Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Akgemci, E. Güler , Ersöz, Mustafa and Atalay, Tevfik(2005) 'Transport of Formic Acid Through Anion Exchange Membranes by Diffusion Dialysis and Electro-Electro Dialysis', Separation Science and Technology, 39: 1, 165 — 184

To link to this Article: DOI: 10.1081/SS-120027407

URL: http://dx.doi.org/10.1081/SS-120027407

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 1, pp. 165–184, 2004

Transport of Formic Acid Through Anion Exchange Membranes by Diffusion Dialysis and Electro-Electro Dialysis

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ABSTRACT

In this study, first, the diffusion dialysis method was used for the transport of formic acid through anion exchange membranes (polysulfone SB-6407, Neosepta AFN, ACM, and AMH). The transport of formic acid was carried out at different concentration ranges and quantified with the membrane mass-transfer coefficient and diffusion coefficient parameters. Neosepta AFN and SB-6407 membranes were efficient for formic acid transport by the diffusion dialysis method at low concentrations. The second method, electro-electro dialysis was applied as a function of some parameters, such as concentration ratio and polarization curves at constant flow rate ($1.17 \times 10^{-6}\ \mathrm{m^3\ s^{-1}}$), and at 0.1-M concentration of formic acid. In this method, AMH membrane was

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DOI: 10.1081/SS-120027407 0149-6395 (Print); 1520-5754 (Online)

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found to be effective due to its higher mechanical stability, lower proton leakage, lower water content and higher current efficiency.

Key Words: Formic acid; Anion exchange membranes; Diffusion dialysis; Electro-electro dialysis; Acid recovery; Mass transfer coefficient.

INTRODUCTION

Recovery of acids from hydrometallurgical process waste is one of the beneficial recycling technologies. Many metal-finishing processes generate low-grade acidic waste streams and involve treating metal with acids for stripping, cleaning, and pickling.[1] Diffusion dialysis (DD) has been used for recovering various inorganic acids from waste streams, because of its operational simplicity, compatibility, and particularly, economic advantages in terms of energy saving.[2–5] The principle of diffusion dialysis are discussed in detail elsewhere.[6–9] The operation of DD uses the difference in concentration of permeable species in solutions partitioned by a anionic membrane and requires no external forces to promote separation, only electrical energy to pumps are needed.[10–12] Diffusion dialysis is a recovery technology that uses an anion exchange membrane, allowing anions and the protons to pass through into a water stream. The acid is reconstituted on the water side of the membranes and directed back to the process tank.

Electro-electro dialysis (EED) is a separation method for acid recovery in which the anion exchange membrane is essential and the electrochemical reactions occur at the electrodes. Metals can be recovered on a cathode while acid is simultaneously transferred across the membrane.[13] Electro-electro dialysis displaces acids by permselective transport of acids anion through an anion-exchange membrane and electrodialysis of protons.[14] A good anionic membrane has to have the following characteristics; low proton leakage, high limiting current density, low membrane voltage, and high mechanical resistance.

The objective of this study was to conduct an extensive study of recovering formic acid from pickling solution in the leather industry by applying diffusion dialysis and electro-electro dialysis processes. Emphasis was placed on examining the effects of various operating variables on the process performances with an aim of deriving the optimum operating conditions for both processes by using a polysulfone SB-6407 membrane and Neosepta AMH, AFN, and ACM membranes.

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EXPERIMENTAL

Materials

All chemicals were purchased from Merck and were reagent grade. SB-6407 anion exchange membrane was obtained from Gelman Sciences, and Neosepta AMH, AFN, ACM anion-exchange membranes, produced by the Japanese firm Tokuyama Soda Co. Ltd., were kindly supplied by Eurodia Co. (Wissous, France).

Acid Concentration in Membranes

The concentration of acid in the membrane was determined by a method based on saturation of the membrane with the acid in different concentration ranges from 0.05 to 0.5 M, followed by extraction of acid into water.

At the beginning of the tests, membrane pieces ($A = 20$ to $25\,\text{cm}^2$, in Cl^- form) were washed with distilled water until no salt residues could be detected in the water. Then, the sheets were soaked in 100 mL of acid solution and then the solution was stirred for 24 h. The membrane sheets were rinsed with distilled water for a short time to remove the acid remaining at the surface of the membrane. The surface-rinsed membranes were immersed in distilled water for 24 h. This extraction step was repeated three times. Then, the amount of the acid extracted from the membrane was measured by microtitration with 0.05-M NaOH standard solution.

