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

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A B S T R A C T

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, MgCl₂, Na₂SO₄). 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 counter-ion 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.

Keywords:
Electrodialysis
Desalination
Mass transfer
Hydration
Organic solute

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 electro dialysis [2,3]. But once separation of salt and organic solute is concerned, membrane processes with selectivity like nanofiltration (NF) or electro dialysis (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.

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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, MgCl₂, Na₂SO₄) 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_s^{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_s^{mig} , caused by the electrical current. [3]. Then the salt transfer is expressed by the following equation:

$$j_s = j_s^{diff} + j_s^{mig} \quad (1)$$

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:

$$j_s \approx j_s^{mig} = \alpha I \quad (2)$$

2.2. Water transfer

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

$$j_w = j_w^{os} + j_w^{eo} \quad (3)$$

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_w^{eo} is also proportional to the current. Introducing an electroosmotic coefficient, β (m³ m⁻² s⁻¹ A⁻¹), the expression of the water flux density can be written as in Eq. (4):

$$j_w \approx j_w^{eo} = \beta I \quad (4)$$

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):

$$j_{org} = j_{org}^{diff} + j_{org}^{conv} \quad (5)$$

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

$$j_{org}^{diff} = P_{org} \Delta C_{org} \quad (6)$$

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]:

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

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):

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

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):

$$j_{org} = j_{org}^{diff} + \gamma I \quad (9)$$

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):

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

3. Materials and methods

3.1. Chemicals

Three different salts containing ions of various hydrations were selected: NaCl, Na₂SO₄, MgCl₂. The corresponding ion hydration numbers are given in Table 1, with the order of sequence for cations: Na⁺ < Mg²⁺ and anions: Cl⁻ < SO₄²⁻ [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

Table 1
Ion hydration number (mole of H₂O per mole of ion) [11].

Na ⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻
6	15–16	8	13–14

Table 2
Relevant characteristics of the organic solutes.

Name	Chemical Formula	M _w (g.mol ⁻¹)	pKa	pH	log P [*]
Glucose	C ₆ H ₁₂ O ₆	180.16	12.28	6.0 ± 0.5	-2.93
Phenol	C ₆ H ₅ OH	94.11	9.99	5.4 ± 0.3	1.48
Acetic acid	CH ₃ COOH	60.05	4.76	3.0 ± 0.2	-0.32

* Solute hydrophilicity (P as partition coefficient between octanol and water.) [41].

(lowest log P value), followed by acetic acid, while phenol is hydrophobic (highest log P value). This is mainly due to the functional groups as hydroxyl, carboxyl and benzene [42].

Experiments were carried out with synthetic solutions containing organic solutes in water on one hand (referred as organic solute/water systems) and organic solutes in salt solutions on the other hand (referred as organic solute/salt systems).

The salt concentration was fixed at 0.8 eq L⁻¹. The concentration of organic solute was fixed at 0.1 mol L⁻¹.

3.2. Membrane and electrodialysis set-up

The ED experiments were performed with an EUR 2B-10 stack (Eurodia, France). The ED stack comprises 10 cells of anion-/cation-exchange membrane (AEM and CEM respectively) as Neosepta AMX/CMX, Tokuyama Corp, Japan [7,11,31]. For each type of membrane, the effective membrane surface is 0.02 m² per cell, i.e. the total effective membrane surface is 0.2 m².

The ED experiments were operated in batch mode (complete

recycling of diluate, concentrate and electrode solutions). The set-up consists of three separated circuits, for diluate, concentrate and electrode solution, with three 4 L vessels. The feed flow rates were set at constant values of 180 L h⁻¹ for both diluate and concentrate compartments, and 360 L h⁻¹ for the electrode solution. All the experiments were carried out at constant temperature 25 ± 1 °C using a circulating thermostatic bath [11].

The electrode compartment was fed with 3 L of Na₂SO₄ solution at a concentration of 10 g L⁻¹. For the study of the transfer of organic solutes, the diluate was initially fed with 2 L of the salt solution containing the organic solute, while the concentrate was fed with 2 L of the solution at the same salt composition but without organic solute (Section 3.3).

3.3. Experimental procedures

For each salt composition, the membranes were first soaked in a solution exactly the same as that used in ED experiments, using a procedure reported elsewhere [11,27,28]. Since the quantity of ions in the soaking solutions is about 40 times higher than the total ion-exchange capacity of AMX and CMX membranes in the ED stack, one can consider that this soaking procedure ensures a complete exchange of the membrane counter-ion. Even for acidic conditions, i.e. with acetic acid, the IEMs were considered to be equilibrated with the counter-ion present in the salt solution because of the much higher salt concentration compared to that of protons (i.e. concentration ratio $C_{counter-ion}/C_{H^+}$ about 1000).

Then, experiments were carried out without current ($I=0$), under diffusion conditions, and with current ($I\neq 0$) under normal ED conditions. The experimental protocol is illustrated in Fig. 1.

Diffusion experiments were carried out with organic solute/water (Case 1) and the organic solute/salt (Case 2) systems as shown in Fig. 1(a). Due to the concentration difference, diffusion of the organic solute across the membrane from the diluate to the concentrate was observed. The possible water flux in reversed direction due to the osmotic pressure difference between the two

