



Title	Removal kinetic model of oil droplet from o/w emulsion by adding methylated milk casein in flotation
Author(s)	Maruyama, Hideo; Seki, Hideshi; Satoh, Yuuki
Citation	Water Research, 46(9), 3094-3100 <a href="https://doi.org/10.1016/j.watres.2012.03.016">https://doi.org/10.1016/j.watres.2012.03.016</a>
Issue Date	2012-06-01
Doc URL	<a href="http://hdl.handle.net/2115/49431">http://hdl.handle.net/2115/49431</a>
Type	article (author version)
File Information	WR46-9_3094-3100.pdf



[Instructions for use](#)

**Removal kinetic model of oil droplet from o/w emulsion by adding  
methylated milk casein in flotation**

**Hideo MARUYAMA<sup>\*</sup>, Hideshi SEKI, Yuuki SATOH**

Division of Marine Biosciences, Graduate School of Fisheries Sciences, Hokkaido  
University

*Minato 3-1-1, Hakodate JAPAN, 041-8611*

*Telephone: +81-138-40-8813, Facsimile: +81-138-40-8811, E-mail:*

*maruyama@elsie.fish.hokudai.ac.jp*

\* corresponding to the author

## Abstract

In this study, o/w emulsion flotation experiments were conducted by ~~with~~ adding methylated milk casein (MeSC). Emulsion used in this study was prepared by ultrasonic emulsification of heavy oil (bunker-A) and sodium dodecyl sulfate (SDS) solution. A simple kinetic model was proposed to estimate the removal rate of the oil droplets within the column. The model was based on main assumption that adsorption of single droplet adsorbed MeCS or floc onto bubble surface within flotation column. Removal rate constant,  $K$ , was defined by  $k_a X_s (S_b \tau / V)$ , where  $k_a$  and  $X_s$  are overall adsorption rate and saturated adsorption density of oil droplet or floc,  $S_b$ ,  $\tau$  and  $V$  are bubble surface production rate, retention time of bubble swarms and emulsion volume within the column, respectively. The experiments were conducted with varying operating conditions; superficial gas velocity, column dimension and emulsion volume.  $K$  was evaluated from slope value of obtained straight line by plotting time versus  $\ln(T/T_0)$ , where  $T/T_0$  is relative turbidity.  $K$  was mostly proportional to  $(S_b \tau / V)$ , which corresponds to specific surface area of bubble swarms per unit volume within the column, in the present experimental region. This result suggested that efficiency of this removal process was mainly controlled by the specific surface area of bubble swarms, and proposed model was fundamentally verified.

**KEYWORDS:** flotation; o/w emulsion; removal model; methylated milk casein; separation

## 1. Introduction

Oil in water (o/w) emulsion has been used in several industrial processes, e.g., petroleum, chemical, food, pharmaceutical, electronic, machine industries. Because wastewater including o/w emulsion has influences on aqueous environments, for removal of oil droplets from aqueous environments, several techniques have been proposed, such as filtration (Belkacem et al., 1999; Hilal et al., 2004; Lobo et al., 2006; Hu et al., 2007), chemical destabilization (Rios et al., 1998), dissolved air flotation (Abo-El Ela et al., 1980; Fukushi et al., 1998; Zouboulis et al., 2000; Al-Shamrani et al., 2002a; Al-Shamrani et al., 2002b), electrocoagulation (Carmona et al., 2006; Cañizares et al., 2008), flotation (Maruyama et al., 2009) and so on.

As one of these techniques, the authors proposed flotation involving adding flocculant to o/w emulsion for enhancement of removal (Maruyama et al., 2009). In the previous study, the authors used biodegradable methylated milk casein (MeCS) as flocculant, which is a poly-cationic polymer, and reported that addition of MeCS to oil droplets charged negatively enhanced removal of the oil droplets as flocs from o/w emulsion. The removal kinetics could be evaluated by adopting the pseudo first-order kinetic equation (Maruyama et al., 2009). However, the rate constant,  $k$ , in the previous study is practical coefficient and lacks physical or physicochemical meaning. For improvement of process design for this technique, it is important to clarify what operating variables and conditions or physical properties of objective substances affect the removal kinetics by this technique. Kinetic modeling of flotation for solid particles has been reported by some researchers (Ityokumbul, 1992; Bloom and Heindel, 2003). However, few kinetics model for removal of oil droplet from o/w emulsion involving oil breaking by adding a flocculant have been reported.

In this study, the authors propose a simple kinetic model to evaluate removal rate by the proposed flotation technique. The experiments were conducted with varying

superficial gas velocity, column dimension, emulsion volume within the column and concentration of droplets. The authors discuss verification of the proposed model and influences of the operating variables and conditions for this technique in this study.

## 2. Flotation model

Emulsified droplets using sodium dodecyl sulfate (SDS) hardly attached on bubble surface, since SDS adsorbed on oil droplets surface and its polar head is oriented in the direction of bulk liquid, resulting the droplet surface is hydrophilic. Therefore, droplets and their floc adsorbed MeCS can adsorb on bubble surface because of hydrophobic groups existing on MeCS, thus droplets and their floc adsorbed MeCS can be removed by flotation. During a bubble's rise in a column, the coverage,  $\theta$ , of droplets or flocs adsorbed MeCS onto bubble surface during the residence time,  $\tau$ , is expressed as,

$$\frac{d\theta}{d\tau} = k_a C(1 - \theta) - k_d \theta \quad (1)$$

where,  $k_a$  and  $k_d$  are adsorption and desorption rate constant, respectively. During  $\tau$ , adsorption equilibrium between oil droplets and bubble surface could not be attained, and desorption of oil droplets from bubble surface is negligible small. In addition, the adsorption density should be much smaller than the saturated adsorption density. Thus,  $\theta$  could be very smaller than 1. Eq. (1) can be simplified as,

$$\frac{d\theta}{d\tau} = k_a \theta C \quad (2)$$

Eq. (2) is integrated with initial conditions;  $C = 0$  at  $\tau = 0$ , and  $C = C$  at  $\tau = \tau$ .

$$\theta = \frac{X}{X_S} = k_a C \tau \quad (3)$$

where,  $X_S$  is the saturated surface density of oil droplets or their floc. In batch operation, the mass balance of the bubble column is expressed as,

$$V \frac{dC}{dt} = -S_b X = -S_b k_a X_S \tau C \quad (4)$$

where,  $S_b$  and  $V$  represent bubble surface production rate and volume of treated emulsion within the column, respectively. By solving Eq. (4) with respect to  $C$ , the following equation is obtained.

$$\ln \frac{C}{C_0} = -Kt \quad (5)$$

where,  $C_0$  and  $K$  represent the initial concentration of oil droplet in o/w emulsion and the oil droplets removal rate constant, respectively.  $K$  is defined as:

$$K \equiv k_a X_S \left( \frac{S_b \tau}{V} \right) \quad (6)$$

In this equation, the product,  $k_a X_S$ , corresponds to influence of adsorption properties of adsorption of bubble surface and oil droplet and floc covered by MeCS. Moreover, the product,  $(S_b \tau/V)$ , corresponds to influence of operating variables.

