

## Concentration polarization in electrodialysis: Buffer solutions experimental method

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### Abstract

This research work presents a simple, original and illustrative experimental method to investigate the concentration polarization using a cation exchange membrane (CEM). The nature of the overlimiting current ( $I_{ov}$ ) and the water dissociation (WD) on the CEM are particularly studied. They are still widely discussed nowadays. Our experimental method is based on the comparison of the  $i$ - $v$  (current transmembrane voltage) curves of the same counter ion with and without buffer coions. For example we compare  $\text{Na}_2\text{SO}_4$  and  $(\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4)$ , or  $\text{K}_2\text{SO}_4$  and  $(\text{KH}_2\text{PO}_4 + \text{K}_2\text{HPO}_4)$ . The role of the mixture hydrogen-dihydrogen phosphate coions is to buffer the solution at a neutral pH. The protons, whatever their origin, do not contribute to the current transport. The distance between the two  $i$ - $v$  curves of  $\text{Na}_2\text{SO}_4$  and  $\text{NaT}$  ( $T =$  buffer coions) represents then the contribution of the protons, issued from the WD, to the current transport. This comparison gives unexpected and interesting results: the superposition of  $\text{Na}_2\text{SO}_4$  and  $\text{NaT}$   $i$ - $v$  curves shows clearly that the WD occurs on the CEM and the protons contribute to the  $I_{ov}$ ; the superposition of  $\text{K}_2\text{SO}_4$  and  $\text{KT}$   $i$ - $v$  curves shows a larger distance between the 2 curves: the water dissociation is many times higher with  $\text{K}^+$  than with  $\text{Na}^+$ ; the superposition of  $\text{NaT}$  and  $\text{KT}$  gives identical  $i$ - $v$  curves. It is an unexpected result:  $\text{Na}^+$  and  $\text{K}^+$  have the same membrane mobilities if the protons do not contribute to the current transport. The overlimiting current increases with voltage: the WD is not a necessary condition to obtain  $I_{ov}$ ; the contribution of  $\text{H}^+$  to  $I_{ov}$  is not negligible. It represents more than 20% of the total current. The distance between  $\text{K}_2\text{SO}_4$  and  $\text{KT}$   $i$ - $v$  curves measures this contribution. This experimental method contributes strongly to a better understanding of the concentration polarization phenomenon. It is only based on experimental evidences and not on hypothesis, speculations or calculations.

**Keywords:** Electrodialysis; Polarization; Polarizability; Overlimiting current; Water dissociation; Buffer co-ions; Accumulating layer

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## 1. Introduction

A better understanding of the water dissociation mechanisms in the bipolar membranes explains the recent interest to the concentration polarization studies [1].

The other classical interest is the limiting current which constitutes a serious obstacle to the progress of the electrodialysis process.

Until today the following questions are still widely discussed:

- What is the nature of the overlimiting current?
- Is there a water dissociation on the cation exchange membrane?

We summarize the main ideas and results found in the literature:

- The loss of permselectivity and the water dissociation cannot be responsible for the overlimiting current, in the two types of membranes [2]. It is particularly true with the CEM [2–4]. With the AEM the WD is negligible with new membranes before the degradation of tetraalkyl ammonium fixed sites into tertiary amines [5]. These amines catalyse the water dissociation [5].
- The overlimiting current is generally explained by space charges which promote a very high local electric field [6]. The Wien effect is the direct consequence.
- The overlimiting current is often studied through pH measurements and transport numbers calculations [2,3].
- The main causes of the concentration polarization are the concentration decrease in the diluate boundary layer and the difference of the counterion transport numbers between the membrane and the solution.

In this paper we propose another experimental and theoretical approach to provide

original information about the concentration polarization phenomenon.

The experimental approach is based on the comparison of the *i-v* curves of an alkaline counterion, with and without a buffer coion, with a CEM.

For example we compare the *i-v* curves of  $K_2SO_4$  and KT ( $T = [H_2PO_4^-] + [HPO_4^{2-}]$ ). The role of T is to maintain a neutral pH and to eliminate any contribution of the protons, whatever their origin, to the current transport. The distance between the two *i-v* curves represents, then, the contribution of protons to the overlimiting current with  $K_2SO_4$ .

This experimental method will answer directly to the question: is there a WD on the CEM?

We will study also the influence of the counterion nature on the *i-v* curves. The influence of the polarizability is particularly studied.

The theoretical approach is based on new theory and ideas already presented in our previous studies [7–9]. Our basic idea is simple: the counterion mobility in the membrane shows one or more order lower than in aqueous solutions.

We have then an accumulating layer instead of a depleting layer.

