

FINAL REPORT
U.S. Department of Energy

Office of Environmental Management
Environmental Management Science Program

Project Title: Phase Equilibria Modification by Electric Fields

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Project Number: 55119
Grant Number: DE-FG07-96ER55119

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Project Duration: 10/1/96-3/31/00

2. Table of Contents

1.0	Cover Sheet	1
2.0	Table of Contents	2
3.0	Executive Summary	3
4.0	Research Objectives	4
5.0	Methods and Results	4
5.1	Gas-Liquid Systems	4
5.2	Liquid-Liquid Systems	9
5.3	Solid-Liquid Systems	16
6.0	Relevance	19
7.0	Project Productivity	21
8.0	Personnel Supported	21
9.0	Publications	22
10.0	Interactions	23
11.0	Transitions	24
12.0	Patents	24
13.0	Future Work	24
14.0	Literature Cited	24
15.0	Feedback	24
16.0	Appendices	25

3. Executive Summary

The goal of this project was to investigate the use of electric fields to favorably manipulate the thermodynamic and transport properties of mixtures, so that higher separation efficiencies can be achieved. The main focus was to understand and quantify the influence of electric fields on vapor-liquid, liquid-liquid, and solid-liquid systems, which have applications in solvent extraction, sorption, distillation, and vapor stripping. Such processes are widely used by DOE for treatment of wastes and sites contaminated with heavy metals, radionuclides, and organic solvents. Particular examples of applications of vapor-liquid-equilibria modification can be found in the separation of volatile organic compounds by either vapor stripping or distillation. Improvements can also be made in liquid-liquid extraction processes of TRU, Sr, Tc, and Cs by both thermodynamic and transport enhancements. Enhanced separations of metal ions by sorption can be used to remove such metal ions as Cs, Sr, Co, Pu, Cr, Cd, and Hg from aqueous solutions.

Several people from Oak Ridge National Laboratory, University of Tennessee, and Georgia Institute of Technology collaborated on this project and several discoveries have been made regarding the application of electric fields to modify equilibrium and enhance transport in multiphase systems. Technologies, such as electroextraction and electrosorption, have been identified for further research and development activities because they offer several benefits for tank waste treatment and environmental cleanup efforts. In electroextraction, electric fields are applied to solvent extraction systems to improve transport of chemical species and phase separation. A novel means for inducing phase inversion in a liquid dispersion that provides the opportunity for increased performance and improved process control has been devised. In electrosorption, an electric field is employed to enhance the capacity and kinetics of sorption of metal ions and anions by sorbents of high electrical conductivity and porosity. This process can be used in situ for groundwater treatment, and the sorbent can be readily regenerated by simply removing the electric field.

Results of this project can be used for improved solvent extraction approaches in high-priority tank waste applications. They also provide a basis for intensified separations that can solve many environmental problems at DOE sites.

4. Research Objectives

This project has been focused on equilibrium and transport properties of gas-liquid, liquid-liquid, and solid-liquid systems under electric fields. The objective was to intensify separations methods that are used or can be used to process liquid waste or contaminated groundwater within DOE sites. Examples of processes that have been investigated are distillation (gas-liquid), extraction (liquid-liquid), and sorption (solid-liquid). Effects of electric fields on phase equilibria and interfacial transport have been investigated. So far, this project was directed at basic research on a broadly crosscutting concept. The results advocate continuation of this research in two directions, with the objective to solve problems related to solvent extraction of tank waste and groundwater treatment.

5. Methods and Results

A summary of the findings of this project is presented here. Gas-liquid and liquid-liquid systems have been studied at the Chemical Technology Division of ORNL, while solid-liquid studies focused on electrosorption were conducted in collaboration of ORNL with the School of Civil and Environmental Engineering of Georgia Tech.

5.1 Gas-Liquid Systems

Vapor-Liquid Equilibria: Experimental studies of electric-field effects on vapor-liquid equilibria have been conducted using a modified Othmer still shown in Figure 1 in which the interface was subjected to an electric field. The experimental setup for these experiments is shown in Figure 2, where a sample is obtained for concentration measurements using a gas chromatograph. In cases of binary mixtures of nonpolar fluids, the electric field had no effect

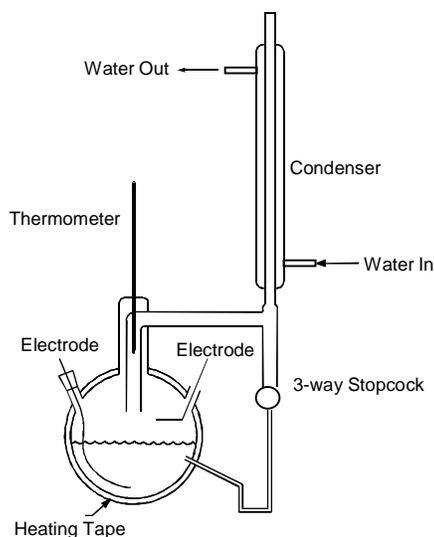
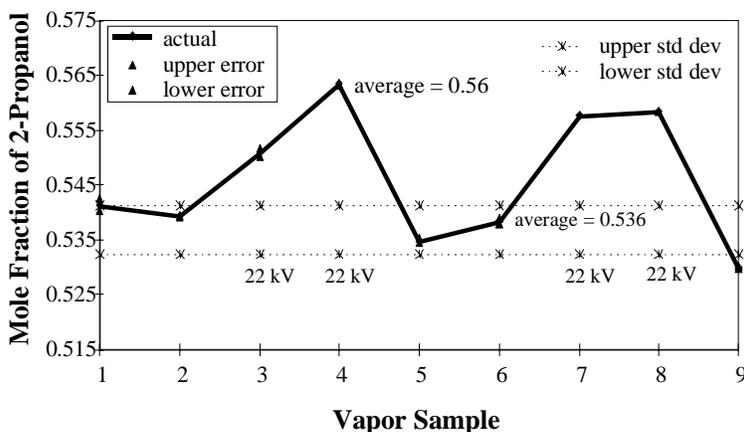


Figure 1. Modified Othmer still for vapor-liquid-equilibria experiments using electric fields.



Figure 2. Experimental setup for vapor-liquid-equilibria experiments using electric fields.

on vapor-liquid equilibria. However, when one of the constituents of the mixture was a polar component, there was an increase in the equilibrium concentration of the more volatile component in the vapor phase (Figure 3).



Because of this modification of the equilibrium, a 10% increase of the separation factor was achieved.

The mechanism has been investigated by Raman and FTIR spectroscopy. It was concluded that concentration changes in the vapor phase are caused by charge accumulation on the vapor-liquid interface.

Figure 3. Effect of a periodic electric field on vapor equilibrium concentration of 2-propanol in a water/2-propanol mixture.

Transport Enhancement: In addition to equilibrium modification, transport effects of electric fields in gas-liquid systems have been examined. The experimental setup of Figure 4 has been used to form microbubbles in water and thereby increase the interfacial area for mass transfer. As shown in Figure 5, under a sufficiently strong electric field, a stream of microbubbles is

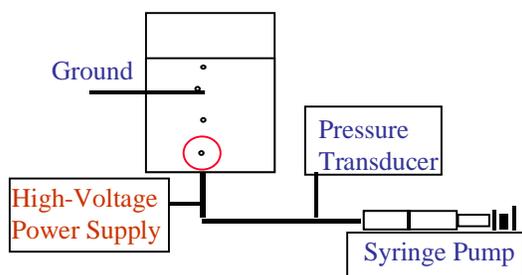


Figure 4. Experimental setup for microbubble formation by means of electric fields.

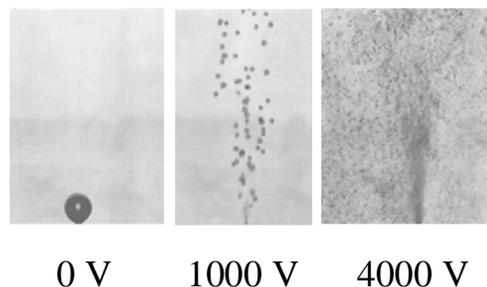


Figure 5. Microbubbles formed in water by electric fields.

ejected from an electrified capillary. Furthermore, it was also found that electric fields cause a pumping action. For example, if the syringe pump of Figure 4 is removed, air from the ambient atmosphere is pumped in the water column through the electrified capillary and is atomized to form microbubbles upon entering the water phase. This phenomenon is demonstrated in Figure 6.

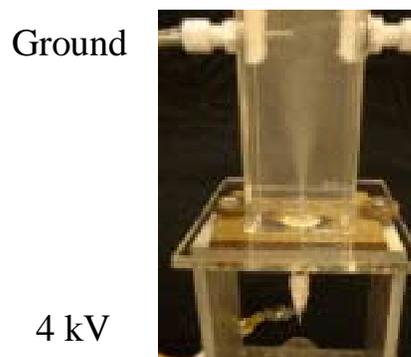


Figure 6. Pumping and atomization of air in water by an electric field.

