

Effect of solvent polarity and adsorbed water on reaction between
hexyltriethoxysilane and fumed silica

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Abstract

The effects of a solvent on the surface modification progress of fumed silica were investigated. Hexane, toluene, and acetone as the reacting solvent and hexyltriethoxysilane as the surface modifier were used. After a 1 hour reaction at 50°C, the surface modifier density was calculated from the weight loss of the reacted modifier at the silica surface. With a decrease in the solvent polarity (in the order of acetone, toluene, and hexane), the surface modifier density increased. Hexane and toluene have similar solvent polarities. However, behavior of the surface modifier density as a function of the modifier amount was totally different. By considering the solubility of the modifier in the solvents, hexane has a higher solute ability for the modifier than toluene. The reaction between the modifier and silica was promoted in hexane, but not promoted in toluene. In addition to the solvent property, adsorbed water on the silica surface is important for the reaction. In hexane and toluene, the amounts of adsorbed water at the silica surface showed the maximum surface modifier density of about 30 mg and 50 mg, respectively. It can be postulated that the adsorbed water layer could be fixed in hexane while diffused in toluene. Based on these results, it can be concluded that the solvent polarity, solubility of the modifier, and adsorbed water amount at the silica surface should be considered in order to achieve the desired surface modification.

Keywords: fumed silica, surface modification, solvent, adsorbed water, hexyltriethoxysilane, modifier density

1. Introduction

Nano-sized fumed silica has been widely used in many fields, such as cosmetics [1, 2], CMP and electronics [3], sealants and adhesives [4-6], paints and coatings [8-10], silicone rubber [11], toners [12], etc., to improve their functionalities. For these applications, dispersion of the fumed silica in the desired medium, such as organic solvents, polymers, water, etc., is required. However, aggregation of the fumed silica easily occurs, induced by many hydrophilic silanol (SiOH) groups on the silica surface [13]. To obtain such a desired dispersion in organic solvents, affinity control between the silica surface and solvent is effective through surface modification using a modifier such as silane coupling agents and alcohols [14, 15].

Silane coupling agents mostly have one functional group with various physico-chemical properties such as hydrophobic, hydrophilic, polar, non-polar, etc. The other groups are alcoxyde (OR) which turns into SiOH via hydrolysis in the presence of water then forms hydrogen bonds with the SiOH of the silica surface. The functional groups of the modifier should be suitable for the organic solvent. The methods to induce a reaction between these modifiers and the silica surface can be categorized into a gas phase [16, 17], liquid phase [17, 18], and autoclaving [19]. In the liquid phase, the modifier was dissolved in the selected organic solvent. Hydrolysis and condensation are then induced and progress by heating or the addition of a catalyst [20].

In the liquid phase reaction, the surface modification process can occur as follows.

- a) Hydrolysis of modifier occurs with water to form the SiOH group
- b) The hydrolyzed modifier forms hydrogen bonds between its SiOH and the SiOH of the silica surface
- c) Dehydration between SiOH provides the covalent bond

In reaction a), the water necessary for the hydrolysis of the modifier can be adsorbed at the silica surface; reaction b) depends on the stability of the modifier-adsorbed silica in the reaction solvents;

and reaction c) is promoted by heating or a catalyst. The progress of reaction b) could be dominated by the physical properties of the selected solvents such as their polarity, solubility of the modifier, etc.

As a reacting solvent for surface modification via the liquid phase, hexane and toluene are often utilized [21, 22]. These solvents are chemically stable so that there is a low probability to limit the reaction between the modifier and silica surface.

For hydrolysis of the modifier, only a small amount of water, which is at least equivalent molar to the modifier, was necessary. As the silica surface has many SiOHs, a certain amount of water chemically and physically adsorbs which can be controlled by the relative humidity [23]. In hexane and toluene, the adsorbed water on the silica surface could be useful for hydrolysis because extra water in the atmosphere is not going into these hydrophobic solvents. The hexane and toluene seem to be definitely effective reacting solvents for the surface modification, however, the different progress of the reaction between the modifier and solvents has never been investigated in terms of their physical properties.

