1996)

Cetyltrimethylammonium bromide에서 Eriochrome Cyanine R에 의한 스칸듐(III)의 분광광도법 정량

차기원[†] · 박찬일 · 김종훈*

인하대학교 화학과

*전주대학교 화학과

(1996. 3. 8. 접수)

Abstract: The spectrophotometric determination method of scandium with eriochrome cyanine R(ECR) and the composition ratio of the complex were investigated in the presence of surfactants. The absorbance increase and red shift of maximum adsorption wavelength of Sc(III)-ECR complex were observed in cetyltrimethylammonium bromide (CTMAB), but those changes were not observed in the sodium dodecyl sulfate(SDS) and Triton X-100. A volume of 5ml of 1×10^{-3} M ECR and 10ml of 2×10^{-4} M CTMAB are necessary for the determination of $1 \times 10^{-7} \sim 3.0 \times 10^{-6}$ M Sc(III) at pH 6.5. The apparent molar absorption coefficient of the Sc(III)-ECR-CTMAB, ternary complex at 610nm is $5.6 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$ and its detection limit is 1.0×10^{-7} M. The binary complex composition of Sc(III)-ECR is 1:2 and the ternary complex composition of Sc(III)-ECR-CTMAB is 1:3:1.

요약: 발색제로 eriochrome cyanine R(ECR)을 사용하여 여러 가지 계면활성제에서 스칸듐을 분광광도법으로 정량하는 방법과 그 착물의 조성을 연구하였다. Sc(III)-ECR 착물의 흡광도와 최대 흡수 파장은 cetyltrimethylammonium bromide (CTMAB)에서 크게 변하지만, sodium dodecyl sulfate(SDS)나 Triton X-100의 계면활성제에서는 변화가 없다. $1 \times 10^{-7} \sim 3.0 \times 10^{-6}$ M Sc(III)을 ECR로 정량할 때는 pH 6.5에서 1×10^{-3} M ECR 5ml와 2×10^{-4} M CTMAB 10ml가 필요했다. Sc(III)-ECR-CTMAB, 삼성분 착물의 몰흡광계수는 610nm에서 $5.6 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$ 이며 검출한계는 1.0×10^{-7} M이었다. Sc(III)-ECR-CTMAB 삼성분 착물의 조성은 1:3:1이었다.

Key words: Eriochrome cyanine R(ECR), Cetyltrimethylammonium bromide (CTMAB), Ternary complex.

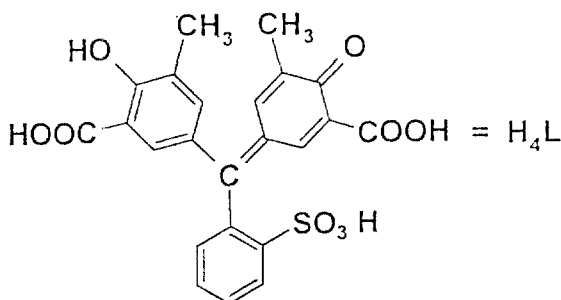
1. Introduction

Triphenylmethane dye has been extensively used for the spectrophotometric determination of scandium ion. Numerous methods such as arsenazo III¹, chrome azurol S(CAS)², methyl thymol blue(MTB)³, xylenol orange (XO)⁴⁻⁶ are available for the spectrophotometric determination of scandium ion. Typically, those metal-dye complexes have molar absorptivities ranged $1 \times 10^4 \sim 5 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$.

The sensitivity of spectrophotometric determination is often enhanced by addition of surfactants to metal-dye complex solution. The sensitization effect is characterized by an increase in molar absorptivity and red shifts of λ_{max} (approximately 50~150nm).^{7,8} Generally there are two models for sensitization mechanism : micellar solubilization and formation of ternary complexes containing surfactant monomers.

