



Potassium nitrate synthesis by electro dialysis-metathesis: The effect of membrane type

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A B S T R A C T

The applicability of four commercially available ion exchange membranes: (Ralex AM-PP, CM-PP; Neosepta AMX, CMX; Selemion AMV, CMV; Ionsep AM-A, AM-C) for potassium nitrate synthesis by electro dialysis-metathesis was investigated. Solute back-diffusion, solvent transport, and potassium nitrate synthesis performance (the product purity, concentration and energy consumption) were evaluated for each IEM. The ED-M synthesis efficiency indicators: potassium nitrate concentration, purity, and current efficiency decreased with membrane type in the following order: Selemion > Neosepta > Ionsep > Ralex. A Selemion AMV-CMV membrane pair performed the best among the membranes tested. Heterogeneous membranes were found to constitute a more efficient barrier for water transport by osmosis than homogeneous ones. Water transport along with ions was found to be the main source of water transport to products, leading to an undesired dilution of product solutions. All of these: back-diffusion, osmosis and water electrotransport can, however, be diminished by the selection of favorable ED-M conditions. The high performance of ED-M synthesis can be provided by using membranes with high fixed ion concentration and low water content. High selectivity, high conductivity and low water electrotransport ability are the most important membrane properties in terms of providing concentrated product under low energy consumption through ED-M.

1. Introduction

Electrodialysis metathesis (ED-M) is a modification of electro dialysis in which two separate feed streams are simultaneously desalinated and two separate product streams are concentrated. Among possible applications of ED-M are syntheses of: inorganic salts (especially potassium salts for fertilizers) [1–3], ionic liquids [4,5], and explosives [6]. ED-M can also be applied for softening of waters and industrial effluents [7,8].

The efficiency of ED-M, as in the case of any electro dialysis-based process, is determined by both operating parameters (current density, feed concentration and composition, etc.) and the performance of ion-exchange membranes (IEMs). Most commercial IEMs are polymeric materials with attached charged ion groups (fixed ions). Due to their ion selectivity, IEMs are divided into cation-exchange membranes (CEMs) with negatively charged groups and anion-exchange membranes (AEMs) with positively charged groups fixed to a polymer backbone. Furthermore, IEMs are classified as heterogeneous, made by introducing ion-exchange resin particles to a polymer, or homogeneous, with ion groups chemically bound to a polymer backbone [9,10].

Homogeneous membranes generally exhibit more favorable electrochemical properties, while heterogeneous membranes are more robust and cheaper to produce [9,10]. In ED-M synthesis, IEMs play a two-fold role: a physical barrier separating products and a selective barrier allowing ion transport to the suitable compartments. Transport properties of IEMs (such as: selectivity, conductivity, diffusion and electroosmotic permeability) are known to be dependent upon the membrane structure and determine the magnitude of phenomena such as: transport of counter and co-ions, diffusion, and transport of solvents [9–11]. Transport of co-ions across the membranes determines the product purity and can be caused either by diffusion or co-ion transport through the membrane [1,10,16,17]. Transport of water increases the volume of concentrate, decreasing the effective salt concentration [3,16,18]. Water can be transported either by osmosis or in an ion hydration shell [12–14] and the dominating mechanism depends on membrane and electrolyte properties and on process conditions [11,15]. Moreover, the IEM structure and material affect process parameters, such as limiting current density and stack resistance [9]. Therefore, IEMs have an impact both on process indices and on product quality parameters [2,16,17].

