Effects of Interfacial Tension and Viscosities of Oil and Water Phases on Monodispersed Droplet Formation Using a Shirasu-porous-glass (SPG) Membrane

Masato Kukizaki^{1)*} and Masahiro Goto²⁾

1) Miyazaki Prefectural Industrial Technology Center

16,500-2 Higashi-kaminaka, Sadowara, Miyazaki 880-0303, Japan

2) Department of Applied Chemistry, Graduate School of Engineering, Kyushu University

744 Moto-oka, Fukuoka 819-0395, Japan

Membrane emulsification using Shirasu-porous-glass (SPG) membranes is a novel method for preparing monodispersed emulsions. In this study, effects of interfacial tension, and viscosities of dispersed and continuous phases on droplet formation were investigated using various surfactant concentrations and various dispersed and continuous phases. Decane was pressurized into a stirring sodium dodecyl sulfate (SDS) aqueous solution in an interfacial tension range of 4.7 to 35.7 mN·m⁻¹ through a SPG membrane with a mean pore diameter of 3.1 μ m, at a transmembrane pressure larger than capillary pressure. Under these conditions, monodispersed oil-in-water emulsions with a mean droplet diameter of approximately 10 μ m were stably prepared. Oil-water interfacial tension barely affected the resulting droplet diameter. In a system composed of decane containing liquid paraffin and SDS solution containing polyethylene glycol, experimental results showed that the resulting droplet diameter increased with increasing water-phase viscosity, while droplet diameter decreased with increasing oil-phase viscosity. Droplet diameter decreased as the ratio of oil-phase to water-phase viscosity increased. However, droplet diameter did not change in the case of a constant viscosity ratio.

Key words : Shirasu-porous-glass membrane / monodispersed emulsion / droplet formation / interfacial tension / viscosity

1. Introduction

Emulsification is an important process in food, cosmetic, and pharmaceutical industries. Size and size distribution of emulsion droplets determine their characteristics and abilities^{1, 2)}. For instance, physicochemical properties including rheology and emulsion stability are influenced by size and size distribution of emulsion droplets. Size control of emulsion droplets is also significantly important for studying their characteristics, because interpretation of experimental results in a system composed of monodispersed emulsions is much simpler than in systems composed of polydispersed emulsions.

In the early 1990s, we proposed a novel method for preparing monodispersed emulsions using Shirasu-porous-glass (SPG) membranes, which have cylindrical, tortuous uniform pores forming a three-dimensional interconnected network^{3 ~ 6)}. We named our emulsification method 'membrane emulsification', which allowed the preparation of monodispersed emulsions by permeating a dispersed phase into a continuous phase through a membrane with uniform pores^{3, 4)}. The biggest advantage of this method is that the resulting droplet size can be controlled by varying pore size of the membrane employed. This method requires lower energy input, and smaller mechanical stress than conventional emulsification methods such as those using colloid mills, rotor-stator systems, and high pressure homogenizers^{7, 8)}. With membrane emulsification using SPG membranes, monodispersed oil-in-water^{3, 4)}, water-in-oil⁹⁾, and water-in-oil-in-water emulsions can

* Corresponding author

Tel : 0985-74-4311 Fax : 0985-74-4488,

e-mail : kukizaki@iri.pref.miyazaki.jp

Fig. 1 Schematic diagram of the experimental apparatus used for preparing oil-in-water emulsions using an SPG membrane.

(a) : SPG membrane module, (b) : Compressed nitrogen gas, (c) : Oil-phase container, (d) : Water-phase and emulsion container, (e) : Magnetic stirrer, (f) : Dispersed oil phase, (g) : Continuous water phase

be prepared⁴⁾. Over the last decade, a number of studies investigated process parameters affecting droplet size and size distribution including transmembrane pressure^{3, 4, 9, 10)}; velocity of continuous phases^{9 ~ 16)}; surfactant types¹⁷⁾; pore shapes¹⁴⁾; and surface wettability of the membrane⁹⁾. However, there has been no investigation reporting effects of interfacial tension and viscosities of dispersed and continuous phases on droplet formation behaviors in detail. In the present study, we investigated effects of interfacial tension between dispersed oil phase and continuous water phase on the resulting diameter of droplets produced from an SPG membrane. The effects of both viscosities on the resulting droplet diameter were also examined.

