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

Back-Extraction of Carboxylic Acids by Two-Phase Electrophoresis

S. Pan[a]; G. S. Luo[a]; J. G. Liu[a]; J. D. Wang[a]
[a] Department of Chemical Engineering, Tsinghua University, Beijing, China

To cite this Article Pan, S. , Luo, G. S. , Liu, J. G. and Wang, J. D.(2003) 'Back-Extraction of Carboxylic Acids by Two-Phase Electrophoresis', Separation Science and Technology, 38: 15, 3731 — 3746

To link to this Article: DOI: 10.1081/SS-120024226

URL: http://dx.doi.org/10.1081/SS-120024226

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 15, pp. 3731–3746, 2003

Back-Extraction of Carboxylic Acids by Two-Phase Electrophoresis

S. Pan, G. S. Luo,* J. G. Liu, and J. D. Wang

Department of Chemical Engineering, Tsinghua University,
Beijing, China

ABSTRACT

In this work, two-phase electrophoresis as a more highly effective back-extraction method was studied. With 33% TOA in n-hexanol as organic solvent, citric acid and succinic acid can be back-extracted to the aqueous phase by two-phase electrophoresis. Compared with the traditional back-extraction ways, there is no phase mixing, phase separation, or other chemicals requirement. So, the process can be called an environmentally friendly process. Some influence factors, such as the distance between the electrode to the interface, time, initial concentration, and electric current density, are discussed. Our experimental results show that the distance from the upper electrode to the interface has little

---

*Correspondence: G. S. Luo, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China; Fax: 8610 62770304; E-mail: gsluo@mail.tsinghua.edu.cn.

DOI: 10.1081/SS-120024226
0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

influence on the mass transfer performance. Hence, it is better to keep the distance as low as possible, but the interface cannot be destroyed. The overall mass transfer quantity increases but the electric current efficiency decreases with an increase in the time. A higher electric current density gives better mass transfer performance. With the initial concentration increasing, both the overall mass transfer quantity and electric current efficiency increase. For the acids with lower distribution coefficient at normal conditions, a much higher back-extraction ratio can be reached.

Key Words: Back-extraction; Two-phase electrophoresis; Carboxylic acids.

INTRODUCTION

Recovery of carboxylic acids from their dilute solutions with acid concentrations lower than 10% (w/w), such as fermentation broth and wastewater, has received increasing attention.[1] Until now, the classic recovery method by precipitation of calcium salt with the addition of calcium hydroxide to the aqueous phase is still regarded as one of the most useful methods. But this method leads to lower yield and the generation of a large amount of calcium sulfate, which has a heavy impact on the environment.[2] Therefore, it is a higher demand to find alternative methods for the production of carboxylic acids.[3–8]

Extraction has been proposed as an alternative to the classical recovery method of carboxylic acids. Organic solvents used for extraction can be categorized into as 1) conventional oxygen-bearing and hydrocarbon extractants, 2) phosphorous-bonded oxygen-bearing extractants, and 3) high-molecular weight aliphatic amines.[2] Aliphatic amines, especially long-chain tertiary amines, have received the most attention because they are the most effective and less expensive.[9] It has been found that a higher recovery ratio can be reached by extraction. But, there is a lack of a more highly effective back-extraction method for getting the products in the form of carboxylic acids, not as salts, and for the regeneration of the organic solvents. It is largely considered that changing pH values is the most effective approach, and there are many published studies related to this method. King et al.[1] pointed out that its major drawback was some of the extra chemicals required and the waste salts formed in this process. Tamada et al.[10] made a detailed investigation of carboxylic acids back-extraction from amine extractants by a swing of temperature and diluent composition, respectively. They also found that the two approaches may be used in combination.[9] King et al.[1] proposed a novel back-extraction method by using thermal decomposition for the extraction of volatile tertiary amines, such as trimethylamine. This novel back-extraction system was found to work rather satisfactorily. In general, successful back-extraction can be achieved by shifting extraction equilibrium through changing the experimental conditions.

