Transfer of neutral organic solutes during desalination by electrodialysis: Influence of the salt composition

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ABSTRACT

Electrodialysis is a promising process to treat saline water containing organic solute. The desalination performances are fixed by the transfer of salts and organic solutes. On the contrary to the transfer of salts, few results were reported regarding that of organic compounds. This is the objective of this work to investigate the transfer of neutral organic solutes (acetic acid, phenol, glucose) through ion-exchange membranes, focusing on the influence of the salt (NaCl, $MgCl_2$, Na_2SO_4). Results show that the water transfer due to electroosmosis depends on the salt composition following the ion hydration. Two contributions, diffusion and convection, are pointed out for the transfer of organic solutes. Both are important and mainly fixed by steric effect. Concerning the influence of the ion hydration, reverse trends are found for both contributions. Decreasing diffusion flux is observed for increasing membrane counterion hydration showing the influence of the membrane structural properties. Increasing convection flux is observed for increasing ion hydration showing the influence of the solute hydration.

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1. Introduction

Increasing quantities of saline water are produced most of the time with an organic content [1]. The organic content can be either hazardous pollutants to treat (e.g. pharmaceutically active compounds, hormones, pesticides etc.) or valuable resource to recycle (e.g. organic acids, sugar, protein etc.). Considering the tightening environmental regulations and further economic value, the treatment and disposal of such saline waters has to be improved.

Membrane based separation can play a primary role in desalination as shown by many successful applications using reverse osmosis (RO) and electrodialysis [2,3]. But once separation of salt and organic solute is concerned, membrane processes with selectivity like nanofiltration (NF) or electrodialysis (ED) are required. ED can be used in a wide range of salinity unlike NF for which osmotic pressure is a limit. The desalination can also be controlled by fixing the current and time, and this makes ED a very flexible process [3,4]. ED was used for desalination of complex saline solutions in food, beverage, drug and chemical industries as well as in biotechnology and wastewater treatment [5–8].

Although ED is a mature process for many applications, some fundamental bottlenecks remain concerning the transfer of solutes through ion-exchange membranes (IEM) during desalination [3,9].

The salt and water transfer was already investigated in previous studies [10–13]. Indeed, during desalination by ED, the salt

transfer is accompanied by a transfer of water due to electroosmosis, resulting from the shell of water carried by the migrating ions.

A thorough understanding of transport phenomena of organic solutes through IEM is also necessary. However, previous studies mainly focus on the transfer of organic solutes in the case of pressure-driven membrane operations like NF or RO [14,15]. The few works dealing with the transfer of organic solutes through IEM concern a limited number of solutes like trace organic contaminants and organic acids [16–18]. Moreover, these studies focus on the solute sorption in the membrane and on the process performance while the solute transfer mechanisms are very little discussed.

The influence of salt on the transfer of organic solutes through IEM, e.g. in brines, is also an important concern. Recent studies have pointed out that the transfer of organic solutes is strongly dependent on the salt composition. Again, it was mainly reported in NF conditions [19–26] but also with IEM [27–29]. The salt concentration and nature, more specifically the ion hydration, was reported to modify the diffusion of saccharides through IEM because of the change of the membrane properties according to the counter-ion hydration [27]. Further computational approach considering the CMX-cation-glucose system has demonstrated that the polymer chain-chain interaction inside the membrane matrix varies according to the hydration of the membrane counter-ion [30]. However, such studies are limited to saccharides, while the influence of the salt on the transfer of other kinds of organic solutes remains to be explored.

The aim of this study is thus to investigate the transfer of organic solutes during the desalination of saline waste waters by ED. The mechanism controlling the transfer of organic solutes through IEM and the influence of the salt are systematically studied in different conditions, without and with current. Synthetic solutions of different compositions, containing neutral organic solutes of varying characteristics (acetic acid, phenol and glucose) and different salt compositions (NaCl, MgCl$_2$, Na$_2$SO$_4$) are used.

2. Mass transfer mechanisms

2.1. Salt transfer

In the ED process, the salt flux, j_s (eq m^{-2} s^{-1}), is the sum of two contributions. The first one is a flux due to the chemical potential gradient, i.e. a diffusion flux, j^{diff}, caused by the difference of solute's concentration across the membrane and directed towards the compartment of decreasing concentration. The other one is the flux due to the electrical potential gradient, i.e. the migration flux, j^{mig}, caused by the electrical current. [3]. Then the salt transfer is expressed by the following equation:

$$j_s = j^{diff} + j^{mig} \tag{1}$$

It was shown that the diffusion contribution can be neglected compared to that of migration in most of the ED conditions [7,31]. Furthermore, since the migration flux is proportional to the current, the following equation is obtained for the flux density, in which α (eq m^{-2} s^{-1} A^{-1}) will be referred as the current coefficient:

$$j_s \approx j^{mig} = \alpha I \tag{2}$$

2.2. Water transfer

In the same manner, the water transfer in ED is the result of two contributions, osmosis (j^{os}) and electroosmosis (j^{eo}), as expressed in the following equation:

$$j_w = j^{os} + j^{eo} \tag{3}$$

where the osmotic flux is due to the chemical potential gradient across the membrane, while the electroosmotic flux is due to the water transfer caused by the ion migration through the membranes [3].

