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Use of Electric Fields in Solvent Extraction: A Review and Prospectus

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USE OF ELECTRIC FIELDS IN SOLVENT EXTRACTION:
A REVIEW AND PROSPECTUS

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1. INTRODUCTION

Electric fields have been used in applications related to
solvent extraction for nearly seventy years, primarily to break
aqueous-in-organic emulsions. It was not until about twenty years
ago that the use of electric fields was contemplated as a means of
driving and controlling extraction processes. The initial ideas
revolved around droplet formation from charged nozzles and have
led to development of several designs for continuous contacting
devices. Electric field driven devices are not used to any
significant extent in industry, but recent results in this area,
some of which are described in this paper, suggest that this tech-
nique may produce systems that are an order of magnitude more
effective than present day machines.

The purpose of this paper then is to inform the separation
science community of this alternative approach to operating solvent
extraction processes. In order to understand the underlying
principles of operation, the second section describes the inter-
actions of electric fields with liquids while the third discusses
important phenomena related to droplet behavior in electric
fields. Sections four and five present electric field effects as
they are manifested in the several steps that comprise extraction
and give some idea as to the state of the research area and
future directions which may lead to interesting discoveries.

2. ELECTRICAL FORCE EFFECTS ON FLUIDS

In contrast to electrochemical applications, the use of
electric fields to control solvent extraction processes involves

primarily physical interactions between charges, fields and con-
ducting and/or dielectric liquids. The interactions of electric
fields with fluids are the subject of a branch of fluid mechanics
called electrohydrodynamics. Although this area of research
encompasses both liquid-liquid and gas-liquid systems, we will
restrict ourselves to the discussion of multiphase liquid systems
– a combination which is characteristic of solvent extraction
operations. First, one must understand the effect of an electric
field and a volumetric charge density upon a single stagnant
fluid. Once these fundamental relationships are in place one can
then proceed to determine what happens to electric field and
charge effects at a discontinuity of electrical properties — an
interface. Generally speaking, these interfacial effects manifest
themselves as a resultant force or shear stress that can induce
a static deformation of the interface and even steady or transient
fluid motion. It is the understanding the nature of the electric-
field-induced forces that arise at liquid-liquid interfaces which
forms the basis for exploration of possible application of
electric fields in solvent extraction systems.

2.1 Governing Mathematical Relationships

    In 1864, Maxwell described how Ampere's law of force between
moving charges or currents and Faraday's law of induction can be
transformed into field equations.[1] In addition, he postulated the
need for the existence of a displacement current in Ampere's law
in order to satisfy conservation of charge in a system. His
treatment resulted in a set of four equations, known as "Maxwell

TABLE I: DIFFERENTIAL FORMS OF MAXWELL EQUATIONS AND APPROPRIATE
           BOUNDARY/INTERFACIAL CONDITIONS UTILIZED IN ELECTRO-
           HYDRODYNAMICS

Differential Laws	Boundary/Interfacial Conditions
Faraday's Law	Continuity of Tangential Electric Field
$$\nabla \times \underline{E} = \underline{0} \quad (1)$$	$$\underline{n} \times (\underline{E}^A - \underline{E}^B) = \underline{0} \qquad (5)$$
Gauss' Law	Change in Normal Electric Displacement
$$\nabla \cdot \underline{D} = \rho_E \quad (2)$$	$$(\underline{D}^A - \underline{D}^B) \cdot \underline{n} = \sigma_E \qquad (6)$$
Charge Conservation Equation	Boundary Condition for Current
$$\frac{\partial \rho_E}{\partial t} + \nabla \cdot \underline{J} = 0 \quad (3)$$	$$\frac{\partial \sigma_E}{\partial t} + \nabla_S \cdot (\sigma_E \underline{v}) = \qquad (7)$$
Electric Displacement – Electric Field Relationship	$$- [(\underline{J}^A - \rho_E^A \underline{v}) - (\underline{J}^B - \rho_E^B \underline{v})] \cdot \underline{n}$$
$$\underline{D} = \varepsilon_0 \underline{E} + \underline{P} \quad (4)$$	$$- \nabla_S \cdot (\underline{i}_S - \sigma_E \underline{v})$$

equations," which are the starting point of all theoretical

analyses involving electromagnetic fields.[2]

   When fluid velocities are sufficiently low such that dynamic

currents are very small, magnetic induction can be ignored and the

electrostatic form of the Maxwell equations may be utilized as

shown in Table I.[3],[4]

A feature important to the analysis of electrohydrodynamic appli-

cations is the irrotational nature of the electric field intensity,

$\underline{E}$, as shown in Equation 1 (Faraday's law). Gauss' law, Equation 2,

relates the free charge density ρ_E to the electric displacement,

$\underline{D}$, while Equation 3 is simply the charge conservation equation which takes into account the free current density, $\underline{J}$. The relationship between the electric displacement and the electric field is shown in Equation 4, where the polarization, $\underline{P}$, is the dipole moment per unit volume.[5] Hence, the electrical displacement takes into account the "background electric field" as well as electric field contributions from induced polarization of the media. The differential laws displayed in Table I have analogous integral forms which provide the starting points for derivation of the boundary and the interfacial conditions that pertain to the electric field, $\underline{E}$, electric displacement, $\underline{D}$, and current density, $\underline{J}$ (Equations 5-7, respectively).

The differential equations represented in Table I can be written in terms of the associated fields through the use of constitutive relationships for electric displacement, $\underline{D}$, and current density, $\underline{J}$:

$$\underline{D} = \varepsilon \, \underline{E}, \tag{8}$$

$$\underline{J} = \gamma \, \underline{E}, \tag{9}$$

where ε and γ are the permittivity and conductivity, respectively. Upon comparison of Equations 4 and 8, it is evident that the permittivity can be thought of as a measure of the polarizability of a material. In the polarization relationship, Equation 8, the value of the permittivity is generally considered to be a function of electric field strength and fluid density. Equation 9, Ohm's law, concerns the electrical conduction process in a stagnant liquid. For the case of fluid in motion, the total current density measured from

a stationary frame of reference is given by

$$\underline{J} = \gamma\underline{E} + \rho_E\underline{v},\qquad(10)$$

where $\underline{v}$ is the velocity vector of the fluid.

2.2 Behavior of Electrical Charges in Liquids

Examination of the continuity of charge relationship
(Equation 3) in light of the constitutive relationships shown in
Equations 8 and 9 reveals that the time rate of change of charge
density, ρ_E, observed when one is convecting with the fluid is
given by

$$\frac{D\,\rho_E}{Dt} = -\rho_E\,\nabla\cdot\underline{v} - \frac{\gamma}{\varepsilon}\rho_E - \gamma\underline{E}\cdot\left(\frac{\nabla\gamma}{\gamma} - \frac{\nabla\varepsilon}{\varepsilon}\right)\qquad(11)$$

Assuming the liquid to be incompressible, $\nabla\cdot\underline{v} = 0$, and that γ and
ε remain constant, Equation 11 can be integrated to yield

$$\rho_E = \rho_{E,0}e^{-t/\tau_e},\qquad(12)$$

where τ_e, the relaxation time constant, is defined as the ratio of
the permittivity to the conductivity, ε/γ.[3,6] This ratio yields
a qualitative indication of the propensity of a material to retain
a charge distribution versus allowing charge transport to occur.
In this case the bulk charge density displays an exponential decay
from the initial value, $\rho_{E,0}$, with a characteristic time constant,
τ_e. In addition, because the description involves motion
following along with the fluid, this result implies that a given
element of liquid will not contain any charge unless its stream-
line can be traced back to a source of charge.[3]

Evaluation of the behavior of the decay of bulk charge den-
sity yields insight into the behavior of electric fields in fluids.

A perfect conductor would have a relaxation time that approaches zero; hence, the bulk charge density would instantaneously decay to zero. On the other hand, a perfect insulator would have a τ_e which approaches infinity and therefore the bulk charge density does not decay at all. The relaxation time in seawater is 2×10^{-10} seconds (conducting) while the corresponding value in distilled water is approximately 1×10^{-6}. It is evident that in all but the very poorest of liquid conductors the relaxation time is extremely small. For comparison, fused quartz (a good electrical insulator) has a value of about a million for τ_e.[7] The analysis in Equations 11 and 12 brings to light an extremely important concept which is useful in liquid phase applications. Charges that are initially in the interior of most liquids (except for exceedingly poor conductors) will in general quickly move through the liquid and seek out an area where there is a discontinuity of electric conductivity and permittivity — an interface. In solvent extraction this is generally a liquid-liquid interface; however, in real systems one also encounters solid-liquid, solid-gas, and gas-liquid, interfaces associated with the physical equipment.

