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Three compartment bipolar membrane electro dialysis of sodium formate

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Abstract:

Bipolar membrane electro dialysis is used in three compartment configuration to regenerate formic acid and sodium hydroxide from sodium formate. The preceding study [7] showed that diffusion of molecular formic acid is responsible of 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 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 in the membranes is proportional to acid concentration. The transfer coefficients vary with the temperature.

A model based on mass balance is proposed to describe the electro dialysis. Some experimental parameters like volume variations are needed. It is seen that, following the model, 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 formic acid among 5 tested membranes. The flux of hydroxide ion through the CMB cation exchange membrane is evaluated.

Keywords: Bipolar membrane electro dialysis, formic acid, diffusion through bipolar membrane, diffusion through the anion exchange membrane, hydroxide ion leakage through the cation exchange membrane, modelling.

1. Introduction

Bipolar membrane electro dialysis (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 figure 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 a 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 electro dialysis 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 diffusion 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, transfer coefficients 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 approaches 80%. The transfer coefficient values at ambient temperature near 20°C were 0.0024 dm h^{-1} and 0.0061 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 is its diffusion and that, among the three membranes the less permeable is the AMX membrane. Wodzki et al. [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. [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 point out diffusion of acetic acid through the bipolar and anion-exchange membranes. Koter S. [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 is defined by the relation:

$$\eta = \frac{\Delta N}{iA\Delta t / F} \quad (1)$$

where ΔN is the variation of mole number of a component, i the current density, A is the membrane area, F is the faraday ($96485 \text{ A s mol}^{-1} = 26.8 \text{ Ah mol}^{-1}$) and Δt the interval of time chosen for integration.

The aim of this study is to validate the equations describing the three compartment configuration, to evaluate the current efficiency of formic acid, sodium hydroxide and sodium formate and to predict the effect of varying the operating conditions.

2. Experimental details

2.1. Ion exchange membranes

The homopolar membranes used are listed in table 1 where some of their properties are summarised. Besides, BP-1 and BP-1E bipolar membranes were used. All these membranes were supplied by Eurodia Industries except the PC acid 100 membrane supplied by PCA GmbH. Each membrane is conditioned in the wetting solution and rinsed with demineralised water before use.

2.2. Diffusion studies

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

2.3. Stack

Electrodialysis was performed with a cell stack EUR 2C-BIP supplied by Eurodia Industries. It was composed of 4 cells with three compartments (figure 1). Two nickel electrodes with $\text{NaOH } 2 \text{ mol dm}^{-3}$ rinsing solution terminate the stack. They do not interfere with the

electrodialysis. Active membrane surface area was 2 dm² per cell. Temperature was measured but not controlled. In these experiments the initial volume per unit area (dm²) values were the following: 0.151 dm, base circuit:0.145 dm and salt circuit: 0.537 dm. A constant current is applied.

2.4. Reagents and solutions:

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

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

3. Results and discussion

The subscripts a, s and b refer to acid, salt and base solutions. The subscript w refers to water. Formic acid concentrations up to 5 mol dm⁻³ (23%) are considered. According to figure 1, formic acid may diffuse through bipolar membrane into sodium hydroxide solutions and through anion-exchange membrane into sodium formate solution.

Figure 1 summarise the exchange of species in the electrodialysis device.

To model the electrodialysis the following assumptions are made:

- The loss of formic acid is due to its diffusion through the membranes
- The cation-exchange membrane presents an hydroxide leakage
- The OH⁻ concentration in the salt compartment is low and the flux of OH⁻ through the anion-exchange membrane is negligible
- The diffusion of formate ion (opposite to the electric field) through the cation-exchange membrane is negligible
- The average temperature is taken

The mass-balance equations may be written

The formic acid balance is written (neglecting the migration of ionic species other than H⁺ and OH⁻ through the bipolar membrane i.e. the efficiency of production of H⁺ by the bipolar membrane is 100%):

$$d(V_a [\text{HCOOH}]_a) = \frac{iA dt}{F} - (k_{\text{bip}} + k_{\text{aem}}) [\text{HCOOH}]_a A dt \quad (6)$$

The acid accumulation results from the acid production (positive term) and diffusion through the membranes (negative terms). V_a is the volume of acidic solution, A the membrane area and i the current density.

The balance of sodium formate is the following neglecting its diffusion through cation exchange membrane and leakage of H^+ through the anion-exchange membrane due to its very low concentration [13].

$$d(V_s [NaHCOO]_s) = -\frac{iAdt}{F} + k_{aem} [HCOOH]_a Adt \quad (7)$$

The first term assume that the transport number of formate ion through the AEM is almost 1 and the second term that formic acid in the salt compartment (diffusion through the AEM) is neutralised by OH^- coming from the basic compartment.

The balance on the sodium hydroxide may be written:

$$d(V_b [NaOH]_b) = \frac{iAdt}{F} - k_{bip} A [HCOOH]_a dt - \alpha' [NaOH]_b dt \quad (8)$$

α' is the transfer coefficient of OH^- through the CEM. The mechanism is different for OH^- compared to $HCOOH$. Migration is responsible of the hydroxide ion transfer. Thus, α' is proportional to the current. $\alpha' = \alpha i A$. [14-15].

Equation (6) may be written as follows:

$$V_a d[HCOOH]_a = \frac{iAdt}{F} - (k_{bip} + k_{aem}) [HCOOH]_a Adt - [HCOOH]_a dV_a \quad (9)$$

k_{bip} and k_{aem} vary with temperature. Starting from ambient for the first electro dialysis and not far from 313 K, the temperature reaches rapidly (less than 1 h) a stable value around 313 K under a current density of 5 A dm^{-2} . The values of transfer coefficients are corrected for temperature effect knowing the activation energy.

The relation (10) gives the concentration of formate anion in sodium hydroxide solution:

$$d(V_b [HCOO^-]_b) = k_{bip} A [HCOOH]_a dt \quad (10)$$

This means that the only source of formate ion in sodium hydroxide solution is the passage through the bipolar membrane.

The integration of the equation (9) is possible analytically.

$$[HCOOH]_a = \frac{iA/F - (iA/F - (k_{bip} + k_{aem} + \lambda_a i)A[HCOOH]_0)(1 + \lambda_a iAt/V_a^0)^{-(k_{bip} + k_{aem} + \lambda_a i)/\lambda_a i}}{(k_{bip} + k_{aem} + \lambda_a i)A} \quad (11)$$

where $[\text{HCOOH}]_0$ and V_a^0 are the initial values of the formic acid concentration and volume and λ_a the acid volume variation per current quantity. Nevertheless resolution of equations (7-10) is undertaken numerically. The numerical solving is based on calculation of small variations of concentrations during a small laps of time.

3.3.4.1. Fitting of formate ion in sodium hydroxide:

This fitting of formate ion concentration in sodium hydroxide solution enables the determination of k_{bip} . Equation (10) is considered (it is assumed when writing this equation that, when current is on, no formate ion is transferred through the cation-exchange membrane to the base circuit). The only transport of formate to the base circuit occurs by diffusion of formic acid through the bipolar membrane. The associated anion-exchange membrane is ACS or AMX membranes. The coefficient k_{bip} is obtained by minimizing the least squares errors between experimental points and calculated values applying relation (). The temperature varies between 293 and 303 K in the two experiments with AMX membrane. The experiment with ACS membrane is done at an average temperature of 311 K. The value of k_{bip} is: 0.005 dm h^{-1} for the experiment at 311 K. Others determination of k_{bip} : 0.0045 dm h^{-1} and 0.0048 dm h^{-1} at an average temperature of 298K. Figure 3 shows the agreement of experimental values with the predicted ones for three experiments where the concentration of formic acid is increased in the range indicated. The leakage is more important where acid concentration is higher.

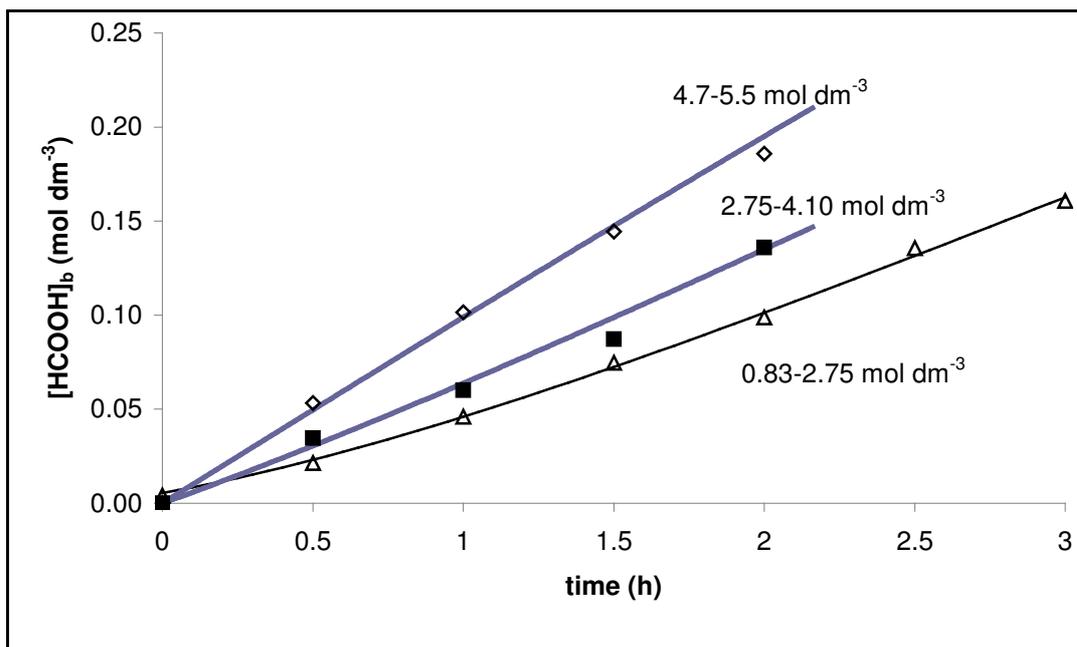


Figure x: variations of formate concentration in sodium hydroxide solution – experimental points and calculated curves (Δ $i = 500 \text{ A m}^{-2}$, V_{0b} (NaOH initial volume) = 1.16 dm^3 , acide range $0.8\text{-}2.7 \text{ mol dm}^{-3}$; \blacklozenge $i = 1000 \text{ A m}^{-2}$, $V_{0b} = 1.73 \text{ dm}^3$, acide range $2.75 - 4.1 \text{ mol dm}^{-3}$; \diamond $i = 1000 \text{ A m}^{-2}$, $V_{0b} = 1.73 \text{ dm}^3$, acide range $4.4\text{-}5.5 \text{ mol dm}^{-3}$).

