

# Fabrication and Photochromism of Langmuir-Blodgett Films Composed of Polyoxometalate Anions and n-Alkylamines

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**Abstract:** Polyoxometalate anions possess some opto-electronics functionality, such as electrochromism, photochromism and so on. The composite films in that these anions were ordered with long-chain alkylamines, were made up using Langmuir-Blodgett technique. The film built up from vanadate anion ( $[V_4O_{12}]^{4-}$ ) and  $CH_3(CH_2)_{18}NH_2$  was accumulated at pH ranging from 8.0 to 9.8, and another film composed of heptamolybdate anion ( $[Mo_7O_{24}]^{6-}$ ) and n-alkylamine ( $CH_3(CH_2)_{18}NH_2$ , or  $CH_3(CH_2)_{21}NH_2$ ) was prepared from 5.8 to 6.3. These films were characterized by X-ray diffraction analysis, infrared spectroscopy. After irradiating u. v. light to them for 12 h, change in color was measured by ultraviolet-visible spectroscopy. The films of vanadate and molybdate anions were observed photochromism at 500 nm and 350 nm respectively.

**Key words:** Polyoxometalate, n-Alkylamine, Langmuir-Blodgett, composite film, photochromism

## 1. INTRODUCTION

Langmuir-Blodgett (LB) technique is more effective methods to form artificially molecular assemblies under mild condition. Using the technique, we have studied on fabrication of multilayer films composed of inorganic/organic molecules, such as (clay unit layers)/alkylamines [1], (metal oxalates)/alkylamines and so on.

Polyoxometalate are receiving increasing interest in materials science owing to their chemical structural, and electronic versatility [2]. At the application of polyoxometalates to molecular electronics and opto-electronics, the films consisting of well-ordered polyoxometalates with organic molecules have been tried to prepare by LB technique recently [3-4].

We chose  $[V_4O_{12}]^{4-}$  and  $[Mo_7O_{24}]^{6-}$  from many kinds of polyoxometalate anions (Fig. 1). Here we describe optimum conditions for fabrications of two composite films of  $[V_4O_{12}]^{4-}/C_{19}H_{39}NH_2$  and  $[Mo_7O_{24}]^{6-}/(C_{19}H_{39}NH_2$  or  $C_{22}H_{45}NH_2)$ . We also show the photochromic behaviors of their films [5].

## 2. EXPERIMENTAL PROCEDURES

$[(CH_3)_5CNH_3]_4[V_4O_{12}]$  was synthesized accordingly to

literature [6].  $C_{22}H_{45}NH_2$  was prepared from  $C_{22}H_{45}Br$  using  $NaN_3$  [7]. All commercial compounds, such as  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (Wako Pure Chemical Industries, LTD),  $C_{19}H_{39}NH_2$  (Tokyo Kasei Kogyo Co., LTD), and so on, were used without further purification.

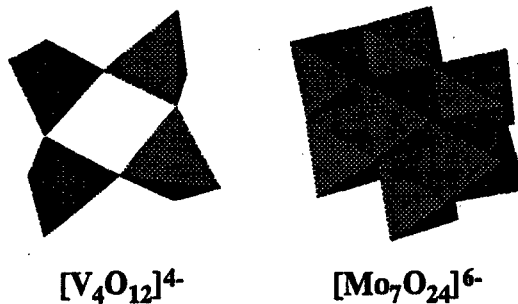


Fig.1 Polyhedral structural model of (a)  $[V_4O_{12}]^{4-}$  and (b)  $[Mo_7O_{24}]^{6-}$

The composite films were obtained at room temperature by a vertical lifting method. Solution dissolved  $[V_4O_{12}]^{4-}$  or  $[Mo_7O_{24}]^{6-}$  in distilled water was used as a subphase, and pH-values were adjusted with 1N NaOH. N-alkylamines were dissolved in benzen (concentration ca.  $2.0 \times 10^{-3}$  M). Maintaining the subphase ( $1000 \text{ cm}^2$ ) of a Kyowa Interface Science trough at  $16 \sim 18^\circ\text{C}$ ,  $200 \mu\text{l}$  of the spreading solution was dropped by

a microsyringe onto its surface. After evaporation of Benzen for 20 min, a monolayer on which polyoxometalate anions deposited was compressed by a barrier at a rate of 20 cm<sup>2</sup>/min to a surface pressure (20–30 dyne/cm). The monolayer was transferred onto hydrophilic silica or glass substrate, keeping the surface pressure. Dipping speed was generally set to 0.5–1.0 cm/min.

