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The Electronic Absorption Spectra of Fatty Acid Mono-, Bi-, and Multilayers with Bivalent Metal Ions

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The electronic absorption spectra of fatty acid multilayers with bivalent metal ions were studied in the vacuum ultraviolet (VUV) to ultraviolet (UV) energy region below 8 eV; they are due to transitions in the carboxylic acid and metal carboxylate moieties. Infrared (IR) absorptions due to the C–O stretching vibration in the carboxylate moiety are also studied. Stearic acid multilayers without metal ions are shown to form hydrogen-bonded dimers. The spectra of multilayers with metal ions show a marked dependence on the subphase pH which is different for different kinds of adsorbed metal ions. Their VUV spectra are conspicuously dependent on the kind of metal ions adsorbed. All the multilayers with alkaline earth metals, metals of the 2B group, transition metals, Cu, and Pb have at least two bands in the VUV region, 7.3—6.3 eV. The polarization spectra of the Ba stearate multilayer suggest that the two transitions may be the intramolecular π-π^* and n-π^* transitions in the carboxylate anion moiety. The multilayers with Cu and Pb have another band in the UV region. The spectra of the UV bands of the Pb and Cu stearate mono-, bi-, and multilayers were studied. In the Pb stearate layers, the positions of the UV bands in the bi- and multilayers are the same, but those in the monolayers are at considerably shorter wavelengths. The positions of the UV band in the Cu stearate mono-, bi-, and multilayers are successively red shifted. The polarization spectra of the UV bands of the mono- and bilayers showed that they are charge-transfer bands between the Pb or Cu ion and the coordinated carboxylate moiety.

In an accompanying paper[1] (hereafter we will refer to it as I), we have shown that the vacuum ultraviolet (VUV) absorption spectra of fatty acid multilayers in the energy region below 10 eV consist of two parts, a strong absorption in the region above 8 eV (Region 1) and a weaker absorption in the region below 8 eV (Region 2). From the chain length and pH dependences of the spectra, we have assigned the absorption in Region 1 to the σ-σ^* transitions in the alkane chain moiety, and that in Region 2 to the transitions in the carboxylic acid and metal carboxylate moieties.

In this paper, we wish to present the results of our detailed studies of the absorption spectra of fatty acid multilayers and monolayers in Region 2. Fatty acid multilayers prepared on the water subphase containing metal ions adsorb the metal ions to a varying extent, depending on the pH of the subphase.[2,3] The pH profile of the metal ion adsorption is characteristic of the kind of metal ion. The physical properties of fatty acid monolayers such as the π-A profiles and the surface potential are dependent of the kind and amount of adsorbed metal ions. However, little direct information has been obtained about the interaction of metal ions with carboxylic acid moieties in fatty acid mono- and multilayers. The absorption spectra in Region 2 of fatty acid multilayers, that are due to the electronic transitions in the carboxylic acid and metal carboxylate moieties, provide direct information about the interaction of metal ions with fatty acid monolayers. In this paper, we will study the pH and metal ion dependencies and polarization of the spectra in Region 2. We will study also the infrared (IR) absorptions due to the carboxylic acid and carboxylate moieties.

Experimental

Materials. The fatty acids and other materials used in the present study were the same as those described in I. The spectrograde acetic acid and dichlorodimethylsilane were purchased from Nakarai Chemicals, Ltd. Optically flat quartz plates were obtained from the Takahashi Giken Co.

Methods. Fatty acid multilayers with metal ions and pure stearic acid multilayers were deposited on CaF_2 plates, as has been described in I. Monolayers of Cu stearate and Pb stearate were deposited on quartz plates with hydrophilic surfaces, as has been described by Matsuki *et al.*[4] Bilayers of Cu stearate and Pb stearate were deposited on quartz plates whose surfaces had been made hydrophobic by rinsing with a dichlorodimethylsilane solution.[5] All the multilayers and monolayers were prepared at 19±0.5 °C.

The measurements of VUV absorption spectra were performed as has been described in I. The IR spectra were measured on Shimadzu-IRG and JASCO-IRA-2 spectrometers; the latter apparatus was five times more sensitive than the former. The measurements of the ultraviolet (UV) spectra of the monolayers and bilayers of Cu stearate and Pb stearate were performed on a high-sensitivity spectrometer using the single-beam and sample in-sample out technique described by Matsuki *et al.*[4] The apparatus was equipped with a CaF_2 Glan-Thompson prism for measurements of the polarized spectra.

The UV spectra of $PbCl_2$, $Pb(CH_3COO)_2$, and $Cu(CH_3COO)_2$ in water and acetic acid were measured with a Shimadzu-UV-180 spectrometer. To minimize the absorption of the solvent, acetic acid, the spectra were measured for solutions of high concentrations in the order of 10^{-2} M with the use of a thin cell, with the path length of 12 microns and the cell was made of two quartz plates and a polyethylene film spacer.

All the measurements of the VUV spectra in Region 2 (below 8 eV) and of the IR specrta in the region from 1000 cm^{-1} to 4000 cm^{-1} were performed for multilayers prepared by 15 dippings of the substrate.

