

## **Extraction and separation of iridium(IV) and rhodium(III) from hydrochloric acid media by a quaternary ammonium-based hydrophobic eutectic solvent**

V. Zakusilova,<sup>1,2</sup> G. Zante,<sup>1,3</sup> E.E. Tereshatov,<sup>2</sup> C.M. Folden III,<sup>2,4</sup> and M. Boltoeva<sup>1</sup>

<sup>1</sup>*Université de Strasbourg, CNRS, IPHC, UMR 7178, F-67000 Strasbourg, France*

<sup>2</sup>*Cyclotron Institute, Texas A&M University, College Station, Texas 77843*

<sup>3</sup>*ADEME, 20 Avenue du Grésillé, 49004 Angers Cédex 01, France*

<sup>4</sup>*Department of Chemistry, Texas A&M University, College Station, Texas 77843*

The main goal of green chemistry is to reduce the hazardous environmental impact of solvents used in chemical production, including extraction and separation of analytes [1]. Over the past twenty years, a new type of solvents called eutectic solvents were actively being developed. Alternative solvents should be more environmentally friendly, less toxic and non-flammable compared to conventional molecular solvents. Ideally, they should also be less expensive, easy to prepare and biodegradable. Moreover, eutectic solvents can be recycled owing to their low vapor pressure. For these reasons, they are also called “green solvents” [2].

To date, the majority of published investigations are devoted to the utilization of hydrophilic eutectic solvents. In contrast, hydrophobic eutectic solvents have attracted attention only recently due to their effective extraction of metal ions from aqueous solutions [3-5].

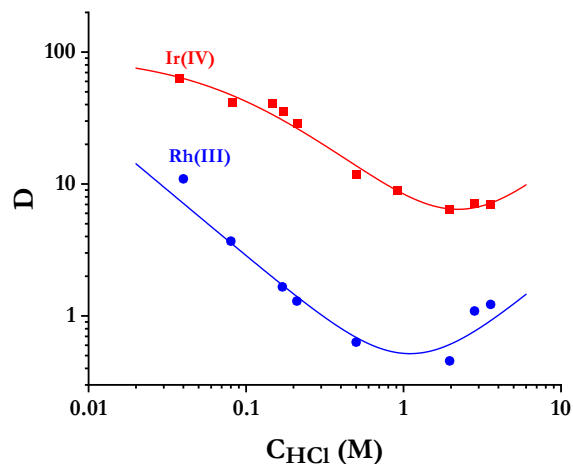
Currently, the demand for platinum group metals (PGMs) is increasing due to the shift in the global energy sector towards low-carbon-emission technologies and renewable energy sources [6]. In addition, mining of these metals and their application in a number of industries leads to significant pollution of the environment, endangering people’s health [7]. Thus, their recycling is crucial from both the ecological and economical points of view. The focus of our work is to find a greener way to extract two PGMs, namely iridium (Ir) and rhodium (Rh), from HCl solutions. These metals’ similar chemical behavior and the existence of multiple metallic species in chloride solutions make their separation a challenging task.

We studied the extraction performance of a hydrophobic eutectic solvent composed of a quaternary ammonium salt and a fatty acid, namely tetraheptylammonium chloride and decanoic acid (C10:0) in a 1:2 molar ratio; this ratio was chosen based on literature data [3]. This is the first time that this eutectic solvent has been used for extraction and separation of PGMs. The effects of the main experimental factors (HCl concentration and initial metal concentration in the aqueous phase) on the extraction behavior of Ir(IV) and Rh(III) have been investigated. Concentrations of metals in the aqueous phase before and after extraction were analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Solvent extraction trials were performed by mixing 0.1 g of the synthesized eutectic solvent with 1.5 mL of an aqueous phase (volume ratio of aqueous to organic phase,  $V_{aq}/V_{org} = 13.4$ ). This choice was made based on the significant extraction of Ir(IV) with a distribution ratio (D) value around 10 under such experimental conditions. In the described experiment the initial metal concentration for Ir(IV) was  $5.2 \times 10^{-4}$  M in 0.4 M HCl solution [initial metal concentrations for ultraviolet-visible (UV-Vis) analysis (discussed below) and acidity dependency test were different].

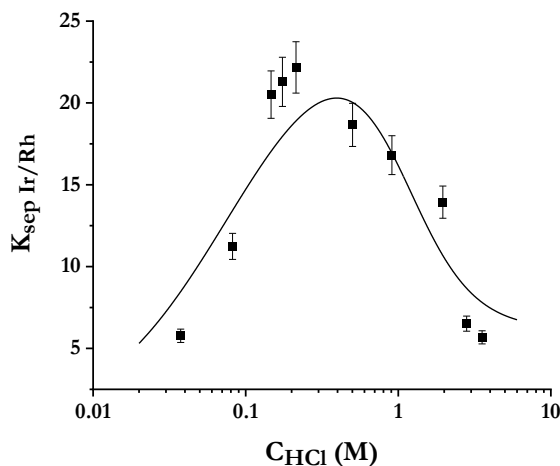
The extraction equilibrium for both metals is reached within 1 min of shaking. However, to simplify technical conditions of the performed experiments and minimize any discrepancies associated with short time of phase contact, in all solvent extraction experiments the shaking time was extended to 30 min.

The highest D values represented in Fig. 1 were obtained at 0.04 M HCl, reaching ~60 and ~10



**Fig. 1.** Distribution ratio variation for Ir(IV) and Rh(III) as a function of the initial HCl concentration in the aqueous phase.  $[\text{Ir}]_{\text{init, aq}} = 5.2 \times 10^{-5}$  M,  $[\text{Rh}]_{\text{init, aq}} = 9.7 \times 10^{-5}$  M,  $V_{\text{aq}}/V_{\text{org}} = 13.4$ . The lines are drawn to guide the eye.

