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Synthesis and transport of impurities in electrodialysis metathesis: Production of choline dihydrogen phosphate

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Abstract

The production of ionic liquids involves a metathesis step in which the desired anion and cation are combined. Depending on the desired product purity, this step can be accomplished by different methods, including acid base neutralisation reactions, the use of silver salts and electrodialysis. In this paper, electrodialysis metathesis is used for the production of choline dihydrogen phosphate. The influence of operating parameters was investigated. It was found that a high current density, low diluate and choline dihydrogen phosphate concentration yield the highest product purity. Furthermore, it was illustrated for the first time that electrodialysis metathesis is able to yield a product purity comparable with that obtained by using silver salts. An electrical efficiency of 94.0% for choline and 58.6% for dihydrogen phosphate was achieved. The total cost of the electrodialysis process was estimated at 0.06 € per mole of choline dihydrogen phosphate. The second aim of this paper is the characterization of the flow of impurities in electrodialysis metathesis. In addition, the effect of operating variables on this flow of impurities was quantified. In the further optimization of the electrodialysis metathesis process, this knowledge is likely to be of great interest in conducting salt metathesis reactions.

1. Introduction

Ionic liquids are salts that are completely melted at a temperature lower than 100°C [1]. Due to their versatility, they possess a whole range of possible applications including the use as a solvent for chemical synthesis and catalysis [2-4], liquid-liquid extractions [5, 6], lubricant [7], electrochemical applications [8], etc.

In general, the synthesis of ionic liquids is composed of two steps, namely the synthesis of the desired cation and a metathesis step. In this metathesis, the anion used in the synthesis of the cation is exchanged by the desired anion to yield the product. In most cases, the cation is commercially available as a halide salt and only an anion exchange is required. The metathesis process for the production of water-miscible ionic liquids is demanding because of the difficult separation of desired and undesired ions.

Several methods can be applied. The use of silver salts of the desired anion results in the precipitation of silver halides and the formation of the corresponding ionic liquid. This process yields a very high purity but is too expensive for large scale application [9]. For example, 1-butyl-3-methylimidazolium nitrate prepared by this method contained, on water free basis, less than 0.22 mol% Na⁺ and 0.45 mol% Cl⁻ [10]. Moreover, the use of silver salts entails a potential problem for human health and for the environment [11, 12]. Other production methods include the simple mixing of the desired cation (as a halide) with an alkali metal salt or the use of an acid base neutralization reaction. For water soluble ionic liquids, the feasibility of these methods depends on the ability to isolate the ionic liquid from the alkali metal halide. This isolation is difficult and therefore the removal of halides is only mediocre [10, 13]. For example, 1-butyl-3-methylimidazolium nitrate prepared by the mixing of 1-butyl-3-methylimidazolium chloride and NaNO₃ still contained, on water free basis, 1.1 mol% Na⁺ and 18 mol% Cl⁻. For this ionic liquid, the acid base neutralization reaction yielded a lower amount of impurities, namely less than 0.22 mol% Na⁺ and 0.22 mol% Cl⁻ [10]. However, the use of acid base neutralization is not possible for all types of ionic liquids. Quaternary ammonium bases, such as choline hydroxide, may undergo a reverse Menshutkin reaction or Hofmann degradation [14] which disables this synthesis route.

In the literature, it has been shown that the use of electrodialysis for the processing of ionic liquids has several promising applications. Electrodialysis was used for the recovery of ionic liquids from dilute solutions [15-17]. For example, Yan et al. [17] investigated the concentration of waste ionic liquids using electrodialysis. Different commercial membranes, the influence of the voltage difference, operating modes and the concentration ratio between the diluate and concentrate compartment were studied. Electrodialysis can also be used for the purification of ionic liquids [18]. Endo et al. [19] studied the transport properties of various ionic liquids during electrodialysis. The authors found that ionic liquids having large cations were transported more slowly than ionic liquids with large anions. Using Selemion AMV and CMV membranes, the pore size of the membranes was comparable with the size of the ionic liquid ions.

