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Concentration of Formic Acid Solution by Electro-electrodialysis

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ABSTRACT

The traditional production process for formic acid is a high-energy-consumption process. To save energy when concentrating formic acid solutions, anion-exchange membranes 3362W and AM-203 were evaluated for facilitating the concentration of formic acid solution by electro-electrodialysis. The effects of concentration, temperature, electric current, and time on the electro-electrodialysis process were studied. Experimental results indicated that electro-electrodialysis was an effective method for concentrating formic acid solutions at 30°C. Higher efficiencies were not obtained at higher temperatures. If the concentration of a working system was greater than 10 wt%, the overall current efficiency was greater than 100%. The overall current efficiency was 80–95% when the concentration of a system was less than 10 wt%. In general, the overall current efficiency was increased with an increase of low current density. After a certain value, the overall current efficiency would begin to drop. The performance of the AM-203 membrane was better than the 3362W membrane. With the AM-203 membrane it was found that the overall current efficiency was decreased if the concentration difference between the cathodic and anodic compartments was increased.

Key Words. Electro-electrodialysis; Anion exchange membrane; Formic acid

INTRODUCTION

Formic acid is an important reagent. One of the main methods of production is hydrolysis of methyl formate prepared by Leonard Co. and SD/Bethlehem Co. This process has the advantage of a high conversion rate. The process

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of separation and concentration of formic acid is a high-energy-consumption process. Three different distillation columns are used in the process. Corrosion of formic acid at higher temperatures makes it very difficult to maintain equipment in a normal state.

Electrodialysis has many industrial applications, such as water desalination (1), table salt production (1), acid recovery (2–9), heavy metal recovery (2, 10–11), separation of protein solutions (12), radioactive solution separation (13), wastewater treatment (3–5, 7, 13), and so on. Electrodialysis has also been considered for conversion of salts into their respective acids and bases by bipolar membranes (14–17). Slightly modified electrodialysis is also used to separate mixtures of amino acids or even proteins (18).

Electro-electrodialysis is a separation technique involving the permselectivity of an ion-exchange membrane. The electro-electrodialyzer is divided into two compartments by means of an anion-exchange membrane. Touaibia et al. (19) used the technique to treat wet industrial phosphoric acid with two kinds of membranes. The concentrated phosphoric acid (4 M) was obtained with an interesting yield and a low concentration of metal impurities.

In this work electro-electrodialysis is used to concentrate formic acid solution, especially a high-concentration solution with two kinds of anion-exchange membranes.

EXPERIMENTS

Reagents

All reagents were purchased from Beijing Chemical Products Company and used without any further purification. Formic acid was of AR grade.

Anion Exchange Membranes

Two types of anion-exchange membranes were evaluated for this process. AM-203 and 3362W were obtained from Shanghai Shengle Chemical Plant and Shanghai Chemical Plant, respectively. The exchange capacity of the 3362W membrane was 1.8 meq/g, the membrane resistance was less than 13 Ω/cm^2, and the thickness 0.4 mM. For the AM-203 membrane, the exchange capacity 1.9 meq/g, the membrane resistance was less than 5 Ω/cm^2, and the thickness was 0.3 mM.

Experimental Setup

Figure 1 is a schematic diagram of the experimental setup employed in this work. The system was comprised of an electro-electrodialyzer, two storage tanks, two pumps, a DC power source, and a water bath. The electro-electrodialyzer was divided into an anolyte and a catholyte compartment by an anion-exchange membrane. The working area of the membranes and electrodes was

