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Influence of methylated milk casein flocculant dosage on removal rate of oil droplet removal from o/w in flotation

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Abstract

In previous study, we conducted removal of oil droplets in o/w emulsion by flotation involving addition of methylated milk casein (MeCS) as a flocculant in a batch system and proposed a simple kinetic model to evaluate the removal rate constant, K, which is proportional with two adsorption parameters and one experimental conditional parameter. The formers are adsorption rate constant, k_a, of oil droplet and its floc onto bubble surface and the saturated adsorption density, X_s, the latter is the specific surface area per unit column volume, which is expressed as a product, $(S_b\ \tau)/V$, where S_b, τ, and V are bubble surface production rate, bubble residence time within the column and the treated volume of o/w emulsion. This proportional relationship was verified from flotation experiments at the optimum dosage of MeCS, which was determined by the clarification experiment of flocculation. In this study, especially, the influence of MeCS dosage on the removal kinetics of the flotation and the variation of K was investigated. The result suggested that the flotation efficiency in the case of varying MeCS dosage was mainly controlled by the specific surface area of bubbles and the flocculation condition within the flotation column.

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, for example, petroleum, chemical, pharmaceutical industries and so on. Wastewater including o/w emulsion has influences on aqueous environments. For this reason, several techniques to remove oil droplets from aqueous environments have been proposed: for examples, filtration [1-3], chemical destabilization [4], dissolved air flotation [5-9], electrocoagulation [10,11], magnetic demulsification [12] and so on. From the view point of wastewater treatment, removal of hydrocarbon from aqueous environments is very important operation because these substances cause high organic loading in the effluent, which, for example, these resulted excess sludge in activated sludge treatment process.

Flotation method has been employed for this purpose as one of effective and low cost techniques. As one of these techniques, we previously conducted flotation involving addition of flocculant to o/w emulsion to enhance oil removal. In the previous study [13], the removal kinetic model was proposed, which is expressed by the following equation.

$$\ln\frac{T}{T_0} = -Kt \tag{1}$$

Where, T and T_0 represent turbidity and the initial turbidity, respectively. The removal rate constant, K, is defined as the following equation.

$$K = k_{\mathrm{a}} X_{\mathrm{S}} \left(\frac{S_{\mathrm{b}}\tau}{V} \right) \tag{2}$$

By using this first order type equation, that is, Eq. (1) the removal rate constant was evaluated. Traditionally, for evaluation of flotation performance, flotation rate have been determined and estimated by mathematical or empirical models. Many researchers have used to evaluate flotation rate by a first order rate equation as a simple and easy-to-understand [13-16].

In Eq. (2), k_a, X_s, S_b, τ and V represent the adsorption rate constant, the saturated adsorption density of oil droplets and flocs, the bubble surface production area within the column, the residence time of bubbles and the treated emulsion volume within the column, respectively. The removal rate constant, K, is an index of the speed of the flotation process, which is affected by many factors. On the right side of Eq. (2), the first term, k_aX_S, corresponds to the adsorption properties concerning the adsorption ability and capacity of oil droplets, the state of flocs forming by addition of flocculant and flocs covered with flocculant, and, the second term, $(S_b \tau/V)$, corresponds to specific surface area per unit volume of the treated emulsion, which is affected by the operating conditions involving liquid properties, volumetric flow rate of aerated gas, pore size of gas distributor and so on. The state of bubble dispersion, especially, the surface area of bubble swarms generated within the column is very important for removal efficiency.

In the previous study [17,18], we confirmed the proposed removal kinetic model at the most optimum condition of the methylated milk casein (MeCS) dosage based on the oil droplets clarification by flocculation. This condition would rather be considered, where the state of adsorption condition seemed to be constant and the operating condition seemed to be only varied by the volumetric gas flow rate, which resulted in variation of the bubble surface production area within the column. The removal rate constant K should be affected by the variation of MeCS dosage in flotation involving MeCS addition. Several researches have performed and reported floc flotation [19-21], however, there have been few reports which concerned quantitative evaluation of flotation kinetics.

In this study, we investigated the influence of the dosage of MeCS as a flocculant on the removal rate constant, K, of oil droplets and flocs from o/w emulsion. In addition we discuss influence of the dosage on K and also confirm whether the proposed model could be applied in case of different state of floc by varying MeCS dosage.

2. Materials and methods

2.1. Materials

Commercially available heavy oil (bunker A) was used as 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 practical grade and other chemicals were reagent grade. All chemicals were used without further purification.

2.2. Preparation of methylated milk casein

The preparation method of methylated milk casein (MeCS) was almost the same manner in the previous study [22] according to the method reported by Fraenkel-Conrat and Olcott [23]. A casein solution (ca. 10 g/L) was prepared, and 0.1 M HCl solution was added to be precipitated at pH 4.6 (isoelectric point of casein). The precipitated casein was collected by centrifugation (1007 ×*g* (3000 rpm, 20 min)) and was washed with methanol for substituting from water to methanol. The casein was dispersed in a 100-fold volume of methanol containing 0.05 M HCl. This solution was stirred for 24 h at room temperature. The methylated casein was collected in a centrifuge at 3000 rpm for 20 min and then washed with methanol. The degree of methylation was determined by potentiometric titration [24] and MeCS with the degree of methylation of 83 % was used.