In the present study, the dimensionless concentration,  $C/C_0$ , of droplets could be substituted with the specific turbidity,  $T/T_0$ . Eq. (5) can be rewritten as,

$$\ln \frac{T}{T_0} = -Kt \quad (7)$$

By plotting time,  $t$ , versus  $\ln(T/T_0)$ , a straight line will be obtained. The value of  $K$  will be estimated from the slope value of the line. In addition, Eq. (6) predicts that plotting of  $(S_b \tau/V)$  versus  $K$  estimated by Eq. (7) gives a straight line from the origin. By fitting of the experimental data to Eqs. (6) and (7), the proposed model will be verified.

### **3. Experimental**

#### *3.1 Materials*

Commercially available heavy oil (bunker A) was used as dispersed oil droplets. Milk casein, methyl alcohol, sodium hydroxide, and hydrochloric acid and sodium dodecyl sulfate (SDS) were purchased from Wako Pure Chemical Industries (Japan). Milk casein was of practical grade and other chemicals were of reagent grade. They were used with no further purification.

#### *3.2 Methylated egg casein*

Preparation method of methylated milk casein (MeCS) was similar to that in the previous study (Seki et al., 2004). Milk casein was methylated according to the method reported by Fraenkel-Conrat and Olcott (1945). An aqueous solution of casein (ca. 10 g/L) was prepared, and a 0.1 M HCl solution was added. At pH 4.6 (isoelectric point of casein), casein precipitated, and the mixture was centrifuged at 3000 rpm for 20 min. The precipitated casein was washed with methyl alcohol and dispersed in a 100-fold volume of methyl alcohol containing 0.05 M HCl. This solution was stirred for 24 h at room temperature. The methylated casein (MeCS) was collected in a centrifuge at 3000 rpm for 20 min and then washed with methyl alcohol. The degree of methylation was determined from the change in the number of carboxylic groups before and after methylation by a potentiometric titration (Seki et al., 2003). In this study, MeCS with degree of methylation of 83 % was used. Experiments were conducted at room temperature.

#### *3.3 Preparation of emulsion*

Preparation method of o/w emulsion was almost the same manner in the previous study (Maruyama et al., 2009). In the most experiments, 1 mL of heavy oil was added to

500 mL of  $2.0 \times 10^{-5}$  M SDS solution. The solution was stirred by magnetic stirrer and was sonicated by ultrasonic dispersion (20 kHz, 25 W, Powersonic Model 50, POWERSONICS, Inc., CT, US) for 10 min. When 4 mL of heavy oil was dispersed,  $4.0 \times 10^{-5}$  M of SDS solution of the same volume was employed. Hereinafter, the emulsion solutions prepared by the former and latter conditions referred to as A1 and A2 emulsion, respectively. 800, 1200 and 2000 mL of the o/w emulsion was also prepared to use in the flotation experiments as necessary. To confirm diameter distribution for preparation of o/w emulsion by using different sizes glass vessel, the irradiation time were varied as necessary. The droplet size distribution was measured with laser scattering size distribution analyzer (LA-300 HORIBA, Ltd., Japan).

#### *3.4 flocculation (clarification) experiment*

The procedure of flocculation experiment is similar to that in the previous study (Maruyama et al., 2009). This experiment was conducted to determine the optimum amount of MeCS added to the emulsion. 100 mL of o/w emulsion was poured into a 100 mL glass cylinder gently and was stirred by magnetic stirrer at 500 rpm. After beginning of agitation, MeCS solution prepared at a desired concentration was immediately added to the emulsion. This mixture was stirred for 5 min at 500 rpm. After 5 min, agitation was stopped and the mixture was left to stand for 10 min. A clear water region appeared from the bottom of the cylinder because the floc of oil droplets rises upward by adding MeCS. A 2 mL sample was taken from the clear water layer at a position of 3 cm above the bottom of the glass cylinder by using long syringe needle. The turbidity of the sample was measured at 700 nm spectrophotometrically (HITACHI U-1500, or, JASCO V630). The experimental relative turbidity,  $T/T_0$ , was employed for indicator as flocculation efficiency.  $T$  and  $T_0$  represent the turbidity of o/w emulsion in the presence and the absence of MeCS in the clear water sampled at a position of 3 cm above the bottom of the glass cylinder, respectively. All experiments were conducted at room

temperature.

### *3.5 flotation experiment*

Flotation experiments were conducted in batch system. A schematic diagram of the experimental setup is shown in Fig. 1. The experimental setup used in this study was mostly same as that used in the previous our study (Maruyama et al., 2009).

Four columns were employed in response to treated volume of o/w emulsion: (a) 3.2 cm in inside diameter and 31 cm in height transparent acrylic resin, (b) 4.4 cm in inside diameter and 0.4 m in height transparent acrylic resin, (c) 4.4 cm in inside diameter and 60 cm in height polycarbonate resin, and (d) 8.0 cm in inside diameter and 46 cm in height acrylic resin. Sintered glass filter (10-15  $\mu\text{m}$  mean-pore size) was installed as a gas distributor at the bottom of the column. Liquid feed and drain were installed at the center and the bottom of the column, respectively. Pressure taps for measuring gas holdup in the column were installed along the wall.

The o/w emulsion solution was poured into the column gently. Then, air was supplied from air compressor and was dispersed as bubble through the gas distributor. After starting aeration ( $t = 0$ ), MeCS solution was injected at the injection tap by using a syringe. In most runs, MeCS was injected at  $t = 10$  see. The treated solution within the column was sampled at desired time and the concentration of emulsion was measured by turbidimetry at 700 nm.