2.3 Effects of Electric Fields on Hydrodynamics

The previous treatment illustrates that, in general, electric field and charge phenomena in multiphase liquid systems demonstrate the greatest effect at interfaces. Let us now examine the contribution which electric field forces make to the overall hydrodynamical description of the fluids. The motion of fluids under

the influence of an applied electric field is governed by the usual principles of conservation of linear momentum and of mass. For incompressible fluids, the equations of motion and of continuity are given by

$$\rho \frac{D\underline{v}}{Dt} = \nabla \cdot \underline{\underline{T}} + \rho\underline{g},$$ (13)

and

$$\nabla \cdot \underline{v} = 0,$$ (14)

respectively, where ρ is the fluid density, $\underline{g}$ is the gravitational force per unit mass, $D\underline{v}/Dt$ is the substantial derivative of the velocity with respect to time, and $\underline{\underline{T}}$ is the stress tensor.[3] At an interface between two fluids A and B, conservation of momentum requires that

$$\underline{n} \cdot (\underline{\underline{T}}^A - \underline{\underline{T}}^B) + 2H\sigma\underline{n} = 0,$$ (15)

where $\underline{n}$ is a unit normal to the interface, 2H is the local mean curvature, and σ is the interfacial tension which for most applications of interest in this paper will be assumed constant.[8,9]

The stress can be considered to be the sum of two parts: one an equilibrium entity and the other dynamic in nature. The decomposition is relatively arbitrary[3,10]; however, the general notion is that the local state of stress is given by an expression such as

$$\underline{\underline{T}} = \underline{\underline{T}}_{eq} (\rho,T,\underline{E}) + \underline{\underline{T}}_v (\underline{v}; \eta),$$ (16)

where $\underline{\underline{T}}_{eq} (\rho,T,\underline{E})$ is the contribution at mechanical and thermodynamic equilibrium in an externally imposed electric field and

$\underset{=v}{T}$ ($\underline{v}$; η) is the viscous stress tensor. In the case of hydrostatic equilibrium, the momentum equation (13) reduces to

$$\nabla \, (p_o - p_s) + \rho\underline{g} = 0, \tag{17}$$

where $p_o = p(\rho,T,0)$ is the zero field pressure and p_s is the electrostrictive pressure. This relationship holds whenever either the flow field is isothermal or the polarization, $\underline{P}$, is independent of temperature and when the free charge density, ρ_E, is everywhere zero.

As an example, one can explore the case of a liquid that is highly conducting with respect to another liquid with which it is in contact. The electric field vanishes inside the conductor; hence, only the normal component of the electric field on the insulator side of the interface will be of importance. The boundary condition at the interface (see Equation 15) takes on the following form

$$-2H\sigma = \Delta p + \tfrac{1}{2}\epsilon_o E_n^{\,2}, \tag{18}$$

where Δp is thermodynamic pressure on the conductor side minus that on the insulator side of the interface, and E_n is the normal component of the electric field on the insulator side. To calculate the shape of the interface, Δp is eliminated from Equation 18 via integration of Equation 17. The result is the augmented Young-Laplace equation for an equilibrium meniscus shape. This result indicates that imposition of a sufficiently intense electric field on the system may overcome "surface forces" (interfacial tension) and cause deformation of the interface.

The case for fluids in motion is significantly more complex. If the liquids are ohmic conductors with constant conductivities,

are linear, isotropic dielectrics with constant permittivities,
and are incompressible, the total stress tensor $\underline{\underline{T}}$ takes on a
reasonable form which allows investigation of Equation 15. At the
interface between two such liquids,

$$T_e = \underline{nt}: (\underline{\underline{T}}_e^A - \underline{\underline{T}}_e^B) = \sigma_E E_t, \qquad (19)$$

where $\underline{n}$ is a unit normal and $\underline{t}$ is unit tangent to the interface.
The most interesting aspect of Equation 19 is that whenever an
interface simultaneously supports a tangential electric field (E_t)
and a surface charge density (σ_E) an electric shear stress (T_e) acts
upon it.[4] The nature of fluids is such that a mechanical
equilibrium cannot be maintained under the action of a shear
stress; hence, the result of the electric field contribution is to
induce fluid motion in the system.

3. BEHAVIOR OF LIQUID DROPLETS IN ELECTRIC FIELDS

Interaction of drops and bubbles with electric fields is
prevalent in nature and is important in many technological
applications.[4] Similar situations can be found in such diverse
areas as colloidal systems, meteorology and cloud physics,
electrostatic spraying of liquids, power engineering applications,
nuclear physics, aerosol science, and many others.[10-15] The
behavior which links these seemingly unrelated situations together
is the physics describing droplet formation, stability,
oscillation, breakup, and coalescence. To understand the effects
of electric fields upon solvent extraction processes, one must
study these same types of effects for electric field interactions
with liquid droplets.
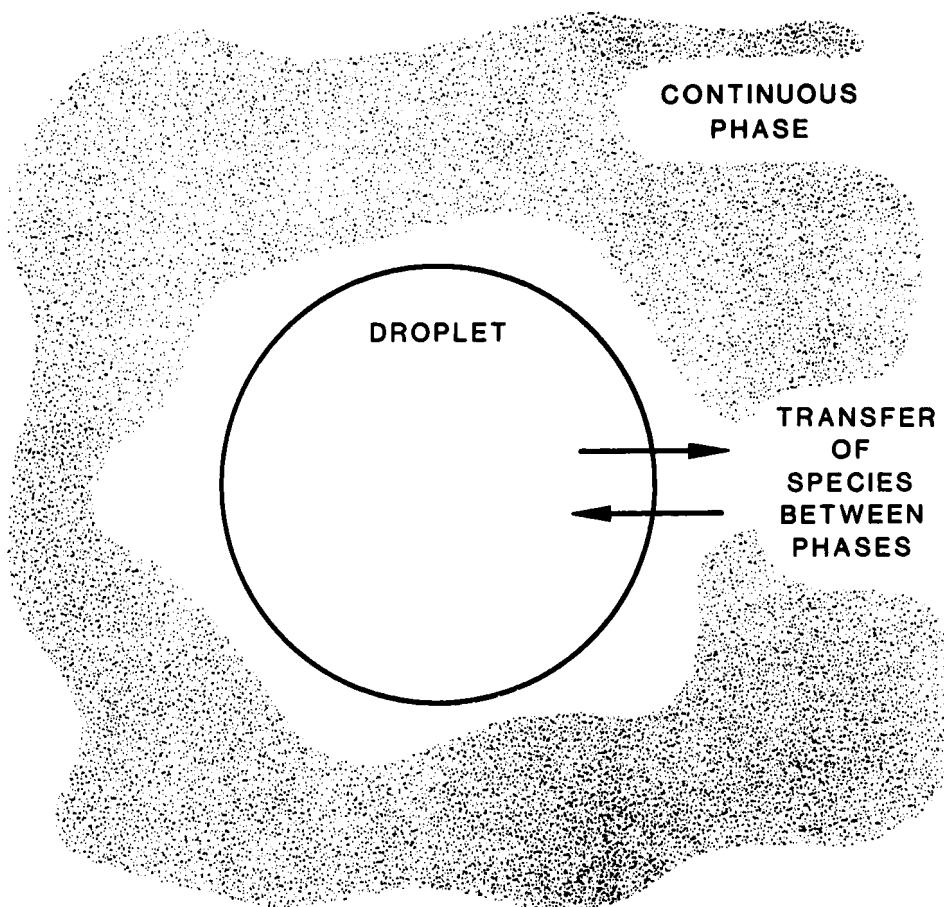
FIGURE 1
Droplet-Continuum System Characteristic
of Solvent Extraction.

Contact of droplets of a dispersed liquid phase with a

surrounding continuous liquid phase represents a basic interaction

in liquid-liquid solvent extraction. Figure 1 is a schematic

diagram representing this "basic building block" which characterizes

the mass transfer behavior in extraction. In terms of the

droplet-continuum system, mass transfer rates from one liquid
phase to another depend upon the physicochemical properties of the
transferring species and solvents as well as on the hydrodynamic
state of the system. Although there are cases in which electric
field and charge effects may affect the physicochemical properties
of the components, the interactions with liquid-liquid systems
generally manifest themselves as changes in the hydrodynamics.
The most important effects will be discussed in terms of the
following types of interactions: droplet translation, deformation,
stability, and oscillation.

