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Adsorption behavior of methyl palmitate onto silica particle surface

Hideo Maruyama *, Hideshi Seki, Akito Furukawa

Division of Marine Biosciences, Graduate School of Fisheries Sciences, Hokkaido University, Minato 3-1-1, Hakodate 041-8611, Japan

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ABSTRACT

Adsorption behavior of methyl palmitate (MP), as a model substance of biodiesel fuel, onto silica surface in the presence of methanol and toluene was investigated, assuming the dry washing purification of biodiesel production process. Methanol and toluene affected amount absorbed of MP, especially methanol greatly affected amount absorbed of MP. The adsorption model was proposed based on the Langmuir type adsorption and two assumptions for competitive adsorption. The equilibrium adsorption constant, K, and the maximum number of the adsorption sites, X_S, were determined by fitting the data to the proposed model. The proposed model agreed well experimental data. The magnitude of K correlated with the dielectric constant of each substance. The occupied surface area of silanol group estimated from X_S was mostly the same as the reported values. These adsorption parameters were verified experimentally with other conditions.

1. Introduction

From the viewpoints of depletion of fossil fuels, concerns about environmental problems, and effective utilization of biomass resources, biodiesel production has attracted much attention during the past decade as a renewable and environmentally friendly fuel [1,2]. Biodiesel is fundamentally and chemically a fatty acid methyl ester (FAME) and can be produced from animal fat, vegetables, and fish oil, in which the corresponding triglyceride (TG) reacts with methanol in the presence of a catalyst.

Several kinds of oil have been employed for biodiesel production. One of the major resources is vegetable oils, for example, rapeseed oil, palm oil, olive oil, and so on. They have been mostly used from waste oil, which is used frying cooking oil. On the other hand, it has been well known that fisheries wastes, especially viscera of fishes and shells include proteins and lipids. The lipid mainly consists of triglyceride, which includes three fatty acids. For example, the triglycerides extracted from squid liver contain mainly oleic acid (C18:1), palmitic acid (C16:0), docosahexaenoic acid (C22:6, DHA), eicosapentaenoic acid (C20:5, EPA), and so on [3]. EPA and DHA have been used in medicines and health supplements because they are well known to have health-promoting effects. The low-value fatty acids other than EPA and DHA can be utilized as a resource of biodiesel. However, fatty acids of fisheries waste have rarely been used as a resource of biodiesel fuel. Few studies have been reported in two decades. We are proceeding study on the effective utilization of fisheries waste for biodiesel [4].

Several purification methods of crude biodiesel have been proposed [5,6]. Among them, recently wet washing method using water or organic solvent was widely used to purify biodiesel and used to remove impurities [2,5]. This technique can process a large amount of crude biodiesel as an advantage, however, has some disadvantages such as increasing cost and producing high wastewater with high chemical oxygen demand (COD). On the other hand, dry purification (washing) which involves adsorption has also been attempted and has been applied to remove impurities (water, glycerin, methanol, unreacted glycerides, free fatty acid, and so on) or to recover biodiesel (fatty acid alkyl ester). For this purpose, several adsorbents was used in dry washing, for example, silicate [7–10], ion exchange resin [11–13], cellulosic [14,15], activated clay [16], activated carbon [17,18], membranes [19–21] and so on. However, there have been few reports on the direct recovery of biodiesel fuel using the adsorption technique.

Extracted lipid or feedstock oil for biodiesel production is not always dissolved well in all kinds of organic solvent, resulting in dispersing lipid oil droplets in the organic solvent because of the difference in polarity between lipid (triglyceride) and these organic solvents. From an empirical viewpoint, this immiscible property affected mass transfer and kinetics of transesterification of triglyceride. The influence on mass transfer of transesterification has been pointed out by many researchers [22–24] and several methods of mixing lipids (oil) and methanol have been developed and proposed (mechanical mixing [25,26], ultrasonic irradiation [27], and so on).

To solve this problem, the relatively highly polar solvents, such as

* Corresponding author.
E-mail address: maruyama@fish.hokudai.ac.jp (H. Maruyama).

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toluene or benzene, should be added to a solution of the reaction system. The lipid could be hereby dissolved in organic solvents, resulting in enhancing the rate of the esterification reaction. This fact has been well known empirically. In the case of usage of the adsorption method to recovery fatty acids methyl ester, it is necessary to understand the influence of these coexisting substances on the adsorption behavior of the objective substance, that is, fatty acid methyl ester (biodiesel).

Adsorption method as separation technique has well known and has been used in various processes, for example, removal of harmful substances, recovery of useful substances, and so on. Some investigations and attempts have been reported. Molecular sieve X 13 [28], rice hull ash [29], silica gel [29], and activated charcoal [30] were used as adsorbents. These researchers would investigate the adsorption of alkyl methyl ester onto these adsorbents from the viewpoint of their oleochemical interests. However, there are few reports on the adsorption behavior of fatty acid alkyl ester onto adsorbents from the viewpoint of biodiesel fuel recovery and on the influence of coexisting substances on the adsorption behavior of fatty acid methyl ester. It is very important to clarify the adsorption behavior of biodiesel fuel from mixture solvent from the viewpoints of design and operation of the adsorptive separation.