3.3.4.2. Fitting of acid concentration

The fitting of formic acid concentration versus time enables to determine k_{aem} . Its value is 0.018 dm h^{-1} for ACS membrane at 308 K average temperature. For AMX membrane the average value is 0.011 dm h^{-1} at 298 K average temperature. Figure 13 shows the fitting is good. The small deviation is due probably to variation of temperature..

3.3.4.3. Fitting of sodium formate concentration:

The fitting of sodium formate concentration enables determination of k_{aem} also. It gives the following value 0.019 dm h^{-1} for the experiment with ACS membrane t average temperature 308 K . for AMX membrane, the values obtained are the following: 0.015 and 0.017 dm h^{-1} . Figures show the quality of fitting for acid and salt concentration. The evolution of salt concentration seems slightly linked to acid concentration. The same variations are observed for two levels of acid concentration but there is a small difference between the 2 cases: the variations are less for higher acid concentration.

The deviation between the predicted values and the experimental ones is probably due to variation of temperature.

3.3.4.4 fitting of sodium hydroxide concentration

The fitting of sodium hydroxide concentration enables the calculation of hydroxide anion leakage through the cation-exchange membrane. The values obtained are given in table x. 0.003 at 298K and 0.004 at 308 K . Figure x reports the variations of sodium hydroxide concentration observed and calculated. The agreement is good.

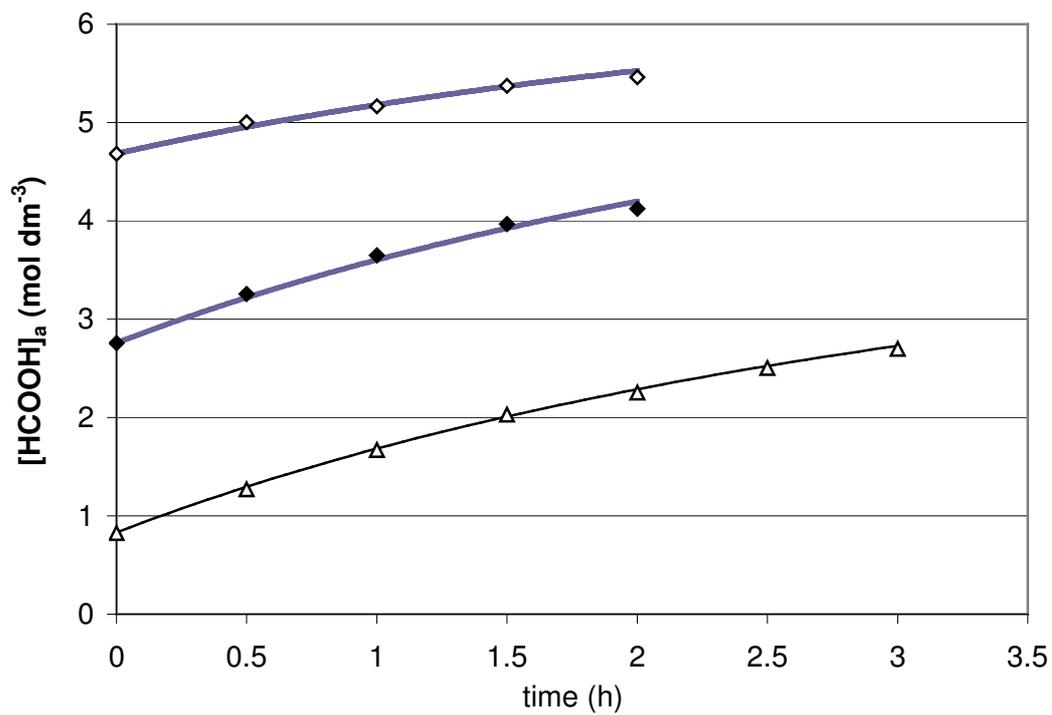


Figure x: variations of formic acid solution concentration vs. time - - experimental points and calculated curves (Δ $i = 500 \text{ A m}^{-2}$, V_{0a} (HCOOH initial volume) = 1.21 dm^3 , acide range $0.8\text{-}2.7 \text{ mol dm}^{-3}$; \blacklozenge $i = 1000 \text{ A m}^{-2}$, $V_{0a} = 1.71 \text{ dm}^3$, acide range $2.75\text{-}4.1 \text{ mol dm}^{-3}$; \diamond $i = 1000 \text{ A m}^{-2}$, $V_{0a} = 1.71 \text{ dm}^3$, acide range $4.4\text{-}5.5 \text{ mol dm}^{-3}$).

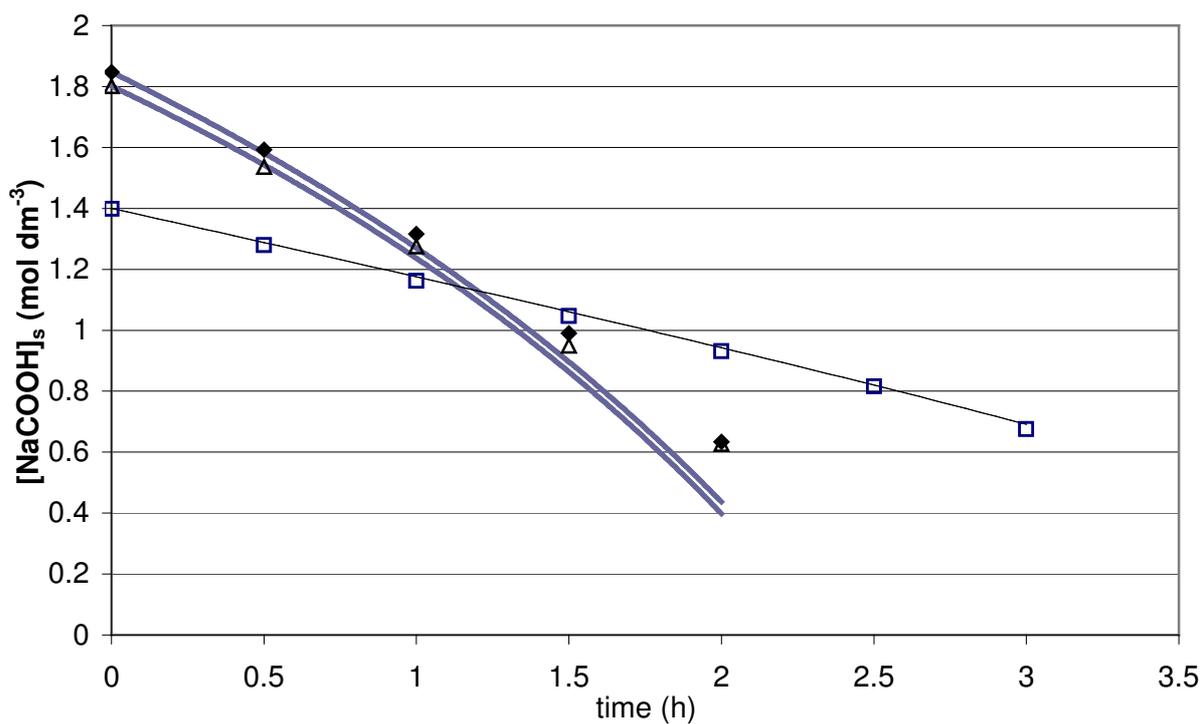


Figure x: variations of formic acid solution concentration vs. time - - experimental points and calculated curves (Δ $i = 500 \text{ A m}^{-2}$, V_{0s} (NaCOOH initial volume) = 4.30 dm^3 , acide range $0.8\text{-}2.7 \text{ mol dm}^{-3}$; \blacklozenge $i = 1000 \text{ A m}^{-2}$, $V_{0s} = 3.36 \text{ dm}^3$, acide range $2.75\text{-}4.1 \text{ mol dm}^{-3}$; \blacktriangle $i = 1000 \text{ A m}^{-2}$, $V_{0s} = 3.36 \text{ dm}^3$, acide range $4.4\text{-}5.5 \text{ mol dm}^{-3}$).