The situation which is of most importance for liquid-liquid
extraction is that of a conducting droplet located in a (relatively)
nonconducting continuous phase under the influence of an electric
field. For a free droplet, even when the continuous phase is a
"very good" insulator, the minute amount of current flow through
the continuum will cause a small amount of charge to be present at
the interface.[16] In the case of droplet formation at an
electrode, the droplet will carry a relatively high surface charge
which approaches a limiting value determined by Rayleigh.[17]
In either case, effects of the tangential electric field at the
interface and the surface charge distribution will generally be
small enough so as not to induce significant fluid motion in the
system (see Equation 19).

Given, then, that all liquid droplets will acquire a finite
amount of charge, it is necessary to take into account electric
field-charge interactions. When a charged droplet is placed in a

SLIGHTLY CHARGED
DROPLET

WILL BECOME
POLARIZED
IN THE FIELD

AND MOVE TOWARD
ELECTRODE OF
OPPOSITE SIGN

DEPENDENT UPON CONDITIONS,
TWO DROPLETS MAY MOVE IN THE FIELD
AND BE ATTRACTED TO EACH OTHER.
THIS IS A POTENTIAL AID TO COALESCENCE.
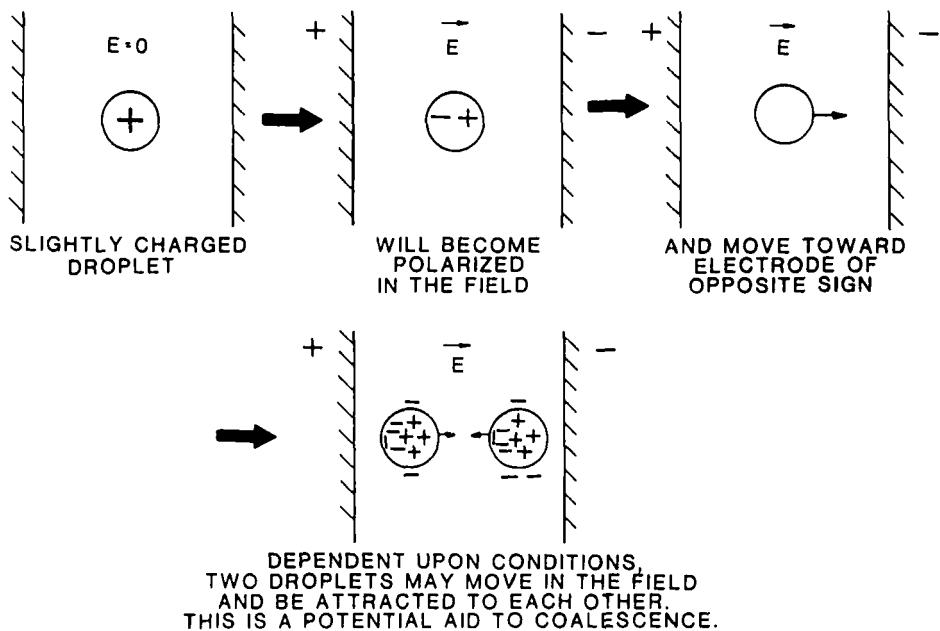
FIGURE 2
Polarization and Translation of a Charged
Droplet in a Steady DC Field.

steady DC field, two important phenomena occur: the droplet is

polarized, and the droplet undergoes electric-field-induced

motion. Figure 2 depicts these two effects on a charged conducting

droplet located in a steady DC field. Polarization of the charge

may have effects upon droplet-droplet interactions because

oppositely polarized ends of separate droplets may attract one

another. The effect of the net charge in the field will be for

the droplet to migrate toward the electrode of opposite sign;

SPHERE   PROLATE SPHEROID

(NO FIELD)   (FIELD ON)
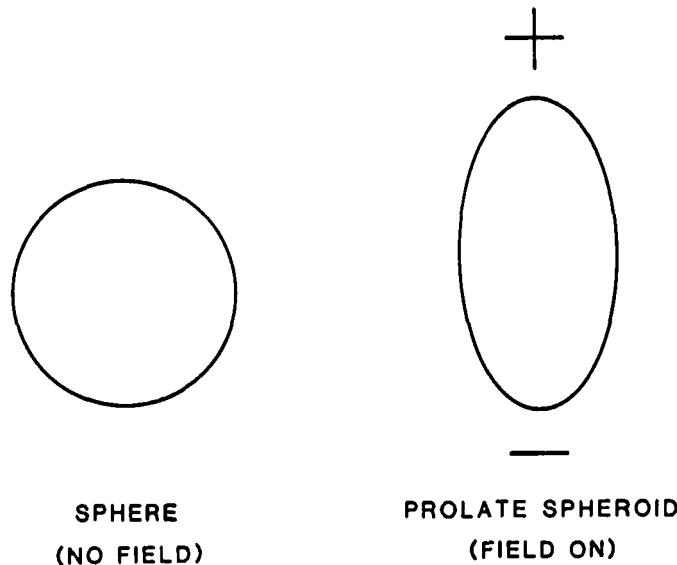
FIGURE 3
Droplet Deformation in a Strong Electric Field.

hence, the steady electric field induces droplet motion in an

otherwise stagnant system.

Placing a spherical, conducting droplet which is surrounded

by a nonconducting continuum in a steady DC electric field will

cause stresses to develop on the droplet.[18] As the strength of

the field is increased, the droplet will deform into an ellipsoid

whose major axis lies parallel to the electric field lines (see

Figure 3).[19] Solving an alternate version of Equation 2 for the

electric field vector, $\underline{E}$, in conjunction with the augmented

Young-Laplace equation enables one to determine the shape of the

droplet.[4],[18] If sufficient field strength is provided, the

(NECKING)   **(JETTING)**
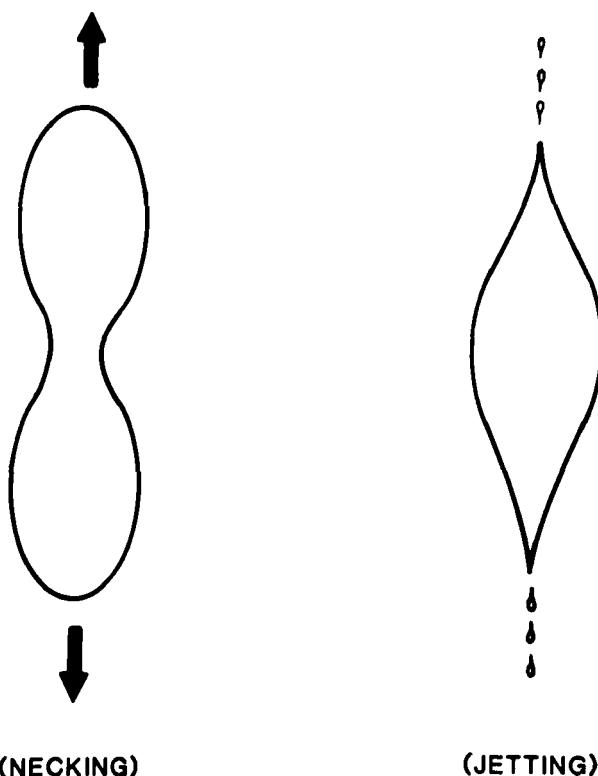
FIGURE 4
Droplet Disintegration in Electric Fields.

droplet deformation will become large enough to overcome inter-

facial tension and cause disintegration of the original droplet

into a large number of smaller daughter droplets.[16],[20],[21]

Dependent upon droplet charge and electric characteristics,

disintegration can occur by necking in the middle of the ellipsoidal

shape prior to break-up, or by cone formation and jetting of small

droplets from either end of the droplet as shown in Figure 4.[22]

When an AC or pulsing DC field is used, the droplet will deform when the field is "on" and relax back toward the spherical shape when the field is "off" thereby forcing the droplet to oscillate about the spherical form. The droplet undergoes deformation each time the DC field pulses and two times per cycle when using an AC field. The main effect of this type of activity is to alter the velocity profiles within the droplet and around the interface in the continuous phase. This alteration can, in turn, affect the interfacial mass transfer rate of the system.[23] Transient fields can also be used to cause droplet disintegration; however, the field strength required is higher than when using a steady DC field.[24]

