EFFECT OF FREQUENCY IN A.C. HIGH VOLTAGE ON COALESCENCE OF WATER-IN-OIL EMULSION STABILIZED WITH SORBITAN MONOOLEATE TYPE NONIONIC SURFACTANT

YASUSHIGE MORI*
Department of Chemical Engineering and Materials Science, Doshisha University, Tanabe, Kyoto 610-03
MASATAKA TANIGAKI, NORIYASU MAEHARA AND THE LATE WATARU EGUCHI
Department of Chemical Engineering, Kyoto University, Kyoto 606-01

Key Words: Extraction, Membrane Separation, Liquid Surfactant Membrane, Emulsion, Demulsification, Phase Separation, Electrical Field, Sorbitan Monooleate Surfactant

The liquid surfactant membrane has advantages superior to those of other types of liquid membranes, but its biggest bottleneck lies in the demulsification process for separating the stripping solution from the organic phase containing surfactant and carrier. This paper is concerned with the electrostatic coalescence of the W/O emulsion stabilized with surfactant in an a.c. high-voltage current applied between two insulated flat electrodes. Effects of the dispersed phase hold-up, the applied voltage and the frequency on the phase separation rate were studied.

The separation rate was larger for lower initial hold-up of the dispersed phase. When the initial hold-up was less than 40 %, the coagulation stage preceded the coalescence stage and the separation rate decreased. The separation rate increased approximately with the second order of the applied voltage. It also increased with frequency and tended to become constant at frequencies in the range of 1000 to 2000 Hz. The water content of the separated oil phase decreased with increase in frequency.

Introduction

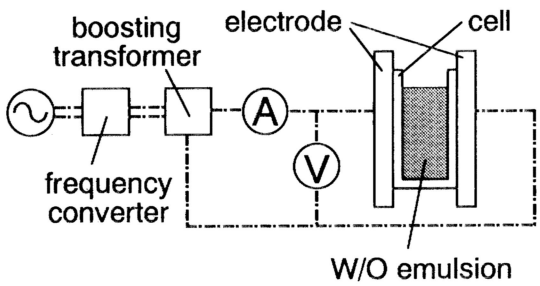
A liquid membrane operation, in which both the extraction and the stripping steps are carried out in a single stage, offers a potentially attractive alternative to solvent extraction operation. Among various types of liquid membranes proposed since the work by N.N. Li[18], the liquid surfactant membrane (LSM) has advantages superior to other types, namely a very large area-to-volume ratio and a highly mobile thin liquid membrane. One bottleneck of LSMs at present lies in the demulsification process of water-in-oil (W/O) emulsion required to separate the inner stripping solution from the outer organic phase containing surfactant and carrier.

Electrical coalescence as a means of demulsification of W/O emulsions seems to be better than other methods, such as heating, centrifugation or filtration[19]. The mechanism of coalescence in the electrostatic field has been studied by many researchers, some of whom observed aggregation and coalescence phenomena under a microscope[15,20,22], and measured the lifetime of water droplets at the oil-water interface[1]. The lifetime of water droplets decreased with increasing frequency of the electric field, but the dependency is not clear[4-6]. Bailes and Larkai[2,3], and Galvin[8] found that a certain lower frequency of pulsed high voltage with d.c. field gave maximum coalescence efficiency for W/O emulsions, but it depended on the electrical properties of the system.

The effect of operating conditions and the design of the electrical coalescer of W/O emulsions stabilized with surfactant in the LSM system have been tested using a.c. high voltage of commercial frequency[7, 9-11, 13, 14], d.c. field[21], and pulsed d.c. field[16, 17, 23]. As for the influence of the frequency of the applied field, Hauertmann *et al.*[12] reported that the breakage rate was correlated linearly with the frequency up to 2000 Hz using a continuous coalescer, although the electrical field strength used was below 1 kV/cm.

