A Method for Preparing A Large Sized, Uniform and Stable Built-up Film of ^{109}Cd Icosanoate as A Radioactive Source by Utilization of an Extremely Small Amount of Substrate Solution

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A stable radioactive source *in vacuo* was obtained by a modified horizontal lifting method of Langmuir-Blodgett (L/B) film. In spite of the slight consumption of the substrate solution (only 2—2.5 ml) for preparing a 15 mm×25 mm sized L/B film containing four molecular layers of ^{109}Cd icosanoate, the deposition of the film was complete. The reliability of the deposited films by this method was confirmed by their radioactivities, deposition ratios and autoradiographs. The condition to obtain a larger sized homogeneous L/B film (20—25 mm×102 mm) was also examined. Two or four molecular layers of nonradioactive Cd icosanote deposited on the L/B film of ^{109}Cd icosanoate did not influence the intensity of the γ-ray of 88.0 KeV. Concequently, it is possible to obtain the high radioactive source by the deposition of the multilayers of ^{109}Cd icosanoate. Spectra of L_2 and L_3 conversion electrons from the ^{109}Cd in its built-up film were also determined. In conclusion, the present depositing method for the L/B film is excellent for the manufacturing the radioactive source and thought to be also applicable for the deposition of other valuable materials.

A Langmuir-Blodgett (L/B) multilayer film is superior to the ordinary vacuum deposition films in the homogeneity of the lateral direction and the uniformity of the thickness together with other advantages of their easy and reliable controllability. The L/B film of soap of a radioactive metal is, therefore, expected to be an excellent radioactive source. There are, however, two problems for the preparation of a high radioactive L/B film by the commonly used depositing method, *i.e.*, the vertical dipping method.[1] One big problem is that a great amount of radioisotope is necessary by the method. Another problem is the contamination by radioactive material on the undesirable side of the substrate plate. To reduce the amount of the radioactive material and prevent the contamination of the back side of the plate in its built-up process, a modified horizontal lifting method was devised and applied to the deposition of ^{109}Cd icosanoate monolayer, combining with an extremely shallow Teflon trough whose inside was treated with oxygen plasma to be hydrophilic. To make sure the reliability of this method, the linear relationship was confirmed between the radioactivity and the deposited amount of the source, and the uniformity of the built-up films was established by the autoradiography. The stability of the source under high vacuum and the influence of the film thickness on the intensity of the γ-ray from ^{109}Cd nucleous were also examined. The built-up film of ^{109}Cd icosanoate was utilized finally as a radioactive source in vacuum.

Experimental

A sample of icosanoic acid (purity of 99.5%, Fulka AG. Swizerland) was dissolved in benzene to make a spreading solution of 1×10^{-3} mol dm^{-3}. 500μCi and 5mCi of carrier-free cadmium-109 were supplied from Amersham (Buckinghamshire, England) as $^{109}CdCl_2$ in 0.1 M HCl. After the isotopic dilution with $CdCl_2$ and the removal of the HCl by distillation from the solutions, the aqueous solutions of radioactive $CdCl_2$ (specific activity of 0.9 or 445mCi mmol^{-1}) were prepared. The pH of the solution was adjusted to be 7—7.8[2] by the addition of a small amount of the aqueous solution of NaOH (electronic grade, Kanto Chemical Co., Tokyo). Iron(III) octadecanoate (the purest grade of Tokyo Kasei Industry Co., Tokyo) was used for the pretreatment of the surfaces of aluminium plates (20 or 25 mm×102 mm×1 mm) and resistive substrate plates (15 mm×25 mm×1 mm or 40 mm×25 mm×1 mm, Japan Fine Co., Tokyo) which were made from a mixture of ruthenium oxide with glass and printed on alumina plates. Water for the underlying ^{109}Cd solution was triply distilled, the second distillation being from alkaline permanganate, and was contained in a very shallow Teflon trough (15 mm×120 mm×0.5 mm or 1mm, 40 mm×200 mm×1 mm, or 20 or 25 mm×280 mm×1 mm) whose inside was hydrophilic by the glow discharge in an oxygen atmosphere,[3] and whose rims remained hydrophobic by protective adhesive tapes. The hydrophilic property of the inside of the trough is very important because an aqueous

