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I. Abou-Nemeh[a]; M. Moors[a]; A. P. van Peteghem[a]
[a] LABORATORY FOR NONFERROUS METALLURGY, UNIVERSITY OF GENT GROTESTEENWEG, ZWIJNAARDE, BELGIUM

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Electrostatic Splitting of the Emulsion Used in Liquid Surfactant Membranes Process for Metals Separation

I. ABOU-NEMEH, M. MOORS, and A. P. VAN PETEGHEM
LABORATORY FOR NONFERROUS METALLURGY
UNIVERSITY OF GENT
GROTESTEENWEG NOORD 2, ZWIJNAARDE B-9052, BELGIUM

Abstract

A study has been carried out to investigate the effect of different parameters on the splitting process of the emulsion used in the liquid surfactant membranes process for metals separation. The influence of electric field strength, frequency of the applied ac voltage, and membrane recycling on emulsion stability have been studied. The investigations have revealed that there exists a unique optimal frequency range in which the best separation of the emulsion phases is obtained. The effect of the membrane composition and the variation of tri-*n*-butyl phosphate (TBP) concentration has been shown to vary linearly with the splitting efficiency. This finding correlates quite well with Sadek and Hendrick's equation on the force causing coalescence in an electric field.

INTRODUCTION

The tremendous use of emulsions and their wide range of practical application in different fields has been expanded enormously, particularly in the last few decades. This is partially due to liquid surfactant membranes (LSM) technology which is an area of interest on the academic as well as the industrial level. Moreover, the need to separate dispersed systems such as intermixed immiscible liquid phases is a fluid processing step causing major difficulty in industry which requires the application of an effective tool for emulsion break down and phases separation. Numerous examples can be found in the hydrometallurgical industry. Metal recovery by solvent extraction leads to a moderately stable liquid–liquid dispersion in crude oil operation where routine processing involves stable emulsions with water. In each instance, the dispersion (emulsion) of interest may, in generic terms, be either an oil-in-water or a water-in-oil type. However, it should be pointed out here that the electrostatic technique exclusively deals only with the latter kind of emulsions.

In LSM technology the aims of emulsion splitting can be summarized as follows:

1. To recover the separated metal in the internal aqueous phase for electrowinning and its further processing.
2. To recover the membrane phase for recycling and its multiusage for fresh emulsion preparation.

In water-in-oil emulsions, the continuous phase (membrane) is rather a good insulator in comparison with the dispersed phase. Therefore, an electric field can be established and maintained in the system where water droplets are encapsulated in the organic phase. Actually, this physical fact has been exploited by the present method. Furthermore, the internal aqueous phase droplets will retain any electrical charge they may acquire.

Practical applications used over eight decades (*1–4*) have shown that any type of electric field applied, either ac or dc, will result in emulsion break down. Moreover, the effect of electric field pulses has also been observed in cell biology and biotechnology (*5–7*). The electrofusion method has been applied successfully—by triggering a fusion process by a high electric field pulse—and has become a powerful tool for cell hybridization and genetic engineering.

The theory of emulsion breaking in an electric field, and particularly in an ac field, has not been completely investigated in spite of a large number of publications (*8–14*). Emulsion splitting and the mechanisms whereby it occurs are not clearly understood. It is generally known that under the influence of electric field forces, which enhance coalescence of small droplets, appropriate and suitable size droplets for gravity separation are more rapidly attained. The effect of applying a dc electric field was also investigated by many researchers (*15–18*). Recently some of them (*19*) have investigated the behavior of emulsion systems by applying pulsed dc fields to parallel horizontal plate electrodes.

EXPERIMENTAL

The experimental unit used for emulsion splitting is a bench-scale electrostatical splitter developed at the Laboratory for Nonferrous Metallurgy (LNFM). It is built of glass and its design resembles a heat exchanger as depicted in Fig. 1. One of the electrodes is the jacket of the heat exchanger. For the jacket to be conductive and to act as an electrode, the jacket was filled with 4 *M* NaOH solution. The second electrode is a cylindrical bar

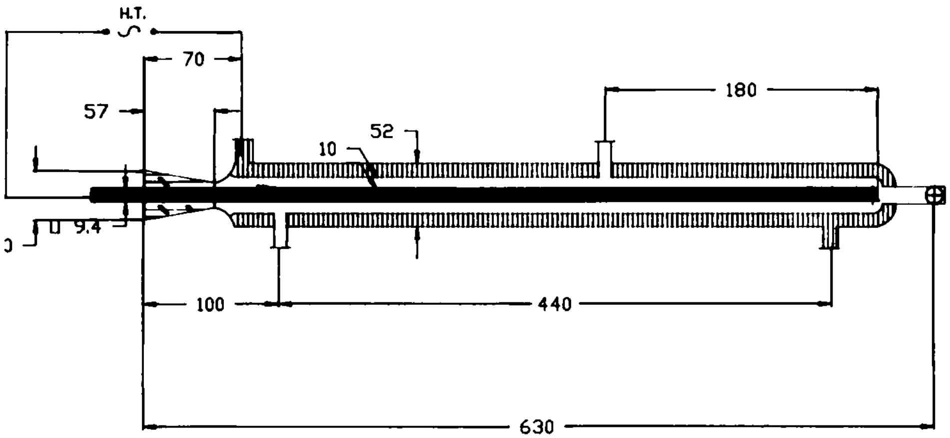

FIG. 1. Electrostatic splitter used for emulsion splitting.

