Monolayers of Triple Long-Chain Salts on the Concentrated Sodium Chloride Solution

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(Received March 28, 1988)

The surface pressure-area (π–A) curves for monolayers of four kinds of cation-anion triple long-chain salts [dialkyldimethylammonium alkanesulfonates] on the aqueous solution of 4.4 M NaCl were measured at various temperatures by the Langmuir method. Some π–A curves of these salts showed two transition points. Judging from the apparent molar entropy change on the transition, the first was assigned to the transition from the expanded state (E phase) to the condensed state (C-I phase) and the second to the transition from the C-I phase to another condensed state (C-II phase). In this paper, another condensed phase (C-I′) was newly observed over a certain temperature range on the phase diagram, which is the intermediate phase between the C-I phase and the C-II phase. There exist two triple points on the phase diagram at which three phases (i.e., E, C-I, and C-I′, and C-I, C-I′, and C-II) coexist. From the apparent molar entropy change, limiting area, compressibility, and phase diagram, the orientation of (2–1) long-chain salts in the monolayer state was assumed.

Many papers have been published on the adsorbed film at the air/water interfaces from the mixtures of cationic and anionic surfactant solutions.[1–11] Some studies concerning the mixed monolayers of cationic and anionic surfactants have also been reported.[12–16] We have recently investigated the surface chemical properties of the insoluble monolayers of double long-chain salts, which are composed of a long-chain cation and a long-chain anion, on water and/or electrolyte solutions.[17–20] The monolayers of double long-chain salts on 4.4 M NaCl solution (1 M=1 mol dm^{-3}) showed such outstanding behavior as some surface pressure-area (π–A) curves had two transition points.[19–20] To investigate the phase transitions of monolayer more deeply, it is necessary to extend the study from the viewpoint of molecular structure and to compare the results with those of other types of long-chain salts at the same experimental conditions, i.e., on 4.4 M NaCl solution.

In the present study then, dialkyldimethylammonium alkanesulfonates [which is denoted as (2–1)long-chain salt or as 2C*n*NC*n*S, in which *n* is the number of carbon atoms in the long-chain cation and anion, while a customary double long-chain salt will be described as (1–1) long-chain salt or as C*n*NC*n*S] were prepared, and the surface pressures of monolayers of these salts have been measured as a function of molecular area at various temperatures. The NaCl concentration of the substrate was fixed at 4.4 M throughout the experiments. The phase type in the monolayer states of the (2–1) long-chain salts could be judged from both the phase diagrams and thermodynamic quantities on the phase transition.

Experimental

The (2–1) long-chain salts (2C*n*NC*n*S), dialkyldimethylammonium alkanesulfonates, were prepared by mixing equimolar solutions of dialkyldimetylammonium bromides from Prof. T. Kunitake of Kyushu University and sodium alkanesulfonates from Tokyo Kasei Kogyo. The precipitates were purified by recrystallization from an acetone/water mixture (7:3 in v/v). The four salts of different hydrocarbon chain length are shown in Table 1. The purity of these salts was confirmed by elemental analyses. Each (2–1) long-chain salt was spread from hexane–ethanol mixture (4:1 in v/v, the former from Merck, Uvasol, and the latter from Nacalai Tesque) at the air/water interface.

The substrate solution of 4.4 M sodium chloride (Nacalai Tesque) was prepared using thrice distilled water. Sodium chloride was roasted at 973 K to remove any surface active impurities.

The surface pressure was measured by an automated Langmuir film balance, which was the same used in the previous study.[17–20] The concentration of NaCl in the substrate was held constant at 4.4 M throughout the experiments in order to observe the reproducible π–A curve and to compare the phase diagrams from the viewpoint of the molecular structures of the two kinds of salts [C*n*NC*n*S and 2C*n*NC*n*S].

