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DIFFUSION AND OSMOSIS IN POTASSIUM NITRATE SYNTHESIS BY ELECTRODIALYSIS METATHESIS

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Abstract

The experimental results of the chosen salts permeation with selected heterogeneous and homogenous membranes were analysed as a part of modelling of mass transport in electrodialysis metathesis process (ED-M) for synthesis of KNO_3. Heterogeneous membranes swelled more in aqueous solutions and they had higher water uptake than homogeneous membranes. Heterogeneous membranes were also more permeable for both the solute and the solvent, which was attributed to higher solubility of salts in heterogeneous membrane's material. Diffusion coefficients in ion-exchange membranes tested in this study were found to be dependent on concentration of the upstream solution, with an exception of Ca^{2+} in anion-exchange membranes and NO_3^- in cation-exchange membranes. The role of osmosis in water transport in ED-M process was found negligible.

Streszczenie

Przedstawiono wyniki transportu bezprądowego roztworów wybranych soli w szerokim zakresie stężeń przez wybrane membrany homo- i heterogeniczne, stanowiące część badań nad modelowaniem transportu masy w procesie elektrodializy z podwójną wymianą. Membrany heterogeniczne charakteryzowały się większym pęcznieniem i sorpcją roztworu niż homogeniczne. Obserwowaną większą przepuszczalność soli dla membran heterogenicznych przypisano ich większej rozpuszczalności w materiale membrany heterogenicznej. Wyznaczone współczynniki dyfuzji rosły ze stężeniem roztworu, za wyjątkiem Ca^{2+} dla membrany anionowymiennej i NO_3^- dla membrany kationowymiennej. Potwierdzono pomijalnie mały, w porównaniu do elektroosmozy, udział osmozy w przenoszeniu wody w procesie elektrodializy z podwójną wymianą.

Keywords: **Electrodialysis metathesis; Potassium nitrate; Diffusion; Osmosis.**

1. INTRODUCTION

Electrodialysis-metathesis (ED-M) is an alternative synthesis route for metathesis (double replacement) reactions:

$$AB + CD = AD + CB \qquad (1)$$

but, contrary to conventional metathesis, it is not an equilibrium process, which eases separation of products from the reaction mixture where all components are highly soluble [1]. Potassium nitrate is an example of chemical compound produced on industrial scale by energy consuming chemical metathesis processes. ED-M can be a promising alternative for its production, both in terms of product quality and environment protection, thanks to reduced water and energy consumption.

Beside electric field-driven transport of ionic species, which was investigated for KNO_3 synthesis in ED-M process [1], non-current transport also takes place, namely: diffusion and osmosis. These processes are driven by the difference in chemical potential between two solutions with a different salt concentration across the ion-exchange membrane (IEM). Insight into these two non-current transport mechanisms in ED-M process is important both for process modeling and practical process realization. For modeling of ion transport through IEMs, Nernst-Planck equation is widely used due to its relative simplicity [2, 3]. In this model, diffusion is one of three forces, next to electric potential difference and drag, driving the compound transport across the membrane. From the process implementation point of view, diffusion and osmosis can affect the ED-M synthesis efficiency. As high product concentration is desired due to reduced water evaporation in subsequent operations for solid product separation, ED-M process encounters typical electrodialysis limitations: back diffusion of ions and solvent transport from the diluate to the concentrate. The former limitation affects product purity and process efficiency while the latter adds up to electroosmosis and limits final product concentration [1].

Permeation experiments are the widely used method for investigation of the mass transport through IEMs using simple laboratory procedures. Transport parameters (namely: diffusion coefficient, permeability, solubility) can be derived directly from experimental data [4]. The interval between the moment solute comes into contact with the membrane and when it emerges at a constant rate on the other side is known as time lag [4, 5]. If the membrane is initially free of permeate, then this lag is positive and reflects the characteristic time required for mass to permeate the membrane. The use of observable time lag to determine diffusion coefficient was developed by Firsh [5]. The time lag has been defined as the intercept on the time axis, determined by the asymptote to the solute mass going out of the membrane. The method of time lags measurements constitutes a useful experimental tool for investigating even very complicated systems and extends the possible analytical descriptions of the various diffusion processes.