A liquid droplet immersed in a viscous continuous phase has a "natural oscillation frequency" which is a complex function of the drop size, physical properties of the two phases, and interfacial tension.[25] If a droplet is deformed with a single disturbing pulse and allowed to dissipate the energy of the pulse, it will do so at this preferred natural frequency. If the droplet is disturbed with a transient field as described above, the amplitude of the droplet oscillation, while holding the electric field strength constant, becomes a complex function of the frequency of the electric field. Figure 5 is a schematic representation of this type of behavior. The amplitude ratio of the disturbance goes through a local maximum at the natural frequency as calculated by Miller and Scriven and then increases to a value approaching the interaction with a steady DC field.[25] For a
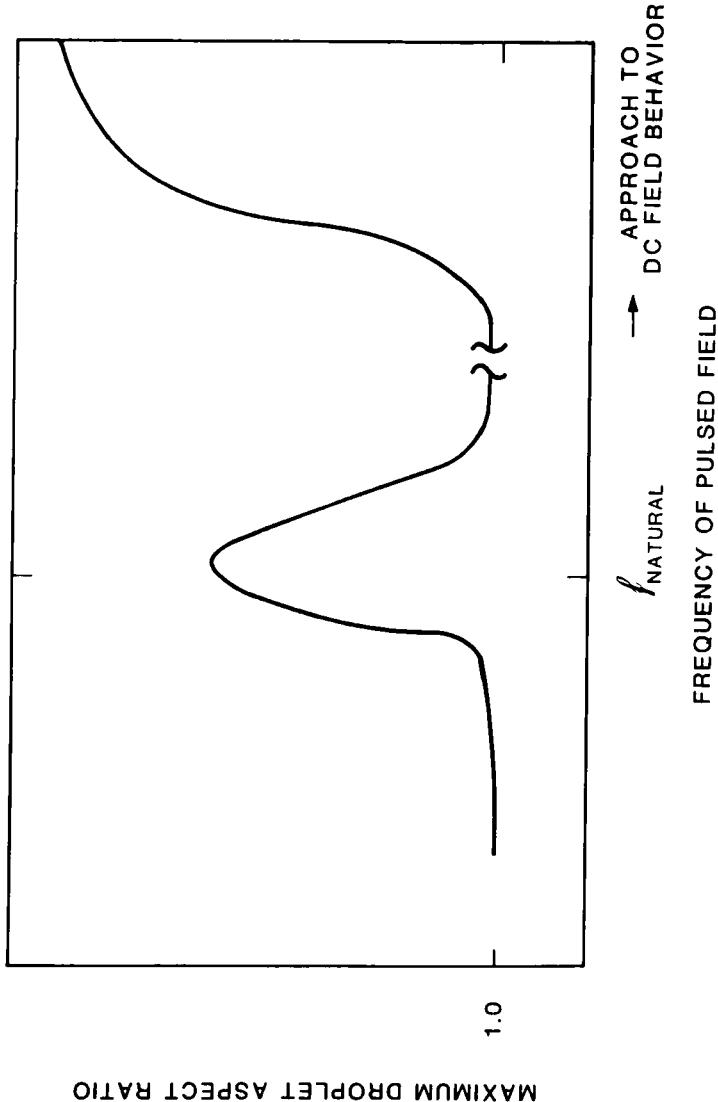
FIGURE 5

Droplet Deformation Behavior as a Function of Pulsed-
Electric-Field Frequency at a Constant Field Strength.

given liquid-liquid system, the natural oscillation behavior is essentially only a function of droplet size; therefore, varying the frequency of an electric field will preferentially affect specific droplet sizes.[24]

4. SYSTEMATIC CONSIDERATIONS

Having laid the groundwork with our discussion of the inter-actions of fluids and droplets with electric fields, we may now proceed to examine how these phenomena become important in altering the performance of liquid-liquid solvent extraction systems. It is convenient to examine extraction "componentwise" in terms of the several types of operations involved in nearly every extraction process. These common features are surface area (droplet) formation, free droplet-continuum interactions, and coalescence and phase separation. Figure 6 is a schematic diagram depicting these important common elements.

4.1 Droplet Formation

Formation of interfacial surface area for mass transfer may be considered as the first step in an extraction process. In practice, interfacial area or droplets are usually created by a form of mechanical manipulation. This general approach may take such forms as extrusion through sieve plates, use of impellers in baffled tanks, forced countercurrent flow through static packing, or combinations thereof.[26-28] As varied as these operations may appear, they all share a requirement for an energy input into the bulk of each of the liquids to create a dispersed phase with a

DROP FORMATION

FREE DROPLET-
CONTINUUM
INTERACTIONS

COALESCENCE
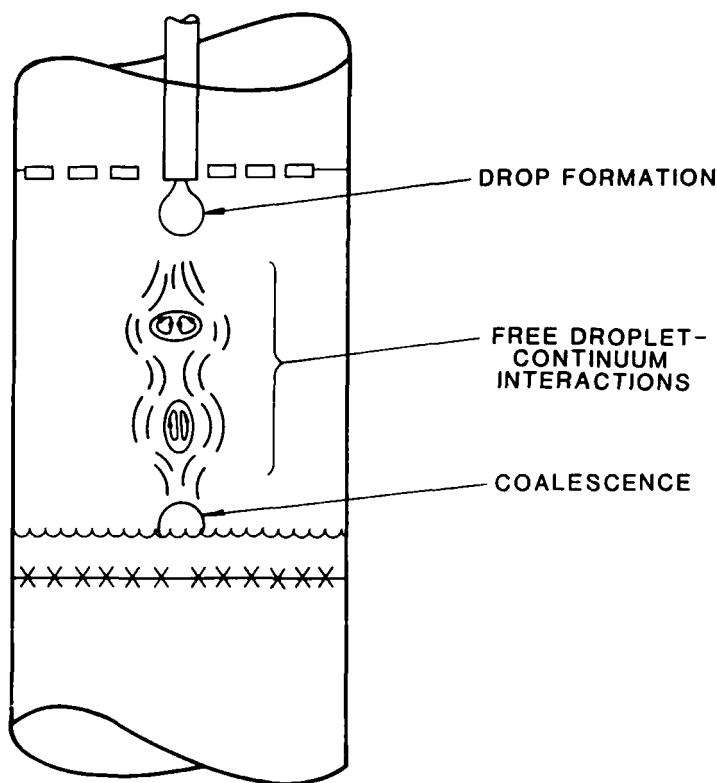
FIGURE 6
Common Features Important to Solvent Extraction Processing.

reasonable amount of surface area. This represents a possibly
inefficient use of energy because the continuous phase must be
manipulated to create the desired effect on the dispersed phase.

Electric field techniques have been investigated for use in
droplet formation from charged nozzles or orifices and to a lesser
extent for surface area creation via emulsification. In drop
formation studies, the size of the drop is determined by the

balance of gravitational, surface tension, and electrostatic forces.[29] The gravitational force is dependent upon the density difference of the two fluids and the droplet volume. The surface force depends the interfacial tension and the diameter of the orifice through which the droplet is formed. If the electrostatic force acts in the same direction as the gravitational force the result is the formation of droplets with a reduced volume. For the same flow rate of material through an orifice, the electrified system produces a larger number of droplets with reduced volume and consequently more surface area per unit volume of dispersed phase.

Numerous studies have been undertaken to investigate the effects of droplet formation from charged nozzles.[29-37] The experiments were performed utilizing a parallel flat plate electrode geometry similar to the apparatus schematically depicted in Figure 7. In these types of studies, single charged droplets are formed at the charged nozzle and are accelerated toward the bottom electrode by gravity and the electric field. The droplet volume, velocity, and formation rate were determined by high-speed photography or video cameras.

