Three-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: Role of diffusion of molecular acid

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A B S T R A C T

Bipolar membrane electrodialysis is used in a three-compartment configuration to regenerate formic acid and sodium hydroxide from sodium formate. A previous study showed that the diffusion of molecular formic acid induces the loss of acid current efficiency. The present study shows the following results: the diffusion of molecular formic acid through the bipolar membrane explains quantitatively the presence of sodium formate in the sodium hydroxide solution. The loss of acid current efficiency is only due to diffusion of molecular acid through both anion-exchange and bipolar membranes. The sodium hydroxide current efficiency is determined by acid diffusion through the bipolar membrane and OH⁻ leakage through the cation-exchange membrane. The flux of acid diffusion through the membranes is proportional to acid concentration and depends on sodium hydroxide concentration for bipolar membrane and on sodium formate concentration for anion-exchange membrane. The flux rates vary with temperature.

A model based on mass balance is proposed to describe the bipolar membrane electrodialysis. Some experimental parameters like volume variations are needed.

It is seen that a low temperature is favourable to the process. So does an increase of current density. The nature of anion-exchange membrane also affects diffusion. It is found that PC acid 100 membrane is the less permeable to diffusion of formic acid among the 5 tested membranes.

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1. Introduction

Bipolar membrane electrodialysis (BMED) is used to regenerate organic acids and sodium hydroxide from sodium organic salts [1–4]. It is based on the ability of a bipolar membrane to split water into H⁺ and OH⁻ at membrane bilayer interface. In the three-compartment configuration represented in Fig. 1, H⁺ produced by the bipolar membrane forms an acid with the anion coming through the anion-exchange membrane while the salt cation crosses the cation-exchange membrane and forms a base with OH⁻ produced by the other face of the bipolar membrane. Among carboxylic acids, formic acid is less studied than others like acetic or lactic acids [5,6]. Ideally, formic acid and sodium hydroxide solutions obtained by three-compartment bipolar membrane electrodialysis are recovered pure and no formate is present in sodium hydroxide solution. However, this is not the case. Some formate pollutes the sodium hydroxide solution. Moreover the current efficiency is not as high as expected. This is principally due to acid diffu-

sion through membranes. Formic acid diffuses through the bipolar membrane and also through the anion-exchange membrane as shown by Jaime-Ferrer et al. [7]. In this study, flux rates were determined for bipolar and anion-exchange membrane. For formic acid concentration around 7 mol dm⁻³ and with 5 A dm⁻² current density the current efficiency approached 80%. The flux rate values at ambient temperature near 20 °C were 2.4 × 10⁻³ dm h⁻¹ and 6.1 × 10⁻³ dm h⁻¹, respectively, for bipolar membrane BP-1 and PC acid 100 membrane.

Carboxylic acids diffusion was mentioned as one factor reducing the current efficiency. Narebska et al. [8] studied diffusion of acetic, propionic and lactic acids through three anion-exchange Neosepta membranes (AMX, AM1 and ACM). They concluded that the smaller the carboxylic acid the higher its diffusion and that, among the three membranes, the less permeable is the AMX membrane. Wodzki and Nowaczyk [9,10] studied diffusion of some carboxylic acids (acetic, propionic, lactic, tartaric, oxalic and citric) through AFN-7 Neosepta membrane and through bipolar membrane. They concluded that acid permeation occurs by two mechanisms: solution-diffusion or reaction-diffusion. The first mechanism is pure diffusion and in the second mechanism a reaction with a carrier is assumed to occur in the membrane. Yu et al.

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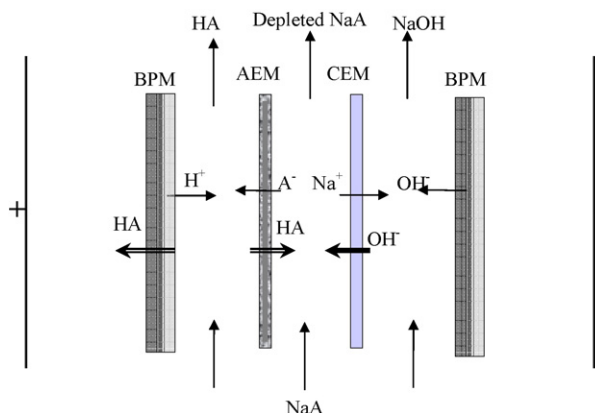*E-mail address:* mohammed.rakib@ecp.fr (M. Rakib).

