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Separation of cobalt(II) from nickel(II) by a hybrid liquid membrane–electrodialysis process using anion exchange carriers

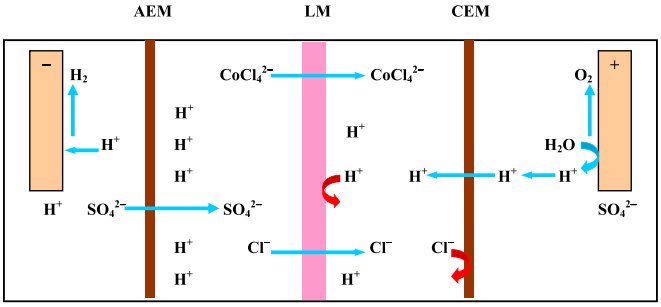
T.Zh. Sadyrbaeva

Riga Technical University, Institute of Inorganic Chemistry, Miera str. 34, Salaspils, LV-2169, Latvia

HIGHLIGHTS

- Galvanostatic electrodialysis was combined with carrier-facilitated transport.
- Selective transport of Co(II) from HCl solutions containing Ni(II) was studied.
- The Co(II) flux depends on the current density, HCl and Co(II) concentration.
- The separation factor rises as the Co(II) or Ni(II) initial concentration increases.
- A possibility of Co(II) transfer into solutions of HCl, H_2SO_4, HNO_3, $HClO_4$ was shown.

GRAPHICAL ABSTRACT



AEM: anion exchange membrane **LM:** liquid membrane **CEM**: cation exchange membrane

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ABSTRACT

Cobalt and nickel are widely used in various branches of industry, are usually present together in industrial and waste solutions and have similar physical and chemical properties; therefore, the separation of the metals is an important practical problem. A hybrid process based on the bulk liquid membrane is proposed as a novel method for the selective separation of cobalt(II) from nickel(II). The process includes the transport of cobalt(II) anionic chlorocomplexes from 3 to 6 mol/L HCl solutions through the liquid membranes containing tri-n-octylamine or trialkylbenzylammonium chloride in 1,2-dichloroethane during galvanostatic electrodialysis. A possibility of cobalt(II) transfer into dilute solutions of sulfuric, hydrochloric, nitric and perchloric acids accompanied by an effective separation from nickel(II) is demonstrated. Effects of the main electrodialysis parameters as well as of the composition of the liquid membranes, feed and strip aqueous solutions on the rate and selectivity of the cobalt(II) transport are studied, and optimum conditions are determined. It is shown that the rate of cobalt(II) transport increases with the increase in current density, hydrochloric acid and cobalt(II) initial concentration in the feed solution. The selectivity of the metal separation increases as the cobalt(II) or nickel(II) concentration in the initial mixture increases.

1. Introduction

Cobalt and nickel are among the most important nonferrous metals. Cobalt- and nickel-based alloys are used for their corrosion, magnetic and wear-resistant properties in stainless steels, electronics, aircraft engines, gas turbines, permanent magnets, coinage and medicine [1]. Cobalt and nickel compounds are used in rechargeable batteries, in electroplating and as industrial catalysts. Cobalt gives a blue color to glass, ceramics, paints and varnishes. Cobalt and nickel also play an important role in biology; cobalt is a component of vitamin B_{12}. Cobalt and nickel are widely used in various branches of industry, are usually

E-mail address: sadyrbaeva@hotmail.com.

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present together in industrial and waste solutions and have similar physical and chemical properties; therefore, the separation of the metals is an important practical problem. Classical chemical methods, such as precipitation, oxidation and crystallization are not effective for the separation of cobalt(II) from nickel(II) ions from dilute solutions [2]. The separation of cobalt(II) from nickel(II) can be based on the different stability of anionic chloride complexes of these metals. Nickel(II) forms only cationic complexes in hydrochloric solutions, whereas cobalt(II) forms anionic complexes $CoCl_4^{2-}$ in the presence of excess chloride ions, so the metals can be separated by solvent extraction with anion exchange extractants, such as amines and quaternary ammonium salts [3].

The liquid membrane technology has great potential for the removal of heavy metals from aqueous dilute solutions. The liquid membrane is a layer of an organic solvent separating two aqueous solutions. The main advantages of the liquid membranes, if compared with the traditional solvent extraction, are the relatively small volume of the organic phase, simultaneous extraction and back-extraction within a single technological stage, higher extraction degrees of target compounds from dilute solutions, more effective separation of elements with similar properties, easy scale-up, and low capital and operating costs [4–6].

The liquid membranes can be classified into different types: bulk, emulsion, supported, and hollow fiber liquid membranes [4]. Bulk liquid membranes consist of an aqueous feed and stripping phases, separated by a water-immiscible liquid membrane (thickness ≥ 0.1 cm). They demonstrate usually stable transport properties. During recent years a significant increase of the applications of liquid membranes for the separation of cobalt from nickel is observed. Tertiary amines are widely used as ion carriers in the liquid membranes. Alamine 336 [7,8] and tri-*n*-octylamine [9] were applied to separate cobalt from nickel in supported liquid membrane (SLM) processes. The applications of emulsion liquid membranes for the separation of cobalt from nickel using trialkylamine [10], tri-*n*-octylamine [11,12] and triisooctylamine [2,13] as mobile carriers have been reported. The separation of cobalt, copper and nickel by polymer inclusion membranes containing tri-*n*-octylamine and triisooctylamine was investigated [14]. However, practical importance of the liquid membranes is not sufficiently high at present. The main issue for all types of supported liquid membranes is the loss of the membrane solvent and carrier. The emulsion liquid membrane process is much more complex than the bulk liquid membrane. The slow transport of metals is a disadvantage of polymeric liquid membranes. Therefore, the development of new membrane extraction processes for the separation of cobalt from nickel is of important environmental and economic interest.