2.3. Preparation of emulsion

The preparation method of o/w emulsion was almost the same manner in the previous study [18]. In almost all experiments, 1 mL of heavy oil was added to 500 mL of 2.0×10^{-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, 4.0×10^{-5} M of SDS solution of the same volume was employed. Hereinafter, the emulsion suspensions prepared by the former and latter condition 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 size glass vessels, the irradiation time was varied as necessary. The average diameter and the size distribution of oil droplets or their flocs were measured with a laser scattering size distribution analyzer (LA-300 HORIBA, Ltd., Japan).

2.4. Clarification experiment

The procedure of the flocculation experiment is mostly same as described in the previous study [17,18]. 100 mL of o/w emulsion was poured into a 100 mL glass cylinder gently and was stirred by magnetic stirrer at 500 rpm. 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. 2 mL sample was withdrawn from the supernatant layer at a position of 3 cm above the bottom of the glass cylinder. The turbidity of the sample was measured at 700 nm spectrophotometrically. The specific turbidity, T/T_0, was employed for indicator as flocculation efficiency. T and T_0 represent the turbidity and the initial turbidity of the emulsion, respectively. Most experiments were performed in two times.

To evaluate the influence of the dosage of MeCS on change in the removal rate constant, K, the dosage of MeCS was varied as described in the next section. In this study, three kinds of MeCS dosages were employed. The flocculation efficiency, R, is defined as:

$$R = 1 - T/T_0 \tag{3}$$

2.5. Flotation experiment

A schematic drawing of the experimental setup is shown in Fig. 1. The setup used in this study was mostly the same as that used in the previous study [17,18,25]. Four columns were employed according to the volume of o/w emulsion prepared: (a) 3.2 cm in inside diameter and 31 cm in height transparent acrylic resin, (b) 4.4 cm in inside diameter and 40 cm 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 transparent acrylic resin, respectively. The experimental conditions about the inside diameter of the column employed, the initial emulsion volume within the column and the superficial gas velocity are summarized in Table 1.

Sintered glass filter (10-15 μm mean-pore size) was installed as a gas distributor (No. 4 in Fig. 1) at the bottom of the column. The injection and sampling taps were installed at the middle and the bottom of the column. Two pressure taps (No. 3 in Fig. 1) for measuring gas holdup in the column were installed along the column wall. The o/w emulsion solution was poured into the column gently. Then, air was supplied from an air compressor and was dispersed as bubbles through the gas distributor. After confirmation of the stable bubbly flow of air within the column, MeCS solution was injected from the injection tap (No. 12 in Fig. 1) by using a syringe. In most runs, MeCS was injected at t = 10 sec. The treated solution within the column was sampled at the desired time and the concentration of emulsion was measured by turbidimetry at 700 nm. Most experiments were performed in two times, and the average value was applied to Eq. 1 to evaluate K. The gas holdup was determined from the difference in static pressure between the clear and aerated liquids using a differential pressure transducer. Voltage signals were recorded by a personal computer.

3. Results and Discussion

3.1. Determination of MeCS dosage for desired flocculation efficiency R

The desired dosages for oil droplet flotation involved the addition of MeCS should be determined to know the influence of MeCS dosage on the removal rate constant, K. These values of dosages were determined based on the result of the clarification experiment. Typical results of the clarification experiment for A1 and A2 emulsions with MeCS are shown in Fig. 2. As seen in Fig. 2, the existence of the minimum value of T/T_0 should suggest that this flocculation was dominated by charge neutralization. The minimum values of T/T_0 were 0.23 for A1 and 0.13 for A2, respectively. In subsequent experiment, MeCS dosages were determined as the dosage making T/T_0 = 0.18 (the average value of 0.23 and 0.13), 0.5 and 0.7, respectively. Thus, each flocculation efficiency, R, corresponds to 0.82, 0.5 and 0.3, respectively.

3.2 Influences of MeCS dosage and superficial gas velocity on flotation efficiency

Fig. 3 shows the typical results of the time course of the specific turbidity, T/T_0 within the column. Time courses of MeCS dosage for R = 0.3 (square symbol) are relatively much slower than the dosage for those at R = 0.5 and 0.82. The results suggest that the flotation at low flocculation efficiency (R = 0.3) is not feasible for the removal of oil droplets from emulsion suspensions. In cases of R = 0.5 and 0.82, the removal efficiency of oil droplets are almost the same in the initial stage (t < 25 minutes), and it finished within ca. 90 minutes. The results in Fig. 3 suggest that the MeCS dosage affects the removal rate of oil droplets even at the same superficial gas velocity. To compare the flotation efficiency at higher R values with those at R = 0.3, the first-order kinetic model represented by Eq. (1) was applied to the experimental data presented in Fig. 3. The results were shown in Fig. 4 with the straight lines calculated by a least-squares regression. The data agreed well with the model up to ca. 60 minutes because T/T_0 decreased to negligible value after 60min. The results show that the larger R value or the appropriate dosage of MeCS gives the steeper slope for lines or the higher flotation efficiency.

3.3. Influence of MeCS dosage on relationship between K and specific surface area within flotation column

Fig. 5 shows the fitting of the data to Eq. (2). The abscissa and the ordinate of Fig. 5 represents the value of K determined from Fig. 4 and the product term of $S_b\tau/V$. S_b and τ were estimated by the following equations [26]:

$$S_b = 6A\varepsilon_G(1-\varepsilon_G)^{4.65}[(4/225)(\rho_L-\rho_G)^2 g^2/(\mu_L\rho_L)]^{1/3}, \tag{4}$$

$$\tau = \varepsilon_G V/(AU_g) \tag{5}$$

where A, ε_G, g, ρ_L, ρ_G and μ_L represent 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.

