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Two-Phase Electro-Electrodialysis with an Emulsion as Anolyte

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ABSTRACT

A new technique of two-phase electro-electrodialysis process has been developed and applied to separate acetic acid from its solution. Normally an aqueous phase is applied as the anolyte solution in a normal electro-electrodialysis process. In the new technique an emulsion composed of 49.9% kerosene, 49.9% water, and 0.2% Tween was used as the anolyte instead of the aqueous phase. The influences of the electrical current and the initial anolyte and catholyte concentration on the performance of the normal or the new process have been studied. The experimental results showed that the new technique could control the electroosmosis and osmosis effectively. Almost no anolyte volume change has been observed during the two-phase electro-electrodialysis process. And also much higher concentrated ratio with almost 100% recovery can be reached

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with the new technique. In the process, the electrical current efficiency was kept around 50%. Furthermore it was found that the concentration difference between the anolyte and the catholyte has less influence in the two-phase electro-electrodialysis process than that in the normal electrodialysis process.

Key Words: Two-phase electro-electrodialysis process; Emulsion; Acetic acid; Electroosmosis.

1. INTRODUCTION

Recovery of organic acids from their dilute solutions is a very important project because the dilute solutions are causing a great amount of material consumption and terrible impacts to the environment. If these organic acids can be recovered and become a great chemical material resource, the environmental impacts can be greatly alleviated. But there are few processes with high performance to treat these dilute solutions nowadays. Thus, new separation methods for the treatment of the organic acid solutions are highly required.

Conventional unit operations such as extraction, adsorption, or ion exchange severed as the common techniques in the recovery of organic acids have been applied for long time. But these methods often consume lots of chemicals to regenerate their separation agents. Electro-electrodialysis, one of the external electric field assisted methods, has been considered as a usable technique in this field. It can be operated in a continuous way and there are no regeneration steps required. Arifal et al.[1,2] studied the electro-electrodialysis of hydriodic acid with a cross-linked cation exchange membrane by accelerated electron radiation. Luo et al.[3] reported their results for concentrating of formic acid solution by electro-electrodialysis. Cattoir et al.[4] did the research in the removal of sulfuric acid from decontamination effluents with electro-electrodialysis. Mazrou et al.[5] reported their experimental results in sodium hydroxide and hydrochloric acid generation from sodium chloride and rock salt by electro-electrodialysis. The technique of electro-electrodialysis was also applied for concentrating and purifying wet industrial phosphoric acid.[6]

However, the electroosmosis and osmosis of water in the process of electrodialysis or electro-electrodialysis are serious.[3,7] Even the overall electrical current efficiencies are much higher; the concentrated ratio of the concentrated solutions cannot be high, sometimes even less than 1.0. So the application of this technique is some how limited strictly. How to control and reduce the electroosmosis became an important project for electro-electrodialysis technique. Two-phase electrophoresis is a novel separation technique, which takes the advantages of extraction and electrophoresis.[8–10] No results about the water eletroosmosis in this process have been reported. But very high electric field strength must be applied due to the weak conductivity of organic solvents in the process. So the energy consumption is very high.

In this work, a new technique of two-phase electro-electrodialysis based on two-phase electrophoresis was designed to control the water eletroosmosis. In order to improve the conductivity of the organic phase, an emulsion was used to replace the organic phase. The new technique was tested for the recovery of acetic acid from its solution. The effects of initial concentration and electrical current density on the electrical current efficiency and the recovery ratio were explored. The results were compared with that of the normal electro-electrodialysis too and the advantages of the new technique were discussed.

2. MATERIALS AND EXPERIMENTAL

2.1. Reagents and Anion Exchange Membranes

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

AM-203 anion-exchange membrane was obtained from Shanghai Shengle Chemical Plant. The exchange capacity was 1.9 meq/g, the membrane resistance was about $10\,\Omega\,\text{cm}^2$, and the selectivity was 96% for the aqueous solution.

