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

DEMULSIFICATION OF W/O EMULSIONS BY MICROWAVE RADIATION

Chih-Chieh Chan[a]; Yeong-Ching Chen[a]
[a] Department of Chemical Engineering, Feng Chia University, Taichung, Taiwan 407, R.O.C.

Online publication date: 23 October 2002

To cite this Article Chan, Chih-Chieh and Chen, Yeong-Ching(2002) 'DEMULSIFICATION OF W/O EMULSIONS BY MICROWAVE RADIATION', Separation Science and Technology, 37: 15, 3407 — 3420
To link to this Article: DOI: 10.1081/SS-120014434
URL: http://dx.doi.org/10.1081/SS-120014434

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 37, No. 15, pp. 3407–3420, 2002

DEMULSIFICATION OF W/O EMULSIONS BY MICROWAVE RADIATION

Chih-Chieh Chan* and Yeong-Ching Chen

Department of Chemical Engineering, Feng Chia University, 100 Wenhwa Road, Seatwen, Taichung, Taiwan 407, R.O.C.

ABSTRACT

Demulsification is an indispensable step in the application of emulsion liquid membrane (ELM) separation process. In this work, a novel microwave demulsification method is first applied in the ELM system to study the phenomenon of breaking water-in-oil (W/O) emulsion. The mechanism of microwave heating is essentially that of dielectric heating. After exposing the emulsion to the microwave electromagnetic (EM) field, molecular rotation, and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. Thus, the application of microwave radiation results in the acceleration of separation of emulsion. In this work, the effects of emulsion conditions and microwave operating conditions on the demulsification rate and the separation efficiency of W/O emulsion were systematically studied. The results exhibited that both the demulsification rate and the separation efficiency increased with

*Corresponding author. Fax: +886-4-24510890; E-mail: ccchan@fcu.edu.tw

DOI: 10.1081/SS-120014434
0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

the increase in droplet size and the concentrations of the carrier (D2EHPA) and acid. However, they decreased with the increase in surfactant (Span 80) concentration and the oil phase-to-aqueous phase volume ratio (O/A). As for the effect of electrolyte concentration, it exhibited a peculiar maximum phenomenon. Both the demulsification rate and the separation efficiency were maximum when the concentration of electrolyte was about 0.5 *M*. The optimum microwave irradiation power and exposure time were suggested to be 420 W and 12 sec, respectively.

Key Words: Microwave demulsification; Emulsion liquid membrane; Surfactant; Carrier

INTRODUCTION

The breaking of the loaded emulsion is one of the key steps in the emulsion liquid membrane (ELM) separation process. After the liquid membrane extraction, the membrane phase must be recycled repeatedly, and the enriched internal phase usually recovered. Therefore, demulsification of the loaded emulsion is unavoidable for the use of this separation process.

Two principal approaches for the demulsification of the loaded emulsion are chemical and physical treatments. Chemical treatment involves the addition of a demulsifier to the emulsion. However, the added demulsifier will change the property of the surfactant, which is intentionally added to the membrane phase and also, the contamination of demulsifier in the membrane phase will change its emulsification power in the recycle ELM process and thus prohibit its reuse. Therefore, chemical treatment is usually not suitable for breaking liquid membrane emulsions.

Physical treatment methods include heating, centrifugation, ultrasonics, solvent dissolution, high shear, and the use of high-voltage electrostatic fields. Among them, demulsification with electrostatic fields appears to be the most efficient and economic way for breaking W/O emulsion in the liquid membrane process.[1] However, a special design of the electrostatic coalescer and a high critical electric field strength are necessary for this method.

Recently, an innovative microwave heating technology has been successfully tested in field operation and laboratory tests for the demulsification of oil–water–solid emulsion.[2] The microwave demulsification does not require chemicals. This is a significant advantage for reusing the membrane phase. Microwaves are electromagnetic (EM) energy. Microwave energy is a nonionizing radiation that causes molecular motion by migration of ions and

rotation of dipoles, but does not cause changes in molecular structure. Microwave energy has a frequency range from 300 MHz to 300 GHz. Microwaves are coherent and polarized and couple effectively with lossy materials, their primary action being very rapid heating. One important characteristic of microwave heating is that the entire volume of sample is heated up internally and selectively.

In conventional thermal heating, energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces, and it is possible to achieve rapid and uniform heating of thick materials. In addition to volumetric heating, microwaves can be utilized for selective heating of materials. The molecular structure affects the ability of the microwaves to interact with materials and transfer energy. When materials in contact have different dielectric properties, microwaves will selectively couple with the higher loss material. In multiple phase materials, such as W/O emulsions, some phases may couple more readily with microwaves.

