

# Water/Oil Emulsions Prepared by the Membrane Emulsification Method and Their Stability

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## ABSTRACT

We developed and tested a simple method to measure dispersed droplet size of W/O emulsions. Then, using a microporous glass membrane treated with oil phase, we produced a W/O emulsion with high water content (40% w/w) at a high emulsification rate by the membrane emulsification method, and assessed its stability. In comparison with emulsions by the stirring methods, variations in dispersed droplet size and viscosity of emulsions by membrane method were small and the emulsions were more stable. Droplet size was not related to the stability of the W/O emulsion prepared by membrane emulsification.

**Key Words:** membrane, water/oil, emulsion, stability, microporous membrane

## INTRODUCTION

CONVENTIONAL METHODS TO PREPARE EMULSIONS RELY ON STIRring equipment, colloid mills, homogenizers, ultrasonics or microfluidizers (Sherman, 1971). However, such methods utilize a strong shearing stress which results in coalescence of the dispersed phase. For emulsions prepared this way, the uniformity of dispersed droplets is not consistent, and it is not possible to directly control droplet size. The dispersed droplet size and distribution affects many of physicochemical properties of the emulsion. In addition, because W/O food products such as margarine contain flavoring components in the dispersed phase, droplet size affects the flavor of such products. Also, it has a great effect on growth of bacteria. When the dispersed droplet diameter is large, bacteria multiply readily; when the dispersed droplet diameter is small, bacterial growth is suppressed due to lack of nutrients in the interior of droplets (Bullock et al., 1969).

Emulsification (Katoh et al., 1996), using a microporous membrane with uniform pore diameter, can produce an emulsion with high uniformity in droplet size and dispersion. Besides being able to control the size of dispersed droplets, there is no strong shear stress during emulsification.

Katoh et al. (1997a) reported the preparation of W/O food products using the membrane emulsification method, but the rate of emulsification was too slow for practical use. Test samples were limited to a dispersed phase concentration of only 10% (w/w). In such emulsion, when the dispersed phase concentration is high phase inversion is promoted. Also, at high concentrations, when the shear stress is great during emulsification phase inversion is readily promoted.

In a membrane emulsification system (Fig. 1), the dispersed phase is permeated under pressure through a microporous membrane with uniform pore diameter, and droplets are uniformly dispersed into the continuous phase. If the membrane surface is wetted by the dispersed

phase, droplet size cannot be controlled. Therefore, an O/W emulsion can best be prepared using a hydrophilic membrane and a W/O emulsion is prepared using a hydrophobic membrane. The Shirasu porous glass membrane "SPG" (Nakashima et al., 1987) is the most suitable microporous membrane available for such an emulsification system.

With a membrane emulsification system, a uniform emulsion can be prepared. By selecting the membrane pore diameter, the size of the dispersed droplet can be controlled. Because it is a "Static Emulsification Method" (Nakashima, 1993), it does not involve the high shear stress of a homogenizer, and even with a highly concentrated dispersed phase, a stable emulsion can be prepared. The apparatus is comparatively simple and is suitable for large or small volumes.

Our objective was to develop a simple method for measurement of droplet size in relation to the quality of W/O food product emulsions. In addition, we prepared high-water-content W/O food emulsions using the membrane emulsification method at a practical rate, to determine whether it was possible to control dispersed droplet size under specified conditions, and we determined the stability of such emulsions.

## MATERIALS & METHODS

WATER PREPARED USING A RO (REVERSE OSMOSIS) MEMBRANE (Osmonics Company, RO apparatus OSMO-43 CHF-SR 12 K/DLX) followed by ion exchange treatment (Organo Co. Ltd., Pure Water Cartridge G70); corn oil (Taiyo Yushi Co. Ltd.), polyglycerin polyricinolate (PGPR, Sakamoto Pharmaceuticals Co. Ltd., SY "Glyster" CR-310) as an emulsifier were used.