Formation of microbubbles and pumping of a gas phase into a liquid phase can both be used to enhance transport in a distillation process. The setup of Figures 7a and b has been used in these experiments.

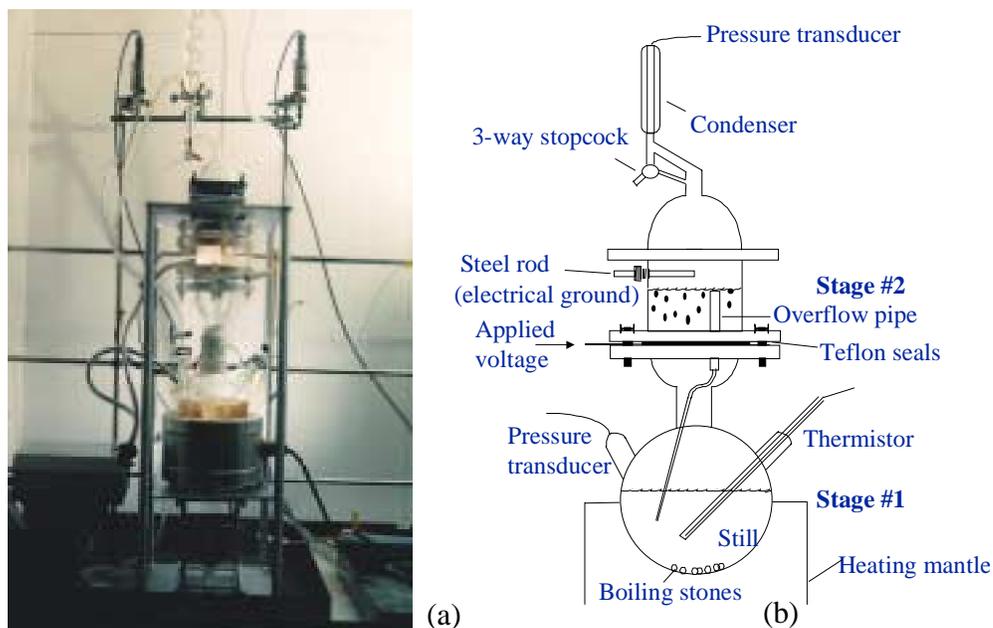


Figure 7. Experimental setup for the investigation of transport enhancement in distillation by means of electric fields.

The effect of applied electric fields on the distillation of a binary mixture of water and 2-propanol was studied. It was found that the distillation column performance, i.e., the plate efficiency and distillate flow rate, could be greatly increased by application of a direct-current (DC) electric field. Figure 8 shows the change of isopropanol concentration in the distillate with an increase in the applied voltage. A comparison for the distillation results obtained under conditions with and without an applied electric field is provided in Table 1.

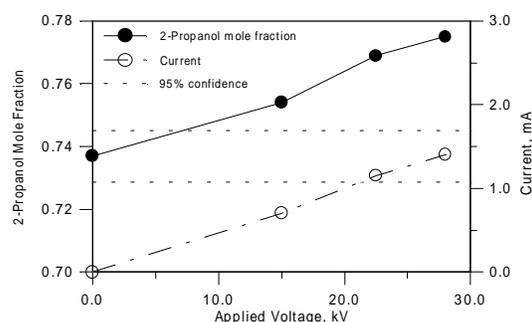


Figure 8. Effect of the applied voltage on the distillate concentration.

Table 1. Comparison of Distillate Concentration With and Without an Applied Voltage.

Parameter	Applied voltage 0 kV	Applied voltage 14 kV
Mole fraction of 2-propanol in distillate	0.738	0.754
Average bubble diameter, mm	4.4	1.8
Vapor flow rate (or distillate rate), mL/min	~2.0	~9.0
Electric energy converted to heat, kJ/min	15	19
$N_{V=14}/N_{V=0}$ *	65.7	
$A_{V=14}/A_{V=0}$ **	11.0	

* $N_{V=14}$ and $N_{V=0}$ are total numbers of bubbles in the liquid under 14 and 0 kV.

** $A_{V=14}$ and $A_{V=0}$ are total vapor-liquid contacting areas under 14 and 0 kV.

For a binary system of water/2-propanol, a 2.2% increase in the plate efficiency of the second stage and a fourfold increase in the distillate flow rate were obtained by applying a voltage of 14 kV. The cause for such an increase in the distillation efficiency is the enhancements in mass and heat transfer rates and the vapor transport rate through the plate under an applied electric field. The vapor bubble size decreased dramatically thus increasing the total vapor-liquid contacting area. Figure 9 shows the images of vapor bubbles in the liquid phase under different voltages.

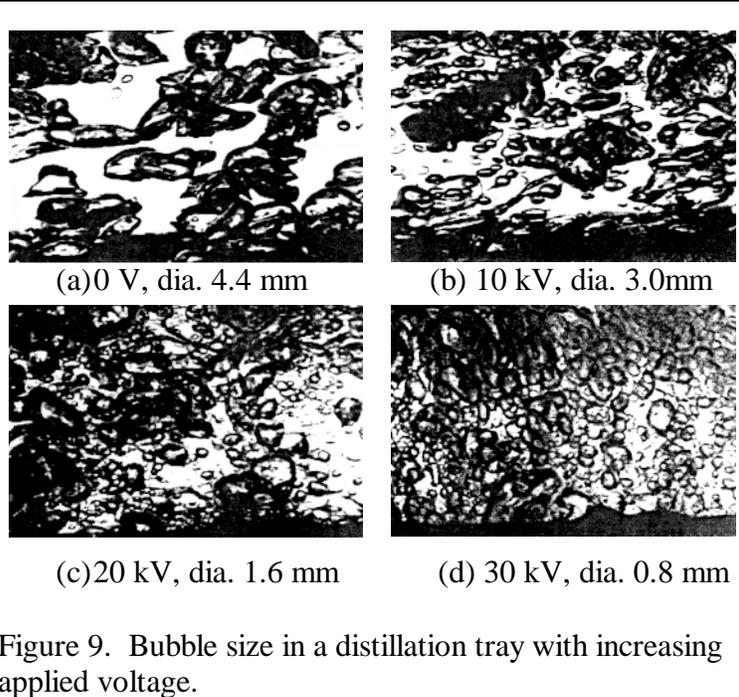


Figure 9. Bubble size in a distillation tray with increasing applied voltage.

A 20% increase in the heating energy input was observed under 14 kV, and the extra energy consumed by the electric field was very small (28 watts) due to the very low current (2 mA). The electric power input and the distillate flow rate are shown in Figure 10.

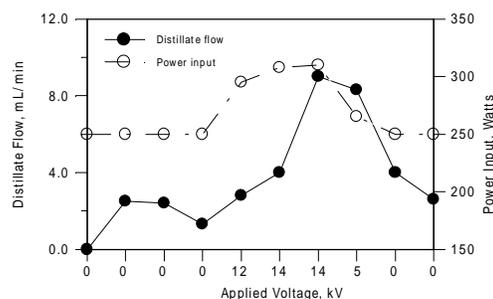


Figure 10. Distillation flow rate and total power input at different applied voltages.

More details about vapor-liquid equilibria and distillation enhancement under electric fields can be found in two peer-reviewed publications (Blankenship et al., 1999a and b; see Accomplishments section) and a Master's thesis (Blankenship, 1999).

Electrooxidation: Microbubbles are particularly desirable in ozonation of organic compounds in water. The use of ozone in water and wastewater treatment systems has been shown to be a mass-transfer limited process. The most effective way to overcome this limitation is to increase the interfacial area available for mass transfer by decreasing the size of the ozone containing gas bubbles that are dispersed in solution. Electrohydrodynamic (EHD) atomization and micromixing of ozone into water has been proven as an energy-efficient method for increasing the rate of mass transfer of ozone into the solution and thus the rate of phenol oxidation. Studies conducted using a laboratory-scale column (Figure 11) demonstrated an increase in the rate of mass transfer on the order of 40%, when the applied voltage was increased from 0 to 4 kV, as a result of the smaller bubbles generated by EHD atomization and micromixing. The EHD approach was also shown to be more effective than conventional systems (Figure 12).

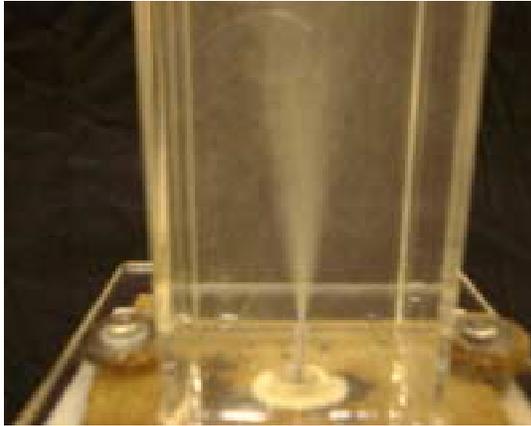


Figure 11. EHD atomization of ozone-containing gas in water.