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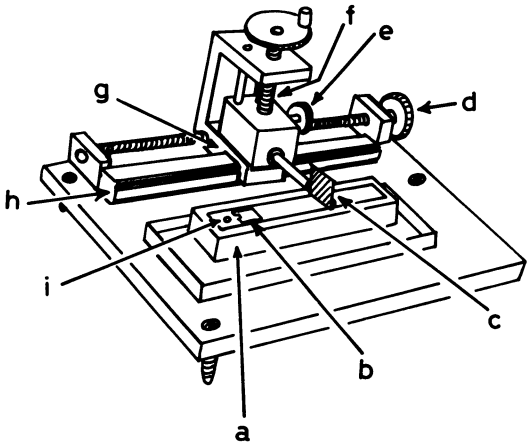

Fig. 1. Apparatus for the deposition of Langmuir-blodgett film. **a** denotes the Teflon trough whose inside is hydrophilic; **b**, Floating barrier (thin mica) coated with paraffin, having a small check at its end for the convenience of setting a small amount of piston oil; **c**, Substrate plate for built-up film; **d**, Wheel for moving the slide unit; **e**, Wheel for turning the substrate plate which was rotated by a hand or a mechanical operation with a motor and gears; **f**, Lifting screw; **g**, Slide unit; **h**, Track rail; **i**, 9-octadecenoic acid drop as a piston oil.

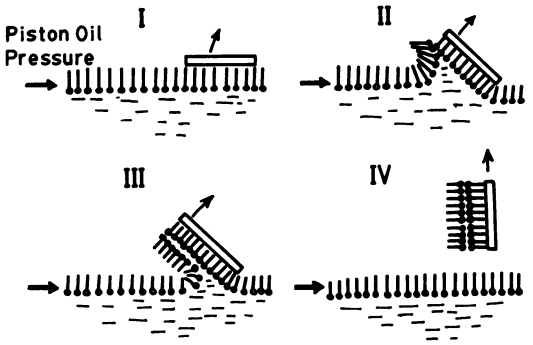

Fig. 2. Scheme of the deposition process of ^{109}Cd icosanoate monolayer on a substrate plate.

solution on a hydrophobic surface has a large contact angle and does not spread fully on the surface. If the inside of the shallow trough is hydrophobic, a small amount of the aqueous solution, therefore, can not fill the trough. Only 2—2.5 ml of solution was required to fill the small hydrophilic trough and 14—16 ml for the another large troughs. After sweeping the solution surface by a hydrophobic glass barrier treated with dimethyldichlorosilane,[4] a thin mica plate (13.5 mm×15 mm×0.1 mm, 38 mm×50 mm×0.1 mm, 18 mm×25 mm×0.1 mm or 23 mm×30 mm×0.1 mm) coated with paraffin[5] was placed on the surface and used as a movable barrier. As shown in the Fig. 1, the mica plate (b) had a small check at its one end for the convenience of setting a small amount of piston oil drop. The piston oil drop should not contact with the movable barrier because such a contact prevents sometimes the smooth movement of the barrier. The oil drop was set therefore in contact with the end wall of the trough. The floating barrier can move smoothly by the repulsion[6] between the hydrophilic trough and the hydrophobic ends of the movable barrier. A thin Teflon plate or a paper plate coated with paraffin was not suitable for the movable barrier in such the shallow trough because of its warping. The monolayer of ^{109}Cd icosanoate was deposited at the surface pressure of 29.5 mN m^{-1} with 9-octadecenoic acid (the purist grade of Merck AG., Darmstadt, German) using an apparatus shown in Fig. 1. After touching the substrate plate almost horizontally and gently on the monolayer surface from its one end, the plate was turned gradually by a hand or a mechanical operation with a motor and gears, lifted and removed finally from the surface (see Fig. 2). Two molecular layers of the ^{109}Cd icosanoate were deposited on the substrate plate by this process. The repetition of this process produced an additional deposition of two molecular layers. In order to achieve the complete deposition of the rigid monolayer onto the substrate plate, we should set the plate as close as possible to the end of the floating mica plate: Its possible smallest distance from the mica plate is apparently two times of the length of the substrate plate. This depositing method giving Y-film resembles the horizontal lifting method,[7] which gives X-film, in the first contact of the plate with the monolayer and the vertical dipping method during the gradual turning and removing of the plate. The radioactivity (characteristic γ-ray of 88.032 KeV of ^{109}Cd) of the L/B film was detected with a coaxial Ge (Li) detector (ORTEC Inc. Co., Oak Ridge, USA); a known amount of ^{109}Cd sample was used for the calibration of the radioactivity. LKB2208 Biofilm (Amuko Co. Ltd, Tokyo) was used for the autoradiography of the built-up film obtained.

