Investigation of the Acid Strength Effects on Bipolar Membrane Electrodialysis

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Abstract: The purpose of this paper is to investigate acid strength effects on the same system for production of two different acids. Production of two different acids from their salts was carried out by electro dialysis (ED) using bipolar membranes (BPM). An virulent acid hydrofluoric acid and an weak acid boric acid were produced, all data were recorded and compared. Result of the study, in electro dialysis of acids and base, acid strength play an important role in terms of the efficiency of the process. Current efficiency was calculated very high at all processes for this electro dialysis (EDBM) system. This results in a growing demand for alternative process solutions such as Electro dialysis with Bipolar Membranes (EDBM).

Keywords: Bipolar Membrane, Ion Migration, Current, Acid Strength.

1. INTRODUCTION

Bipolar membrane electro dialysis (EDBM) is a technology used for the production of protons and hydroxyl ions [1] widely studied and applied for a multitude of technical applications, amongst them the production of organic acids [2-12], in environmental applications such as waste water treatment [13-16] or carbon dioxide recovery [17] and in the food industry [18, 19]. A bipolar membrane consists of an anion Exchange layer (positively charged) and a cation Exchange layer (negatively charged). At the interface of both layers, water splitting takes place. H+ that migrates through the cation Exchange membrane towards the cathode and OH$^-$ that migrates through the anion exchange membrane towards the anode are produced. Overall, at the anode side an alkaline solutions formed and an acidic solution appears at the cathode side [1]. At the same time due to the nature of the membrane, the transport of ions across the bipolar membrane is prevented. This concept can be used to control the pH in electro- dialysis applications and is called BPM-ED.

Until today synthesis of the acid-base from salt was examined in many bipolar membrane processes at different membrane types and in different configurations. For example BMED was studied to regenerate concentrated organic and inorganic acids such as acetic acid [20], gluconic acid [21], citric acid [26], lactic acid [22] or phosphoric acid [23]. Only few papers were published concerning electro dialysis of

formic acid (26). Luo *et al*. [24] and Nagarale *et al*. [25] demonstrate the feasibility of ED in order to concentrate formic acid solution. Current efficiency is generally taken as the first criterion of the electro dialysis performance. When performing electro dialysis of organic acids the molecular acid diffusion contribution to reduce the current efficiency was underlined by several authors like those referenced [21-28]. Several studies have shown that the ED process, involving bipolar membranes, have economic potential for recovering inorganic, organic or amino acids [29]. But in the same process, effects of different two acids on the system were not investigated. The purpose of this paper is determined, that during the production of different two acids changes in the same process.

In this study, the virulent acid hydrofluoric acid from sodium fluoride and weak acid boric acid from borax was produced. All data were recorded and compared during the production of these acids.

2. EXPERIMENTAL

2.1. Materials

Chemicals Borax ($Na_2B_4O_7.10H_2O$), H_2SO_4, H_3BO_3, NaOH, Carmine indicator, NaF, HF, NaOH and TİSAB III (total ionic strength adjustment buffer) used in the experiments and analysis were purchased from MERCK. Ion-exchange membranes and bipolar membranes used in the electrochemical cell were purchased from PCA GmbH Table **1**. Illustrates the main characteristics of the commercial ED membranes used in this study.

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Table 1:   Main Characteristics of Membranes Used in this Work

Manufacturer	PCA GmbH	PCA GmbH
	PC acid 60	PC SK
Transference number KCl (0.1 / 0.5 N)[a] Acid (0.7/3 N)[b]	>0.95 55	>0,95
Resistance / Ω.cm²	~ 2	~ 2.5
Water content (wt%)	~ 17	~ 9
Ion exch. capacity Strong basic (meq.g-1): Weak basic (meq.g-1):	ca 1.14 ca 0.45	n/a

[a]Calculated from potentiometric measurements.
[b]Observed current efficiencies.

