Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hsu, Edward C. and Li, Norman N.(1985) 'Membrane Recovery in Liquid Membrane Separation Processes', Separation Science and Technology, 20: 2, 115 — 130
To link to this Article: DOI: 10.1080/01496398508058354
URL: http://dx.doi.org/10.1080/01496398508058354

SEPARATION SCIENCE AND TECHNOLOGY, 20(2 & 3), pp. 115-130, 1985

Membrane Recovery in Liquid Membrane Separation Processes

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Abstract

The use of conventional electrostatic coalescers with bare metal electrodes for the separation of rich water-in-oil emulsions often causes the formation of a sponge-like emulsion. This effect was eliminated by the use of insulated electrodes in a coalescer that allow the application of high electric fields at the oil/water interface, resulting in a clean separation of oil from water.

ELECTROSTATIC COALESCENCE TO SEPARATE LIQUID MEMBRANE EMULSIONS

Electrostatic coalescence is a technique widely used to separate dispersed aqueous droplets from nonconducting oils (*1*). The petroleum industry has been using it to separate brine emulsified in crude oil; the chemical industry uses it to resolve water-in-oil (w/o) emulsions generated during extraction (such as removal of naphthenic acids from gas-oils). Since this type of demulsification is strictly a physical coalescence process, the technique is most suitable for breaking w/o emulsions used in liquid membrane technology (*2–6*).

The breaking of liquid membrane emulsions is a key step in the liquid membrane (LM) extraction process. In this process, a w/o emulsion is

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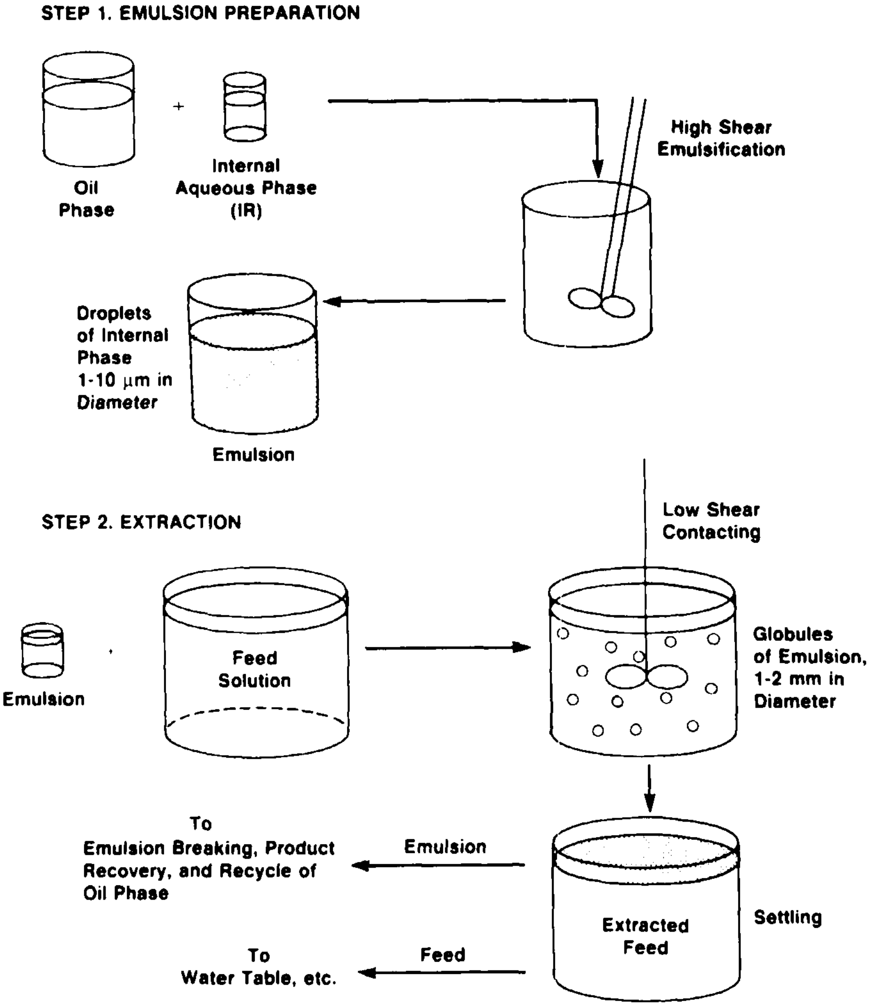

FIG. 1. Formation and use of liquid membranes.

prepared with emulsifying surfactants to ensure adequate stability of the emulsion during extraction (Fig. 1). The emulsion is then dispersed into an aqueous feed containing the chemicals to be extracted. These chemical species migrate from the external aqueous phase through the oil phase of the emulsion and are stripped and concentrated in the internal aqueous droplets which contain stripping reagents. The w/o emulsion is then allowed to separate from the external feed phase, usually by settling. This rich w/o emulsion has to be broken in order to recover the internal reagent phase which contains the extracted species. The oil phase from the broken emulsion is recycled to remake the emulsion and the entire operation repeated.

