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DISTILLATION UNDER ELECTRIC FIELDS*

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ABSTRACT

Distillation is the most common separation process used in the chemical and petroleum industry. Major limitations in the applicability and efficiency of distillation come from thermodynamic equilibria, that is, vapor-liquid equilibria (VLE), and heat and mass transfer rates. In this work, electric fields are used to manipulate the VLE of mixtures. VLE experiments are performed for various binary mixtures in the presence of electric fields on the order of a few kilovolts per centimeter. The results show that the VLE of some binary mixtures is changed by electric fields, with changes in the separation factor as high as 10% being observed. Batch distillation experiments are also carried out for binary mixtures of 2-propanol and water with and without an applied electric field. Results show enhanced distillation rates and separation efficiency in the presence of an electric field but decreased separation enhancement when the electric current is increased. The latter phenomenon is caused by the formation at the surface of the liquid mixture of microdroplets that are entrained by the vapor. These observations suggest that there should be an electric field strength for each system for which the separation enhancement is maximum.

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INTRODUCTION

Distillation is a process used extensively in the chemical, petrochemical, pharmaceutical, food, biochemical, and other industries to separate chemical products or recyclable components from mixtures. It is estimated that, in the United States alone, the energy spent on distillation is approximately 10% of the total energy consumption of the chemical industry. Despite its high energy demands, a distillation process is preferred over other separation methods because of its high efficiency, simplicity in processing, and applicability for a plethora of chemical systems. Any improvement in the distillation process would lead to considerable energy and cost savings. Limitations in applicability and efficiency of distillation come mostly from the mass and heat transfer rates and the vapor-liquid equilibria (VLE) of a system.

This research originated with the hypothesis that applying an electric field to a binary mixture may change the VLE of the mixture and therefore increase the separation of components by distillation. The objective is to determine which types of mixtures are most affected by electric fields and to understand the mechanisms that may cause any modification of the phase equilibria.

BACKGROUND

The enhancement of heat transfer coefficients due to electric fields in boiling or condensation processes has been known for several years (1,2). Electrohydrodynamic (EHD) effects lead to reduction in film thickness and interfacial instability, resulting in wave formation or spraying and enhanced heat transfer coefficients. Didkovsky and Bologa (3) studied the effect of electric field strength, frequency, and uniformity on the hydrodynamics and heat transfer in film condensation of vapor on a short vertical surface. They found a 20-fold enhancement in heat transfer, which they attributed to the formation of transverse waves on the condensed vapor film and reduction in the film thickness caused by the condensate spraying into the vapor phase. Bologa et al. (4) found a sevenfold increase in the heat transfer coefficient for the condensation of a vapor in the presence of a noncondensable gas due to an electric field-induced corona discharge. Yabe et al. (5)

showed that the use of a field strength of 2.3 kV/mm resulted in a 300% increase in boiling heat transfer rates of a nonazeotropic mixture of HCFC-123 and HFC-134a. Yabe et al. (6) have also shown EHD enhancements in heat transfer by a factor of 5–100 for several processes such as nucleate boiling, condensation, and defrosting. Mass transfer effects of electric fields across the gas-liquid interface have also been reported. Bulanov and Butkov (7) found a twofold to sixfold increase in the rate of mass transfer during rectification of an ethanol-water mixture. Recently, Maximuo et al. (8) investigated the effect of electric fields on mass transfer rates in distillation of binary mixtures. They reported a significant increase in mass transfer rates, up to 70%, compared with those found under free conditions.

Effects of electric fields on the boiling point of pure liquids have been studied by several investigators. Katti and Chaudhri (9) reported a decrease in the boiling point of methanol, ethanol, and isopropyl alcohol under the influence of alternating electric fields. Using classical thermodynamics, Lyon (10) calculated the change in the boiling point of these alcohols to be on the order of 10^{-5} °C and claimed that the experiments by Katti and Chaudhri were in error. Anderson and Sardo Infirri (11), Ramakrishna et al. (12), and Sharma (13) carried out experiments similar to those of Katti and Chaudhri and failed to observe a change in the boiling point of liquids under the influence of electric fields. Biswas and Basu (14) used a dc electric field to study its effect on the boiling point of liquids. They found no change in the boiling point of benzene or carbon tetrachloride. They observed, however, a decrease in the boiling point for methanol of 1.63°C at a field strength of 16 kV/cm. Quint, Gates, and Wood (15), using classical thermodynamics, predicted changes on the order of 10^{-4} Pa in the saturation pressure of water at 25–300°C and at field strengths of 10^6 V/m.

