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Surfactant Extraction and Determination of Ruthenium(III) as a Thiocyanato Complex

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Ruthenium(III) was reacted to form a complex with thiocyanate, and extracted into the surfactant phase with Zephiramine (Z) by heating. The structure of this ion-pair was estimated to be $[RuX_2(SCN)_2]^- \cdot Z^+$, in which X was a chloride ion, and was observed to cause an increasing absorbance and a blue shift of the spectrum. The determination of ruthenium(III) was investigated by the surfactant extraction-spectrophotometric method using a nonionic surfactant of Triton X-100 as an extraction solvent. The molar absorptivity was equal to 1.16×10^4 dm^3 cm^{-1} mol^{-1} at 565 nm. Ruthenium(III) could be concentrated from the solution into a surfactant phase having a small volume. The first-order derivative spectroscopic method was used to reduce the interference from other platinum-group elements, such as osmium.

An aqueous solution of surfactant micelles exhibits the property of separating into two liquid phases due to a temperature[1,2] and pressure change,[3] or the addition of salts. One is a concentrated phase containing most of the surfactant, and is termed a surfactant-rich phase, or briefly, a surfactant phase; another is an aqueous phase containing a low concentration of surfactants close to the critical micelle concentration (cmc). Based on these phase separation phenomena, the surfactant-extraction technique was of considerable interest for a chemical analysis for the separation and quantitative determination of a large number of metal ions.[4] Traditionally, organic solvents, such as benzene or chloroform, have been used for liquid–liquid extraction systems; however, these solvents are often classified as having carcinogenic toxicity and as environmental pollutants. Nonionic surfactants have a non-volatile nature and would be classified as either practically non-toxic or relatively harmless reagents.[2,5]

The surfactant-extraction method, based on the characteristic colors and low solubility of metal complexes in water, was initially reported by Watanabe and co-workers[6] with a nonionic surfactant, and was combined with the spectrophotometric method. An aqueous solution of a nonionic surfactant, such as Triton X-100, when heated above the cloud-point temperature, exhibits the property of separating into an aqueous phase and a surfactant phase. There is an advantage in the surfactant-extraction method in which a concentration effect has been expected as a function of the small volume of the separated surfactant phase. However, other sensitive effects, such as a shift in the spectrum or an increasing absorbance, which was often observed in micellar systems, have not been reported in the surfactant-extraction systems.

In the present work, we investigated the surfactant extraction of ruthenium(III) with thiocyanate based on a temperature-induced phase separation. Ruthenium(III) reacts with thiocyanate to form a blue-colored complex in an acidic solution. This reaction has been widely used as a conventional method for the spectrophotometric and extraction-spectrophotometric determination of ruthenium.[7—11] However, the sensitivity of these methods was insufficient for an analysis of micro amounts of ruthenium, because the molar absorptivity of the thiocyanato complex could not exceed 7×10^3 dm^3 cm^{-1} mol^{-1}. An increase in the absorptivity of ruthenium(III) was obtained by the formation of an ion-pair as a thiocyanato complex with high molecular amines, such as Zephiramine. This sensitive ion-pair formation was a characteristic for ruthenium(III) among the platinum-group elements and was extracted into the Triton X-100 phase by heating. The nature of the complex and the extracted ion-pair was examined and utilized for the determination of ruthenium(III).

Experimental

Reagents. Water that had been twice deionized was used in the preparation of all solutions. A stock solution of ruthenium(III) was prepared by dissolving 1.0 g of ruthenium trichloride (Kanto Chemicals) in 1.0 dm^3 of 1.0 mol dm^{-3} hydrochloric acid. The concentration of ruthenium(III) was gravimetrically standardized with thiosalicylamide that was synthesized according to a literature method.[12,13] A 5.0 mol dm^{-3} ammonium thiocyanate (Kanto Chemicals) and 0.10 mol dm^{-3} Zephiramine (Dojindo Chemicals, tetradecyldimethylbenzylammonium chloride) solutions were prepared by dissolving a weighed amount of each in water. A Triton X-100 solution(20%, v/v) was prepared by dissolving 20 cm^3 of Triton X-100 (Katayama Chemicals) in 80 cm^3 of water and heated over its cloud point(about 70 °C). After phase separation, the aqueous phase was discarded. The remaining Triton X-100 was diluted with water to 100 cm^3. All of the other chemicals were of analytical grade.