Micelles have been widely applied to many areas of science and technology.⁹⁻¹² One of the well known abilities of them is to make water insoluble compound to soluble. Because, hydrophobic molecules are surrounded by the micelles, they can be soluble in an aqueous media.¹³

ECR [1], sodium 2⁻-sulpho-3,3-dimethyl-4-hydroxyfuschson-5,5-dicarboxylate, a dye of the triphenylmethane series has been used for spectrophotometric determination of aluminium(III), beryllium(II) and others. It has been reported that addition of 2,2-bipyridine(bpy) to ECR enhanced the absorption sensitivity and selectivity for iron(II).¹⁴



Eriochrome Cyanine R (I)

In this paper, we focused on careful examination of the spectrophotometric behaviors of Sc(III)-ECR complex in various surfactants (cationic, anionic and nonionic). The other aim of this study was improvement of the understanding of those mechanisms underlying surfactant sensitization.

2. Experimental

2.1. Reagents

All solutions were prepared with distilled-deionized water. Stock solution of Sc(III) ($1 \times 10^{-4} \text{ M}$) was prepared from Sc_2O_3 (Sigma, 99.9% purity). Weighed amount of Sc_2O_3 was dissolved in a 0.1M hydrochloric acid and diluted to a constant volume with water.

Stock solution of ECR ($1 \times 10^{-3} \text{ M}$) was prepared by dissolving 0.536g of ECR in 1L water. The cetyltrimethylammonium bromide (CTMAB, 99% : Sigma) and sodium dodecyl sulfate (SDS ; 99% : Sigma) were used without additional purification. The Triton X-100 (octylphenoxypolyethoxyethanol) used in this study was obtained from Sigma Co. and used as received. An average molecular weight of 624 g mol^{-1} was used for concentration calculation.

The surfactant solutions were prepared as $1 \times 10^{-3} \text{ M}$. The sample solution was adjusted to pH 6.5 with hexamethylenetetramine (HTM) buffer and the surfactants should not have any absorbance from 400 to 800nm.

The absorbances were measured with a Perkin Elmer 552S spectrophotometer. The pH was measured with a NOVA-310 pH-meter.

2.2. Procedure

An aliquot of Sc(III) standard solution was transferred to a 50mL volumetric flask, consecutively 5.0mL of the $1 \times 10^{-3} \text{ M}$ ECR solution, 3.0mL of pH 6.5 hexamethylenetetramine(HTM) buffer and 10mL of $2 \times 10^{-4} \text{ M}$ surfactant solution were added. The solution was made up to the mark with deionized

water.

The absorbance of the solution was measured at 400~800nm against a reagent blank as a reference.

3. Results and Discussion

3.1. Absorption spectra of ECR

The absorption spectra of the ECR ligand were studied at various pH adjusted with buffer solutions. The results were shown in Fig. 1. The absorption maxima λ_{max} is 422nm in pH 7~9, 476nm in pH 1~4, and 580nm above pH 11.9.

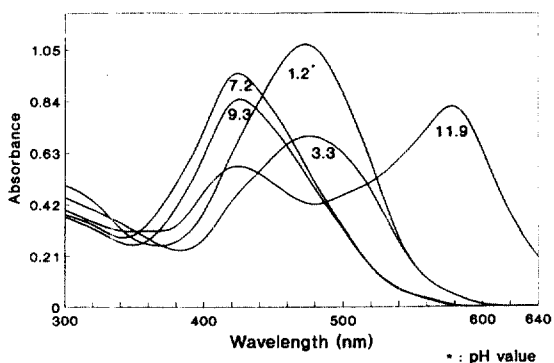


Fig. 1. Absorption spectra of 1×10^{-4} M ECR according to pH change.

Suk and Miketukova⁶ reported that the ECR dissociates in aqueous solution as follows :



The changes of λ_{max} from 420nm to 580nm according to pH variations could be interpreted in terms of increasing dissociation ratio of protons from ECR.

As can be seen in Fig. 1, in pH between 7~9, the primary chemical species of ECR was $HECR^{3-}$ and its λ_{max} was 420nm ($pK_1=1.83$, $pK_2=1.83$, $pK_3=5.74$, $pK_4=11.83$, according to Ref. 15).

