April, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 1217—1221 (1981) 1217

The Vacuum Ultraviolet Absorption Spectra of Fatty Acid Multilayers

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(Received August 28, 1980)

The electronic absorption spectra of fatty acid multilayers were measured in the vacuum ultraviolet region with an energy below 10 eV. From the chain length dependence of the spectra, the strong absorption (above 8 eV) was assigned to the σ-σ^* transitions in the alkane chain moiety, and the weaker one (below 8 eV), to the transitions in the carboxylic acid and metal carboxylate moieties. The polarized spectra of the Ba stearate multilayer showed that the band near 8.8 eV was polarized perpendicularly to the alkane chain. The spectra of the stearic acid multilayer without metal ions and the multilayer of the Zn stearate showed that their alkane chains were titled against the normal of the layer plane.

Fatty acid multilayers prepared by the Langmuir-Blodgett technique[1] are excellent objects for the measurement of the electronic absorption spectra of long alkane chains. In multilayers, the alkane chain and carboxylic acid moieties of fatty acids are arranged in regular two-dimensional layers, and the number of the layer can be controlled at any desired value. This property of multilayers makes it possible to measure the spectra of long alkane chains, which are difficult to measure in crystalline samples. The electronic absorption spectra of alkane chains and carboxylic acids lie in the vacuum ultraviolet (VUV) region. However, by depositing multilayers on a LiF or CaF_2 plate, spectra up to 10 eV can be measured. In a previous paper[2] we reported preliminary results for the VUV spectra of fatty acid multilayers. The VUV spectra of fatty acid multilayers provide information about the structures of multilayers and their interaction with metal ions, as well as basic information about the electronic structures of alkane chains. In this and an accompanying paper, we present the results of a systematic study of the VUV spectra of fatty acid multilayers. In this paper we deal mainly with the contribution of the alkane chain moiety in the VUV spectra. Studies of the chain length dependence and the polarization of the spectra are the main subjects of this paper. The application of the VUV spectra to the study of the molecular arrangement in multilayers is also made. Studies of the spectra of metal carboxylate moieties will be presented in an accompaying paper.[20]

Experimental

The crystalline stearic acid ($C_{17}H_{35}COOH$) was purchased from the Merck Co. The arachidic acid ($C_{19}H_{39}COOH$), heneicosanoic acid ($C_{20}H_{41}COOH$), and behenic acid ($C_{21}H_{43}COOH$) were purchased from Nakarai Chemicals, Ltd. The melting points of theses fatty acids were 70.0 °C, 76.0 °C, 74.0 °C, and 79.0 °C respectively, they agreed with the reported values[3] within an error of 1 °C. Guaranteed-reagent grade metal chlorides and spectrograde benzene were purchased from Nakarai Chemicals, Ltd. These chemicals were used without further purification. Twice-distilled water was used in all the experiments. A single crystal of CaF_2 was purchased from the Hursh Co., Ltd.

The fatty acid multilayers were prepared according to the Langmuir-Blodgett method[1] at 19±0.5 °C in a thermostated room. The pH of the water subphase was adjusted by the use of $KHCO_3$, HCl, or KOH. The fatty acids were spread on the water surface as a 0.1% (w/v) benzene solution, and caster oil was used as the piston oil (pressure, 16.5 dyn/cm). Plates of CaF_2 cleaved from a CaF_2 single crystal by a clean razor were used as the depositing plates. The CaF_2 plates were transparent up to 10 eV; their absorption was confirmed to be unchanged by dipping into water.

The deposition of fatty acid multilayers with bivalent metal ions was performed using CaF_2 plates coated with one layer of Fe stearate by the Langmuir method[4] and on the water subphase containing 10^{-4} M metal chloride at a neutral pH. Under these conditions with $BaCl_2$ and $CdCl_2$ multilayers were deposited as Y layers.[1,4–6] The deposition of multilayers was confirmed by the observation of the meniscus of the subphase near the dipping plate and by the linearity of the VUV absorption strength of the deposited multilayers to the number of times the plates were dipped into the subphase.[2]

The stearic acid monolayer on the subphase without metal ions at an acid pH could not be deposited on the CaF_2 plate coated with one layer of Fe stearate. To make the deposition possible, 4 layers of stearic acid with Ba ions were pre-deposited on the plate from the subphase with 10^{-4} M $BaCl_2$ at a neutral pH. After this treatment of the plate, the deposition of stearic acid multilayers at an acid pH became possible, but not so surely as the deposition at a neutral pH. From the observation of the meniscus when the plate was dipped only a few times, the stearic acid multilayer prepared at an acid pH without metal ions appeared to be of X-type layers.