Apparatus. An absorbance measurement was made with a Shimadzu UV-265 spectrophotometer using quartz cells of 1.0 cm path length. The same spectrophotometer was used for measuring the first-order derivative spectra with a 4.0 nm derivative width. All of the pH measurements were made with a Horiba M-7 pH meter and a combination glass electrode. The solution was warmed in a water bath at a temperature of 80±2 °C that was electrically controlled.

General Procedure. A sample solution containing less than 50 μg of ruthenium(III) was transferred to a 50 cm^3 test tube with a graduation line. After the successive addition of 3.0 cm^3 of 20% Triton X-100, 3.0 cm^3 of 0.10 mol dm^{-3} Zephiramine and 1.5 cm^3 of 5.0 mol dm^{-3} ammonium thiocyanate, the pH of the solution was adjusted to 1.6 with hydrochloric acid and diluted to 40 cm^3 with water. The solution was heated at 80 °C for 80 min and then cooled to room temperature. After the aqueous phase was discarded, the Triton X-100 phase that remained at the bottom of the tube was diluted to 8.0 cm^3, or a selected volume, with water. The absorbance at 565 nm was measured against pure water. The first-order derivative spectra and their absolute values at 515 or 605 nm were also measured against pure water.

Results and Discussion

Formation of the Complex and Ion-Pair. Ruthenium(III) reacted with thiocyanate to form a water-soluble complex, and its molar absorptivity was 4.10×10^3 dm^3 cm^{-1} mol^{-1} at 585 nm in water. This complex was extracted into the Triton X-100 phase in the presence of Zephiramine. Figure 1 shows the spectra of ruthenium(III)–thiocyanato complexes formed in water and extracted with Zephiramine into the Triton X-100 phase. An enhanced absorbance and a slightly blue shift of the spectrum were observed in the surfactant phase. The molar absorptivity of this ion-pair was 1.16×10^4 dm^3 cm^{-1} mol^{-1} at 565 nm in the Triton X-100 phase.

The reaction of ruthenium(III) with thiocyanate was slow at room temperature in the surfactant solution. Figure 2 shows the effect of the reaction temperature and heating time on the absorbance. The formation of the complex was slow at 70 °C. Though an increasing temperature accelerated the reaction of the complex formation, a decrease in the absorbance was observed at a high temperature, such as 90 °C. This decrease was due to a partial decomposition of the complex, which was related to the reduction of ruthenium(III) to ruthenium(II) by thiocyanate.[14,15] The reaction proceeded satisfactorily at 80 °C and for 80 min.

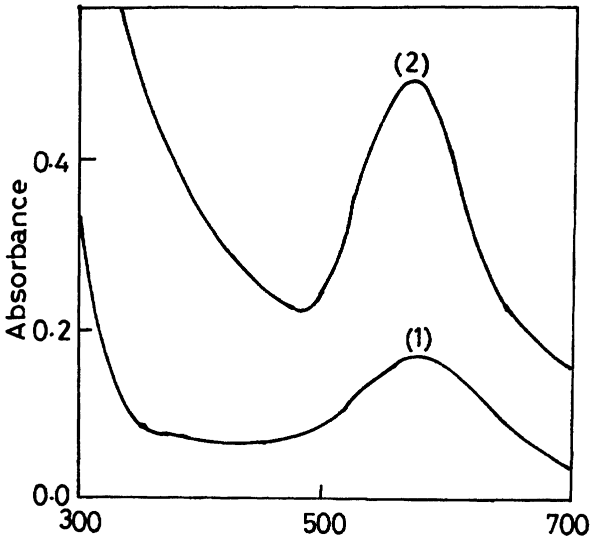

Fig. 1. Absorption spectra of Ru(III) complexes (1) in water and (2) in Triton X-100 in the presence of 4.3×10^{-5} mol dm^{-3} Ru(III) at the final volume of 40 cm^3. For experimental conditions, see general procedure.

