

Analysis of Rubberlike Elasticity in LB Films of Cd Salts of Fatty Acids

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The rubberlike elasticity observed in LB films of Cd palmitate, stearate and arachidate at temperatures above -40°C is analyzed by numerical calculations based on the stiff-chain model combined with the thermal expansion of the molecular chains. The optimized value of the coefficient $\alpha_0 \sim 10^{-5} \text{K}^{-1}$ indicates that the positive contribution mainly originates from the increase in bond lengths. The activation energy $E \sim 10^{-1} \text{eV}$ for the flexural rigidity coincides with those of hindered rotations around C-C bonds, confirming that the alkyl chains are subjected to microbrownian motion above -40°C . The half a decade difference between the values of curvature radius at 60°C and 90°C suggests the relevance of the microbrownian motion to the annealing effect in the dye - fatty acid mixed LB films.

Key words: LB films, Cd salts of fatty acids, rubberlike elasticity, stiff-chain model, simulation

1. INTRODUCTION

Straight chain fatty acids, $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ (C_n) with $n=16-20$, are well known film-forming materials for Langmuir-Blodgett (LB) films (Fig.1). As early as in 1935, K. B. Blodgett reported that stearic acid (C_{18}) forms a metal salt monolayer when it is spread on an aqueous subphase containing Ba^{2+} or other divalent metal ions, and that the monolayer is stable enough to be transferred layer by layer onto a solid substrate which is dipped and raised traversing the air-water interface [1]. This transfer technique is now known as the vertical dipping method, and thus prepared films are called Langmuir-Blodgett (LB) films. As is well known, I. Langmuir, K. B. Blodgett and their collaborators have carried out a series of pioneer works on LB films by utilizing the LB preparation technique.

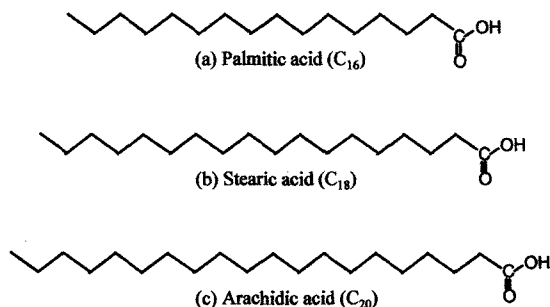


Fig. 1 Chemical formula of straight chain fatty acids. (a) Palmitic acid, (b) stearic acid, and (c) arachidic acid.

In the 1960s, H. Kuhn and his collaborators began to develop a new research field that is now known as molecular engineering. In this field, Cd^{2+} salt films have attracted special interest because of their higher stability in comparison to those of the corresponding free acids other divalent metal salts [2-6]. LB films of Cd^{2+} salt of arachidic acid C_{20} , e.g., are found to retain their LB lamellar structure after several years' storage in a desiccator at room temperature [7].

The Cd^{2+} salt films are utilized in two different ways [2,3,5]. One is to use them as spacers of molecular dimensions: the monolayer thickness linearly increases

with the number n of C atoms involved in an acid chain, and a multilayer possesses a well-defined thickness given as the sum of those of the constituent monolayers. Kuhn's group has successfully applied these molecular spacers in clarifying the mechanisms of energy and electron transfer processes between molecules. The other way is to introduce C_n as additives in functional LB films to stabilize the LB lamellar structure. This usage is also fruitful as we can trace in a vast literature accumulated on various device prototypes based on mixed LB systems.

The thermal properties of the Cd- C_n LB films have attracted considerable attention reflecting the importance of fatty acids for forming molecular spacers and molecular stabilizers.

T. Fukui et al. [8] have examined the structure of Cd^{2+} salt Y-type LB films of C_{16} , C_{18} , and C_{20} for temperatures ranging from -193°C up to 80°C by using X-ray diffraction. They have found that the Cd-Cd spacing or the bilayer thickness for each LB film remains almost constant with a thermal expansion coefficient of $\alpha \sim 1 \times 10^{-5} \text{deg}^{-1}$ up to about -40°C , beyond which the thickness tends to decrease, i.e., $\alpha < 0$ with an upward convex [8,9]. It has been also revealed that the ordering of Cd^{2+} lattice in the Cd- C_{20} LB films remains unchanged up to ca. 80°C [9]. The observed thermal behavior was interpreted as a compromise between the usual expansion due to anharmonic vibrations and the contraction due to the rubberlike elasticity as a result of microbrownian motions in the alkyl chains.