### Membrane emulsification apparatus

The membrane emulsification apparatus (Fig. 2) was the same as that used by Katoh et al. (1996), i.e. a Continuous Phase Circulating System microporous glass membrane tube (Kiyomoto Iron and Machinery Works Co., Ltd.). The continuous phase circulated through the interior and the dispersed phase was forced under pressure from the outside. The circulating pump for continuous phase was a fixed volume pump (Bidell Co. Ltd., VLN-10D-2). The air to pressurize the disperse phase was provided by a compressor (Hitachi Manufacturing Plant Co. Ltd., POD-5.5UTB).

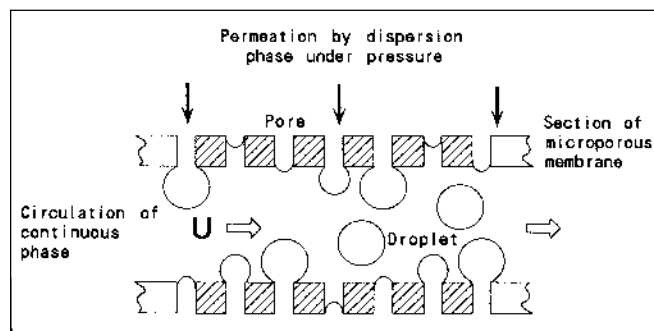


Fig. 1—Schematic of emulsion formation.

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## Preparation of Emulsions by Membrane . . .

Normally, to prepare a monodispersed W/O emulsion of controlled dispersed droplet size, it would be necessary to use a hydrophobic membrane (Nakashima et al., 1991). However, with a hydrophobic membrane, the flux rate is minimal (Katoh et al., 1997a) making it impractical. It has been reported that a simple hydrophobic membrane, made by soaking a hydrophilic membrane (SPG) in the continuous phase (oil phase) and treating it by ultrasonification would increase the flux rate, and a W/O emulsion of controlled dispersed droplet size could be produced (Katoh et al., 1997b). Usually, to make this membrane hydrophobic, silanol on the glass surface would be treated with silane coupler. However, in our research, the emulsifier was adsorbed to the silanol on the glass surface. Fat adsorbed to the hydrophobic base creating a simple hydrophobic membrane. For this reason, SPG (Ise Chemical Industries Co., Ltd., MPG) was treated in the same way with the oil phase to produce the simple hydrophobic membrane we used.

### Preparation of emulsions

The continuous phase (oil phase) consisted of oil and emulsifier, the dispersed phase (water phase) consisted of water and salt (NaCl). As reported by Kato et al. (1997b), in a study in which the monodispersion of emulsions was prepared at emulsifier concentrations in the range of 2 to 10% (w/w), a monodispersed emulsion was achieved when the emulsifier concentration was >5% (w/w). To conserve flavor, it would be desirable to use an emulsifier concentration that is as low as possible. In all tests, the emulsifier concentration was 5% (w/w). In the dispersed phase, to achieve a monodispersion, a solution of sodium chloride 3% (w/w) was used (Katoh et al., 1997a).

With respect to line velocity, i.e. continuous phase circulation, of the continuous phase through the microporous glass membrane tube, the minimum velocity (0.4 m/s) for monodispersion was used, and a dispersed phase concentration of up to 40% (w/w) was achieved. The

difference between the pressure of the dispersed phase when forced into the continuous phase and pressure of the continuous phase circulation was the emulsification pressure, and the dispersed phase flux was the emulsification velocity. The flux of the dispersed phase was established as  $60 \text{ kg (m}^2 \cdot \text{h)}^{-1}$  to prepare the emulsion, and the emulsification temperature was room temperature ( $\approx 23^\circ\text{C}$ ).

### Preparation of emulsion by the stirring method

A small stirring motor (Iuchi Seieido Ltd., NK-1 35) with a 12 cm stirring rod was used. The emulsification container was stainless steel with internal diameter 15 cm and height 17.5 cm. The emulsification temperature was room temperature ( $\approx 23^\circ\text{C}$ ).

### Measurement of the viscosity and pore size

For measurement of viscosity, a B model viscosity meter (Tokimec Co. Ltd.) was used with a No. 2 rotor at 60 rpm and room temperature. A test sample was stored at room temperature.

