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Influence of High Voltage Electric Fields Applied across a Horizontal Liquid–Liquid Interface on the Rate of Metal Extraction Using a Rotating Diffusion Cell

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ABSTRACT

The effect of an applied electrical field across a plane liquid–liquid interface on the rate of metal extraction using hydroxyoximes and dialkylphosphoric acids as extractants is examined. The results indicate that applied electric fields have no marked influence on the observed rate of metal extraction when aliphatic hydrocarbons are employed as the diluents in the organic phase. Increases in mass transfer rates of up to 250% were observed when mixtures of octanol and an aliphatic hydrocarbon were employed as the diluent in the organic phase. The mechanism of transfer is thought to be a combination of movement of charges in the bulk of the nonconducting organic phase and electrohydrodynamic flows due to local variations in the effective interfacial tension as a result of the applied electric fields.

Key Words. Applied electrical field; Liquid–liquid interface; Mass transfer rate; Marangoni phenomena; Electrohydrodynamic flow; Interfacial tension

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INTRODUCTION

A number of studies have been conducted on the effect of applied electrical fields on liquid–liquid mass transfer rates between a drop (the dispersed conducting phase) and a nonconducting continuous phase. Pioneer studies on the effect of applied electric fields on drops showed that they can disintegrate at high voltages (1). Increased liquid circulation within the droplet has been observed even in those cases where such droplets were expected to behave as rigid spheres due to their small size (2). The increased circulation inside a droplet results in better renewal of the interface between the droplet phase and the continuous phase, resulting in an increase in the rate of mass transfer.

The stability of droplets in an electrical field is said to be a complex function of a variety of physical properties of the liquid phases, e.g., viscosities, densities, interfacial tension, difference in dielectric constants, etc., and the characteristics of the applied electrical field (3).

Compared with the number of studies on drops, very little work has been reported on the effect of applied electrical fields on liquid–liquid mass transfer when such fields are applied across a plane interface. Where such work has been reported (4–8), increased interfacial instability and interfacial turbulence, i.e., Marangoni phenomena, have been observed. This is due to local variations in the interfacial tension at the interface.

This study was conducted using a rotating diffusion cell. The study is an attempt to shed more light on the mechanisms involved in the enhancement of rates of mass transfer due to applied high voltage electric fields across a plane liquid–liquid interface of known area. It has been suggested that an applied electrical field across a plane liquid–liquid interface will orientate molecules at the interface (8). Such an accumulation of extractant molecules at a plane liquid–liquid interface could result in enhanced mass transfer rates. If it is true that molecules orientate at the interface, then it is expected that different polarities of the electric field (negative or positive) will result in a favorable or unfavorable orientation of the extractant molecules at the interface, thus resulting in either an increase or decrease in the observed mass transfer rate as the applied voltage increases.

BACKGROUND

Interfacial tension is a function of solute concentration at the interface of interfacial temperature and of the surface density of electric charges. A change in interfacial tension will appear when there exists in the interface region a concentration gradient, a temperature gradient, or a gradient of the density of electrostatic charges. This can result in surface-induced Marangoni instabilities.

Taylor and McEwan (9) studied the stability of a horizontal interface between conducting and nonconducting fluids under the influence of an initially uniform vertical electrical field. They showed that as the field strength increases in a range below a certain critical level of the applied voltage, a part of the heavier conducting phase at the interface which is subjected to the uniform field exhibits a vertical displacement upwards. This was attributed to an electrostatic pressure acting on the interface. If this pressure is great enough to counterbalance the pressure drop due to gravity and surface tension, the interface will become unstable.

In a system consisting of a conducting and nonconducting fluid phase the effect of the electric field is to accumulate charges at the interface. Conditions are thus established in which, as a result of the local variation in interfacial tension, Marangoni-type instabilities may set in. When both phases are perfectly insulating, there is no free charge at the interface.

Terasawa et al. (10) observed that in a system in which one phase is sufficiently conducting relative to the other, DC fields will cause some increase in mass transfer rates by disturbing the interfacial boundary layer in the less conducting fluid with conical projections evenly distributed at the interface. These authors observed that if the density difference between the two fluids is small, the entrainment of tiny droplets of the more conducting fluid increases. Mass transfer is augmented further in these systems due to the amount of area generated by the tiny droplets. The charged tiny droplets of the heavier conducting fluid in the nonconducting fluid are expected to migrate due to electrophoretic forces and thus enhance the macroscopic electrohydrodynamic convection (Marangoni-type phenomena) at the interface.

Onsager (11) found that the dissociation constants of weak electrolytes dissolved in solvents of low dielectric constants change in the presence of applied electrical fields, and he deduced the following expressions on the basis of the interionic attraction theory.

$$\frac{K(E)}{K(0)} = 1 + b + \frac{b^2}{2} + \frac{b^3}{18} + \cdots \tag{1}$$

$$b = 9.639 \,|\, \overline{E} \,|/(\varepsilon T) \tag{2}$$

where $K(E)$ and $K(0)$ are the dissociation constants of the weak electrolyte in the presence of an electric field and in the absence of an electric field, respectively, $\overline{E}$ is the average field strength, ε is the dielectric constant of the solvent, and T is the absolute temperature.

From the above equations it can be seen that the change in dissociation constant of a weak electrolyte, e.g., acidic extractant, in a strong electric field is highest in solvents of low permittivity and at low temperature.

In this work acidic extractants, i.e., 5-nonylsalicylaldoxime (P50) and bis(2-ethylhexyl)phosphoric acid (D2EHPA), were used for the extraction of copper(II) ions from aqueous solution. Acidic extractants form water-insoluble compounds with copper with the release of protons. The insoluble compounds of copper that are formed are readily soluble in the organic phase and thus partition readily into the organic phase on formation.

EXPERIMENTAL PROCEDURE

Reagents

The copper sulfate and the diluents (heptane and octanol) used for this work were of Analar grade. D2EHPA [bis(2-ethylhexyl)phosphoric acid] was 99.1% pure and P50 (5-nonylsalicylaldoxime) was 98% pure. Water for interfacial tension measurements was double distilled.

Kinetic Experiments

A rotating diffusion cell (RDC) was used to study the kinetics of copper extraction with either D2EHPA or P50 in heptane or mixtures of heptane and octanol. The RDC together with the electrodes used to apply the electric field are shown in Fig. 1. An important feature of the RDC is a thin porous membrane which is attached to the bottom of a cylinder rotating around its axis, with Perspex cement (Tensol), and divides the organic and aqueous phases and consequently the RDC into two chambers. The filter is treated so that only a central circular area between 100 and 300 mm^2, shown in Fig. 1 as a dotted line, remains permeable. The porous membrane, in this case a 0.22-μm pore-size Millipore-type GS membrane with a porosity of 68%, provides a constant interfacial area that is undisturbed by flow patterns. The membrane used was hydrophobic in nature. The liquid–liquid interface is therefore set up at the filter surface on the aqueous side of the membrane and not within the membrane pores. Thus, only the organic phase is allowed to transfer through the membrane pores. The diameter and consequently the surface area of the porous membrane was measured with the aid of a traveling microscope. Since the average pore size of the membrane (0.22 μm) is much larger than the average size of the molecules of substances employed in this work (about 5 nm, e.g., the maximum length of molecules of P50 and D2EHPA are estimated to be 1.3 and 1.9 nm, respectively), it is envisaged that the pores offer no resistance to diffusion of molecules across the membrane.