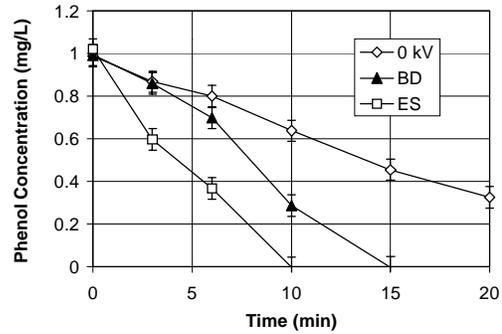


Figure 12. Ozonation of phenol in water; electroatomization of ozone increases the ozonation rate; BD=bubble diffuser; ES=electrostatic spraying.

Ozone is currently used to deactivate microorganisms and remove organic contaminants. However, it was found in our studies that microorganisms and organic species in water can be destroyed without using ozone. As can be seen in the photo (Figure 13), by increasing the applied voltage in an EHD atomization process, a pulseless corona-discharge phenomenon occurs. In the presence of oxygen in water, this phenomenon generates various chemical species, including free radicals (Figure 14) that can be used to destroy organic pollutants in water. This novel approach combines corona discharge with electrohydrodynamic atomization and micromixing of oxygen, forming microbubbles. We have shown that pulseless corona discharge effectively removes organics, such as phenol and methylene blue in water. In Figure 15, the corona-discharge method is comparable to the direct use of ozone at a high voltage. Electrooxidation results have been summarized in a paper submitted for publication in a peer-reviewed journal (Shin et al., 2000).

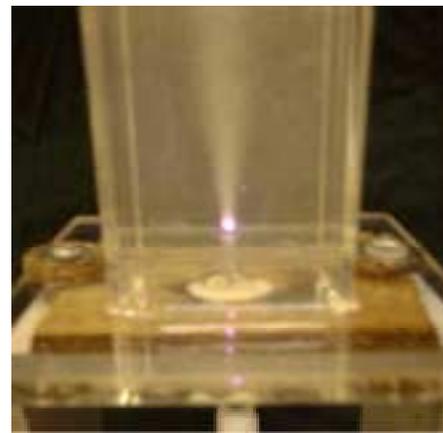


Figure 13. EHD atomization of oxygen under corona discharge.

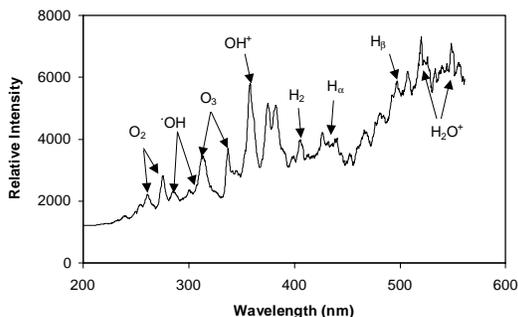


Figure 14. Identification of radical species formed with oxygen atomization under corona discharge.

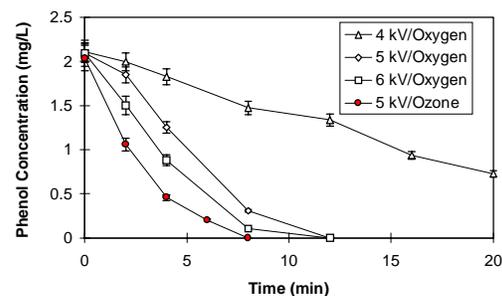


Figure 15. Electrooxidation of methylene blue; the oxidation rate by the corona-discharge method is sufficiently high to remove the need of ozone.

5.2 Liquid-Liquid Systems

Liquid-Liquid Equilibria: Experimental studies of electric-field effects on liquid-liquid equilibria were conducted using the experimental system of Figure 16. Because of interfacial instabilities, the electric-field strength applied across the interface was limited. Under the maximum field strength possible, no changes in liquid-liquid equilibrium were observed in ternary systems including water/2-propanol/toluene and water/hexane/toluene. As the applied voltage was increased, interfacial instabilities were observed that led to the formation of an emulsion in each phase, contaminating the samples taken for concentration measurements. Further studies were focused on interfacial phenomena including column formation at the interface, drop-interface coalescence, and drop-drop coalescence under electric fields and how these phenomena affect the behavior of liquid dispersions.

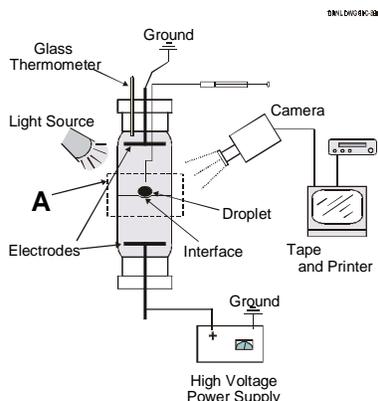


Figure 16. Schematic of the setup for liquid-liquid studies.

Interfacial Instability: The interfacial instability and formation of multiple liquid columns on a liquid-liquid interface has been studied using an apparatus with a large distance between the interface and the parallel mesh-electrodes under a vertically applied, DC electric field (Figure 16). Mixtures of water, toluene, and isopropanol, forming two phases, were used. Liquid columns were then formed on the interface. These columns were drawn from the aqueous phase by the electric force, with their upper ends either free or anchored on the upper electrode, depending on the operating conditions and the system properties. Under the action of the electric field, the columns moved and twisted irregularly on the interface with rotation about the column axis until they disintegrated into streams of droplets. The formation and morphology of the liquid columns were determined by the strength of the electric field and the physical properties of the fluids. Pictures of the columns are shown in Figures 17 and 18.

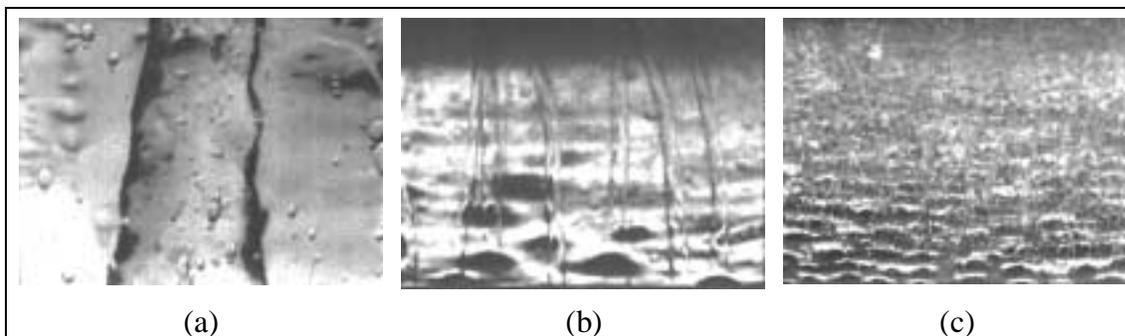
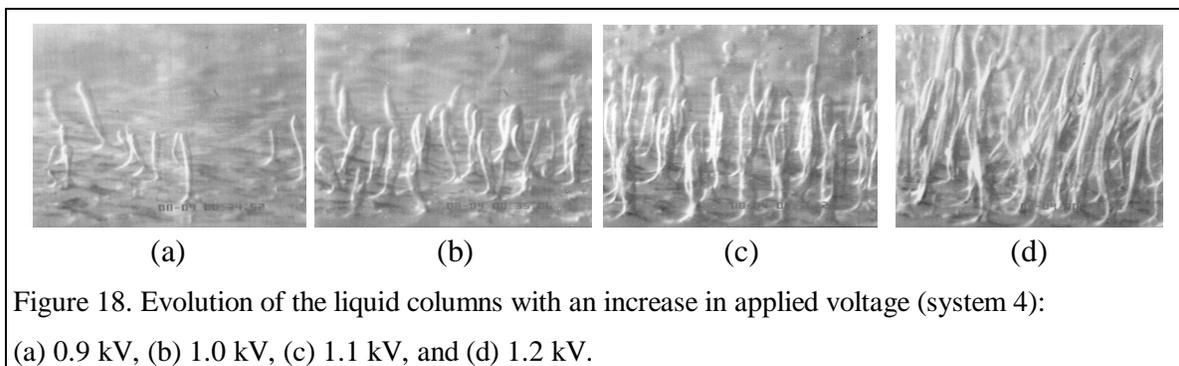


Figure 17. Liquid columns formed at the liquid-liquid interface: (a) system 1, single column at 20 kV; (b) system 2, multiple columns at 4 kV; and (c) system 3, multiple columns at 1.5 kV; systems 1, 2, and 3 have different concentrations.

The total number of columns and their average height, diameter, and slenderness ratio increased with increasing applied voltage. Lowering the interfacial tension, reducing the density difference between the two phases, and increasing the permittivity of the conducting phase decreased the critical voltage for interface instability onset and the threshold voltage for stable column formation.



