To the Graduate Council:

I am submitting herewith a thesis written by Kevin David Blankenship entitled "Distillation With Applied Electric Fields." I have examined the final copy of the thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Jack Watson, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

DISTILLATION WITH APPLIED ELECTRIC FIELDS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Kevin David Blankenship
May 1999

ACKNOWLEDGEMENTS

This research was sponsored by the Environmental Management Science Program, Office of Environmental Management, and Office of Basic Energy Sciences, Office of Chemical Sciences of the U.S. Department of Energy and the Electric Power Research Institute. The writer's appointment with the Separations Group of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) was sponsored by the Science and Engineering Research Program and the Professional Internship Program of the Oak Ridge Institute of Science and Education.

The writer wishes to acknowledge the motivation and the helpful suggestions provided by his major professor, Dr. Jack Watson, his ORNL advisor, Dr. Costas Tsouris, his ORNL group leader, Dr. David DePaoli, and Dr. Vinod Shah, who initiated several of the experiments described in this work. Theoretical calculations described in this work were made in collaboration with Dr. Jim Hylton. The writer also wishes to acknowledge Jerry King who illustrated several of the figures in this work.

ABSTRACT

Distillation is the preferred separation technique in the chemical industry because of its operational simplicity and efficiency. However, distillation has thermodynamic and transport limitations which determine the number of stages and the energy required to separate the components of a mixture. In this study, several types of laboratory-scale experiments were designed and conducted to investigate the hypothesis that an applied electric field on the order of a few kilovolts per centimeter enhances component separation, heat transfer, and mass transfer in a distillation process. For boiling polar-polar and polar-nonpolar mixtures, the relative volatility, known as the separation factor in a distillation process, has been shown experimentally to increase by as much as 10% in a single distillation stage. The electric field effects were only observed when there was a polar component present in the system. In these experiments, the more volatile component was the component whose concentration was increased in the vapor. The results of batch distillation experiments showed an increase in distillate concentration and a small increase in distillate flow rate with negligible power input from the applied voltage.

Experiments were performed to investigate the mechanisms involved in separation enhancements with an applied electric field. These included experiments varying the shape and separation of the electrodes and the strength and polarity of the electric field. The experiments showed that greater voltage differences led to higher separation efficiency. However, varying the electrode separation at a given potential difference, and thus the electric field strength, had little effect on the vapor composition.

The geometry of the system was important in maximizing the separation improvements due to the applied voltage difference because the increase in separation efficiency was reduced under intense electrohydrodynamic conditions where liquid dynamics such as dripping, splashing, or jetting occurred. A large rise in the slope of the current, as opposed to a small, steady increase, as the applied voltage was increased indicated when the electric field enhancements had been reduced. This elevated current was sometimes accompanied by the formation of microdroplets at the surface of the liquid. These findings, in combination with calculations of the interface charge density, suggested that improvements in the separation efficiency achieved by an applied voltage difference were induced by charge accumulation at the vapor-liquid interface rather than electric field effects in the bulk liquid region of the still.

Mass transfer enhancements have been observed in a distillation stage due to electrohydrodynamic spraying. Applying voltage to a distillation tray increased the interfacial contact area between liquid and vapor by decreasing the size of the bubbles rising through the liquid in the distillation stage. This transport enhancement led to increased separation of the components and increased plate efficiency.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
II.	REVIEW OF THE LITERATURE	4
	Effect of Electric Fields on Pure Liquid Boiling Point	4
	Increased Component Separation with Applied Voltage	5
	Summary of Background Information	6
III.	EXPERIMENTAL METHODS	7
	Phase Equilibria Method	8
	Batch Distillation Method	11
	Total Reflux Method	13
	Interfacial Study	17
	Concentric Electrode Distillation Method	17
	Multistage Distillation Method	21
	Analytical Methods	23
IV.	EXPERIMENTAL RESULTS	24
	Phase Equilibria Results	24
	Batch Distillation Results	32
	Total Reflux Results	37
	Experiments With Different Electrode Shapes	45
	Electrode Separation Distance	48
	Concentric Electrode Results	50

Azeotrope Experiments 50

Multistage Distillation Results 52

Interfacial Study Results 56

V. DISCUSSION 58

VI. CONCLUSIONS 63

LIST OF REFERENCES 65

APPENDICES 67

A. PHASE EQUILIBRIA CALCULATIONS 68

B. BATCH DISTILLATION CALCULATIONS 71

C. THEORETICAL CALCULATIONS 76

Theoretical Equations 76

Nomenclature 77

VITA 78

LIST OF TABLES

TABLE		PAGE
I.	Dielectric constants and dipole moments for the chemicals used	7
II.	Mass and Energy Balance for Batch Distillation of 2-Propanol/Water	37
III.	2-Propanol–Water (14:86) Liquid Samples	68
IV.	Gas Chromatograph 2-Propanol–Water Standards	69
V.	2-Propanol–Water (14:86) Vapor Samples	70

LIST OF FIGURES

FIGURE PAGE

1. Schematic of the phase equilibria apparatus 9
2. Schematic of the batch distillation apparatus 12
3. Schematic of the total reflux apparatus 14
4. Setup for the study of the interface of a total reflux experiment with the 2-propanol–water system using Raman spectroscopy 18
5. Concentric electrode condenser apparatus 20
6. Multistage distillation apparatus 22
7. Comparison of vapor-liquid equilibria experimental data with those found in the literature [J. Kohoutova et al., 1970 (ref. 19)].. 25
8. Vapor concentration for the 2-propanol–water system with 23 mol % 2-propanol with an applied electric field at samples 3, 4, 7, and 8 26
9. Liquid concentration for the 2-propanol–water system with 23 mol % 2-propanol and an applied electric field at samples 3, 4, 7, and 8 28
10. Phase equilibria experiment with the cyclohexane–toluene system 29
11. Vapor temperature as a function of high voltage addition for the 2-propanol–water system 30
12. Vapor and liquid temperature measurements for pure 2-propanol, n-butanone, and toluene 31
13. Comparison of distillate concentrations for batch distillation runs of 2-propanol–water with and without an applied electric field 33

14. Comparison of vapor temperatures for batch distillation runs of 2-propanol–water with and without an applied electric field 35
15. Comparison of distillate flow rates for batch distillation runs of 2-propanol–water with and without an applied electric field 36
16. Current measurements as a function of positive (+) and negative (-) applied voltage for a solid electrode, mesh electrode, and spiked (points) electrode ... 38
17. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to spiked electrodes with a separation distance of 6 cm. (a) negative polarity; (b) positive polarity 41
18. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to rod electrodes with a separation distance of 6 cm. (a) negative polarity; (b) positive polarity 43
19. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to mesh electrodes with a separation distance of 10 cm. (a) negative polarity; (b) positive polarity 44
20. Concentration versus applied voltage for the 2-butanone–toluene system with mesh electrodes 46
21. (a) Vapor temperature change as a function of potential difference between electrodes for the 2-propanol–water system. (b) Power input by electric field . 47
22. Total reflux experiments with the 2-propanol–water system at voltage differences of 10, 15, and 20 kVwith varying separation distance between the liquid and vapor electrodes 49

23. 2-Propanol mole fraction at different applied voltages from the center of the concentric electrode condenser with a 2-propanol–water system 51
24. Bubble size reduction in a distillation stage with applied voltage 54
25. (a) Distillate mole fraction for a multistage distillation experiment with the 2-propanol–water system as a function of applied voltage; (b) Distillate flow rate and total power input at different applied voltages 55
26. Raman spectroscopy intensities at a fixed point at the vapor-liquid interface of 2-propanol–water for different applied voltages 57
27. Results of simplified calculations of the charge density at the vapor-liquid interface for a parallel-plate electrode configuration. (a) variation as a function of applied voltage; (b)variation as a function of vertical distance between the vapor electrode and the interface at a fixed voltage 61
28. Gas chromatograph calibration curves for 2-propanol–water standards 69
29. Sample phase equilibria experimental results for 2-propanol–water 70
30. Comparison of depletion of 2-propanol from the bulk liquid for batch distillation runs with and without an electric field 75

CHAPTER I

INTRODUCTION

Distillation is the most important separation process in the chemical, petrochemical, pharmaceutical, biochemical, food, and other industries. It is often the preferred separation technique because of a number of advantages including operational simplicity, high separation efficiency, and availability of vapor-liquid-equilibrium (VLE) data. In contrast to other separation processes, such as membrane separation, distillation is easily scaled to high throughput. However, distillation is also the most energy-consuming step in the process industries.

Major limitations in the applicability of distillation and the number of distillation stages required come from the vapor-liquid equilibria (VLE) of a chemical system. In addition to thermodynamic limitations, the rates of heat and mass transfer are a factor in determining the separation efficiency. Enhancements in the distillation process that result in energy savings and waste reduction would be beneficial to both the chemical industry and the environment. Even small enhancements in tray efficiencies would result in very large savings in capital and operating costs.

Different distillation techniques and column designs are continuously being designed to further increase distillation efficiency and to decrease the net energy consumed. Utilizing heat rejected from the condenser of a distillation column as energy

supplied to the reboiler is one common method. Tray designs and packing arrangements in a column are optimized to maximize vapor/liquid contact while minimizing weeping and entrainment.

The effects of electric fields on thermodynamic and transport properties of pure chemicals and mixtures have been studied by several researchers for decades. These studies include electric field effects on pure substance boiling points, heat and mass transfer in boiling and other rate processes, and separation of components in mixtures. However, viable methods of utilizing the electric field effects in distillation have not been demonstrated. The purpose of this study was to investigate whether application of an electric field can have a significant effect on chemical separations by distillation. For such an approach to be promising configuration, it would improve distillation efficiency with only small increases in the electrical power load by applying high voltage, but relatively low current.

The effect of an electric field applied across the vapor-liquid interface on the relative volatility and the phase equilibrium of binary mixtures was investigated in this study. The electric field effects were compared for binary polar-polar, polar-nonpolar, and nonpolar-nonpolar mixtures. The dielectric properties of the components were also considered. An electric field was applied to pure components at steady state and equilibrium conditions to observe the effect on the phase equilibrium temperature. The relative volatility and distillate flow rate for boiling mixtures were compared for batch distillation experiments with and without applied electric fields. To provide insight into mechanisms involved in the electric field effects, a distillation experiment with a binary

mixture at total reflux was developed with adjustable electrode configurations. Experiments with an electric field applied concentrically to a condensing mixture were run to compare the magnitude of results from this study to results found in the literature. Also, the concentric design was intended to investigate whether a polar component was attracted toward or repelled from an electrified rod. All of these experiments were used to determine the optimum setup for maximizing the benefits from applied electric fields in a distillation process.

Chapter II

REVIEW OF THE LITERATURE

Distillation with applied electric fields has not been the focus of electrotechnology studies. Many of the experimental results in these studies have not been verified or supported with theory and, therefore, are the subject of debate. There are some papers on the effect of electric fields on a pure component's boiling temperature and studies of component separation using applied fields discussed below.

Effect of Electric Fields on Pure Liquid Boiling Point

Several investigators have studied the effects of electric fields on the boiling point of pure liquids. Katti and Chaudhri (1) reported up to a 2°C decrease in the boiling point of methanol, ethanol, and isopropyl alcohol under the influence of alternating electric fields. Using the conservation of energy equation and assuming that an electrical field does both electrical and pressure-volume work, Lyon (2) calculated that the change in the boiling point of these alcohols should rise on the order of 10^{-5}°C and claimed that the experiments by Katti and Chaudhri were in error. His model was based on the assumption that the change in the dielectric constant was small with only a small change in the boiling temperature. Anderson and Sardo Infirri (3) repeated the boiling point experiment with methanol in a Cottrell apparatus and failed to observe any changes due

to an applied alternating field. Ramakrishna et al. (4) used a more precise thermometer in their experimental setup and observed no changes in the boiling point of benzene, ethanol, 2-propanol, and methanol. They discussed the possibility of superheated vapor as an explanation for the results obtained in the earlier experiments. Sharma (5) also carried out experiments similar to those of Katti and Chaudri and failed to observe any change in the boiling point of liquids. Biswas and Basu (6) 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. In each of the boiling point experiments described here, the electric field was applied across two vertically aligned metal plates. However, the electrode geometries and experimental setups were not exactly the same in each experiment.

Increased Component Separation with Applied Voltage

Karagounis (7) applied a 10^6 volts per cm radial electric field to polar/nonpolar mixtures by electrifying a tungsten wire in the center of a metallic cylinder containing the liquid mixture. With p-nitroaniline–benzene, the liquid samples collected near the center wire were enriched with p-nitroaniline by up to 12 per cent with 10 kV applied. Karagounis observed that the ultraviolet absorption curve of this mixture was increased with 10 kV, and attributed this to a change in the energy states of the electrons due to the application of the electric field.

O'Neal (8) studied electrified distillation of polar-nonpolar organic mixtures. He utilized an apparatus that included a vertical condenser in which the total reflux was electrified by a DC high voltage that was applied between concentrically mounted electrodes along the axis of and on the outside of the glass-walled condenser. He found increases in the concentration of the polar component of liquid samples collected at the bottom of the negatively charged central electrode for several mixtures, including: 2-pentanone/*n*-heptane, 2-butanone/*n*-heptane, 2-butanol/*n*-heptane, and *n*-butyl acetate/*n*-heptane. He also reported a shift in the equilibrium form of acetylacetone to its enol form (versus keto form) at the central electrode. The concentration of 2-butanol at the central electrode was 7.5% greater when 4 kV was applied to the butanol/*n*-heptane system than in the no-field sample. O'Neal suggested that dielectrophoretic forces on polar molecules would attract the polar molecules to the central electrode. To explain findings that cited a critical voltage above which the concentration of the polar molecule at the central electrode would decrease from a peak concentration, O'Neal postulated that the polar molecule acquires a charge from the electrode and is repelled.

Summary of Background Information

Several researchers have investigated the effects of electric fields on thermodynamic and transport properties of vapor-liquid systems. Although disagreement exists over the effects, particularly regarding the boiling points of pure components, there is general agreement that some thermodynamic and transport properties are significantly affected by electric fields.

CHAPTER III

EXPERIMENTAL METHODS

Different mixtures were used in these experiments to observe the degree of change caused by an electric field when using polar-polar, polar-nonpolar, and nonpolar-nonpolar mixtures. Mixtures included: 2-propanol–water, 2-propanol–toluene, cyclohexane–toluene, and n-butanone–toluene. The dielectric constant and dipole moment, which indicate the degree of polarity for the pure chemicals used in these experiments, are shown in Table 1. Deionized water and high-grade pure chemicals were used to form the mixtures.

TABLE I. DIELECTRIC CONSTANTS AND DIPOLE MOMENTS FOR THE CHEMICALS USED

Chemical	Polar/Nonpolar	Dielectric Constant of Liquid Phase	Dipole Moment of Gas Phase (debye)
2-Propanol	Polar	18.3 @ 25°C	18.3
Toluene	Slightly Polar	2.4 @ 25°C	0.4
n-Butanone	Polar	18.5 @ 20°C	2.7
Water	Polar	78.54 @ 25°C	1.85
Cyclohexane	Nonpolar	2.0 @ 25°C	0

Phase Equilibria Method

Steady-state isobaric experiments were run with d.c. voltage applied across the vapor-liquid interface of well-mixed binary mixtures. The individual component mole fractions were 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 modified the vapor and liquid concentrations.

In the phase equilibria experiments, a modified Othmer still, as shown in Figure 1, was used to boil a binary liquid mixture. The still was modified to allow an electric field to be applied between two electrodes. Two heating tapes were wrapped around the still for heating and insulation. One tape heated the top or vapor region of the still, while the other was wrapped around the bottom to control the heating of the liquid region. Variac variable power supplies were used to measure and maintain the voltage power used by the heating tapes. The current and, therefore, the power input due to each heat tape was determined using a 0.5-ohm resistor that was connected to the variable power supplies.

The electric field was applied across the vapor-liquid interface of the mixture by a high voltage d.c. power supply (Series EQ, Glassman, Whitehouse Station, N.J.), which generated up to 30 kV. An electrode rod, connected to the high-voltage power supply, was located in the vapor region of the still. A second electrode rod, located in the liquid region, was connected to electrical ground. The voltage drop across a precision resistor was used to measure the electric current and determine the significance of the power added by the electric field. The temperature of the system was measured by using two thermistors located in the vapor and liquid regions of the still. The thermistors were

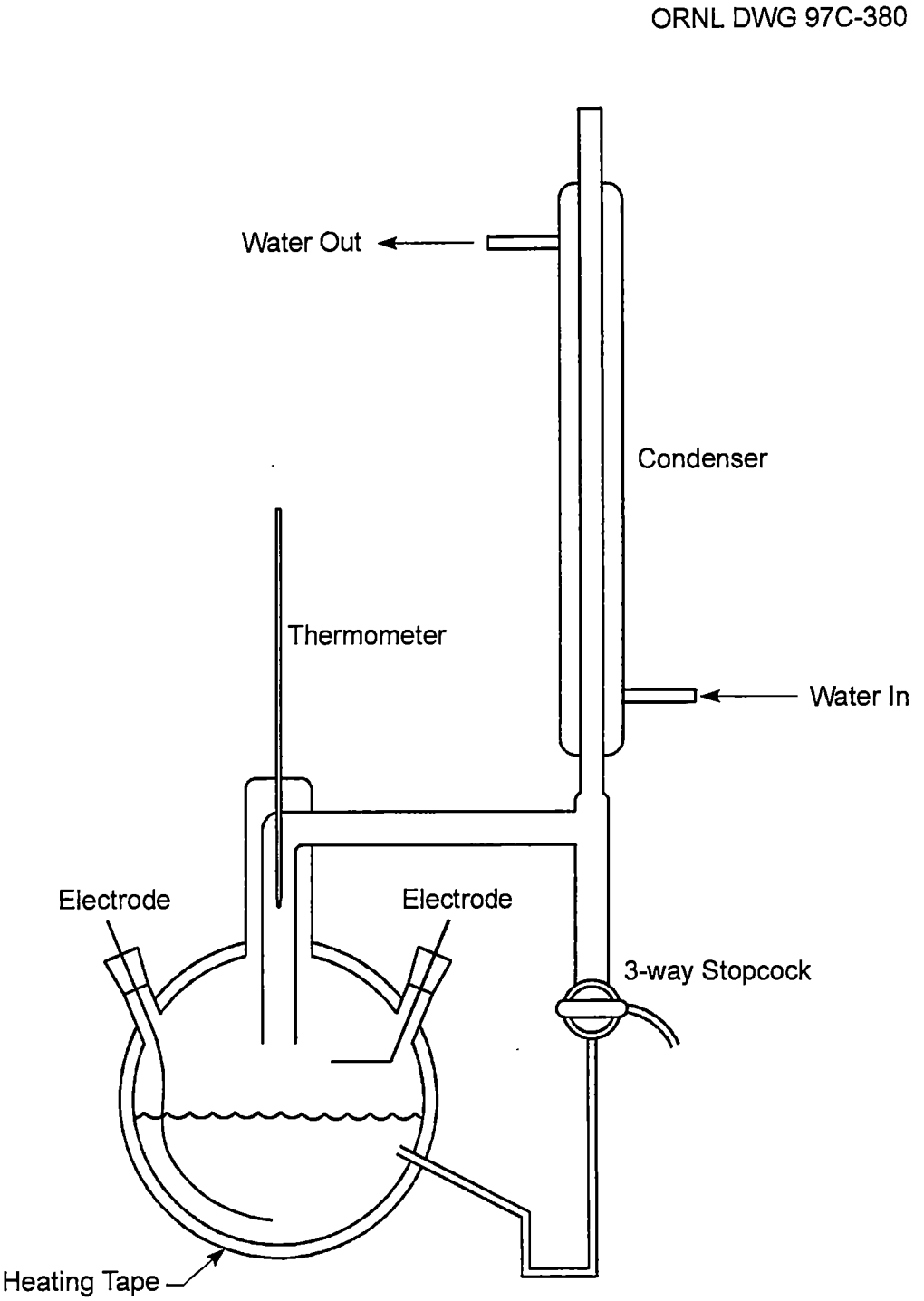


Figure 1. Schematic of phase equilibria apparatus.

connected to a temperature recorder (1560 Black Stack, Hart Scientific, American Fork, UT), which plotted the temperature with an accuracy of 0.01°C for the duration of the experiments. The pressure of the system was measured by using an electronic pressure transducer (Model SC 200, Sensotec, Columbus, OH).

A mixture (500-mL) with a known concentration was heated to its boiling temperature, and the vapor flowed into a water-cooled heat exchanger for condensation. The condensate was completely recycled back into the still. Equilibrium was reached with no applied voltage in the system by modifying the heat input to fix the vapor temperature at the liquid boiling temperature. After steady state was reached, liquid samples were drawn from the bottom stopcock, and vapor samples were drawn from the condensed liquid using a three-way stopcock. 100 μL samples were drawn at 30-min intervals. Initially, several samples were taken with no applied voltage. The concentration of these samples was measured to determine whether the concentrations of the no-field samples were the same, which gave further indication of equilibrium.

When voltage was applied, the system was allowed to reach a psuedo-equilibrium state before several electric field samples were taken at 30-min intervals. The pseudo-equilibrium state was reached when the vapor and liquid temperatures and compositions reached a new steady state due to the applied electric field. The electric field was then removed and the system was again given sufficient time for the temperatures to reach the zero voltage equilibrium state. Sufficient time for the vapor and liquid temperatures to reach steady state was approximately 30 min during the experiments. The compositions

of the samples collected with and without applied electric fields were determined by using a gas chromatograph (GC).