Other experimental conditions were the same as described in the previous paper.[20]

Results and Discussion

The π–A curves obtained of 2C*n*NC*n*S salts with equal number of carbon atoms in three long chains, at

Table 1. Materials

(2–1) Long-chain salt	Structure	Abbreviation
Dialkyldimethylammonium alkanesulfonate	$(C_nH_{2n+1})_2N^+(CH_3)_2\,C_nH_{2n+1}SO_3^-$ where n=12, 14, 16, 18	2C*n*NC*n*S

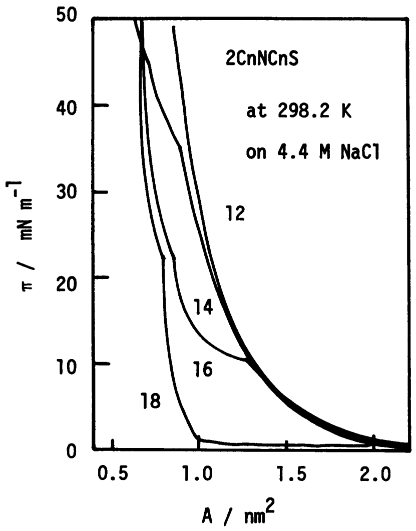

Fig. 1. The π-A curves of (2–1) long-chain salts on 4.4 M NaCl solution at 298.2 K. In the case of 2C*n*NC*n*S type; Curve 12, 2C12NC12S; 14, 2C14NC14S; 16, 2C16NC16S; 18, 2C18NC18S.

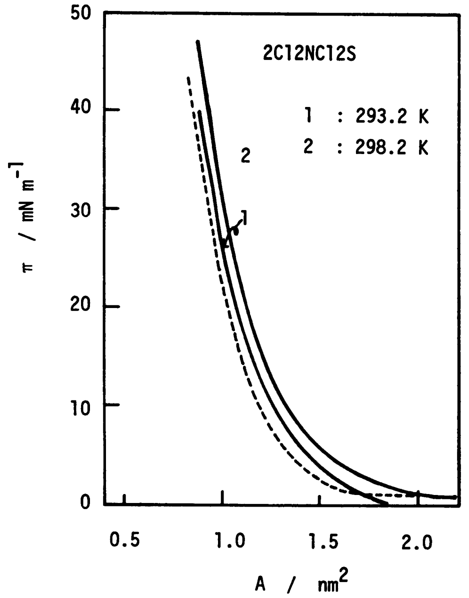

Fig. 2. The temperature dependence of π-A curves of 2C12NC12S salt. Substrate: 4.4 M NaCl solution. Dotted line: on pure water at 298.2 K.

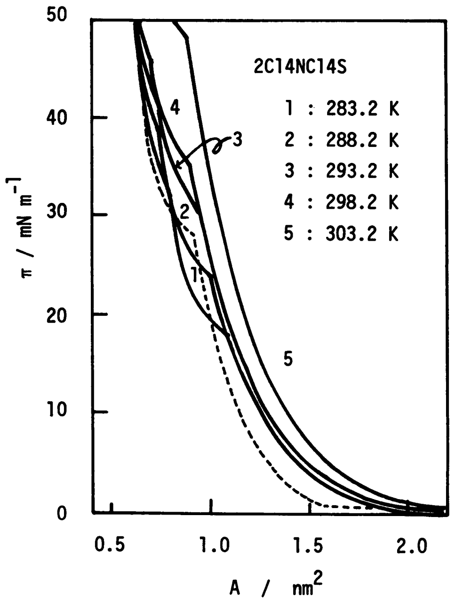

Fig. 3. The temperature dependence of π-A curves of 2C14NC14S salt. Substrate: 4.4 M NaCl solution. Dotted line: on pure water at 298.2 K.

298.2 K on 4.4 M NaCl are shown in Fig. 1. Numerical values in Fig. 1. refer to the number of carbon atoms in the long-chains. The longer the chain length of the salts, the smaller the value of the mean area per molecule at constant pressure. As seen from Fig. 1, all the π-A curves have one or two transition points at 298.2 K except for 2C12NC12S salt. Since the transition pressures remain constant irrespective of the compression rate,19,20) all the transition points on the π-A curves can be regarded as the equilibrium point between two or three phases on the monolayer. The phase transition pressures (π^{eq}) change extensively with varying the chain length. Especially, both π-A curves of 2C14NC14S and 2C16NC16S revealed two distinct break points. The two transitions for these salts, however, have turned out to be different in phase; new intermediate phase appeared during the compression of the monolayer of 2C16NC16S. The first break point at a low surface pressure of the π-A curve for the 2C16NC16S salt indicates the transition from the expanded (E-phase) to the condensed film, and the second break point at a higher surface pressure is as the transition from a condensed film to another condensed film, as described in the previous papers.19,20) These two condensed states are referred to the condensed phase I and the condensed phase II, respectively, in the same manner.19,20) On the other hand, judging from the previous phase diagrams, the break point at a low surface pressure of 2C14NC14S can be assigned to the transition from the expanded phase (E-phase) to the condensed phase I′ (C-I′) which is different from the condensed phase I (C-I) on the monolayer phase diagram. The second break point at a higher surface pressure is regarded as the transition from the condensed phase I′ (C-I′) to the condensed phase II (C-II), which can be also assigned by the aid of thermodynamic quantities and the phase diagram as mentioned later.