The experimental cell was composed of nine membranes. This cell included three paces of three compartments (salt, acid and base compartment). Each of the membranes has 64 cm² surface areas. The cathode is stainless steel and the anode is Pt/Ir alloy coated by titanium in ED cell. A scheme of the experimental set-up is illustrated in Figure **1**. In all compartments, solutions were circulated in a batch mode using centrifugal pumps.
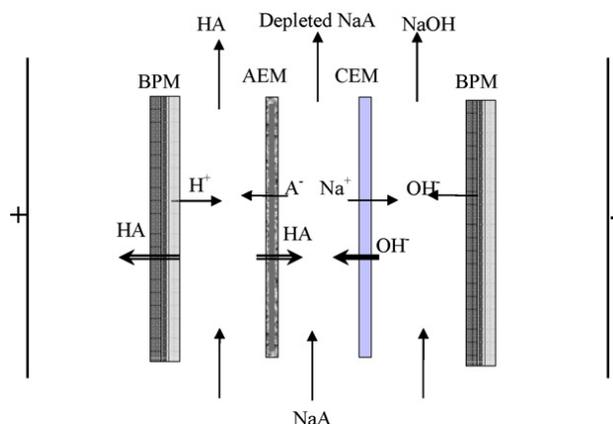
Figure 1: Principles of bipolar membrane electro dialysis and mass fluxes [30].

The streams containing acid, base and its salt solution were held at constant temperature (25°C) with a thermostatic controlled constant temperature water circulator and the serpentines located in each compartment. The changes in concentration of different solutions circulating in the ED unit were measured by samples from the each solution at regular time intervals. The needed constant voltage to the cell was supplied by digital controlled D.C. power supply.

2.2. Methods

The initial compositions of the solutions in each compartment were the following:

- 1 liter NaF solution in the salt compartment

- 1 liter 0, 1.10⁻⁵ M NaOH solution in the base compartment

- 1 liter 0, 1.10⁻⁵ M HF solution in the acid compartment

In this study, the values of chosen parameters were determined as follows: The values of initial NaF concentrations are of 0.025 M and 0.05 M, applied potential values of 5V, 7.5V, and 10V. The solution flow rate is of 0. 38 1/min in all experiments.

The analysis of fluorine was performed by Metler Toledo multi meter, analysis of sodium monitored by flame photometer (Sherwood 410) and analysis of boron was performed by carmine method and was monitored by UV spectrophotometer (Mapada V-1100) at wavelength of 585 nm.

3. RESULTS AND DISCUSSION

The current-time curves for the two acids were given at Figures **2-3** Molar flux was defined as the amount of transition mol in unit of time from unit membrane area. If ion concentration decreases, the amount of substance decreases from unit membrane area. It can be seen clearly at Figures **3-4** from HF 10V curve.