Infrared spectroscopy (IR) was used to monitor as to whether polyoxometalate anions were incorporated in the composite film. IR spectra were recorded on IR-460 Shimadzu spectrometer. X-ray diffraction was also used to study the structures of the films composed of polyoxometalate anions and long-chain alkylamines. X-ray diffraction experiments ( $\theta$ -2 $\theta$  scans) were performed with XD-610 Shimadzu X-ray powder diffractometer.

The color change of the films irradiated with u. v. light for 12h, was observed by UV-265 Shimadzu u. v. – visible recording spectrophotometer. Mercury lamp (NEC GL-15) was used as the source of u. v. light.

### 3. RESULTS AND DISCUSSION

#### 3.1 [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup>/C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub>

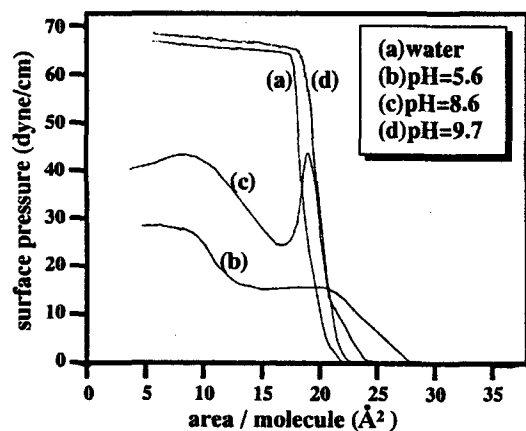


Fig. 2 Surface pressure - area isotherm ( $\Pi$ -A) curves of monolayers spreaded C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> on distilled water (a) and subphases of  $5 \times 10^{-6}$  M ((CH<sub>3</sub>)<sub>3</sub>CNH<sub>3</sub>)<sub>4</sub>V<sub>4</sub>O<sub>12</sub> solutions at various pH-values.

A [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> anion is in the pH-range 5.5–9.7.  $\Pi$ -A curves at different pH-values, for monolayers of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> spread on water and a subphase of  $5 \times 10^{-6}$  M [(CH<sub>3</sub>)<sub>3</sub>CNH<sub>3</sub>]<sub>4</sub>[V<sub>4</sub>O<sub>12</sub>] are shown in Fig. 2. As shown in Fig. 2, the isotherms depend upon the pH. A floating layer ([V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup>/C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub>) was dissolved in the subphase at pH 5.6. On the other hand, the  $\Pi$ -A curve at pH 9.7 was similar to it of the C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> layer on water. It is explained that [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> anions were hardly deposited

below the monolayer due to deprotonating it at high pH. Consequently the pH-range preparing the composite film is ca 8.0–9.0. At pH 8.6, surface pressure sharply went up to about 20 A<sup>2</sup> and then rapidly decreased to collapse the floating layer. [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> anions which bind to C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> got near each other by compression of the floating layer, and then formed the inorganic layer by dehydration and condensation.

Fig. 3 shows IR spectra of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> and the floating layer ([V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup>/C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub>) at pH 8.6. In comparison with IR spectrum of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub>, a few bands are observed below 1000 cm<sup>-1</sup> in it of the floating layer. Their bands are due to symmetric stretching of V-O<sub>1</sub> (V(O)<sub>2</sub>) at 935 and 890 cm<sup>-1</sup>, and asymmetric stretching of V-O<sub>5</sub>-V at 640 cm<sup>-1</sup> for tetrameric anion [3]. Besides V-O stretching of monomer anion (VO<sub>4</sub><sup>3-</sup>) was not observed at 1090 and 1050 cm<sup>-1</sup> in it. The depositing species below the monolayer of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> at pH 8.6, was clearly [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup>.