The rotating cylinder which contains the lighter organic phase is placed in a stationary vessel filled with the heavier aqueous phase. The surface tension locates the interface between the aqueous and organic phases at the membrane. The rotation of the inner cylinder creates laminar flows both below and above the membrane disk. The inner cylinder has an inside baffle which counteracts wall effects on flow and produces rotating disk hydrodynamics on the

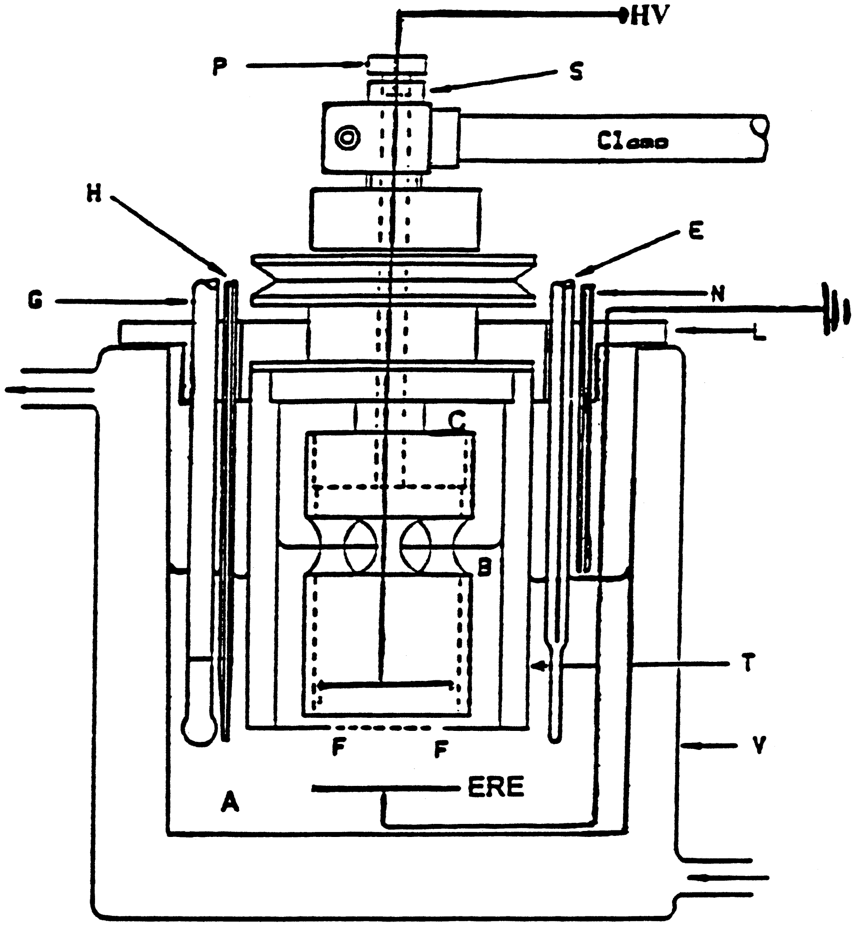

FIG. 1 Diagram of the rotating diffusion cell (RDC). Key: A = aqueous phase, B = organic phase, C = PTFE baffle, E = calomel electrode, F = porous membrane, G = glass electrode, H = titrant delivery tube, L = Perspex lid, N = nitrogen purge tube, P = PTFE plug, V = stationery chamber (thermostated glass vessel), HV = ring electrode to the high voltage source, ERE = earthed ring electrode.

inside of the membrane. The baffle prevents the lighter solution from rotating together with the motion of the cylinder.

The auxiliary equipment associated with the use of the RDC, using the pH-stat technique to follow the release of protons from the organic phase into the aqueous phase, is well documented in the literature (12). The kinetic results were analyzed using linear plots of the inverse flux against the inverse square root of the rotation speed. This is called the Levich plot. The Levich plot was used to estimate the experimental flux at a given rotational speed of the RDC. Thus, the extraction flux at different applied voltages was compared by analyzing the extraction fluxes obtained at the same rotational speed of the RDC (ω = 3 Hz) and other operating variables, e.g., concentration, pH, etc. being constant.

In all the kinetic experiments, 50 mL of the organic phase containing the extractant was contacted with 190 mL of the aqueous phase at a pH of 4.5. The initial concentration of the extractant and copper(II) ions was 0.05 and 0.01 M respectively.

The electric field was introduced into the system via a pair of stainless steel ring electrodes. One electrode was placed in the organic phase (inner rotating cylinder) and the other was placed in the aqueous phase (outer thermostated stationary cylinder). Ring electrodes were used in order to minimize the effect of the electrodes on the hydrodynamics of a rotating disk filter as solved by Levich (13) and Albery (14).

The ring electrodes had outside and internal diameters of 25 and 18 mm respectively, and were 0.8 mm thick. The distance between the electrodes and the membrane surface was 5 mm in the aqueous phase and 2.5 mm in the organic phase. As the aqueous phase is a good conductor, it was assumed that the distance between the grounded ring electrode that was located within the aqueous phase and the surface of the millipore membrane was not important, since the whole of the aqueous phase would be grounded to the aqueous side of the membrane surface. The effective distance between the two electrodes would then be that between the high voltage electrode and the aqueous side of the membrane surface. The electrode in the organic phase was connected to a high voltage DC generator (Brandenburg Photomultiplier Power Supply Unit, Model 475R) with a variable output of up to 2000 V. The electrode in the aqueous phase was grounded through an electrometer (610C Solid State Electrometer, Keithley Instruments) for measurements of the electric current between the electrodes.

