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The effect of the borate/boric acid buffer on the transfer of potassium counter-ion through a cation-exchange membrane: current-voltage characteristics

Ridha Zerdoumi*, Kafia Oulmi, Kamel-Eddine Bouhidel

Laboratory of Chemistry and Environmental Chemistry LCCE, Department of Chemistry, Faculty of Science, University of Batna, Batna 05000, Algeria
Tel. +213 669 780 769; email: zerdoumiridha@yahoo.fr

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ABSTRACT

In this study, we compare the current–voltage (I–V) curves of the same counter-ion with and without buffer coions. We compare the polarization curves of the counter-ion K^+ without and with borate coions which results from boric acid dissociation. The boric acid was added progressively from 0.005 to 0.1 N. The role of the mixture (borate coions/boric acid) is to buffer the solution at pH = 9.23, the protons, whatever their origin, do not contribute to the over-limiting current transport. We have a later onset of the over-limiting current and an increase in the plateau length of the membrane's polarization curves. On the other hand, the addition of boric acid to a potassium sulfate solution does not affect the limiting current density, also the plateau length decreases and its slop increase with increasing boric acid concentration, this unexpected results helps us to better understand the classical electrochemical concentration polarization phenomena in electrodialysis process.

Keywords: Cation-exchange membrane; Limiting current density; Boric acid; Concentration polarization; Plateau length; Over-limiting current; Water dissociation

1. Introduction

In electroplating process, boric acid is a common additive of nickel and zinc sulfate baths. The presence of boric acid results in an increase in current efficiency in the deposition process, in the amount of the deposited metal, and in the nucleation density of the deposit [1,2]. Also, boric acid acts as a buffer to maintain the pH of the electrolyte bath, buffering is especially necessary when hydrogen evolution occurs because the latter leads to higher pH near the electrode as a consequence of H^+ consumption, resulting eventually in metal hydroxide precipitation [3]. As a result the electroplating wastewaters can contain boron up to several grams per liter (g/l) and have to be treated before discharge in nature, significant amounts of boron or its compounds, boric acid or borates, in water constitute substantial environmental risks and are strongly regulated [4–6].

Electrodialysis has been extensively used in the electroplating industry to remove and recycle metal ions from plating bath rinse solutions. In this case, complete recycle of the water and recovery of metal ions can be achieved and treated water may reutilized for cooling or wash bath [7]. So, to ensure a good

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*Corresponding author.

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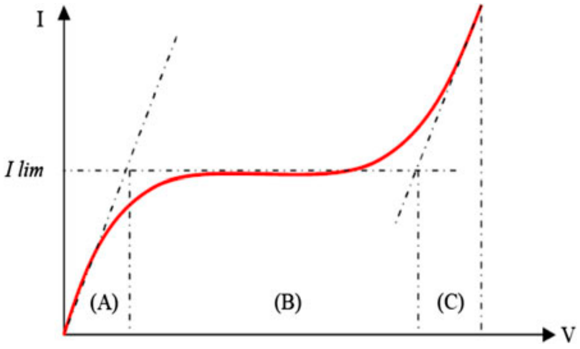

Fig. 1. Typical current–voltage curve of a mono-polar ion-exchange membrane.

performance of electrodialysis, it is necessary to know the effect of the boric acid on the counter-ion transport properties during an electrodialytic process.

In electrodialysis, the current–voltage curve (I–V) of an ion-exchange membrane (IEM) can be divided into three regions (Fig. 1): the Ohmic region (A) followed by a polarization plateau (B) caused by ion depletion in the diffusion boundary layer, and then, an increase in the current density called the over-limiting current region (C).

If the applied current density exceeds the limiting one, operational problems occur, such as the inorganic salts precipitation on the membrane surface, destruction of the membranes and an increase in the energy consumption decreasing the process efficiency. So, the limiting current density is an important parameter to take decisions regarding to which membrane is the most appropriate and which is the maximum current density that can be used for a given application [8–11]. According to the classical concentration polarization theory, the limiting current density is expressed by the following equation:

$$I_{lim} = \frac{c_D^{+} DF}{(t_s - t_m)\delta} \tag{1}$$

The limiting current density (I_{lim}: A/m^2) is dependent on the bulk solution concentration (c_D^{+}: mol/l), the salt diffusion coefficient (D: m^2/s), the boundary layer thickness (δ: m), the counter-ion transport number in the solution t_s, the counter-ion transport number in the membrane $t_{m,}$ and the Faraday constant (F: As/mol). According to this theory, currents larger than the limiting current density should not be expected, but in membrane/solution system, we measures currents much higher than the limiting one, In such situations, the classical theory cannot give an account to the observed phenomena, the nature of the over-limiting current and the physical meaning of the plateau length has not been clearly understand which makes it a serious puzzle for the scientists and was investigated intensively in recent publications [11–17].