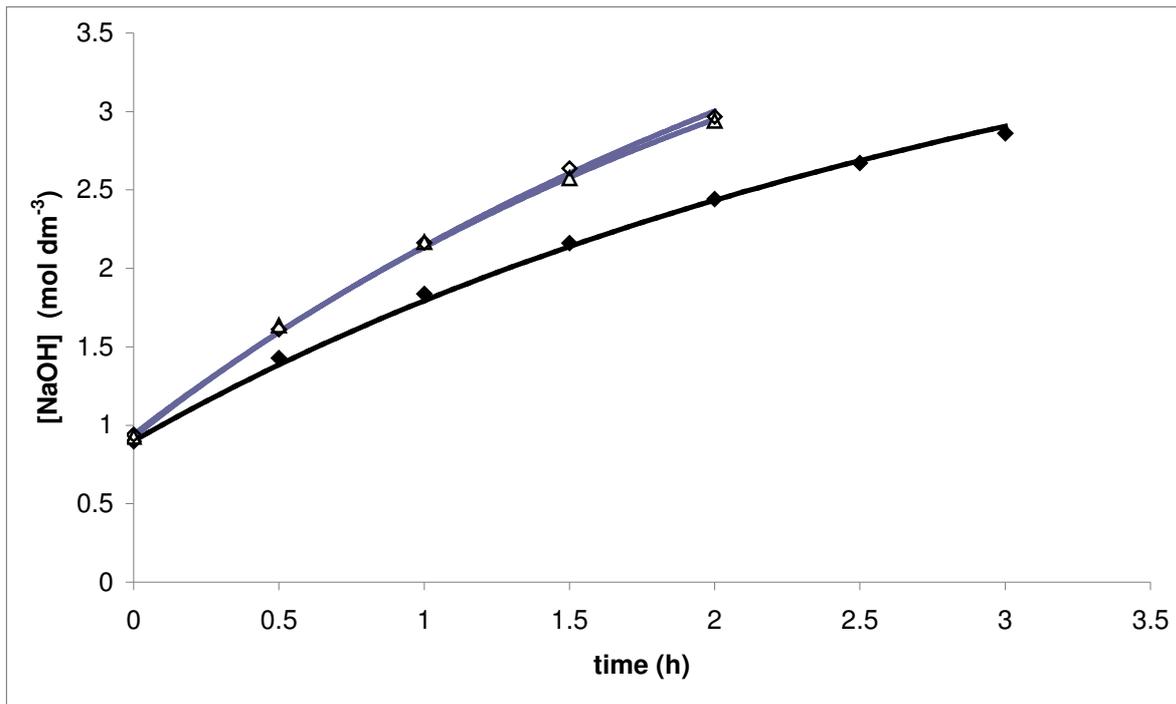


Figure: variations of sodium hydroxide concentration with time . – experimental points and calculated curves (\blacklozenge $i = 500 \text{ A m}^{-2}$, V_{0b} (NaOH initial volume) = 1.16 dm^3 , acide range $0.8\text{-}2.7 \text{ mol dm}^{-3}$; \triangle $i = 1000 \text{ A m}^{-2}$, $V_{0b} = 1.73 \text{ dm}^3$, acide range $2.75\text{-}4.1 \text{ mol dm}^{-3}$; \diamond $i = 1000 \text{ A m}^{-2}$, $V_{0b} = 1.73 \text{ dm}^3$, acide range $4.4\text{-}5.5 \text{ mol dm}^{-3}$)

3.3.4.5 Summary of the values of transfer coefficients

Table x reports the values obtained:

	k_{bip}	k_{aem}	α	Average temperature (K)
BM/ACS/CMB	0.005	0.018-0.019	0.0041	308
BM/AMX/CMB	0.0045	0.011-0.015	0.0028	298
BM/AMX/CMB	0.0047	0.011-0.017	0.0029	298

In order to improve the preceding results, the formic acid diffusion coefficients determination is undertaken and the value compared to those obtained by fitting.

3.1. Formic acid diffusion through bipolar membranes BP-1 or BP-1E

3.1.1. Diffusion of formic acid through BP-1 membrane into water

Formic acid diffuses from solutions into water through the bipolar membrane BP-1 separating the two media. The temperature is kept equal to 298 K.

Formic acid concentration in water varies versus time as reported in figure 2. The total volume of water is practically constant. The water passage is negligible and the aliquots volumes cause variations of the total volume from 0.150 dm³ to 0.146 dm³. An average volume of 0.148 dm³ is taken. Concentration of formic acid in water varies linearly vs. time. This is because acid concentration in the acidic medium does not deplete noticeably during the operation, the quantity that diffuses is negligible compared to the quantity undergone in the acidic solution. The diffusion rate is defined as the slope of the line giving the acid concentration in water vs. time. It is reported vs. acid concentration in the original acidic solution. The variations are linear as reported in figure 3 (the slope of the line is $s = 0.0028 \text{ h}^{-1}$ and the value at $x = 0$ is negligible).

The flux of formic acid through the bipolar membrane is given by the relation:

$$\phi = V_w s [\text{HCOOH}]_a / A \quad (2)$$

where V_w is the water volume $V_w = 0.148 \text{ dm}^3$, A is the membrane area $A = 0.1 \text{ dm}^2$,

That is,

$$\phi = k_{\text{bip}}^w [\text{HCOOH}]_a \quad (3)$$

$$k_{\text{bip}}^w = V_w s / A \quad (4)$$

ϕ is the flux in $\text{mol dm}^{-2} \text{ h}^{-1}$ and the transfer coefficient is the constant $k_{\text{bip}}^w = 0.0041 \text{ dm h}^{-1}$ at 298K.

3.1.2. Diffusion of formic acid through BP-1 membrane into NaOH solutions

The sodium hydroxide concentration is taken equal at 0.5 or 1 or 2 mol dm⁻³. The variations of formate concentration are similar to those obtained with water. The flux is obtained from figure 4 where the slopes of lines (formate concentration in NaOH solutions vs. acid concentration) are reported versus the original acid solution concentration.

$$\phi = k_{\text{bip}} [\text{HCOOH}]_a \quad (5)$$

At 298K, $k_{\text{bip}} = 0.0045 \text{ dm h}^{-1}$ for $[\text{NaOH}] = 0.5 \text{ mol dm}^{-3}$ and 0.005 for $[\text{NaOH}] = 1$ or 2 mol dm^{-3} . (ϕ in $\text{mol dm}^{-2} \text{ h}^{-1}$).

The transfer coefficient varies versus sodium hydroxide concentration. The transfer coefficient increases with the sodium hydroxide concentration until 1 mol dm^{-3} then it stabilises. This is explained by the presence of OH^- in the anion exchange layer. OH^- reacts

with the formic acid to give formate ion and maintain the chemical potential at its maximum. The formate anion is more mobile than formic acid in an anion-exchange membrane. The concentration of OH^- in the membrane is limited so the enhancement is limited and attains a plateau.

3.1.3. Comparison of BP-1 and BP-1E membranes

Figure 5 shows that BP-1E membrane is more favourable to formic acid diffusion in the acid concentration range (0 - 2 mol dm^{-3}). The transfer coefficient is higher in the case of BP-1E membrane. This is explained by the difference in membrane structure. The catalyst is different and BP-1E membrane is more permeable to water. Diffusion of formic acid is also enhanced.

3.1.4. Effect of temperature

Figure 6 shows the effect of temperature on the transfer coefficient between 298 K and 313 K. It reports the variations of $\ln(k_{\text{bip}})$ vs. $1/T$ (Arrhenius equation $k_{\text{bip}} = B \exp(-\Delta E/RT)$ where ΔE is the activation energy for diffusion through BP-1E membrane into sodium hydroxide solution 1 mol dm^{-3} , B a constant, R the ideal gas constant and T the temperature in Kelvin). The activation energy is equal to 18 kJ mol^{-1} in accordance with the physical characteristics of the phenomena (diffusion)..

3.2. Formic acid diffusion through anion-exchange membranes

3.2.1 Diffusion of formic acid through ACS and PC acid 100 membrane into water

Formic acid concentration in water contacted with formic acid solution increases linearly versus time. The flux of acid is unchanged with time. Figure 7 reports the determination of the transfer coefficient through the membrane into water. The value of transfer coefficient obtained is about 0.0083 dm h^{-1} for ACS membrane at 298 K and 0.0045 dm h^{-1} for PC acid 100 membrane.

The diffusion through ACS membrane into sodium formate (1 or 2 mol dm^{-3}) solutions is reported in figure 8 and does not modify noticeably the value obtained with water (0.0083 dm h^{-1})

3.2.3. Effect of temperature

Figure 9 shows Arrhenius diagram for ACS and PC acid 100 membranes for transfer to formate solution 1 mol dm^{-3} . The activation energy is calculated from the slope of line obtained. The slope values are very close and give activation energy around $36\text{-}38 \text{ kJ mol}^{-1}$. This value is higher than the one obtained with bipolar membrane. The activation energy intermediate between physical and chemical limiting phenomena

3.2.4. Comparison of different anion exchange membranes

Different anion exchange membranes were used and formic acid diffusion was measured through them. Figure 10 reports the transfer coefficients for formic acid solution (less than 5 mol dm^{-3}) into water through the chosen membranes. The PC acid 100 membrane is the less permeable and the AMX is the most favourable to diffusion. The order of transfer coefficient of the tested membranes is PC Acid 100 < ACS < ACM < AHA < AMX. This is explained by the difference between membranes such reticulation, membrane thickness, water content, capacity.