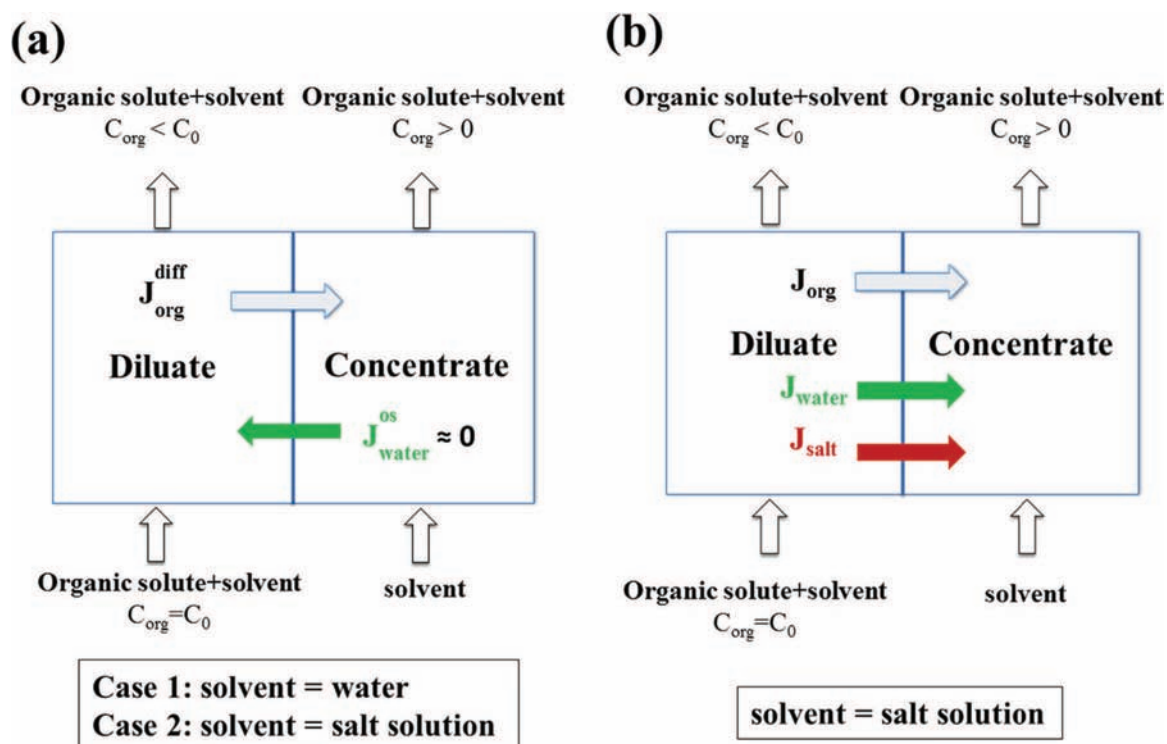


Fig. 1. Protocol for diffusion conditions (a) and normal ED conditions (b).

solutions was found to be negligible because of the low concentration of organic solute.

With the organic solute/water system, the transfer of the organic solute is affected by the interaction between the solute and the membrane, which is previously equilibrated with the counterion. It is thus possible to investigate the influence of the membrane swelling due to different counter-ions on the solute diffusion. In the organic solute/salt system, the transfer of the organic solute results from both effects due to the membrane (i.e. membrane swelling) and the presence of salt in the solution. Thus, the organic solute/salt system enables to study the overall impact of the salt on the transfer [27].

In normal ED conditions, as shown in Fig. 1(b), experiments were carried out at various constant currents (2, 3, 4, 6A), i.e. in the range $0\text{--}300\text{ A m}^{-2}$. The experiment duration was determined according to the final conductivity of the diluate. They were stopped as soon as the conductivity reached 5 mS cm^{-1} in order to keep the current lower than the limiting current for any set of experiments. Consequently, different experiment durations were used according to the operating conditions. The water and solute (ions and organic solute) fluxes were obtained respectively from the variation of the volume and the mass of solute transferred through the membranes versus time.

3.4. Analytical methods

Conductivities, pH and temperature were measured in real-time in the two compartments, as well as the electrical current and voltage.

The salt concentrations were determined by ion chromatography (IEC, Dionex, France) [11]. The concentrations of glucose and acetic acid were measured by high-performance liquid chromatography (HPLC, Jasco, France), using a Shodex SH1011 column, with refractive index detector RI-2031plus. The mobile phase was H_2SO_4 (10 mM) at a flow rate of 1 mL min^{-1} . The injection volume was $20\text{ }\mu\text{L}$ and the temperature was set at $50\text{ }^\circ\text{C}$. Samples from diluate compartment were diluted to a maximum of 200 times and samples from the concentrate compartment to a maximum of 20 times by ultra-pure water (resistivity $>18\text{ M}\Omega\text{ cm}$, Elga, France). The concentration of phenol was measured by ultraviolet (UV) spectroscopy at 270 nm [7]. Samples from the concentrate and the diluate were diluted 20 times and 100 times, respectively.

The mass balances for water and solutes were systematically checked, with a maximum deviation less than 2%, 5% and 10% for

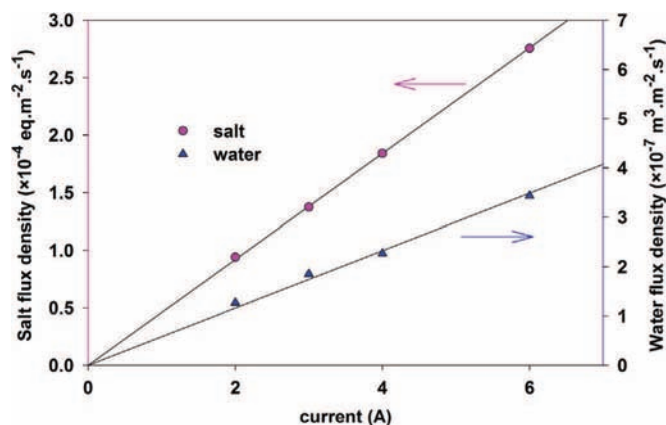


Fig. 3. Variation of salt and water flux densities versus current; glucose/NaCl system, $[\text{organic solute}] = 0.1\text{ mol L}^{-1}$ and $[\text{salt}] = 0.8\text{ eq L}^{-1}$.

water, ions and organic solute respectively.

4. Results and discussion

The transfer of salt and water are firstly investigated, followed by the transfer of neutral organic solute through IEM in two cases (without current and with current). In each case, the influence of the salt on the organic solute transfer is pointed out according to the ion hydration and the corresponding membranes (i.e. AEM and CEM).

4.1. Salt and water transfer

In desalination of the saline water containing organic solute by ED, salt and water transfer are investigated as previously reported in the case of saline water without organic solute [11]. Firstly, the variations of the quantities of salt and water transferred versus time for different current intensities are shown in Fig. 2.

As expected, the quantities of salt (a) and water (b) transferred (from the diluate to the concentrate) increase versus time. As previously mentioned, the mass balance is respected.

One can further observe that the quantities of salt and water transferred increase with the current. For each current, the salt and water transfer vary linearly versus time, which is in agreement with previous results [11]. Then, the salt and water fluxes

