Effect of Post-Treatments on the Stability of the Langmuir-Blodgett Film of Fatty Acid Salt in Vacuum

Makio IWAHASHI,* Yoshimi YAMAGUCHI, Koichi KOBAYASHI,† and Tsutomu SEIMIYA††
Department of Chemistry, School of Hygienic Sciences, Kitasato University, Sagamihara, Kanagawa 228
†Laboratory of Chemistry, Musashi Institute of Technology, Setagaya-ku, Tokyo 158
††Department of Chemistry, Faculty of Sciences, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158
(Received April 24, 1987)

Synopsis. The effects of the following treatments on the stability of the Langmuir-Blodgett (L/B) film of fatty acid salt in vacuo have been investigated by radiotracer method: (I) Skeletonization of the L/B film. (II) Transformation of the fatty acid molecules remaining in the L/B film into its soap molecules. (III) Perfect formation and deposition of the metal soap monolayer.

Langmuir-Blodgett (L/B) films of tritiated fatty acid are expected to be an excellent ^{3}H-source for the measurement of the electron anti-neutrino mass:[1] The measurement requires a source that is highly radioactive, homogeneous, very thin, uniform and nonvolatile in vacuo. Concerning the volatility in vacuo, however, the L/B film of fatty acid is not so stable,[2-4] and the desorption of the source molecules becomes the origin of the main background in the measurement.

Roberts and Gaines[2] reported that almost 90% of the ^{14}C-octadecanoic acid film on a quartz backing was evaporated after one hour evacuation at a pressure of 10^{-4} Pa and room temperature, while only 10% of the barium ^{14}C-octadecanoate film was evaporated at the same conditions. This suggests that the L/B film of metal soap is more stable in vacuo than that of the free acid. Most of L/B films of metal soap, in addition, do not consist of only pure metal soap molecules: They include more or less the original acid molecules which evaporate easily.[5] The increase of the metal soap content in the molecules consisting the L/B film is therefore expected to make the L/B film more stable even under high vacuum conditions.

In the present study we investigated the desorption behaviours of ^{3}H-molecules from the L/B films of barium or cadmium $^3H_2$-octadecanoate in solvent and/or in vacuo, trying to improve the stability of the L/B film with various procedures such as (I) preremoval of the free acid molecules by rinsing the L/B film in a solvent (skeletonization), (II) transformation of the free acid molecules in the L/B film to the metal soap molecules by immersing the L/B film in a concentrated $BaCl_2$ aqueous solution under high pH conditions, and (III) complete formation and deposition of monolayer of pure metal soap.

Experimental

A sample of 9,10-$^3H_2$-octadecanoic acid (sp. ac. of 16 Ci mol^{-1}) was synthesized[6] the addition of hydrogen gas to 9,10-$^3H_2$-octadecenoic acid (sp. ac. of 5700 Ci mol^{-1}, Amersham Co.) diluted with pure 9-octadecenoic acid (purity $\gg$ 99.5%, Merck Co.). The sample was purified by repeated recrystallization from hexane and dissolved in benzene to make a spreading solution of 1×10^{-3} mol dm^{-3}.

Organic solvents and inorganic salts were the purest grade reagents of Wako Pure Chemical Co., Osaka. The former were distilled prior to use and the latter were used without further purification. Iron(III) octadecanoate (the purest grade of Tokyo Kasei Industry Co., Tokyo) was used for the pretreatment of surface of substrate plate (ferrotype plate whose size was 15 mm ×25 mm×0.8 mm).

Water for the subphase solution was triply distilled, the second distillation being from alkaline permanganate, and was contained in a Teflon trough (8 cm×20 cm×1 cm) with a waxed silk thread as the movable barrier. The trough had a pocket (1.5 cm×4 cm×1 cm) in its bottom for the dipping of the substrate plate. The pH of the solution was adjusted by adding a solution of NaOH or $Ba(OH)_2$. All the solutions were not buffered. The pH value was determined prior to and after the built-up procedure. The change of pH was less than 0.3 unit. L/B films were deposited at a surface pressure of 29.5 mN m^{-1} using 9-octadecenoic acid (Merck reagent grade) as a piston oil. The plate was dipped to 10 mm in depth of the subphase water and withdrawn through the monolayer at a velocity of 0.1—0.5 cm s^{-1} by means of a synchronous motor. In order to determine the transfer ratio of the monolayer onto the substrate plate, we used an another Teflon trough (2.5 cm×20 cm×2 cm) with an inside that was hydrophilic.[7] A thin mica plate (23 mm×30 mm×0.1 mm) coated with paraffin was placed on the surface of the solution in the trough and used as a movable barrier. The floating barrier can move smoothly by the repulsion[8] between the hydrophilic trough and the hydrophobic ends of the movable barrier. From the movement of the barrier in the deposition process we evaluated the transfer ratio of the monolayer. The transfer ratio, thus obtained, for each deposition process was almost unity (0.97—1.00).