On the other hand, the π-A isotherms of 2C18NC18S have only one transition point, which is the transition from one condensed state to another condensed state by the aid of thermodynamic quantities as mentioned later. The π-A curve of 2C12NC12S salt shows only an expanded film at 298.2 K.

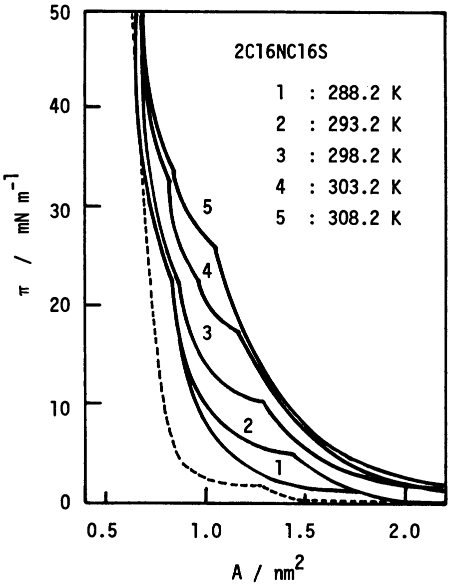

Fig. 4. The temperature dependence of π-A curves of 2C16NC16S salt. Substrate; 4.4 M NaCl solution. Dotted line: on pure water at 298.2 K.

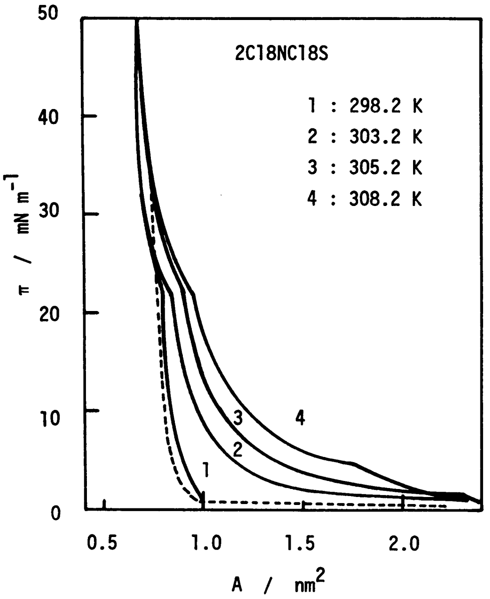

Fig. 5. The temperature dependence of π-A curves of 2C18NC18S salt. Substrate; 4.4 M NaCl solution. Dotted line: on pure water at 298.2 K.

Table 2. Limiting Areas of (2-1) Long-Chain Salts and (1-1) Long-Chain Salts at 298.2 K (on 4.4 M NaCl)

Chain length (n) of salts	Limiting area (A/nm^2)	
	CnNCnS	2CnNCnS
	Condensed phase I	
n=12	—	—
n=14	—	1.12(E→C-I′)[a]
n=16	0.728	1.06
n=18	0.700	—
	Condensed phase II	
n=12	—	—
n=14	—	0.910(C-I′→C-II)[b]
n=16	—	0.868
n=18	0.599	0.755

a) This value is the limiting area for the condensed phase I′(C-I′). b) This value is the limiting area for the condensed phase II(C-II).

In order to clarify the effect of the chain lengrh on the phase diagram, the π-A curves for the four (2-1) long-chain salts were compared at various temperatures in Figs. 2—5. The limiting area is found to be larger by about 0.6 nm^2 than threefold area of corresponding single long-chain fatty acids.[21] This is due to the bulky cationic head group. From these figures the π-A curves clearly have two or three transition points depending on the chain length of the cations and anions. In the previous experiments of (1-1) long-chain salt monolayer on 4.4 M NaCl solution, only two kinds transitions [E phase→C-I phase and C-I phase→C-II phase] have been observed. Therefore, the three kinds of transitions [E phase→C-I phase, C-I phase→C-I′ phase, and C-I′ phase→C-II phase] are characteristic of the present systems.