In electromagnetic field, there exist a number of properties that contribute to the dielectric response of materials. These properties include electronic polarization, atomic polarization, ionic conduction, dipole polarization, and Maxwell–Wagner polarization mechanisms. At microwave frequencies, dipole polarization is thought to be the most important mechanism for energy transfer at the molecular level. In composite materials, Maxwell–Wagner polarization, which results from the accumulation of charge at the material interface, is also an important heating mechanism.[3] In addition, in aqueous solutions, ionic conduction, which is the conductive migration of dissolved ions in the applied electromagnetic field, should also be taken into account.[4] This ionic migration is a flow of current that results in I^2R losses (heat production) due to the resistance to ion flow.

Due to these unique heating characteristics, microwave radiation has been widely used in domestic, laboratory, and industrial applications since the pioneering work in food processing.[5] Excellent reviews have been published on various aspects of microwave-assisted treatment and chemistry.[6–14] However, only a few reports were concerned about the application of microwave to demulsification. Petrowski[15] first used microwave irradiation to determine the stability of emulsion. Patents developed in microwave demulsification of water-in-oil (W/O) emulsions were first awarded to Klaila[16] and Wolf.[17] Fang et al.[2] demonstrated the microwave demulsification of dispersed water–oil mixtures and emulsified water–oil–solid sludge in laboratory and field tests. In their conclusions, microwave-induced molecular rotations were believed to reduce zeta potential, which suspends water droplets and solid particles in an emulsion, and that was considered to play a role in addition to the primary heating effect in

the acceleration of microwave demulsification. Lai[18] and Fang,[19–21] in their laboratory and field tests, showed that viscous and stable W/O emulsions can be demulsified and separated into oil and water layers by the combined process of microwave heating and gravity sedimentation. Barringer et al.[22] compared the heating rates of various W/O emulsions, oil-in-water emulsions, and layered systems in microwave oven. Alternately, Takahashi et al.[23] proposed a novel treatment of waste oils from ships by decomposition of oil-in-water emulsions with microwave or ultrasonic wave irradiation. Fu and Wu[24] recently proposed the microwave radiation method to break oil-in-water emulsions. Zeta potential of the oil droplets in water was measured in their study.

However, most of the emulsion systems discussed in the previously mentioned papers are limited to waste oil emulsions or dispersions of hydrocarbons and water. The volume fraction of dispersed phase is usually small and contains no or slight amount of emulsifiers. The viscosity and stability of these emulsions are usually not too high. In contrast, for liquid membrane emulsions, the volume fraction of dispersed phase is usually between 0.25 and 0.75 and significant amount of special emulsifiers and carriers are often

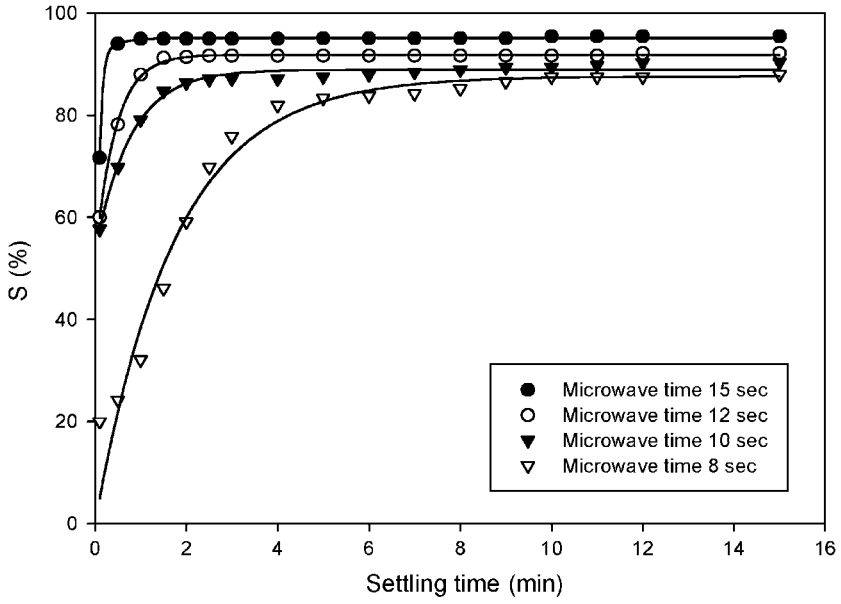

Figure 1. Typical plot of separation efficiency. Emulsion volume = 25 mL, O/A = 1, power = 420 W. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 40 wt%, kerosene = 52 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

intentionally added to the continuous phase to stabilize and facilitate the emulsion systems. Thus, both viscosity and stability of these tailor-made emulsions are usually too high to be demulsified easily by most conventional methods. In the present work, the novel microwave radiation method is first adopted to study the demulsification of liquid membrane emulsions.