The radioactivity of the L/B films of Ba- or Cd-$^3H_2$-octadecanoate was measured with a 2π-windowless gas flow counter (Aloka Model FC-1E) using Q-gas as the counting gas.

Results and Discussion

A good linear relationship was obtained between the radioactivity and the number of layers of barium $^3H_2$-octadecanoate film deposited on the ferrotype plate under the conditions of pH=6.2—11.2. From the radioactivity results and the movements of the movable barrier, it was confirmed that two monolayers were always deposited onto the substrate plate in one dipping and withdrawing process of the plate even at high pH region. Autoradiographs of the other samples with two molecular films of Ba-$^3H_2$-octadecanoate similarly prepared were taken using LKB Biofilm-^{3}H (Akom Co., Tokyo); they were fairly uniform.

Five kinds of L/B films were prepared under the following depositional conditions and by post-treat-

Table 1. The Effects of Immersing in $BaCl_2$ Solution and Rinsing in Benzene on the Stability for the L/B Film of Octadecanoic Acid

Film	No. of monolayer	Built-up condition[a)]	Fraction of remaining radioactivity after immersing in $BaCl_2$ solution of 1×10^{-3} mol dm^{-3} at pH=9.2	Fraction of remaining radioactivity after rinsing in benzene for 30 s
(a)	4	pH=6.2		
(b)	4	pH=9.0		
(c)	4	pH=6.2		0.885
(d)	2	pH=11.2		0.940
(e)	4	pH=6.2	1.00 (1 min immersing)	0.679
(f)	4	pH=6.2	0.935 (1.5 h immersing)	0.822

a) Built-up process for these L/B film was carried out at the surface of $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at ca. 288K.

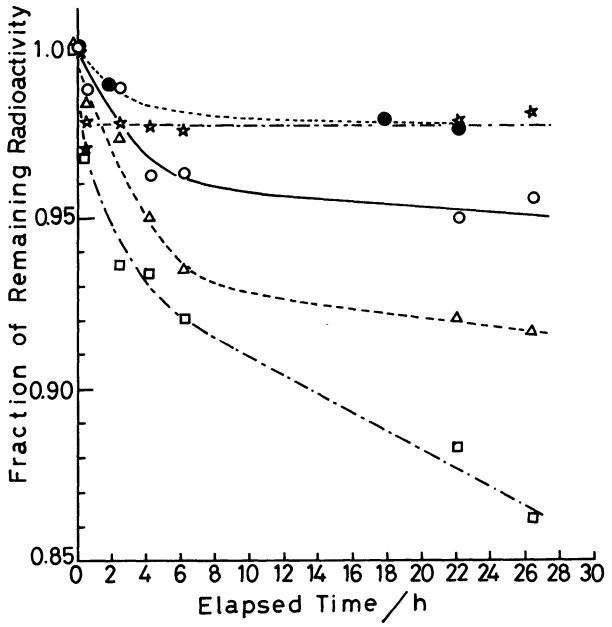

Fig. 1. The effect of post-treatments of the L/B film on its removal at a pressure of 133 Pa and a source temperature of 288 K; ○, L/B film (a) was composed of four molecular layers transfered from the $^3H_2$-octadecanoic acid monolayer spread on an aqueous $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at pH=6.2; ●, film (b), four layers transfered from the acid monolayer spread on $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at pH=9; △, film (c), the same as the film (a), but was rinsed in benzene for 30 seconds; □, film (e), the same as the film (a), but was immersed in $BaCl_2$ solution of 1×10^{-3} mol dm^{-3} at pH=9.2 for one minute and then rinsed in benzene for 30 seconds; ☆, film (f), the same as the film (a), but was immersed in the above $BaCl_2$ solution for 1.5 hours and then rinsed in benzene for 30 seconds.