The ion exchange between the membrane and formic acid solution can be calculated using the difference between the initial acid solution and either the final solution or the partially extracted solution which contains acid.

Diffusion Dialysis Experiments

The diffusion coefficients of the acid were determined from a batch dialysis cell made from Teflon cell that consisted of two chambers of equal volume separated by the membrane with an active area of $7.07\,\text{cm}^2$. Initially, one chamber contained an acid solution (0.05 to 0.5 M) and the other deionized water. The cell temperature was maintained at 25°C. Both chambers were stirred at identical rates to minimize concentration polarization effects on the membrane surface. The initial volume of solution in each chamber was 50 mL. The acid concentrations in both chambers were measured every 30 min by acid–base titration. Diffusion coefficients were determined from initial concentration gradients obtained from experiment data.

Current–Voltage Curves

Current–voltage curves were determined using the two-compartment cell already described,[13] as shown in Fig. 1. The cell was composed of two symmetrical 50-cm^3 half-cells. In the geometric center there was a cylindrical hole between which the membrane was clamped. The voltage drop across the test membrane was measured by two Ag/AgCl electrodes immersed into Lugging capillaries. Mechanical stirrers were placed in each compartment. The electrical current was supplied by means of two platinum electrodes with the power supply [Thurlby-thender PL 320 (32V-2A)].

Electro-Electro Dialysis Experiments

Electro-electro dialysis experiments were carried out for 0.1-M HCOOH in our laboratory-scale EED set-up (Fig. 2), a circular piece of the anionic membrane (exposed area: = 7.07 cm^2) was placed between two smooth graphite electrodes of identical shape and size. The anolyte and catholyte half-cells thus formed had a volume of 25 mL. Through these half-cells run an anolyte and a catholyte solution of 300 mL. It was supplied by peristaltic pumps at a constant flow rate ($1.17 \times 10^{-6} m^3 s^{-1}$).

The temperature was controlled by water bath. The voltage across and the constant current in the electro-electro dialysis were controlled by the DC

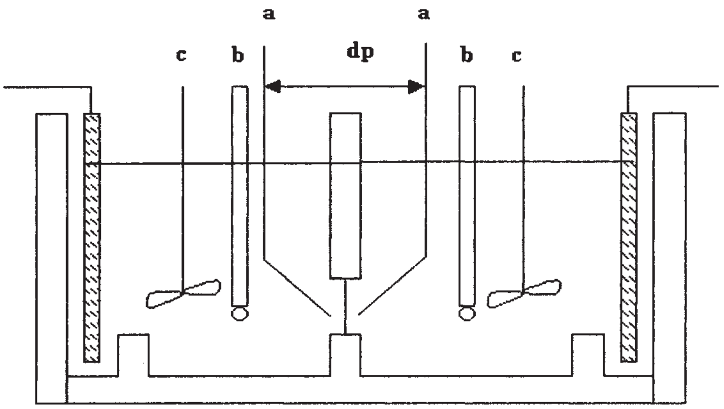

Figure 1. The polarization experimental cell. (a) Ag/AgCl probes. (b) pH electrodes. (c) Mechanical stirrers.

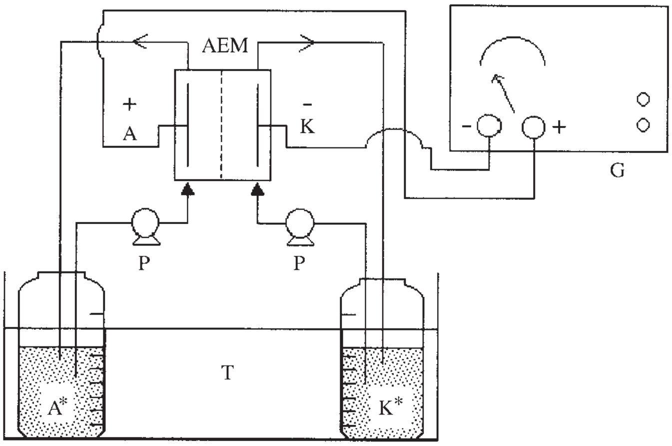

Figure 2. Schematic diagram of experimental set-up for electro-electro dialysis process. P, pumps; T, water bath; A, anode; K, cathode; G, DC power; A*, anolyte; and K*, catholyte.

power supply. The experimental conditions were $i = 3,\ 5,\ 10,\ 15\,\text{mA/cm}^2$, $t = 6\,\text{h}$, and the initial concentration of poured anolyte and catholyte solutions was 0.1 M. The current efficiency was determined with these experiments.

