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Electrostatic Coalescence: Reactor, Process Control, and Important Parameters

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Abstract

An optimal breakage of liquid membrane emulsions is desirable for the industrial application of liquid membrane extraction. The electrostatic emulsion breakage process was investigated with regard to its parameters. The results show that the breakage efficiency increases with the applied field strength, frequency, and the achievable polarization of the membrane phase molecules. An on-line measurement of the applied field strength allows control of the process efficiency.

I. INTRODUCTION

Liquid membrane extraction (LME) represents a new separation technique for special applications (*1*, *2*) (Fig. 1). LME can be applied on an industrial scale by optimizing the extraction process and the breakage of the emulsion. However, chemical processes for deemulsification have failed because the advantage of minimizing the amount of organic substances of the used W/O emulsions was lost.

Therefore, deemulsification requires a physical process. An electrostatic separation of the emulsion is promising because it requires only small amounts of electrical energy. For example, the petroleum industry relies on electrostatic coalescence for the purification of crude petroleum, which is washed with water to remove corrosion-inducing salts (*3*). Basically, there are two types of processes for the electrostatic separation of liquid-liquid dispersions (Fig. 2):

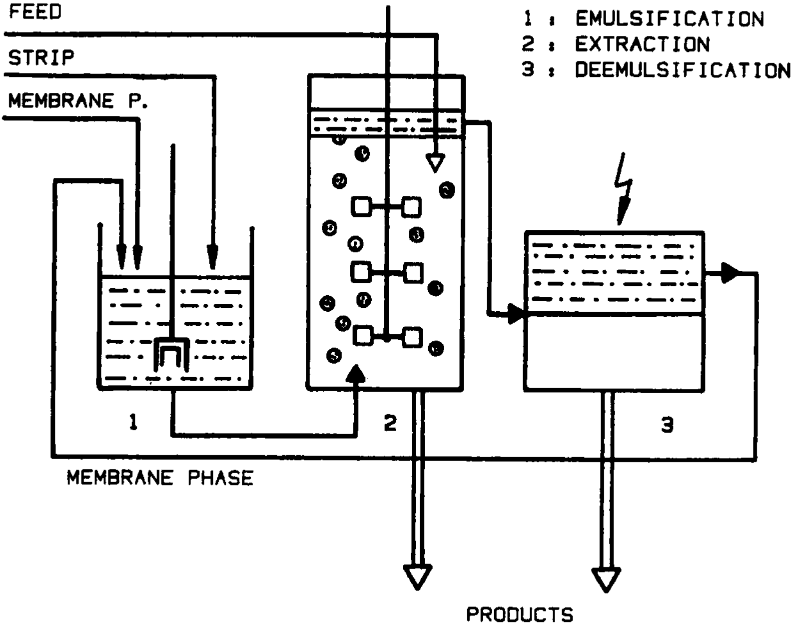


FIG. 1. Extraction with the liquid surfactant membrane process scheme.

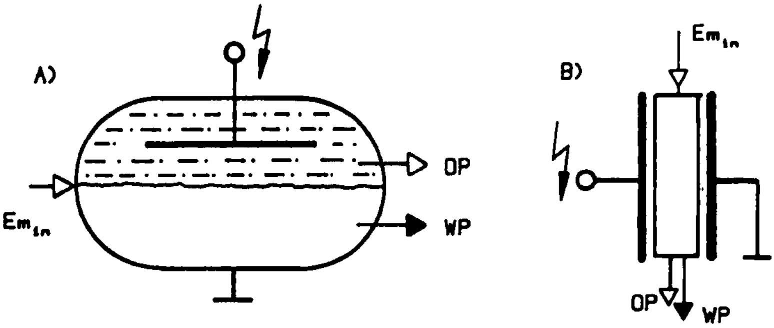


FIG. 2. Typical coalescence reactors: A) tank reactor, B) cellular reactor.

A. Tank coalescence reactors with (non)isolated electrodes
B. Cellular reactors with isolated electrodes and an external settler

Reactors of Type A are utilized in the petroleum industry (*4–6*). For special emulsions used in liquid membrane extraction, Li et al. developed a reactor with isolated horizontal electrodes (*7*).

In this work, a reactor of Type B was investigated; a high voltage alternating current of variable frequency was used.

A. Electrical Properties of the Deemulsification Process

The coalescence of encapsulated water droplets in organic solutions containing surfactants can be induced by both dc and ac fields. However, dc fields cause electrolysis in the encapsulated water phase and are less effective in inducing coalescence (*8*, *9*). Coalescences induced by pulsed dc and high-powered ac voltages with low frequencies have also been investigated. Bailes and Larkai (*10*) stated that the coalescence efficiency of complex water-in-oil emulsions depends on the frequency of the applied pulsed dc field. In the range of lower frequencies (0–60 Hz), they observed maximum coalescence rates near 10 Hz.

Electrically induced coalescence strongly depends on such electric parameters as field strength and frequency (Table 1). Some publications on electrical coalescence have shown that the efficiency of the coalescence decreases with increasing field strength, and also that the frequency dependence is unpredictable (*11*). In our investigations we used alternating current to induce the emulsion breakage in all experiments.

B. Influence of Emulsion Composition on Electrostatically Induced Coalescence

As discussed previously (*9*, *12*, *13*), coalescence also depends on the properties of the dielectric medium in the reactor. The main parameter is

TABLE 1
Parameters of Electrostatic Coalescence

i. Field strength
ii. Frequency
iii. Emulsion composition

the water content of the emulsion. Hanai et al. (*19*) project various equations to describe the relative permittivity of emulsions with regard to the water content (e.g., Brüggeman's, Wagner's, or Wiener's equation). However, the water content depends on the parameters of the extraction (e.g., residence time of the emulsion) and effects such as osmosis and occlusion (*20*). The composition of the membrane phase is an important parameter for extraction and also for emulsion breakage behavior.