Batch Distillation Method

Time-dependent batch distillation experiments were used to compare the vapor concentration versus time and the total component separation for experimental runs with and without an applied electric field. A binary mixture was boiled in a 165-mm-high, 108-mm-diameter, 1000-mL flat bottom reaction flask (Ace Glass, Inc., #6511) with three in-line joints (24/40) and a #7 ace-thred in the flask head, as shown in Figure 2. An electric jacket controlled by a variable power supply heated this apparatus. The exposed top portion of the still was wrapped with insulating tape to reduce heat loss. The vapor was condensed in a single-pass glass heat exchanger and collected in a graduated cylinder. A thermometer was located at the exit to the heat exchanger to measure the vapor temperature. Two circular electrodes, made of SS-316 wire mesh, were used to generate a uniform electric field across the vapor-liquid interface. The electrodes were held in a constant position with a separation distance of 6-cm during the experiment. Samples were 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 was placed in the batch distillation still. The mixture was heated by applying electrical power to the heating jacket using the variable power supply. The power supplied was calculated as in the phase equilibria experiments by measuring the applied voltage and current passing through the jacket. When the mixture began to boil,

ORNL DWG 97C-379

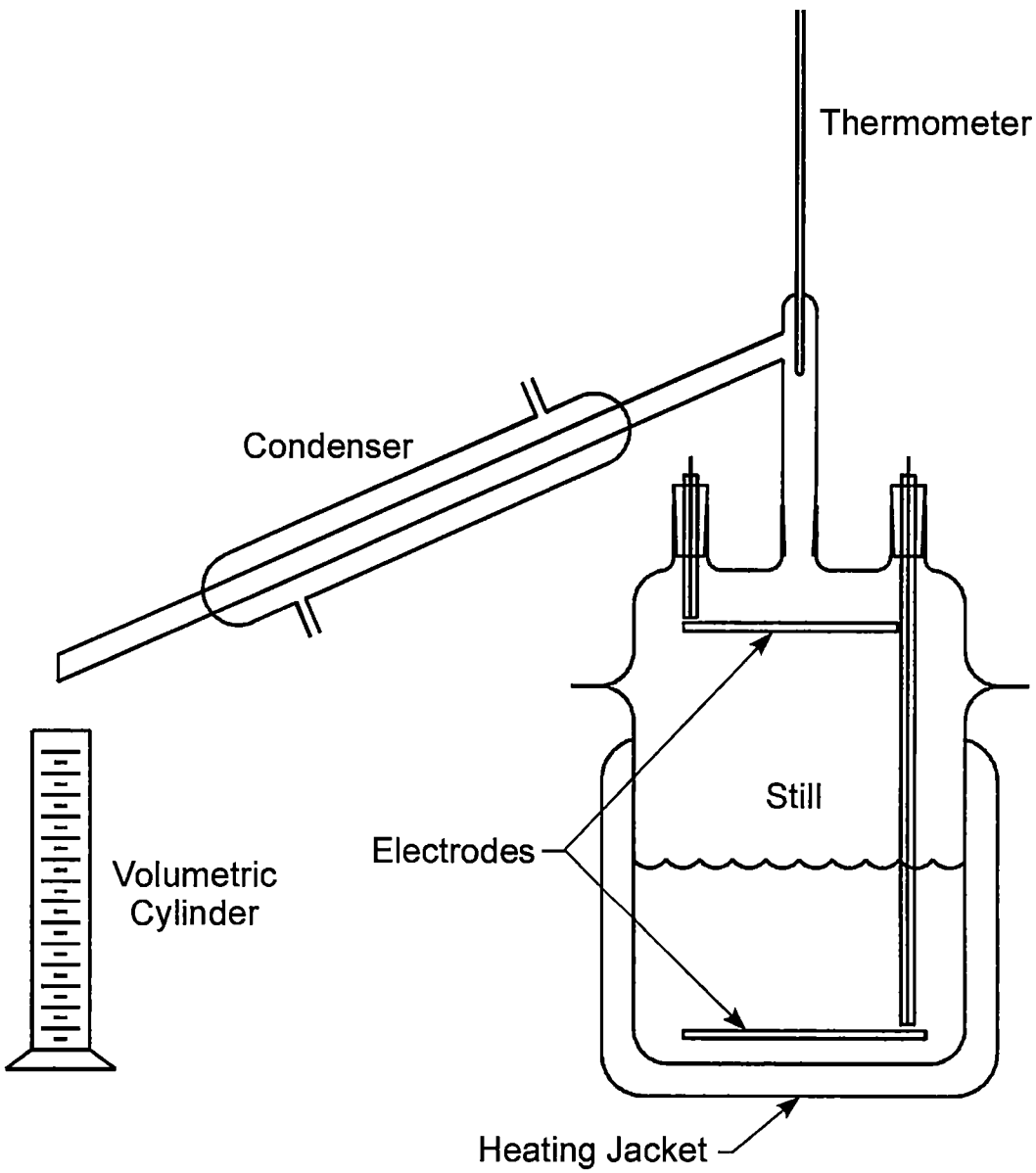


Figure 2. Schematic of the batch distillation apparatus.

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

Total Reflux Method

The kettle still used in the batch distillation experiment was modified by attaching a water-cooled condenser to the still for total reflux of the distillate, as shown in Figure 3. This setup was designed to allow flexibility in adjusting electrode configurations.

Experiments were carried out at a hood pressure that was slightly less than atmospheric pressure and essentially constant over the course of a single experiment. A distilling receiver (Ace Glass, #6635-20) was located at the base of the condenser where samples of the distillate were removed via a three-way stopcock. Two Teflon®-covered rods (3-mm diameter), mounted by Teflon stoppers at the flask head, supported two stainless-steel electrodes inside the apparatus. To prevent electrical arcing at high voltages, the electrodes were positioned a sufficient distance away from the walls of the apparatus. Furthermore, in the majority of the experiments, a Teflon sheet (15 cm x 6

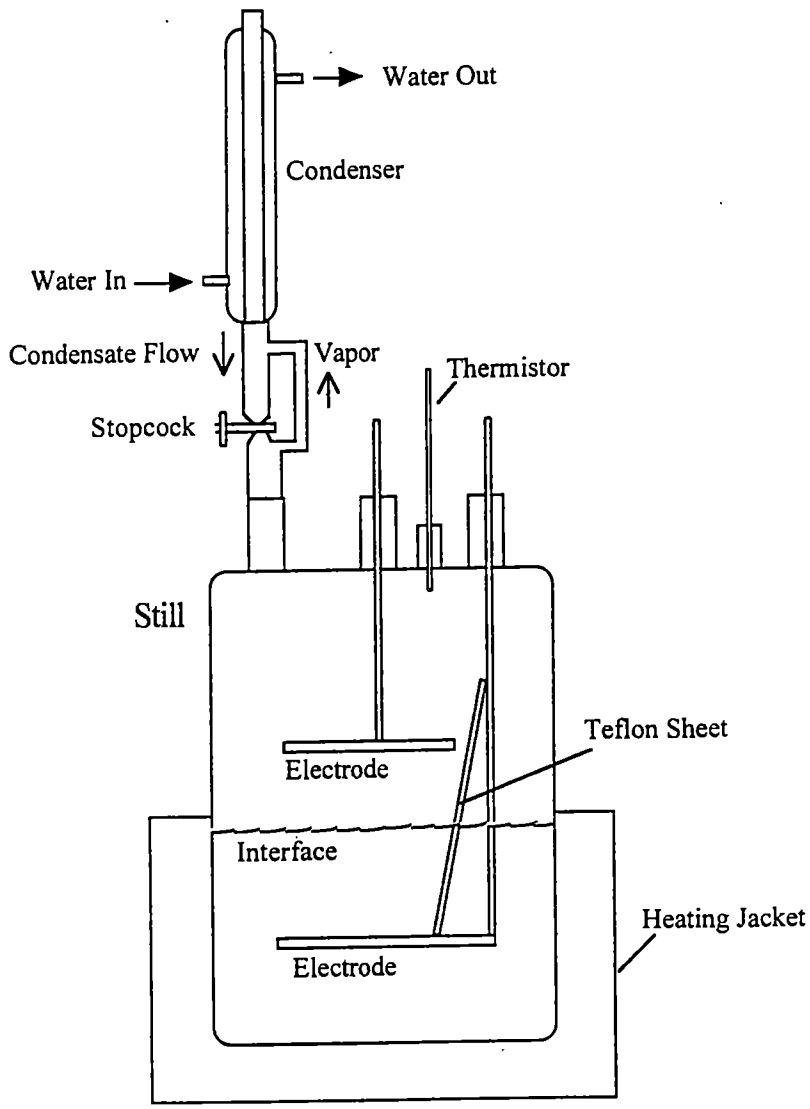


Figure 3. Schematic of the total reflux apparatus.

cm, 1 mm thick) was inserted between the vapor electrode and the liquid electrode support for insulation against electrical arcing and charge transfer. This apparatus design allowed the height of the two electrodes to be adjusted while maintaining a gas-tight seal. A 500-mL mixture of 2-propanol–water with a starting 0.25 mole fraction of 2-propanol was heated by an electric jacket controlled by a variable power supply at a constant power input of 200 W. The exposed top portion of the still was wrapped with insulating tape to reduce heat loss.

The experiments were carried out at total reflux and at a hood pressure that was slightly less than atmospheric pressure. The vapor temperature was measured using thermistors connected to a temperature recorder. The thermistor was positioned 4 cm into the apparatus in a glass thermowell filled with oil that was sealed in the threaded joint.

Before samples were taken, the mixture was heated at total reflux until a steady vapor temperature was reached. Several samples of condensed vapor were taken at 30-min intervals with no applied voltage to establish a baseline for the vapor mole fraction of 2-propanol. For operation with an applied voltage, the system was allowed to stabilize for 30 min prior to sampling. The Glassman high-voltage power supply was used to apply voltage to one electrode in the apparatus, and the second electrode was attached to an electrical ground. The polarity of the electric field could be reversed by placing a negative-polarity module in the power supply or by applying the high voltage to the second electrode and attaching the first to an electrical ground. The current in the system was monitored using a multimeter attached to the interface of the remote control of the high-voltage power supply. The mole fractions of the components in the vapor were

measured by taking a 100-μL sample of the distillate from the stopcock located at the base of the condenser.

Four electrode shapes were employed in the experiments: a 7.7-cm-diameter, flat, solid electrode; a 5.3-cm-diameter wire mesh (16 mesh squares/in^2) electrode; a 7.5-cm-diameter, ring-shaped electrode with eight 1-cm vertical spikes extending toward the interface; and a 0.6-cm-diameter, L-shaped rod with a 6-cm length parallel to the interface. The solid, mesh, and rod electrodes were used to observe the effects of electrode surface area. The spiked electrode was used to observe the effect of injecting charge into the vapor region, since charge accumulates at the sharpest points on irregularly shaped electrified objects. For electrodes with sharp edges, the phenomenon of luminosity (corona discharge) occurs at voltages much lower than that leading to the breakdown of a dielectric.

The effect of electrode separation on the vapor mole fraction of 2-propanol and current was investigated by adjusting the distance between two mesh electrodes. The liquid electrode was positioned 1, 2.5, and 5.5 cm below the vapor–liquid interface. For each liquid electrode position, the vapor electrode was positioned 2.5, 4.5, 7.5, and 9.5 cm above the interface. The separation reported in the results of these experiments was the total separation between the liquid and the vapor electrode. However, due to the significantly larger dielectric constant and conductivity of the liquid region to the vapor region (67 to 1), the voltage drop was primarily between the vapor electrode and the vapor-liquid interface. The effect of electric field direction was studied experimentally

by applying high voltage to the liquid electrode in some experiments and high voltage to the vapor electrode in others.

Interfacial Study

The total reflux apparatus with a 2-propanol–water system was modified to allow an argon laser to be focused at the vapor-liquid interface in an attempt to detect a change in the hydrogen bonding characteristics at the vapor-liquid interface due to an applied electric field. For this experimental setup, shown in Figure 4, the still was heated using a hotplate and was completely wrapped with heating tape for insulation except for a small window in the sidewall for focusing the laser at the interface. An electric field was formed across two mesh electrodes separated by a distance of 6 cm. The intensities of peaks from carbon–hydrogen bonds and carbon–oxygen bonds measured using a Raman spectrometer with a 500M SPEX Detector were compared for varying electric field strengths. The laser position could be adjusted 1-mm at a time vertically using a Newport 855C Controller with an 850-05 actuator. The laser was determined to be focused at the interface when the measured Raman intensity reflected that of the liquid region rather than the vapor region as the laser was lowered toward the interface.

Concentric Electrode Distillation Method

A distillation column, based on the design used by O'Neal (8), was fashioned to examine a different arrangement of high voltage electrodes for comparison with separation results achieved in the previously described experimental setups. A glass

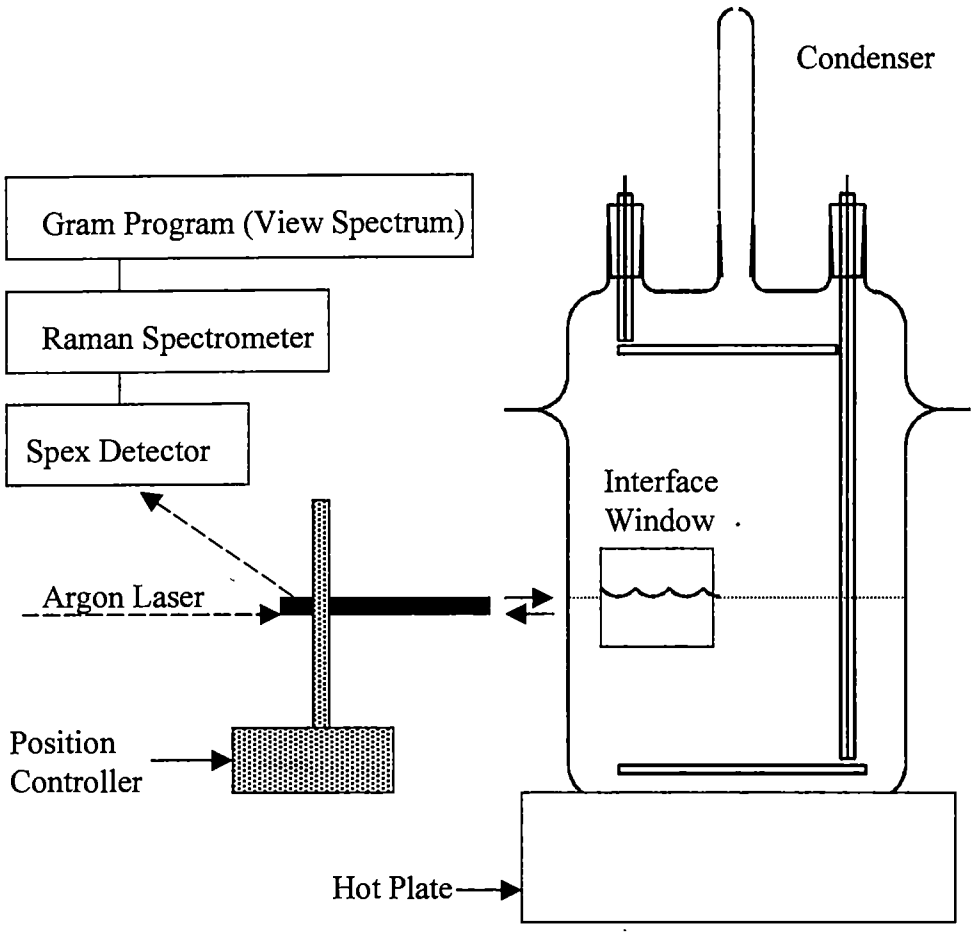


Figure 4. Setup for the study of the interface of a total reflux experiment with the 2-propanol–water system using Raman spectroscopy.

condenser attached vertically to a round-bottom kettle flask, shown in Figure 5, featured total reflux of condensate through an electric field applied radially in the condenser. This concentric electrode condenser (CEC) design also examined which component in the mixture would be attracted to the center of the condenser where the voltage was applied.

The CEC contained a stainless steel rod at the center where high voltage was applied. A steel cylindrical mesh, acting as the electrical ground, was attached to the inside wall of the CEC. The vapor from a boiling binary mixture flowed upward through the CEC and then into a second glass condenser which was cooled by water. The distillate was then totally refluxed back through the electrode condenser and into the still. Condensate flowed back through the CEC along the walls and the central rod. Liquid dripping from the central rod was sampled from a sample port and a stopcock located directly below the tip of the rod. The concentration was then determined for the liquid at the center of the condenser.

Mixtures of 2-propanol–water and 2-propanol–toluene were used in the CEC experiment. For each experiment, 500 mL of the mixture was heated until the vapor temperature and the vapor concentration reached steady-state. Several condensate samples were taken in each experiment before an electric field was applied to ensure steady-state conditions. An electric field was then applied and samples were taken at 30-min intervals to observe the effect on the condensate. It proved difficult in these experiments to apply voltage across the small region in the condenser without electrical arcing and the complex method used to take samples from the center of the condenser made some of the results unreliable and limited the amount of results presented.

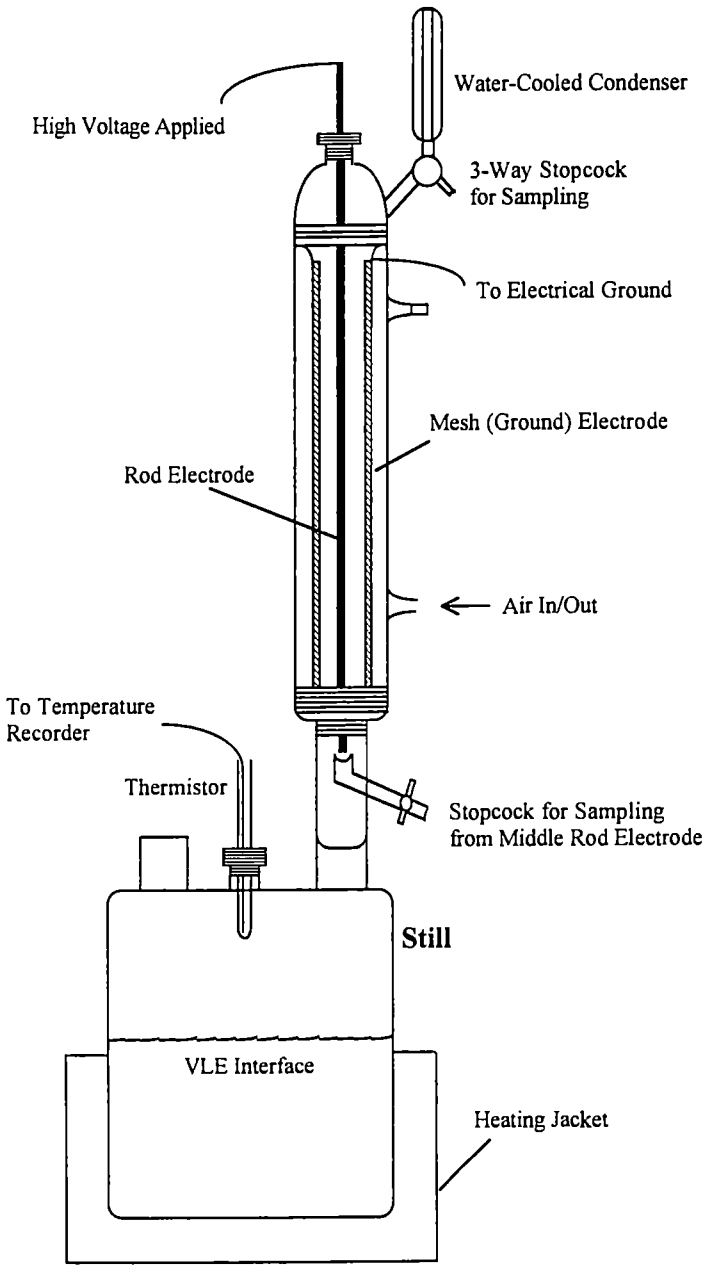


Figure 5. Schematic of the concentric electrode condenser.

Multistage Distillation Method

A larger-scale distillation column was designed that included distillation trays and multiple stages, as shown in Figure 6. Liquid mixtures were boiled in a 2000 mL round-bottom flask (Ace Glass) heated by an electric heating jacket. The vapor flowed upward through 0.02-in holes in an aluminum distillation tray into the second stage of the column, which was an 8-cm diameter Pyrex pipe. The vapor then flowed into a vertical water-cooled glass condenser and then was refluxed as condensate back into the second stage of the column. A Teflon overflow pipe in the second stage returned liquid to the first stage of the column through Teflon tubing which extended down into the reaction flask. This overflow maintained the liquid level in the second stage at a fixed height above the distillation tray.

Two types of experiments were attempted in the multi-stage column. First, the attempt was made to recreate the separation enhancements that were observed in the smaller scale experiments by applying high voltage to the distillation tray in the second stage. In this experiment, the ground electrode was a stainless-steel rod held in the vapor region in the sidewall above the overflow level of the stage by a Teflon seal and chemical resistant o-rings. An electric field was therefore formed across the interface as in the phase equilibria experiments.