Average pore size ( $D_m$ ) was measured using a Mercury Porosimeter (Shimadzu Corp., PC9300).

### Measurement with an image analyzer

For measurement of sample droplet size and distribution, an image analyzer (Nikon Co. Ltd., COSMOZONE R500) and appropriate software (Nireco Corp., LUZEX F) were used. Measurement of the W/O emulsion was done at room temperature. For measurement, a  $20\times$  objective lens was used and an objective micrometer was used to calibrate length. Digitization was based on gray level and the diameter was estimated based on the equivalent circular diameter. For measurement, using six views per test, from the average volume of thousands of dispersed droplets, the average droplet size was estimated. For picture preparation, a color video printer (Sony Co. Ltd., UP-1850) and CCD color video camera (Sony Co. Ltd., DXC930) were used.

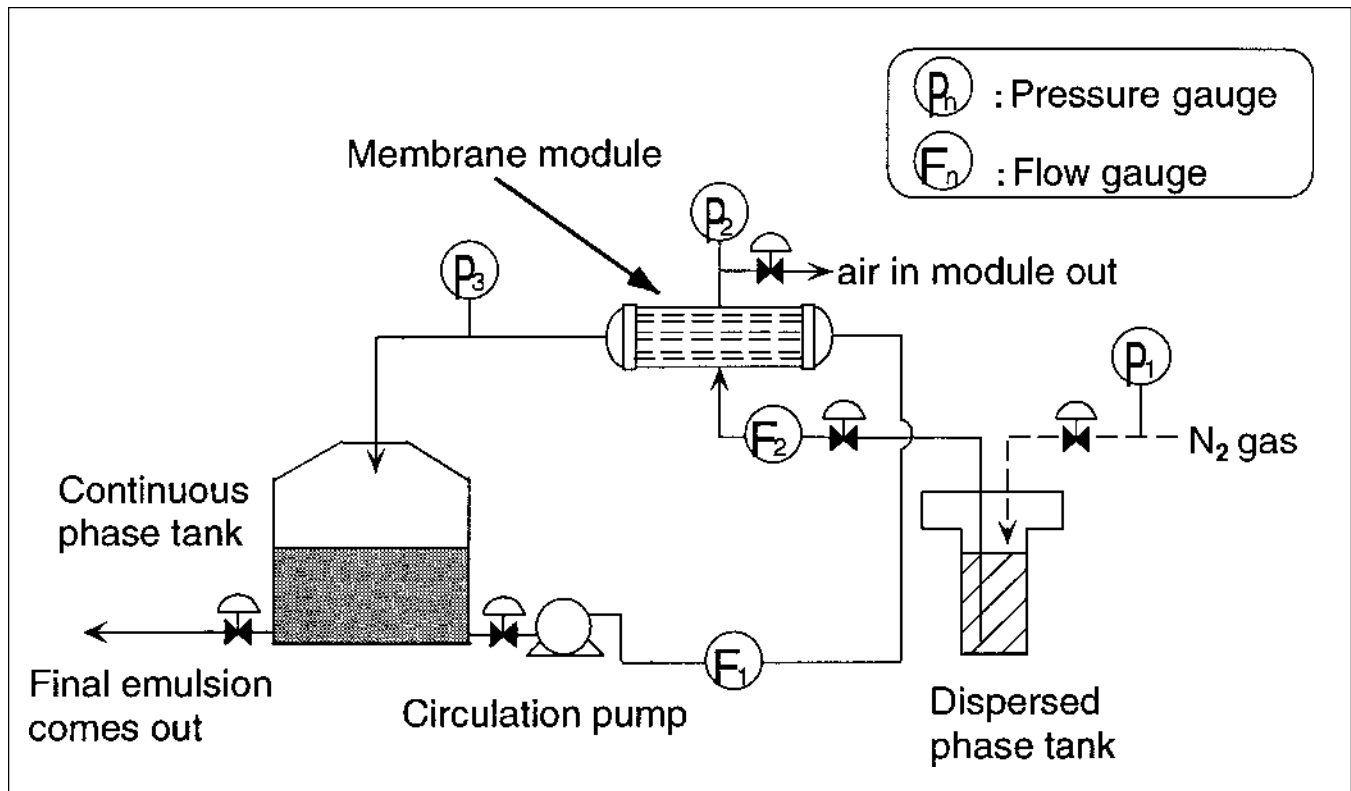


Fig. 2—Membrane emulsification apparatus.