made of stainless steel (ϕ = 9.4 mm). It is installed exactly in the center of the internal tube of the "heat exchanger" so that the distance separating the metallic electrode and the glass wall of the second electrode is 10 mm. One end of the metallic electrode is fixed to a conical Teflon seal to ensure equidistance between the electrodes. The Teflon sealing functions as an insulator and mechanical stabilizer. Hence, the internal electrode length can be regulated by sliding it through the Teflon sealing. The splitting apparatus was maintained by 2 inlets and 3 outlets. Two openings (inlet and outlet) of the jacket are used for electrolyte filling and draining. Another two (inlet, outlet) are used for emulsion feed to the splitter and internal aqueous phase evacuation respectively. The third one is the membrane (organic phase) outlet and is located in the upper part of the splitter (see Fig. 1). This construction enables a continuous mode of exploitation of the splitter. The industrial splitters used in LSM are similar to this one. However, the internal electrode is actually a bundle of electrodes connected to each other. This type has been shown to be quite effective and efficient. Different types of electrostatic splitters can be found in the literature (*13*, *17*, *19*, *20*).

The second element, which is equally important, is the high tension generator (H.T.G.). It has also been developed at LNFM. The maximum ac field that can be generated is approximately 3000 V/cm. The following apparatus is a digital voltmeter (MX 579 ITT) which is used for a readout of the applied field. The signal generator (GX 239 ITT) is used exclusively to set the required frequency. The oscilloscope (OX 170 C ITT) is used to control the sinusoidal signal.

a. Emulsion Preparation

The emulsion used for the splitting study was prepared by adding the internal aqueous phase (Co^{2+}, 10,000 ppm in 2 *M* H_2SO_4) to the organic phase. The membrane contained 5.5 v% di-2-ethylhexyl phosphoric acid (D2EHPA) of 98.6% purity (Lot 31291608 purchased from Johnson Matthey Ltd.) and 2.5 v% Span 80 (Lot V-3106 supplied by ICI Essen, Germany). The solvent used was paraffinic and isoparaffinic kerosene (Shellsol T) purchased from Shell-Belgium. This mixture was homogenized in an ultraspeed mixer (Ultra-Turrax T-45) for 7 min total mixing time. The emulsification was carried out at a fixed impeller speed of 10,000 rpm. The choice of surfactant concentration was decided upon after a series of preliminary experimental runs. The trials were conducted on a "real emulsion," i.e., an emulsion rich in metal after permeation and with a membrane phase containing 3 v% Span 80 and other ingredients. The splitting of an emulsion rich in metal after 30 min residence time can be simulated by using 2.5 v% Span 80 instead of 3 v%.

b. Emulsion Splitting Procedure

Emulsion splitting experiments have been carried out in a continuous mode, i.e., the emulsion was pumped to the splitting zone and the internal aqueous phase was drained from the electrostatic splitter during emulsion breakdown. Only the residue of the unsplit emulsion and the organic phase remain in the system. However, it should be pointed out that several runs were conducted with simultaneous draining of both the organic phase and the internal aqueous phase from the splitting zone, while the emulsion was fed continuously to the system. Nonetheless, only the former mode of emulsion breakdown will be considered in this paper. In other words, 150 mL of emulsion loaded the splitter and was split versus time. The residue of the unsplit emulsion and the organic phase were then centrifuged for 45 s to obtain a clear separation of the phases. This was done to correlate the residual volume of the aqueous phase—if any was left—with the final aqueous phase volume obtained in order to check the mass balance of the emulsion.

To start the splitting experiment, the high tension generator (H.T.G.) was turned on and the required voltage was built up in the system. The digital voltmeter, which is interfaced to the H.T.G., was used to set the desired value. The frequency was set on the signal generator apparatus. To control the output signal and other parameters (amplitude, frequency, etc.), an oscilloscope was interfaced to the H.T.G. so that a clear picture was obtained on the operating conditions of the system. After setting all the required parameters, the H.T.G. was switched off in a "stand-by" position. Meanwhile, the emulsion was fed to the splitting zone. As soon as all the emulsion was present in the splitting zone, the H.T.G. was turned on and the time for splitting was recorded.

RESULTS AND DISCUSSION

The course of the splitting experiment was evaluated by measuring the internal aqueous phase volume drained off from the splitting system versus time.

The emulsion splitting efficiency is defined as the ratio of the measured volume of the internal aqueous phase at time *t* to its initial volume before splitting. This can be represented by

$$S_p = (V_{i,t}/V_{i,0}) \times 100 \qquad (1)$$

Therefore, by knowing the initial aqueous phase volume and that measured during splitting, the efficiency can be found.