In this study, the effect of the solvents on the surface modification progress was investigated. As the dispersed silica, fumed silica was chosen because of its nonporous and the surface smoothness. Hexane and toluene were used as low polar solvents. As a comparison, acetone was used as a high polar solvent. The relative permittivity was used as an index of the solvent polarity. Hexyltriethoxysilane was used as a modifier. In addition, the relationship between the amount of adsorbed water at the silica surface and in the reacting solvent was investigated and the optimum water amount was determined for the surface modification.

2. Experimental

2-1. Materials

Hexane (Hex), toluene (Tol), and acetone (Ace) of special chemical grade (Wako Pure Chemical Industries, Ltd.) were used as organic solvents after overnight removal of the dissolved water by dried molecular sieves (3A Wako Pure Chemical Industries, Ltd.). Fumed silica powder was supplied by Nippon Aerosil Co., Ltd., as Aerosil200 (abbreviated A200) with the specific surface area of 200 m²/g calculated by applying the Brunauer-Emmett-Teller (BET) equation [24] to the nitrogen adsorption isotherms. To adjust the amount of water adsorbed on the A200 surface, the A200 was dried under reduced pressure at 180 °C for 2 hours then the A200 was exposed to the various relative humidities (RH) of 42.8, 68.8, and 92.0 % for one week at 25 °C by the corresponding saturated salt solutions of K₂CO₃, KI, and KNO₃ (Wako Pure Chemical Industries, Ltd.), respectively [25-28]. The amounts of water at for 2g of the A200 surface were determined to be as 30, 50, and 190 mg, respectively. As a the surface modifier agent, hexyltriethoxysilane (HTES, CH₃(CH₂)₅Si(OCH₂CH₃)₃, Tokyo Chemical Industry Co., Ltd.) with a hydrophobic chain was used.

2-2. Surface modification

The A200 (2.0 g) samples with the controlled adsorbed water were dispersed in the dehydrated solvents (150 ml) containing 0.3 - 4.2 ml/g of dissolved HTES. The suspensions were stored at 50 °C for 1 hour. The treated A200 samples were separated by centrifugation and dried under reduced pressure at 80 °C for 2 hours.

2-3. Characterizations

How many CH₃(CH₂)₅Si (-C₆) groups of HTES introduced on the A200 surface was determined using thermogravimetric and differential thermal analysis (TG-DTA, Thermo Plus 8120, Rigaku Co.,

Ltd.) as shown in Fig. 1. The measurement was carried out under air. The value was calculated from the difference in the weight loss between modified sample (W_{CH}) and unmodified sample (W_{OH}). Described as the surface HTES density were determined by the following equation (1) [29, 30].

$$d_A (-C_6/nm^2) = \frac{(\Delta W_{CH} - \Delta W_{OH}) N_A}{M_w S_{N_2}} \times 10^{-18} \quad (1)$$

where d_A is the surface density ($-C_6/nm^2$), M_w is the the molecular weight of the modifier, S_{N_2} is the BET specific surface area measured from the nitrogen adsorption isotherm, and N_A is Avogadro's number. ΔW_{CH} and ΔW_{OH} are the weight loss of the modified and unmodified A200 measured by thermogravimetric and differential thermal analyse, respectively.

3. Results and discussion

To investigate the effect of the solvent polarity on the surface HTES density, the A200 sample with 30 mg of adsorbed water was treated in each solvent at 50 °C for 1 hour. The relative permittivities (ϵ/ϵ_0) of Hex, Tol, and Ace were 1.88, 2.38, and 20.7, respectively [32, 33]. Fig. 2 shows the surface HTES density as a function of the added amount of HTES from 0.3 to 4.2 ml/g in (a) Hex, (b) Tol, and (c) Ace. In the order of Hex, Tol, and Ace (i.e., with an increase in ϵ/ϵ_0), the surface HTES density increased. In Hex, the surface HTES density was almost constant at about 0.3 ($-C_6/\text{nm}^2$) for the amount of HTES, while in Tol, it increased with an increase in the HTES amount. In Ace, it showed a low and constant value of about 0.1 $/\text{nm}^2$.

Ace is a polar solvent, therefore, the reaction between HTES with the non-polar C_6 group and the polar A200 surface is not promoted in Ace. Tol and Hex can be categorized as hydrophobic solvents being non-polar. The affinity of A200 for both Tol and Hex is low. HTES molecules can work as stabilizers for A200 adsorbing on the A200 surface. However, from Fig. 2, the behavior of the surface HTES density with the HTES amount was totally different.