#### 4. Results and Discussion

Oil droplet diameter distribution is shown in Fig. 2 as a typical result of A2 emulsion. To confirm diameter distribution for preparation of o/w emulsion by using different sizes glass vessel, the irradiation time of ultrasonic were varied. Each sonication time was employed as follows: 500 mL for 10 min, 800 mL for, 15 min, 1200 mL for 20 min, and, 2000 mL for 30 min, respectively. As shown in Fig. 2, each diameter distribution is seemed to be mostly same.

The optimum dosage of MeCS was determined from clarification experiments by similar method (Maruyama et al., 2009). Typical result of the clarification experiment for A2 emulsion with MeCS is shown in Fig. 3. A minimum value of the relative turbidity,  $T/T_0$ , was observed. This fact suggests that flocculation of the emulsion used in this study by MeCS should be dominated by charge neutralization. In almost runs, pH value of emulsion solution after flocculation was ca. pH 5.5. At this pH, oil droplet is charged negatively due to SDS adsorption onto the droplet surface, and MeCS charged positively. Due to electrostatic attraction, bridging flocculation between MeCS and oil droplet occurs. According to these results, the optimum dosage of MeCS was determined to conduct flotation experiments. Therefore, the dosage of MeCS making  $T/T_0$  minimum corresponds to the optimum dosage for flocculation. In this study, optimum dosage of MeCS as flocculant was determined as  $4.38 \times 10^{-4}$  g for A1 and  $2.01 \times 10^{-3}$  g for A2 emulsion, respectively. These values were almost same as the values previously reported (Maruyama et al., 2009).

Time course of the relative turbidity,  $T/T_0$ , is shown in Fig. 4. The experiment results with 4.4 cm in inside diameter (I.D.) of column for 400 mL of A1 (Fig. 4a) and A2 (Fig. 4b) emulsion were shown as typical results. Arithmetic mean value was employed as the value of data shown in Fig. 4. The experimental error was within 4 %. In the experiment without adding MeCS (solid circle), oil droplets were not removed by flotation (Fig. 4b).

By addition of MeCS, the oil droplets would be removed from bulk liquid within the column due to adsorption of MeCS and formation of oil droplet floc. For both case of A1 and A2 emulsion, the degree of oil droplet removal increased with increasing the value of the superficial gas velocity,  $U_g$ , under same column dimension and treated emulsion volume within the column. This result might support that the frequency of bubbles generated within the column was proportional to increase in  $U_g$ . This tendency is mostly same as previous study (Maruyama et al., 2009).

Typical results of fitting of the data obtained with various conditions to Eq. (7) are shown in Fig. 5. The straight lines in Fig. 5 were calculated by a least squares method. The data agreed well to Eq. (7) up to about 60 min of the present flotation process. Therefore, the value of  $K$  was determined from the value of slope obtained by plotting of Eq. (7).

The flotation experiments were conducted by varying superficial gas velocity, column size, and treated emulsion volume within the column. The values of  $K$  were determined from the plot of Eq. (7). Figure 6 shows plotting of  $S_b\tau/V$  versus the estimated value of  $K$  from Eq. (7). Both  $S_b$  and  $\tau$  were estimated from the following equations (Suzuki et al., 1995):

$$S_b = 6 A \varepsilon_G(1-\varepsilon_G)^{4.65} \left\{ (4/225)(\rho_L-\rho_G)^2 g^2 / (\mu_L \rho_L) \right\}^{1/3}, \quad (8)$$

$$\tau = \varepsilon_G V / (A U_g) \quad (9)$$

where  $A$ ,  $\varepsilon_G$ ,  $g$ ,  $\rho_L$ ,  $\rho_G$  and  $\mu_L$  denote a cross-sectional area of the column, the gas holdup, the gravitational acceleration, the densities of the liquid and the gas and the viscosity of the liquid, respectively. Eq. (8) was derived from the assumption that bubbles are homogeneous sphere and their terminal rising velocity can be calculated by Allen`s equation (Allen, 1900). An equation proposed by Lewis et al. was employed for voidage compensation (Lewis et al, 1949). As seen in Fig. 6, the value of  $K$  is linearly

proportional to that of  $S_b \tau / V$ , although some scatter is observed. This result supports that the proposed model in this study could be verified fundamentally according to the prediction by Eq. (6). The straight line in Fig. 6 is obtained by least squares method. The value of the slope for the straight line in Fig. 6 corresponds to the value of  $k_a X_s$  in Eq. (6), and the value of  $k_a X_s$  is estimated as  $1.68 \times 10^{-3}$  cm/s.

The quantity,  $S_b \tau / V$ , corresponds to the surface area of bubbles per unit volume of the column. In other words,  $S_b \tau / V$  is regarded as the specific surface area of bubbles based on the column volume. The oil droplets removal rate constant,  $K$ , was proportional with the specific surface area of bubbles based on the column volume,  $S_b \tau / V$ . In the present system, the proportional coefficient,  $k_a X_s$ , could be considered as constant. The adsorption rate constant and the saturated adsorption density of each oil droplet or floc adsorbed MeCS might be different because of difference in both size distributions. However, these values for assemblage of oil droplet or its floc adsorbed MeCS should be estimated as average values apparently. In the present system, adsorption properties of oil droplet and floc covered by MeCS onto bubble surface could be considered to be mostly same condition. Varying dosage of MeCS to treated o/w emulsion, in these conditions, the value of  $k_a X_s$  could be varied from that of the present case because of change in adsorption properties of oil droplet and floc covered by MeCS onto bubble surface.

## 5. Conclusions

In this study, the authors proposed a flotation model based on adsorption of oil droplets or their flocs adsorbed MeCS onto bubble surface. The flotation experiments were conducted with adding the optimum amount of MeCS which determined from clarification experiments. The experimental results were verified with the proposed model. The removal rate constant,  $K$ , was estimated from fitting of the data to Eq. (7). In addition, the removal rate constant,  $K$ , was linearly proportional to the generated bubble surface area per unit working column volume,  $S_b z/V$ , that is, the specific bubble surface area in the present system as predicted by Eq. (6). From the slope value, adsorption property,  $k_a X_s$ , of oil droplet and floc covered by MeCS onto bubble surface was estimated as constant value,  $1.68 \times 10^{-3}$  cm/s. These results support verification of the proposed model fundamentally. In further study, influence of dosage of MeCS on the proposed flotation process would be discussed.