The use of electrostatic coalescence to separate LM emulsions is different from the conventional application of such coalescence. First, the LM emulsions contain much more aqueous phase (as high as 50% versus roughly 5%), and the recovered oil may contain more water (~1%) than pipeline quality dehydrated crude (about 0.3%). Second, since these emulsions are intentionally made, they contain high concentrations of potent emulsifying surfactants. Finally, the properties of the oil phase must be preserved for reemulsification. The last requirement excludes the conventional use of chemical demulsifiers for coalescence assistance and the sparking (localized electrical discharges of high power dissipation) inside a coalescer, which usually causes deterioration of the oil and the surfactants.

This paper reports the development of an insulated electrode coalescer for separating LM emulsions.

MECHANISM OF COALESCENCE AND THE CAUSE OF UNRESOLVED "SPONGE EMULSION"

An electric field has several effects on water droplets dispersed in oil. The insulative nature of the continuous oil phase allows the establishment of a high electric field across the emulsion. This electric field can polarize and elongate the water droplets. It can cause unidirectional migration of the droplets in dilute emulsions by either an electrophoresis mechanism (dc) or a dielectrophoresis mechanism (movement of dipoles in inhomogeneous fields). When the concentration of the droplets becomes high, it can also cause the coalescence of the droplets into larger droplets. At very high electric field strengths, a single water droplet could also burst into several small droplets.

The entire emulsion-breaking process can be divided into three stages. The first stage involves droplet coalescence and growth, the second stage involves droplet settling, and the third stage involves coalescence of the large water and oil droplets with their respective continuous phases in the coalescer. Coalescer throughput can be limited by any of these three stages.

When Pearce (7) applied an electric field to a relatively concentrated (~10% water) w/o emulsion under a microscope, he found that instead of unidirectional movement of water droplets, the droplets formed chains of closely spaced droplets oriented along the electric field direction (Fig. 2). The mutual attractive force between droplets in an electric field has the following proportionality (*8*):

$$f \propto \frac{E^2 r^6}{d^4}$$

where f = attractive force between droplets
E = electric field strength (V/cm, rms)
r = droplet radius (cm)
d = droplet separation (cm)

This equation indicates that the high electric field, not the conduction current, is the main cause of the droplet coalescence and growth. Thus the excess current caused by electrical breakdowns in the coalescer is not required nor advisable for the coalescence operations in LM applications.

After the water droplets have been coalesced to sufficient sizes under the electric field, they start to settle rapidly. Reducing the viscosity of the oil

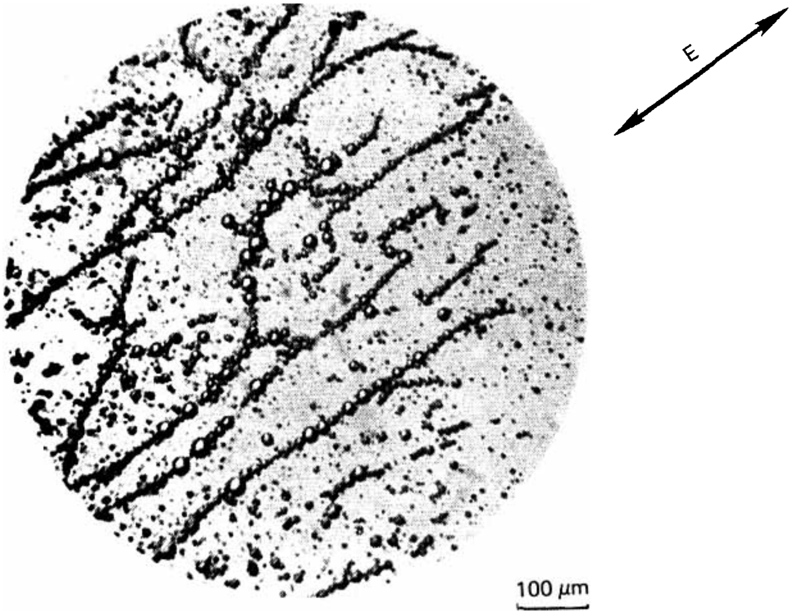

FIG. 2. Mechanism of coalescence (*7*): Electric field induces dipoles in water droplets, dipoles cause chains of droplets, and coalescence occurs between droplets in chains.