The physical parameters of the emulsion (e.g., viscosity and surface tension) are also altered with the amount of surfactant or extractant in the membrane phase (*21*). In order to discuss the influence of these parameters on electrically induced coalescence, the mechanism of this process must be described in a schematic model.

The coalescence of two adjacent droplets takes place in a two-step mechanism. In the first step the separating layer between the droplets is removed as the droplets approach an equilibrium distance due to the electrical field strength (*23*). Coalescence can only take place if the thin separating layer can be ruptured in the second step. Instabilities in the film layer or sparking due to the applied field strength induce this final disruption, and the droplets coalesce (*22*). With the application of an electrical field, the layer can be compared with a dielectric medium between two electrodes (the water droplets) in a capacitor. Typically, the thickness of the layer lies between 3 and 5 nm (*23*). Thus the chemical and physical properties of the membrane phase influence both steps:

Removal of the separating layer
Changes of the dielectric properties of the layer

The dielectric properties of the layer are influenced by the solvent. The first step seems to be dependent on the viscosity of the membrane phase. The measurement of surface tension is a difficult task, but fortunately, its influence can be neglected since its value remains constant due to the large amount of surfactant. For these investigations the breakage rate of various emulsions was measured under the same electrical conditions.

II. EXPERIMENTATION AND APPARATUS

A. Reactor Equipment

A high water content is typical of LM emulsions. This condition requires the use of a reactor with a high disruptive strength. We chose vertically mounted electrodes on a cellular reactor with separated coalescence and settling areas. This system provides a constant emulsion composition in the reactor. A high disruptive strength is attained by a two-stage liquid/solid insulation which decreases the air content in the insulating system (Fig. 3). In order to increase the disruptive strength, the liquid insulation oil may be cooled in regard to the thermal character of the disruptions. Before the start of an experiment, the unit must be completely filled with emulsion. The process of emulsion breakage is controlled by monitoring the lower liquid-liquid interface (water/emulsion) in the settler.

Complete emulsion breakage is achieved by the recirculation of the unbroken emulsion. In a semicontinuous operation the unbroken emulsion in the settler is separated and recycled. For a continuous process the reactor is supplied with fresh emulsion using pumps P_1 and P_2. By increasing the pumping performance of P_1 as compared to that of P_2, we can also recycle the emulsion for continuous emulsion breakage.

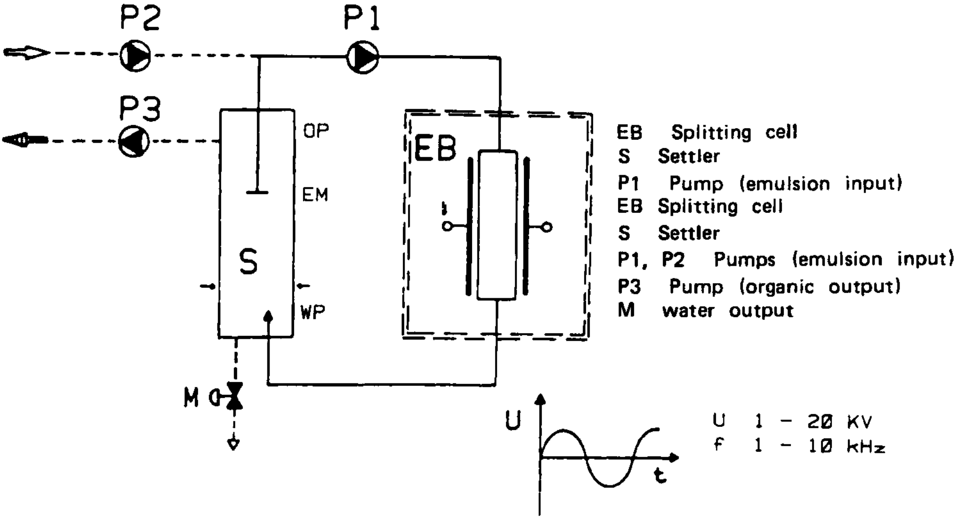


FIG. 3. Schematic of the apparatus for the electrostatic coalescence of a liquid membrane emulsion.

B. High Voltage Supply

High voltage was supplied by the combination of a function generator, an amplifier, and a transformer. This combination gave frequencies up to 10 kHz with a maximum voltage of up to 3 kV (Fig. 4).

C. Emulsion Preparation and Breakage

With regard to more commonly used extraction systems, breakage was obtained by using liquid membranes for copper and zinc extraction (*1*, *2*). Span 80 was chosen as the surfactant. In all experiments the encapsulated water phase contained 10–20 g/L metal in sulfuric or hydrochloric acid solution (Fig. 5). The emulsions were prepared with a high-speed stirrer. The water phase was dispersed within 45 s (5000 rpm) into the organic phase. Complete dispersion was achieved by vigorous stirring for 120 s (20,000 rpm).

Emulsion breakage was investigated at various field strengths and frequencies. The process was controlled by monitoring the liquid–liquid interface in the settler. The voltage vs time curve was digitally recorded to obtain the coalescence efficiency.

D. Variation of the Electrical Parameters

In order to investigate the effects of the electrical coalescence during a semicontinuous coalescence experiment, an on-line measurement of the applied voltage was installed. The system can be compared to a wiring diagram that includes a capacitor and a resistor which corresponds to the insulation and the emulsion inside the reactor (Fig. 6). The emulsion composition changed as a function of time because the water content decreased due to the coalescence process.

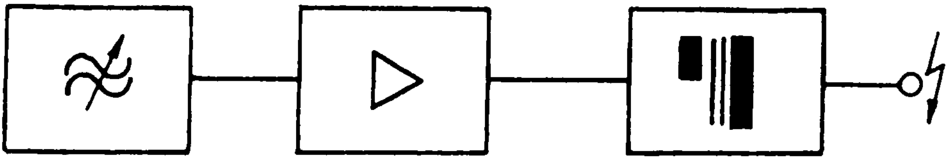


FIG. 4. High voltage supply. Function generator, Philips PM 5127; amplifier, Dynacord LV 200; transformer, MWB TEG 20/3.