## Notation

$A$	= a cross sectional area of bubble column	$[\text{m}^2]$
$\varepsilon_G$	= gas holdup	$[-]$
$g$	= gravitational acceleration	$[\text{m}/\text{s}^2]$
$C$	= concentration of oil droplet at $t$	$[\text{kg}/\text{m}^3]$
$C_0$	= initial concentration of oil droplet	$[\text{kg}/\text{m}^3]$
$k_a$	= adsorption rate constant of oil droplet or floc onto bubble surface	$[\text{m}^3/(\text{kg s})]$
$k_d$	= desorption rate constant of oil droplet or floc onto bubble surface	$[\text{s}^{-1}]$
$K$	= removal rate constant	$[\text{s}^{-1}]$
$\mu_L$	= liquid viscosity	$[\text{kg}/(\text{m s})]$
$\rho_L$	= liquid density	$[\text{kg}/\text{m}^3]$
$\rho_G$	= gas density	$[\text{kg}/\text{m}^3]$
$S_b$	= bubble surface area production rate within the column	$[\text{m}^2/\text{s}]$
$t$	= time	$[\text{s}]$
$T$	= turbidity at 700 nm	$[-]$
$T_0$	= initial turbidity at 700 nm	$[-]$
$\tau$	= residence time of bubbles within the column	$[\text{s}]$
$U_g$	= superficial gas velocity	$[\text{m}/\text{s}]$
$X$	= adsorption density of oil droplet or floc onto bubble surface	$[\text{kg}/\text{m}^2]$
$X_s$	= saturated adsorption density of oil droplet or floc onto bubble surface	$[\text{kg}/\text{m}^2]$

## References

- Abo-El Ela, S.I., Nawar, S.S., 1980. Treatment of wastewater from an oil and soap factory via dissolved air flotation. *Environment International* 4(1), 47-52.
- Allen, H. S., 1900. The motion of a sphere in a viscuos fluid. *Philosophical Magazine* 50(306), 323-338.
- Al-Shamrani, A.A., James, A., Xiao, H., 2002a. Separation of oil from water by dissolved air flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 209(1), 15-26.
- Al-Shamrani, A.A., James, A., Xiao, H., 2002b. Destabilisation of oil–water emulsions and separation by dissolved air flotation, *Water Research* 36(6), 1503-1512.
- Belkacem, M. Bensadok, K., Nezzal, G., Aurelle, Y., 1999. Applicabilité du model du gel au traitement des huiles de coupe par ultrafiltration. *Entropie* 219, 30-35.
- Bloom, F., Heindel, T.J., 2003. Modeling flotation separation in a semi-batch process. *Chemical Engineering Science* 58, 353-365.
- Cañizares, P., Martínez, F., Jiménez, C., Sáez, C., Rodrigo, M.A., 2008. Coagulation and electrocoagulation of oil-in-water emulsions, *Journal of Hazardous Materials* 151(1), 44-51.
- Carmona, M., Khemis, M., Leclerc, J., Lopicque, F., 2006. A simple model to predict the removal of oil suspensions from water using the electrocoagulation technique. *Chemical Engineering Science* 61, 1237-1246.
- Fraenkel-Conrat, H., Olcott, H.S., 1945. Esterification of proteins with alcohols of low molecular weight, *Journal of Biological Chemistry*. 161, 259-268.
- Fukushi, K., Matsui, Y., Tambo, N., 1998. Dissolved air flotation: experiments and kinetic analysis. *Journal of Water Supply: Research and Technology-Aqua* 47, 76-86.
- Hilal, N., Busca, G., Hankins, N., Mohammad, A.W., 2004. The use of ultrafiltration and

- nanofiltration membranes in the treatment of metalworking fluids. *Desalination* 167, 227-238.
- Hu, B., Scott, K., 2007. Influence of membrane material and corrugation and process conditions on emulsion microfiltration. *Journal of Membrane Science* 294, 30-39.
- Ityokumbul, M.T., 1992. A new modelling approach to flotation column design. *Minerals Engineering* 5, 685-693.
- Lewis, W. K., Gilliland, E. R., Bauer, W. C., 1949. Characteristics of fluidized particles. *Industrial & Engineering Chemistry* 41(6), 1104-1117.
- Lobo, A., Cambiella, Á., Benito, J.M., Pazos, C., Coca, J., 2006. Ultrafiltration of oil-in-water emulsions with ceramic membranes: influence of pH and crossflow velocity. *Journal of Membrane Science* 278, 328-334.
- Maruyama, H., Tada, Y., Seki, H., 2009. Enhancement of oil droplet removal from o/w emulsion by adding methylated milk casein in flotation technique, *Asia-Pacific Journal of Chemical Engineering* 4, 211-217.
- Rios, G., Pazos, C., 1998. Destabilization of cutting oil emulsions using inorganic salts have coagulants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 138(2-3), 383-389.
- Seki, S., Suzuki, A., 2003. Flocculation of diatomite by methylated egg albumin, *Journal of Colloid and Interface Science* 263, 42-46.
- Seki, H., Suzuki, A., Shinguh, M., Maruyama, H., 2004. Flocculation of diatomite by methylated milk casein in seawater, *Journal of Colloid and Interface Science* 270, 359-363.
- Suzuki, A., Maruyama, H., Seki, H., Hayashi, T., 1995. Application of nonfoaming bubble separation to enrichment of dilute dye solution, *Journal of Chemical Engineering of Japan* 28, 115-117.
- Zouboulis, A.I., Avranas, A., 2000. Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation. *Colloids and Surfaces A: Physicochemical and*

Engineering Aspects 172(1-3), 153-161.

## Figure captions

**Fig. 1.** Schematic diagram of experimental setup for flotation. 1. bubble column; 2. gas distributor; 3. pressure measuring tap; 4. gas flow meter; 5. flow control valve; 6. air compressor; 7. pressure/voltage transducer; 8. amplifier; 9. volt meter; 10. personal computer; 11. sampling tap; 12. injection tap.