Balster et al. [12] investigated the influence of the membrane surface heterogeneity on the plateau length, they prepared membranes with designed undulations and found that the plateau length of the undulated membranes is reduced by up to 60% compared with that of a flat membrane. Also, the commercial CMX membrane coated with polyethylenimine (PEI) led to a strong increase in the plateau length and a later occurrence of the over-limiting current density.

In this work, we are studied the effect of the weak electrolytes (boric acid) and the buffer solutions (potassium borate/boric acid) on the plateau length in current–voltage curves of the CMX cation-exchange membrane.

2. Methods

2.1. Ion-exchange membrane and electrolyte solutions

The ion-exchange membrane used in this study was the CMX cation-exchange membrane. This is a homogenous acrylic fiber-backed membrane containing sulfonic acid groups as fixed charges. The potassium borate and boric acid solutions were used in this study. The experiments were accomplished after a membrane equilibration period of at least 24 h in a solution with the same characteristics used in the experiments.

2.2. Electrochemical cell and current–voltage measurements

The current–voltage curves were obtained using a two compartment electrochemical cell as shown in

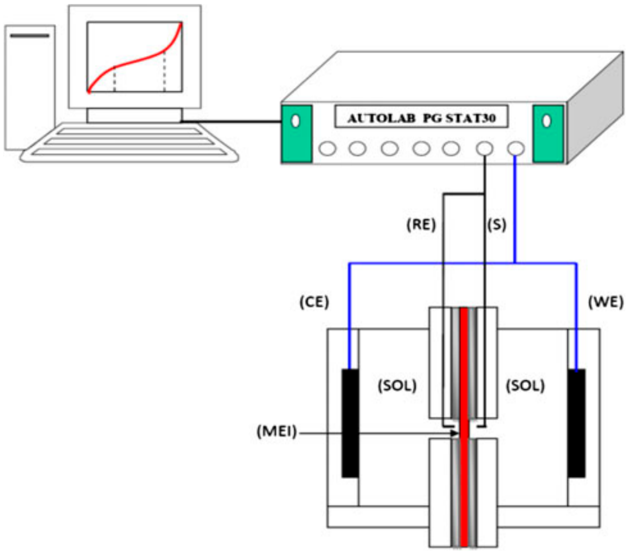

Fig. 2. Schematic description of the experimental setup. RE: reference electrode, S: sensor electrode, CE: counter electrode, WE: working electrode, SOL: solutions, MEI: ion-exchange membrane.

Fig. 2. This cell was composed of two 25 -ml symmetrical half-cells, In both compartments, solutions of identical concentration and composition were utilized, The circular exposed area of the membrane surface was 0.5 cm^2. The potential drop through the membrane was measured using two references golden Luggin electrodes. Moreover, all measurements were carried out in a galvanostatic mode, two graphite electrodes were used to impose the current density by a potentiostat/galvanostat (Autolab, PGSTAT 30) at a current scanning rate of 10 μA/s. All experiments were conducted at room temperature and without stirring.

3. Results and discussion

3.1. Effect of the K_2SO_4 concentration on the I–V curves

Fig. 3 shows typical current–voltage curves obtained for a K_2SO_4 solution at different concentrations. As it can be observed, the current–voltage curves are typical for a mono-polar cation-exchange membrane. The three characteristic regions can be distinguished. It is also observed that the value of the limiting current density increases with increasing K_2SO_4 concentration, because at the highest concentrations, it is more difficult to reach the zero concentration value at the membrane surface. In addition, the plateau length decreases as the concentration increases, the same effect was also observed by Barragan and Ruiz-Bauza [18].

Plotting the limiting current density values, as a function of the K_2SO_4 concentration, a good linear relationship was achieved as shown in Fig. 4.

If it is assumed that D, t_m and t_s remain constant, Eq. (1) predicts a proportional relationship between the limiting current density and the solution concentration, as experimentally observed in the study carried out by Krol et al. [19].

As shown in Fig. 5, a good linear relationships were obtained between the ohmic region slops (conductivity $1/R_o$) and the plateau slops ($1/R_p$) as a function of the potassium sulfate concentration.

This result suggests that in the ohmic region, the solution resistance was controlled by K_2SO_4 concentration but in the plateau region, the concentration differences between the membrane interface and the bulk solution controls the diffusion boundary layer resistance. What is happening now if we add boric acid when K^+ transfers through the CMX cation-exchange membrane?

3.2. Effect of the boric acid on the K_2SO_4 transfer

Fig. 6 shows the current–voltage curves of K_2SO_4 without (black), with boric acid 0.05 N (red) and 0.075 N (green). The obtained results showed that the addition of boric acid to a potassium sulfate solution does not affect the limiting current density and has no effects on the first ohmic region. The non-influence of boric acid on the limiting current density value and on the potassium ohmic transport through the CMX cation-exchange membrane should be associated with the boric acid properties in aqueous solutions, boric acid is a very weak electrolyte, therefore its dissociation is negligible and do not contributes to the migration current transport.

