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Novel Multibilayer Film Incorporating Electro- and Photo-Chemically Active Decatungstate Anion

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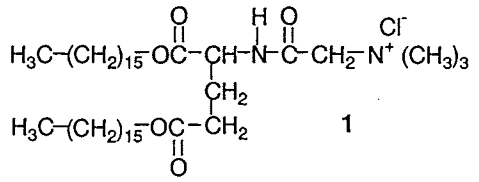
The ionic complex between a cationic double-chain amphiphile and a decatungstate anion formed a well-organized multibilayer film, not only with keeping inherent properties of both the amphiphile and decatungstate anion almost intact but also with generating unique temperature dependence of the redox reaction regulated by the phase transition of bilayer.

Recently, syntheses of inorganic cluster in molecular assembled films such as Langmuir-Blodgett films$^{1)}$ and bilayer membranes$^{2)}$ have been attracting a lot of attention from the viewpoints of not only stabilization of nanosized inorganic cluster but also regularization of the arrangement of them in a sandwich structure. However, synthesized species of inorganic compounds so far reported in these systems have been limited to metal calcogenides and halides. We propose herein an organization of cluster ions by ion-complexing with oppositely charged amphiphiles forming a bilayer membrane to give an inorganic-organic composite film. Inorganic isopolyanions (tungstate, vanadate, molybdate, etc.) and heteropolyanions (molybdophosphate, tungstophosphate, etc.) are well known to have electrochemical, photochemical, photochromic and/or catalytic properties.$^{3)}$ Thus the polyion-complexed bilayer films containing such inorganic polyanions, if formed, would be novel functionalized bilayer systems as well as novel organized organic-inorganic composite films. As representative example, this paper reports the preparation and electro- and photo-chemical characterization of ion-complexed multibilayer film of the dialkylammonium amphiphile, **1**, and decatungstate anion ($W_{10}O_{32}{}^{4-}$).



$$\begin{array}{l} H_3C{-}(CH_2)_{15}{-}O\overset{O}{\overset{\|}{C}}{-}\underset{|}{C}H{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}N^+(CH_3)_3\ Cl^- \\ \qquad\qquad\qquad\qquad CH_2 \\ H_3C{-}(CH_2)_{15}{-}O\underset{O}{\underset{\|}{C}}{-}CH_2 \end{array}$$

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Dialkylammonium amphiphile, **1**,$^{4)}$ (4 mmol) was dispersed in 50 ml of water by sonication, to which was added 50 ml of aqueous decatungstate anion (pH=2, conc.=0.02 M, 1 M=1 mol·dm^{-3}) prepared by the procedure previously reported.$^{6)}$ The obtained precipitate was collected by filteration, washed with water and dried. The molar ratio of **1**:$W_{10}O_{32}^{4-}$ evaluated from elementary analysis was 4:1, being consistent with the value expected from the electric charges of **1** and $W_{10}O_{32}^{4-}$. The appearance of IR absorption bands characteristic of both $W_{10}O_{32}^{4-}$ 7) and **1**, coupled with the observed molar ratio, clearly suggests the formation of ionic complex between **1** and $W_{10}O_{32}^{4-}$. The ionic complex, **1**/$W_{10}O_{32}^{4-}$, was soluble in chloroform, but insoluble in water, ethanol and aqueous KCl used as electrolyte for the measurement of cyclic voltammograms. Transparent thin films were obtained by casting chloroform solution (5.0 mM) of **1**/$W_{10}O_{32}^{4-}$ on plates of borosilicate glass and quartz, respectively, for X-ray diffraction (XRD) measurement (Rigaku 2034, CuK_α radiation) and UV-VIS measurement (Shimadzu UV-3100). Before the measurements, the cast films were subjected to a water-annealing treatment which consisted of the successive immersion for a few minutes in hot water (80 ℃) and then in cold water (5 ℃). Differential scanning calorimetry (DSC) (Shimadzu DSC-50) of **1** and the **1**/$W_{10}O_{32}^{4-}$ cast films (20 mg) which were directedly formed in DSC sample pans was performed between 0 ℃ and 90 ℃ at a heating rate of 2 ℃·min^{-1} with and without 0.1 M aqueous KCl (20 µl). Cyclic voltammograms (CVs) were measured in deoxygenated 0.1 M aqueous KCl (pH=2) within the potential range from +0.2 to -0.6 V vs Ag/AgCl by using a polarized unit (Toho Technical Research, PS06), an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode was prepared by casting 5 µl portion of chloroform solution of **1**/$W_{10}O_{32}^{4-}$ (1 mM) on a polished glassy carbon disk electrode (diameter: 3 mm, Bioanalytical System Co. Ltd) and then evaporating the solvent at ambient temperature. The electrode thus obtained was annealed in 0.1 M aqueous KCl (pH=2) at 80 ℃ and 5 ℃ before CV measurements. No change in the molar ratio, **1**:$W_{10}O_{32}^{4-}$, was observed before and after these annealing treatments by elementary analysis.