The efficiency of the deposition of multilayers may change from sample to sample depending on the subphase pH, the kinds of metal ions, and the substrate.[6–10] In order to avoid uncertainty in the deposition ratio, we measured both the VUV and IR spectra for each multilayer sample. We nomalized the deposition ratio using the 2910 cm^{-1} IR band, which is attributable to the antisymmetric stretching vibration

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of the CH_2 groups in the alkane chain moiety.[2,11-13] The 2910 cm^{-1} IR band of the Ba heneicosanoate multilayer was used as the standard for the normalization of the deposition ratio. The Ba heneicosanoate multilayer prepared at a neutral pH forms Y layers with a nearly perpendicular molecular arrangement.[1,13] Its deposition on a CaF_2 plate coated with Fe stearate was confirmed by the linearity of the VUV[14] and IR spectra to the dipping number. The number, L, of fatty acid layers deposited on a plate by 15 dippings was calculated by means of:

$$L = 60 \times \frac{20}{n} \times \mathrm{OD}(2910\ \mathrm{cm}^{-1})/\ \mathrm{OD}(2910\ \mathrm{cm}^{-1}\ \text{Ba heneicosanoate}),$$

where n is the carbon number in the alkane chain, we assumed the deposition of 4 layers of Ba heneicosanoate on the substrate per dipping into the subphase.

For pure stearic acid and Zn stearate multilayers with molecular arrangements tilted against the normal of the layer plane, the intensity of the 2910 cm^{-1} band was corrected for the tilting of molecular axes by the method of Akutsu *et al.*[15]

All the VUV and UV spectra of multilayers except for Fig. 1 are normalized to the per-layer value. The molar extinction coefficient, ε, is obtained from the per-layer absorption, A, by means of:

$$\varepsilon = A \cdot a \cdot N = 12 \times 10^5 \times A,$$

where N is the Avogadro's number and a is the area (in cm^2) occupied by a fatty acid molecule, which is estimated to be about 20×10^{-16} cm^2 from the limiting area in the π-A profile of fatty acid monolayers.[16,17]

Results and Discussion

VUV Spectrum of Pure Stearic Acid Multilayer. The deposition of the pure stearic acid monolayer, which was spread on the subphase without any metal ions at acid pH (3.1), onto the CaF_2 plate was most uncertain, as was mentioned in I. The number of deposited layers appropriate for the measurements of the VUV spectra in Region 1 was limited to only a few layers because of the strong absorption of Region 1, so the intensity of the 2910 cm^{-1} IR band was too weak to use for the nomalization of the deposition ratio. However, in the measurements of the spectra in Region 2 much thicker multilayers could be used because of the weaker absorptions in that region, so the 2910 cm^{-1} IR band could be effectively used in the normalization of the deposition ratio. The pure stearic acid multilayer prepared at the acid pH was reported to have a molecular arrangement with chain axes tilted against the normal of the layer plane by about 30°.[12] The VUV spectrum in Region 1 also gave a tilting angle of about 30°, as has been discussed in I. Therefore, in the normalization of the deposition ratio, the intensity of the 2910 cm^{-1} band was corrected for the tilting by assuming the tilting angle of 30°. The Region 2 VUV spectrum of the pure stearic acid multilayer is shown in Fig. 1, as well as the spectra of the acetic acid dimer and the monomer in the gas state obtained by Barnes and Simpson.[18] The spectrum of the pure stearic acid multilayer has a band at 7.7 eV which resembles, in position and strength, the lowest energy band of the acetic acid dimer, but which has no absorption in the region near 7.2 eV where the absorption of the acetic acid monomer exists. This shows that the carboxylic acid moieties in the pure stearic acid multilayer are not in the monomeric states but form hydrogen-bonded dimers. The existence of hydrogen bonding in pure fatty acid multilayers was also suggested by Koyama *et al.* from the broadness of the 1700 cm^{-1} IR band.[19]

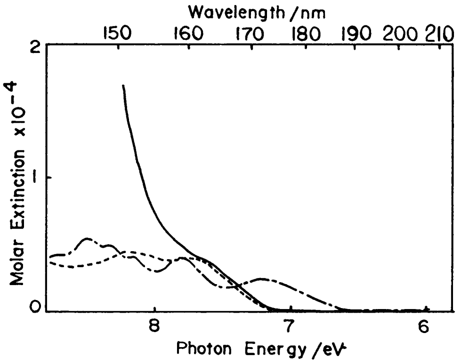

Fig. 1. Spectrum of pure stearic acid multilayer in molar extinction scale (——). The multilayer was prepared on the subphase without metal ions at pH 3.1. The spectra of acetic acid monomer (–·–) and dimer (----) obtained by Barnes and Simpson[18] were also shown.

pH *Dependencies of the VUV and IR Spectra of Fatty Acid Multilayers with Bivalint Metal Ions.* Fatty acid multilayers prepared on the subphase with metal ions adsorb the metal ions to a varying extent, depending on the pH of the subphase.[2,3] Corresponding to the pH dependencies of the metal ion adsorptions, the VUV spectra in Region 2 of the multilayers show marked dependencies on the subphase pH. In Figs. 2a and 3a we show the pH dependencies of the Region 2 spectra of the arachidic acid multilayers with Sr^{2+} and Cd^{2+} ions respectively.

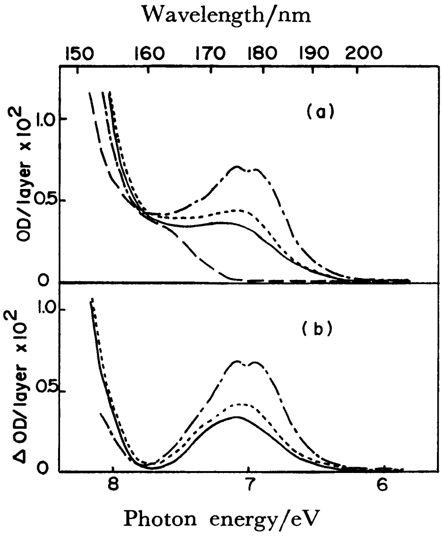

Fig. 2. (a): The pH dependence of the spectra of arachidic acid multilayers with Sr^{2+} ions prepared on the subphases with 10^{-4} M $SrCl_2$ at pH 6.6 (——), at pH 9.3 (----) and pH 10.7 (—-—). The spectrum of pure stearic acid multilayer prepared at pH 3.1 (——) is also shown. (b): The difference spectra presentation of the spectra in (a) with the reference of the pure stearic acid multilayer spectrum. The notation is the same as (a).