EXPERIMENTAL

Paraffin oil and kerosene, which comprised the membrane phase solvent, were obtained from Union Chemical Works, Ltd. (Taiwan). The surfactant Span 80 (sorbitan monooleate) was obtained from Wako Pure Chemical Industries Ltd. (Japan). The carriers used were D2EHPA (di(2-ethylhexyl)phosphoric acid), M2EHPA (mono(2-ethylhexyl)phosphoric acid), TBP (tributyl phosphate), and naphthenic acid, and all were obtained from Fluka Chemie AG (Switzerland). Inorganic salts NaCl, KCl, $NaNO_3$, Na_2SO_4, and inorganic acids HCl, HNO_3, H_2SO_4, obtained from Wako Pure Chemical Industries Ltd. (Japan), were used to prepare the necessary internal aqueous phase. All chemicals were used as supplied.

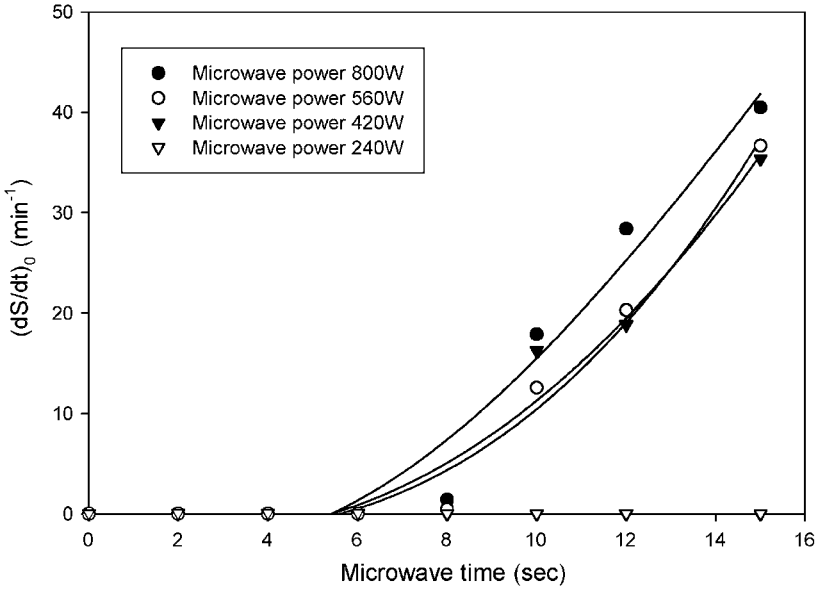

Figure 2. Effect of microwave irradiation power. Emulsion volume = 25 mL, O/A = 1. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 40 wt%, kerosene = 52 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

Water-in-oil emulsion systems were studied throughout all experiments. Liquid membrane emulsions (300 mL), with oil phase-to-aqueous phase volume ratio (O/A) = 0.5–2, were prepared each run by dispersing internal aqueous phase into oil membrane phase with the help of either Waring blender Model CB-6, Dynamics Corporation of America or rotor–stator homogenizer (IKA Ultra-Turrax model T25, Janke & Kunkel GMBH & Co. KG). After emulsification, the freshly made emulsions were allowed to stand for 30 min of relaxation time and then aliquots of the prepared emulsions were sampled for microwave heating experiments and drop size analysis. The prepared emulsions had good stability for several days. Drop sizes were analyzed by particle size analyzer (Model CAPA-300, Horiba Ltd. Japan). A commercial microwave oven (Model NN-7450, 2450Mz, Matsushita Electric Co. Ltd., Taiwan) was used for microwave heating experiments in this work. Four kinds of power output (240, 420, 560, and 800 W) with time control were easily adjustable as the experiment required. Emulsion sample (25 mL) was placed in a 50 mL beaker, which was located in the same position in the microwave oven each time to eliminate heating difference due to standing waves. After microwave irradiation, emulsions were poured into graduated cylinders for settling measurements. The volumes of

