The Stability of (W/O)/W Liquid Surfactant Membranes

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The stability of liquid membranes, which is a basic and important subject in (W/O)/W liquid surfactant membrane process, was studied. In general, a lot of dispersed droplets with a diameter of around 2×10^{-6} m exist in the stable emulsion. The effects of various factors on the dispersed droplet sizes in (W/O) emulsion were investigated, and the conditions for forming such a stable emulsion were determined. The fraction of liquid membrane breakage, which represents the degree of the stability of liquid surfactant membranes, was measured by using hydrochloric acid as a tracer, and the effects of various factors on the stability were clarified.

1. Introduction

The separation technique using liquid membranes has been noted as an energy-efficient and very selective separation method. In the practical application of this technique, the use of liquid surfactant membranes is promising because of their large specific contact area. The key point of such a separation process is to maintain stable liquid surfactant membranes during the permeation of solute through the membranes. Therefore, it is important first of all how to make the stable liquid surfactant membranes. The stability of liquid membranes is influenced by various factors such as the kind of surfactant and its concentration, volume ratio of each phase forming liquid surfactant membranes, and emulsifying time, etc., and hence in the practical separation and concentration process, suitable operational conditions should be selected. However, there have been a few studies on the stability of liquid surfactant membranes[1, 3−6] and most of them are fragmentary, so researches in more detail are desired.

In this work, in order to study the stability of (W/O)/W liquid surfactant membranes, the dispersed droplet sizes of inner water phase, which are of importance for the estimation of contact area and the stability of (W/O) emulsion, were measured. The effects of emulsifying time, rotational speed of emulsification and surfactant concentration on the droplet sizes were examined. Furthermore, (W/O)/W liquid surfactant membranes were formed by dispersing the generated (W/O) emulsion into an outer water phase, and then the stability of liquid membranes was experimentally investigated by measuring a fraction of liquid membrane breakage, which represents the stability of three phase emulsion, and the droplet sizes of inner water phase.

2. Experimental Apparatus and Procedure

An oil phase O(II) was prepared by dissolving a non-ionic surfactant, Span (sorbitan fatty acid ester), in xylene and a xylene solution containing liquid paraffin or polybutadiene as a membrane-strengthening agent. A deionized water and hydrochloric acid solution of 1 kmol/m³, respectively, saturated with xylene were used as an inner water

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phase W(I).

A (W(I)/O(II)) emulsion was produced by agitating W(I) of $6 \times 10^{-5} \, m^3$ and O(II) of the same volume by the homogenizer with emulsifying head (Silverson Machines Ltd., England) in the glass vessel of $2 \times 10^{-4} \, m^3$. A rotational speed of the homogenizer was measured with the photo-tachometer. Taking only a small amount of the formed emulsion, photographs (magnifying power: 154-fold) were taken by using the microscope with phase contrast device. The film was projected on a screen of the projector with scale (magnifying power: 10-fold), and one hundred dispersed droplet sizes in the emulsion, that is, those of W(I) were measured.

Next, (W(I)/O(II))/W(III) liquid surfactant membranes were formed by dispersing $1 \times 10^{-4} \, m^3$ of the (W(I)/O(II)) emulsion into the deionized water W(III) of $7 \times 10^{-4} \, m^3$ in the glass agitation vessel (inner diameter: 0.1 m) with four buffle plates. The turbine impeller with six flat-blades of $5.4 \times 10^{-2} \, m$ fitted at the near center of liquid depth were driven by the stirrer with rotational meter in the vessel. A precision of the meter was checked with the photo-tachometer. About $2 \times 10^{-5} \, m^3$ of samples were taken with a pipette cutted the tip at regular intervals to analyze the hydrochloric acid concentration of W(III), and the fraction ϵ of liquid membrane breakage was evaluated by the following equation.