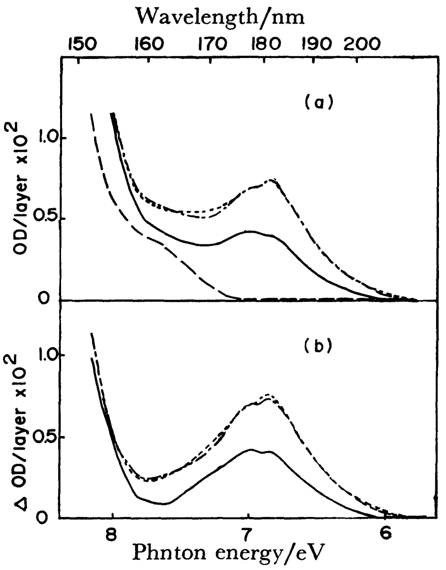

Fig. 3. (a): The pH dependence of the spectra of arachidic acid multilayers with Cd^{2+} ions prepared on the subphases with 10^{-4} M $CdCl_2$ at pH 6.15 (——), at pH 6.9 (----) and at pH 8.15 (— — —). The spectrum of pure stearic acid multilayer prepared at pH 3.1 is also shown (——). (b): The difference spectra presentation of the spectra in (a) with the reference of the pure stearic acid multilayer spectrum. The notation is the same as (a).

At pH 3.1 little adsorption of these ions took place, and the spectra in Region 2 were almost the same as that of pure stearic acid multilayer. As the subphase pH was increased up to the pH region where the adsorption of the metal ions took place, however, new bands appeared in the energy region around 7 eV, where little absorption existed at pH 3.1, and their intensities increased with an increase in the pH. To establish the shapes of the new bands more clearly, in Figs. 2b and 3b we show the difference spectra with reference to the pH 3.1 spectra. The new bands depend on the kinds on metal ions adsorbed. At least two peaks can be discriminated for the multilayers with both Sr^{2+} and Cd^{2+} ions, at 7.10 and 6.95 eV for Sr^{2+} and at 7.00 and 6.85 eV for Cd^{2+}.

We show in Fig. 4 the pH dependencies of the absorption strengths at the positions of the two peaks. We note that the shapes of the spectra had a dependence on the pH. The relative strength of the lower energy peak to the higher energy one increased with the increase in the pH. This suggests that the metal ion dependent absorption around 7 eV contains contributions from at least two different molecular species.

To elucidate the nature of the molecular species responsible for the absorption, we inspected the pH dependencies of the IR spectra of the same multilayer samples in the wavenumber region from 1350 to 1850 cm^{-1} (Figs. 5 and 6). In this wavenumber region, there were two bands with marked pH dependencies, the broad band at 1700 cm^{-1} and the band at 1515 cm^{-1} (Sr^{2+}) or 1546 cm^{-1} (Cd^{2+}). The intensity of the 1700 cm^{-1} band was maximal at an acid pH and decreased with the increase in the pH. Its position was independent of the kinds of metal ions adsorbed. The 1700 cm^{-1} band can be assigned to the C=O stretching vibration in the unionized carboxylic acid moiety, because its position is identical with that of the C=O stretching band in the stearic acid crystal.[11] The metal ion dependent band at 1515 cm^{-1} (Sr^{2+}) or 1546 cm^{-1} (Cd^{2+}), on the other hand, was absent at an acid pH, but emerged in the pH region where the adsorption of the metal

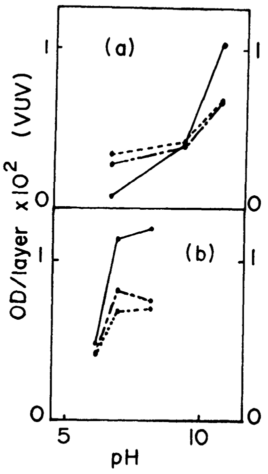

Fig. 4. (a): The pH dependences of the intensities of the VUV bands at 7.10 eV (– – –) and 6.95 eV (—·—) and of the IR band at 1515 cm^{-1} (——) of arachidic acid multilayers with Sr^{2+}. (b): Those of the VUV bands at 7.00 eV (– – –) and 6.85 eV (—·—) and of the IR band at 1546 cm^{-1} (——) of arachidic acid multilayer with Cd^{2+}.