The feasibility of using electrodialysis for the production of ionic liquids was illustrated earlier in the literature [20-22]. Meng et al. [20] used a four compartment configuration to synthesize 1-butyl-3-methylimidazolium tetrafluoroborate starting from 1-butyl-3-methylimidazolium chloride and sodium tetrafluoroborate. Under the tested conditions, a maximum ionic liquid concentration of 0.40 mol L⁻¹ was obtained with a product purity over 95%. Haerens et al. [21] investigated the synthesis of choline thiocyanate, choline acetate and choline dicyanamide and reported an electrical efficiency between 65% and 78%. The ionic liquid produced contained, on water free basis, less than 3 mol% of sodium. It was also found that the chloride content strongly depends on the product purity of the starting products. An ionic liquid concentration approximating 1 mol L⁻¹ was achieved. Bipolar membrane electrodialysis was used by Himmeler et al. [22] to synthesize a 5% [EMIM]OH solution starting from [EMIM][EtOSO₃] with a product purity higher than 98%.

In the production of ionic liquids with electrodialysis, aqueous solutions with a low concentration of ionic liquids were produced. Because of the low concentration, large amounts of water had to be removed to yield the pure ionic liquids. The feasibility of producing a highly concentrated ionic liquid was not tested. In addition, the product purity of ionic liquids produced by electrodialysis metathesis did not exceed 99%. To be competitive with other synthesis routes, such as the use of silver salts, a higher product purity is required. In this study, the production of choline dihydrogen phosphate is investigated. The focus is on the production of highly concentrated solutions combined with a high product purity. Moreover, choline dihydrogen phosphate has several promising potential applications. For example, choline dihydrogen phosphate is identified as one of the most promising candidates to be used as a medium for the stabilization of proteins [23] and DNA triplex formation [24]. The ionic liquid can potentially be used as proton conducting electrolyte in fuel cells [25, 26].

The second aim of this study is to investigate the transport of impurities in the electrodialysis metathesis process. Pisarska investigated the transport of co-ions in the production of MgSO_4 and KCl by electrodialysis metathesis [27]. It was found that the flux of co-ions gradually pollutes all compartments. Jaroszek et al. discussed the transport of impurities (Na^+ , Cl^- and SO_4^{2-}) during the synthesis of KNO_3 [28]. The use of analytical and technical grade salts revealed a difference in transport of impurities. By using technical salts, the feed or diluate streams were contaminated by impurities. As a consequence of competing transport of counter-ions in the diluate compartments, the product streams were polluted. The use of analytical grade salts resulted in a lower transport of impurities. Nevertheless, the pathways of this transport of impurities using high purity salts remain to be resolved. Moreover, the effect of operating parameters such as ion concentration, current density and voltage difference is of great interest in the minimization of the impurities in salt synthesis with electrodialysis metathesis. In this paper, a systematic approach is used to quantify the transportation pathways of impurities in the four compartment electrodialysis configuration.

2. Materials and methods

2.1. Experimental setup

Electrodialysis experiments were conducted in a four compartment electrodialysis setup by using a PCCell ED 64-004 Stack (PCCell GmbH, Heusweiler, Germany). The four compartment stack (cf. Figure 1) is composed of two diluate compartments (NaH_2PO_4 and choline chloride (ChCl)) and two concentrate compartments (choline dihydrogen phosphate (ChH_2PO_4) and NaCl). The relative error on the mass balances of choline and dihydrogen phosphate was below 5%. In this work, the concentrate compartment containing the ionic liquid (in this case choline dihydrogen phosphate) is referred to as the product compartment. As a cation-exchange membrane, Neosepta CMS was used. Neosepta ACS was used as an anion-exchange membrane. Based upon own non-published research and Veerman et al. [29], these membranes were chosen because of their high permselectivity compared to other commercial ion-

exchange membranes. Two repeating units were used in one stack. The active surface area of one membrane was 0.0064 m^2 .

The flow rate of all salt streams in the stack was 6 L h^{-1} per compartment, the flow rate of the electrode rinsing solution was 150 L h^{-1} . These flow rates correspond with a linear flow velocity of $4.2 \cdot 10^{-2} \text{ m s}^{-1}$ for the streams in the stack and $5.2 \cdot 10^{-1} \text{ m s}^{-1}$ for the electrode rinsing solution. Every experiment was performed in batch mode during two hours. Samples of 30 mL were taken of all vessels at the beginning and every interval of 30 minutes. The initial volume of all streams was 500 mL . The effect of osmosis and electro-osmosis was taken into account by measuring the difference in volume height in long cylindrical vessels containing the salt streams. Unless mentioned otherwise, a $1 \text{ L } 0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution was used as the electrode rinsing solution.