RESULTS AND DISCUSSION

Acid Concentration in Membranes

Transport through dialysis membrane is quantified by the membrane mass-transfer coefficient and diffusion coefficient of the component. Before utilizing of DD, it is necessary to know the data on solution to membrane equilibrium by sorption experiments. The concentration of formic acid dissolved in the membrane was calculated on the basis of mass balance between initial and final concentrations of acid. The dependence of acid concentration in membrane with the external solution concentration is presented in Fig. 3, in which C_m values increased with increasing initial formic acid concentration. As shown in Fig. 3, the sorption isotherms data were fitted by a Langmuir type expression, which is written as;

$$\frac{C_i}{C_m} = \frac{1}{K_b A_s} + \frac{C}{A_s} \qquad (1)$$

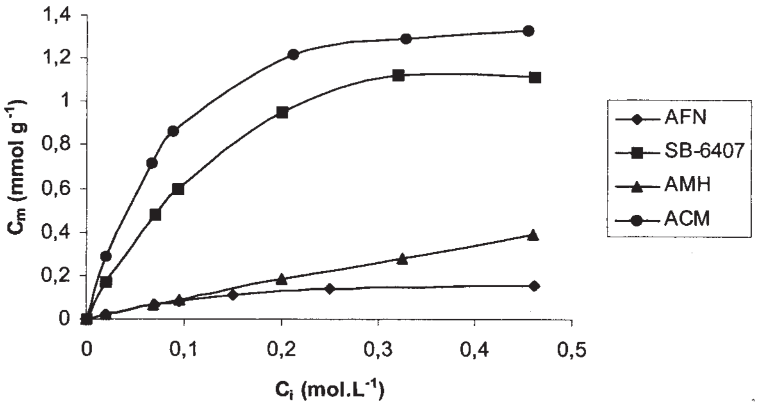

Figure 3. Dependence of acid concentration in membranes with external concentration.

where C_m and C_i represent the acid concentration in the membrane and solution, respectively, the parameters K_b and A_s are the sorption binding constant (1/mmol) and saturation capacity (mmol acid/g dry wt. of membrane), respectively. The obtained data for the membranes are listed in Table 1. The sorption data with respect to formic acid provide an excellent fit to Langmuir isotherm, giving a correlation coefficient of 0.98 or above for all membranes.

The highest acid sorption was observed for ACM membrane. Comparing the dependence of acid concentration in membranes with external concentration of solution between ACM and SB-6407 membranes, acid sorption increases as a parabola, except the AMH and AFN membranes. The graph shows that the sorption of formic acid depends on the external concentration for all membranes. In case of ACM membrane, the equilibrium is quickly attained. This indicates that the ACM membrane shows the lowest proton leakage.

Table 1. Parameters of Langmuir isotherm for each membrane.

Membranes	K_b (1/mmol)	A_s (mmol/g memb.)	Correlation coefficient
SB-6407	6.731	1.541	0.983
AFN	6.385	0.214	0.981
ACM	12.657	1.583	0.996
AMH	0.326	2.654	0.986

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Membrane Mass-Transfer Coefficients and Diffusion Coefficients

The transported formic acid concentration in the membranes as a function of different initial concentrations is presented in Fig. 4, where it can be seen that the transport increases at higher initial acid concentrations. SB-6407 and AFN membranes show considerable affinity for formic acid and particularly, marked in the external solution up to 0.5 M. The membrane mass-transfer coefficient in liquid is determined with the aim of obtaining information about the effect of mixing where unsteady-state mass transport takes place. In the experiment, when the concentration and volume changes were taken into account, the unsteady-state transport of the i component is described by the following differential equation upon the equilibrium and experimental determination of the membrane mass-transfer coefficient for acid. The theoretical treatment and the treatment of the experimental data in a differential equation is described in detail in previous works.[6,7] The membrane mass-transfer coefficient was determined using of the following equation:

$$\frac{dc_i{}^d}{dt} = -\frac{A}{V^d}\frac{K_i{}^d c_i{}^d - K_i{}^r c_i{}^r}{(K_i{}^d/k_l{}^d) + (l/k_m) + (K_i{}^r/k_l{}^r)} - \frac{c_l{}^d}{V^d}\frac{dV^d}{dt} \tag{2}$$