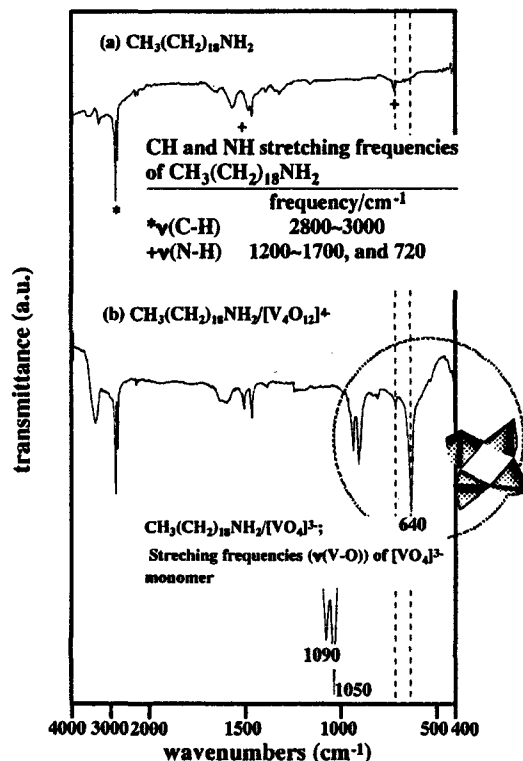


Fig. 3 IR spectra of CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>NH<sub>2</sub> (a) and the monolayer spreaded CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>NH<sub>2</sub> on the  $5 \times 10^{-6}$  M [(CH<sub>3</sub>)<sub>3</sub>CNH<sub>3</sub>]<sub>4</sub>[V<sub>4</sub>O<sub>12</sub>] aqueous solution at pH 8.6 (b).

Table I d(001)-values of the film of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub> and the composite film of C<sub>19</sub>H<sub>39</sub>NH<sub>2</sub>/[V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup>.

	d(001) / Å
C <sub>19</sub> H <sub>39</sub> NH <sub>2</sub>	54.2
C <sub>19</sub> H <sub>39</sub> NH <sub>2</sub> /[V <sub>4</sub> O <sub>12</sub> ] <sup>4-</sup>	57.5

$d(001)$ -value of the film composed of  $[V_4O_{12}]^{4-}$  and  $C_{19}H_{39}NH_2$  was shown in Table I, and was 56.1 Å.  $[V_4O_{12}]^{4-}$  was sandwiched with  $C_{19}H_{39}NH_2$  (27.6 Å).

### 3.2 $[Mo_7O_{24}]^{6-}/C_{19}H_{39}NH_2$ and $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$

$\Pi$ - $A$  curves for monolayers of  $C_{19}H_{39}NH_2$  on water and  $7 \times 10^{-6}$  M  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  solutions at various pH are shown in Fig. 4. As shown in Fig. 4, the pH-value transferring onto a hydrophilic substrate is at around 6.3. However  $[Mo_7O_{24}]^{6-}$  is unstable at the pH. Because  $[Mo_7O_{24}]^{6-}$  is in the pH-range 4.0~6.0. However, at the low pH, a floating layer ( $[Mo_7O_{24}]^{6-}/C_{19}H_{39}NH_2$ ) was sunken into the solution. Consequently,  $C_{22}H_{45}NH_2$  which was more hydrophobic compared with  $C_{19}H_{39}NH_2$ , was used as a monolayer. Fig. 5 shows  $\Pi$ - $A$  isotherms of monolayers of  $C_{22}H_{45}NH_2$  spread on water at 5.5 and the subphase of a  $7 \times 10^{-6}$  M  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  solution at

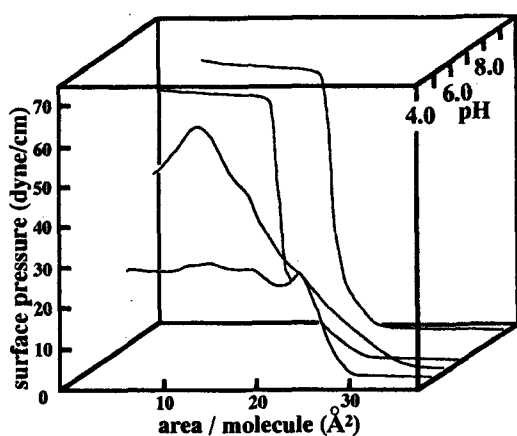


Fig. 4 Pressure-area isotherm obtained with  $CH_3(CH_2)_{18}NH_2$  spread on  $7 \times 10^{-6}$  M  $[Mo_7O_{24}]^{6-}$ -subphases containing 1N NaOH adjusted to give values of pH between 4.7 and 9.0, shown as a three dimensional graph.