In this study, we conducted adsorption experiments on the assumption of recovery of fatty acid methyl ester (FAME) from the solution after the esterification reaction of triglycerides in the biodiesel production process. Methyl palmitate was employed as a model fatty acid alkyl ester. Silica gel was used as an adsorbent because it is a widely used adsorbent. The adsorbed amounts of the objective substance (methyl palmitate) and the coexisting substances (methanol and toluene) were measured. Based on the obtained experimental results, we proposed the Langmuir type adsorption model considering the influence of the coexisting substances on the adsorption behavior of the subjective substance. We discussed the influence of coexisting substances on the adsorbed amount of methyl palmitate and verified the proposed adsorption model with varying the initial solution conditions.

2. Experimental

2.1. Materials

Silica particle (silica gel 60, diameter distribution 100–210 μm, specific surface area 730 ± 50 m^2/g) as an adsorbent, palmitic acid, hydrogen chloride-methanol (10 wt%) solution, and hexane were purchased from Kanto Chemical Co. Inc. (Japan). Methyl alcohol, toluene, and glycerin were purchased from Fujifilm Wako Pure Chemical Co. (Japan). All purchased reagents were used without further purification.

2.2. Preparation of methyl palmitate

The desired amount of palmitic acid was taken in a 100 mL bottle. A desired amount of toluene was added to the bottle and palmitic acid was dissolved in toluene. An aliquot of hydrogen chloride-methanol (10 wt %) solution was added as a liquid catalyst of the esterification reaction. The bottle was set in a water bath and was heated at 90 °C for 120 min. After open cooling, methyl palmitate (MP) was collected by liquid extraction and was stocked in a refrigerator.

2.3. Procedure of adsorption experiment

All adsorption experiments in this study were conducted with a batch-wise operation. Silica gel particles were washed with distilled water and were dried at 180 °C for two hours in an incubator. After cooling to be room temperature, they were stocked in a desiccator. A certain amount of silica gel was taken in a 100 mL flask with a lid. By pouring a small amount of hexane into the flask, the adsorbent was soaked in hexane and was deaerated by decompression using an aspirator. Predetermined amounts of MP, methanol, and toluene were taken into another glass vessel and were mixed well. The adsorption experiment was started by adding the required amount of the mixed solution to the flask. In most experiments, the liquid volume of the adsorption system was 49.5 mL. It was stirred with a magnetic stirrer for the time necessary to attain the adsorption equilibrium, and then the silica particle was separated from the liquid phase by filtration with a 3 μm membrane filter. The concentrations of toluene, methanol, and methyl palmitate were determined by ultraviolet spectrometry [31], colorimetric spectrometry [32,33] (Jasco V-630, Japan) and, gas chromatography (Shimadzu GC-2014, Japan), respectively. The adsorbed amount of each substance onto the silica surface was determined from the difference between the concentrations in the initial and the equilibrium state.

3. Results and discussion

3.1. Influence of coexisting substances on adsorption of methyl palmitate

We suppose that the adsorption operation is performed after the esterification reaction of triglyceride in a biodiesel production process. Firstly the adsorption experiment was conducted with the same initial mole ratio of methanol (ME), toluene (TL), methyl palmitate (MP), and glycerin. The ratio was employed as 1:1:1:0.33. The reason why we employed this mole ratio is as follows; 3 mol of alkyl methyl ester and 1 mol of glycerin are produced stoichiometrically from 1 mol of triglyceride by the esterification reaction. Also, we conducted the same adsorption experiments without adding glycerin. The results are shown in Fig. 1. As seen in Fig. 1, the adsorbed amount of ME, TL, and MP in both cases were mostly the same, although some scatter could be observed. Glycerin could adsorb onto the silica surface because some investigators have reported the adsorption of glycerin onto the silica surface. In the fixed bed adsorption experiment to refine biodiesel as methyl ester of soybean oil, the saturated adsorption density of glycerin was 1.41×10^{-3} mol/g [34]. For the same aim of biodiesel refining, in the batch adsorption experiment, the saturated adsorption density of glycerin was 2.6×10^{-3} mol/g [35]. In our experimental system, glycerin should adsorb onto the silica surface. However, in the present concentration range and the stoichiometrically restricted condition, it could be considered that the adsorbed amount of glycerin did not affect the adsorbed amount of the other coexisting substances (ME, MP, TL). Therefore, in further experiments, we conducted the adsorption experiments without glycerin.