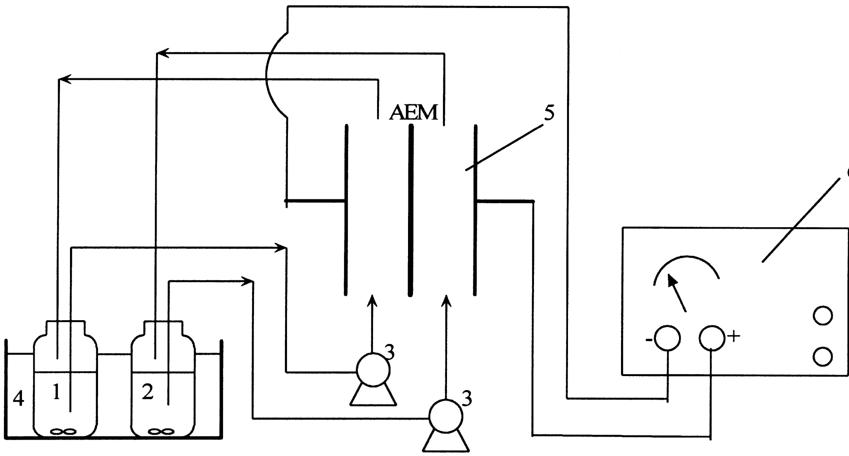

FIG. 1 Schematic diagram of experimental set-up. (1) Concentrate solution storage; (2) dilute solution storage; (3) pumps; (4) water bath; (5) electro-electrodialysiser; (6) DC power.

100 cm^2. The electrodes were made of platinum. The voltage across and the constant current in the electro-electrodialysis were controlled by the DC power supply. Two storage tanks and two pumps were used for continuously circulating concentrate and dilute solutions. The flow rate in the dilute and concentrate solution compartments was maintained at 0.005 $m^3 h^{-1}$. The temperature of the dilute and concentrate solutions was controlled by the water bath.

Principle of Electro-electrodialysis

For concentration of formic acid, a predetermined volume of various solutions was circulated in the anolyte and catholyte compartments. Formate 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 anolyte compartment increases, while it decreases in the catholyte compartment. The pK_a value of formic acid is 3.77, so ion strength is not high even when the concentration of the formic acid solution increases. This property facilitates increase of the concentration of organic acid by electro-electrodialysis. During the electro-electrodialysis process, samples of the anolyte solution were removed at regular intervals. The concentration of acid was analyzed by acid titration.

In this work two parameters of the overall current efficiency η and concentration ratio ω were used to evaluate the performance of the electro-electrodialysis. Overall current efficiency and concentrated ratio were defined by

$$\eta = \frac{(V_{f2}C_{f2} - V_{i2}C_{i2})F}{\mathrm{It}} \times 100\%$$

$$\omega = \frac{C_2}{C_{i2}}$$

where η is overall current efficiency, F is Faraday's constant, I is the applied current, and t is the time. 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. ω is the concentrated ratio, and C_2 is the molarity of formic acid solution in the anolyte compartment.

RESULTS AND DISCUSSION

Effect of Temperature on Overall Current Efficiency

To determine the effect of temperature on the overall current efficiency, experiment No. 1 was carried out at different temperatures using a 3362W anion-exchange membrane (AEM). The experimental conditions were I = 20 mA/cm^2, t = 6 h, and the initial concentration of poured anolyte and catholyte solutions was 30 wt%. Three repetitions of each trial were performed. The standard deviations were in the range of ±3%. The experimental results are shown in Fig. 2.

The overall current efficiency increases until a maximum value is reached, then slightly decreases with an increase of temperature. The main reason for the decrease at higher temperature 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 of the overall current efficiency. As the temperature increases, selectivity of the anion exchange membrane will drop, and the effect of electroosmosis will become serious, which results in an increase in water transfer through the anion-exchange membrane. As the experiment proceeded, the color of the surface of the anion-exchange membrane changed as the experimental temperature was increased to 38°C. This is due to corrosion of the formic acid solution at higher temperature. Thus, the negative effect of the temperature will result in a decrease in the overall current efficiency. Consequently, in the following experiments the experimental temperature was controlled at about 30°C to maintain a high overall current efficiency.

Fig. 2 also shows that the overall current efficiency is greater than 100%. This phenomenon will be discussed in the next section.