The VUV absorption spectra were measured with a Shimadzu-SGV-50 VUV spectrometer (Seya-Namioka type with 50 cm focus concave grating blazed at 1500 Å and with 1200 rulings/mm. Light source, Tousey-type hydrogen discharge arc.). The apparatus was equipped with a beam splitter made of grazing incidence mirrors, and both the reference and sample signals were recorded. We used as the reference a CaF_2 plate coated with one layer of Fe stearate, so that the reflection at the surface of the sample plate was almost completely compensated for. A spectrum was measured after a plate with a multilayer had stood *in vacuo* for about three hours. An LiF polarizer with the Brewster angle reflection was used to obtain plane polarized VUV light. The polarizer was inserted between the light source and the entrance slit of the monochrometer.

Plates deposited with 8 layers of fatty acid (with 2 dippings of the plates for Y-type layers or 4 dippings for X-type layers) were used in all the spectral measurements to make the optical density in an appropriate range. The background spectra due to the pre-coating of the plates were substrated from the apparent spectra. All the spectra shown in this paper are those normalized to the per-layer value except for that of the pure stearic acid multilayer prepared at an acid pH, in which

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the deposition at each dipping is not sure (see text).

Results and Discussion

We show in Fig. 1 the VUV absorption spectra of the stearic acid, arachidic acid, and behenic acid multilayers prepared on the water subphase containing Ba ions at a neutral pH. The spectra can be divided into two regions; the region of high absorption above 8 eV (Region 1), and the region of weaker absorption below 8 eV (Region 2). The spectra in Region 2 all have the same strength and shape, which do not depend on the carbon number, *n*, of the alkane chain moiety. The spectra in Region 1, on the other hand, have a broad maximum near 8.8 eV, and their strengths increase with the carbon number, *n*, though their shapes are homologous. We show in Fig. 2 the *n* dependence of the absorption in Region 1 (at 9 eV). The multilayers were prepared on the subphase containing Ba, Sr, Mg, Mn, or Cd ions at a neutral pH. In all the cases, the shapes of the spectra in Region 1 were homologous. We show in Fig. 2 that the absorption in Region 1 is proportional to *n* except for the stearic acid ($n=17$) multilayers with Mn, Sr, or Ba. The absorptions of these stearic acid multilayers, which showed deviations from the proportionality to *n*, were found to decrease slowly with the time, keeping their spectral shapes homologous in the whole wavelength region when they were kept *in vacuo*. This shows that stearic acids in the multilayers sublime slowly *in vacuo*, leading to the formation of a skeletal film.[4] The sublimation of stearic acids from the multilayers can explain the deviation from the proportionality to *n*.

From these results, we can assign the absorption in the Region 1 mainly 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. The absorption edge of polyethylene was reported to lie at 7.5 eV. The edge of the strong absorption of Region 1 is at the same position as the absorption edge of polyethylene, supporting our assignment.

In order to ascertain the polarization of the σ-σ^* transitions of the alkane chain moiety in Region 1, we measured the polarization spectra of a stearic acid multilayer with Ba ions prepared at a neutral pH (Fig. 3). The polarization spectra of normal incidence had no anisotropy, showing that the multilayer was uniaxial. The polarization spectra of 45° angle incidence showed a stronger absorption for the light with an electric field vector perpendicular to the plane of incidence (S-polarization) than the light with an electric field vector parallel to it (P-polarization) in both the regions, 1 and 2. We show in Table 1 the photon energy dependence of the dichroic ratio, A_S/A_P,

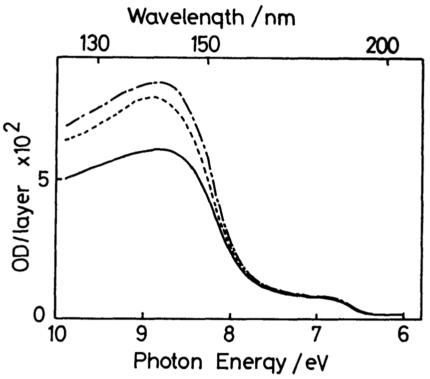

Fig. 1. Per layer absorption spectra of the stearic acid (——), arachidic acid (– – –) and behenic acid (—·—) multilayers prepared on the subphase with 10^{-4} M $BaCl_2$ at pH 7.6.