Interfacial Tension Measurements

The effective interfacial tension between the organic and aqueous phases in the presence of applied electric fields was measured by a modified drop volume method, equipped with a high voltage unit. Figure 2 is a schematic diagram of the experimental device used. The drop volume method was chosen because it could easily be adapted to work involving charged droplets. A variable voltage of up to 2000 V was applied to the base of the stainless steel syringe. The outside diameter of the tip of the stainless steel syringe was measured with a traveling microscope and found to be 0.88 mm; this is where the drops were formed. The disk electrode in the organic phase was earthed and its diameter was 25 mm. If the average drop volume at a particular electric field strength is known, the effective interfacial tension can be roughly estimated by the Harkins–Brown formula (15):

$$\gamma_e = V_E(\rho_1 - \rho_2)gF/r \qquad (3)$$

where ρ_1 and ρ_2 are the densities of the aqueous and organic phases, respectively, r is the outer radius of the tip of the stainless steel syringe, g is the ac-

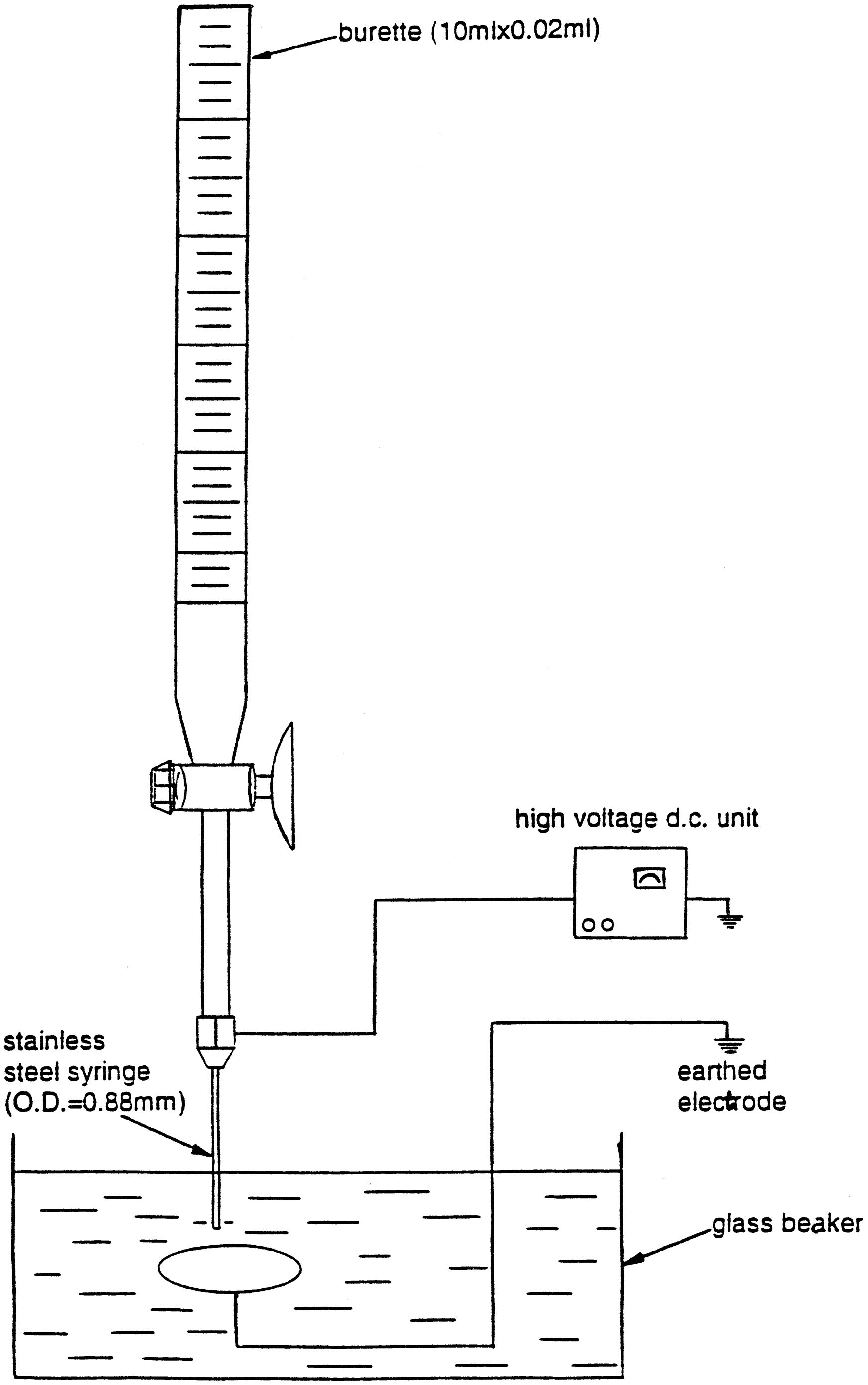

FIG. 2 A schematic of the apparatus used in this work to measure the interfacial tensions of liquid–liquid systems under the influence of applied voltages.

celeration due to gravity, V_E is the average drop volume of the aqueous phase at a particular field strength, and F is the Harkins–Brown correction term for the small amount of liquid left behind when the drop falls off the nozzle and is a function of V_E/r^3, the value of the latter (V_E/r^3) ranging from 1.0 to 270 in this work. The range of values for V_E/r^3 from 1.0 to 270 corresponds to drop volumes of 0.68 and 184 mm^3 and F values of 0.2603 and 0.1979, respectively. Values of F were obtained through the extrapolation of tabulated values of F against v/r^3, v being the drop volume (16). In general, F values range from 0.159 to 0.2559 for corresponding v/r^3 values of ∞ and 0.403, respectively.

In this work, the use of the Harkins–Brown formula to estimate the effective interfacial tension in the presence of an applied electrical field assumes that the correction factor, F, is the same for a drop detaching from either an uncharged and a charged nozzle. In reality, this might not be the case because the drop will be subjected not only to an acceleration force due to gravity but also to an acceleration force (QE_0) due to the electric field, where Q is the droplet charge and E_0 is the actual field strength acting on the drop. However, the use of the Harkins–Brown formula for the calculation of the effective interfacial tension of a system under electrical stress, i.e., electrical field, will give a good approximation of the real values.

The volume of liquid corresponding to a number of drops was read off from a 10 mL $\times$ 0.02 mL burette. All measurements were performed at room temperature, 25 ± 1°C.

RESULTS

In parallel plate electrode geometry, as a result of the difference in the mobilities of the positive and negative charge carriers, the applied electric field is nonlinear because space charges accumulate at the electrodes and the electric field is distorted. The mobility of positive charge carriers is generally higher than that of negative charge carriers, and as a result the electric field distortion is highest at the cathode (17). Consequently, in the absence of field probe measurements, the results below have been presented in terms of applied voltage rather than as variables dependent upon the absolute magnitude of the applied electric fields.

The effect of the applied voltage on the copper extraction flux using D2EHPA and P50 as extractants in the organic phase is summarized in Figs. 3 and 4, respectively. Increases in copper ion transfer flux ranging between 0 and 145% were observed for extraction with P50 in 50% octanol/heptane diluent at applied voltages above 900 V (Fig. 4). For extraction with D2EHPA in a 50% octanol/heptane diluent (Fig. 3), increases ranging between 5 and 250% were observed in the whole range of applied voltages employed in this work.