Conventional electrodialysis with solid ion exchange membranes was used for the separation of cobalt and nickel in the presence of EDTA [15–17]. This process exploits the greater stability of the anionic EDTA complex with nickel. Continuous electrodeionization process in the presence of EDTA, used for the separation of cobalt and nickel ions, is described in [18]. In this hybrid process a fixed bed of cation exchange resins was placed into an electrodialysis cell. It has been demonstrated that the electrodeionization process was more effective than the electrodialysis process. The application of a new membrane free electrostatic shielding-based electrodialysis/electrodeionization process for the removal of cobalt from aqueous solutions is reported in [19]. Graphite powder beds were used as intermediate electrodes inside an electrolytic set up in this process. Bipolar membrane electrodialysis method with EDTA chelation proposed in [20] for the separation of cobalt and lithium ions. This process uses the greater stability of the anionic EDTA complex with cobalt at pH > 4.

Electrodialysis with liquid membranes combines carrier-mediated transport and electrodialysis. Application of a direct electric field significantly intensifies the transport of ions through the liquid membranes and facilitates the back-extraction of metals from the organic phase [21,22]. The electric field gradient is a driving force of the membrane extraction process at electrodialysis. If compared with traditional electrodialysis, the liquid membranes provide a greater selectivity and permeability than the solid ion-exchange membranes. If compared with the traditional liquid membranes, electrodialysis negates the sole dependence on the properties of the carrier to provide the selectivity, kinetics and thermodynamics necessary for efficient separation [23]. Data on the electrodialysis of liquid membranes are insufficient in comparison with that on membrane extraction. A first study on the electrodialysis of liquid membranes had been conducted by Purin [24,25], who concentrated rhenium from industrial solutions. Wipf and Simon studied the selective transport of potassium over sodium through bulk liquid membranes containing monactin and nonactin at a potential difference [26]. A theoretical model for the description of the transport of cations through thick neutral carrier membranes at electrodialysis has been developed by Morf and Simon [27]. The mechanism of the transport of cations through liquid membranes containing Dibenzo-18-Crown-6 as the carrier was investigated in [28]. Electroassisted solvent extraction for the separation of Ni(II), Cu(II) and Cd(II) ions using supported liquid membranes was studied in [29]. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was used to extract copper from a copper, nickel and iron sulfate solution by the liquid membranes in electrodialysis [30]. Electromembrane potentiostatic microextraction (EME) through supported liquid membranes was introduced some years ago [31] as a sample preparation technique for chromatography, electrophoresis and mass spectrometry. This technique was used to remove lead ions from various biological fluids [32], as well as to extract Ni(II), Mn(II), Cd(II), Cu(II), Co(II) and Zn(II) cations [33]. However, the electromembrane extraction method is associated with some drawbacks [34]. The voltages above 300 V cause bubble formation at the electrodes, instability problems, punctuation of the SLM and sparking. Hansen and Fyles recently used carrier-mediated electrodialysis through supported liquid membranes containing valinomycin or calyx [4] arene for the separation of sodium and potassium [35].

Galvanostatic electrodialysis through bulk liquid membranes containing D2EHPA was used by the author previously to separate copper(II) from palladium(II) and platinum(IV) extracted from binary hydrochloric mixtures [36], to recover silver(I) extracted from nitric acid solutions during hybrid electrodialysis-electrolysis process [37] and to remove manganese(II) from sulfuric acid solutions [38]. Effective separation of platinum(IV) from palladium(II) extracted from hydrochloric mixtures using liquid membranes containing organic derivatives of thiourea at electrodialysis has been achieved [39]. In the present work, results obtained for the membrane extraction of cobalt(II) from nickel-containing solutions using TOA or TABAC as carriers in the bulk liquid membranes are discussed. The main parameters influencing the transport process, such as current density, acid concentration of the feed solution, extractant concentration, type of the strip solution, initial cobalt(II) and nickel(II) concentrations are studied. The selectivity of the system against nickel(II) and the stability of the liquid membranes are also reported.

2. Materials and methods

2.1. Instrumentation

The experiments were carried out in a five-compartment cylindrical Teflon electrodialysis cell (Fig. 1). The liquid membranes had a thickness of 0.5 cm and volume of 4 cm^3 or a thickness of 0.8 cm and a volume of 5.5 cm^3. In both cases the liquid membrane had a diameter of 3 cm and a surface area of 7.1 cm^2. The liquid membrane was separated from the aqueous solutions by two vertical cellophane films (Khimvolokno, Russia). The films had a thickness of 20–30 μm and a surface area of pores of $1 \cdot 10^{-3}$ cm^2 per 1 cm^2. It has been demonstrated earlier that electrodialysis influences the structure of the cellophane film [40]. The number of pores and their diameter increase significantly after electrodialysis. These films serve as an aqueous phase continuation and allow