These studies have created a debate among researchers, and the effect of electric fields on the boiling point remains unclear. Recently, however, molecular simulations on dipolar fluids have shown that there should be a significant effect of electric fields on the pure fluid VLE of polar compounds. Molecular simulations of dipolar hard spheres (DHS), dipolar soft spheres (DSS), and Stockmayer (ST) fluids have been recently reported (16,17,18,19). These studies showed a significant effect on the vapor pressure and VLE of these fluids under the influence of external electric fields. Boda et al. (20) used perturbation theory to study the VLE of a DSS fluid under an electric field. A decrease in

the vapor pressure and an increase in the critical temperature of the fluid with increasing field strength were reported. Boda et al. (19) studied the vapor-liquid equilibria of a ST fluid in an applied field using perturbation theory and *NpTE* molecular simulations along with test particle insertions to obtain the chemical potential. They found a qualitative agreement between simulation results and perturbation theory calculations. These simulation data, however, need to be substantiated with experiments.

Research Approach

Two types of experiments are conducted to investigate the effect of electric fields on the VLE of mixtures and on such dynamic processes as heat transfer and the rate of boiling. Steady-state isobaric experiments are run with high voltage applied across the vapor-liquid interface of a binary mixture to study the effect of an electric field on the VLE of binary liquid mixtures. The individual component mole fractions are measured and compared with existing VLE curves found in the literature to ensure the validity of the experimental data and to observe whether an applied electric field modifies the vapor and liquid concentrations.

The time-dependent batch distillation experiment is used to compare the vapor concentration versus time and the total component separation for experimental runs with and without an applied electric field. The direction and position of the electric field remain constant during the runs but have been altered in previous experiments to find optimum field strength, location, and direction. Different electrode types are used to observe the effect of the uniformity of the electric field. Phase equilibria modification is studied by comparing the degree of change caused by a nonuniform electric field on polar-polar, polar-nonpolar, and nonpolar-nonpolar mixtures, as well as mixtures with and without hydrogen bonding.

EXPERIMENTAL METHODS

VLE Apparatus

In the VLE experiments, a modified Othmer still, as shown in Figure 1, is used to boil a binary liquid mixture. The still was modified to allow an electric field to be applied

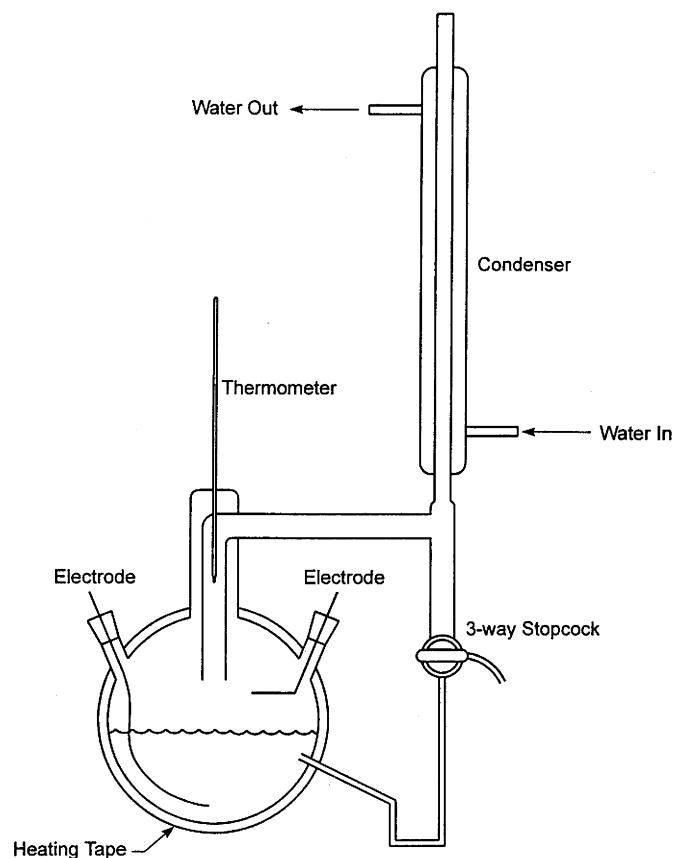


FIGURE 1. Schematic of the VLE apparatus.

between two electrodes. Two heating tapes are wrapped around the still for heating and insulation. One tape heats the top or vapor region of the still, while the other is wrapped around the bottom to control the heating of the liquid region.