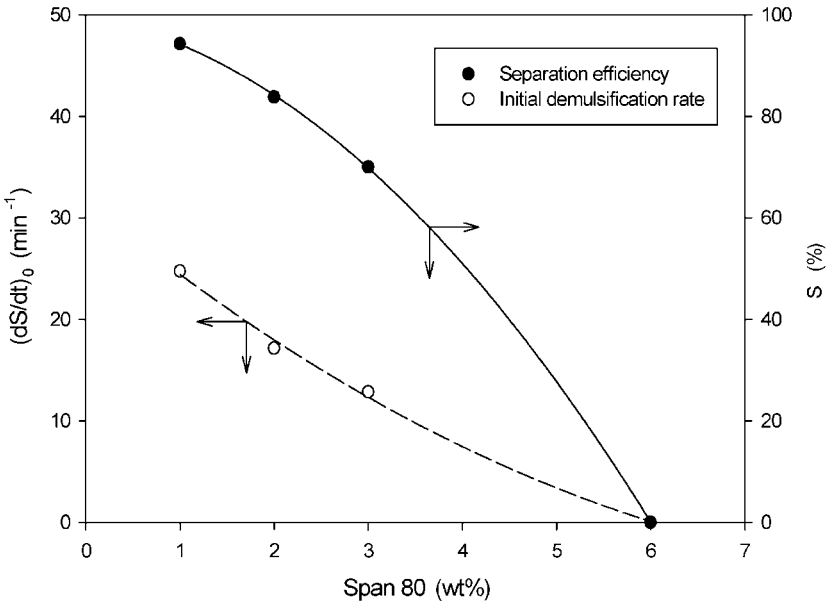

Figure 3. Effect of Span 80. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: D2EHPA = 5 wt%, paraffin oil = 5 wt%, kerosene = 84–89 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

the separated water phase were recorded as settling time. The separation efficiency (S) is defined as follows

$$\text{Separation efficiency, } S = \frac{\text{volume of separated water phase (mL)}}{\text{original volume of water phase in emulsion (mL)}} \times 100\% \quad (1)$$

A typical plot of separation efficiency is shown in Fig. 1. A small amount of sponge emulsions were observed at the interface between the separated oil and aqueous phases under some experimental conditions. This might be accounted for the separation efficiencies less than 100%, as shown in Fig. 1. After least square curve-fitting, the initial demulsification rates were calculated by the initial slope of the curves, i.e.,

$$\text{Initial demulsification rate} = \left(\frac{dS}{dt}\right)\Big|_{t=0} \quad (2)$$

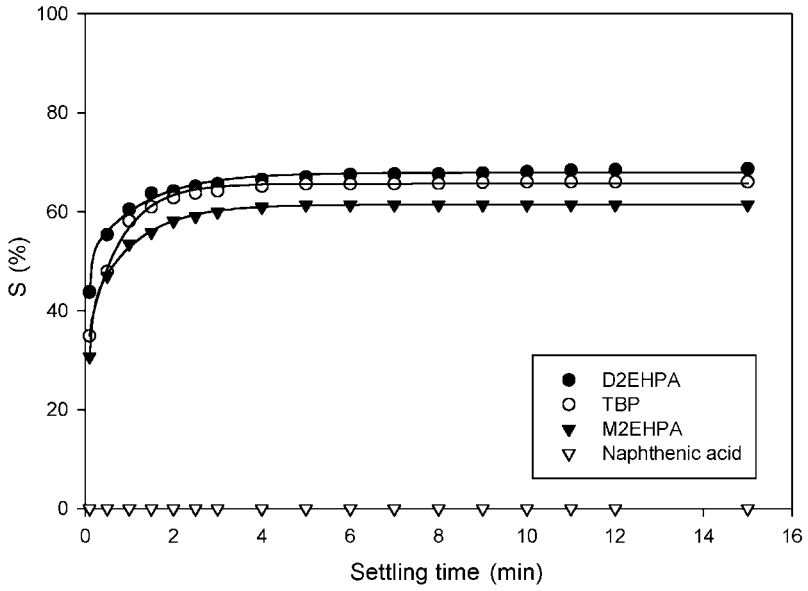

Figure 4. Effect of carriers. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, carrier = 5 wt%, paraffin oil = 5 wt%, kerosene = 87 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

Both limiting separation efficiency (i.e., final separation efficiency achievable) and initial demulsification rate were used to discuss and compare the influences of parameters on the microwave demulsification for each experimental run.

RESULTS AND DISCUSSION

Figure 2 shows the effects of both microwave power output and irradiation time on demulsification. No aqueous phase can be separated with a 240 W power output. Even with power output above 420 W, a critical irradiation time greater than 6 sec is necessary to give significant demulsification rate. Power output greater than 420 W seems unnecessary since its improvement is insignificant. Demulsification rate increases with the irradiation time. However, irradiation time longer than 15 sec suffered from boiling over. Therefore, 420 W and 12 sec were used for all subsequent experimental runs.