3.3. Electrodialysis pilot tests

Bipolar membrane electrodialysis on pilot scale was performed using the three compartment cell described in the experimental details with BP-1, CMB and ACS membranes. The volumes of the solutions and the concentrations of all species were measured included the minor species resulting from leakage through the membranes.

3.3.1. Modelling

The formic acid concentration versus time may be predicted from the data given above if the loss is due to diffusion only. This assumption was made and checked. All the electrodialysis experiments were made with a constant current during all the experiment.

3.3.2. Volume variations:

V_a , V_b and V_s vary linearly versus time at constant current density [14]

$$V = V_0 + \frac{dV}{dt} t \quad (12)$$

Figure 11 shows that volume variations are linear versus time for a given current density (5 A dm^{-2}) and given set of membranes (BP-1, ACS and CMB membranes). Moreover they depend only on current density and surface area of membranes [7, 14-15]. dV/dt may be written:

$$dV/dt = \lambda i A \quad (13)$$

The values of dV/dt are the following;

Acid circuit: $0.136 \text{ dm}^3 \text{ h}^{-1}$

Salt circuit: $-0.296 \text{ dm}^3 \text{ h}^{-1}$

Base circuit: $0.107 \text{ dm}^3 \text{ h}^{-1}$

Table 2 summarises the volume variations obtained per current quantity for the three solutions

3.3.3. Cell voltage

For $i = 5 \text{ A dm}^{-2}$, the cell voltage is about 12-13 V for 4 cells and the electrodes. Thus the voltage is less than 3 V per cell for the cited value of current density. The electrochemical specific energy consumption assuming a current efficiency near 100% is about 1.8 kWh per kg of formic acid and 0.88 kg of sodium hydroxide. If the current efficiency is far from 100% then this number is to divide by the value of current efficiency.

3.3.4. Optimisation

3.3.4.4. Fitting of sodium hydroxide concentration

Adjusting the parameter α fits the sodium hydroxide concentration versus time. Figure 15 shows the result and the fitting gives the value of $\alpha = 0.0042 \text{ dm}^3 (\text{Ah})^{-1}$ or $11.3 \text{ dm}^3 \text{ Faraday}^{-1}$.

3.3.4.5. Results of fitting

Table 3 reports the values obtained with ACS membranes and compares them to those obtained in diffusion tests. The agreement is good. The equations describing the bipolar electro dialysis with three compartments fit well the experimental results. The transfer coefficients are close to those determined by diffusion studies. This strengthens the model.

3.3.5. Current efficiency

The current efficiency is calculated from the data above for the following set of values k_{bip} (at 298 K) = 0.0028 dm h^{-1} , k_{aem} (at 298 K) = 0.007 dm h^{-1} and $\alpha = 0.0042 \text{ dm}^3 (\text{Ah})^{-1}$. Considering OH^- leakage, its contribution to sodium hydroxide current efficiency reduction is near 11% at 5 A dm^{-2} current density. Formic acid, sodium formate and sodium hydroxide current efficiencies are given in figure 16. They decrease when the acid concentration increases. The values are in good agreement with experimentally determined values: the final values are 82% (calculated for the formic acid range $0.83 - 2.7 \text{ mol dm}^{-3}$) versus 77%

experimental value for formic acid and 74% (calculated) versus 74% (experimental) for sodium hydroxide. The deviation between experimental value of acid efficiency and calculated value is due to variation of temperature. The salt current efficiency is also given in figure 16. Its value is 85% (calculated) and the experimental value is 83%. The deviation is explained as temperature effect.

3.4. Model validation

An experiment during 9 h was undertaken using PC acid 100 membrane as anion-exchange membrane. Figure 17 gives the experimental points and the calculated curve with $k_{aem} = 0.004$ at 298 K. The temperature of the electrodialysis was around 313 K except during the first hour. The agreement is very good.

3.5. Prediction of operating conditions effect on current efficiency

The operating conditions (current density, temperature) affect the process performance.

3.5.1. Prediction of the effect of temperature

The variation of temperature of electrodialysis results in variation of the two coefficients k_{bip} and k_{aem} . A priori, the other parameters are not affected noticeably. For the same range of acid concentration (0.83 – 2.7 mol dm⁻³) and a current density of 5 A dm⁻², the current efficiency varies from 0.82 to 0.87 when temperature varies from 313 K to 298 K. the effect of temperature is important. One must maintain the temperature as low as possible.

3.5.2. Prediction of the effect of membrane choice

The anion-exchange membrane is to select judiciously. The value of k_{aem} depends on the chosen membrane. Among the membranes studied the less permeable to acid is PC acid 100 membrane. The value of k_{aem} for this membrane is 0.004 dm h⁻¹ at 298 K. The current efficiency for the same range of acid concentration (0.83-2.7 mol dm⁻³) and a current density of 5 A dm⁻² is 0.88 instead of 0.82 for ACS membrane. For AMX membrane $k_{aem} = 0.01425$ dm h⁻¹ at 298 K and the current efficiency value is 0.64.

3.5.3. Prediction of the effect of current density

For the same range of acid concentration 0.83-2.7 mol dm⁻³ and the same temperature, the acid and base current efficiency for PC acid 100 and ACS membranes varies as shown in table 4. A high current density is favourable to production of acid and sodium hydroxide since

the diffusion is proportional to time while migration depends on current quantity. But high current implies high voltage and high energy consumption.

4. Conclusion:

The regeneration of formic acid and sodium hydroxide from sodium formate using bipolar membrane technique was studied in a three compartment electro dialysis cell.

The transfer of formic acid by diffusion explains quantitatively the observed presence of formate ion in sodium hydroxide solution and the current efficiency of acid production. The current efficiency of sodium hydroxide production depends on both diffusion of formic acid through the bipolar membrane and OH^- leakage through the cation exchange membrane.

The best current efficiencies are obtained for a high current density and low temperature. The anion exchange membrane nature is also important (the transfer coefficient varies in a large extent between PC acid and AMX membranes). The hydroxide anion leakage through the cation exchange membrane must be minimised. The effect of temperature is more pronounced on the anion-exchange membrane than on the bipolar membrane. The modelling of the electro dialysis enables to predict the effect of the operating parameters.

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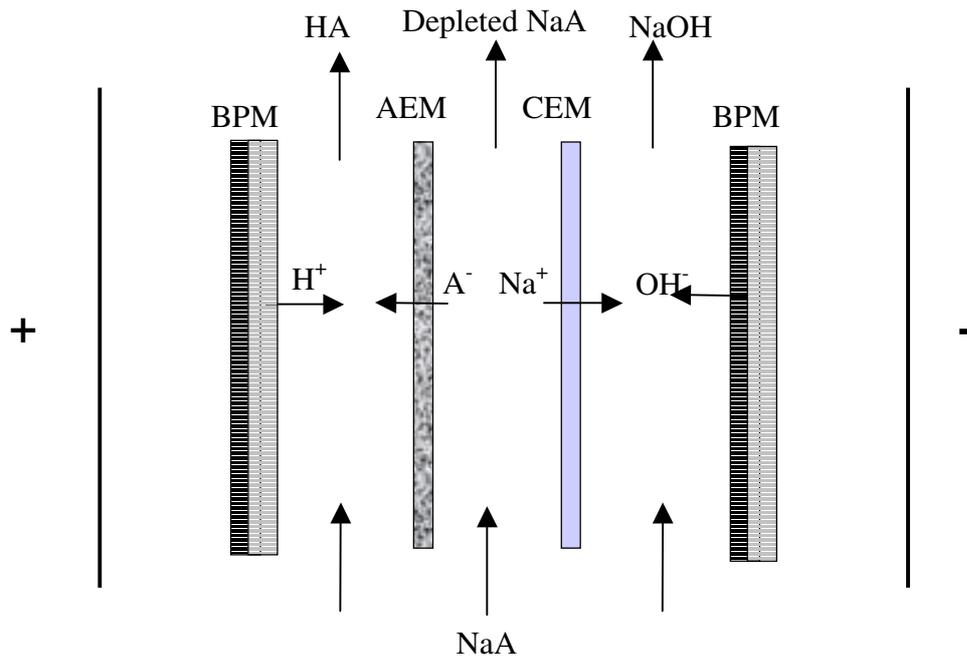


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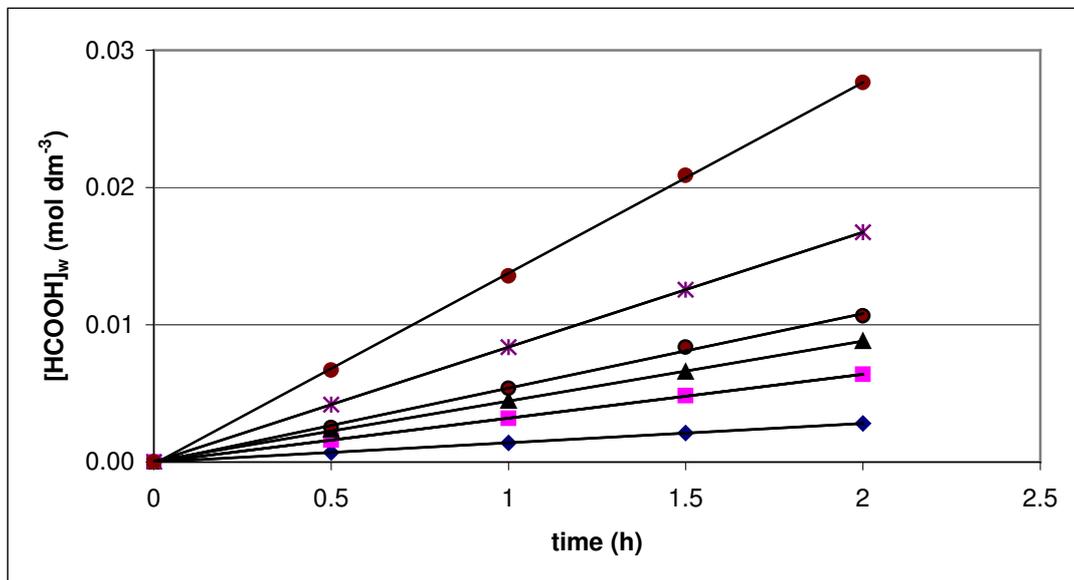


