March, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 657—661 (1989) 657

The Meaning of the Equilibrium Spreading Pressure of Fatty Acid Being Relatively Soluble in an Underlying Subphase

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(Received July 15, 1988)

The spreading pressure of a lipid monolayer in equilibrium with its crystal placed at the air/water interface is a thermodynamical property—i.e., the equilibrium spreading pressure (ESP). It is, however, quite likely that the apparently constant spreading pressure of a lipid with a relatively large desorption rate into the underlying subphase is not a thermodynamical property but merely a steady-state one. Mutual comparisons were, therefore, carried out for the rate constants of the six possible processes associated with the spreading pressure of tetradecanoic acid, whose monolayer has a relatively large desorption rate into the underlying subphase; it was found that monolayer formation from its crystal was predominant and that the desorption from the monolayer little affected the spreading pressure, even at high temperatures. Consequently, the apparently constant spreading pressure for the tetradecanoic acid can be regarded as the ESP even at high temperatures, in which the dissolution of the monolayer into the subphase occurs very rapidly.

Many lipids spread spontaneously when placed in a solid or liquid form at the air/water interface, thus giving monolayers in apparent equilibrium with the excess bulk lipid phase. The corresponding surface pressure (Π) of the monolayer is generally known as the equilibrium spreading pressure (ESP). The ESP is, in principle, useful for obtaining thermodynamic information on the crystal-monolayer transition; monolayer experiments carried out beyond the pressure of ESP are thought to be thermodynamically invalid. However, it appears to be doubtful that the apparently constant spreading pressure for the lipid, which has a relatively large desorption rate into the underlying subphase, is a true equilibrium property; that is, it seems quite likely that the apparent constancy of the spreading pressure is attributable not to the genuine ESP, but to a steady-state caused by the monolayer material being lost from the interface by desorption. Six processes (see Fig. 1) are, in general, possible in accounting for the spreading of a relatively soluble and nonvolatile lipid crystal: (1) a monolayer formation by the spreading of the lipid from its crystal; (2) the re-binding of the molecule in the monolayer to the crystal; (3) the dissolving of the monolayer into the underlying subphase; (4) the adsorption from the subphase to the monolayer; (5) the dissolution of lipid molecules from its crystal into the subphase; and (6) the adsorption from the subphase to the crystal.

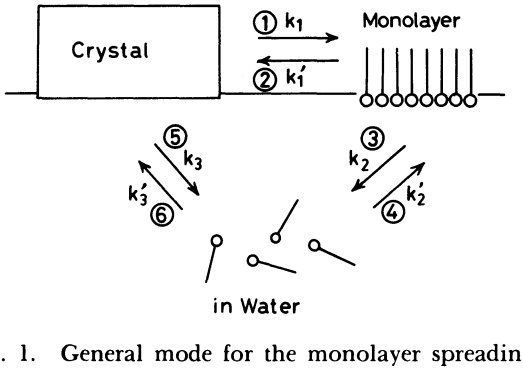

Fig. 1. General mode for the monolayer spreading process.

In the present study we investigated the above processes for tetradecanoic acid, which has a relatively large desorption rate into the underlying water, and discussed kinetically the meaning of the ESP by comparing the rate constants for the above processes with one another.

Experimental

The sample of tetradecanoic acid (purity: 99.7%; Applied Science Co., Ltd.) was further purified by repeated slow crystallizations overnight from hexane. Needle-like (small) and plate-like (large) crystals formed from the hexane solution were both freed of the solvent by being pumped out for a week on a vacuum line. The crystallographic forms were determined for the two types of crystals with a X-ray diffraction instrument (Rigaku Denki Model Geigerflex RAD-1A). The needle-like and plate-like crystals were A-super-type and C-type forms respectively.[1] The purest grade hexane from the Wako Co., Ltd. (Tokyo), was redistilled two times before being used for the preparation of the above crystal samples and as the spreading solvent in the monolayer-desorption experiment. The subphase solution consisted of triply distilled water whose pH has been adjusted to 2 with twice-distilled HCl.