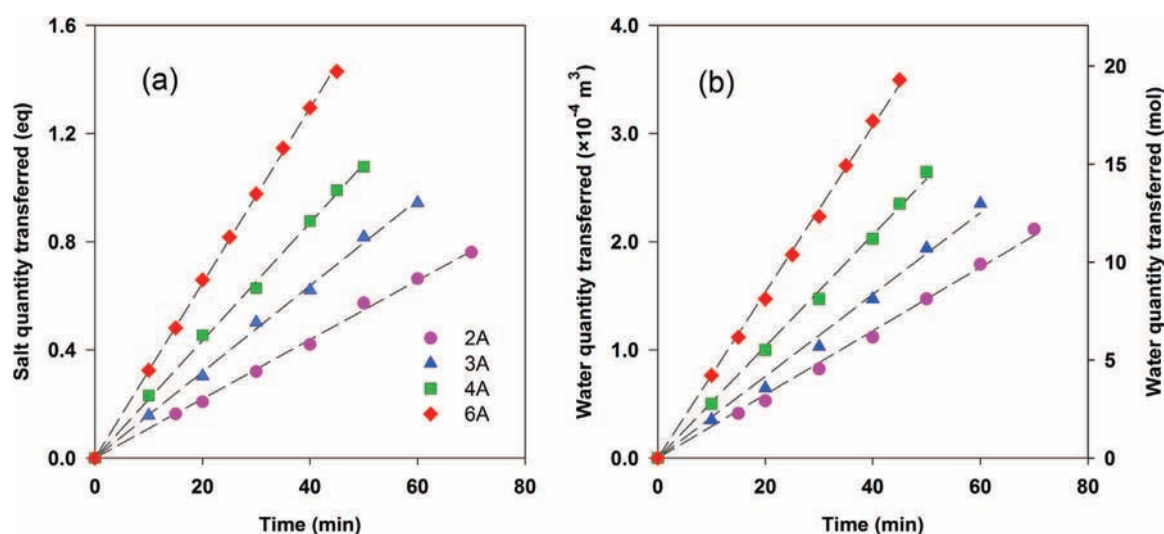


Fig. 2. Variation of salt (a) and water (b) quantity transferred versus time; influence of the current; glucose/NaCl system, $[\text{organic solute}] = 0.1\text{ mol L}^{-1}$ and $[\text{salt}] = 0.8\text{ eq L}^{-1}$.

Table 3
Current coefficient (α , $\text{eq m}^{-2} \text{s}^{-1} \text{A}^{-1}$) for different organic solute/salt systems according to Eq. (2); [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

$\alpha \times 10^{-4} \text{ eq m}^{-2} \text{s}^{-1} \text{A}^{-1}$	Acetic acid	Phenol	Glucose	No organic solute [11]
MgCl ₂	4.7	4.5	5.1	4.9
NaCl	5.1	4.5	5.0	4.6
Na ₂ SO ₄	4.8	4.4	4.9	4.8

Table 4
Electroosmotic coefficient (β , $\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{A}^{-1}$) for different organic solute/salt systems according to Eq. (4); [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

$\beta \times 10^{-8} \text{ m}^3 \text{m}^{-2} \text{s}^{-1} \text{A}^{-1}$	Acetic acid	Phenol	Glucose	No organic solute [11]
MgCl ₂	7.0	6.1	6.6	6.8
NaCl	6.3	5.5	5.9	5.8
Na ₂ SO ₄	5.9	5.1	5.6	5.6

can be obtained from the corresponding slopes. The values of the flux densities (flux divided by the membrane surface) are further plotted on Fig. 3 versus current.

Fig. 3 shows that the variations of both salt and water flux densities are proportional to the current ($R^2 > 99\%$). Same variations are obtained for any condition. This observation confirms that under current, migration dominates the salt transfer as indicated by Eq. (2), while electroosmosis dominates the water transfer as indicated by Eq. (4). Then, the contribution of diffusion to the salt flux and that of osmosis to the water flux are negligible [7].

Then, the corresponding coefficients α and β can be obtained, according to Eqs. (2) and (4), as the slope of the corresponding variations of the salt and water transfer versus current. The values of current coefficients α for all the solutions investigated are reported in Table 3.

One can find that for a given organic solute, the current coefficient α has very small variation according to the salt. Indeed, since the experiments are carried out at a constant current, the total quantity of the salt transferred is fixed.

Concerning the different solutes, one can observe that values obtained with acetic acid and glucose are very close, and also close to those obtained without organic solute. For any salt composition, slightly but systematically lower values are obtained with phenol, compared to those obtained with the two other solutes.

Then, the obtained electroosmotic coefficients characterizing the water transfer are reported in Table 4 for the different systems investigated.

For a given solute, one can observe that β varies according to the salt composition (variation ca. 30%). Moreover, for any solute, the same trend is observed for β according to the salt composition, i.e. MgCl₂ > NaCl > Na₂SO₄. Concerning different organic solutes, Table 4 shows that the values with acetic acid and glucose are close, approximating those obtained without organic solute (difference below 8%). Again, the values obtained with phenol are systematically slightly lower (difference below 12%).

Table 5
Ratio between water and salt transfer (β/α , $\text{m}^3 \text{eq}^{-1}$) for different organic solute/salt systems; [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

$\beta/\alpha \times 10^{-4} \text{ m}^3 \text{eq}^{-1}$	Acetic acid	Phenol	Glucose	No organic solute [11]
MgCl ₂	1.5	1.3	1.3	1.4
NaCl	1.2	1.2	1.2	1.3
Na ₂ SO ₄	1.2	1.2	1.2	1.2

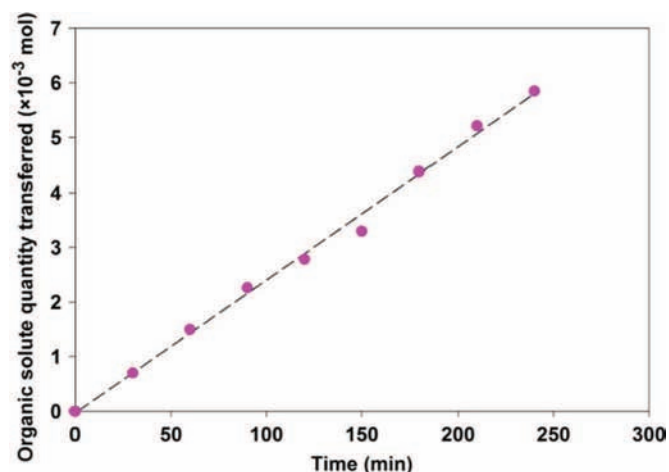


Fig. 4. Variation of the organic solute quantity transferred versus time; diffusion conditions; glucose/NaCl system, [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

Since the coefficient β characterizes the water transfer due to electroosmosis, i.e. the water accompanying the salt migration, the ratio between water and salt transfer, which can be calculated as β/α , characterizes the salt hydration, as explained in a previous work [11]. The values of this ratio obtained for the different systems are reported in Table 5.

For a given salt, very close values of β/α are obtained for the different solutes, including phenol, despite the fact that the respective values of α and β with phenol are slightly lower than those for the other solutes. It means that the salt hydration is constant for the different conditions investigated. Then, the presence of any kind of organic solute (of different nature, size, hydrophilicity, solution pH) doesn't affect the hydration of the ions migrating through the membranes.

4.2. Neutral organic solute transfer

The transfer of organic solute through IEM is studied in two conditions: without current ($I=0$), i.e. diffusion condition, and with current ($I \neq 0$), i.e. normal ED conditions. As previously explained, the transfer of the neutral organic solute with current consists of two contributions, diffusion and convection. The transfer of organic solute without current is firstly discussed, followed by that observed with current [28].