The electric field is applied across the vapor-liquid interface of the mixture by a Glassman (Series EQ) power supply, which generates high voltage (up to 30 kV). An electrode rod, connected to the high-voltage power supply, is located in the vapor region of the still. A second electrode rod, located in the liquid region, is connected to an electrical

ground. The shape of the electrodes causes a nonuniform field in the horizontal and vertical directions. Also, the polarity of the electric field can be reversed. An electrical circuit connected to an oscilloscope is used to measure electric current and determine the significance of the power added by the electric field. The temperature of the system is measured by using two thermistors located in the vapor and liquid regions of the still. The thermistors are connected to a temperature recorder (1560 Black Stack, Hart Scientific, American Fork, UT), which plots the temperature with an accuracy of 0.01°C for the duration of the experiments. The pressure of the system is measured by using an electronic pressure transducer (Model SC 200, Sensotec, Columbus, OH).

A mixture (500 mL) with a known concentration is heated to its boiling temperature, and the vapor flows into a water-cooled heat exchanger for condensation. The condensate is completely recycled back into the still. Equilibrium is reached for a system by modifying the heat input to fix the vapor temperature at the liquid boiling temperature and by allowing the system to reach steady state in vapor and liquid concentration. After steady state is reached, liquid samples are drawn from the bottom stopcock, and vapor samples are drawn from the condensed liquid using a three-way stopcock. Three samples are drawn at 15-min intervals before applying a voltage between the two electrodes and repeating the measurements. The size of each sample is about 70 μL . The electric field is turned off and the system is allowed to reach steady state. The compositions of the samples collected with and without applied electric fields are determined by using a gas chromatograph (GC).

Batch Distillation Apparatus

A binary mixture is boiled in a batch distillation still, which is heated by an electric jacket controlled by a variable power supply, as shown in Figure 2. The exposed top portion of the still is wrapped in insulating tape to reduce heat loss. The vapor condenses in a single-pass glass heat exchanger and is collected in a graduated cylinder. The thermometer is located at the exit to the heat exchanger to measure the vapor temperature. Two circular electrodes, made of SS-316 wire mesh, are used to generate a more uniform electric field across the vapor-liquid interface. The electrodes can be vertically spaced up

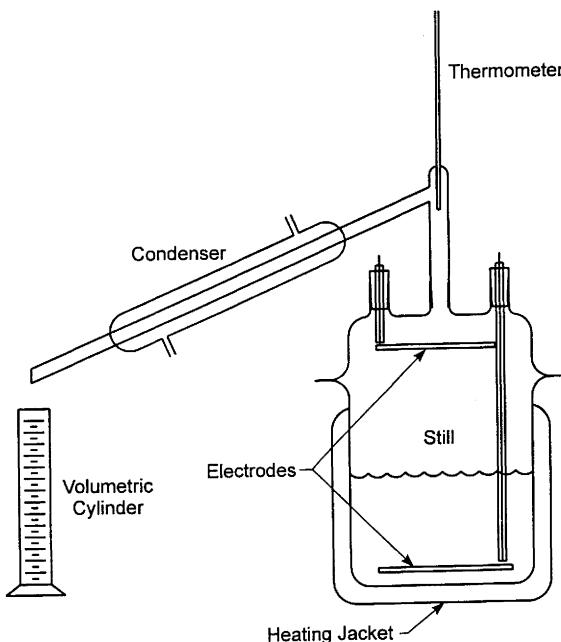


FIGURE 2. Schematic of the batch distillation apparatus.

to 20 cm apart, but they are held in a constant position during the experiment. With this geometry, a more uniform electric field can be formed across the vapor-liquid interface inside the still. A Glassman power supply is used to apply a high voltage to one of the electrodes. The second electrode is grounded. Samples are taken using 2-mL sample bottles and analyzed using a GC.