## 2. Experimental

A plexiglass 2 compartments polarization cell with a Selemion CMV cation exchange membrane is used to plot the *i-v* curves. It is free convection cell. The voltage drop across the membrane is measured by golden Luggin electrodes.  $Na_2SO_4$ ,  $K_2SO_4$ ,  $Li_2SO_4$ ,  $NaH_2PO_4$ , and  $Na_2HPO_4$  (Merck, analytical grade) was used to prepare solutions at different concentrations. The couple  $[NaH_2PO_4 + Na_2HPO_4]$  is used as a buffer solution where  $Na^+$

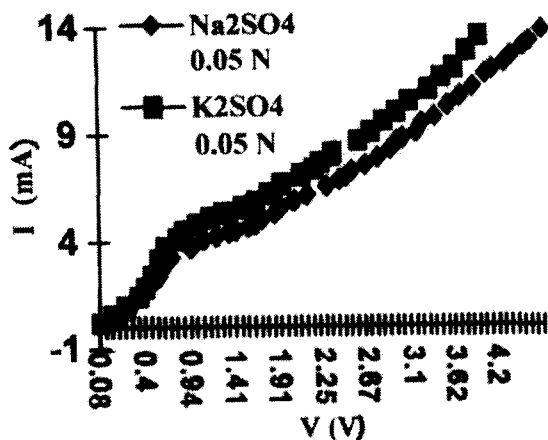


Fig. 1.  $i$ - $v$  curves of  $\text{Na}^+$  and  $\text{K}^+$  without buffer.

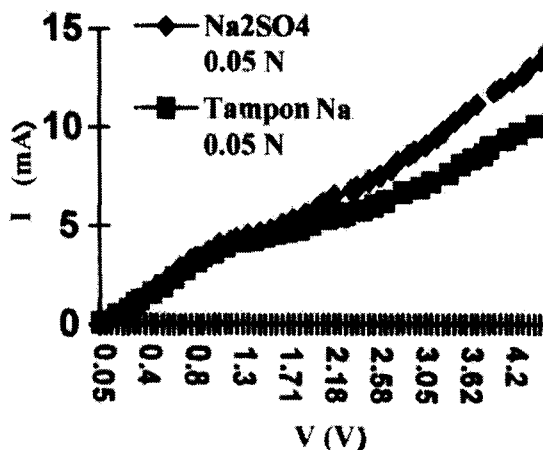


Fig. 2.  $i$ - $v$  curves of  $\text{Na}^+$  with and without buffer.

is the counter ion and  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^-$  is the buffer coion which maintains a neutral pH.

The experimental method is based on the comparison of  $i$ - $v$  curves with and without buffer coions. For example we compare  $\text{K}_2\text{SO}_4$  and  $[\text{K}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4]$ . The distance between the two curves must represent the contribution of the water dissociation, with  $\text{K}_2\text{SO}_4$ , to the current transport.

### 3. Results and discussion

#### 3.1. Comparison of $\text{Li}_2\text{SO}_4$ , $\text{Na}_2\text{SO}_4$ and $\text{K}_2\text{SO}_4$ $i$ - $v$ curves

Fig. 1 compares  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$   $i$ - $v$  curves, without buffer coions. At low transmembrane voltages the three curves are almost identical. They diverge, particularly at the polarization where distinct limiting current densities are obtained.

The order of  $I_{\text{lim}}$  values of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  agree, apparently, with the classical equation of  $I_{\text{lim}}$ :

$$I_{\text{lim}} = (z \cdot D \cdot C) / (\delta \Delta t)$$

Apparently this order depends, mainly, on the diffusion coefficient  $D$ . The use of our experimental method, based on buffer solutions, gives other experimental evidences. The next experiment presents these results and permits a better understanding of Fig. 1. The classical approaches of concentration polarization, such as the previous equation, are not sufficient to explain the  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  behavior in the membrane.

#### 3.2. Comparison of $\text{Na}_2\text{SO}_4$ and $(\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4)$ $i$ - $v$ curves

Fig. 2 compares the  $i$ - $v$  curves of the counter ion  $\text{Na}^+$ , with and without buffer coions. At low transmembrane voltages, the two curves are almost identical. The hydrogen phosphate coions do not influence the  $\text{Na}^+$   $i$ - $v$  curves. These coions play their predicted role at higher voltages: the pH remains constant and neutral.

At higher voltages, near the limiting current zone, we observe a slight difference between the two curves. In the third zone, (overlimiting current), the distance increases sensitively. This difference represents apparently, the contribution of protons to the current transport in the un-

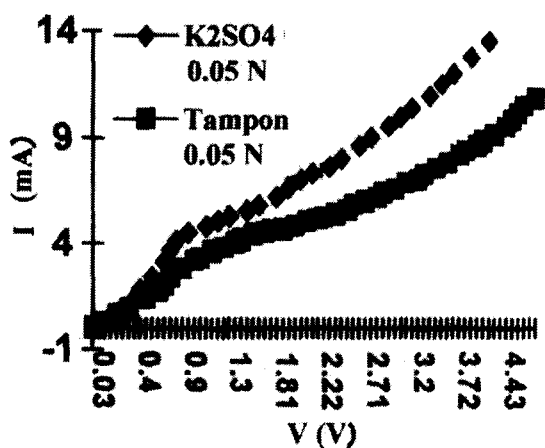


Fig. 3.  $i$ - $v$  curves of  $K^+$  with and without buffer.

buffered solution ( $Na_2SO_4$ ). This contribution is not negligible. It may represent more than 20% of the total current.