Figure 3 gives the concentration effect of Span 80 on demulsification. It shows that both separation efficiency and demulsification rate decrease with the

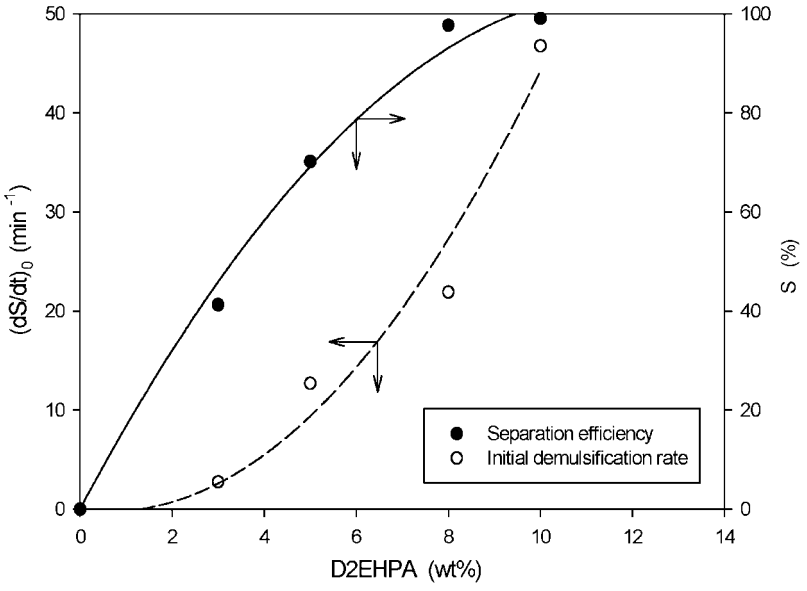

Figure 5. Effect of D2EHPA. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, paraffin oil = 5 wt%, kerosene = 82–92 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

increase in Span 80 concentration. It is also noted that no separation is observed when the amount of Span 80 is above 6 wt%. The reason is obvious since Span 80 increases the oil viscosity, strengthens the interface, hinders the water droplet coalescence, and thus stabilizes the emulsions.

The addition of carrier to oil membrane phase is often necessary for improving the separation rate and selectivity. However, some types of carriers with some kinds of functional groups, such as carboxylic acid or phosphate, were proven to have negative interaction with Span 80, destroying the function of surfactant and resulting in the instability of emulsions. Four types of carriers, i.e., D2EHPA, M2EHPA, TBP, and naphthenic acid, were used for comparison. The results are shown in Fig. 4. It is noted that emulsion with D2EHPA is the most easily broken system while that with naphthenic acid is the most stable system. For further investigation, the concentration effect of D2EHPA is shown in Fig. 5. Surprisingly, without D2EHPA, the emulsion is very stable and no separation is observed. As the concentration of D2EHPA increases, both separation efficiency and demulsification rate increase significantly. When D2EHPA is beyond 8 wt%, 100% of separation efficiency is attained quickly. The interaction effect and high

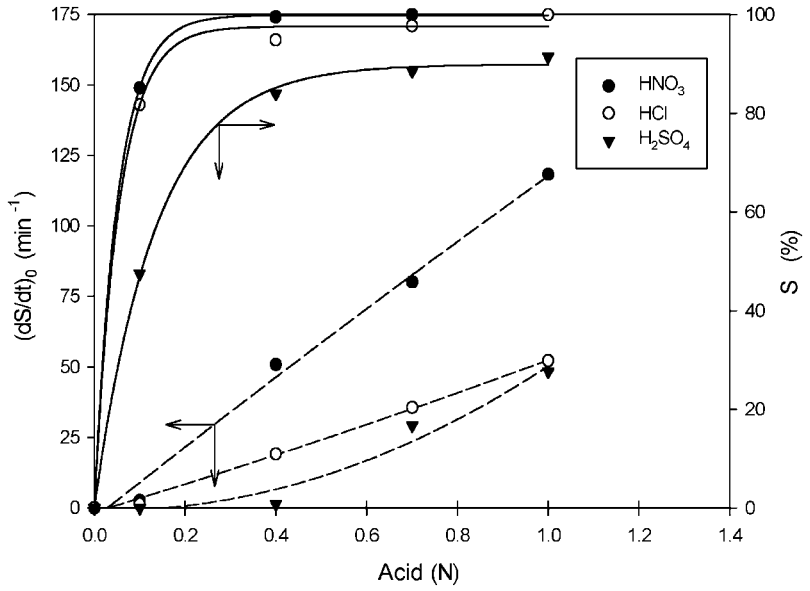

Figure 6. Effect of acids. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 5 wt%, kerosene = 87 wt%. Aqueous phase: acid solution.

microwave absorption power of D2EHPA are considered to be responsible for this phenomenon.