A known volume (usually 500 or 750 mL) of a binary mixture of known composition is placed in the batch distillation still. The mixture is heated by applying electrical power to the heating jacket using the variable power supply. The power supplied is calculated by measuring the applied voltage and current passing through the jacket. When the mixture begins to boil, samples of the distillate are taken at regular intervals and the total volume of the distillate collected is recorded throughout the experiment. After the distillate is

collected for 5–10 min, up to 24 kV of high voltage is applied and maintained for a designated period. The current passing between the electrodes is measured to determine the additional power added to the system. The high voltage is turned off about 5–10 min before the electrical power to the heating jacket is turned off. After the completion of the experiment, samples are taken from the total distillate collected and the remaining bottoms for analysis. Control experiments are carried out in the absence of the electric field. The volume collected over time gives the condensate flow rate.

Analytical Methods

The Hewlett Packard 5890 Series II Gas Chromatograph equipped with a thermal conductivity detector and a Porapak Q 1/8-in., 6-ft-long column is used to determine the concentrations for both the VLE and the batch distillation experiments. The GC response peaks are computer integrated to give an area percentage for each component and a calibration curve is generated using the area percentage of known standards. The mole fraction of the samples can then be determined. Results are plotted on a spreadsheet with the standard deviation and the experimental uncertainty of the mole fractions. The mass balance for the batch distillation runs and the separation that has been achieved in the system are then evaluated.

Experimental Systems

The polar-polar 2-propanol–water system has been examined closely because of results indicating electric field effects on systems that contain hydrogen bonding. Mixtures of varying polarities have also been investigated.

RESULTS AND DISCUSSION

VLE Results

Literature data (21) are plotted against data obtained in this work for 2-propanol (isopropanol) mole fractions of 10, 14, 23, 50, 68, and 87% in 2-propanol–water mixtures, as shown in Figure 3. The addition of an electric field to these systems at equilibrium

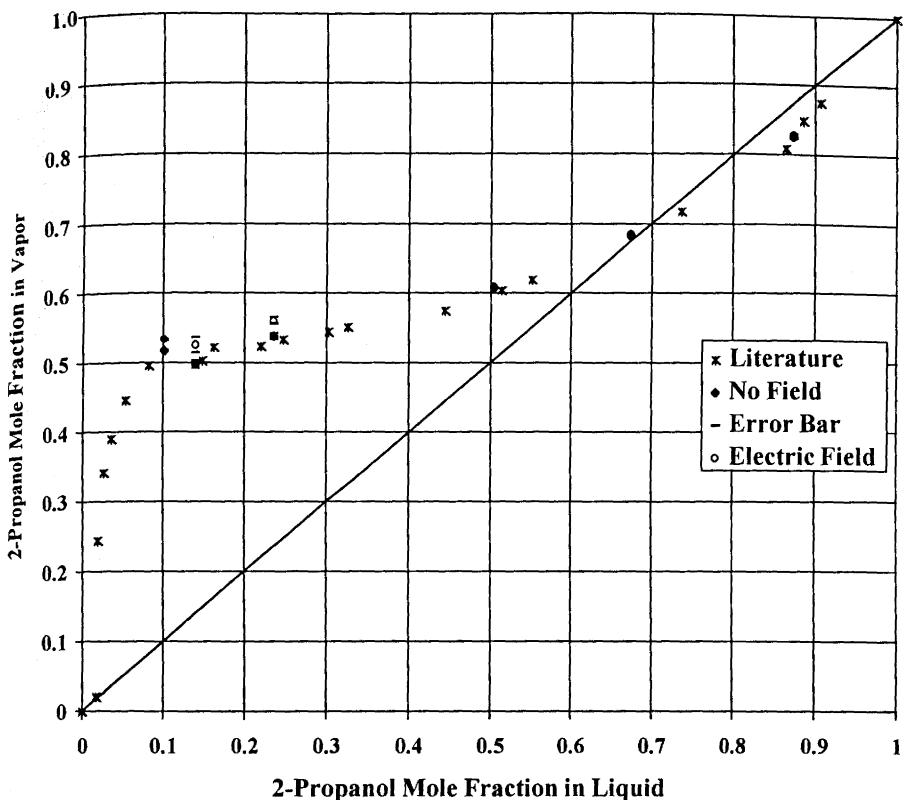


FIGURE 3. Comparison of VLE experimental data with those found in the literature [J. Kohoutova et al., 1970 (ref. 21)].