### Index for evaluation of emulsion stability

From the results of average dispersed droplet diameter ( $D_p$ ) and viscosity ( $\eta$ ) measurement, the W/O emulsion stability index was determined. A larger numerical value indicates an unstable emulsion:

$$\text{Change in } D_p(\%) = \{[(D_p \text{ on day 7 after emulsification}) - (D_p \text{ on day of emulsification})] / (D_p \text{ on day of emulsification})\} \times 100$$

$$\text{Change in } \eta(\%) = \{[(\eta \text{ on day of emulsification}) - (\eta \text{ on day 7 after emulsification})] / (\eta \text{ on day of emulsification})\} \times 100$$

### RESULTS & DISCUSSION

WHEN W/O EMULSIONS ARE OBSERVED DIRECTLY UNDER A MICROSCOPE, high dispersed droplet density, the mass of the droplet etc., make it not possible to measure the diameter of dispersed droplets.

Therefore, a sample diluted with corn oil was used for observation. Next, the effect of the cover glass on the shape of the dispersed droplets was examined (Fig. 3). When a cover glass was used on the sample, a large number of dispersed droplets were compressed by the glass (Fig. 3a) and they appeared to collapse. The use of a cover glass for microscopic observation of W/O emulsions was not suitable. It was possible to view the sample using a microscope without the use of a cover glass (Fig. 3b). However, some collapsing of dispersed droplets was observed when the dispersion was diluted using only corn oil.

In order to stabilize the dispersed droplets, a hydrophobic emulsifier was added to the dispersion oil at 1.0% (w/w) or 3.0% (w/w). In the sample with 1.0% (w/w) emulsifier (Fig. 4b), a few collapsed dispersed droplets were detected, however, in the sample with 3.0% (w/w) added (Fig. 4b), no collapsed droplets were observed. In addition,