The stability of the L/B film *in vacuo* was confirmed by the following method. An aluminum plate was fixed in front of the L/B film of the ^{109}Cd icosanoate (the specific activity of 0.9 mCi/mmol) with a 1 mm gap; the whole source, including the plate and the ^{109}Cd film, was set in a vacuum chamber and evacuated to a pressure of 10^{-3} Pa at room temperature (*ca.* 298 K) for a week. After the experiment, the radioactivities of the L/B film and the Al plate were detected, respectively.

Spectra of L_2 and L_3 conversion electrons (84.508 and 84.681 KeV,[8] respectively) from ^{109}Cd source prepared was measured with an INS double forcusing $\pi\sqrt{2}$ air-core β-ray spectrometer[9] and a position sensitive single-wire proportional counter[10] which had the position resolution of 1.3 mm. The momentum resolution of the counter was 0.04%.

Results and Discussion

Figure 3 shows the relationship between the relative radioactivity, R_r, of the two molecular layers of ^{109}Cd icosanoate deposited on the 15 mm×25 mm sized resistive plate and the concentration of the underlying ^{109}Cd solution. The relative radioactivity is defined as the following equation,

$$R_r = \frac{R_{obs}}{R_c}, \quad (1)$$

where R_{obs} denotes the experimental value of radioactivity and R_c, the calculated value assuming the stoichiometric bonding of a ^{109}Cd ion and two icosanoic acid molecules in the deposited L/B film. The characteristic S-shaped curve was obtained and saturated to unity above at the concentration of 1×10^{-4} mol dm.$^{-3}$ The result agrees with that by Petrov *et al.*[2] using the neutron activation analysis of cadmium species. This radioactive saturation indicates that the binding between cadmium ion and the monomolecular film of the fatty acid is complete.

We used therefore the ^{109}Cd solution of 1.2×10^{-4} mol dm^{-3} as the substrate solution for the further experiment.

Figure 4 shows the relationship between the radioactivity and the number of monolayers of ^{109}Cd icosanoate deposited on the resistive plate. A good linearity was obtained. In this fugure the full diamond, whose value is calculated from the specific activity of the $^{109}CdCl_2$, the molecular area of the icosanoic acid on the $CdCl_2$ solution of 1.2×10^{-4} mol dm^{-3} at the pressure of 29.5 mN m^{-1} and the number of layers, agrees exactly with the experimental result. A simular good linearity was observed when using the large resistive plate (40 mm×25 mm),

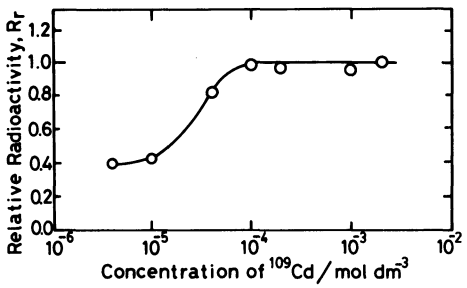

Fig. 3. The relationship between the relative radioactivity, R_r, of the two-molecular layers of ^{109}Cd icosanoate deposited on the 15 mm × 25 mm sized resistive plate and the concentration of the underlying ^{109}Cd solution.