$$\epsilon = (1 - \phi') \, C_{III}/\phi \, \phi' \, (C_{Ii} - C_{III})$$

where C_{Ii} is the initial concentration of hydrochloric acid in W(I) and C_{III} the hydrochloric acid concentration in W(III). Furthermore, ϕ and ϕ' are the volume fraction of W(I) in (W(I)/O(II)) emulsion and that of (W(I)/O(II)) emulsion in (W(I)/O(II))/W(III) emulsion, respectively. In this case, neglecting the occlusion of the outer water phase W(III) into the membrane and the permeation of hydrochloric acid from W(I) to W(III) phase, the transfer of hydrochloric acid into W(III) was assumed to be attributed to the leakage of W(I) to W(III) only by the breakdown of liquid membranes.

After the operation was stopped, taking only a small amount of (W(I)/O(II)) emulsion separated upward in the vessel, droplet sizes of W(I) were measured by the above method.

The experiments were performed at 303 K by circulating water of a constant temperature.

3.   Experimental Results and Discussion

3.1.   Dispersed droplet sizes in (W/O) emulsion

(1) Effect of Emulsifying Time

A variation with the emulsifying time t_E in the dispersed droplet size distribution in the (W/O) emulsion generated at the volume fraction of inner water phase of $\phi = 0.5$ and the rotational speed of emulsification of $N_E = 67 \, s^{-1}$ is shown in Fig. 1. In this case, W(I) is the deionized water and O(II) is the xylene solution containing 4 vol% Span 80. The distribution becomes narrow and shifts to small droplet size as t_E increases, but its variation is only a little beyond $t_E = 600 \, s$.
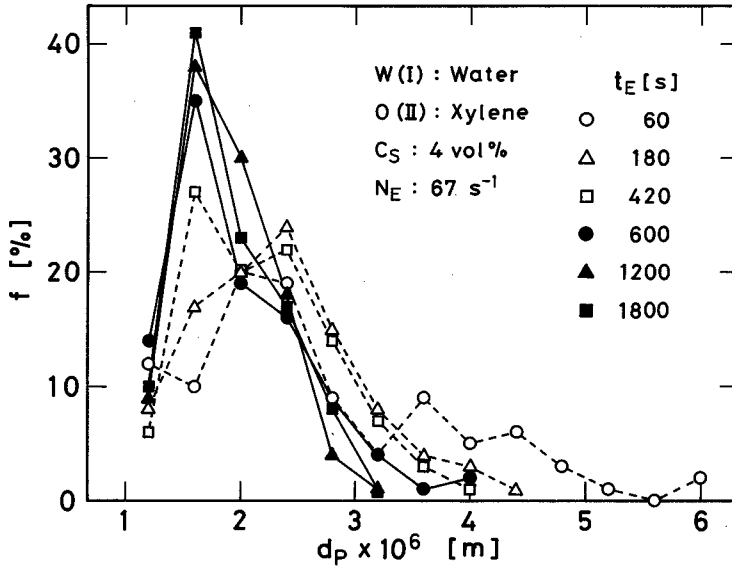
Fig. 1   Effect of emulsifying time t_E on the dispersed droplet size distribution.
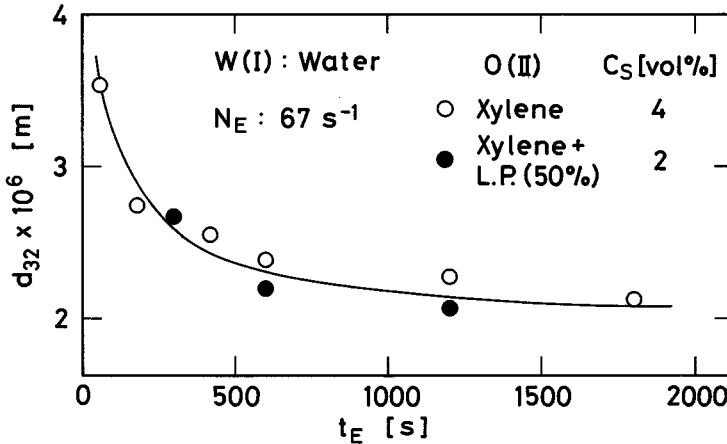

Fig. 2   Effect of emulsifying time t_E on d_{32}.