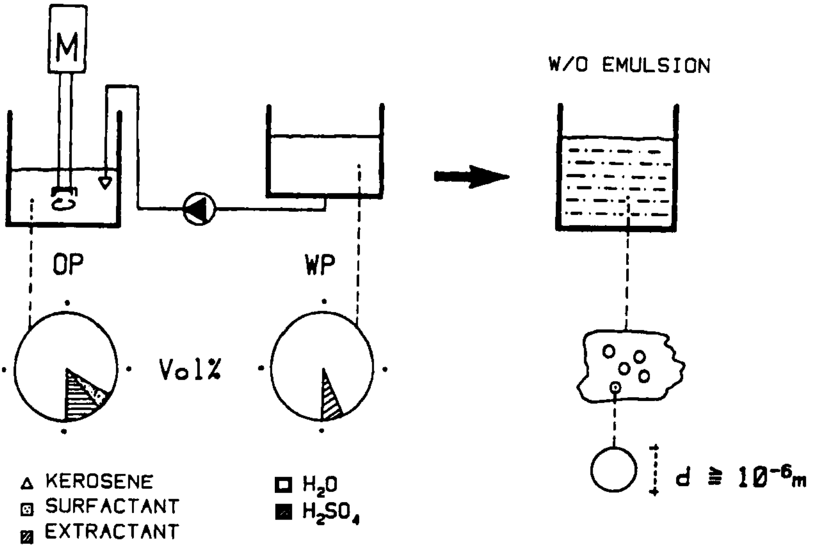


FIG. 5. Emulsion production.

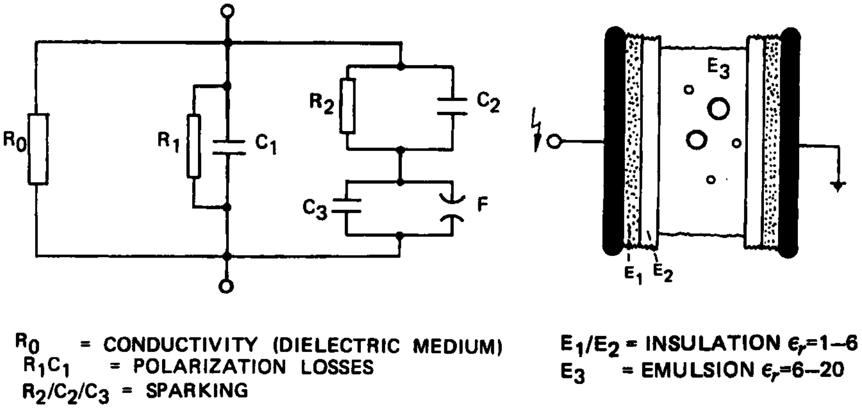


FIG. 6. Left: Wiring diagram for an nonhomogeneous dielectric medium. Right: Liquid membrane emulsion as a dielectric medium.

III. RESULTS AND DISCUSSION

The relative permittivity of the emulsion is, of course, a function of the water content (*14*), and, therefore, the value of this parameter decreased during the process. Thus, changes in the permittivity, measured as changes in the applied voltage, can be used to monitor the deemulsification process. Figure 7 presents a plot of the field strength vs time for a semicontinuous coalescence experiment. The change of electrical field strength obviously correlates with the inner resistance R_1 of the media. In order to describe the process, the field strength curve was divided into three parts. These three segments were observed in all experiments and are designated as follows:

Precoalescence period. In the precoalescence period the field strength decreases sharply due to the immediate coalescence of bigger and unstable droplets.

Main coalescence period. The decrease of the water content in the emulsion causes an increase of the applied field strength. The slope of the field strength curve can be correlated with the time needed for total coalescence, and it therefore decreases.

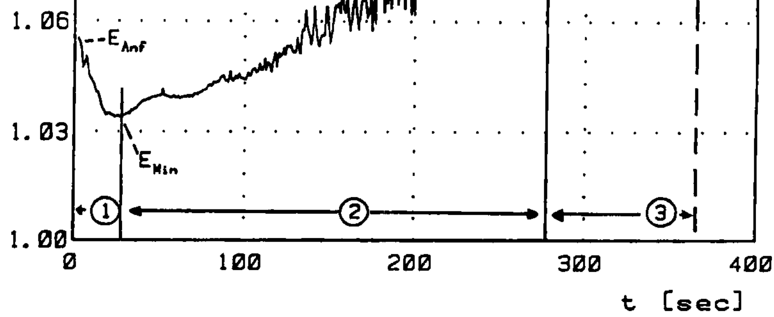


FIG. 7. Field strength vs time curve for a fast emulsion breakage experiment. Parameters: $E = 1.05$ kV/cm, $f = 1$ kHz, $F_v = 130$ mL/min.

Final coalescence period. The dielectric medium in the reactor becomes more homogeneous. With further progress in the coalescence process, the field strength approaches a maximum value. There are still only a few coalescence steps in the media.

The slope of the field strength curve in the main coalescence period is generated by strong and weak losses of the dispersed phase. The sudden dip in field strength in the precoalescence period is proportional to the initial breaking rate. If bigger water droplets are generated in the reactor by many coalescence steps, we found a proportionality to the decrease of the field strength.

Therefore, it is possible to describe the coalescence efficiency by the variation in the field strength, and primarily by means of the positive slope of the field strength curve. Figures 8a and 8b show the correlation between the altered coalescence due to variations in the surfactant content and the field strength as a function of dimensionless time. The coalescence efficiency is determined from the field strength–time curve.

In further investigations the coalescence should be altered by varying the electric parameters. Several authors (*18–21*) describe the influence of the applied field strength on emulsion breakage. The results shown in Fig. 9 also indicate that an increase in the field strength causes an increase in coalescence efficiency.