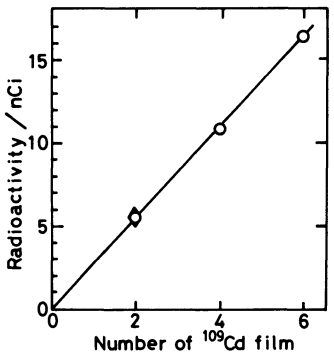

Fig. 4. Relationship between the radioactivity and the number of ^{109}Cd icosanoate monolayers deposited on the 15 mm × 25 mm sized resistive plate at 298 K. A full diamond denotes the calculated value.

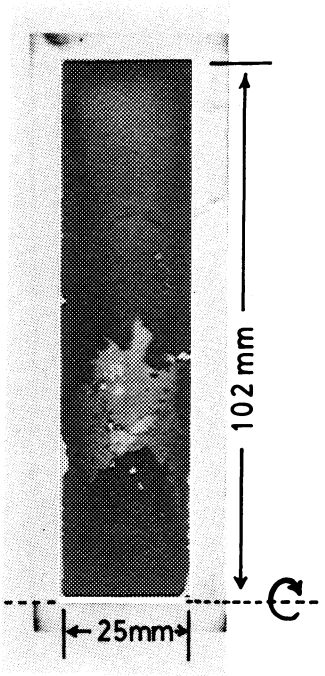

Fig. 5. Autoradiograph of the built-up film of two layers of ^{109}Cd icosanoate monolayer deposited on a 25 mm × 102 mm sized almuminium plate. Dotted line denotes the rotation axis of the substrate plate. The dark part expresses the depostion of two layers of monolayers and grayish part, one layer.

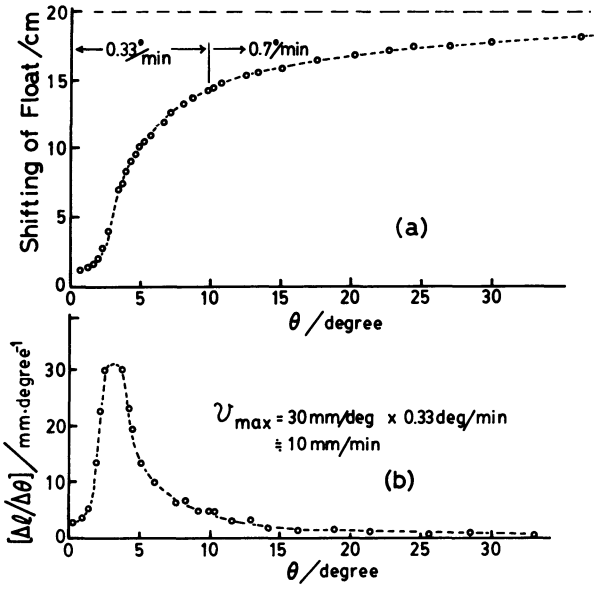

Fig. 6. (a) A typical relationship between a shift of the movable float, l, and an angle, θ, of the turning substrate plate (102 mm in length) to water surface. (b) The relationship between a slope of the tangent to the above curve of (a) and an angle, θ. The largest shift velocity, V_{max}, of the float was obtained to be about 10 min/min at $\theta = ca.$ 3°.