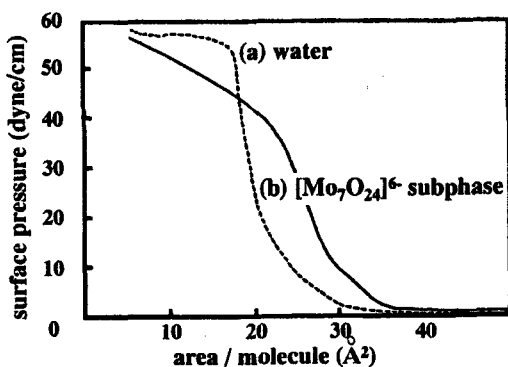


Fig. 5 Pressure-area ( $\Pi$ - $A$ ) isotherm of  $CH_3(CH_2)_{21}NH_2$  on water at pH 5.5 and  $T=16^\circ C$  (a). Isotherm of  $CH_3(CH_2)_{21}NH_2$  on a  $7 \times 10^{-6}$  M  $[Mo_7O_{24}]^{6-}$  subphase at pH 4.2 and  $T=16^\circ C$  (b).

pH 4.2. At pH 4.2, the layer ( $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$ ) floated on the subphase.

Fig. 6 shows IR spectra of  $C_{22}H_{45}NH_2$  and the floating layer ( $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$ ) at pH 4.2. A few bands are observed below  $1000\text{ cm}^{-1}$  in only the spectrum of the floating layer. Their bands agreed with the peaks in the IR spectrum of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (c). It is obviously that  $[Mo_7O_{24}]^{6-}$  deposited below the monolayer of  $C_{22}H_{45}NH_2$  at pH 4.2.

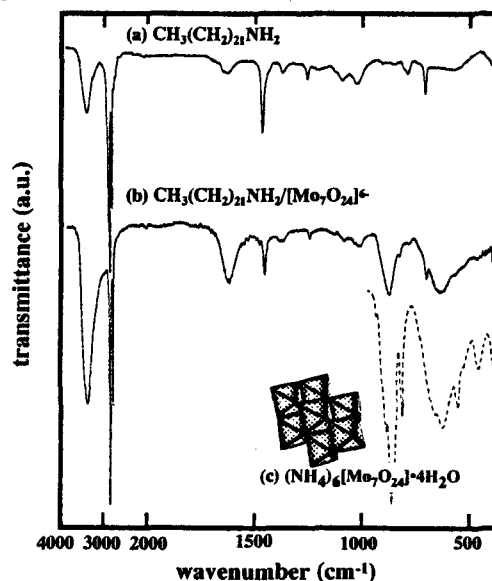


Fig. 6 IR spectra for films of  $CH_3(CH_2)_{21}NH_2$  (a),  $CH_3(CH_2)_{21}NH_2/[Mo_7O_{24}]^{6-}$  (b) and  $(NH_4)_6[Mo_7O_{24}]^{6-} \cdot 4H_2O$  (c).

The  $d(001)$ -value of the LB films of  $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$  was 56.3 Å. The  $d(001)$ -value was shorter than it estimated from length of  $C_{22}H_{45}NH_2$  and thickness of  $[Mo_7O_{24}]^{6-}$  anion. It is concluded that molecules of  $C_{22}H_{45}NH_2$  in the film inclined on the substrate.

### 3.3 Photochromism of $[V_4O_{12}]^{4-}/C_{19}H_{39}NH_2$ and $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$

Fig. 7 shows photochromic behavior of the LB film composed of vanadate anions ( $[V_4O_{12}]^{4-}$ ) and  $C_{19}H_{39}NH_2$ . After irradiating u. v. light to the film for 12 h, it turned brown. It was furthermore observed in Fig. 6 (b) that the absorption band at 500nm slightly increased. Lying the film in the dark, brown returned to colorless as before.