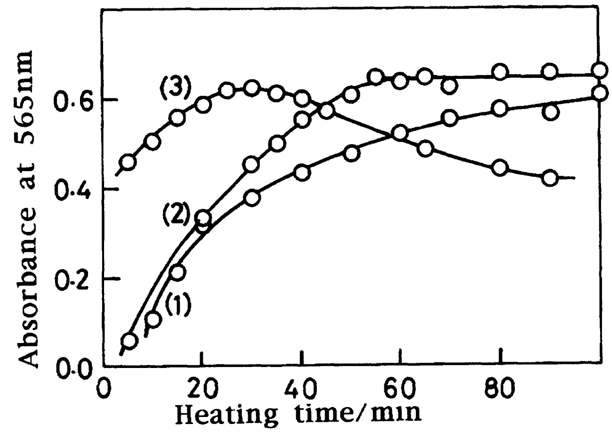

Fig. 2. Effect of heating time on the absorbance at (1) 70 °C, (2) 80 °C, and (3) 90 °C in the presence of 1.0×10^{-5} mol dm^{-3} Ru(III) at the final volume of 8.0 cm^3.

Table 1 summarizes the molar absorptivities of the ruthenium(III) thiocyanato complex in various media with the reported values.[11,14—17] Bakyrdzhieva and co-worker[11] reported a molar absorptivity of 6.8×10^3 dm^3 cm^{-1} mol^{-1} as the thiocyanato complex extracted with di(2-ethylhexyl) amine into 1,2-dichloroethane. It seems that the molar absorptivity (about $\varepsilon=7\times10^3$) of this system is the highest one ever reported. They recommended a preheating procedure in which the solutions were heated on a sand bath for 5 min, and rapidly cooled with ice. Further heating led to a decrease in the absorbance. Their system resembles our system with respect to ion-pair extraction with amine; however, there is a distinct result concerning the molar absorptivity and spectrum.

We examined the extraction of the complex into acetonitrile with tetraethylammonium bromide and Zephiramine. After 30 min of heating at 60 °C, the maximum absorbance was obtained in both cases. The molar absorptivities were 4.3×10^3 at 599 nm with tetraethylammonium bromide and 9.5×10^3 dm^3 cm^{-1} mol^{-1} at 544 nm with Zephiramine. The spectrum changes, such as the blue shift and increasing absorbance, were related to the presence of Zephiramine, rather than the character of the solvents. Some scatter of the molar absorptivities shown in Table 1 was also due to the conditions of the preheating procedure, such as the time, temperature and coexisting acids. During preheating, the two reactions were indicated by increasing the absorbance due to complex formation and decreasing it due to the reduction of ruthenium. This opposite propensity affected the sensitivity and reproducibility of the measurements.

Figure 3 shows the effect of the thiocyanate concentra-

Table 1. Molar Absorptivities of Ruthenium(III) Thiocyanate Complex

Method	ε/dm^3 cm^{-1} mol^{-1}	λ_{max}	Medium
Heat at 70 °C	3.0×10^3	590 nm	Aqueous soln[a]
Heat at 70 °C	5.9×10^3	585 nm	Aqueous soln[b]
Heat at 90 °C	4.2×10^3	590 nm	Aqueous soln[c]
Heat at 80 °C	4.1×10^3	585 nm	Aqueous soln
Back extraction from CCl_4	3.2×10^3	590 nm	Aqueous soln[d]
Heat on a sand bath and extract with amine	6.8×10^3	585 nm	$C_2H_2Cl_2$[e]
Heat at 80 °C and extract with Zephiramine	1.16×10^4	565 nm	Triton X-100

a) Ref. 16. b) Ref. 14. c) Ref. 15. d) Ref. 17. e) Ref. 11.