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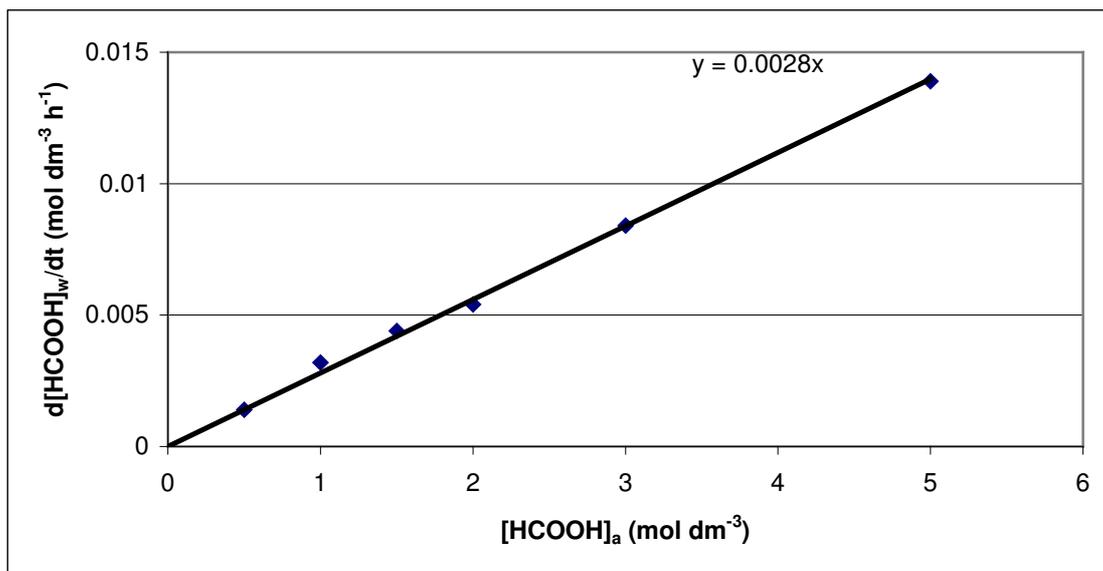


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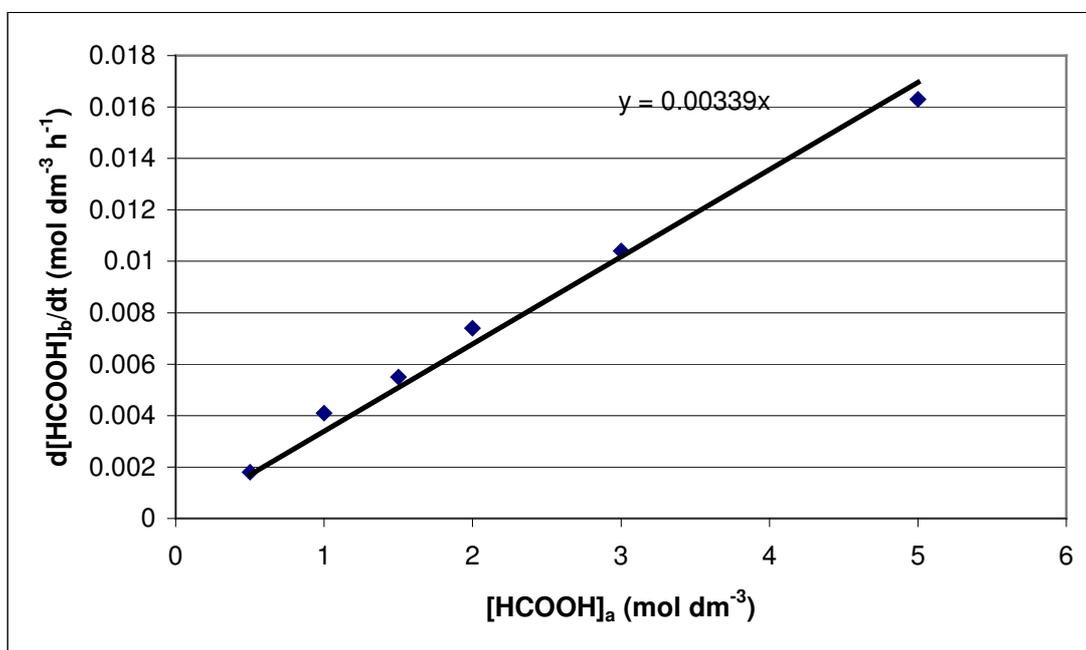


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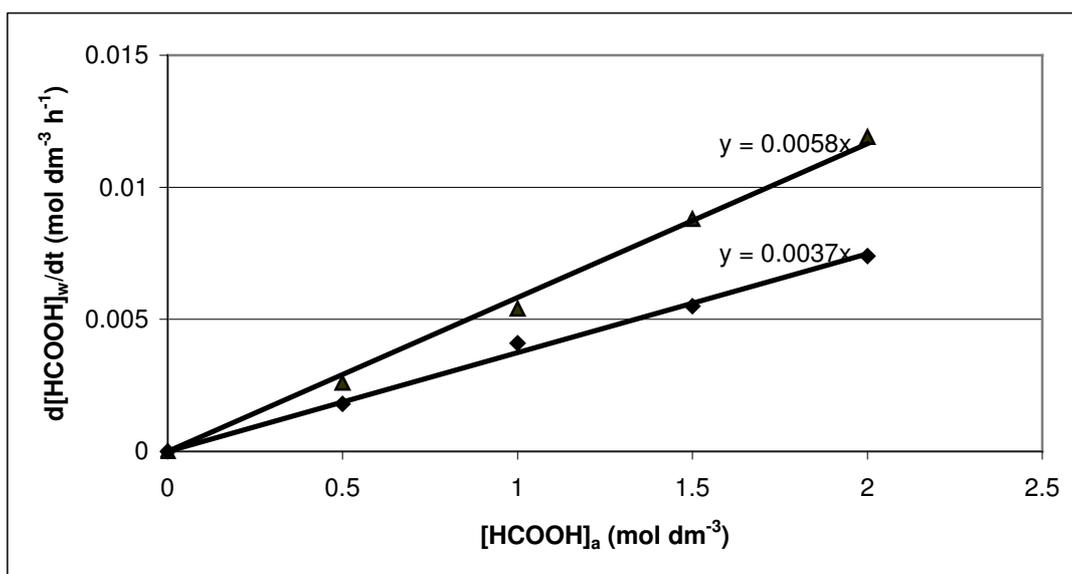


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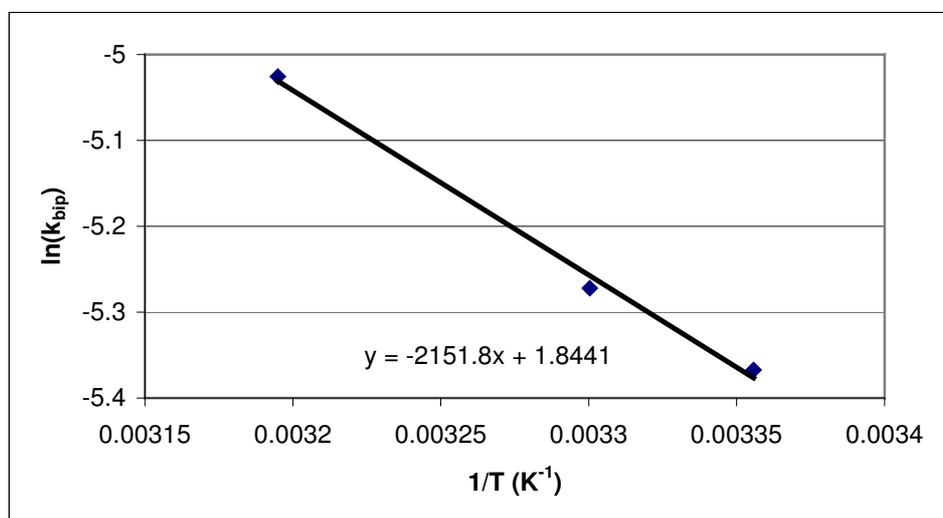