As the strength of the electric field is increased, the electrostatic force increases and the characteristic droplet size decreases until the transition is made from single-droplet formation into the jetting regime. Increasing the field strength not only decreases the droplet volume, but also increases the droplet velocity through the continuous phase because of the
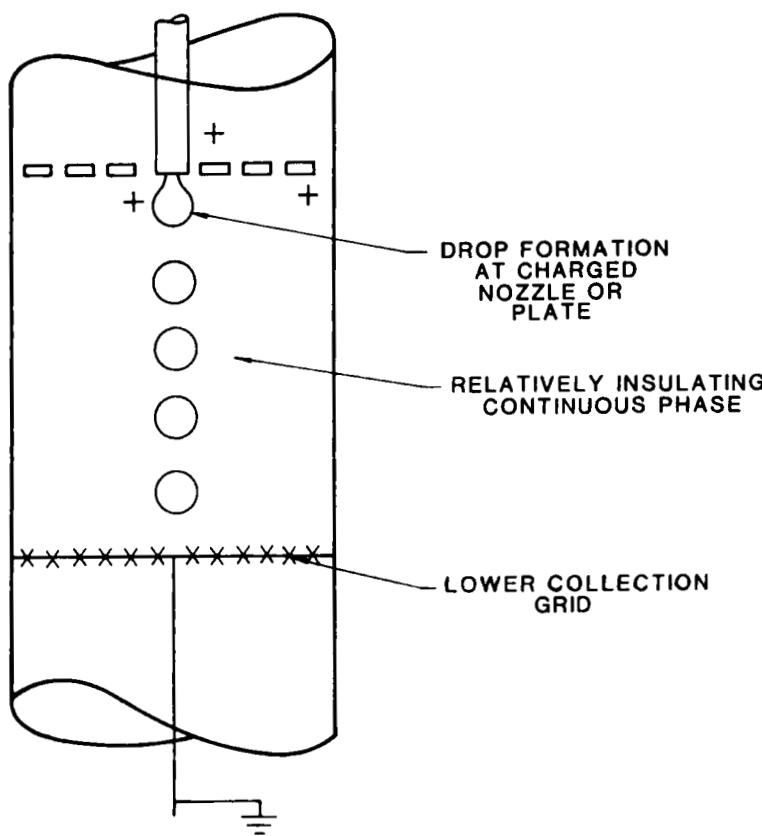
FIGURE 7
Typical Electrified Single Droplet Formation Apparatus.

accelerating affect of the field on the charged droplet. Due to

the increasing "pull" of the electric field the droplet is deformed

into a prolate spheroid as it detaches from the nozzle, thus,

giving it the tendency to oscillate after detachment.

To predict the resultant droplet size, given the physical

apparatus and electric field strength, Takamatsu et. al assumed a

spherical drop shape was formed in an electric field between two parallel plates.[34] This physical model did not predict well the effects at significant field strengths. Perona and Byers added the effects of the prolate spheroidal shape to obtain a better approximation to the electrostatic force on the forming droplets and met with improved results.[29] Using a more realistic model for the electric field by taking into account electrode geometry, Perona and Byers have extended their work and are now able to satisfactorily predict droplet sizes under conditions of high droplet deformation.[38] In the aforementioned studies, field strengths generally ranged between 0.2 and 2.0 kV/cm, with millimeter-sized droplets having volumes that were typically 2 to 10 times smaller than in the no-field case.

The potential benefits of electric field droplet formation are severalfold. First, the amount of surface area per unit volume increases over the no-field case, thus allowing more effective use of processing equipment. Second, the velocity of charged droplets through the continuous phase under the influence of the field is significantly higher, thereby increasing mass transfer rates on individual droplets. Last, the presence of charge on the droplets, in principle, should allow electric fields to be used to perform effective coalescence and phase separation operations on the dispersed phase.

Another approach to surface area formation (less well investigated) is electric-field-induced emulsification. If the electric field strength near a nozzle is increased past the point

of single droplet formation, jetting occurs which results in the

formation of an electrically charged emulsion of micron-sized

droplets. This phenomenon has been noted in DC, AC, and pulsing

DC electric fields.[24,39-42] Two interesting aspects of this type

of approach are the droplet-size characteristics and the energy

requirements for creation of the emulsion. The average droplet

size for these types of aqueous-in-organic emulsions is between 2

and 5 μm with associated droplet size distributions in the range

of 1 to 10 μm. Thus, using this method, there is a possible 200

to 500 times increase in the amount of surface area per unit volume

of dispersed phase compared to using millimeter-sized droplets

for conventional extraction processes. In addition, the droplet

size distribution is fairly narrow in the charged emulsion, so

perhaps hydrodynamic and electric field conditions in vessels

could be "tuned" to manipulate the small droplets.

A final word about droplet formation should include a state-

ment concerning the energy input required to obtain the smaller

droplet sizes. If the electric-field-induced droplet size

reduction requires a large amount of energy, the increase in

transport efficiency could be offset by increases in energy costs.

An investigation of this type has been performed for electric

emulsification.[40] In the experiments, a stream of droplets was

continuously emulsified between a parallel plate electrode system

utilizing a pulsing DC field. Energy inputs required to con-

tinuously form the emulsion were approximated by treating pulsed-

field behavior of the emulsion-electrode system as the charging

and discharging of a parallel plate capacitor. Comparison of this
value to droplet size and agitated-tank power input correlations
revealed that the electric field energy input was significantly
less than 1% of that required when using mechanical agi-
tation.[27,43,44] The assumed average droplet size was 5 μm with a
correspondingly narrow size distribution — conditions easily
obtainable in the electrical system but not (if at all possible)
in the mechanical one. In fact, agitated tank correlations had
to be significantly extrapolated to obtain this analysis; hence,
the comparison was considered to be a conservative one.

4.2 Free Droplet-Continuum Interactions

After droplet formation occurs, the dispersed phase to some
degree translates with respect to the continuous phase, all the
while allowing transport of material, until coalescence and phase
separation are carried out (see Figure 6). Dependent upon the
extent of separation achieved during this time as compared to the
needs of the particular operation, the coalesced phase may either
be redispersed to allow further mass transport to occur, thus re-
peating the cycle, or the process is terminated, with the resultant
liquids being sent to other operations for further processing.
During the free droplet-continuum interaction stage of the process,
the rate of mass transport is strongly dependent upon the hydro-
dynamic state of the system. The contribution of electrically
based processes to increasing rates or enhancing separation is
generally due to alteration of the velocity profiles within and
around individual droplets.

The hydrodynamic state of the system may vary widely from a stagnant droplet surrounded by a nearly stagnant continuous phase to a droplet that displays vigorous internal motion and translation with respect to the continuous phase. The two primary modes of velocity profile alteration produced by the aforementioned electric field methods are increased relative velocity between the phases and inducement of droplet oscillation.[45] Either of these effects can lead to significant enhancement in overall mass transfer rates. Increased droplet velocity occurs as a result of inter-action of charged droplets with the imposed electric field (see Section 3). It has been illustrated that the terminal velo-city of droplets formed at charged nozzles can easily exceed two times that of uncharged droplets of the same size.[46] Therefore, using an electric field for droplet formation not only produces smaller droplets, but causes them to move through the continuous phase at a higher velocity than the no-field case. Hence, the rate of mass transfer is enhanced by the greater amount of inter-facial area per unit volume and by the increase in the local mass transfer coefficient provided by the higher droplet velocity.

Oscillation of droplets in an electric field can be caused by either relaxation of the droplet from an initial deformation or by periodic forced deformation which occurs as a result of transient electric fields. As mentioned in Section 3, droplets formed at charged nozzles in steady fields tend to start out as prolate ellipsoids. The aspect ratio of this deformation increases as the electric field is increased. To dissipate the stress imposed by

the initial deformation, the liquid droplet undergoes damped
oscillations at a frequency which is characteristic of the physical
properties of the two liquids as it is accelerated through the
continuous phase.[25]

The effects of these oscillations are twofold: the amount of
surface area available for mass transfer is greater, and the
velocity profiles within and around the droplet are altered. The
increase in interfacial surface area for oscillating droplets has
been treated as the primary mode for the enhancement of mass
transfer by several researchers.[47,48] Neither of these approaches
takes into account the actual velocity profiles involved in the
oscillating droplet system, and subsequently they have been shown
to underpredict the effect of oscillation upon mass transfer. [45,49]

Evidently, the increase cannot be adequately described unless
the effect of droplet oscillation upon the actual velocity profiles
is also taken into account. This hypothesis is supported by
oscillating-circulating droplet mass transfer data for the
dissolution of water droplets in 2-ethyl-1-hexanol (2EH).[49] In
this study aqueous droplets were suspended in upflowing 2EH and
forced to oscillate about the spherical form by a pulsed DC
electric field which was parallel to the flow field. The fre-
quency of droplet oscillation was varied from 0 to 50 Hz, with an
amplitude of oscillation that was 10% of the initial droplet
radius. Based on surface area arguments, the increase in mass
transfer for the highest oscillation rate should have been only a
matter of several percent; however, the reported enhancement was a

40% increase in the rate of mass transfer for an oscillation frequency of 50 Hz.