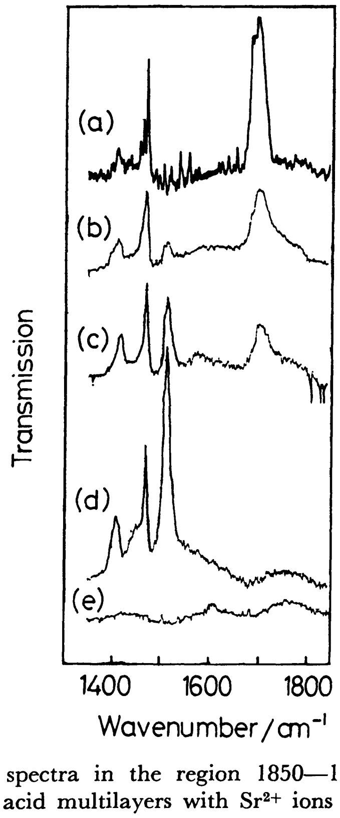

Fig. 5. IR spectra in the region 1850—1350 cm^{-1} of arachidic acid multilayers with Sr^{2+} ions prepared at pH 6.6 (b), at pH 9.3 (c), and at pH 10.7 (d). The spectrum of the pure stearic acid multilayer is also shown (a). (e) is the base line of the spectra.

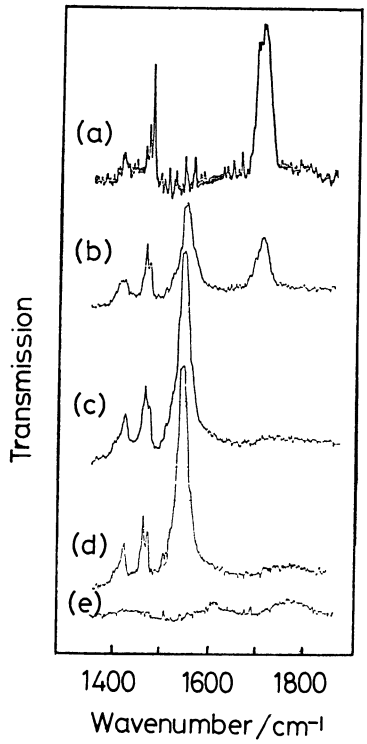

Fig. 6. IR spectra in the region 1850—1350 cm^{-1} of arachidic acid multilayers with Cd^{2+} ions prepared at pH 6.15 (b), pH 6.9 (c), and pH 8.15 (d). The spectrum of the pure stearic acid multilayer is also shown (a). (e) is the base line of the spectra.

ions begun to occur, and its intensity increased with the increase in the pH. The band can be assigned to the COO$^-$ antisymmetric stretching vibration in the metal carboxylates moiety, because its position is very close to the position, 1514 cm^{-1} or 1548 cm^{-1}, of the vibration mode in Sr or Cd stearate crystal respectively.[11] The intensity of the band, therefore, is considered to be proportional to the amount of the metal ions adsorbed to the multilayer.

We show in Fig. 4 the pH dependencies of the 1515 cm^{-1} and 1546 cm^{-1} IR bands. One may see in Fig. 4 that there is a difference in the pH dependencies of the VUV and IR absorptions. The strength of the VUV absorption relative to that of the IR absorption was larger in the lower pH region, where the adsorption of the metal ions was incomplete, than in the high pH region, where the adsorption of the metal ions had been completed. This indicates that a molecular species which is present in the pH region with a partial adsorption of the metal ions contributes to the VUV absorption, but not to the IR band. This molecular species is considered to be unionized fatty acid molecules unhydrogen-bonded in their carboxylic acid moieties. As is shown in Fig. 1, the carboxylic acid moieties in pure fatty acid multilayers form hydrogen-bonded dimers. As the pH of the subphase is increased, a fraction of the fatty acid molecules is ionized and adsorbs metal ions. Therefore, the hydrogen bonds in a fraction of the remaining unionized molecules may be broken by the disturbance of the regular structure of the multilayer by the partial adsorption of metal ions. The unionized fatty acid monomers thus produced will have an absorption near 7.2 eV, as judged from the absorption spectrum of the acetic acid monomer shown in Fig. 1, and will contribure to the VUV absorption, but not to the IR band due to the metal salts of fatty acids. This mechanism can explain also the pH dependent change in the shape of the VUV absorption. The two peaks in the VUV spectra which were most clearly seen in the high pH region are