This differential equation also describes the time dependence of the concentration of component i in the donor compartment. Given the experimental data, the partition coefficients K_i, is as follows

$$\left(K_i = \frac{C_m}{C_i}\right) \tag{3}$$

The relationship between the mass-transfer coefficient and the diffusion coefficient for liquid–solid interfaces in the case of the membrane is given as

$$k_m = \frac{D_m}{\delta} \tag{4}$$

where, k_m is membrane mass-transfer coefficient and δ membrane thickness, which are given in Table 2. Table 3 shows mass-transfer and diffusion coefficients of the anion-exchange membranes used in tests.

As pointed out by many workers, mass transport through ion-exchange membranes is very complex and in addition to diffusion, the influence of electrical potential distribution inside the membrane, such as migration effects, swelling, hydration, water content, and the dissociation degree, must be taken into consideration.[15,16] However, linear concentration gradients of

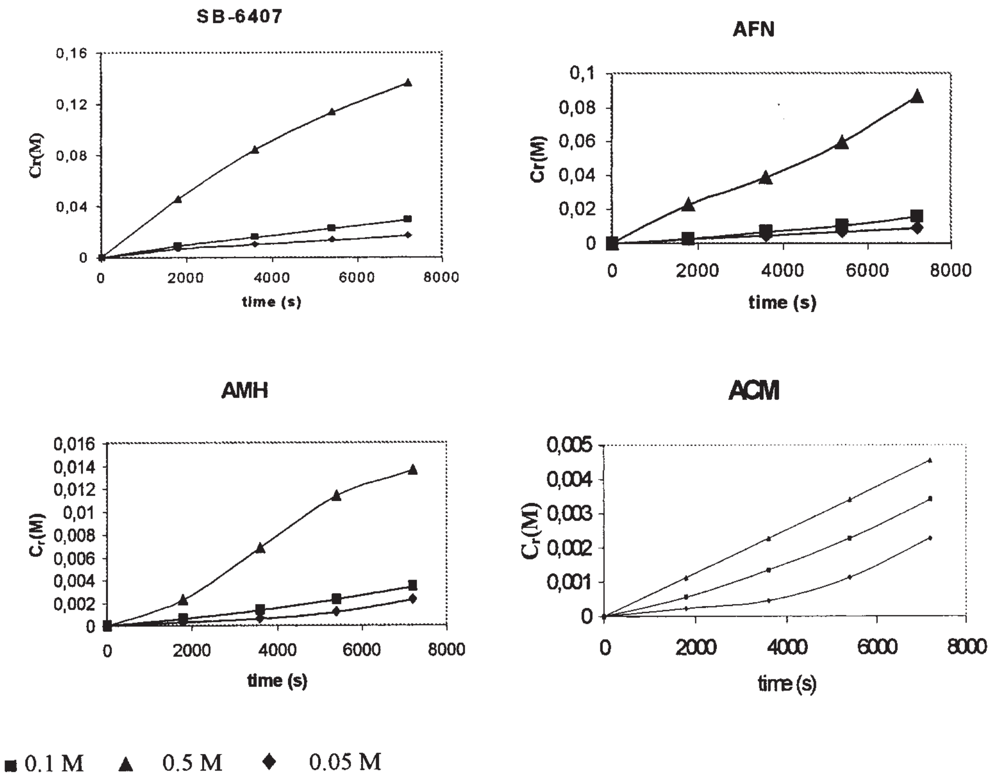

Figure 4. Time dependence of HCOOH concentration through the membranes.

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Table 2. Main characteristics of studied membranes.

Membranes	Type	Specifications	Water content (%)	Ion exchange capacity (meq g^{-1})	Thickness (mm)	Resistance (ohm cm^{-2})	Burst strength (kg cm^{-2})
SB-6407	Strongly basic anion permeable		50–55[a]	2.15[a]	0.152	0.3–1.2[a]	—
AFN	Strongly basic anion permeable	Resistant against organic fouling	40–55	2.0–3.5	0.15–0.20	0.4–1.5	2–3.5
ACM	Strongly basic anion permeable	Low H$^+$ transport	13–18	1.4–1.7	0.11–0.13	4.0–5.0	2–3
AMH	Strongly basic anion permeable	High mechanical, chemical strength	17–22	1.3–1.5	0.26–0.28	11.0–13.0	12

[a] Determined at laboratory.