The use of quantitative and qualitative flow visualization techniques for the oscillating-circulating droplet system has confirmed the complex nature of the problem.[23] This study has shown that forced oscillation of a fully circulating droplet which is translating through a continuous phase simply imposes a secondary flow upon the internal droplet motion. Both the altered internal droplet and continuous phase motion display smooth, continuous streamlines. The velocity profiles were modeled as the vectorial addition of low-Reynolds-number circulatory Hadamard flow and flow due to oscillations of an ellipsoid about the spherical form.[50,51] Numerical solution of the convective-diffusion equations describing droplet-continuum mass transport utilizing these altered velocity profiles yields predictions of mass transport increases on the order of 29 to 59% for the water-2EH system.[52] This type of approach appears to be in much better agreement with the limited amount of mass transfer data. Furthermore, it has been noted that the rate of heat and mass transfer in oscillating droplets is a complex function of both the frequency and amplitude of oscillation with the rate of transfer increasing upon augmentation of each of these parameters.[53-55] To best take advantage of these relationships, one would wish to operate a system in which relatively small droplets would be formed and forced to undergo high-amplitude oscillations as they move through the continuous phase.

4.3 Coalescence and Phase Separation

The final step in extraction operations involves coalescence of the dispersed phase to enable separation of the immiscible liquids and to allow redispersion or further processing. Of the three steps shown in Figure 6 this is the least understood, particularly when one is taking into account the effects of steady or transient electric fields upon the coalescence of charged droplets. Although the mechanisms involved are not known, several applications of steady and transient electric fields have been made to carry out phase separation in liquid-liquid systems.[33] Electrically enhanced settling has seen limited use in solvent extraction for quite some time. Researchers at Lurgi developed a multistage mixer-settler which allows for improved settler performance through the use of electric fields.[56] Additional applications of electrical techniques have been noted in hydro-metallurgy and dehydration of crude oil emulsions.[57-59]

A qualitative approach to understanding this complex phenomenon can be obtained by taking into account several interactions that can occur in electrified emulsions. A number of coalescence mechanisms based upon electric field interactions have been suggested. Hypotheses along these lines include chain formation, dielectrophoresis, electrophoresis, dipole coalescence, electrofining, and random collisions.[60] The formation of chains of droplets prior to coalescence has been observed by several authors.[61-63] It is speculated that the chains are formed by forces due to the potential differences between drops as a

result of induced charges. Dielectrophoresis and electrophoresis are involved with droplet motion induced by polarization and charge interactions with the electric field, respectively.[64],[65] In both of these cases, the net result is for the imposed electric field to induce droplet motion in the continuous phase, thereby increasing the probability for droplet-droplet interactions. Dipole coalescence as defined by Waterman occurs as a result of droplets acquiring an induced dipole in either AC or DC fields, while electrofining relies on the combined effects of electro-phoresis, induced dipoles, and differential droplet velocities to enhance coalescence.[65]

Another approach involves explaining enhanced coalescence rates in fields in terms of an increase in the number of random collisions between droplets due to induced droplet motion between electrodes.[66] This work has proposed a model for electrostatic coalescence based on a random collision/coalescence mechanism; however, the model parameters are not readily measured, so correlation of experimental data is not easily carried out. The collision frequency approach has also been investigated by Bailes and Larkai.[60] The intent of this work was to develop an expression which allows straightforward correlation of coalescence efficiency versus the enhanced droplet collision rate. In this study the enhanced collision frequency was determined by taking into account the additional force imposed on liquid droplets by electric fields. Several data sets obtained using a pulsing DC field were examined with this method. A plot of coalescence efficiency

versus enhanced collision frequency containing all of the data
sets yielded a single, smooth curve. Use of this correlation to
explain the behavior in steady DC fields was not successful.

5. EXTRACTION SYSTEM CONCEPTS

Currently, there are no industrially significant solvent
extraction systems that are controlled by utilizing electric
fields. However, as mentioned in the preceding section, several
applications of electric-field systems to enhance emulsion
coalescence are now in operation. Although not yet on the market,
two general types of electrically controlled extraction systems
have been proposed and tested on the laboratory scale. The first
kind is based upon formation of millimeter-sized droplets at
charged nozzles and is designed to operate in vessels resembling
sieve-plate columns. The second is based on electric field
emulsification/coalescence phenomena and may require new equipment
configurations.

Three examples of charged nozzle devices have been reported
in the literature.[45,46,67] Figure 8 is a schematic diagram of an
electrical extractor designed by Thornton.[46] The device repre-
sents a single stage in a sieve-plate column. The top plate is at
a higher electrical potential so as to force droplet formation
through the top plate and accelerate the droplets downward. Mass
transfer tests on this device using the water-benzoic acid-toluene
system indicated that for the same flow conditions the extraction
rate could be increased by a factor of 3. The factor of 3 was
obtained by comparison of the electric field to the no-field case
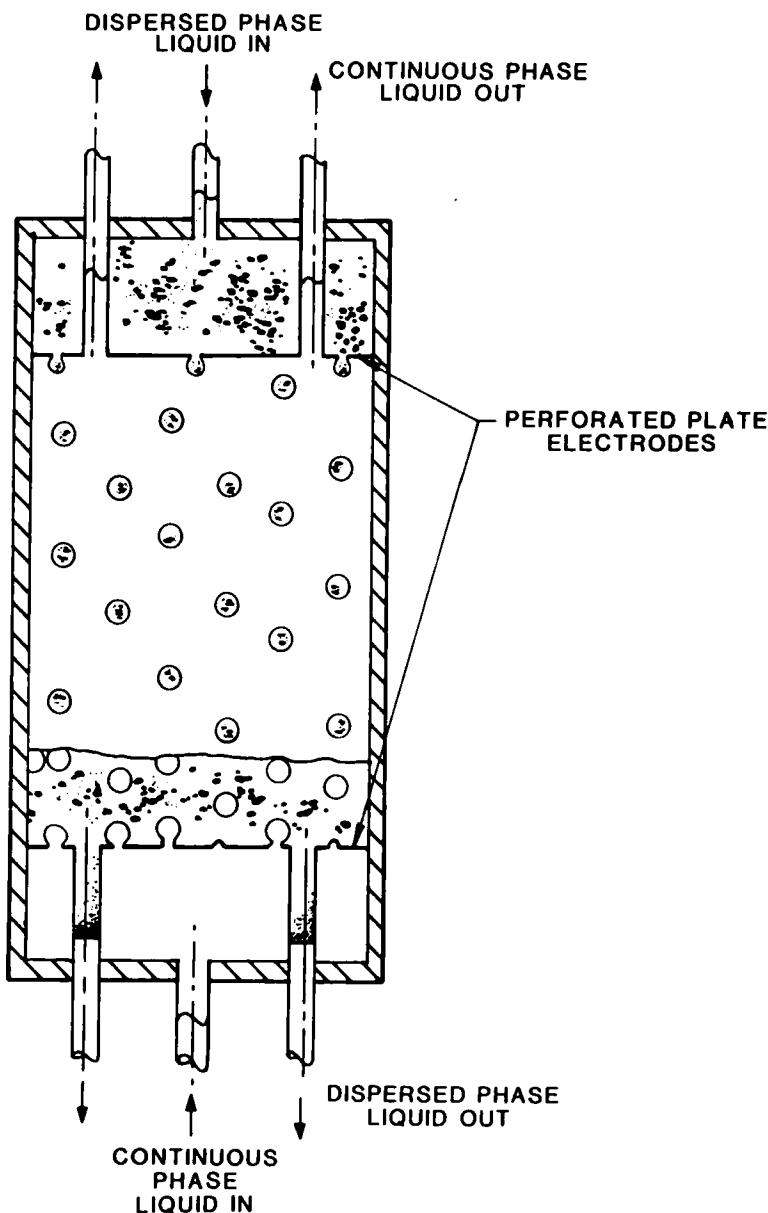
FIGURE 8
Electric Field Driven Solvent Extraction Device.

in this particular apparatus. No comparisons were made to the
performance of existing industrial devices. It was noted that if
the continuous phase was "too conductive," significant current
flow could be realized. Therefore, the basic design was modified
by Bailes to provide a nitrogen gas gap between the top electrode
and the upper surface of the continuous phase.[45] This second
design is depicted in Figure 9. Mass transfer tests were carried
out using the water-acetone-n-butyl acetate system. The reported
results were in terms of the Murphree tray efficiency for the
single stage device. Upon imposition of a 50-kV electric field
across the distance between electrodes (including the air gap
and liquid phase), the tray efficiency of the apparatus approached
85%, or nearly double that of the no-field case. Again, no
comparison to industrial devices was quoted.