The aim of this work was to evaluate non-current transport of water and solute through two membranes: heterogeneous Ralex-PP (Mega, Czech Republic) and homogeneous Neosepta (Tokuyama Soda, Japan). The obtained data will help to select optimal membranes and conditions for ED-M synthesis of KNO_3.

2. METHODS AND APPARATUS

The diffusion/osmotic permeability experiments were conducted in EDR-Z module (Mega, Czech Republic), with one membrane separating two compartments: the downstream and the upstream. Both process solutions were circulated with a peristaltic pump, the linear flow velocities inside the ED compartment equaled to 2.78 cm/s. Four membranes: two homogeneous and two heterogeneous type were tested in an independent experiments. Their properties are given in Table 1. The downstream solution was initially 65 cm^3 of deionized water. The changes in downstream volume were measured with high accuracy (±0.08%) by application of a burette with a ±0.05 cm^3 accuracy as a flow tank for downstream solution. The conductivity of the downstream solution was measured on-line with CC-401 conductometer (Elmetron, Poland) equipped with CF-201 electrode. Downstream conductivity was recorded every 5 s with PC software. The upstream solution was 500 cm^3 of salt of a given concentration, prepared from analytical grade salt (POCH, Poland). The range of upstream concentrations used in this study is provided in Table 1. Due to upstream large volume, the change in upstream salt concentration during experiments was assumed to be negligible. The downstream and upstream solutions were thermostated at 25°C. The downstream solution salt concentration was calculated from conductivity based on the data from [6].

Table 1.
Membranes, solutions and their concentrations used in diffusion/osmosis experiments

Membrane	Tested solutions (role in ED-M synthesis)	Upstream concentrations, mol/dm^3
Anion-exchange:	$NaNO_3$ (feed)	0.2, 0.4, 1, 2, 4.6
Ralex AM-PP	$Ca(NO_3)_2$ (feed)	0.2, 0.4, 1, 2, 3.5
Neosepta AMX	KNO_3 (main product)	0.2, 0.4, 1, 2, 2.5
Cation-exchange:	KCl (feed)	0.2, 0.4, 1, 2, 3.5
Ralex CM-PP	K_2SO_4 (feed)	0.1, 0.2, 0.3, 0.4, 0.5
Neosepta CMX	KNO_3 (main product)	0.2, 0.4, 1, 2, 2.5

To determine the change of membrane properties (thickness, water content) with ionic strength of solution, 5x5 cm slices of each membrane: Ralex AM-PP, Ralex CM-PP, Neosepta AMX or Neosepta CMX were placed in a solution of given ionic strength for 24 h (three pieces for each concentration). Thickness of the swollen membrane was measured with a micrometer screw. Membrane slice was then carefully wiped-out with a paper towel, weighted, and subsequently dried to constant weight in a vacuum oven at 105°C. Prior to drying, TGA analysis was conducted to ensure thermal stability of each membrane in such conditions. Water content in the membrane was calculated from the mass change of wet membrane equilibrated with solution of given ionic strength and dried membrane:

$$W = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Membranes behavior in a solution

An ion-exchange membrane consists of a cross-linked polymer structure which swells anisotropically when immersed in water. This is caused by both electric repulsion and solvatation of fixed ions [7]. The swelling degree of a membrane is limited and depends on ionic strength of the solution (linked to availability of water in a solution) and degree of cross-linking of the polymer [8]. Figs. 1 and 2 show changes of membranes properties with increasing ionic strength of external solution.

For all the membranes tested, the water content decreased with ionic strength of the solution. The highest water content and degree of swelling was observed for Ralex CM-PP membrane. Moreover, it was found that heterogeneous membranes sorbed more water than homogeneous ones. This swelling was also linked to changes in the membrane thickness: it was the highest in dilute solutions and lower for more concentrated solutions. The thickness of Ralex membranes was strongly dependent upon ionic strength of the solution, whereas for Neosepta membranes thickness remained almost constant in the tested range of the solution ionic strength. The membrane dimensions stability is desirable, as it provides mechanical strength of membrane. Greater swelling of heterogeneous IEMs is mostly attributed to swelling of the ion-exchange particles incorporated into the membrane, while for homogeneous membrane it is the result of swelling of the polymeric net [8]. For most of the membranes tested, minimum thickness was observed at ionic strengths higher than 2 mol/dm^3 while for CM-PP – higher than approx. 5 mol/dm^3.

