



Transport of impurities and water during potassium nitrate synthesis by electro dialysis metathesis



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ARTICLE INFO

Article history:

Received 19 September 2015

Received in revised form 4 December 2015

Accepted 7 December 2015

Available online 8 December 2015

Keywords:

Electrodialysis metathesis

Potassium nitrate

Synthesis

ABSTRACT

The applicability of KNO₃ synthesis by electro dialysis metathesis (ED-M) following: NaNO₃ + K₂SO₄ → KNO₃ + Na₂SO₄ reaction scheme using Ralex PP membranes was examined. The effects of operating parameters: current density, feed concentration and composition on a current efficiency, solute and solvent transport were investigated. Current efficiencies observed were close to 100% and purity of the products exceeded 99%. It was found that electroosmosis contributed to water transport the most. At the same time, osmosis and solute back diffusion did not influence the process.

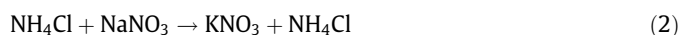
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1. Introduction

Potassium nitrate (KNO₃) has a wide range of uses: as a fertilizer, in production of explosives, for glassmaking, as a preservative, and even as a storage medium of thermal energy in concentrating solar power plants [1]. Due to insufficient KNO₃ mineral (niter) deposits, it is artificially produced mainly *via* chemical processes. Of many known methods of synthesis, only a few are used on an industrial scale [1]. The most commonly used one is a metathesis reaction between sodium nitrate and potassium chloride:



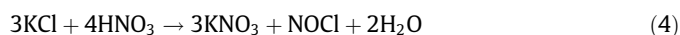
This process is governed by the difference in KNO₃ and NaCl solubility at varying temperatures and requires extensive heating/cooling cycles for crystallization of separate products, and further recrystallization to products with high purity [1]. The alternative route involves the reaction between potassium chloride and ammonium nitrate and is used mostly in China, where the by-product is used as fertilizer for rice cultivation:



Another route involves the reaction of potassium chloride with nitric acid:



To proceed toward KNO₃ formation, HCl is either extracted with organic solvent or distilled off – in the latter case the process is conducted at elevated temperatures and NOCl is reused to improve the overall process economy [1]:



The reaction of KCl with HNO₃ can also be carried out as continuous ion exchange in a column with an acidic cation-exchanger, with subsequent evaporation and crystallization of the product [2]. The above-mentioned processes used for KNO₃ synthesis are hard to control and suffer from limited conversion degree, high energy consumption, low product purity (in the metathesis production route), the use of expensive corrosion resistant equipment or organic solvents (for reaction with HNO₃) and low concentration and large waste streams (in the ion-exchange process) [1,2]. Despite many years of industrial-scale KNO₃ production, there is still a strong need for development of an inexpensive and continuous process for production of potassium nitrate at ambient temperatures.

Electrodialysis (ED) satisfies most of requirements for an environmentally and economically feasible method of KNO₃ synthesis. Ion exchange membranes (IEMs), placed in an external electric field, retain ions of the same charge as the charge of fixed groups

Abbreviations: AEM, anion-exchange membrane; CE, current efficiency; CEM, cation-exchange membrane; ED, electro dialysis; IEM, ion-exchange membrane; ED-M, electro dialysis-metathesis; *c*, concentration, mol/L; *d*, density, g/cm³; *F*, Faraday constant, 96500 A s/mol; *I*, electric current, A; *j*, electric current density, A/m²; *J*, flux, mol/(m² s); *m*, mass, g; *t*, time, s; *t_D*, electroosmotic drag coefficient, mol/mol; *t_R*, transport rate, mol/A h; *t_w*, water transport number, mol/mol; *V*, volume, cm³; *z*, the valence of an ion, eq./mol.

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attached to polymer matrix (co-ions) and pass ions of opposite charge (counter-ions) on the base of the so-called Donnan exclusion [3,4]. This property, widely used for desalination of aqueous solutions, can also be used for conducting double decomposition reactions. Electrodialysis-metathesis (ED-M) is conducted in a four-compartment electrodialyzer with each compartment separated by alternately placed cation-(CEM) and anion-selective (AEM) membranes. The overall cell configuration can be described as follows:



where $\{ \dots \}_n$ denotes the repeating unit, F1, F2 are the separate feeds (potassium and nitrate salts respectively) and P1, P2 are the products – KNO_3 and a by-product. Such a configuration allows for ion transport from the two feed streams into two streams of products where new salts are formed. In this arrangement, ED has been successfully applied for controlled synthesis of azide salts [5], synthesis of ionic liquids [6,7], recovery of organic acids from their salts [8–11] and for conversion of soluble inorganic salts [12–15]. In contrast to the chemical method, metathesis conducted by electrodialysis is not an equilibrium process, so separation of products from the reaction mixture where all components are highly soluble does not require extraction or multi-stage crystallization. It also extends the range of applicable raw materials, as it prevents formation and precipitation of double salts. Earlier works demonstrated the advantages of ED-M application for chemical synthesis: the current efficiencies were high [8,12–14] and the purity of products exceeded 98% [9,12–14].