Figure 6 compares the effects of internal aqueous solution with different amounts of acids on the demulsification. It is shown that both separation efficiency and demulsification rate are increasing with the acid concentration. Ionic migration is thought to be responsible for the concentration effect. Among the three kinds of acids, HNO_3 solution caused the emulsion to be broken most easily. For comparison, the effect of internal solution with different amounts of electrolytes is shown in Fig. 7. According to the study of Neas and Collins,[4] the microwave dissipation factor of NaCl solution increases with the electrolyte concentration when its range is below 0.5 *M*. A solution with high dissipation factor gives good microwave absorption capability and thus shows high microwave heating effect. That is why both separation efficiency and demulsification rate increase with the electrolyte concentration in dilute range. However, when the electrolyte is concentrated ($> 0.5\,M$), the dependence is totally different as shown in Fig. 7. The limitation of dipole rotation of water molecules due to "salting effect," especially in the concentrated range, is thought to be responsible for the results.

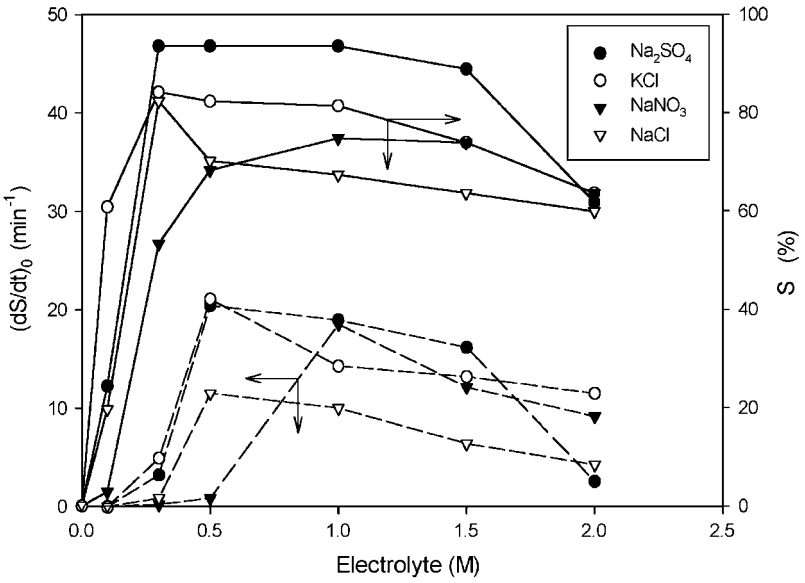

Figure 7. Effect of electrolytes. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 5 wt%, kerosene = 87 wt%. Aqueous phase: electrolyte solution.

Due to the effects of both dipole rotation and ionic conduction, aqueous solution has higher dissipation factor, and thus higher microwave heating effect, than oil membrane solution. It is expected that the relative volume ratio of O/A will significantly influence the demulsification rate and separation efficiency. Figure 8 depicts the results of O/A ratio effect. As expected, both separation efficiency and demulsification rate decrease with the increase in O/A ratio. The influence is greatly significant when the value of O/A ratio is greater than 1.

Three mechanisms, i.e., drop–drop coalescence, sedimentation, and interface coalescence are responsible for the separation of water droplet phase during demulsification. Drop size is the key factor to all these mechanisms and plays an important role in the demulsification rate. The smaller the drop size is the harder the emulsion will be broken. It was found that drop sizes of emulsions prepared by rotor–stator homogenizer were smaller than that prepared by Waring blender. As can be seen in Fig. 9, both separation efficiency and demulsification rate do increase with drop size. For systems with drop size greater than 10 μm, W/O emulsion can be demulsified easily by microwave radiation.