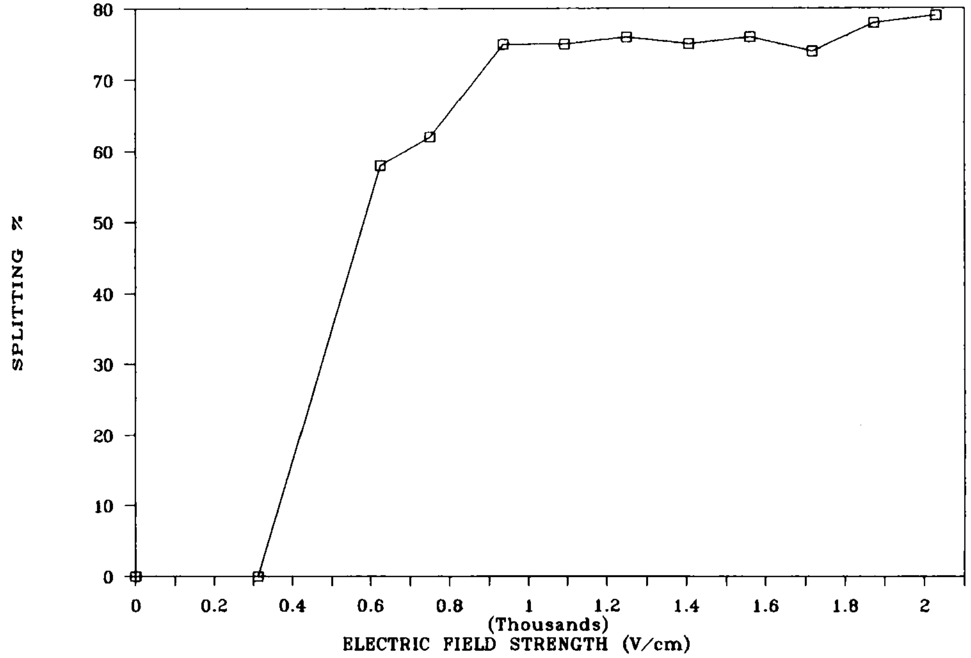

FIG. 2. Electric field effect on emulsion splitting (splitting time, 240 s; frequency, 500 Hz).

a. Effect of the Electric Field

A series of experimental runs was carried out to study the effect of an electric field on emulsion splitting. The applied voltage ranged in field strength from 312 to 2029 V/cm and at frequencies of 500 and 1000 Hz. It is known that emulsion breakdown increases with increasing field strength. Increasing the field strength from 312 to 624 V/cm increases the splitting efficiency by 58%, as shown in Fig. 2. However, any further increase in the field strength, particularly beyond 900 V/cm, has been shown to have a marginal impact on splitting (see Fig. 3). It can be deduced that the emulsion breakdown has reached its asymptotic value where any further escalation of the applied voltage will not result in a significant enhancement in the rate of emulsion splitting. An analogous phenomenon has been observed by many researchers (*13*, *14*). Bailes and Larkai (*17*) observed the same tendency on applying a pulsed dc field at 60 Hz.

Moreover, it has been noted that when the strength of the applied field is 312 V/cm or lower, no emulsion splitting is observed.

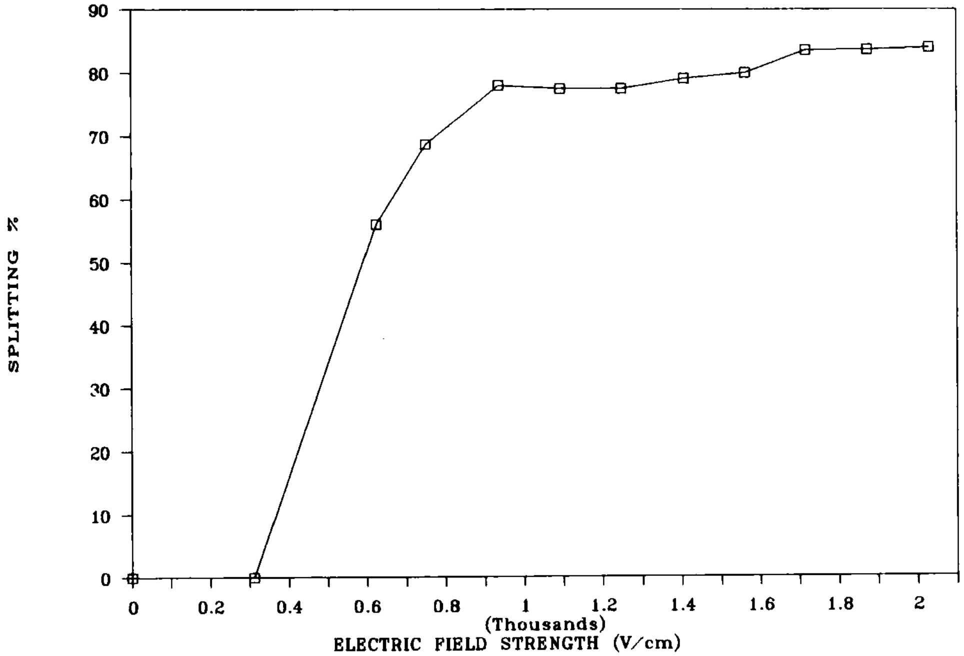

FIG. 3. Electric field effect on emulsion splitting (splitting time, 240 s; frequency, 1000 Hz).

b. Effect of Frequency

It has been seen that the higher the field strength, the higher the rate of coalescence of the internal phase droplets and, consequently, the higher the emulsion breakdown. However, as far as the frequency is concerned, only Bailes and Larkai (*16–18*) have reported the presence of an optimal frequency in a pulsed dc field for maximum emulsion splitting efficiency. Gutknecht et al. (*14*) investigated the effect of frequency, but they did not report an optimal frequency.

The elucidation of this important fact in ac fields has been investigated by conducting a series of experimental runs. The experiments covered applied fields from 360 to 1208 V/cm. Frequencies from 150 to 2000 Hz have been scanned for each electric field strength.