Fig. 2 shows the influences of the coexisting species, methanol, and toluene, on the adsorbed amount of MP. The initial concentration of MP was 0.1 mol/L. In both results as seen in Fig. 2, the adsorbed amount of MP decreased with increasing the concentrations of coexisting ME or TL. The influence of the concentration of ME greatly affected the adsorbed amount of MP than that of TL. The concentration of existing ME at a lower concentration than that of TL sufficiently affected the adsorbed amount of MP. Thus, it is important to understand how the coexisting species affect the adsorption behavior between each other for stating the adsorption behavior of MP.

The adsorption isotherms of MP, TL, and ME were anew shown in Fig. 3a–c. The initial mole ratio of each substance in the solution was set for MP: TL: ME = 1: 1: 1. Fig. 3d shows the adsorbed amount of all these substances to clarify the difference in the adsorbed amount of each other for comparison. In the equilibrium concentration of ca. 1.6 mmol/L or less, the adsorbed amounts of ME and MP increased abruptly and the adsorbed amount of methanol indicated an extremely higher value than that of TL and MP. In contrast, the adsorbed amount of TL increased slightly. In the equilibrium concentration range of ca. 1.6 mmol/L or more, the adsorbed amount of TL increased largely, on the other hand, the adsorbed amount of MP decreased largely and that of methanol kept the most high-level amount (ca. 5.4 mmol/g). This experimental result should suggest that these variations of the adsorbed amount described above were affected by some competitive adsorptions among methyl

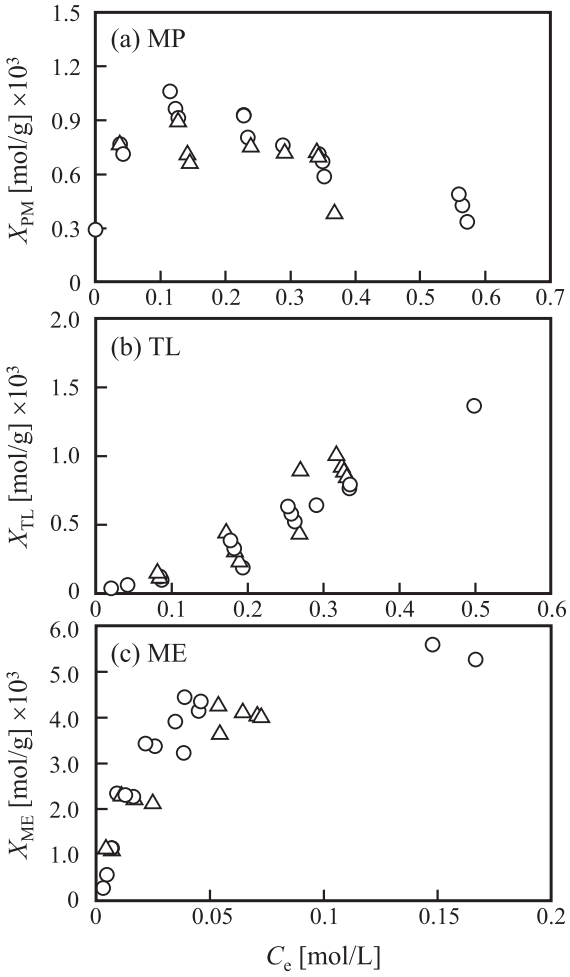


Fig. 1. Influences of glycerin on the amount adsorbed of methyl palmitate (a), toluene (b) and methanol (c) onto silica gel surface. The symbols of open circle and triangle correspond to the results of without and with glycerin in the adsorption systems.

palmitate, methanol, and toluene. The present adsorption model proposed in this study would be explained in the following.

3.2. Competitive adsorption model

Considering the present experimental results described above, we assumed that the following two types of competitive adsorption occurred; (1) competitive adsorption between MP and ME onto the hydrogen atom of the silanol functional group at silica surface; (2) competitive adsorption between MP and TL onto methyl functional group of methanol adsorbed onto silanol group at silica surface. A scheme of two assumptions and these adsorption reactions are shown in Fig. 4. Reactions 1 and 2 correspond to the adsorption of ME onto the silanol group at the silica surface. Reaction 1 represents the binding between the oxygen atom of ME and the hydrogen atom of the silanol group, in addition, reaction 2 represents the binding between the hydrogen atom of ME and the oxygen atom of the silanol group. Reaction 3 represents the binding between MP and the hydrogen atom of the silanol group. We assumed that one of the competitive adsorptions could occur between ME and MP onto the hydrogen atom of the silanol group. Reactions 4 and 5 correspond to the adsorption of TL or ME onto methyl group of ME adsorbed onto silanol group, respectively. We also assumed that the other competitive adsorption could occur between ME and MP onto the methyl group of adsorbed ME. It is well known that the silanol groups exist on the silica surface. Yamauchi and Kondo [36] and Christy

