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Nuclear Magnetic Relaxation Study of the Organic-Inorganic Hybrid Systems $(C_nH_{2n+1}NH_3)_2SnCl_6$

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The ^{1}H NMR spin-lattice relaxation in a series of the organic-inorganic hybrid systems $(n\text{-}C_nH_{2n+1}NH_3)_2SnCl_6$ ($n = 8, 10, 12, 14$) undergoing two successive phase transitions was studied. A discontinuity characteristic of a first order phase transition was observed at the high-temperature conformational transition. Besides, the spin-lattice relaxation rate below the conformational transition temperature was well fitted by four types of molecular motions, from which the chain-length dependence of the activation energies of the molecular groups was obtained.

Key words : Nuclear magnetic relaxation, Organic-inorganic hybrid systems, Phase transitions

1. Introduction

The hexahalometallates of the general formula A_2MX_6 ($A=K^+$, Rb^+, Cs^+, NH_4^+; M=Pd, Pt, Sn, Pb, Re, Se, Te, Ir, Os, ···; X = Cl, Br, I) normally crystallize in the cubic antiflurite structure with space group $F3m3m(O_h^5)$ in the high temperature phase [1, 2]. They usually undergo structural phase transitions lowering their symmetry with decreasing temperature. If A is replaced with the alkylammonium ion, $(R_nNH_{4-n})_2MX_6$ type compounds are formed and the dimensionality of the overall structure is reduced from 3D to 2D. Several examples have been reported for the Sn, Pt and Te metals [3-6].

The bis-*n*-alkylammonium hexachlorostannates $(n\text{-}C_nH_{2n+1}NH_3)_2SnCl_6$ (C_nSn for short) are layer compounds, where the $SnCl_6^{2-}$ octahedra do not form a 2D macroanion but exist separately [2-4]. The NH_3 group of the alkylammonium ion links the three closest octahedra through equivalent hydrogen bonds of the N-H···Cl type, forming a layer. The distance between the ammonium groups or between the tin atoms in C_nSn is great enough (7.3~7.5 Å, depending on the chain length) for interdigitated interlayer alkylchains. The alkylammonium groups are statically disordered around the three fold-axes at (1/3, 2/3, z) and (2/3, 1/3, $\dot{z}$), with the alkylchains alternately pointing upwards and downwards [4].

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In our previous ^{1}H NMR studies of $C_{10}Sn$ and $C_{18}Sn$, two phase transitions, i.e., an order-disorder and a conformational transition, were clearly identified and the molecular motions of the methyl and ammonium groups, as well as some defects were characterized in each phase [7-9]. In this work, ^{1}H NMR was employed for the systematic study of the chain-length dependence of the phase transitions and molecular motions.

2. Experiment

The C_nSn ($n = 8, 10, 12, 14$) samples used in this work were synthesized with much care in order to avoid impurities by the chemical reaction: $2(n\text{-}C_nH_{2n+1}NH_3Cl) + SnCl_4 \cdot 5H_2O \rightarrow (n\text{-}C_nH_{2n+1}NH_3)_2SnCl_6 + 5H_2O$. After filtering and two recrystallizations, white sugar-like crystals were finally obtained, and then vacuum-dried and kept in a dry condition. The stoichiometry and the structure were checked by elemental analysis and x-ray diffraction (XRD). Differential scanning calorimetry (DSC) carried out between 123 K and 453 K shows two reversible phase transitions. The spin-lattice relaxation time measurements were made using 200-MHz ^{1}H NMR in the temperature range 150~400 K.