In Fig. 2, the Sauter mean diameter d_{32} obtained from one hundred droplet sizes in Fig. 1 is plotted against t_E. Although d_{32} gradually becomes small up to $t_E = 600$ s, it varies slightly in the region of t_E longer than 600 s. Thus, the variation of d_{32} with t_E shows a similar tendency to that of the droplet size distribution. The results for a 50 vol% liquid paraffin-xylene solution containing 2 vol% Span 80 which was used as O(II) are also shown in Fig. 2, and the variation of d_{32} with t_E is similar to that for xylene alone.

It is generally said that a lot of dispersed droplets with a diameter of around 2×10^{-6} m exist in the stable emulsion[2]. In the present results, d_{32} is $2.4 \sim 2.0 \times 10^{-6}$ m beyond 600 s and thus the stable emulsions are generated.

(2) Effect of Rotational Speed of Emulsification

The droplet sizes in the emulsions generated by varying N_E from 33 to 133 s^{-1} at $t_E = 600$ s were measured to examine the effect of N_E on the dispersed droplet sizes. The relations between d_{32} and N_E are shown in Fig. 3. It was found that d_{32} decreases slightly with N_E above $N_E = 67$ s^{-1} and is a value of around 2×10^{-6} m, but it increases rapidly below 50 s^{-1}.

(3) Effect of Surfactant Concentration

It is necessary to determine an optimum concentration of surfactant from the standpoints of the permeation rate through the liquid membrane, the stability of liquid membranes and the demulsification of emulsion. In this experiment, the effect of Span 80 concentration C_S on the dispersed droplet sizes was investigated. Fig. 4 shows the
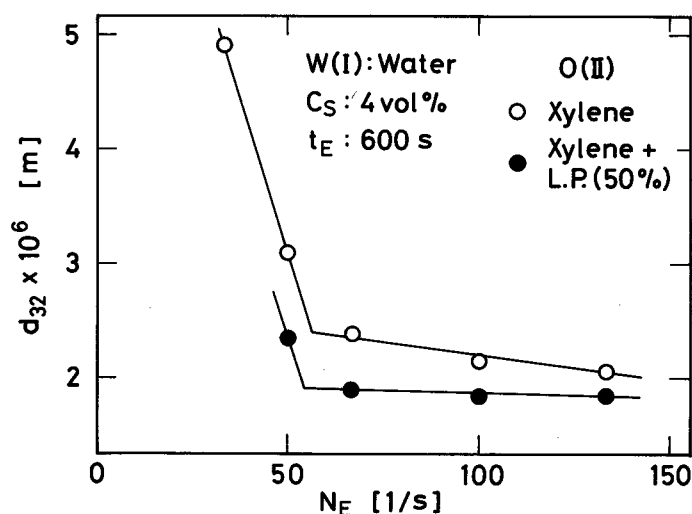

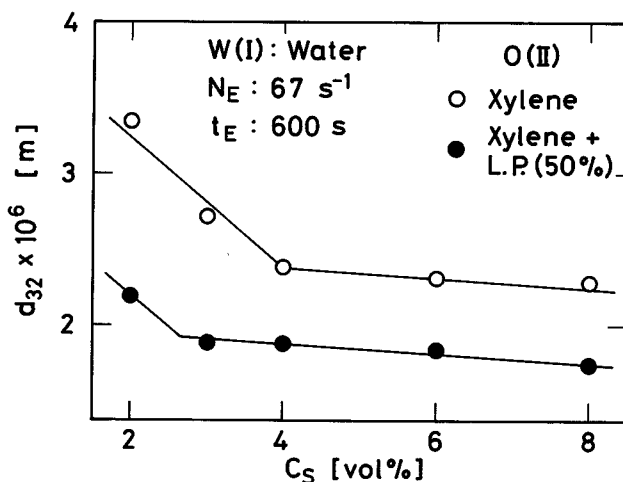Fig. 3   Effect of rotational speed N_E of emulsification on d_{32}.