Two-phase electrophoresis, i.e., electroextraction was proposed by Stichlmair et al.[11] in 1987. It is similar to electrophoresis and electrodialysis on one hand, and to traditional extraction on the other. One of the phases contains the mixture to be separated and the other acts as a solvent to remove the required components. An electric field perpendicular to the phase interface is imposed on a liquid–liquid system, so oppositely charged particles move into different phases. In this technique, the distinct interface between the two liquid phases can nullify the harmful effects of convection caused by the concentration gradient and temperature difference. Levine and Bier[12] studied the electrophoretic mobility of a protein in an aqueous two-phase system by using a U-tube electrophoresis device. Marando and Clark[13,14] used a dextran–polyethylene glycol–water system to separate the mixtures of hemoglobin and albumin. Their results showed that a significant change of distribution partition for different components was caused when an electric field was applied on the two-phase system. In our previous research, we examined the separation effect of organic acids and dyestuffs by electroextraction.[15–18] We also found that the external electric field would induce a change in the distribution coefficients. Most of carboxylic acids could be concentrated into organic phase by two-phase electrophoresis effectively. But there is no research on back-extraction by two-phase electrophoresis.

The aim of this work was to test the performance of two-phase electrophoresis for back-extraction of carboxylic acids, and to make solvent extraction be an effective method in the separation of carboxylic acids. The influence of time, electric current density, and initial concentration were studied.

Materials and Experimental

N-hexanol (CP) was purchased from Beijing Gold Dragon Chemical Reagent Ltd. and was presaturated by deionized water prepared by our laboratory. TOA (CP) was bought from Chemical Reagent Supply Station of Beijing Military Science Academy. Citric acid and succinic acid were afforded by Beijing Yili Fine Chemical Reagent Ltd.

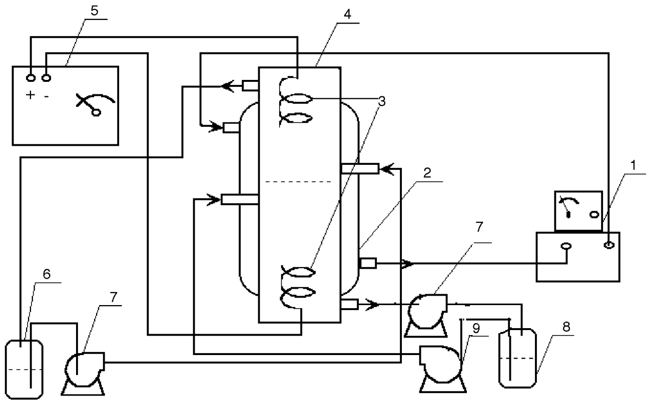
The aqueous solutions with different concentrations were mixed with prepared organic phase over 12 hours. After the phase equilibrium was achieved, the phase separation was allowed for 12 hours, and the loaded organic phase was ready for back-extraction. The carboxylic acid concentrations in both phases were titrated with 0.05-M NaOH solutions. To compare the back-extraction results, we define the back-extraction ratio E and the overall electric current efficiency η as

$$E = (C_{o0} - C_o)/C_{o0} \tag{1}$$

$$\eta = (96500 \times N)/(I \times t \times 60) \tag{2}$$

where C_{o0} is the initial concentration of organic phase and C_o is the concentration of organic phase at a certain time. N is the overall mass transfer quantity. I is the electric current, and t is the experimental time. As to the overall electric current efficiency, ion form of citric and succinic acid can be considered as univalent anion, because they both are weak acids.

The experimental setup is shown in Figure 1. The main part is a glass tube 30 mm in diameter and 70 mm high. It wears a water jacket. Two platinum electrodes connected to the electrophoresis apparatus are made of platinum wire of 0.5 mm in diameter. The water jacket is connected to the thermostatic bath to keep the system at a required temperature. Thirty mL of organic phase and 30 mL of aqueous phase in equilibrium status were filled into the organic phase tank and the aqueous phase tank, respectively.



