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LIQUID-LIQUID PHASE EQUILIBRIUM UNDER EXTERNAL ELECTRIC FIELDS

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ABSTRACT

With the development of novel combined-field separation techniques, the influence of external fields on the thermodynamic properties of working systems is an important area of study. A study on the phase equilibrium of *n*-butanol/citric acid/water under an electric field was carried out. The effects of field strength, temperature, and solute concentration in the aqueous phase on the distribution coefficients were investigated, and the results were analyzed through chemical potential equations. The experimental results show that, if enough time is allowed, an equilibrium state will be reached for the working system under the action of an electric field. Increased voltages and temperatures resulted in higher distribution coefficients between butanol and water. If the solute concentration in the aqueous phase is lowered, the distribution coefficient is strongly increased with an increase of the field strength. However, at unchanged field strength, a higher solute concentration will cause a decrease in the distribution coefficient. Also, the logarithm of the ratio defined by the distribution coefficient under an electric field to the distribution coefficient without an electric field is directly proportional to the voltage applied to the system.

Key Words: Equilibrium; Electric field; Liquid-liquid; Citric acid

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INTRODUCTION

Separation processes are very important in the chemical process industries. They are used for the removal of contaminants from raw materials, for the recovery and purification of primary products, and for the elimination of contaminants from effluent streams. The novel separation techniques bring additional driving forces (electric, magnetic, ultrasonic, microwave, etc) into a separation system, which is considered an effective way to enhance mass transfer performance (1–2).

Electro-extraction, a novel combined-field separation technique, is showing good prospects for many applications. In 1987, J. Stichlmair (3) proposed this technique. It is similar to electrophoresis and electrodialysis on one hand and to traditional extraction on the other hand. In this technique, 2 distinct liquid phases within the separation device compensate for the harmful effects of thermal convection. One of the phases contains the mixture to be separated and the other one acts as a solvent to remove the components separated (4). An electric field perpendicular to the interface is imposed on the system, making oppositely charged particles move into different phases. Levine and Bier (5) studied the electrophoretic mobility of a protein in an aqueous 2-phase system by using a U-tube electrophoresis device. Theos and Clark (6) and Marando and Clark (7) used the dextran/polyethylene glycol/water system to separate mixtures of hemoglobin and albumin. The experimental results showed significant improvements of the separation obtained with the application of an electric field over that obtained from the same 2-phase system without an applied field. In our previous research, we examined the separation effect of organic acids and dyestuffs (8–11) by electro-extraction. In these studies, we showed that purification can be significantly enhanced by the electric field. Electro-extraction can be utilized in many separation processes, particularly for diluted or multicomponent systems. Because it is widely applicable and easily controllable, electro-extraction has the prospect for a variety of industrial uses.

All current research focuses on the performance of mass transfer. As stated in Astarita's textbook, *Thermodynamics,* an electric field penetrates into a dielectric fluid so that the field energy contributes to the internal energy of a system. The interaction has a great effect on thermodynamic properties of a dielectric medium, which leads to a change of the phase equilibrium (12). However, the question of strong field influence on the thermodynamics of phase equilibrium is not yet clear (13–16). Therefore, the study of phase equilibrium under an external electric field is important for developing novel separation techniques. In the present work, a study on the liquid-liquid phase equilibrium under an electric field has been carried out with *n*-butanol/citric acid/water in an experimental system.

MASS TRANSFER MECHANISM

In the electro-extraction process, the stable interface plays an important role in mass transfer performance. The whole space where mass transfer activity occurs is divided into 4 sections: an anode zone, a cathode zone, an aqueous phase, and an organic phase. Figure 1 shows how the solutes permeate through the interface from one phase to the other one. To describe the mass transfer mechanism, we denote the molecule of organic acid as HA. The cathode is allocated in the aqueous phase, and the mass transfer direction of A^- is from the aqueous phase into the organic phase. The mass transfer mechanism is discussed under the assumption that water and *n*-butanol are mutually saturated, so dissociation of organic acid molecules occurs because H^+ and A^- ions are present in both phases. However, the dissociation constant in the organic phase is much lower than it is in the aqueous phase. If the organic solvent molecule and A^- ions are inert to electrode reactions, the cathode reaction is $2H^+ + 2e \rightarrow H_2 \uparrow$, and the anode reaction is $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 \uparrow + 2e$.