In order to investigate the molecular orientation on the surface films, the limiting areas of the condensed film were estimated from the π-A curves by the same method described previously.[19,20] The values of the limiting area can be classified into two groups as shown in Table 2: one is the limiting area for the condensed phase I (for 2C14NC14S salt, the value is the limiting area for the condensed phase I', this will be made clear later by the phase diagram), and the other is that for the condensed phase II. The π-A curves of 2C18NC18S (curve of n=18 in Fig. 1) and C16NC16S [curve of n=16 in Fig. 2 of Ref. 20], for example, have one transition point. As seen from Table 2, the limiting area (0.364 nm^2) per alkyl chain for C16NC16S quite resembles the limiting area (0.350 nm^2) per alkyl chain for the condensed phase I of the C18NC18S salt with two break points on the π-A curve, whereas the value of the limiting area (0.252 nm^2) per alkyl chain for 2C18NC18S should be classified to another condensed phase, the condensed phase II of the 2CnNCnS salt.

As seen from Figs. 2 to 5, there exists evidently an appreciable difference in the limiting area of the π-A curves for (2-1) long-chain salt between on pure water and on the 4.4 M NaCl solution, which amounts to about 0.1 nm^2. The monolayer of the 2C18NC18S salt on pure water at 298.2 K exhibits a direct transition to condensed film and has no break point on the π-A curve. On the other hand, the monolayer on the 4.4 M NaCl solution is somewhat more loosely packed in the condensed state (C-I) than that on pure water and has a break point due to the transition from the condensed phase I to II at 298.2 K. The values of somewhat expanded limiting area for the condensed phase I and the occurrence of the phase transition from the condensed phase I to II are attributable to the substrate of concentrated NaCl solution.

The film compressibilities of (2–1) long-chain salts are also useful for a discussion of the molecular interaction in the film. Compressibility is taken as $C^s = -1/A(\mathrm{d}A/\mathrm{d}\pi) \fallingdotseq (a_0 - a_1)/a_0\pi_1$, where a_1 is the area at a certain surface pressure π_1, and a_0 is the area extrapolated to zero pressure. A suitable surface pressure was chosen 49 mN m^{-1} because above this surface pressure all the films are the state of the condensed phase II, as is clear from the π-A curves of Figs. 3 to 5. For the salts 2C*n*NC*n*S, the values of the compressibility decrease with increasing the chain length (*n*) of (2–1) long-chain salts (Table 3) and approach to that of octadecanoic acid. On the other hand, the condensed monolayer (C-II) of C18NC18S has twice the compressibility of the condensed films (C-II) of 2C18NC18S, and presents approximately similar compressibility to the 2C16NC16S monolayers (C-II), as seen in Table 3. This indicates that the cohesive interaction between the long chains increases with the number of alkyl chains, while decreasing with shortening of alkyl chain.

Table 3. Compressibilities of (2–1) Long-Chain Salts and (1–1) Long-Chain Salts in the Condensed Film at 298.2 K (on 4.4 M NaCl)

Chain length (*n*) of salts	Compressibility/m mN^{-1} [a)]	
	C*n*NC*n*S	2C*n*NC*n*S
n=12	—	—
n=14	—	0.0056
n=16	—	0.0047
n=18	0.0039	0.0020

a) Octadecanoic acid, 0.0015 (m mN^{-1}); Dipalmitoyl phosphatidylcholine, 0.0064 (m mN^{-1}) at 298.2 K. Compressibility is taken as $(a_0 - a_1)/a_0\pi_1$, where a_1 is the area at π_1=49 mN m^{-1}, and a_0 is the area extrapolated to zero pressure.

The studies of the temperature effect on the transition pressure are of much interest, since they provide us with thermodynamic information about the state of monolayers. Figures 3—5 show, the π-A isotherms of 2C14NC14S, 2C16NC16S, and 2C18NC18S at various temperatures, which have two break points. As for 2C16NC16S salt in particular, three break points are observed on the π-A isotherm. As was expected, the transitions pressures increased with an increase in the temperature.

In Fig. 6 are illustrated the three types of phase diagrams from the transition pressure (π^{eq}) and temperature for 2C*n*NC*n*S salts, where the slope of the π^{eq} against temperature is a key point to assign the phases.