In this paper, the electrostatic coalescence of the W/O emulsion stabilized with surfactant was tested in the range of 40 to 2000 Hz, up to 8 kV a.c. voltage. The two insulated flat electrodes were employed because the electric field is well defined and the design for scale-up is easy. Effects of the dispersed phase hold-up, the surfactant, the applied voltage and the frequency on the phase separation rate of the emulsion were studied.

* Received October 12, 1993. Correspondence concerning this article should be addressed to Y. Mori.



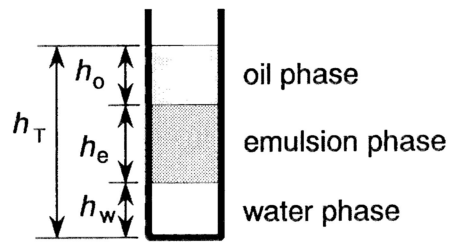


Fig. 1 Experimental apparatus and definition of the height of various phases in the cell during demulsification

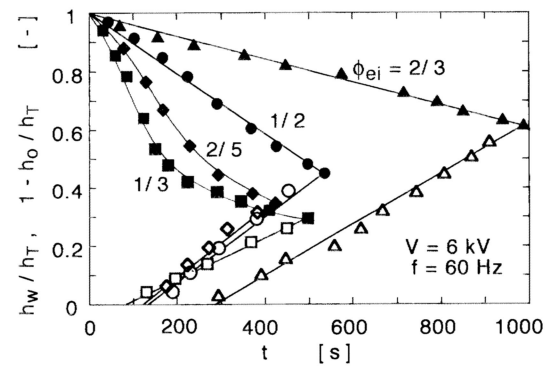


Fig. 2 Change of interfaces during demulsification

1. Experimental

1.1 Liquid systems studied

Kerosene and 50 mol/m^3 hydrochloric acid aqueous solution were used as the organic and the aqueous phases respectively. Rheodol SP-O10 nonionic surfactant (Kao Co.), which consists mainly of sorbitan monooleate, was used. It is equivalent to Span 80, manufactured by ICI Specialty Chemicals. The aqueous and organic phases were presaturated with each other in the absence of surfactant. The surfactant was dissolved in the organic phase after the two phases were separated. Its concentration was 3 wt. % in the organic phase.

The organic and aqueous phases were charged in a glass container, which was kept at 273 K in a bath of ice water, to produce an emulsion of predetermined water content. A mixer-type emulsifier (Ystral GmbH, Germany; LD-X10/20) was first used for 15 minutes at 167 rps, followed by the use of an ultrasonic emulsifier (Nihon Seiki Co., Japan; US150) for 2 minutes.

The size distribution of the emulsion produced was determined with a particle-size analyzer (Horiba Co., Japan; CAPA 500). It was found that this size distribution changed considerably within about an hour, and was stable for several hours thereafter. The emulsion produced, consequently, was allowed to stand for more than ninety minutes at 273 K, before it was used in the demulsification experiment. The stable size distribution was log-normal on a projected area basis. The surface-volume mean diameter was 3.4 μm, and the geometric standard deviation was 2.1.

1.2 Apparatus and procedure

Figure 1 shows the schematic set-up of the experimental apparatus. The width and height of electrodes were bigger than those of the cell in order to ensure a uniform electrical field in the cell. A quartz glass cell with an interior width of 10 mm and a wall thickness of 1.25 mm was used. The mean value of the applied a.c. voltage ranged from 4 to 8 kV and the frequency was changed from 40 to 2000 Hz. The appearance of the separated oil and water phases in the cell was observed with a television camera and was recorded by a video tape recorder.

2. Results and Discussion

2.1 Demulsification phenomena

When high a.c. voltage was applied, the coalesced drops were observed to line up in the direction of the electric field in accordance with the observation by C.A.R. Pearce *et al.*[20] The grown-up water drops settled at the cell wall and finally fell downward to grow the clear water phase at the bottom of the cell. The emulsion phase decreased and finally disappeared with the elapse of time.