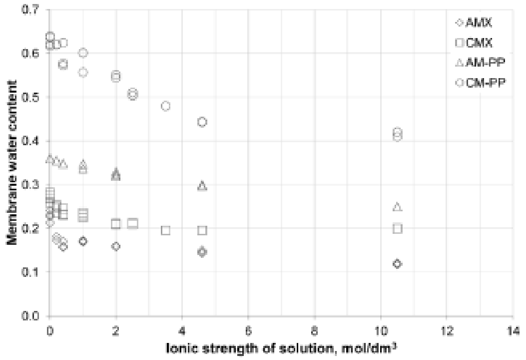

Figure 1.
Membrane water content upon ionic strength of solution

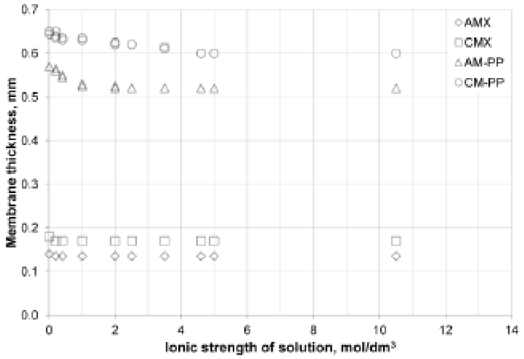

Figure 2.
Membrane thickness upon ionic strength of solution

Examination of membrane's swelling and water uptake dependency upon ionic strength of the solution allows to estimate parameters necessary to evaluate mass transport through IEMs. The membrane thickness is the minimum diffusion path length for particles in their diffusive transport (assuming one-dimensional transport). Membrane thickness was measured for membrane equilibrated with a solution of given ionic strength. However, in permeation experiments, membrane is facing salt solution on the one side and deionized water on the other. Therefore, diffusion path length in permeation experiments (l_{mean}, m) was calculated as a logarithmic mean of thickness measured for those two cases: for membrane soaked in deionized water (l_{water}) and equilibrated with a solution of given ionic strength (l_{soln}):

$$l_{mean} = \frac{l_{water} - l_{soln}}{\ln\left(\frac{l_{water}}{l_{soln}}\right)} \tag{3}$$

The calculated diffusion path length in conditions of each permeation experiment set is given in Tables 2 and 3.

3.2. Non-current transport of salts through IEMs

The diffusivity of the component in membrane is one of basic mass-transfer characteristics. For evaluation of mass transport through membranes, two models are commonly used: pore-flow transport and solution-diffusion transport model. These are two extreme cases, in which transport is explained by, respectively, the presence and the absence of pores. Herein, solution-diffusion model was applied for data analysis.

In this study, a wide range of upstream solution concentrations was used. This is because in the envisioned ED-M system, both high and low concentrations can be encountered, due to simultaneous desalting of feeds and concentration of products. The salt molar flux was determined based on the slope of number of the moles vs. time curve in a steady-state region:

$$J = \frac{dn}{dt} \cdot \frac{1}{s} \tag{4}$$

where: J – steady-state flux, mol/(m^{2}s); n – moles of salt, mol; t – time, s; S – geometric active membrane surface, m^2.

Simultaneously, time lag was determined as the intercept of the rate of mass transported through IEM to downstream solution vs time curve, in the same region.

The determined steady-state flux and time lag for each membrane and feed used are given in Tables 2 and 3.

From the solution of 1st Fick's law for diffusion through a layer of thickness l, the one-dimensional diffusion mass flux through the membrane is proportional to concentration difference across the IEM by the permeability coefficient (P, m/s):

$$J = -\frac{P}{l}\left(c_1 - c_0\right) \tag{5}$$

If downstream solution concentration was negligible, $c_l \ll c_0$, then:

$$\left(c_1 - c_0\right) \approx -c_0 \tag{6}$$

thus, the concentration difference across the IEM was assumed equal to upstream feed concentration.