In a second type of experiment, the ground rod was located entirely in the liquid region to observe the effect on the vapor bubbles rising through the liquid. Improved mass transfer through greater interfacial contact area induced by electrohydrodynamic spraying was investigated by measuring the final stage distillate concentration with and

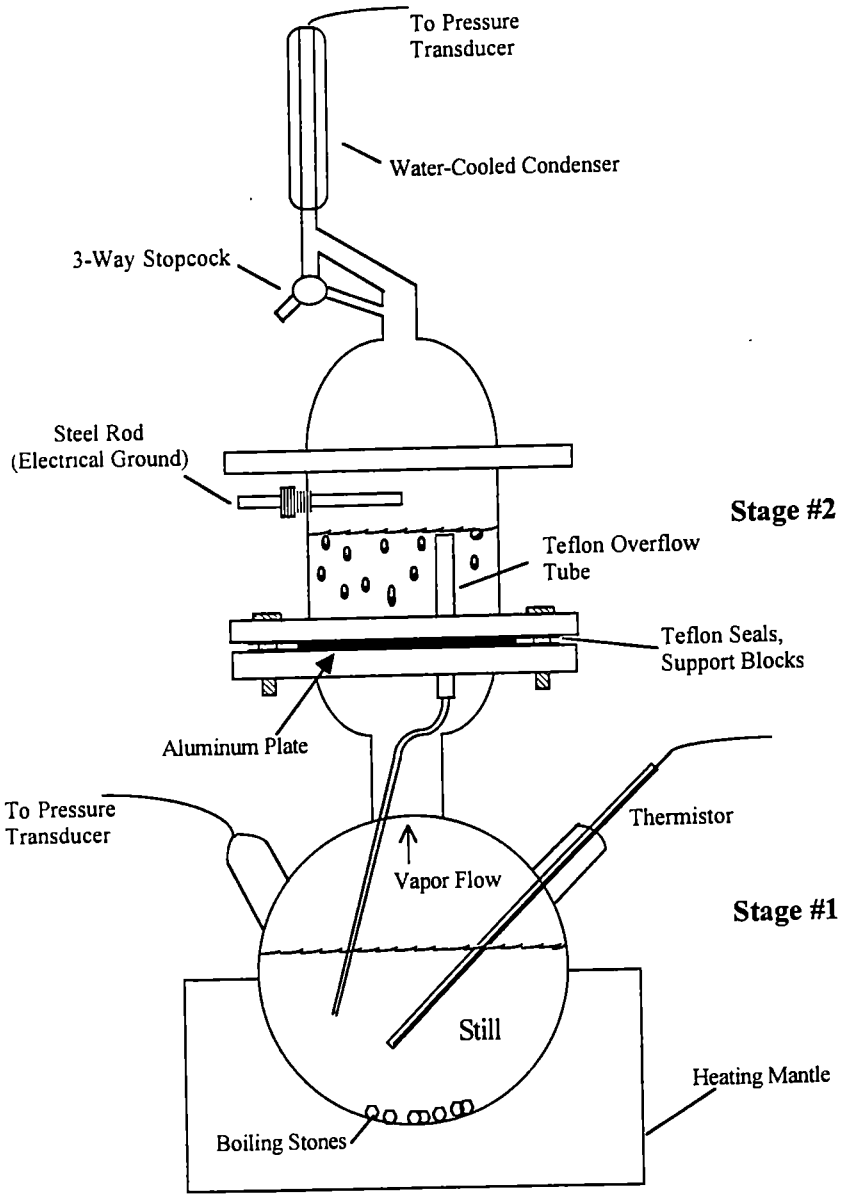


Figure 6. Schematic of the multistage distillation column.

without an electric field applied in the second-stage region of the distillation stage. A CCD camera was used to photograph and record the bubbles flowing through the liquid. Still shots of the bubbles with and without an applied electric field were used to observe changes in the bubble diameter and the number of bubbles. The size of the region photographed remained constant throughout an experiment. The bubble diameters were determined by comparing their size to the known length of sections of the overflow tube included in the photographed region.

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 was used to determine the concentration when 2-propanol, water, and toluene were used in the experiments. An FID detector with a 30-ft-long capillary column was used to measure the concentration for experiments with n-butanone and cyclohexane. The GC response peaks were computer-integrated to give an area percentage for each component and a calibration curve was generated using the area percentage of known standards. The mole fraction of the samples was then determined. Results were plotted on a spreadsheet with the standard deviation and the experimental uncertainty of the mole fractions. An example of these calculations for a phase equilibria experiment is shown in Appendix A.

CHAPTER IV

EXPERIMENTAL RESULTS

Phase Equilibria Results

Data obtained in this work were plotted against literature data (9) for 2-propanol starting (liquid) mole fractions of 10, 14, 23, 50, 68, and 87% in 2-propanol–water mixtures, as shown in Figure 7. The addition of an electric field to these systems at steady-state caused an increase in the 2-propanol vapor concentration (mole fraction) for the mixtures containing lower concentrations of 2-propanol. The increases were significantly above the 95% confidence lines (2 times standard deviation) of the no-field samples. The largest field effects for the 2-propanol–water system, shown in Figure 8, were observed for a 23% initial concentration. The average vapor concentration of 2-propanol shifted from 53.6 to 56%. For this case the separation factor α, given by Eq. [1] was enhanced by 10% from 3.80 to 4.19.

$$\alpha = \frac{y(1-x)}{x(1-y)} \qquad [1]$$

The separation factor, or relative volatility, was calculated using the mole fraction of the high key component in the liquid, x, and the vapor, y. Measurement error was determined by analyzing repetitive samples to show error bars for each point, as shown in Figure 9. The electric field samples consistently showed an increase above the standard deviation lines of all the no-field samples for lower starting concentrations. This enhancement was

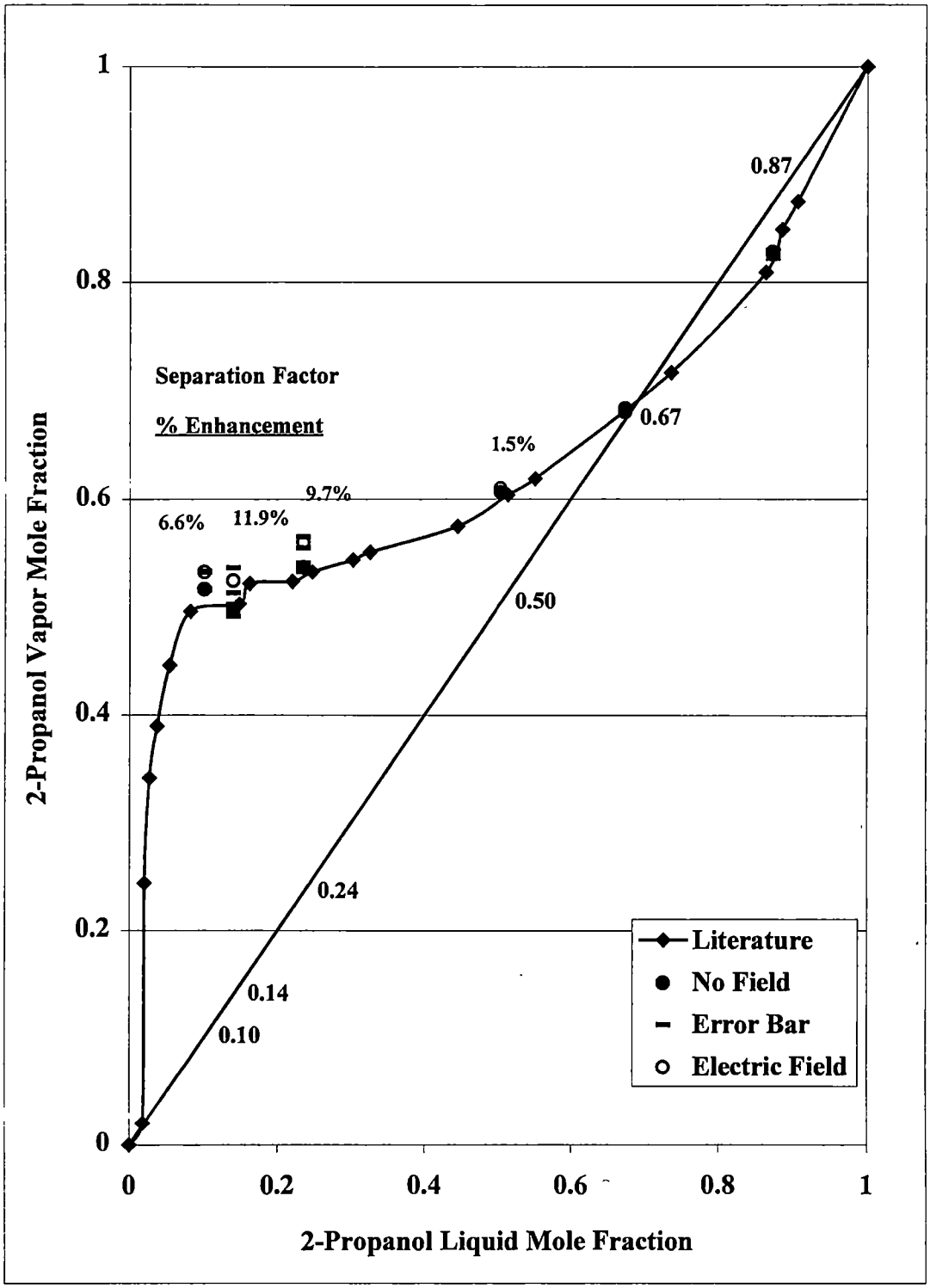


Figure 7. Comparison of 2-propanol/water phase equilibria experimental data with data found in the literature [J. Kokoutova et al., 1970 (ref. 19)].

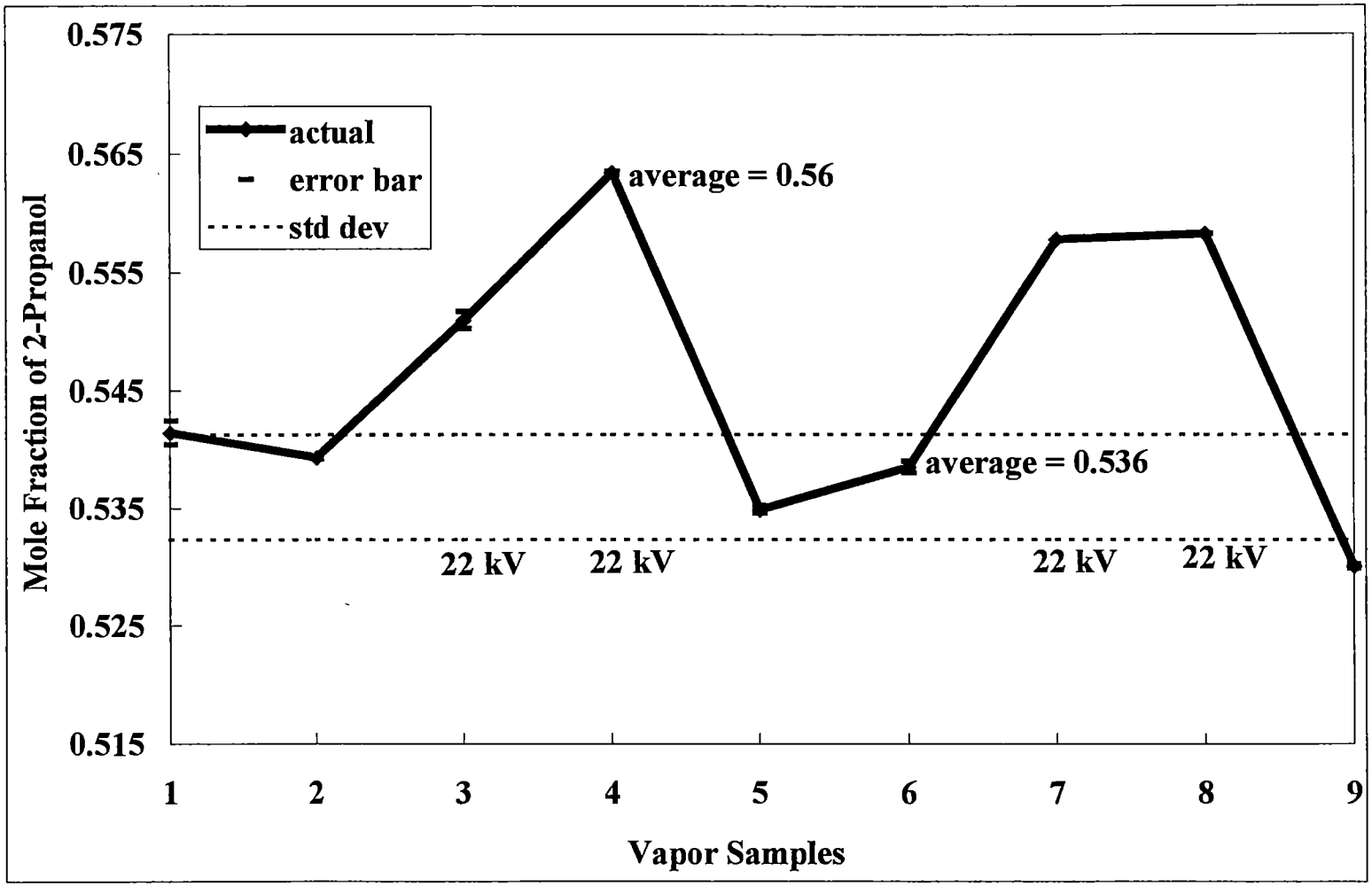


Figure 8. Vapor concentration for the 2-propanol/water system at phase equilibrium with 23 mol % 2-propanol starting concentration and with an applied electric field at samples 3, 4, 7, and 8.

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 9, which was expected due to the larger liquid volume.

Similar results to the 2-propanol–water system were obtained with 2-propanol–toluene systems and n-butanone–toluene systems. Each of these systems has at least one polar component. The phase equilibrium of the cyclohexane–toluene system was not affected by an applied electric field, as shown in Figure 10, because cyclohexane is a nonpolar component and toluene behaves essentially as a nonpolar component.

An interesting observation in this experiment was that when the concentration enhancement was observed due to an applied electric field, there was also a decrease in the vapor temperature below the liquid temperature. This new steady state that was reached when the electric field was applied is referred to in this work as a psuedo-equilibrium state. As shown in Figure 11, the vapor temperature during a phase equilibria experiment with 2-propanol–water decreased by more than half a degree when high voltage was added.

Experiments run with pure 2-propanol and pure n-butanone at their equilibrium boiling temperatures showed a similar temperature drop with an applied electric field, as shown in Figure 12. The equilibrium temperature of the slightly polar toluene was also examined with an applied electric field. A significant observation was that the applied voltage did not affect toluene's vapor temperature. These observations supported an assumption that electric field effects on concentration and vapor temperature will occur nly if there is a strong polar component present (toluene being weakly polar). When a

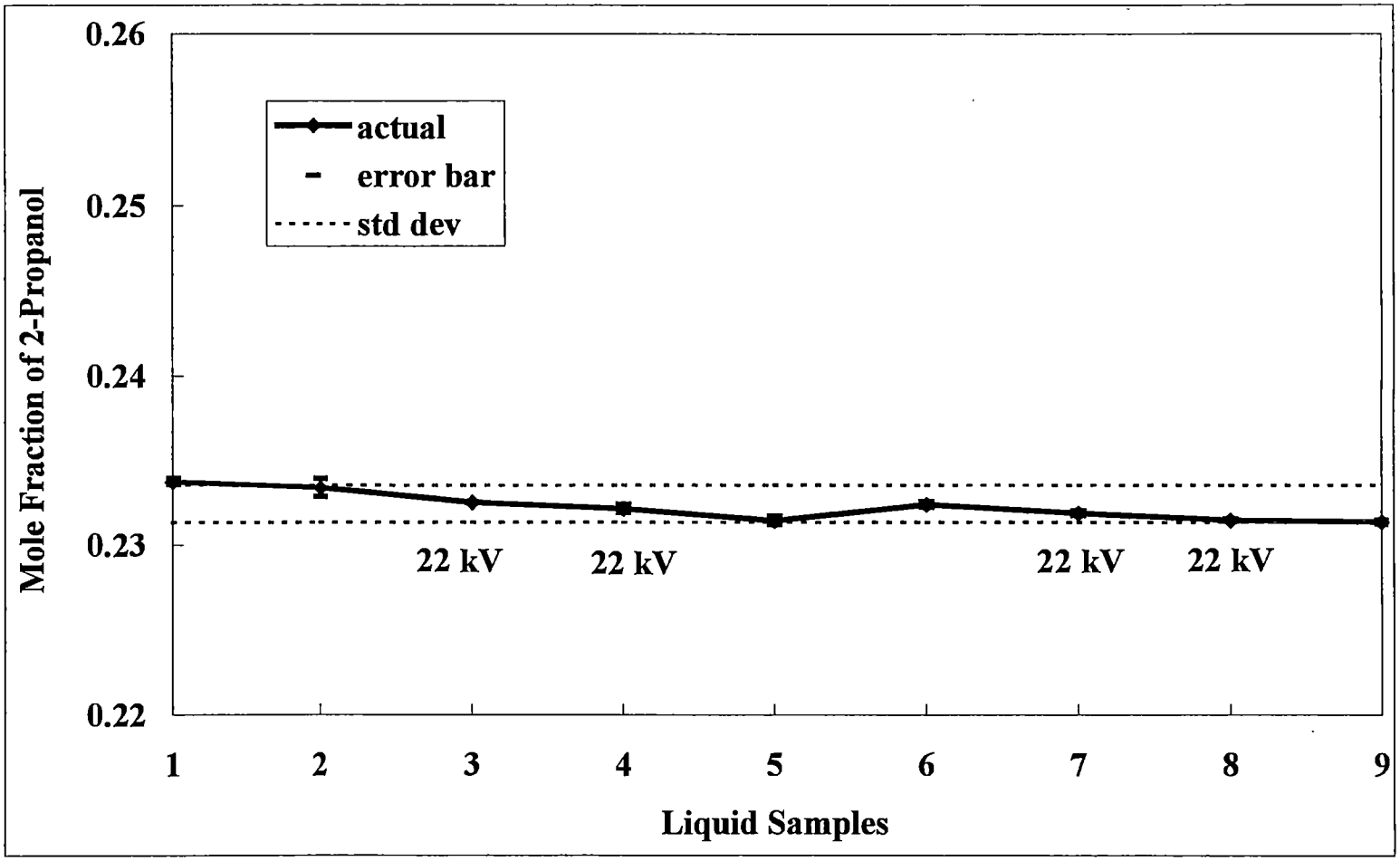


Figure 9. Liquid concentration for the 2-propanol/water system at 23 mol % 2-propanol starting concentration and an applied electric field at samples 3, 4, 7, and 8.

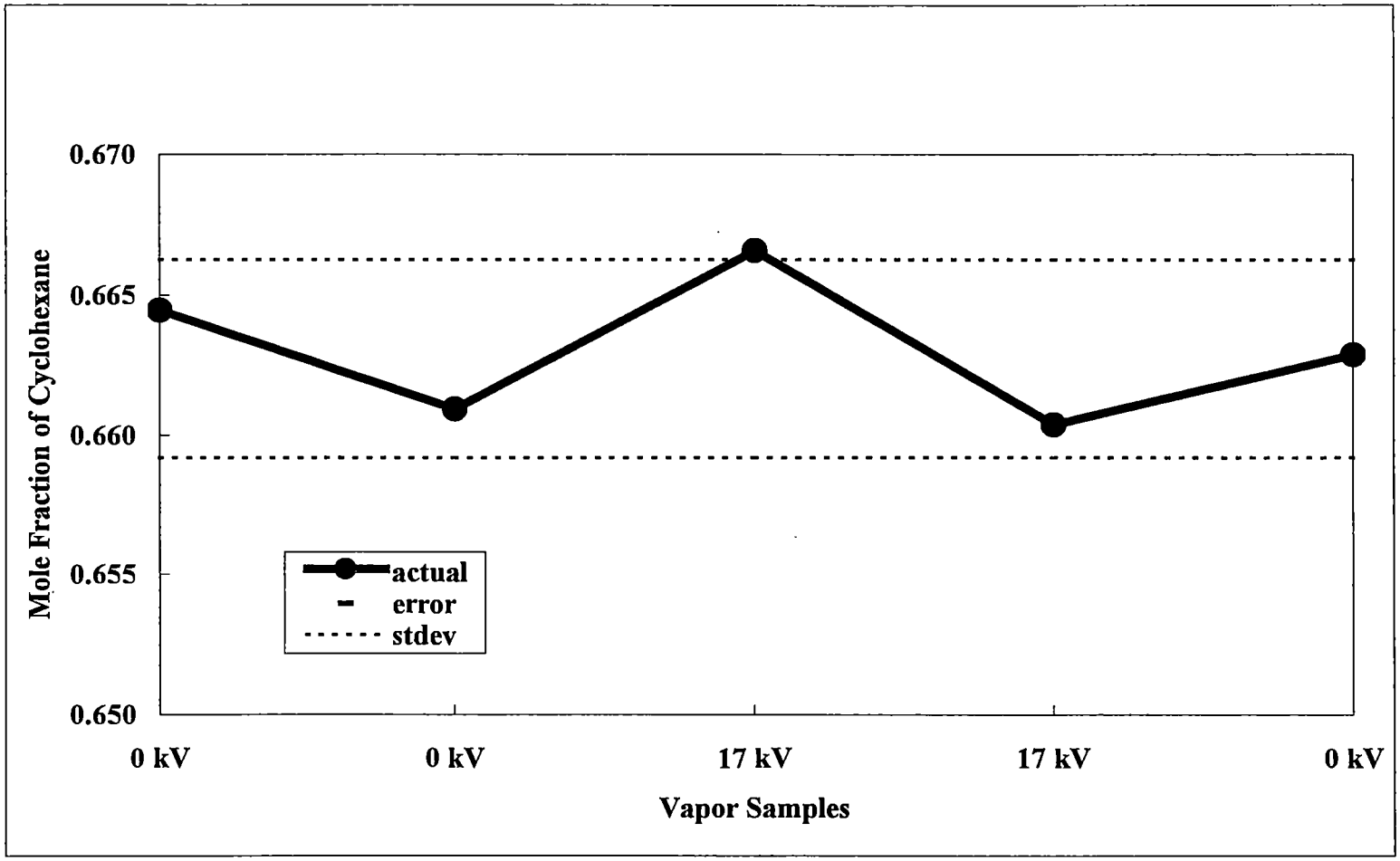


Figure 10. Phase equilibria experiment with the cyclohexane/toluene system.