This experiment shows clearly that:

- The water dissociation, or a similar phenomenon, occurs on the cation exchange membranes.
- The proton contribution to the overlimiting current is relatively important (20% or more).
- The water dissociation is not a necessary condition to obtain the overlimiting current.

Most authors find that the proton contribution to  $I_{ov}$  is negligible [2–4]. Their methods are based on pH and transport membranes measurements.

Our method is direct, simple and explicit. Why these controversies? We prefer firstly to present the  $K^+$  experimental case, which is more illustrative and confirms these results.

### 3.3. Comparison of $K_2SO_4$ and $[KH_2PO_4 + K_2HPO_4]$ $i$ - $v$ curves

Fig. 3 compares the  $i$ - $v$  curves of  $K^+$  with and without buffer coions. The same phenomenon is

obtained as with  $Na^+$ . However, with  $K^+$  the water dissociation, measured by the distance between the two curves, is more accentuated and starts precocely (before the limiting current). Then the proton contributes strongly, not only to the overlimiting current, but also to the limiting current and before. With  $Na^+$ , this last contribution is very small.

The difference between  $Na^+$  and  $K^+$ , in unbuffered solutions, is then due to a higher water dissociation with  $K^+$ , than with  $Na^+$  (Fig. 1). These two experiments show clearly that the buffer coions, the hydrogen-dihydrogen phosphate mixture, play their predicted role: they do not permit the proton to contribute to the current transport. We can, then, observe the actual behavior of the alkaline counter ion ( $Na^+$  or  $K^+$ ) in the membrane.

Our experimental method permits to observe and to confirm an interesting phenomenon: The overlimiting current increases with the transmembrane voltage, even in buffered solutions. Then, the water dissociation is not a necessary condition to obtain  $I_{ov}$ .

The sensitivity is another advantage of the buffer solution experimental method. We observe distinctly the proton contribution to the current transport in the cation exchange membrane.

Many other authors [2–4] with similar polarization cells and more sophisticated measurement methods, exclude any proton contribution to  $I_{ov}$  in the CEM. We notice that this contribution cannot be neglected because it represents more than 20% of  $I_{ov}$ .

### 3.4. Comparison of $[NaH_2PO_4 + Na_2HPO_4]$ and $[KH_2PO_4 + K_2HPO_4]$ $i$ - $v$ curves

Fig. 4 compares the  $i$ - $v$  curves of  $Na^+$  and  $K^+$  with buffer coions. The result is quite unexpected and remarkable: the two curves are almost identical. We have the same limiting and overlimiting currents.  $Na^+$  and  $K^+$  have very

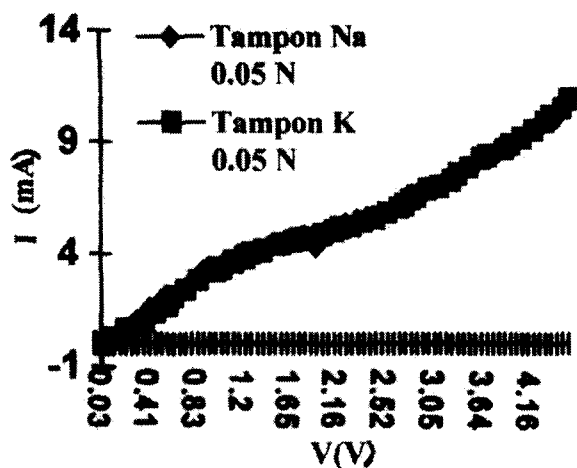


Fig. 4.  $i$ - $v$  curves of  $K^+$  and  $Na^+$  with buffer.

similar electrochemical mobilities, or diffusion coefficients, in the cation exchange membrane is the direct and evident interpretation of this experimental result. This result has never been obtained previously.

In the previous example (Fig. 1) with unbuffered solutions,  $Na^+$  and  $K^+$  give distinct curves. The other direct interpretation is the proton contribution to the current transport if the solution is not buffered. This contribution is ore important with  $K^+$  than with  $Na^+$ .