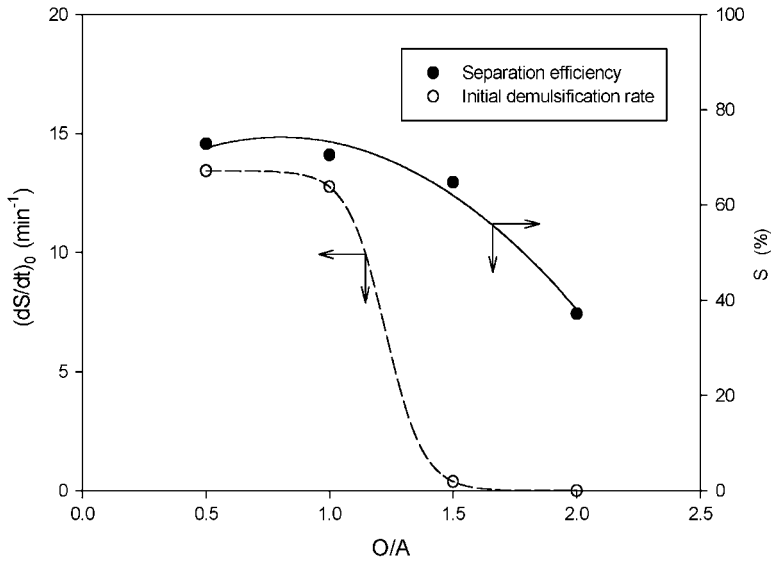

Figure 8. Effect of O/A ratio. Emulsion volume = 25 mL, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 5 wt%, kerosene = 87 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

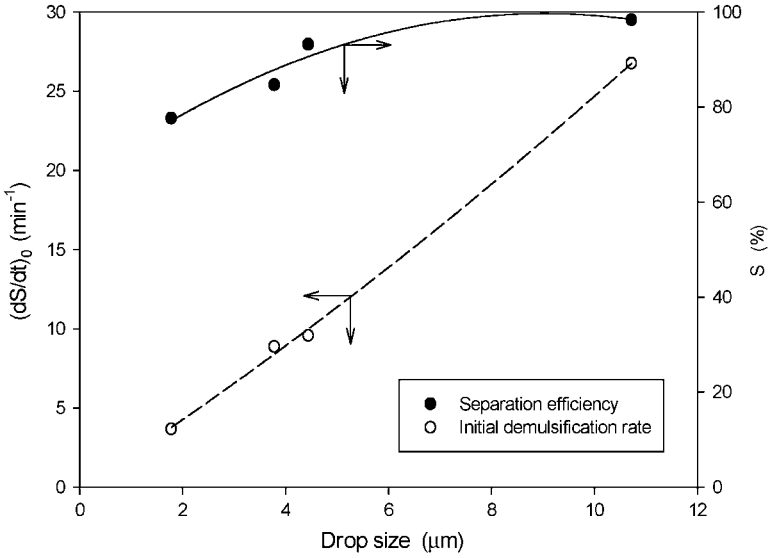

Figure 9. Effect of water droplet size in emulsion. Emulsion volume = 25 mL, O/A = 1, power = 420 W, microwave time = 12 sec. Oil phase: Span 80 = 3 wt%, D2EHPA = 5 wt%, paraffin oil = 5 wt%, kerosene = 87 wt%. Aqueous phase: [NaCl] = 1.0 *M*.

CONCLUSIONS

Microwave radiation is first applied in breaking the liquid membrane emulsions. This kind of tailor-made emulsion is usually considered as a system that is hard to be demulsified by conventional methods. The results of this work show that microwave radiation, a dielectric heating technique with the unique characteristics of fast, volumetric, and selective heating is feasible and has the potential to be used as an alternative way in the demulsification process. This new separation technology does not require chemical addition and high electric voltage. Furthermore, since microwaves can penetrate thick, viscous emulsions, it is more effective in heating viscous liquid membrane emulsions than other methods and is considered to play an important role in the acceleration of demulsification.

ACKNOWLEDGMENT

Financial support for this work from the National Science Council of the Republic of China (Grant No. NSC-82-0402-E035-070) is gratefully acknowledged.