would aid the settling rate. (It also benefits droplet coalescence.) Since it is relatively easy to reduce the viscosity by heating the emulsion, coalescence at high temperature appears to be a desirable option for the oils having high viscosities.

Associated with the third stage in the emulsion-breaking process is the coalescence of the falling water droplets with the bulk water phase in the coalescer where the "sponge emulsions" problem could occur. Initial coalescence experiments with two vertical electrodes indicated that small droplets would coalesce to large sizes (~50 μm) and settle rapidly to the bottom of the coalescer. But instead of coalescing with the continuous water phase immediately, they form a stable, viscous, high-water-internal-phase (volume fraction about 94%), sponge-like emulsion. This indicates an ineffective coalescence of large water droplets with the bulk water phase in an electrostatic coalescer.

Mason et al. (*9, 10*) studied the coalescence of water droplets falling through an oil medium onto a flat oil/water interface. They showed that the droplets tended to rest at the interface for a few seconds before coalescence. The rest time increased significantly when oil-soluble surfactants were present. However, with the application of an electric field of sufficient strength (above a critical field strength), the falling droplet could coalescence instantaneously with the water. This critical field strength appears to be the same for a dc or ac field up to 10,000 Hz (*11, 12*). This decreased droplet rest time was interpreted as the result of accelerated drainage of the oil layer separating the water droplet from bulk water when an electric field is applied. Thus, to prevent the sponge emulsion formation in the coalescer, an electric field above some critical strength acting perpendicular to the interface has to be maintained. For this reason, a horizontal electrode configuration is necessary for LM emulsion.

However, coalescence using horizontal metal electrodes inside the coalescer only worked effectively with a few unstable emulsions. For most of the stable emulsions, the coalescence rate was unacceptably low. Attempts to increase the coalescence rate at high voltage was accompanied by frequent sparkings, which severely deteriorate the surfactant and oil, or by a growing accumulation of sponge emulsion.

Apparently the LM surfactant system is so effective in stabilizing the water droplets that it requires an unusually high critical electric field at the oil/water interface to prevent sponge emulsion formation. The increase of electric field, on the other hand, triggers frequent sparkings when the emulsion was feeding into the coalescer at any reasonable rate. One way to solve the problem is to employ electrodes insulated with solid dielectrics (*5, 6*).

INSULATED ELECTRODE COALESCER

The coalescence due to insulated electrodes is explained in Fig. 3. As mentioned previously, instantaneous formation of chains of water droplets occurs during coalescence. In a conventional coalescer, if a single chain happens to extend from one electrode to the other, sparking will occur. In an insulated electrode coalescer, the surface of the top electrode is coated by a layer of nonconductive, nonwater wetting insulation material. In this configuration, part of the applied *ac* voltage would be consumed by the insulation, but part of it would still be transmitted through the dielectric to act upon the emulsion. This is like transmitting an ac voltage through a capacitor. Since the surface of the dielectric is not water-wetting and the surface conductivity of the dielectric is low, this capacitor can be regarded as a parallel array of tiny *independent* capacitors. They are independent because when a water chain grows from the bottom electrode to touch the top electrode, this conducting chain only grounds one side of that tiny capacitor touched by the small water droplet. The other part of the