2.2. Experimental Setup

The mechanism of the electro-electrodialysis for concentrating the organic acids from their dilute solutions has been explained elsewhere.[3,7] Figure 1 is a schematic diagram of the experimental set-up. The effective membrane surface is $20\,\text{cm}^2$. The two electrodes are made of platinum. The cathode is located in the aqueous phase and the anode located in the emulsion phase. Two peristaltic pumps were used for circulating water solution and emulsion solution. The electrical current density is controlled by the DYY-III DC power supply. Two magnetic stirrers are used to avoid phase separation of the emulsion solution and to keep the uniform concentration of the aqueous phase and the emulsion. In the two-phase electro-electrodialysis process, one phase was water solution and the other one was emulsion solution. The emulsion comprised 49.9% kerosene, 49.9% water and 0.2% Tween.

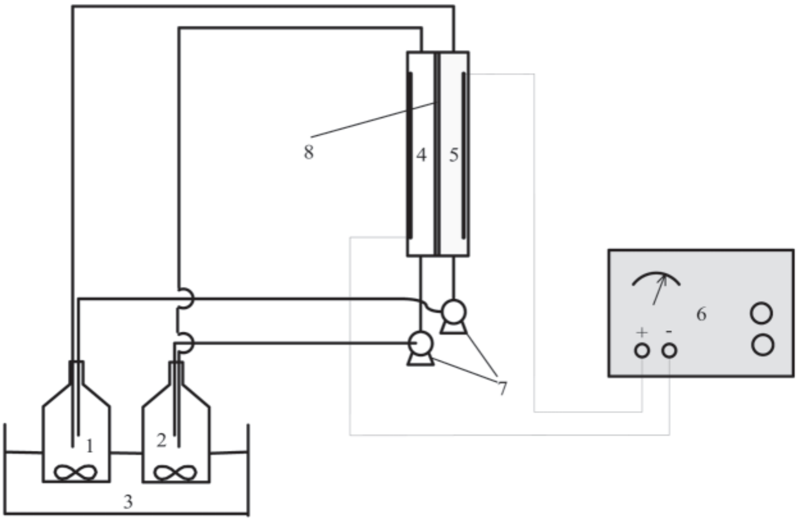

Figure 1. Schematic diagram of experimental set-up: 1, emulsion phase tank; 2, water phase tank; 3, water bath; 4, cathode chamber; 5, anode chamber; 6, power; 7, pumps; 8, and AM203 anion-exchanger membrane.

For a style of water in oil emulsion, the surfactant of Tween was selected due to its hydrophobic nature. As to the emulsion no phase separation happened during our experimental process. The volume of the aqueous phase and the emulsion phase was 60 mL, respectively. During the two-phase electro-electrodialysis, samples of the aqueous phase were collected and analyzed by titration at a certain interval.

In this work, three parameters current efficiency η, concentrated ratio ω, and recovery ratio R were used to evaluate the performance of the two-phase electro-electrodialysis. They are defined as

$$\eta = \frac{(C_{i1}V_{i1} - C_{f1}V_{f1})F}{It} \times 100\%$$

$$R = \left(1 - \frac{C_{f1}V_{f1}}{C_{i1}V_{i1}}\right) \times 100\%$$

$$\omega = \frac{C_{f2}}{C_{i2}}$$

where η is overall current efficiency, F is the Faraday constant, I is the applied electric current, and t is time. V_{f1} and V_{i1} are the final and initial volume of the diluted solution, respectively. C_{f1} and C_{i1} are the final and initial molarity of the diluted solution, respectively. ω is the concentrated ratio and C_{f2} and C_{i2} are the final and initial molarity of the concentrated solution. R is the recovery ratio.

3. RESULTS AND DISCUSSIONS

3.1. Normal Electro-Electrodialysis Results

In order to have a comparison of the two-phase electro-electrodialysis with the normal electro-electrodialysis, the normal electro-electrodialysis process in the same set-up has been carried out. Figures 2–4 are the results under the normal process when the initial volume of anolyte and catholyte were 40 and 80 mL, respectively, and the initial concentration of anolyte and catholyte was 0.55 mol/L. The electrical current was 100 mA. The catholyte sample of 2 mL was taken out every 60 min.