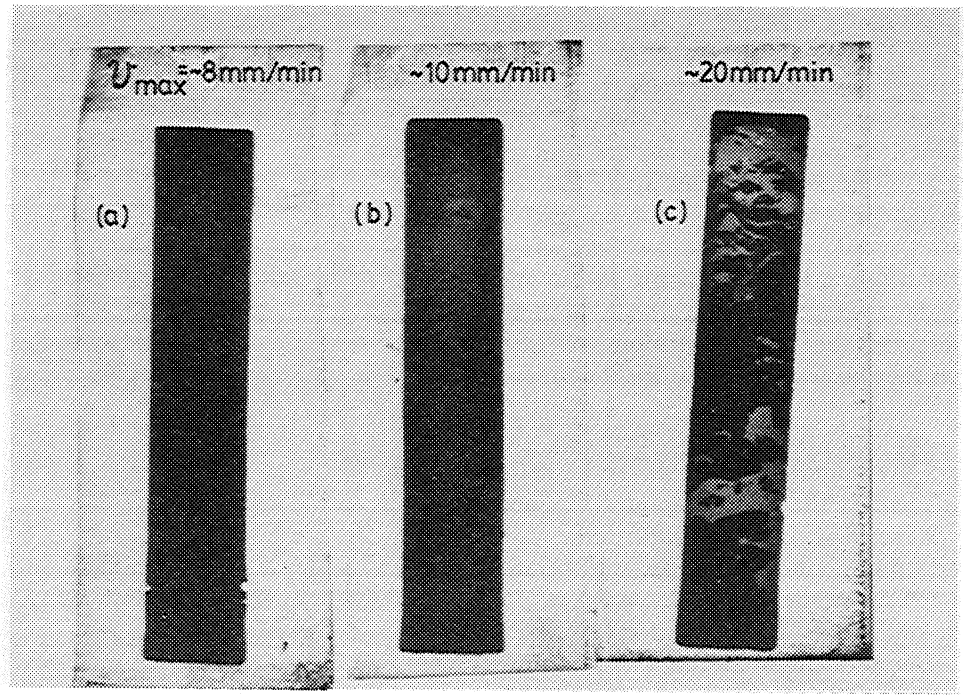

Fig. 7. Autoradiographs of built-up films of two-molecular layers of ^{109}Cd icosanoate deposited on 20 mm × 102 mm sized aluminium plates by various V_{max} values. (a) $V_{max} = \approx 8$ mm min^{-1}. (b) $V_{max} = \approx 10$ mm min^{-1}. and (c) $V_{max} = \approx 20$ mm min^{-1}.

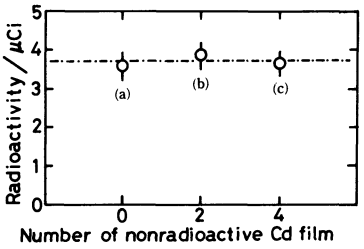

Fig. 8. Radioactivities of three samples of ^{109}Cd icosanoate (two-molecular layers) deposited on the substrate plates. **b** and **c** express the values of radioactivity for the samples containing the additional two and four layers of nonradioactive Cd icosanoate monolayer deposited on the radioactive two layers, while **a** is for the original sample.

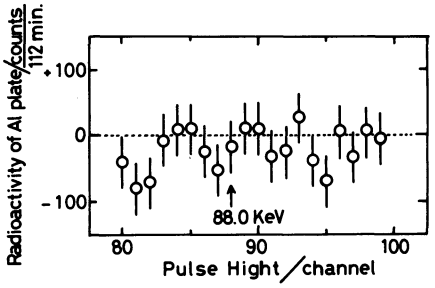

Fig. 9. Radioactivity of Al plate; arrow expresses the peak position of the characteristic γ-ray of ^{109}Cd (88.0 KeV). One channel in the abscissa denotes 1 KeV.

the wide trough and the higher specific active $^{109}CdCl_2$ subsolution. These evidences suggest that the deposition of the ^{109}Cd icosanoate monolayer on the substrate plate was perfectly achieved by this method. This suggestion has been also confirmed by the facts that the trasfer ratio of the ^{109}Cd icosanoate monolayer on the substrate plate was exactly unity and that the autoradiographs taken for these built-up films (15 mm×25 mm or 40 mm×25 mm) deposited by manual operation were entirely uniform. For the larger substrate plate (102 mm in length), however, the deposited film, especially the second layer of the film, peeled off the plate (see Fig. 5) regardless of a careful turning of the plate by the manual operation. Thus we adopted a motor and gears to rotate the substrate plate with a constant angular velocity. Figure 6a shows a typical example of the relationship between a shift of the movable float, l, and an angle, θ, of the turning substrate plate (102 mm in length) to the water surface. By θ being 10° the angular velocity was regurated to be 0.33° min^{-1} and, beyond the angle, 0.7° min^{-1}. Up to 30° the most monolayer (*ca.* 90%) was transfered from water surface to the substrate plate.