4.2.1. Transfer of neutral organic solute without current

To investigate diffusion, experiments were carried out using water (organic solute/water systems) and salt solutions (organic solute/salt systems) as two different solvents, respectively. Firstly, the variation of the quantity of organic solute transferred through the membranes versus time is shown in Fig. 4, using glucose/NaCl system as an example.

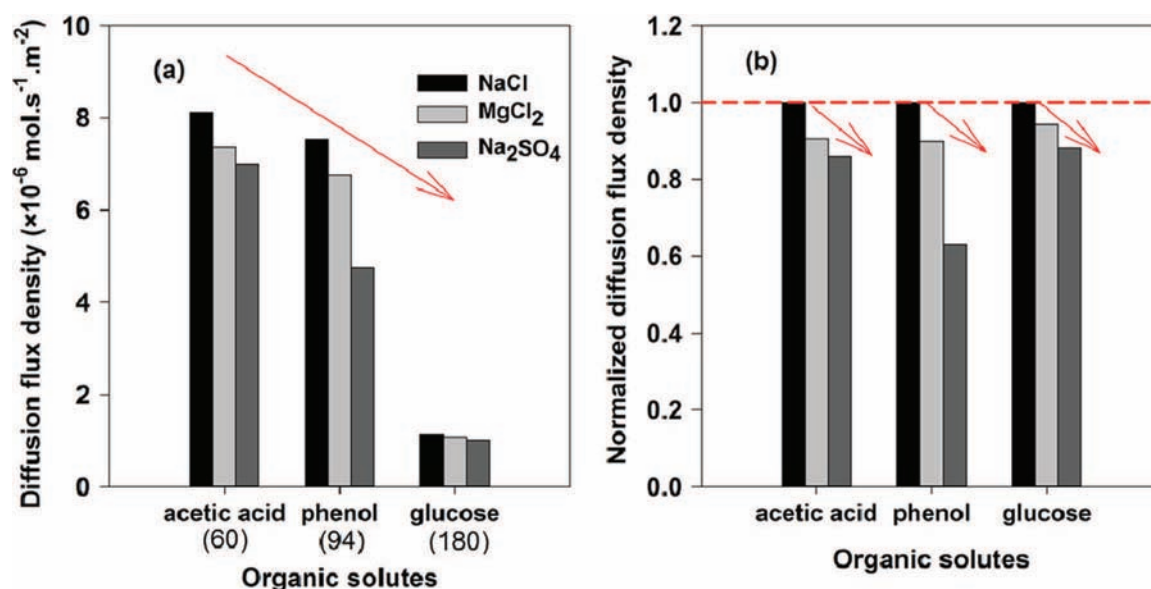
Fig. 4 shows a linear increase of the quantity of organic solute transferred in the concentrate compartment versus time ($R^2 > 98\%$). This is in agreement with Eq. (6), showing that the diffusion flux is proportional to the concentration gradient of the solute across the membrane, which can be assumed to remain constant (variation less than 10%). The same finding is observed for any system investigated in this work.

The diffusion results for organic solute/water systems are reported in Table 6, in comparison with those obtained with organic solute/salt systems.

Some similarities between organic solute/water and organic solute/salt systems can be firstly pointed out.

Table 6Organic solute diffusion flux density for different organic solute/water and organic solute/salt systems; [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

$j_{org}^{diff} \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$	Organic solute/water			Organic solute/salt		
	Acetic acid	Phenol	Glucose	Acetic acid	Phenol	Glucose
NaCl	7.5	7.3	1.1	8.1	7.5	1.2
MgCl ₂	7.2	-	1.0	7.4	6.8	1.1
Na ₂ SO ₄	6.9	4.5	0.9	7.0	4.5	1.0

**Fig. 5.** Variation of organic solute diffusion flux density for different organic solute/salt systems: (a) influence of the solute size; solute M_w , shown in bracket (unit: g mol⁻¹); (b) influence of the salt; [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹; normalized diffusion flux density with the value for NaCl as reference.

Concerning the different organic solutes, for a given salt, the same sequence of the solute diffusion flux in both the organic solute/water and the organic solute/salt systems can be drawn as: acetic acid > phenol > glucose. Indeed, the results show that the diffusion flux densities vary ca. 8 times between glucose and acetic acid in the organic solute/salt systems, e.g. from glucose ca. $1.0 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ to acetic acid ca. $8.0 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$.

Then, concerning the different salts, one can state a same sequence for each organic solute as: NaCl > MgCl₂ > Na₂SO₄. Finally, comparing the two systems, i.e. organic solute/salt and organic solute/water, one can find that even if the values observed are not very different (variation below 10%), those in the organic solute/salt systems are systematically higher than those in the organic solute/water systems.

The results are also illustrated in Fig. 5, using the organic solute/salt systems as an example, in order to discuss the influence of the solute and the salt.

Fig. 5(a) shows a decreasing trend of the solute diffusion flux for increasing solute M_w . One can thus consider that steric effect fixes the diffusion in the organic solute/salt systems. Since similar results are obtained with the organic solute/water systems, one can confirm the role of the steric effect on the diffusion of the neutral solute, with or without salt.

Then, concerning the influence of salt, normalized diffusion flux are plotted for the different systems, using the solute diffusion flux obtained with NaCl as a reference, as illustrated in Fig. 5(b).

It is important to keep in mind that the observed organic solute transfer is due to the flux through two different kinds of membranes (AEM and CEM). Since it was demonstrated that the IEM properties varies according to its counter-ion (cation for CEM and

anion for AEM), it is interesting to consider separately the effect of cation and anion respectively on the diffusion flux of the organic solute. The following trend is obtained:

Cation: NaCl > MgCl₂; Anion: NaCl > Na₂SO₄

When comparing the values obtained with NaCl and MgCl₂, one can consider that the solute transfer through the AEM is identical because of the fixed counter-ion (Cl⁻) and that only the transfer through the CEM is affected. One can state that Mg²⁺, as the more hydrated counter-ion, results in the lower diffusion flux compared to Na⁺ through the CEM. Accordingly, for the AEM, the more hydrated counter-ion, i.e. SO₄²⁻, leads to the lower diffusion flux, compared with Cl⁻. These results show that the sequence of diffusion flux through IEM (CEM and AEM) is reversed compared to the counter-ion hydration. More hydrated counter-ion results in lower flux.

As previously discussed, the objective to study the organic solute/water systems is to investigate the influence of the membrane properties, while the overall influence (membrane swelling and additional salt effect on the solute) can be studied with the organic solute/salt systems. Then, the influence of the salt observed in the organic solute/water systems is firstly discussed, followed by that in the organic solute/salt systems.

