Application of Electron Spectroscopy for Chemical Analysis to Studies of the Composition of Icosanoic Acid Monolayer

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Synopsis. Electron spectroscopy for chemical analysis (ESCA) was used to determine the composition of icosanoic acid (n-$C_{19}H_{39}COOH$) monolayer deposited on the microscope glass slide from the water surface containing Cd^{2+} at varying pH. It was found that the monolayers deposited from substrate at pH<4.6, pH>6.6, and pH=4.6—6.6 consist of icosanoic acid, cadmium icosanoate, and mixture of both substances, respectively.

A knowledge of the composition of a Langmuir-Blodgett film (L-B film) is important for understanding of its properties and structures. The compositions of L-B films have been studied by means of IR spectroscopy,[1,2] neutron activation analysis,[3] and photomeric measurements.[4]

Electron spectroscopy for chemical analysis (ESCA) has been attracting attention as a powerful method for determining structure and composition on the surface layer of materials. Few ESCA studies of Langmuir-Blodgett films, however, have been reported.[5,6]

In the present investigation, the attempt was made to determine the composition of icosanoic acid monolayer deposited on a microscope glass slide from cadmium substrate at various pHs by ESCA.

Experimental

Materials. Icosanoic acid (purity of 99%), cadmium chloride and potassium hydrogencarbonate were obtained from Sigma Chemical Co., Wako Pure Chemical Ind., and Kanto Kagaku Co., respectively and were used without further purification. Other chemicals used were of analytical reagent grade. Icosanoic acid was dissolved in purified chloroform to make a spreading solution of 3×10^{-4} mol dm^{-3}. The pH of the solution in the trough was adjusted by the addition of aqueous solutions of NaOH and HCl.

The water used was distilled three times after refluxing ordinary distilled water with acid permanganate, and then distilling it from an alkaline permanganate solution.

Apparatus. The substrates for film deposition were commercially available microscope glass slides (24 mm×50 mm×0.5 mm). The surfaces of the microscope slides were cleaned in the following manner: they were first sonicated with distilled water, subsequently soaked in a cleaning solution of concentrated acid permanganate overnight, rinsed repeatedly with distilled water, and then dried in a desiccator. The monolayer was prepared in a Langmuir trough (40 mm×385 mm×7 mm) with a well of a water depth of 37 mm and was deposited on the microscope glass slide by lifting the previously immersed glass slide at a velocity of 7 mm min^{-1} at constant surface pressure of 29.5 mN m^{-1}, which was given by the use of piston oil (*cis*-9-octadecenoic acid).

The solution in the trough was 3×10^{-4} mol dm^{-3} $CdCl_2$ and 5×10^{-4} mol dm^{-3} $KHCO_3$ with varying pH. Under these conditions, no visible drops of water occurred on the microscope slides. The deposition ratio was monitored by comparing the geometric area of the microscope slide to the change in the monolayer area during the deposition process at constant surface pressure. Only monolayer films whose deposition ratio was maintained within 100±1% were used in this experiment.

ESCA measurements were made with a JEOL JESCA-4 spectrometer using Mg $K\alpha$ X-ray source (1253.6 eV). The samples were mounted to give a take-off angle of 45°. The peak areas of the C_{1S} and Cd_{3d} bands of the samples were measured to calculate the composition of the cadmium icosanoate monolayer.

All the experiments were carried out at about 20 °C.

Results and Discussion

It is important to know the escape depth of photoelectrons in the case of quantitative analysis using ESCA. Brundle et al.[7] reported that the escape depth of photoelectrons from gold, silver, and indium substrates through cadmium icosanoate (2.68 nm thick) was 3.6—4.1 nm. In our study, the escape depth for photoelectrons emitted from Cd through the icosanoate moiety is generally expected to be larger than that determined for cadmium icosanoate. In addition, recent studies[8—10] on the structure of L-B film indicate that the orientation of molecules to the substrate surface is perpendicular in the first layer of the deposited monolayers either of long chain fatty acids or their salts. Therefore, the peak areas of the Cd_{3d} and C_{1S} bands observed are assumed to be proportional to the amount of Cd and C in the monolayer films, respectively.

The vacuum stability of the monolayer film deposited at pH 7.4 were studied. Figure 1 shows the effect of time on the peak areas of C_{1S} and Cd_{3d} bands under a pressure of about $(2—4)\times10^{-8}$ mmHg (1 mmHg=133.322 Pa). As can be seen in Fig. 1, the peak areas of C_{1S} bands decrease linearly with increasing time, while the peak areas of Cd_{3d} bands are almost invariable within experimental error. The investigations of the vacuum stability of deposited films of cobalt octadecanoate[11] and cadmium icosanoate[12] show that the salts of these fatty acids are stable even under high vacuum. Thus, the decrease in peak area of C_{1S} band is considered to be caused by the breaking of the hydrocarbon chain in cadmium icosanoate under the X-ray radiation. Accordingly, all subsequent ESCA experiments were performed over a time period during which the damage to the hydrocarbon chain was negligible.