The whole reaction can be regarded as a process of splitting water. In the bulk of the aqueous phase, the H^+ move toward the anode and take part in the anode reaction. At the same time, A^- migrates to the anode. When the A^- passes through the interface, it combines with H^+ from the anode reaction to form an HA molecule because the HA molecule in the organic phase could dissociate little. With the increase in the concentration of organic acid in the organic phase, the organic acid molecule will diffuse back to the aqueous phase. When the mass flux caused by the electric driving force is equal to that caused by the concentration difference, an equilibrium state (a quasi equilibrium) is reached.

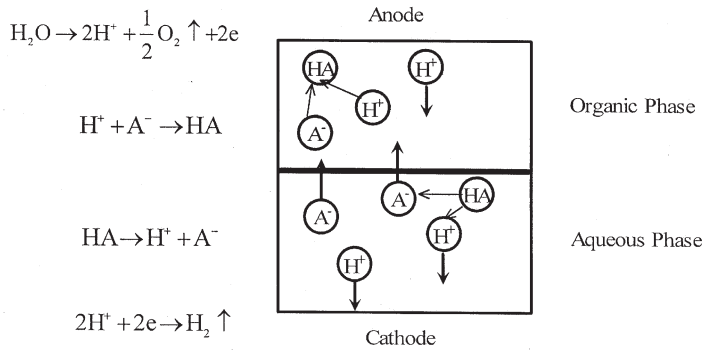

Figure 1. Mass transfer mechanism in the electro-extraction process.

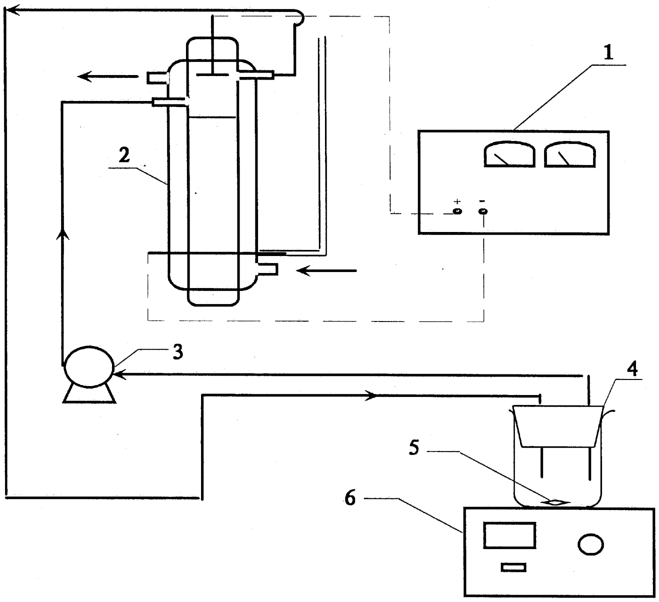

Figure 2. The setup of experimental apparatus. 1, electrophoresis apparatus; 2, electro-extraction equipment; 3, pumps; 4, organic phase tank; 5, magnetic stirring apparatus.

MATERIALS AND EXPERIMENTAL

The experimental apparatus is shown in Fig. 2. A glass tube, which is 1.5 cm in diameter, 12 cm high, and enclosed in a water jacket is the principal component. The 2 platinum electrodes connected to the electrophoresis apparatus are made of 0.5-mm diameter platinum wire. The distance between the 2 electrodes is 7.5 cm. The lower electrode is covered with a micropore hollow fiber to discharge the gas produced by the electrode reactions. The cut-off molecule weight of the membrane is 30 000. The water jacket is connected with a thermostatic bath to keep the system at a constant temperature.

To avoid the phase volume change caused by mutual dissolution, the system of *n*-butanol/citric acid/water was fully mixed for more than 24 hours without an applied electric field. After the two phases were mutually saturated, the equilibrium state was achieved, and 23 mL of water phase was fed into the electro-extraction tube. Then, 10 mL of organic phase was fed to a beaker and pumped into the electro-extraction tube. The distance between anode and interface was 1 cm, and that from cathode to interface was 6.5 cm. After the system was stable, a constant electric field was applied to the working system. To overcome the volume changes of the 2 phases due to the electrode reactions, the electric currents were limited to less than 5 mA.

After the electric field was applied, the solute concentration in the organic phase was analyzed at different times until the relative deviations of the concentration in the organic phase were less than ± 5%, and we could assume that a new equilibrium state had been reached. Then the 2 phases were separated, and the solute concentrations in the 2 phases were analyzed with titration. The relative deviation of this analysis method was determined to be less than ± 2%. In this work, the distribution coefficient was defined as a ratio of the solute concentration in the organic phase to solute concentration in the aqueous phase at an equilibrium state.