The spreading pressure of the crystal was measured by the Wilhelmy plate method, using the apparatus shown in Fig. 2 and under temperatures (constant to ±0.01 K) over the range of 290—318 K and at almost a 100% humidity. A Wilhelmy

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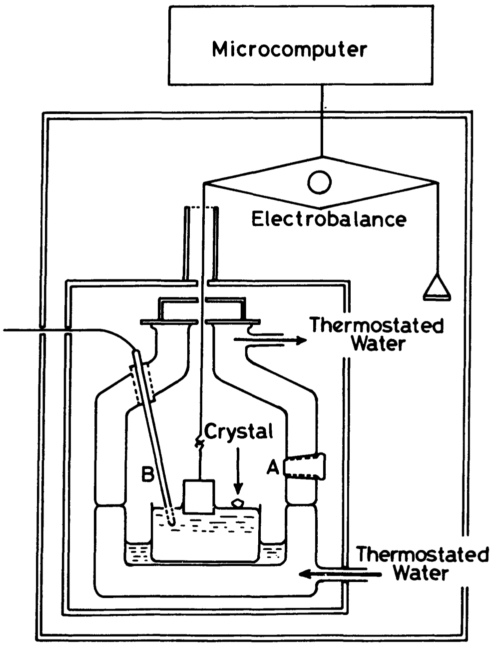

Fig. 2. Schematic representation of apparatus for measurement of surface pressure. A denotes a hole though which samples are introduced onto clean water surface and B, an IC-thermometer.

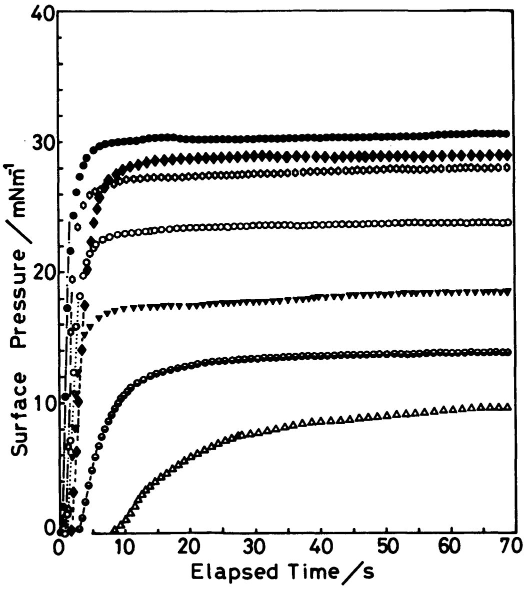

Fig. 3. Time dependences of spreading pressure of tetradecanoic acid crystal on the water surface at various temperatures. Diamond denotes plate-like crystal and other symbols needle-like crystal. △: T=292.1 K, ○: 296.1 K, ▽: 303.1 K, ○: 308.1 K, □: 313.1 K, ● and ◆: 318.1 K.

plate was connected to an electrobalance (Shimadzu Model TGA-31), whose output was in turn connected to a digital multimeter (Hewlett-Packard Model 3478A) and a personal computer (NEC Model PC-8001MKII). Needle-like crystals (or a single crystal of a plate-like form) were introduced onto the clean surface through the hole A (shown in Fig. 2); the surface pressure was recorded every half-second. The sensitivity of the balance was $\pm 0.01\ \mathrm{mN\,m^{-1}}$, and the reproducibility was $\pm 0.1\ \mathrm{mN\,m^{-1}}$. A constant surface pressure was obtained 5—10 min after the crystal has been placed onto the water surface; the constancy of the pressure for the plate-like crystal did not change for 120 h, while that for the needle-like crystals varied somewhat with the time. The constant values thus obtained were taken as the apparent ESP (see Table 1).

For desorption experiments on the monolayer at constant surface pressures, we used a Langmuir glass trough (600 mm×109 mm×57 mm) whose surface has been treated with dimethyldichlorosilane in order to make it hydrophobic. Two glass pipes were set on the bottom of the trough for temperature control (±0.1 K). The surface pressure was also observed by the Wilhelmy plate method. After spreading a monolayer and evaporating the spreading solvent, compression was carried out to a surface pressure below about $0.3\ \mathrm{mN\,m^{-1}}$ of the apparent ESP so as to avoid spontaneous monolayer collapse. This pressure was maintained constant within $0.1\ \mathrm{mN\,m^{-1}}$ by further manually decreasing the area. This area decrease was measured as a function of the time.