Theoretical analysis was carried out by a model developed by Taylor and McEwan with assumptions of instantaneous charge relaxation and negligible interaction of electric and viscous shear forces.

$$V_c = \left(\frac{2}{\epsilon_{org}} \right)^{1/2} [(\rho_{aqu} - \rho_{org})g\gamma]^{1/4} h_0 \quad (1)$$

$$\lambda = 2\pi \left[\frac{\gamma}{(\rho_{aqu} - \rho_{org})g} \right]^{1/2} \quad (2)$$

The model overestimates the critical voltage for instability onset and underestimates the Taylor wavelength because it does not consider the effect of free surface charge, which may be important in the present systems. Qualitative analysis was also made for column growth, using an idealized electrohydrodynamic model that balances the electric force, gravity force, and interfacial tension force.

$$2 \frac{dK_c}{dx} \gamma + g(\rho_{aqu} - \rho_{org}) \frac{dh(x)}{dx} = \frac{\epsilon_{org} [d(E^2)/dx]}{8\pi}, \quad (3)$$

The experimental results can be qualitatively explained by these simplified theoretical models. However, the mechanisms of the tornado-like motion, periodic formation and disappearance, and size change of the columns are not well understood. The results obtained here may be useful in the development of new type of liquid-liquid contactors for solvent extraction and floating zone reactors. Details on interfacial behavior under electric fields can be found in Dong et al. (2000; see Accomplishments section).

Drop–Interface Coalescence: Drop-interface coalescence was investigated in terms of coalescence time to better understand the effects of electric fields on drop coalescence (Dong et al., 2000). Coalescence time, which is defined as the period between the arrival of the drop at the interface and its coalescence with its homophase, was studied under varying applied voltage for aqueous and organic drops. Figure 19 shows the images of aqueous and organic drops in contact with the liquid-liquid interface. The immiscible liquid–liquid systems used in the drop–interface coalescence experiments are listed in Table 2, along with some important physicochemical

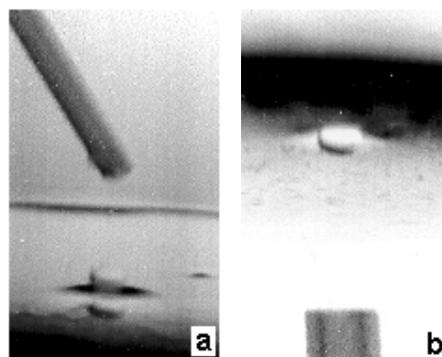


Figure 19. Drops in contact with the interface: (a) aqueous and (b) organic.

properties adjusted by additions of a small amount of specific chemicals. These systems had an identical volumetric composition of 0.34 water–0.24 toluene–0.42 isopropanol except system 1, which had a volumetric composition of 0.29 water–0.29 toluene–0.42 isopropanol.

Table 2. Liquid-Liquid Systems Used in this Work^a

Sys. no.	Additive	$\sigma_{\text{org/aqu}}$ (dyn/cm)	C_{org} (μMHO)	C_{aqu} (μMHO)	pH	ζ^c (mv)	ρ_{org} (g/cm^3)	ρ_{aqu} (g/cm^3)	η_{org} (cP)	η_{aqu} (cP)
1	None	< 0.2 ^b	0.006	0.35	6.22	---	0.872	0.929	1.17	3.12
2	None	< 0.2	0.008	0.45	6.32	---	0.869	0.936	1.16	3.09
3	NaCl	< 0.2	0.120	35.6	6.25	- 5.7	0.869	0.936	1.15	2.92
4	HCl	< 0.2	0.100	34.8	2.52	0.0	0.869	0.936	1.17	2.98
5	NaOH	< 0.2	0.116	56.2	10.1	-16.2	0.869	0.936	1.17	3.01

^a $\sigma_{\text{org/aqu}}$ is the organic/aqueous interfacial tension; C_{org} and C_{aqu} are the conductivities of organic and aqueous phases, respectively; ρ_{org} and ρ_{aqu} are the densities of organic and aqueous phases, respectively; η_{org} and η_{aqu} are the viscosities of organic and aqueous phases, respectively. ^b The lowest interfacial tension measurable by the instrument. ^c ζ potential of the organic phase drops in the aqueous phase.

Results of the measurements of coalescence time for aqueous and organic drops are presented in Figure 20. For an organic drop, the coalescence time decreased when the applied voltage increased, under negative polarity (i.e., the lower electrode was electrified by a negative-polarity voltage), and increased when the applied voltage increased, under positive polarity. For an aqueous drop, the coalescence time decreased when the applied voltage increased, regardless of the electric field polarity. When the applied voltage was higher than a certain level, the aqueous drop coalesced upon arrival at the interface.

For the case of an organic drop, the drop–interface coalescence is driven by the buoyant force. Because of the preferred adsorption of OH^- on the organic surface, the drop has a negatively charged double layer (see zeta-potential measurements in Table 2). Thus, when a positive polarity is used, an electrostatic force directed toward the lower electrode is applied on the drop acting against buoyancy and inhibiting coalescence. In contrast, when a negative polarity is used, the coulombic force is directed toward the upper electrode facilitating drop–interface coalescence. Because of higher conductivity, aqueous drops are polarized. The interface charge under the electric field is of opposite sign than that of the drop fraction approaching the interface. Therefore, an attractive coulombic force acts between the drop and interface, facilitating coalescence regardless of the field polarity.

To further investigate the effects of an applied electric field on drop–interface coalescence, experiments were performed using liquid–liquid systems with varying levels of ionic strength and pH values and with the lower electrode at positive polarity. For aqueous drops, higher ionic strength resulted in a faster coalescence time in the absence of an electric field and a more rapid

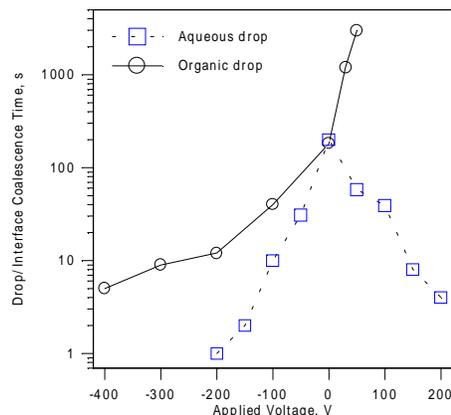


Figure 20. Coalescence time vs. applied voltage for system 1 in Table 2. Drop-dia.: organic 1.8mm and aqueous 1.6mm.

decrease in the coalescence time with an increase in the applied voltage. The organic drop–interface coalescence time was similar for systems 3 (pH 6.25) and 4 (pH 2.52), while the coalescence time for system 5 (pH 10.1) was significantly longer than those for systems 3 and 4, both with and without applied electric fields. This phenomenon was explained by the increasing negative values of zeta-potential with increasing pH. A high pH value enhances the double-layer force and prolongs the coalescence time of organic drops.

Drop–Drop Coalescence: Drop-drop coalescence was investigated to better understand the coalescence mechanism under an applied electric field. Drop–drop interactions were studied under different applied electric voltages using the apparatus shown in Figure 21. Drop-drop coalescence was visualized for the case of water-in-organic with and without an applied electric

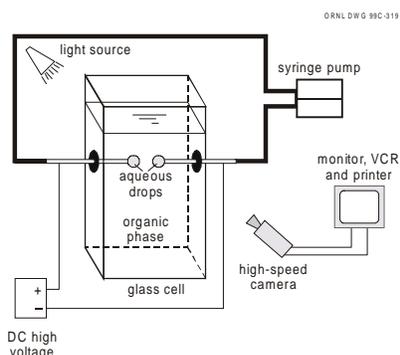


Figure 21. Setup for drop-drop coalescence studies.

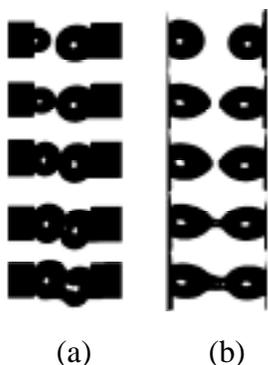


Figure 22. Coalescence of water drops in toluene:(a) 0 V; (b) 1 kV.

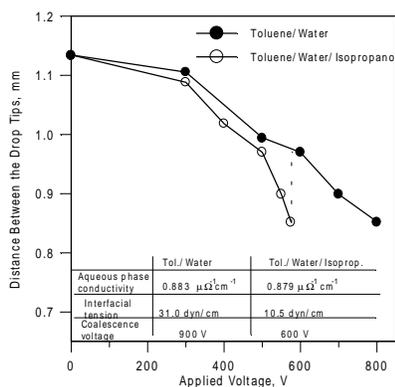


Figure 23. Drop coalescence under electric fields for systems with different surface tension.

field (Figures 22a and b). Without an electric field applied, drop coalescence occurs only if the drops are pushed in contact with each other and squeeze out the organic film between the drops. This is shown in Figure 22a, where the drops are deformed before coalescence. In Figure 22b, two aqueous drops were first loaded at the tips of the capillary tubes with a distance of 1.13 mm between the drop tips. Then, a voltage of 1 kV was applied to one of the capillaries while the other was connected to an electrical ground. Under the electric field, the two aqueous drops deformed and stretched to each other due to polarization that caused an attractive coulombic force to appear. The drops coalesced as soon as their tips made a physical contact and the coalescence process took only 5 ms.

