Synergism in the Extraction of Ru(III) by a Tri-\(n\)-Octylamine–Di-\(n\)-Hexylsulfide System

Tomoya SUZUKI*, Takeshi OGATA, Mikiya Tanaka and Hirokazu NARITA

Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 16-1, Onogawa, Tsukuba, Ibaraki 305-8569, Japan

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We have found that a mixture of tri-\(n\)-octylamine (TOA) and di-\(n\)-hexylsulfide (DHS) in CHCl\(_3\) displays synergistic extraction of Ru(III) from aqueous HCl. Approximately 55% of Ru(III) was extracted by a 0.25 M TOA–0.25 M DHS system, whereas a single extractant, 0.25 M TOA or 0.25 M DHS, achieves hardly any Ru(III) extraction. Job plots of the extraction of Ru(III) from 5 M HCl aqueous solution indicate formation of a complex with 1:2:1 Ru(III):TOA:DHS stoichiometry. UV-Vis absorption spectra of the extracted Ru(III) complexes suggest that a DHS molecule is bound to the Ru(III) ion in the inner coordination sphere.

1. Introduction

In general, the extraction of trivalent platinum group metal (PGM) ions such as Rh(III) and Ru(III) from HCl solutions is more difficult than of their divalent or tetravalent PGM equivalents. The reason for this is that trivalent ions are kinetically inert and their complex anions in HCl solutions, [MCl\(_4\)(H\(_2\)O)\(_2\)]\(^-\), [MCl\(_5\)(H\(_2\)O)]\(^2-\), and [MCl\(_6\)]\(^3-\), have lower affinities than their divalent and tetravalent counterparts for hydrophobic organic cations like protonated extractants [1,2]. In most refining processes for PGMs therefore, ruthenium is recovered by distillation after oxidation to RuO\(_4\), which is so toxic that specific, careful handling operations needed [3].

We have been investigating the extraction of trivalent PGM ions from HCl solutions by facilitating ion-pair reactions. In studies of rhodium extraction (as Rh(III)) we have found that the recovery efficiency is greatly enhanced when amide-containing tertiary amine (ACTA) compounds are used as extractants [4,5] or when a mixture of tri-\(n\)-octylamine (TOA) and a thioether-type extractant is used [6]. Recently, we have demonstrated that 2-ethylhexyl-bis\((N,N\)-di-2-ethylhexyl-ethylamide)amine (EHBAA), which is an ACTA derivative, displays high extraction efficiency with respect to Ru(III) in HCl solution. An investigation has been carried out on the speciation of Ru(III) in the aqueous phase at various HCl concentrations and in the organic phase containing EHBAA. The species formed in the organic phase is an ion-pair-type assembly in which two protonated EHBAA molecules are associated with a single [RuCl\(_3\)(H\(_2\)O)]\(^2-\) ion [7].

This paper records investigations of the synergistic extraction of Ru(III) from HCl solutions using a mixture of TOA and di-\(n\)-hexylsulfide (DHS) in CHCl\(_3\). We discuss the mechanism of extraction and the origins of the synergism, making comparisons with work reported on the extraction of Rh(III) with TOA–DHS [6].
2. Experimental

2.1 Reagents
TOA and DHS were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The extractants, not subjected to further purification, were dissolved in CHCl₃. All solutions containing Ru(III) were prepared by dissolving RuCl₃ dihydrate (Soekawa Chemicals Inc., Sendai, Japan) in aqueous HCl. The Ru(III) solutions were kept in the dark at room temperature for two weeks to allow them to achieve equilibrium [7]. All chemicals were of reagent grade.