During the surface modification process, the following reactions can be generated; a) hydrolysis of HTES occurs with water to form the silanol (SiOH) group, b) the hydrolyzed HTES forms a hydrogen bond between its SiOH and SiOH of the A200 surface, and c) these SiOHs dehydrate to form a covalent bond. In reaction a), the water necessary for the hydrolysis of HTES can be adsorbed water at the A200 surface, reaction b) depends on the stability of the A200 adsorbed by HTES in the reaction solvents, and reaction c) is promoted by the heating process [34-37].

The physical properties of the solvents affect the progress of the reaction b). Except for ϵ/ϵ_0 , the solubility of HTES in the solvents can be obtained. In a good solvent for the HTES, HTES can easily move toward the A200 surface. That is, the solubility parameter (SP) value between HTES and the solvents should be close.

Table 1 shows the SP values of Hex and Tol, the difference of the SP value between the solvents and before/after the hydrolyzed HTES. The SP value difference of Hex with HTES was as low as 0.63 while for both Tol at 1.23 and Ace at 1.26 showed a two times higher values than that of Hex. It seems that Tol has a lower solubility power than Hex which is derived from the pi bond in Tol and not in HTES. On the other hand, the solubility of the hydrolyzed HTES becomes worst in Hex and also low in Tol and Ace, because there are polar SiOHs in the HTES molecules.

The adsorbed water at the A200 surface corresponding to the RH of 42.8 % is 30 mg. It seems that this is the sufficient amount to hydrolyze 0.3 ($-C_6/nm^2$) HTES at the A200 surface (Fig. 2(a)). The adsorbed water at A200 in Hex could be fixed like a “layer” because Hex and water are immiscible. The solute HTES in Hex tends to stabilize the polar A200 surface by adsorbing the alcoxyl group. Once the alcoxyl group of HTES attaches the adsorbed layer on the A200, the hydrolyzed HTES forms a hydrogen bond with the A200 surface. The 0.3 ml/g as the lowest added amount of HTES (Fig. 2) corresponds to 2.8 SiOH/ nm^2 on the A200 [30], nonetheless, the actual surface HTES density was only 0.3 ($-C_6/nm^2$). This could be due to the steric hindrance of the C6 groups of the modified HTES.

Unlike Hex, Tol has a slight water miscibility of 0.067 wt% (at 23.5 °C) [38]. Therefore, the adsorbed water layer on the A200 can be diffused into Tol to form a “diffused layer” near the A200 surface. The solubility of HTES without the pi bond is relatively lower in Tol than in Hex. Despite this, if HTES is added to Tol, HTES works as a stabilizer for A200. When HTES reaches the diffused layer, hydrolysis of the HTES progresses step by step with a small amount of water. Because the solubility of the hydrolyzed HTES in Tol is low, it moves to the silica surface to form hydrogen bonds. The reason why that surface HTES density increased with an increase in the HTES amount (Fig. 2(b)) can be derived due to the low solubility of HTES in Tol [39].

As these factors affect the progress of the surface modification, the amount of adsorbed water on

the A200 can be determined. Effects of the adsorbed water amount on the surface HTES density in Hex or Tol were investigated. Fig. 3 shows the surface HTES density of the 42.8~90.0 % RH controlled A200 in (a) Hex and (b) Tol. The reaction was conducted at 50 °C for 1 hour. In this figure, 0 mg means the modified A200 without RH control just after drying under reduced pressure at 180 °C for 2 hours. It seems that the weight of the adsorbed water which provides the maximum surface HTES density is different between in Tol and Hex. In Hex, the surface HTES density was 0.12 (-C₆/nm²) without RH control and it showed the maximum value of 0.37 (-C₆/nm²) with 30 mg adsorbed water. It Then decreased to 0.20 (-C₆/nm²) with the increase in the weight of the adsorbed water to 190mg. While in Tol, with an increase up to 30 mg, it remained almost constant at 0.17 (-C₆/nm²), reached the maximum of 0.47 (-C₆/nm²) at 50 mg of adsorbed water, then it decreased.