Figure 1: Scheme of the four compartment electro dialysis metathesis configuration for the production of choline dihydrogen phosphate.

Before each experiment, all ion-exchange membranes were subject to a pretreatment. Hereby, the membranes were placed in the stack and rinsed with a $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ solution. The linear flow velocity was chosen identical as in the electrodialysis experiments, namely $4.2 \cdot 10^{-2} \text{ m s}^{-1}$. One KNO_3 solution was used for both diluate compartments, the other solution was used for both concentrate compartments. A $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution was used as an electrode rinsing solution. During one hour a current density of 200 A m^{-2} was applied.

The operating parameters of the electrodialysis metathesis process were optimised using a 2^3 design of experiments. This means that the influence of three variables (namely the current density, the ionic liquid concentration and the concentration of both diluate compartments) were investigated on two levels. The current density was varied from 100 to 200 A m^{-2} , the choline dihydrogen phosphate concentration (concentrate 2) was changed from 1 to 3.4 mol L^{-1} . The diluate concentration for both compartments (NaH_2PO_4 and ChCl) was chosen equal and was set at either 1 or 4 mol L^{-1} . The initial concentration of NaCl (concentrate 1) was 0.3 mol L^{-1} in every experiment. The repeatability of the results was checked by

performing an experiment at intermediate levels of all variables twice (150 A m^{-2} , 2.2 mol L^{-1} choline dihydrogen phosphate and 2.5 mol L^{-1} diluate concentration).

The origin of impurities in the product compartment was investigated in a following set of experiments. The migration of sodium was examined by systemically substituting all sodium salts by potassium salts. In a first experiment, the NaCl concentrate was replaced by KCl to quantify the sodium flux originating from the diluate compartment containing NaH_2PO_4 . In the second experiment, the sodium salt of phosphoric acid was substituted by KH_2PO_4 . Hereby, the contribution of the NaCl concentrate to the total sodium flux towards the product compartment was examined. In addition, both experiments were repeated whereby the Na_2SO_4 electrode rinsing solution was replaced by a K_2SO_4 solution.

Based upon these experiments, the optimal operating parameters were selected. At these settings, a current voltage profile was recorded. This is done in order to investigate the occurrence of a limiting current density. The profile was recorded by linearly increasing the current density at $50 \text{ A m}^{-2} \text{ min}^{-1}$ and measuring the voltage difference across the stack. Subsequently, an experiment at the optimal current density was performed to estimate the product purity and to perform an economic evaluation. The current density was chosen as high as possible but below the limiting current.

2.2. Analytical methods

The sodium concentration was measured by means of atomic emission spectroscopy with a Unicam AAS Solar 989 (ThermoFisher Scientific, USA). The choline concentration was monitored by the change in non-purgeable organic carbon and was measured by a TOC analyzer (TOC-Vcph Total Organic Carbon Analyzer, Shimadzu, Japan). The phosphate concentration was determined by ion chromatography (Dionex ICS-1100 RFIC system, Thermo Scientific Dionex, USA). The chloride concentration was measured by a chloride selective electrode (Cole Parmer, USA).

The water content of samples was determined by volumetric Karl Fisher titration, for which a Metrohm 787 KF Titrino was used. The conductivity was measured using a conductivity electrode (Consort, Belgium). Viscosity was measured with a Brookfield DVII+ equipped with a small sample adapter (Brookfield, USA).

2.3. Data analysis

The electrical efficiency of an ion A η_A was calculated using Eq. 1 [30].

$$\eta_A = \frac{\dot{n}_A z F}{i N} \quad (1)$$

With $\dot{n}_A$ the flux of ion A [$\text{mol s}^{-1} \text{ m}^{-2}$], z the valence of ion A, F the Faraday constant [96485 C mol^{-1}], N the number of repeating units and i the current density [A m^{-2}]. The flux was calculated by measurement of the ion concentration and taking into account the change in volume due to the samples taken, osmosis and

electro-osmosis. This flux corresponds with the increase in molar amount of ion A in the product compartment or the decrease in molar amount in the diluate compartment. It was found that both values correspond well. However, the best accuracy was achieved when a large variation in concentration was measured. The change in concentration was larger in the compartment with the lowest salt concentration.