2.2 Extraction procedure
Solutions of the extractant(s) (TOA and/or DHS) in CHCl₃ and an aqueous HCl solution containing no Ru(III) were mixed in 10-mL glass tubes with a vertical shaker (Yayoi, Japan) (amplitude: 100 mm; frequency: 200 strokes/min). After centrifugation, 1 mL of the pre-equilibrated organic phase and an equal volume of the aged HCl solution of Ru(III) were shaken and subsequently centrifuged. The metal concentrations in the aqueous solutions were determined using an inductively-coupled plasma atomic emission spectrometer (Ultima2, Horiba, Ltd.). Values for the extraction percentage ($E\%$) and the distribution ratio ($D$) were calculated on the basis of the mass balance of ruthenium in the aqueous phases; the Ru(III) extracted in the TOA–DHS phase was scarcely back-extracted into an aqueous solution using the procedure reported in studies of the Rh(III)–TOA–DHS system [6].

2.3 UV-Vis spectroscopy
Solutions prepared by the solvent extraction experiments were transferred to quartz cells with optical path lengths of 0.20 or 1.0 cm. Absorption spectra were collected using a UV-Vis spectrometer (UV-2550PC, Shimadzu Corporation).

3. Results and Discussion

3.1 Equilibrium time
Figure 1 shows the Ru(III) $E\%$ values in the 0.25 M TOA–0.25 M DHS system as a function of the contact time. Ru-uptake reaches a plateau after 6 h. Consequently all extraction experiments conducted subsequently were run for 6 h.

3.2 Dependence of Ru-loading on HCl concentration
The variations of Ru(III) uptake by the TOA-DHS mixture with changes of HCl concentration are compared with those for the single extractants in Figure 2. As we have already reported [7], TOA hardly extracts any Ru(III) in the HCl concentration range investigated. DHS alone also proved ineffective in Ru(III)-extraction, even though its thioether moiety, an electron-donating group, displays the characteristics of a soft base and should show a strong coordination ability for the Ru(III) ion, characterized by its soft acidity [8,9]. In contrast, the TOA–DHS mixture gives much higher Ru $E\%$ values which greatly exceed the sum of the $E\%$ values for TOA and DHS alone, indicating a synergetic effect. The $E\%$ values increase with HCl concentration, up to a value of 5 M after which they begin to decrease. This extraction profile mirrors by that obtained using 0.5 M EHBAA [7]; for this system we suggested that [RuCl₅(H₂O)]⁻ was extracted by two protonated EHBAA molecules. The extraction mechanism of the TOA–DHS system is discussed later in this article.
Figure 1. Relationship between the $E\%$ of Ru(III) shown by a 0.25 M TOA–0.25 M DHS solution in CHCl$_3$ and the contact time with an equal volume of 5 M HCl aqueous solution containing 1 mM Ru(III).

Figure 2. Variation of values for the $E\%$ of Ru(III) vs the aqueous HCl concentration in the aqueous phase after 6 h contacts with equal volumes of CHCl$_3$ solutions of: 0.5 M TOA (open circles), 0.5 M DHS (open triangles), 0.25 M TOA–0.25 M DHS (filled triangles), and 0.5 M TOA–0.5 M DHS (filled circles). The aqueous HCl solutions contained 1 mM Ru(III). The data for $E\%$ of Rh(III) in 0.5 M TOA–0.5 M DHS system (dashed line) and $E\%$ of Ru(III) in 0.5 M EHBAA system (solid line) are from refs. 6 and 7.

3.3 Effect of Ru(III) concentration on the extraction process

Figure 3 shows that the $D$ values are independent of ruthenium concentration. The observation that the $D$ values were constant implies that the Ru(III) complex extracted in the organic phase is mononuclear.
3.4 Job plots

The stoichiometry of the Ru(III) complex formed by the TOA–DHS mixture was determined by an analysis of the Job plots for the E% of Ru(III) at 5 M HCl. Figure 4 shows the E% values of Ru(III) as a function of the mole fraction of DHS in the TOA–DHS system at constant total molarity: [DHS] + [TOA] = 0.5 M. The maximum E% value was obtained when the value of the DHS mole fraction falls in the 0.30–0.35 range, suggesting that two molecules of TOA and one of DHS are involved in the extraction of a single Ru(III) ion from an aqueous 5 M HCl solution.
3.5 Proposed extraction mechanism