As already described, 30 mg adsorbed water seems to be enough for hydrolysis of 0.3 (-C₆/nm²) HTES. With an increase in the weight of the adsorbed water, the “adsorbed water layer” on the A200 in Hex seems to increase in thickness. The hydrophilicity of A200 with a thick water layer becomes high and the affinity with Hex becomes low. The alkoxy groups of HTES approached the “adsorbed water layer” on the A200 and were hydrolyzed. However, the hydrolyzed HTES could not contact the A200 due to of the thickness of the “adsorbed water layer”. Additionally, the solubility of the hydrolyzed HTES in Hex is low which resulted in preventing of hydrolysis and modification.

The adsorbed water layer on the A200 in Tol is diluted by Tol. To hydrolyze HTES, which reaches the “diffused water layer” of A200, it needs more water than 30 mg. Accordingly 50 mg could be the proper amount. With the increase in weight of the adsorbed water, the diffused layer thickness increases. Similar to the reaction in Hex, the solubility of the hydrolyzed HTES in Tol is low and the thick water layer prevents approach of HTES to the A200 surface. Therefore, the surface modification of HTES is not promoted as shown in Fig. 3(b).

Zheng Yang reported that preferential adsorption of the Tol vapor at the silica surface occurs

when silica was exposed to the Tol and Hex vapor mixture due to the interaction between polar structures derived from the pi bond in the Tol molecules and SiOH in the silica surface [40]. In this experiment, the effect of Tol in the diffused water layer on the A200 surface was investigated. Fig. 4 shows the surface HTES density of A200 prepared in different Hex/Tol mixtures with 100/0, 75/25, 50/50, 25/75, and 0/100 volume ratios. The adsorbed water of A200 was controlled at 42.8 % RH and reacted at 50 °C for one hour, thus the addition of the HTES amount of 3.0 ml/g was selected.

In Hex (100/0), the surface HTES density was shown to be 0.37 ($-C_6/nm^2$) and it decreased to 0.11 ($-C_6/nm^2$) for the Hex/Tol=75/25. With an increase in the Tol ratio, it remained almost constant at around 0.11/ nm^2 ($-C_6/nm^2$) though it slightly increased. In Tol (0/100), the surface HTES density was then 0.20 ($-C_6/nm^2$). Based on these results, it clearly indicated that Tol prevents progress of the reaction between HTES and the A200.

Whether Tol adsorbs on the A200 surface due to the existence of Tol in the reaction media was investigated. A certain amount of Tol was added to Hex where the A200 was dispersed. The suspension was heated at 50 °C for 1 hour in the same way as the surface modification process. Based on a GC-MS analysis, the adsorption of Tol on the A200 surface was confirmed at 300 °C.

As already described, in Hex, the hydrolysis of HTES occurs when HTES reaches the water adsorbed “layer” of the A200. When Tol was added to Hex at 75/25, Tol approaches the water layer due to its slight water miscibility to form a “diffused layer”. It can be said that A200 with a diffused layer was dispersed in the Hex/Tol mixture. Tol molecules in the diffused layer gradually approach the A200 surface and adsorb at the SiOH of A200 which prevents HTES from forming hydrogen bonds with the SiOH of A200. In addition, HTES before hydrolysis dissolves in a sufficient amount of Hex in the mixture, therefore, the hydrolysis of HTES is not promoted. Consequently, the surface HTES density decreased.

Even if the Tol ratio increases (50/50 and 25/75), the thickness of the diffused layer does not

remarkably change and the the surface HTES density did not increase. In Tol (0/100), the solubility of HTES before hydrolysis in Tol is low. HTES rather hydrolyzes using water at the diffused water layer of the A200 than dissolves in the Tol. Consequently, the surface HTES density in Tol increases compared to that in the Hex/Tol mixture.

Conclusion

Effects of the physical properties of a solvent and amount of adsorbed water on the A200 on the surface HTES density were investigated.

a) With an increase in the solvent polarity in the order of Hex, Tol, and Ace, the the surface HTES density decreased. The difference in the surface HTES density in Hex and Tol, which have a similar polarity, can be derived from the low solubility of HTES in Tol.

b) The maximum the surface HTES densities in Hex and Tol were shown with different RHs controlled at 42.8% (weight of adsorbed water is 30 mg) and 68.8% (weight of adsorbed water is 50 mg), respectively. In Hex, the water adsorbed layer on the A200 can be fixed like a “layer”, while in Tol, the layer can be diffused with Tol as a “diffused layer”. For hydrolysis of the HTES, it needed more water in Tol than in Hex.

c) Tol in the diffused layer tends to adsorb at the SiOH of the A200. Therefore, the hydrolysis of HTES does not approach the A200 surface and the reaction between HTES and the A200 is not promoted.