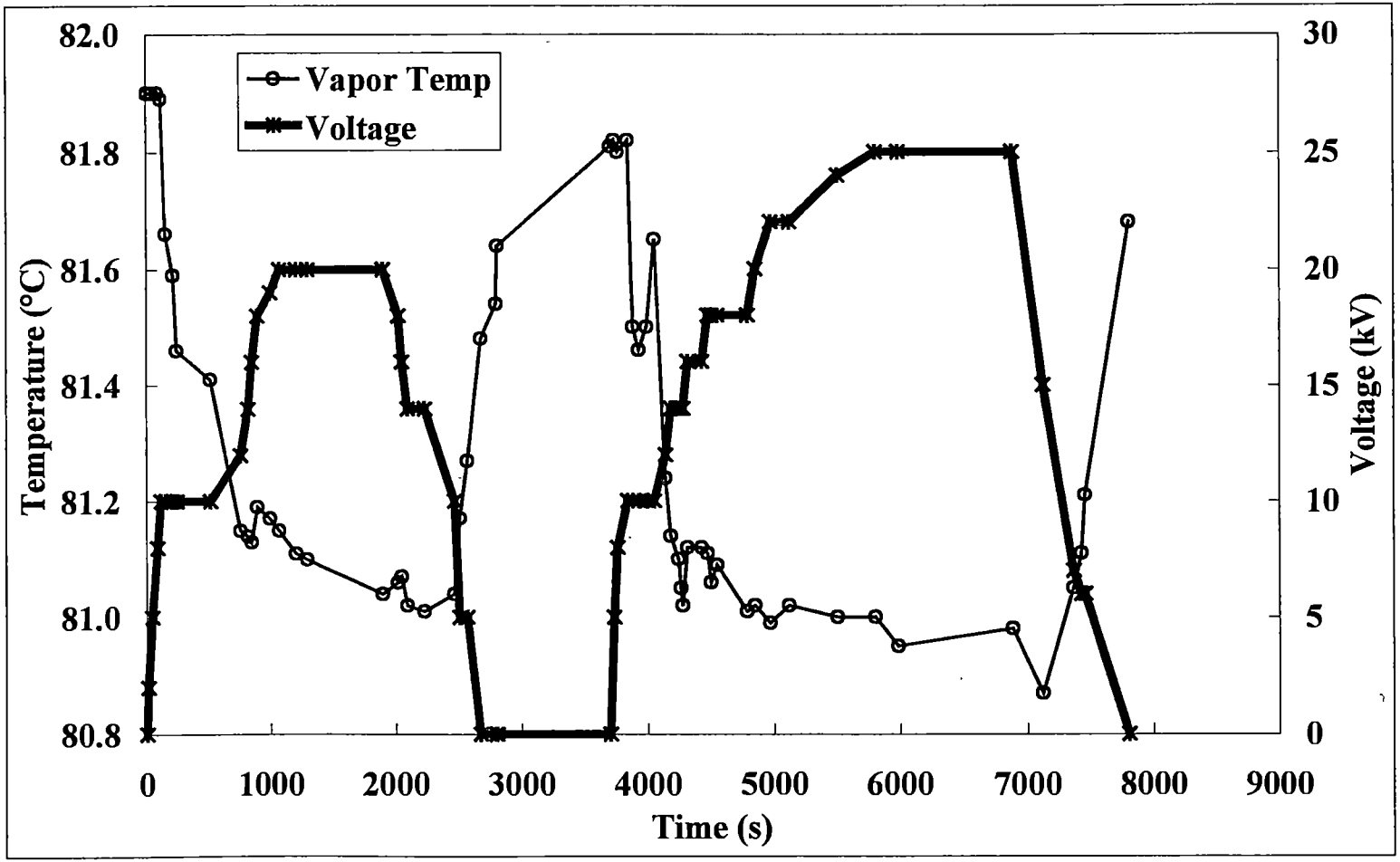


Figure 11. Vapor temperature as a function of high voltage addition for the 2-propanol/water system.

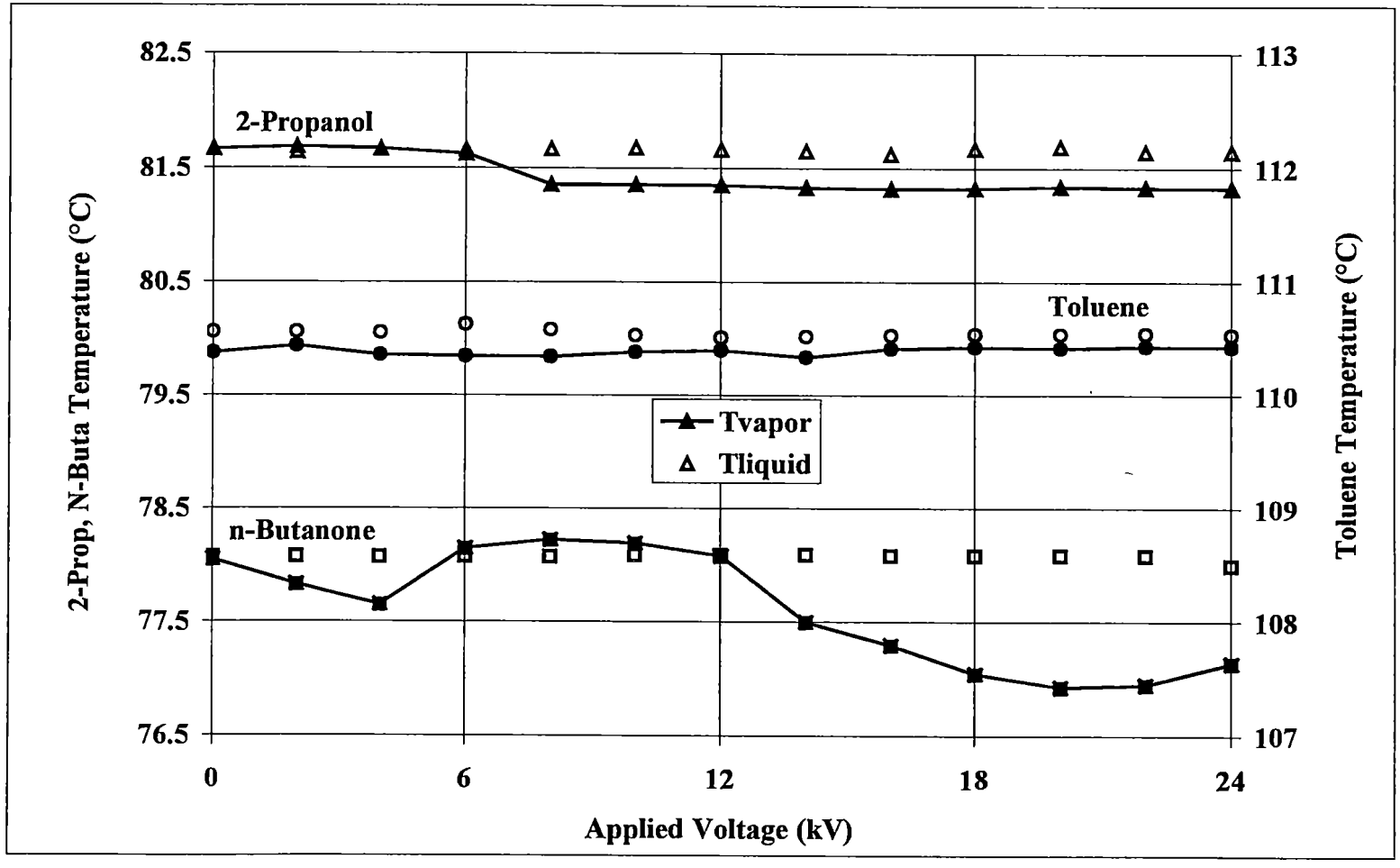


Figure 12. Vapor and liquid temperature measurements for pure 2-propanol, n-butanone, and toluene.

temperature drop was observed in the phase equilibria experiments with mixtures, the possibility that the change in vapor temperature was due to the change in concentration was considered. The one degree drop in vapor temperature, for the 2-propanol–water case for example, seemed to closely follow the required rise in concentration that is observed in the literature data if the concentration were manipulated manually. However, as evident from the pure component experiments, the temperature drop was not caused by concentration changes in the liquid and vapor. Though the power input in the phase equilibria experiments was small, there could have been small changes in the volume of liquid and vapor due to the extra power.

Batch Distillation Results

The distillate concentration and the rate of distillation for the 2-propanol–water system were 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 13. Before the application of the field (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 was noted for the electric field run. For the samples taken after the electric field was removed from the system, the distillate concentration of 2-propanol did not match the concentration of the no-field samples as the electric field effects did not immediately end when the field was removed. When the liquid concentration of 2-propanol became depleted during longer experimental runs, the distillate concentration for the electric field

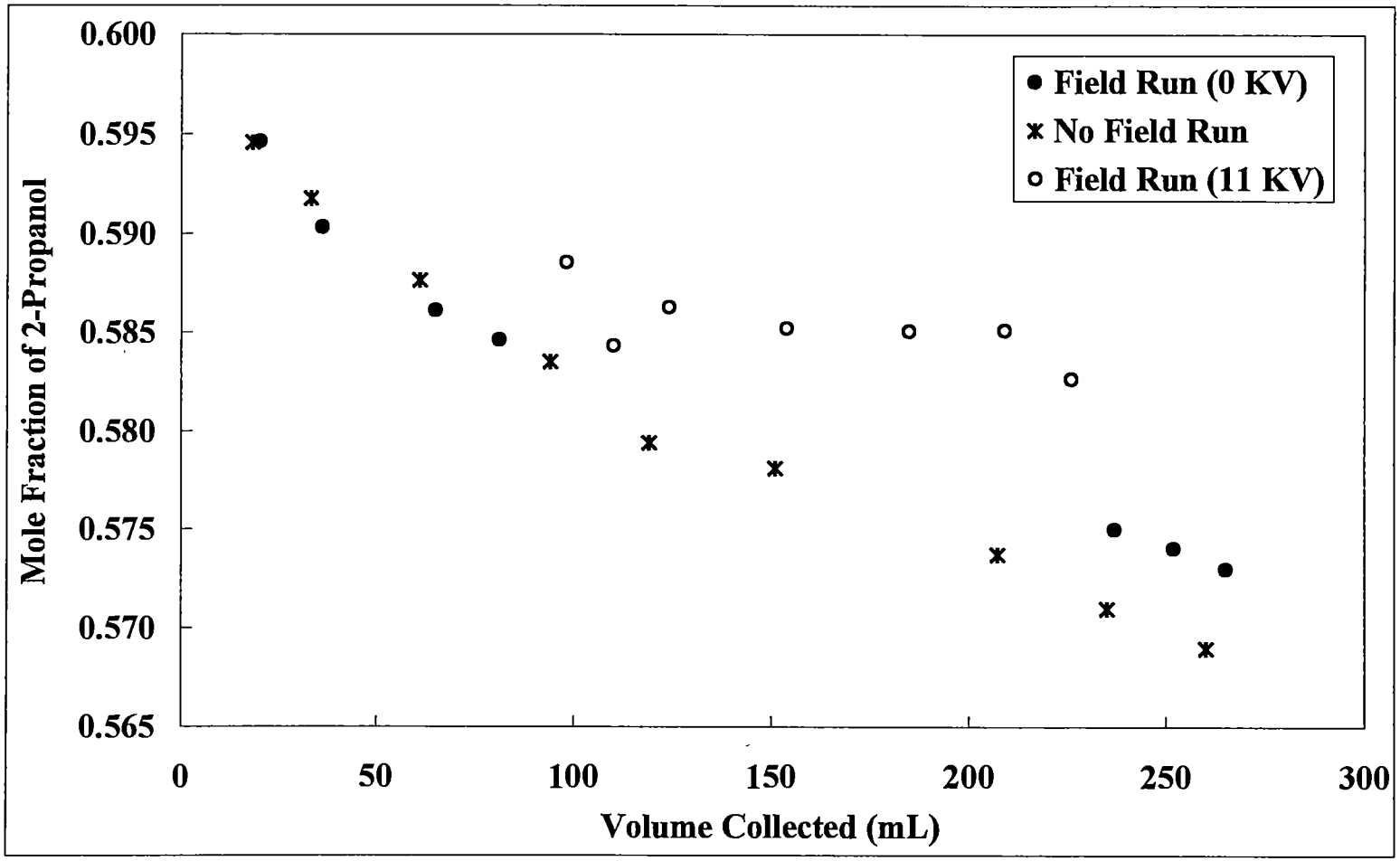


Figure 13. Comparison of distillate concentrations for batch distillation runs of 2-propanol/water with and without an applied electric field.

run eventually dropped below the no-field concentration curve as shown in Figure 30 (Appendix B). The batch distillation results resembled the phase equilibria results for the 2-propanol–water system as there were changes in the vapor mole fraction reflected by changes in the vapor temperature, as shown in Figure 14. It did not appear that the higher concentration of 2-propanol in the vapor with the applied electric field was the reason for the reduced vapor temperature because the reduced temperature was also observed in single component experiments, as discussed in the phase equilibria section. The distillate flow rate, compared for field and no-field runs in Figure 15, showed small increases in rate with applied voltage, which can partially be explained by the added power of the electric field. Assuming constant heat supplied to boil the mixture, there was not enough heat added by the small additional flow rate to explain the change in the vapor temperature.

As shown in Table 2, the addition of an electric field increased the overall efficiency of the batch distillation of 2-propanol from water, as the volume of 2-propanol removal increased and the total volume increased for similar lengths of time and power inputs. Less heat was required to vaporize the greater volume of distillate for the electric field run because of the increase in 2-propanol concentration which has a lower heat of vaporization than water. The calculations were made using the program shown in Appendix B.

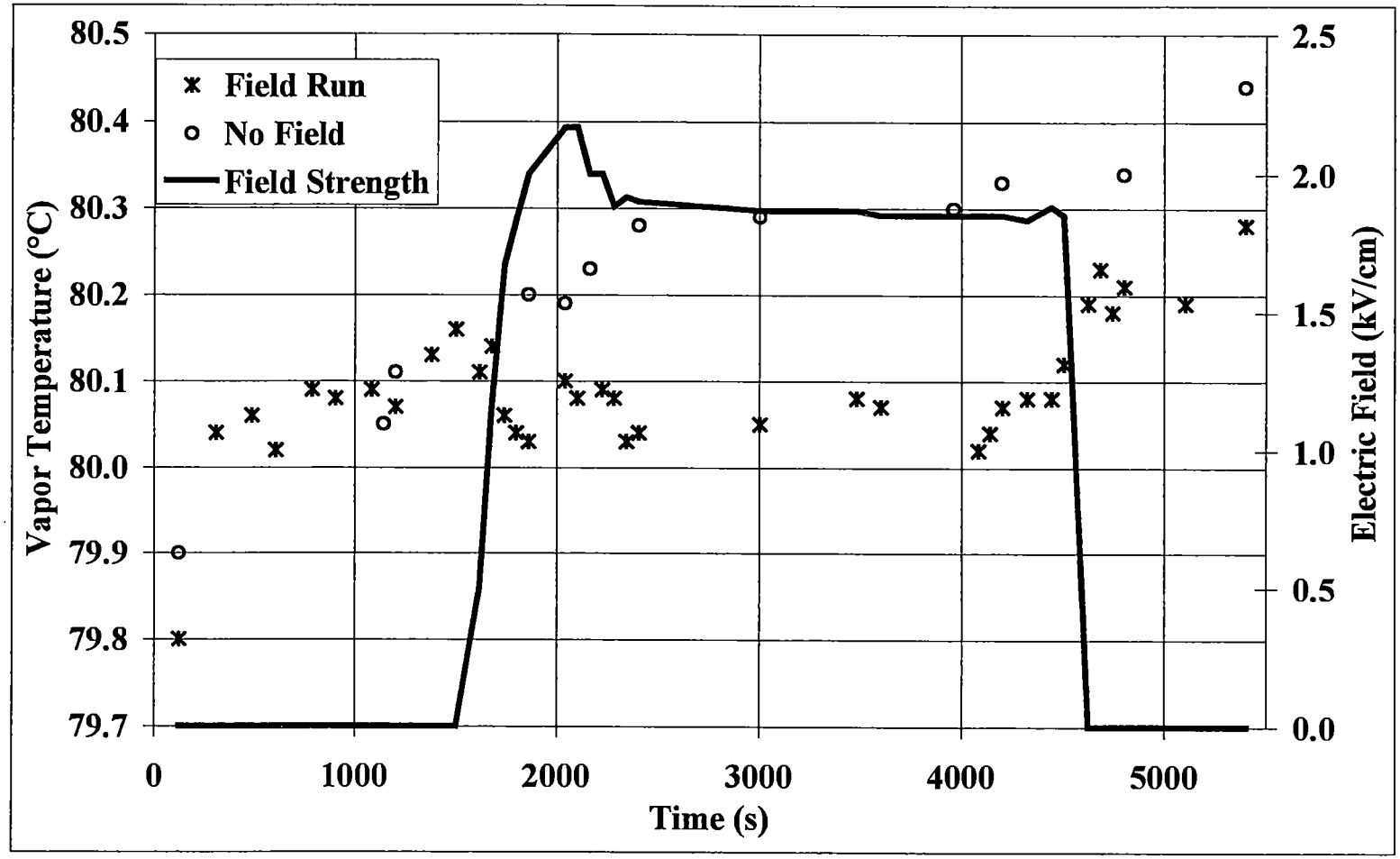


Figure 14. Comparison of vapor temperatures for batch distillation runs of 2-propanol/water with and without an applied electric field.

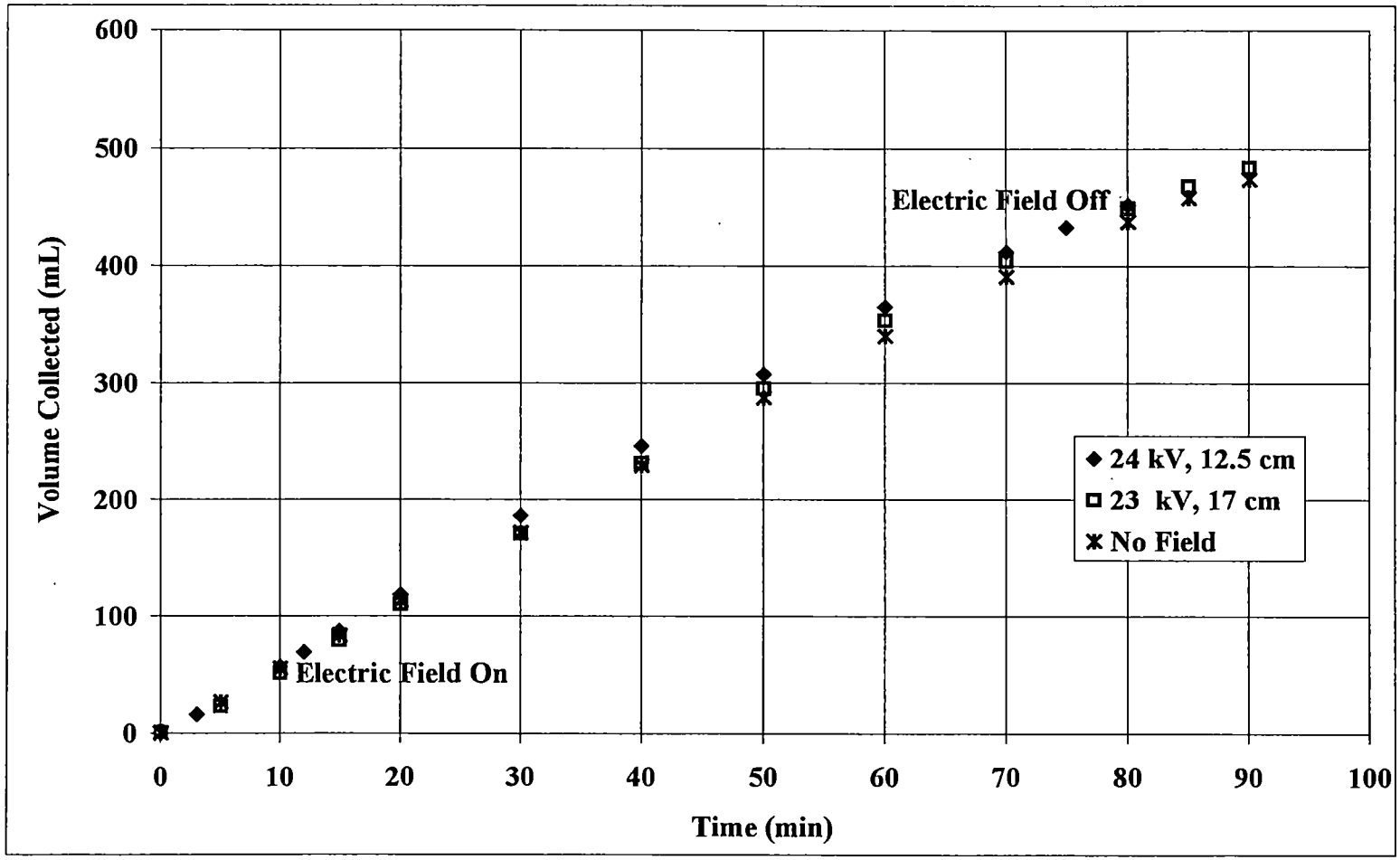


Figure 15. Comparison of distillate flow rates for batch distillation runs of 2-propanol/water with and without an applied electric field.