Table 3. Membrane mass-transfer and diffusion coefficients at various initial formic acid concentrations for studied membranes.

	Membranes							
	Membrane mass-transfer coefficients ($k_m \cdot 10^7\,\mathrm{m\,s^{-1}}$)				Diffusion coefficients ($D \cdot 10^{11}\,\mathrm{m^2\,s^{-1}}$)			
Initial concentration	SB-6407	AFN	AMH	ACM	SB-6407	AFN	AMH	ACM
0.045	3.47	4.04	2.19	2.41	5.27	6.67	5.48	2.89
0.0976	3.59	4.41	2.22	2.67	5.46	7.28	5.55	3.20
0.4903	3.71	5.32	2.63	3.64	5.64	8.78	6.58	4.37

acids through the membranes could not be assumed under steady-state conditions due to the external solution concentration changes during time.

The numerical integration equation is used to calculate the membrane mass-transfer coefficient of acid. Parameters such as the partition coefficient were determined from the sorption equilibrium measurement and the liquid mass-transfer coefficient in liquid phase is estimated. It can be seen from Table 3 that the membrane mass-transfer seems to depend on the initial acid concentration, giving a slope of around 8.8×10^{-8}, 1.8×10^{-8}, 1.64×10^{-7}, and 2.5×10^{-7}.

It is assumed that thermodynamic equilibrium exists at the phase boundaries between membrane and solution; thus, the experimental data concerning the time dependence of concentration of acids on both solutions is available. The dependence of the membrane mass-transfer coefficient on the initial HCOOH concentration is presented in Fig. 5, where the membrane mass transfer coefficient (k_m) increases slightly with increasing initial acid concentration. D_m is calculated from Eq. (4). It was found that the thickness of the membrane is independent of the HCOOH concentrations in the range from 0.05 to 0.5 M. Thus, the thickness of the membrane is taken as the average constant value given in Table 2 in the studied concentration ranges.

Anion-exchange membranes are ideally impermeable to cations, while, in practice, no membrane is ideal and some leakage of cations will occur, particularly proton mobility through these membranes is abnormally high. Proton migration can occur by two mechanisms: diffusion, in a manner similar

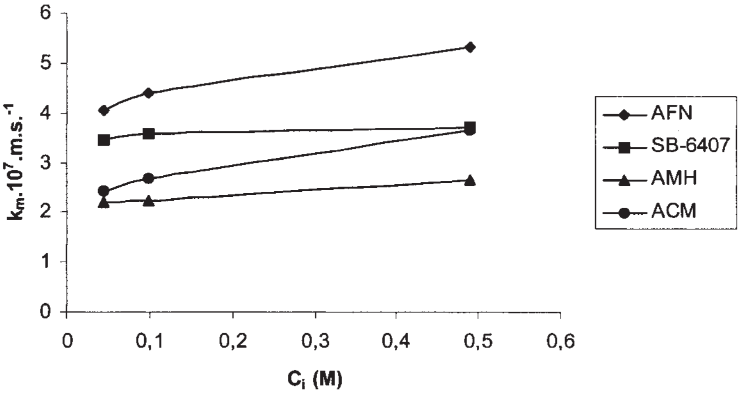

Figure 5. Dependence of membrane mass transfer coefficient for HCOOH upon the initial concentration in compartment 1 of cell.

to other ions, or the Grotthus mechanism in which protons transfer from one water molecule to another. Strathmann reported that the permeability of anion-exchange membranes for organic acids can be varied by adjustment of the degree of cross-linking and the chain length of the cross-linker in the polymer network.[17] As the degree of cross-linking proceeds, the diffusion coefficient decreases because of the increase in intermolecular cross-linking.[18] The ACM membrane has a large degree of cross-linking.[17] This is the reason that the diffusion coefficient in the ACM membrane is lower with respect to others.

Current–Voltage Curves

Current–voltage curves measured for the membranes at 0.1-M formic acid concentration are presented in Fig. 6. It can be seen from Fig. 6 that the highest membrane limiting current density at 0.1-M HCOOH solution for AMH and AFN membranes are 3.5 and 3 $\mathrm{mA/cm^2}$, respectively. In case of the SB-6407 and ACM membranes, their current densities were found to be very low.