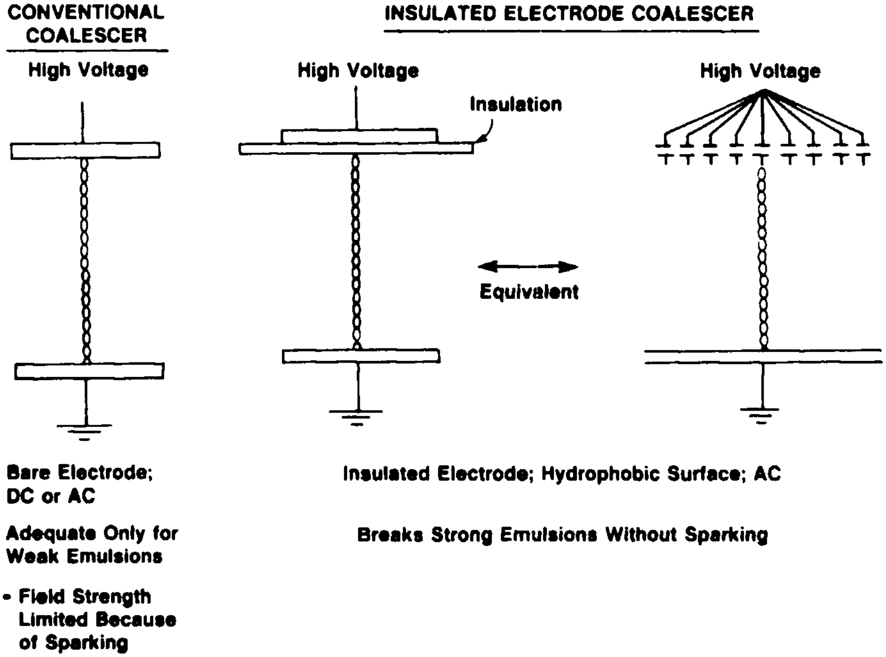

FIG. 3. Comparison of conventional and insulated electrode coalescer.

dielectric surface can still be at its original coalescing potential to continue coalescence action. Since the current passing through this conducting chain is limited by the reactance of this tiny capacitor (the smaller the capacitor, the lesser the current), sparking is suppressed. The maximum voltage can be determined by raising the applied voltage without causing sparking until the breakdown voltage of the insulation layer is reached.

EXPERIMENTAL

To test the insulated electrode for breaking liquid membrane emulsions, a model coalescer equipped with a glass-insulated electrode, shown in Fig. 4, was made by bending a Pyrex glass tube of 7 mm o.d. and 5 mm i.d. to form a horizontal grid with two vertical stems. The external surface of the glass grid was coated with a very thin layer of FEP (fluorinated ethylene-*co*-propylene) to reduce the water wettability of the surface. The horizontal portion of the grid was filled with an aqueous electrolyte to serve as a conductor for transmitting high voltage. The vertical stems of the grid were filled with transformer oil. The glass-insulated electrode was placed inside a cylindrical Plexiglas coalescer body with the two vertical stems protruding through two holes at the top of the coalescer cylinder. A flexible wire, inserted through the oil to the electrolyte, connected the electrolyte conductor of the electrode to the high voltage terminal of a transformer. A metal electrode was placed above the glass electrode. This electrode and the coalesced aqueous phase at the bottom of the coalescer were connected to the ground terminal of the transformer.

Prior to continuous coalescence operation, the coalescer was filled with the aqueous component of the emulsion to about 1 in. below the glass electrode, then with the oil until the coalescer was full. The 60-Hz high voltage was then activated and the emulsion was gradually fed into the coalescer. To obtain a steady-state coalescence at a specified applied voltage, the pumping rate of both the inlet emulsion feed and the outlet aqueous phase were adjusted so that the oil/water interface stayed at a constant level. The oil phase was allowed to overflow from the top of the coelescer with its water content monitored.

Two major parameters can be used to quantify the coalescence: the emulsion feed rate and the water remaining in the recovered oil. The higher the feed rate, the more the water would remain in the recovered oil. For stable liquid membrane emulsions, however, there exists a maximum emulsion feeding rate above which a layer of sponge emulsion begins to form at the oil/water interface of the coalescer, indicating the onset of a