2. Experimental

2.1 Materials

A tubular SPG membrane (outer diameter, 10 mm; thickness, 0.5 mm; length, 30 mm) was purchased from SPG Technology Co., Ltd. (Miyazaki, Japan). The SPG membrane was prepared by leaching phase-separated glass in a $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ sys-

tem synthesized from volcanic ash called “Shirasu”, which was used as the main raw material. Preparation methods of membranes were described previously⁶⁾. Mean pore diameter and porosity of the membrane determined by the mercury penetration method were $3.1 \mu\text{m}$ and 0.58, respectively.

The emulsion system consisted of decane as the dispersed oil phase, and distilled water containing sodium dodecyl sulfate (SDS, $M_w = 288 \text{ g}\cdot\text{mol}^{-1}$) as the continuous water phase. To examine effects of oil- and water-phase viscosities, liquid paraffin and polyethylene glycol (PEG, $M_w = 20000 \text{ g}\cdot\text{mol}^{-1}$) were added to the oil and water phases, respectively. Decane, SDS, liquid paraffin, and PEG were purchased from Wako Pure Chemical Industries Co., Ltd. (Tokyo, Japan).

2.2 Preparation of oil-in-water emulsions

Emulsification preparation was carried out using the experimental apparatus shown in Fig. 1. The oil phase was stored in a pressure-tight vessel, and was allowed to permeate through the SPG membrane into the stirring water phase at a transmembrane pressure larger than capillary pressure. Under these conditions, emulsion droplets were produced from the SPG membrane. During the emulsification experiments, the temperature was kept at 298 K using a constant temperature chamber (AE-215, Toyo Seisakusyo Kaisya, Co., Ltd., Chiba, Japan). The stirring speed of the magnetic stirrer (HPS-100P, AS ONE Co., Ltd., Osaka, Japan) in the emulsion container was maintained at 150 rpm.

2.3 Measurement and analysis of the emulsions prepared

Diameter distributions of emulsion droplets prepared were determined using a laser diffraction particle size analyzer (SALD2100, Shimadzu Co., Ltd., Kyoto, Japan). Refraction index of decane was 1.4. Monodispersity of emulsion droplets was characterized using the particle size dispersal coefficient, δ ³⁾.

$$\delta = ({}^{90}D_o - {}^{10}D_o) / {}^{50}D_o \quad (1)$$

where ${}^{90}D_o$, ${}^{50}D_o$, and ${}^{10}D_o$ are diameters corresponding to 90 vol.%, 50 vol.%, and 10 vol.%, respectively, on a relative cumulative droplet diameter distribution curve; and ${}^{50}D_o$ expresses the mean droplet diameter. The smaller the value of δ , the narrower the diameter distribution.

Fig. 2 Relationship between SDS concentration and oil-water interfacial tension.

Fig. 4 Schematic illustration of the droplet formation process from a pore.

2. 4 Analytical methods

Interfacial tensions between oil and water phases were measured by the pendant droplet method using an automatic interfacial tensiometer (DM500, Kyowa Interface Science Co., Ltd., Saitama, Japan). Viscosities of oil and water phases were measured using a rotational viscometer (DVL-B, TOKIMEC Co., Ltd., Tokyo, Japan). All experiments were performed at 298 K.

3. Results and Discussion

3. 1 Effects of oil-water interfacial tension on capillary pressure

First, oil-water interfacial tension was measured by varying SDS concentrations between 0.17 and 10.0 mol·m⁻³. The results in Fig. 2 show that the critical micelle concentration (cmc) of SDS was 7.0 mol·m⁻³. Next, capillary pressure was measured using an SPG membrane with a mean pore diameter of 3.1 μm.

Fig. 3 Relationship between oil-water interfacial tension and capillary pressure. The mean pore diameter of an SPG membrane is 3.1 μm.

Fig. 5 Diameter distributions of emulsion droplets produced from an SPG membrane with a mean pore diameter of 3.1 μm. The emulsion system consisted of decane and SDS aqueous solutions with an interfacial tension of (a) 4.7 and (b) 39.8 mN·m⁻¹.