The solid lines in Fig. 5 were obtained by a least-squares regression. The value of the slope of the straight line corresponds to the value of k_aX_s in Eq. (2). For comparison, regression lines for R = 0.82, R = 0.5 and R = 0.3 were presented in the figure as dotted, dashed and dashed-dotted lines, respectively. Although some scatter of the plots was observed in Fig. 5, the linear relationship of Eq. (2) was held even when the MeCS dosage was not the optimum dosage. As increasing the MeCS dosage, the value of slope also increased. This fact suggests that the MeCS dosage obviously affect flotation efficiency and k_aX_s, that is, the adsorption properties of oil droplets or their flocs onto bubble surface within the flotation column because the variation of the value of $S_b\tau/V$ is mostly same in Fig. 5. The MeCS dosage should affect the adsorption properties rather than the operating variables, especially, the surface area of bubbles per unit volume of the column. The values of k_aX_s were determined from the values of the slopes of the lines as 1.68×10^{-3}, 1.44×10^{-3} and 6.54×10^{-4} cm/s in case of R = 0.82, 0.5 and 0.3, respectively.

The typical time course of the size distribution of oil droplets and flocs within the column is shown in Fig. 6. The results shown in Fig. 6 are in case of R = 0.82 (Fig. 6a) and 0.3 (Fig. 6b), respectively. In both cases, the average diameter of the droplet increased with time, however, the degree of increase in the average diameter was larger in the case of R = 0.82 than in the case of R = 0.3. At 60 minutes, the average diameter for R = 0.8 became ca. six hold (129.1 μm) of that for R = 0.3 (20.7 μm). The time course of change in the average diameter in Fig. 6 is shown in Fig. 7. The average diameters apparently increased linearly in both cases. Two straight lines in Fig. 7 are regression lines drawn through the 5.9 and 6.0 μm (t = 0) for R = 0.82 (Fig 6a) and R = 0.3 (Fig. 6b), respectively. The rate of increase in the average diameter during the flotation process was obviously much faster at the optimum dosage (R = 0.82) than the dosage for R = 0.3 within the column. The values of slopes of the lines were 1.93 and 0.23 for R = 0.82 and 0.3, respectively. The changing rate of R = 0.82 was ca. 8.4 fold higher than that of R = 0.3.

The surface properties of the bared part or the adsorbed MeCS part of the oil droplets were considered to be not changed even though the droplet size became larger. The variation of MeCS dosage should affect rather the saturated surface density of oil droplets or their flocs, X_s than the adsorption rate constant of them, k_a.

5. Conclusions

In this study, we conducted the oil droplet removal involving flocculant (MeCS) addition in air dispersed flotation and verified the kinetic model of the flotation proposed previously by varying amounts of the MeCS dosage. The flotation experiments were conducted with adding the desired amount of MeCS which made the flocculation clarification efficiency, R = 0.3, 0.5 and 0.82, respectively.

The removal rate constant, K was affected by varying the MeCS dosage even for the same superficial gas velocity. As increasing the MeCS dosage, the value of K also increased. The determined K was linearly proportional to the bubble surface area per unit column volume, $S_b \tau/V$. From this plotting, the product term, $k_a X_s$, could be determined from the value of the slope. The value of $k_a X_s$ increased with increase in the value of R even so the same range of $S_b \tau/V$. These facts should suggest that the kinetic model proposed previously could be verified even in the case of varying the flocculant (MeCS) dosage. As consider the time course of change in the average diameter of oil droplets or its flocs, the variation of MeCS dosage should be considered as affecting the saturated surface adsorption density, X_s rather than the adsorption rate constant, k_a.

Notation

A = a cross sectional area of bubble column [m^2]

ε_G = gas holdup [-]

g = gravitational acceleration [m/s^2]

k_a = adsorption rate constant of oil droplet or floc onto bubble surface [m^3/(kg s)]

K = removal rate constant [s^{-1}]

μ_L = liquid viscosity [kg/(m s)]

ρ_L = liquid density [kg/m^3]

ρ_G = gas density [kg/m^3]

R = flocculation efficiency [-]

S_b = bubble surface area production rate within the column [m^2/s]

t = time [s]

T = turbidity at 700 nm [-]

T_0 = initial turbidity at 700 nm [-]

τ = residence time of bubbles within the column [s]

U_g = superficial gas velocity [m/s]

X_s = saturated adsorption density of oil droplet or floc onto bubble surface [kg/m^2]

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Figure and table captions

Fig. 1. Schematic drawing 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 conputer; 11. sampling tap; 12. injection tap.

Fig. 2. Typical results of change in the specific turbidity, T/T_0, with varying the MeCS dosage for A1 (a) and A2 (b) emulsion, respectively.

Fig. 3. Influences of the superficial gas velocity, U_g, and variation in MeCS dosage on the time course of the specific turbidity, T/T_0, within the column. The experimental conditions: (a) column I.D. 2.3 cm, 230 mL A1 emulsion, $U_g = 0.0497$ cm/s; (b) column I.D. 4.4 cm, 400 mL A1 emulsion, $U_g = 0.0548$ cm/s; (c) column I.D. 4.4 cm, 400 mL A2 emulsion, $U_g = 0.0548$ cm/s; (d) column I.D. 4.4 cm, 800 mL A2 emulsion, $U_g = 0.11$ cm/s.