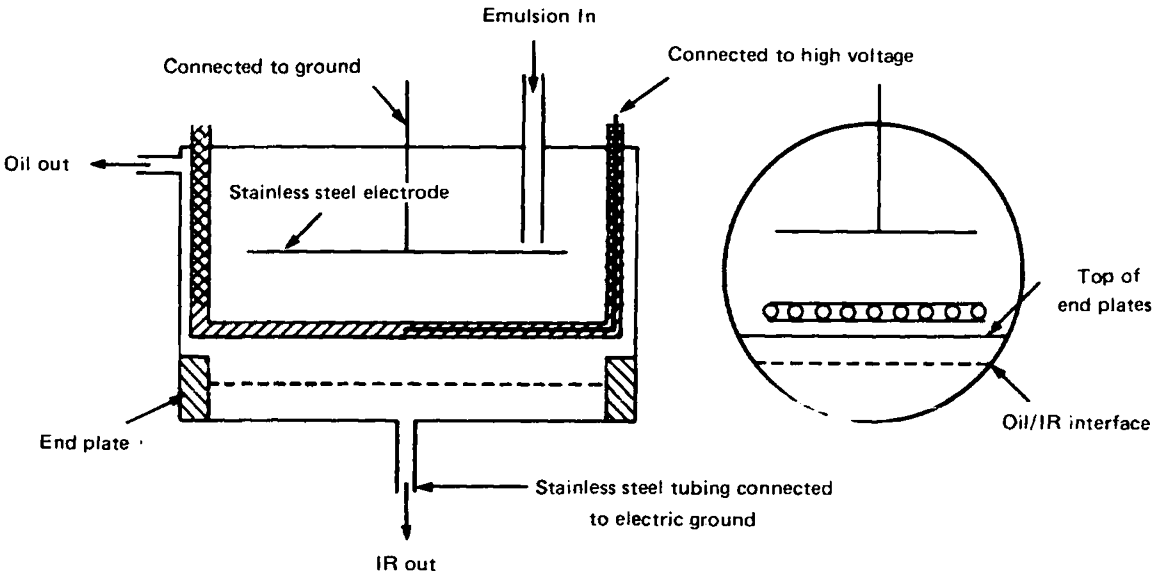

FIG. 4. Sketch of the continuous insulated electrode coalescer.

TABLE 1
Continuous Electrical Coalescence Studies with Uranium Emulsions

Applied voltage (kV)	20	20	20	20	13	13	13	13	13	13	15
Mean droplet size of feed emulsion (μm)	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9
Emulsion feed position	←Below Interface→			←Above Interface→							
Electrode to interface distance (cm)	1.2	2.0	1.5	2.0	3.0	2.5	2.0	1.5	1.0	1.5	1.7
Maximum coalescence rate (cm^3/min)	48	64	64	86	17	30	30	30	30	45	17
Sponge emulsion formation	Slight	Excess	*None*	*None*	Slight	Slight	*None*	*None*	Excess	None	None
Internal phase reagent content of recovered oil (% v/v)	1.8	1.8	1.8	1.8	1.6	1.6	1.6	1.6	1.6	1.6	2.8

coalescer upset. Thus the maximum *steady-state* coalescence rate of a coalescer is limited by the onset of sponge emulsion formation.

In addition to the compositional variables which determine the coalescibility of a specific emulsion, the performance of the coalescer also depends upon many operating variables, e.g., the applied voltage, the aqueous concentration, the emulsion feed, the position of the feed inlet, and the separation between the glass electrode and the oil/water interface. The performance of the coalescer in breaking an emulsion formulated for uranium extraction (oil/aqueous = 2/1) was studied at various operating conditions. The results of this study are shown in Table 1. To demonstrate the rate limit because of the formation of sponge emulsion, this table also includes *unsteady-state* results where sponge emulsion was slowly accumulating in the coalescer.

RESULTS AND DISCUSSIONS

As shown in Table 1, the maximum *steady*-state rate of the coalescer appears to depend upon the distance separating the electrode and the oil/water interface. As mentioned earlier, a stream of relatively large water droplets is continuously falling to the interface during coalescence. These water droplets tend to decrease the electric field at the interface by reducing the impedance of this zone, thus increasing the chance for some of these water droplets to contact the interface without coalescence. If this happens, the electric field alone cannot cause drop coalescence. Raising the applied voltages will set up a hydrodynamic disturbance at the oil/water interface, which will help droplet coalescence. Apparently, the use of insulated electrodes not only provides the initial critical field needed to maximize the instantaneous coalescence of falling droplets with bulk water, but also generates a complex electrohydrodynamic turbulence at the interface to break up sponge emulsions. At the high field strengths needed to sustain turbulence, a bare electrode would cause excessive sparkings. This turbulence phenomenon is a complex function of insulation characteristics of the electrode, the distance between the electrode and interface, and the flux of the water droplets falling to the interface.