Capillary pressure is defined as the transmembrane pressure at which oil droplets begin to permeate through the membrane into a water phase. In the present study, capillary pressure was determined by measuring transmembrane pressure at which oil droplet formation could be observed by eye. Fig. 3 shows the relationship between oil-water interfacial tension γ , and capillary pressure P_c . Capillary pressure increased with increasing interfacial tension and can be calculated from the following equation⁹⁾ (Fig. 4(a)) :

$$P_c = \frac{4 \gamma \cos(\pi - \theta)}{50 D_m} = - \frac{4 \gamma \cos \theta}{50 D_m} \quad (2)$$

Fig. 6 Effects of oil-water interfacial tension on mean droplet diameter and particle size dispersal coefficient. The mean pore diameter of an SPG membrane is $3.1 \mu\text{m}$.

where θ is the contact angle between the membrane surface and the oil-phase, and $^{50}D_m$ is the membrane pore diameter. These results showed that by increasing SDS concentration in a range of $0.17\text{--}7.0 \text{ mol}\cdot\text{m}^{-3}$ (i.e., at the SDS concentrations less than the cmc concentration), capillary pressure decreased due to a decrease in the oil-water interfacial tension.

3.2 Effects of oil-water interfacial tension on mean bubble diameter

Effects of oil-water interfacial tension on droplet diameter formed were investigated using different concentrations of SDS aqueous solutions. Fig. 5 shows typical diameter distributions of emulsion droplets produced in a system composed of decane as the oil phase and the SDS aqueous solution (γ of (a) 4.7 and (b) $= 39.8 \text{ mN}\cdot\text{m}^{-1}$) as the water phase. Fig. 6 shows the effects of interfacial tension on mean droplet diameter and particle size dispersal coefficient within an interfacial tension range of 4.7 to $39.8 \text{ mN}\cdot\text{m}^{-1}$. Monodispersed emulsion droplets were stably produced in this range; that is, even at an SDS concentration below the cmc. In this range, interfacial tension barely affected resulting droplet diameter and the particle size dispersal coefficient. However, increases in mean droplet size diameter and the particle size dispersal coefficient were observed with an increase in interfacial tension

Fig. 7 Schematic representation of droplet formation (a) at relatively high surfactant (SDS) concentrations, and (b) at very low surfactant concentrations.

Fig. 8 Effects of oil-phase viscosity on mean diameter and particle size dispersal coefficient of emulsion droplets produced from an SPG membrane with a mean pore diameter of $3.1 \mu\text{m}$. The oil phase consisted of different fractions of liquid paraffin containing decane.

within a range of 37.7 to $39.8 \text{ mN}\cdot\text{m}^{-1}$. This was probably due to unsaturated adsorption of SDS molecules at the newly formed oil-water interfaces during droplet formation with decreasing SDS concentration. Consequently, the probability of droplet coalescence at the membrane surface increased, and thus, large emulsion droplets with a broad diameter distribution formed (Fig. 7 (b)). On the other hand, at relatively high surfactant concentrations (in an interfacial tension range of 4.7 to $35.7 \text{ mN}\cdot\text{m}^{-1}$ in this study), the probability of coalescence of droplets formed at pore open-

Fig. 9 Effects of water-phase viscosity on mean diameter and particle size dispersal coefficient of emulsion droplets produced from an SPG membrane with a mean pore diameter of $3.1 \mu\text{m}$. The water phase consisted of different concentrations of PEG aqueous solutions containing $8.0 \text{ mol}\cdot\text{m}^{-3}$ SDS.

ings decreased. This was probably due to SDS molecules being adsorbed in a saturated condition at newly formed oil-water interfaces during droplet formation, and electrostatic repulsion worked between the negatively charged hydrophilic groups of SDS molecules. In that case, monodispersed emulsion droplets formed (Fig. 7 (a)).

3.3 Effects of oil- and water-phase viscosities on mean droplet diameter

The effects of dispersed oil-phase viscosity on mean droplet diameter were investigated. Decane containing different fractions of liquid paraffin in a viscosity range of $0.88\text{--}52.3 \text{ mPa}\cdot\text{s}$ was used as the oil phase. An SDS aqueous solution of $8.0 \text{ mol}\cdot\text{m}^{-3}$, corresponding to a water-phase viscosity of $0.95 \text{ mPa}\cdot\text{s}$, was used as the water phase. Fig. 8 shows the effects of oil-phase viscosity on the mean diameter and particle size dispersal coefficient of the emulsion droplets produced. Mean droplet diameter decreased with increasing oil-phase viscosity. This was probably due to an increase in oil-phase viscosity causing a decrease in supply rate of the oil phase during droplet formation.