3. Results and Discussion

Fig. 1 shows the order-disorder (T_{c1}) and conformational phase transition (T_{c2}) temperatures for the C_nSn

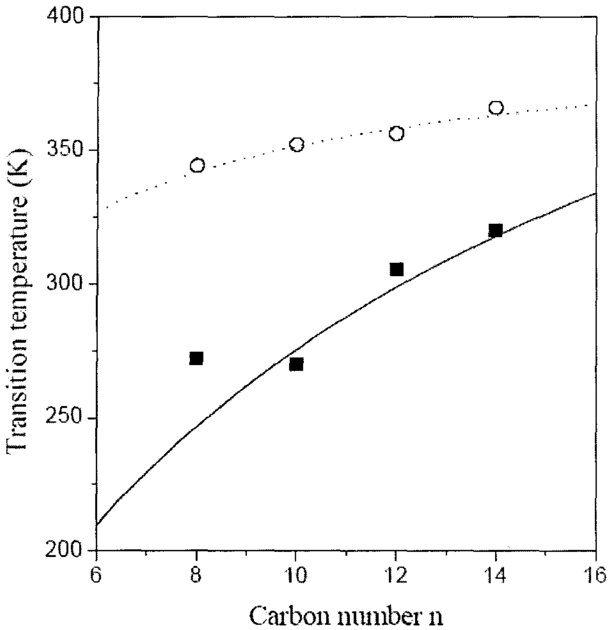

Fig. 1. The chain length dependence of the order-disorder (solid squares) and conformational (open circles) phase transition temperatures in C_nSn.

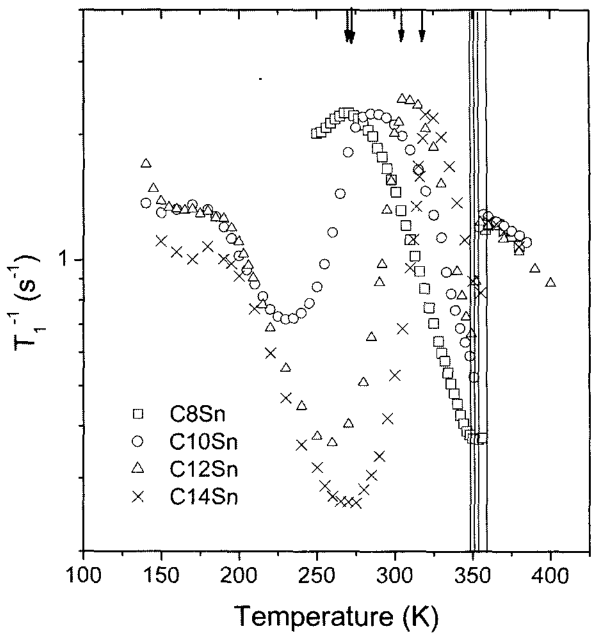

Fig. 2. The [1]H NMR spin-lattice relaxation rates in C_nSn as a function of temperature. Arrows indicate the order-disorder transition temperatures (T_{c1}) and vertical lines indicate the conformational transition temperatures (T_{c2}).

series as determined by the DSC and NMR measurements. A general tendency of increasing phase transition temperatures with increasing chain length, especially for the order-disorder phase transition, is noticed for the phase transition temperatures. The spin-lattice relaxation of the C_nSn samples showed a single-exponential pattern over the entire temperature range except around the transition temperatures, where negligible nonexponentialities were found. The spin-lattice relaxation rate measurements in Fig. 2 show a discontinuity at T_{c2}, characteristic of a first order phase transition. While T_{c1} represents the order-disorder transition temperature in this system, no anomaly is apparent in Fig. 2 as previously reported [7].

The spin-lattice relaxation rate data below T_{c2} were well fitted to the intramolecular dipole-dipole interactions modulated by various types of molecular motions following examples in similar systems [10];

$$T_1^{-1} = \sum_i \frac{2}{3}\gamma^2 M_{2i}\left[\frac{\tau_{ci}}{1+(\omega\tau_{ci})} + \frac{4\tau_{ci}}{1+(2\omega\tau_{ci})^2}\right] \quad (1)$$