For the maximum voltage 10V, the current-time curve was shown at the Figure **4**. The transport process of salts through the membrane is diffusion controlled and depends on the hydrodynamic of system [31]. The selectivity of the membrane is dependent on concentration of fixed charge, concentric to the valence of the ions, to the valence of the counter ion and concentration of the electrolyte solution [32]. Hence,
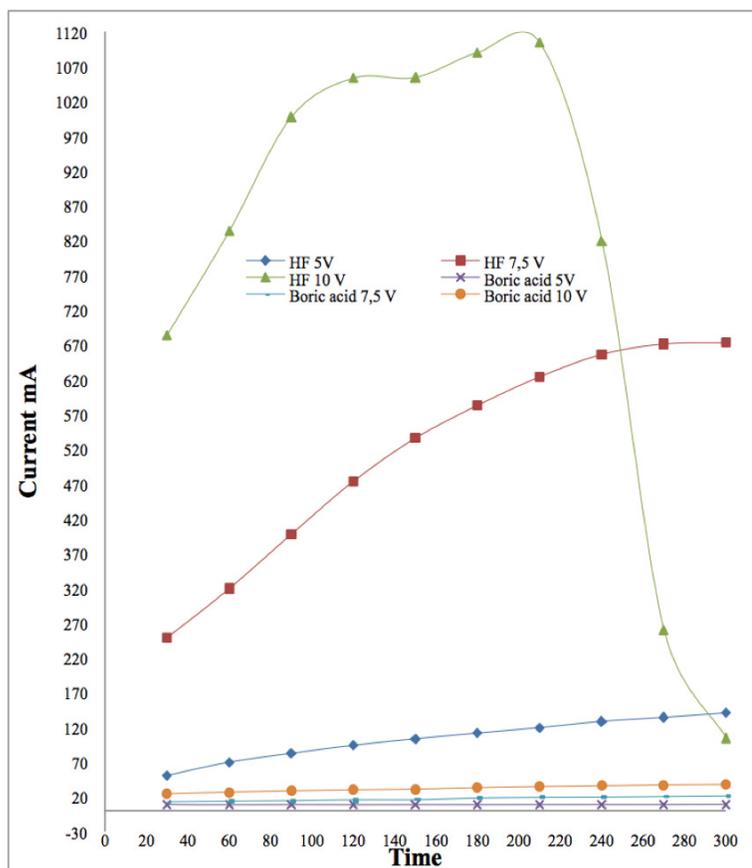
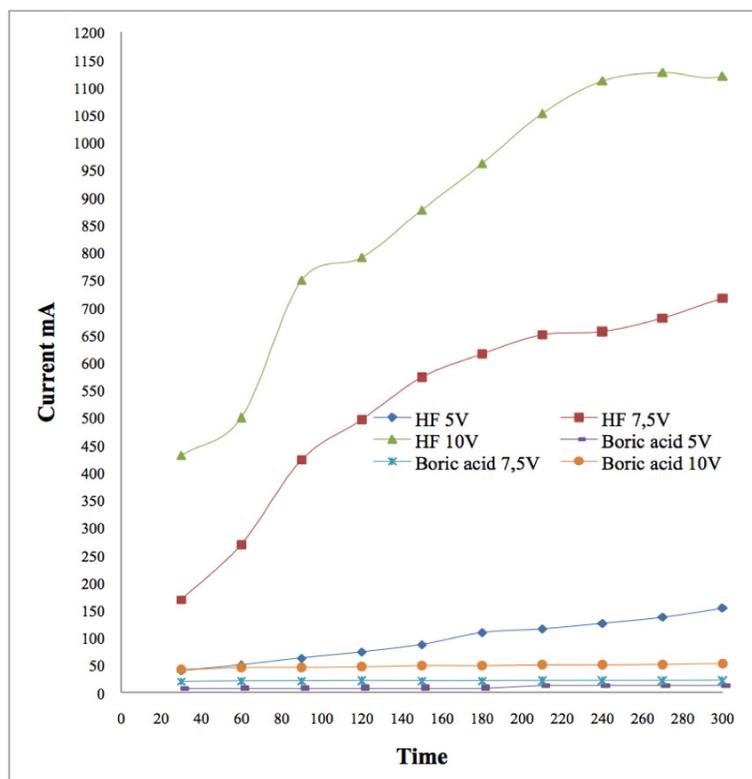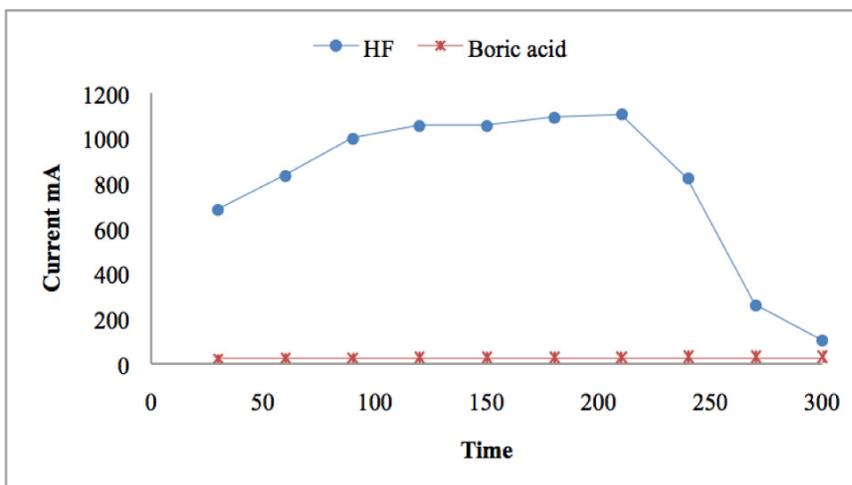**Figure 2:** Current-Time curves comparison of systems at 0.025 M HF and 0.025 M H_3BO_3 starting concentration.