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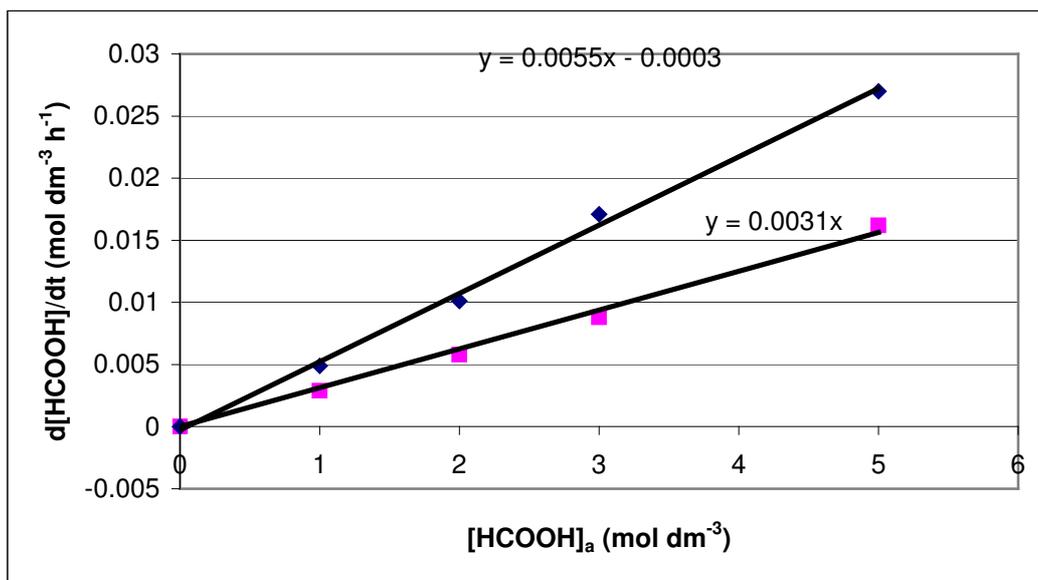


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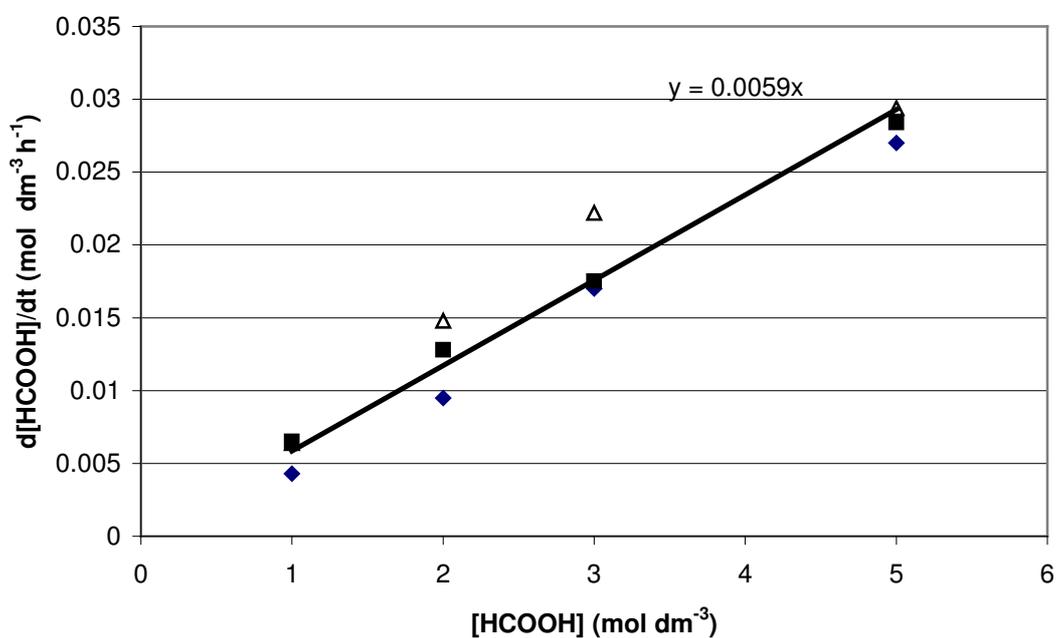


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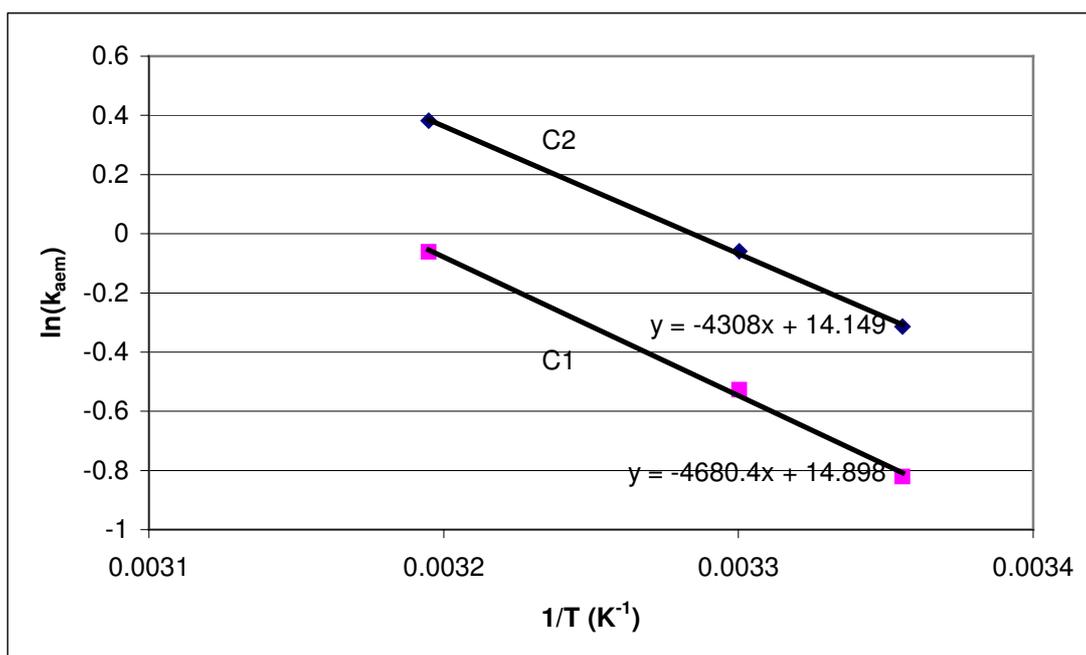


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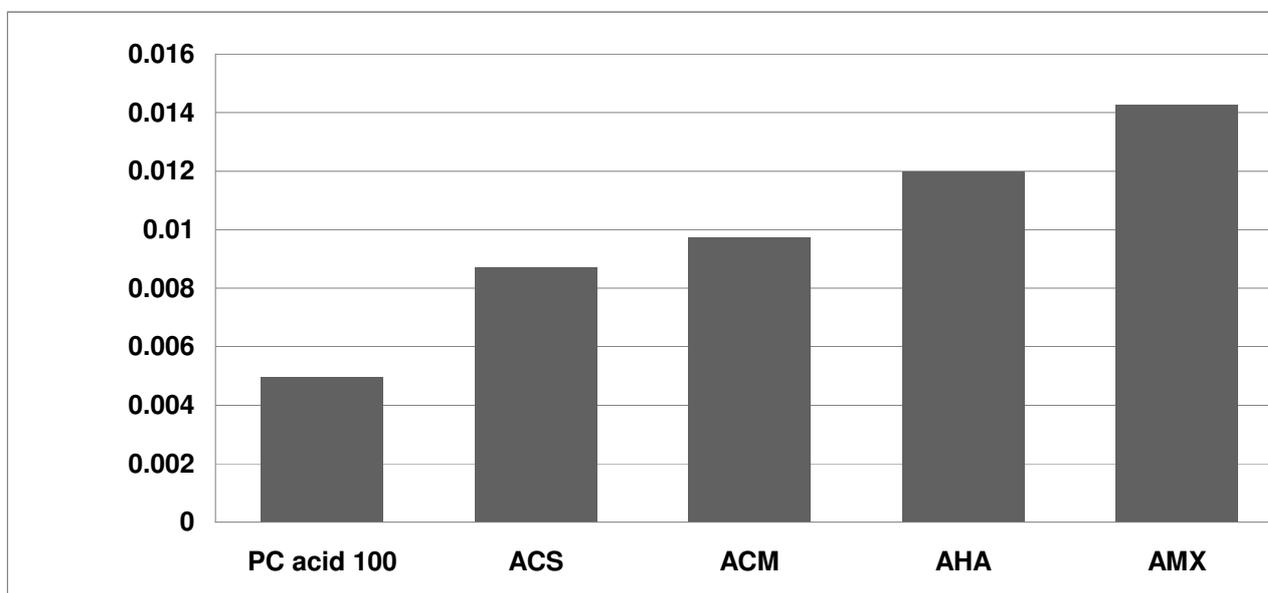