In DSC thermograms, the **1**/$W_{10}O_{32}^{4-}$ film showed an endothermic peak at 45 ℃ (in air) and 46 ℃ (in aqueous KCl), which were close to the phase transition temperature (Tc) of the aqueous bilayer 8) and cast film of **1** (43 ℃). On the other hand, tetrabutylammonium/$W_{10}O_{32}^{4-}$ film 9) obtained by casting N,N-dimethylformamide solution did not show any endothermic peaks between 0 ℃ and 90 ℃. This clearly indicates that the **1**/$W_{10}O_{32}^{4-}$ film possesses the typical thermal characteristic of the bilayer system. In addition, XRD measurement (Fig. 1) revealed that the **1**/$W_{10}O_{32}^{4-}$ film, which gave distincter 00*l* Bragg peaks

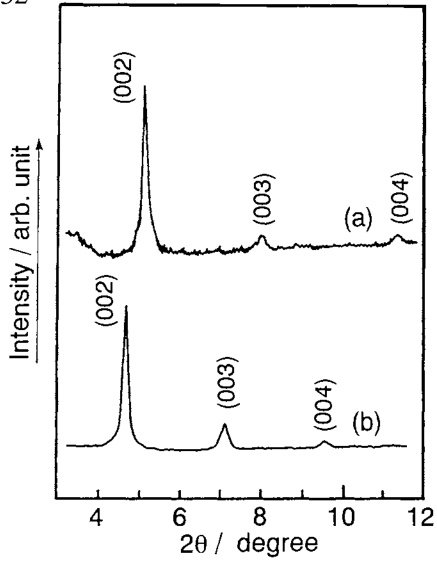

Fig. 1. XRD patterns of cast films of (a) **1** (800 counts·s^{-1}) and (b) **1**/$W_{10}O_{32}^{4-}$ (8000 counts·s^{-1}).

than that in original film of **1**, had well-organized multibilayer structure. The basal-plane spacing of the **1**/$W_{10}O_{32}^{4-}$ film (37.2 Å) was found to be larger than that of the cast film of **1** (33.8 Å). This would be due to the large ionic size of $W_{10}O_{32}^{4-}$ as compared with that of Cl^-. The results obtained by DSC and XRD measurements suggest that $W_{10}O_{32}^{4-}$ might be arranged and orientated in the hydrophilic interlayers while keeping the orientation of the original bilayer film of **1**. This suggestion is supported by the geometric consideration that the occupied area of $W_{10}O_{32}^{4-}$ (ca. 96 Å^2) evaluated from the product of lengths of long and short axes$^{7)}$ just fits with twice that of molecular cross section of **1** (49 Å^2).$^{10)}$