ments. Film (a): four-layers film deposited from the $^3H_2$-octadecanoic acid monolayer spread on the aqueous $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at pH=6.2, film (b): four-layers film deposited from the acid monolayer spread on a $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at pH=9, film (c): the same as the film (a) but was rinsed in benzene for 30 seconds, film (d): two-layers film deposited from the acid monolayer spread on a $BaCl_2$ solution of 1×10^{-4} mol dm^{-3} at pH=11.2 and then rinsed in benzene for 30 seconds, film (e): the same as the film (a) but was immersed in a $BaCl_2$ solution of 1×10^{-3} mol dm^{-3} at pH=9.2 for one minute and then rinsed in benzene for 30 seconds, film (f): the same as the film (a) but was immersed in the above $BaCl_2$ solution for 1.5 hours and then rinsed in benzene for 30 seconds.

The desorption ratio of the above films (c—f) into solvent are tabulated in Table 1 as a remaining fraction of the radioactivity. Film (d) deposited at high pH was more stable against rinsing in benzene than film (c) deposited at low pH. Barium octadecanoate, being resistant against dissolution in benzene,[5)] might be easily formed at a high pH region. The fatty acid monolayer, however, tends to desorb into the subphase solution at the highest pH region, even during the deposition process. The radioactivity of the film (e) was not changed by one-minute immersing in the $BaCl_2$ solution of pH=9.2. The succeeding rinsing of the film (e) in benzene, however, decreased its radioactivity considerably. The one-minute immersing of the L/B film of fatty acid in $BaCl_2$ solution of high pH does not improve the conversion of fatty acid to its barium soap in the film, but seems to distort the arrangement of the acid molecules and to loosen the lateral bondings among the molecules by the electrical repulsions of their dissociated carboxyl groups. Although the long period of immersing of the L/B film in the $BaCl_2$ solution is expected to progress the conversion, a slight removal of the film material was resulted.

Figure 1 shows the evaporation profiles of the $^3H_2$-octadecanoic acid from the L/B films under a condition of 133 Pa and 288 K. For the films (c), (e), and (f), the initial radioactivity is defined as that obtained just after their rinsing in benzene. Evaporation of the acid molecules from the film (e), was most significant. This is also due to the distortion of the arrangement of the molecules. Film (b) strongly resisted the removal of molecules. The evaporation rate for the skeletonizated film (c) was much higher than that for film (a); the skeletonized films did not resist the thermal desorption of the film molecules. Beischer[9)] reported that copper 1-^{14}C-octadecanoate molecules, whose neighboring octadecanoic acid molecules were excluded, evaporated much easier than copper octadecanoate molecules in the pure L/B film.

Film (f) seems to be better than film (a) in the resistance against the thermal removal of film molecules. However, the total remaining fraction of the radioactivity (0.749=0.935×0.822×0.975) of film (f) is smaller than that (0.929) of film (a).

Consequently, an increase of the metal soap content in the film is essential to obtain a L/B film stable in vacuum without the skeletonization for the film.

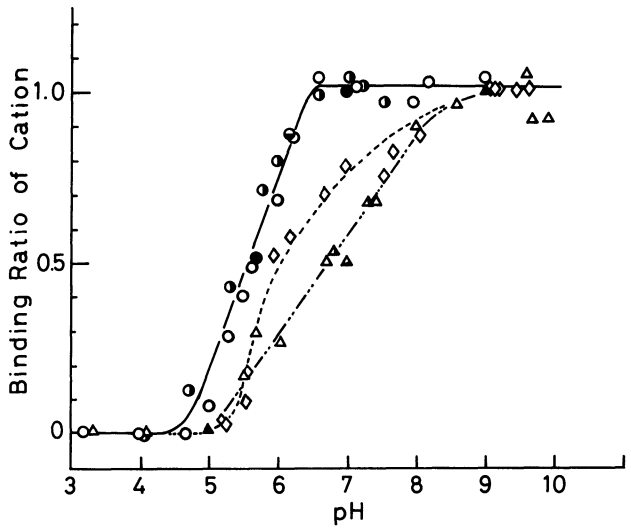

Fig. 2. The pH dependence of the ratio of binding of divalent cations to fatty acid monolayers. Circles denote the ratio of binding for cadmium ion, diamonds that for calcium ion and triangles that for barium ion. The marks ○ and △ are from neutron activation analysis study[10] for icosanoic acid; ● and ▲ are the Blodgett's data[11] for icosanoic acid and ◭ is the Ehlert's data[12] for octadecanoic acid (both data were obtained by the skimming method); ▲ and ◇ are IR-spectroscopic data[13,14] for octadecanoic acid; ◒ is from the photometric study of dissolved multilayers of icosanoic acid;[15] ◑ is the Kobayashi's data[16] for icosanoic acid by ESCA.