TABLE 2. MASS AND ENERGY BALANCE FOR THE BATCH

DISTILLATION OF 2-PROPANOL–WATER

NO-FIELD RUN	Total Volume (mL)	Mole Fraction of 2-Propanol	Volume of 2-Propanol (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 2-Propanol	Volume of 2-Propanol (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 due to evaporation.*

Total Reflux Results

Experiments conducted in the total reflux apparatus with various electrode shapes illustrate the effect that electrode shape has on the current that is conducted through the boiling mixture. The current was measured in the 2-propanol–water system at steady state for different applied voltages. Figure 16 shows the measured current as a function of applied voltage for two solid electrodes, two mesh electrodes, and two spiked electrodes, each arrangement at a spacing of 6 cm and constant position. In each case, the measured current remained relatively small at low voltages and then increased rapidly as

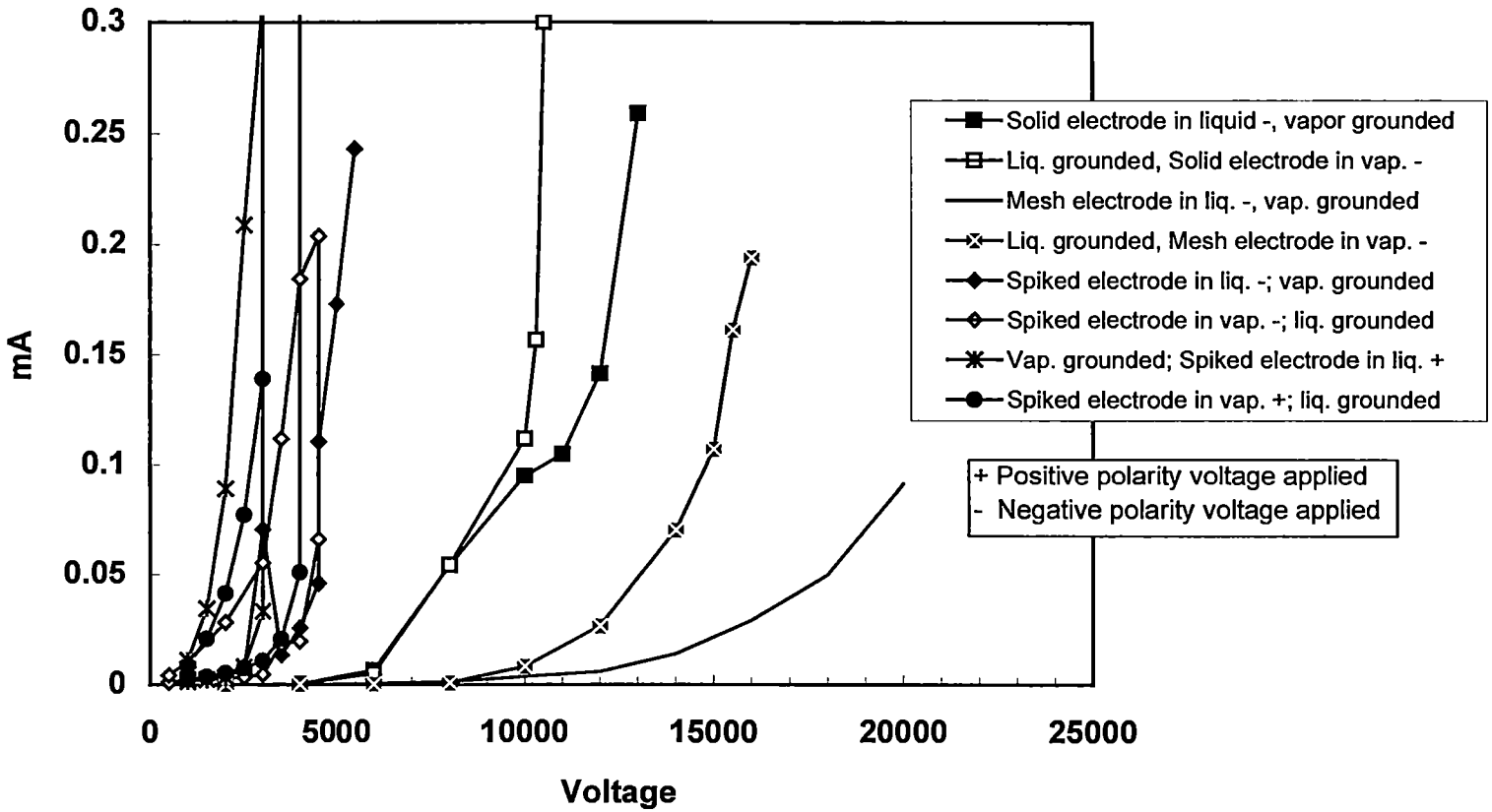


Figure 16. Current measurements as a function of positive(+) and negative(-) applied voltage for a solid, mesh, and spiked (points) electrode.

greater voltage was applied. The highest current was measured when positive high voltage was applied to the spiked electrode in the vapor phase or negative high voltage in the liquid phase. The lowest current was measured when negative high voltage was applied to a mesh electrode in the liquid. At those conditions, the current did not rise sharply until 12 kV. The measured current for the solid electrode case was intermittent and higher than the mesh, which was unexpected because of the low curvature of the surfaces. This is believed to be due to liquid dynamics, including both (1) splashing of liquid from the liquid surface by escaping vapor bubbles that collected under the liquid electrode during boiling and (2) pooling and dripping of condensate from the edges of the vapor electrode.

A common trait that was observed for each of the electrodes was the lower current measured when the vapor electrode was held at a positive potential relative to the liquid electrode. At higher voltages, the accumulation of condensate along the walls of the container close to the vapor electrode and arcing to the wall across liquid cones were observed. These effects were minimized by positioning the vapor electrode a sufficient distance from the wall and with the addition of a Teflon sheet between the electrode and the support rods. The curves in Figure 16 indicated that electrodes could be designed that reduce hydrodynamic effects and limit the current in the system.

Experiments with Different Electrode Shapes

The shape of the electrode used and the extent of current and hydrodynamics in the system affected the vapor concentration in the experiments. Results of experiments

with a 7.5-cm-diameter open circular electrode with eight 1-cm vertical points extending toward the vapor-liquid interface are shown in Figure 17. This figure and the following two figures show the mole fraction of 2-propanol in distillate samples and current as a function of applied voltage for both negative and positive polarities. They also show, as in the phase equilibria experimental results, 95% confidence (2 times sigma) intervals around the average mole fraction of the no-field samples. Data points outside the bands were considered to be significantly affected by the application of the electric field. When positive or negative high voltage was applied to the spiked electrode in the vapor, the mole fraction of 2-propanol in the vapor increased significantly over a voltage range of approximately 10–20 kV. For both polarities, there was a peak mole fraction of 2-propanol. A unique characteristic of the spiked electrode was that at low field strengths (about 1 kV/cm), there was a decrease in the vapor mole fraction of 2-propanol. This appeared to coincide with observations of liquid jetting from the edges of the vapor electrode toward the wall of the apparatus. Transfer of charge from the vapor electrode to the vapor-liquid interface was facilitated in this situation. The determination was made that such disruptions needed to be avoided to enhance separation. The current was lower when a positive potential was applied to the vapor electrode rather than a negative potential; however, in spite of the higher current levels, the peak in 2-propanol concentration occurred at a higher voltage for the positive polarity case. The vapor temperature did not drop significantly for this setup, but it did rise as current (power) increased.

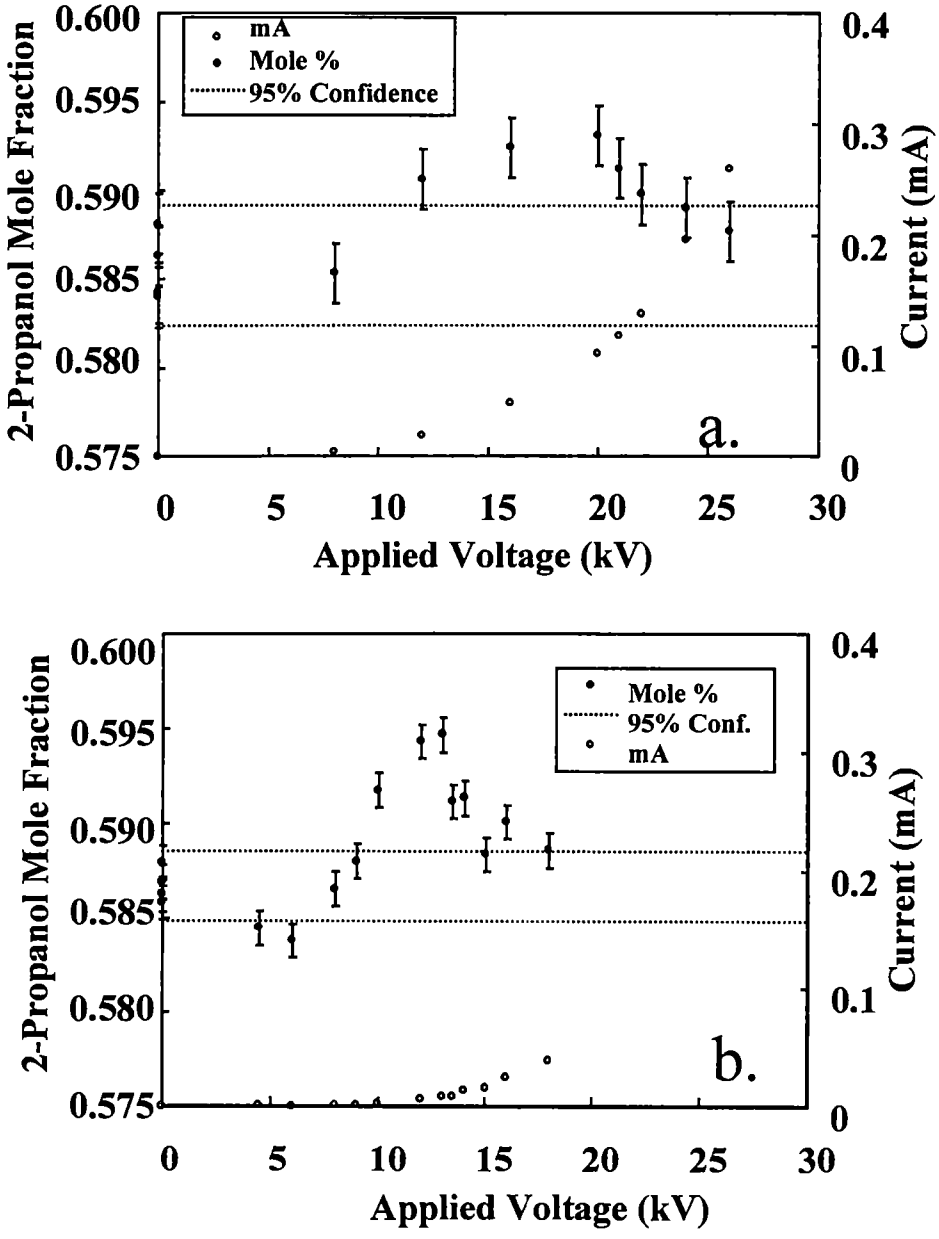


Figure 17. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to spiked electrodes with a separation distance of 6 cm. (a) negative polarity; (b) positive polarity.

During experiments employing rod electrodes and high voltage applied to the vapor or the liquid electrode, liquid cones formed on the vapor electrode and sprayed microdroplets toward the vapor-liquid interface and the apparatus wall. The cones became smaller and more numerous with increasing applied voltage. At higher voltages, up to nine liquid cones were observed on the electrode. As shown in Figure 18, the separation enhancement was small for this setup, even though the measured current was low for voltages less than 18 kV. For the negative polarity run, there was an apparent drop in the 2-propanol vapor mole fraction that corresponded to a large increase in the measured current. It is postulated that the vapor mole fraction was influenced in this setup by the charge carried by the liquid spraying from the vapor electrode.

The results of experiments conducted with mesh electrodes positioned 10 cm apart are shown in Figure 19. These results show an increase in the vapor mole fraction of 2-propanol when an electric field was applied. When positive high voltage was applied to the vapor electrode or negative high voltage was applied to the liquid electrode, a steady rise in the vapor mole fraction of 2-propanol was observed. Also, a small current increase was observed as the voltage was increased between 0 and 30 kV, which was the voltage range of the power supply. For the opposite-polarity situation, that is, when positive high voltage was applied to the liquid electrode or negative high voltage was applied to the vapor electrode, a peak in the vapor mole fraction of 2-propanol was observed. This corresponded to a point above which there was a significant increase in current. In both polarity cases, this peak in concentration occurred at a current of

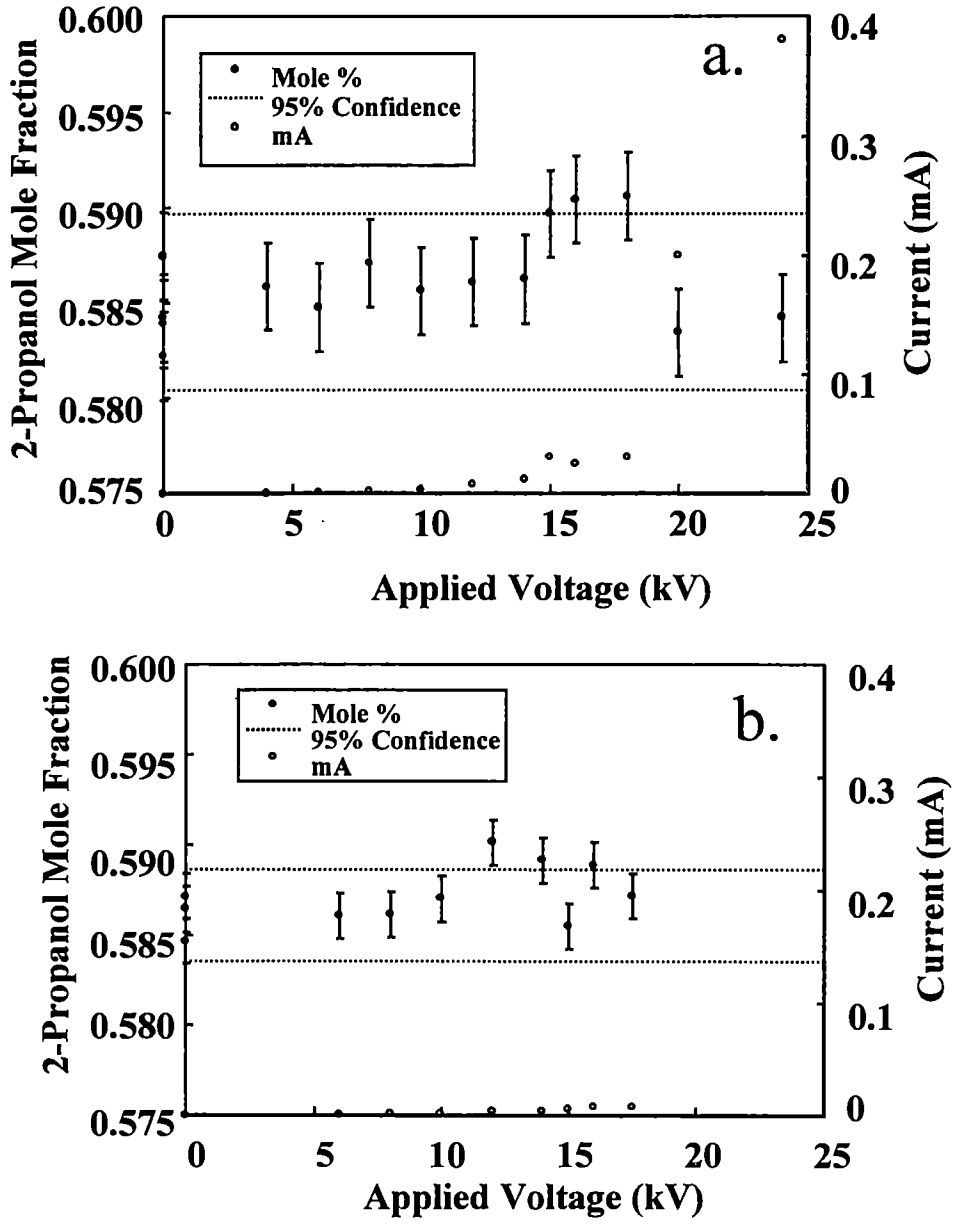


Figure 18. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to rod electrodes with a separation distance of 6 cm. (a) negative polarity; (b) positive polarity.

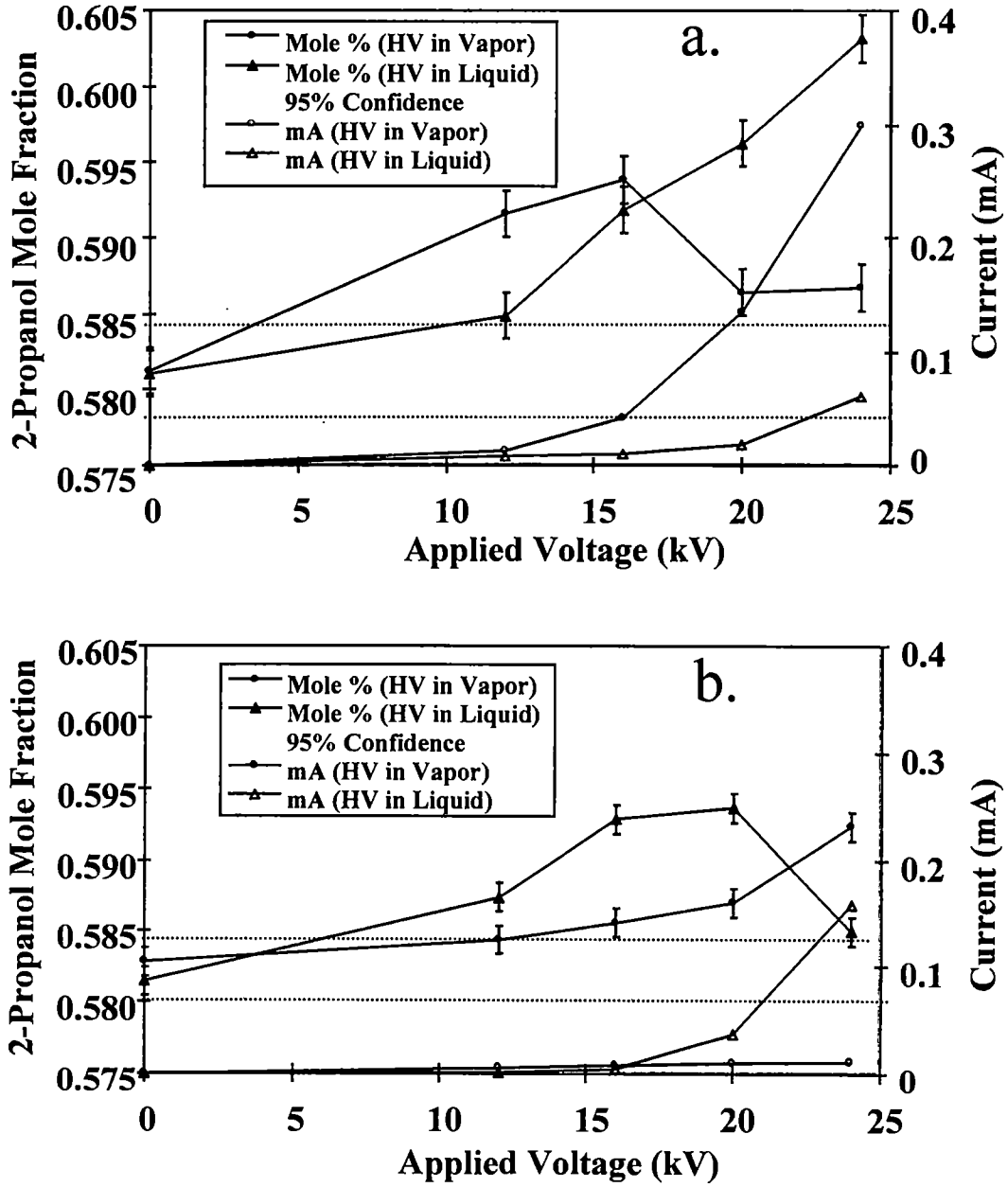


Figure 19. Vapor mole fractions and current measurements in a 2-propanol–water system for a voltage difference applied to mesh electrodes with a separation distance of 10 cm. (a) negative polarity; (b) positive polarity.

approximately 0.04 mA, which suggested that the increased current offset the concentration enhancement.