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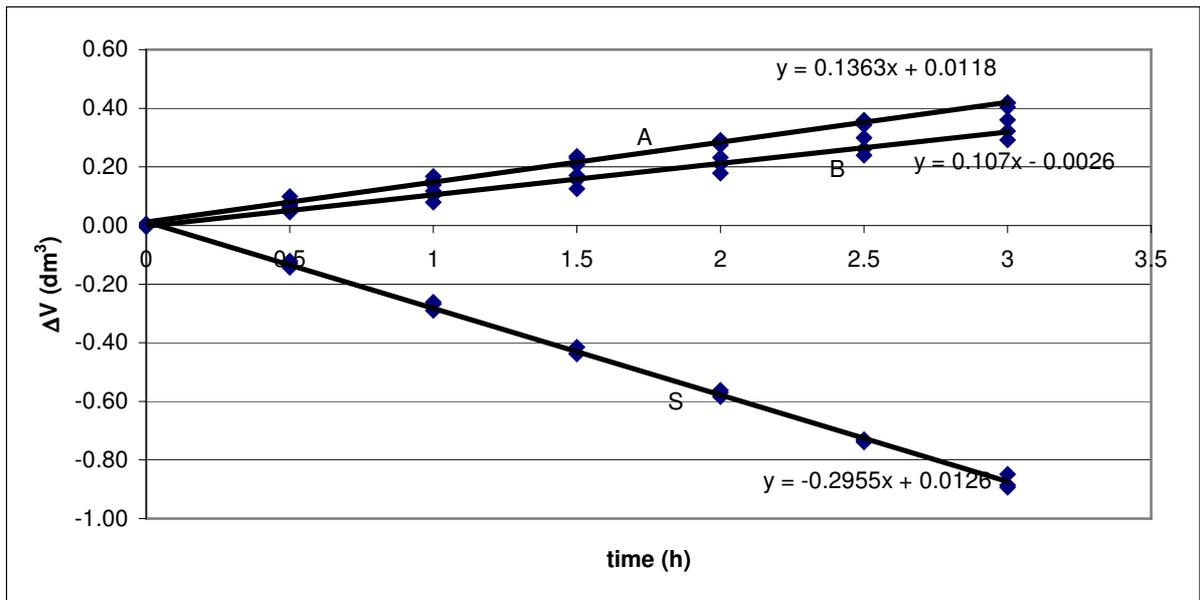


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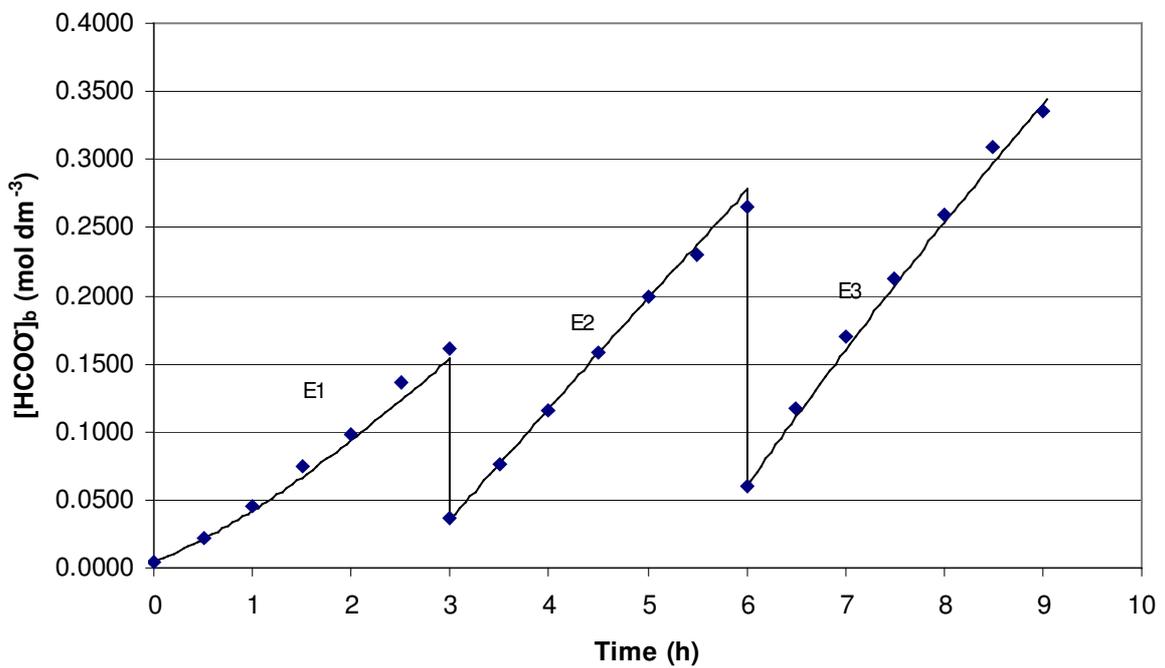


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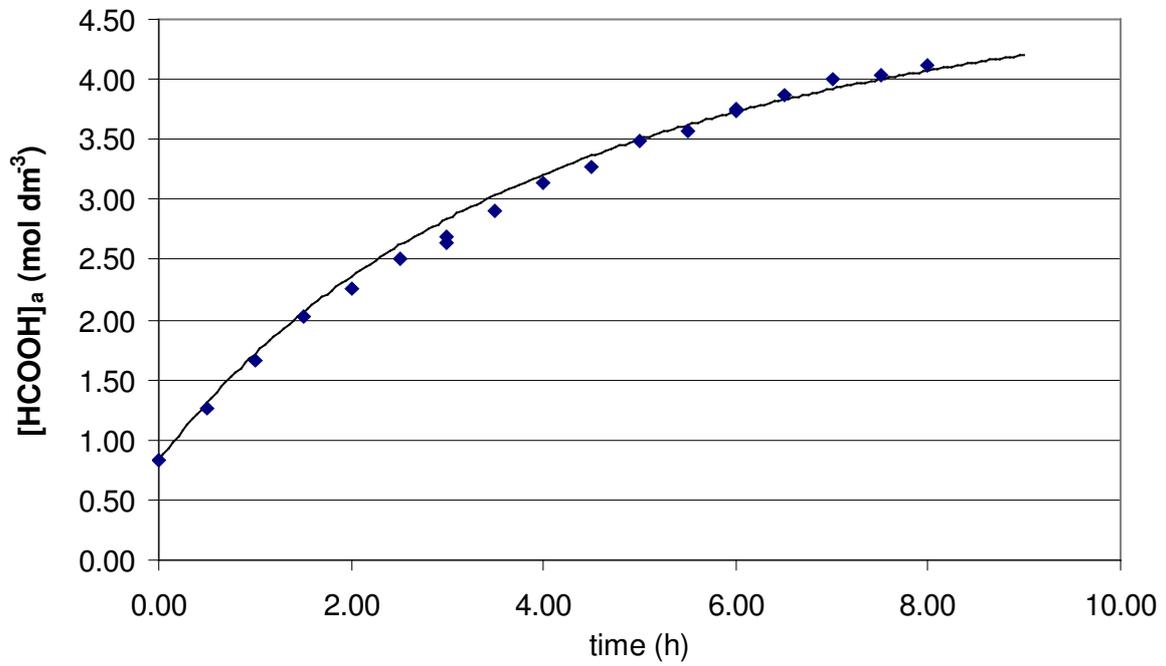


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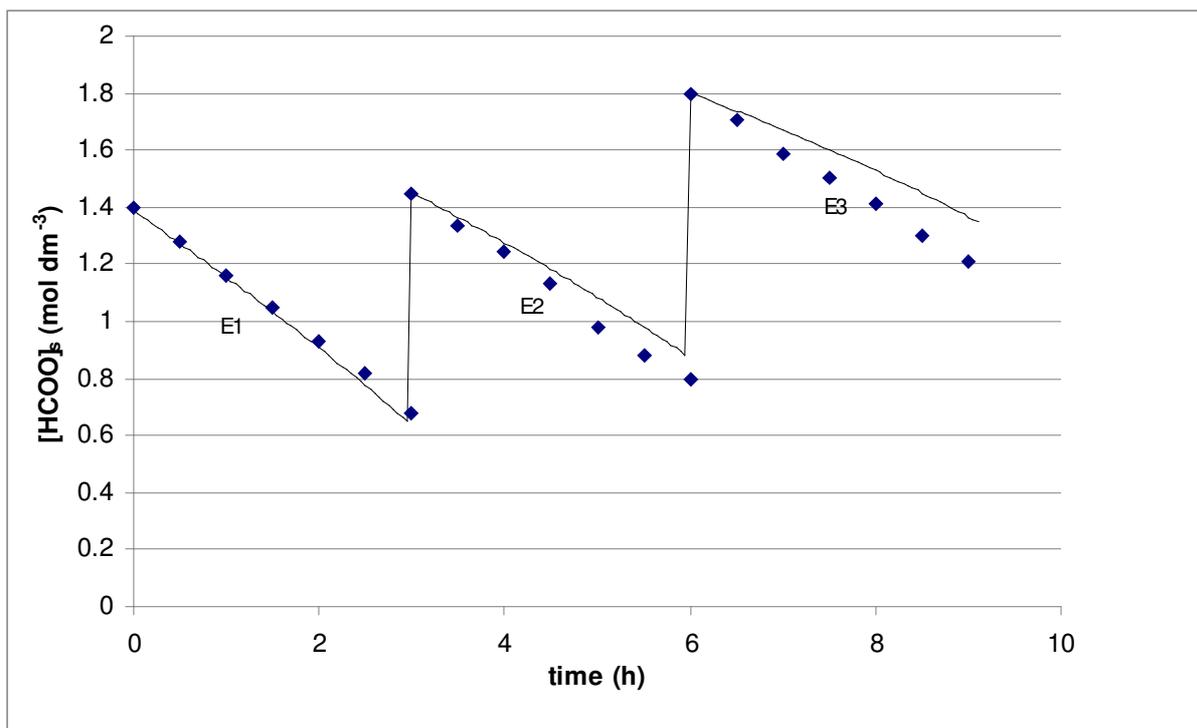