We can also see that the plateau length decreases and its slop increase when the boric acid concentration increases. We explain this behavior by the second

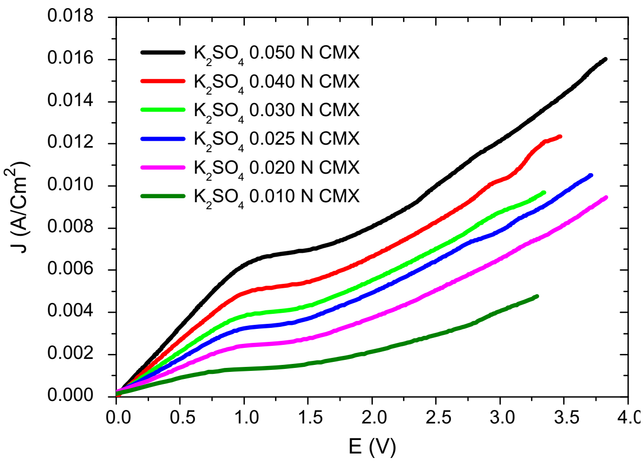

Fig. 3. Effect of K_2SO_4 concentration on the I–V curves of the CMX membrane.

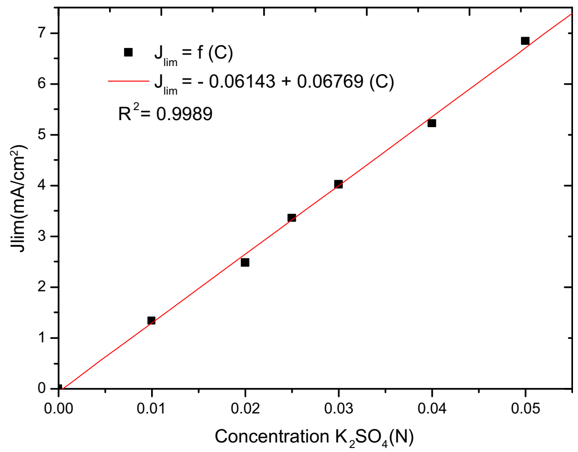

Fig. 4. Limiting current density as a function of K_2SO_4 concentration for the CMX membrane.

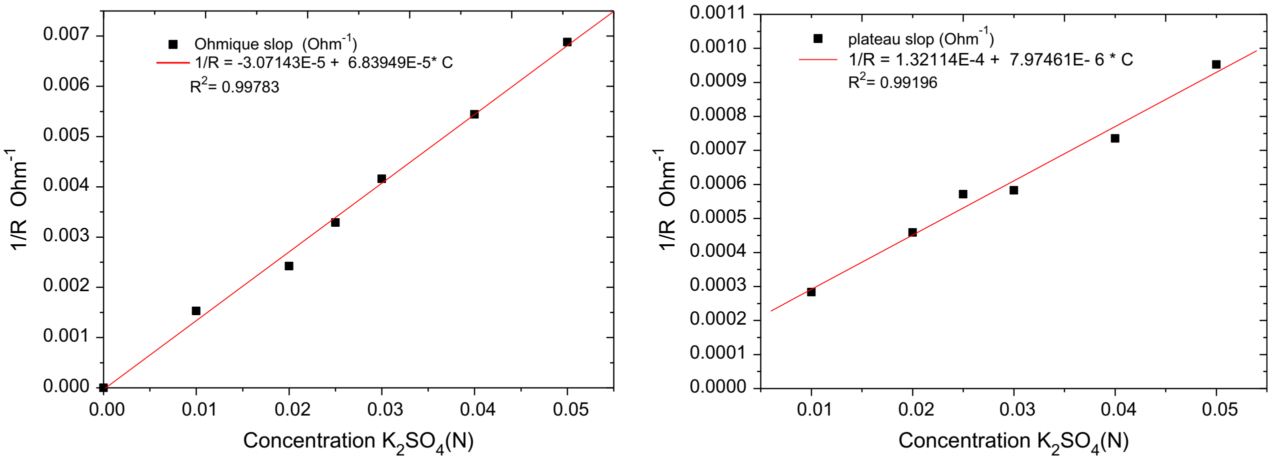

Fig. 5. The ohmic region slops and the plateau slops as a function of K_2SO_4 concentration for the CMX membrane.