Fig. 4   Effect of Span 80 concentration C_S on d_{32}.

plot of d_{32} against C_S. The value of d_{32} decreases with increasing C_S, though the variation is slight above 4 vol%. The values of d_{32} for the xylene solution containing 50 vol% liquid paraffin are smaller than those for xylene alone.

It became clear from the above results that in the present experimental conditions, the stable (W/O) emulsion having the dispersed droplets with a diameter of around 2×10^{-6} m is formed under the following conditions; $C_S \geqslant 4$ vol%, $N_E \geqslant 67$ s^{-1}, and $t_E \geqslant 600$ s.

3.2. Stability of (W/O)/W emulsion

(W(I)/O(II))/W(III) liquid surfactant membranes were formed by dispersing two phase emulsion prepared at $t_E = 600$ s and $N_E = 67$ s^{-1} into W(III), and then the fraction ϵ of liquid membrane breakage was measured as a function of time.

(1) Effect of HLB Value of Surfactant

It is reported that a surfactant with a particular HLB value must be used to obtain the satisfying emulsified state[2]. The effect of HLB value on the stability of liquid membranes was investigated using four kinds of Span as the surfactant. The results are shown in Fig. 5. The values of ϵ increase with the operational time t but are fairly small values except those for Span 20 (HLB = 8.6). The viscosity of two phase emulsion may be considered to influence the stability. The values of viscosity η' measured with the rotary viscometer (the generated emulsions show the pseudoplastic behavior except for Span 40) are represented in the figure. The value of η' for Span 20 is similar to that for Span 80, so the difference in ϵ between both the surfactants may depend on the effect of HLB value. It is therefore considered that the stable liquid membranes are formed in the HLB range of 4.3 to 6.7. In most of the studies on (W/O)/W liquid surfactant membranes which have been reported to date, Span 80 has been used as the surfactant. However, the results presented in Fig. 5 show that the stabilities for Span 60 and 40 are slightly better than that for Span 80.
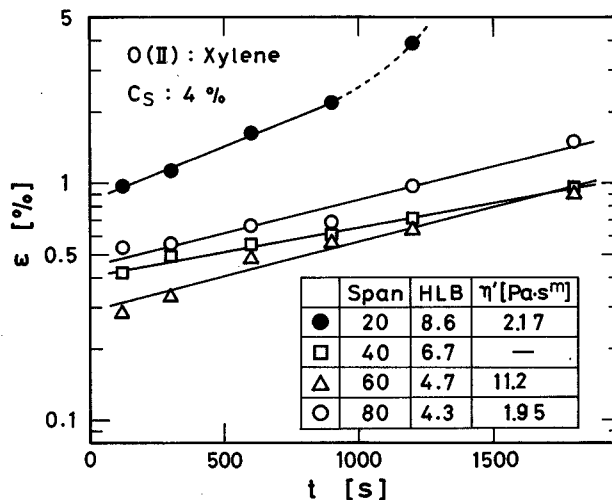

Span	HLB	η'[Pa·s^m]
● 20	8.6	2.17
□ 40	6.7	—
△ 60	4.7	11.2
○ 80	4.3	1.95

Fig. 5   Effect of HLB value of surfactant on ϵ.