REFERENCES

1. Gu, Z.; Ho, W.S.W.; Li, N.N. Emulsion Liquid Membranes—Design Considerations. In *Membrane Handbook*; Ho, W.S.W., Sirkar, K.K., Eds.; Van Nostrand Reinhold: New York, 1992; Part IX.
2. Fang, C.S.; Chang, B.K.L.; Lai, P.M.C.; Klaila, W.J. Microwave Demulsification. Chem. Eng. Commun. **1988**, *73*, 227–239.
3. Thostenson, E.T.; Chou, T.W. Microwave Processing: Fundamentals and Applications. Composite, Part A **1999**, *30*, 1055–1071.
4. Neas, E.D.; Collins, M.J. Microwave Heating—Theoretical Concepts and Equipment Design. In *Introduction to Microwave Sample Preparation*; Kingstor, H.M., Jassie, L.B., Eds.; American Chemical Society: Washington, 1988; 7–32.
5. Spencer, P.L. US Patent 2,605,383, 1952.
6. Mingos, D.M.P.; Baghurst, D.R. Applications of Microwave Dielectric Heating Effects to Synthetic Problems in Chemistry. Chem. Soc. Rev. **1991**, *20*, 1–47.
7. Strauss, C.R.; Trainor, R.W. Developments in Microwave-Assisted Organic Chemistry. Aust. J. Chem. **1995**, *48*, 1665–1692.
8. Berlan, J. Microwaves in Chemistry: Another Way of Heating Reaction Mixtures. Radiat. Phys. Chem. **1995**, *45* (4), 581–589.
9. Wei, J.B.; Shidaker, T.; Hawley, M.C. Recent Progress in Microwave Processing of Polymers and Composites. TRIP **1996**, *4* (1), 18–24.
10. Xia, D.K.; Pickles, C.A. Applications of Microwave Energy in Extractive Metallurgy: A Review. CIM Bull. **1997**, *90* (1011), 96–107.
11. Jassie, L.; Revesz, R.; Kierstead, T.; Hasty, E.; Matz, S. Microwave-Assisted Solvent Extraction. In *Microwave-Enhanced Chemistry*; Kingston, H.M., Haswell, S.J., Eds.; American Chemical Society: Washington, DC, 1997; 569–609.
12. Kingman, S.W.; Rowson, N.A. Microwave Treatment of Minerals—A Review. Mater. Eng. **1998**, *11* (11), 1081–1087.
13. Haque, K.E. Microwave Energy for Mineral Treatment Processes—A Brief Review. Int. J. Miner. Process. **1999**, *57*, 1–24.
14. Larhed, M.; Hallberg, A. Microwave-Assisted High-Speed Chemistry: A New Technique in Drug Discovery. DDT **2001**, *6* (8), 406–416.
15. Petrowski, G.E. Determination of Emulsion Stability by Microwave Irradiation. J. Am. Oil Chem. Soc. **1974**, 110–111.
16. Klaila, W.J. Method and Apparatus for Controlling Fluency of High Viscosity Hydrocarbon Fluids. US Patent 31,241, 1983.
17. Wolf, N.O. Use of Microwave Radiation in Separating Emulsions and Dispersions of Hydrocarbons and Water. US Patent 4,582,629, 1986.

18. Lai, P.M.C. Demulsification and Activated Carbon Regeneration Using Microwave Radiation. DAI **1990**, *51* (09B), 4482.
19. Fang, C.S.; Lai, P.M.C.; Chang, B.K.L.; Klaila, W.J. Oil Recovery and Waste Reduction by Microwave Radiation. Environ. Prog. **1989**, 235–238.
20. Fang, C.S.; Lai, P.M.C. Temperature Profile of W/O Emulsions Under Microwave Radiation. AIChE Annual Meeting, April 15, 1991.
21. Fang, C.S.; Lai, P.M.C. Microwave Heating and Separation of W/O Emulsions. J. Microw. Power Electromagn. Energy **1995**, *30* (1), 46–57.
22. Barringer, S.A.; Ayappa, K.G.; Davis, E.A.; Davis, H.T.; Gordon, J. Power Absorption During Microwave-Heating of Emulsions and Layered Systems. J. Food Sci. **1995**, *60* (5), 1132–1136.
23. Takahashi, R.; Uchida, H.; Ishihara, M. Treatment of Waste Oils from Ships by Decomposition of Emulsions with Microwave or Ultrasonic Wave Irradiation. Jpn. Kokai Tokyo, Koho JP 08010509 A2, 1996.
24. Fu, D.; Wu, H. Laboratory Tests for Microwave Radiation Demulsification. Zhongguo Jishui Paishui **1998**, *14* (4), 4–6.
25. Anantheswaran, R.C.; Liu, L. Effect of Viscosity and Salt Concentration on Microwave Heating of Model Non-Newtonian Liquid Foods in a Cylindrical Container. J. Microw. Power Electromagn. Energy **1994**, *29* (2), 119–126.
26. Little, R.C.; Patterson, R.L. Breaking Emulsions in Navy Bilge Collection and Treatment Systems. Environ. Sci. Technol. **1978**, *12* (5), 584–590.
27. Battelle Institute B.V. Separation Oil–Water Emulsions by Electrocoagulation May Be Far Cheaper. Chem. Eng. **1989**, 19.
28. Datta, A.K. Heat and Mass Transfer in the Microwave Processing of Food. Chem. Eng. Prog. **1990**, 47–53.
29. Ayappa, K.G.; Davis, H.T.; Grapiste, G.; Davis, E.A.; Gordon, J. Microwave Heating—An Evaluation of Power Formulations. Chem. Eng. Sci. **1991**, *46*, 1005–1016.

Received September 2001
Revised February 2002