A total reflux experiment with mesh electrodes was also used to observe the effect of an electric field on the phase equilibria of the polar–slightly polar n-butanone–toluene system. The electric field effects observed on concentration and temperature for this system, shown in Figure 20, were slightly larger than the effects on the 2-propanol–water system.

Another characteristic of the system behavior with a mesh electrode was a drop in the vapor temperature as high voltage was applied. In the phase equilibria experiments, a correlation was noted between a drop in the vapor temperature and an increase in the vapor mole fraction of 2-propanol. As shown in Figure 21, the mesh electrode was the only type tested that showed a temperature drop with increasing voltage for this apparatus at similar starting mole fractions of 2-propanol. When positive high voltage was applied to the liquid (or negative to the vapor), the vapor temperature decreased as the concentration approached its peak and increased as greater voltage was applied. In each case, an increase in the vapor temperature corresponded to a significant increase in power input via the electrode, indicating that the temperature rise was due to Ohmic heating. The vapor temperature decreased for both the 2-propanol–water and the n-butanone–toluene systems. Since vapor temperature drops were also observed with pure 2-propanol and n-butanone, observing the effect of an electric field on a pure component could indicate whether electric field effects will be observed on the concentration and temperature of mixtures containing that component.

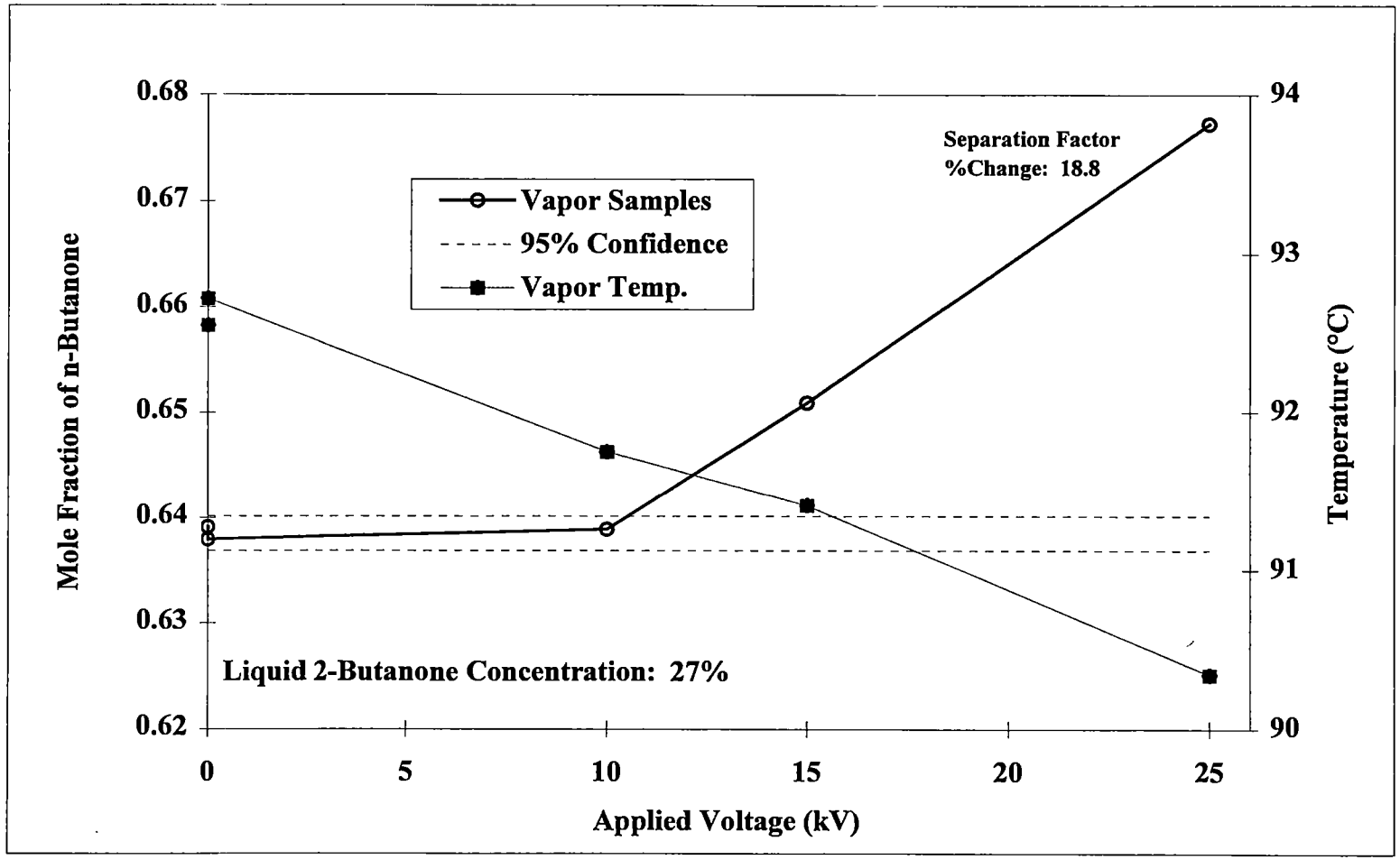


Figure 20. Concentration versus applied voltage for the 2-butanone/toluene system with mesh electrodes.

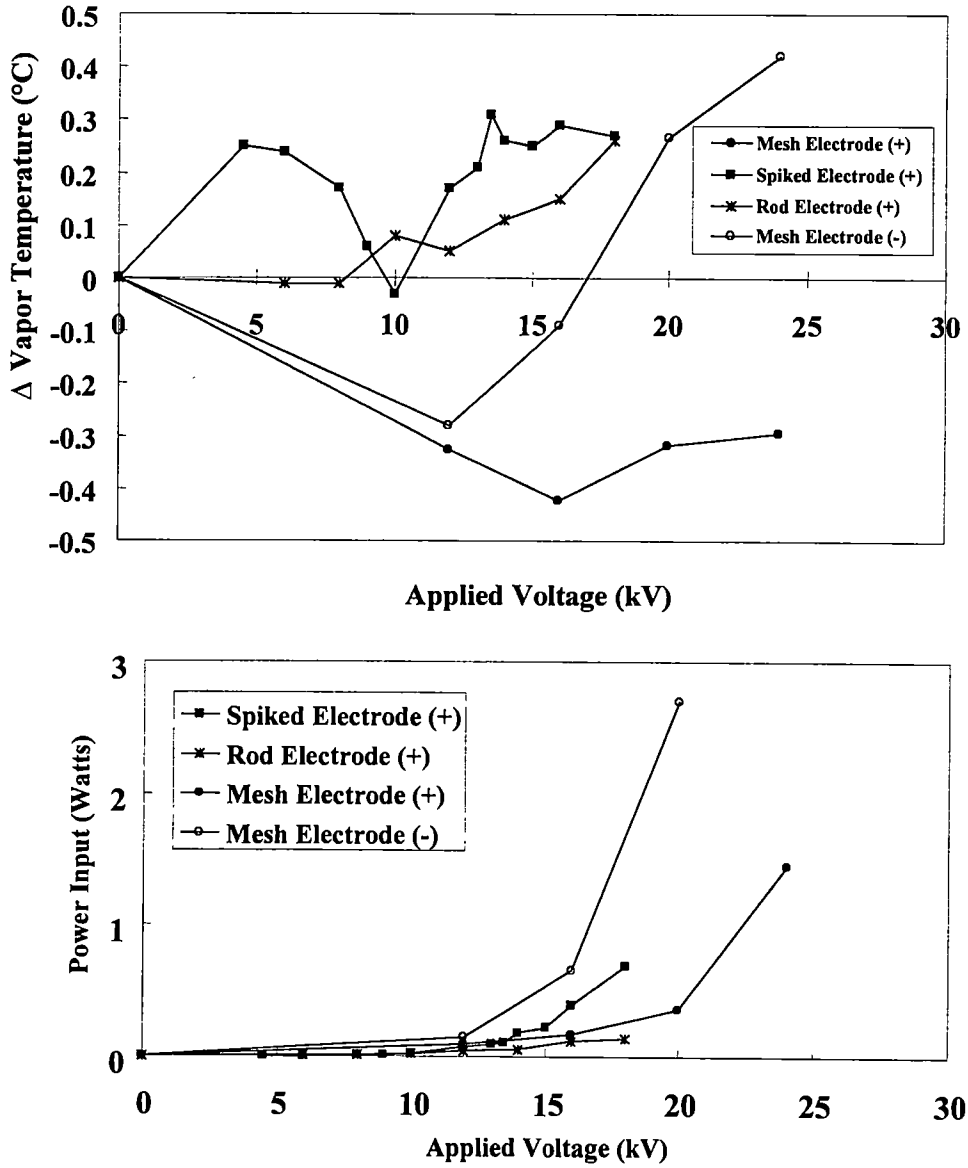


Figure 21. (a) Vapor temperature change as a function of potential difference between electrodes for the 2-propanol–water system. (b) Power input by the electric field.

Electrode Separation Distance

As the applied voltage to the refluxing 2-propanol–water system at steady state was increased from zero, the vapor mole fraction of 2-propanol did not vary until a transition voltage of approximately 6 kV was reached. Varying the electrode separation distance, and thus the electric-field strength, had no significant effect on the mole fraction for experiments conducted close to the transition voltage. The compositions of 4- and 5-kV samples were not significantly different from the no-field samples 95% confidence level, while the mole fraction of 2-propanol in 6-kV samples was consistently slightly higher than the no-field samples, independent of the electrode positions.

Figure 22 shows the results of adjusting the vapor and liquid electrode heights at specific applied voltages. When 10 or 15 kV was applied, the current and the vapor mole fraction of 2-propanol remained relatively constant as the electric field strength, calculated using the separation distance between the vapor electrode and the interface, was increased from 1 to 6 kV/cm. These results suggest that the increase in the separation factor is dependent on the applied voltage but not on the electric-field strength. When 20 kV was applied, the vapor mole fraction and current were relatively constant up to the point (5 kV/cm) where the electrodes were relatively close (4 cm) to the interface. At this point, there was a rise in current and a noticeable decrease in vapor mole fraction. There were two possible reasons for this behavior that pertain to the close proximity of the vapor electrode to the vapor-liquid interface. Liquid dynamics at the interface and possible electrostatic spraying of liquid under those conditions would have caused transfer of charge from the liquid surface to the vapor electrode. Another possible reason

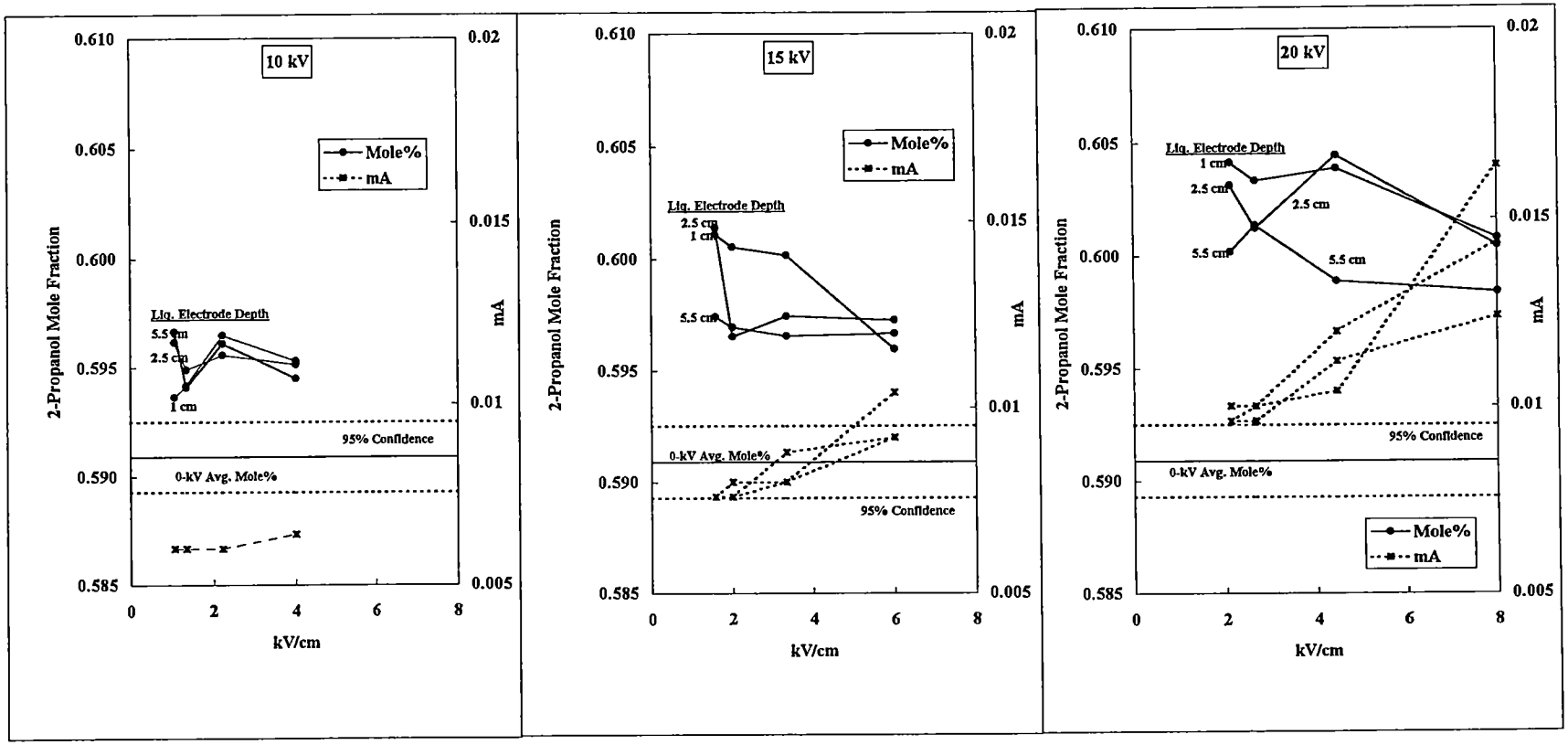


Figure 22. Total reflux experiments with the 2-propanol/water system at voltage differences of 10, 15, and 20 kV with varying separation distance between the liquid and vapor electrodes.

was the proximity of the vapor electrode to a region of charge buildup near the vapor-liquid interface, which would have increased the number of charge carriers in the vapor and thus increased the conductivity for a direct current.

Concentric Electrode Condenser Results

For a 30% solution of 2-propanol in toluene, samples taken from the base of the electrified central rod were more enriched with 2-propanol with an applied voltage, as shown in Figure 23. With 8-kV applied, the change in 2-propanol concentration at the center was greater by 9%, which is similar to the amount of separation achieved in the phase equilibria experiments. With 12-kV applied to the central rod, the 2-propanol concentration was the same as when 8-kV was applied. With greater voltage applied, arcing of current was observed in the condenser. Results were similar using a 25% solution of 2-propanol in water as 2-propanol was enriched at the central electrode with applied voltage. In both cases, however, the more volatile component (2-propanol) was enriched at the center. Since water is more polar than 2-propanol, it cannot be assumed from these findings that the more polar component will be attracted to the area of applied voltage.

Azeotrope Experiments

In each experimental setup described above, experiments were run with electric fields applied to mixtures of 2-propanol–water and 2-propanol–toluene at or near their respective azeotrope (inseparable) points. In each case, the vapor mole concentrations

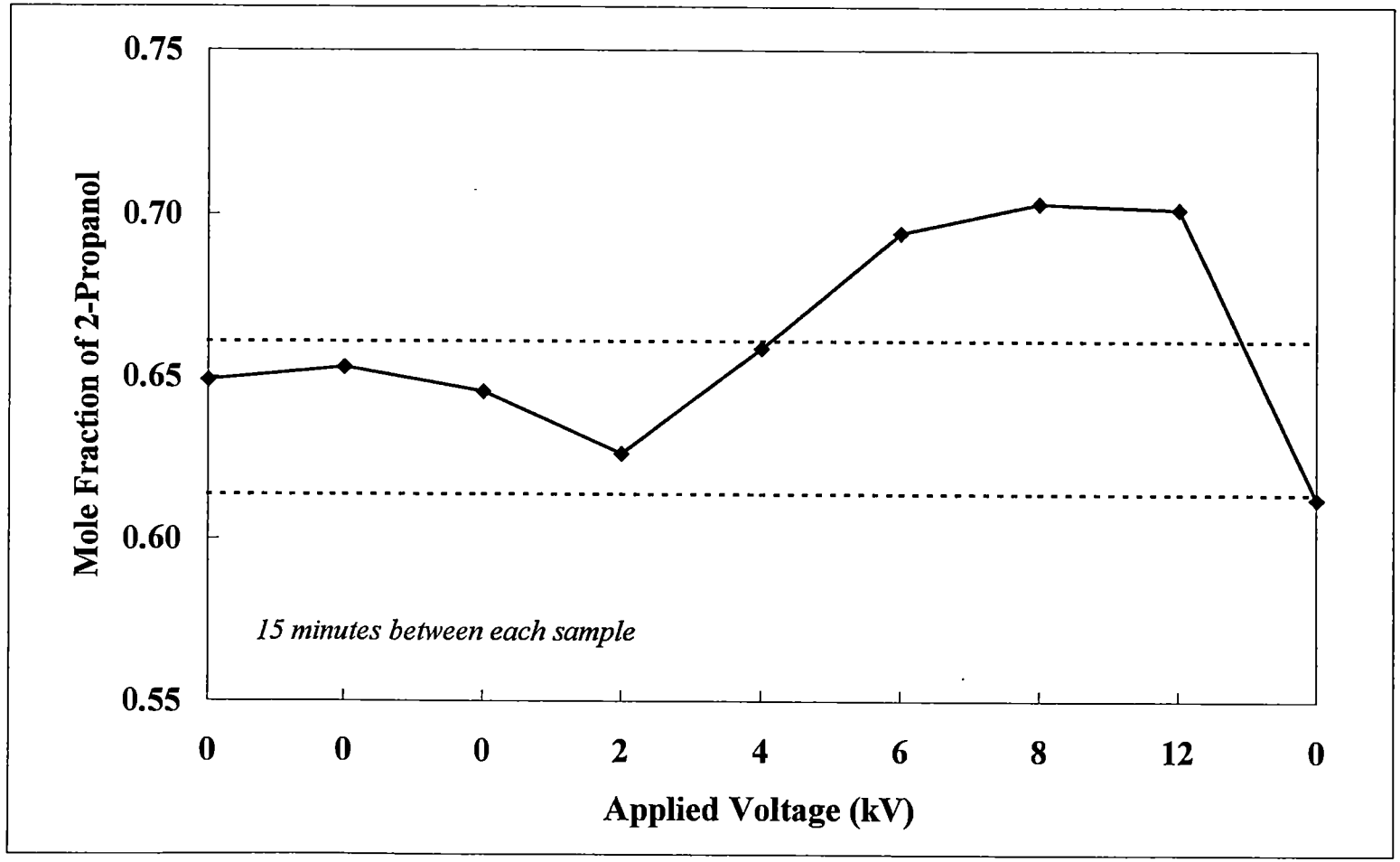


Figure 23. 2-Propanol mole fraction at different applied voltages from the center of the concentric electrode condenser with a 2-propanol/toluene system.

did not deviate from the starting azeotrope concentrations, as could be seen for the 2-propanol–water case in Figure 8. Also, for each experiment, the percent enhancement in the separation factor decreased as the starting (liquid) concentration was moved closer to the azeotrope.

Multi-Stage Distillation Results

In the experimental setup with the electric field applied across the gas-liquid interface in the second stage of the multistage distillation, several problems were encountered due to limited space. Based on the previous experiments, the attempt was made to limit the current in the system with the design of the electrode configuration. The first observation that was made was that high voltage could not be applied to one distillation tray and grounded by the tray in the next stage. When this was attempted, electrical arcing and spraying was noticeable along the length of the stage via liquid on the inside wall. Therefore, the addition of the rod from the side wall into the center of the stage was necessary. Further dynamic problems were encountered due to space, such as weeping of liquid onto the vapor electrode and flooding in the upper stage. Also, the multiple stages pushed the mixtures to their azeotrope where the applied electric field effects were diminished. These factors prevented the reproduction of the results observed in the one-stage columns where there was more space in the vapor region to isolate the vapor electrode.

Better results with an applied electric field were found in multistage distillation experiments with the ground rod totally immersed in liquid below the overflow level. In

these experiments, close attention was paid to the size and quantity of the vapor bubbles rising through the liquid. With a 2-propanol–water system, there were significant increases in the number of bubbles and bubble size reduction due to an applied electric field. As shown in Figure 24, the vapor bubbles flowing upward through liquid in the second stage of the column decreased in diameter from 4.4 mm to 0.8 mm with 30 kV applied to the plate. The number of bubbles increased from 20–25 to around 250. The current was low (0.3-mA) at 30-kV, so little power was added by the electric field. To investigate whether there were indeed mass transfer and concentration enhancements due to increased surface area, distillate samples were analyzed with different applied voltages. As shown in Figure 25, the mole fraction of 2-propanol was increased monotonically in the distillate with increasing applied voltage. Figure 25 also shows the results of a multistage experiment where the distillate was collected in a graduated cylinder rather than refluxed back into the column. The distillate rate increased fourfold with 14 kV applied and a 20% increase in the energy supplied to the system. These experiments were found to be somewhat limited to the conductivity of the system. The 2-butanone–toluene, which was not very conductive, showed little mass transfer improvements with applied voltage. Highly conductive systems with high concentrations of water tolerated only a limited applied voltage because the current and the power addition were larger for these systems.