The thermodynamic quantities on the phase transition of monolayers were calculated by the same method as described in our previous study.[17–20,22,23] The apparent molar entropy change (Δs^{r}) on the phase transition were evaluated by employing Eq. 29 of Ref. 22.

The apparent molar entropy changes on the various types of phase transition are given in Table 4 for (2–1) long-chain salts. As seen from in Table 4, the first

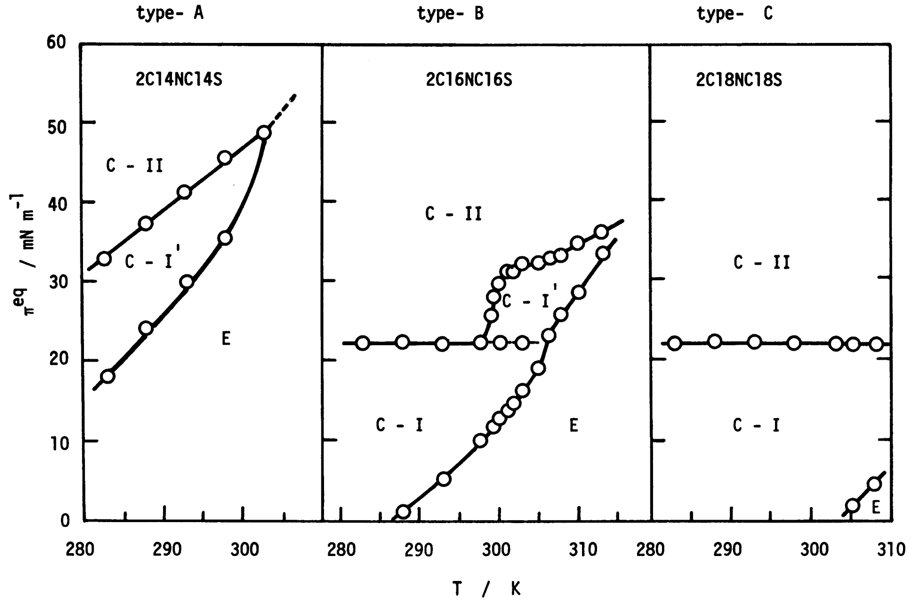

Fig. 6. The transition pressure (π^{eq}) as a function of the temperaure, and the transition pressure-temperature diagrams for the monolayers of 2C14NC14S, 2C16NC16S, and 2C18NC18S salts on the 4.4 M NaCl solution.

Table 4. The Apparent Molar Entropy Changes on the Phase Transition of (2–1) Long-Chain Salts at Various Temperature (on 4.4 M NaCl)

Temp/K / Transition	Entropy change ($-10^{-2}\Delta s^{\gamma}$/J K^{-1} mol^{-1})					
	2C14NC14S	2C16NC16S			2C18NC18S	
	298.2	298.2	303.2	308.2	298.2	305.4
E →C-I	—	2.9	5.0	—	—	9.6
E →C-I′	1.2	—	—	3.4	—	—
C-I →C-II	—	0.14	—	—	0.07	0.16
C-I →C-I′	—	—	0.2	—	—	—
C-I′→C-II	0.3	—	0.5	0.68	—	—

transition includes two kinds of transitions; one from the expanded phase (E) to the condensed phase I (C-I) and the other from the expanded phase (E) to the condensed phase I′ (C-I′). The values of the apparent molar entropy change of 2C16NC16S salt increases with the temperature. Normally, the value of the apparent molar entropy change increases with an increase in the temperature. The smaller value at 308.2 K than that at 303.2 K reflects the difference in type of the phase transition between the E→C-I and the E→C-I′. The phase transition for the 2C14NC14S salt at 298.2 K can be classified as the transition from the expanded phase (E) to the condensed phase I′ (C-I′) by the aid of the phase diagram (Fig. 6), and the slope of π^{eq} vs. T curves. The longer the chain length of the salt, the larger the apparent molar entropy on the transition from their expanded to their condensed states.