Figure 2 shows steady-state CVs of the **1**/$W_{10}O_{32}^{4-}$ film at 20, 40, 50, 60 ℃, which were obtained after multiple scans at a sweep rate of 30 mV s^{-1}. Two redox waves are clearly observed at temperatures above 40 ℃, but not at 20 ℃. Formal redox potentials of two waves, -0.20 and -0.42 V, were almost the same as those of aqueous $W_{10}O_{32}^{4-}$ (0.1 M KCl, pH=2). In Fig. 3 are depicted the temperature dependences of anodic (at -0.17 V) and cathodic (at -0.23 V) peak currents of the **1**/$W_{10}O_{32}^{4-}$ film together with those of aqueous $W_{10}O_{32}^{4-}$ (5×10^{-2} mM). The peak currents of aqueous $W_{10}O_{32}^{4-}$ are independent on temperature, whereras those of the **1**/$W_{10}O_{32}^{4-}$ film are remarkably dependent on temperature. The temperature-dependence behavior was reversible. The coincidence between the onset temperature of peak currents (Fig. 3) and Tc of the **1**/$W_{10}O_{32}^{4-}$ film in aqueous KCl (46 ℃) suggests that the redox reaction of $W_{10}O_{32}^{4-}$ is associated with the phase transition of the bilayer film. The peak current of the first redox wave at 60 ℃ was found to be proportional to the square root of the sweep rate in the range of 5-200 mV·s^{-1}, indicating that the present redox system is diffusion-controlled. The phase-transition regulated electrochemistry in multibilayers has been already reported with a "foreign" (doped) flavin located in the hydrophobic region$^{11)}$ and charged metal complexes uptaken in the

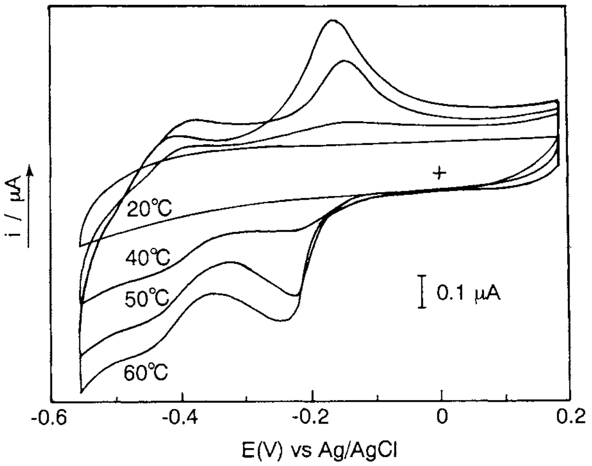

Fig. 2. Steady-state cyclic voltammograms of **1**/$W_{10}O_{32}^{4-}$ film loaded on a carbon electrode in 0.1 M aqueous KCl (pH=2). Sweep rate: 30 mV·s^{-1}

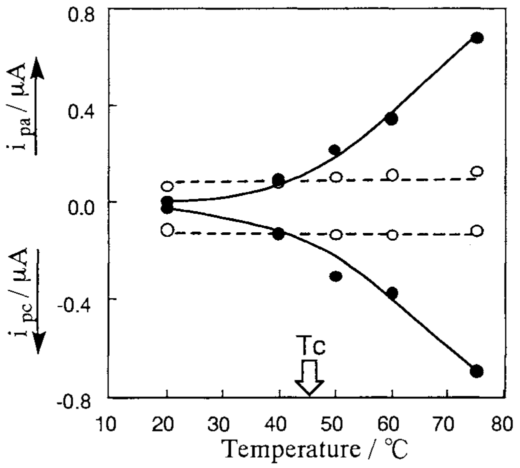

Fig. 3. Temperature dependence of anodic (i_{pa}) and cathodic (i_{pc}) peak at the first redox wave around -0.2V. (●) the **1**/$W_{10}O_{32}^{4-}$, (o) aqueous $W_{10}O_{32}^{4-}$ (5×10^{-2} mM)

hydrophilic region through ion-exchange reaction.$^{12)}$ However, the present results is the first example that the phase transition of a bilayer film regulated the electron transfer reaction of a redox-active inorganic cluster fixed in the hydrophilic region through the complexation with a bilayer-forming ionic amphiphile. The origin of the temperature-dependent electrochemistry might be the change in the rate of self-exchange electron transfer between $W_{10}O_{32}^{4-}$ species and/or in the rate of diffusion of $W_{10}O_{32}^{4-}$ itself which is regulated by the bilayer fluidity.