Figure 3: Current-Time curves comparison of systems at 0.05 M HF and 0.05 M H_3BO_3 starting concentration.
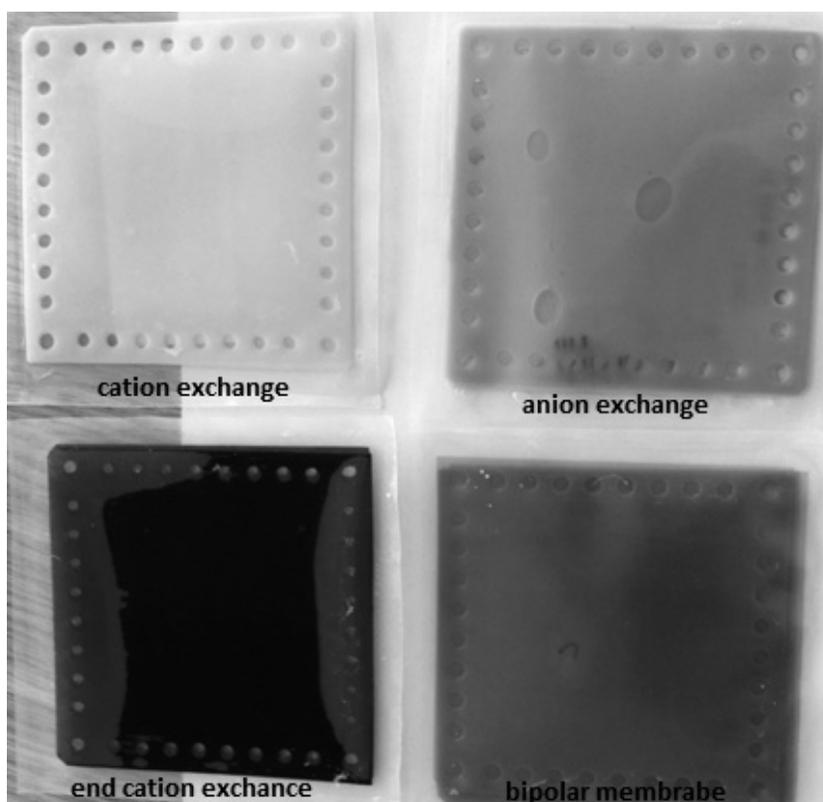
Figure 4: Current-Time curves comparison of systems at 0.025 M HF and 0.025 M H_3BO_3 starting concentration, 10V operating voltage and 0,38 l/min flow rate.

when looking at test results under the employed conditions and used system in this study, it can be seen easily the rate of production acid and base increases with increasing concentration.

However, membranes were damaged at high concentration and high voltage. As shown in Figures **5-6** for HF at 0.05 M concentration and 12.5 V applications, it was observed that due to excessive current density, membranes were seriously damaged.

In electro dialysis of acids, pH changes play an important role in terms of the efficiency of the process [33]. The change in the moles numbers of HF was more impressed to pH. Therefore, at the low voltage of the HF production rate was greater than the boric acid production rate.