RESULTS AND DISCUSSION

Distribution Coefficient Without Electric Field

An experimental study of the phase equilibrium without electric field was carried out. The results are listed in Table 1. The distribution coefficient was between 0.3 and 0.4, and slightly increased with increasing temperature.

Phase Equilibrium Under Electric Fields

Figure 3 shows the curve of the citric acid concentration in the organic phase versus time at 26.5°C under 100 V. The initial solute concentration in the organic phase and in the aqueous phase was 0.025 N and 0.066 N, respectively. The concentration in the organic phase increased after an electric field had been applied to it, which demonstrated that the conventional 2 phase equilibrium state can be broken by the application of an electric field. At first, the concentration increased

Table 1. Distribution Coefficients Obtained Without Electric Field

Temperature (°C)	1	2	3	4	5	6	7
25.6							
Y (N)	0.008	0.013	0.024	0.031	0.046	0.050	0.062
D	0.33	0.33	0.32	0.32	0.34	0.33	0.34
30.0							
Y (N)	0.010	0.015	0.028	0.039	0.044	0.052	0.063
D	0.37	0.34	0.34	0.36	0.37	0.33	0.34
35.0							
Y (N)	0.009	0.014	0.027	0.032	0.040	0.052	0.066
D	0.38	0.38	0.36	0.34	0.36	0.35	0.36

Y = organic phase concentration.

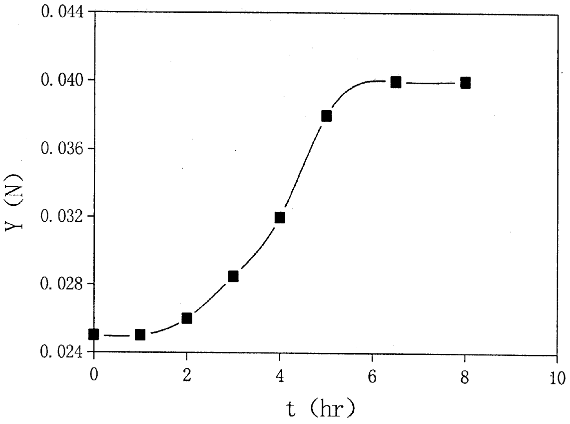

Figure 3. The concentration of organic phase vs. time.

only slowly, then sharply, then slowly again. Finally, almost no change occurred over time as a new equilibrium state was achieved. For the system considered, 6.5 hours were required to reach the equilibrium state. In subsequent experiments, the equilibrium was considered to be reached when the concentration in organic phase varied by less than ± 5%.

The influence of the electric field on the 2-phase equilibrium was studied under 100, 200, 300, 400, 500, and 600 V at 26.5°C for different initial concentrations. The initial concentrations in the organic and water phases were 0.018 N, 0.040 N; 0.026 N, 0.066 N; 0.033 N, 0.095 N; 0.044 N, 0.122 N. Figure 4 shows the experimental results.

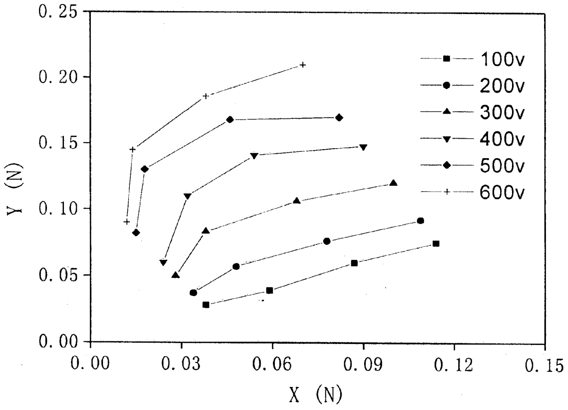

Figure 4. The influence of field strength and concentration on equilibrium. Y is organic phase and X denotes the aqueous phase.

The equilibrium concentration in the organic phase and, in turn, the distribution coefficients increased with increasing voltage for experiments conducted at the same initial concentrations. Table 1 shows that the distribution coefficients do not depend on the initial concentrations. However, when an electric field was applied, the influence of the initial concentration was considerable. When the applied electric field strength was low, the linear relationship between the concentrations in the 2 phases was still evident. As the electric field strength increased, the influence of electric field on the system gradually increased. When the concentration in the water phase was low, the increase of the concentration in the organic phase was greater under high electric field. However, the concentration in the organic phase increased only slowly if the solute concentration in water phase was high.