Drop-pair coalescence under electric fields was also conducted to examine the effect of interfacial tension on the coalescence process. Two aqueous drops were first loaded at the tips of the capillary tubes with a distance of 1.13 mm between the drop tips. The applied voltage was increased from zero to the level at which the drops coalesced and the distance between the tips of the two drops was measured under different applied voltages. As shown in Figure 23, under the same applied voltage, the distance between the drop tips was shorter for the lower interfacial tension system. In addition, drops coalesced at a lower applied voltage in the system with the lower interfacial tension. These observations indicate that lowering interfacial tension facilitates aqueous drop coalescence in an organic phase in the presence of an applied electric field because the drops with lower interfacial tension can be deformed and elongated more readily under an applied electric field. An opposite effect occurs in the absence of the electric field, i.e., lower interfacial surface tension increases the coalescence time.

Phase Inversion: Liquid-liquid dispersions are involved in many environmental and chemical processes such as solvent extraction and emulsion polymerization. In this work, experiments were conducted to study the effect of an electric field on turbulent liquid-liquid dispersions. The objective was to provide basic knowledge and data necessary to develop energy-efficient and cost-effective separations. Phase inversion of a liquid-liquid dispersion occurs when the dispersed phase becomes continuous and the continuous phase becomes dispersed. In a plot of organic volume fraction versus agitation speed, there is a region called ambivalence regime between two lines in which either phase can be dispersed or continuous, depending on the initial status. Phase inversion and the ambivalence regime of liquid-liquid dispersions were studied under applied alternating-current (AC) and direct-current (DC) electric fields, using a stirred tank (Figure 24). The phase inversion point was determined by on-line monitoring of abrupt changes in electrical conductivity for nonelectric field condition and electrical current under electric fields.

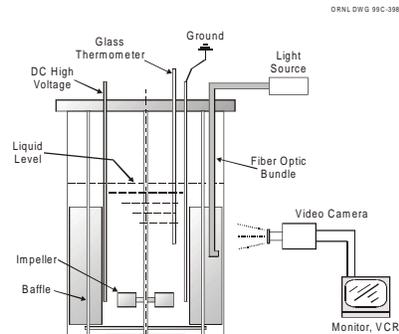


Figure 24. Stirred-tank used for phase inversion studies.

The ambivalence behavior of liquid-liquid dispersions in a stirred vessel was determined under AC and DC electric fields. The immiscible liquid-liquid systems contained water and toluene as the two basic components, with the interfacial tension adjusted by addition of isopropanol. The pH and ionic strength were also adjusted by addition of hydrochloric acid, sodium hydroxide, and sodium chloride. Effects of operating conditions, such as agitation speed and applied voltage, and physical properties, such as aqueous-phase conductivity, organic-phase viscosity, pH, and interfacial tension, were investigated. By increasing the applied voltage, the ambivalence regime was narrowed and shifted toward higher volume fractions of the organic phase (Figure 25).

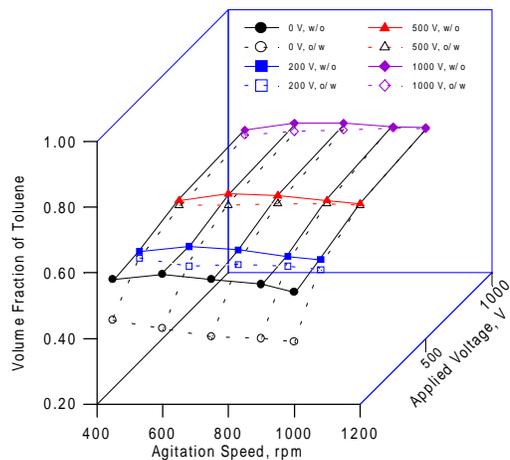


Figure 25. Phase inversion under AC electric fields for a toluene/water system. — inversion from O/W to W/O; - - - inversion from W/O to O/W.

When the dispersed system reaches a steady state, the droplet breakup rate is equal to the coalescence rate. If the dispersed phase is more conductive than the continuous phase, an applied electric field facilitates coalescence of the droplets, thus shifting the dynamic equilibrium. The mechanism of electric-field effects on phase inversion is depicted in Figure 26. Water droplets, which are more conductive than toluene, are polarized under an electric field. Two drops approaching each other are attracted because

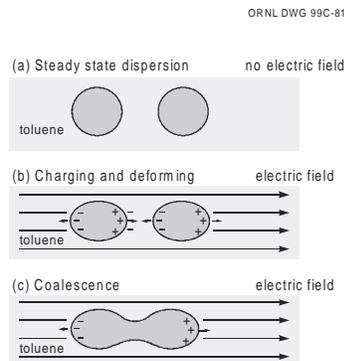


Figure 26. Coalescence of water drops under an electric field.

they have opposite charges at the approaching tips. The attractive coulombic force draws the droplets together into coalescence. On the other hand, breakup of the polarized drops leads to the formation of charged droplets, which also have higher collision and coalescence rates. Induced phase inversion by an electric field indicates that the presence of larger droplets in the dispersion, due to enhanced coalescence under the electric field, increases further the coalescence rate of droplets so that the breakup rate cannot follow.

The phenomenon of electric field-induced phase inversion may offer several advantages for manipulation and control of liquid-liquid processes, including the following: (i) To ensure that the aqueous phase remains the continuous phase, even at a high volume fraction of the organic phase. (ii) To increase the volume fraction of a dispersed organic phase without causing phase inversion. (iii) To correct a phase inversion, which is currently considered a catastrophic event, without having to shut down the process. (iv) To enhance mass-transfer rates from one phase to the other by inducing a phase-inversion cycle. For example, as illustrated in Figure 27, point **A** is located above the ambivalence regime in the absence of an electric field meaning that the dispersion is water-in-oil (W/O, organic continuous). When an AC voltage of 183 V is applied,

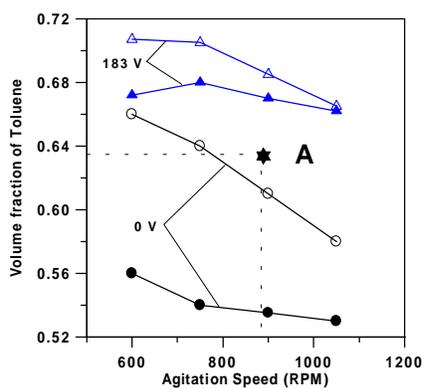


Figure 27. Effects of electric fields on phase inversion in the toluene-water system.

the ambivalence regime is narrowed and shifted upward so that point **A** is located below the ambivalence regime meaning that the dispersion is oil-in-water (O/W, organic dispersed). Therefore, by switching the voltage ON and OFF, the dispersion status of point **A** will be inverted from W/O to O/W and from O/W to W/O, correspondingly. It has been shown that such a phase inversion cycle induced by a periodic electric field enhances the mass-transfer rate across the interface. The effects of the physical properties of the liquid-liquid system on the ambivalence regime were also studied. Results have been summarized in two papers that have been submitted for publication in peer-reviewed journals.

Drop-Size Distribution: The steady-state drop-size distribution of turbulent liquid-liquid dispersions was determined as a function of electric-field strength. The effects of electric fields on drop-interface and drop-drop coalescence indicated that electric fields can be used to control the drop size of liquid-liquid dispersions in stirred tanks. To further investigate this hypothesis, we conducted experiments using the tank of Figure 24. Experiments were performed in an applied voltage range of 0–3 kV. Drop-size distributions were measured at a fixed agitation speed of 500 rpm. A ratio of 1:9 for dispersed:continuous volume was used for both water-in-toluene and toluene-in-water dispersions. The results of cumulative drop-size-distribution measurements are graphically shown in Figures 28 and 29. Figure 28 shows that application of an electric field did not change the size distribution of the toluene droplets. For a water-in-organic dispersion, the effect of the electric field was stronger. An increase in the applied voltage significantly increased the size of the dispersed aqueous drops. As shown in Figure 29, the cumulative size distribution shifted to larger size as the applied voltage was increased. The average drop diameters were 0.34 and 0.62 mm under applied voltages of 0 and 3.0 kV (positive

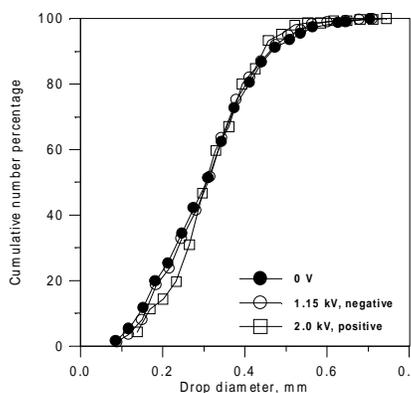


Figure 28. Cumulative size distribution of toluene drops in water.