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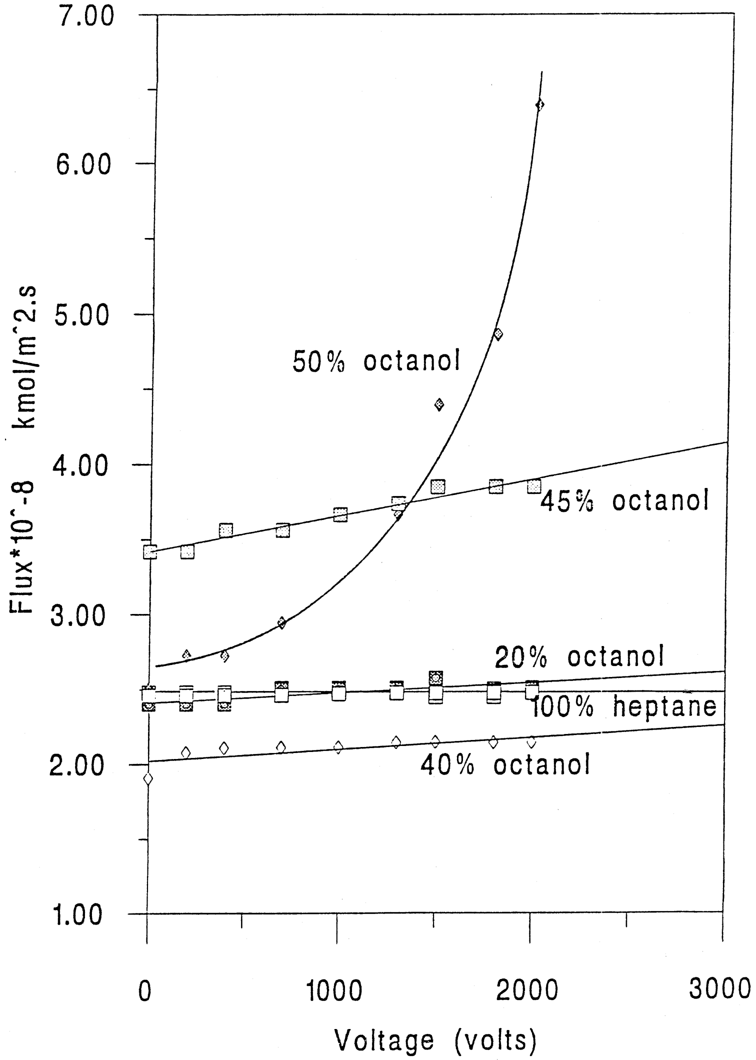

FIG. 3 The effect of an applied voltage across a liquid–liquid interface on the extraction flux for the Cu^{2+}–SO_4^{2-}/D2EHPA/octanol–heptane diluent mixture system, $C_{D2EHPA} = 0.05$ M, $C_{Cu^{2+}} = 0.01$ M, pH 4.5, $\omega = 3$ Hz.

These observed increases are within the range of those increases reported in the literature. Thus, Iyer and Sawistowski (4) observed increases in mass transfer rate of between 20 and 1000% for the transfer of propionic acid and acetone from toluene into water at applied voltages ranging from 0 to 2500 V. Hund and Lancelot (8) observed increases of up to 60% for the extraction of copper ions using a 30% solution of LIX65N (2-hydroxy-5-nonyl benzophenone oxime) in Escaid 110 (a type of kerosene) at an applied voltage of +12 kV. Our extraction fluxes at zero applied voltage compare well with those in the literature (18, 19).

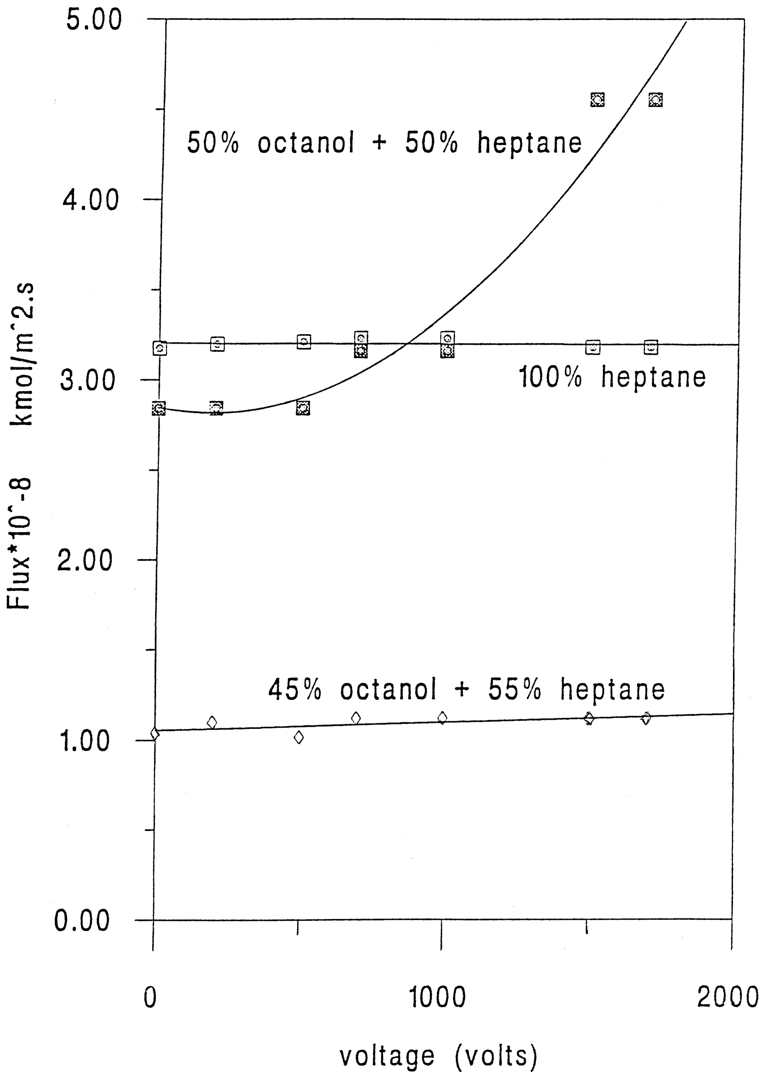

FIG. 4 The effect of an applied voltage across a liquid–liquid interface on the extraction flux for the Cu^{2+}–SO_4^{2-}/P50/octanol–heptane diluent mixture system, $C_{P50} = 0.05$ M, $C_{Cu2+} = 0.01$ M, pH 4.5, $\omega = 3$ Hz.

The effect of the applied voltage on the effective interfacial tension of the liquid–liquid systems investigated in this work is summarized in Figs. 5 and 6 for the water/D2EHPA/octanol–heptane diluent mixture and the water/P50/octanol–heptane diluent mixture systems, respectively. The effect of applied voltages on the effective interfacial tension between octanol–heptane diluent mixtures and water including between heptane and water, when no extractant is present in the diluent, is summarized in Fig. 7.

The current passing between the electrodes at different applied voltages was measured by an electrometer and is summarized in Figs. 8 and 9 for the

Cu^{2+}–SO_4^{2-}/D2EHPA/octanol–heptane diluent mixture and the Cu^{2+}–SO_4^{2-}/P50/octanol–heptane diluent mixture systems, respectively. The current measurements may be interpreted in terms of the number of charge carriers present in the organic phase as the octanol content of the octanol–heptane diluent mixture increases.