A slope of the tangent to the l—θ curve is plotted against θ in Fig. 6b. We can find that the float shifts most significantly at *ca.* 3°. From the $\Delta l/\Delta\theta$ value at

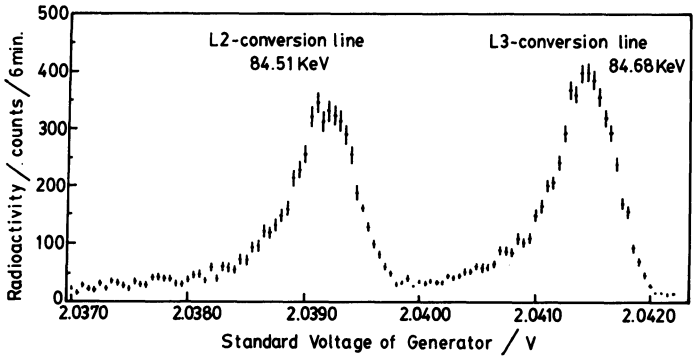

Fig. 10. A spectrum of 88 KeV-L_2 and L_3 conversion electrons (84.508 and 84.681 KeV) from ^{109}Cd source obtained. The source thickness was two-molecular layers; the source activity, 3.7 μ Ci; the source area, 40 mm × 25 mm. SVG (standard voltage of generator[9]) step: 0.00005/V.

this angle and the constant angular velocity (0.33°/min), the largest shift velocity (V_{max}) of the float was calculated to be *ca.* 10 mm min^{-1}. The V_{max} is defined in general by the length of the substrate plate and the angular velocity. The uniformity of the autoradiographs and the deposition ratios of the several built-up films were thus examined to their corresponding V_{max} values. The monolayers were deposited completely at V_{max}<10 mm min^{-1} while the deposited monolayer often peeled off the plate at V_{max}> 10 mm min^{-1}. Several examples are shown in Fig. 7.

In order to obtain a high radioactive source of the L/B film, it is necessary to deposit many number of radioactive molecular film. For such the source, the absorption of the radiation by the films themselves comes into a problem. Figure 8 shows the radioactivities of three samples of the two molecular layers of ^{109}Cd icosanoate (sp. ac. 445 mCi mmol^{-1}) deposited on 40 mm×25 mm sized resistive plate. The second (b) and the third (c) samples contain the additional two and four layers of nonradioactive Cd icosanoate monolayer on the radioactive two hayers, respectively. These three values are almost equal to each other within the experimental error. For the γ-ray of 88.0 KeV, therefore, the influence of its absorption seems to be almost negligible. In addition the result of these constant radioactivities suggests that the additional deposition of the nonradioactive Cd monolayers does not cause the isotope exchange between the ^{109}Cd in the deposited monolayers and the nonradioactive Cd ion in the subsolution in the short period of the additional depositing process (*ca.* 12—3 min).

For the application of the L/B film of ^{109}Cd icosanoate as the radioactive source, its stability *in vacuo* is essential, because the radioactive sources are often used under high vacuum. The test of the stability of the L/B film of ^{109}Cd icosanate (two-molecular layers) *in vacuo* was, threrefore, carried out. After the one week evacuation of the sample at 10^{-3} Pa any reduction of the radioactivity of the L/B film was not observed and the radioactivity was also not detected from the Al plate as shown in Fig. 9. Futhermore, the contents in a liquid nitrogen trap did not show any radioactivity of ^{109}Cd. The stability of the L/B film *in vacuo* was thus confirmed.

Figure 10 shows a spectrum of L_2 and L_3 conversion electrons from the two layers of ^{109}Cd icosanoate (40 mm×25 mm, 3.7μCi). Two peaks due to the above conversion electrons, whose energies are very close each other, were sharp and apparently distinguishable each other. The momentum resolutions obtained from the half-value widths of the peaks were 0.029 and 0.030% for the peaks of L_2 and L_3 conversion electrons, respectively.

The depositing method for the L/B film is excellent, therefore, for preparing the radioactive source and thought to be also applicable for the deposition of other valuable materials.

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