Scanning electron micrographic observation (SEM) for the plate-like crystals used in the spreading-pressure experiments was carried out with a JOEL JXA-840 scanning electron microscope.

Results and Discussion

Figure 3 shows the time dependence of the spreading pressure of the tetradecanoic acid crystal introduced at the air/water interface. After a retardation time, the surface pressure Π increased rapidly for a few seconds, followed by a gradual increase before it reached a constant value. The yield point was dependent on the crystal type or on the temperature. In the case of the needle-like crystal at a higher temperature (318.1 K), we could not recognize the retardation time. The yield point was defined as time zero for the spreading process of the molecules from the crystal.

In the six processes illustrated in Fig. 1, the contributions of Processes (4) and (6), i.e., the k_2' and k_3' terms, to the whole system appear to be negligibly small because of the extremely small concentration of the tetradecanoic acid in the water,[2] especially at the initial stage. Furthermore, the k_3 (the desorption constant from the crystal into water) in Process (5) is thought to be smaller than the k_2 (the desorption constant from monolayer into water) in Process (3), for the molecules in the crystal are more ordered and are combined more tightly with one another than the molecules in the monolayer.

Spreading Process. Assuming the first-order mode for every process, the rate equation for the monolayer formation (spreading) is given by:

$$\mathrm{d}\Gamma/\mathrm{d}t = k_1C - (k_1' + k_2)\Gamma \qquad (1)$$

where Γ is the amount of molecules in the monolayer; t, the elapsed time after the yield point of the spreading pressure; C, the amount of crystal directly in contact with the water; k_1, the rate constant for the spreading process of the molecules from the crystal to form the monolayer (Process (1)), and k_1', the rate constant for the re-binding of the molecules to the crystal (Process (2)).

In the initial stage of the spreading from the crystal, the molecular density in the monolayer is so small that Γ can be almost zero. Consequently, Eq. 1 is expressed as:

$$\mathrm{d}\Gamma/\mathrm{d}t = k_1 C \tag{2}$$

In the temperature range of 290—318 K in our experiment, the monolayer of tetradecanoic acid is in the liquid-expanded state.[3,4] For the liquid-expanded film, Langmuir proposed the following equation:[3]

$$(\Pi - \Pi_0)(A - A_0) = RT \tag{3}$$

where Π is the surface pressure (mN m^{-1}): Π_0, the characteristic surface pressure of the film material ($\Pi_0 = -11.2$ mN m^{-1} for tetradecanoic acid[5]); A, the occupied area per mole (m^2 mol^{-1}) of the film material; A_0, the excluded area per mole (m^2 mol^{-1}); R, the gas constant and T, the absolute temperature.

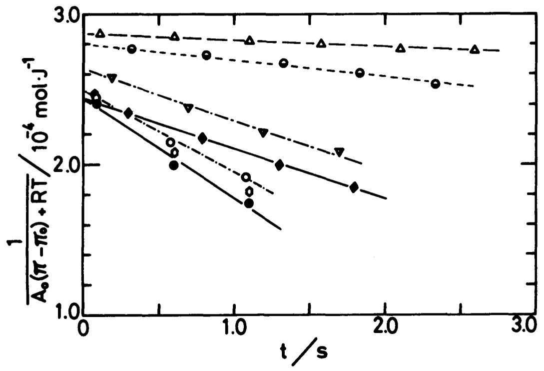

Fig. 4. $1/[A(\Pi-\Pi_0)+RT]$–t relationships for tetradecanoic acid monolayers on 0.01 M HCl at various temperatures. Diamond denotes plate-like crystal and other symbols needle-like crystal. △: T=292.1 K, O: 296.1 K, ▽: 303.1 K, O: 308.1 K, □: 313.1 K, ● and ◆: 318.1 K.