Figures 8 and 9 illustrate the fact that the number of charge carriers increases substantially as the octanol content in the diluent mixture increases above 45%. Thus, for example, the current passing between the electrodes is shown to be 9.0×10^{-5} and 1.0×10^{-5} amperes for extraction of copper ions with P50 in

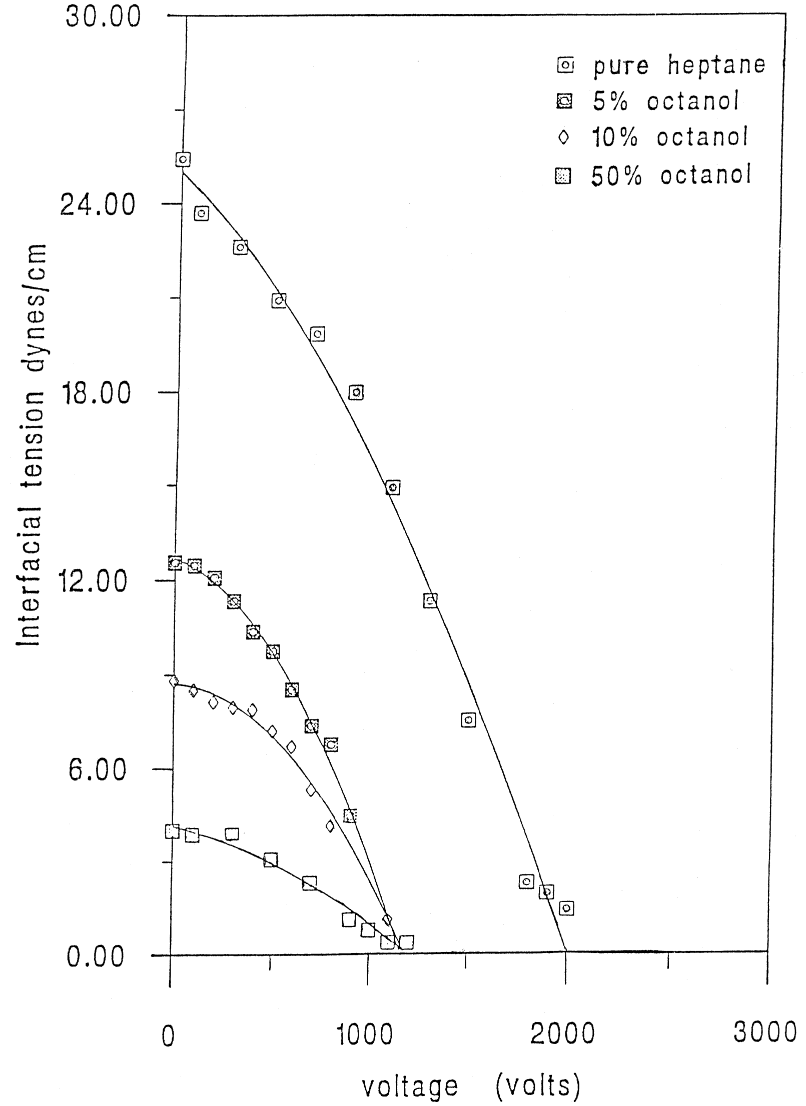

FIG. 5 The effect of an applied voltage across a liquid–liquid interface on the interfacial tension for the water/D2EHPA/octanol–heptane diluent mixture system, $C_{D2EHPA} = 0.05$ M, pH 4.5, $T = 23.5$°C.

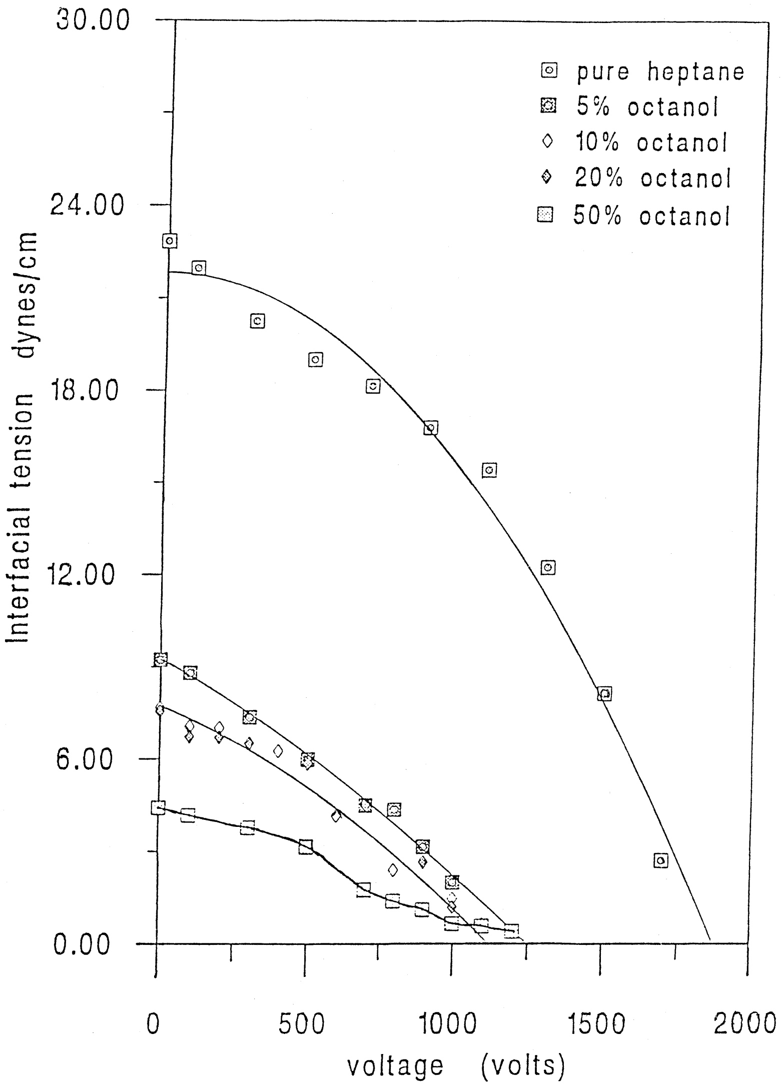

FIG. 6 The effect of an applied voltage across a liquid–liquid interface on the interfacial tension for the water/P50/octanol–heptane diluent mixture system, $C_{P50} = 0.05$ M, pH 4.5, $T = 23.5°C$.

a 50% octanol/heptane diluent and P50 in a 45% octanol/heptane diluent, respectively (Fig. 9). The large difference in amounts of charge carrier present in 50 and 45% octanol/heptane diluent explains why the critical voltage for the onset of instabilities is much lower for the 50% octanol/heptane diluent.

DISCUSSION

The discussion in this section is based on the range of applied voltages studied in this work, i.e., 0 to 2000 V. The discussion on the main findings in this work can be summarized as follows.

1. The enhancement of the extraction rate under the influence of electrical fields is negligible when heptane alone is used as diluent for the extractants, D2EHPA and P50, in the extraction of copper from sulfate media.