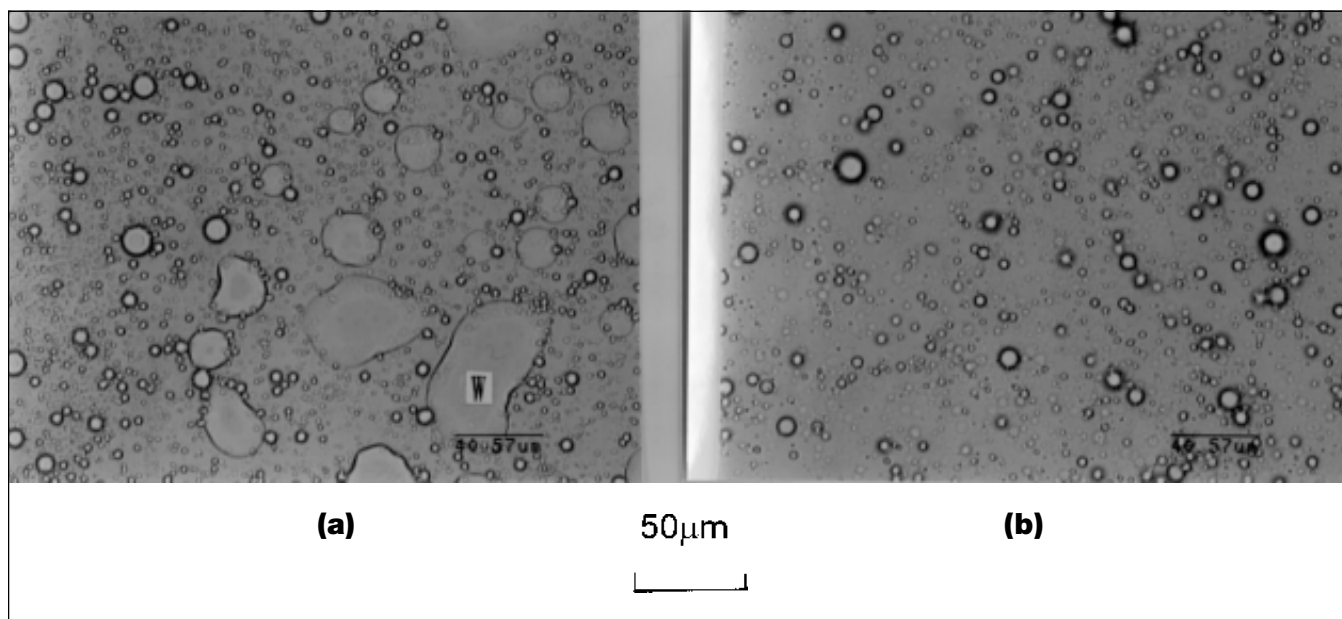


Fig. 3—Micrographs of W/O emulsions: (a) using cover glass; (b) without cover glass; W=collapsed droplet. (50 μm)

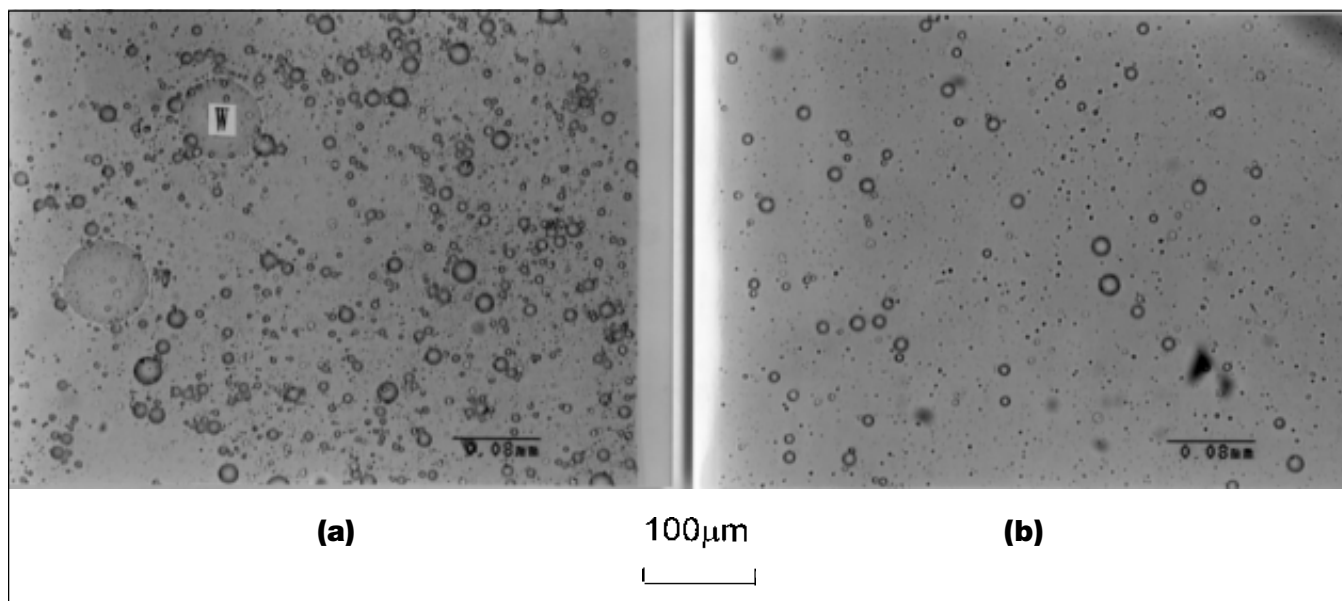


Fig. 4—Micrographs of W/O emulsions: (a) using corn oil with 1% (w/w) emulsifier; (b) using corn oil with 3% (w/w) emulsifier; W=collapsed droplet. (100 μm)