It has been pointed out that a good anionic membrane should have the following characteristics: low proton leakage, high limiting current density,

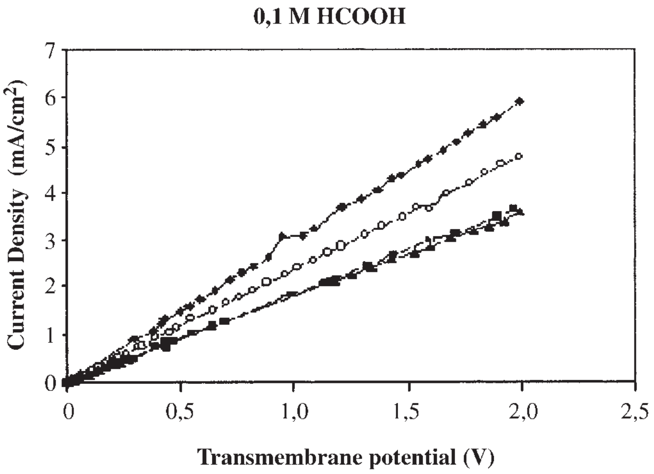

Figure 6. Current–voltage curves measured for membranes in 0.1-M HCOOH solution.

low membrane voltage, and high mechanical resistance.[10] From this statement, the AMH membrane has the mentioned characteristics, thus it is good for electro-electro dialysis applications.

Electro-Electro Dialysis Results

One of the main methods for production of formic acid is hydrolysis of methyl format. This process needs very high energy consumption for separation and concentration of formic acid. In this work, the electro-electro dialysis process was used to concentrate by using four kinds of anion-exchange membranes.

The principle of electro-electro dialysis of formic acid is described as follows: Format anions ($HCOO^-$) pass through the anion-exchange membrane into the anolyte compartment to form formic acid by combining with the protons produced by the anodic water oxidation. While in the catholyte compartment, H^+ is retained, and reacts with hydroxide ions to form water. Therefore, the concentration of formic acid in the catholyte compartment increases, while it decreases in anolyte compartment. The dissociation constant K_a of formic acid is 1.75×10^{-4} with a pK_a value of 3.76.

$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
$$\text{Anode: } H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^-$$

In this work, two parameters of the overall current efficiency, η and concentration ratio, ω were used to evaluate the performance of the electro-electro dialysis. Overall current efficiency:

$$\eta = \frac{(V_{f2}C_{f2} - V_{i2}C_{i2})F}{I \cdot t} \times 100 \qquad (5)$$

and concentration ratio was defined by the following relation:

$$\omega = \frac{C_2}{C_{i2}} \qquad (6)$$

where, V_{f2} and V_{i2} are the final and initial volume of the anodic solution, respectively. C_{f2} and C_{i2} are the final and initial molarities of formic acid solution in the anodic side. F is Faraday's constant, t is time, and I is the applied current. C_2 is the molarity of formic acid solution in the anolyte compartment.

Effect of Temperature on Overall Current Efficiency

To determine the effect of temperature on the overall current efficiency, an AFN membrane was used. In these experiments, the following experimental conditions were chosen; $I = 15\,\mathrm{mA/cm^2}$, $t = 6\,\mathrm{h}$, and the initial concentration of poured anolyte and catholyte solutions was 0.1 M. The obtained experimental results for variation of the current efficiency with time for AFN membrane is presented in Fig. 7, in which the temperature increases at first with an increase in the current efficiency and then it levels off. The main reason in this is that the mobility of ions moving in solutions and velocity of the anodic ions passing through the anion-exchange membrane increase as the temperature increases. This results in an increase in the overall current efficiency.

As the temperature increases, selectivity of the anion-exchange membrane will drop, and the effect of electro-osmosis will become serious, which results in an increase in water transfer through the anion-exchange membrane.[12] Thus, the experimental temperature was controlled at about 25°C.

Effect of Current Efficiency and Concentration Ratio

The effect of current density on overall current efficiency was investigated by using all membranes at 25°C for 0.1-M HCOOH concentration. The effect of current density on overall current efficiency at 25°C for AMH and AFN membranes is illustrated in Fig. 8, in which there is a difference of 3 to $10\,\mathrm{mA/cm^2}$ current density ranges for AMH membrane. The selectivity was not observed in the range of 5 to $15\,\mathrm{mA/cm^2}$ current efficiency for ACM and SB-6407 membranes. It can be seen from Fig. 8 that the current efficiency for AMH membrane was determined to be over 100% at $5\,\mathrm{mA/cm^2}$