Figure 2 shows the changes of the dimensionless heights of the interfaces with time (see Fig. 1). Solid keys indicate the position of the interface between the oil and the emulsion phases. Open keys indicate the interface between the emulsion and water phases. The time of complete demulsification, in general, decreased with the decrease in the initial water content of the charged emulsion, ϕ_{ei}. For high ϕ_{ei}, the oil phase grew almost linearly with time. For lower ϕ_{ei}, the oil phase initially grew much faster than for higher ϕ_{ei}, but the rate decreased as demulsification proceeded. The water phase grew almost linearly after a certain lag time in all cases.

The position of the interface between the oil and water phases at the end of demulsification does not agree with ϕ_{ei}. The difference is somewhat larger at higher applied voltage. But when the applied voltage was shut off at the end of the experimental run, the interface between the oil and water phases coincided with ϕ_{ei}. This is due to enhanced convection under the electrical field of the coalesced water drops, which were much larger than the original emulsion droplets existing in the oil phase. The number of convecting water drops in the oil phase was observed to be higher at higher voltages.

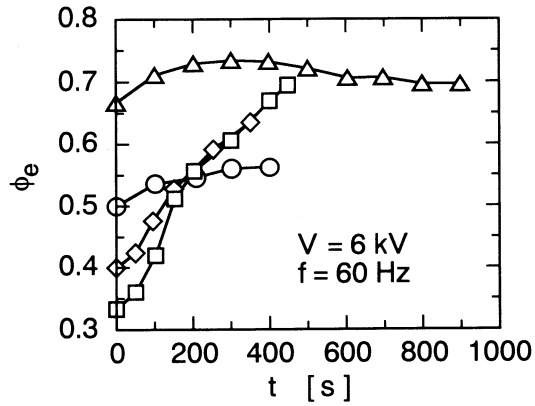


Fig. 3 Change of water content in the emulsion phase (Keys are the same as in Fig. 2)

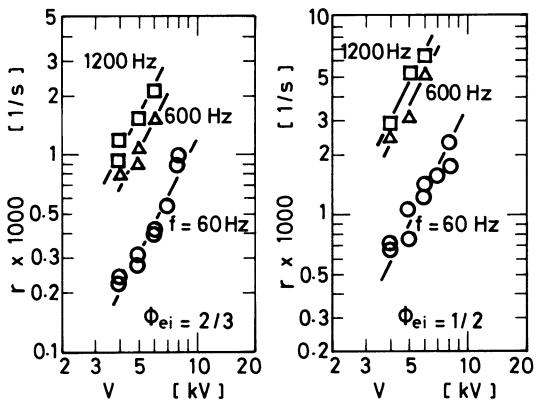


Fig. 4 Relationship between phase separation rate, r, and applied voltage

The water content in the emulsion phase during demulsification, ϕ_e, could be calculated from the data in Fig. 2 if the water content in the produced oil phase, ϕ_o, was assumed to be same as that after complete demulsification, ϕ_{of}. **Figure 3** shows the change in calculated water content of the emulsion phase with time. Demulsification by electrostatic force could consist of the approach of two water droplets to each other (coagulation stage), and water droplet growth that breaks the oil membrane between them (coalescence stage). For high ϕ_{ei}, the coagulation process is less likely, because the water content in the emulsion phase, ϕ_e, is nearly constant, except in the early stage. For lower ϕ_{ei}, the coagulation rate is anticipated to be larger than the coalescence rate, and this tendency is larger for lower ϕ_{ei}.