4.2.1.1. Influence of the membrane soaking. These results for the organic solute/water systems agree with our previous work dealing with the transfer of sugar through AEM and CEM [27]: the more hydrated counter-ion to equilibrate the membrane, the lower transfer for both water and sugar (Mg²⁺ < Ca²⁺ < Na⁺ < NH₄⁺ and SO₄²⁻ < Cl⁻). It was concluded

that such trend shows a membrane modification, i.e. changes in the membrane structural properties like its free-water content or free volume [27,43,44]. Then, a recent computational investigation considering CMX-cation-glucose-water as case study further demonstrated that this membrane modification takes place at the molecular level [30]. It was observed that the polymer chain-chain interactions inside the membrane are very sensitive to the membrane counter-ion. Then, a more hydrated counter-ion leads to a stronger chain-chain interaction, and thus to a lower sugar transfer.

4.2.1.2. Influence of the presence of salt in solution. Concerning the influence of salt, the present results for the three solutes with the organic solute/salt systems are in agreement with the previous finding with saccharide/salt systems (solute diffusion trend: $\text{Na}^+ > \text{Mg}^{2+}$ and $\text{Cl}^- > \text{SO}_4^{2-}$) [27]. Similar trends with other neutral solutes were also reported, i.e. the diffusion coefficient of boron through CEM for various cations, with a sequence as $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ [38,45] and that of arsenite with a sequence as $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+}$ [45]. It shows that with organic solute/salt systems also, more hydrated counter-ion induces lower solute diffusion flux.

Another result shown in Table 6 is that the solute transfer in the presence of salt is systematically higher than that obtained in water. Considering that thanks to soaking the membrane properties are identical in the two systems, the results suggest a variation of the solute properties due to the presence of salt in the solution. Then, since the transfer is mainly fixed by the steric effect, a higher transfer indicates a decrease of the solute size in the presence of salt compared to water.

These results are in agreement with previous ones [27], showing that the transfer of a neutral solute through IEM is increased by the addition of salt. Such observations were also reported in NF systems [19–24]. Indeed, Boy et al. [24] reported a solute dehydration effect induced by the salt, i.e. a variation of sugar hydration according to the salt composition as demonstrated with apparent molar volume measurements. The hydration of the sugars was found to decrease in the presence of more hydrated ions or with increasing amount of salts, which explains the increase of sugar transfer observed in NF for the organic solute/salt systems. The present results agree with the solute dehydration assumption, not only for glucose, but also for acetic acid and phenol.

Meanwhile, the small diffusion increase due to the solute dehydration and the same trend of diffusion transfer according to the

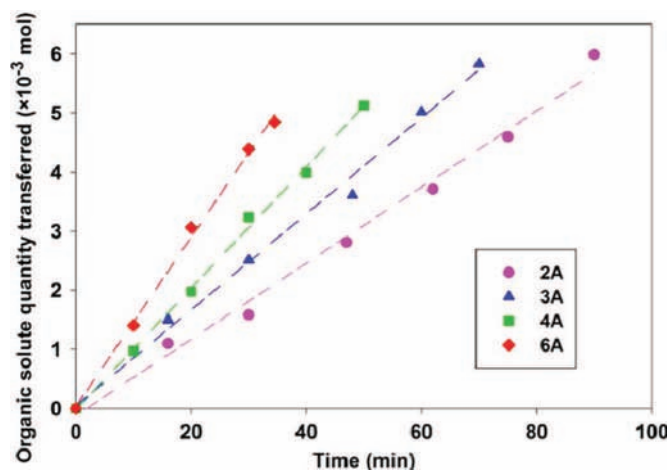


Fig. 6. Variation of the organic solute quantity transferred versus time: influence of the current; glucose/NaCl system, [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

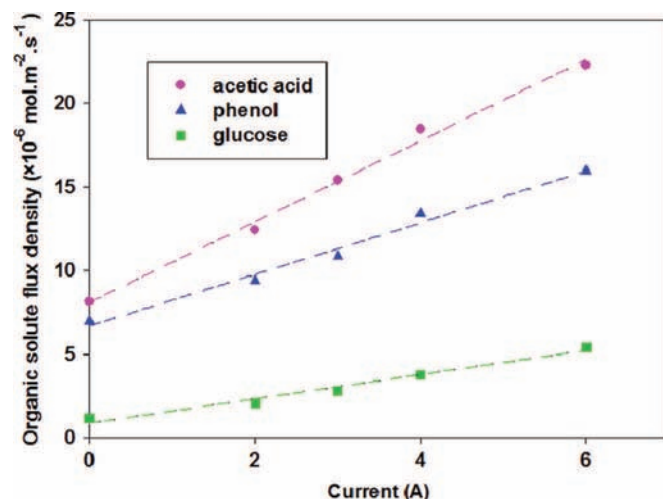


Fig. 7. Variation of organic solute flux density versus current for different organic solute/NaCl systems; [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

salt for the organic solute/salt and organic solute/water systems, suggest that the membrane modification is the main contribution governing the solute diffusion.

Then, the present results concerning the solute diffusion through IEM show that both effects, i.e. the salt induced membrane swelling and solute dehydration, are involved in the different systems with different organic solutes and salt composition. Specifically, one would have expected different behavior with phenol, which is a hydrophobic solute. However, the influence of the salt composition on the phenol diffusion follows exactly the same trends compared to acetic acid and glucose, which are more hydrophilic solutes. The more hydrated membrane counter-ion leads to a lower diffusion of phenol, and the increased concentration of salt leads to a higher phenol transfer. In addition, with acetic acid, i.e. in acidic pH conditions, the findings agree with those at neutral pH conditions (for phenol and glucose).

4.2.2. Transfer of neutral organic solute with current

With current, the transfer of organic solute is subject to the overall impacts of the membrane swelling and the solute dehydration, as in diffusion case for the organic solute/salt systems.

Firstly, the variations of the organic solute quantity transferred versus time for the different applied currents are plotted in Fig. 6, using glucose/NaCl system as an example.

A linear increase of the solute quantity transferred versus time (from diluate to concentrate) can be found under each current. Fig. 6 shows that a higher current intensity leads to a higher solute transfer through the membranes. The same phenomenon is observed for all the conditions investigated.

Then, the organic solute flux density under each current can be determined from the corresponding slope of the linear variation for all the systems ($R^2 > 98\%$). These values are plotted versus current including previous diffusion results ($I=0$) in Fig. 7, showing the variation of different organic solute flux densities with NaCl as an example.

Table 7

Convective coefficients γ for different organic solute/salt systems; [organic solute]=0.1 mol L⁻¹ and [salt]=0.8 eq L⁻¹.