Based on these results, in addition to $\varepsilon/\varepsilon_0$ between the modifier and solvent, the solubility of the modifier in the solvent before/after hydrolysis, the amount of water adsorbed at the particle surface should be considered for control of the surface modification progress.

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Table 1 (a) Solubility parameter (SP) of Hex and Tol, (b) SP difference between solvents and HTES, and (c) SP difference between solvent and hydrolyzed HTES [30].

Solvent	(a) Solubility Parameter (SP)	(b) $\Delta\sigma(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_6\text{H}_{12}$	(c) $\Delta\sigma(\text{OH})_3\text{SiC}_6\text{H}_{12}$
Hexane	7.28	0.63	5.11
Toluene	9.14	1.23	3.25

Figure captions

Fig. 1 Estimation of the number of HTES (C6) groups introduced onto the A200 surface from thermogravimetric analysis (TG) differential thermal analysis (DTA) (a) DTA curve for modified A200, (b) TGA curve for modified silica, (c) TGA curve for unmodified A200

Fig. 2 Surface HTES density in (a) Hex, (b) Tol, and (c) Ace as a function of added HTES amount.

Fig. 3 Effects of various weights of adsorbed water on silica surface which were controlled at RH of 42.8, 68.8, and 90.0 % for A200 reacted in (a) Hex and (b) Tol on surface HTES density.

Fig. 4 Effects of different Hex/Tol volume ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 on surface HTES density.