The absorption spectra of complexes between

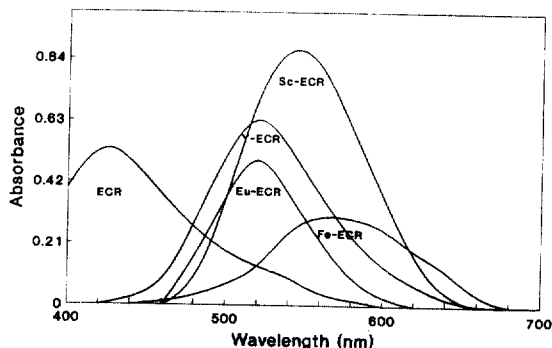


Fig. 2. Absorption spectra of ECR and ECR-metal complex at pH 6.5.

Metal : $5 \mu\text{g} / \text{mL}$, ECR : 1×10^{-4} M.

ECR and several metal ions at pH 6.5 were shown in Fig. 2. As shown in Fig. 2, λ_{max} of ECR-metal complexes were similar to ECR^{4-} species.

3.2. Effects of surfactants

The effects of various surfactants were investigated. As shown in Fig. 3, a remarkable absorbance increase of Sc(Ⅲ)-ECR system were made in the CTMAB surfactant but those effects were not found in Triton X-100 and SDS system.

The addition of CTMAB to the Sc(Ⅲ)-ECR solution led to the red-shift of λ_{max} (608~615nm) and an increase of absorbance at λ_{max} .

The absorbance change of Sc(Ⅲ)-ECR-CTMAB

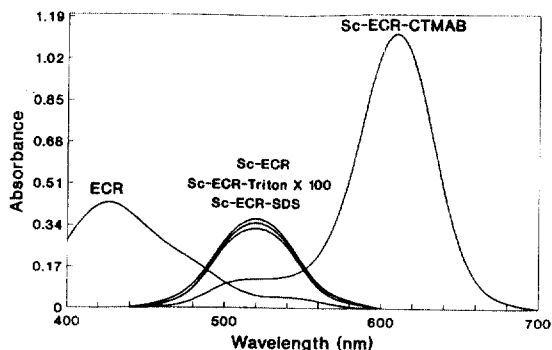


Fig. 3. Absorption spectra of Sc(Ⅲ)-ECR complex with surfactants at pH 6.5.

Sc(Ⅲ) : 2.0×10^{-6} M, ECR : 1×10^{-4} M, surfactants : 2.0×10^{-4} M.

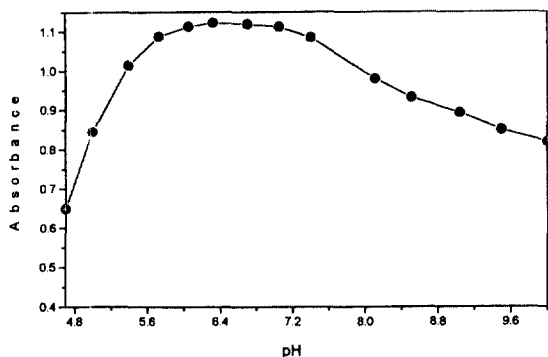


Fig. 4. Effect of pH. Sc(III) : 2.0×10^{-6} M, ECR : 1×10^{-4} M, CTMAB : 2.0×10^{-4}

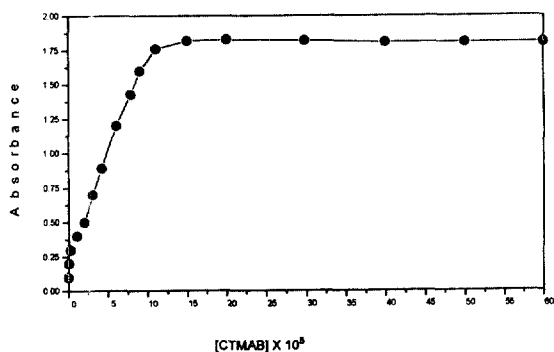


Fig. 5. Effect of CTMAB concentration on the absorbance of Sc-ECR complex : ECR : 1×10^{-4} M, Sc(III) : 3.0×10^{-6} M.

system according to pH change was obtained against the reagent blank (Fig. 4). From the result of Fig. 4, pH 6.5 which give absorption maximum was chosen for the further investigation.