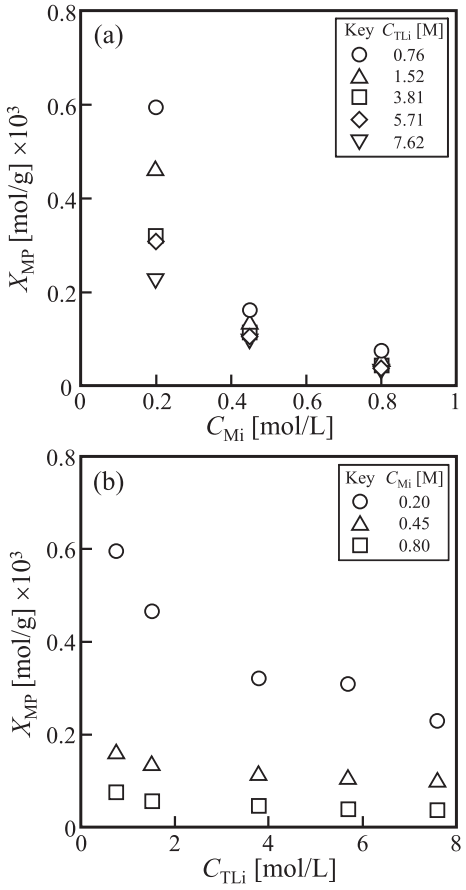


Fig. 2. Influences of the initial concentration of methanol (a) and toluene (b) on the amount adsorbed of methyl palmitate onto silica gel surface.

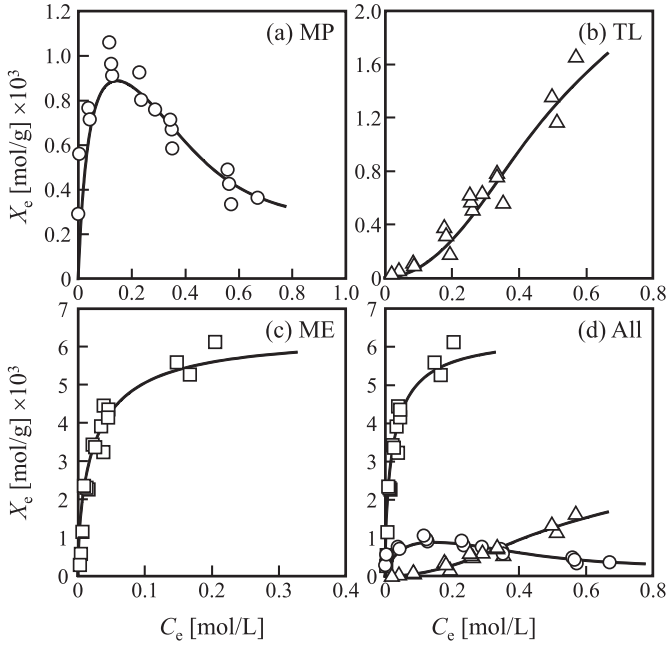


Fig. 3. Adsorption isotherms of (a) methyl palmitate (MP), (b) toluene (TL) and (c) methanol (ME), respectively. Fig. 4d corresponds to the overlay of Fig. 4a, b and c. The initial condition of the mole ratio of each substance in the solution was employed for MP: TL: ME = 1: 1:1. The solid lines are calculated values by fitting of the data to the proposed adsorption model (Eqs. (13)–(15)).

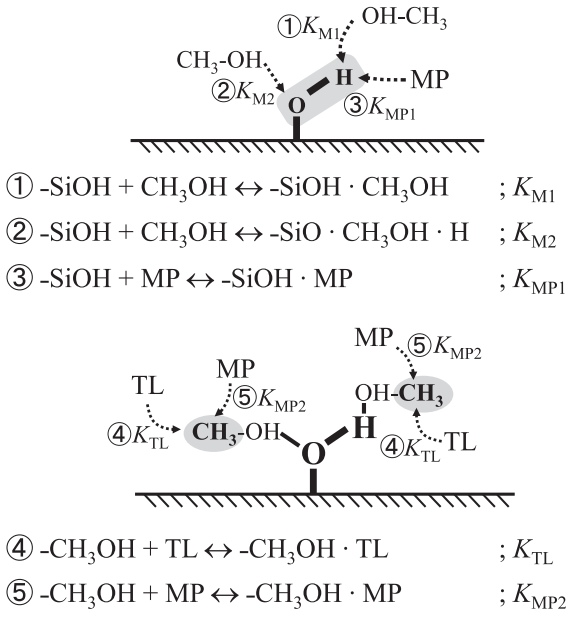


Fig. 4. Schematic drawing of the competitive adsorption mechanism proposed in this study.

[37] reported that methanol could bind with hydrogen or oxygen atoms in the silanol group by hydrogen bond formation. We think that these reports support our assumptions.

