

Separation of cobalt and nickel with a thermomorphic ionic- liquid-based aqueous biphasic system

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Electronic Supplementary information

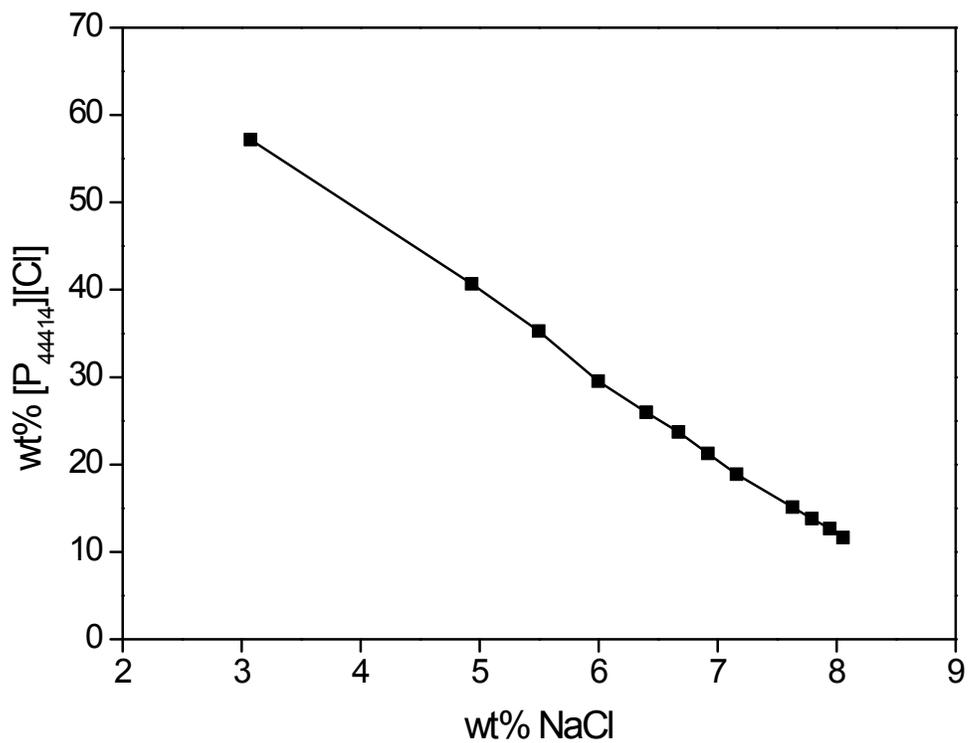


Figure S1: Orthogonal ternary phase diagram of the [P₄₄₄₁₄][Cl]-NaCl-H₂O system at room temperature (22 °C).

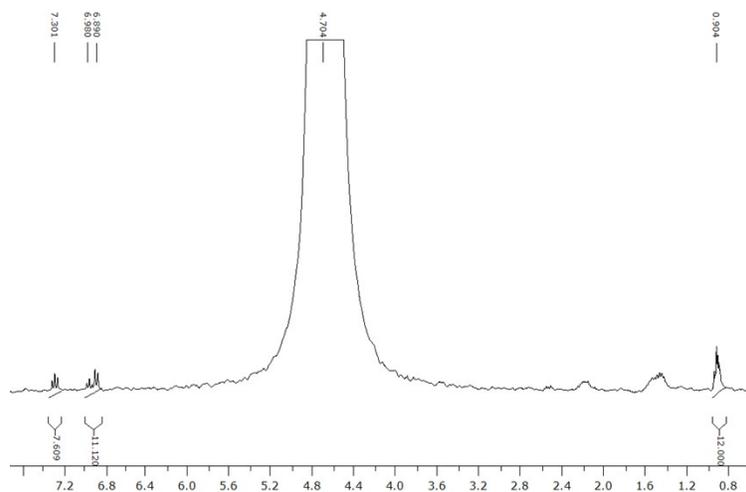


Figure S2: Quantitative ¹H NMR spectrum: sample of the aqueous phase (0.419 g) of a [P₄₄₄₁₄][Cl]-NaCl-H₂O ABS extraction mixture containing 40 wt% [P₄₄₄₁₄][Cl], 5.4 wt% NaCl, [Co(II)] = 1 g·kg⁻¹ and [Ni(II)] = 1 g·kg⁻¹, mixed with 0.062 g phenol as internal standard and diluted with D₂O to 600 mg.

