



Short communication

Evaluation of tri-*n*-octylamine oxide as phenol extractant in a solvent impregnated resin

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ABSTRACT

Tri-*n*-octylamine oxide (TOAO) is evaluated as alternative to the state-of-the-art phenol extractants tri-*n*-octylphosphine oxide (TOPO) and Cyanex 923. Liquid–liquid equilibrium experiments show that TOAO in 1,3-dimethylnaphthalene achieves higher phenol distribution coefficients in an extractant concentration range of 0.1–1.25 mol L⁻¹ than respective TOPO/1,3-dimethylnaphthalene or Cyanex 923/1,3-dimethylnaphthalene solutions. In a solvent impregnated resin (SIR) application, the SIRs impregnated with TOAO/1,3-dimethylnaphthalene have a higher phenol capacity than the SIRs impregnated with Cyanex 923/1,3-dimethylnaphthalene. Regeneration of the SIRs with alkaline solution of pH 13 shows that both SIRs maintain a constant phenol capacity during at least seven cycles. Based on these observations TOAO can be considered as a better alternative to Cyanex 923.

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1. Introduction

Phenol is a toxic and environmentally hazardous component found in wastewaters of, e.g. coking plants or phenolic resin production, and thus needs to be removed from these streams [1]. The most suitable process for phenol removal from aqueous effluents within a concentration range from 50 ppm [2] up to 6000 ppm [1] is liquid–liquid extraction, which has high selectivity and high solute capacity. In order to avoid possible drawbacks, such as persistent emulsification and the leaching of the extractant, a solvent impregnated resin (SIR) can be applied [3]. A SIR consists of a macroporous polymer support, which is impregnated with a liquid extractant. The immobilization of the extractant inside the pores by, e.g. physical sorption, prevents emulsification and extractant leaching [4]. SIRs have already been applied for heavy metal recovery and removal of organic substances, such as aldehydes [5] and organic acids [6] from aqueous media. In case of phenol extraction, tri-*n*-octylphosphine oxide (TOPO) and the organophosphorous blend Cyanex 923, see Fig. 1, are very effective phenol extractants [7]. Although alkyl amine oxides are suggested to be even more effective for phenol removal than organophosphorous components [8], alkyl amine oxides have not yet been studied in a SIR application.

In this study, tri-*n*-octylamine oxide (TOAO) is compared with the state-of-the-art phenol extractants TOPO and Cyanex 923 in

liquid–liquid equilibrium experiments and SIR experiments. TOAO has to be synthesized, as it is not commercially available. TOPO is not used for SIR impregnation, as it is comparable to Cyanex 923 and Cyanex 923 is more convenient to use [7]. The regenerability of the prepared SIRs is also studied.

2. Materials and methods

2.1. Materials

The materials used for amine oxide synthesis are ethanol (99.9%, Merck, Germany), *n*-hexane (98%, Fluka, Germany), hydrogen peroxide (35%, Fluka, Germany), magnesium sulfate (98%, Fluka, Germany), *n*-pentane (99%, Riedel-de Haën, Germany), tri-*n*-octylamine (98%, Fluka, Japan). Demineralized water is obtained from a Millipore Milli-Q-plus 185 system. The substances used for liquid–liquid equilibrium experiments are phenol (99%, Merck, Germany), tri-*n*-octylamine oxide, which is synthesized in-house, Cyanex 923 (mixture of tertiary octyl and hexyl phosphine oxides, 93%, Cytec Canada Inc.), tri-*n*-octylphosphine oxide (93%, TOPO, Cytec Canada Inc.) and the diluents toluene (99%, Fluka, Switzerland) and 1,3-dimethylnaphthalene (96%, Sigma–Aldrich, Germany). Regeneration experiments are done with barium hydroxide (98%, Fluka, Italy) dissolved in demineralized water (pH 13). Above listed substances are all utilized without further treatment.

For the preparation of the SIR particles, acetone ($\geq 99.5\%$, Sigma–Aldrich, Germany), *n*-hexane (98%, Fluka, Germany) and

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Nomenclature

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$c_0^{\text{aq}}(\text{PhOH})$	initial phenol concentration in aqueous phase, mol L^{-1}
$c_{\text{eq}}^{\text{aq}}(\text{PhOH})$	equilibrium phenol concentration in aqueous phase, mol L^{-1}
c_0^{E}	initial extractant concentration in organic phase, mol L^{-1}
K_D	overall distribution coefficient, $\text{mol L}^{-1} (\text{mol L}^{-1})^{-1}$
p_{vap}	vapor pressure, Pa
w.s.	water solubility, mg L^{-1}

toluene (99%, Fluka, Switzerland) are used as solvents. The polymeric resin particles used for impregnation are macroporous polypropylene particles (MPP) (VWS MPP Systems, Netherlands). The MPP particles are sieved, then washed with each toluene, acetone and *n*-hexane, and left in a rotary evaporator (BÜCHI Rotavapor R-200, BÜCHI Labortechnik AG, Switzerland) equipped with a heating bath (BÜCHI Heating Bath B-490, BÜCHI Labortechnik AG, Switzerland) for 12 h at vacuum and 70 °C to remove solvent residues.

The characteristics of the MPP particles used are given in [4].