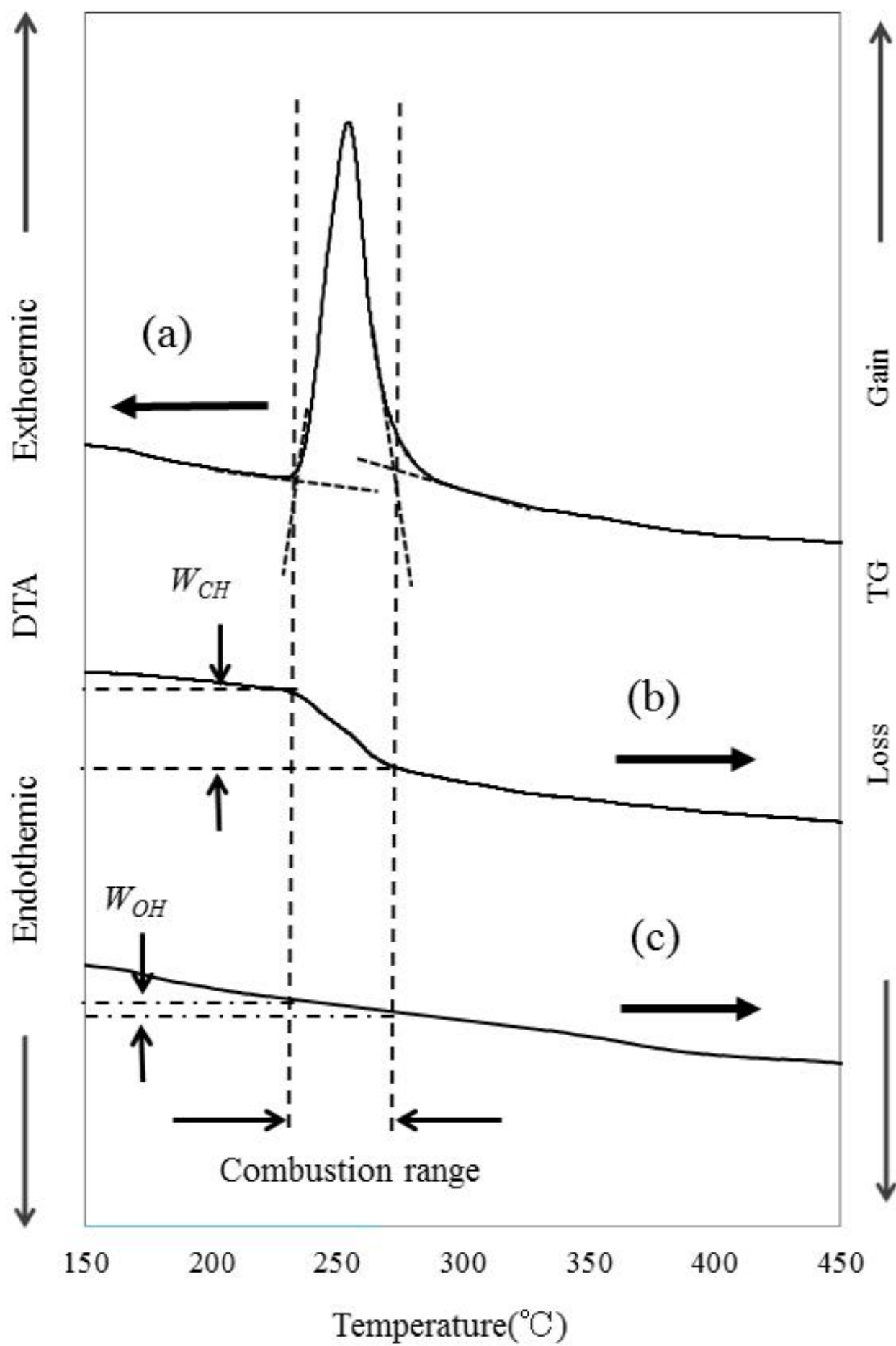


Fig.1