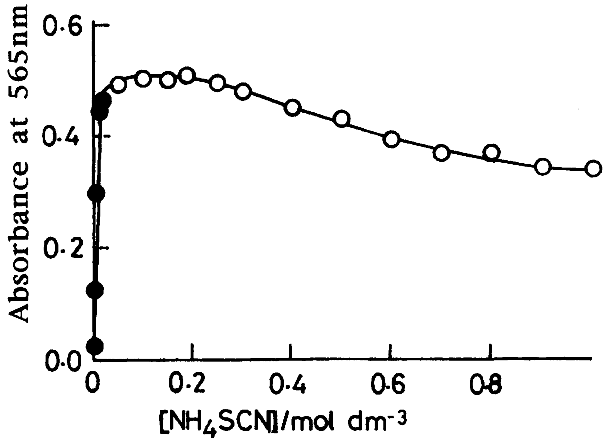

Fig. 3. Effect of the thiocyanate concentration on the absorbance in the presence of 8.6×10^{-6} mol dm^{-3} Ru(III), 1.5% Triton X-100 and 7.5×10^{-3} mol dm^{-3} Zephiramine at pH 1.6. The conditions for the phase separation were at 80 °C for 80 min in the (○) absence of and (●) presence of 0.75 mol dm^{-3} $(NH_4)_2SO_4$.

tion. The phase separation did not occur below a thiocyanate concentration of 2.5×10^{-3} mol dm^{-3}. Therefore, ammonium sulfate was added as a salting-out reagent in these low thiocyanate concentration ranges. The decrease in the absorbance at high concentration was mainly due to the reduction of ruthenium(III) by thiocyanate. In the absence of Zephiramine, the phase separation was incomplete; a constant and maximum absorbance was then obtained at greater than a 6.5×10^{-3} mol dm^{-3} Zephiramine concentration. A constant absorbance was obtained from pH = 1.5 to 3.5. The optimum concentration of Triton X-100 was 1.0—2.0%(v/v).

In the presence of Zephiramine, a stable and high absorbance was obtained by the surfactant extraction. Though a slight disadvantage remained in relation to the heating time, this method was simple because one needed only to heat the solution for the sake of both the complex formation and phase separation, and the upper aqueous phase was easily discarded.

Extraction of the Complex and Calibration Graph. Under the conditions of the present experiment, approximately 3 cm^3 of the surfactant phase was obtained from a 40 cm^3 solution. Therefore, ruthenium was concentrated more than ten times. In practical use, since the Triton X-100 phase had a relatively high viscosity, the transfer of a sample into the optical cell was slightly difficult. Dilution with water gave good a reproducibility, and caused no influence, such as a decomposition or dissociation of the complex on the measurements. The values of the ordinate shown in Fig. 4, that is the product of the measured absorbance at 585 nm and the final volume, were constant.

We attempted to dilute the final volume to 8.0 cm^3, which corresponded to a five-fold concentration of ruthenium. Under this condition, the calibration graph obeyed Beer's law between ruthenium concentrations of 3.4×10^{-7} and 1.3×10^{-5} mol dm^{-3}. The apparent molar absorptivity was 5.80×10^4 dm^3 cm^{-1} mol^{-1}, and the variance in the reproducibility was within 3% at 8.6×10^{-6} mol dm^{-3} ruthenium(III) concentration. Linear calibration graphs passing through the origin were obtained for each of the derivative measurements at 515 and 605 nm for the same ruthenium concentration ranges.

Influence of Diverse Ions. The influence of diverse ions on the spectrophotometric and first-order derivative methods was mainly tested for the platinum-group elements and other metals that form a colored complex with thiocyanate. The results are summarized in Table 2 as the weight ratio of ions within an error of ±3.0%.