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Abbreviations			
AEM	anion-exchange membrane	N	number of repeating units (pairs or quartets of membranes) in a stack
CE	current efficiency	Q	electric charge, Ah
CV	coefficient of variation	R	normal gas constant, 8.314 J/(mol K)
DD	diffusion dialysis	r ²	coefficient of determination
CEM	cation-exchange membrane	s	membrane geometric surface, m ²
ED	electrodialysis	t	time, s
EC	electric energy consumption, kWh/kg	T	temperature, K
FIC	fixed ion concentration, meq/g _w	t _D	electroosmotic drag coefficient, mol/mol
IEM	ion-exchange membrane	W	water content of membrane
IEC	ion exchange capacity, meq/g _{dry}	V	volume, mL or L
ED-M	electrodialysis-metathesis	z	the valence of an ion, eq./mol
SE	standard error		
c	molar concentration, mol/L	<i>Greek letters</i>	
d	density, g/cm ³	π	osmotic pressure, Pa
D _{app}	apparent diffusion coefficient, m ² /s	φ	osmotic coefficient
E	voltage drop, V	ω _{app}	apparent osmotic water transport coefficient, mol/(m ² s Pa)
F	Faraday constant, 96,500 As/mol or 26.8 A h/mol		
I	electric current, A	<i>Subscripts</i>	
i	number of dissociated ions	i	of compound <i>i</i>
j	electric current density, A/m ²	osm	osmotic
J	molar flux, mol/(m ² s)	el	related to migration of ions
k _{app}	apparent mass transfer coefficient, m/s	w	of water
L	thickness of swollen membrane, mm	s	of salt
m	mass, g or kg		
M	molar mass, Da		

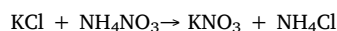
Recently, Camacho et al. attempted to optimize ED-M parameters in softening RO concentrates using a 2⁴ factorial experimental design [2] and concluded that applied potential and concentration (dependent on the origin of the RO concentrate) had more impact on the desalination rate than membrane type (the linear flow rate had no significant effect). Thus, under the same experimental conditions, membrane type may determine the process efficiency. Various commercial membranes have been used in ED-M synthesis of inorganic compounds: homogeneous (Neosepta), perfluorinated (Nafion) and heterogeneous (Ionsep, Ralex, Lab), as presented in Table 1. Sharma et al. [3] synthesized styrene and divinyl benzene based interpolymer ion exchange membranes with satisfactory mechanical properties and low electroosmotic water transport. These membranes allowed to obtain low impurity in the product, but the current efficiency was rather low. Given the various experimental conditions used in each work, no firm conclusions on the effects of membrane type can be drawn based on existing data.

Ideally, IEMs used in ED-M synthesis should provide complete exclusion of co-ions (thus excluding the transport of impurities), a low rate of water transport and a low back-diffusion rate of a product. In addition, IEMs should indicate low electric resistance. All of the above

should allow for the attainment of concentrated solutions of pure products with low energy consumption.

1.1. The objective

The aim of this work was to investigate the effect of membrane type on the efficiency of KNO₃ synthesis by ED-M according to the following general reaction:



The IEMs chosen for this study come from leading manufacturers and are originally designed for electrodialysis. In our previous study, the effects of operating parameters (current density, feed concentration and composition) on the effectiveness of KNO₃ synthesis using Ralex membranes only were determined [1]. Herein, the performance of four pairs of commercially available ion-exchange membrane brands (Ralex, Neosepta, Selemion and Ionsep) was analyzed to select the most suitable pair of IEMs for KNO₃ synthesis and to determine the process indices that strongly depend on IEM type.

Table 1
Results and conditions of ED-M synthesis of inorganic compounds.

Ref.	Reaction (main product bolded)	Membranes	Main product		
			Current efficiency	Energy consumption, kWh/kg	Impurity content per solid salt, %
[18]	MgCl + Na ₂ SO ₄ → MgSO₄ + NaCl	Neosepta AMX and CMX	1.06	0.85–1.30	1.3–1.6
[19]	MgSO ₄ + 2KCl → K₂SO₄ + MgCl ₂	Neosepta AMX and Nafion 423	0.94	n/a	0.2
[16]	Na ₂ SO ₄ + 2KCl → K₂SO₄ + 2NaCl	Neosepta AMX and Nafion 423	0.94–0.95	n/a	1.2–2.5
[20]	2KCl + Na ₂ SO ₄ → K₂SO₄ + 2NaCl	Ionsep	0.67–0.74	0.97–1.42	2.1–4.8
[21]	2KCl + (NH ₄) ₂ SO ₄ → K₂SO₄ + 2NH ₄ Cl	LabA and LabC	0.37	0.43	39.46
[1]	K ₂ SO ₄ + NaNO ₃ → KNO₃ + NaCl	Ralex AM-PP and CM-PP	0.99	n/a	< 0.3
[3]	KCl + NaNO ₃ → KNO₃ + NaCl	prepared from styrene and DVB base	0.72–0.84	0.74–1.31	1

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