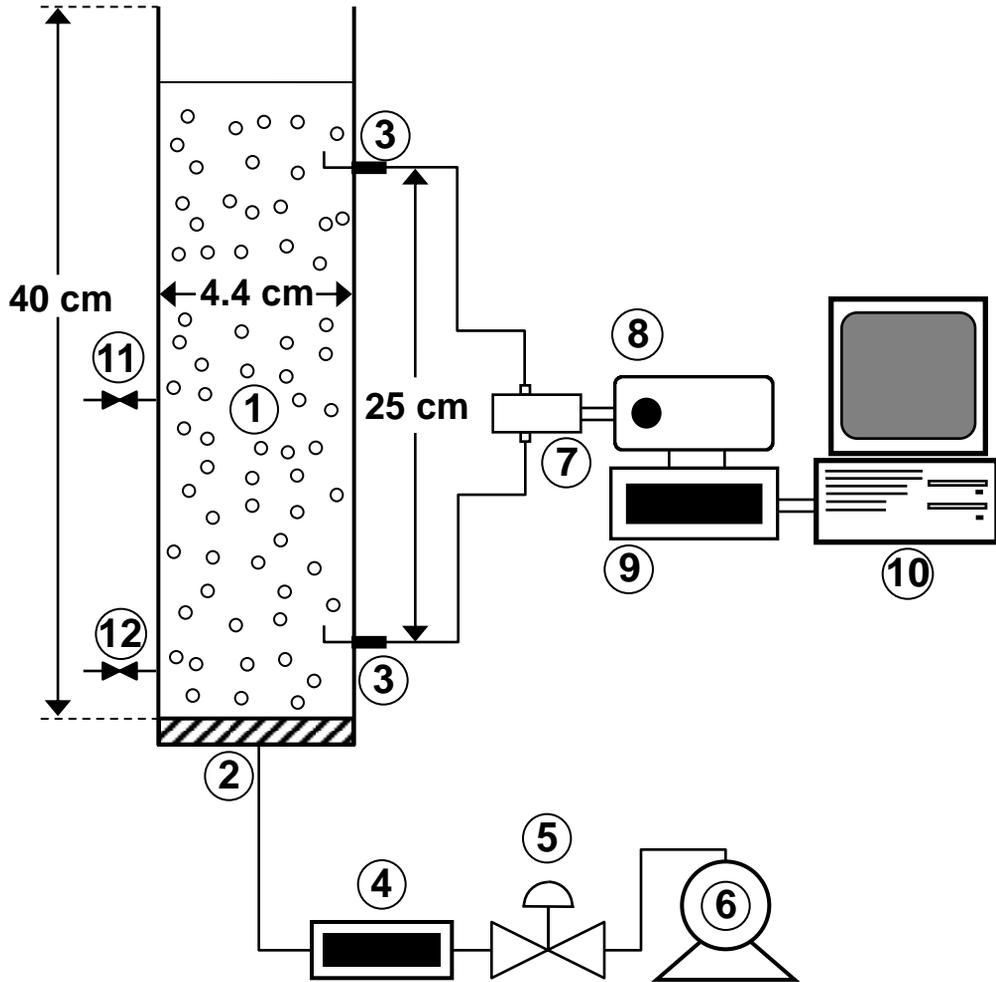
**Fig. 2.** Typical oil droplet diameter distribution of A2 o/w emulsion prepared in this study. Sonication time for 500, 800, 1200 and 200 mL are 10, 15, 20 and 30 min, respectively.

**Fig. 3.** Typical relationship between dosage of MeCS and the relative turbidity,  $T/T_0$ , for A2 emulsion. The experiments were conducted with 100 mL of o/w emulsion solution.

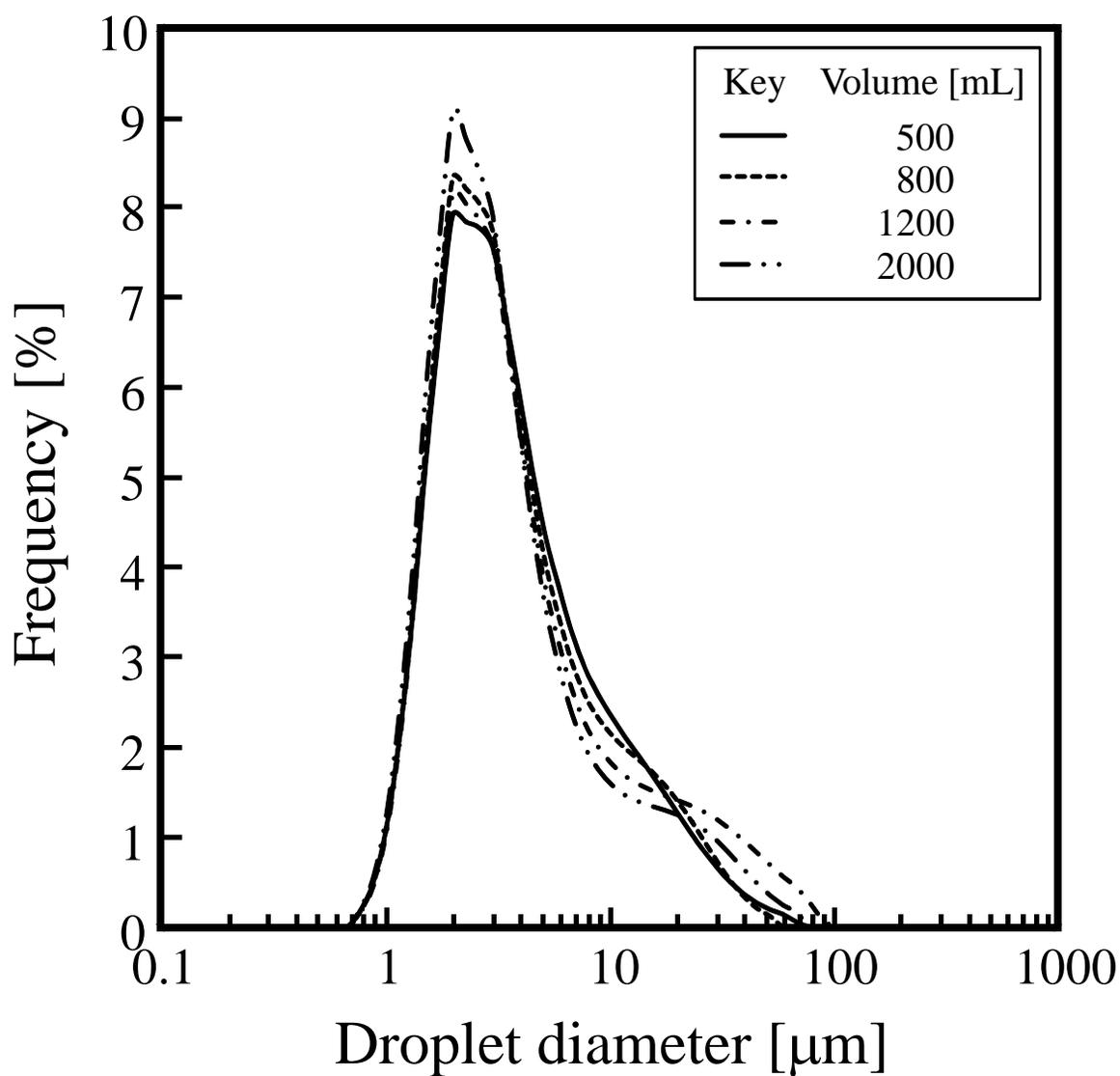
**Fig. 4.** Typical time course of the relative turbidity,  $T/T_0$ , for (a) A1 and (b) A2 emulsion (400 mL), respectively. The column I.D. was 4.4 cm. Solid circle in (b) is a control (without MeCS).