0 kV Applied: 20-25 bubbles, 4.4-mm dia.

30 kV Applied: 250-300 bubbles, 0.8-mm

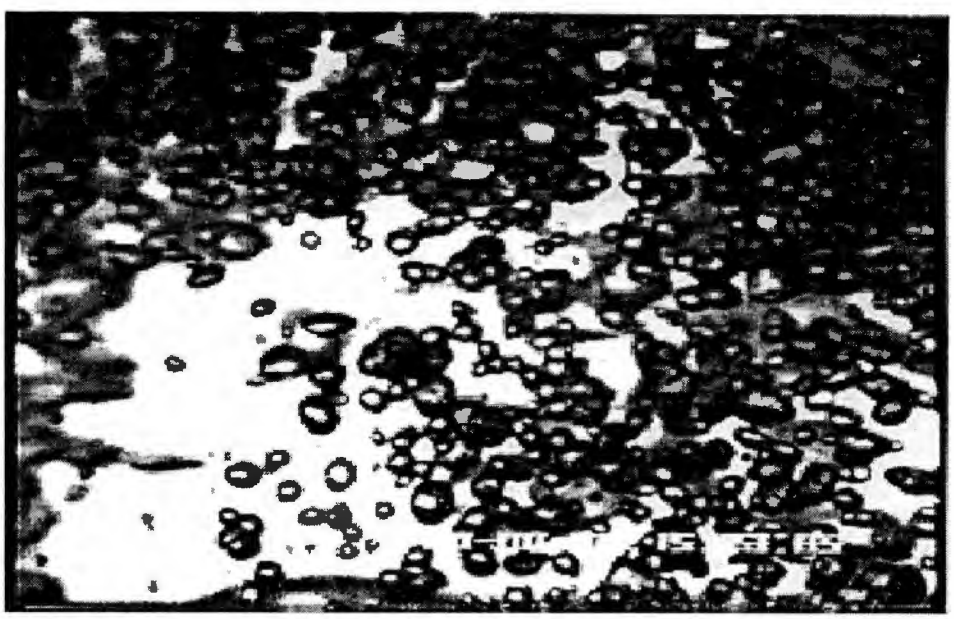


Figure 24. Bubble size reduction in a distillation stage with applied voltage.

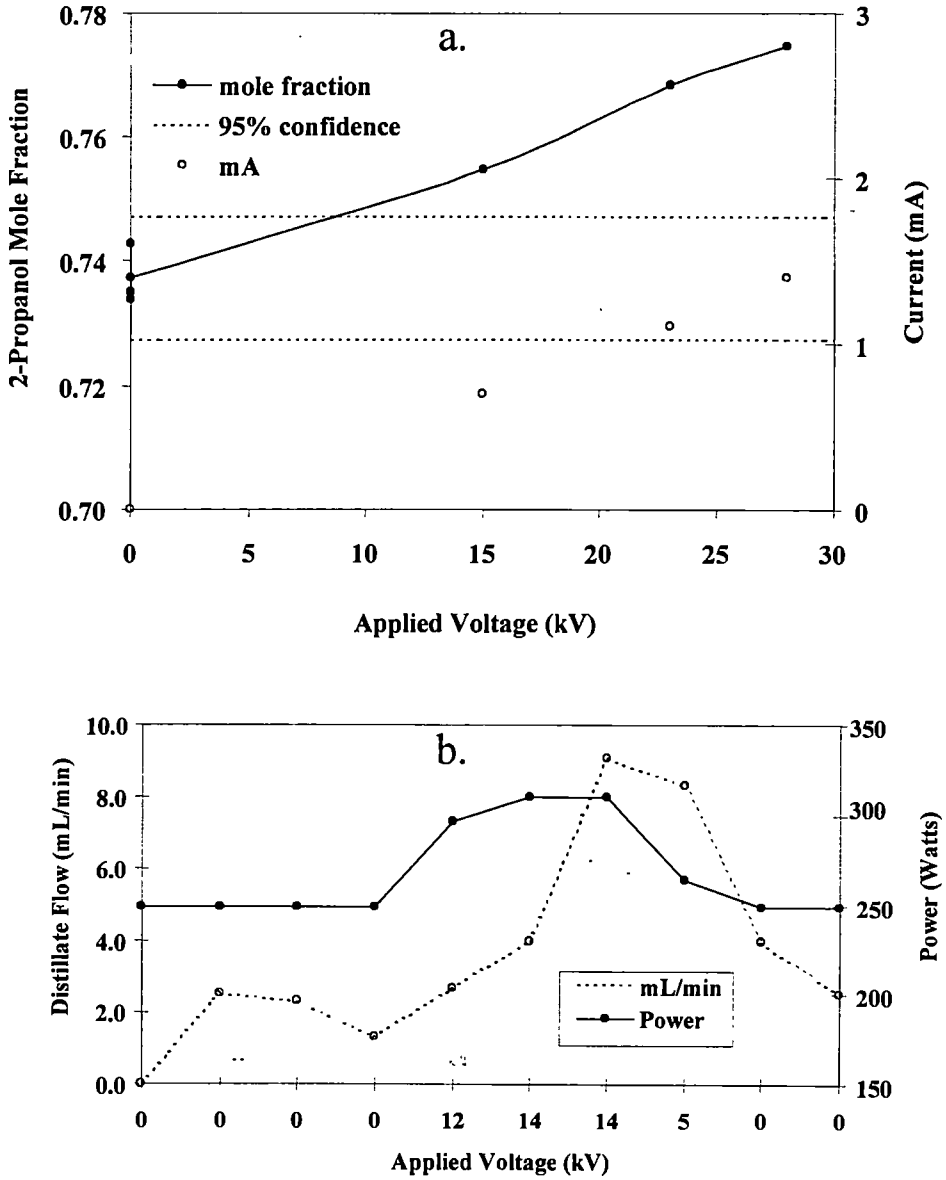


Figure 25. (a) Distillate mole fraction for a multistage distillation experiment with the 2-propanol/water system as a function of applied voltage; (b) Distillate flow rate and total power input at different applied voltages.

Interfacial Study Results

Based on the calculations of charge density and experimental findings of applied voltage effects at the vapor-liquid interface, a closer investigation was made of the interface and the bonding characteristics of the 2-propanol–water system in the total reflux experiment using Raman spectroscopy with an argon laser. A common trend was observed in the Raman intensity of the 2-propanol peak at the interface and slightly below the interface. With increasing applied voltage, as shown in Figure 26, the intensity of the 2-propanol peak increased, indicating possible increases of 2-propanol at the interface or changes in the physical characteristics of the interface. These results did resemble the results found by Karagounis (7), with the difference that Raman spectroscopy measures vibrational energy rather than electronic energy. Also, the position of the peak was not changed and there were no new peaks that would have indicated a new species or changes in the bonding characteristics of the system.

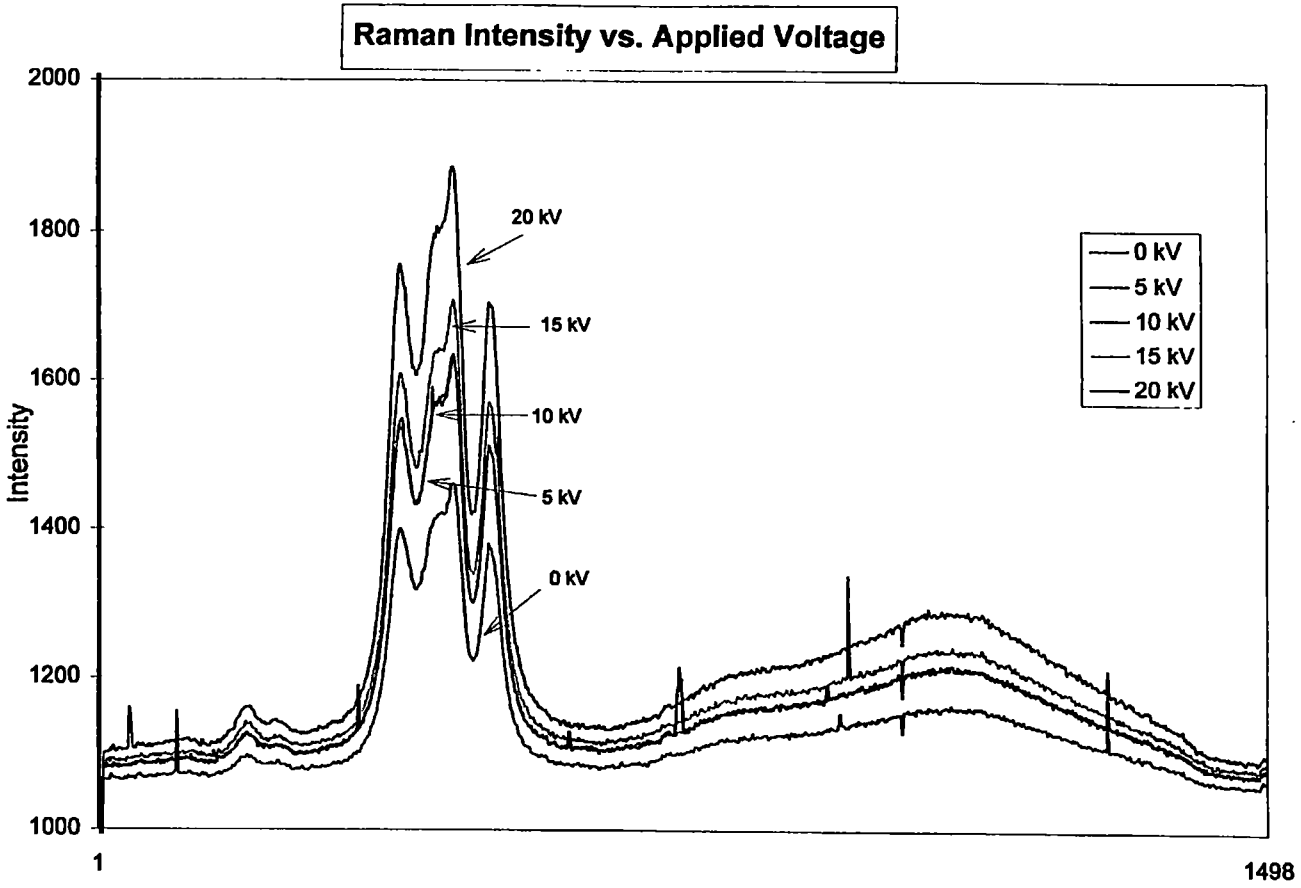


Figure 26. Raman spectroscopy intensities at a fixed point at the vapor-liquid interface of 2-propanol–water for different applied voltages.

CHAPTER V

DISCUSSION

Several observations may be made in consideration of the results presented that may provide insight as to the mechanisms responsible for a shift in composition when an electric field is applied across the interface of a boiling mixture. During experiments with different chemical systems, electric field effects were only observed for systems including a polar component.

The general shapes of the majority of the curves for vapor composition as a function of applied voltage generated in the phase equilibria and total reflux experiments were very similar to those of O'Neal [8]. These curves can be described as having three parts: (1) a low-voltage regime where there was no apparent effect, (2) a regime in which the vapor concentration of one of the species increased with increasing voltage, and (3) a higher-voltage portion in which the concentration decreased with increasing voltage. The similarities in the experiments and results suggested that the same mechanisms were responsible for the separation enhancement in the two studies. Although, as conclude by O'Neal, there may be an alignment of the polar molecules in the direction of the electric field lines in these experiments, it was unlikely that there was an attraction of these molecules toward the region of charge. This phenomenon, known as dielectrophoresis, is not considered to be the responsible mechanism due to the fact that most of the

experiments in this study were conducted with a parallel-plate-electrode geometry that employed essentially a homogeneous field. Also, the direction of the applied field did not qualitatively alter the results; for example, 2-propanol was increased in the vapor for either field direction for the 2-propanol–toluene system.

In the total reflux experiments with 2-propanol–water, two circumstances coincided with decreases in the vapor concentration of 2-propanol. These are: (1) liquid dynamics in the electric field, including splashing of liquid up from the interface, dripping of liquid from the vapor electrode, and jetting of liquid from the vapor electrode, and (2) higher current and electrical arcing from the vapor electrode. Both led to transfer of charge between the vapor electrode and the liquid, an observation that provides support for a hypothesis that electric charge at the vapor-liquid interface may be responsible for the observed separation enhancement in the phase equilibria and batch distillation experiments. Another possible explanation, based on experimental observation, for the decrease in separation enhancement with higher currents was that at a sufficiently high voltage, the liquid surface became unstable and microdroplets were sprayed in the vapor region.

Whereas the applied voltage was directly related to separation enhancement over a wide range, the electric field strength was found to have little effect. For a given applied voltage, the results for a range of electrode spacings in the vapor varied little, with the exception of closer spacings for which liquid dynamic effects were magnified. These results suggest that the effects of the applied field on separation enhancement are not due to the electric field in the bulk liquid region.

A hypothesis was made that surface charge at the vapor-liquid interface was responsible for the observed effects on the electric field in the phase equilibria and the total reflux experiment. Maxwell equations relating the electric field, potential, and charge as a function of media permittivities and conductivities were solved for a case with parallel-plate electrodes. Since the experiments were conducted at steady-state with relatively small, steady currents, the assumption was made that the bulk fluids were charge-free and bulk flow did not contribute so that a Laplace equation of voltage could be solved for the charge density at the vapor-liquid interface. The results of calculations supported this hypothesis for the case of an ac signal applied to the liquid and vapor of two media having properties similar to those of the 2-propanol/water mixture and using the equations and further assumptions shown in Appendix C. Results indicated that the charge density at the vapor-liquid interface varied as a function of applied voltage and electrode position as presented in Figure 27. It was seen that the charge density at the interface increased with the applied voltage. This was consistent with the experimental findings of increased separation with increased voltage. In contrast, the charge density was a nonlinear function of electrode distance. For small spacings, the charge density varied greatly with electrode distance. For large distances, representative of the experimental conditions, the charge density at the interface was relatively insensitive to the changing electric field strength. This also is consistent with the hypothesis that the enhancement in the vapor concentration was not dependent on electric field strength.

Recommendations for future work include a further detailed investigation of the mechanism and a more precise look at the properties of the interface under an electric

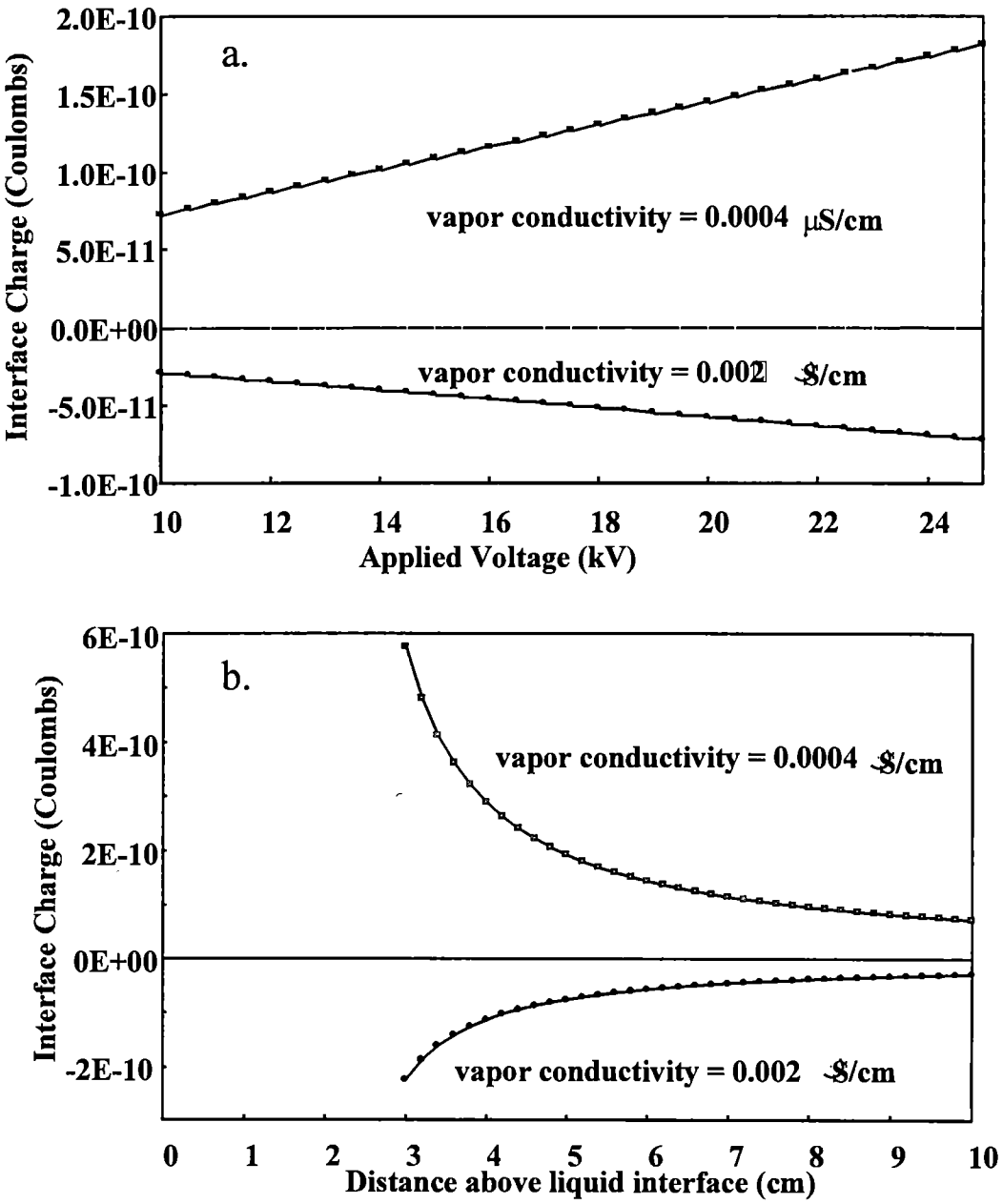


Figure 27. Results of simplified calculations of the charge density at the interface for a parallel-plate electrode configuration. (a) variation as a function of applied voltage; (b) variation as a function of distance between the vapor electrode and the interface at a fixed voltage.

field. The debate in the literature about the effect of an electric field on pure component properties, such as boiling point, was continued by the experimental observation that an applied electric field reduced the vapor temperature. The mechanism behind this phenomenon also requires further study. Measuring and comparing the heat of vaporization of pure 2-propanol with and without an electric field could indicate if increased heat transfer enhancement played a role in the observed concentration enhancements. The combination of the mass transfer enhancement and separtion enhancement would increase the practicality of implementing applied voltage in distillation. Also, further experimentation with larger scale versions of the distillation experiments presented in this work would be useful in demonstrating that electric fields could be viable configurations in separation processes.

CHAPTER VI

CONCLUSIONS

These experiments have shown that an electric field applied across the interface of a boiling mixture can have a significant effect on the vapor composition. It cannot be concluded from these results that the electric field affected the vapor-liquid equilibria of a mixture because of the change in the vapor temperature observed with applied voltage. However, an applied voltage did enhance separation efficiency, which implied more efficient distillation when there was at least one strong polar component (toluene was not affected) present in the mixture and when the initial concentration was not at an azeotrope point. In each of the experiments described in this work, the concentration of the more volatile component increased in the vapor samples or near the high voltage electrode. Experiments conducted with different electrode configurations indicated that the magnitude of the effect varies monotonically with applied voltage for conditions with low current and without disruptive liquid dynamics. When there was increased current in the system, there was a peak in the concentration, consistent with some results found in the literature. The effects were maximized when current flow between electrodes and liquid transport between the vapor-liquid interface and the vapor electrode was minimized.

The results of the experiments with the electric field applied across the interface suggested that the observed effects were localized at the vapor-liquid interface. The

effect of an applied electric field was surprisingly found relatively independent of field strength. The optimum electrode configuration for maximized separation enhancement was mesh electrodes with voltage applied to the electrode in the vapor region. Hydrodynamics and current was also reduced when the vapor electrode was not located near the vapor-liquid interface. For the experiments with an electric field applied in a liquid region with vapor bubbles rising through it, the interfacial contact area between the phases was increased by the field, which led to increased separation efficiency.

LIST OF REFERENCES

LIST OF REFERENCES

1. P. K. Katti and M. M. Chaudhri, Effect of strong electric fields on the boiling points of some alcohols, Nature 190 (1961) 80.
2. R. K. Lyon, Effect of strong electrical fields on the boiling points of some alcohols, Nature 192 (1961) 1285.
3. R. A. Anderson and S. S. Infirri, Effect of electric and magnetic fields on the boiling point of alcohol, Nature 196 (1962) 267.
4. V. Ramakrishna, P. K. C. Pillai, and P. K. Katti, Effect of electric field on the boiling points of liquids, Nature 198 (1963) 181.
5. R. C. Sharma, Effects of electric fields on the boiling points of liquids, J. Appl. Phys. 42 (1971) 1234.
6. S. Biswas and S. P. Basu, Effect of electric field on the boiling points of liquids, Indian J.Technol. 14 (1976) 165.
7. G. Karagounis, Separation of polar from non-polar molecules, Nature 156 (1948) 855.
8. J. M. O'Neal, The compositional behavior of selected binary mixtures in the presence of a non-uniform electric field, University of Southern Mississippi, Ph.D. Dissertation (1973).
9. J. Kohoutova, J. Suska, J. P. Novak, and J. Pick, Collect. Czech. Chem. Commun. 35, (1970) 3210.