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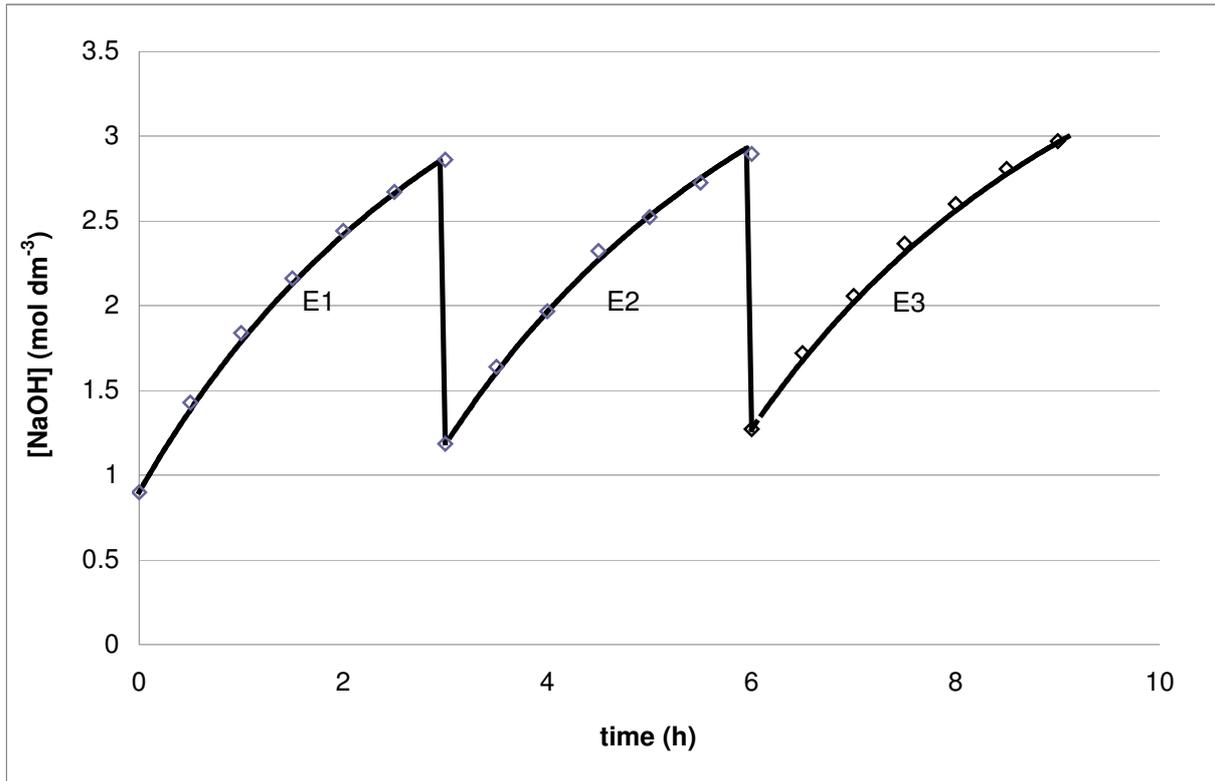


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$$\alpha = 0.0046 \text{ dm}^3 (\text{Ah})^{-1}, \text{ ACS membrane, } T = 313 \text{ K}$$

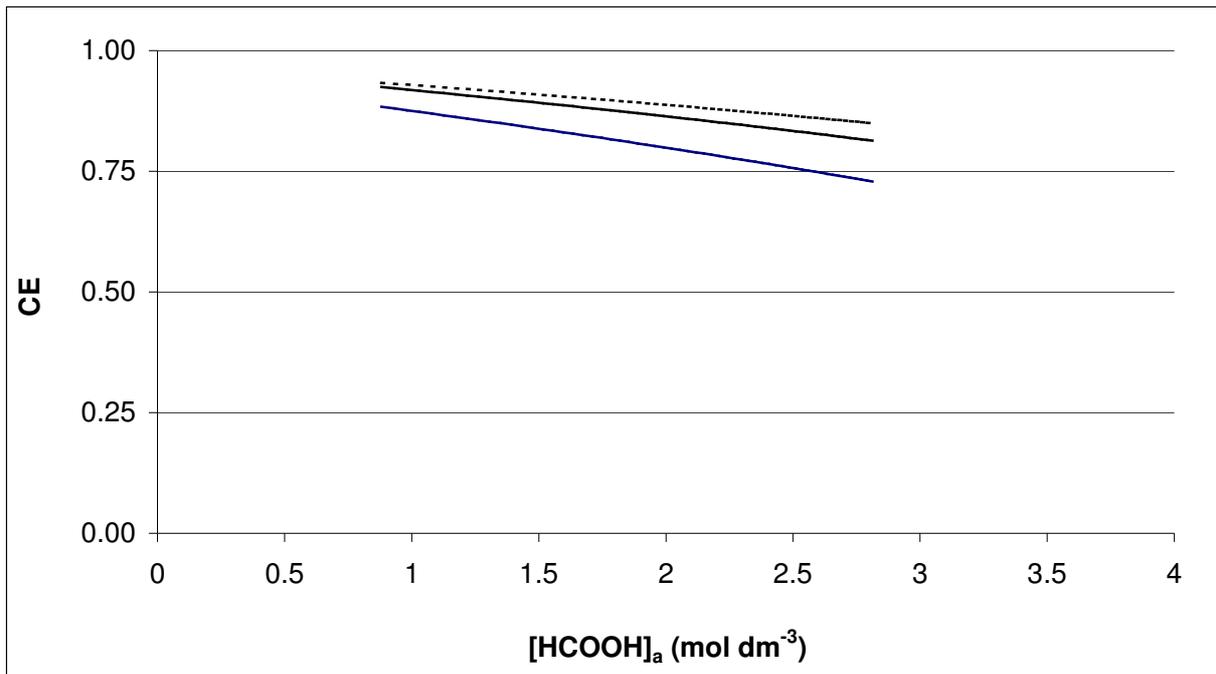


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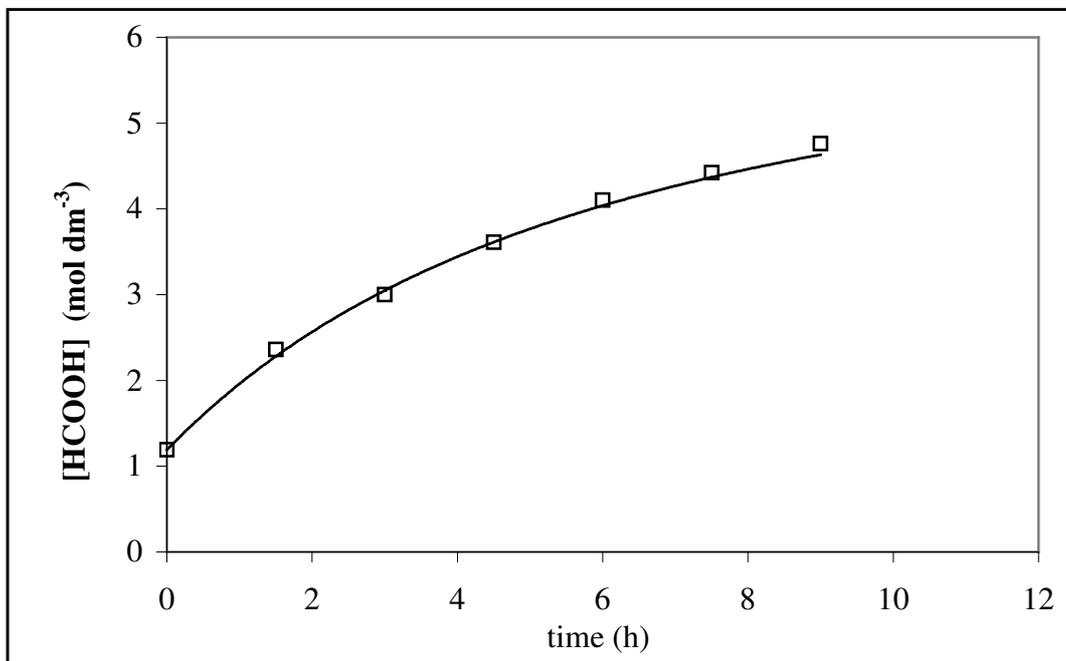


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 $T = 313$ K and $I = 5$ A dm⁻² and $V_0 = 0.347$ dm³ cell⁻¹

Table 1: Membrane properties*

	Membrane	Nature	Capacity (equiv. kg ⁻¹)	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.

Table 2: Volume variations per current quantity

	$\frac{dV_a}{iAdt} = \lambda_a$	$\frac{dV_s}{iAdt} = \lambda_s$	$\frac{dV_b}{iAdt} = \lambda_b$
dm ³ (Ah) ⁻¹	0.0034	0.0074	0.0027
dm ³ Faraday ⁻¹	0.091	0.198	0.072

Table 3: Comparison of fitting and diffusion studies results (ACS membrane)

	k_{bip} (dm h ⁻¹) at 298 K	k_{acem} (dm h ⁻¹) at 298 K	α (dm ³ (Ah) ⁻¹)
Fitting	0.0028	0.007	0.0042
Diffusion	0.004	0.008	
Diffusion at 298 K [7]	0.0027		

Table 4: Current efficiency vs. current density for PC acid 100 membrane (ACS membrane) for acid concentration range (0.83 - 2.7 mol dm⁻³), T = 298K

i (A dm ⁻²)	2.5	5	10
Current efficiency for formic acid (%)	75 (61)	88 (82)	94 (92)
Current efficiency for sodium hydroxide (%)	48 (37)	76 (74)	79 (78)