Electro-electrodialysis Under High Initial Concentration

Experiment No. 2 was designed to study the effects of current density on the overall current efficiency and concentration ratio at 32°C. Formic acid solu-

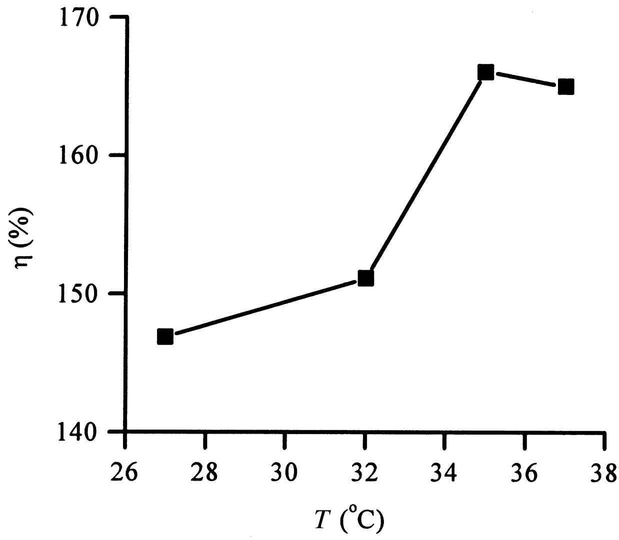

FIG. 2 Effect of temperature on overall current efficiency.

tion (500 mL at 30 wt%) was poured into the anolyte and catholyte compartments, respectively. Three repetitions of each trial were performed. The standard deviations were in the range of ±3%. The experimental results for membranes 3362W and AM-203 are shown in Fig. 3–4.

The overall current efficiency was increased with an increase in current density when the current density was low. When a maximum value was reached, the overall current efficiency decreased. The reason is that if the current is less than the limiting current density (80% of the maximum current density), the increase of current density will not cause negative effects such as higher electrical resistance, proton leakage through the anion-exchange membrane, or protons generated by the dissociation of water molecules at the interface of the AEM. Therefore, the overall current efficiency increases with an increase of the current density, but if the current density is greater than the limiting current density, proton transport increases. An increase in current density will make the overall current efficiency decrease.

At high concentration (>10 wt%) the overall current efficiency is greater than 100% in Figure 2–3. This is because there is a strong hydrogen bond between formic acid molecules, which causes two or three formic acid molecules to form associated bonds when the concentration of formic acid solution is high. These bonds may become monovalent or multivalent anions. This action leads the overall current efficiency to be greater than 100%. But this phenomenon will not happen if the concentration of formic acid solution remains low, for example, as much as 4 wt%.

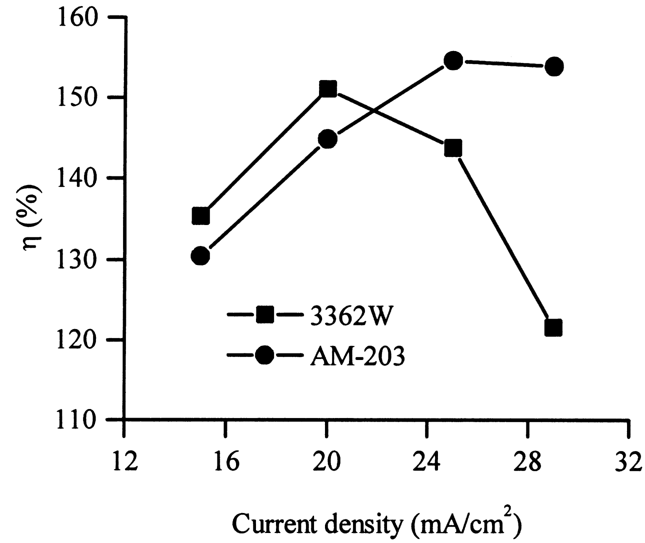

FIG. 3 Effect of current density on overall current efficiency.

When comparing the results of the two anion-exchange membranes, the performance of the AM-203 membrane is better than the 3362W membrane. This is because the membrane resistance of the AM-203 membrane is less than that of the 3362W membrane as explained in the Experiments section above. The stability of the AM-203 membrane is better than that of the 3362W membrane, because during long-term testing the AM-203 membrane remained stable. Under the same experimental conditions as in experiment No. 2, the performance of the 3362W membrane decreased more than 10% after 30 tests. Each test lasted 6 hours. But the performance of the AM-203 membrane remained almost the same as a new one.