Our experimental method is also a powerful tool to investigate the mechanisms of current transport before, during and after limiting conditions. This result is in apparent contradiction with the classical laws of ionic conduction in solutions. It is well known that  $Na^+$  and  $K^+$  have very different electrochemical mobilities in aqueous solutions.  $Na^+$  is slower because it has a higher hydrated radius than  $K^+$ . The ionic size constitutes the main dissipative force under an applied voltage. Why do  $Na^+$  and  $K^+$  have similar mobilities in the cation exchange membrane if the solution is buffered? Is this result physically acceptable? We try to explain this phenomenon.

Contrarily to the aqueous solutions, we have not only size resistance forces (Stokes law) but also affinity dissipative forces (attraction forces between the ion exchange fixed site and the counter ion). It is well known that  $Na^+$  has a lower affinity than  $K^+$  towards the fixed site. Under an applied transmembrane voltage  $Na^+$  moves better than  $K^+$  if we consider only this effect. However, we have a second resistance which is due to the ionic size. In this case  $K^+$  moves better than  $Na^+$ . We have then a compensation:  $Na^+$  has a weaker affinity towards the fixed site, but has a higher ionic hydrated size.  $K^+$  has opposite properties to  $Na^+$ . These effects may explain qualitatively the Fig. 4.

### 3.5. Comparison of $K^+$ and $Cl^-$ $i$ - $v$ curves in their respective membranes

$K^+$  and  $Cl^-$  give identical limiting currents in their respective membranes (CMV and AMV) [4]. The plateau length of  $K^+$  is shorter than that of  $Cl^-$ .  $Cl^-$  needs a higher voltage to obtain  $I_{ov}$ .

The classical comparison, between  $Na^+$  and  $Cl^-$  [2] and its consequences (higher WD in the AEM) is not a good choice to compare the CEM and the AEM. We must compare counterions with similar properties such as  $K^+$  and  $Cl^-$ , or  $Li^+$  and  $CH_3COO^-$ . We notice that  $Cl^-$  is less polarizable than  $K^+$ . We think that this property explains the higher WD in the AEM: the WD depends much more on counterion properties than on the fixed sites catalysis effect.

## 4. Conclusions

We have compared the  $i$ - $v$  curves of a given counter-ion, with and without a buffer coion, for a Selemion CMV membrane. The buffer coion is a hydrogeno-dihydrogeno phosphate, noted T. Its role is to maintain a neutral pH and to avoid the contribution of protons to the current transport in the membrane.

The distance between the two i-v curves (for example  $\text{Na}_2\text{SO}_4$  and NaT) measures directly the contribution of WD to the overlimiting current in the CEM; It is the experimental originality of this research work.

Unexpected and interesting results have been obtained:

- Comparison of  $\text{Na}_2\text{SO}_4$  and KT: the distance between the two curves is much more accentuated with  $\text{K}^+$  than with  $\text{Na}^+$ . This distance measures the contribution of  $\text{H}^+$  to  $I_{ov}$ . It may also represent a change in  $pK_w$  of the water molecule under interfacial conditions (Wien effect).
- Comparison of NaT and KT: the two curves are almost identical.  $\text{K}^+$  and  $\text{Na}^+$  have the same mobilities in the membrane, in the presence of T. The difference between  $\text{Na}^+$  and  $\text{K}^+$ , in the absence of T is due to a higher water dissociation with  $\text{K}^+$  than with  $\text{Na}^+$ . We explain this phenomenon by the difference of polarizabilities.
- The contribution of the WD in the CEM represents more than 20% of  $I_{ov}$ . It is not negligible as related in the literature.
- The WD is not a necessary condition to obtain  $I_{ov}$ .

The classical definition and theory of the concentration polarization (depleting layer, transport numbers) are not sufficient to explain our results, the WD, the nature of  $I_{ov}$ , etc.

We have already introduced a new theory and ideas [7–9] to explain these phenomena. For example we think that the plateau (zone II of i-v curve) is due to the limiting velocity of the counter ion in the membrane and not to the resistance of the depleting layer. The counterion velocity in the membrane shows one or more order lower than in aqueous solutions. This explains easily the accumulation of counterions at the interface.

We have then an accumulating layer instead of a depleting layer. This accumulation promotes the Wien effects with these results:

- When we increase the voltage the distance counterion-counterion decreases at the interface. It creates a very strong local electric field which may promote a Wien effect with different consequences.
- If the counterion is highly polarizable (for example a hydrated counterion as  $\text{Li}^+$ ), the strong electric field deforms the counterion and the overlimiting current is due to the first Wien effect.
- If the counterion is less polarizable ( $\text{K}^+$ ), the local electric field is stronger and promotes the dissociation of weak electrolytes, even  $\text{H}_2\text{O}$ . the dielectric properties of the solvent are changed. The  $pK_w$  decreases and the conductivity increases by the second Wien effect. This explains the overlimiting current with  $\text{K}^+$ .
- The addition of T ( $\text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^-$ ), the buffer coion, reduces the WD and shows clearly the influence of the second Wien effect.

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