$\gamma \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ A}^{-1}$	Acetic acid	Phenol	Glucose
NaCl	24.3	15.5	7.3
MgCl ₂	25.1	17.9	7.6
Na ₂ SO ₄	30.3	8.8	8.4

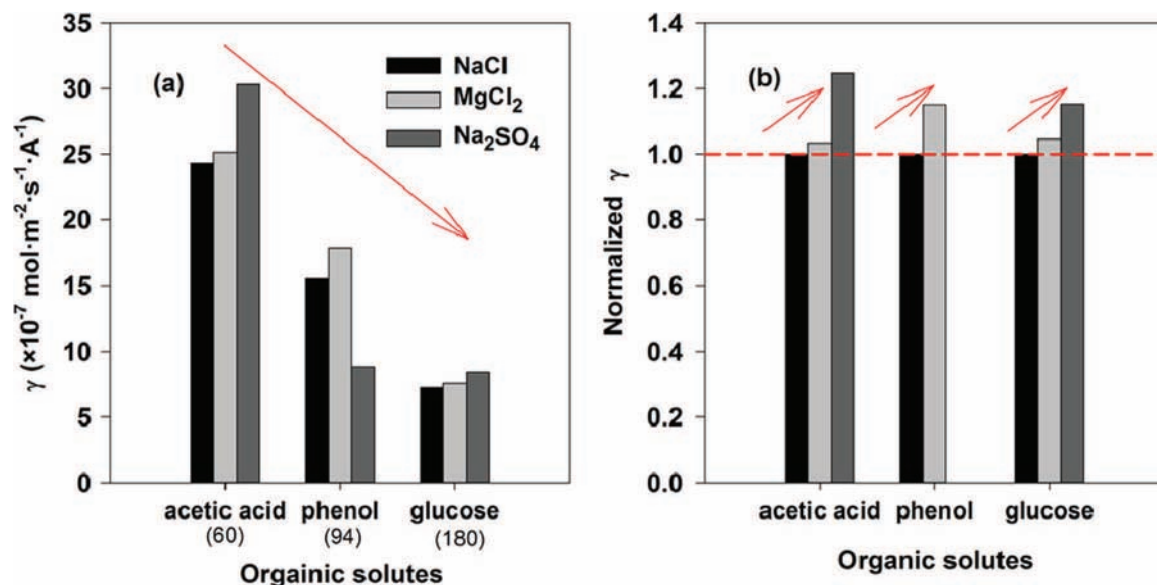


Fig. 8. Variation of convective coefficients γ for different organic solutes: influence of the solute size (a); solute M_w shown in bracket (g mol^{-1}); influence of the salt (b); [organic solute]=0.1 mol L^{-1} and [salt]=0.8 eq L^{-1} ; normalized γ with the value for NaCl as reference in (b).

For each current, the following sequence is observed for the flux: glucose < phenol < acetic acid. This sequence is also found in any system with different salts. These results suggest that the transfer of neutral organic solutes through IEM is governed by steric effect, both without current and with current.

Moreover, Fig. 7 shows a linear increase of the flux density versus the current starting from the value for diffusion ($I=0$). This shows that the additional transfer is proportional to the current. Similar variations are observed for all the organic solute/salt systems investigated in this work, i.e. proportionality of flux with the current ($R^2 > 98\%$).

Such results are in agreement with Eq. (9), considering the two contributions to the solute transfer, i.e. diffusion and convection due to the electroosmosis flux. Moreover, the slope of the linear variation of the flux density versus current provides the convective coefficient γ ($\text{mol m}^{-2} \text{s}^{-1} \text{A}^{-1}$). The γ values obtained for the different systems investigated are reported in Table 7, and plotted in Fig. 8, in the same manner as for diffusion.

Very different γ values are obtained for the different solutes. For a given salt, there is always the order of sequence as: acetic acid > phenol > glucose. It shows that convection flux is mainly fixed by the steric effect. Then, considering the results for diffusion (Table 6) and total flux (Fig. 7), one can state that the steric effect governs the solute transfer through IEM.

Then, for a given solute, concerning the influence of the salt on the convection term, the results in Fig. 8 show the following sequence: $\text{NaCl} < \text{MgCl}_2 < \text{Na}_2\text{SO}_4$ for both glucose and acetic acid.

Concerning phenol, the sequence of γ is $\text{NaCl} < \text{MgCl}_2$, as for the other two solutes. But the γ value of phenol with Na_2SO_4 is surprisingly low. In fact, the observed value is about half those obtained for phenol with other salts, and it is almost as low as the

Table 8
Reflection coefficient σ for different organic solutes: influence of the salt composition [organic solute]=0.1 mol L^{-1} and [salt] = 0.8 eq L^{-1} .

σ	Acetic acid	Phenol	Glucose
MgCl_2	0.64	0.71	0.89
NaCl	0.61	0.72	0.88
Na_2SO_4	0.48	(0.83)	0.85

value obtained for glucose with Na_2SO_4 , despite a much lower size of phenol compared to that of glucose. Then, an additional mechanism rather than steric effect is involved in the phenol convective transfer through the Na_2SO_4 soaked IEM. This exception of phenol convection with Na_2SO_4 will be discussed later. The following discussion begins with the results for the other organic solute/salt systems.

Concerning the influence of salt, Na^+ induces a lower convection than Mg^{2+} , for a given anion (Cl^-); Cl^- induces a lower convection than SO_4^{2-} , for a given cation (Na^+). One can observe that the sequence of the counter-ion effect on the convection contribution is the opposite of that previously pointed out for diffusion (4.2.1), for cation and anion respectively.

These results are in agreement with the previous ones obtained with the same type of IEM and glucose showing an opposite trend of glucose convective transfer ($\text{Na}^+ < \text{Ca}^{2+}$ and $\text{Cl}^- < \text{SO}_4^{2-}$) compared to the diffusion one [28]. Similar finding on solute convection was also reported ($\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$) for the transfer of boric acid as neutral solute through various AEM [38]. All these results suggest that the more hydrated ion (membrane counter-ion) leads to the higher convection flux.

Then, the observed salt effect on the solute convection flux can be further illustrated by using the reflection coefficient σ calculated according to Eq. (10). Table 8 reports the values of the reflection coefficient σ obtained for different organic solute/salt systems.

First, considering the different solutes, one can find an identical sequence for the different salts as: acetic acid < phenol < glucose. These results are consistent with the solute M_w since a higher M_w is expected to give a lower transfer, i.e. higher σ values. They also agree with those previously reported with the same membranes for the transfer of phenol with the phenol/ NaCl system (σ value ca. 0.7) and for the transfer of glucose in different salt systems (σ value ca. 0.9) [7,28].

Concerning the influence of the salt for a given organic solute, one can draw the sequence as $\text{MgCl}_2 \approx \text{NaCl} > \text{Na}_2\text{SO}_4$. It shows that for each solute, the difference between SO_4^{2-} and Cl^- is higher than that between Na^+ and Mg^{2+} , suggesting a stronger anion effect. Specifically, the result as $\text{SO}_4^{2-} < \text{Cl}^-$ of σ value is found for glucose and acetic acid. It means that the solute transfer is higher with Na_2SO_4 than with NaCl or MgCl_2 .