APPENDICES

APPENDIX A

PHASE EQUILIBRIA CALCULATIONS

2-Propanol/Water [14:86]

Liquid Samples

			Measurement					
	Actual	Error	Error	Std Dev.	Std Dev.			
L1	0.1396	0.1392	0.1401	0.1407	0.1389	30.2836	30.205	30.362
L2	0.1411	0.1413	0.1409	0.1407	0.1389	30.5178	30.548	30.488
16KV	0.1381	0.1379	0.1382	0.1407	0.1389	30.0209	29.994	30.048
16KV	0.1393	0.1389	0.1397	0.1407	0.1389	30.2274	30.155	30.300
L5	0.1389	0.1389	0.1389	0.1407	0.1389	30.1655	30.164	30.167
L6	0.1395	0.1396	0.1394	0.1407	0.1389	30.2606	30.279	30.242
16KV	0.1361	0.1358	0.1365	0.1407	0.1389	29.7019	29.650	29.754
16KV	0.1367	0.1364	0.1370	0.1407	0.1389	29.7960	29.747	29.845

No Field avg =	0.1398	Stdev =	0.0009
Field Avg =	0.1380	%Change	1.26

Gas Chromatograph
2-Propanol/Water Standards

Area %	Mole Fraction		
12.07	0.0476	12.0415	12.0984
22.816	0.0983	22.8751	22.7567
30.068	0.1368	30.0786	30.0583
33.349	0.1596	33.3830	33.3157
68.643	0.4451	68.6293	68.6571
78.581	0.5594	78.5656	78.5966
84.511	0.6591	84.5063	84.5158

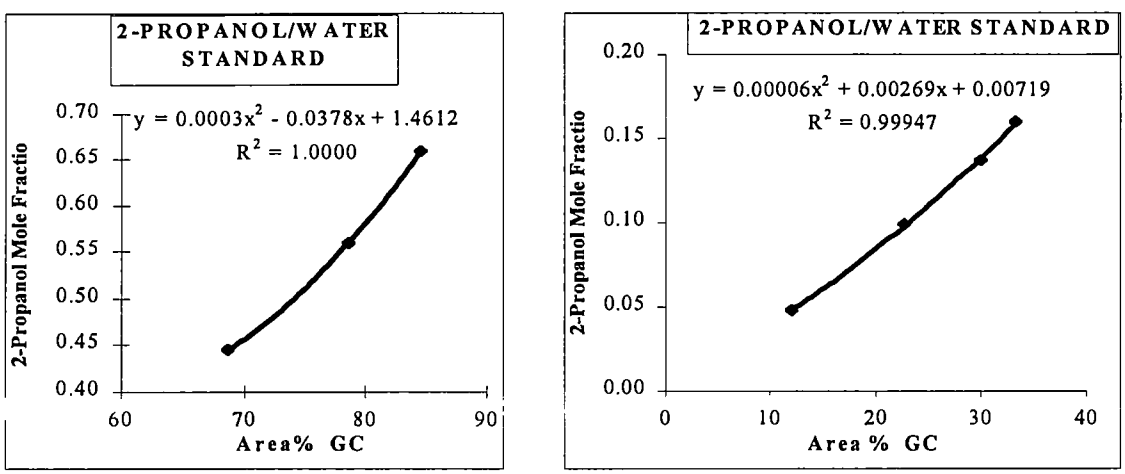


Figure 29. Gas chromatograph calibration curves for 2-propanol–water standards.

2-Propanol/Water [14:86]

Vapor Samples

			Measurement					
	Actual	Error	Error	Std Dev	Std Dev			
V1	0.5034	0.5035	0.5034	0.5023	0.4889	73.3923	73.386	73.399
V2	0.4971	0.4973	0.4969	0.5023	0.4889	72.8374	72.853	72.822
16KV	0.5226	0.5221	0.5230	0.5023	0.4889	75.0025	74.965	75.040
16KV	0.5240	0.5228	0.5251	0.5023	0.4889	75.1176	75.020	75.215
V5	0.4946	0.4942	0.4949	0.5023	0.4889	72.6137	72.584	72.643
V6	0.4873	0.4844	0.4902	0.5023	0.4889	71.9646	71.700	72.229
16KV	0.5308	0.5308	0.5309	0.5023	0.4889	75.6731	75.669	75.677
16KV	0.5288	0.5294	0.5283	0.5023	0.4889	75.5151	75.559	75.472

No Field avg = 0.4956 Stdev = 0.0067
Field avg = 0.5265 %Change 6.24

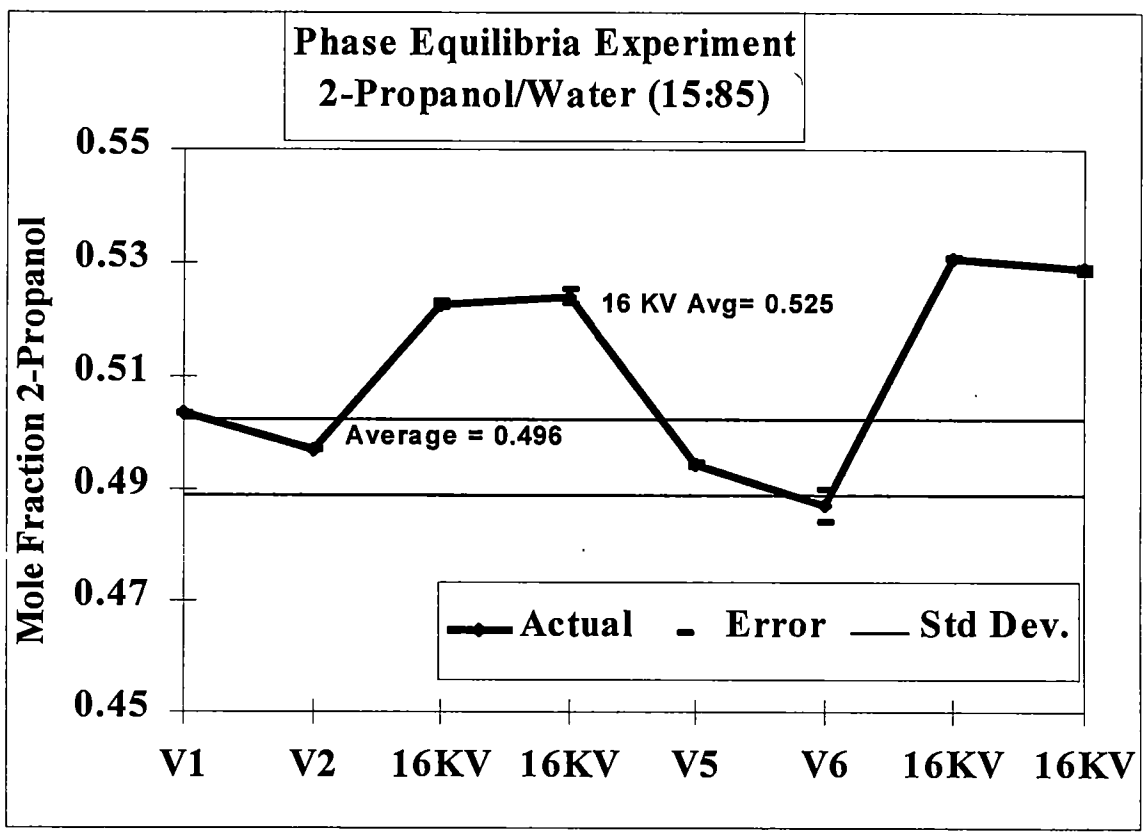


Figure 30. Sample phase equilibria experimental results for 2-propanol–water system.

APPENDIX B

BATCH DISTILLATION CALCULATIONS

Mass/Energy Balance for Batch Distillation with an Applied Electric Field

```
REM The experimental system is 2-propanol/water.
CLS
MWX = 60.096, MWY = 18.0159, DENSEX = .7855, DENSEY = 1
REM The density of water is already included in the equations as 1.
L$ = STRING$(75, "-")
REM  2-propanol is the X component
REM  3 significant decimals
FRACX = .254, FRACXD = .539, FRACXS = .034
REM  Recorded initial volume, total distillate volume, final still volume.
VOLT = 750, VOLD = 487, VOLS = 263
INPUT "GUESS TOTAL MOLES"; MOLT
REM  Power Calculation is in KJ/min.  Heat input is in Volts, resistance is in Ohms.
HEAT = 90.6, HEATR = 1.171, RESIST = .488
POWERSEC = HEAT * HEATR / RESIST
PKJMIN = POWERSEC * 60 / 1000
REM  An electric field is applied which adds extra power to the heat input.
REM  The average recorded current due to the applied field is used for calculations.
FIELDMIN = 50
KILOVOLT = 11
MILLIAMP = .09
EFPOWER = 60 * KILOVOLT * MILLIAMP * FIELDMIN / 1000
REM  Experiment time is in min; Reduced temperature (T_R) is needed in the Clapeyron
     equation.  The liquid temperature rises as the low boiler concentration decreases.
```

```
MINUTE = 80, TEMPC = 81.5, TEMPMID = 86.5, TEMPEND = 92
TEMPK = 273.15 + TEMPC, TMIDK = 273.15 + TEMPMID, TENDK = 273.15 +
    TEMPEND
CRITICAL = 508.3
TR = TEMPK / CRITICAL, TRMID = TMIDK / CRITICAL, TREND = TENDK /
    CRITICAL
REM The heat of vaporization equation used for 2-propanol is from Clapeyron equation.
REM Units are J/kmol.
VAPORI = (5.698E+07) * (1 - TR) ^ (.087 + .3007 * TR)
VAPIMID = (5.698E+07) * (1 - TRMID) ^ (.087 + .3007 * TRMID)
VAPIEND = (5.698E+07) * (1 - TREND) ^ (.087 + .3007 * TREND)
JKMOLI = VAPORI * .63 + VAPIMID * .25 + VAPIEND * .12
KJMOLI = JKMOLI / 1000000!
REM  The heat of vaporization for water was found in steam tables. KJ/MOL
VAPWAT = (-.04656 * TEMPC + 41.59847) * .63
VAPWAT2 = (-.04656 * TEMPMID + 41.59847) * .25
VAPWAT3 = (-.04656 * TEMPEND + 41.59847) * .12
KJMOLW = VAPWAT + VAPWAT2 + VAPWAT3
GOSUB 1000
GOSUB 2000
GOSUB 3000
VOLX = MASSX / DENSEX, VOLXD = MASSXD / DENSEX, VOLXS = MASSXS /
    DENSEX
HEATADD = PKJMIN * MINUTE + EFPOWER
HEATNEED = KJMOLI * (MOLD * FRACXD) + KJMOLW * (MOLD * (1 -
    FRACXD))
PRINT
PRINT "          MASS BALANCE OF BATCH DISTILLATION SYSTEM"
PRINT
```

```
PRINT "Date of Experiment:  xx/xx/xx"
PRINT "2-PROPANOL/WATER MIXTURE"
PRINT L$
PRINT "        "; "  VOLUME (mL)  "; " TOTAL MOLES  "; "  MOLEFR 2-
PROPANOL  "; " 2-PROPANOL (mL)"
PRINT L$
PRINT "INITIAL"; "      "; VOLT; "       "; MOLT; "       "; FRACX; "          "; VOLX
PRINT
PRINT "DISTILLATE"; "   "; VOLD; "       "; MOLD; "       "; FRACXD; "          ";
      VOLXD
PRINT
PRINT "FINAL"; "       "; VOLS; "       "; MOLS; "       "; FRACXS; "          ";
VOLXS
PRINT
PRINT "TOTAL HEAT ADDED TO THE SYSTEM (KJ):"; HEATADD
PRINT "HEAT REQUIRED TO VAPORIZE DISTILLATE (KJ):"; HEATNEED
END
1000 REM Subroutine to iterate for total moles entering still.
10 MASST = (FRACX * MWX + (1 - FRACX) * MWY) * MOLT
MASSX = DENSEX * (VOLT - MASST) / (1 - DENSEX)
NEWMOLT = (MASSX / MWX) + (MASST - MASSX) / MWY
DELTA = (MOLT - NEWMOLT)
IF ABS(DELTA) < .01 THEN RETURN
MOLT = MOLT + DELTA / 3.5
GOTO 10
2000 REM Subroutine to iterate for total distillate moles.
MOLD = MOLT / 2.5
20 MASSD = (FRACXD * MWX + (1 - FRACXD) * MWY) * MOLD
MASSXD = DENSEX * (VOLD - MASSD) / (1 - DENSEX)
```

```
NEWMOLD = (MASSXD / MWX) + (MASSD - MASSXD) / MWY
DELTA = (MOLD - NEWMOLD)
IF ABS(DELTA) < .01 THEN RETURN
MOLD = MOLD + DELTA / 5
GOTO 20
3000 REM Subroutine to iterate for final still moles.
MOLS = MOLD / 2.5
30 MASSS = (FRACXS * MWX + (1 - FRACXS) * MWY) * MOLS
MASSXS = DENSEX * (VOLS - MASSS) / (1 - DENSEX)
NEWMOLS = (MASSXS / MWX) + (MASSS - MASSXS) / MWY
DELTA = (MOLS - NEWMOLS)
IF ABS(DELTA) < .01 THEN RETURN
MOLS = MOLS + DELTA / 5
GOTO 30
```

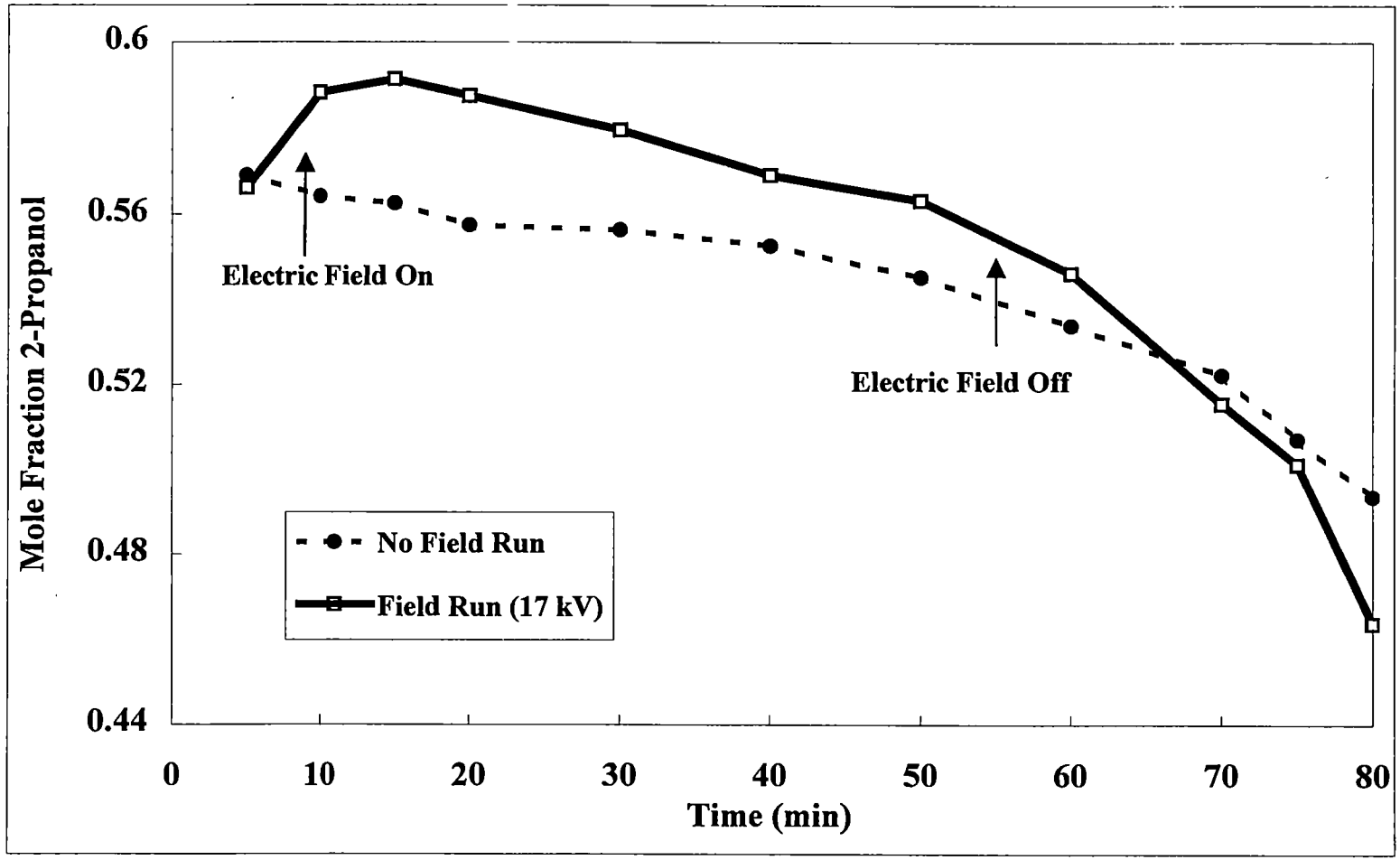
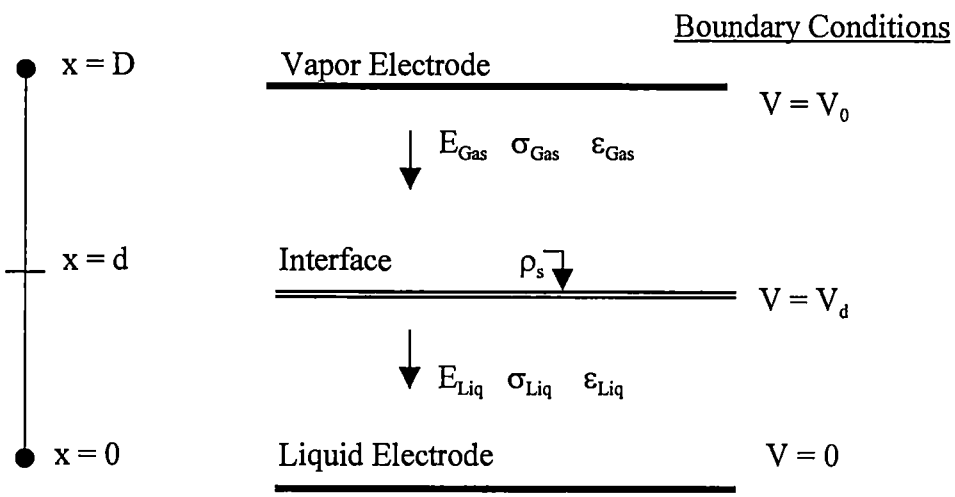


Figure 30. Comparison of depletion of 2-propanol from the bulk liquid for batch distillation runs with and without an electric field.

APPENDIX C

THEORETICAL CALCULATIONS

A one-dimensional Laplace equation was solved for the conditions of a steady-state parallel-plate capacitor with a vapor region, vapor-liquid interface, and a liquid region between the plates. The surface charge density at the interface was determined for different electrode separation distances and applied voltages using the gas and liquid properties of a 2-propanol–water system. The results were shown in Figure 28.



Theoretical Equations

$$\nabla \bullet E = \frac{\rho_v}{\varepsilon_0} \text{ (Gauss Law)} \quad @\, x = d, \quad V_{liq} \bullet \frac{\partial V_{liq}}{\partial x} = V_{gas} \bullet \frac{\partial V_{gas}}{\partial x} \qquad [2]$$

$$\nabla^2 V = 0 \qquad \text{(1-D Laplace Equation)} \qquad [3]$$

$$\nabla \bullet J = -\frac{\partial V_{liq}}{\partial t} = 0 \quad \text{(Current density at steady-state condition)} \qquad [4]$$

$$\rho_s = \frac{V}{D}\frac{\varepsilon_{gas}\gamma_{liq} - \varepsilon_{liq}\gamma_{gas}}{(1-\eta)\gamma_{liq} + \eta\gamma_{gas}}$$ Surface charge density at the interface. [5]

$$\eta = \frac{d}{D}$$ Ratio of distance between the liquid electrode and the interface to the total electrode separation. [6]

$$J = \sigma E + \varepsilon\frac{\partial E}{\partial t} = \gamma E$$ [7]

Nomenclature

D = Total distance between the vapor and liquid electrode (cm).

d = Distance between the liquid electrode and the interface (cm).

E = Electric field strength (V/cm).

J = Electrical current density (mA/cm^2).

V= Voltage at a distance from the liquid electrode (V)

V_0 = Applied voltage (V).

ε = Dielectric constant of region.

ε_0 = Permittivity of free space, 8.85×10^{-14} (F/cm).

σ = Electrical conductivity of region (S/cm).

γ = Parameter for electrical conductance.

α = Separation factor for distillation.

VITA

The author, born Oct. 27, 1973, in Birmingham, Alabama, is the son of David and Kay Blankenship and has one brother, Keith Blankenship. The author attended W. A. Berry High School in Hoover, Alabama. He was graduated from Mississippi State University in 1996 with a B. S. degree in chemical engineering.

In 1997, the author took part in research activities with the Separations Group of the Chemical Technology Division at Oak Ridge National Laboratory as part of the Professional Internship Program (ORISE). The author began graduate study in the chemical engineering program at the University of Tennessee, Knoxville in 1997.

The author is a member of the American Institute of Chemical Engineers, TAPPI, and is registered in Mississippi as an Engineer-in-Training.