2.2. Synthesis of tri-*n*-octylamine oxide (TOAO)

The synthesis which is used in this work is an altered version of the oxidation of tri-*n*-octylamine with hydrogen peroxide in ethanol as performed by Ejaz [9]. In order to increase conversion, the reaction time is prolonged from 4 days [9] to 6 days and the molar ratio between tri-*n*-octylamine and hydrogen peroxide is increased from 1:2 [9] to 1:9.

To a solution of approximately 17 g (approximately 0.05 mol) tri-*n*-octylamine and approximately 15 g (approximately 0.44 mol) hydrogen peroxide 150 ml ethanol are added. The liquid system is magnetically stirred at 260 rpm in an open flask for 6 days at ambient temperature (20 °C). After stirring, 750 mL demineralized iced water is added. A two-phase system is formed. This two-phase system consists of an aqueous phase containing water and remnant reactants and an organic phase containing TOAO and remnant reactants. The phases are separated in a separating funnel. The aqueous phase is washed three times with 100 mL *n*-hexane in a separating funnel in order to recover residual TOAO from the aqueous phase. After this, the aqueous phase is discarded. The resulting 300 mL *n*-hexane containing the recovered TOAO is added to the organic phase. This organic phase is washed three times with 100 mL demineralized water to remove ethanol and remaining starting materials. The residual water in the organic phase is

removed with an excess amount of magnesium sulfate. Magnesium sulfate is subsequently removed by vacuum filtration. *n*-Hexane is then evaporated from the organic phase in a rotary evaporator (BÜCHI Rotavapor R-200, BÜCHI Labortechnik AG, Switzerland) equipped with a heating bath (BÜCHI Heating Bath B-490, BÜCHI Labortechnik AG, Switzerland) at vacuum and 60 °C. The resulting white crystals are purified by recrystallization in *n*-pentane. *n*-Pentane is boiled and added to the crystals in a ratio of 10:1, v/w. Initially, the previously obtained white crystals completely dissolve. Cooling of this solution at ambient temperature (20 °C) without disturbance causes the precipitation of white crystals, which are separated from the solution using filter papers (Whatman 595, 150 mm) at atmospheric conditions. The crystals are air dried for at least 24 h. The prepared TOAO crystals are analyzed with Nuclear Magnetic Resonance spectroscopy (NMR) conducted in a Varian Mercury Vx 400 MHz NMR-spectrometer to determine successful conversion. Deuterated chloroform (CHCl_3) ($\geq 99.96\%$, Aldrich, USA) is used as a solvent. The proton NMR analysis shows a shift of the peaks for the hydrogen atoms of the carbon directly adjacent to the functional amine/amine oxide group (C1) of 3.08 ppm (6H, t). The hydrogen atoms attached to the next carbon (C2) show a peak shift of 1.70 ppm (6H, m). This proves that the synthesis is performed successfully. The purity of the synthesized TOAO is approximately 94%. The error of the NMR analysis is approximately 10%. Additionally, the thermal stability of TOAO is determined with thermogravimetric analysis (Netzsch TG209 F1 with an AC Manager autosampler) under nitrogen atmosphere. The decrease of sample weight is measured over a temperature range of 20–250 °C at a temperature increase rate of 5 °C per minute. With the performed measurements the thermal stability threshold of 125 °C reported for TOAO in literature [9] is confirmed, which is considered as additional proof that the synthesis of TOAO is successful.

2.3. Experimental determination of K_D with LLE experiments

The liquid–liquid equilibrium extraction setup consists of magnetically stirred, temperature controlled glass flasks. With this setup the influence of the extractant concentration on the overall phenol distribution coefficient between the organic extractant phase and the aqueous phase is determined. The ratio between organic and aqueous phase is 1:10. The aqueous phase consists of 40 g demineralized water presaturated with the extractant solution. The aqueous phase is spiked with phenol to give a phenol concentration $c_0^{\text{aq}}(\text{PhOH})$ of 1 g kg^{-1} (approximately 0.01 mol L^{-1}). The organic extractant phase consists of 4 g of extractant solution, which consists of extractant and diluent. The extractant concentrations of the extractant solutions range up to 1.25 mol L^{-1} . The extractants used are tri-*n*-octylamine oxide (TOAO), tri-*n*-octylphosphine oxide (TOPO) and Cyanex 923. 1,3-Dimethylnaphthalene and toluene are separately used as diluents. 1,3-Dimethylnaphthalene

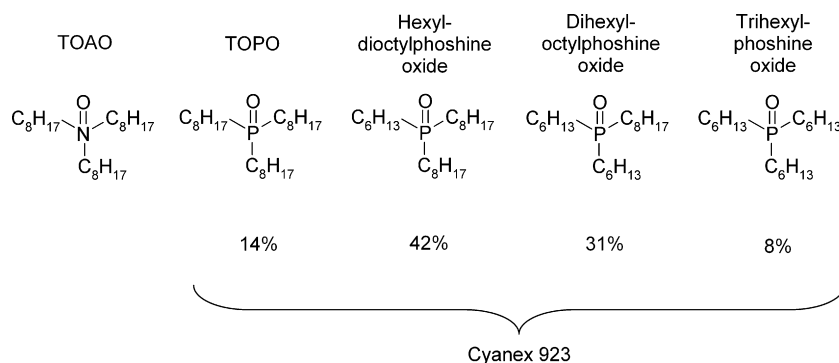


Fig. 1. Chemical structures of tri-*n*-octylamine oxide (TOAO), tri-*n*-octylphosphine oxide (TOPO) and Cyanex 923.

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