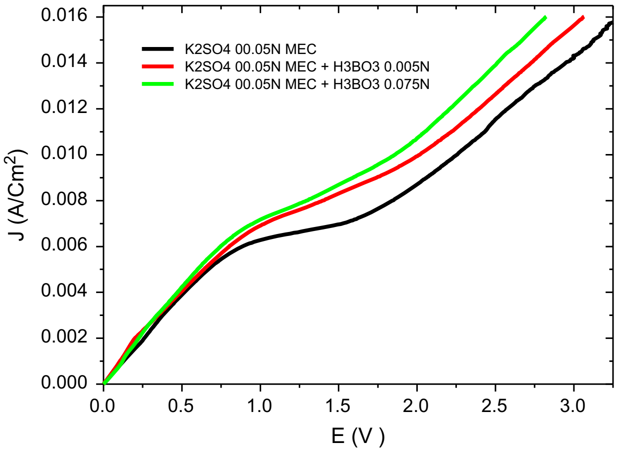

Fig. 6. Current–voltage curves of K_2SO_4 without (black), and with boric acid.

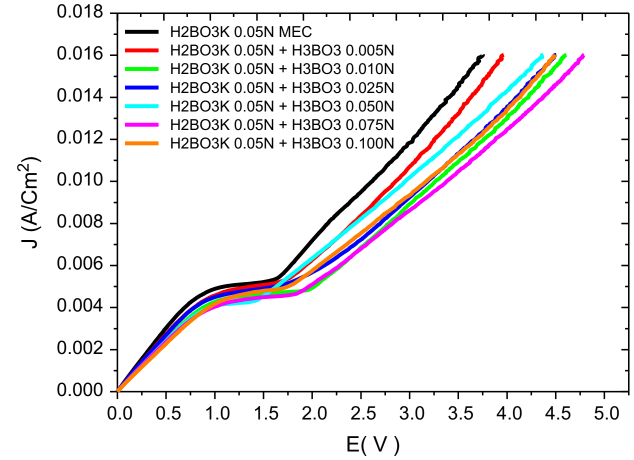

Fig. 7. Effects of the current density (mA cm^{-2}) vs. membrane voltage (V) curves of the CMX: (black) without boric acid and (others) with boric acid as a function of boric acid concentration.

Wien effect [20]; the boric acid (pKa = 9.23) plays a sacrificial role. It is dissociated before the water molecule (pKw = 14) causing then a sooner over-limiting current transport [21].

3.3. *Effect of the borate/boric acid buffer on the K_2SO_4 transfer*

In this case, we add boric acid to a potassium borate solution (0.05 N), as shown Fig. 7. It can be seen that by varying boric acid concentration progressively from 0.005 N to 0.1 N, the plateau length increases and we have a later onset of the over-limiting current regime.

Comparing the plateau length of the potassium counter-ion to that with the buffer solution mixture, the plateau length becomes larger with the buffer solution. The distance between the I–V curves measures directly the contribution of water dissociation (WD) to the over-limiting current transport, because when we use boric buffer, we eliminate the contribution of protons due to water dissociation at the membrane solution interface by their association with various poly-borates species presented in the investigated system (Fig. 8). However, The appearance of the over-limiting current with the buffer solution indicate that the K^+ counter-ion was transported in the over-limiting mode and WD is not a necessary condition to obtain the over-limiting current. The obtained results suggest that, the electro-convection phenomena is not the principal origin of the over-limiting current, it is due to a coupled mechanisms [6,23].

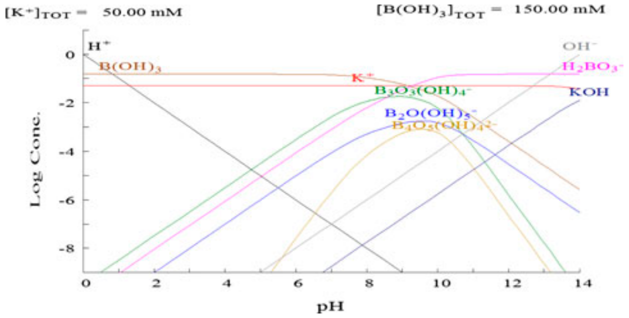

Fig. 8. Various poly-borates species present in the investigated solutions using the Hydra–Medusa program [22].

4. Conclusions

According to this study, we conclude that:

- In the case of potassium sulfate, the boric acid addition reduces the plateau length and we have a sooner over-limiting current that can explained by the second Wien effect.
- In the case of the potassium borate, we found a later onset of the over-limiting current and an increase in the plateau length with increasing boric acid concentration. This behavior was associated with the elimination of water dissociation contribution by various poly-borates species formed in the investigated system.
- The boric acid addition increases and decreases the polarization plateau length, it can play two different roles, depending on pH and boron concentration in the system.
- The appearance of the over-limiting current with the buffer solution indicates that the K^+ counter-ion was transported in the over-limiting mode, and WD is not a necessary condition to obtain the over-limiting current.
- The adapted electro-convection theory cannot explain the increase (buffer effect) and the decrease (weak electrolyte effect) in the polarization plateau length.

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