The kinetic profiles of emulsion splitting for a sample of six frequencies are presented in Fig. 4. The efficiency of emulsion splitting has been shown to pass through a global maximum between 700 and 1200 Hz. Nevertheless, to reveal the exact optimal frequency, the entire spectrum of frequencies

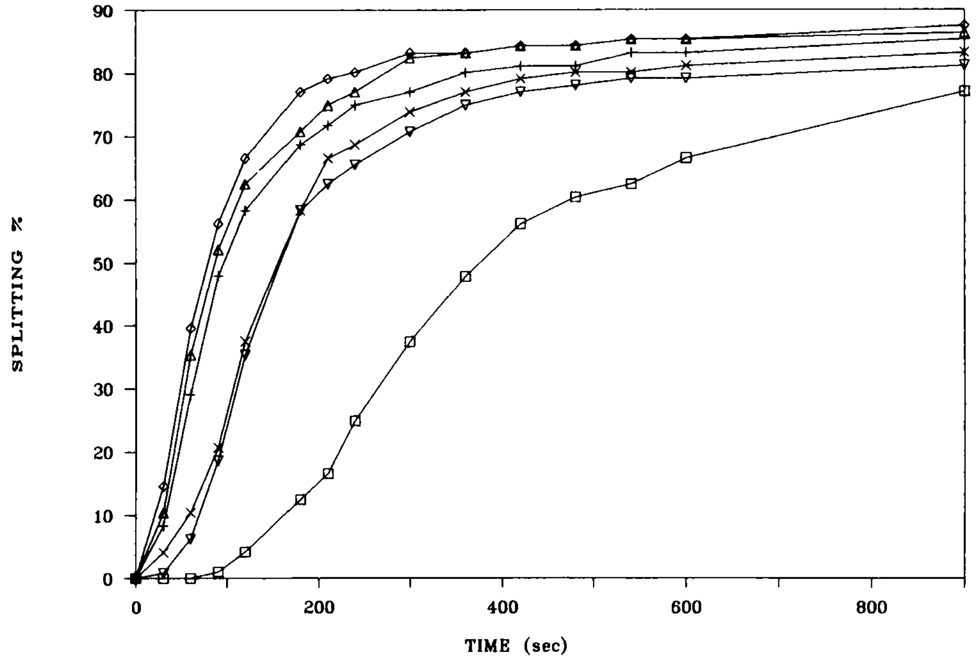

FIG. 4. Kinetics of emulsion splitting. The frequency effect (E = 1208 V/cm; □ 150, + 600, ◇ 1000, △ 1200, × 1500, ▽ 1900 Hz).

investigated is plotted in Fig. 5. As can be seen, the optimal frequency is 1000 Hz. Nearly 80% of the emulsion is split within 240 s. On the other hand, when the applied field is decreased from 1208 to 750 V/cm, a clear, well-defined peak of the optimal frequency at 1000 Hz is also obtained, as depicted in Figs. 6 and 7.

A third series of experimental runs dealt with the effect of frequency on droplet coalescence at an electric field strength of 360 V/cm. It has been observed that the effect of frequency can be more easily identified at lower fields than at higher fields. A sharp peak indicating the critical frequency is obtained. What is worth mentioning here is that the effect of frequency on emulsion splitting is almost the same at 150 and at 1900 Hz, i.e., no emulsion splitting is noted at all (see Figs. 8 and 9).

The existence of a "critical frequency" is of prime importance. It suggests that the mechanism of emulsion splitting which proceeds via the coalescence of internal aqueous phase droplets involves a mechanism of chain formation of the droplets. This fact has been identified microphotographically (*22*). At a frequency below the "critical," the field changes very slowly so that the chains become more and more well established. In other

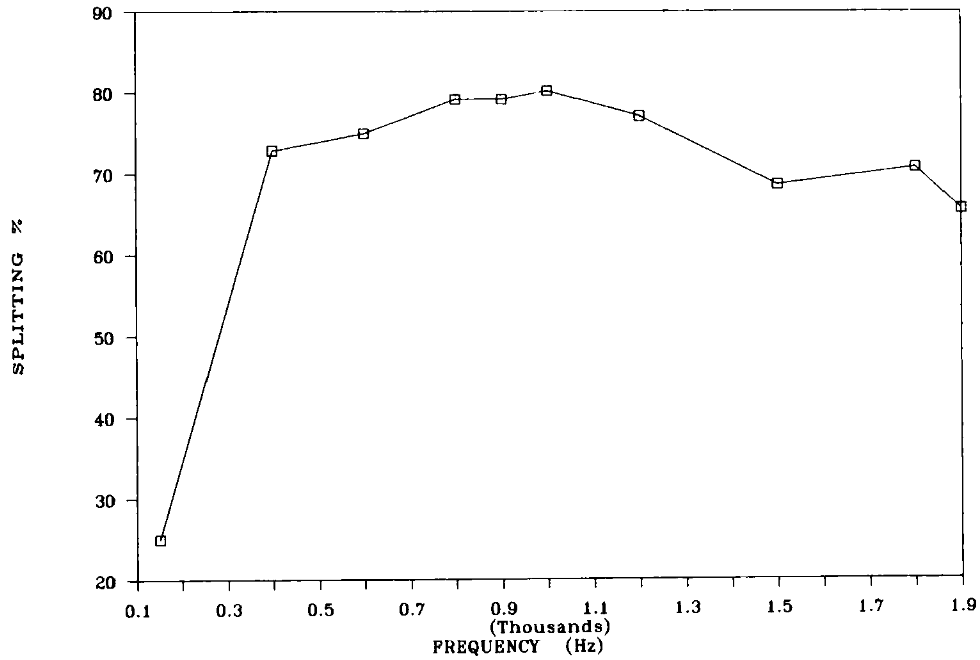

FIG. 5. Effect of frequency on emulsion splitting (splitting time, 240 s; E = 1208 V/cm).