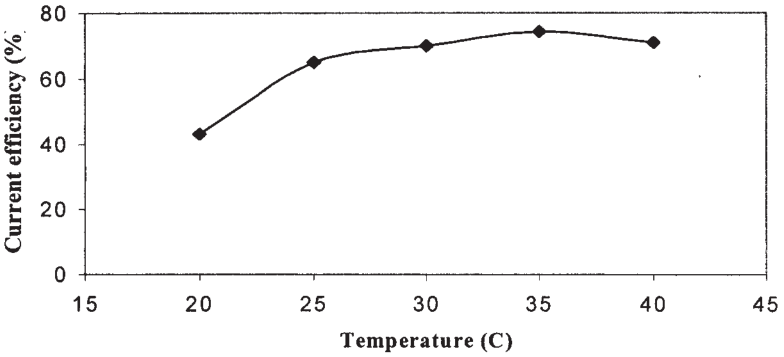

Figure 7. Variation of the current efficiency vs. the temperature for AFN membrane.

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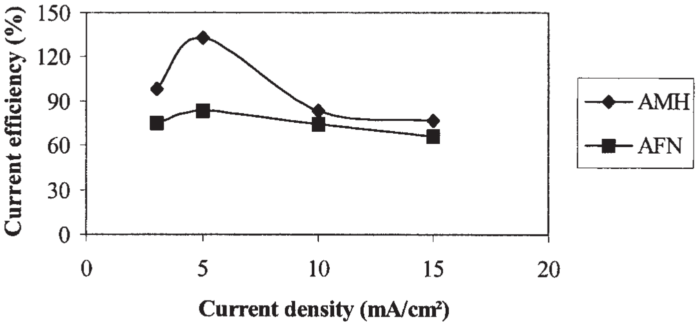

Figure 8. Effect of current density on overall current efficiency at 25°C for 0.1-M HCOOH.

current density. This indicates that water transport did not occur through the AMH membrane due to the formation of hydrogen bonds between formic acid molecules at higher concentrations.[19] The overall current efficiency was increased with an increase in current density when the current density was low. When a maximum value ($5\,\mathrm{mA/cm^2}$) was reached, the overall current efficiency decreased. For this reason, the experiment was carried out in the above limiting current value. It can be concluded that the solution passed from the catholyte compartment to the anolyte compartment because of water transport of electro-osmosis.

Figure 9 shows the variation of fractional ionization of HCOOH with pH. HCOOH ionization equilibrium can be illustrated as follows:

$$\mathrm{HCOOH} \leftrightharpoons \mathrm{H^+} + \mathrm{HCOO^-}$$

$$K_a = \frac{[\mathrm{HCOO^-}][\mathrm{H^+}]}{[\mathrm{HCOOH}]} \qquad K_a = 1.75 \times 10^{-4}$$

$$f_1 = \frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

where, f_1 is the fractional ionization, which is low at 0.1 M for HCOOH. However, OH^- ions, which are produced by the electro-electro dialysis process, increase the pH of the cathode compartment and thus the fractional ionization increases during the time. In other words, the proton leakage was prevented in the cathode compartment. It was established that the best membranes suitable for the reconcentration of H_2SO_4 by electro dialysis are those in which the sorption of acid and diffusion of protons are minimized.[18] Moreover, any proton being electrolytically reduced is replaced by a proton migration through the membrane. Figure 10 shows the curves of the

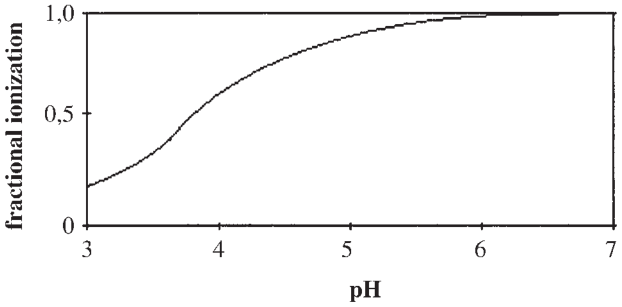

Figure 9. Variation of fractional ionization with pH for HCOOH.