Table 2.
Average membrane thickness, molar fluxes and measured time lag for permeation experiments with anion-exchange membranes

	$c_{upstream}$, mol/dm^3	AM-PP			AMX		
		l_{mean}, mm	$J \cdot 10^{-5}$, mol/(m^{2}s)	t_{lag}, s	l_{mean}, mm	$J \cdot 10^{-5}$, mol/(m^{2}s)	t_{lag}, s
$NaNO_3$	4.6	0.545	13.15	354	0.135	21.37	48
	2	0.547	3.23	559	0.135	6.27	52
	1	0.553	0.82	600	0.135	3.35	65
	0.4	0.561	0.61	712	0.135	0.62	80
	0.2	0.563	0.24	720	0.135	0.20	131
KNO_3	2.5	0.545	7.53	463	0.135	6.84	52
	2	0.547	6.24	488	0.135	5.67	55
	1	0.553	3.20	499	0.135	2.78	56
	0.4	0.561	1.04	571	0.135	0.77	57
	0.2	0.563	0.40	721	0.135	0.27	57
$Ca(NO_3)_2$	3.5	0.545	3.72	708	0.135	4.63	214
	2	0.547	2.49	726	0.135	2.77	199
	1	0.550	1.47	772	0.135	1.02	218
	0.4	0.551	0.65	729	0.135	0.20	226
	0.2	0.558	0.32	756	0.135	0.05	310

The membrane surface concentration of diffusing specie can be obtained from characteristic numbers and hydrodynamics conditions. However, as high linear flow velocities ensured turbulent flow inside the ED compartments, the role of polarization layers was found to be negligible (calculated difference between concentration in bulk solution and at the IEM surface was < 1%).

In solubility-diffusion mechanism, P is defined as:

$$P = s \cdot \overline{D} \tag{7}$$

where s is the solubility of compound in membrane, given as ratio of concentrations of compound *i* in and outside the membrane:

Table 3.
Average membrane thickness, molar fluxes and measured time lag for permeation experiments with cation-exchange membranes

	$c_{upstream}$, mol/dm^3	CM-PP			CMX		
		l_{mean}, mm	$J \cdot 10^{-5}$, mol/(m^{2}s)	t_{lag}, s	l_{mean}, mm	$J \cdot 10^{-5}$, mol/(m^{2}s)	t_{lag}, s
KCl	3.5	0.623	11.76	345	0.175	11.63	69
	2	0.632	6.98	393	0.175	5.01	68
	1	0.640	3.07	425	0.175	1.72	74
	0.4	0.646	0.93	506	0.175	0.39	80
	0.2	0.648	0.35	647	0.175	0.12	84
KNO_3	2.5	0.629	9.19	490	0.175	7.90	84
	2	0.632	7.83	498	0.175	6.73	83
	1	0.640	3.94	516	0.175	3.10	94
	0.4	0.646	1.20	526	0.175	0.80	97
	0.2	0.648	0.52	527	0.175	0.37	100
K_2SO_4	0.5	0.636	0.27	1126	0.175	0.16	239
	0.4	0.639	0.20	1281	0.175	0.13	233
	0.3	0.641	0.13	1278	0.175	0.06	257
	0.2	0.644	0.07	1406	0.175	0.02	279
	0.1	0.646	0.02	1805	0.175	0.01	330

$$s = \frac{\overline{c_i}}{c_i} \tag{8}$$

For diffusion into slab membrane and boundary conditions as in experimental setup herein (membrane initially contains no diffusing species, upstream concentration is constant and downstream concentration is negligible, compared to upstream concentration) time lag (t_{lag}) in steady state is given by Eq. 9, as according to [4,9]:

$$t_{lag} = \frac{L^2}{6\overline{D}} \tag{9}$$

which enables an immediate calculation of diffusion coefficient (D, m/s) for a measured time lag value, taking l_{mean} as diffusion path length (L). Calculated values of D are presented in Fig. 3 and Fig. 4 for each membrane, salt and concentration tested.