(2) Effect of Surfactant Concentration

The effect of Span 80 concentration on the stability of liquid membranes is shown in Fig. 6. The liquid membranes are fairly unstable in the case of $C_S = 2$ vol%, but above 4 vol%, the difference in ϵ is slight and the values of ϵ at $t = 1800$ s are lower than 1.5%, thus the stable liquid membranes are formed. Fujinawa et al. indicated that for stabilization of the membranes, there is a critical value n_{cr} for the number n of the surfactant molecular layer adsorbed at the oil-water interface and if $n > n_{cr}$, ϵ is approximately independent of C_S[1]. In this experimental system, the value of n calculated by their method for the case of 2 vol% in which the stability is especially bad is about 1.5, corresponding to the value of n_{cr} obtained from their results. The stabilization of liquid membranes in Span 80 concentration greater than 4 vol% also seems to relate to the formation of the stable (W(I)/O(II)) emulsion, because the value of d_{32} of W(I) droplets for $C_S = 4$ vol% is 2.4×10^{-6} m. In the case of 4 vol%, d_{32} of W(I) droplets measured after (W(I)/O(II))/W(III) liquid surfactant membrane operation is 2.6×10^{-6} m and becomes slightly larger than that before the operation mentioned above. As shown in the figure, the value of η' increases with increasing C_S and this increase in viscosity of (W(I)/O(II)) emulsion contributes to the stabilization.

The value of ϵ was similarly measured by varying C_S from 1 to 4 wt% for Span 60. The results show that the stability of liquid membranes increases with increasing Span 60 concentration. In the case of 2% Span 60, ϵ at $t = 1800$ s is 1.8% and thus the stability is pretty good compared to the case of 2% Span 80 represented in Fig. 6.

(3) Effect of Membrane-Strengthening Agent

A membrane-strengthening agent has been frequently added to the membrane phase to stabilize the liquid membranes. In this experiment, using liquid paraffin (L.P.) and
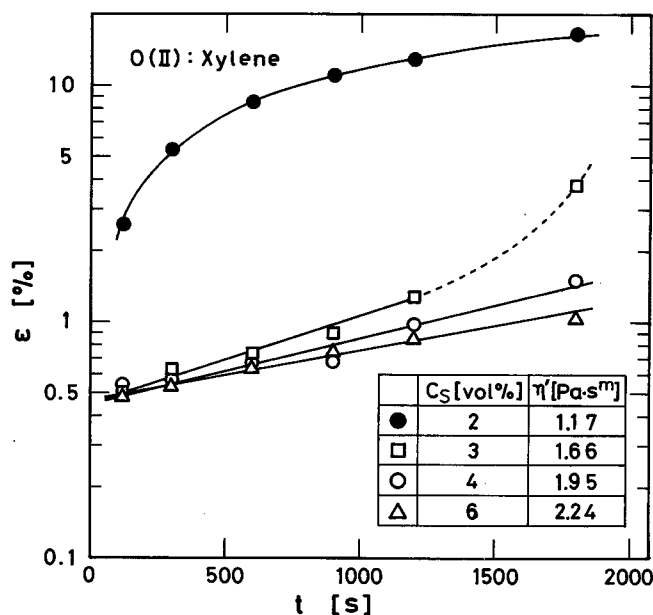

C_S [vol%]	η' [Pa·s^m]
● 2	1.17
□ 3	1.66
○ 4	1.95
△ 6	2.24

Fig. 6   Effect of Span 80 concentration C_S on ϵ.

polybutadiene (P.B.) as the membrane-strengthening agent, their effects on the stability were investigated.

