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# Normal mode analysis of zinc caprate (Zn)<sup>1/2</sup>O<sub>2</sub>C(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>

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#### Abstract

A normal mode analysis was made for zinc caprate with using the Wilson GF matrix method. Based on the analysis and infrared spectra, structural transition behavior of zinc caprate was discussed. © 2007 Elsevier B.V. All rights reserved.

Keywords: Zinc caprate; Infrared spectra; Normal mode analysis

#### 1. Introduction

Structure and thermal transition behavior of metal salt of saturated fatty acid (soap) depend on its chain length. For example, potassium soaps take the monoclinic A form crystal for C4 to C12 where C is the carbon number and the triclinic B form crystal for C12 to C18 at room temperature [1]. A kind of metal affects the thermal transition behavior, e.g., potassium stearate has eight thermal transitions in the temperature region from 50 to 300 °C [2] but zinc stearate has only one transition around  $130 \degree C$  [3]. We have studied two zinc soaps, i.e., zinc palmitate (C16) [4] and stearate (C18) [5]. Both zinc soaps have one thermal transition around 130 °C. At the transition, both chain molecules go into liquid like conformation and some structural disorder occurs around the COO group. A normal mode analysis of long chain compound is rather difficult by using Gaussian program, since its assignment is complicated without using potential energy distribution. Empirical calculation is still valuable for such as metal salts of saturated fatty acids. In this study, we treated zinc caprate (C10) in order to clarify its structure and thermal transition behavior with using infrared spectroscopy and a normal mode analysis.

## 2. Experimental

Zinc caprate specimen was synthesized as follows. Sodium caprate ( $\sum$  Company, 99% purity) was dissolved into a solvent

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which consists of ethanol and water (50:50, v/v). Zinc chloride aqueous solution was titrating slowly into the above solution and stirred for 2-3 h. The resultant solution was precipitated in diethyl ether over night. These procedures were repeated twice. Based on only this synthesis, enough thermal data could not be obtained. And therefore, the synthesized result was purified by washing with water, ethanol and acetone. The product was recrystallized from benzene. These procedures were repeated two times. Then, three endothermic peaks appear in the thermal analysis [3]. Thermal behavior was measured by a Rigaku DSC PTC-10A. Infrared spectra were observed with a JASCO R-800 spectrophotometer. Temperature dependence of infrared spectra  $(\pm 1 \,^{\circ}\text{C} \text{ accuracy})$  was measured with a JASCO HC-12 heating unit with a heating rate of 10 K/h. Temperature was measured by a sealed CA thermocouple with an ADVANTEST TR2114 digital multi-thermometer.

## 3. Results and discussion

In order to investigate the molecular conformation of zinc caprate at room temperature and assign the intramolecular modes, a normal mode analysis was made by the Wilson GF matrix method using an IBM RS/6000-580 computer. The details have been reported elsewhere [6]. The molecule was assumed to have all-*trans* conformation and belongs to the Cs point group symmetry with the A' and A'' species. A tetrahedral geometry was assumed for C–C–C, C–C–H and H–C–H angles with C–C and C–H bond lengths equal to 1.54 and 1.093 Å, respectively. The C–C–O and O–C–O angles were assumed to be 120° with a C–O length equal to 1.27 Å. The valence force constants were estimated as follows. Zinc caprate

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Fig. 1. Infrared spectra of  $CO_2(CH_2)_{14}CH_3$ ,  $CO_2CD_2(CH_2)_{13}CH_3$  (2,2-D<sub>2</sub>) and  $CO_2(CD_2)_{14}CD_3$  (D31) from 400 to 4000 cm<sup>-1</sup> region at room temperature.