Figure 4 shows the curves for concentration ratio versus time and current density for each of the anion-exchange membranes. The concentration ratio is increased if current density and time are increased. The reason is the same as that for the effect of the current density and time on the overall current efficiency. For each membrane, the concentration ratio with the AM-203 membrane is greater than that with the 3362W membrane under the same experimental conditions.

Electro-electrodialysis Under Low Initial Concentration

Experiment No. 3 was carried out under the same experimental conditions as those of the high-concentration solution. The effects of current density on the overall current efficiency and concentration ratio were studied with 4 wt%

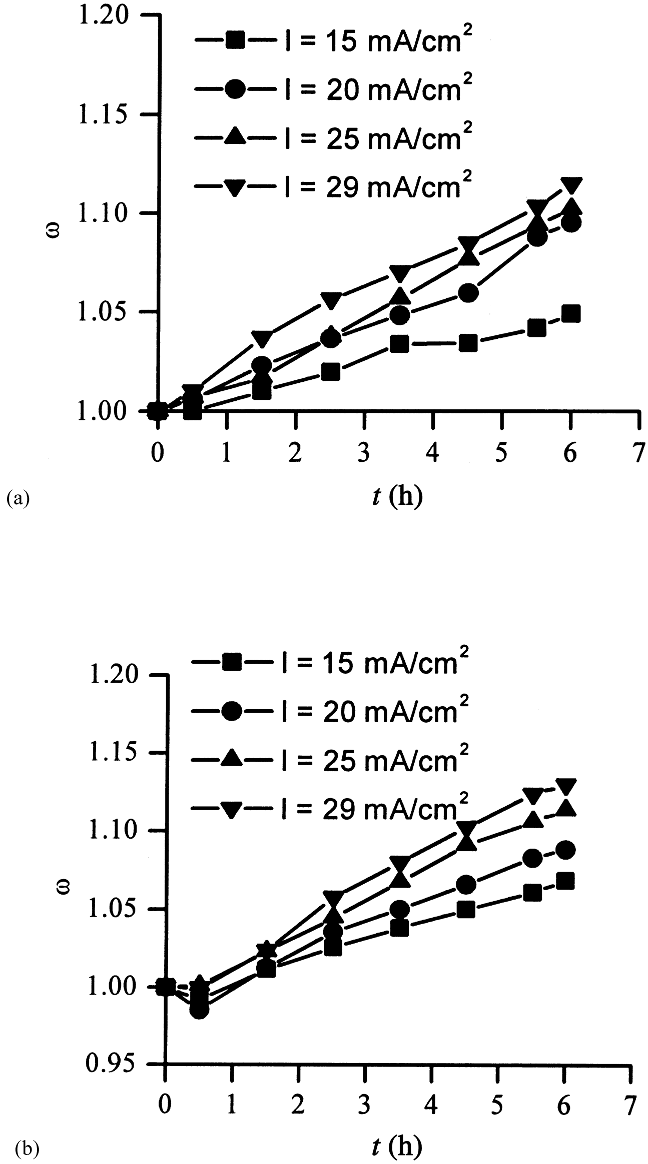

FIG. 4 Effect of time and current density on concentration ratio. (a) 3362W; (b) AM-203.

formic acid solution. Three repetitions of each trial were performed. The standard deviations were in the range of ±3%. The experimental results for the 3362W and AM-203 membranes are shown in Fig. 5–6.

In Fig. 5 the trend lines of the overall current efficiency with the changes of the current density are almost the same as those in Fig. 3. The changes of the overall current efficiency under low concentration are the same as those under high concentration.

Unlike the phenomenon at high concentration, the overall current efficiency shown in Fig. 5 is less than 100% at low concentration. This is because there is no hydrogen-bond action between the molecules of formic acid in the dilute solution. All molecules in the solution exist as individual molecules. Therefore, the anion ions of formic acid move from the catholyte compartment to the anolyte compartment as they migrate through the anion-exchange membrane. In the electro-electrodialysis process, there is electrical resistance from electrode reactions, water transfer, and protons leakage, so that the overall current efficiency is less than 100% under low concentration.