At preliminary experiments made for this study, because of the strength of both acids, the effects of acids on membrane was found to be different. While at
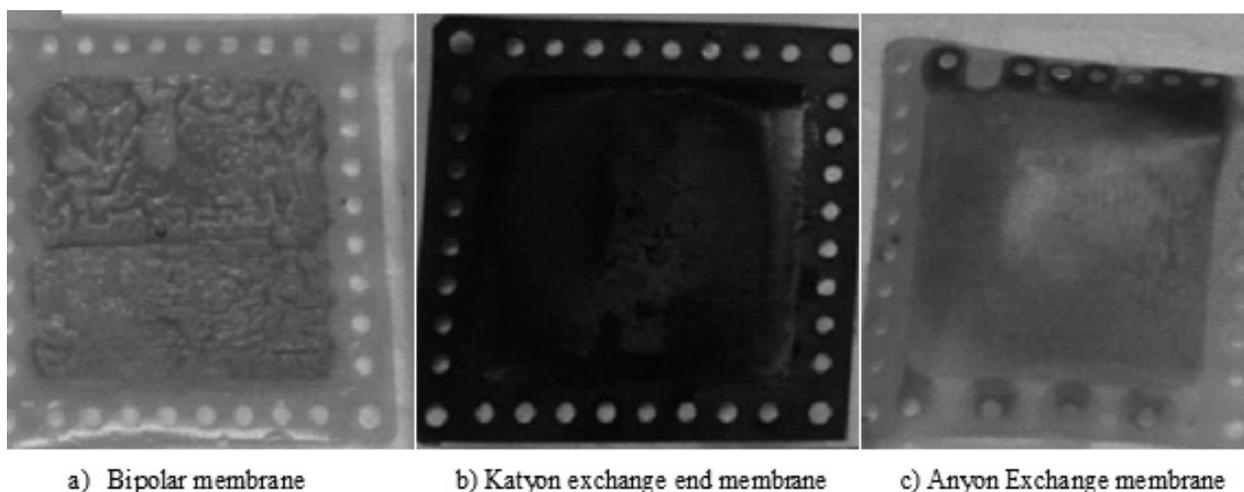

Figure 5: New membranes.

a) Bipolar membrane   b) Katyon exchange end membrane   c) Anyon Exchange membrane

Figure 6: Damaged membranes.

Table 2: Current Efficiency All Operations at End of 300 Minute

	Current Efficiency			
	Boric acid (0,025M)	**HF (0,025M)**	**Boric acid (0,05M)**	**HF (0,05M)**
10 V	0,88328	0,99179	0,960025	0,938402
7,5 V	0,99807	0,969363	0,940056	0,962072
5 V	0,96915	0,985128	0,922401	0,967055

the 0.05 M HF study can be applied maximum 10 V, at the 0.05 M boric acid study can be applied maximum 15 volt.

Current efficiency was calculated using the following equation. Starting from Faraday's law M theoretically was calculated.

$M_{theoretically}$: the mass of the substance liberated at an electrode in grams.

M: molecular weight (g)

n: valence effect

i: current (amperes)

t: time (sec)

F: faraday constant 96485 As / eg.

Current efficiency was calculated as the ratio actual value and theoretical value. The obtained values were shown in Table **2**.

4. CONCLUSION

Despite, working conditions and using membrane were same, because of different charges and different molecular diameters F^- and $B_3O_4^=$ ions were need different driving forces. Because of F^- ionic strength greater than $B_3O_4^=$, hydrofluoric acid production was needed less energy consumption more than boric acid. And fluorine ion diameter is smaller than the diameter of borate ions, fluorine ions passing through the membrane pores were more rapid than $B_3O_4^=$ ions, Figure **4** good example for this situation.

This results in a growing demand for alternative process solutions such as Electro dialysis with Bipolar Membranes (EDBPM). These must be simultaneously economically attractive and have a low impact on the environment.

Over-voltage application was caused separation anion and cation exchange layers of bipolar membrane from each other. In the industrial sense BPM processes, despite in this process acid and base can be obtained pure and in one step, it was required after concentrated study. Because the virulent acid was processed in this process wasn't concentrate. Using anion exchange and cation exchange membranes together bipolar membranes can be improved process which has high energy efficiency and low investment costs.

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