From Figs 2–4, one can see that the recovery ratio is increased with an increase of time. The overall electrical current efficiency can be larger than 100%, but it is decreased after the concentrated ratio is larger than 1.5. The concentrated ratio and the concentration of anolyte are increased quickly when the different concentration between the anolyte and catholyte is lower. After the concentrated ratio is larger than 1.6, the concentrated ratio and the concentration of anolyte are not increased, but decreased. The change of anolyte volume was measured and plotted in Fig. 4. It is shown that the

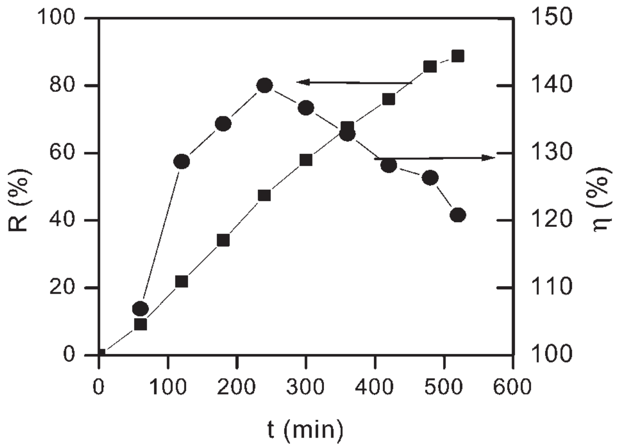

Figure 2. Effect of time on recovery ratio and overall current efficiency.

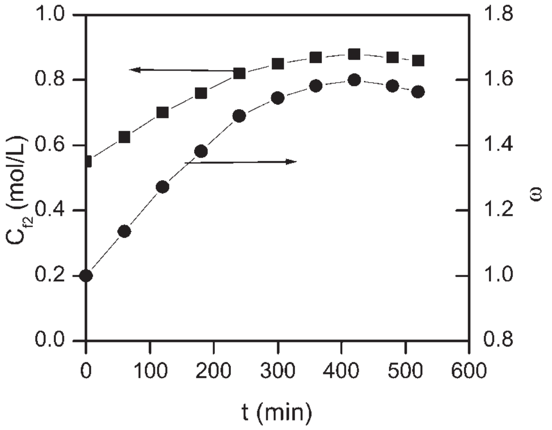

Figure 3. Effect of time on concentrated ratio and concentration of anolyte.

anolyte volume has grown up fast. The similar phenomenon has been observed for treatment of formic acid solutions.[7] The reason why the electrical current efficiency is larger than 100% has been explained in our previous work.[3,7] The main reason for the volume change is due to the leakage of proton, eletroosmosis and osmosis, which causes the water flux to increase. So, to control the water flux during the electro-electrodialysis for organic acids is the key factor for getting higher concentrated ratio.

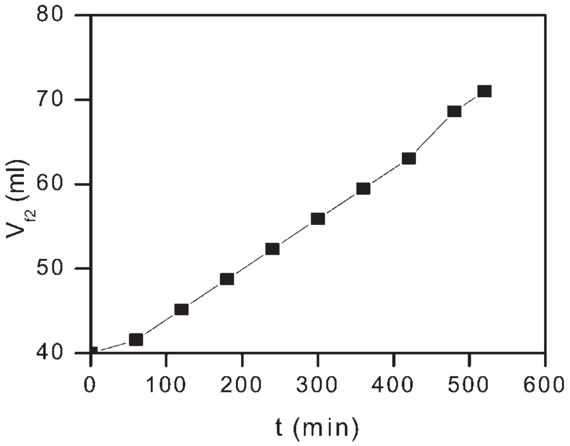

Figure 4. Effect of time on anolyte volume.

3.2. Electro-Electrodialysis with an Emulsion Solution as Anolyte

3.2.1. Influence of Initial Catholyte Concentration

The influences of initial catholyte concentration on the recovery ratio and the overall electrical current efficiency are shown in Fig. 5. The initial anolyte concentration was 0.44 M, and the electrical current was 100 mA. If the time is allowed enough long, it can be seen that almost 100% recovery ratio for all the test solutions can be reached. During the process, the electrical current efficiency is kept around 50%. It is slowly decreased with an increase of time.