Next, effects of continuous water-phase viscosity on mean droplet diameter were investigated. Different concentrations of PEG aqueous solutions containing

Fig. 10 Effects of the ratio of oil-phase to water-phase viscosity on mean droplet diameter.

The mean pore diameter of an SPG membrane is $3.1 \mu\text{m}$. The oil phase consisted of different fractions of liquid paraffin containing decane. The water phase consisted of different concentrations of PEG aqueous solutions containing $8.0 \text{ mol}\cdot\text{m}^{-3}$ SDS.

Table 1 Effect of viscosities of dispersed oil phase and continuous water phase on the droplet diameter

Experimental system	η_d [mPa·s]	η_c [mPa·s]	η_d/η_c [-]	$^{50}D_0$ [μm]	δ [-]
A	0.88	0.95	0.93	10.5	0.34
B	0.88	2.10	0.42	13.2	0.37
C	0.88	5.30	0.17	15.1	0.40
D	0.88	13.4	0.07	21.2	0.33
E	0.88	25.1	0.04	26	0.35
F	1.77	10.5	0.17	15.2	0.37
G	25.3	10.5	2.41	9.3	0.35
H	12.6	13.4	0.94	10.3	0.33
I	12.6	30.0	0.42	13.8	0.37
J	18.3	0.95	19.26	7.5	0.41
K	25.3	0.95	26.63	6.2	0.33
L	52.3	0.95	55.05	5.4	0.40

$8.0 \text{ mol}\cdot\text{m}^{-3}$ SDS were used as the water phase. Decane, corresponding to an oil-phase viscosity of $0.88 \text{ mPa}\cdot\text{s}$, was used as the oil phase. Fig. 9 shows effects of water-phase viscosity on mean diameter of emulsion droplets formed. Mean droplet diameter increased with increasing water-phase viscosity. It is assumed that the increase in viscosity of the water phase delays the release of droplets, and increases the oil-phase supply during the formation of each droplet. Therefore, emulsion droplets would become large.

Fig. 10 and Table 1 show the relationship between

the ratio of oil-phase viscosity to water-phase viscosity and the resulting droplet diameter. Mean droplet diameter decreased with increasing viscosity ratio. In the case of a constant viscosity ratio, the resulting droplet diameter did not change, as shown in experimental systems of (A) vs. (H), (B) vs. (I), and (C) vs. (F) in Table 1. These results suggested that if the flow between oil and water phases was analogous, the resulting droplet diameter did not change.

4. Conclusions

Effects of interfacial tension and viscosities of dispersed and continuous phases on droplet formation behavior with various surfactant concentrations and various dispersed and continuous phases were investigated by membrane emulsification using an SPG membrane. Monodispersed oil-in-water emulsions were prepared by permeating decane into an SDS aqueous solution in a interfacial tension range of 4.7 to 35.7 mN·m⁻¹ through an SPG membrane at a transmembrane pressure larger than capillary pressure. Interfacial tension of the water phase barely affected the resulting droplet diameter. In a system composed of decane containing liquid paraffin and an SDS solution containing polyethylene glycol, our experimental results showed that resulting droplet diameter increased with increasing water-phase viscosity, while resulting droplet diameter decreased with increasing oil-phase viscosity. Droplet diameter decreased with an increasing ratio of oil-phase to water-phase viscosity. However, droplet diameters did not change when the viscosity ratio was constant.

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Symbols

$^{50}D_o$	mean oil droplet diameter	(m)	δ	particle size dispersal coefficient	(-)
nD_o	oil droplet diameter at n % of the cumulative volume	(m)	η_c	continuous water-phase viscosity	(Pa·s)
$^{50}D_m$	mean pore diameter	(m)	η_d	dispersed oil-phase viscosity	(Pa·s)
M_w	molecular weight	(g·mol ⁻¹)	η_r	ratio of dispersed oil-phase viscosity to continuous water-phase viscosity	(-)
P_c	capillary pressure	(Pa)	θ	contact angle between membrane surface and dispersed oil phase	(-)
(Greek letters)					
γ	oil-water interfacial tension	(N·m ⁻¹)			