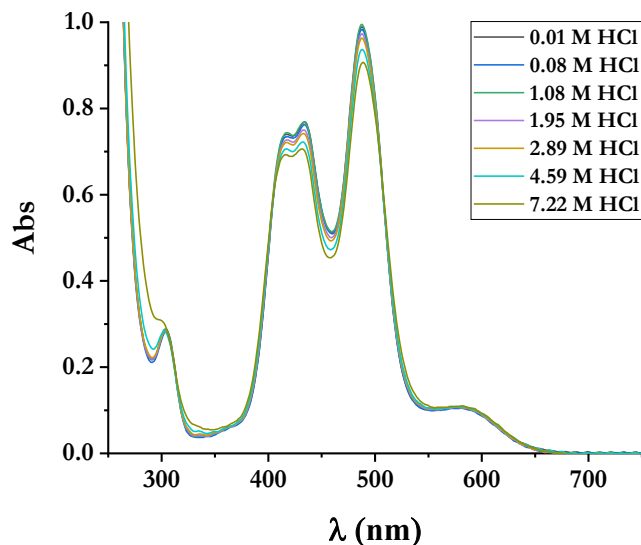
for Ir(IV) and Rh(III), respectively. High D values for Ir(IV) and low D values for Rh(III) indicate that the preceding eutectic solvent is efficient for Ir(IV)/Rh(III) separation. The highest Ir(IV) and Rh(III)



**Fig. 2** Separation factor of Ir(IV) and Rh(III) as a function of the initial HCl concentration in the aqueous phase.  $[\text{Ir}]_{\text{init, aq}} = 5.2 \times 10^{-5}$  M,  $[\text{Rh}]_{\text{init, aq}} = 9.7 \times 10^{-5}$  M,  $V_{\text{aq}}/V_{\text{org}} = 13.4$ . The line is drawn to guide the eye.

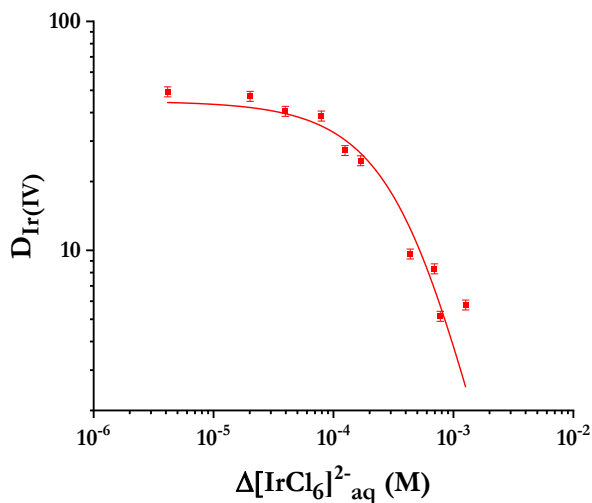
separation factor  $K_{\text{sep}}$  (which is a ratio of corresponding D values) at a level of ~20 was obtained at ~0.4 M HCl as shown in Fig. 2.

Results of UV-Vis spectroscopy displayed in Fig. 3 provide insight on the Ir(IV) speciation in HCl solutions. Observation of distinct characteristic peaks for  $[\text{IrCl}_6]^{2-}$  complexes at 433 nm and 488 nm leads to the conclusion that the major extracted species is a doubly charged complex  $[\text{IrCl}_6]^{2-}$  in the entire HCl concentration range.



**Fig. 3.** Selected experimental UV-Vis absorption spectra of  $[\text{IrCl}_6]^{2-}$  complexes at different HCl concentrations.  $[\text{IrCl}_6]^{2-} = 2.6 \cdot 10^{-4}$  M.

The impact of the metal loading on the extraction yield is shown in Fig. 4. The results indicate that while the initial Ir(IV) concentration in the aqueous phase increases, D values decrease. This is most



**Fig. 4.** Distribution ratio variation for Ir(IV) as a function of complex concentration difference in the aqueous phase before and after extraction.

likely due to the limited capacity of the organic phase. The most efficient extraction ( $D_{Ir} \sim 50$ ) was observed for  $5.2 \times 10^{-6}$  M Ir(IV) solution at 0.12 M HCl.

We developed a mathematical model to fit the experimental data illustrated in Fig. 4. This model is based on the comparison of two possible mechanisms of Ir(IV) extraction: ion pair formation (the corresponding extraction constant is  $K_{ip}$ ) and ion exchange (the corresponding extraction constant is  $K_{ie}$ ).

A high value of  $R^2 = 0.864$  shows a good quality of the fit and confirms that the major extracted species is a doubly charged complex  $[\text{IrCl}_6]^{2-}$ . Results of this independent method are in good agreement with those obtained by UV-Vis analysis.

The comparison of the extraction constants ( $K_{ip}$  and  $K_{ie}$ ) from the developed mathematical model testifies that the predominant mechanism of extraction is ion pair formation between  $[\text{IrCl}_6]^{2-}$  and  $[\text{N}_{7777}]^+$ , while ion exchange is a negligible process:

$K_{ip} = (1.1 \pm 0.4) \times 10^8$  and  $K_{ie} = (1.8 \pm 0.4) \times 10^{-5}$ . The mathematical model also allowed us to estimate the conditional constant of the eutectic solubility product:  $K_{sp} = (3.6 \pm 0.9) \times 10^{-7}$ .

A publication based on these results is in the late stages of preparation.

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