Figure 2 shows typical C_{1S} and Cd_{3d} photoelectron spectra obtained from the deposited monolayer at pHs' 4.7, 5.8, and 7.6. In Fig. 2, we can see the photoelectron signals for C_{1S} at 288.0 eV, which correspond to the carbon (284.3 eV) of the ordinary hydrocarbon chain. The shift in the C_{1S} peak occurs by the electrical insulating properties of the monolayer and glass. In addition, it is evident from Fig. 2,

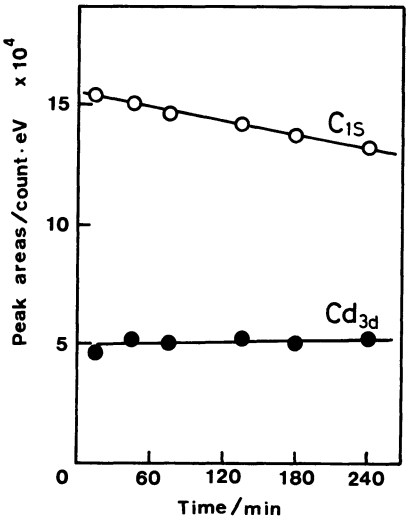

Fig. 1. Vacuum stability of cadmium icosanoate monolayer. The monolayers were deposited from cadmium substrate with pH=7.4.

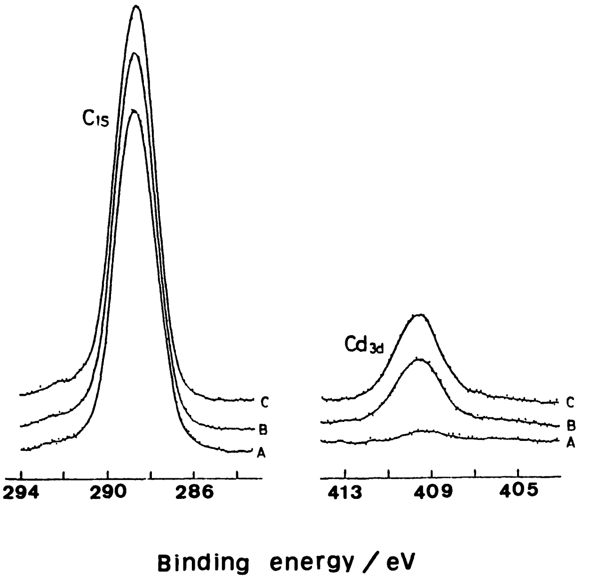

Fig. 2. C_{1s} and Cd_{3d} peaks for monolayer deposited from cadmium substrate with varying pH.
A: pH 4.7, B: pH 5.8, C: pH 7.6

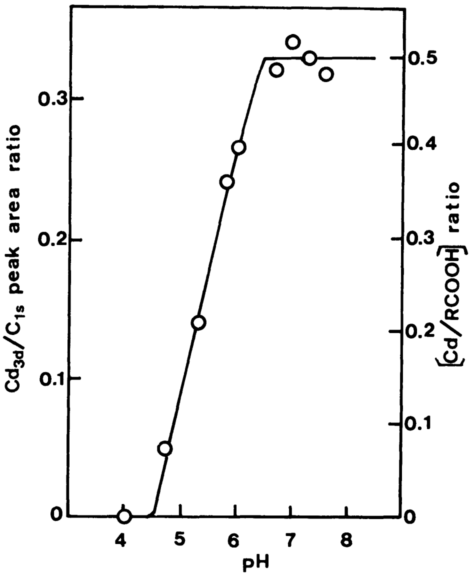

Fig. 3. Dependence of Cd_{3d}/C_{1s} peak area ratio or [Cd/RCOOH] ratio on pH.

that the carboxylic carbon band appears as a shoulder on the high energy side.[13] Also, we observed that the peak area of Cd_{3d} band was nearer to 0 in the lower pH region than about 4.6 and showed a constant value in the higher pH region than about 6.6. The near zero value at lower pH indicates no formation of cadmium icosanoate([Cd/RCOOH]=0), while the constant value at higher pH indicates the formation of cadmium icosanoate([Cd/RCOOH]=0.5), considering the pK_s value of 5.6. In order to calculate the [Cd/RCOOH] ratio at various pH, we assumed a linear relationship between the peak area of the Cd_{3d} band and the pH. The Cd_{3d}/C_{1s} peak area ratio calculated from the peak area of Fig. 2 and the [Cd/RCOOH] ratio were plotted against pH. The results are shown in Fig. 3. In this figure, the Cd_{3d}/C_{1s} peak area ratio or the [Cd/RCOOH] ratio increases from about pH 4.6 and reaches a plateau above about pH 6.6. In the lower pH region, the value of [Cd/RCOOH] is 0 which means the absence of cadmium ions. In the higher pH region, the value of [Cd/RCOOH] is about 0.5 which corresponds to the equivalent proportion of one bivalent cation to two fatty acids. Therefore, the monolayer deposited from solutions with pH<4.6 and pH>6.6 consist of icosanoic acid and cadmium icosanoate, respectively, and the monolayer deposited from solutions with pH=4.6—6.6 consist of the mixture of free acid and cadmium salt. Our experimental results are in good agreement with the observations of Petrov et al.,[3] using a combination of Langmuir-Blodgett technique and neutron activation analysis.

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