3. Results and discussion

3.1. Properties of choline dihydrogen phosphate

Choline dihydrogen phosphate is a solid at room temperature with a melting point of 119°C [31]. Starting from a water content of approximately 20 (w/w)%, a viscous liquid is formed [23]. To estimate which is the maximum concentration of an aqueous solution at which choline dihydrogen phosphate can be synthesized using electrodialysis metathesis, two physical properties of aqueous choline dihydrogen phosphate solutions are determined. An overview of the conductivity at various choline dihydrogen phosphate concentrations is shown in Figure 2a. Up to a concentration of 2 mol L⁻¹, an increase in conductivity is observed for an increase in choline dihydrogen phosphate concentration. At higher concentrations, the conductivity starts decreasing as a result of the increasing viscosity. This principle is known as the Walden Rule, which states that the product of the limiting molar conductivity and the solvent's viscosity is constant for infinitely diluted electrolyte solutions [32]. Regarding the metathesis process, the decreasing conductivity also limits the maximum obtainable ionic liquid concentration. The lower conductivity at high choline dihydrogen phosphate concentration will result in a higher energy consumption for the production of highly concentrated solutions.

The viscosity was determined at two temperatures, namely 25 and 40°C (cf. Figure 2b). Above a concentration of 3.5 mol L⁻¹ choline dihydrogen phosphate, a strong increase in viscosity is observed. In an electrodialysis stack, a high viscosity of a solution will result in large pressure drops across a compartment, a poor distribution of the fluid over the membrane and consequently a concentration polarisation. Therefore, the maximum choline dihydrogen phosphate concentration that can be achieved with electrodialysis metathesis would be between 3.5 and 4 mol L⁻¹. These concentrations correspond to a water content of approximately 36(w/w)% and 26 (w/w)%, respectively. To perform the electrodialysis experiments, 3.4 mol L⁻¹ was chosen as the high initial value for the choline dihydrogen phosphate concentration.

Figure 2: Conductivity (a) and viscosity (b) of aqueous solutions of choline dihydrogen phosphate.

3.2. Optimization of the electrodialysis process

3.2.1. Electrical efficiency

The electrical efficiency for the transportation of dihydrogen phosphate and choline ion from the two diluate compartments towards the product compartment is shown in Figure 3 and Figure 4, respectively. The highest electrical efficiency is observed for the migration of choline to the product compartment. In all experiments, dihydrogen phosphate is transported with a lower electrical efficiency. In the experiments with intermediate level of all parameters, the electrical efficiency for choline and dihydrogen phosphate amounts to $98.0 \pm 0.2\%$ and $84.8 \pm 0.9\%$, respectively.

The efficiency of dihydrogen phosphate is calculated assuming that the ion is transported as a monovalent ion. However, in a typical experiment, the pH in the product compartment increases from 3.15 at the beginning to 3.43 at the end of the experiment. Beside the transport of dihydrogen phosphate, the transport of hydrogen phosphate (HPO_4^{2-}) occurs as well. This results in a lower phosphate concentration compared to choline in the product compartment.

In addition, the electrical efficiency for the migration of dihydrogen phosphate decreases strongly if the current density increases. At the same time, the use of a higher current density results in a larger voltage difference across the stack. For example, at a diluate concentration of 1 mol L^{-1} and a product concentration of 1 mol L^{-1} choline dihydrogen phosphate, the voltage difference increases from 2.8 to 4.5 V per repeating unit for an increase in current density from 100 to 200 A m^{-2} . The higher voltage difference facilitates the transport of the bivalent hydrogen phosphate. Furthermore, it is also observed that the electrical efficiency for choline transport (cf. Figure 4) is lower at a higher current density.

Figure 3: Overview of the electrical efficiency of dihydrogen phosphate as a function of current density, diluate concentration and choline dihydrogen phosphate concentration.

A change in choline dihydrogen phosphate concentration and diluate concentration has a similar result on both the electrical efficiency of choline and dihydrogen phosphate. The increase in choline dihydrogen phosphate concentration and decrease in diluate concentration results in a lower electrical efficiency. This tendency is a result of the concentration gradient between the diluate and concentrate compartment. As a consequence of the applied electrical field, ions are transported from the diluate towards the concentrate compartment. At a high concentrate concentration, this concentration gradient results in diffusion of ions from the concentrate to the diluate compartment. Due to the two opposite tendencies a decrease of electrical efficiency is observed. This phenomenon is commonly referred to as back diffusion [33]. On the contrary, if the concentration gradient between the diluate and concentrate compartment is positive, electrical efficiencies for choline transport higher than 100% are obtained due to the combination of migration and diffusion.