1. Water bath 2. Water jacket 3. Electrodes 4. Two-phase electrophoresis equipment

5. Electrophoresis apparatus 6. Organic phase tank 7. 9. pumps 8. Aqueous phase tank

Figure 1. Setup of experimental apparatus.

The aqueous phase was pumped into the two-phase electrophoresis equipment at first. Then, the organic phase was pumped into the electrophoresis equipment. The distance from the interface to the bottom electrode was about 30 mm. When the two-phase system was stable, i.e., the volume flow rates of the organic phase and the aqueous phase were under the required value, the electrophoresis apparatus was turned on to carry out the back-extraction. The electrical current density across the system was adjusted through the electrophoresis apparatus. In the course of back-extraction, the acid concentration in aqueous phase was analyzed by titration, and the acid concentration in organic phase was calculated from the concentration of the aqueous phase and the initial concentrations of the two phases.

RESULTS AND DISCUSSION

Selection of Working System

Identification of an appropriate extraction system is the most important requisite of our work, because the working system used in two-phase electrophoresis should meet some special demands, such as a much higher extraction efficiency and much better electric conductivity. Based on our knowledge of extraction and two-phase electrophoresis, the following rules were drawn for the selection of the organic solvent.

1. The organic solvent must have good electric conductivity. Usually the solvents with higher polarity or in which the solubility of water is higher are preferred.
2. The density difference between the organic solvent and the aqueous phase must be distinct and there is a well-defined liquid–liquid interface.
3. The organic solvents can extract carboxylic acids from aqueous phase effectively.
4. The organic solvents have as low as possible toxicity and solubility to reduce the effect on fermentation process and to avoid the loss of organic solvents.

As to the selection of the extraction of carboxylic acids, TOA (trioctylamine), a long-chain tertiary amine has been proved to be one of the excellent extractants. So TOA was selected as the extractant in our work. Besides the extractant, a suitable diluent should be chosen to meet the above rules. Alcohols are widely used as diluent in carboxylic acids

Table 1. Physical properties of some alcohols.

Alcohols	Relative density to water	Dielectric constant	Solvent solubility in water (wt%)	Water solubility in solvent (wt%)
n-butanol	0.8097	17.1 (25°C)	7.8 (20°C)	20 (20°C)
n-pentanol	0.8144	13.9 (25°C)	2.1 (30°C)	7.2 (30°C)
n-hexanol	0.8186	13.3 (25°C)	0.58 (20°C)	7.2 (20°C)
n-heptanol	0.8219	9.21 (20°C)	Immiscible	Immiscible
n-octanol	0.8239	10.34 (20°C)	Immiscible	Immiscible

extraction because of their high polarity. Physical properties of some alcohols[19] are listed in Table 1.

From Table 1, we can see that n-hexanol has low solubility in water, and high water solubility content when it contacts with water. The properties make n-hexanol be a good diluent for two-phase electrophoresis because of its electric conductivity. But to confirm the detailed contents of TOA and hexanol, the electrical conductivity and extraction ability of different contents are still required to be studied. The compared results are listed in Table 2. To evaluate the extraction ability, the mixed solvents of different TOA content were used to extract citric acid from 9 wt% aqueous solution at a phase ratio of 1:1. The distribution coefficients are defined as the indictor of the extraction ability.

It is shown that the solvent electrical conductivity increases while the extraction ability decreases with a decrease in the TOA content. When the volume ratio of TOA to hexanol is 4:8, both the electrical conductivity and the extraction ability of the mixed solvent can meet the requirement of solvent extraction and two-phase electrophoresis. Therefore, the organic phase with 4:8 of the volume ratio of TOA to hexanol was be used in the work.

Table 2. Compared results of different TOA content solvents.