The abundance of \([\text{RuCl}_5(\text{H}_2\text{O})]^2^-\) in the aqueous phase is dependent on the HCl concentration [7] and mirrors the dependence on HCl concentration of the uptake of Ru(III) by a CHCl₃ solution of a TOA–DHS mixture (see Figure 2). This implies that the TOA–DHS system preferentially extracts \([\text{RuCl}_5(\text{H}_2\text{O})]^2^-\). After a TOA–DHS mixture in CHCl₃ is equilibrated with aqueous HCl, TOA molecules forms a 1:1 TOA:HCl assembly. The formation of these assemblies does not depend on the presence of DHS [6]. The two protonated TOA molecules that are required to neutralize the double negative charge of the pentachloridoruthenate, \([\text{RuCl}_5(\text{H}_2\text{O})]^2^-\), do not enter the inner coordination sphere of the Ru(III) ion.

The role of DHS in the synergistic extraction was investigated by UV-Vis absorption spectrometry (Figure 5). Intense absorption bands at 383 and 443 nm were characteristic of the Ru(III)-loaded TOA-DHS mixture in CHCl₃. These peaks were not observed in the spectra of the Ru(III) complex extracted with TOA (362 nm) or of the aqueous solutions of either \([\text{RuCl}_5(\text{H}_2\text{O})]^2^-\) (329 nm) or \([\text{RuCl}_6]^3^-\) (304 and 348 nm) [7]. Ru(III) complexes with sulfide donor ligands contain two bands (at 358–393 and 418–472 nm), which are assigned to a ligand-to-metal charge-transfer and a d–d transition, respectively [10-12]. Consequently, evidence suggests that a DHS molecule is bound to the Ru(III) ion in the extractions.

As mentioned above, a \([\text{RuCl}_5(\text{H}_2\text{O})]^2^-\) is likely to be the predominant species extracted from the aqueous phase. Displacement of the coordinated water molecule by DHS will reduce the energy required to transfer the Ru(III) ion to the water-immiscible phase; in other words, a synergism arises because hydrophobicity of the complex transferred organic phase is enhanced [13]. Accordingly, the following equilibrium best defines the extraction reaction:

\[
[\text{RuCl}_5(\text{H}_2\text{O})]^2^-_{\text{aq}} + 2(\text{TOA} \cdot \text{HCl})_{\text{org}} + \text{DHS}_{\text{org}} \rightleftharpoons [\text{RuCl}_5(\text{DHS})]\cdot(\text{TOA} \cdot \text{H})_2_{\text{org}} + 2\text{Cl}_{\text{aq}}^- + \text{H}_2\text{O} \quad (1)
\]

Figure 5. UV-Vis spectra (optical path length, 0.20 cm) of CHCl₃ solutions of 0.25 M TOA and 0.25 M DHS (solid lines) containing: 0 (green), 0.11 (red), 0.24 (purple), 0.36 (blue), and 0.51 mM (black) Ru(III). The dashed lines are the spectra (optical path length 1.00 cm) of CHCl₃ solutions of 0.5 M TOA containing: 0 (green) and 0.04 mM of Ru(III).
3.6 Comparison with the mechanism of extraction of Rh(III)

A previous study reported the extraction of Rh(III) by the TOA–DHS system [6]. For both Ru and Rh the $E\%$ values increased with increasing HCl concentration, reaching a maximum before decreasing. The $E\%$ values for maximum loading of Rh(III) and Ru(III) occur at different HCl concentrations. Speciation diagrams for Rh(III) and Ru(III) in aqueous acidic chloride solutions [7,14] indicate that for Rh(III), a pentachlorido di-anion $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ is the predominant species at lower HCl concentrations than is the case for the corresponding Ru(III) complex. This is consistent with the TOA–DHS mixture extracting the pentachloridoaquo dianions $[\text{MCl}_5(\text{H}_2\text{O})]^{2-}$ for both metals. Further structural and theoretical investigations are needed to clarify the rationale for this selectivity. In the context of the separation between Rh(III) and Ru(III), Ru(III) complexes are preferentially transferred into the organic phase at higher HCl concentration.

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