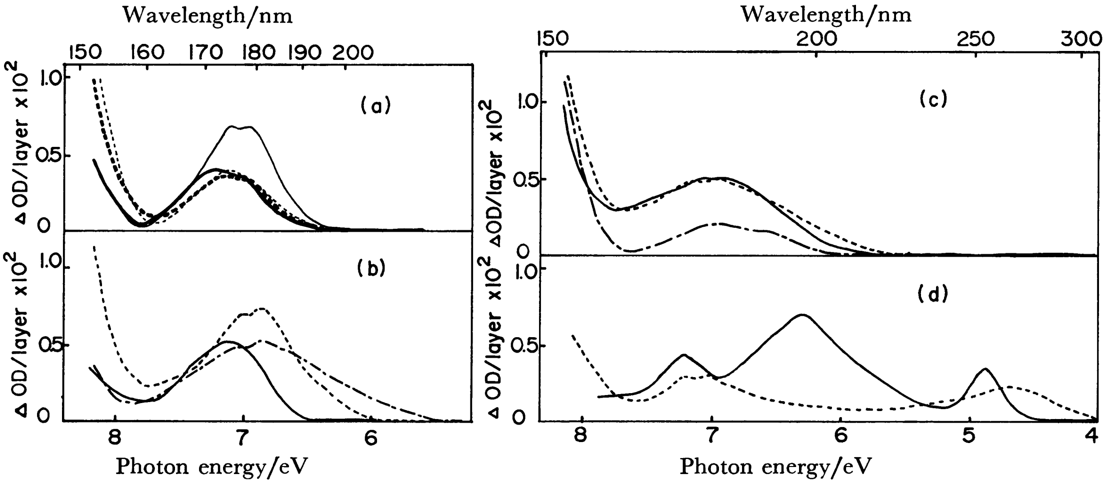

Fig. 7. The VUV difference spectra of fatty acid multilayers with alkaline earth metals (a), with 2B group metals (b), with transition metals (c), and with Cu and Pb (d). The reference is the spectrum of pure stearic acid multilayer prepared at pH 3.1. The metal ions and the pH's of the subphases are (a) Mg^{2+}, pH 10.1 (——), Ca^{2+}, pH 7.6 (- - -), Sr^{2+}, pH 10.7 (——), and Ba^{2+} at pH 9.6 (–––), (b) Zn^{2+}, pH 7.3 (——), Cd^{2+}, pH 8.15 (–––), and Hg^{2+}, pH 5.4 (—·—), (c) Mn^{2+}, pH 8.4 (——), Co^{2+}, pH 8.4 (–––), and Ni^{2+}, pH 5.8 (—·—) and (d) Pb^{2+}, pH 5.7 (——) and Cu^{2+}, pH 5.4 (–––). All the subphases contained 10^{-4} M metal chloride except for the Pb case with 6×10^{-7} M PbCl$_2$. The fatty acids used are indicated in Table 1. In the case of the multilayer with Zn^{2+} ions, the layer number was calculated assuming the tilted arrangement of molecules with the angle 26°[1,11] against the normal of the layer plane.

TABLE 1. POSITIONS OF THE ELECTRONIC ABSORPTION BANDS AND THE COO^- ANTISYMMETRIC STRETCHING VIBRATIONS OF FATTY ACID MULTILAYERS WITH BIVALENT METAL IONS

	Metal ions	Carbon[a)] number	Metal[b)] adsorption	Electronic bands	The COO^- band	Crystals[c)]	
			%	eV	cm^{-1}	The COO^- band/cm^{-1}	State of hydration
Alkaline earth metals	Mg	17	100	7.22 7.00	1560(b)	1564(b)	$3H_2O$
	Ca	17	50	7.15 6.95	1540 1575	1540 1581	H_2O
	Sr	19	100	7.10 6.95	1515(s)	1514(s)	Anhydrous
	Ba	20	50	7.10 6.85	1510 1530	1513	Anhydrous
2B group metals	Zn	17	100	7.30 7.10	1540(s)	1540	Anhydrous
	Cd	19	100	7.00 6.85	1546(s)	1548	Anhydrous
	Hg	17	50	7.00 6.85	1590(s)	1570	Anhydrous
Transition metals	Mn	17	100	7.10 6.85	1560(b)	1550(sh) 1574	H_2O
	Co	17	100	7.20 6.95	1550(b)	1530(b)	H_2O
	Ni	17	100	7.00 6.60	1550(b)	1550(b)	$2H_2O$
Others	Cu	17	—	7.20 7.05 4.70	1590(s)	1588	Anhydrous
	Pb	17	—	7.20 6.30 4.86	1510(s)	1512	Anhydrous

(b): broad band, (s): sharp band, (sh): shoulder. a) The carbon number of the alkane chain of fatty acids used as the multilayer samples. b) Calculated from the intensity of the 1700 cm^{-1} IR band. c) The IR and hydration data for metal stearate crystals obtained by R. Matsuura.[11)]

considered to be due to the metal carboxylate moieties. The absorption due to the unionized monomer carboxylic acid moieties is superimposed on them in the low pH region, so that a pH dependent change in the spectral shape is produced. The swelling near 7.2 eV present only in the low pH VUV spectra may be due to the absorption of the unionized monomer species.

Metal Ion Dependence of Region 2 Spectra of Fatty Acid Multilayers. The Region 2 spectra of fatty acid multilayers with bivalent metal ions have a conspicuous dependence on the kinds of metal ions adsorbed. We show in Fig. 7 the difference spectra of the multilayers with metal ions of an alkaline earth group (Fig. 7a), the 2B group (Fig. 7b), a transition metal group (Fig. 7c), and Cu^{2+} and Pb^{2+} (Fig. 7d). The reference was the spectrum of the pure stearic acid multilayer prepared at pH 3.1. The depositions of the multilayers were performed at the pH's where the adsorptions of the metal ions were almost complete, except in a few cases in which the efficiency of deposition was not so good in such a pH region. The spectra, therefore, represent the absorptions of the metal carboxylate moieties. In Table 1 we list the positions of the absorption peaks which could be clearly discriminated.

We measured also the IR spectra of the same samples. In Table 1 we list the positions of the IR bands which were assigned to the COO^- antisymmetric stretching vibration in the metal carboxylate moieties. We show also the data of the positions of the vibration mode in the metal stearate crystals.[11)] Several multilayers have two bands for the vibration mode that may be ascribed to different hydration states. It has previously been reported that, in crystals, the band width of the vibration mode was broadened by hydration to metal carboxylate moieties.[11)] We show also the qualitative data about the band width and the data of hydration in crystals. We may see in Table 1 that there are good correspondences between multilayers and crystals in the band positions and the states of hydration, as judged by the band splitting and the band width. We also show in Table 1 the extent of metal ion adsorption in the multilayers, as estimated by the intensity of the 1700 cm^{-1} IR band.

We may see in Fig. 7 and Table 1 that all the multilayers have a band in the 7.0—7.3 eV energy region. This band may have a common origin in all the multilayers. A possible origin is the intramolecular π-π^* transition in the carboxylate anion moiety. The spectrum of the carboxylate anion has not been obtained. Barnes and Simpson suggested, from their observation of its absorption edge, that the π-π^* transition of the carboxylate anion may lie near 7.2 eV.[18)] The position of the π-π^* transition may be shifted a little depending on the kind of bound metal ion.