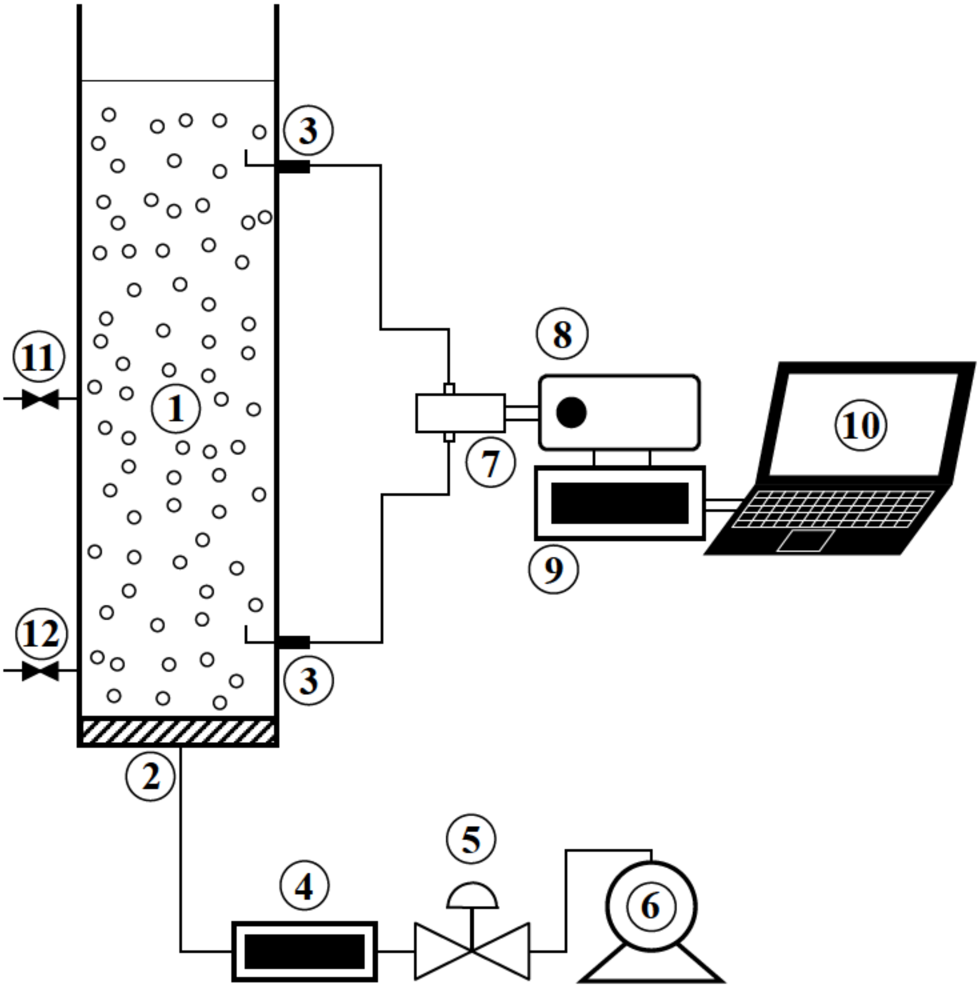
Fig. 4. Fitting of the data of Fig. 3 to Eq. (1) to evaluate the removal rate constant, K. The experimental conditions and the symbols in this figure are same as these in Fig. 3.

Fig. 5. Influence of the MeCS dosage on the relationship of Eq. (2) for various experimental conditions for $R = 0.82$ (a), 0.5 (b) and 0.3 (c), respectively.

Fig. 6. Typical results of the time course of the oil droplets or its flocs size distribution for $R = 0.82$ (a) and $R = 0.3$ (b), respectively. D in the figure legend corresponds to the average diameter.

Fig. 7. Typical time course of change in the average diameter of the droplets and their flocs within the flotation column. The average diameter values were obtained from Fig. 6 for R = 0.82 (Fig. 6a) and R = 0.3 (Fig. 6b), respectively.

Table 1 Summary of the column dimensions and the experimental conditions (the initial emulsion volume and the superficial gas velocity).