When the experimental results of each membrane are compared, the performance of the AM-203 membrane is better than that of the 3362W membrane. This is because the membrane resistance of the AM-203 membrane is less than that of the 3362W membrane. These results are the same as those of the high-concentration solution.

Figure 6 shows the curves of the concentration ratio versus changes of time and current density for each anion-exchange membrane for low concentra-

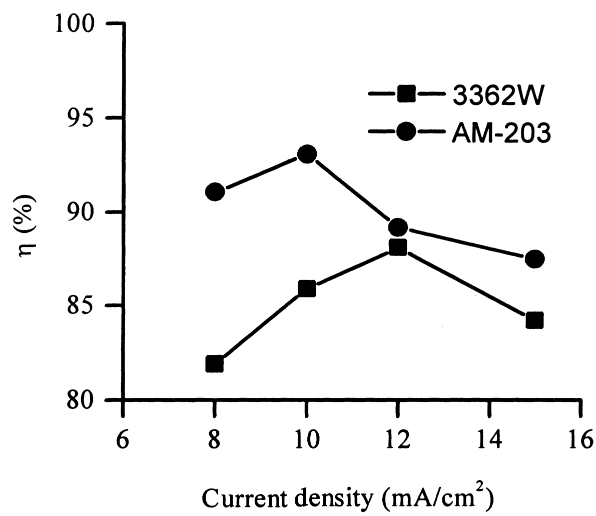

FIG. 5 Effect of current density on overall current efficiency.

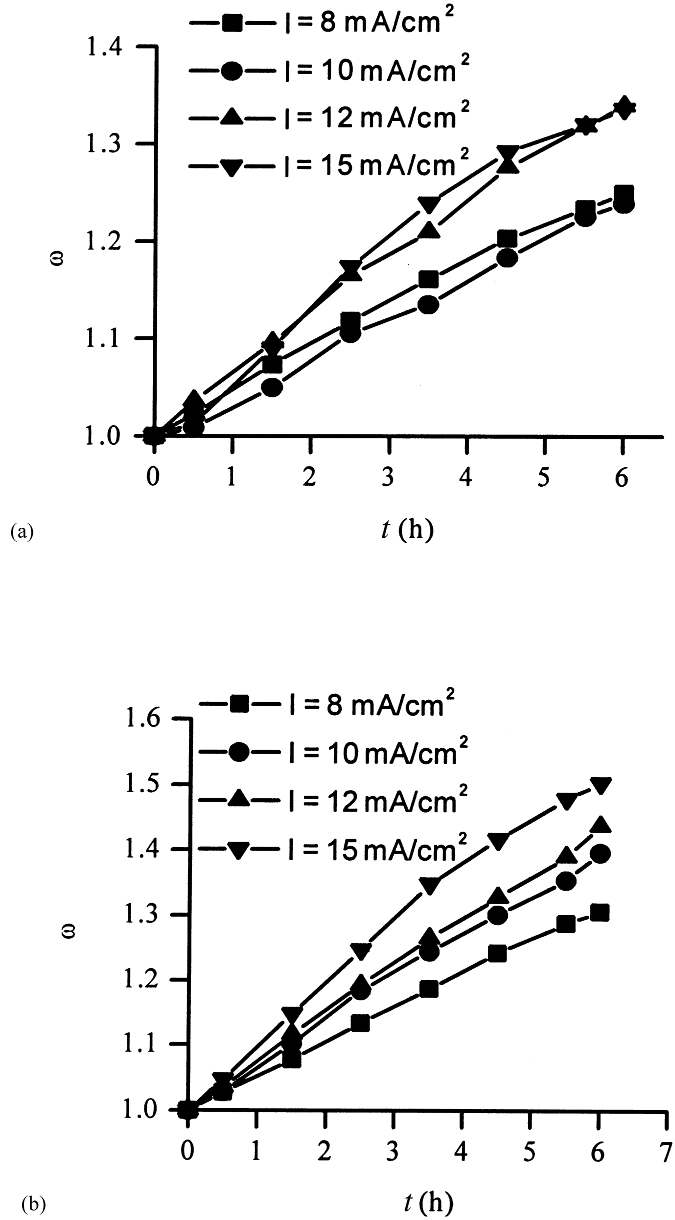

FIG. 6 Effect of time and current density on concentration ratio. (a) 3362W; (b) AM-203.