All the multilayers also have another band in the 6.3—7.1 eV energy region. The assignment of this second band is not clear. In the Ba stearate multilayer it has a polarization perpendicular to the first band, as we shall show in the next section. Hence, it may be due to an intramolecular transition in the carboxylate anion moiety, possibly the n-π^* transition. The intensity of the n-π^* transition may be enhanced by the distortion of the n electron orbital caused by the interaction with bound metal ions. In the case of the multilayer with Pb^{2+}, the intensity of the second band is too strong to be assigned to the n-π^* transition, though, its position is shifted to a much lower energy compared to the other multilayers. The nature of the second band in the multilayer with Pb^{2+} may, therefore, be different from those of the other multilayers. To obtain a certain assignment of the transitions, further studies seem to be necessary.

The absorptions of the multilayers with Cu^{2+} and Pb^{2+} extend up to the UV region and have their bands at

4.70 and 4.86 eV respectively. The UV band is due to the charge-transfer transition between the carboxylate anion moiety and the bound metal ion, as we shall show later by means of the polarization spectra in the UV region.

The absorption edges of the multilayers with transition metals and 2B group metals, except for Zn, extend to a much lower energy region (up to about 5.5 eV) than do the multilayers with alkaline earth metals. The low energy tails of the absorptions of those multilayers may, therefore, contain weak transitions with the charge-transfer character.

Polarization Spectra of the Ba Stearate Multilayer. We show in Fig. 8 the polarization spectra of the Ba stearate multilayer measured with a 45° angle incidence of plane polarized lights. The absorption of the light polarized perpendicularly to the plane of incidence (S-polarization) was stronger than that of the light polarized parallel to the plane of incidence (P-polarization) throughout the energy region. The Ba stearate multilayer has been reported to have a layer structure with molecular axes arranged perpendicularly to the layer plane.[13,20–25] Assuming the perpendicular molecular arrangement and using Akutsu *et al.*'s method, we calculated the angle, θ, of the transition moment against the molecular axis. In the calculation, we used as the refractive index, n, of the multilayer both the value, $n=1.70$, of quartz near 7.0 eV[26] and the value, $n=1.50$, of the multilayer in the visible region,[20] as we have done in I. The theoretical value of the dichroic ratio, $R=A_S/A_P$, where A_S and A_P are the absorbances for S and P polarized lights respectively, became maximal for $\theta=90°$. The theoretical maximal value of R is 1.21 for $n=1.70$ and 1.29 for $n=1.50$. In all the energies, the observed dichroic ratio was close to the theoretical maximal value; for instance, $R=1.29$ at 7.1 eV. Therefore, we can conclude that $\theta=90°$ within the limits of experimental error.

This result shows that the transitions near 7 eV in the Ba stearate multilayer are intramolecular transitions in the carboxylate anion moiety. The π-π^* transition in the carboxylate anion has its direction along the line connecting the two oxygen atoms, and the n-π^* transition is perpendicular to the carboxylate plane, so that they are polarized perpendicularly to the molecular axis. The charge-transfer transition between the carboxylate anion moiety and the bound metal ion, on the other hand, is expected to have its direction of the transition moment not perpendicular to the molecular axis, because bound metal ions are arranged outside

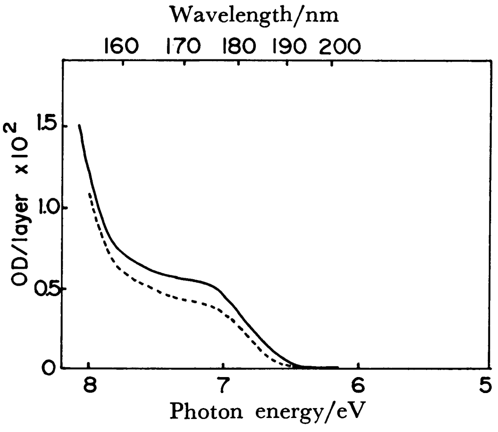

Fig. 8. Polarized absorption spectra of stearic acid multilayers with Ba^{2+} ions prepared on the subphase with 3×10^{-5} M $BaCl_2$ at pH 7.2 with 45° angle incidence of the light plane polarized perpendicularly (——), or parallely (– – –) to the plane of incidence.

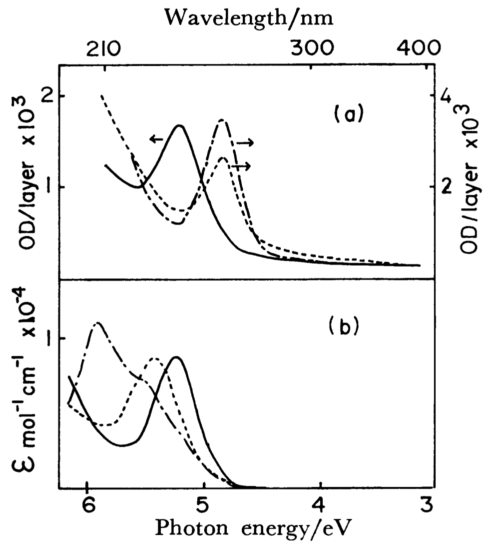

Fig. 9. (a): UV spectra of stearic acid mono- (——), bi- (– – –) and multi- (—·—) layers prepared on the water subhases with 1.2×10^{-6} M $PbCl_2$ at pH 5.4 (mono-) and 5.7 (bi- and multilayers). (b): UV spectra of $Pb(CH_3COO)_2$ (0.03 M) in CH_3COOH (——) and H_2O (– – –) solutions and $PbCl_2$ (0.02769 M) in H_2O (—·—) solution. The path length of the cell was 12 microns.