causes an increase in the 2-propanol vapor mole fractions for the mixtures containing lower concentrations of 2-propanol. The largest field effects for the 2-propanol–water system, shown in Figure 4, are observed for a 23% initial concentration. It is shown that the average vapor concentration of 2-propanol shifts from 53.6 to 56%. The separation factor α , given by Eq. (1) (ref. 22, page 978) is enhanced by 10% from 3.80 to 4.19.

$$\alpha = \frac{y(1-x)}{x(1-y)} \quad (1)$$

The separation factor, or relative volatility, is calculated using the mole fraction of the high

key component in the liquid, x , and the vapor, y . Measurement error is determined by analyzing repetitive samples to show error bars for each point, as shown in Figure 4. The electric field samples consistently show an increase above the standard deviation lines of all the no-field samples for lower starting concentrations and the data shift is confirmed by a student t-test of unequal variances for a 99% confidence limit. This enhancement is not due to changes in the liquid concentration. The liquid mole fraction of 2-propanol for this experiment remains around 23%, as shown in Figure 5, which is expected due to the larger liquid volume.

A change in the vapor temperature is observed when the electric field is applied. As shown in Figure 6, the vapor temperature, during a VLE experiment with 2-propanol-water, decreases by more than half a degree when high voltage is added, indicating a possible heat transfer effect. The temperature drop is not caused by concentration changes in the liquid and vapor. Experiments run with pure 2-propanol at its equilibrium boiling temperature have shown a similar temperature drop with an applied electric field. The largest increase in the vapor concentration of 2-propanol in the binary mixture is observed at the greatest decrease in the vapor temperature.

During runs, stronger electric fields have caused larger temperature changes until the point at which increasing current causes disruptions in the system. When the current rises due to high-voltage addition, the rise in concentration is smaller. One explanation for this, based on experimental observation, is that at a sufficiently high voltage, the liquid surface becomes unstable and microdroplets are formed due to electrostatic spraying. Electric fields have not shown any effect on the pressure during the VLE experiment. Also, the same electric field effects on concentration and temperature are observed for pressures of 740 and 760 mm Hg.

The azeotrope (inseparable) point at constant pressure for the 2-propanol-water mixture is 68 mol % 2-propanol. Experiments were conducted at 68 and 87% concentrations of 2-propanol. However, no significant effects of electric fields on the vapor concentration of these systems were observed.

Batch Distillation Results

The batch distillation experiment differs from the VLE experiment in that the batch experiment is time dependent. Therefore, the distillate concentration and the rate of

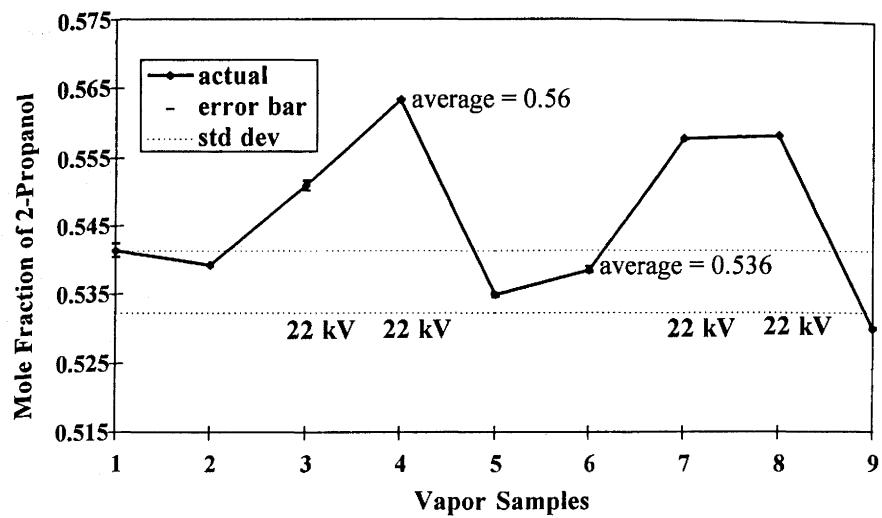


FIGURE 4. Vapor concentrations for the VLE of the 2-propanol–water system at 23 mol % 2-propanol with an applied electric field at samples 3, 4, 7, and 8. Time between samples is 30 min.