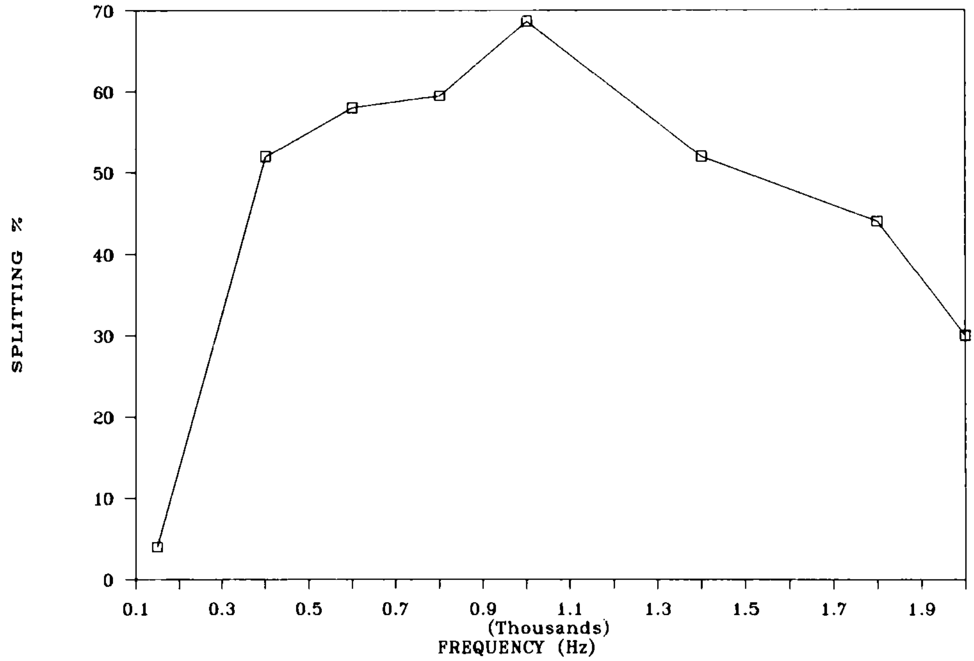

FIG. 6. Effect of frequency on emulsion splitting (splitting time, 240 s; E = 750 V/cm).

words, film rupture between droplets—which leads to coalescence—is slower due to the slow changes of the field. However, when the frequency of the field is higher than the "critical," the field changes too fast and film rupture between droplets is slow. This is because the response of "bypassed" droplets results in a lower rate of coalescence and, consequently, a lower splitting efficiency.

c. Effect of Splitting on Emulsion Stability

From the previous sections it has been seen that the application of an electric field drastically affects emulsion stability. Consequently, enhanced coalescence of the internal aqueous phase droplets takes place under the influence of the field forces. Nonetheless, there are no data on the behavior of the emulsion after its breakdown. Only a few researchers (*14*, *21*) have highlighted the problem, however, but without any further details on the issue. Therefore, the need to clarify the effect of splitting on membrane recycling is obvious.

The main principle behind the experiments relies on emulsion preparation, splitting, and then recycling of the membrane phase and the internal

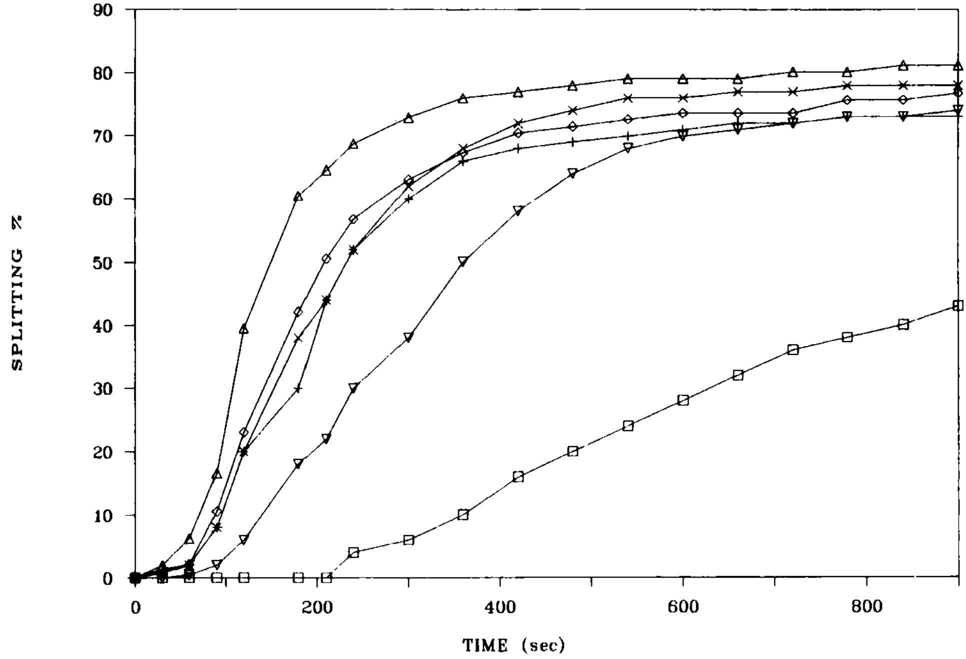

FIG. 7. Kinetics of emulsion splitting. The frequency effect (E = 750 V/cm; □ 150, + 400, ◇ 800, △ 1000, × 1400, ∇ 2000 Hz).

aqueous phase, and finally emulsification. The process is depicted in Fig. 10.

