Features of feed concentration and temperature effects on membranes operation in electrodialysis systems – a review

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Abstract. Electrodialysis (ED) is a significant method in saline water desalination and industrial wastewater treatment. Ion exchange membranes (IEMs) are an important part of the electrodialysis process. An ion-exchange membrane is a semipermeable membrane that transports ions through an oppositely charged membrane and blocks the passage of a co-ion under an electric field. This review describes the effects of feed concentration and its operating temperature on different sides of IEMs in an electrodialysis system. The influence of feed solutions and temperature gradients on diffusion and osmotic membrane permeability was clarified. The distribution of feed concentration under thermostat and thermodynamic conditions are also discussed. Temperature changes in ED systems may increase ion transport selectivity and charge separation efficiency. The rate of ions transport depends on the number of ions diffusion toward the membrane. To date, there are very few studies reporting diffusion and osmotic permeability of IEMs at high temperature.

1. Introduction
Electrodialysis (ED) is a common method of treating salty brackish water or industrial wastewater [1]. In industry, electrodialysis methods are mainly used to desalinate brackish water, remove nitrates, and deionized whey [2]. In recent years, Ion exchange membranes (IEMs) are extensively used in Donnan dialysis, capacitive deionization, diffusion dialysis, and electrodialysis. IEMs play an important role in the ED system, due to their ability to selectively move water and certain ions, as well as the chemical stability of membrane [3]. In addition, a higher operating temperature (up to 50°C) is one of the advantages of using the IEMs in the ED [4]. Many studies were carried out to characterize IEMs’ performance, but some researchers have optimized thermodynamic data [5, 6].

An electric field is applied to selectively transport ions through an ED stack containing alternately arranged membranes: cation exchange membranes (CEMs), and anion exchange membranes (AEMs), which lead to the formation of dilute and concentrated solutions. Counter-ions pass through the membrane with the opposite charge, while co-ions often do not pass through the membrane with the
same charges according to Donnan-exclusion [2]. In addition, there are two mechanisms of water penetration through IEMs: osmosis and electro-osmosis. As shown in Fig. 1, Osmosis refers to water diffusion, whereas electro-osmosis refers counter-ions of water molecules transport through IEMs as a result of electric field migration [7].

![Figure 1. Phenomena of mass transfer in ED stacks.](image-url)

Since IEMs are widely used in ED, there is a great interest in optimizing its performance, which is strongly influenced by many factors. The most significant factors are the initial feed composition, flow rate, temperature, pH, and IEMs characteristics [1]. Feed concentration and temperature are the most important factors affecting the membrane operating process [6]. Kamcev et al. [8] noted that membrane permeability coefficients increase with an increase in external concentration. Furthermore, when feed temperature increases, the separation of ions increases due to the influence of temperature on the electrical resistance of solutions and the mobility of ions [2]. Hong et al. [9], they studied the effect of operating temperature on the performance of a Nafion membrane in ED. They concluded that as the solution temperature increases, the proton conductivity increases, and water and proton selectivity of Nafion membrane type decreases. They noted that an increase in temperature does not always lead to an improvement in ED performance. Thus, the thermodynamics in the ED method would be more complicated than expected, and the efficiency of the membrane and its temperature dependence would have to be examined more closely.

To date, there are a few researchers have evaluated the effect of discharged feed solutions at different temperatures on diffusion and osmotic permeability of IEMs in the ED process to verify the effectiveness of membrane separation. Therefore, the aim of this study is to clarify the thermodynamic phenomena of contacting different concentrations and temperatures of solutions with IEMs in an electrodialysis system.
2. Temperature dependence on Nernst-Einstein equation

In ED, the Nernst-Einstein equation is mainly used to study the influence of temperature. The Nernst-Einstein equation (1) shows that the mobility of ions and separation of ions improves at higher temperature as a result of an increase in diffusivity of ions [10].

\[ u_i = \frac{|z_i| F D_i}{R T} \]  

(1)

where \( u_i \), \( z_i \), \( D_i \), \( F \), \( T \), and \( R \) are mobility of ion, electrical charge of ion, diffusivity coefficient of ion, Faraday constant, temperature, and molar gas constant, respectively.