Figure 4: Overview of the electrical efficiency of choline as a function of current density, diluate concentration and choline dihydrogen phosphate concentration.

3.2.2. Electrical potential difference

In this paragraph, the electrical potential or voltage difference needed for the electrodialysis metathesis process is discussed. All experiments are performed at a fixed current density of either 100 or 200 A m⁻². Therefore, the voltage difference directly indicates the change in electrical resistance of the electrodialysis process (cf. Figure 5). In electrodialysis, the stack resistance is predominately determined by the conductivity of the least conducting compartment. For all profiles, the voltage difference decreases as a function of time. This is caused by the increase in temperature of the different vessels and increasing conductivity of the salt streams. For example, in a typical experiment, the temperature of the product stream increases from 295 K at the beginning towards 303 K at the end of the experiment.

The highest voltage differences are observed for the highest current density. In addition, the increase in diluate concentration results in an decrease in electrical resistance (34.1 and 49.5 mS cm^{-1} at a concentration of 1 and $4 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$, 46.6 and 71.1 mS cm^{-1} at a concentration of 1 and 4 mol L^{-1} choline chloride). The choline dihydrogen phosphate concentration in the product compartment has only a minor influence on the electrical resistance. This tendency is caused by the small difference in conductivity of both choline dihydrogen phosphate solutions (21.5 and 10.9 mS cm^{-1} at a concentration of 1 and 3.4 mol L^{-1}).

Figure 5: Voltage difference across the stack as a function of current density, diluate concentration and choline dihydrogen phosphate concentration (a: 1 mol L^{-1} CHDP and b: 3.4 mol L^{-1} CHDP).

3.2.3. Transport of impurities

The analytical method used for the determination of chloride reveals that the chloride concentration in the product compartment does not increase significantly. As a consequence, it is assumed that the chloride flux is very small and comparable to or smaller than the sodium flux. Similar observations concerning the magnitude of unwanted cation or anion fluxes were made for other electrodialysis metathesis processes [28, 34]. For example, Jaroszek et al studied the synthesis of KNO_3 by electrodialysis metathesis; it was found that the product stream was more contaminated by cations (Na^+) than by anions (SO_4^{2-}). In addition, the production of MgCl_2 and Na_2SO_4 by electrodialysis metathesis was investigated by Alhritire et al. The result show that the MgCl_2 stream was more contaminated by Na^+ than the Na_2SO_4 stream by Cl^- [34].

An overview of the sodium flux towards the product compartment is shown in Figure 6. An increase in flux is observed for an increase in current density and diluate concentration. To investigate the influence of these operating parameters on the sodium transport and the origin of this flux, one experiment was studied in more detail. Additionally, the sodium flux increases with an increase in choline dihydrogen phosphate concentration in the product compartment. The thickness of the Neosepta CMS membrane

decreases from $158 \pm 1 \mu\text{m}$ to $153 \pm 1 \mu\text{m}$ in contact with a 1 mol L^{-1} and 3.4 mol L^{-1} choline dihydrogen phosphate solution, respectively. This phenomenon is known as osmotic de-swelling [35]. It is assumed that this de-swelling facilitates the transport of smaller ions such as sodium compared to large ions such as choline.

Figure 6: Overview of the sodium flux towards the product compartment as a function of the current density, diluate concentration and choline dihydrogen phosphate concentration.

In Figure 7, an overview of the transport rate of sodium to the product compartment in different experiments is shown. In the first experiment, the sodium flux of a typical metathesis experiment (concentrate 1: $0.3 \text{ mol L}^{-1} \text{ NaCl}$, diluate 1: $1 \text{ mol L}^{-1} \text{ ChCl}$, concentrate 2: $1 \text{ mol L}^{-1} \text{ CDHP}$, diluate 2: $1 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$ and $i: 200 \text{ A m}^{-2}$) with a sodium salt in the electrode solution (Na_2SO_4), concentrate 1 and diluate 2 compartment is shown. This flux amounts to a total of $2.7 \mu\text{mol s}^{-1} \text{ m}^{-2}$. In the other experiments, the sodium salts are systematically replaced by potassium salts. A summary of the different contributions to the total sodium flux is shown in the rightmost bar of Figure 7.