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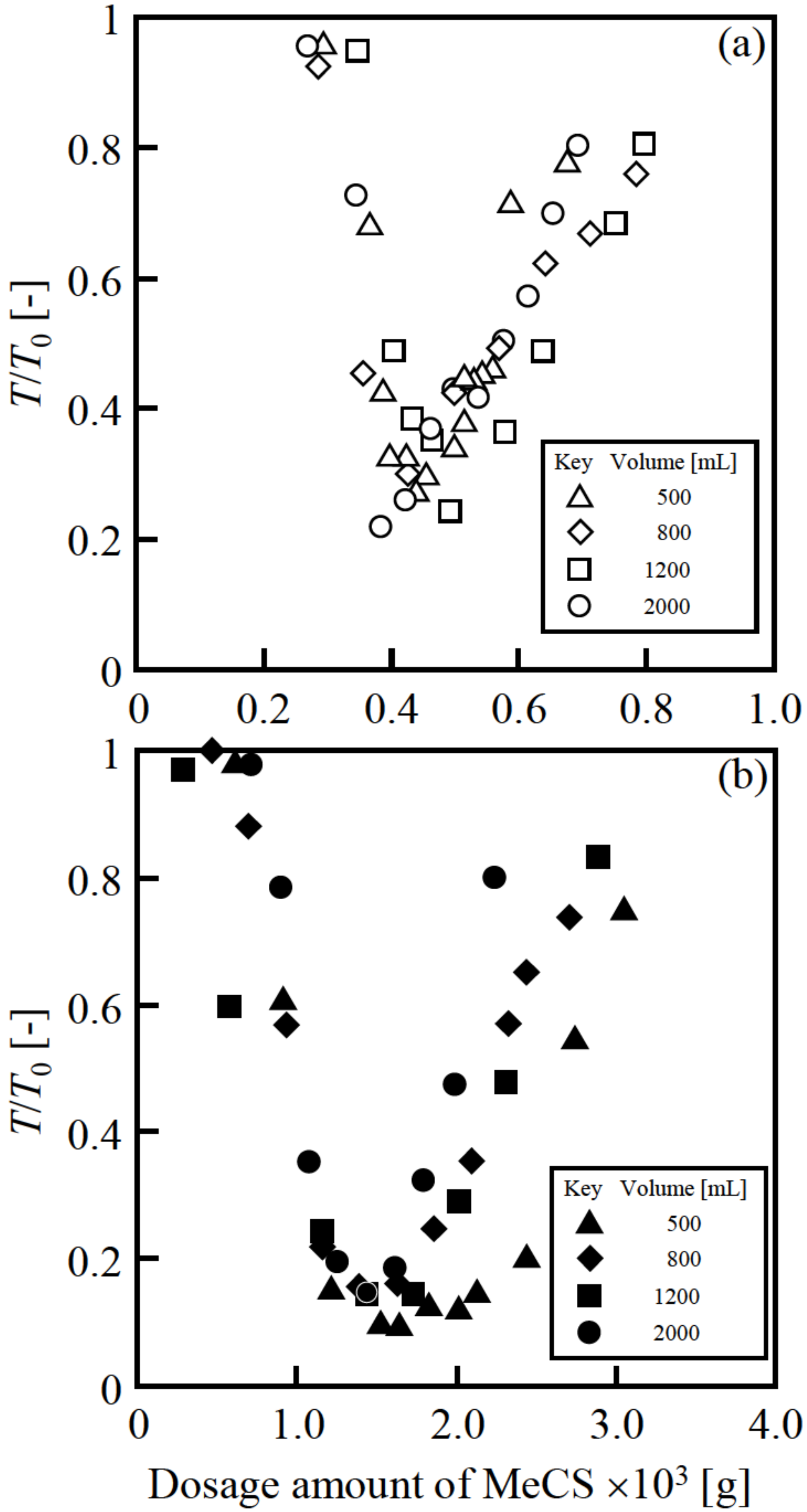

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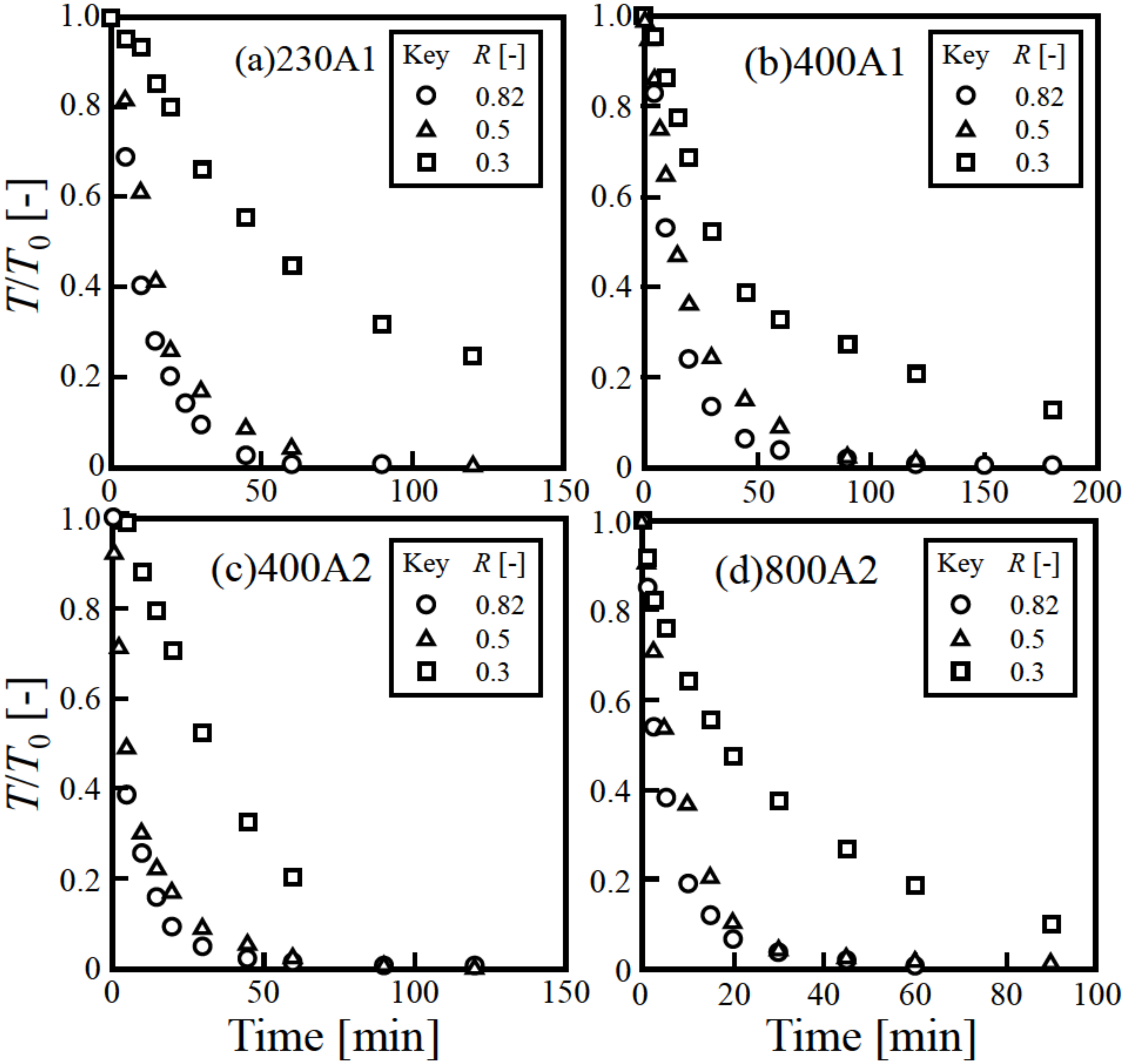