The diffusion coefficient of a solution varies inversely with viscosity and linearly with temperature, as shown in equation (2) [11]:

\[ D_i(T) = \frac{D_i(T_0) \times T \times \mu(T_0)}{T_0 \times \mu(T)} \]  

(2)

where \( D_i(T) \) and \( \mu(T) \) are diffusivity coefficient and dynamic viscosity of solution at a certain temperature \( (T) \), respectively; \( D_i(T_0) \) and \( \mu(T_0) \) are diffusivity coefficient and dynamic viscosity of solution at reference temperature \( (T_0) \), respectively [11]. Temperature is highly dependent on experimental conditions such as stack type and flow rate, especially in the case of a pilot stack [12]. As temperature increases, ions diffusion, and ions transport of solution increases. In contrast, the viscosity of the solution decreases [2]. In general, an increase in temperature is the main factor to increase ion transfer rate and reducing energy consumption in ED. However, to avoid additional costs, feed water should be heated using waste heat sources.

3. Membrane permselectivity

Permselectivity is a key to identifying the restriction of ion transport across the IEM boundary or penetrating the membrane wall depending on the membrane charge. The concentrations of ions within the membrane, especially co-ions, are important for characterizing the permselectivity of membranes. According to Donnan exclusion, the permselectivity membrane excludes all co-ions. Membrane permselectivity (\( \psi \)) can be determined according to equation (3) bellow:

\[ \psi_{\text{membrane}} = \frac{T_{\text{membrane}}}{T_{\text{counter-ions}}} - \frac{T_{\text{counter-ions}}}{T_{\text{co-ions}}} \]  

(3)

where \( (T_{\text{membrane}}) \) is transport number of counter-ions in membrane, \( (T_{\text{counter-ions}}) \) is counter-ions of bulk solutions, and \( (T_{\text{co-ions}}) \) co-ions of bulk solutions [13]. Fundamentally, the concentration of the initial solution and operating temperatures had a significant effect on the diffusion and osmotic permeability of ion-exchange membranes.

3.1 Effect of concentration on diffusion-osmotic membrane permeability

In ED, the size of the system, as well as dilute and concentrated concentrations influence on the osmotic and diffusion permeability of IEMs operation [14]. In IEMs, the specific amounts of ions transported from the high-concentration region to the low-concentration region is considered a negative phenomenon in the electrodialysis process. Moreover, changing the operating parameters is the most important way to improve the diffusion permeability coefficient of the membranes and can be practically determined [7]. Geise et al. [15] found that with an increase in the NaCl salt concentration from 0.58 to 58 g/L, the diffusion permeability increases by more than 10% in charged polymers and decreases by 16% in the uncharged hydrogel. Kamcev et al. [16] showed that ion transfer in a membrane with high water content occurs faster than in a membrane with a low water content. The water content in the membrane is relatively unchanged at low NaCl concentrations (<5.8 g/L) and decreases at higher NaCl concentrations (>5.8 g/L) as the result of osmotic deswelling. This concluded that the diffusion permeability of membranes depends on the concentration of the solution.
Permeability $P$ (m².s⁻¹) is the steady flow of a molecule through a membrane, determined by the thickness of the membrane and the driving force. In addition, permeability is the result of molecular diffusion coefficient $D$ (m².s⁻¹) and molecular partition coefficient $K$, as shown in equation (4) [7].

$$P = DK$$

The diffusion coefficient is defined as the rate of substances to pass through the membrane, while the partition coefficient is measured depending on the concentration of substance inside the membrane divided by the concentration in bulk solution. As demonstrated by Kozaderova et al. [17], when the external solution has low concentrations, the conductivity of IEMs is relatively high. Długolecki et al. [18] showed that the electrical resistance of IEMs highly depends on the concentration of the solution, they investigated the phenomena of ion transport in two cation exchange membranes (Neosepta CMX and Fumasep FKD) and two anion exchange membranes (Neosepta AMX and Fumasep FAD) for the concentration of NaCl in the range from 0.017 to 0.5 M under different hydrodynamic conditions. They found that ion transport is high for a process operating in a low concentration range.