The equilibrium of a liquid-liquid system can be analyzed from the chemical potential. For any working system, with no electric field, the chemical potential of the solute in the 2 phases can be written as

$$\mu_a = \mu_a^\theta + RT \ln(\gamma_a C_a) + ZF\Phi_a \tag{1}$$

$$\mu_o = \mu_o^\theta + RT \ln(\gamma_o C_o) + ZF\Phi_o \tag{2}$$

where μ is the chemical potential; γ is activity coefficient; C is concentration; Z is the charge number of the ion, F is the Faraday constant; and Φ is the electric potential in the bulk phase. The subscripts a or o represent the water and organic phases, and superscript θ represents normal condition. If an equilibrium state is reached, then

$$\mu_a = \mu_o \tag{3}$$

According to the first and second Wien effects, the dissociation constant and the ion activity coefficient vary with the strength of the electric field. When the applied electric field is larger than 10^5 V/cm, the effect is considerable. Obviously, the applied electric field in our experiment was so small that the Wien effect could be neglected (17). Therefore, when an electric field is applied to the system and the system is in the equilibrium state, the chemical potential will change according to the Eqs. (4–6).

$$\mu_a' = \mu_a^\theta + RT \ln(\gamma_a' C_a') + ZF\Phi_a' \tag{4}$$

$$\mu_o' = \mu_o^\theta + RT \ln(\gamma_o' C_o') + ZF\Phi_o' \tag{5}$$

$$\mu_a = \mu_o' \tag{6}$$

When an electric field is applied, the first equilibrium state will shift to a new one, and $ZF\Phi_a$ and $ZF\Phi_o$ are changed greatly. The changes lead to a mass transfer of citric acid from the water phase into the organic phase.

For the relation of the first equilibrium state to the new equilibrium state, the variation of electrochemical potential of citric acid in the water phase and in the organic phase can be described by Eqs. (7–9).

$$\Delta\mu_a = RT \ln(\gamma_{a1} \mathrm{C}_a' / \gamma_{a1} C_{a1}) - F(\Phi_a' - \Phi_a) \tag{7}$$

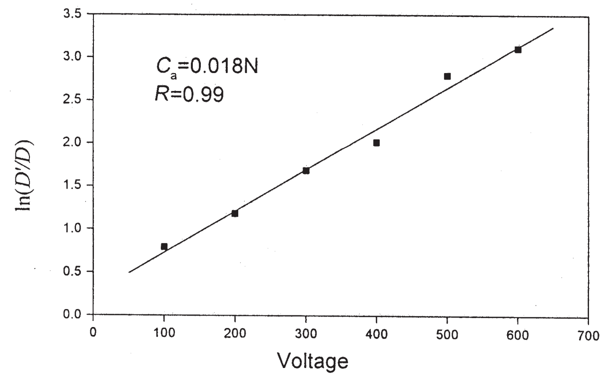

Figure 5. ln (D'/D) vs. voltage at initial concentration of 0.018 N.

$$\Delta\mu_o = RT \ln(\gamma_o' C_o' / \gamma_o C_o) - F(\Phi_o' - \Phi_o) \tag{8}$$

$$\Delta\mu_1 = \Delta\mu_2 \tag{9}$$

Because the system is dilute, we suggest that $\gamma = 1$, and the following equation is obtained:

$$\ln\left(\frac{D'}{D}\right) = F(\Phi_a - \Phi_o)/RT + F(\Phi'_a - \Phi'_o)/RT \tag{10}$$

Here D'/D is the ratio of the distribution coefficient obtained for phases under an electric field to that measured for phases without an applied electric field.

In Eq. (10), $F(\Phi_a - \Phi_o)/RT$ is not related to the electric field, but $F(\Phi_a' - \Phi_o')/RT$ is strongly dependent on the applied electric field. Hence, ln (D'/D) is a function of the voltage applied. Figures 5–8 show the relationships between ln (D'/D) and the applied voltage for different initial concentrations.

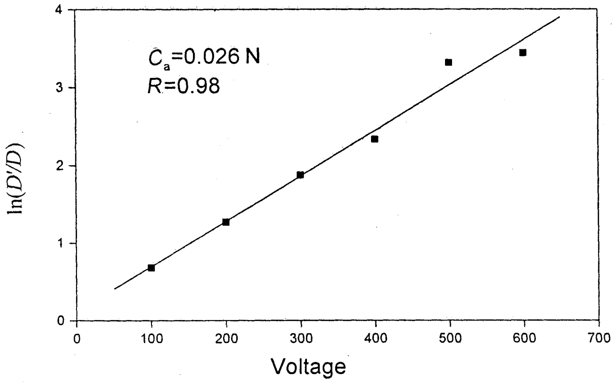

Figure 6. ln (D'/D) vs. voltage at initial concentration of 0.026 N.