A series of experimental runs was conducted by preparing the emulsion according to the operating conditions given in Table 1. Such an emulsion was split at 2000 V/cm electric field strength and a frequency of 1000 Hz.

A significant deterioration in emulsion stability was observed after 3 cycles. The faster the rate of splitting, the greater the emulsion instability. This fact has been taken as a measure of emulsion stability, and thus, freshly prepared emulsion, i.e., cycle 0, has shown the highest stability (see Fig. 11). However, the higher the frequency of recycling, the more pronounced the effect of emulsion instability, with a pattern showing the attainment of a state of equilibrium. This finding can be attributed to surfactant decomposition as a result of hydrolysis. Abou-Nemeh and Van Peteghem (*23*, *24*) recently studied the kinetics of the surfactant decomposition during metal extraction. They found that upon emulsifying the ingredients of the membrane phase with 2 *M* H_2SO_4 (internal aqueous phase), the concentration of the oleic—as a result of sorbitan monooleate

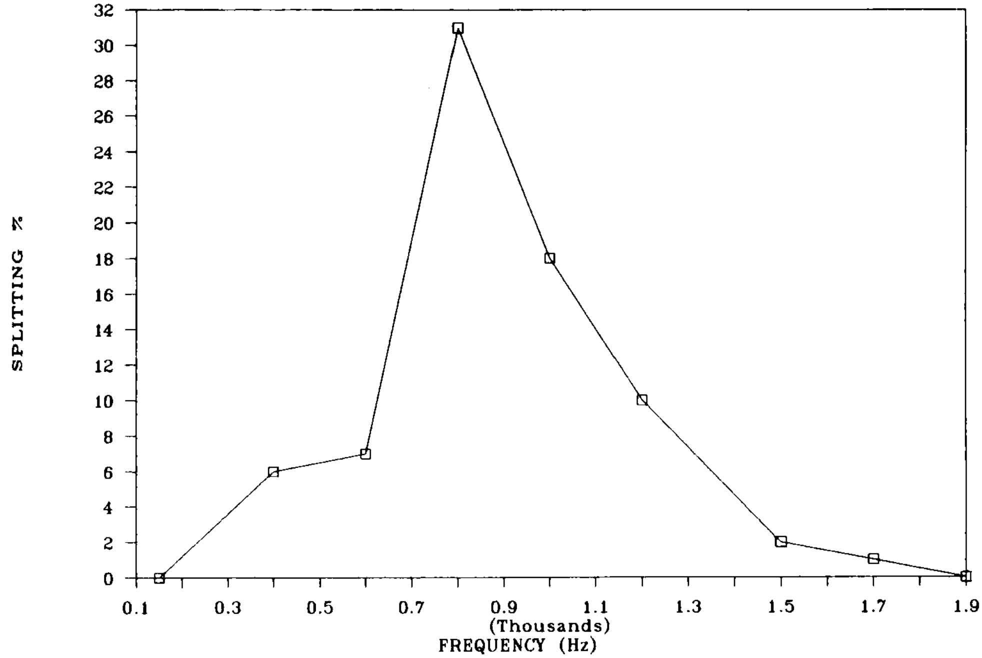

FIG. 8. Effect of frequency on emulsion splitting (splitting time, 540 s; E = 360 V/cm).

(Span 80) hydrolysis—was doubled from its initial concentration after 7 minutes of mixing time. Therefore, it is difficult to identify any effect of electric field splitting on the chemical stability of the compounds involved in the membrane composition.

d. Effect of Membrane Composition on Emulsion Splitting

Emulsion composition is essential as far as emulsion stability is concerned. Any change in membrane composition will dramatically affect emulsion stability. This is due to the change in the viscosity, the phase ratio (the membrane phase to the internal aqueous phase), the surfactant concentration, the interfacial activity of the surfactant, and to many others factors. In this work it was decided to study the effect of membrane phase composition by varying the tri-*n*-butyl phosphate concentration in the membrane from 0 to 3 v%.

Sadek and Hendricks (*25*) reported that the magnitude of the force causing coalescence in an electric field can be represented by