When a specific emulsion was fed from beneath the interface, the maximum steady-state coalescence rate appeared to be 64 cm^3/min at 20 kV at a 1.5-cm gap. Increasing the gap to 2.0 cm tended to cause accumulation of sponge emulsion. Decreasing the gap (in theory, this increases the electric field) also causes sponge emulsion accumulation, even at lower feed rates. Similar phenomena occurred when the emulsion was fed above the interface. Here, at an applied voltage of 13 kV, the maximum rate was 30 cm^3 at a 1.5–2.0 cm gap. Increasing the voltage to 20 kV increased the rate to 84 cm^3/min, which is much higher than that when feed was introduced beneath the interface.

Figure 5 shows the effect of the applied voltage on the maximum steady-state coalescence rate of the emulsion using the data in Table 1. It is apparent that the relation is linear and that the extrapolation of the straight line to lower voltage does not pass the origin but has an intercept at about 9 kV. This type of nonzero intercept is observed with many other LM emulsions. It may be related to the diminishment of the electrohydrodynamic turbulance at low applied voltages.

As we expected, the maximum coalescence rate of the emulsion decreases with decreasing droplet size of the emulsion. As shown in Table 1, an emulsion with 1.8 μm mean droplet size can be broken at a rate of 45 cm^3/min with the application of a 15-kV voltage. The coalescence rate dropped to 17 cm^3/min when the mean droplet size was reduced to 0.9 μm. In general, smaller droplets require more collisions than a large droplet to coalesce to a settling size. On the other hand, emulsions with smaller

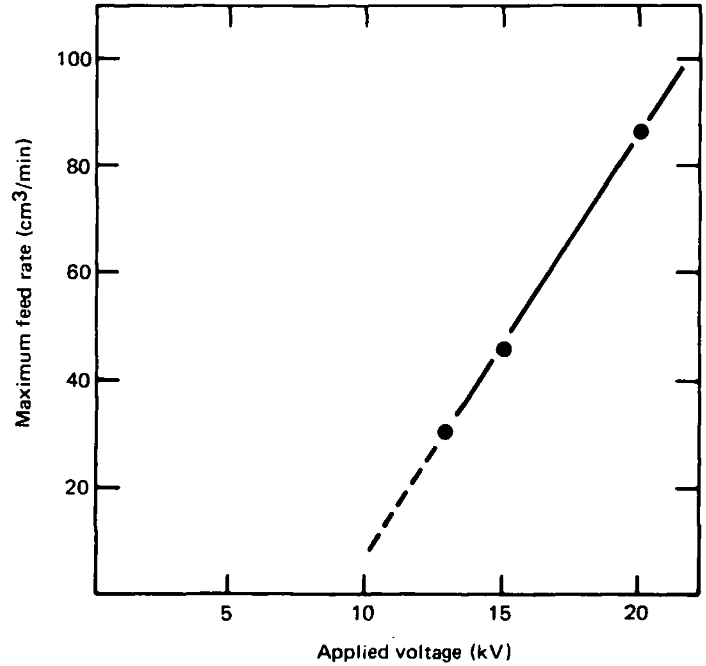

FIG. 5. Effect of applied voltage on the maximum coalescence rate of a uranium emulsion.

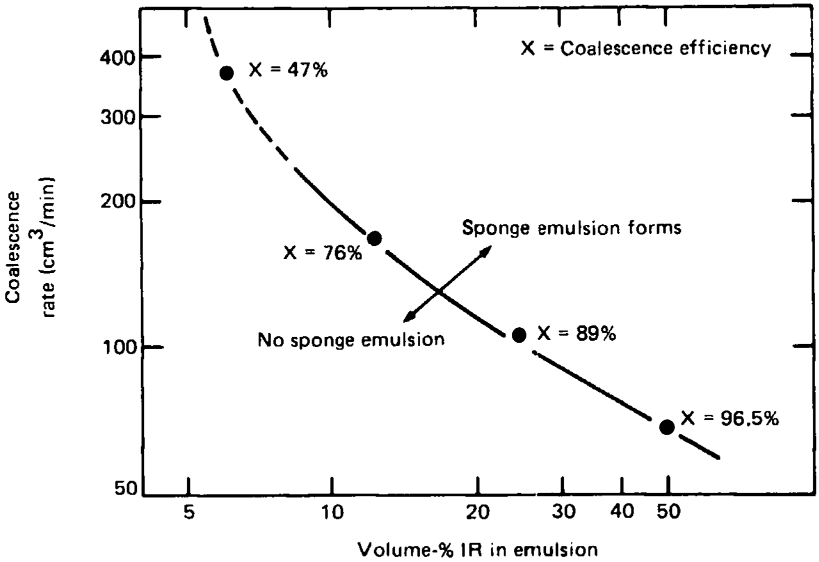

FIG. 6. Dependence of the coalescence rate on the volume-% IR in the emulsion feed.

droplets have a higher chance of mutual collision than emulsions with larger droplets.