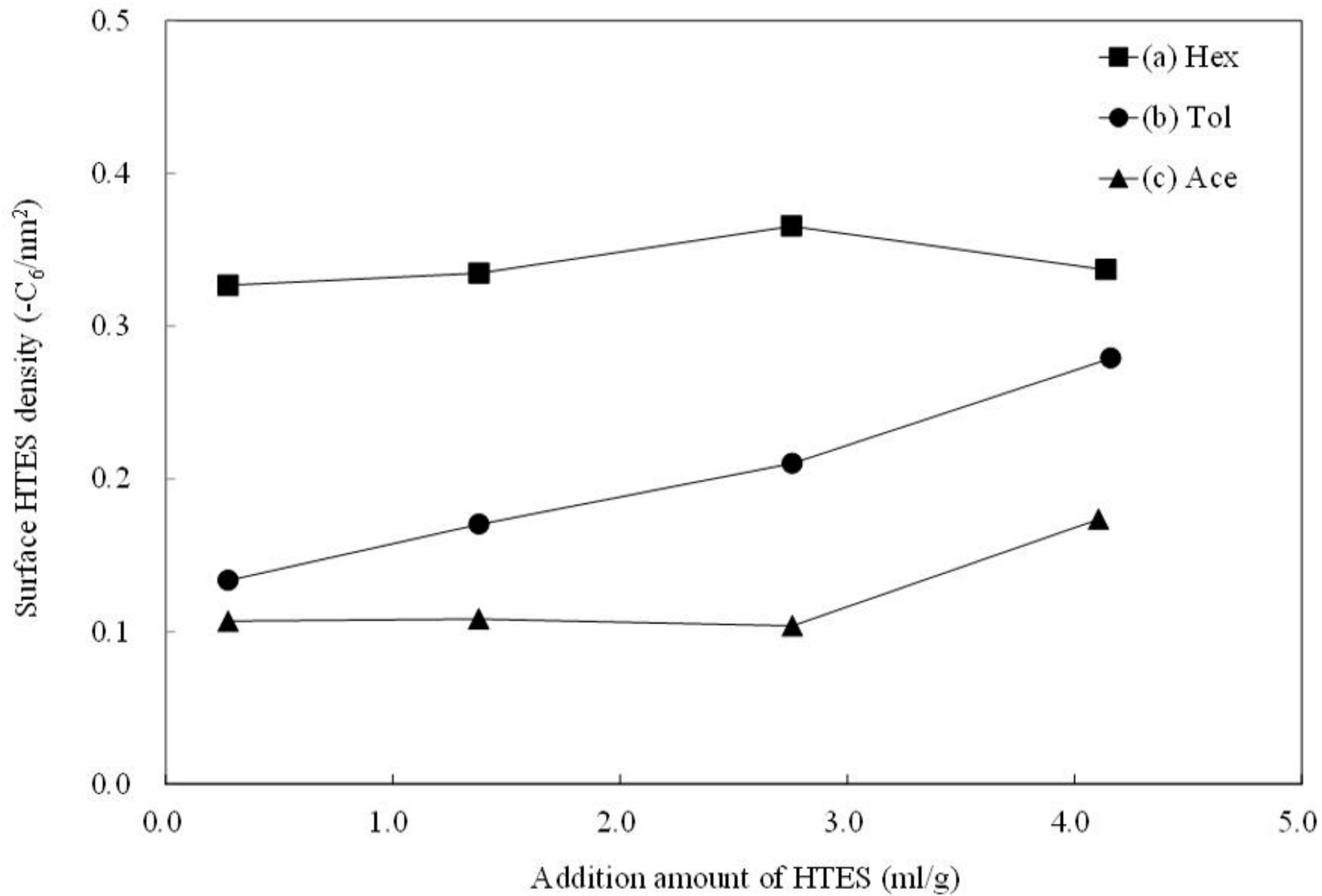


Fig.2

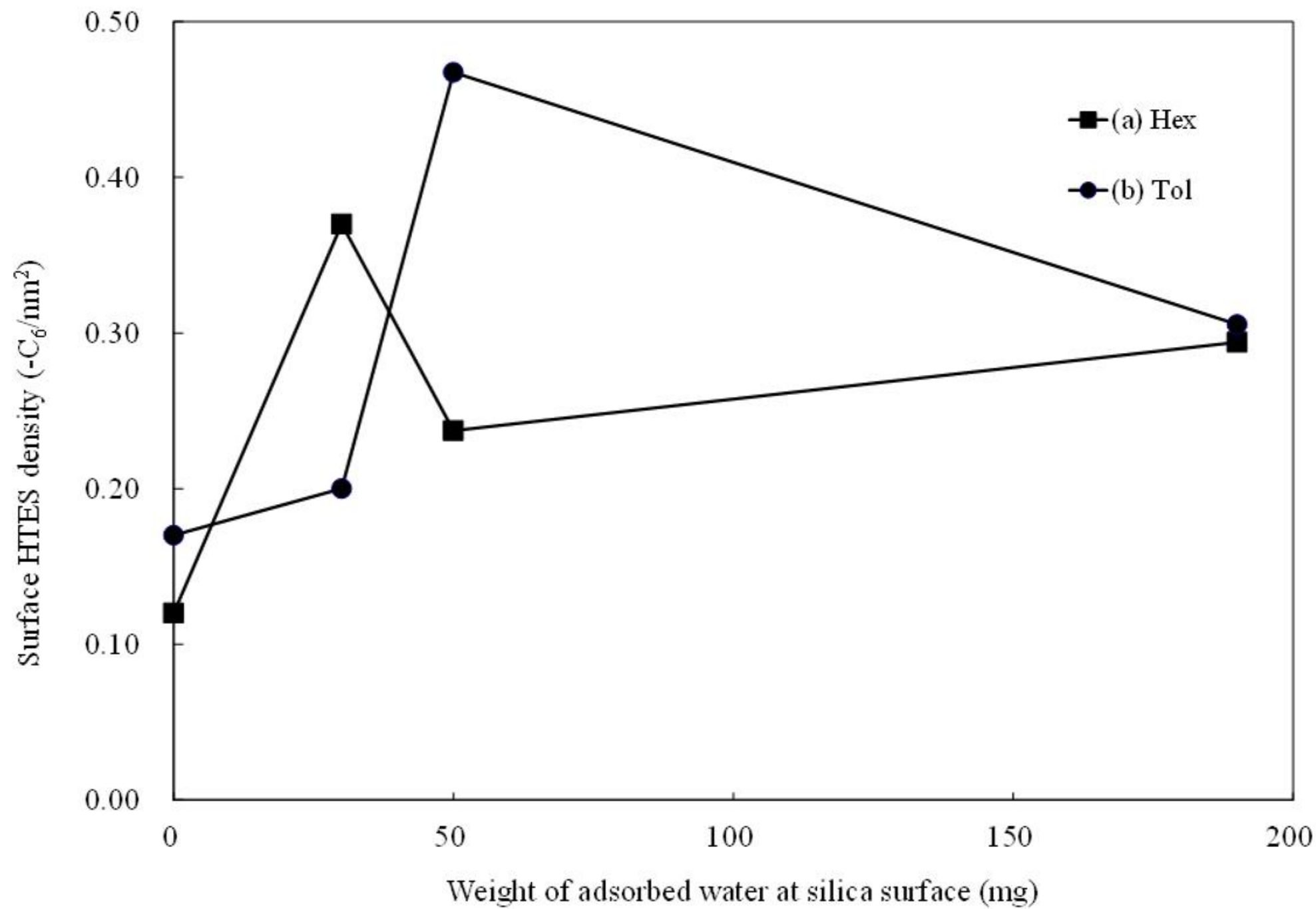