The system, therefore, was tested with different initial field strengths. However, increasing the field strength requires a high disruptive strength of the reactor and also a suitable high voltage power supply. In our investigations the maximum achievable electrical field strength was 2 kV/cm near 1 kHz.

A. Influence of Frequency

Bailes and Larkai investigated coalescence induced by pulsed dc fields in the range between 0 and 60 Hz. Our investigations were performed with ac fields and frequencies up to 10 kHz. Because the transformer failed at higher frequencies, effective coalescence could only occur up to 2 kHz.

The breakage rate correlates linearly with the frequency for identical emulsion compositions. Also, the field strength vs time curves show that an increase in frequency promotes coalescence (Figs. 10a and 10b). The coalescence-promoting effect of higher frequencies can be shown by sharply decreasing field strength in the precoalescence period. This

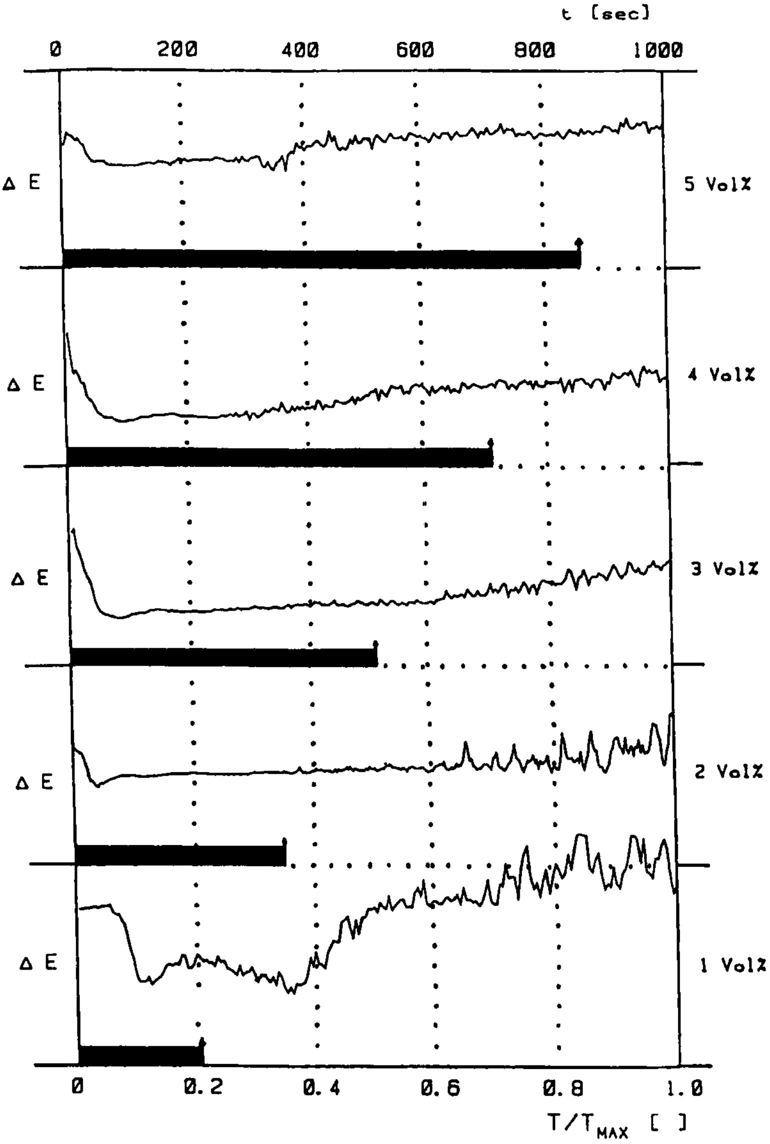


FIG. 8a. Field strength vs time curves for different emulsion surfactant contents.

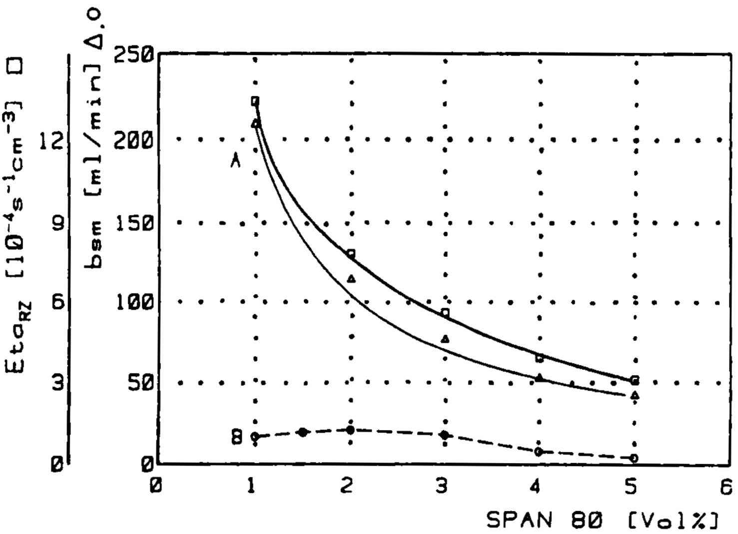


FIG. 8b. Space-time yield and mean breakage rate as a function of the surfactant content. Parameters: E = 1.07 kV/cm, f = 1 kHz, F_v = 130 mL/min, ΔE = 0.1 kV/cm.