Many theoretical equations[6—9] of the state for liquid-expanded monolayers have been proposed; Smith[9] compared the equations with the experimental data for fatty acids and concluded that Langmuir's equation described the experimental data better than any other equation in spite of the variation in Π_0. Consequently, by using Langmuir's equation and by defining $\Gamma = A_T/A$, where A_T is the area of the trough (m^2) containing the subphase solution, we obtain:

$$\Gamma = A_T(\Pi - \Pi_0)/[A_0(\Pi - \Pi_0) + RT] \tag{4}$$

wherefrom we obtain:

$$\begin{aligned}\mathrm{d}\Gamma/\mathrm{d}t &= (\mathrm{d}\Gamma/\mathrm{d}\Pi)(\mathrm{d}\Pi/\mathrm{d}t)\\ &= \{A_T RT/[A_0(\Pi - \Pi_0)+RT]^2\}(\mathrm{d}\Pi/\mathrm{d}t).\end{aligned} \tag{5}$$

The substitution of Eq. 2 in Eq. 5 and subsequent integration yield:

$$\{1/[A_0(\Pi - \Pi_0) + RT]\} = -(A_0 k_1 C/A_T RT)t + 1/(RT - A_0\Pi_0). \tag{6}$$

Figure 4 shows the relationship between $\{1/[A_0(\Pi - \Pi_0) + RT]\}$ and t at various constant temperatures. Good linearities are observed. The slopes for these lines give us k_1C values by the use of A_T=59.17×10^{-4} m^2 and A_0=6022×[12.0+0.178(T−273.15)] m^2 mol^{-1} for the tetradecanoic acid monolayer.[5] The k_1C values thus obtained are listed in Table 1.

The surface pressure, especially at the initial spreading process of the film, is thought to be associated with the number of acid molecules, which are directly in contact with the water, in the crystal. Consequently, we can evaluate the k_1 value only if we know the actual amount of molecules, C.

Figure 5 shows the relationship between the k_1C and the amount of crystal placed on the water surface at 318.1 K. The k_1C value for the needle-like crystals (circle) is always larger than that for the plate-like crystal (square). This may be attributable to the fact that the needle-like crystals have many sharp points[10] at the ends of the crystal, as is shown in the SEM

Table 1. ESP, k_1, k_2, and k_1' Values for the Needle-Like Crystal at Various Temperatures

T	ESP	k_1C	k_1	k_2	k_1'
K	mN m^{-1}	mol·s^{-1}	s^{-1}	s^{-1}	s^{-1}
292.1	14.0	9.96×10^{-10}	13.8	1.2×10^{-5}	2.0×10^{-2}
296.1	16.7	1.81×10^{-9}	25.1	1.8×10^{-5}	5.6×10^{-2}
303.1	20.4	6.15×10^{-9}	85.2	2.8×10^{-5}	19.2×10^{-2}
308.1	24.3	8.08×10^{-9}	112	5.9×10^{-5}	25.3×10^{-2}
313.1	27.0	8.45×10^{-9}	117	33.8×10^{-5}	26.3×10^{-2}
318.1	30.9	8.88×10^{-9} 5.25×10^{-9} a)	123 72.8 a)	74.0×10^{-5}	27.7×10^{-2}

a) These values are for a plate-like crystal.

photograph **A** in Fig. 6, rather than to the difference in the crystallographic forms. The k_1C for the plate-like crystal is independent of the crystal size, while that for the needle-like crystals is also independent of their amounts. Consequently, the number of molecules which are directly in contact with the water seems to be restricted and to be almost constant, regardless of the size or amount of the crystal placed onto the water surface: there is never a time when all the crystal is in contact with the water. In fact, as is shown in the SEM photograph **B** in Fig. 6, the surface of the plate-like crystal used for the spreading-pressure experiment was found to be corroded only partially, even after the crystal has stood on the water surface for 7 days at 318.1 K.

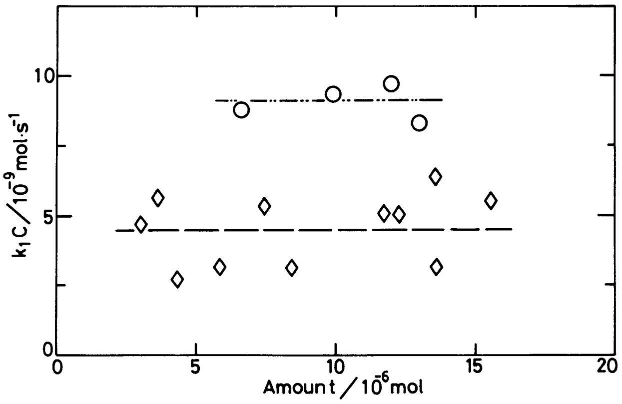

Fig. 5. Relationship between k_1C and amount of crystals placed on water surface at 318.1 K. Circles denote needle-like crystals; diamonds, plate-like crystals.