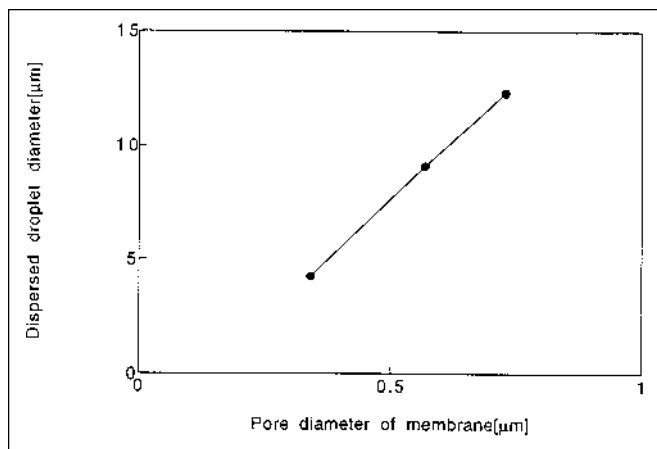


Fig. 5—Relationship between pore diameter of membrane and dispersed droplet diameter.

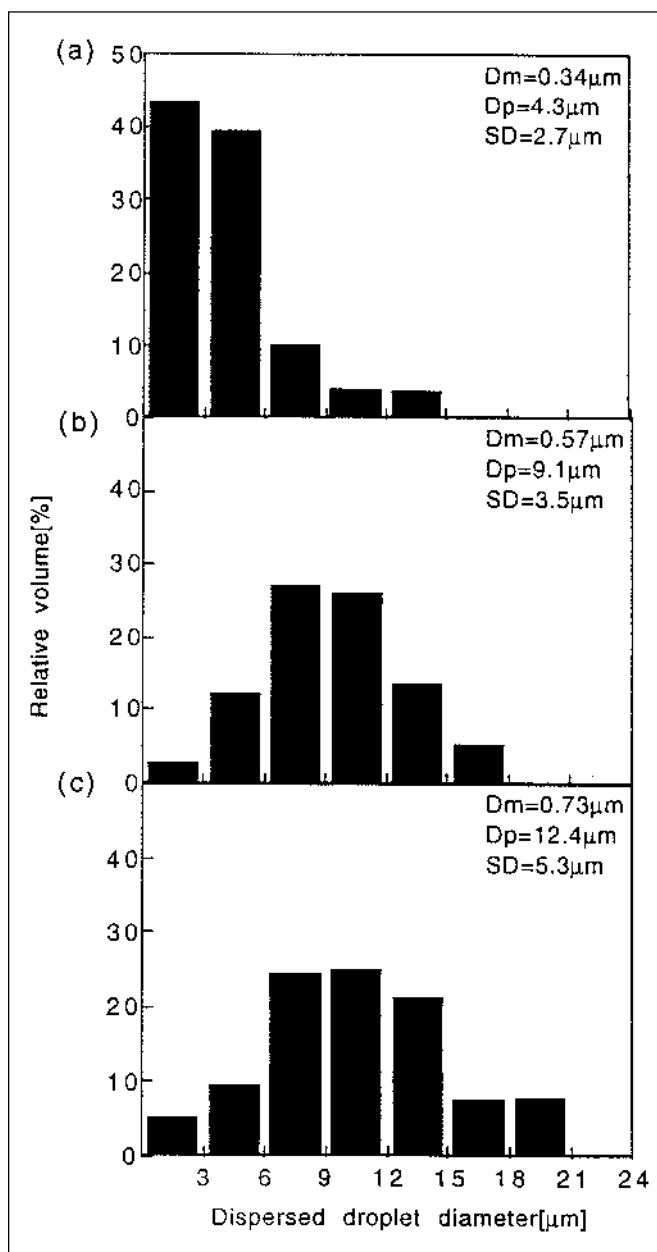


Fig. 6—Droplet size distribution of W/O emulsions prepared by means of membrane.

tion, in the sample with 3.0 % (w/w) added, no remarkable change to the shape of the droplets was observed. Subsequent measurements of the dispersed droplet diameter in a W/O emulsion were performed with 3.0% (w/w) hydrophobic emulsifier added to the dispersion dilution oil.