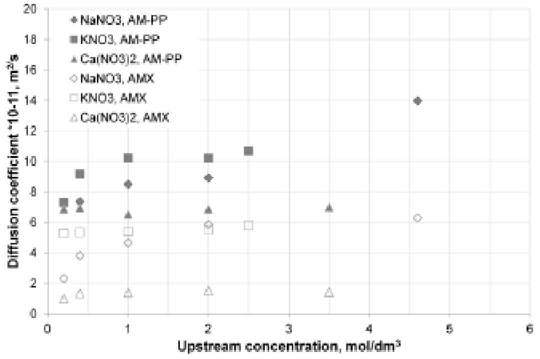

Figure 3.
Diffusion coefficient of the limiting ion upon upstream solution concentration for the anion-exchange membranes

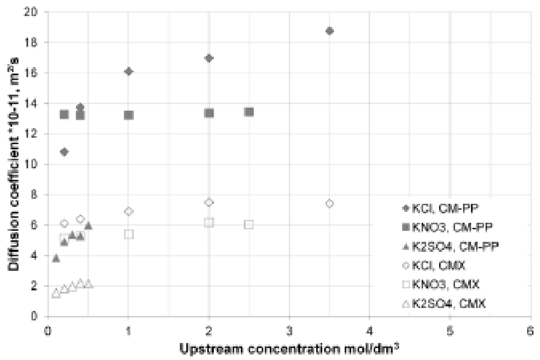

Figure 4.
Diffusion coefficient of the limiting ion upon upstream solution concentration for the cation-exchange membranes

Diffusion coefficients in AEMs tested in this study were found to be dependent on concentration of the upstream solution in non-linear, asymptotic manner, except for $Ca(NO_3)_2$ (for both membranes) and KNO_3 in AMX membrane, where the diffusivities remained approximately constant. For CEMs, almost constant diffusivities were observed for KNO_3 exclusively. For all membranes, diffusivities in the presence of bivalent ion (Ca^{2+}, SO_4^{2-}) were the lowest. Also, it was observed that diffusivities in heterogeneous membranes were relatively higher than in homogeneous membranes. This is a little counter-intuitive: heterogeneous membrane should be less permeable due to its thickness than thin, homogeneous membrane. This tendency can also be seen from data presented Tables 2 and 3: salt fluxes through homogeneous membranes were relatively lower than for heterogeneous membranes. The origin for the above differences can be explained by salt solubilities in the heterogeneous membranes being generally higher than in homogenous, as shown in Figs. 5 and 6. The solubility of each compound in the membrane was found to depend non-linearly upon external solution salt content, in the manner similar to diffusivity.

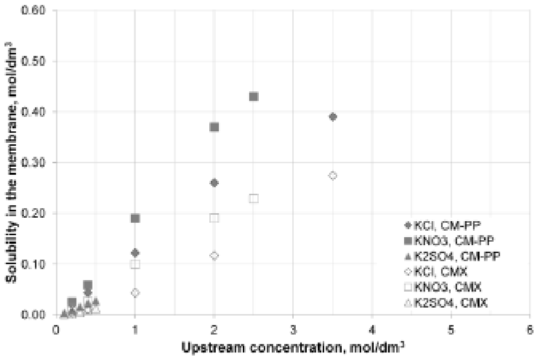

Figure 5.
Relation between salt solubility in the membrane and upstream concentration for cation-exchange membranes

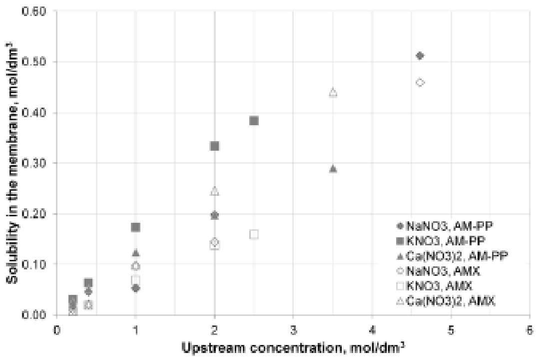

Figure 6.
Relation between salt solubility in the membrane and upstream concentration for anion-exchange membranes