Once again, the equations for the adsorption reactions are shown in Eqs. (1)–(5) as follows,

$$-\mathrm{SiOH} + \mathrm{CH_3OH} \leftrightarrow \mathrm{SiOH{\cdot}ME};\ K_{M1} \tag{1}$$

$$-\mathrm{SiOH} + \mathrm{ME} \leftrightarrow \mathrm{SiO{\cdot}ME{\cdot}H};\ K_{M2} \tag{2}$$

$$-\mathrm{SiOH} + \mathrm{MP} \leftrightarrow -\mathrm{SiOH{\cdot}MP};\ K_{MP1} \tag{3}$$

$$-\mathrm{SiOH{\cdot}MeOH} + \mathrm{TL} \leftrightarrow -\mathrm{SiOH{\cdot}Me{\cdot}(TL){\cdot}OH};\ K_{TL} \tag{4}$$

$$-\mathrm{SiOH{\cdot}MeOH} + \mathrm{PM} \leftrightarrow -\mathrm{SiOH{\cdot}Me{\cdot}(PM){\cdot}OH};\ K_{MP2} \tag{5}$$

where, each K represents the equilibrium adsorption constant for each adsorption reaction. From Eqs. (1)–(5), the equilibrium constants for these adsorptions are obtained as follows,

$$K_{MP1} = \frac{X_{MP1}}{(X_S - X_{MP1} - X_{M1})C_{MP}} \tag{6}$$

$$K_{MP2} = \frac{X_{MP2}}{(X_M - X_{MP2} - X_{TL})C_{MP}} \tag{7}$$

$$K_{M1} = \frac{X_{M1}}{(X_S - X_{MP1} - X_{M1})C_M} \tag{8}$$

$$K_{M2} = \frac{X_{M2}}{(X_S - X_{M2})C_M} \tag{9}$$

$$K_{TL} = \frac{X_{TL}}{(X_M - X_{PM2} - X_{TL})C_{TL}} \tag{10}$$

where, X_S represents the maximum adsorption sites existing silica surface, which correspond to the all silanol groups at silica surface. As for MP and TL, The maximum adsorbed amount of both MP and TL is regarded as the same as the amount adsorbed of ME (Eqs. (7) and (10)). The total adsorbed amounts of ME and MP, X_M and X_{MP}, are represented as the following equations, respectively.

$$X_M = X_{M1} + X_{M2} \tag{11}$$

$$X_{MP} = X_{MP1} + X_{MP2} \tag{12}$$

From Eqs. (6)–(10), the adsorbed amounts of each substance at each adsorption site, X, were obtained as follows,

$$X_{MP} = \frac{X_S K_{MP1} C_{MP}}{1 + K_{MP1}C_{MP} + K_{M1}C_M} + \frac{X_M K_{MP2} C_{MP}}{1 + K_{MP2}C_{MP} + K_{TL}C_{TL}} \tag{13}$$

$$X_M = \frac{X_S K_{M1} C_M}{1 + K_{MP1}C_{MP} + K_{M1}C_M} + \frac{X_S K_{M2} C_M}{1 + K_{M2}C_M} \tag{14}$$

$$X_{TL} = \frac{X_M K_{TL} C_{TL}}{1 + K_{MP2}C_{MP} + K_{TL}C_{TL}} \tag{15}$$

By fitting the data to Eqs. (13)–(15) using a least-squares regression, the equilibrium adsorption constants and the saturated adsorbed amount were determined. The calculated lines by using the estimated adsorption parameters are shown in Fig. 3. The solid curves in Fig. 3a–d correspond to these values. Judging from the fact that the data are in good accordance with the model calculation, the adsorption of MP, TL, and ME should be expressed by the proposed adsorption model.

Üstün conducted adsorption experiments by using FAME of tail oil and molecular sieve 13× as an adsorbent in various solvents [28]. In the case of methanol used as a solvent, a maximum adsorbed amount of FAME (fatty acid methyl ester) was ca. 350 mg/g. Damasceno et al. [30] reported adsorbed amounts of relatively short molecular chain (C8, C10, and C12) FAME produced from macauba oil. They used a commercial molecular sieve 13× and activated charcoal prepared from macauba cake remaining after press-defatting macauba fruit kernel. The total adsorbed amount of these FAMEs were 27 mg/g and 1225 mg/g for X13 and the activated charcoal, respectively. As seen in Fig. 3, the maximum adsorbed amount of MP was ca. 0.9 mmol/g, which corresponds to 243.4 mg/g. This adsorbed amount of MP was not especially lower than these reported values in the literature.

3.3. Consideration of the validity of the estimated adsorption parameters

The evaluated values of the adsorption parameters are summarized in Table 1. Comparing the adsorption equilibrium constant, K_{MP1} of MP and K_{M1} of ME, for the hydrogen atoms of the silanol group, the value of K_{M1} was larger than that of K_{MP1}. This suggests that the adsorbed amount of MP decreased as the initial concentration of ME increased because ME is more selective to the hydrogen atom of the silanol group than MP.

The dielectric constants of ME, TL, and MP [38] were also summarized in Table 1. The dielectric constant could become an indicator of the magnitude of polarity. The value of the dielectric constant of methanol is larger than that of toluene. It means that the magnitude of polarity for methanol should be stronger than that for toluene, thus, methanol molecule was tended to adsorb at silanol group than at methyl group, on the other hand, toluene molecule was tended to adsorb at methyl group. Therefore, the relationship between the dielectric constant and the adsorption equilibrium constant was compared. As for the competitive adsorption between ME and MP at the hydrogen atom of the silanol

Table 1
The equilibrium adsorption constants and the maximum adsorbed amount estimated by the proposed adsorption model.