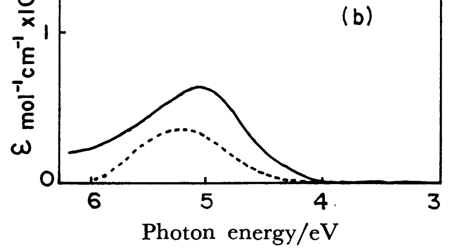

Fig. 10. (a): UV spectra of stearic acid mono- (——), bi- (– – –) and multi- (—·—) layers with Cu^{2+} ions prepared on the water subphase with 5×10^{-4} M $CuCl_2$ at pH 5.1 for the mono- and bilayers and with 10^{-4} M $CuCl_2$ at pH 5.4 multilayer. (b): UV spectra of $Cu(CH_3COO)_2$ (0.05 M) in H_2O (– – –), CH_3COOH (——) solutions. The path length of the cell was 12 microns.

TABLE 2. THE UV BANDS OF MONO-, BI-, AND MULTILAYERS OF Pb AND Cu STEARATE AND OF Pb AND Cu ACETATE AND $PbCl_2$ IN SOLUTION

Ion	Sample	Position/nm	OD/layer	$\varepsilon^{a)}$/mol^{-1} cm^{-1}
Pb	Multilayer	254	3.3×10^{-3}	6300
	Bilayer	255	2.4×10^{-3}	6400
	Monolayer	237	1.6×10^{-3}	4100
	$Pb(CH_3COO)_2$ in CH_3COOH	237	—	8700
	$Pb(CH_3COO)_2$ in H_2O	228	—	8700
	$PbCl_2$ in H_2O	208 225	—	11000 —
Cu	Multilayer	263	2.1×10^{-3}	5000
	Bilayer	260	1.9×10^{-3}	4600
	Monolayer	254	1.8×10^{-3}	4300
	$Cu(CH_3COO)_2$ in CH_3COOH	245	—	3600
	$Cu(CH_3COO)_2$ in H_2O	235	—	6600

a) The molar extinctions of the L B layers were calculated as has been described in the Materials and Methods section.

the layer plane of the carboxylate anion moieties. The above conclusion is considered to be valid for the multilayers with alkaline earth metals. However, for the multilayers with metal ions of other kinds, further studies to check the validity of the assignment are necessary because their electronic structures are so different from those of alkaline earth metals that their interactions with the carboxylate anion moiety may be different from the interaction of the alkaline earth metals.

UV Spectra of Pb Stearate and Cu Stearate Mono- and Bilayers. As is shown in Fig. 7d, the Pb and Cu stearate multilayers have an absorption band in the UV region. The UV absorptions of the mono- and bilayers as well as those of the multilayers can be measured by using the high-sensitivity spectrometer for thin layers with the sample-in, sample-out technique developed in Kuhn's laboratory.27) We show in Figs. 9a and 10a the UV spectra of the Pb and Cu stearate mono-, bi-, and multilayers. We also show, in Figs. 9b and 10b, the UV spectra of Pb acetate, $PbCl_2$ and Cu acetate in acetic acid and water solutions. The positions and molar extinctions of the UV bands are listed in Table 2.

The positions of the UV band in the bi- and multilayers with Pb ions were the same, though the breadth of the band was a little different, perhaps because of the larger light scattering in the bilayer. The coincidence of the peak position suggests that the structure and arrangement of the chromophores in the bilayer were unchanged by the formation of multilayer. The intensity of the absorption was larger in multilayer than in bilayer. This hyperchromicity of the multilayer may be due to the interlayer excitonic interaction of chromophores, as we shall discuss later. The peak position in the monolayer, on the other hand, was at a considerably shorter wavelength than those of the bi- and multilayers, and the intensity was stronger than that of the bilayer. This shows that the structure of coordination in the Pb carboxylate moieties is different between the mono- and bilayers. The peak position and the band width were almost the same in the monolayer and Pb acetate in an acetic acid solution. Therefore, the coordination of Pb ions in the monolayer is considered to be similar to that in an acetic acid solution.

The peak position of the UV band in the Cu stearate multilayer was red shifted a little against that of the bilayer, and the absorption intensity was a little stronger in the multilayer, showing that the structure and arrangement of chromophores in the bilayer are affected by the formation of the multilayer. The UV band in the bilayer was red shifted against that of the monolayer. This indicates that there is a difference between the mono- and bilayers in the coordination of Cu ions with the surrounding carboxylate anion moieties. The position of the UV band of the monolayer was closest to the UV band of Cu acetate in the acetic acid solution, though it was at a little longer wavelength position. Therefore, the coordination of Cu ions in the monolayer is considered to be similar to, but not identical with, the coordination in the acetic acid solution.