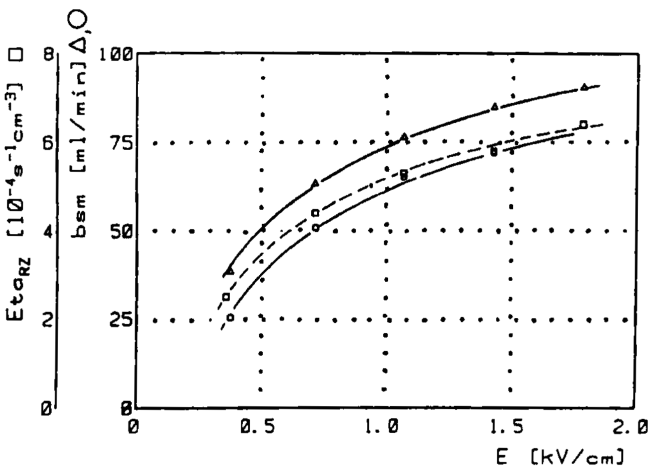


FIG. 9. Space-time yield and mean breakage rate as a function of the applied field strength. Parameters: f = 1 kHz, F_v = 130 mL/min.

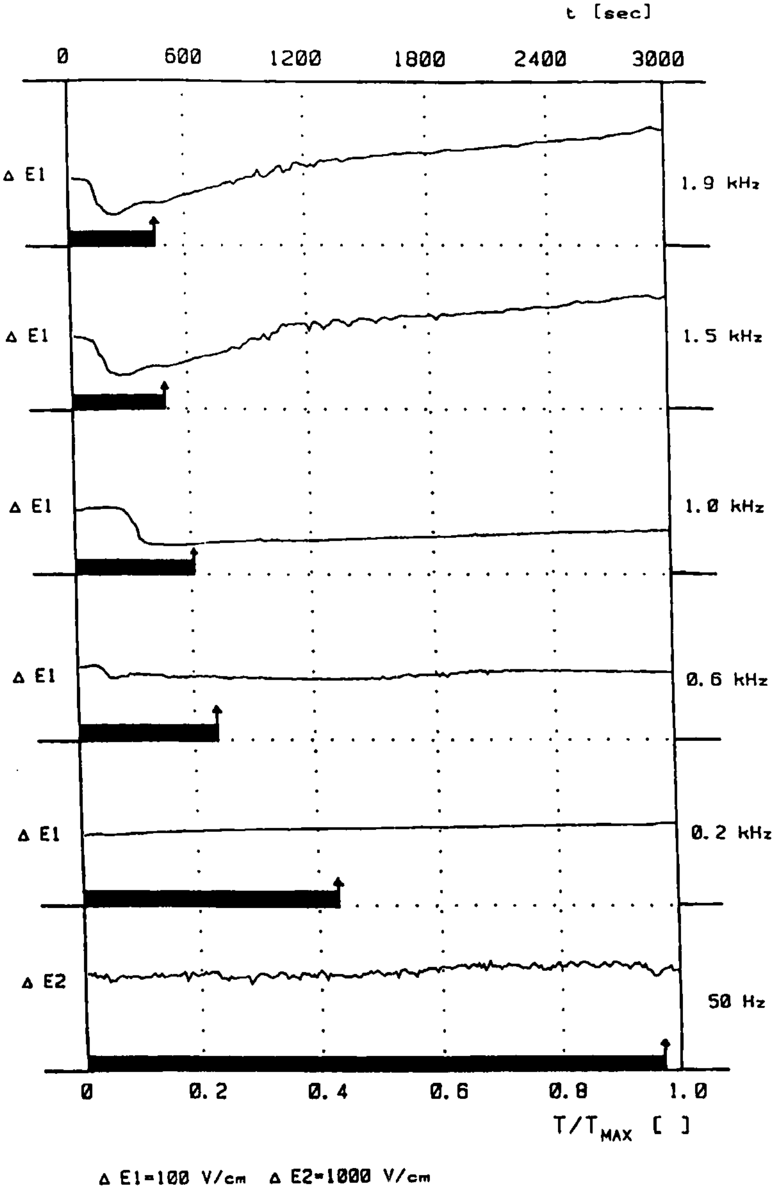


FIG. 10a. Field strength vs time curves for various frequencies.

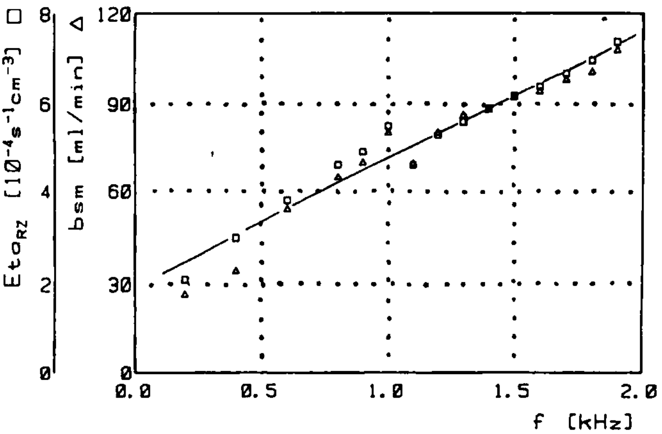


FIG. 10b. Space-time yield and mean breakage rate as a function of frequency. Parameters: $E = 0.54$ kV/cm, $F_v = 130$ mL/min.

hypothesis is supported by the latest investigations of Lin which involve frequencies above 2.5 kHz (*21*).

B. Variations of the Membrane Phase Properties

We usually used kerosene as the solvent for LME with additional surfactants and extractants. In order to investigate the influence of the solvent on the coalescence phenomenon, we generated emulsions with pure solvents of different chemical configurations and dielectrical properties. These were prepared as shown in Section II-B.

Specifically, we investigated emulsion breakage under two conditions: High field strength/low frequency and low field strength/high frequency.

The results shown in Figs. 11a and 11b indicate that the use of branched or cyclic aliphatic hydrocarbon as solvents accelerated the breakage rate. These effects can also be forced by adding aromatic compounds to the solvent systems. The content of aromatic compounds, however, is limited by the stability of the emulsion.

The influence of the composition of the membrane phase on the mechanism of coalescence, and particularly on the removal of the separating layer, can possibly be correlated to the solvent viscosity.