	Methanol		Methyl palmitate		Toluene	
Estimated adsorption parameters	K_{M1} [L/mol]	K_{M2} [L/mol]	K_{MP1} [L/mol]	K_{MP2} [L/mol]	K_{TL} [L/mol]	X_S [mmol/g]
	212	30.7	8.97	0.01	0.61	3.24
Dielectric constant* [F/m]	32.7		3.1		2.4	

* Ref. [38].

group, the equilibrium adsorption constant, K_{M1}, for ME is larger than K_{MP1} for MP. As for the alternate competitive adsorption between TL and MP at methyl group of methanol adsorbed onto silanol group, K_{TL} was larger than K_{MP2} for MP. These relations of the magnitude of the equilibrium constants mostly corresponded to the tendency of the relations of the magnitude of the dielectric constants. These suggest that the relative strength of the adsorption of ME, TL, and MP onto the silica surface was affected by the polarity of these substances.

Takamuku et al. [40] reported that methanol molecules were strongly hydrogen-bonded to the silanol group according to large-angle X-ray scattering measurement and suggested the hydrogen bond has consisted of the binding between the methanol O atom and the H atom of the silanol group. Yoon and Vivek [41] reported the strong adsorption of methanol onto silica surfaces judging from atomic force microscopy measurement. These reports support the present experimental results and our assumption of reaction 1 presented in Fig. 4 (selective adsorption of methanol onto silanol group and the methyl group of adsorbed methanol could be the adsorption site for MP and TL). The proposed adsorption model could evaluate the equilibrium constant as an indicator of the adsorption strength.

We considered the number of the maximum adsorption sites, X_S, as the same as the number of the silanol groups existing at the silica surface. Based on the value of X_S, the occupied area of silanol site, A_{OH}, by using the following equation,

$$A_{OH} = (X_S N_A)/S_m \quad (16)$$

where, N_A and S_m represent Avogadro's number and the specific surface area of silica gel based on unit mass, respectively. The value of S_m was employed the data supplied by the company (Kanto Chemical Co., Inc. Japan) and was 730 ± 50 m^2/g. A_{OH} was calculated as 2.7 OH groups/nm^2. Christy determined the silanol group number per unit area of different silica gel samples with different surface areas, particle sizes, and pore sizes by the deuterium exchange technique. The silanol group numbers were reported to be ranging 2.6–3.5 OH groups/nm^2 [37,39]. These values are listed in Table 2. The average value of silanol numbers reported by Christy is 3.18 OH groups/nm^2. Aoki et al. [42] measured the number of silanol groups on the surface of hydrophilic silica at low water content and reported that it was about 2.5 OH groups/nm^2 at 1 wt % water content. The estimated value of the silanol group derived from X_S is also considered to be a reasonable value.

3.4. Verification of equilibrium adsorption parameters

We verified whether the estimated equilibrium adsorption constants and the number of maximum adsorption sites were adequate for other different initial concentration conditions. Figs. 5 and 6 show the experimental results of the adsorbed amount and the calculation lines when the initial mole ratio of each substance in the solution was set in MP: TL: ME = 1: 1: 0.5 or 1: 1: 1.5, respectively. The solid lines shown in Figs. 5 and 6 represent the calculated values of the adsorbed amount by using Eqs. (13)–(15) with the adsorption parameters determined from the results shown in Fig. 3. The experimental values mostly agreed with the calculated values although some scatters were observed. Moreover, by conducting the adsorption experiments in various cases of the mole ratio of MP, TL, and ME in the initial concentrations, the verification of the equilibrium adsorption constants and the maximum adsorbed amount was confirmed. Fig. 7 shows the comparison of the experimental and the calculated adsorbed amount of MP, TL, and ME in the various mole ratio conditions. The experimental results almost agreed with the calculated adsorbed amounts for MP, TL, and ME, respectively. This suggests that the estimated adsorption parameters were sufficiently adequate values and that the assumptions in the proposed adsorption model were also verified.

Table 2
Comparison of the numbers of the silanol groups at silica surface.

The numbers of the silanol groups [OH groups/nm^2]						
A[a]	B[a]	C[a]	D[a]	E[b]	F[b]	this study
3.1	2.6	2.9	3.0	3.5	3.0	2.72

[a] Ref. [37].
[b] Ref. [39].

Table 3
The initial concentration conditions shown in Fig. 7.