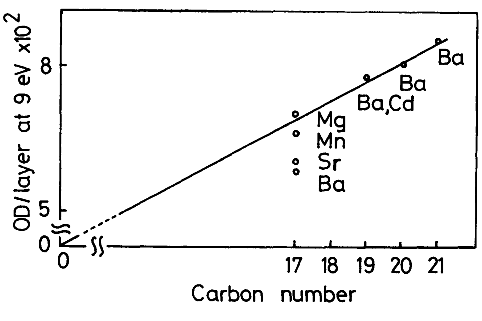

Fig. 2. Dependence of the per layer absorption strength at 9.0 eV of fatty acid multilayers on the carbon munber *n* of the alkane chain moiety. The multilayers were prepared on the subphase with 10^{-4} M metal chloride at neutral pH.

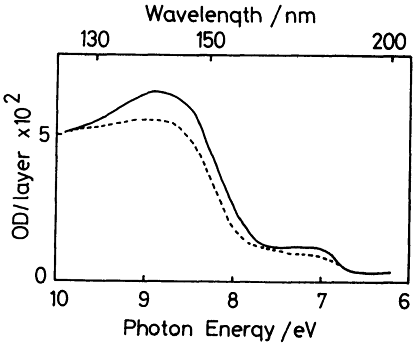

Fig. 3. Per-layer polarized spectra at 45° incidence of the stearic acid multilayer prepared on the subphase with 3×10^{-5} M $BaCl_2$ at pH 7.2. The spectrum for S polarized light (——) and the one for P polarized light (– – –).

TABLE 1. THE ANGLE OF THE TRANSITION MOMENTS OF REGION 1 AGAINST THE MOLECULAR AXIS

Photon energy/eV	$R(=A_s/A_p)$	$\theta(n=1.70)$	$\theta(n=1.50)$
8.3	1.30	90°a)	90°b)
8.4	1.29	90°a)	90°
8.5	1.29	90°a)	90°
8.6	1.22	90°a)	73°
8.7	1.22	90°a)	73°
8.8	1.20	82°	71°
8.9	1.17	74°	67°
9.0	1.16	72°	66°
9.1	1.15	70°	65°

a) The observed value of *R* exceeds the theoretical value, 1.21, for $\theta=90°$. b) The observed value of *R* exceeds the theoretical value, 1.29, for $\theta=90°$.

in Region 1, where A_S and A_P are the absorption strengths for the S and P polarized lights respectively. In the present system, the apparent dichroic ratio, A_S/A_P, represents the true dichroic ratio because the chromophores, *i.e.*, the alkane chains, are distributed nearly uniformly in the multilayer, and so no correction for the interference effect,[7] such as is necessary for multilayers with chromophores distributed only in a restricted layer, is necessary.

Stearic acid multilayers with Ba ions prepared at a neutral pH have been reported to have a layer structure with the molecular axes arranged near perpendicularly to the layer plane.[1,4,6,8–11] Assuming a perpendicular arrangement of alkane chains, and using the method of Akutsu *et al.*,[12] we calculated, from the observed dichroic ratio, the angle, θ, between the chain axis and the transition moment of the σ-σ^* transition near the absorption maximum of Region 1. (Akutsu *et al.*'s method assumes that the alkane chains in a monolayer have a uniform uniaxial distribution in their directions, with a tilting angle, γ, against the normal of the layer plane and that the transition moments with an angle, θ, against the chain axis, also have a uniform distribution around chain axis). The results are shown in Table 1. In the calculation of the angle, the value of the refractive index, n, in the VUV region is necessary. However, no data are available for it, and so we used $n=1.70$, that is, the value of quartz near 8 eV.[13] Since quartz has a refractive index with a value in the visible region similar to that of the fatty acid multilayer ($n=1.46$ for quartz and $n=1.49$—1.51, depending on the mixing ratio of stearic acid and metal stearate, for the fatty acid multilayer at the visible wavelength of 5890 nm[4,13]), and has an absorption edge near 7.5 eV, that is, close to that of the Region 1 absorption of fatty acid multilayers, the refractive index of fatty acid multilayers in the VUV region is considered to have a value similar to that of quartz. For the sake of comparison, we also show in Table 1 the results of the calculation using the value of $n=1.50$ in the visible region.