These remarks on the Cd- C_{20} films have been later supported by an infrared spectroscopic study including the Cd- C_{20} LB system by C. Naselli et al. [10,11]. They have reported that a pretransitional disordering of alkyl chains is observed followed by a catastrophic breakup of the Cd^{2+} -ion lattice at a temperature corresponding to the melting point, $100-120^{\circ}\text{C}$. This pretransitional behavior has further been confirmed by J. P. Rabe et al. [12] and M. R. Buhaenko et al. [13].

As to the Cd^{2+} -salt additives to stabilize the LB lamellar structure, an annealing effect has been recently found in the mixed LB films of a merocyanine and C_{20} by mild heat treatments at temperatures $60-70^{\circ}\text{C}$, which causes narrowing of the 590-nm red-shifted band of the as-deposited films with a further red shift by several nanometers. This process has been understood as a total

reorganization rather than an additional growth of the original band [14,15]. This annealing effect in the merocyanine chromophores presents a keen contrast to the heat treatments at 80–90°C that enhances the ordering of the Cd²⁺-ion lattice at the expense of the dissociation of J-band [16].

For the better understanding of these different effects of heat treatments at 60–70°C and 80–90°, we have analyzed the temperature-dependence of the Cd-Cd bilayer spacing of the fatty acid salt films by numerical calculations based on the stiff-chain model. The results are reported in the present paper.

2. THEORETICAL FRAMEWORK

Three different mechanisms are considered to be relevant to the temperature-dependent thickness observed for the present Cd²⁺ salt LB films:

- (1) Thermal expansion of the distances between the adjacent atoms and/or segments due to anharmonic vibrations,
- (2) Rubberlike elasticity due to the increased fraction of dynamic disorders in each alkyl chain, which arise from the rotations around C–C axes resulting in a negative contribution to the thermal expansion coefficient, and,
- (3) Change in the tilt angle of the alkyl chains, which may, however, lead to a first- or second-order transition with discontinuities in thermodynamic functions and their derivatives.

In the present model, Mechanism (1) and (2) are allowed for. Mechanism (1) is represented by a single temperature-independent thermal expansion coefficient, while the contribution from Mechanism (2) is evaluated by the stiff-chain model [17].

The contour length L of a C_n molecule is defined as the total length of a smooth curve connecting the middle points of adjacent bonds one after another along the principal chain. The temperature-dependent L is assumed to be written as,

$$L = L_0(1 + \alpha_0 T), \quad (1)$$

where α_0 and T are the thermal expansion coefficient and the absolute temperature, respectively.

The molecular chain is represented by a piece of elastic wire that is characterized with a single flexural rigidity ε written as,

$$\varepsilon = \varepsilon_0 \exp\left(\frac{E}{k_B T}\right), \quad (2)$$

where E and k_B are the activation energy and the Boltzmann constant, respectively. The elastic energy U stored in the wire is then given by,

$$U = \frac{1}{2} \int_0^L \varepsilon \left(\frac{\partial^2 \mathbf{r}}{\partial s^2}\right)^2 ds, \quad (3)$$

where s denotes the contour coordinate, \mathbf{r} is the position vector of a point on the contour.