	ME [mol/L]	TL [mol/L]	MP [mol/L]	Mole ratio ME: TL: MP
1	0.05	0.80	0.682	13.6: 16:1
2	0.10	0.80	0.682	6.8: 8: 1
3	0.05	1.59	0.695	13.9: 31.7:1
4	0.10	1.59	0.695	7: 15.9: 1
5	0.05	5.87	0.771	15.4: 117.3: 1

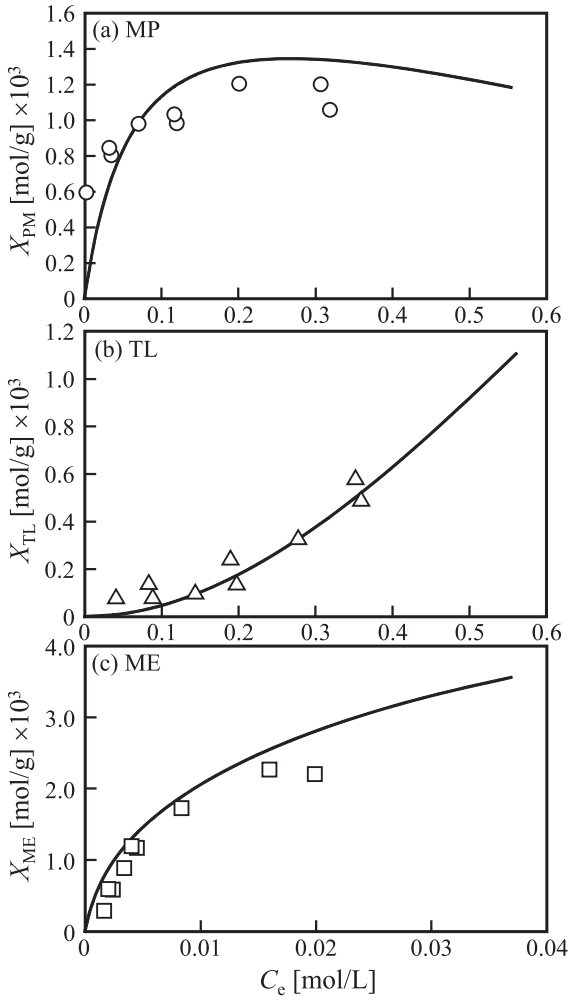


Fig. 5. Verification of the adsorption parameters of the proposed model. The initial concentration condition of mole ratio, ME: TL: MP was 0.5: 1: 1 for adsorption experiment.

4. Conclusions

The influence of coexisting methanol and toluene on the adsorption behavior of methyl palmitate onto silica surface was investigated, assuming the adsorption of diesel fuel from the solution after the reaction in the biodiesel production process. Methyl palmitate was used as a model substance for biodiesel fuel.

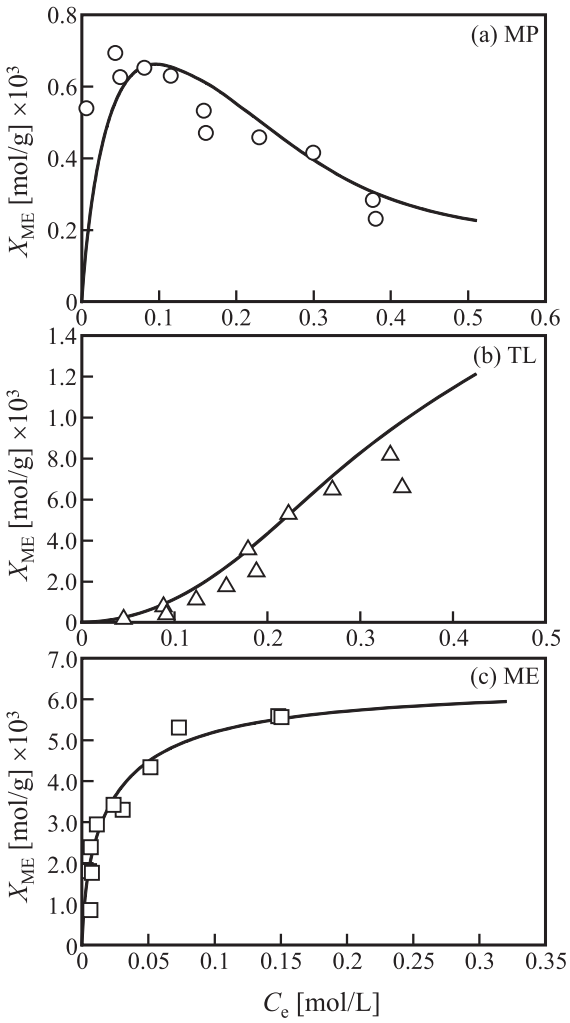


Fig. 6. Verification of the adsorption parameters of the proposed model. The initial concentration condition of mole ratio, ME: TL: MP was 1.5: 1: 1 for adsorption experiment.

Under the experimental condition of the present study, coexisting glycerine did not affect the adsorbed amounts of methyl palmitate, methanol, and toluene in comparison with the case without glycerine. Among the three species, methyl palmitate, methanol, and toluene, methanol was found to have the largest adsorbed amount, in addition, methanol greatly affected the methyl palmitate and toluene adsorption.