3.3. Osmotic water flux

As time lag for water permeation through IEM cannot be determined, the analysis of water non-current transport presented herein is less detailed. The water molar flux through IEM was calculated from the mass balance at a steady-state (by Eq. 4) and is presented in Figs. 6 and 7. The water flux in each case increased with increasing upstream salt concentration. For both Ralex and Neosepta membranes, water flux was higher for CEMs than for AEMs. In the case of Neosepta membranes, water flux increased more strongly with upstream concentration than for Ralex membranes. The differences observed between water flux for various salt solutions for each IEM in Figs. 6 and 7 can be attributed to inaccuracy in measurements and its resulting random scattering of the experimental data. The water osmotic molar flux found was around four orders of magnitude lower than molar diffusive flux of salts. The above confirms conclusion of negligible, compared to electroosmotic flux, role of osmosis in water transport during ED-M [1].

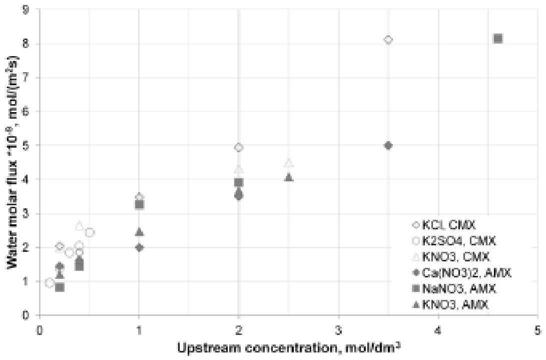

Figure 7.
Measured water flux vs. upstream salt concentration for Neosepta membranes

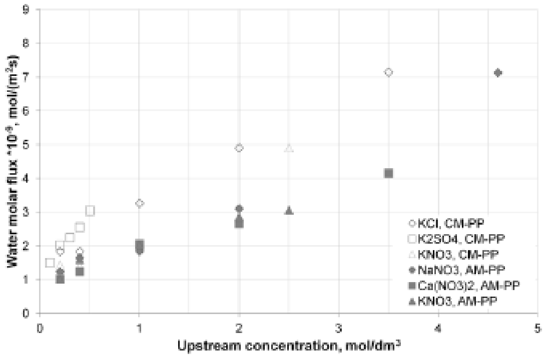

Figure 8.
Measured water flux vs upstream salt concentration for Ralex membranes.

4. CONCLUSIONS

In this work, the results of selected salts permeation experiments with selected heterogeneous and homogenous membranes were analyzed as a part of modeling of mass transport in ED-M synthesis of KNO_3. ED-M is an interesting and potentially more environmental-friendly alternative for KNO_3 synthesis. It was found that heterogeneous membranes swelled more in aqueous solutions and had higher water uptake than homogeneous. Similarly, heterogeneous membranes were more permeable for both: the solute and the solvent, than homogeneous membranes, which was attributed to higher solubility of tested salts in heterogeneous membrane's material. The more soluble the compound was in the membrane, the higher was its diffusivity. Diffusion coefficients in IEMs tested in this study were found to be dependent on concentration of the upstream solution, with an exception of $Ca(NO_3)_2$ in AEMs and KNO_3 in CEMs.

The diffusion of neutral specie through IEM is limited by a co-ion of membrane ion of the same charge as IEM's fixed ion. This is due to electroneutrality condition requirement. Co-ions, retained by membranes' fixed ions, penetrate through and finally leave the membrane surface combined with counter ion (whose concentration in the membrane is high due to high concentration of fixed ions). Thus, diffusion coefficients determined herein apply to membrane co-ions: Na^+, Ca^{2+}, K^+ for AEMs and Cl^-, NO_3^-, SO_4^{2-} for CEMs. These findings will be useful for further modeling of mass transport in ED-M.

The osmotic molar flux of water was found to be independent on salt solution and due to its small value even at high salt concentrations, the negligible role of osmosis in water transport in ED-M was confirmed.

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