Figure 6 shows the changes of the anolyte concentration and the concentrated ratio. It can be found that there is almost linear relationship between the time and C_{f2} or ω, it is almost not influenced by the initial catholyte concentration. But it is shown that the deviations from the straight line for both lower initial concentration solutions with greater time. This is because almost all solute has been recovered from its dilute solution before the allowed time. It means that less time for 100% recovery ratio is required than that in this experiment. So the deviations from the straight line for both lower initial concentration solutions with greater time are shown. Figure 7 is the change of the anolyte volume. In the two-phase electro-electrodialysis process, no change of the anolyte volume has been observed. So we can conclude that the electroosmosis and osmosis can be controlled very well with an emulsion as the anolyte. Although no phase separation phenomenon has been observed,

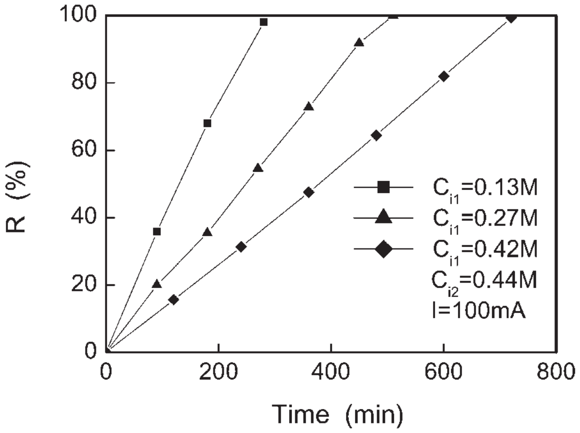

Figure 5. Influence of initial catholyte concentration on recovery and η.

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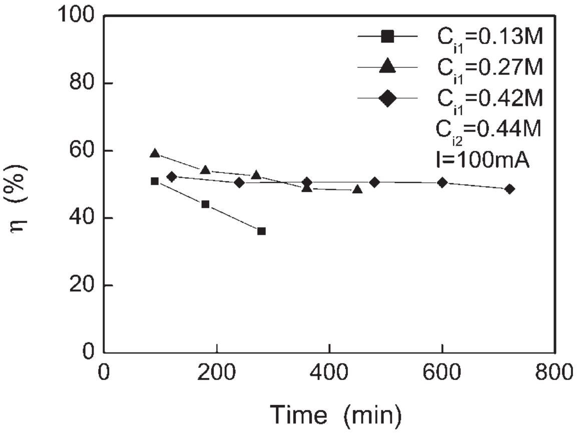

Figure 6. Influence of initial catholyte concentration on C_{f2} and ω.

it is believed that the oil phase should be adsorbed on the surface of the anion membrane because of their hydrophobic interaction. But it will not influence the emulsion composition very much. The most likely reason for no change of the anolyte volume is that the characteristic of the membrane surface has been changed due to the adsorbed oil phase. In this case the membrane not only can select ions, but also can block water transfer through the membrane. The detail mechanism will be studied further.

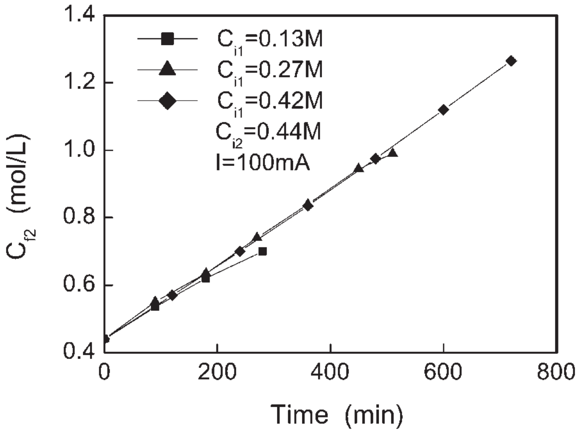

Figure 7. Influence of initial catholyte concentration on V_{f2}.

3.2.2. Influence of Electrical Current Density

Figures 8 and 9 are the results when the initial concentration of anolyte and catholyte is 0.44 and 0.42 M, respectively. Figure 8 shows that the recovery ratio is increased with an increase of the electrical current if the same time is allowed. But the overall electrical current efficiency is little influenced by the electrical current. The changes of the anolyte concentration and the concentrated ratio are plotted in Fig. 9. We can find the linear increase of the anolyte concentration and the concentrated ratio with the time for all the electrical current conditions. The volume of the anolyte was recorded and no volume change has been observed too.