Contrary to conventional metathesis, during the course of ED-M products cannot be separated from the reaction mixture by crystallization, because an accumulation of crystalline matter on the membrane surface will cause blockage and/or destruction of the membrane [16]. The ED-M product stream is subject to evaporative crystallization, therefore its KNO_3 content should be as high as possible, to reduce the amount of water to evaporate and reduce energy consumption during crystallization. The usual maximum concentration achieved in ED is 100–200 g/L, this can be omitted i.e. by use of a special stack configuration, like in the electrodialysis-concentrating process [17]. Obtaining concentrated solutions by electrodialysis encounters two major obstacles: back diffusion of ions and the solvent transport from the feeds to the product compartments [16,18]. Both affect the possibility for obtaining deeply desalinated feeds and highly concentrated product streams in conventional ED. Thus, besides the limitation in electric current efficiency, the extent of these two phenomena determines the overall efficiency of the ED-M process.

When a current is passed through an ion-exchange membrane, the water can be transported *via* osmosis, in a hydration layer of ions or dragged by friction. Hydration and dragged water, in both cases associated with electric transport of counter-ions, is often referred as electroosmotic water [19,20]. Osmotic flux occurs when the membrane is much more permeable for solvent than for solute [4] and is generally less significant but can become comparable to electroosmotic flux, especially at low currents [21]. Water transport results in a significant increase in volume of the concentrate, decreases the overall process efficiency and limits the maximum salt concentration achievable by electrodialysis [6,8,14].

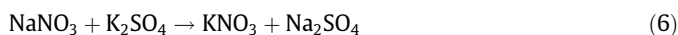
Back diffusion results from concentration gradient across the IEM and increases with an increase in the concentration ratio between the concentrate and diluate streams [18,22]. It also leads to a decrease in the production rate (and current efficiency) – the greater the concentration difference, the stronger decrease in the rate.

Purity of the products is determined by both: purity of feeds [6] and properties of membranes, mainly their selectivity [15,18]. In the case of ED-M, impurities transport mechanism across IEMs is

quite complicated. Co-ions transported through IEMs became counterions in the adjacent product compartment, and can be transported further in the electric field along with product ions, thus spreading contamination. Another source of impurities present in the product may be diffusion [8,12]. All the above makes it hard to investigate the transport of impurities in this variant of electrodialysis directly in ED-M units [15,18].

1.1. The objective

A deep understanding of the efficiency-limiting factors enables selection of the process conditions to minimize their effects. In this work we investigated the effects of operating parameters: current density, feed concentration and composition on a current efficiency, solute and solvent transport in KNO_3 synthesis by metathesis electrodialysis, following the reaction below:



Examination of phenomena determining process efficiency and their dependency upon chosen operating parameters allowed us to assess the applicability of ED-M for KNO_3 synthesis. We also attempted to quantify impurities transport and to make generalizations on mechanisms of their transport.

2. Experimental

2.1. Apparatus and analytical methods

The principle of ED-M is aptly explained by one of its names: *four-compartment electrodialysis*, because at its heart lies four adjacent compartments (referred to as repeating unit) that repeatedly builds up the whole ED-M stack. The repeating unit consists of four compartments: two product compartments (corresponding to concentrate compartments in conventional ED) and two feeds (corresponding to diluate compartments). The cations from both feed streams move under applied electric field toward the cathode through CEM and anions move toward the anode through AEM. In each product compartment, further ion movement in the electric field is restricted by IEMs. As a result, in each of the two product compartments different salts are formed and their concentrations increase during the course of ED-M. In electrode compartments, electrolysis of water occurs and by linking electrode solutions, electrode reaction products are neutralized. Fig. 1 shows the summary of ions flow in ED-M.

Experiments were conducted in a plate and frame electrodialyzer with active membrane area of 16 cm², equipped with electrodes made of Pt-coated titanium. Ralex AM-PP anion-exchange membranes and CM-PP cation-exchange membranes supplied by MEGA (Czech Republic) were used.

Experiments were carried out in a batch mode at room temperature at constant current density. Solutions were circulated through an ED-M stack with flow rates corresponding to a linear flow velocity of 1 cm/s. Graduated cylinders were used to monitor change in volumes during the course of experiments. All solutions were prepared from analytical grade salts (POCH, Poland). In every case, the current density applied did not exceed the limiting value, which was determined separately for solutions with the lowest concentrations applied in this work.

Samples of product solutions were collected periodically. Concentrations of ions were determined by ion-chromatography system ICS-5000 (Thermo Dionex, USA) equipped with AS-19 anion-exchange and CS-16 cation-exchange columns operated in a suppressed conductivity mode.

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