The use of K_2SO_4 (black bars) instead of Na_2SO_4 (grey bars) in the electrode rinsing solution results in a large decrease in sodium flux of on average $1.8 \mu\text{mol s}^{-1} \text{ m}^{-2}$. Moreover, the decrease is approximately identical comparing both black and grey bars. This tendency is caused by the pretreatment of the membranes. Before every experiment, membranes were placed in the stack and rinsed with two $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ solutions during one hour with an applied current density of 200 A m^{-2} . One KNO_3 solution was used for both diluate compartments, the other KNO_3 solution was used for both concentrate compartments. Because a Na_2SO_4 electrode rinsing solution was used, the concentrate 1 compartment and the KNO_3 solution were polluted by sodium ions (cf. Figure 1). After one hour, the total amount of sodium in the concentrate stream amounts theoretically to $4.8 \cdot 10^{-2} \text{ mol}$ at a current density of 200 A m^{-2} .

Further, it is hypothesized that sodium is sorbed into the cation-exchange membranes and released during the electrodialysis metathesis process. A sodium flux of $2 \mu\text{mol s}^{-1} \text{m}^{-2}$ during two hours requires a sorbed sodium amount of $9.2 \cdot 10^{-5} \text{ mol}$. Taken into account the ion-exchange capacity of Neosepta CMS membranes ($2.0 - 2.5 \text{ mmol (g dry membrane)}^{-1}$ [36]), the required sodium amount corresponds with a substitution rate of 5%. Because this pathway of impurities is solely caused by the procedure used, these type of impurities are not expected to occur in a longterm metathesis process.

Figure 7: Influence of the use of different sodium and potassium salts on the sodium flux towards the product compartment (concentrate 1: $0.3 \text{ mol L}^{-1} \text{ NaCl}$, diluate 1: $1 \text{ mol L}^{-1} \text{ ChCl}$, concentrate 2: $1 \text{ mol L}^{-1} \text{ CDHP}$, diluate 2: $1 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$ and $i: 200 \text{ A m}^{-2}$).

By replacing NaCl with KCl in the concentrate 1 compartment, the contribution of the sodium salt in the diluate 2 compartment to the total sodium flux is investigated. As can be seen in Figure 7, the use of a sodium salt in the second diluate compartment results in a very small sodium flux towards the product compartment. The flux amounts to $0.02 \mu\text{mol s}^{-1} \text{m}^{-2}$, which corresponds with 1% of the total sodium flux and can be considered negligible. This flux is caused by migration of sodium as a co-ion through the adjacent Neosepta ACS membrane opposed to the direction of the electrical field. This flux is obtained at a diluate concentration of 1 mol L^{-1} . Using the results in Figure 6, a change in diluate concentration from 1 to 4 mol L^{-1} , results in a sodium flux increase of $1.1 \mu\text{mol s}^{-1} \text{m}^{-2}$ on average. This is a large increase compared to the sodium migration caused by a 1 mol L^{-1} diluate. Therefore, it is recommended to use a low diluate concentration to minimize this type of impurity pathway.

Subsequently, the sodium transport originating from the NaCl concentrate 1 compartment was studied. This transport is larger and amounts to $0.8 \mu\text{mol s}^{-1} \text{m}^{-2}$, which corresponds to 30% of the total sodium flux. This flux is caused by co-ion transport of Na^+ from the NaCl compartment to the ChCl compartment, followed by migration as a counter-ion towards the product compartment. Under the tested conditions, this sodium flux is more than 30 times higher than the sodium flux caused by the use of the NaH_2PO_4 diluate.

However, this type of impurity transport can be minimized by maintaining a low NaCl concentration in the concentrate 1 compartment. Additionally, an increase in current density facilitates this type of sodium pollution. The results in Figure 6 show that the sodium flux is increased on average $1.0 \mu\text{mol s}^{-1} \text{m}^{-2}$ for an increase in current density from 100 to 200 A m^{-2} .