Fig. 7 shows the results of ϵ vs t in the case that Span 80 was used as the surfactant and P.B. was added to xylene. It was found that the stability highly increases when P.B. is added to the unstable system such as C_S = 2 vol%, but the effect in the addition of P.B. is a little in the originally, relatively stable system such as 4 vol%. The similar results were obtained in the cases of using Span 60 and L.P.. This improvement in the stability by the addition of the membrane-strengthening agent may be considered to be due to the increase of viscosity of (W(I)/O(II)) emulsion.
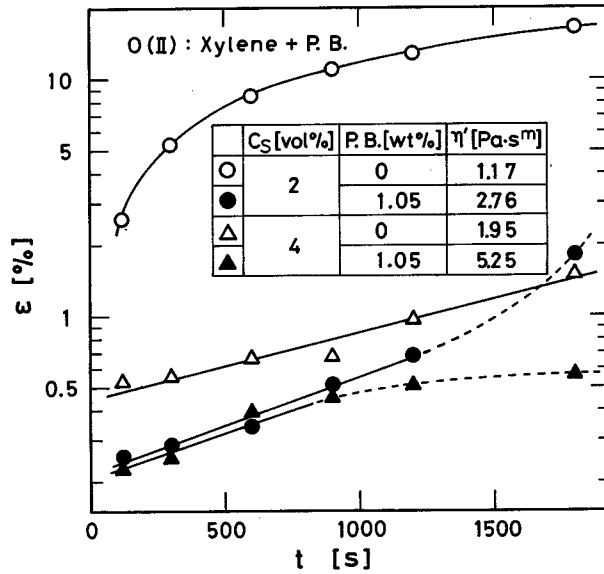

Fig. 7　Effect of the addition of polybutadiene on ϵ.

(4) Effect of Volume Ratio

The effect of volume ratio, namely volume fraction ϕ of the dispersed phase in (W(I)/O(II)) emulsion on the stability was investigated. The results for Span 60 are shown in Fig. 8. In the case of C_S = 1 wt%, ϵ decreases with decreasing ϕ and increases linearly with time. The slopes r_B of these straight lines are plotted against ϕ in Fig. 9 and it shows that r_B is nearly proportional to 0.6 power of ϕ. As shown in Fig. 8, the liquid membranes are stabilized though η' decreases extremely as ϕ decreases. This may be due to the reasons that n becomes greater than n_{cr} (= 1.5) when ϕ is less than 0.33 and the oil membrane encapsulating the dispersed droplets thickens with a decrease of ϕ. In the case of 4 wt%, however, the stabilizing effect by the decrease of ϕ may be counteracted by the unstabilization by the decrease of viscosity.

(5) Effect of Stirring Speed

Fig. 10 shows the effect of stirring speed N on ϵ. The value of ϵ varies linearly with time. The breakage of liquid membranes proceeds fast in the cases of Span 80 and 60, respectively, as N increases.
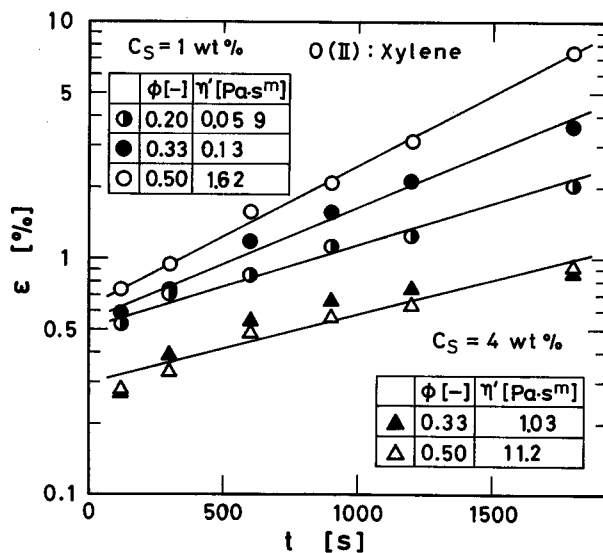
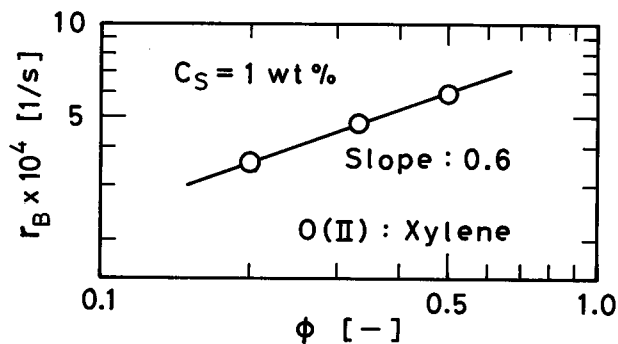Fig. 8　Effect of volume fraction ϕ of W(I) in (W(I)/O(II)) emulsion on ϵ.
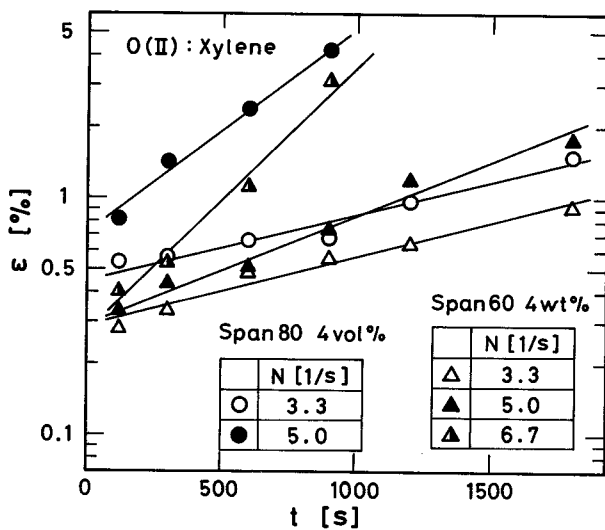
Fig. 9