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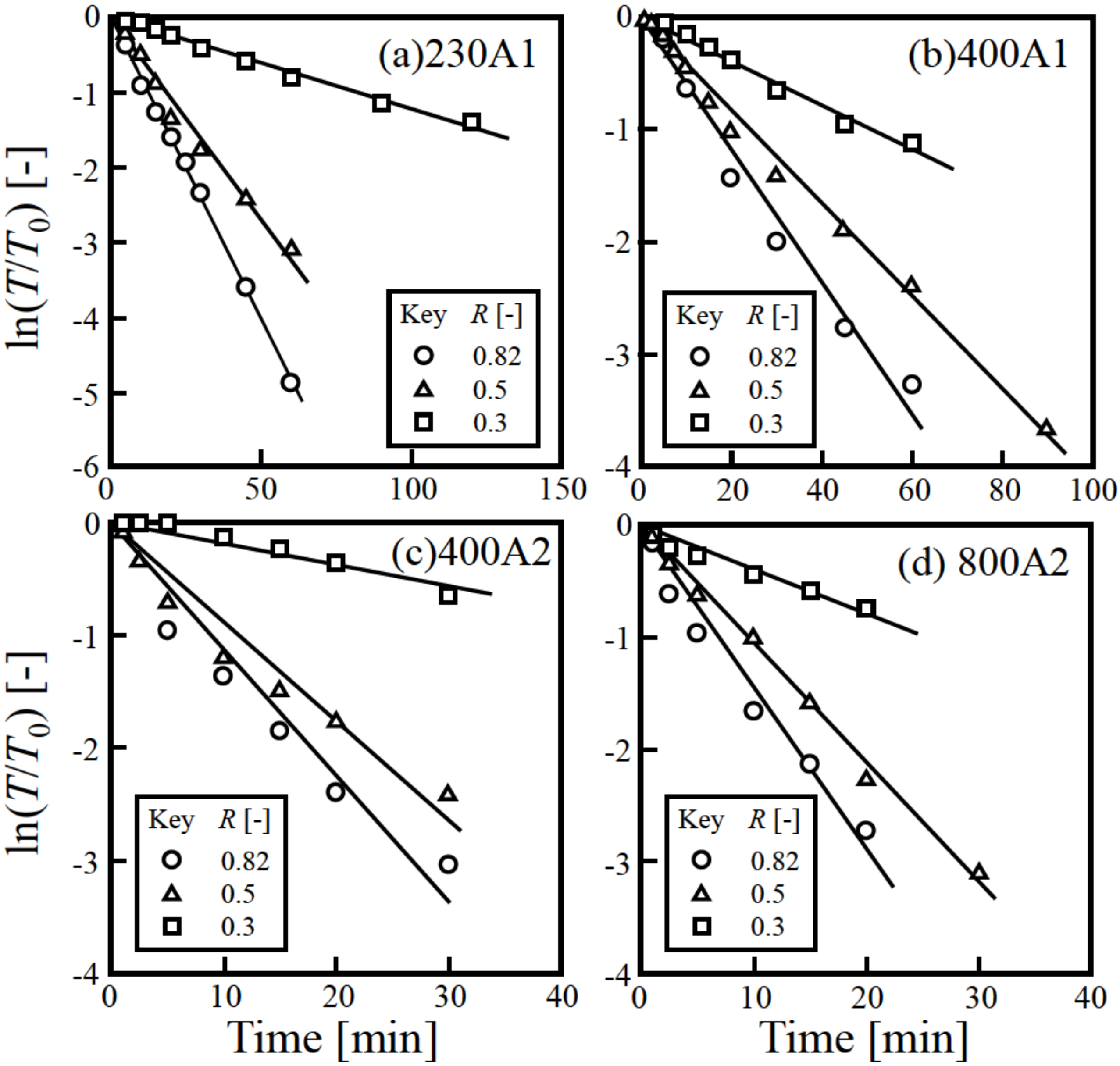

Fig. 4. Fitting of the data of Fig. 3 to Eq. (1) to evaluate the removal rate constant, *K*. The experimental conditions and the symbols in this figure are same as these in Fig. 3.