Volume ratio (TOA:hexanol)	Electrical conductivity (μS/cm)	Indicator of extraction ability	Electrical conductivity of loaded solvents (μS/cm)
1:11	1.603	1	110.2
2:10	1.235	2	165
4:8	0.559	10	136
6:6	0.188	> 50	80.7

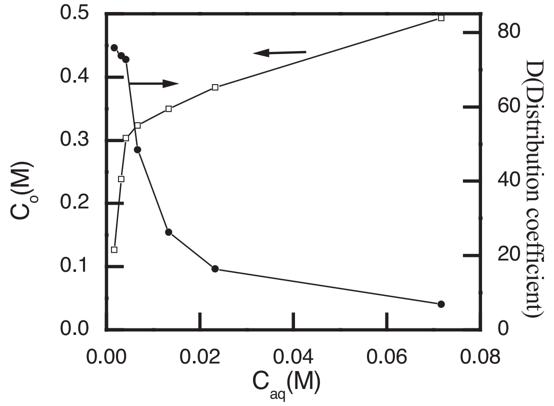


Figure 2. Distribution coefficients for citric acid.

Extraction Ability

The extraction experiments were carried out with the solvent for citric acid and succinic acid at 25°C. The distribution coefficients are plotted in Figures 2 and 3 for citric acid and succinic acid, respectively.

From the above curves, it can be seen that the selected solvent shows a very high extraction ability for carboxylic acids, especially for the dilute solutions. The results prove that the solvent is a good choice for the recovery of carboxylic acids. But as we know, for a proper choice, there

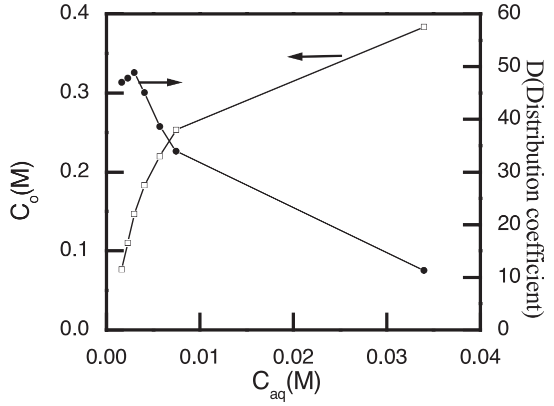


Figure 3. Distribution coefficients for succinic acid.

must be a good back-extraction method for this solvent. Otherwise, we cannot set a complete process for the production of carboxylic acids. So, a back-extraction way with higher performance should be developed.

Test of Back-Extraction Under an Electric Field and the Influence of Distance Between Upper Electrode and Liquid–Liquid Interface

Our previous studies proved that the two-phase electrophoresis is a higher performance separation method for the recovery of carboxylic acids from their dilute solutions. In this work, an experiment was carried out to see if the two-phase electrophoresis could be used for back-extraction. The experimental results under the electric current density $i = 10.6\ \mathrm{mA/cm^2}$ are shown in Figure 4. The initial concentration in aqueous phase is $C_{aq0} = 0.07$ M and in organic phase $C_{o0} = 0.483$ M. The distance from the upper electrode to the liquid–liquid interface, L_1, is 5 mm.

Figure 4 shows that the concentration of aqueous phase is increased with time during the back-extraction process, which tells us that the two-phase electrophoresis is an effective back-extraction method.

But, because the electrical conductivity of organic phase is much lower than that of aqueous phase, most of the electrical resistance in the two-phase electrophoresis circuit is focused in the organic phase. Therefore, the distance between upper electrode and liquid–liquid interface, L_1, is an important factor for the consumption of electrical energy. It is necessary to study the influence of L_1 on the performance of the back-extraction process. Figure 5 is the back-extraction ratio for citric acid at $L_1 = 5$ mm and 35 mm, respectively.

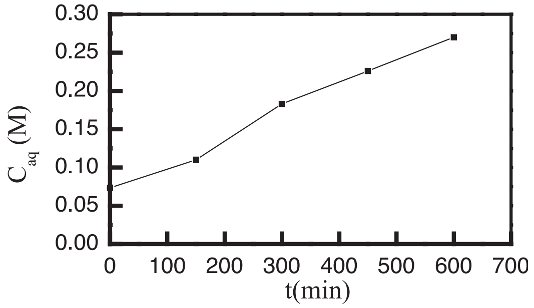


Figure 4. The curve of concentration of aqueous phase with time.