$i = 1, 2, ..., n.$

$$\tau_c = \tau_0 e^{E_a/RT}, \quad (2)$$

where γ is the proton gyromagnetic ratio, M_2 the second moment, ω the Larmor frequency, and E_a is the activation energy. Four different types of the molecular motions ($n = 4$), as previously reported for $C_{10}Sn$, were introduced for the fits, and the fitting was done according to Eqs. (1) and (2). From comparison of the second moment of each motion contributing to our relaxation data with the results in C_nSn as well as in C_nCd and C_nZn [7], two of the molecular motions were assigned to those of NH_3 and CH_3 groups. In other words, two of the second moments M_{2i} needed for the fit to Eq. (1), 3.1 G^2 and 2.5 G^2, were easily assigned to the NH_3 group and the CH_3 group, respectively, and the corresponding activation energies were obtained from the fits to Eqs. (1) and (2). An unidentified motion is needed to fit the spin-lattice relaxation rate data as in $C_{10}Sn$ and is attributed to a chain defect in each of the low and the intermediate temperature phases.

Fig. 3 shows the activation energies for the CH_3 and NH_3 groups as a function of the chain length n. In Fig. 3, it is noticed that the NH_3 group is much more sensitive to the chain length change than the CH_3. For example, the activation energies of the CH_3 group are 8 and 16 kJ/mol in C_8Sn and $C_{14}Sn$, respectively. In comparison, the activation energy of the NH_3 group in $C_{14}Sn$, 58 ± 5 kJ/mol, was found to be much greater than that of 14 kJ/mol, in C_8Sn. The conformational transition temperatures in C_8Sn and $C_{14}Sn$ are 346 K and 365 K, respectively. In comparison, the order-disorder transition temperature in $C_{14}Sn$ is 320 K, which temperature is much higher than

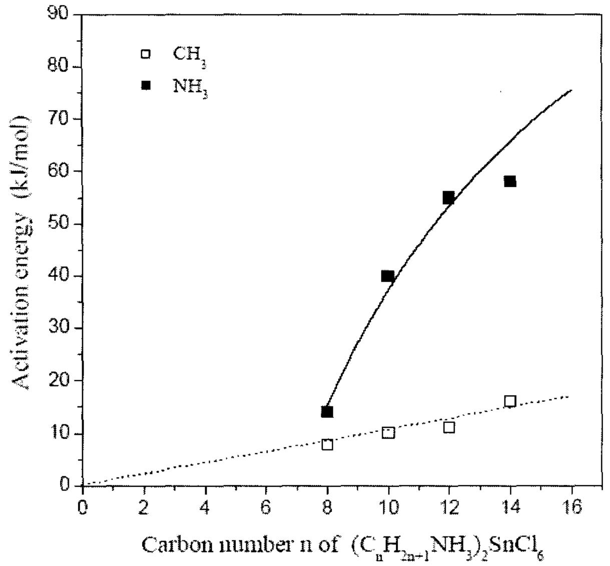

Fig. 3. The activation energies in the C_nSn series obtained from the ^1H NMR spin-lattice relaxation measurements.

that of 273 K in C_8Sn. Thus, the activation energy of the ammonium group may dictate the order-disorder transition of the hydrocarbon chain in the C_nSn systems. In fact, in similar lipid membranes the greater chain length has commonly been observed to lead to the higher transition temperature [11], and attributed to an increase in the interchain interaction, presumably the van der Waals interaction, with increasing chain length. It can thus be inferred that the potential well, in which the ammonium group lies, is strongly affected by the interchain interaction as well as by the N-H-Cl hydrogen bonding. In Fig. 3, it is indeed worthwhile to note the strong chain-length dependence for the NH_3 group despite the presumably similar hydrogen bonding in the systems with different chain lengths.

In summary, the chain-length dependence of the phase transitions in the C_nSn systems, an order-disorder phase transition and a conformational transition, were investigated by means of the ^1H NMR spin-lattice relaxation measurements. By fitting the spin-lattice relaxation rates with four types of molecular motions, the activation energies of the methyl and the ammonium groups were obtained, from which their roles in the phase transitions were assessed.

Acknowledgments

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