Change in color for the film which was accumulated  $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$  on the substrate, was presented in Fig. 8. As shown in Fig. 8, the absorption band at 350 nm went up by irradiation of u. v. light for 12 h.

Photochromic behavior has been explained by T.

Yamase *et al.* [8]. The absorption bands at 500 and 350 nm for the LB films are due to d-d transition. The d-d transition results from formation of a charge-transfer complex through photoreduction of  $V^V \rightarrow V^{IV}$  or  $Mo^{VI} \rightarrow Mo^V$ . The photoreduction takes place by irradiating u. v. light to  $O \rightarrow M$  (V, or Mo) charge-transfer absorption band. After that, a charge-transfer complex is formed by stabilization of the hole at O with the unpaired electron at N.

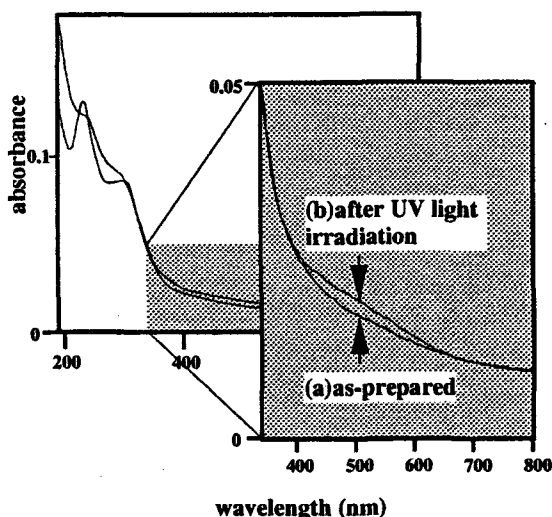


Fig. 7 UV-Vis spectra of the 15 layered LB film of  $CH_3(CH_2)_{18}NH_2/[V_4O_{12}]^{4-}$  (a) and it after u. v. light irradiation for 12h (b).

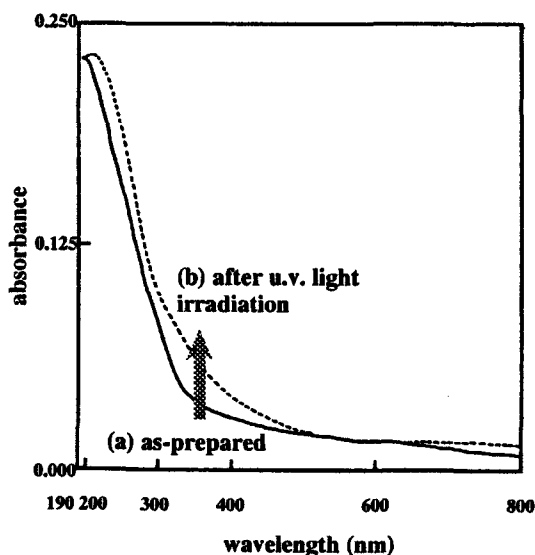


Fig. 8 Uv-Vis spectra for the composite film of  $CH_3(CH_2)_{21}NH_2/[Mo_7O_{24}]^{6-}$  (a) and it after irradiation u.v. light for 12 h (b).

#### 4. CONCLUSION

We prepared LB films composed of polyoxometalate anions and n-alkylamines. The film of  $[V_4O_{12}]^{4-}/C_{19}H_{39}NH_2$  was prepared at pH 8.6. On the other hand,

the film of  $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$  was also obtained at pH 4.2. Their films of  $[V_4O_{12}]^{4-}/C_{19}H_{39}NH_2$  and  $[Mo_7O_{24}]^{6-}/C_{22}H_{45}NH_2$  both have photochromism at 500 and 350 nm respectively.

LB technique is most useful to order polyoxometalate anions in the films. It is expected that The LB films composed of polyoxometalate anions and n-alkylamines was applied to opto-electronics field, as inorganic/organic composite materials.

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