To determine the optimal operating parameters for the production of choline dihydrogen phosphate, the ratio of the molar choline and sodium flux towards the product compartment is discussed (cf. Figure 8). The highest ratios are observed at a low choline dihydrogen phosphate concentration and high current density. Although a high current density increases the sodium flux towards the product compartment, the increase in choline flux is larger and results in a higher ratio. An increase in diluate concentration reduces the product purity because of the smaller ratio. As a consequence, a low diluate and product concentration are preferred to maximize the product purity.

Figure 8: Ratio of the choline and sodium flux towards the product compartment as a function of current density, diluate concentration and choline dihydrogen phosphate concentration.

3.3 Transport of impurities at high current density

To investigate the maximum current density at which the electrodialysis metathesis can be conducted, a current voltage profile is included (cf. Figure 9). This profile is recorded at the optimal salt concentrations regarding product purity (concentrate 1: $0.3 \text{ mol L}^{-1} \text{ NaCl}$, diluate 1: $1 \text{ mol L}^{-1} \text{ ChCl}$, concentrate 2: $1 \text{ mol L}^{-1} \text{ CDHP}$ and diluate 2: $1 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$). A linear increase in voltage difference is observed for an increase in current density. In the occurrence of a limiting current density, a steep increase in voltage difference would be observed [37]. Therefore, under the conditions tested, no limiting current is observed.

According to data provided by the manufacturer of the stack [38], the voltage drop per compartment should not exceed 1 V. In this four compartment metathesis setup, this corresponds with a voltage drop of 4 V per repeating unit. As can be seen in Figure 9, the maximum current density in this setup is 300 A m^{-2} .

Figure 9: Current voltage profile of the electrodialysis metathesis process (concentrate 1: 0.3 mol L^{-1} NaCl, diluate 1: 1 mol L^{-1} ChCl, concentrate 2: 1 mol L^{-1} CDHP and diluate 2: 1 mol L^{-1} NaH_2PO_4).

Subsequently, an experiment at a current density of 300 A m^{-2} was performed. In this experiment, a K_2SO_4 electrode rinsing solution is used to avoid contamination by the pretreatment (cf. Paragraph 3.2.3). The results of this experiment are summarized in Table 1. At the optimal settings (current density of 300 A m^{-2} , 1 mol L^{-1} diluate solutions, 0.3 mol L^{-1} NaCl concentrate and 1 mol L^{-1} choline dihydrogen phosphate in the product compartment), a current efficiency of 94.0% and 58.6% was achieved for choline and dihydrogen phosphate, respectively. The molar flux ratio of choline compared to sodium amounts to $3.6 \cdot 10^2$ approximately. In this case, an aqueous choline dihydrogen phosphate solution is produced with a composition (solvent-free basis) of 61.6 mol% choline, 38.3 mol% H_2PO_4^- , 0.017 mol% Na^+ and <0.017 mol% Cl^- . The purity of the ionic liquid can be compared with data reported in the literature describing the purity of other synthesis routines [10]. As described in the introduction of this paper, the impurity of the ionic liquid 1-butyl-3-methylimidazolium nitrate made by a metathesis reaction of 1-butyl-3-methylimidazolium chloride with NaNO_3 amounts to 1.1 mol% Na^+ and 18 mol% Cl^- . Compared to the metathesis reaction, a higher purity can be achieved by using silver salts. For example, the use of AgNO_3 instead of NaNO_3 for the metathesis reaction results in a very low impurities concentration, namely <0.22 mol% Na^+ and 0.22 mol% Cl^- . Based on these data, the electrodialysis metathesis process yields a product purity which is comparable with a metathesis process using silver salts.

Table 1: Characteristics of the optimal experiment (concentrate 1: 0.3 mol L⁻¹ NaCl, diluate 1: 1 mol L⁻¹ ChCl, concentrate 2: 1 mol L⁻¹ CDHP, diluate 2: 1 mol L⁻¹ NaH₂PO₄ and $i = 300 \text{ A m}^{-2}$).