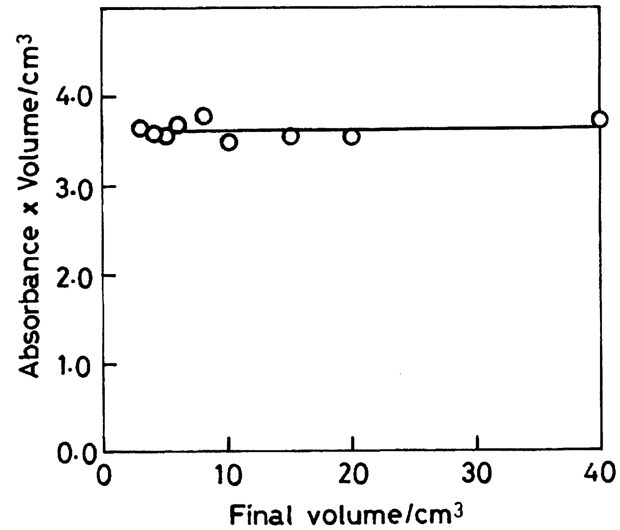

Fig. 4. Effect of the dilution with water on the absorbance measurements in the presence of 8.6×10^{-6} mol dm^{-3} Ru(III), 0.19 mol dm^{-3} thiocyanate, 1.5% Triton X-100 and 7.5×10^{-3} mol dm^{-3} Zephiramine.

Table 2. Tolerance Limit of Diverse Ions[a)]

Diverse ions	Added as	Tolerance limit of ions/Ru(III),w/w	
		Spectro-photometry	First-order derivative
Pd(II)	$PdCl_2$	<1	5
Fe(III)	$(NH_4)Fe(SO_4)_2$	1	10
Ir(IV)	Na_2IrCl_6	<1	10
Rh(III)	$Rh(NO_3)_3$	1	10
Ag(I)	$AgNO_3$	5	20
Au(III)	$HAuCl_4$	5	20
Co(II)	$Co(NO_3)_2$	1	20[b)]
Cu(II)	$CuSO_4$	<1	20
Ni(II)	$NiSO_4$	5	20
Os(VI)	K_2OsO_4	1	20
Pt(IV)	H_2PtCl_6	20	100
Ca(II)	$CaCl_2$	100	100
Mg(II)	$MgCl_2$	100	100

a) Contained 0.87 $\mu g\,ml^{-1}$ Ru(III). b) Measured at 515 nm.

Tetra- and hexavalent osmium formed the same orange complex that corresponds to the osmium(III)–thiocyanato complex due to the reduction of osmium by thiocyanate.[14,18)] Palladium(II) formed a yellow complex. These colored complexes of platinum-group elements gave the same spectrum in the presence and absence of Zephiramine. The other metal ions of the platinum-group elements did not form a colored complex; however, an excess of these ions interfered.

At high temperature in the presence of the other metal ions, the thiocyanate was inclined to be oxidized. The absorption of the oxidation products of thiocyanate, those colors being yellowish, tailed widely into the visible region. Therefore, many ions interfered with the absorbance measurement at 565 nm.

The first-order derivative analysis at 605 nm reduced the influence of diverse ions. A 5-times excess of palladium, a 10-times excess of iridium and of rhodium, a 20-time excess of osmium and a 100 times excess of platinum did not interfere.

For over a 100-times excess of magnesium and calcium ions, the solution was turbid and the phase separation was incomplete. The solution involving cobalt(II) gave a blue color at room temperature before and after heating. This coloration was due to the characteristic reaction of cobalt(II) with thiocyanate in nonionic surfactant solutions, and had an absorption peak at 628 nm.[19)] The first-order derivative analysis at 515 nm was used for this ion, and a good result was obtained.

Structure of Complex. The thiocyanato complex of ruthenium(III) formed an ion-pair with Zephiramine, which was extracted into the Triton X-100 phase,

$$\mathrm{Ru^{III}_w} + n\mathrm{SCN^-_w} + m\mathrm{Z^+_w} = [\mathrm{Ru^{III}SCN}_n\cdot\mathrm{Z}_m]_\mathrm{s}, \qquad (1)$$

where Z^+ denotes the Zephiramine cation, and n and m denote the number of the thiocyanate and Zephiramine, respectively. The subscripts w and s denote the aqueous and Triton X-100 phases, respectively. The distribution ratio (D) is defined as

$$D = [\mathrm{Ru^{III}SCN}_n\cdot\mathrm{Z}_m]_\mathrm{s}/[\mathrm{Ru^{III}}]_\mathrm{w}. \qquad (2)$$