Fig. 5 indicates the absorbance changes of the complex according to the concentration change of CTMAB. The absorbance of Sc(III)-ECR complex increased with the increase of CTMAB concentration up to 1.2×10^{-4} M. The approximately constant absorbance was obtained in higher concentration than 1.2×10^{-4} M. Thus, 2×10^{-4} M CTMAB was chosen as an optimum experimental condition. The enhancement factor (absorbance of Sc(III)-ECR-CTMAB vs. that of Sc(III)-ECR) was calculated as 7 times in the 2×10^{-4} M CTMAB solution.

The mechanism of the red shift and absorbance increase in the presence of CTMAB can be interpreted with the formation of Sc(III)-ECR-CTMAB ternary complex.

3.3. Change of composition of the Sc(III)-ECR complex with CTMAB

In order to examine the composition of Sc(III)-ECR-CTMAB ternary complex, we measured the mole ratio of Sc(III) and ECR in Sc(III)-ECR complex with and without CTMAB. The molar composition of the Sc(III)-ECR complex was ascertained using the continuous variation method.

The molar composition of the Sc(III) to ECR was 1:2 in the absence of CTMAB and 1:3 in the presence of CTMAB. The stoichiometric mole ratio of Sc(III) and ECR of Sc(III)-ECR complex changed from 1:2 to 1:3 in the presence of CTMAB.

The molar ratio of Sc(III) and CTMAB in the Sc(III)-ECR-CTMAB complex was determined by the method mentioned above. It appeared that the molar ratio of Sc(III) and CTMAB in the ternary complex of Sc(III)-ECR-CTMAB was 1:1.

The positive charge of the cationic surfactant would attract the negatively charged complex of mixed-ligand complex, so 1:1 (mole ratio) complex of CTMAB and Sc(III)-ECR was formed.

3.4. Calibration curves

The calibration curve for the determination of

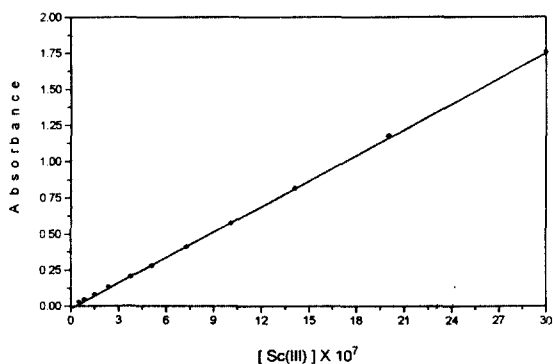


Fig. 6. Calibration curve of Sc(III) in the presence of CTMAB.

Sc(III) by this method was prepared in the range of $1.0 \times 10^{-7} \text{M}$ to $3.0 \times 10^{-6} \text{M}$. The results are plotted in Fig. 6.

The equation obtained by least-squares method ($n=11$) is : $A=5.61 \times 10^5 C + 0.003$ ($r=0.9996$), where A is the absorbance, C is molarity of scandium and r is the correlation coefficient. The calculated molar absorptivity is $5.61 \times 10^5 \text{ mol}^{-1} \text{cm}^{-1} \text{L}$.

3.5. Effects of foreign ions

To assess the usefulness of this method, the effects of foreign ions which often interfere for the determination of scandium were studied.

The tolerance limits given in Table 1 are the concentrations that cause error of less than $\pm 3.0\%$ in the absorbance of 1ppm Sc(III) solution.

Table 1. Effects of interfering ions on determination of $1 \mu\text{g}/\text{mL}$ of Sc(III).

Foreign ion	Tolerance ($\mu\text{g}/\text{mL}$)
Ni (II)	0.7
Cr (III)	1
Cd (II)	0.15
Cu (II)	0.15
Al (III)	0.008
Zn (II)	0.3
Fe (III)	0.06
Mg (II)	500
Zr (IV)	0.5
Pt (II)	3.5
Pb (II)	1.5
Au (II)	5
Ti (IV)	0.6
Pd (II)	0.3
Malic acid	45
Tartaric acid	50
EDTA	1
Sulfate	100
Phosphate	5
Nitrate	30

Aluminium, iron(III), cadmium and copper, which form strong complexes with ECR, give strong inter-

ference. EDTA and phosphate ions inhibit color formation of the ternary complexes of Al and Cu.