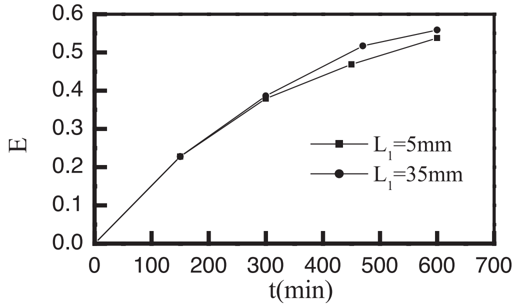


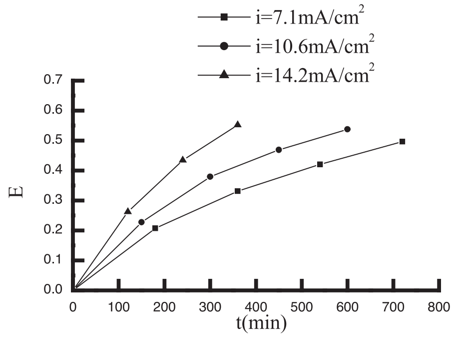
Figure 5. Influence of L_1 on back-extraction of citric acid (i = 10.6 mA/cm^2, $C_{aq0} = 0.07$ M, $C_{o0} = 0.483$ M).

From the results at different L_1, we can see that the extraction ratio is slightly higher when the distance is longer. But the difference between the two conditions is not as much as the change of the distance. So it can be concluded that L_1 is not a sensitive factor on back-extraction. Considering the consumption of electrical energy, L_1 should be set as low as possible if only that the liquid–liquid interface is not destroyed. In the other parts of this work, L_1 is fixed at 5 mm.

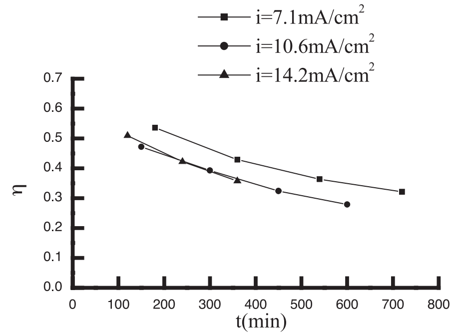
Influence of Time on Back-Extraction

The influence of time on the back-extraction of citric acid and succinic acid by two-phase electrophoresis is exhibited in Figures 6 and 7. It is shown that with the time increasing, a satisfactory back-extraction ratio is achieved. The back-extraction ratio improves but the improving tendency is slowed down and, hence, the overall electric current efficiency decreases.

The explanation of the experimental results is based on the mass transfer mechanism of two-phase electrophoresis. There are two main mass transfer modes of carboxylic acids in two-phase electrophoresis. One is due to the action of electromigration. It is a mass transfer process combined with electrode reactions. To describe the mass transfer mechanism, we suppose that the molecule of carboxylic acid is expressed as HA. The anode is allocated in the aqueous phase, and the mass transfer direction of A^- is from the organic phase to the aqueous phase. Because water is dissolved in organic phase in some content, dissociation of carboxylic acid can be occurred as H^+ and A^- ions in both phases. If the carboxylic acid molecule and relevant ions are inertia to the electrode reactions, the cathode reaction will be $2H^+ + 2e \rightarrow H_2\uparrow$, and the anode reaction is $H_2O \rightarrow 2H^+ +$