**Fig. 5.** Typical results for fitting of the data to Eq. (7). (a) 230 mL A1 emulsion, column ID 3.2 cm; (b) 400 mL A1 emulsion, column ID 4.4 cm; (c) 800 mL A2 emulsion, column ID 4.4 cm; (d) 1200 mL A1 emulsion, column ID 8.0 cm.

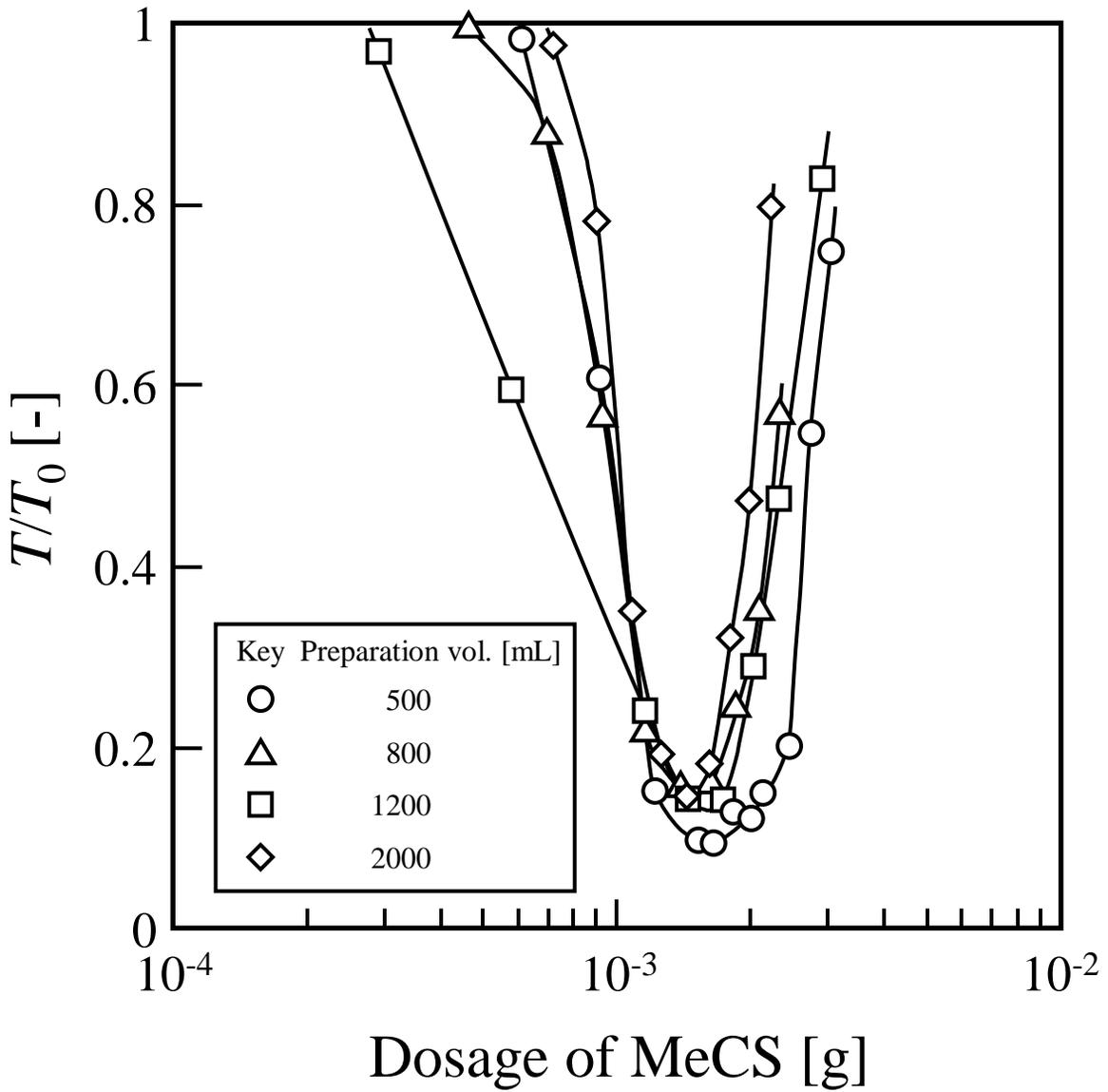
**Fig. 6.** Fitting of the data to Eq. (6) for A1 and A2 emulsions.