Although it is essential to know the amount of the molecules, C, directly in contact with the water in the initial stage of the spreading process, the estimation of the genuine amount is impracticable at the present time. Accordingly, a rough approximation was carried out as follows.

C is assumed to be the amount of the molecules in the outermost molecular layer of the crystal facing the underlying water, disregarding the fact that only a part of the crystal surface is directly in contact with the water. The area of the plate-like crystal used in our experiment was determined to be in the range of 7.83—26.7 mm^2 by means of photographic observations. The amount of C for the 7.83 mm^2-sized crystal was estimated to be 7.22×10^{-11} mol by using the cross-section of the 18 Å^2/molecule for the fatty-acid molecule. The k_1 values thus obtained from this C amount at various temperatures are listed in Table 1. Although the ESP increases linearly with the temperature, the k_1 increases in an S-shape. The rapid increase in the k_1 value between 296 and 308 K seems to due not only to the increase in its genuine value, but also to the increase in the wettability of the crystal to water-that is, the increase in the amount of C which is directly in contact with the water. The k_1 value at low temperatures is, therefore, probably smaller than the genuine value because water has a low wettability against the crystal surface because of the higher surface tension of water at low temperatures. The magnitude of k_1 is, however, sufficiently large in comparison with the other rate constants which will be mentioned below.

Desorption Process. In order to estimate the rate constant k_2 in the process of dissolving tetradecanoic acid from its monolayer (Process (3)), desorption

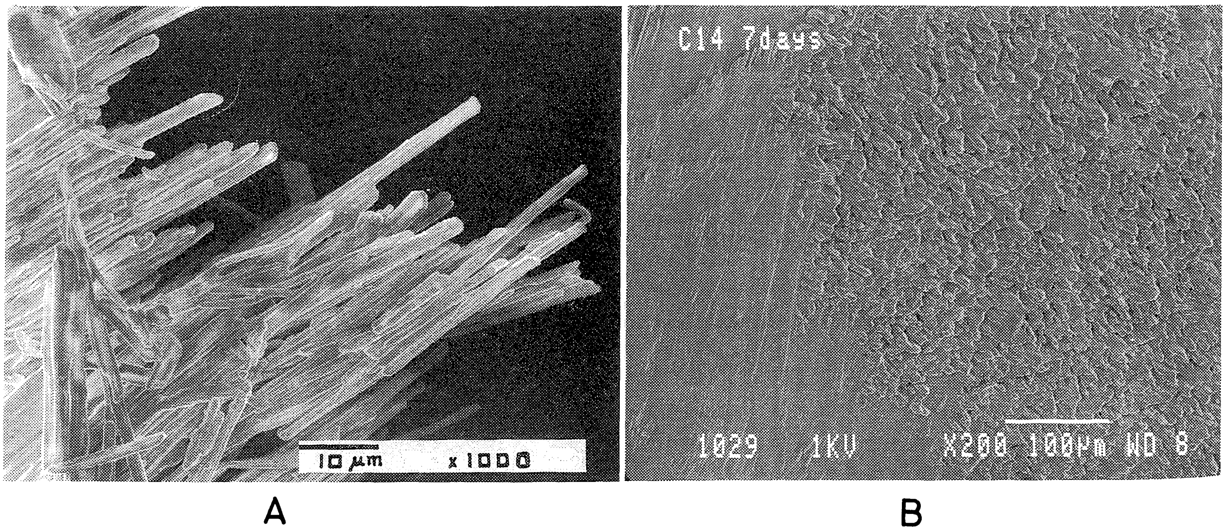

Fig. 6. Photograph **A** represents the needle-like crystals which have sharp ends. Photograph **B** represents a plate-like crystal which was kept for standing on water surface for 7 days at 318.1 K. Only right side of the crystal is corroded.