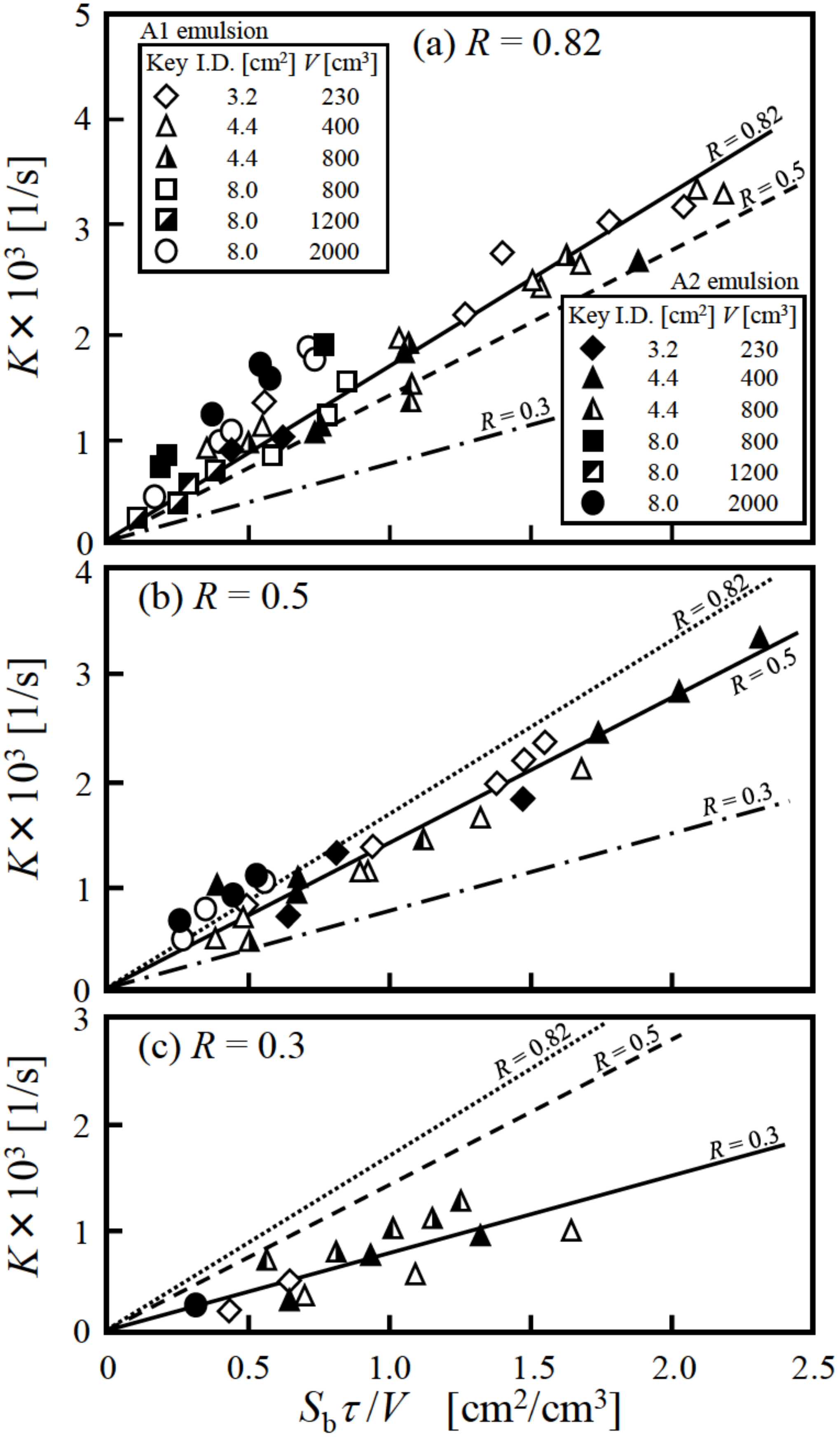

Fig. 5. Influence of the MeCS dosage on the relationship of Eq. (2) for various experimental conditions for R = 0.82 (a), 0.5 (b) and 0.3 (c), respectively.