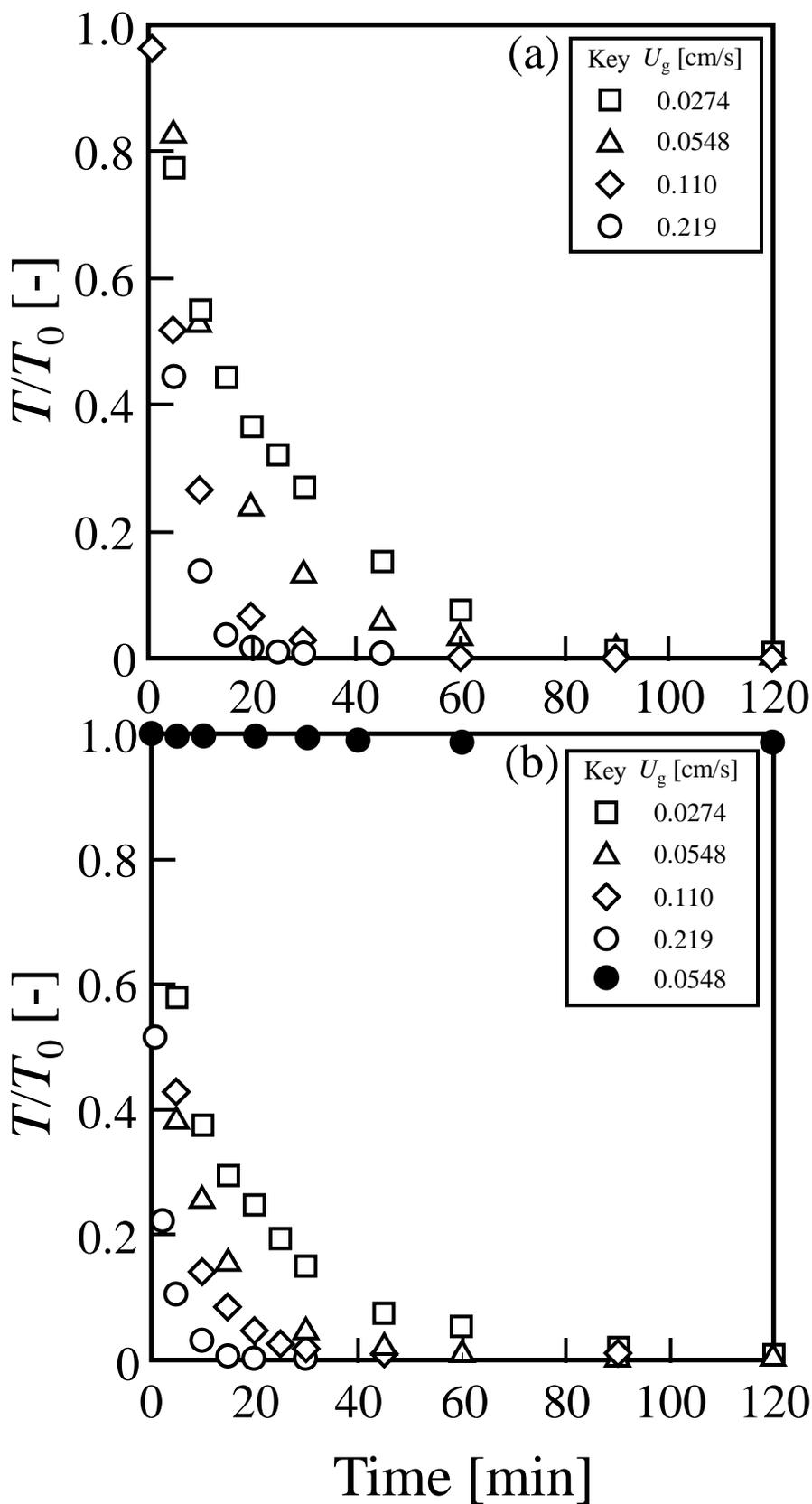
**Fig. 1.** Schematic diagram of experimental setup for flotation. 1. bubble column; 2. gas distributor; 3. pressure measuring tap; 4. gas flow meter; 5. flow control valve; 6. air compressor; 7. pressure/voltage transducer; 8. amplifier; 9. volt meter; 10. personal computer; 11. sampling tap; 12. injection tap.



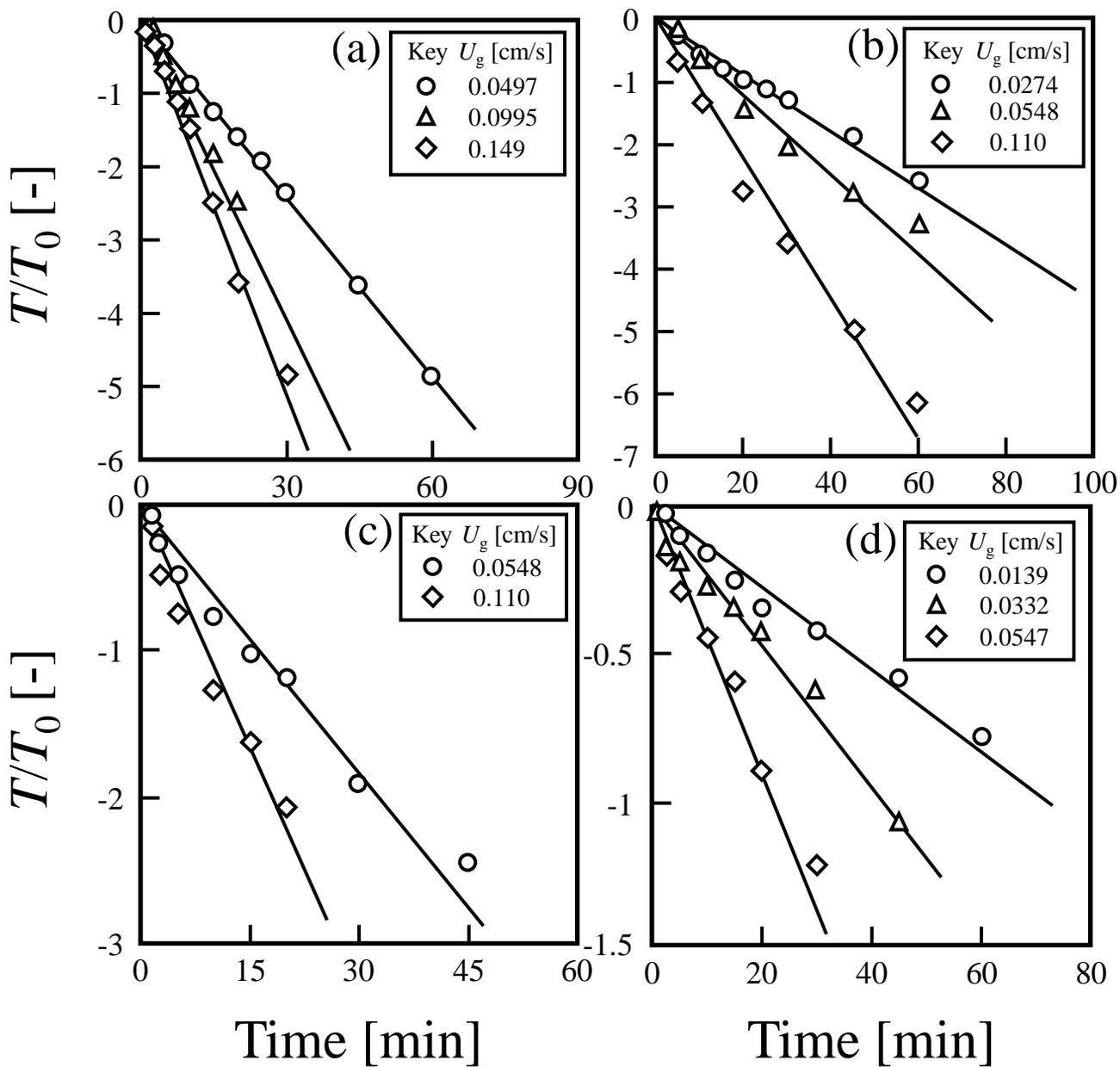
**Fig. 2.** Typical oil droplet diameter distribution of A2 o/w emulsion prepared in this study. Sonication time for 500, 800, 1200 and 2000 mL are 10, 15, 20 and 30 min, respectively.