(a) Back-extraction ratio

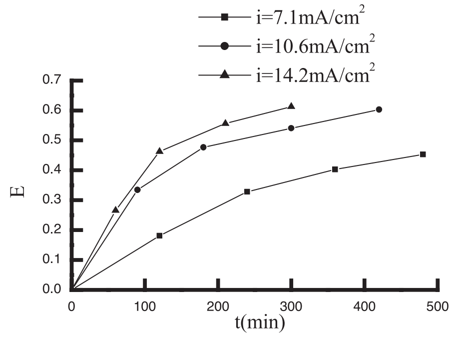


(b) Electric current efficiency

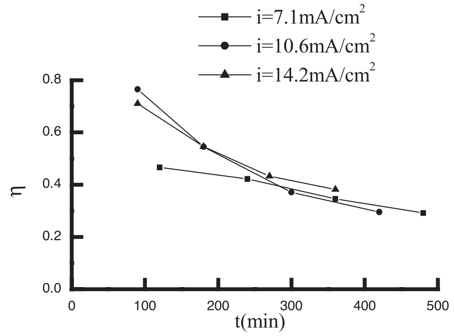
Figure 6. Influence of time on back-extraction of citric acid ($C_{aq0} = 0.073$ M, $C_{o0} = 0.483$ M).

$1/2O_2\uparrow + 2e$. In the bulk of organic phase, the ions of H^+ move toward the cathode, and take part in the cathode reaction. At the same time, A^- migrates to the anode. When A^- ions pass through the interface, some of them combine with H^+ from anode reaction to form HA molecule.

The other mode for mass transfer of carboxylic acids is driven by the concentration difference between two phases. Because before the back-extraction is started the two phases are at an equilibrium state, there is not yet any net mass transfer between the two phases. But when the equilibrium state is broken by an electric field, the mass transfer due to the mass gradient will be produced.



(a) Back-extraction ratio



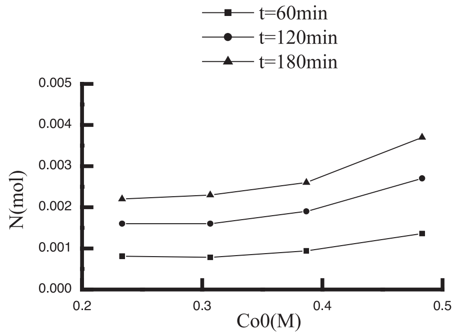
(b) Electric current efficiency

Figure 7. Influence of time on back-extraction of succinic acid ($C_{aq0} = 0.009$ M, $C_{o0} = 0.320$ M).

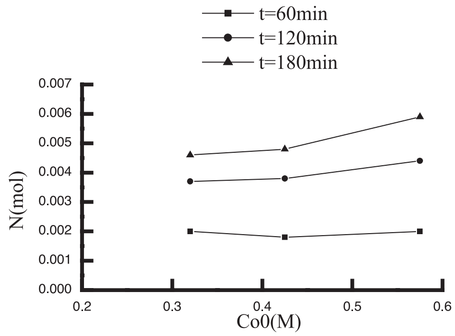
At the beginning of back-extraction, the mass transfer of carboxylic acids is mainly electromigration from the organic phase to the aqueous phase. The electromigration mass flux is determined by the electric current density. So the overall electric current efficiency can be kept at higher value and the back-extraction ratio is increased quickly. But with our experiment continued, the concentration of aqueous phase is grown, and the concentration difference between the two phases is improved. The back diffusion from the aqueous phase to the organic phase increases with the increment of time. Hence, the net flux from the organic phase to the aqueous is decreased, and the overall electric current efficiency is decreased too.

Influence of Electric Current Density

Figures 6 and 7 also show that under the same conditions, the back-extraction ratio is higher if the electric current density is higher. The reason is that the higher electric current density leads to higher electromirgation flux, and the net flux from organic phase to aqueous phase is higher. Therefore, a much higher back-extraction ratio can be reached in a shorter time when the electric current density is higher. And also, we can see that the overall electric current efficiency is decreased with time. This result means that it is helpful for back-extraction to improve the current density.



(a) citric acid



(b) succinic acid

Figure 8. Influence of initial concentration on overall mass flux ($i = 10.6\ mA/cm^2$).