tions. Concentration ratio is increased as current density and time are increased. Concentrated ratio with the AM-203 membrane is greater than that with the 3362W membrane under the same experimental conditions. The results are also the same as those of the high-concentration solution.

Effect of Concentration and the Concentration Difference Between the Two Sides on Overall Current Efficiency

As reported above, the solution concentration has a strong effect on the overall current efficiency. To study the effects of the concentration on the overall current efficiency, experiment No. 4 was designed. Solutions of 4 wt%, 13 wt%, 21 wt%, and 30 wt% were used with the AM-203 anion-exchange membrane in this experiment. The results are listed in Table 1 where the experimental conditions are $T = 32°C$, $I = 15 mA/cm^2$, $t = 6$ h, and the volumes of the solutions is 500 mL.

From Table 1 it can be seen that the overall current efficiency is high. Even for the 4 wt% solution the overall current efficiency is 87.5%. Accordingly it may be concluded that the electro-electrodialysis is a good way to concentrate formic acid solutions. With the increase of the initial concentration the overall current efficiency will increase quickly. At under 30 wt%, the overall current efficiency is slightly decreased.

As the concentration difference between the concentrated and dilute compartments increases, the overall current efficiency decreases. The effect of initial concentration on the overall current efficiency was studied under the experimental conditions of $T = 32°C$, $I = 20$ mA/cm^2, $t = 6$ h, and the volumes of the solutions are 500 mL with the AM-203 anion-exchange membrane. The experimental results are listed in Table 2.

Table 2 shows that eventhough the concentration difference between the two sides is much greater, the overall current efficiency is not very low. Thus, as long as enough time is provided, good performance of electro-electrodialysis can be reached for concentrating formic acid solutions. It was also found

TABLE 1
Effect of Solution Concentration on Overall Current Efficiency

No.	Initial concentration: Anolyte	Initial concentration: Catholyte	Overall current efficiency (%)
1	4 wt%	4 wt%	87.5
2	13 wt%	13 wt%	117.9
3	21 wt%	21 wt%	139.9
4	30 wt%	30 wt%	130.5

TABLE 2
Effect of Solution Concentration Difference on Overall Current Efficiency

No.	Initial concentration		Overall current efficiency (%)
	Anolyte	Catholyte	
1	20 wt%	10 wt%	125.9
2	40 wt%	20 wt%	109.5
3	60 wt%	30 wt%	69.3

that the overall current efficiency decreased when the concentration difference increased because protons leakage through the anion-exchange membrane increases as the concentration is increased.

CONCLUSION

From the above experimental results it may be concluded that the electro-electrodialysis process is an effective method to concentrate formic acid solutions as opposed to distillation. The performance of the AM-203 membrane is better than that of the 3362W membrane. The suitable temperature (30°C) would make for high efficiency. At higher temperatures current efficiency decreased. At higher concentration the overall current efficiency was greater than 100%. The overall current efficiency for low concentration systems was 80–95%. In general, the overall current efficiency was increased with an increase of the current density at lower current densities. After a certain value (about 25 mA/cm^2 in these experiments), the overall current efficiency began to drop. With the AM-203 membrane the overall current efficiency decrease if the concentration difference between the cathodic and anodic compartments was increased.

Because there are no phase changes in the electro-electrodialysis process, the process is probably less energy consumptive compared with distillation, for concentrating formic acid solutions. But it is still necessary to study the suitable concentration range with this process to maintain higher efficiency. Anion-exchange membranes with much higher performance levels need to be found.

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