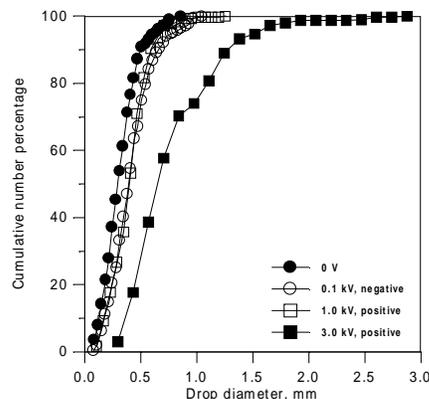


Figure 29. Cumulative size distribution of water drops in toluene.

polarity), respectively.

Electropumping and Electroatomization: Electric fields were also used to form microdroplets in a similar geometry where microbubbles were formed. Using the setup of Figure 6 for example, which was used to investigate pumping and atomization of a gas in a liquid, we were able to show the same effects of electric fields for kerosene (colored red) in water. Results are demonstrated in Figure 30, where the color of the liquid becomes red with time due to the presence of kerosene microdroplets in water. For more details, see Tsouris et al. (1998).

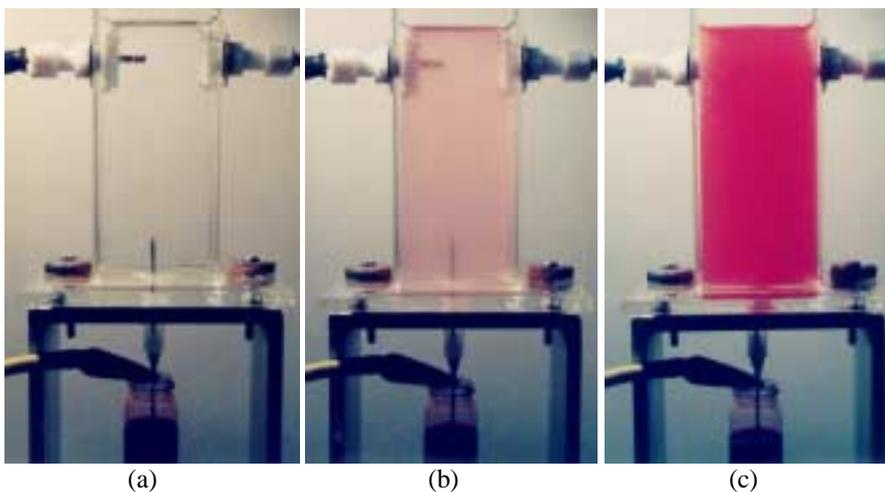


Figure 30. Pumping and atomization of kerosene (colored red) from a reservoir underneath the tank in water by means of an electric field. A voltage of 4 kV is applied on the capillary immersed in kerosene and an electrical ground is connected to water. (a) time=0; (b) time=2 min; (c) time=10 min.

Liquid-liquid phenomena investigated in this project can be readily employed to enhance mass transfer in liquid-liquid extraction. Preliminary investigations discussed in the Project Narrative indicate that the rate of mass transfer under a phase-inversion cycle is significantly increased. In addition, drop-drop and drop-interface coalescence enhanced by electric fields can be used in phase separation, especially in cases where a stable emulsion or foam is formed. Electric fields can therefore be applied to intensify existing and new extraction processes.

5.3 Solid-Liquid Systems

Equilibrium Experiments of Electrosorption: Bench-scale equilibrium experiments of electrosorption were conducted by applying a DC voltage (V) between two parallel-plate carbon aerogel electrodes. Carbon aerogel electrodes were made by attaching two carbon aerogel composites (Marketech, Port Townsend, WA) on two titanium plates that served as both current collectors and structural supports for the electrodes. Each sheet of carbon aerogel has dimensions of $15.6 \times 8 \times 0.0127 \text{ cm}^3$. The separation distance between the electrodes was maintained at 0.6 cm. The effects of experimental parameters, such as type of chemical species, solution concentration, applied voltage, pH, and flow-rate, on the deionization capacity of electrosorption were investigated. In most of the experiments, NaF solutions were used. Other species such as NaCl, NaBr, and NaI were also used to study the effect of type of anions on metal ion removal.

The effect of type of anion species on the electrosorption capacity at different concentrations is shown in Figure 31. In each set of columns, the blue bar represents the chemisorption capacity and the red one represents the electrosorption capacity. The chemisorption capacity is defined as the amount of ion removal without an applied voltage. On the other hand, the electrosorption capacity is defined as the amount of ion removal with an applied voltage. From the experimental results, it was found that the chemisorption capacity is relatively small compared to the electrosorption capacity. Also, the capacity of anion removal increases in the order of Cl^- , Br^- , and I^- . The reason is probably because the iodide ions have a higher partial charge-transfer coefficient than the bromide and chloride ions. The partial charge-transfer coefficient is an indicator of how many electrons can be released from an adsorbate to an adsorbent during adsorption. In addition, it was observed that at higher concentrations, the electrosorption capacity is increased. Since sodium ions are the only cations shown in the system, it can be concluded that the electrosorption capacity for these electrolytes is limited by anions.

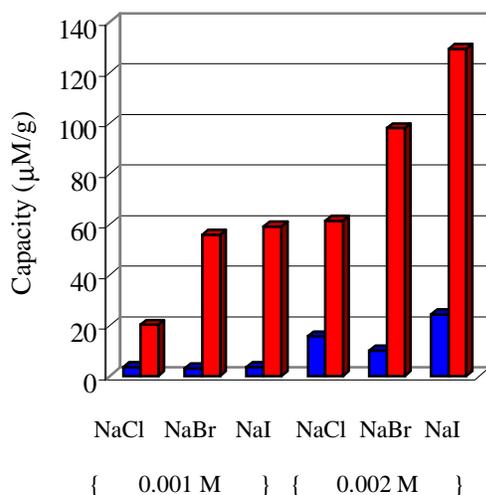


Figure 31. Effect of different anions on the electrosorption capacity; $V=1.2 \text{ V}$.

The deionization capacity of carbon aerogel was found to increase with an increase of the initial solution concentration and applied voltage. Although the electrosorption capacity increased as the initial concentration was increased, the removal efficiency of NaF dropped from 70% to 15% as the initial concentration was increased from 30 ppm to 1000 ppm. Figure 32 also indicates that the electrosorption capacity did not increase much at low applied voltage ($< 0.6 \text{ V}$), and then increased quickly when the applied voltage was increased from 0.6 to 1.3 V. The increasing rate of deionization capacity decreased at high voltage ($> 1.3 \text{ V}$), and also bubbles were observed as

applied voltage became higher than 1.2 V. The reason that electrosorption capacity does not increase much as voltage is increased may be due to the electrical capillary maximum (ECM) of the carbon aerogel composite. It was found from experimental results that the value of ECM is around 0.18 V with respect to one electrode. The electrostatic driving force, therefore, will be used to balance the ECM voltage until the applied voltage increases beyond 0.36 V. From the experimental results, it was also observed that electrosorption capacity changed with the age of the carbon aerogel. It can be concluded that electrosorption is more efficient in dilute systems and a set of optimizing operating conditions can be obtained for the application of the process.

During the experiments, it was observed that solution pH increased very quickly from about pH 7 to pH 10 when voltage was applied and slowly dropped back to its initial pH value. It implies that when voltage is applied, OH⁻ ions are released from the electrode surface. Single-side carbon aerogel experiments were therefore conducted, in which one of the electrodes (anode or cathode) was made by carbon aerogel and the other by platinum. It was observed that the solution pH did not change much when carbon aerogel electrode served as cathode; the solution pH, however, increased when carbon aerogel electrode served as anode. This result indicates that the increase of pH in the experiments of two-side carbon aerogel electrodes is due to anode reactions.

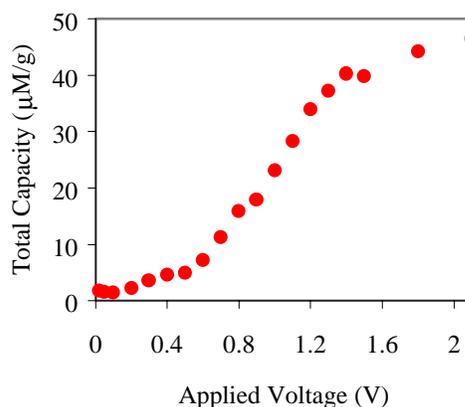


Figure 32. Effect of applied voltage on electrosorption capacity; 100 ppm NaF.

The effect of flow-rate on the equilibrium electrosorption capacity was studied by varying the flow-rate from 8 mL/min to 54 mL/min. The experimental results showed that the difference of equilibrium capacities at different flow-rates was insignificant. It means that the change of flow rate does not affect the equilibrium capacity of electrosorption.