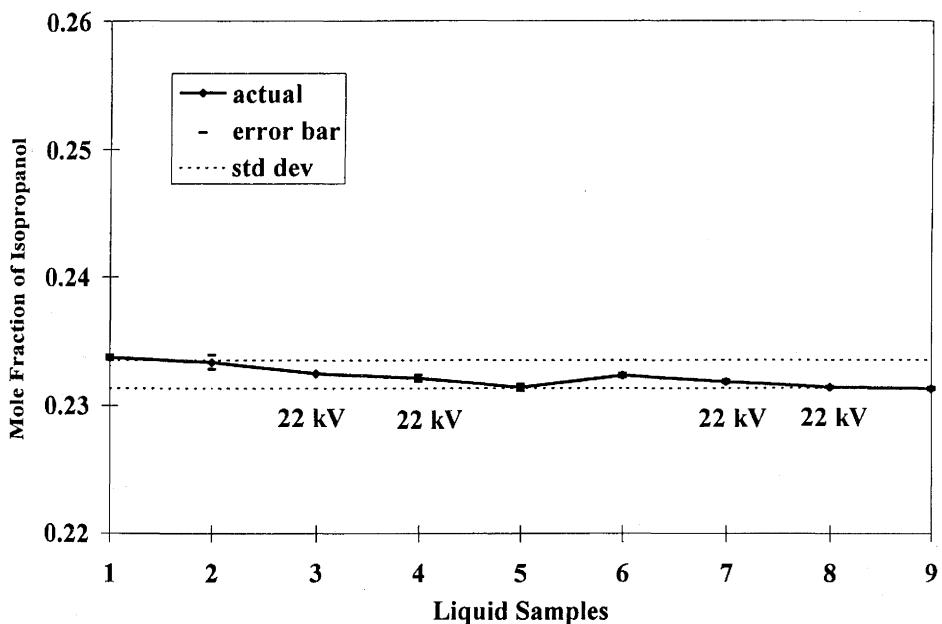


FIGURE 5. Liquid concentrations for the VLE of the 2-propanol–water system at 23 mol % 2-propanol with an applied electric field at samples 3, 4, 7, and 8. Time between samples is 30 min.

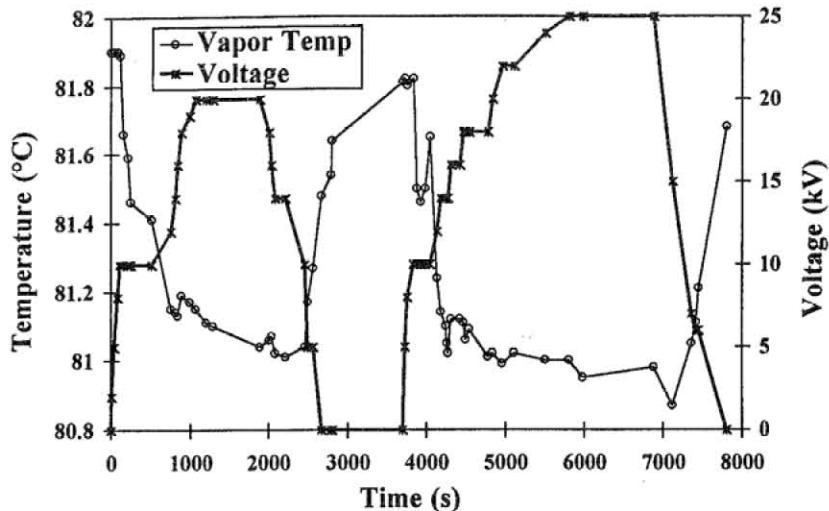


FIGURE 6. Vapor temperature as a function of high-voltage addition for the VLE 2-propanol-water system.

distillation for the 2-propanol-water system are compared for runs with and without an applied electric field, using similar power inputs for both runs. A 2-kV/cm electric field was applied to a 28% 2-propanol mixture, as shown in Figure 7. Before the addition (up to 100-mL volume of the distillate collected), the concentration curve for the field run resembled the concentration curve for the no-field run. A rise in the concentration of 2-propanol in the distillate and an increase in the separation were noted for the electric field run. Table 1 compares the mass balance of the electric field run with that of the no-field run. High voltage was added to the mixture for 50 min, and the result was a higher concentration of 2-propanol in the distillate for the electric field run. As can be seen in Figure 8, the vapor temperature decreased when the voltage was applied to the batch distillation experiment. This decrease is similar to the temperature change observed in the VLE experiment. Also, the concentration enhancement is again diminished when more than 0.1 mA (varies for different systems) of current is added to the system by the high voltage.