The relationship between the  $D_m$  and  $D_p$  of the W/O emulsification at the time of preparation using microporous glass membranes was compared (Fig. 5) for three different pore diameters. The dispersed droplet size distributions were also compared (Fig. 6).  $D_p$  and viscosity data obtained immediately after emulsification were evaluated (Table 1). Examination of the average  $D_p$  for emulsions prepared under these conditions showed a significant difference ( $p \leq 0.01$ ). These results were used to compare the characteristics of all emulsions. Within this range of  $D_m$ , we concluded that by changing the membrane pore size it was possible to control the dispersed droplet diameter.

The dispersed droplet size distribution for W/O emulsions prepared by the stirring method (Fig. 7) was compared with the  $D_p$  and the viscosity data obtained directly after emulsification (Table 1). Comparing the  $D_p$  under the beginning stage conditions (membrane emulsification method as shown in Fig. 6c), and the  $D_p$  in emulsions by stirring, monodispersion of emulsions by membrane emulsification using the hydrophobic membrane was better.

The time course of changes in  $D_p$  and viscosity was followed (Fig. 8) for emulsions prepared by membrane emulsification and by stirring. The stability index was also compared (Table 2). To make the  $D_p$  conditions at the beginning stage the same, an emulsion with a  $D_m$  of 0.73  $\mu\text{m}$  prepared by membrane emulsification and an emulsion by stirring were compared, to define the index for assessment of stability. The rate of increase of  $D_p$  in the emulsion prepared by the membrane emulsification method was small. Also the rate of decline in viscosity of the membrane emulsion was lower.

In the time course of changes in  $D_p$  during storage, there was a difference in coalescence rate of the dispersed droplets. This is believed to be due to a difference in monodispersion and the adsorption mechanism of the emulsifier at the oil/water interface.

Generally, emulsions with a large dispersed droplet size are less stable. However, under our conditions, this trend was not observed (Fig. 9) and it was confirmed to be possible, using the membrane emulsification method, to prepare W/O emulsions of almost the same level of stability with a  $D_p$  ranging from 4  $\mu\text{m}$  to 12  $\mu\text{m}$  (Table 2). These results confirm the potential for the membrane emulsification system to be used on a practical level.

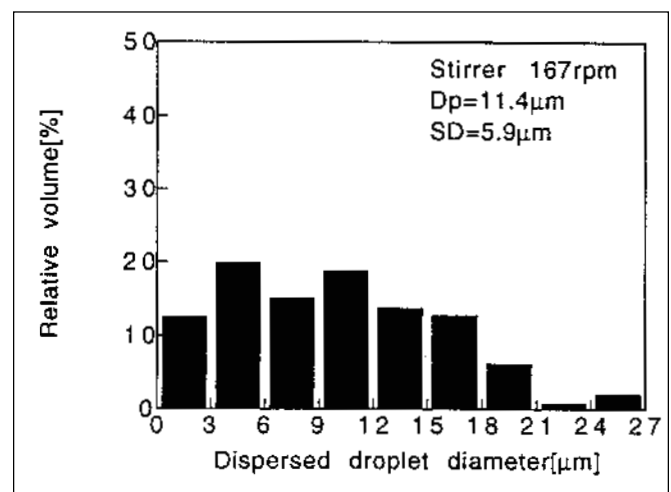


Fig. 7—Droplet size distribution of W/O emulsion prepared by means of stirring.

**Table 1—Properties of W/O emulsions**

Emulsification method	Dm (μm)	Dp (μm)	Std dev of Dp (μm)	Significance level of statistical test	Dp/Dm <sup>a</sup>	Viscosity (mPa·s)
Membrane	0.34	4.25	2.74	>1%*	12.5	202
	0.57	9.11	3.45		16.0	220
	0.73	12.3	5.30		16.8	201
Stirrer 160 rpm 2h	—	11.4	5.92	—	—	200