One may see in Table 1 that the dichroic ratio is nearly constant and that the angle between the transition moment and the chain axis calculated with $n=1.70$ is nearly perpendicular in the energy region from 8.6 eV to 8.8 eV. The angle calculated with $n=1.50$ is somewhat smaller. It is certain that the refractive index is larger in the VUV region than in the visible region and that the true value of the angle is larger than the one calculated with $n=1.50$.

Thus, the present measurement of the polarized spectra leads to the conclusion that the σ-σ^* transitions forming the absorption maximum in Region 1 are polarized perpendicularly to the molecular axis. The dichroic ratio begins to decrease in the higher energy region over 9 eV and becomes unity at 9.94 eV. This suggests that weak σ-σ^* transitions polarized in a parallel direction are present in this energy region or that the low energy tail of a strong σ-σ^* transition polarized in a parallel direction which may be present in the high energy region over 10 eV extends up to this energy region.

Based on the intramolecular exciton theory, Partridge estimated that the lowest parallel and perpendicular σ-σ^* transitions in polyethylene lie at 8.16 eV and 10.08 eV respectively.[14] Therefore, his estimates contradict our data. Based on the interband transition theory, McCubbin calculated that the lowest three transitions in polyethylene lie at 12.6, 13.6, and 16.9 eV and that all of them have perpendicular polarization.[15] The calculated peak positions are too high, but the direction of the transition moments is consistent with our data.

The polarization of the σ-σ^* transitions in Region 1 can be used for the study of the molecular arrangement in fatty acid multilayers. We show in Fig. 4 the normal incidence spectrum of the stearic acid multilayer prepared on the subphase with Zn ions at a neutral pH. The spectrum in Region 1 is apparently different from that of the stearic acid multilayer with Ba ions, with a weaker absorption strength in the energy region near 8.8 eV. We show in Table 2 the ratio of the absorption of the multilayer with Zn to that of the multilayer with Ba in the energy region near the absorption maximum. The ratio is nearly constant, though there is a weak decrease with the photon energy. The difference in the spectral shape can be ascribed to the fact that the multilayer with Zn ions has a tilting of the alkane chain axes against the normal of the layer plane. Assuming that the alkane chain axes in the multilayer with Ba ions are arranged perpendicularly to the layer plane, and that the σ-σ^* transitions near the absorption maximum are perpendicularly polarized against the chain axis, we calculated from the ratio the angle, γ, of the tilting of the chain axes in the multilayer with Zn ions using the method of Akutsu *et al.*[12] The results are shown in Table 2. The calculation gives angles of tilting in the range from 20° to 28°. The X-ray data about Ba stearate and Zn stearate crystals[16] showed that the inter-layer distances in these crystals were 47.5 Å and 42.6 Å respectively. The inter-layer distance of the Ba stearate crystal is consistent with the perpendicular packing of molecules against the layer plane. On the other hand, the inter-layer distence of the Zn stearate crystal shows that the axes of molecules are tilted against the normal of the layer plane. Assuming the perpendicular arrangement of molecules in the Ba stearate crystal, the angle, γ, of the tilting in the Zn

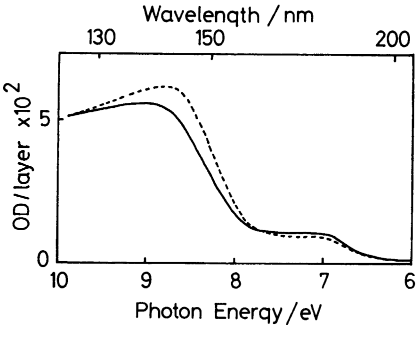

Fig. 4. Per-layer absorption spectrum of the stearic acid multilayer prepared on the subphase with 10^{-4} M $ZnCl_2$ at pH 6.5 (——). The per-layer spectrum of the stearic acid multilayer prepared on the subphase with 10^{-4} M $BaCl_2$ at pH 6.9 is also shown (---).

Table 2. The tilting angle of the molecular axis against the normal of the layer plane in the Zn stearate multilayer

Photon energy/eV	$t^{a)}$	$\gamma^{b)}$
8.4	0.90	19°
8.5	0.87	21°
8.6	0.85	23°
8.7	0.82	25°
8.8	0.80	27°
8.9	0.78	28°

a) t is the ratio of the per-layer absorptions of the Zn stearate multilayer to the Ba stearate multilayer. b) γ is the tilting angle of the molecular axis calculated from t.

stearate crystal is estimated from the $\cos\gamma = 42.6/47.5$ relation to be $\gamma = 26°$. The tilting angle estimated from our spectral data is in agreement with this X-ray value. We note also that the spectrum of the multilayer with Zn ions has the same intensity as that of the multilayer with Ba ions at the photon energy of 9.94 eV, just the energy where the S and P polarized spectra at the 45° incidence of the multilayer with Ba ions have the same strength (Fig. 3). This fact is also consistent with our interpretation that the change in the spectral shape of the multilayer with Zn ions is due to a change of polarization caused by a tilting of the molecular axis.