$$F = QE = 6.6\pi\mu\epsilon\epsilon_0 r^2 E^2 \quad (2)$$

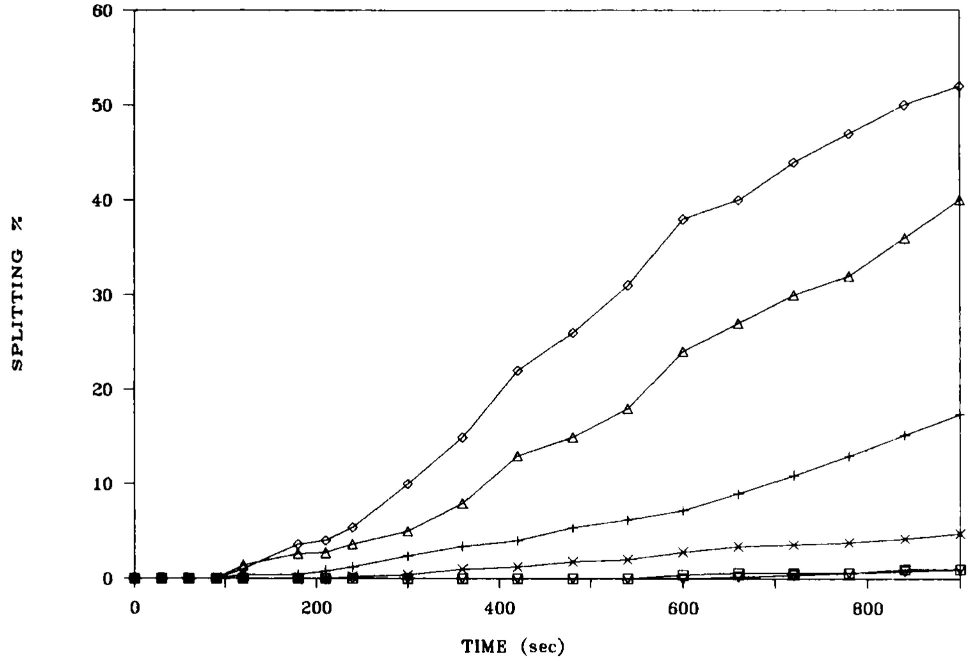

FIG. 9. Kinetics of emulsion splitting. The frequency effect (E = 360 V/cm; □ 150, + 600, ◇ 800, △ 1000, × 1500, ▽ 1900 Hz).

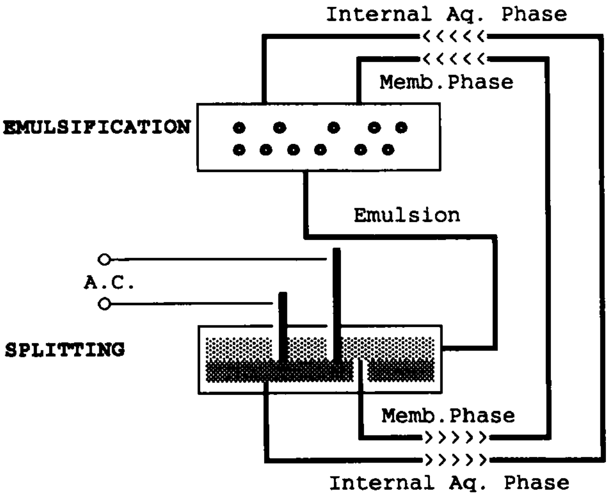

FIG. 10. Schematic diagram of the emulsion stability test.

TABLE 1
Operating Conditions for Emulsion Splitting

Temperature	20°C
Stirring speed (emulsion preparation)	10,000 rpm
Total stirring time	7 min
Emulsion volume	150 mL
Phase ratio (membrane/internal aqueous phase)	2/1
ac electric field strength	300-2050 V/cm
Frequency range	150-2000 Hz
Membrane composition (v%):	
1. D2EHPA	5.5
2. Span 80	2.5
3. Shellsol T	92
Internal phase composition:	
CO^{2+} in 2 M H_2SO_4	10,000 ppm

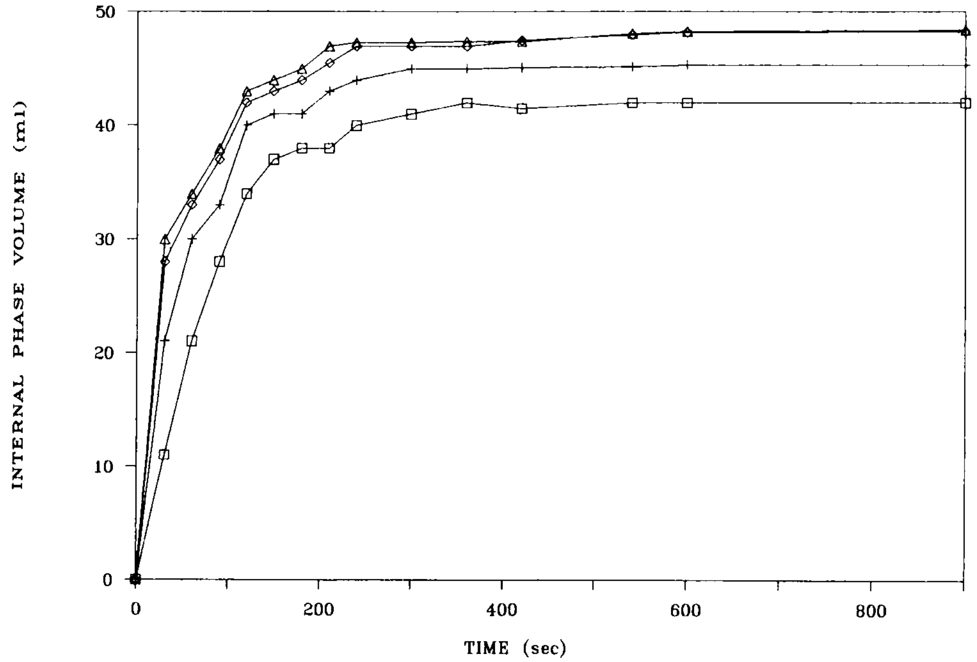

FIG. 11. Effect of splitting and membrane recycling on emulsion stability. (E = 2000 V/cm; frequency = 1000 Hz; □ Cycle 0, + Cycle 1, ◇ Cycle 2, △ Cycle 3).