For explaining these influences by each other, the adsorption model was proposed based on Langmuir type adsorption and two assumptions for competitive adsorption; (1) competitive adsorption between ME and methanol onto hydrogen atom of silanol group; (2) competitive adsorption between ME and toluene onto methyl group of methanol adsorbed onto silanol group. The proposed model was in good agreement with the experimental results and explained them well.

The estimated adsorption parameters, each equilibrium adsorption constant, K, and the maximum number of the adsorption sites, X_S, were verified with several initial concentration conditions. In these cases, the experimental adsorbed amounts of each substance also agreed well with the calculated those. The magnitude of each K tended to be similar to each dielectric constant of MP, methanol, and toluene in a liquid state. The occupied surface area of a single silanol group estimated from X_S was mostly the same as the reported values in the literature.

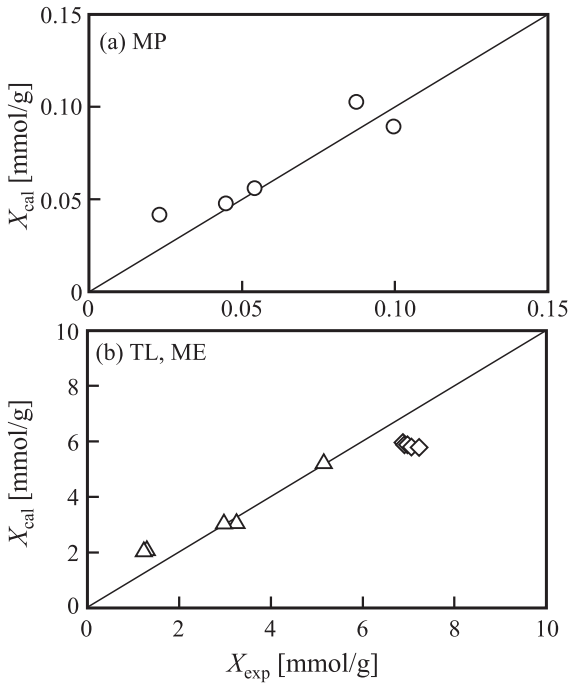


Fig. 7. Comparison of the experimental and the calculated amount adsorbed of MP (open circle), TL (open triangle), and ME (open diamond) at various initial concentration conditions. The experimental conditions are summarized in Table 3.

Notation

A_{OH}	Estimated occupied area of silanol group based on saturated adsorbed amount [groups/nm^2]
C_e	Equilibrium concentration of methanol, toluene, or methyl palmitate [mol/m^3]
C_M	Equilibrium concentration of methanol [mol/m^3]
C_{Mi}	Initial concentration of methanol [mol/m^3]
C_{MP}	Equilibrium concentration of methyl palmitate [mol/m^3]
C_{TL}	Equilibrium concentration of methyl toluene [mol/m^3]
C_{TLi}	Initial concentration of toluene [mol/m^3]
K_{M1}	Equilibrium adsorption constant of methanol binding with hydrogen atom of silanol group [m^3/mol]
K_{M2}	Equilibrium adsorption constant of methanol binding with oxygen atom of silanol group [m^3/mol]
K_{MP1}	Equilibrium adsorption constant of methyl palmitate binding with hydrogen atom of silanol group [m^3/mol]
K_{MP2}	Equilibrium adsorption constant of methyl palmitate binding with methyl group of methanol adsorbed onto silica group [m^3/mol]
K_{TL}	Equilibrium adsorption constant of toluene binding with methyl group of methanol adsorbed onto silica group [m^3/mol]
N_A	Avogadro's number [/mol]
S_m	Specific surface area of silica gel based on unit mass [m^2/kg]
X_M	Total equilibrium adsorbed amount of methanol [mol/kg]
X_{M1}	Equilibrium adsorbed amount of methanol binding with hydrogen atom of silanol group [mol/kg]
X_{M2}	Equilibrium adsorbed amount of methanol binding with oxygen atom of silanol group [mol/kg]
X_{MP}	Total equilibrium adsorbed amount of methanol [mol/kg]
X_{MP1}	Equilibrium adsorbed amount of methyl palmitate binding with hydrogen atom of silanol group [mol/kg]
X_{MP2}	Equilibrium adsorbed amount of methyl palmitate binding with methyl group of methanol adsorbed onto silica group [mol/kg]
X_S	maximum number of silanol groups onto silica gel [mol/kg]
X_{TL}	Equilibrium adsorbed amount of toluene binding with methyl group of methanol adsorbed onto silica group [mol/kg]

Credit authors statement

Hideo Maruyama: Planning the experiments of this research,

Assisting the experiments, Analysis of the experimental data, Writing original manuscript.

Hideshi Seki: Advising experimental method, Discussions about results, Writing-Reviewing and Editing.

Akito FURUKAWA: Running the experiments, Analysis of the experimental data.

Declaration of Competing Interest

The authors declare no conflicts of interest associated with this manuscript.

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