2. It is now known that, in general, metal transfer fluxes in liquid–liquid systems are higher when the extractant is dissolved in a nonpolar diluent like kerosene or heptane than when the extractant is dissolved in a polar diluent like benzene or octanol. As the octanol content of a heptane–octanol diluent mixture is increased, it is expected that the metal transfer flux should decrease for zero applied voltage conditions. The fact that a decrease in metal transfer flux is observed in Figs. 3 and 4 when the octanol content of the diluent mix-

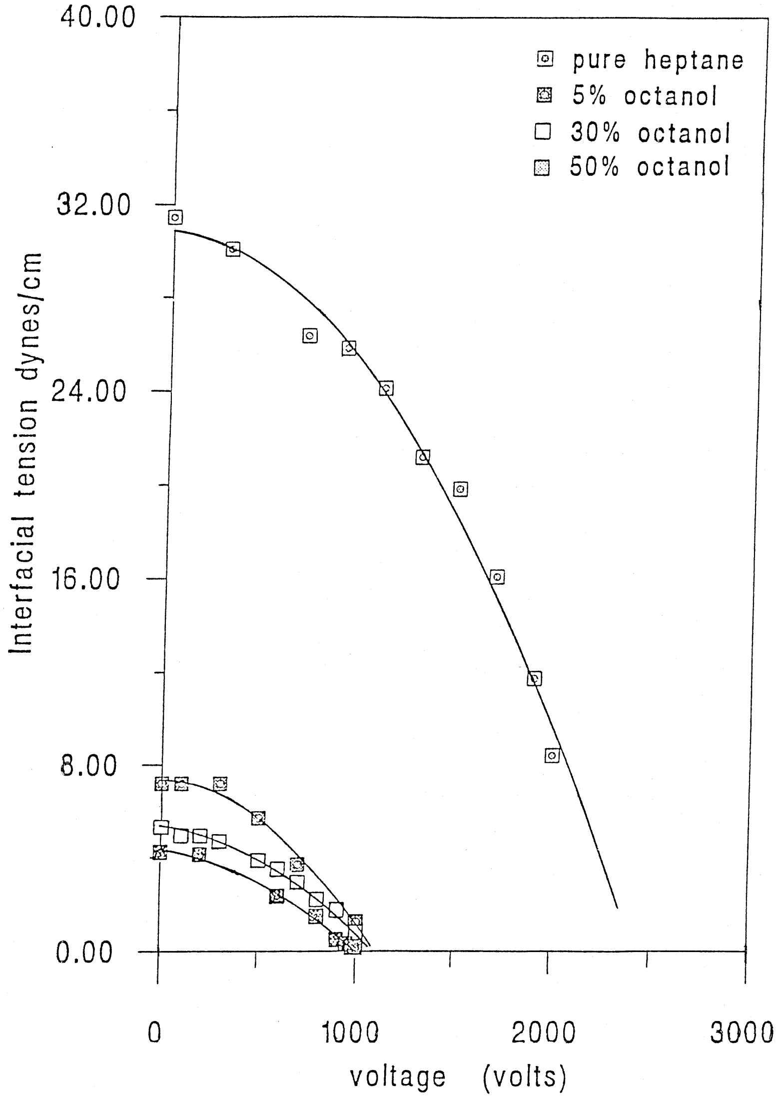

FIG. 7 The effect of an applied voltage across a liquid–liquid interface on the interfacial tension for the water/octanol–heptane diluent mixture system, pH 4.5, T = 23.5°C.

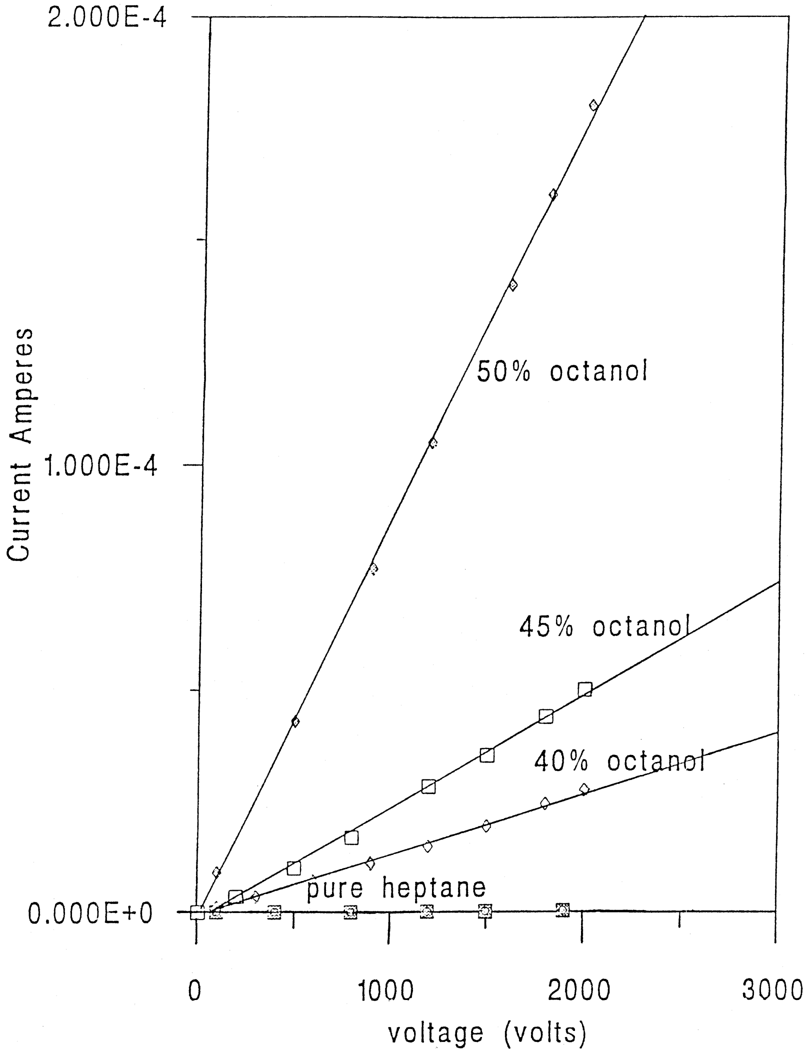

FIG. 8 The applied voltage–electric current relationship for the Cu^{2+}–SO_4^{2-}/D2EHPA/octanol–heptane diluent mixture system, $C_{D2EHPA} = 0.05$ M, $C_{Cu2+} = 0.01$ M, pH 4.5, $\omega = 3$ Hz.

ture is increased from 0 to 40% in the presence of an applied electric field, signifies that at these concentrations of octanol in the diluent the critical voltage for the onset of instabilities, V_C, is out of the range of values employed in this work. The high voltage source used for this work was only capable of delivering 2000 V. The critical voltage for the onset of instabilities, in this work, is thus a function of the octanol content in the diluent. Bailes and Thornton (20) found the critical voltage for the onset of instabilities to be more than 2000 V in their single drop studies on the extraction of furfuraldehyde from heptane into water. It seems that we can also discuss our results in terms of a critical concentration of octanol in the diluent mixture, for the onset of electric-field-induced instabilities, which is about 50% octanol in the case of extraction of copper ions using P50 as extractant and between 45 and 50% for the case of extraction with D2EHPA. While V_C for extraction of copper ions with P50 is about 900 V (Fig. 4), it is close to zero for extraction with D2EHPA (Fig. 3) when a 50% octanol/heptane diluent mixture is employed.