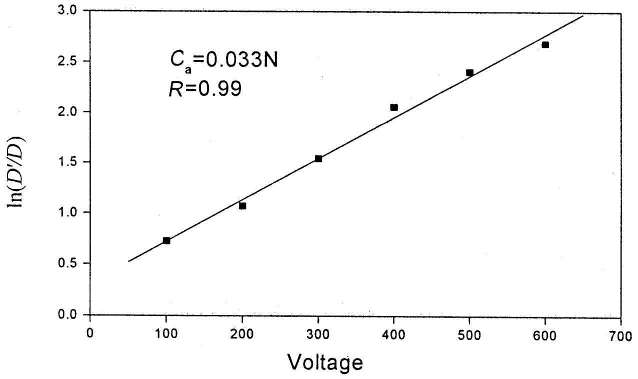

Figure 7. ln (D'/D) vs. voltage at initial concentration of 0.033 N.

Under the experimental conditions, ln (D'/D) and applied voltage can be described by a linear relation. From this result and Eq. (10), we found that ($\Phi'_a - \Phi'_o$) is directly proportional to the voltage applied on the working system.

Influence of Temperature on Equilibrium Under An Electric Field

To study the influence of temperature on the distribution coefficients obtained from phases under electric field, experiments were carried out with an initial concentration in the organic phase of 0.018 N and in the water phase of 0.040 N at different temperatures. The experimental results obtained at 26.5°C and 30°C are shown in Fig. 9. At low voltage, the influence of the temperature on the distri-

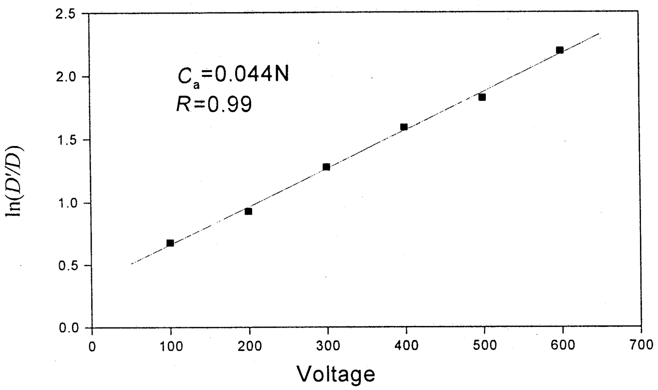

Figure 8. ln (D'/D) vs. voltage at initial concentration of 0.044 N.

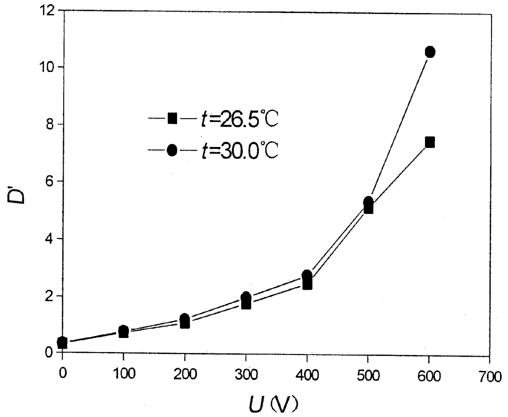

Figure 9. The influence of temperature on distribution coefficients.

bution coefficient was inconspicuous. However, if the applied voltage was higher, the partition coefficient at 30°C was considerably larger than it was at 26.5°C. Obviously, the increase in temperature caused a considerable increase in the electrical conductivity for the working system, especially for the organic phase.

CONCLUSION

From the above experimental and theoretical results, we concluded that, if enough time is allowed, a new equilibrium state (a quasi equilibrium state) can be reached under the action of an electric field. Higher voltages and temperatures result in higher distribution coefficients. When the concentration of the aqueous phase is low, the distribution coefficient is increased rapidly with an increase of the field strength. However, under the same field strength, the higher concentration will cause the decrease of the distribution coefficients. Also, the logarithm of the ratio defined by the distribution coefficient for phases under electric field to the distribution coefficient for phases without electric field is directly proportional to the applied voltage.

Although some mass transfer mechanisms have been briefly discussed in the present work, a more detailed study of the dynamic mass transfer equation is needed. Further study will help us to understand the equilibrium state more clearly.

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