To study the effect of aqueous content of the initial emulsion feed, a large batch of uranium extraction emulsion (*4*) with 50% v/v aqueous content was prepared. This emulsion happened to have larger droplets than the previous emulsion. Dilution of this emulsion with oil at different ratios was used to obtain a series of emulsion feeds of different aqueous content. Such a dilution with oil should not change the droplet size distributions of the emulsions involved. The continuous coalescence was then performed on this series of emulsions at maximum steady-state feed rates as well as at lower feed rates. The aqueous phase remaining in the recovered oil phase was carefully monitored. A coalescence efficiency, defined as percent reduction of the aqueous content of the stream from the inlet emulsion to the outlet oil, was determined for each experimental condition.

As expected, the maximum steady-state feed rates were limited by the formation of sponge emulsions. Figure 6 shows that the larger the dilution, the higher the apparent maximum feed rate. However, as shown in Fig. 7, a log-log plot of the maximum recovery rate of *aqueous* phase vs volume percent aqueous phase in the feed emulsion yields a straight line. (The dashed portion indicates uncertainty.) Thus, the dilution of the emulsion with oil not only is not advantageous but even has an adverse effect on the

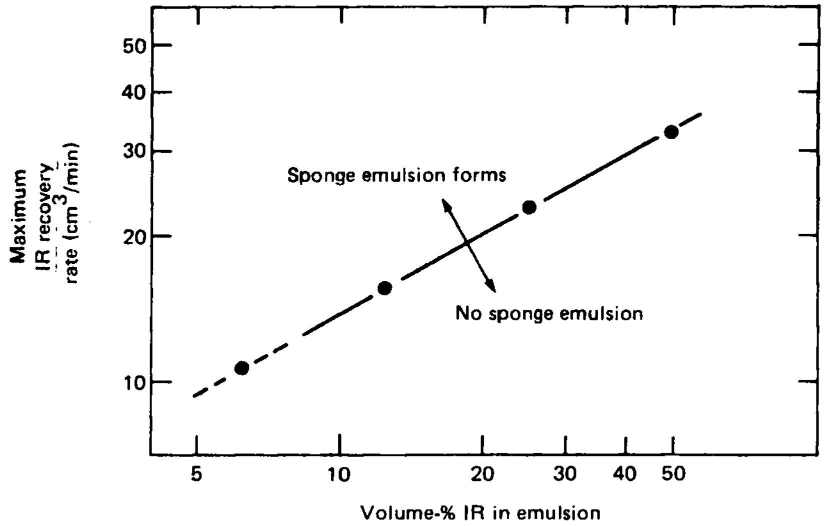

FIG. 7. Dependence of the maximum IR recovery rate on the volume-% IR in the emulsion feed.

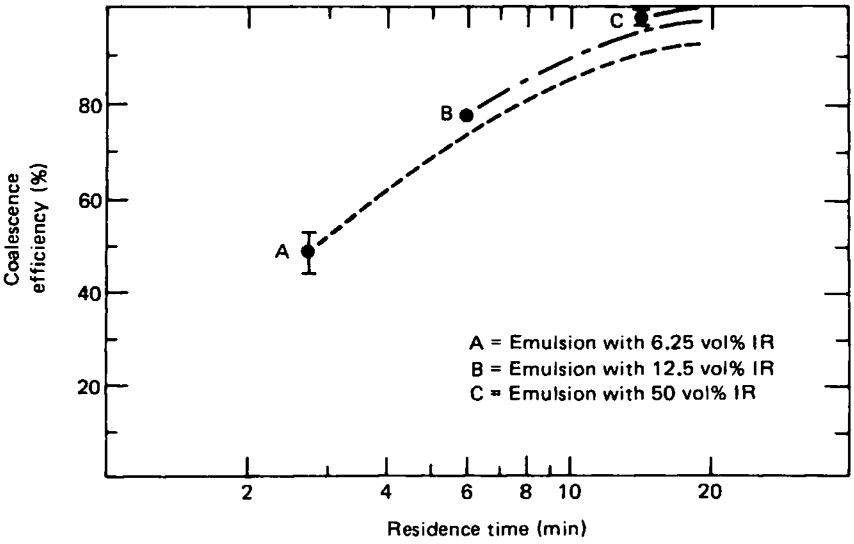

FIG. 8. Dependence of the coalescence efficiency on the residence time of the emulsions.