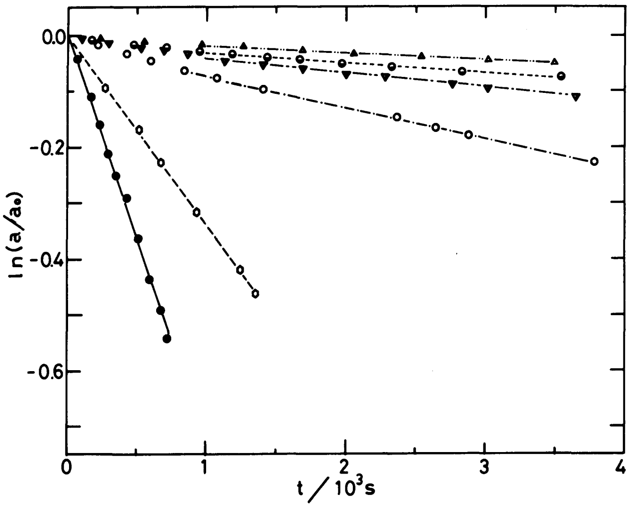

Fig. 7. Desorption performance of tetradecanoic acid from its monolayer into subphase of 0.01 M HCl under 0.3 mN m^{-1} below ESP values at various temperatures. △: T=292.1 K, ◒: 296.1 K, ▼: 303.1 K, ○: 308.1 K, Ȯ: 313.1 K, and ●: 318.1 K.

experiments on the tetradecanoic acid monolayer were carried out under the conditions of constant surface pressures and at various temperatures. In Fig. 7, the logarithm of the relative area, ln(a/a_0), is plotted against t, in which a_0 is the initial area of the monolayer immediately after the monolayer had been compressed to a desired surface pressure, and a, the area of the monolayer at time t. The desorption curve for an experiment at a low temperature has two parts: a curved part at the beginning and a linear one for a higher value of t, as has also been reported by Ter Minassian-Saraga.[10] That is to say, the first desorption stage (shown as a curved part) is diffusion-controlled, while the second one (shown as a linear part) is steady-state. At lower temperatures the steady-state commences at t=ca. 15 min, while at higher temperatures it appears to begin immediately. The rate constant k_2 of the dissolving process was consequently obtained from the ln(a/a_0) vs. t relationship in the steady-state; it also is listed in Table 1. The k_2 value is found to increase very rapidly with the temperature above 308 K.

Re-binding Process. Next we must consider the re-binding process of the film molecule to the crystal (Process (2)). The variation in the surface concentration of the acid molecules, dΓ/dt, expressed by Eq. 1, is zero after the spreading pressure becomes constant:

$$\mathrm{d}\Gamma/\mathrm{d}t = k_1C - (k_1' + k_2)\Gamma_s = 0 \tag{7}$$

where Γ_s is the saturated amount of molecules in the monolayer possessing the area of A_T. Consequently, k_1' is expressed as:

$$k_1' = (k_1C/\Gamma_s) - k_2. \tag{8}$$

The Γ_s value for an insoluble monolayer is, in general, obtainable as the inverse of the molar area of the monolayer at the ESP in its Π–A relationship. The Γ_s for the tetradecanoic acid monolayer at 318.1 K could not be, however, obtained from its Π–A relationship because of the rapid dissolving of the monolayer into the underlying subphase solution. Therefore, by substituting the values of A_t, A_0, Π (ESP), and Π_0 into Eq. 4, the Γ_s value was obtained. For example, the Γ_s value thus obtained at 318.1 K was 3.19×10^{-8} mol, the molecular area being 30.8 Å^2/molecule. This value is reasonable for the acid monolayer at that temperature. On the other hand, the value of C, 7.22×10^{-11} moles, used for the evaluation of the k_1 value seems to be too small compared with this Γ_s value. The C value is, however, the molar amount of the acid in the outermost molecular layer of its crystal directly in contact with the water surface. Even if the outermost layer is desorbed from the crystal into the monolayer, the next layer will appear continuously.

The k_1' value obtained from k_1C, k_2, and Γ_s is also listed in Table 1. When comparing these rate constants with one another, the k_1 is found to be much larger than k_2 at various temperatures. Therefore, the constant spreading pressure, even at high temperatures, at which the monolayer dissolves into the subphase very rapidly, can be regarded as a property in the equilibrium state, namely, the ESP.

The authors wish to express their thanks to Professor Koichi Kobayashi and Mr. Akira Yoshida of Musashi Institute of Technology for their technical help in performing the SEM observations. The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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