Influence of Initial Concentrations

The relationship between overall mass transfer quantity and initial acid concentration in the organic phase is plotted in Figure 8. From the figure, it can be seen that the overall mass transfer quantity N improves with the increasing of the initial concentration.

This relationship is a result of the decreasing of distribution coefficient D with the improving of C_o, as is shown in Figures 2 and 3. The back-diffusion mass flux n, which is from the aqueous phase to the organic phase driven by the concentration difference, can be described as

$$n = K(C_{aq} - C_{aq}*) = K(C_{aq} - C_o/D) \quad (3)$$

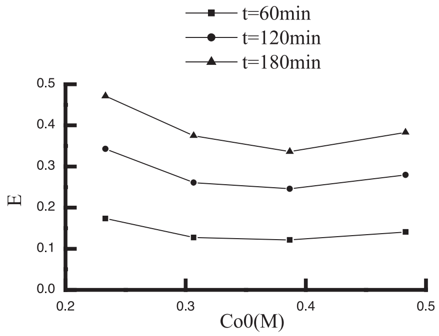
where K is the mass transfer coefficient of carboxylic acid. When a certain mole of carboxylic acid is transferred from the organic phase into the aqueous phase, the value of n is much higher for the system with a higher distribution coefficient. Therefore, a higher initial concentration results in a lower mass transfer flux from the aqueous phase to the organic phase and much higher overall mass flux from the organic phase to the aqueous phase.

Figure 9 is the influence of initial concentration on the back-extraction ratio. It can be seen that the back-extraction ratio is decreased with an increase in the initial concentration for succinic acid. As to citric acid, the back-extraction ratio is decreased with the initial concentration increasing. If the initial concentration is high enough, the back-extraction ratio will increase slightly. The results are strongly related to the distribution coefficients of the system.

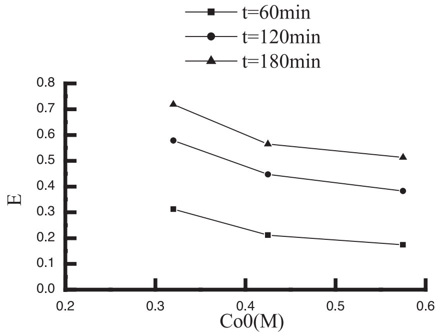
Comparison of Citric Acid and Succinic Acid

Figures 8 and 9 also show that under similar conditions, the back-extraction of succinic acid is much better than that of citric acid. The overall mass transfer quantity and the back-extraction ratio of succinic acid are much higher than that of citric acid. There are probably two reasons. One is that that at a certain C_o, the distribution coefficient and, therefore, the back-diffusion mass flux of succinic acid, is lower than that of citric acid. The other reason is that succinic acid with lower molecule weight has higher electrophoretic mobility and more contribution to the electric conduction. Under the similar initial concentration and electric current density, the electromigration of succinic acid is higher than that of citric acid as well as the over mass transfer quantity.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016



(a) citric acid



(b) succinic acid

Figure 9. Influence of initial concentration on back-extraction ratio (i = 10.6 mA/cm^2).

CONCLUSION

In this work, we successfully back-extracted citric acid and succinic acid from the phase of TOA + n-hexanol to the aqueous phase by a new way of two-phase electrophoresis. Our experimental results show that two-phase electrophoresis is a more highly effective back-extraction method. Also, in this back-extraction process, there is no phase mixing, phase separation, or other chemicals requirement. Coupling the new technique with the normal extraction may provide a higher efficiency and lower material cost process for the production of carboxylic acids. It has been found that the distance from the upper electrode to the interface has little influence on the mass transfer performance. Therefore, to save electric energy, the distance may be set as low as possible. The overall mass transfer quantity increases while the electric current efficiency decreases as the time is increased. A higher electric current density results in better mass transfer performance. With the initial concentration increasing, both the overall mass transfer quantity and electric current efficiency increase. Compared with the results of the two kinds of acid, it has been found that the acid with lower distribution coefficient at normal condition can be back-extracted more effectively.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the National Science Foundation of China and Tsinghua University Science Foundation for this work.