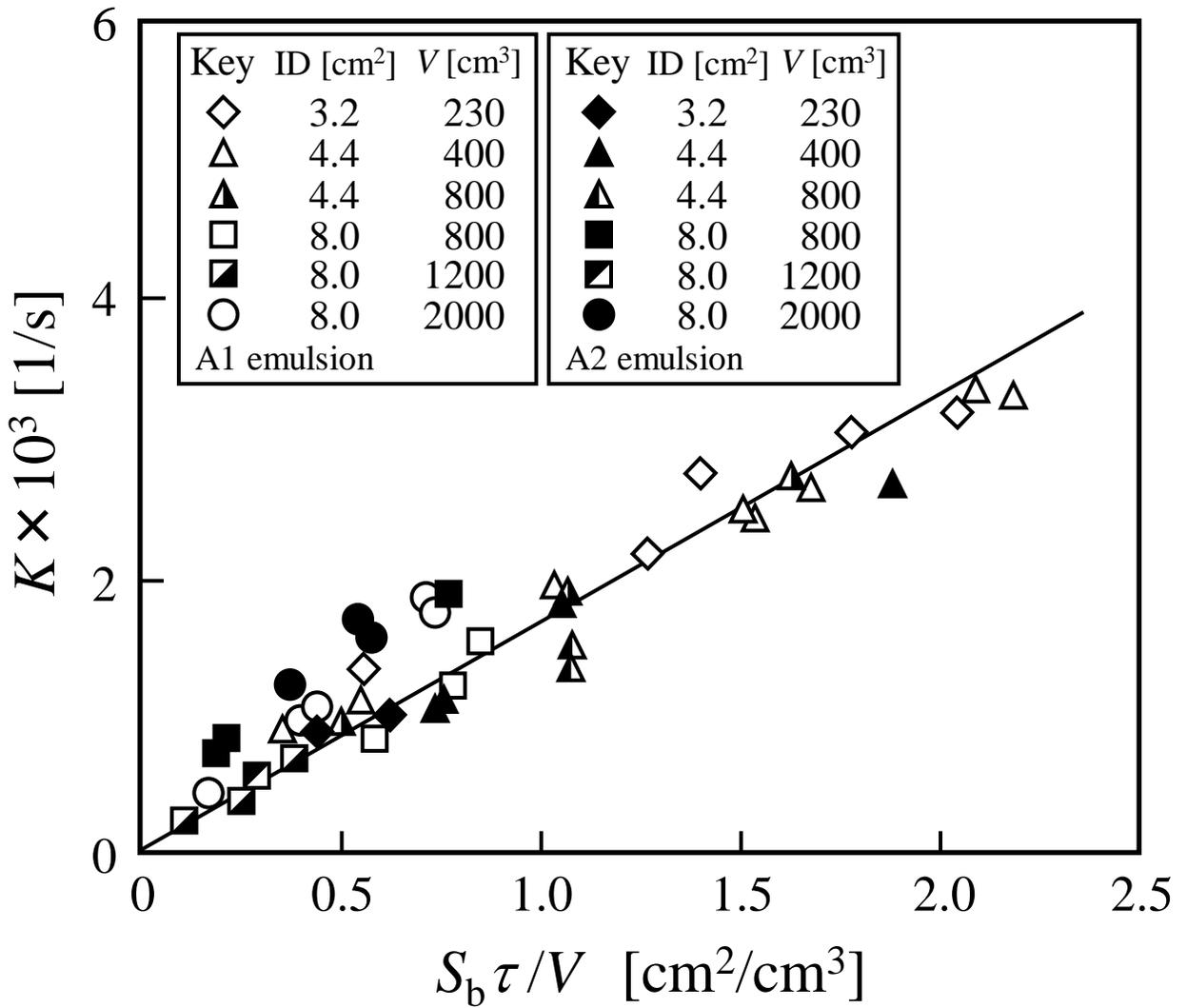
**Fig. 3.** Typical relationship between dosage of MeCS and the relative turbidity,  $T/T_0$ , for A2 emulsion. The experiments were conducted with 100 mL of o/w emulsion solution.



**Fig. 4.** Typical time course of the relative turbidity,  $T/T_0$ , for (a) A1 and (b) A2 emulsion (400 mL), respectively. The column I.D. was 4.4 cm. Solid circle in (b) is a control (without MeCS).



**Fig. 5.** Typical results for fitting of the data to Eq. (7). (a) 230 mL A1 emulsion, column ID 3.2 cm; (b) 400 mL A1 emulsion, column ID 4.4 cm; (c) 800 mL A2 emulsion, column ID 4.4 cm; (d) 1200 mL A1 emulsion, column ID 8.0 cm.



**Fig. 6.** Fitting of the data to Eq. (6) for A1 and A2 emulsions.