3.3. Comparison of the Two-Phase Electro-Electrodialysis with the Normal Electro-Electrodialysis

Table 1 is the comparison of the two-phase electro-electrodialysis with the normal electro-electrodialysis. As we have discussed in Section 3.2, the major advantage of the two-phase electro-eletrodialysis is its ability to overcome the electroosmosis and osmosis of water, which cause the volume of the anolyte to increase. Compared with the normal electro-electrodialysis, there is almost no volume change of the anolyte in the process of the two-phase electro-electrodialysis with the emulsion as the anolyte. Just because no water passes through the membrane to the anode chamber, the concentrated ratio can be increased linearly with an increase of the time. The concentrated

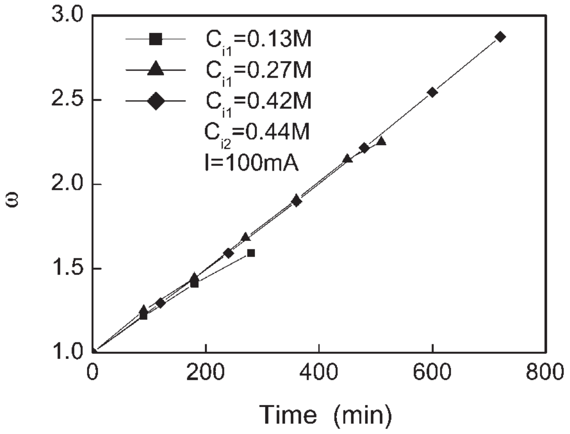

Figure 8. Influence of electrical current on recovery and η.

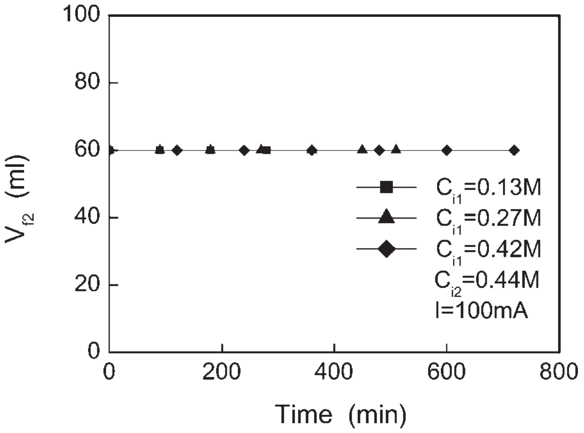

Figure 9. Influence of electrical current on C_{f2} and ω.

ratio can be as much as 2.89, which is much greater than that of the normal electro-electrodialysis. The result tells us that there is almost no influence of the concentration difference between the anolyte and the catholyte on the recovery ratio, concentrated ratio, and the electrical current efficiency in the two-phase electro-electrodialysis. But in the normal electro-electrodialysis process, the anolyte volume will be increased quickly with the concentration

Table 1. Comparison of the two-phase electro-electrodialysis with the normal electro-electrodialysis.

	Electro-electrodialysis ($C_{i1} = C_{i2} = 0.55\,M$)		Two-phase electrophoresis ($C_{i1} = 0.42\,M$, $C_{i2} = 0.44\,M$)		
Electrical current (mA)	50	100	100	150	200
Initial catholyte volume (mL)	60	80	60	60	60
Initial anolyte volume (mL)	40	40	60	60	60
Operation time (min)	540	520	720	480	340
Final volume of the anolyte (mL)	55	71	~60	~60	~60
Concentrated ratio	1.34	1.56	2.88	2.88	2.89
Recovery ratio (%)	56.25	88.77	99.4	99.4	~100
Overall electrical current efficiency (%)	117.3	120.8	49.95	48.59	45.23

difference between the anolyte and the catholyte, or with an increase of the time, although the electrical current efficiency is much higher than that of the two-phase electro-electrodialysis. Therefore, it can be concluded that much higher organic acid solutions can be obtained with the two-phase electro-electrodialysis. But it should also be mentioned that the conductivity of the emulsion is still a little lower than that of the aqueous phase, so in the new process the energy consumption will be a little higher than in the normal process.

4. CONCLUSIONS

In order to overcome the disadvantages of the normal electro-electrodialysis, a new technique of two-phase electro-electrodialysis with an emulsion as the anolyte has been developed and studied in this work based on the study of two-phase electrophoresis. The experimental results showed that the electro-osmosis and osmosis could be controlled very well. Water flux was limited and almost no change of the anolyte volume happened in the two-phase electro-electrodialysis process. For the treatment of the organic acid solutions, very high concentrated ratio and high recovery ratio can be reached with a suitable electrical current efficiency. But the energy consumption will be a little higher than a normal electro-electrodialysis process.

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