We can not offer a plausible explanation as to why the curve for extraction with D2EHPA (Fig. 3) in a 45% octanol/heptane diluent is initially above that for extraction with D2EHPA in a 50% octanol/heptane diluent.

When the octanol content of the octanol/heptane diluent mixture is increased above 50%, the diluent starts to "leak" through the membrane into the aqueous phase when a voltage is applied. The leaking is thought to be con-

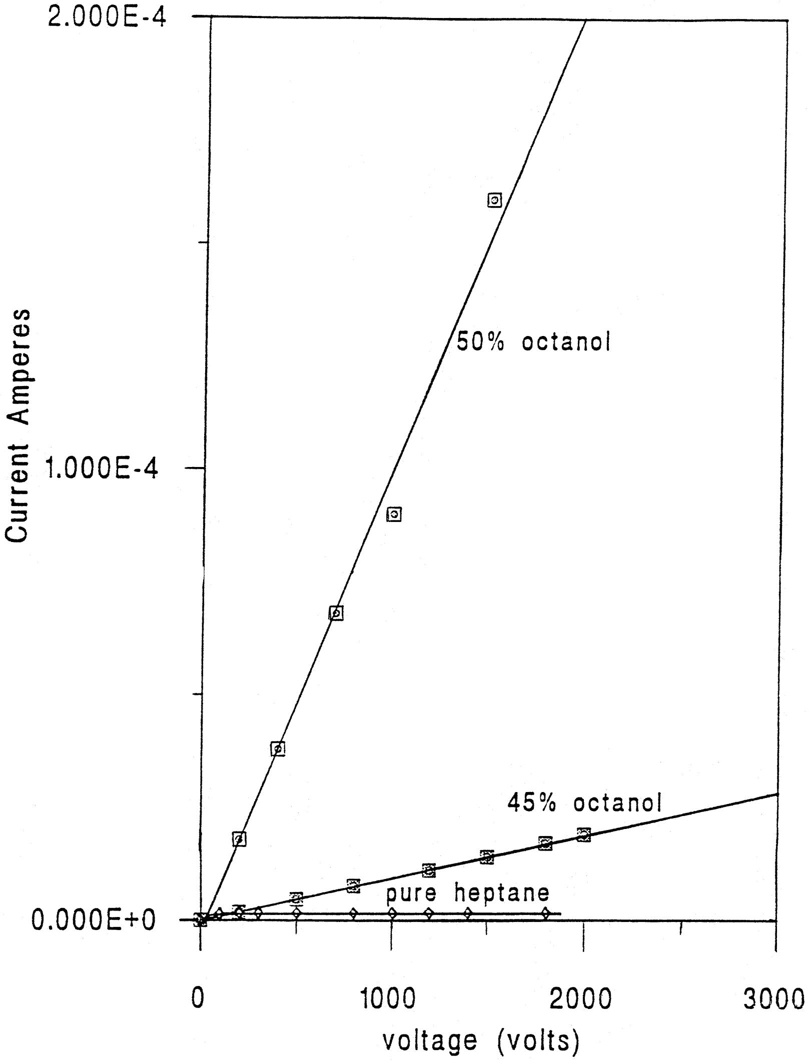

FIG. 9 The applied voltage–electric current relationship for the Cu^{2+}–SO_4^{2-}/P50/octanol–heptane diluent mixture system, $C_{P50} = 0.05$ M, $C_{Cu2+} = 0.01$ M, pH 4.5, ω = 3 Hz.

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nected with the lowering of the effective interfacial tension to very low values by the electric field for the octanol–heptane diluent mixtures in which the octanol content exceeds 50%. The leakage is not observed in the absence of an electrical field. The effect of increasing the octanol content in the diluent mixture on the enhancement of the extraction rates in the presence of applied electric fields is twofold.

(i) An increase in the octanol content of the diluent mixture increases the number of charge carriers and, as a result, space charges in the diluent. This is due to the fact that octanol is a weak electrolyte and is thus slightly dissociated, and that a small amount of water is present in the organic phase as water is slightly soluble in octanol. An increase in the number of charge carriers in the diluent mixture increases the electrical fields near the electrodes and the conductivity of the organic phase, hence the observed increase in the electric current for systems with increasing octanol content in the diluent mixture (Figs. 8 and 9). An increase in the space charges in the organic phase thus favors a steeper gradient of the density of electrostatic charges at the liquid–liquid interface. This creates favorable conditions for electric-field-induced instabilities of the Marangoni type to set in.

(ii) An increase in the octanol content in the octanol–heptane diluent mixture results in a lower interfacial tension for the liquid–liquid system. A low interfacial tension system is more susceptible to Marangoni type of instabilities. An increase in the octanol content of the diluent mixture will also result in a lower density difference between the aqueous and organic phases. A lowering of both the density difference between the two phases and the interfacial tension of the liquid–liquid system favors a lower value of the so-called Taylor wavelength (1) which may be used to characterize the stability of a liquid–liquid system subjected to an external electrical field. The lower the value of the Taylor wavelength, the higher the instability of the liquid–liquid system.

3. The effective interfacial tensions of the liquid–liquid systems explored in this work decrease with an increase in the applied voltage. This phenomenon is true for systems with and without extractant in the organic phase.

4. The sign of the applied voltage does not affect the enhancement of the extraction rate. This indicates that the electric field strength rather than the sign of the applied voltage is responsible for the enhancement of extraction rates. However, it is expected that the field strength at the cathode would be higher than that at the anode because of the difference in mobilities of the positive and negative charge carriers; the mobility of the positive charge carriers is faster. Since enhancement of extraction rate is independent of the sign of the applied voltage, it is reasonable to conclude that enhancement is not due to preferential orientation of extractant molecules at the liquid–liquid interface as suggested by Hund and Lancelot (8), but rather to electrohydrodynamic ef-

fects which are a consequence of the effect of electrical fields on the effective interfacial tension of the system under consideration. Iyer and Sawistowski (4) observed no general trend with respect to polarity in their work, with the behavior of some of their systems being independent of polarity.

According to Stishkov (21), for most dielectrics the onset of electrohydrodynamic flows in the bulk phase occur when electrical fields of 0.5 to 5 kV/cm are applied. The electric field required for the onset of electrohydrodynamic flows will depend on the amount of charge carriers present in the dielectric, the viscosity of the dielectric, and the geometry of the electrodes. If the enhancement of the extraction rates in the presence of applied electric fields was due to the preferential alignment of extractant molecules at the interface, it would be expected that the extraction rate would decrease to values lower than those observed without the electrical field, when the sign of the applied voltage is reversed, because in this instance the extractant molecules would be “non-preferentially” orientated at the liquid–liquid interface.