It can be seen from this equation that the force acting on a droplet is directly proportional to the square of the electric field and droplet radius. However, it varies linearly with the dielectric constant of the continuous phase (membrane) of the emulsion. For a constant field strength and frequency and a known radius of the internal aqueous phase droplets, Eq. (2) can be rewritten as

$$F = C\epsilon \tag{3}$$

and thus

$$S_p \propto F = C\epsilon \tag{4}$$

where

$$C = 6.6\pi\mu\epsilon_0 r^2 E^2 \tag{5}$$

Indeed, as a result of TBP addition to the membrane phase, the splitting efficiency of the emulsion is higher. The higher the TBP concentration, the faster the emulsion breakdown. The results are shown in Fig. 12. Regardless of the slight conductivity of the membrane phase [$\Gamma = 2.6438 \times 10^{-10}$ $(\Omega\cdot\text{m})^{-1}$], a trace addition of TBP of a relatively high dielectric constant ($\epsilon = 8$) in comparison with kerosene ($\epsilon = 2.2$) to the membrane phase causes a significant increase in the conductivity of the system. Consequently, a higher dielectric constant for the membrane is obtained. The other aspect that could arise is the effect of TBP's viscosity on the resultant viscosity of the membrane, which in turn may alter the emulsion stability. This view has been dropped because of the irrelevant influence of TBP's viscosity on the membrane's viscosity because the former's viscosity is only 4 times lower than that of kerosene. Hence, within the range of applied concentrations, this effect is of minor significance.

The presence of TBP in the membrane phase below 1 v% stabilizes the emulsion (*26*), and as a result the emulsion breakdown is slowed. However, when the TBP concentration exceeds 1 v%, its presence destabilizes the emulsion performance and consequently the emulsion splitting is faster. In the present study, the reverse was noted; that is, the higher the TBP concentration, the higher the splitting. This fact ultimately supports Sadek and Hendrick's view, that the force and, consequently, the splitting is a linear function of the dielectric constant of the continuous phase of the dispersion.

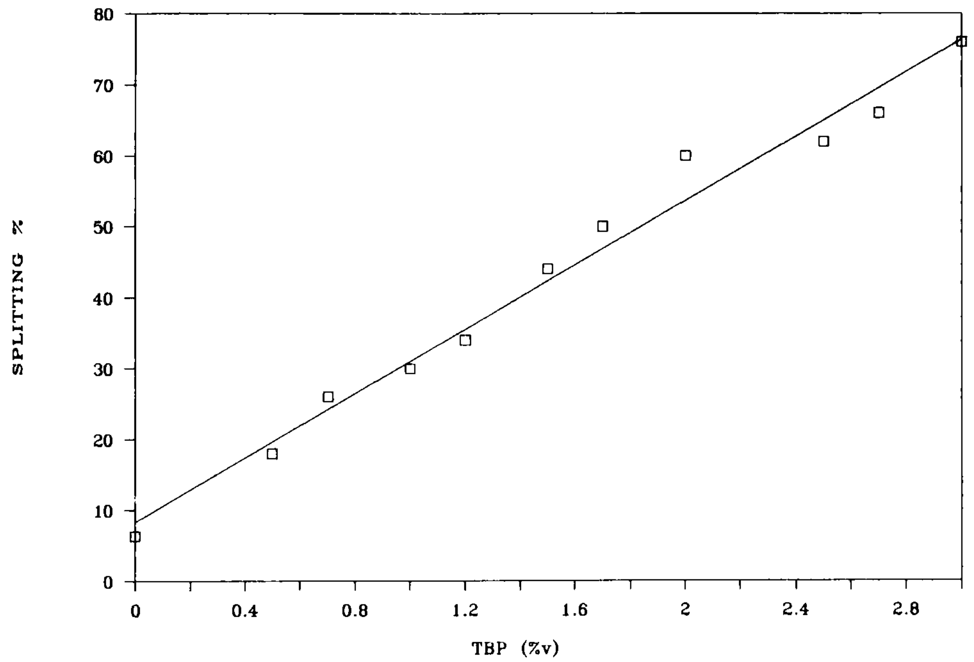

FIG. 12. Effect of membrane composition on emulsion splitting (splitting time, 60 s; E = 936 V/cm; frequency = 1000 Hz; □ experimental data, —— estimated data).

CONCLUSIONS

Emulsion splitting in an electric field is a function of many variables: electric field strength, frequency, membrane composition, emulsification operating conditions, and many others.

1. The electric field has no influence on the physicochemical properties of the membrane components and, consequently, no chemical decomposition as a result of electric field application has been noted.
2. The optimal frequency found for this electrostatic splitter is valid for this specific dispersion. Nonetheless, it should be borne in mind that any constructional modification of the splitter, such as the distance between the electrodes, the electrode diameter, or the thickness of the insulation layer, will definitely alter the optimal frequency.
3. The emulsion preparation and its consistency have a significant impact on the splitting efficiency. Therefore, it is necessary to determine the optimal stirring time, the composition, etc. needed to secure a good

stable emulsion for metal extraction and later to be split within a short time by a minimum energy input.

4. Membrane recycling is affected by surfactant hydrolysis during the emulsification process and metal permeation. As a result, the need for a fresh supplementary surfactant seems to be inevitable in order to reproduce the same emulsion stability.
5. The effect of the membrane composition and, more precisely, TBP content has a pronounced impact on emulsion splitting. This can be attributed to the increase in the dielectric constant of the membrane phase.

SYMBOLS

C	constant value in Eq. (4) (C·m/V)
E	mean electric field (V/m)
F	force causing coalescence in electric field (N)
Q	charge on a droplet (C)
r	radius of a droplet (m)
$S_p\%$	splitting efficiency
$V_{i,t}$	internal aqueous phase volume at time t (mL)
$V_{i,0}$	initial internal aqueous phase volume (mL)

Greek

ϵ	dielectric constant of the membrane
ϵ_0	dielectric constant of a free space (F/m)
μ	correction factor in Eq. (2) which accounts for the charge saturation on a drop; its value varies between 0 and 1

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