The spectrum in Region 1 of a pure stearic acid multilayer prepared on the subphase without metal ions at an acid pH is also different from that of the multilayer with Ba ions, as is shown in Fig. 5. In the case of the pure stearic acid multilayer, the deposition of monolayers on the plate is not so sure as in the case of the multilayers with bivalent metal ions. Furthermore, observation of the meniscus showed that the deposition occurred in such a manner as to give X-type layers for the first several dippings of the plate, but they became Y-type layers after several dippings. Therefore, it is difficult to determine the number of deposited layers in a pure stearic acid multilayer. The multilayers of our samples, prepared with only four dippings, are too thin to apply the interference and infrared techniques in measuring their thicknesses. Therefore, we normalized the spectrum of the pure stearic acid multilayer by the following indirect method.

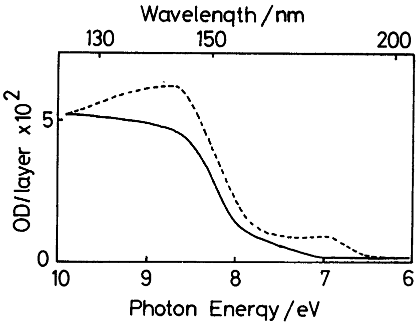

Fig. 5. Absorption spectrum of the stearic acid multilayer prepared on the subphase without metal ions at pH 3.0 (——). For the normalization of the spectrum, see text. The per layer spectrum of the stearic acid multilayer prepared on the subphase with 10^{-4} M $BaCl_2$ at pH 6.9 is also shown (----).

As may be seen in Figs. 3 and 4, the absorption of the alkane chain of stearic acid has the same strength at 9.94 eV irrespective of the polarization of incident light or the tilting of the chain axis. Hence, the photon energy of 9.94 eV is considered to be the isosbestic point for stearic acid multilayers with different directions of the σ-σ^* transition moments. Therefore, we normalized the spectrum of the pure stearic acid multilayer so as to have the same absorption strength at 9.94 eV as the multilayer with Ba ions.

We show in Table 3 the ratio of the absorption strength of the pure stearic acid multilayer thus normalized to the absorption strength of the stearic acid multilayer with Ba ions in the energy region near the absorption maximum. The ratio is fairly constant in this energy region. We calculated from the ratio the tilting angle of alkane chain axis in the pure stearic acid multilayer (Table 3). The calculation showed that alkane chain axes in the pure stearic acid multilayer are tilted by about 30° against the normal of the layer plane. This tilting is in good agreement with the reported value, ≈30°, measured with the infrared spectra.[17)]

Table 3. The tilting angle of the molecular axis against the normal of the layer plane in the pure stearic acid multilayer

Photon energy/eV	$t^{a)}$	$\gamma^{b)}$
8.4	0.74	31°
8.5	0.76	30°
8.6	0.73	32°
8.7	0.75	30°
8.8	0.76	30°
8.9	0.78	28°

a) t is the ratio of the per-layer absorptions of the pure stearic acid multilayer to the Ba stearate multilayer. b) γ is the same as Table 2.

The spectrum in Region 2 of the stearic acid multilayer lacks the absorption near 7 eV which is present in the spectrum of the multilayer with Ba ions. The absence of the band near 7 eV cannot be explained by the tilting of the molecules, rather, it is attributable to the difference in the state of the carboxylic acid moiety. The former multilayer consists only of unionized stearic acids, but the latter is a mixture of Ba stearate and unionized stearic acid.[18,19)] As we shall show in the accompanying paper, the band near 7 eV can be ascribed to the Ba carboxylate and unhydrogen-bonded carboxylic acid moieties, but the carboxylic acid moieties in the pure stearic acid multilayer are hydrogen-bonded. We stress that the marked pH dependence (and the metal ion dependence discussed in the accompanying paper) of the absorption in Region 2 support the assignment of it to the transitions in the carboxylic acid and metal carboxylate moieties.

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