Extractants and surfactants can be considered as highly surface-active species. Essentially, most of these molecules remain at the inner surface

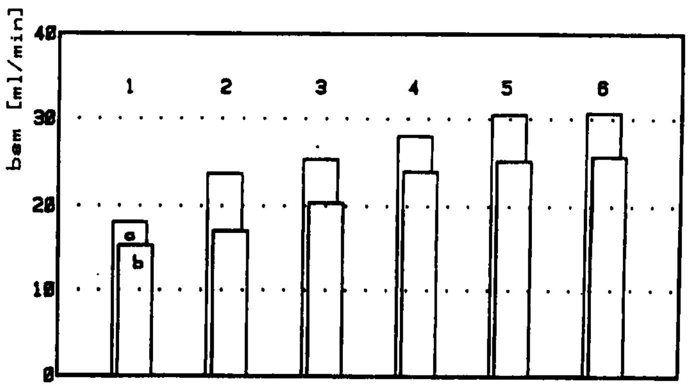


FIG. 11a. The influence of various solvents on the mean emulsion breakage rate. (See Fig. 11b for keys.) Emulsion breakage induced by high field strength. Parameters: $E = 5.6$ kV/cm, $f = 50$ Hz, $F_v = 130$ mL/min.

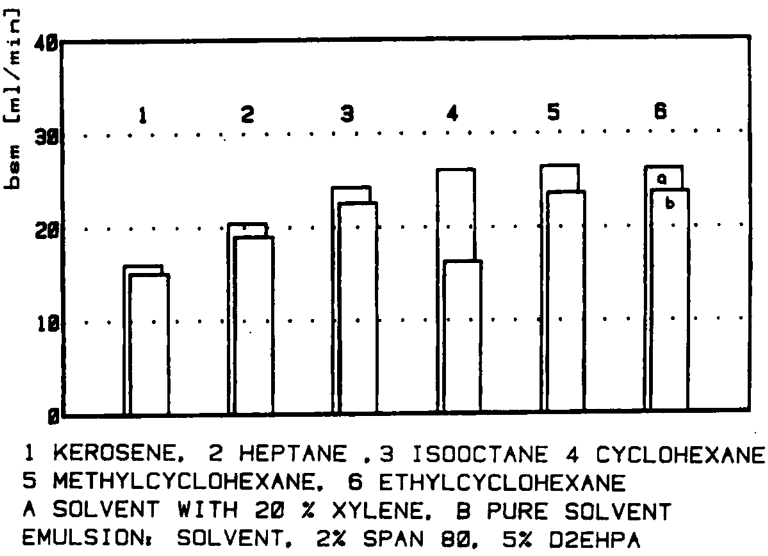


FIG. 11b. The influence of various solvents on the mean emulsion breakage rate. Emulsion breakage induced by high frequency. Parameters: $E = 0.7$ kV/cm, $f = 1$ kHz, $F_v = 130$ mL/min.

of the emulsion. Therefore, their concentration in the bulk phase can be neglected up to a certain degree of approximation for lower concentrations. However, the viscosities of pure solvents and extractant/surfactant solutions show no correlation with the breakage rate (Table 2). All viscosities were measured with an Ubbelohde viscometer at 25°C. The solutions contain a commonly used amount of surfactant and extractant.

The influence of different solvents on the coalescence mechanisms chiefly depends on their molecular conformations. With regard to the displacement of the membrane molecules, the dispersed water droplets may be viewed as inflexible spheres. Under a high field strength, the solvent molecules gain inductive charges, and polarization takes place (*24*). Thus, the total polarization is a combination of the partial polarizations due to electronic effects and the orientation of the molecules in the applied field.

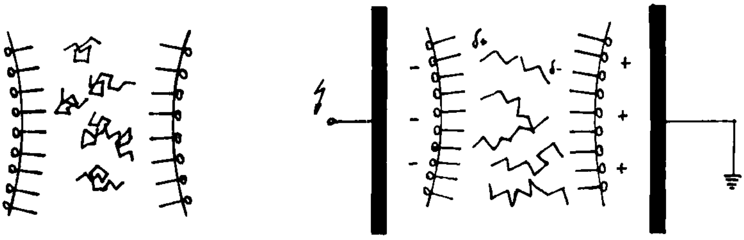
Due to inductive charges on the molecules, the conformations of long-chain aliphatic solvent molecules are altered in the applied electrical field (Fig. 12).

Without any applied electric field, the molecules form a statistical coil; under an electrical field strength, the molecules are extended. In a schematic model the extended solvent molecules must be folded before the separating layer is removed and final coalescence occurs. In this way the water droplets lose energy by displacing the organic layer. The investigation results indicate that increased coalescence rates should be expected when using cycloaliphatic or branched hydrocarbons as solvents. These molecules are limited to a few conformations (e.g., cyclohexane), or certain conformation alterations are sterically restrained. Therefore, the energy loss in this first step of the coalescence mechanism may be minimized.

TABLE 2
Viscosities of Various Membrane Materials[a]

	Kinematic viscosities		Mean breakage rates	
Solvent	Pure solvents (mm^2/s)	Solution (mm^2/s)	20 kV/50 Hz (mL/min)	2.5 kV/1 kHz (mL/min)
Heptane	0.588	0.720	19.0	17.0
Octane	0.741	0.913	15.0	15.3
Isooctane	0.737	0.887	22.5	20.3
Cyclohexane	1.223	1.480	20.0	23.9
Methylcyclohexane	0.905	1.110	23.6	25.2

[a] Solution: Pure solvent, 5 vol% D2EHPA, 2 vol% Span 80.



SOLVENT MOLECULES WITHOUT ELECTRICAL INFLUENCE

SOLVENT MOLECULES IN A ELECTRICAL FIELD

FIG. 12. Conformations of solvent molecules (schematic model).

This effect also takes place when aromatic compounds (e.g., xylene, toluene) are added to the solvent.