Experimental section

Chemicals

Tributylphosphine (97%), 1-chlorotetradecane (98%), sodium chloride, cobalt(II) chloride (anhydrous) and nickel(II) chloride (anhydrous) were obtained from Sigma Aldrich (Diegem, Belgium). Tributyl(tetradecyl)phosphonium chloride was both synthesized (*vide infra*) and purchased from IoLiTec. Heptane (99+%) and the gallium nitrate 1000 mg·L⁻¹ standard solution were obtained from Chem-Lab (Zedelgem, Belgium). Phenol (99%) was purchased from Acros Organics (Geel, Belgium). All products were used as received, without further purification.

Experimental equipment

Cobalt and nickel concentrations were measured on a Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer. Sample preparation was performed by adding 100 µL of gallium nitrate 1000 mg·L⁻¹ standard solution to an aliquot (mostly 100 µL) of the solution to be measured and diluting it with 1 mL of Milli-Q water. Next, a small droplet (5 µL) was placed on a quartz sample carrier, pretreated with silicone solution in isopropanol (SERVA) and dried for 30 min before the measurement. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ¹H, 75 MHz for ¹³C). ³¹P NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 162 MHz. The water content of the IL-rich phase was determined with Karl Fischer titration (Mettler-Toledo). Kinematic viscosities were determined using a type IIc and a type III micro-Ubbelohde viscometer (Lauda), densities were measured with a 5 mL pycnometer. The dynamic viscosity was calculated by multiplying the kinematic viscosity with the density.

Synthesis of tributyl(tetradecyl)phosphonium chloride

The ionic liquid tributyl(tetradecyl)phosphonium chloride, [P₄₄₄₁₄][Cl], was synthesized by reacting tributylphosphine with 1-chlorotetradecane in equimolar amounts under reflux at 140 °C. Purification was performed by washing with heptane under reflux at 120 °C. The remaining heptane was removed *in vacuo*. The structure and purity of the compound were confirmed with ¹H NMR, ¹³C NMR and ³¹P NMR.

Cloud point temperature and composition

Determination of the cloud point composition was performed via cloud point titration. A solution of NaCl in water was added dropwise to a solution of [P₄₄₄₁₄][Cl] in water under constant stirring until the mixture became cloudy. Using the mass of the initial [P₄₄₄₁₄][Cl] solution and the mass of the added NaCl solution, the cloud point composition was calculated. The cloud point temperature was determined by heating or cooling the biphasic ABS mixture under constant stirring until a homogeneous mixture was obtained. Next, the mixture was slowly cooled or heated, respectively, and the temperature at which the mixture became cloudy was visually detected. Cloud point temperature measurements were performed in triplicate.

Quantitative ¹H NMR

Quantitative ¹H NMR was performed by dissolving an aliquot of the aqueous phase of the [P₄₄₄₁₄][Cl]–NaCl–H₂O mixture in deuterated water and adding a small amount of 1,4-dioxane or phenol as internal standard. The concentration of [P₄₄₄₁₄][Cl] was calculated using the relative integration of the peaks in the ¹H NMR spectra.

Extraction of Co(II) and Ni(II)

Extractions were performed by weighing a certain amount of [P₄₄₄₁₄][Cl], NaCl, CoCl₂, NiCl₂, depending on the required final composition, and diluted with ultrapure water (Milli-Q) to a final mass of 5 g was obtained. The [P₄₄₄₁₄][Cl] was always equal to 40 wt% and the metal ion concentrations over the entire mixture were 1 g·kg⁻¹ for both metals. The mixtures were shaken for 30 min at room temperature to obtain extraction equilibrium. Next, the phases were separated and analyzed with total reflection X-ray fluorescence (TXRF) spectroscopy to determine the distribution ratio D and separation factor α_{Ni}^{Co} , as defined by following equations:

$$D = \frac{c_{IL}}{c_{aq}} \quad (1)$$

$$\alpha_{Ni}^{Co} = \frac{D_{Co}}{D_{Ni}} \quad (2)$$

where c_{aq} and c_{IL} are the metal concentrations in the aqueous and IL-rich phase, respectively.