2.2 Effect of applied voltage on phase separation rate

The process of demulsification by electrostatic force is very complicated, as was stated in the preceding section. The effect of voltage on the phase separation rate can be discussed in this section for the cases of $\phi_{ei} = 0.5$ and 0.667, because ϕ_e was almost constant during demulsification, as shown in Fig. 3. The phase separation rate of the oil phase from the emulsion phase was taken to be the rate of demulsification in this case, and this rate, r, was approximated by the slope of the straight line linking the measured points in Fig. 2. **Figure 4** shows the effect

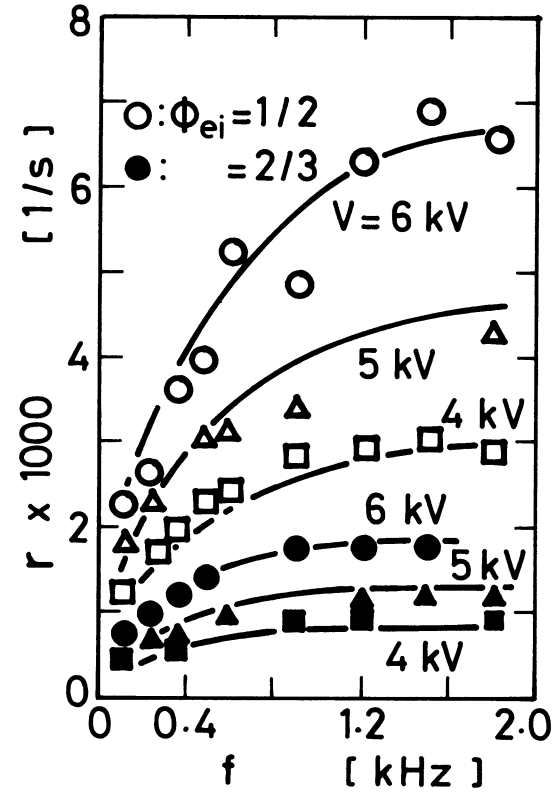


Fig. 5 Effect of frequency on phase separation rate

of the applied voltage on this rate of demulsification. The rate r is approximately proportional to the square of the applied voltage at all frequencies examined. This should be related to the fact that the mutual attractive force between the droplets in a uniform electric field is proportional to the square of the applied voltage.

2.3 Effect of frequency on demulsification

Figure 5 shows the effect of frequency on the rate of demulsification. The rate r increases with the increase in frequency in the low-frequency range, but tends to be constant at higher frequencies. Due to the limitations of the experimental apparatus, whether an optimal frequency at which the rate of demulsification becomes maximum exists or not could not be investigated. The amount of coalesced water drops convecting in the oil phase did not depend on the frequency. The solid lines in Fig. 5 were drawn by using the solid lines in Fig. 4, which indicates that the rate of demulsification was proportional to the square of the applied voltage.

As the current increases with the frequency, the energy input into the emulsion is roughly proportional to the frequency although the field strength inside the cell was not measured. The energy performance of the phase separation may have a maximum point around 1000 Hz.

The effect of the frequency on the water content in the oil phase after demulsification, ϕ_{of}, was not affected by the initial water content in the charged emulsion. ϕ_{of} was very low and was nearly the same as the water content of the spontaneous emulsion (about 0.4 %), which was observed when the aqueous and the organic phases

were allowed to stand in contact with each other for four days. It was concluded that the emulsion in the present study was almost completely separated into the aqueous and organic phases by the electrostatic coalescer.

Conclusions

The electrostatic coalescence behavior of W/O emulsion stabilized with surfactant was studied when a.c. high voltage was applied between two insulated flat electrodes, especially with changing frequency.

1) Complete phase separation of the emulsion into aqueous and the oil phases was possible with the present electrostatic coalescer.

2) The phase separation rate of the oil phase from the emulsion phase was faster for smaller initial hold-up of the dispersed phase, but when the initial hold-up was less than 40 %, the coagulation stage preceded the coalescence stage and the separation rate decreased.

3) The separation rate increased approximately with the second order of the applied voltage when Rheodol SP-O10 (or Span 80) was used as the surfactant.

4) The effect of frequency on the separation rate was very large. The rate increased with increase in frequency and tended to become constant at a certain frequency in the range between 1000 to 2000 Hz. As the current increased with the frequency, the suitable frequency seemed to be around 1000 Hz from the viewpoint of energy performance.