Viscosity generally increases by using cyclic compounds as diluent. In experiments with higher field strengths, the acceleration of the breakage rate dominated over the viscosity influence. For investigations with high frequencies and low field strengths, the correlation between steric behavior of the solvent molecules and the breakage rate no longer holds true.

Nevertheless, in experiments in the presence of aromatic hydrocarbons at all frequencies and field strengths, the breaking rates increased as compared with experiments in which pure hydrocarbons were used.

Also, the viscosity enhancement using benzene derivates increased with the number of alkyl side groups. Thus, the use of toluene or xylene results in a diminished breakage rate (Table 3). (See also Tables 4 and 5.)

TABLE 3
Mean Breakage Rate for Various Added Aromatic Compounds in the Membrane Phase[a]

Additive, 20 vol%	Mean breakage rate (mL/min) 20 kV/50 Hz	2.5 kV/1 kHz
Benzene	30.2	30.4
Toluene	27.7	26.5
Xylene	24.7	25.3

[a] Solvent: Pure heptane.

TABLE 4
Breakage Rates of Emulsions with Various Diluents[a]

Solvent (%)	Leakage	Breakage rate (mL/min)
Heptane	4.0	17.0
Kerosene	7.0	15.3 (20 kV/50 Hz)
Isooctane	4.0	22.5
Methylcyclohexane	5.0	25.2

[a] Membrane phase: Solvent, 5 vol% D2EHPA, 2 vol% Span 80.

TABLE 5
Mean Breakage Rate for Various Solvents and Electrical Field Properties[a]

	Breakage rate (mL/min)	
Solvent	20 kV/50 Hz	2.5 kV/1 kHz
Kerosene	15.3	15.0
Heptane	17.0	19.0
Isooctane	20.3	22.5
Cyclohexane	23.9	16.0
Methylcyclohexane	25.2	23.6
Ethylcyclohexane	25.7	23.5

[a] Membrane phase: Solvent, 5 vol% D2EHPA, 2 vol% Span 80.

However, coalescence is a result of both steps of the proposed mechanism. As discussed previously, the final disruption of the separating layer depends on the dielectric behavior of the organic phase. To correlate the breakage rate with an overall value, the polarization due to the applied electrical field must be calculated. Polarization P correlates linearly to the local field strength E at a constant frequency.

$$P = (\varepsilon_r - 1)\varepsilon_0 E$$

Figure 13 shows the linear dependence between the breakage rate and the calculated polarization of the solvent molecules using hydrocarbons with 6–10 carbon atoms. For all experiments, the same amounts and kinds of surfactant and extractant were used. Increasing the polarization of the solvent molecules leads to a diminished stability of the dispersed

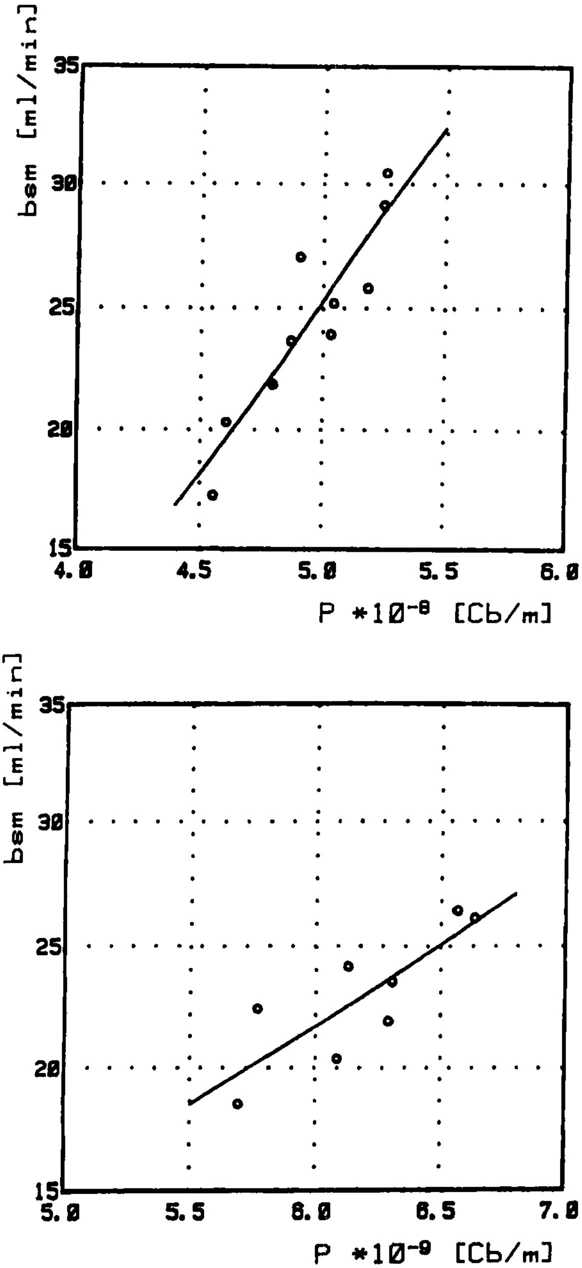


FIG. 13. Mean breakage rate as a function of polarization. Top: For high electrical field strength ($E = 55.5$ kV/cm, $f = 50$ Hz). Bottom: For low electrical field strength ($E = 0.8$ kV/cm, $f = 1$ kHz).

system due to an increased number of charges at the interface. With increasing interaction between the organic and the water phase, the adsorption of surfactant molecules at the interface should be disturbed. The correlation between this simple model and the results at high field strengths is good because the influence of the various viscosities of the membrane phases can be neglected under these conditions.

Thus, the breakage rate for various amounts of xylene in the membrane phase may be calculated with these correlations (Fig. 14).