The extraction constant (K_{ex}) is

$$K_\mathrm{ex} = [\mathrm{Ru^{III}SCN}_n\cdot\mathrm{Z}_m]_\mathrm{s}/[\mathrm{Ru^{III}}]_\mathrm{w}[\mathrm{SCN^-}]^n_\mathrm{w}[\mathrm{Z^+}]^m_\mathrm{w}, \qquad (3)$$

and is rewritten as

$$\log D = \log K_\mathrm{ex} + n\log[\mathrm{SCN^-}]_\mathrm{w} + m\log[\mathrm{Z^+}]_\mathrm{w}. \qquad (4)$$

When the concentration of thiocyanate was sufficiently

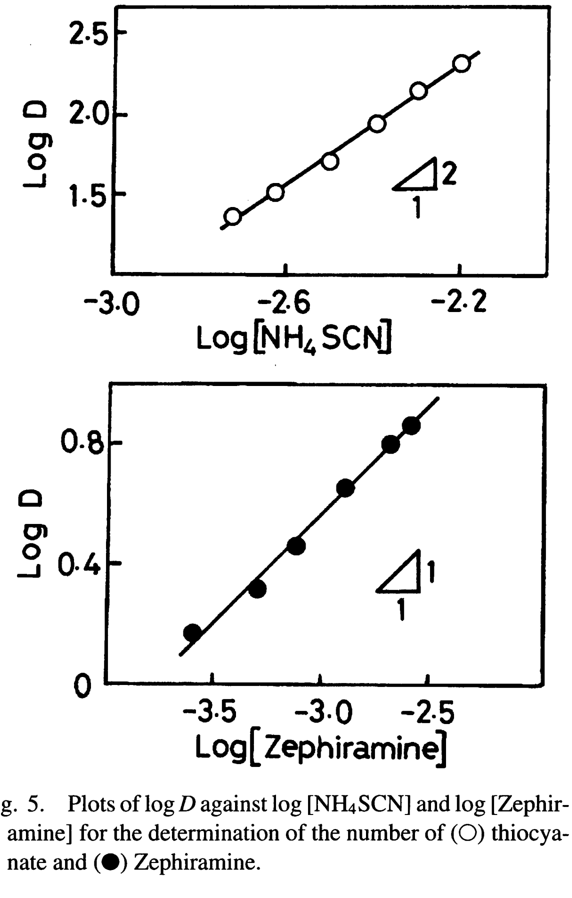

Fig. 5. Plots of log D against log [NH_4SCN] and log [Zephiramine] for the determination of the number of (○) thiocyanate and (●) Zephiramine.

large compared to the metal concentration, the value of $\log[\mathrm{SCN}^-]_\mathrm{w}$ was regarded as a constant. The value of m was obtained from the slope of a plot of $\log D$ vs. $\log[\mathrm{Z}^+]$. The value of n was obtained in the same manner (Fig. 5). The values of n and m were 2 and 1, respectively.

Several structures have been suggested for the ruthenium(III) complexes;[20] i.e., cationic complexes, such as $[\mathrm{Ru(SCN)}]^{2+}$, and an anionic complex $[\mathrm{Ru(SCN)_6}]^{3-}$ adsorbed on polyurethane foam[15] and in thiocyanate molten salt.[18] In the present study, since there were two thiocyanates and one Zephiramine, we performed the ion-exchange experiments in order to confirm the charge of the complex. The blue complex was retained by an anionic-exchange resin (Dowex 1X4), but was not adsorbed on a cationic-exchange resin (Dowex 50WX4). In consideration of the electric balance, the ion-pair, whose structure is $[\mathrm{RuX_2(SCN)_2}]^-\cdot\mathrm{Z}^+$ was extracted into the surfactant phase. Considering the stability constant of the chloro complex of ruthenium(III),[20,21] X may be Cl^- in an aqueous solution of hydrochloric acid.

It is interesting that a stable and sensitive ion-pair was characteristically obtained with Zephiramine in the surfactant phase. The concentration by the volume effect and the large absorptivity of this method should be available for the sensitive determination of a micro amount of ruthenium.

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