The apparent molar entropy changes on the other types of the phase transition are also given in Table 4. The second transition includes three kinds of transitions; C-I→C-II, C-I→C-I′, and C-I′→C-II. The apparent molar entropy change on the second phase transition decreased in magnitude by one order, compared with the apparent molar entropy change on the first phase transition (E→C-I, and E→C-I′). The column of 2C16NC16S salt at 303.2 K includes three numerical values. Especially in this case, the assignment of the type of phase transition is difficult only by the aid of the apparent molar entropy change. The values of the apparent molar entropy changes are too small to compare with those of other phase transitions. So, the phase transition for 2C16NC16S at 303.2 K was classified judging from the slope of π^{eq} vs. T curves in Fig. 6. The classification of the phase transitions on other salts were also done by the same method. The 2C18NC18S salt also has the transition from C-I to C-II on the π–A curve at 298.2 K. The longer the chain length of (2–1) long-chain salts, the smaller the apparent molar entropy change on the phase transition from C-I to C-II. The larger entropy change on the first transition (i.e.; E→C-I, and E→C-I′) suggests the considerable change of the molecular orientation in the monolayers, whereas the small entropy change on the second transition (i.e.; C-I→C-II, C-I→C-I′, and C-I′→C-II) suggests the slight change in the monolayer configuration. As a result, five types of classifications are possible for the phase transitions on the monolayers of (2–1) long-chain salts (2C*n*NC*n*S).

The monolayers of (2–1) long-chain salts turned out to have two or three transition points on their π–A curves. Figure 6 shows the phase diagrams of the monolayers of 2C14NC14S (type-A), 2C16NC16S (type-B) and 2C18NC18 (type-C) as expmples. Judging from the slope of the π^{eq} vs. T curve of the type B in Fig. 6, it is possible to distinguish between the phases of C-I and C-I′. But, there remains some question that the C-I and the C-I′ phases are distinguishable from the phase diagram of the types A and C in Fig. 6. This distinction may be made clearer by other techniques such as surface potential measurement and ellipsometric measurement. It is noteworthy that two triple points exist on the phase diagram of type-B and that three phase transitions, E→C-I, C-I→C-I′, and C-I′→C-II are possible depending on a particular temperature range. At higher temperature, the phase transition of E→C-II will be observed, which is a conventional phase transition in monolayer research. There are some studies on the polymorphism in monolayers of docosanoic acid and 1-octadecanol.[24,25] As for these compounds, the condensed phase I has not appeared on the 0.1 M NaCl solution or water, but it appears on the 4.4 M NaCl solution. Especially, in this (2–1) long-chain salt, another condensed phase I′ (C-I′) appears. The C-I′ phase is the intermediate phase between the C-I and C-II phases. In the condensed phase II, the (2–1) long-chain salts are probably aligned perpendicular to the water surface judging from the limiting area. From the small entropy change from the condensed phase I to II (Table 4), the hydrocarbon tail interaction in the condensed phase I might be similar to that in the condensed phase II. However, the limiting areas for the condensed phase I are considerably larger than those for the condensed phase II as shown in Table 2.

For the condensed phases I and I′, therefore, the elongated distance can be imagined between the ionic head groups, because Na^+ and Cl^- ions are probably incorporated into the two-dimensional ionic crystal structure, causing the pronounced cohesive interaction between the long chains. This model may be clarified by data from other techniques such as surface potential measurement and ellipsometric measurement, which will be reported in a separate paper.

In conclusion, the monolayer of a (2–1) long-chain salts on the concentrated NaCl solution was found to have two triple points in the phase diagram. From the phase transitions, the phase diagrams can be classified into three types: type-A is of two phase transitions, expanded phase (E) → the condensed phase II (C-II) via the condensed phase I′ (C-I′); type-B is of three phase transitions, namely the expanded phase (E) → the condensed phase I (C-I), the condensed phase I (C-I) → the condensed phase I′ (C-I′), and the condensed phase I′ → the condensed phase II (C-II); and type-C is two phase transitions, the expanded phase (E) → the condensed phase II (C-II) via the condensed phase I (C-I). New finding of this study is the appearance of the condensed phase I′ (C-I′) which wasn't present for the (1–1) long-chain salts.

One of authors (O. S.) wants to express his deep gratitude to Prof. Makoto Nakamura of College of General Education, Kyushu University and Dr. Akira Yamauchi of the Department of Chemistry, Kyushu University, for many valuable and most stimulating discussions during this work and would like to thank Dr. Yoshikiyo Moroi of the department of Chemistry, Kyushu University for help with preparation on this manuscript for publication.

This work has been financially supported in part by a Grant-in-Aid for Scientific Research No. 59540268 from the Ministry of Education, Science and Culture.

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