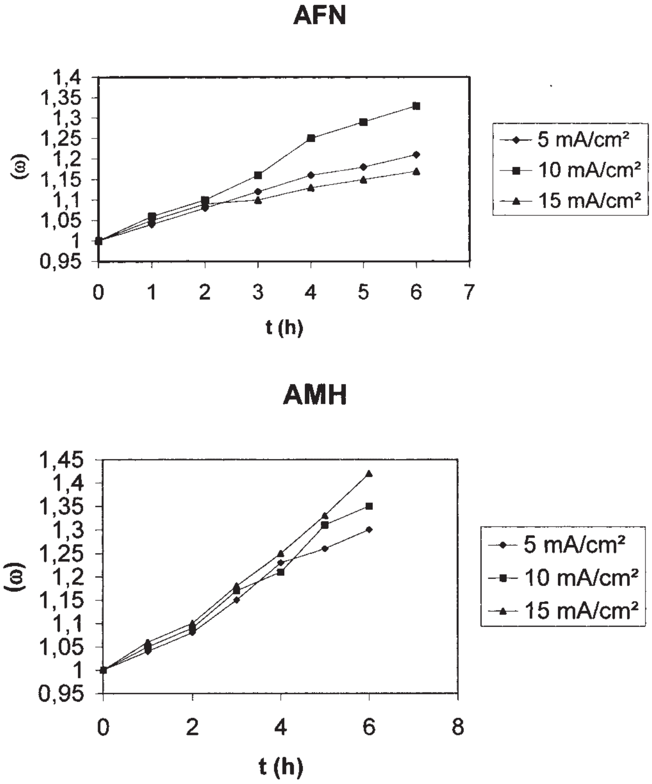

Figure 10. Effect of time and current density on concentration ratio for AFN and AMH membranes.

concentration ratio vs. changes of time and current density for AFN and AMH membranes for 0.1-M HCOOH. Concentration ratio is increased as current density and time are increased. The concentration ratio was found to be higher for AMH membranes. This shows that the recovered acid concentration is more concentrated compared to the AFN membrane. Figure 8 confirms also this result.

CONCLUSION

This study highlights the selection of anion exchange membranes and compare the diffusion dialysis and electro-electro dialysis to recovery of formic acid from the pickling solution in leather industry. The four anionic membranes discussed are: the Neosepta ACM, AFN, and AMH and SB-6407 membranes used in EED and DD. Results show that the highest mass-transfer coefficient was obtained for AFN membrane at a low concentration of formic acid. This indicates that the AFN membrane is suitable for diffusion dialysis application of formic acid as it has been suggested as a very suitable application of diffusion dialysis for inorganic acids.[18]

The most efficient membrane for electro-electro dialysis application of formic acid was determined to be the AMH membrane due to the low electro-osmotic water transport, low acid sorption, high ion permselectivity, and low proton leakage properties.

When both methods were compared in terms of recovering acid, the most important parameter is the proton leakage of the used membranes. The proton leakage of the anion exchange membrane is required for a diffusion dialysis process, while, the membrane has no proton leakage properties for a electro-electro dialysis process. However, the transport of proton through an ACM membrane was found to be higher due to high electro-osmosis water flow at electricity field in spite of lower proton leakage of ACM membrane with considered its specific properties, as shown in Table 2.

LIST OF SYMBOLS

$A =$ surface area of membrane (m).
$c =$ molar konsantrasyon ($\mathrm{k\,mol\,m^{-3}}$).
$c_i =$ acid concentration in solution.
$c_m =$ acid concentration in the membrane.
$D =$ diffusivity ($\mathrm{m^2\,s^{-1}}$).

$F =$ Faraday's constant.
$I =$ current (A).
$f_1 =$ fractional ionization.
$K_i =$ partition coefficient.
$k_l =$ mass-transfer coefficient in liquid ($\mathrm{m\,s^{-1}}$).
$k_m =$ membrane mass-transfer coefficient ($\mathrm{m\,s^{-1}}$).
$K_a =$ dissociation constant of acid.
$A_s =$ Langmuir isotherm parameters in Eq. (1) (mmol/g memb.).
$K_b =$ Langmuir isotherm parameters in Eq. (1) (1/mmol).
$V =$ volume ($\mathrm{m^3}$).

Indexes

$i =$ related to component.
$m =$ related to membrane.
$d =$ related to donor phase (acid).
$r =$ related to receiver phase (water).

Greek Symbols

$\delta =$ membrane thickness (m).
$\omega =$ concentration ratio.
$\eta =$ overall current efficiency.

ACKNOWLEDGMENT

The authors are grateful for the financial support provided by Selcuk University Research Foundation (SUAF) under Project FEF 018/2000.

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Received January 2003
Revised June 2003

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