5. A small heating effect might occur due to the passage of an electric current between the electrodes. This would result in a decrease of the viscosities of the liquids contained in the region between the electrodes. For the liquids used in this study, the current passing between the electrodes was only a fraction of a milliampere, even with 2000 V between the electrodes. The rise in temperature in our liquid–liquid system is thus expected to be negligible.

6. It is thought that the enhancement of the extraction rate in this work is not high because the eddies generated at the interface due to the Marangoni instabilities are damped out within the membrane pores (the pore size of the membrane is 0.22 μm while the size of a typical eddy is reported to be about 16 μm) (22).

7. A number of researchers have reported a small increase in the viscosity of polar liquids subject to an electrical field, i.e., the so-called viscoelastic effect (23). However, this effect was not observed for nonpolar liquids, including those which contained enough impurities to pass a substantial current. The effect was explained by noting that the applied electric field produces a directional ordering of polar molecules, which is favorable to the communication of momentum from molecule to molecule, thus resulting in an increase in the viscosity. Such an increase in the viscosity when applied to a liquid–liquid system would result in lower diffusivities of the reacting species in the interfacial reaction zone, and result in lower extraction rates. It thus seems that this effect is negligible in the systems studied in this work.

8. The observed increase in extraction rates in an electric field when high octanol content diluents are used may be explained in terms of the second Wien effect, or the dissociation field effect, i.e., the fact that the degree of dissociation of weak electrolytes is increased by high fields. The report on the Wien effect by Eckstrom and Schmelzer (24) cites work by Schiele who

showed that acids having a low conductance, i.e., weak acids, exhibit a high field effect. The extractants studied in this work are weak acids, and it is possible that the presence of high electric fields near the electrodes, due to increased charge carriers for high octanol content diluent mixtures, will cause these extractants to dissociate more readily in the aqueous phase reaction zone, thereby increasing the amount of extractant available for reaction in this zone and thus the extraction rates.

CONCLUSIONS

The effect of the electric field on the extraction rate is more pronounced as the amount of charge carriers in the organic phase increases. The behavior of interfacial tension in the presence of an applied electrical field is the same for systems with and without extractant in the organic phase. This means that the observed decrease in interfacial tension of a liquid–liquid system under the influence of an applied electrical field is due to the accumulation of charge carriers at the interface rather than the accumulation of extractant at the liquid–liquid interface. Accumulation of charges at the interface makes the interface unstable, resulting in local variations in interfacial tension which may cause instabilities of the Marangoni type and consequently interfacial turbulence to set in. The interfacial turbulence results in better renewal of the interface between the aqueous and organic phases, thereby increasing the rate of mass transfer.

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REFERENCES

1. G. I. Taylor, “Disintegration of Water Drops in an Electric Field,” *Proc. R. Soc. London, A280*, 383–397 (1964).
2. R. M. Wham and C. H. Byers, “Mass Transport from Single Droplets in Imposed Electric Fields,” *Sep. Sci. Technol., 22*(23), 447–466 (1987).
3. T. C. Scott and R. M. Wham, “An Electrically Driven Multistage Countercurrent Solvent Extraction Device: The Emulsion-Phase Contactor,” *Ind. Eng. Chem. Res., 28,* 94–97 (1989).
4. P. V. R. Iyer and H. Sawistowski, “Effect of Electric Field on Mass Transfer across a Plane Interface,” *Proc. Int. Solv. Extr. Conf. ISEC’80*, pp. 1029–1046 (1980).
5. V. Mohan, K. Padmanabhan, and K. Chandrasekharan, “Marangoni Effects under Electric Fields,” *Adv. Space Res., 3*(5), 177–180 (1983).
6. L. J. Austin, L. Banczyk, and H. Sawistowski, “Effect of Electric Field on Mass Transfer across a Plane Interface,” *Chem. Eng. Sci., 26*, 2120–2121 (1971).

7. V. Mohan, P. Jayasankar, and K. Padmanabhan, "Interfacial Phenomena of Liquid–Liquid Systems under Electric, Magnetic and Gravitational Fields," *Proc. Int. Solv. Extr. Conf. ISEC'86*, *1*, 507–510 (1986).
8. M. Hund and F. Lancelot, "Interfacial Transfer under Electrostatic Field in Solvent Extraction," *Ibid.*, *1*, 511–517 (1986).
9. G. I. Taylor and A. D. McEwan, "The Stability of a Horizontal Fluid Interface in a Vertical Electric Field," *J. Fluid Mech.*, *22*(1), 1–15 (1965).
10. H. Terasawa, Y. H. Mori, and K. Komotori, "Instability of Horizontal Fluid Interface in a Perpendicular Electric Field: Observational Study," *Chem. Eng. Sci.*, *38*(4), 567–573 (1983).
11. L. Onsager, "Deviations from Ohm's Law in Weak Electrolytes," *J. Chem. Phys.*, *2*, 599 (1934).
12. M. A. Hughes and P. K. Kuipa, "Kinetics and Mechanism of Copper Extraction with Dialkylphosphoric Acids and Hydroxyoximes Studied by a Rotating Diffusion Cell," *Ind. Eng. Chem. Res.*, *35*(6), 1976–1984 (1996).
13. V. G. Levich, *Physico-Chemical Hydrodynamics*, Prentice-Hall, Eaglewood Cliffs, NJ, 1962, p. 60.
14. W. J. Albery, *Electrode Kinetics*, Clarendon Press, Oxford, 1975, p. 75.
15. A. Findlay and J. A. Kitchener, *Practical Physical Chemistry*, Longmans, London, 1960.
16. *International Critical Tables*, *Vol. 4*, McGraw-Hill, New York, NY, 1928.
17. G. Stewart and J. D. Thornton, "Charge and Velocity Characteristics of Electrically Charged Droplets in Liquid–Liquid Extraction," *IChemE Symp. Ser. 26*, pp. 29–42 (1967).
18. P. R. Fisk, Ph.D. Thesis, Imperial College, University of London, London, 1981.
19. H. V. Patel, Ph.D. Thesis, Department of Chemical Engineering, University of Bradford, Bradford, 1986.
20. P. J. Bailes and J. D. Thornton, "Electrically Augmented Liquid–Liquid Extraction in a Two Component System I. Single Droplet Studies, *Proc. Int. Solv. Extr. Conf. ISEC'71*, *2*, 1431 (1971).
21. Yu. K. Stishkov, "Elektricheskiye protsesi v teknike i khimii," *Elektron. Obrab. Mater.*, *6*, 29 (1977) (in Russian).
22. R. E. Treybal, *Mass Transfer Operations*, McGraw-Hill, New York, NY, 1980.
23. E. N. Da C. Andrade and J. Hart, "The Effect of an Electric Field on the Viscosity of Liquids," *Proc. R. Soc. London*, *A225*, 463–472 (1954).
24. H. C. Eckstrom and C. Schmelzer, "The Wien Effect: Deviations of Electrolytic Solutions from Ohm's Law under High Field Strengths," *Chem. Rev.*, *24*, 367 (1939).

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