Finally, the photochemical property of the **1**/$W_{10}O_{32}^{4-}$ film is briefly described. The electronic spectrum of the original cast film of **1**/$W_{10}O_{32}^{4-}$ exhibited an absorption band at 325 nm cheracteristic of $W_{10}O_{32}^{4-}$. The irradiation of UV light by a super high-pressure Hg lamp (500 W) in the presence of ethanol caused the 325-nm band to diminish and a new band at 630 nm to appear. The 630-nm band is characteristic of 2-electron reduced polyanion ($H_2W_{10}O_{32}^{4-}$).$^{13)}$ Stopping the irradiation of UV light, the absorbance of 630-nm band decreased and that of 325-nm band increased gradually to return to those of original cast film completely. The photochromism (colorless ⇔ blue) was confirmed by UV-VIS spectroscopy as well as visual observation.

In conclusions, it has turned out that the ionic complex between **1** and $W_{10}O_{32}^{4-}$ is a novel bilayer-forming system and that the presence of $W_{10}O_{32}^{4-}$ in the hydrophilic interlayer causes little influence on the thermal behavior (phase transition) as well as on the organization of the multibilayer structure. Decatungstate anion incorporated in the bilayer film keeps its inherent electrochemical and photochemical properties intact. In addition, the incorporation of $W_{10}O_{32}^{4-}$ into the bilayer results in the temperature-dependent redox reaction regulated by the phase transition of bilayer.

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References

1) I.Moriguchi, I.Tanaka, Y.Teraoka, and S.Kagawa, *J.Chem.Soc., Chem.Commun.*, **1991**, 1401.
2) N.Kimizuka, T.Maeda, I.Ichinose, and T.Kunitake, *Chem.Lett.*, **1993**, 1991.
3) For example, T.Yamase, and T.Ikawa, *Bull.Chem.Soc.Jpn.*, **50**, 746 (1977).
4) **1** was synthesized according to the procedure reported in reference 5 and was identified by IR and NMR measurement, elementary analysis and DSC measurement.
5) T.Kunitake, N.Nakashima, S.Hayashida, and K.Yonemori, *Chem.Lett.*, **1979**, 1413.
6) A.Chemseddine, C.Sanchez, J.Livage, J.P.Launay, and M.Fournier, *Inorg.Chem.*, **23**, 2609 (1984).
7) V.J.Fuchs, H.Hartl, W.Schiller, and U.Gerlach, *Acta.Cryst.*, **B32**, 740 (1976).
8) T.Kunitake, R.Ando, and Y.Ishikawa, *Memories of the Faculty of Engineering, Kyusyu Univ.*, **46**, 221 (1986).
9) Tetrabutylammonium / $W_{10}O_{32}^{4-}$ was obtained by the same procedure as that of **1**/$W_{10}O_{32}^{4-}$.
10) The molecular area in the pressure-area isotherm of monolayer of **1** was used as the molecular cross section.
11) N.Nakashima, K.Masuyama, M.Mochida, K.Kunitake, and O.Manabe, *J.Electroanal.Chem.*, **319**, 355 (1991).
12) J.F.Ruslig and H.Zhang, *Langmuir*, **7**, 1791 (1991).
13) N.Takabayashi and T.Yamase, *Nippon Kagaku Kaishi*, **1984**, 264.

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