A related extractor geometry has been suggested which utilizes
a horizontal AC- rather than vertical DC-electric field.[67] Figure
10 contains a schematic diagram of the device. The extractor
contains four vertical-rod electrodes. Two rods opposite one
another serve as positive poles, while the other pair act as nega-
tive poles. The nonuniform electric field causes the formation of
relatively small droplets from the top nozzle and then aids in
translating the droplets down the column in the presence of
countercurrent flow of the continuous phase. Mass transfer tests
with the water-acetic acid-carbon tetrachloride system indicated
that the fraction of material extracted from the organic phase
improved by a factor of 2 to 3.5 over the no-field case.
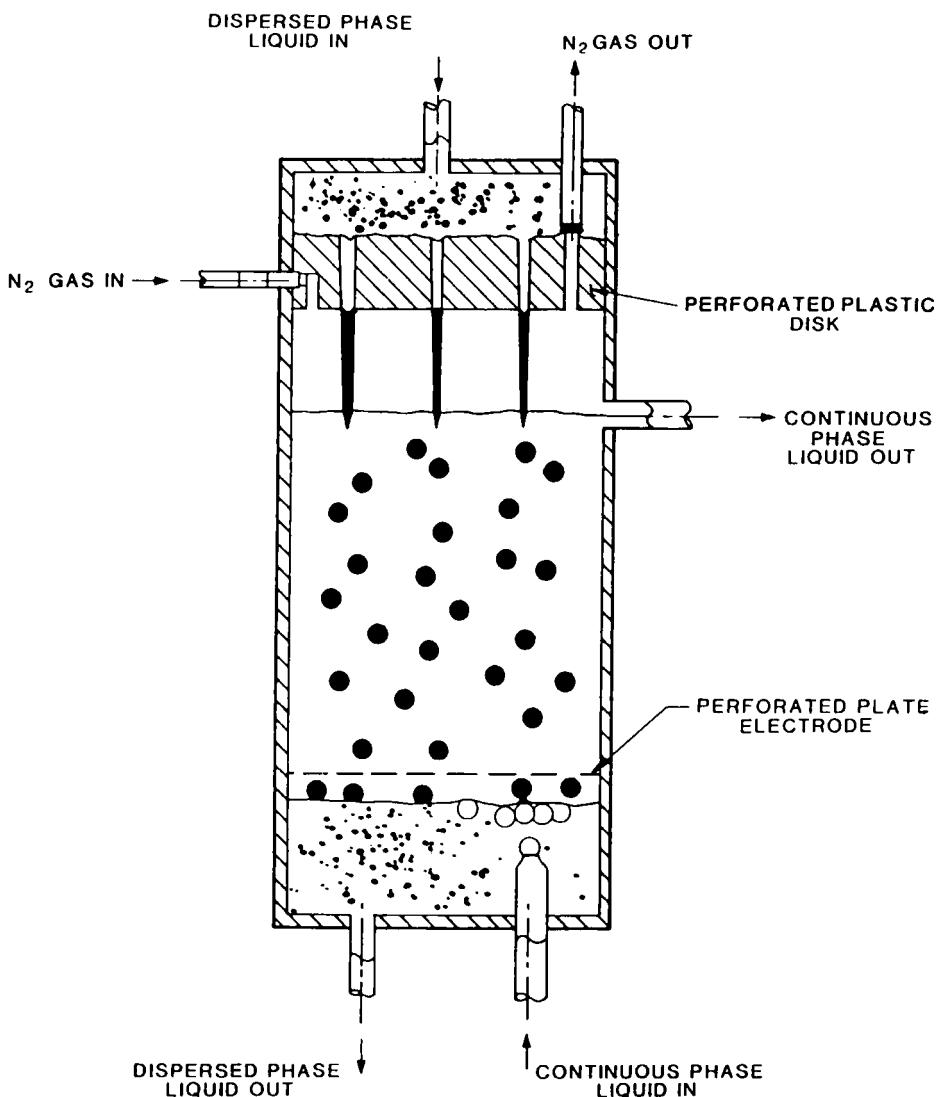
FIGURE 9
Modified Electric Field Driven Extractor.

DISPERSED PHASE
LIQUID IN

CONTINUOUS PHASE
LIQUID OUT

POLYETHYLENE-
COVERED
METAL ROD
ANODES

METAL ROD
CATHODES

DISPERSED PHASE
LIQUID OUT

CONTINUOUS PHASE
LIQUID IN
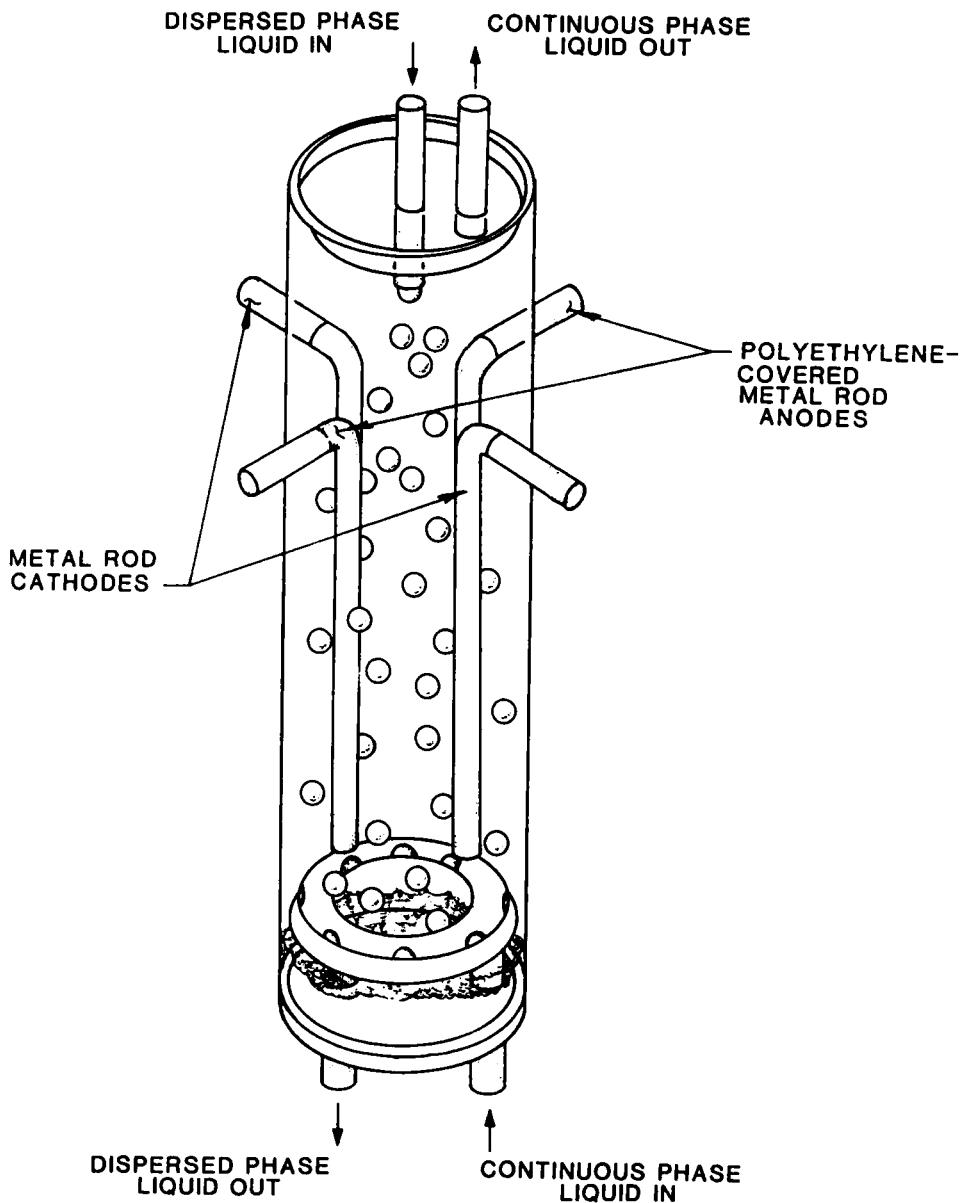
FIGURE 10
Vertical Rod Electrode Extraction Device.