Relation between r_B and ϕ.
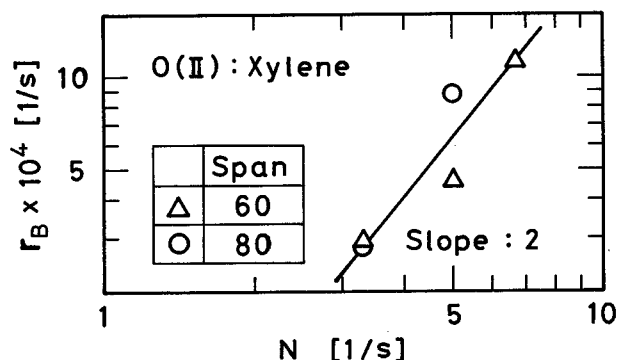
Fig. 10

Effect of stirring speed N on ϵ.

Fig. 11
Relation between r_B and N.

A relation between r_B obtained from Fig. 10 and N is shown in Fig. 11. The value of r_B is nearly proportional to the second power of N and thus the stability of liquid membranes was found to be remarkably affected by the stirring speed. Furthermore, it should be noticed that the dispersed drops of (W(I)/O(II)) emulsion in W(III) deform from sphere and then the tendency to occur large flocs with the progress of flocculation appears early as the stirring speed increases.

4. Conclusion

The dispersed droplet sizes in (W(I)/O(II)) emulsion were measured by the photographic method utilized the microscope to investigate experimentally the stability of (W(I)/O(II))/W(III) liquid surfactant membranes. Furthermore, the variation of the fraction of liquid membrane breakage with time and the droplet sizes of W(I) in the liquid surfactant membranes were measured.

In the present experimental conditions, it became clear that the stable (W(I)/O(II)) emulsions which have the dispersed droplets with a mean diameter of around 2×10^{-6} m are generated under the following conditions; $C_S \geqslant 4$ vol%, $N_E \geqslant 67$ s^{-1}, and $t_E \geqslant 600$ s.

The stable liquid surfactant membranes are formed when the surfactant, Span, with HLB value from 4.3 to 6.7 is used at the concentration of 4%. The addition of the membrane-strengthening agent is very useful to stabilize the unstable system, but the effect of the addition is a little in the relatively stable system. The stability of liquid membranes is remarkably affected by the stirring speed. It was found that the more stable liquid membranes are formed when Span 60 rather than Span 80 was used as the surfactant under the present experimental conditions.

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