Figure 2 shows the metal-ion bindings in the monomolecular films of octadecanoic and icosanoic acids[10-16] in their L/B films. The binding ratio of the barium cation to the above fatty acids is only 0.4 at pH=6.2, that is, ca. 60 mole-percent of the fatty acid seems to remain as the original fatty acid at the surface of the barium solution of pH=6.2. Cadmium cation binds perfectly in the icosanoic acid monolayer above at pH=6.5, whereas both calcium and barium cations do above pH=9. The former pH is close to the pH of distilled water (pH=5.8): This is suitable for preparing a perfect metal soap L/B film because we need not use much undesirable ions such as Na^+, K^+, PO_4^-, or CO_3^{2-} for adjusting the pH of the subphase solution.

New samples of L/B film of Cd-$^3H_2$-octadecanoate were therefore prepared by using a $CdCl_2$ solution of 1×10^{-3} mol dm^{-3} (pH=7.2; the NaOH concentration of the solution was ca. 1.7×10^{-6} mol dm^{-3}) as the subphase solution and evacuated under the pressure of 133 Pa and temperature 288 K. The radioactivities of the L/B films remained unaltered for two days within an error of ±3%; the fatty acid molecule anchored by the cadmium ion seems not to evaporate from the L/B film.

Concequently, in order to obtain a L/B film stable in vacuum, the increase of metal soap content in the L/B film is absolutely essential without skeletonization of the film or without new formation of metal soap. For the increase of the metal soap content, in addition, the cadmium solution can be more advantageously used than the calcium or barium solution.

References

1) V. A. Lubimov, E. G. Novikov, V. Z. Nozik, E. F. Tretyakov, and V. S. Kosik, *Phys. Lett.*, **94B**, 266 (1980).
2) R. W. Roberts and G. L. Gaines Jr., Trans. Ninth Natl. Vacuum Symp., Am. Vacuum Soc., 515, (1962); *Nature (London)*, **197**, 787 (1963).
3) H. Schonohorn, *J. Colloid Soi.*, **18**, 445 (1963).
4) J. A. Spink, *J. Colloid Interface Sci.*, **24**, 61, (1967).
5) J. E. Young, *Australian J. Chem.*, **8**, 173 (1955).
6) M. Iwahashi and K. Tajima, *J. Labelled Comp.*, **7**, 501 (1971).
7) M. Iwahashi, F. Naito, N. Watanabe, T. Seimiya, N. Morikawa, N. Nogawa, T. Ohshima, H. Kawakami, K. Ukai, I. Sugai, S. Shibata, T. Yasuda, Y. Shoji, T. Suzuki, T. Nagafuchi, H. Taketani, T. Matsuda, Y. Fukushima, M. Fujioka, and K. Hisatake, *Bull. Chem. Soc. Jpn.*, **58**, 2093 (1985).
8) J. J. Bikerman, "Physical Surfaces," Academic Press, New York (1970), p. 39.
9) D. E. Beischer, *J. Phys. Chem.*, **57**, 134 (1953).
10) J. G. Petrov, I. Kuleff, and D. Platikanov, *J. Colloid Interface Sci.*, **88**, 29 (1982).
11) K. B. Blodgett, *Phys. Rev.*, **55**, 391 (1939).
12) R. S. Ehlert, *J. Colloid Sci.*, **20**, 387 (1965).
13) J. W. Ellis and J. L. Pauley, *J. Colloid Sci.*, **19**, 755 (1964).
14) J. Bagg, M. B. Abramson, M. Fichman, M. D. Haber, and H. P. Gregor, *J. Am. Chem. Soc.*, **86**, 2759 (1964).
15) J. G. Petrov, H. Kuhn, and D. Möbius, *J. Colloid Interface Sci.*, **73**, 66 (1980).
16) K. Kobayashi and K. Takaoka, *Bull. Chem. Soc. Jpn.*, **59**, 933 (1986).