Model Development of Electrosorption: Electrical double layer capacity can be interpreted by the Gouy-Chapman theory on a flat surface. For porous electrodes such as carbon aerogel, the electrical double-layers form inside the pores instead of the electrode surfaces, which greatly increase the effective area of the porous electrode and the electrical capacity as well. However, when the pore size is of the same order of magnitude as the electrical double-layer thickness, the electrical double-layers inside the pore will overlap onto each other and lose their electrical capacities. Since this overlapping effect only exists in microporous (< 2 nm) and part of mesoporous (2-50 nm) regions, most of the electrical double-layer models do not take this effect into consideration. Carbon aerogel composites have a significant fraction of micropores; it is, therefore, necessary to consider this overlapping effect. The cut-off diameter is the smallest pore size that the electrical double layer can exist, and can be determined by

$$d_m = \frac{2}{-\kappa} \ln \frac{[\exp(e\psi_d / kT) + 1](e\psi_d / kT)}{8[\exp(e\psi_d / 2kT) - 1]} \quad (4)$$

where d_m is the cut-off diameter, κ is the Debye-Hückel parameter, e is the elementary charge, k is the Boltzmann constant, T is the absolute temperature, and ψ_d is the diffuse layer potential of the electrical double layer. The cut-off diameter d_m usually ranges from 10 to 100 Å, depending upon the diffuse layer potential and Debye-Hückel constant κ . Pores with diameter less than the cut-off value will not contribute to the electrosorption of ions. Figure 33 shows the effect of pore size on total capacity and also the cut-off diameter at different concentrations. It is found that when the pore size is smaller than 40 Å, the total capacity decreases rapidly and reaches zero after a specific pore size. This cut-off diameter decreases as the concentration is increased.

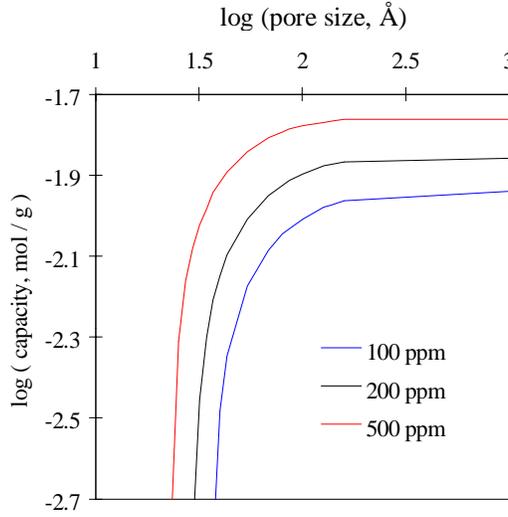


Figure 33. Cut-off diameter at different concentrations; $V=0.6$ V.

An electrical double layer model that considers double-layer overlapping correction has been developed to predict the total capacity of electrosorption on carbon aerogel. This model can be used to predict the total capacity under various values of concentration and applied voltage. In this electrical double layer model, the diffuse layer potential, ψ_d , is one of the most important parameters needed to calculate the electrosorption capacity. For a carbon aerogel electrode with applied voltage V , the diffuse layer potential can be expressed as follows:

$$\psi_d = \frac{V}{2} - \phi_{ecm} - \int_0^{\sigma_0} \frac{1}{C_1(\sigma_0)} d\sigma_0 \quad (5)$$

where ϕ_{ecm} is the electric potential at the electric capillary maximum, C_1 is the inner layer capacitance, V is the applied voltage, and σ_0 is the surface charge density. By inserting this equation into the Poisson-Boltzmann equation, the surface charge density can be calculated. The electrosorption capacity is, thus, calculated by integrating the individual capacity in each pore over the pore size distribution data. The theoretical charge density can be calculated using the following equation:

$$\sigma_0 = \sqrt{4\varepsilon RTI} \left[\cosh \left(\frac{e \left(\frac{V}{2} - \phi_{ecm} - \frac{\sigma_0}{32} \right)}{kT} \right) - \cosh \left(\frac{e\psi_m}{kT} \right) \right]^{1/2} \quad (6)$$

where R is the ideal gas constant, I is the ionic strength, ε is the dielectric constant, and ψ_m is the electrical potential at the centerline of the pore. The surface charge density equation can be solved by iteration. The comparison between modeling results and experimental data is shown in Figure 34. It shows that the total capacity increases with applied voltage. It is also demonstrated that without including the overlapping effect, the electrosorption capacity (indicated in the figure with blue line) will be largely overestimated. On the other hand, by including the overlapping effect (indicated in the figure with red line), a good agreement between experimental results and theoretical calculations is found. The deviations observed at high voltage are attributed to faradaic reactions that may become significant at high voltage and decrease the total capacity. More details on the model developed in this work can be found in a paper that has been submitted for publication in a peer-reviewed journal (see Yang et al., 2000, in the Accomplishments section.)

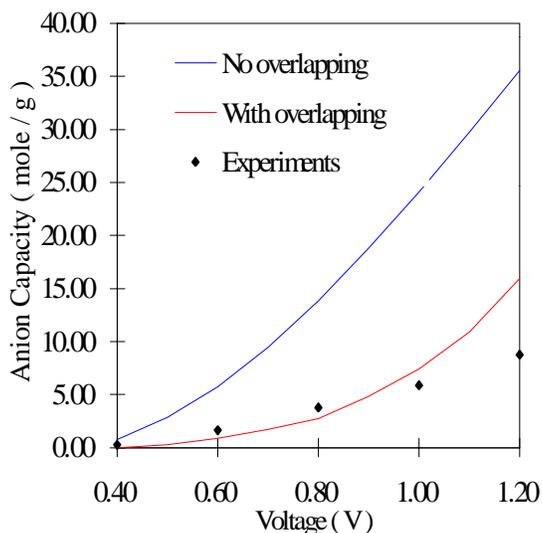


Figure 34. Modeling and experimental results of total anion capacity as a function of applied voltage; 100 ppm NaF.

Electrosorption phenomena investigated in this project can be readily employed to enhance the separation of metal ions and anions from aqueous solutions. Preliminary investigations discussed in the Project Narrative indicate that electrosorption is an ideal process for groundwater treatment. It can be applied in situ, and can be readily regenerated by removing the electric field and redirecting the flow. The basic knowledge obtained here can be used to design the properties of the electrode material so that the electrosorption capacity is maximized.

6. Relevance, Impact, and Technology Transfer

- a. The scientific knowledge obtained by this project focuses on solvent extraction and electrosorption. Novel solvent extraction approaches are directly applicable in high-priority tank waste problems that are currently critical for DOE Environmental Management. Electrosorption is also addressing critical DOE Environmental Management problems related to subsurface contamination and liquid waste treatment.

- b. The new scientific knowledge generated by this project can be used to enhance the efficiency of solvent extraction and electrosorption. In solvent extraction, a novel liquid-liquid contactor using an electric field can achieve a higher separation factor than those of conventional contactors in a shorter time and with less energy consumption. An electric field can also be applied to existing contactors, such as the centrifugal contactor, to eliminate undesirable back-flow of the liquid phases. Electrosorption can be used to enhance sorption capacity so that lower sorbent quantity and reactor volume will be needed to remove metal ions from aqueous solutions, such as contaminated subsurface water. Electrosorbent can be readily regenerated by just turning the electric field off and can be used in-situ for groundwater treatment. These features of both solvent extraction and electrosorption will lead to lower cost and reduced risks and schedules, while meeting DOE compliance requirements.
- c. During the first two years of the project, work was mainly focused on fundamental research investigating the effects of electric fields on equilibria and transport of multiphase systems. In the third year, the effort was to bridge the knowledge obtained in the first two years with applications. That effort was partially successful. More time and effort is needed to complete the bridging of fundamental knowledge with applications in solvent extraction of tank waste and electrosorption of aqueous wastes and groundwater.
- d. The project produced knowledge at Oak Ridge National Laboratory and Georgia Institute of Technology that had a significant impact in other research activities. At ORNL, this knowledge was used in collaboration with BES separations and materials research projects to develop the Electrohydrodynamic Micromixing Reactor (EMR) for controlled synthesis of ceramic particles:



Figure 35. The Electrohydrodynamic Micromixing Reactor submitted for R&D100 Award, 2000.

In addition, knowledge from this project was used in two projects with the Electric Power Research Institute: one on electrodistillation, and the other on electro-ozonation. The project had also an educational impact for students and postdoctoral researchers at the University of Tennessee and Georgia Institute of Technology. The project supported an undergraduate student at Tennessee Tech, a graduate student at the University of Tennessee and three graduate students at Georgia Tech. Graduate students from Georgia Tech were partially supported by NSF through a CAREER Award to Professor Yiacoumi, and visited ORNL for at least one semester to complete their studies. Their results will or have been included in their theses.