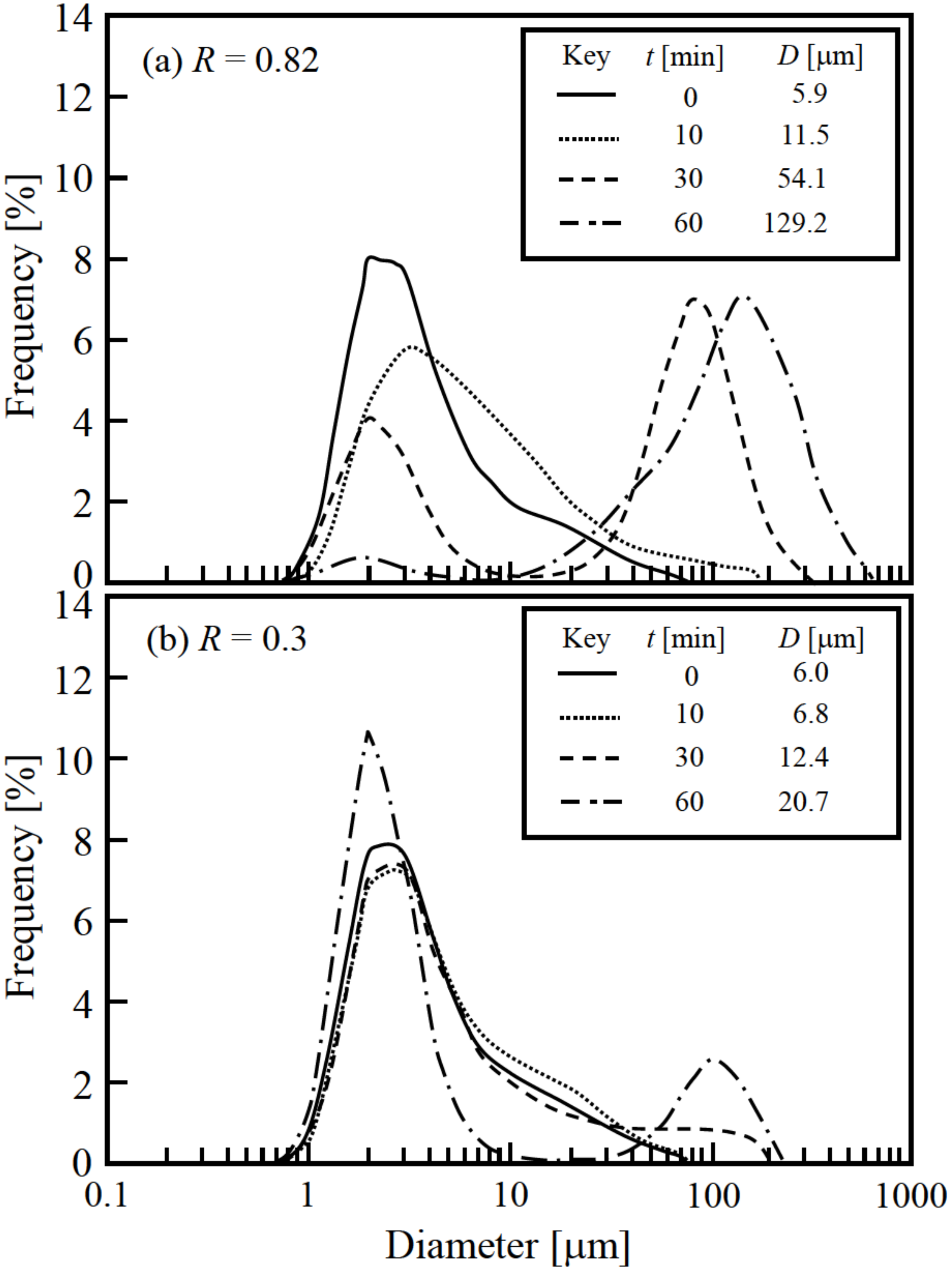

Fig. 6. Typical results of the time course of the oil droplets or their flocs size distribution for R = 0.82 (a) and R = 0.3 (b), respectively. D in the figure legend corresponds to the average diameter.

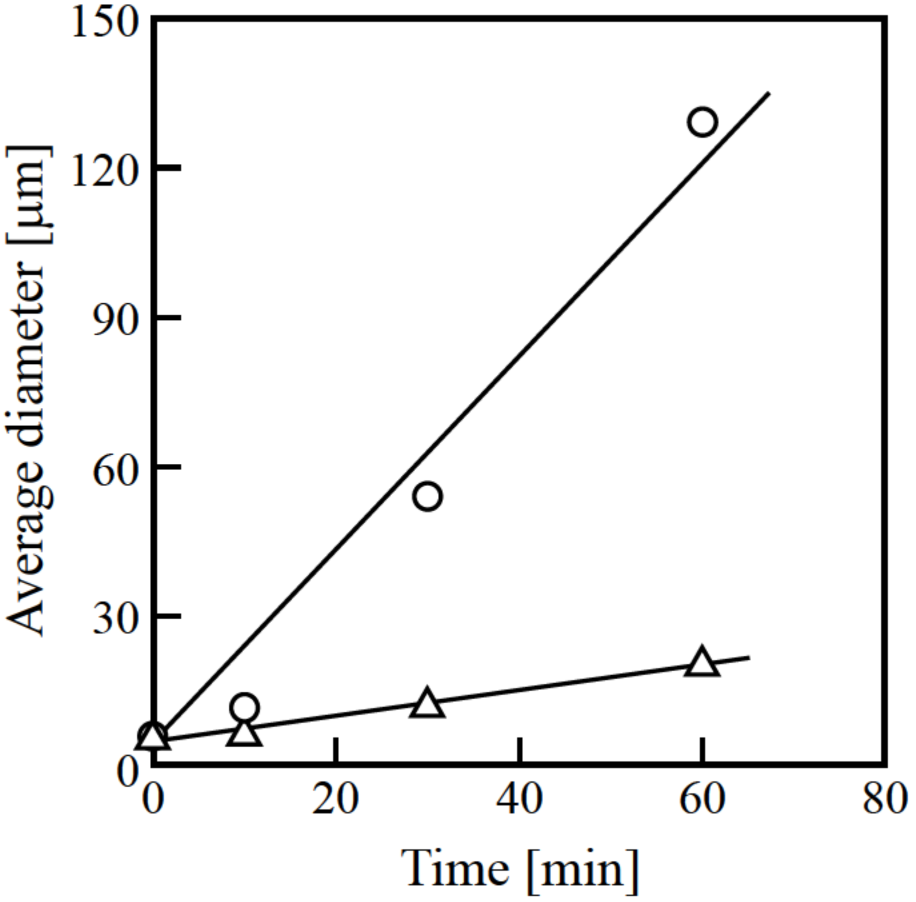

Fig. 7. Typical time course of change in the average diameter of the droplets and their flocs within the flotation column. The average diameter values were obtained from Fig. 6 for R = 0.82 (Fig. 6a) and R = 0.3 (Fig. 6b), respectively.

Table 1
Summary of the column dimensions and the experimental conditions (the initial emulsion volume and the superficial gas velocity).

Emulsion type	I.D. [cm]	V_i [cm^3]	U_g [cm/s] ×10^2
A1	3.2	230	5.0, 9.94, 14.9, 19.9, 24.9
	4.4	400	2.74, 5.48, 10.9, 15.0, 17.5, 21.9, 43.8
	4.4	800	2.74, 5.48, 10.9, 15.0, 17.5, 21.9, 43.8
	8.0	1200	1.39, 2.78, 4.11, 5.47
	8.0	2000	5.47, 9.94, 11.6, 13.2
A2	3.2	230	4.90, 9.90, 19.9
	4.4	400	2.74, 5.48, 10.9, 17.5, 27.4,
	4.4	800	2.74, 5.48, 10.9
	8.0	800	2.75, 5.48
	8.0	2000	9.94, 11.6, 13.2