As aforementioned, in the organic solute/salt systems, both the membrane modification (swelling effect) and the solute dehydration are concerned regarding the influence of the salt composition. The previous results thus show that the variation of the reflection coefficient is due to the dehydration effect. A more hydrated ion makes the neutral solute less hydrated, decreasing the solute size consequently. Then, a higher convection transfer is obtained, which gives decreasing values of the reflection coefficient.

It was reported that, in the case of saccharides, dehydration comes from the interaction between the ions and the hydrophilic sites of the saccharide i.e. $-OH$, $-O-$ [24]. In the present work, all the solutes considered have polarized functional groups ($-OH$, $-O-$, $-COOH$), through which they can be influenced by the presence of strongly charged ions, thus resulting in decreasing hydration in presence of salts. Phenol has only one $-OH$ as hydrophilic site, which is much less compared to glucose (five $-OH$ and one $-O-$) and acetic acid (one $-COOH$). Nevertheless, our results show that phenol can be dehydrated in presence of salt since lower convection flux is observed with NaCl compared to $MgCl_2$. Then, both

the hydrophilic and hydrophobic solutes are subject to the dehydration induced by the salt.

In this study, the solute dehydration is highlighted in both diffusion and convection. However, while the solute dehydration governs the organic solute convection, in the diffusion case, the transfer is governed by the membrane swelling.

It was also previously mentioned that the convection flux of phenol in the phenol/ Na_2SO_4 system is surprisingly lower than those in the phenol/ Cl^- salt systems (Fig. 8). Indeed, Table 8 shows that the calculated value of σ_{phenol} with Na_2SO_4 is ca. 0.8, higher than those obtained for NaCl or $MgCl_2$ (ca. 0.7), which is unexpected following the solute dehydration effect.

In fact, a different behavior of phenol can be also observed regarding its diffusive transfer compared with the other two solutes, since the phenol flux with SO_4^{2-} is more obviously lower than that with Cl^- , as shown in Fig. 5. Thus, a singular behavior of phenol with SO_4^{2-} is pointed out. Since the diffusion transfer observed for phenol/water and phenol/ Na_2SO_4 are similar (Table 6), one can conclude that such singular behavior probably

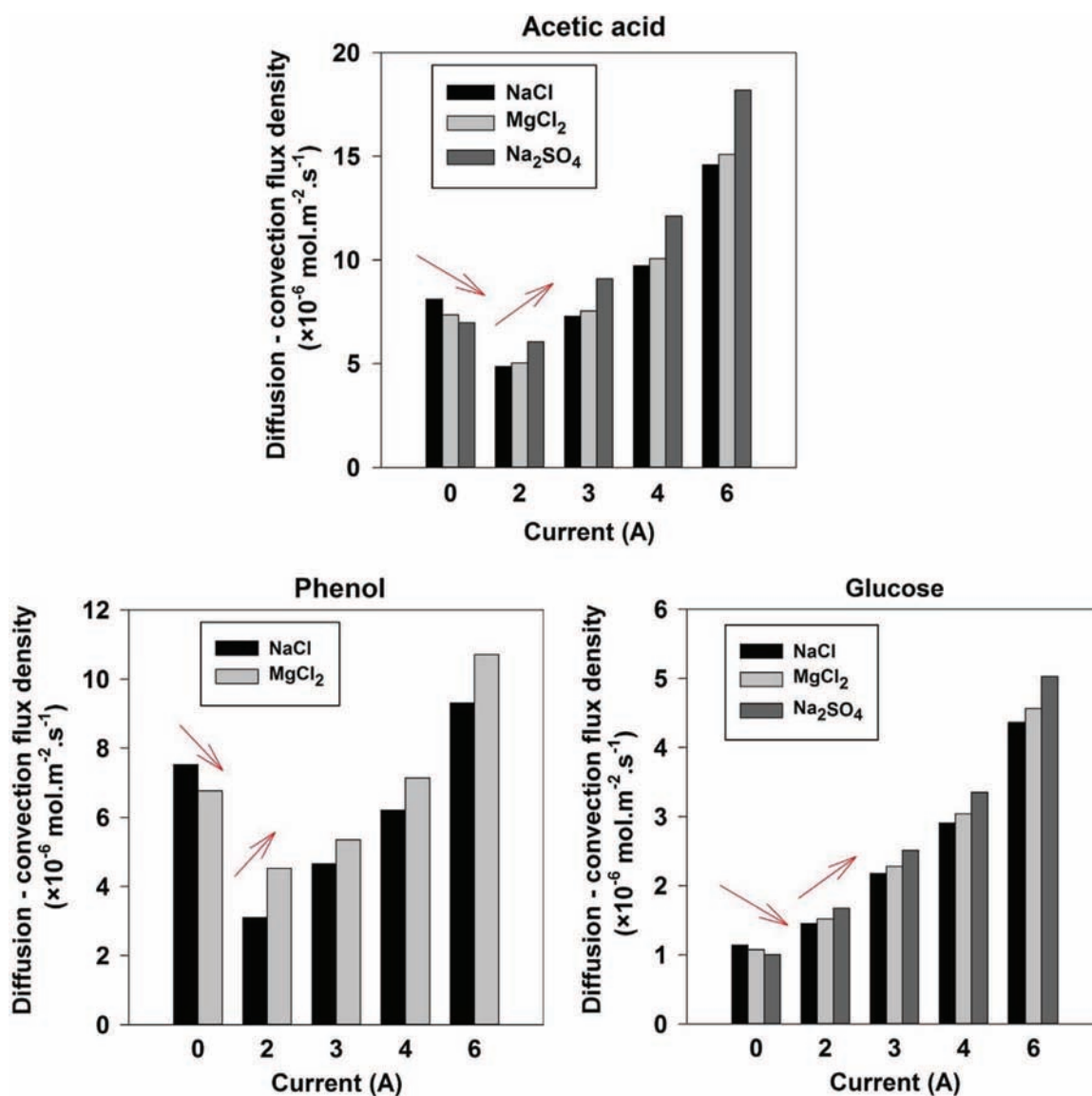


Fig. 9. Comparison of diffusion ($I=0$) and convection ($I \neq 0$) transfer of organic solutes versus current: influence of the salt composition; [organic solute]= 0.1 mol L^{-1} and [salt]= 0.8 eq L^{-1} .