- e. More research and development work is needed before large-scale trials are warranted. The difference the project has made for DOE is that it provided a means to intensify processes that address critical DOE Environmental Management problems and make them more efficient, economically better, and with less risk. For ORNL, expertise on electric-field effects on fluids has been enhanced. For visiting students and professors, they had the opportunity to perform multidisciplinary work with researchers at ORNL laboratories.
- f. Collaborating scientists in this project benefited significantly in terms of knowledge and the approach to acquire knowledge by the multidisciplinary interaction among them at various levels. Graduate students and postdoctoral associates shared most of these benefits because multidisciplinary collaboration is better facilitated at national laboratories than at universities.
- g. The action of electric fields at fluid-fluid and fluid-solid interfaces is still not well understood. Although there is still a long way before we can completely understand all the phenomena occurring under electric fields, this project contributed significantly in this direction.
- h. Fundamental knowledge from this project helped us identify DOE problems that can be solved using this knowledge. Before the results can be successfully applied to DOE Environmental Management problems, additional research is needed to investigate better the specific applications, demonstrate the approach and results, and quantify the benefits.
- i. Interest in this project has been expressed by the Electric Power Research Institute for enhanced distillation and water treatment. The current effort is to link with DOE Environmental Management problems.

7. Project Productivity

The project accomplished all the proposed goals. It has been found that the original hypothesis that electric fields can significantly affect phase equilibria is true for certain types of fluids, i.e., polar fluids. For these fluids, the projected reduction in energy consumption associated with the application of an electric field is on the order of 10%. Transport studies to investigate whether an additional electric-field effect could further increase energy savings were then pursued. These studies were additional and did not alter the schedule of the research program.

8. Personnel Supported

Twelve researchers have been involved in this project at ORNL, University of Tennessee, and Georgia Tech:

Costas Tsouris, David W. DePaoli, Michael Z.-C. Hu, James O. Hylton
Oak Ridge National Laboratory

Junhang Dong, Michele Dinsmore, Kevin D. Blankenship
Oak Ridge Institute of Science and Education

Vinod M. Shah
University of Tennessee

Sotira Z. Yiaccoumi, T.-Y. Ying, K.-L. Yang, W.-T. Shin
Georgia Institute of Technology

Two of the researchers were Postdoctoral Research Associates:

Dr. Vinod M. Shah

Dr. Junhang Dong

Four of the researchers were graduate students:

K. D. Blankenship, M.S., University of Tennessee, 1999.

W.-T. Shin, Ph.D., Georgia Institute of Technology, 2000.

T.-Y. Ying, Ph.D., Georgia Institute of Technology, 2001 (expected).

K.-L. Yang, Ph.D., Georgia Institute of Technology, 2002 (expected).

Michele Dinsmore is an undergraduate student at Tennessee Tech.

9. Peer-Reviewed Publications

Shin, W.-T., S. Yiaccoumi, and C. Tsouris, "Experiments on Electrostatic Dispersion of Air in Water," Industrial and Engineering Chemistry Research, **36**, 3647-3655 (1997).

Norato, M.A., C. Tsouris, and L.L. Tavlarides, "Phase Inversion Studies in Liquid-Liquid Dispersions," The Canadian Journal of Chemical Engineers, **76**, 486-494 (1998).

Tsouris, C., W.-T. Shin, and S. Yiaccoumi "Pumping, Spraying, and Mixing of Fluids by Electric Fields," The Canadian Journal of Chemical Engineers, **76**, 589-599 (1998).

Blankenship, K.D., V.M. Shah, and C. Tsouris "Distillation under Electric Fields," Separation Science and Technology, **34**, 1393-1409 (1999).

Blankenship, K.D., D.W. DePaoli, J.O. Hylton, and C. Tsouris "Effect of Electrode Configurations on Phase Equilibria with Electric Fields," Separation and Purification Technology, **15**, 283-294 (1999).

Tsouris, C., A.P. Borole, and E.N. Kaufman, D.W. DePaoli "An Electrically Driven Gas-Liquid-Liquid Contactor for Bioreactor and Other Applications," Industrial and Engineering Chemistry Research, **38**, 1877-1883 (1999).

Tsouris, C., and J. Dong, "Effects of Electric Fields on Phase Inversion of Liquid-Liquid Dispersions," Chemical Engineering Science, **55**, 3571-3574 (2000).

Tsouris, C., D.W. DePaoli, J.T. Shor, M.Z.-C. Hu, and T.-Y. Ying, "Electrocoagulation for Magnetic Seeding of Colloidal Particles," accepted for publication in Colloids and Surfaces (2000).

Tsouris, C., W.-T. Shin, S. Yiaccoumi, and D.W. DePaoli, "Electrohydrodynamic Velocity and Pumping Measurements in Water and Alcohols," accepted for publication in Journal of Colloid and Interface Science (2000).

- Shin, W.-T., S. Yiacoumi, and C. Tsouris, "Application of Electric Fields in Ultrapure Water Production," submitted for publication in Industrial and Engineering Chemistry Research, February 2000.
- Yang, K.-L., T.-Y. Ying, S. Yiacoumi, C. Tsouris, and E. S. Vittoratos, "Modeling of Electrosorption of Ions from Aqueous Solutions by Carbon Aerogel," submitted for publication in Journal of Physical Chemistry, B, June 2000.
- Dong, J., and C. Tsouris, "Phase Inversion of Liquid-Liquid Dispersions Under Applied Electric Fields," in preparation.
- Dong, J., V. F. DeAlmeida, and C. Tsouris, "Liquid Column Formation on Liquid-Liquid Interfaces Under Electric Fields," in preparation.

Theses:

- Blankenship, K.D., "Distillation with Applied Electric Fields," Master Thesis, Department of Chemical Engineering, University of Tennessee, April 1999.
- Shin, W.-T., "Effects of Electric Fields on Fluids: Applications in Ozonation," Ph.D. Thesis, School of Civil and Environmental Engineering, Georgia Institute of Technology, March 2000.
- Ying, T.-Y., "Influence of Electromagnetic Fields on Environmental Processes," Ph.D. Thesis, School of Civil and Environmental Engineering, Georgia Institute of Technology, May 2001 (expected).
- Yang, K.-L., "Electrosorption of Ions by Porous Materials", Ph.D. Thesis, School of Civil and Environmental Engineering, Georgia Institute of Technology, May 2002 (expected).

10. Interactions

- a. Results from this project have been presented at major technical conferences:
- American Institute of Chemical Engineers (1997, 1998, 1999, 2000)
 - Colloid and Surface Science Symposium (1997, 1998, 1999, 2000)
 - Symposium on Separation Science and Technology for Energy Applications (1997, 1999)
 - North American Mixing Forum (1997, 1999)
 - American Chemical Society (2000)
- Invited seminars have also been presented at:
- Electric Power Research Institute
 - Pulp and Paper Research Institute of Canada
 - Auburn University
 - Georgia Institute of Technology
 - Clarkson University
 - University of Missouri Rolla
- b. Collaborations have been pursued with Dr. Vinod M. Shah at the University of Tennessee, and Dr. Sotira Z. Yiacoumi at Georgia Institute of Technology.

11. Transitions

Knowledge from this project has been used for the development of the Electrohydrodynamic Micromixing Reactor (see page 20) for the controlled synthesis of particles. The EMR is available for commercialization.

12. Patents

Tsouris C., D.W. DePaoli, and J.T. Shor, "A Method to Electrolytically Produce High-Purity Magnetite Powder," Application No. 09/371,638 (1999).

Tsouris C., and J. Dong, "Methods to Control Phase Inversions and Enhance Mass Transfer in Liquid-Liquid Dispersions," Application No. 09/397,281 (1999).

DePaoli, D.W., and C. Tsouris, "Continuous Flow, Electrohydrodynamic Micromixing Apparatus and Methods," Application No. 09/398,675 (1999).

13. Future Work

In future work, the capabilities of electroextraction will be explored using solutions characteristic of the separation of cesium from tank waste at the Savannah River Site. Two approaches will be investigated: (1) novel mixer-settler and other geometries that capitalize on our phase-inversion discovery and (2) electrified centrifugal contactors. In both cases, drop/drop and drop/interface coalescence under electric fields will play significant roles and thus will be investigated in detail. Electrosorption will be used to enhance the removal of metal ions, including cesium, strontium, chromium, and cobalt, and anions, including chloride and iodide, that are present in several groundwater streams. Experimental and theoretical studies will be performed to improve the predictive capability of electrosorption models. Collaborative work with two industrial partners will be aimed at developing a scientifically based means for aerogel design, synthesis, and selection to greatly improve the performance of this powerful technology for water treatment. This work will explore the possibility for improved solvent extraction approaches to high-priority tank waste applications. It will also provide a basis for intensified separations that can solve many environmental problems at DOE sites.

14. Literature Cited

Further information on the results of this project and the relevant literature can be found in the peer-reviewed publications that have been produced by this project as listed on page 22.

15. Feedback

More time and effort are needed for the bridging between fundamental knowledge obtained by this project and applications solving DOE Environmental Management problems.

16. Appendices

Theses produced by this project:

Blankenship, K.D., "Distillation with Applied Electric Fields," Master Thesis, Department of Chemical Engineering, University of Tennessee, April 1999.

Shin, W.-T., "Effects of Electric Fields on Fluids: Applications in Ozonation," Ph.D. Thesis, School of Civil and Environmental Engineering, Georgia Institute of Technology, March 2000.