Usually in ED, the water flux caused by osmosis can be neglected compared to that of electroosmosis [7,11,31–33]. Owing to its link to the salt transfer, this flux j^{eo} is also proportional to the current. Introducing an electroosmotic coefficient, β (m^3 m^{-2} s^{-1} A^{-1}), the expression of the water flux density can be written as in Eq. (4):

$$j_w \approx j^{eo} = \beta I \tag{4}$$

2.3. Transfer of a neutral organic solute

The first contribution to the transfer of a neutral solute is diffusion caused by the concentration gradient across the membrane. This is the most reported contribution [34]. But it was demonstrated that an additional convective contribution is also involved [7] and that this contribution may not be negligible compared to diffusion [35–38]. Then, the neutral organic solute flux, j_{org}, can be expressed as the sum of the diffusion flux, j_{org}^{diff}, and the convective flux, j_{org}^{conv}, according to Eq. (5):

$$j_{org} = j_{org}^{diff} + j_{org}^{conv} \tag{5}$$

The diffusion flux due to concentration gradient can be further expressed as:

$$j_{org}^{diff} = P_{org} \Delta C_{org} \tag{6}$$

where ΔC_{org} is the concentration gradient across the membrane ($\Delta C_{org} = C_{org,D}^0 - C_{org,C}^0$) and P_{org} (m s^{-1}) is the solute permeability. In this study ΔC_{org} is assumed to be constant and equal to the concentration in the diluate (feed), $C_{org,D}^0$, since the amount of neutral organic solute transferred is negligible compared to the initial amount in the diluate compartment. This will be further discussed later.

The convective flux of a solute through a permeable membrane separating two well-mixed compartments can be expressed from the equation, derived from irreversible thermodynamics [7,39]:

$$j_{org}^{conv} = \bar{C}_{org}(1 - \sigma)j_w \tag{7}$$

where $\bar{C}_{org}$ is the mean solute concentration on either side of the membrane, assumed to be equal to the initial concentration in the diluate compartment, $C_{org,D}^0$ as aforementioned. σ is the reflection coefficient, which varies from 0 for a freely permeable solute to 1 for a non-permeating solute.

Therefore, the total flux can be expressed as follows, combining Eqs. (4 to 7):

$$j_{org} = j_{org}^{diff} + \bar{C}_{org}(1 - \sigma)j_w = j_{org}^{diff} + \bar{C}_{org}(1 - \sigma)\beta I \tag{8}$$

where the aforementioned water transfer under current refers to the electroosmotic flux, which is proportional to current. Thus, one can consider that the convection flux is proportional to the current in the ED process. The equation can be further simplified as Eq. (9):

$$j_{org} = j_{org}^{diff} + \gamma I \tag{9}$$

introducing the convective coefficient γ (mol m^{-2} s^{-1} A^{-1}) to characterize the convective contribution to the solute transfer.

From Eqs. (8) and (9), one can also determine the reflection coefficient of the organic solute, σ_{org}, as shown in Eq. (10):

$$\sigma_{org} = 1 - \frac{\gamma}{\beta \times C_{org,D}^0} \tag{10}$$

3. Materials and methods

3.1. Chemicals

Three different salts containing ions of various hydrations were selected: NaCl, Na$_2$SO$_4$, MgCl$_2$. The corresponding ion hydration numbers are given in Table 1, with the order of sequence for cations: Na$^+$ < Mg^{2+} and anions: Cl$^-$ < SO$_4^{2-}$ [11,40]:

The organic solutes used in the experiments are listed in Table 2. They were chosen to be representative of the ones that can be found in industrial effluents or other saline waters, and have different molecular weights (M$_w$) and hydrophilicity.

The pH values of the solutions containing organic solute, without any adjustment, are shown in Table 2, regardless of the presence of salt. One can see that the acetic acid solution has a pH value ca. 3.0. Then, according to its pKa, less than 5% of the acetic acid can be in the dissociated form (acetate). Moreover, the organic solute concentration is very low compared to that of inorganic salts in all conditions. It will be thus further considered for the discussion that all the solutes are neutral in the pH conditions investigated. Glucose is the most hydrophilic solute in this study