3.6. Determination of Sc(III) in Tin slag solution

The proposed method was applied for the determination of Sc(III) in Tin slag. The matrix ions, such as Sn^{4+} , Fe^{3+} , Pb^{2+} , Cr^{3+} are coexisted in tin slag solution. To eliminate the interference ions in the slag solution, the separation of Sc(III) from the tin slag solution was needed.¹⁶

Five to 10ml of sample solution was transferred to a 100ml beaker and 10ml of $3 \times 10^{-2} \text{M}$ di-(2-ethylhexy)phosphate(DEHPA) solution dissolved in ethanol was added. Then, the solution was diluted to 50ml with ethanol and was stirred thoroughly. The precipitate generated was filtered, then washed with 20ml ethanol three times and ignited at 900°C . The residue dissolved with 1:1 HCl and Sc(III) was determined by this method.

Table 2 shows that the analytical values obtained by this method are in good agreement with the data by ICP-AES. The relative standard deviation for the determination of scandium in tin slag solution was 0.9~1.2%.

Table 2. Analytical data of scandium in tin slag solution

Sample	Present method		ICP method	
	Found (ppm)	RSD (%)	Found (ppm)	RSD (%)
Tin slag solution ^{a)}	56.40	0.91	54.35	0.1

a : The solution was received from Lucky Metal Co.

4. Conclusion

The absorption spectra of ECR, Sc(III)-ECR and Sc(III)-ECR-CTMAB have been investigated. The mole ratio of Sc(III) and ECR in Sc(III)-ECR binary complex is 1:2 and 1:3 in Sc(III)-ECR-CTMAB ternary complex, and the mole ratio

of Sc(III) and CTMAB in Sc(III)-ECR-CTMAB ternary complex is 1 : 1.

The calibration line of Sc(III) is obtained over the range $0 \sim 3.0 \times 10^{-6}$ M. The apparent molar absorption coefficient and the detection limit of Sc(III)-ECR-CTMAB at 610m is $5.61 \times 10^5 \text{ mol}^{-1} \text{ L}$, and 1.0×10^{-7} M, respectively. The enhancement factor of Sc(III)-ECR-CTMAB over Sc(III)-ECR is 7.0.

Acknowledgment

This work was supported by research foundation of Inha university, 1995.

References

1. B. J. Bornong and J. L. Moriaty, *Anal. Chem.*, **34**, 871(1962).
2. T. Kawashima, H. Ogawa, and H. Hamaguchi, *Talanta*, **8**, 552(1962).
3. K. W. Cha and E. S. Jung, *J. Korean, Chem. Soc.*, **37**, 496(1993).
4. K. W. Cha and C. I. Park, *J. Korean, Anal. Soc.*, **7**, 277(1993).
5. K. Tonosaki and M. Otomo, *Bull. Chem. Soc. Japan*, **35**, 1683(1962).
6. V. Suk and V. Miketukova, *Collect. Czech. Chem. Commun.*, **24**, 3629(1959).
7. M. P. San Andres, M. L. Marina and S. Vera, *Talanta*, **41**, 179(1994).
8. A. Sanz-Medel and M. F. Fernandez Perez, *Anal. Chem.*, **58**, 2161(1986).
9. W. L. Hinze, *Solution Chemistry of Surfactants, Plenum Press : New York*, 1979 ; Vol. 1, p. 79.
10. E. Pelizzetti, and E. Pramauro, *Anal. Chim. Acta*, **168**, 1(1985).
11. B. Lindman and H. Wennerstrom, *Top. Curr. Chem.*, **87**, 1(1980).
12. D. Atwood and A. T. Florence, *Surfactant System*, Chapman & Hall : London, 1983.
13. J. F. Rusling, C. N. Shi and T. F. Kumosink, *Anal. Chem.*, **60**, 1260(1988).
14. R. Ishida and V. Miketukova., *Nippon Kagaku Kaishi*, 1496(1975).
15. J. Rosendorfova and J. Cermakova, *Talanta*, **27**, 1998(1980).
16. Ki-Won Cha and Eui-Sik Jeong., *Bull. Korean Chem. So.*, **15**, 9(1994).