The partition function Q for a single chain in the configurational space is written by means of a Feynman path integral as,

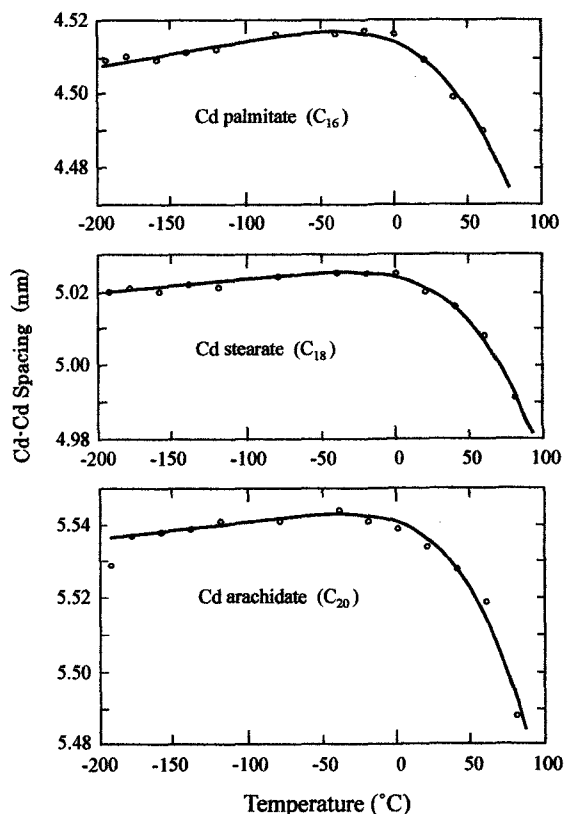


Fig. 2 Temperature-dependence of the Cd-Cd bilayer spacing. Each curve is the least squares fit obtained using Eqs. (1)–(7) in the text.

$$Q = \int \exp\left\{-\frac{\varepsilon}{2k_B T} \int_0^L \left(\frac{\partial^2 \mathbf{r}}{\partial s^2}\right)^2 ds\right\} d(\text{conf}), \quad (4)$$

where $\int \dots d(\text{conf})$ is to take the sum over all possible molecular configurations [17].

Equation (4) is reduced to a differential equation as,

$$\frac{\partial Q}{\partial s} = D \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Q}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Q}{\partial \varphi^2} \right\}, \quad (5)$$

which may be regarded as a diffusion equation describing the random walk on a unit sphere when we compare the contour s to the time t [17]. The “diffusion coefficient” D for this process is given by,

$$D = \frac{k_B T}{2\varepsilon}. \quad (6)$$

The mean-square end-to-end distance is derived as,

$$\langle R^2 \rangle = \frac{e^{-2DL} - 1 + 2DL}{2D^2}, \quad (7)$$

where $\langle R^2 \rangle^{1/2}$ is identifiable with the monolayer thickness (i.e., half of the Cd-Cd spacing), which tends to L and $(L/D)^{1/2}$ for $T \rightarrow 0$ and ∞ , respectively.

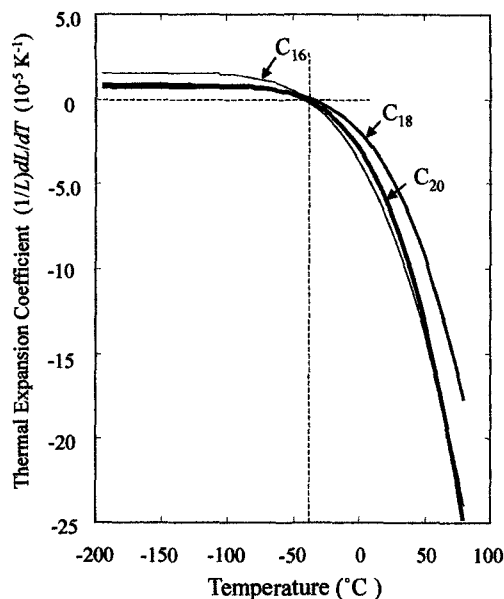


Fig. 3 Thermal expansion coefficient calculated using the optimized values of parameters given in Table I.