molecule consists of the alkyl chain and carboxylate group. The force constants of the alkyl chain have been well established by Schachtschneider and Snyder [7]. We used his values of calculation V which were obtained for a series of normal alkanes. The contribution of  $\alpha$ -methylene group to the spectra should be considered for zinc palmitate as in the case of normal fatty acids. We transferred the constants of Umemura [8]. All torsional constants used were also Umemura's value. The constants of the carboxylate group were evaluated for zinc palmitate and zinc stearate by us [5] but it was found that these constants have a slight mistakes [9]. We have reported the assignment of the bands around 1400 and  $1464 \text{ cm}^{-1}$  for zinc palmitate. The spectral pattern of zinc palmitate and zinc caprate is almost the same except the mthylene progressive bands. We measured the infrared and Raman spectra of zinc palmitate, and considered the band around  $1400 \,\mathrm{cm}^{-1}$  as the overlapped band of the COO symmetric stretch and  $C_{\alpha}H_2$  bend and the 1464 cm<sup>-1</sup> was assigned to the CH<sub>2</sub> bend. However, there remain a question, i.e., the band width of at about  $1400 \,\mathrm{cm}^{-1}$  was narrow but  $1464 \text{ cm}^{-1}$  was broad. In order to clarify the question. We carry out infrared measurements and normal coordinate analysis again. Fig. 1 shows the infrared spectra of zinc palmitates of CO<sub>2</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>, CO<sub>2</sub>CD<sub>2</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>3</sub> and CO<sub>2</sub>(CD<sub>2</sub>)<sub>14</sub>CD<sub>3</sub>. In the  $CO_2CD_2(CH_2)_{13}CH_3$ , 1397 cm<sup>-1</sup> band disappeared, indicating the band is assigned to  $C_{\alpha}H_2$ . For  $CO_2(CD_2)_{14}CD_3$ ,  $1433 \text{ cm}^{-1}$  band disappeared. This band is assigned to CH<sub>2</sub> bend. The  $1400 \text{ cm}^{-1}$  band remained for  $\text{CO}_2(\text{CD}_2)_{16}\text{CD}_3$ . Therefore, this band is assigned to the COO symmetric stretch. By the spectra of the deutrated homologous compounds, we revised the assignments of the bands of zinc caprate as the wavenumber of the COO symmetric stretch from 1464 to  $1417 \text{ cm}^{-1}$ . Here, the force constants were changed for the C–O stretch and the O-C-O interction from 9.420 mdyn/Å to 9.532 and from 1.640 to 2.793, respectively. The observed infrared spectrum of zinc caprate at room temperature is shown in Fig. 2. Their assignments are also shown in Fig. 1. The agreement between the observed and calculated frequencies were satisfactory, indicating that the molecule has an all-trans conformation at room temperature. In the long-chain compounds, the alkyl chains usually packed in a small periodic cell. This small periodic structure is called as subcell. There are two types of subcell which have parallel and perpendicular forms of lateral chain packing. In the perpendicular case, we observe the correlation split in the subcell for the CH<sub>2</sub> bending and the CH<sub>2</sub> rocking regions, but in the parallel case we do not observe it. In this case of zinc caprate, we did not observe the split in the CH<sub>2</sub> bending and rocking regions, and therefore the subcell is parallel type. Some saturated fatty acids have a polymorphism, e.g., for stearic acid, the B form has a gauche conformation at the  $C_{\alpha}$ - $C_{\beta}$  position [10]. But in this case of zinc palmitate, no such a polymorphism was found at the present stage.

Zinc caprate has three thermal transition points at 99, 105 and 134 °C and four phase I, II, III and IV from lower temperature side [3]. The phases I, II and III are crystalline phases, and phase IV is liquid phase. In order to clarify the structural change at these transitions, we measured the temperature dependence of infrared spectra (Fig. 3). As a result, the bands in the methylene progressive region from 700 to  $1400 \text{ cm}^{-1}$  which are characteristic of the all-trans conformation gradually decrease their intensity in phases III and IV, indicating the alkyl chains go into liquid like conformation.  $\Delta H$  and  $\Delta S$  of zinc caprate from phase III to phase IV are 11.71 kcal/mol and 28.77 kcal/mol K at 407 K, respectively. In the case of *n*-decane having the same carbon number of 10,  $\Delta H$  is 6.86 kcal/mol and  $\Delta S$  28.23 kcal/mol K at the melting point of 241 K. Between these two compounds,  $\Delta S$  is the similar value, but  $\Delta H$  of zinc caprate is almost twice larger than that of *n*-decane. This indicates that in zinc caprate,



Fig. 2. Infrared spectrum of zinc caprate from 400 to  $3250 \text{ cm}^{-1}$  at room temperature where the symbols are the same as ref. [6].



Fig. 3. Temperature dependence of infrared spectra of zinc caprate from 40 to 180  $^\circ\text{C}.$ 

the disorderliness of the alkyl chain at the melting is almost the same, but the COO group bonding to the Zn atoms stabilize the chain melt at higher temperature and large  $\Delta H$  was required for the melt. The coordination structure of the carboxylate groups to a metal is sometimes decided from the frequency difference ( $\Delta$ ) between the antisymmetric and the symmetric COO stretch bands [11]. Unidentate structure exhibit the  $\Delta$  values which are much greater than the ionic structure of 160–200 cm<sup>-1</sup>. Chelating structure exhibit  $\Delta$  values for bridging structure are greater than those of chelating structure, and close to the ionic values.

ues. In this case of the coordination structure of COO groups to Zn atom is decided as bridging bidentate, since the difference of the carboxylate COO antisymmetric and symmetric stretch is  $140 \text{ cm}^{-1}$ . The carboxylate antisymmetric stretch  $\nu_a(COO)$ band at 1539 cm<sup>-1</sup> split in phases III and IV. This means not only coordination structural change but also slight structural distortion around the COO group occurs in these phases as confirmed by XAFS study [5]. Annearing effect occurred for zinc palmitate [4] and zinc stearete [12]. Annealing means that increasing sample's temperature up to 150 °C, and cooling to room temperture slowly. In the case of zinc palmitate and stearate, the satellite bands were observed around the CH<sub>2</sub> rocking band which are ascribed to TGT conformation at the COO end where T means trans and G means gauche conformation for this annealing procedure. But in this case of zinc caprate, no annealing effect was observed. A series of zinc soaps were studied by us for even carbon numbers from 10 to 18. Over the carbon number larger than 12, a single thermal transition behavior was observed, but less than the number 12, multiple thermal structural change occur. This may be explained that crystal structure is different at the boundary of the carbon number 12, as in the case of potassium soaps [1].

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