As shown in Figure 9, the distillation rate has been increased with increased field strength for batch experiments at lower concentrations of 2-propanol, suggesting a mass

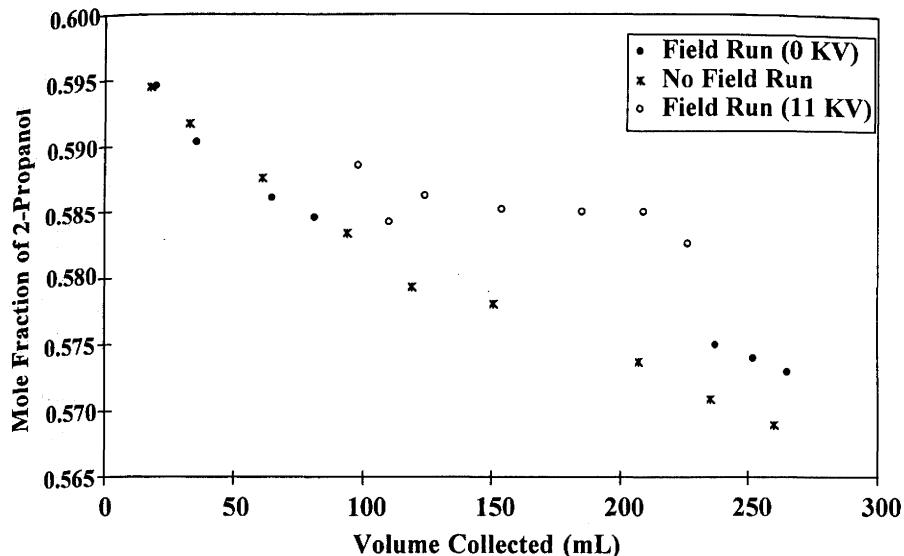


FIGURE 7. Comparison of distillate concentrations for batch distillation runs of 2-propanol–water with and without an applied electric field.

TABLE 1. MASS AND ENERGY BALANCE FOR THE BATCH DISTILLATION OF 2-PROPANOL–WATER

NO-FIELD RUN	Total Volume (mL)	Mole Fraction of Isopropanol	Volume of Isopropanol (mL)
Initial Still	600	0.284	373.7
Distillate	265	0.571	224.9
Final Still	331*	0.160	148.1

Total heat added to the system (kJ): 623.48

Heat required to vaporize distillate (kJ): 203.24

2-kV/cm RUN	Total Volume (mL)	Mole Fraction of Isopropanol	Volume of Isopropanol (mL)
Initial Still	600	0.284	373.9
Distillate	270	0.589	232.2
Final Still	325*	0.152	139.4

Total heat added to the system including electric field heat (kJ): 626.45

Heat required to vaporize distillate (kJ): 201.40

Heat added by the electric field (kJ): 2.97

*Some losses in volume were due to evaporation during the run.