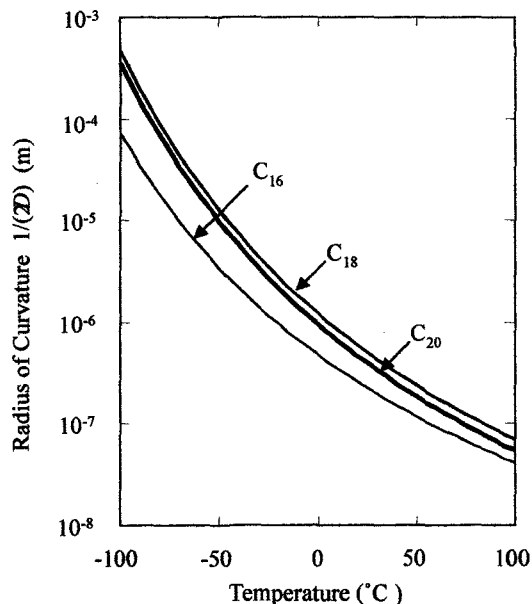


Fig. 4 Temperature dependence of averaged radius of curvature $1/(2D)$.

The mean-square curvature is written as,

$$\langle K^2 \rangle = 4D^2, \quad (8)$$

where K is the curvature vector, where the average radius of curvature is estimated as $\langle K^2 \rangle^{-1/2}$ [18]. The average elastic energy is given by [18],

$$\langle U \rangle = k_B T D L. \quad (9)$$

3. RESULTS AND DISCUSSION

The temperature dependence of the Cd-Cd bilayer spacing is shown in Fig. 2 for C_{16} , C_{18} and C_{20} . The curves in the figure is the best, least-squares fits obtained applying Eqs. (1)-(7) to the corresponding data points taken from Ref. [9]. Each fitted curve satisfactorily reproduces the characteristic upward convex exhibiting its maximum around -40°C , below and above which the spacing is mainly governed by Mechanism (1) and Mechanism (2), respectively.

Table I Optimized values of the four parameters.

	Cd- C_{16}	Cd- C_{18}	Cd- C_{20}
$2L_0$ (nm)	4.502	5.018	5.533
α_0 (10^{-5} K^{-1})	1.56	0.75	0.84
ε_0 (10^{-31} Nm^2)	6.62	3.39	2.76
E (eV)	0.186	0.224	0.223
(kJ/mol)	17.9	21.6	21.6
(kcal/mol)	4.30	5.19	5.18

$2L_0$: d-spacing at 0 K

α_0 : thermal expansion coefficient of the contour length

ε_0 : preexponential factor of flexural rigidity

E : activation energy of flexural rigidity

Of the values of four parameters given in Table I, α_0 is mainly related to Mechanism (1). The values of the order of 10^{-5} K are by about a decade smaller than those of bulk crystals of fatty acids and their metal salts and comparable to those of solid metals as previously reported [8], while the values of $2L_0$ support the picture that the alkyl chain stand upright with a nearly all-trans conformation. It is therefore suggested that the observed behavior is actually governed by the anharmonic vibration. The other two, ε_0 and E , represent Mechanism (2). It is noted that the estimated values of E , about a decade larger than the thermal energy at room temperature, fall in a range of the activation energies of hindered rotations around C-C bond axes in various organic molecules [19].

Figure 3 shows the temperature dependence of the thermal expansion coefficient $\alpha(T) = (1/L)dL/dT$ for each case obtained using the parameter values given in Table I. For $T < -40^\circ\text{C}$, the α -values for C_{18} -Cd and C_{20} -Cd are identical with each other, while the value for C_{16} -Cd are about twice as large as those of the others. This may reflect the weaker interaction between the adjacent bilayers due to the shorter chain length, resulting in looser stacking in the normal direction. For $T > -40^\circ\text{C}$, the curves for C_{16} -Cd, C_{18} -Cd and C_{20} -Cd are similar to one another, and the α -values around room temperature remain within a range of about $\pm 15\%$.

It is noted that the present model does not allow for the glass transition temperature that is characterized as a second-order phase transition accompanied by discontinuities in the thermal expansion coefficient and other differential derivatives with respect to T . The satisfactory coincidence between the model and the experiment indicates that the contribution from entropy term is negligibly small.