$\eta_{\text{Ch}^+}/\%$	$\eta_{\text{H}_2\text{PO}_4^-}/\%$	$\dot{n}_{\text{Na}^+}/$ $\mu\text{mol s}^{-1} \text{ m}^{-2}$	Flux ratio Ch ⁺ /Na ⁺ / -
94.0	58.6	0.80	$3.6 \cdot 10^2$

3.4. Economic evaluation

To estimate the operating and investment cost of the electrodialysis metathesis process, an economic evaluation was performed. The investment cost includes the cost of the stack, power source, membranes, pumps and peripheral cost. The peripheral cost is estimated as 50% of the total cost of the stack, power source, membranes and pumps. An amortization period of 7 years for the equipment [39] and an annual interest rate of 8% was used [40]. The operating cost includes the electricity cost of the stack and pumps, the replacement of membranes and maintenance cost. The maintenance cost is estimated as 10% of the peripheral cost. The electricity cost is estimated as 0.1 € kWh⁻¹. The membrane lifetime is estimated as 5 years [41, 42]. Either Neosepta CMS cation-exchange membranes or Neosepta ACS anion-exchange membranes were used.

The evaluation is performed using one stack containing 60 repeating units with each a membrane area of 0.16 m² (ED Q1600, PCCell GmbH). The process is evaluated for the optimal conditions, namely a current density of 300 A m⁻², 1 mol L⁻¹ diluate (choline chloride and sodium dihydrogen phosphate) and production of a 1 mol L⁻¹ choline dihydrogen phosphate solution and a 0.3 mol L⁻¹ NaCl solution. Further, it is assumed that the stack is operated in feed and bleed mode. This means that pure water is added to the product compartment and as a bleed the desired choline dihydrogen phosphate concentration of 1 mol L⁻¹ is obtained. An estimation of the operating and investment cost is shown in Figure 10.

Figure 10: Estimation of the investment and operating cost of the electrodialysis metathesis process.

The investment cost amounts to a total of approximately 140,000 euro and is predominately determined by the stack and power source cost. Regarding the operating cost, an annual total cost of 26,000 euro is estimated. The cost of electricity used for the metathesis process in the stack (i.e., migration of ions) is higher than the electricity cost required to operate the pumps for the recirculation of the salt streams. This installation will yield a total of 8.9×10^5 mol choline dihydrogen phosphate per year. Therefore, the total cost of the electrodialysis metathesis process amount to 0.06 € mol^{-1} or 0.30 € kg^{-1} of choline dihydrogen phosphate.

However to obtain a solid product, the remaining water content must be removed. This production step is not included in the economical evaluation. A possible process flow diagram of this process is shown in Figure 11. After the electrodialysis process, an addition of phosphoric acid is necessary to obtain equimolar amounts of choline and dihydrogen phosphate. Solid choline dihydrogen phosphate can be obtained by crystallisation.

Figure 11: Process flow diagram for the recuperation of choline dihydrogen phosphate.

4. Conclusion

In this work, the production of choline dihydrogen phosphate by means of electrodialysis metathesis is investigated. Several operating parameters are examined in view of the optimization of the product purity and overall process performance. The experiments indicate that the metathesis process is preferably conducted at a high current density (300 A m^{-2}), a low diluate concentration (1 mol L^{-1} choline chloride and 1 mol L^{-1} sodium dihydrogen phosphate) and a low choline dihydrogen phosphate concentration (1 mol L^{-1}). At optimal conditions, the electrical efficiency of choline and dihydrogen phosphate amount to 94.0% and 58.6%. Due to the lower flux of dihydrogen phosphate, an addition of phosphoric acid is necessary to achieve an equimolar amount of choline and dihydrogen phosphate in the final product.

Additionally, an economic evaluation was performed to estimate the cost of the electrodialysis metathesis process. Under the conditions tested, the cost amounts to 0.06 € per mole of choline dihydrogen phosphate.

In the electrodialysis metathesis process, the impurities in one concentrate compartment originate from the two diluate compartments and the other concentrate compartment. The magnitude of the flow of impurities is determined by the voltage difference across the stack and the ion concentration in the salt streams. In the experiments in this paper, the flow of impurities originating from the diluate compartment becomes insignificant at a diluate concentration of 1 mol L⁻¹ or lower. At high current densities, it was observed that the flux of desired ions increased more than the flux of undesired ions. Therefore, it is possible to achieve a higher product purity at high current densities. A product purity comparable with metathesis processes using silver salts can be obtained using electrodialysis metathesis.

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Highlights

- Production of choline dihydrogen phosphate using electrodialysis metathesis
- Very high product purity obtained, comparable with silver metathesis reaction
- Quantification of transport mechanism of impurities in electrodialysis metathesis
- Economic evaluation of electrodialysis process was performed