In order to determine the directions of the transition moments of the UV bands in Pb and Cu stearate mono- and bilayers, we measured their polarization spectra with the 45° oblique angle incidence of plane polarized lights, as is shown in Figs. 11 and 12. The absorption for the S-polarized light was stronger than that for the P-polarized lights, in all the cases. From the dichroic

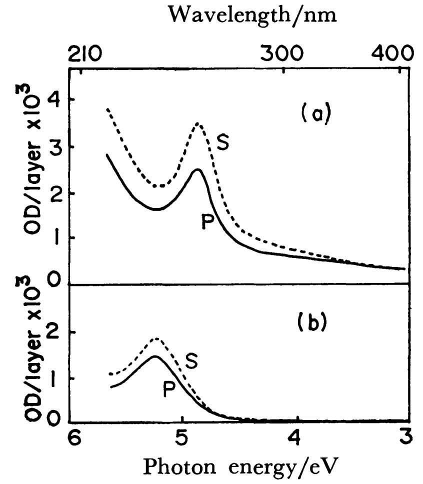

Fig. 11. UV polarization spectra of stearic acid bilayer (a) and monolayer (b) with Cu^{2+} prepared on the subphases containing 6×10^{-7} M $PbCl_2$ at pH 5.4 and 5.7, respectively. The angle of incidence was 45° with the lights plane polarized perpendicularly (----) and parallely (——) to the plane of incidence.

Table 3. The direction of the transition moment of the UV bands of Pb and Cu stearate mono- and bilayers

Ion	Layer number	$\mathrm{R_{app}}$ a)	R b)	n c)	θ d)
Pb	Monolayer	1.28 (at 237 nm)	1.07	1.515	59°
	Bilayer	1.41 (at 255 nm)	1.18	1.505	69°
Cu	Monolayer	1.37 (at 254 nm)	1.15	1.506	65°
	Bilayer	1.30 (at 260 nm)	1.09	1.503	61°

a) The apparent dichroic ratio at the wavelength in parentheses. b) The dichroic ratio after the correction for the interference effect.[27] c) The refractive index of quartz at the peak position that was used in the calculation as the refractive index of the mono- or bilayer. d) The angle of the transition moment against the normal of the layer plane

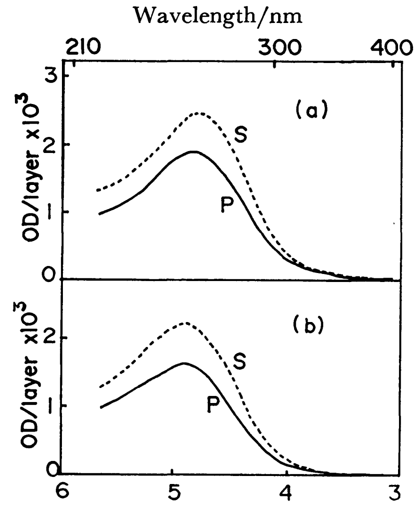

Fig. 12. UV polarization spectra of stearic acid bilayer (a) and monolayer (b) with Cu^{2+} prepared on the subphase containing 5×10^{-4} M $CuCl_2$ at pH 5.1. The angle of incidence was 45° with the lights plane polarized perpendicularly (-----) and parallely (——) to the plane of incidence.

ratios at the peak positions, we calculated the angle, θ, of the transition moment against the molecular axis (Table 3). In the calculation, the molecular axes were assumed to be arranged perpendicularly to the layer plane; we used as the refractive index of the mono- and bilayers the values of quartz[26] at the peak positions, since we had no data about the refractive index at the peak positions and since quartz had a refractive index with a value close to those of the fatty acid multilayers at the Na D line, as was mentioned in I. We also made a correction for the interference effect[27] according to Matsuki *et al.*,[4] because, in the present systems, chromopores are arranged in a restricted layer.

The directions of the transition moments are tilted against the normal of the layer plane, as may be seen in Table 3. From the X-ray data of the Pb stearate multilayer,[28] we can estimate as about 40° the angle of the direction connecting the Pb ion and the oxygen atom in a lead(II) carboxylate complex against the normal of the layer plane. This angle is smaller than the angles of the transition moment obtained by us. However, the X-ray value is not so reliable because of the technical difficulty in the X-ray analysis of multilayers.

The tilting of the transition moments against the normal of the layer plane shows that the transitions are of a charge-transfer character. The same assignment was made for the UV bands of $PbCl_2$ and $CuCl_2$ in an aqueous solution.[29]

The θ angle in the Pb stearate bilayer is larger by about 10° than that in the Pb stearate monolayer. This shows that the lead(II) carboxylate complexes in the bilayer are distorted compared to the complexes in the monolayer in a manner to arrange the Pb ions closer to the layer plane of the carboxylate anions. The large red shift of the peak position in the bilayer may be due to this distortion, that may accompany an increase in the coordination number.[29]

The θ angles in Cu stearate mono- and bilayers are nearly the same. The small red shift in the peak position of the bilayer suggests that there may be a small distortion in the copper(II) carboxylate complexes, accompanied by the formation of a bilayer. Our data about the θ angle are consistent with the smallness of the red shift, but, unfortunately, are not of so high a precision as to enable us to detect conclusively such a small change in θ as only a few degrees.

It was shown that hyperchromicity is produced by the excitonic interaction of chromophores when they are packed in a head to tail arrangement of their transition moments.[30,31] The hyperchromicity of Pb and Cu stearate multilayers against the bilayers may be due to the interlayer excitonic interaction of the Pb and Cu carboxylate complexes. The tilting of the transition moments against the layer plane may produce a head to tail like packing of them. The interlayer distance is too long to produce a strong excitonic interaction between individual chromophores. However, in multilayers, chromophores form infinitely wide, two-dimensional layers, so that the integrated excitonic interaction between layers may become strong in spite of the weak interaction between individual chromophores. To elucidate the origin of the hyperchromocity, it is necessary to develop theory for excitonic interaction and its optical consequences in multilayers.

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