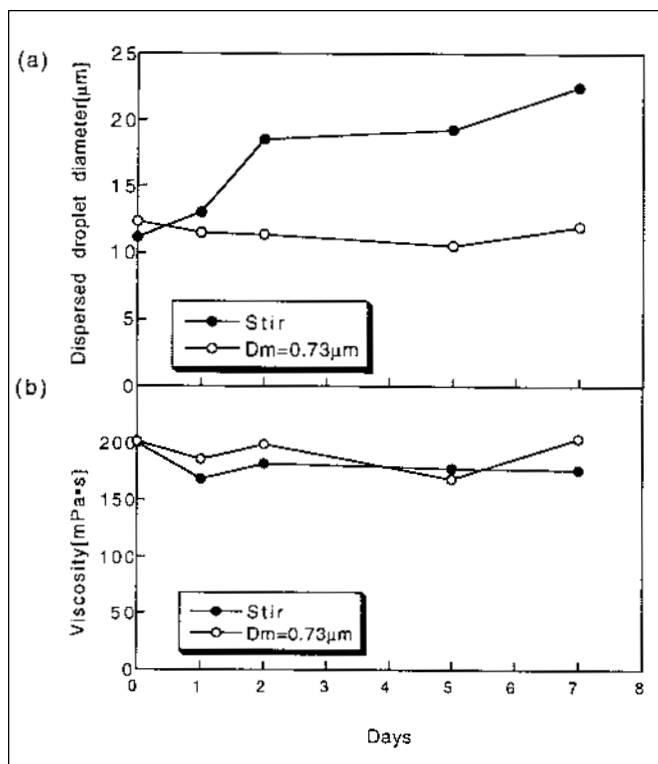
<sup>a</sup>Dm=avg pore diameter of membrane; Dp=avg dispersed droplet diameter.  
\*1% was considered statistically significant.

**Table 2—Stability indices of W/O emulsions**

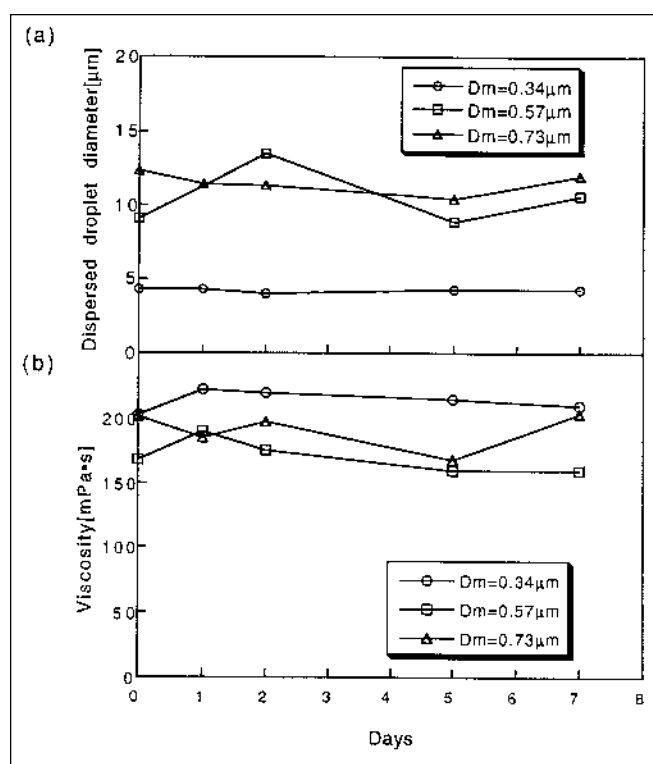
Emulsification method	Dm (μm)	Stability value	
		*1 Rate of increase in Dp (%)	*2 Rate of decrease in viscosity (%)
Membrane	0.34	1.6	-4.0
	0.57	17.5	14.5
	0.73	-2.4	-1.0
Stirrer 160 rpm 2h	—	100.9	12.0

\*1 = [(Dp on day 7 after emulsification - Dp on day of emulsification)/Dp on day of emulsification] × 100.

\*2 = [(η on day of emulsification - η on day 7 after emulsification)/η on day of emulsification] × 100. (η = viscosity)



**Fig. 8—Stability of viscosity and dispersed droplet size of emulsions from the stirring method and the membrane method.**



**Fig. 9—Comparison of W/O emulsions prepared with membranes of three different Dm.**

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