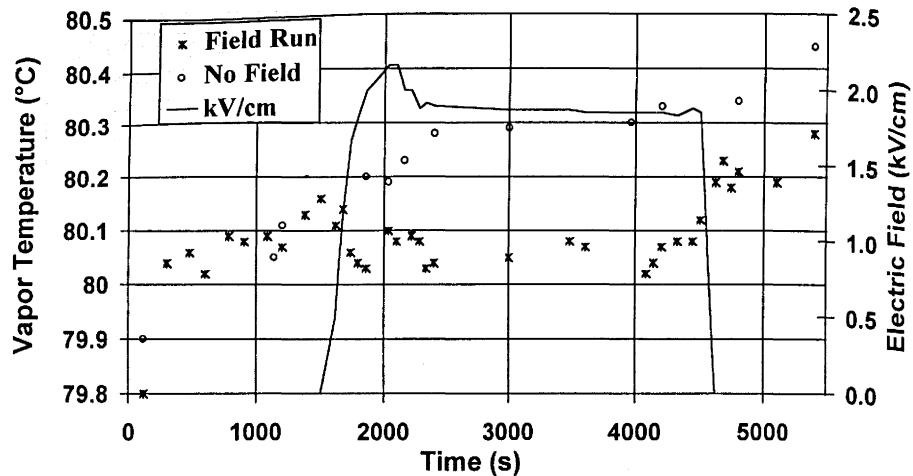


FIGURE 8. Comparison of vapor temperatures for batch distillation runs of 2-propanol-water with and without an applied electric field.

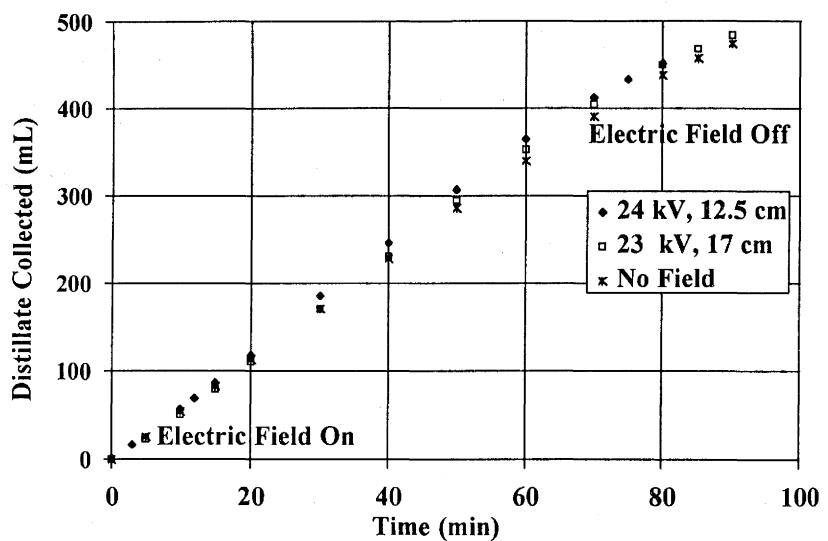


FIGURE 9. Comparison of distillate flow rates for batch distillation runs of 2-propanol-water with and without an applied electric field.

transfer effect. As expected based on VLE results, an 85% starting concentration, which is past the azeotrope point, showed very little difference in the distillation concentrations or rates for runs with and without an applied electric field.

The results of the VLE and the batch experiments for the 2-propanol–water system indicate that electric fields can alter equilibrium. Concentration changes in the vapor for both experiments were reflected by changes in the vapor temperature, a finding that suggests heat transfer effects caused by an electric field. Also, the addition of an electric field increases the overall efficiency of the batch distillation of 2-propanol from water, as the volume of 2-propanol removed increases and the total volume increases for similar lengths of time and power inputs. No significant electric field effects were observed on either the vapor pressure of the system or the concentration of a system at the azeotrope point, though further experiments need to be conducted.

Initially, mixtures of differing polarities were investigated to determine if component separation could be significantly affected by the location of positive and negative high-voltage electrodes. Several different mixtures were used for VLE and batch experiments, including cyclohexane and toluene (nonpolar–nonpolar), isopropanol and water (polar–polar), isopropanol and toluene (polar–nonpolar), and methyl isobutyl ketone and cyclohexane (polar–nonpolar). Significant electric field effects were noticed only in systems that contained hydrogen bonding. Therefore, the 2-propanol–water system will be further studied in future work to determine if alterations occur in the hydrogen bonding or vapor pressure when an electric field is present in the system.

CONCLUSIONS

This work has shown that electric fields can be utilized to modify the vapor-liquid equilibria for some binary mixtures. The addition of an electric field to 2-propanol–water mixtures enhanced separation by distillation as the initial concentration is moved further away from the azeotrope. The relationship between increasing concentration and decreasing vapor temperature indicates enhanced transport effects for the system. The optimum high-voltage addition to the system appears to be the point at which the temperature change is greatest. This point is the level of the highest voltage addition at

which no disruptions occur in the system due to electrical current. Experiments are currently being conducted to further determine the mechanisms for the electric field-induced evaporation enhancements.

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