However, the model requires a constant stability of the emulsion for various membrane phases with no applied electric field. For stability measurements the emulsions used were stirred in a cylindrical bottle for 2 h, at which time the emulsion formed globules in the outer water phase. Because stability data are required for the comparison of the emulsions, a solution of a potassium salt was encapsulated, and the amount of potassium in the outer water phase was measured as a function of time. The extractant D2EHPA did not form a complex with potassium, so the amount of potassium in the outer water phase may be correlated directly with the emulsion stability. These investigations show that the emulsion leakage varies statistically and is not dependent on the solvent used.

The different dielectric behavior of the membrane phase should only appear at a minimal applied electric field strength. For the optimal efficiency of the electrostatic coalescence process it is useful to break different emulsions with various electrical fields. Emulsions with cyclo-

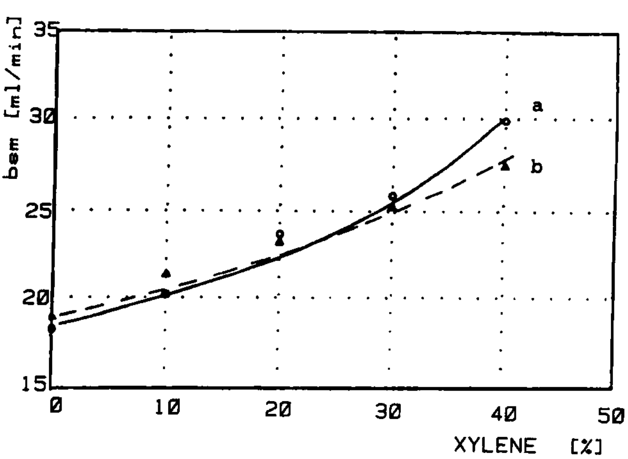


FIG. 14. Mean breakage rate for various levels of xylene in the membrane phase: (a) measured, (b) calculated.

aliphatic solvents may be broken with a high field strength and low frequency, while emulsions with aliphatic solvents require lower field strengths and higher frequencies for more efficient breakage.

IV. CONCLUSION

Process control for the electrostatic emulsion breakage process requires an on-line measurement of the electrical parameters, particularly of the electrical field strength. Highly efficient electrostatic coalescence may be obtained by using lower field strengths and high frequencies.

Further acceleration of the breakage rate may be achieved by optimizing the emulsion composition. Using easily polarizable diluents, emulsions become more unstable under an applied electrical field. The influence of viscosity may be neglected in the investigated systems in the range of higher field strengths. All studied systems can be used in liquid membrane extraction.

The breakage rate correlated well with the polarization of the solvent molecules. It was found that it was possible to optimize the electrical parameters of the two-step coalescence mechanism. Due to limitations of the usable field strength, it was also useful to prepare emulsions with branched or cyclic hydrocarbons as the solvent.

ABBREVIATIONS

Lm	liquid membrane
Em	emulsion
W/O	water in oil
OP	organic phase
WP	water phase
M	stirrer
D2EHPA	bis(2-ethylhexyl)phosphoric acid
Span 80	isosorbitanmono-oleate

SYMBOLS

ε_r	permittivity
E	field strength (kV/cm)
f	frequency (Hz)

R	resistance (Ω)
C	capacity (F)
P	polarization (Cb/m)
F_v	flow (mL/min)
t, T	time (s)
Eta	space-time yield (s^{-1}cm^{-3})
bsm	mean breakage rate (water) (mL/min)
bd	breakage degree

REFERENCES

1. D. Melzner, J. Tilkowski, A. Mohrmann, W. Poppe, W. Halwachs, and K. Schügerl, *Hydrometallurgy, 13,* 105 (1984).
2. J. Draxler, W. Fürst, and R. Marr, *Proc. ISEC '86, 1,* 563 (1986).
3. L. C. Waterman, *Chem. Eng. Prog., 61*(10), 51 (1965).
4. L. C. Waterman, U.S. Patent 3,579,346 (1971).
5. F. L. Prestridge, U.S. Patent 3,847,775 (1974).
6. R. N. Lucas, U.S. Patent 3,582,527 (1971).
7. N. N. Li, European Patent 82 30 3823.7.
8. G. Sander, Diploma Thesis, University of Hanover, 1982.
9. H. B. Hauertmann, Diploma Thesis, University of Hanover, 1983.
10. P. J. Bailes and S. K. L. Larkai, *Trans. Inst. Chem. Eng., 60,* 115 (1982).
11. A. Brown and C. Hanson, *Trans. Faraday Soc., 61,* 1724 (1955).
12. P. J. Bailes and S. K. L. Larkai, *Chem. Eng. Res. Des., 62,* 33 (1984).
13. W. Degener, Diploma Thesis, University of Hanover, 1986.
14. P. Sherman, *Emulsion Science,* Academic, London, 1968, p. 355.
15. A. D. Hovarongkura, Thesis, University of West Virginia, Morgantown, 1979.
16. S. E. Sadek and C. D. Hendricks, *Ind. Eng. Chem., Fundam., 13*(2), 139 (1974).
17. L. K. Tsabek, G. M. Panchenkow, and V. V. Papkov, *World Pet. Congr. Proc., 8*(4), 423 (1971).
18. Z. X. Juan et al., Paper Presented at the 2nd International Conference of Separation Technology, Ellmau, Germany, May 1987.
19. P. Sherman (ed.), *Rheology of Emulsions* (Proc. Symp. Br. Soc. Rheol.), Harrogate, Great Britain, 1982, p. 91.
20. J. Draxler and R. Marr, *Ber. Bunsenges. Phys. Chem., 86,* 64 (1982).
21. B. A. Mikucki and K. Osseo-Asare, *Solv. Exch. Ion Exch., 4*(3), 503 (1986).
22. P. J. Bailes and S. K. L. Sadek, *Trans. Inst. Chem. Eng., 59,* 229 (1981).
23. H. Sonntag and J. Netzel, *Kolloid Z., 22*(1-2), 121 (1966).
24. J. D. Jackson, *Klassische Elektrodynamik,* Walter de Gruyter, Berlin, 1983.

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