Fig. 1. Principles of bipolar membrane electrodialysis and mass fluxes.

[11] studied acetic acid recovery from a diluted effluent in a three-compartment apparatus. They obtained a 30% acid solution but with a current efficiency around 40% under 1.5 A dm^{-2}. To explain this low current efficiency they pointed out diffusion of acetic acid through the bipolar and anion-exchange membranes. Koter [12] studied the weak acids production. The modelling given is very complex. Except [7], literature is poor concerning the conversion of sodium formate to formic acid and sodium hydroxide.

The performance of an electromembrane process is given in term of current efficiency which represents the ratio of the mole number produced or transferred and the number of faradays passed in the system. The integral current efficiency (ICE) between time 0 and time t is defined by the relation:

$$ICE_{0,t} = \frac{\Delta N}{iAt/F} \tag{1}$$

where ΔN is the variation of mole number of a component between time 0 and time t, i the current density assumed constant, A is the membrane area, F is the faraday (96,485 A s mol^{-1} = 26.8 Ah mol^{-1}).

The differential current efficiency (DCE) is defined as:

$$DCE_t = \frac{dN}{iA\,dt/F} \tag{2}$$

The aim of this study is to propose a model to predict the current efficiency of a three-compartment bipolar membrane electrodialysis. The model predicts also the contamination of sodium hydroxide solution by formate ion. The mechanism of leakage through the membranes is elucidated. Diffusion of molecular acid through the bipolar and anion-exchange membrane and migration of hydroxide ion through the cation-exchange membrane are the major limiting factors.

2. Experimental details

2.1. Ion-exchange membranes

The ion-exchange membranes used are listed in Table 1 where some of their properties are summarised. All these membranes were supplied by Eurodia Industries except the PC acid 100 membrane supplied by PCA Gmbh. Before use, the membranes were equilibrated with solutions during one night. Sodium hydroxide and sodium formate solutions were used respectively for the bipolar and anion-exchange membranes. The membranes were rinsed with demineralised water before use.

2.2. The experimental set-up

Diffusion was studied in a micro cell supplied by Electrocell AB. The cell was in two compartments configuration with the studied membrane as separator. The surface area was 0.1 dm^2. Circulation of the solutions was insured by two pumps from two thermostated reservoirs. In the case of bipolar membrane, the acid solution was fed in the compartment in contact with the cation-exchange layer of the membrane. The total volume of acid solution was 150 cm^3. 1 cm^3 or 2 cm^3 aliquots were taken every 30 min. The tests made to study diffusion were performed without electric current.

Electrodialysis was performed with a cell stack EUR 2C-BIP supplied by Eurodia Industries. It was composed of four cells with three compartments (Fig. 1). Two nickel electrodes with NaOH 2 mol dm^{-3} rinsing solution terminated the stack. They did not interfere with the electrodialysis. Active membrane surface area was 2 dm^2 per cell. Temperature was measured but not controlled. A constant current was applied.

The same hydrodynamic regime was insured in the small cell and in the stack by the circulation at the same velocity and by the use of the same spacer.

2.3. Reagents and solutions

Formic acid 97% was supplied by Avogado, sodium formate 98% and sodium hydroxide 37% were supplied by VWR.

The solutions were titrated for acid and base contents. Formate (as formic acid or sodium formate) and sodium ion in low concentration were determined using ionic chromatography (Dionex).

3. Results and discussion

The model proposed is based on diffusion of molecular acid as the only phenomenon reducing the current efficiency of production of formic acid. This assumption is validated because of its consequences.

Table 1
Membrane properties

	Membrane	Nature	Capacity (equiv. kg^{-1})	Electric Resistance (Ω cm^2)	Water content (%)
AEM	PC acid 100	Strong and weak bases	0.4–0.6		18
	ACS	Strong base	1.4–2	2–2.5	20–30
	ACM	Strong base	1.5	4–5	15
	AHA	Strong base	0.5–3	3–5	13–20
	AMX	Strong base	1.4–1.7	2–3.5	25–30
CEM	CMB	Strong acid	2.4–2.7		37–42
BP	BP-1	Bipolar	0.2 (AEL) 1.12 (CEL)		25
	BP-1E	Bipolar			

These data are from different sources.