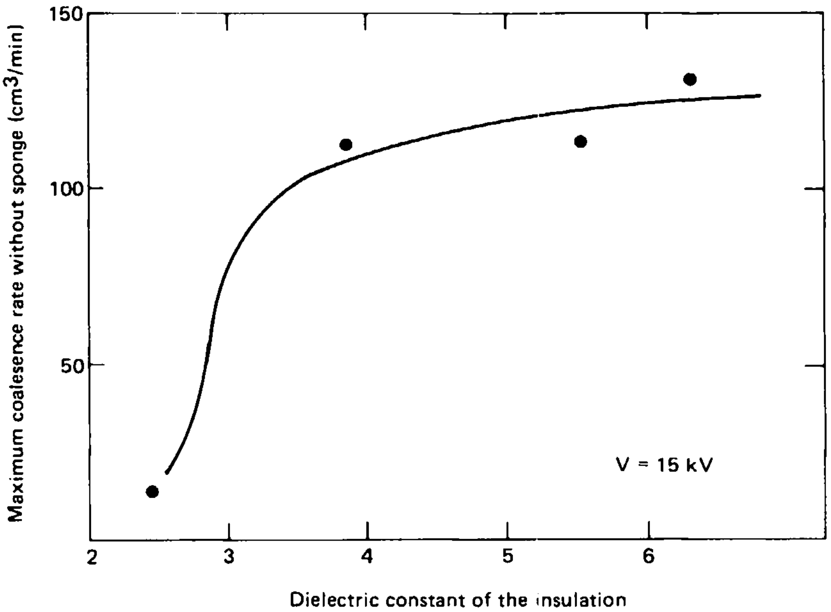

FIG. 9. Effect of dielectric constant of electrode insulation on the maximum coalescence rate.

coalescence efficiency (Figs. 6 and 8). The efficiencies can be improved when the rate is reduced or the residence time is increased. It is interesting to note that better coalescence was obtained when the emulsion was fed to the oil phase than when it was fed beneath the oil/aqueous interface.

Although the coalescence of LM emulsions has been studied with electrodes insulated with a 1-mm glass layer, we have also briefly explored the effect of the dielectric constant of the insulation material on the maximum coalescence rate of the coalescer. The result is shown in Fig. 9. There appears to be a minimum dielectric constant value of about 4, below which the coalescer starts to perform poorly. This peculiar behavior is probably related to the previously mentioned nonzero intercept in the voltage effect (Fig. 5) and the existence of an optimum gap distance between the glass-insulated electrode and the interface for maximum coalescence. It is worth mentioning here that the dielectric constant of the glass used in our coalescence study was 5.58 (at 60 Hz). Polymeric insulation materials having dielectric constants higher than 4 are also available.

CONCLUSIONS

Because of the intentional incorporation of potent surfactants in LM systems to stabilize the emulsions, the LM emulsions have a very high tendency to form residual sponge emulsions during electrostatic coalescence. This makes it impractical to break the LM emulsions with a conventional electrostatic coalescer equipped with bare metal electrodes.

The coalescer with its electrode insulated by a solid dielectric medium having a dielectric constant of at least about 4 and a hydrophobic surface can break LM emulsions at a faster rate and with excellent quality of the recovered oil suitable for reemulsifications. These insulated electrodes, when operated at high voltages, generate intense vertical electric fields, and the associated electrohydrodynamic turbulence at the oil/water interface suppresses the accumulation of sponge emulsion. Ac fields must be used with the insulated electrodes.

Even with the insulated electrodes operated at high voltages, the maximum coalescence rate is still limited by the onset of the sponge emulsion. This maximum coalescence rate is a function of applied voltages, the position of the feed inlet, and separation between the insulated electrode and the aqueous level in the coalescer.

The ease of coalescence is a very sensitive function of droplet size of the emulsion. While emulsions with smaller droplets are preferred to maximize the mass transfer in the LM process, the reduction in emulsion droplet size greatly reduces the ease of coalescence. Surfactant concentration also affects the coalescence of the emulsion. For emulsions with oil viscosities greater than about 10 cP, operation at elevated temperature may be necessary to accelerate coalescence.

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Received by editor September 10, 1984