REFERENCES

1. Tung, L.A.; King, C.J. Sorption and extraction of lactic and succinic acids at ph > pKa1. Ind. Eng. Chem. Res. **1994**, *33*, 3217–3229.
2. Kertest, A.S.; King, C.J. Extraction chemistry of fermentation product carboxylic acids. Biotechnol. Bioeng. **1986**, *28*, 269–282.
3. Katikaneni, S.P.R.; Cheryan, M. Purification of fermentation-derived acetic acid by liquid–liquid extraction and esterification. Ind. Eng. Chem. Res. **2002**, *41*, 2745–2752.
4. Hirth, J.; Bicker, M.; Vogel, H. Isolation of carbohydrate carboxylic acids from aqueous solution by reactive extraction. Chem. Ing. Tech. **2002**, *74*, 345–350.
5. Wodzki, R.; Nowaczyk, J. Propionic and acetic acid pertraction through a multimembrane hybrid system containing TOPO or TBP. Sep. Purif. Technol. **2002**, *26*, 207–220.
6. Malmary, A.U.G.; Albet, J.; Putranto, A.M.H.; Molinier, J. Recovery of carboxylic acids from aqueous solutions by liquid–liquid extraction with a triisooctylamine diluent system. Braz. J. Chem. Eng. **2001**, *18*, 441–447.
7. Kyuchoukov, G.; Marinova, M.; Molinier, J.; Albet, J.; Malmary, G. Extraction of lactic acid by means of a mixed extractant. Ind. Eng. Chem. Res. **2001**, *40*, 5635–5639.
8. Hong, Y.K.; Hong, W.H. Extraction of succinic acid with 1-octanol/

n-heptane solutions of mixed tertiary amine. Bioprocess Eng. **2000**, *23*, 535–538.

9. Yang, S.-T.; White, S.A.; Hsu, S.-T. Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH. Ind. Eng. Chem. Res. **1991**, *30*, 1335–1342.
10. Tamada, J.A.; Kertes, A.S.; King, C.J. Extraction of carboxylic acids with amine extraction, 1, 2. Ind. Eng. Chem. Res. **1990**, *29*, 1319–1326.
11. Stichlmair, J.; Schmidt, J.; Proplesch, R. Electroextraction: a novel separation technique. Chem. Eng. Sci. **1992**, *47* (12), 3015–3022.
12. Levine, M.L.; Bier, M. Electrophoretic transport of solutes in aqueous two-phase systems. Electrophoresis **1990**, *11*, 605–611.
13. Theos, C.W.; Clark, W.M. Electroextraction two-phase electrophoresis. Appl. Biochem. Biotechnol. **1995**, *l54*, 143–157.
14. Marando, M.A.; Clark, W.M. Two-phase elelctrophoresis of proteins. Sep. Sci. Technol **1993**, *28* (8), 1561–1577.
15. Luo, G.S.; Zhu, S.L.; Fei, W.Y.; Wang, J.D. A coupled separation technique of solvent extraction with electrophoresis. Solv. Extrac. Res. Dev., Japan **1997**, *4*, 135–139.
16. Luo, G.S.; Yu, M.J.; Zhu, S.L.; Dai, Y.Y. Electro-extraction separation of dyestuffs. Sep. Sci. Technol. **1999**, *34* (5), 781–792.
17. Zhai, S.L.; Luo, G.S.; Liu, J.G. Aqueous two-phase electrophoresis for separation of amino acids. Sep. Purif. Technol. **2001**, *21*, 197–203.
18. Luo, G.S.; Pan, S.; Liu, J.G., et al. Liquid–liquid phase equilibrium under external electric fields. Sep. Sci. Technol. **2001**, *36* (12), 2799–2809.
19. Cheng, N.L. *Handbook of Organic Solvents (in Chinese)*, 2nd Ed.; Chem. Ind. Press: Beijing, China, 1994.

Received August 2002
Revised January 2003