Nomenclature

f	=	frequency	[Hz]
h_e	=	height of emulsion phase during demulsification	[m]
h_o	=	height of oil phase during demulsification	[m]
h_w	=	height of water phase during demulsification	[m]
h_T	=	initial height of charged emulsion ($= h_o + h_e + h_w$)	[m]
r	=	phase separation rate of oil phase from emulsion phase	[s^{-1}]
t	=	time	[s]
V	=	applied voltage	[V]
ϕ_e	=	water content in emulsion phase	[-]
ϕ_o	=	water content in oil phase	[-]

<Subscripts>

i	=	initial or charged
f	=	final

Literature Cited

1) Allan, R.S. and S.G. Mason: *Trans. Faraday Soc.*, **57**, 2027-2040 (1961)
2) Bailes, P.J. and S.K.L. Larkai: *Trans. I. Chem. E.*, **60**, 115-121 (1982)
3) Bailes, P.J. and S.K.L. Larkai: *AIChE Symp. Ser.*, **80**, 170-77 (1984)
4) Bashirova, R.M., F.L. Sayakhov and V.S. Khakimov: *Chem. Technol. Fuels Oils*, **19**, 84-85 (1983)
5) Brown, A.H. and C. Hanson: *Trans. Faraday Soc.*, **61**, 1754-60 (1965)
6) Brown, A.H. and C. Hanson: *Chem. Eng. Sci.*, **23**, 841-48 (1968)
7) Fujinawa, K., M. Morishita, M. Hozawa, N. Imaishi and H. Ino: *J. Chem. Eng. Japan*, **17**, 632-636 (1984)
8) Galvin, C.P.: *Inst. Chem. Eng. Symp. Ser.*, **88**, 101-113 (1987)
9) Goto, M., J. Irie, K. Kondo and F. Nakashio: *J. Chem. Eng. Japan.*, **22**, 401-6 (1989)
10) Hano, T., T. Ohtake, F. Hori and F. Nakashio: *Water Treat.*, **5**, 202-13 (1990)
11) Hano, T., T. Ohtake and K. Takagi: *J. Chem. Eng. Japan.*, **21**, 345-51 (1988)
12) Hauertmann, H.B., W. Degener and K. Schuegerl: *Sep. Sci. Technol.*, **24**, 253-73 (1989)
13) Hsu, E.C. and N.N. Li: *Sep. Sci. Technol.*, **20**, 115-30 (1985)
14) Ino, H., N. Imaishi, M. Hozawa and K. Fujinawa: *Kagaku Kogaku Ronbunshu*, **9**, 263-269 (1983)
15) Ise, T., M. Yamaguchi and T. Katayama: *Kagaku Kogaku Ronbunshu*, **15**, 1087-94 (1989)
16) Kataoka, T. and T. Nishiki: *Kagaku Kogaku Ronbunshu*, **12**, 16-22 (1986)
17) Kataoka, T. and T. Nishiki: *Sep. Sci. Technol.*, **25**, 171-85 (1990)
18) Li, N.N.: U.S. Patent, 3410794 (1968)
19) Lissant, K.J.: "Demulsification: Industrial Applications", Surfactant Science Series vol. 13, (ed.) Marcel Dekker, New York (1983)
20) Pearce, C.A.R.: *British J. Appl. Phys.*, **5**, 136-143 (1954)
21) Yamaguchi, M., A. Kobayashi, K. Ohbori and T. Katayama: *Kagaku Kogaku Ronbunshu*, **11**, 729-34 (1985)
22) Yamaguchi, M., K. Ohbori, O. Kondo and T. Katayama: *Kagaku Kogaku Ronbunshu*, **14**, 483-9 (1988)
23) Zhong, T., L. Siya, Y. Yaochuan and Z. Xuelun: *Desalination*, **62**, 323-28 (1987)