

The Solvent Extraction Performance of *N,N'*-Dimethyl-*N,N'*-Dibutylmalonamide Towards Platinum and Palladium in Chloride Media

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The solvent extraction performance of *N,N'*-dimethyl-*N,N'*-dibutylmalonamide (DMDBMA) in 1,2-dichloroethane (1,2-DCE) towards platinum(IV) and palladium(II) in hydrochloric acid media was systematically evaluated. Pt(IV) extraction (%E) increases with the HCl concentration in the aqueous phases, being always higher than 72%, whereas Pd(II) extraction decreases from 65% at 1 M HCl to 22% at 8 M HCl. Several stripping agents for the two metals were tested: Pt(IV) is successfully recovered by a 1 M sodium thiosulfate solution, whereas the best result for Pd(II) was achieved with 0.1 M thiourea in 1 M HCl. The loading capacity of DMDBMA for Pt(IV) is high, and data obtained from successive extraction-stripping cycles suggest a good DMDBMA stability pattern. Attempts to replace 1,2-DCE by more environmentally-friendly diluents showed, in general, worse %E for Pt(IV). The dependence of Pt(IV) distribution coefficients on DMDBMA and chloride ion concentrations, as well as on acidity, are the basis of a proposal for the composition of Pt(IV) extracted species.

Keywords platinum; palladium; *N,N'*-tetrasubstituted malonamide derivative; solvent extraction; hydrochloric acid

INTRODUCTION

Platinum-group metals (PGMs) are rather valuable and considered critical raw materials (1), mainly due to their scarcity in the Earth's crust, and also to their difficult replacement in most applications, such as fuel cells, electronics, and catalysis

(for example, in automotive catalytic converters, oil refining, and fine chemistry industries) (2). To allow the sustainable continuous supply for actual and emerging applications, recycling of PGMs-containing wastes is crucial, contributing to their natural resources preservation as well, together with more effective environmental protection and economic revenues.

The hydrometallurgical recovery of PGMs is usually carried out in aqueous chloride phases, as these media dissolve PGMs well and allow high recovery performances (3), especially in the refining steps. Hence, solvent extraction (SX) is one of the most successful unit operations used for separating PGMs from chloride leach solutions, showing remarkable efficiency and selectivity patterns. Since the wastes containing PGMs are nowadays increasingly complex (4), dedicated research in the hydrometallurgical field is plenty justified, either by adapting current technologies or developing new ones.

For a convenient design of a SX pathway, knowledge about PGMs speciation in concentrated chloride media is advisable. Accordingly, some of the most comprehensive articles about PGMs speciation also focus on the development of SX processes. For Pt(IV), it is known that $[\text{PtCl}_6]^{2-}$ is the predominating Pt(IV) species (5,6) from 0.1 M HCl onwards (5), whereas $[\text{PdCl}_4]^{2-}$ is the Pd(II) main species (5–8) at 1 M and higher chloride concentrations ($\geq 95\%$) (5,8).

The most common organic extractants used in industrial SX to recover Pt(IV) and Pd(II) usually allow the direct extraction of the respective chlorocomplexes through ion-pairs, thus involving the protonation of the organic compound. Amines and ammonium salts are the typical extractants involved (6). For Pd(II), neutral organophosphorus compounds (9) and some acidic/chelating extractants have proved to be useful,

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