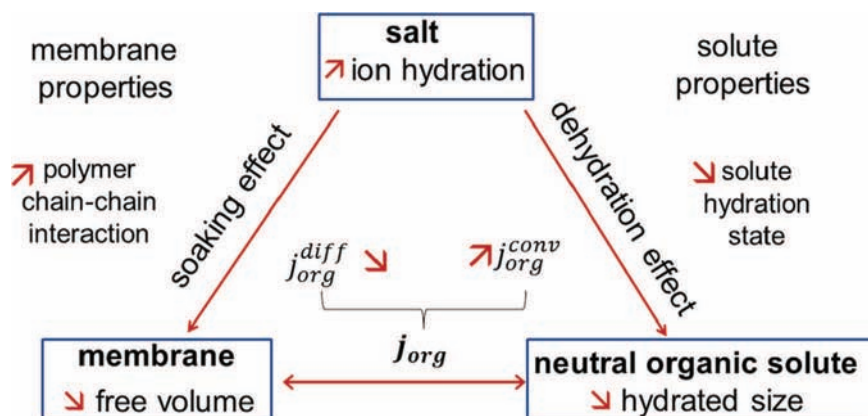


Fig. 10. Influence of salt (ion hydration) on the transfer of neutral organic solutes in ED.

takes place in the membrane, i.e. AEM, rather than in the aqueous solution. It suggests that the SO_4^{2-} soaked AEM lowers the phenol transfer, in both diffusion and convection conditions. This requires further investigation in the future.

4.2.3. Diffusion and convection contributions: influence of the salt

Concerning the salt effect on the transfer of organic solutes, diffusion and convection contributions are further compared for each solute, as illustrated in Fig. 9.

Reversed trends of the salt effect on diffusion and convection are found for each solute. A more hydrated ion induces a lower diffusion and a higher convection. As already mentioned, in the organic solute/salt systems, the ion hydration can modify both the membrane and solute properties, while these modifications lead to different contribution to the solute transfer, for diffusion and convection.

Then, for a given solute, diffusion and convection flux densities (j_{org}^{diff} and j_{org}^{conv}) are in the same order of magnitude, emphasizing that both contributions are important. Since the convection flux is current dependent, its contribution can become dominant for the highest current [36], while the diffusion is still not negligible.

At low current, diffusion can be the main contribution to the solute transfer especially for the solutes of low M_w (i.e. diffusion contribution > 50% under 2A). At higher current, convection is dominant with respect to diffusion, especially for solute of higher M_w like glucose (ca. 80% under 6A).

Finally, one can summarize the main results of this study as follows. The transfer of neutral organic solutes in ED consists of diffusion due to the concentration gradient and convection due to the electroosmosis water flux, and both are important. In any case, the solute transfer is governed by the steric effect due to the relative solute size and membrane free volume. Then, in saline solutions, the transfer of organic solutes varies according to the salt composition. The triple interaction in salt-organic solute-membrane system is illustrated in Fig. 10.

The salt can modify both the membrane and solute properties. On one hand, concerning the membrane, more hydrated counter-ion results in stronger polymer chain-chain interaction that governs the diffusion. Stronger chain-chain interaction further results in a decreasing fragment-fragment distance in the membrane materials, and thus a lower diffusion of the organic solute [30]. On the other hand, concerning the solute, a more hydrated ion results in a decreasing of the solute hydration, which governs the convection. The ion dehydrates some water molecules bound to the solute hydration shell, causing a decreasing hydrated size of the solute, and thus a higher convection. Finally, dealing with the influence of the salt, an opposite trend is expected for diffusion and convection.

5. Conclusions

The aim of this paper was to investigate the transfer of neutral organic solutes through ion-exchange membranes and specially the influence of the salt composition. Varying salts of different hydration and solutes of different size and hydrophilicity were used.

Firstly, the salt and water transfer were studied. As expected, it was found that the salt transfer is mainly fixed by the current and does not show significant variations according to the solution composition. Meanwhile, the water transfer was found to vary with the salt composition according to the following sequence $\text{MgCl}_2 > \text{NaCl} > \text{Na}_2\text{SO}_4$. Both the salt and water transfer were found not influenced by the presence of organic solutes.

Secondly, the influence of the salt on the transfer of neutral organic solutes was studied, using a specific procedure to dissociate the diffusion and convection contributions. This study has shown that both contributions are important. For any solute and both contributions, the following sequence was pointed out: acetic acid > phenol > glucose. It was thus concluded that the transfer of neutral organic solutes is mainly fixed by the steric effect.

Then, concerning the influence of the salt, the sequence for the diffusion flux was found as: $\text{Na}^+ > \text{Mg}^{2+}$ (cation) and $\text{Cl}^- > \text{SO}_4^{2-}$ (anion), showing a reversed trend compared to that of the counter-ion hydration. These results are in agreement with the membrane swelling effect since the more hydrated counter-ion leads to the stronger polymer chain-chain interaction, and thus the lower diffusion flux. On the contrary, the convection flux was found to vary as $\text{Na}^+ < \text{Mg}^{2+}$ (cation) and $\text{Cl}^- < \text{SO}_4^{2-}$ (anion), same to the sequence of ion hydration. These are in agreement with the solute dehydration effect. Indeed, the more hydrated ion gives the stronger solute dehydration, causing a decrease of the solute hydrated size, and thus an increase of the convection flux. In ED, the salt modifies the membrane and solute properties simultaneously and the solute transfer is thus affected by the salt under the combination of these two effects.

Finally, similar transfer mechanisms were pointed out for all the organic solutes considered in this study despite the different size, hydrophilicity and the different pH conditions.

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Nomenclature

List of symbols

j_{org}	organic solute flux density ($\text{mol m}^{-2} \text{s}^{-1}$)
j_s	salt flux density ($\text{eq m}^{-2} \text{s}^{-1}$)
J_w	water flux density ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)
P_{org}	solute permeability (m s^{-1})
ΔC_{org}	solute concentration gradient across the membrane (mol m^{-3})
\bar{C}_{org}	mean solute concentration (mol m^{-3})
$C_{org,D}^0, C_{org,C}^0$	initial solute concentration in diluate and concentrate, respectively (mol m^{-3})
S_m	total surface of one type of membrane (m^2)
I	current intensity (A)
M_w	molecular weight (g mol^{-1})

Greek symbols

α	current coefficient ($\text{eq m}^{-2} \text{s}^{-1} \text{A}^{-1}$)
β	electroosmotic coefficient ($\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{A}^{-1}$)
γ	convective coefficient ($\text{mol m}^{-2} \text{s}^{-1} \text{A}^{-1}$)
σ	reflection coefficient

Superscripts and subscripts

<i>conv</i>	convection
<i>diff</i>	diffusion
<i>eo</i>	electroosmosis
<i>mig</i>	migration
<i>os</i>	osmosis
<i>org</i>	organic solute
<i>s</i>	salt
<i>w</i>	water

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