The mean square curvature of an alkyl chain is calculated using Eq. (8) in the present model [18]. The average radius of curvature is therefore represented by a quantity $1/(2D)$ as a measure of swaying motion of a

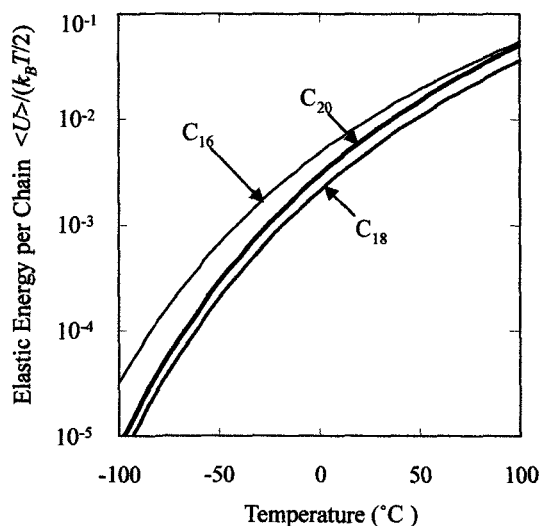


Fig. 5 Average elastic energy per chain normalized to $k_B T/2$

molecular chain. Figure 4 shows thus estimated average values plotted against temperature T in a semi-logarithmic scale. The radius is far larger than the contour length L at lower temperatures, but it monotonically decreases, starting from $1/(2D)=\infty$ at $T=0$, with increasing T until the lamellar structure of LB system is irreversibly destroyed by the melting Cd^{2+} -ion lattice. A difference in the average radius by a factor of 2 or more is seen between the 60°C and 90°C cases for each film species. This much of difference may be relevant to the different effects, annealing and dissociation of J-aggregates, observed for the mixed films of merocyanine and C_{20} .

Figure 5 shows the average elastic energy stored in an alkyl chain $\langle U \rangle$ (Eq. (9)) divided by $k_B T/2$ plotted against T in a semi-logarithmic scale, where the same amount of energy is ascribed as the kinetic energy according to the equipartition theorem. This quantity may increase with temperature up to the number of C-C bonds, $n-1$, involved in a chain, since it corresponds to the degree of freedom with respect to the swaying of the chain. For each case, however, the value remains less than 10^{-1} , indicating the rotation around the C-C bonds is strongly hindered in the pretransitional region. In this respect, it is noted that no discontinuity has been so far reported as to the specific heat in the present temperature range.

4. CONCLUDING REMARKS

We have analyzed the rubberlike elasticity observed as negative thermal expansion coefficients in LB films of Cd salts of fatty acid, C_{16} , C_{18} and C_{20} , by numerical calculations based on the stiff-chain model combined with a linear expansion due to the anharmonic vibrations of atoms and/or segments. In the present model, the molecular chain is represented a piece of elastic wire characterized with a temperature-dependent flexural rigidity obeying an Arrhenius law and a linear thermal expansion of the contour length.

Of four parameters involved, the optimized value $\alpha_0 \sim 10^{-5} \text{K}^{-1}$ of the linear thermal expansion coefficient of contour length for each case suggests that the positive

contribution to the expansion mainly originates from the expansion of bond lengths rather than that of spacing between the dipole-coupled segments.

The activation energy E of the order of 10^{-1} eV for the Arrhenius-type flexural rigidity is found to coincide in the order of magnitude with those of hindered rotations around C-C bonds in various materials, indicating that the microbrownian motion of thermally activated alkyl chains actually takes place at temperatures above -40°C .

The difference by a factor of 2 or more between the values of curvature radius at 60°C and 90°C is suggested to be relevant to the annealing effect in the dye – fatty acid mixed LB films, which may open up a new possible method for modifying the film properties.

For the further understanding of the annealing process in the mild heat treatments, it is necessary to accumulate experimental data by applying such methods as IR spectroscopy, morphological study of the LB films and *in situ* observation of precursor monolayers at the air-water interface besides X-ray analysis. The studies along this line are now in progress.

ACKNOWLEDGEMENT

The present authors wish to express their thanks to Dr. S. Morita for his valuable discussion in the early stages of the present work.

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