In contrast, an increase in the diffusion of water from the dilute concentration chamber to the concentrated solution chamber occurs when the concentration of feed solution is high, which increases osmosis and leads to a decrease in osmotic permeability coefficients of the membrane [7]. Melnikov et al. [19] concluded that in order to minimize the flow of distilled water from the dilution chamber to the salt concentration chamber due to osmosis, the salt concentration chamber should be significantly low, which leads to an increase in the osmotic permeability coefficient. The main reason for water flow is associated with concentration polarization as a result of an increase in salt concentration in the boundary layer of the membrane. Another study by Kingsbury et al. [7], they investigated the osmotic permeability coefficient of water for many types of IEMs, for example: Selemion CMV and Neosepta CMX as cation exchange membranes (CEMs), using 4 m NaCl solution, the results were 4.72×10⁻¹¹ and 7.39×10⁻¹¹ (m²/s), respectively. Also, they investigated osmotic permeability coefficients of anion exchange membranes (AEMs), for example: Selemion AMV and Neocepta AMX, the results were 4.21×10⁻¹¹ and 6.76×10⁻¹¹, respectively. It can be concluded that CEMs have a higher water permeability than AEMs, which means that energy losses will be higher. Moreover, a higher salt concentration significantly reduces the diffusion and osmotic permeability coefficients of the IEMs.

3.2 Effect of temperature on diffusion-osmotic membrane permeability

The influence of temperature on the diffusion and osmotic permeability of IEMs has not been sufficiently studied in the literature. Guesmi et al. [20], they found in their study that when the temperature of feed solution increases from 10°C to 40°C have a significant influence on the equilibrium of the cation exchange membrane, especially with monovalent and divalent ions. Gatapova et al. [6], investigated the diffusion permeability coefficient of ion exchange membrane (MK-40) for NaCl solution under thermostatic conditions (25°C, 37.5°C, and 50°C) and thermodynamic conditions (solution temperature = 25°C, water temperature = 50°C). They found a significant difference in the values of the diffusion permeability coefficient when the temperature of two sides of the membrane was the same, and the temperature of the two sides was different. Furthermore, Tanaka [21], who studied the properties of two types of IEMs, Aciplex K172/A172 and Neocepta CIMS/ACS3, showed that the total hydraulic permeability increases from (1.218×10² to 2.765×10²) cm³.eq.-1.s⁻¹ and (1.254×10² to 2.059×10²) cm³.eq.-1.s⁻¹, when the temperature of the feed solution increases from 25 to 60°C, respectively. This means that membrane diffusion permeability increases as the temperature of feed solution increases, and this leads to a decrease in the efficiency of the membrane.

Gubari et al. [1] indicated that the osmotic permeability coefficient of IEMs decreases with decreasing salt solution temperature. Zhao and Zou [22], studied the effect of temperature on membrane efficiency during osmotic desalination and their results showed that water flow increases with increasing temperature. It can be concluded that an increase in the concentration of the NaCl solution
and an increase in the temperature of the dilute solution significantly affect the osmotic permeability coefficient. Eventually, the diffusion permeability of salt is correlated with the osmotic permeability of water.

3.3 Effect of temperature on mono- and divalent ions transport
The percentage of removal of monovalent ions is better when the initial solution contains only monovalent ions, compared to the removal percentage when the initial solution is a multi-ionic solution. In addition, there is a lower percentage of divalent ion removal when the feed solution consists of only divalent ions compared to a solution containing multi-ionic ions [23]. The separation of divalent ions from monovalent ions is most commonly used in an industrial desalination process [24]. Electrodialysis is one of the most common methods for mono and divalent ion separation [25]. According to a study by Benneker et al. [2], the relative flux of monovalent Na\(^+\) was significantly reduced by adding divalent Mg\(^{2+}\) or Ca\(^{2+}\) ions, while the effects of adding Mg\(^{2+}\) to Na\(^+\) ions were insignificant in flux. In addition, they concluded that the effect of temperature on the diffusion permeability coefficient for both ions (monovalent or divalent) is slightly different and may affect the selectivity of the ED process. In general, the relative variations between the diffusivity of different ions are typically increased at higher temperatures, which leads to a change in the transport characteristics. Furthermore, Lokhande et al. [26] studied the effect of temperature on ion exchange equilibrium for monovalent solutions (Cl\(^-\)/Br\(^-\)) and (Cl\(^-\)/I\(^-\)), and univalent-divalent solutions (Cl\(^-\)/C\(_2\)O\(_4\)\(^{2-}\)) and (Cl\(^-\)/SO\(_4\)\(^{2-}\)) using Duolite ion exchange resin A-113, and they found that affinity of resin for metal ions increases with increasing temperature. In the same context, Chaabouni et al. [3] indicated that with an increase in the temperature of the systems (Zn\(_{2+}\)/H\(^+\)), (Cu\(_{2+}\)/H\(^+\)), and (Cd\(_{2+}\)/H\(^+\)) from 10 to 30°C using cation exchange resin system of the Amberlite IR 120 type, the affinity order of resin to metal ions increases.