Fig.3

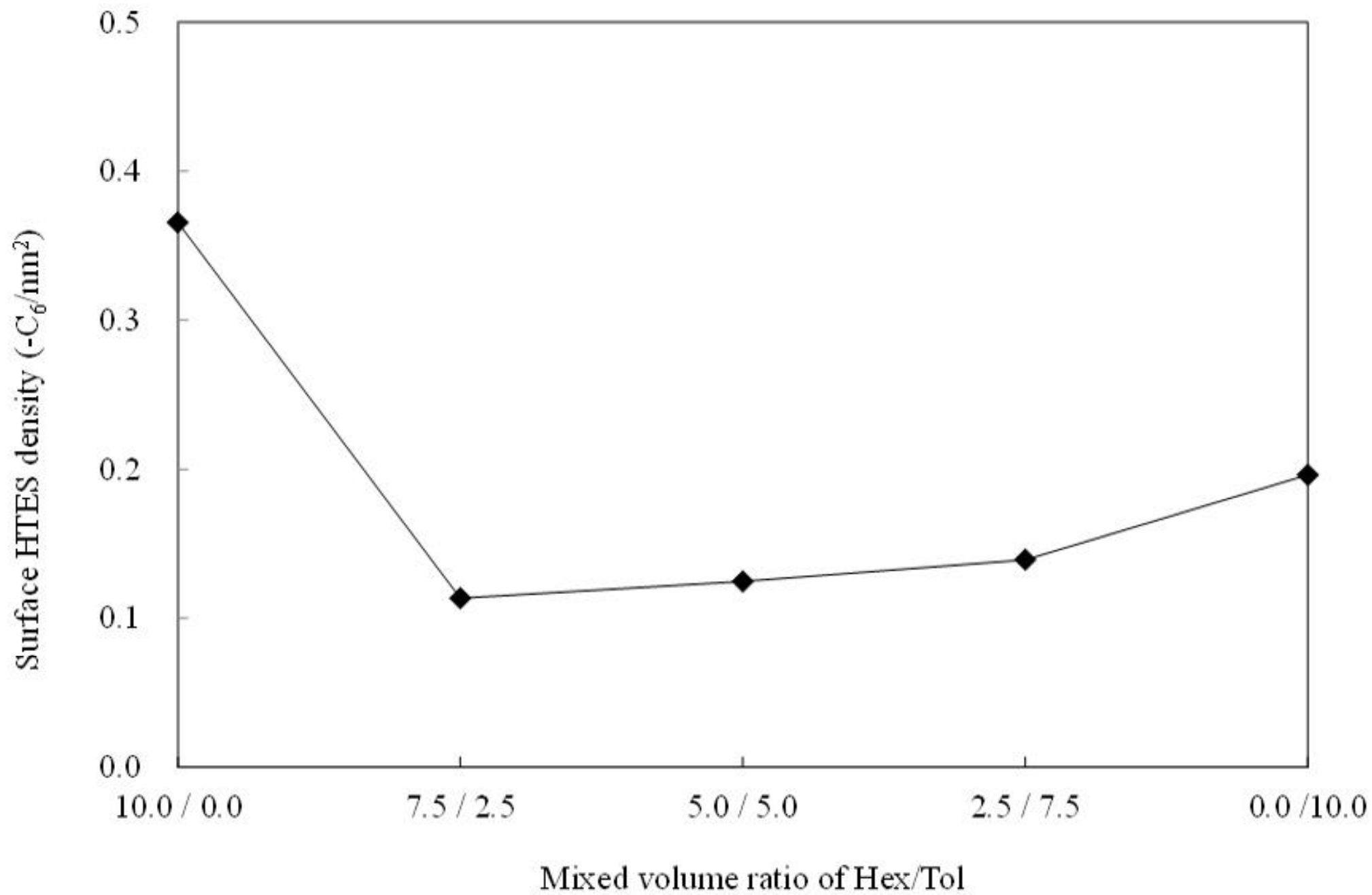


Fig.4