Although the charged nozzle devices appear to provide improve-
ment over the corresponding "no-field" cases, it is not clear that
these systems represent significant improvements over the best
existing technology. One type of system which clearly shows
promise for enhanced operations is based upon the simultaneous
emulsification/coalescence phenomena which can occur in transient
electric fields.[41,42] A schematic diagram of this device is
illustrated in Figure 11. During operation, the electric field is
used to create a high-surface-area emulsion, to hold the emulsion
in place against upward flow of the continuous phase, and to induce
coalescence. Coalescence of the emulsion occurs at a point below
the area of droplet rupture, but still within the electric field.
The resulting large droplets fall through the lighter organic phase
and form a separate, aqueous phase in the bottom section of the
vessel. During emulsification, the continuous phase enters near
the bottom of the vessel, flows upward, and is withdrawn at the
top of the vessel. The (relatively) conducting and slightly
charged emulsion remains in the vicinity of the electric field
around and between the electrodes and is therefore separated from
the upflowing organic phase. Thereby, the system achieves disper-
sion to form mass transfer surface area, coalescence, and phase
separation in a single vessel utilizing a single electric field.
The emulsion behaves as a separate, fluidized phase; hence, the
device has been named the emulsion-phase contactor (EPC). Bench-
mark mass transfer tests for this device have been carried out
with the water-acetic acid-methyl isobutyl ketone system. Results
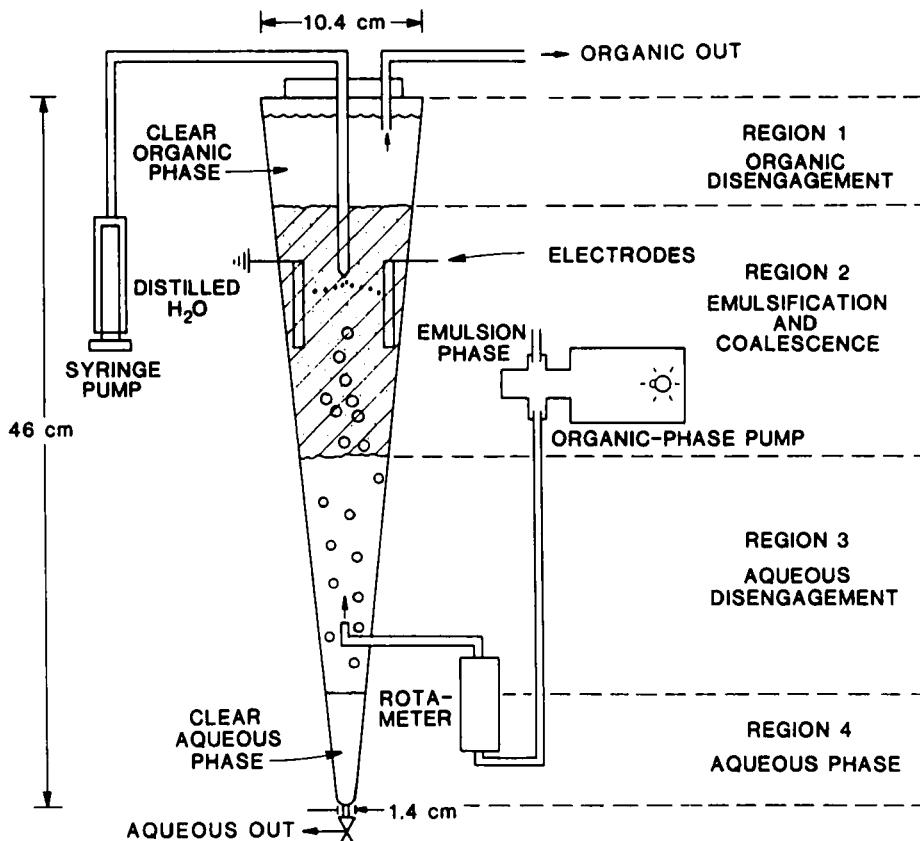
FIGURE 11
The Emulsion-Phase Contactor.

were reported in terms of the number of theoretical transfer stages

per cm of emulsion height. The EPC with 1.7 stages per cm (6

stages in 3.5 cm) outperformed laboratory-scale versions of the

York Scheibel (0.1 stages/cm) and Podbielniak (0.17 stages/cm)

contactors by factors of 17 and 10, respectively. In light of

these promising results, the potential for industrial applications

appears to be present; however, further experimentation needs to be carried out in order to determine throughput capabilities and equipment geometry.

6. PROSPECTS FOR POSSIBLE USE AND FURTHER RESEARCH

Although a minimal impact has been felt to date in the chemical processing industries, it still is possible that electrically controlled solvent extraction systems will provide significant contributions to separations processing. These types of techniques are limited to fluids with appropriate electrical properties, but, a significant portion of the fluid pairs utilized in industry today meet these requirements and could potentially benefit from such electric field effects if the process can be operated in the "insulating-phase-continuous mode." To assess the utility of electrohydrodynamic effects for extraction operations, future research should focus on several important areas: droplet formation/dispersion phenomena, coalescence of electrified emulsions, and the possibility of interactions of electric-field-induced charge effects with physical and chemical charge effects.

It is obvious from the earlier discussion of droplet formation that a healthy research thrust exists on the formation of macroscopic (millimeter-sized) droplets from nozzles and orifices. The treatment to date has been largely empirical. Often, in lieu of proper first principles arguments, authors have resorted to indefensible speculation involving complex electric field and interfacial tension effects to explain deviations from simple models. This is an area which deserves further refinement in

order to take advantage of state-of-the-art hydrodynamical
numerical analyses so that one can calculate resultant droplet
sizes and velocity profiles involved in electrified droplet
formation. It is evident that a significant fraction of mass
transfer in extraction systems occurs during droplet formation;
hence, it is very important that future studies address the
calculation of formation hydrodynamics in a very fundamental
fashion and then use these results to infer effects upon the rate
of mass transfer.

Formation of micron-sized emulsions via electric field
dispersion of material from a nozzle or of free droplets repre-
sents an area of great promise for vastly increasing the
performance of extraction devices. The primary question involved
in developing this approach is one of controlling the microscopic
droplets after formation. In current liquid-liquid systems, the
formation of such droplets is avoided because of potential
entrainment problems in the continuous phase. The electric field
approach yields some hope for control as the droplets that are
formed will be (at least) slightly charged and therefore subject
to interaction with electric fields. The numerical simulation of
droplet fissioning in high intensity electric fields is a subject
on the forefront of electrohydrodynamic research. Thus, initial
investigation into this area may tend to be approached from a
practical point of view until more general treatments can be
formalized.

An important issue related to emulsion formation is
electrified emulsion coalescence. The simultaneous emulsification/

coalescence phenomenon observed in preliminary experiments seems
to indicate that electric fields can be used to control emulsions;
however, the design criteria for electrode configuration and
vessel geometry which would allow industrial application are still
to be determined. Apart from designing a useful extraction system,
fundamental studies need to be carried out to understand the
coalescence mechanism. Coalescence of electrified liquid droplets
in air (cloud physics) is an area of active research. In contrast,
surveying the literature one finds that reasonable treatments of
electrified liquid-liquid interactions do not exist. The com-
plicating factor of the liquid-liquid system is the effect of
continuous phase viscosity upon momentum transfer and the resultant
effect upon coupling of charge, momentum, interfacial, and viscous
transfer processes which allow droplet collisions to result in
coalescence events. At this point in time, about all that can be
said is that transient electric fields appear to be more efficient
than steady fields for emulsion coalescence; hence, this area
harbors a great potential for fruitful research.

Other possible areas for consideration could involve
investigation of the interactions of electric-field-induced
charges with physical and chemical phenomena. For example,
adsorption of charged, surface-active material onto the droplet-
continuum interface could provide the means for controlling or
altering behavior in electric fields. It is also conceivable that
significant differences in transport rates involving reactions
with ions could be realized because of effects caused by droplet

charge and high intensity electric fields. At the present time,
these type of interactions have not been investigated to any
significant extent for extraction systems.

In summary, although significant applications do not currently
exist for the use of high-intensity electric fields in solvent
extraction, several prototype systems are candidates for further
testing and several areas of potentially beneficial research
should be investigated before the concept is abandoned.

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8. NOMENCLATURE

$\underline{D}$ – electric displacement vector

$\underline{D}^i$ – electric displacement of phase i at the interface

$\underline{E}$ – electric field vector

$\underline{E}^i$ – electric field vector of phase i at the interface

$\underline{g}$ – gravitation force per unit mass

2H – local mean curvature

$\underline{J}$ – current density vector

$\underline{i}_s$ – surface current density vector

$\underline{n}$ – unit normal vector

$\underline{P}$ – polarization vector

P_0 — zero field pressure

P_s — electrostrictive pressure

T — temperature

T_e — electric shear stress

$\underline{\underline{T}}$ — stress tensor

$\underline{v}$ — velocity vector

γ — conductivity

ϵ — permittivity

ϵ_0 — permittivity of free space

η — liquid viscosity

ρ — liquid density

ρ_E — volume charge density

$\rho_{E,0}$ — initial volume charge density

σ — interfacial tension

σ_E — surface charge density

τ_e — electrical relaxation time

∇ — nabla

∇_S — surface nabla

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