In addition, in a mixture of a monovalent and a divalent solution, when the concentrated and dilute solution streams are heated to a certain temperature, the separation of monovalent ions for the concentrated solution is higher than the dilute solution. This indicated that when a mixture of monovalent and divalent ions of dilute solutions is heated, the main reason for decreases in monovalent ions transport is a competitive transport between ions. While in the case of divalent ions, when the temperature of the solution changes, there is no significant decrease in ion transport observed. This implies that in the case of a hot dilute solution, the competitive transport of divalent ions is more considerable than monovalent ions [2].

4. Concentration and temperature distributions in ED stack
Electrodialysis is a process of alternating anion-exchange membranes (AEMs) and cation-exchange membranes (CEMs), it should be noted that the concentration values of solutions differ depending on the position in the electrodialysis stack, as shown in Figure 2 (a). The alternation of ion exchange membranes (1 - 9) provides the distribution of streams of desalinated chambers (II, IV, VI, and VIII) and concentrated chambers (I, III, V, and VII) solutions. In the stream of desalted solution (dilute), the concentration of electrolytes decreases, while in the stream of concentrated solution (concentrate), the concentration of electrolytes increases. Taking into account the phenomenon of concentration polarization in the membrane which occurs as a result of different rates of ions migration in solution through the membrane. During the electrodialysis separation process, aqueous solutions and membranes are exposed to an electric current, which is accompanied by the release of heat, which leads to an increase in the temperature of both solutions and membranes. The specific amount of the released heat \(q\) depends on the values of the electric current density \(i\) and the electrical resistance \(R\) of both membranes and solutions. The value of the electrical resistance of the solution is inversely proportional to the electrical conductivity. In contrast, it’s directly proportional to the concentration of the electrolyte in the solution \(c\), therefore [6]:

\[
q = f \left( i; \frac{1}{c} \right)
\]
As a result, due to changes in the concentration of the solution along the length of the electrodialysis stack, a change in temperature $T$ is observed in Figure 2 (b), for the concentrate stream from $T_i$ to $T_c$, and for the dilute stream from $T_i$ to $T_{dil}$. Thus, under operating conditions, IEMs are in contact with solutions of various concentrations and temperatures. For an adequate assessment of diffusion flux through the membrane during experimental studies, it is necessary to create concentrations and temperatures conditions close to the working ones. The solution with a lower concentration must have a higher temperature, since it has a high electrical resistance. From the literature review, there are a large number of studies mentioned that temperature effected on the diffusion permeability coefficient. However, numerous studies have been carried out under conditions of the same temperatures in each chamber (thermostatic mode) and different temperatures in each chamber (thermodynamic mode).

Figure 2. Scheme of changes in (a) concentration and in (b) temperature of the electrolyte during electrodialysis. K and A are cathode and anode chambers, respectively; $T_i$ is the initial temperature of the solution; $T_{con}$ and $T_{dil}$ are final temperatures of the concentrate and dilute solution, respectively.
5. Conclusion

- Electrodialysis (ED) is an important method of alkaline treatment of industrial wastewater.
- Ion exchange membranes characteristics as well as operating conditions have a great impact on the properties of transporting ions during electrodialysis.
- An increase or decrease in feed concentration and its temperature in ED systems may possibly increase selective ion transfer and membrane separation efficiency.
- The diffusion permeability of IEMs is greatly influenced by the temperature of the surrounding solution.
- Ion charge is important when studying the diffusion permeability of membranes. Many experimental studies have shown a significant difference in the values of the diffusion permeability coefficient of the membrane under thermostatic and thermodynamic conditions.
- It can be concluded that feed concentration and operating temperature have a significant effect on diffusion permeability of membranes and allow us to know the optimal operating conditions for optimizing the efficiency of the electrodialysis process.

6. References

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