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Palladium extraction by malonamides

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Recycling of valuable metals appears as solution of growing interest for a sustainable supply strategy nowadays. Palladium (Pd), along with other platinum group metals (PGM) and rare earth elements (REEs), represents one of the crucial issues in recovery processes. Malonamides are neutral amphiphilic molecules which have proved their potency for the extraction of f-elements and the recovery of minor actinides. Also, these compounds were demonstrated to be suitable extractants for the recovery of Pd(II) from hydrochloric media. Nitric media were thoroughly studied in frame of nuclear fuel treatment towards lanthanide-actinide separation. However, valuation of nitric effluents containing REEs and PGM is rarely envisioned.

Within this framework, our purpose is to study liquid/liquid (L/L) extraction towards Pd recovery in nitric media, and especially to focus on the molecular level and understand the key physicochemical parameters necessary for an effective separation.

Various experimental parameters such as equilibration time, pH, extractant and nitrate concentrations were investigated in detail. Similarities and differences between palladium and lanthanides were evidenced: Pd, present at +II oxidation state, and lanthanides, each at +III oxidation state, can be both efficiently extracted but in different conditions. A judicious choice of solvent and aqueous phase composition prevents formation of a Pd-rich solid third phase.

Mechanistic studies involved complete analysis of the organic phases, including chemical speciation at the molecular level (coordination chemistry with NMR, IR, XRD and XPS), and supramolecular ordering characterization (with SAXS, DLS and NMR). Pd(II) complexes were identified and characterized. Emphasis was set on the study of the apparent discrepancy between molecular complexes (1:1 Pd:malonamide) and macroscopic behavior (slope 2 for malonamide).

Keywords: palladium, lanthanides, L/L extraction, speciation, malonamides.

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