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Solid–Solid Phase Transitions of Long-Chain *n*-Alkyltrimethylammonium Halides

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Transition properties of some compounds of the type, n-$C_nH_{2n+1}N^+(CH_3)_3X^-$, with $n = 10, 12, 14, 18, 22$, and X = Cl, Br, and I, were investigated. All these compounds show a solid–solid phase transition with a large enthalpy change in the range of temperature 350 ~ 400 K. The transition behaviors were investigated by the aid of DSC, TG, X-ray, and optical microscope. The solid–solid phase transition is regarded to be caused by melting of the layer of hydrocarbon chains of the compounds, while the rigid ionic layer retains the regular arrangement. Some relationships between the physical properties and the structure of the compounds are discussed.

INTRODUCTION

Until now, some solid–solid phase transition behaviors of a series of compounds $(RNH_3)_2MCl_4$, where R = n-C_nH_{2n+1}, $n = 10 \sim 16$, M = Mn, Cu, Co, Fe, Hg, and Zn, have been reported.[1–6] One of the characteristic points of the crystalline structures of these compounds is the presence of bidimensionally extended layers of MCl_4^{2-}, sandwiched between the layers of alkylammonium ions which face each other with their apolar hydrocarburic end.[1,4] That is, the structure consists of "polar" layers, in which the ionic type bonding force is predominant, separated by pairs of "apolar" layers held together primarily by van der Waals forces. All the compounds show solid–solid phase transitions accompanied by large enthalpy changes in the temperature range, 273 ~ 373 K. The solid state structure of the polar layers remains practically unchanged during the solid–solid phase transition, but the structure of the apolar layers melts at the transition temperature.

We studied the thermochemical properties of some long-chain *n*-alkyl-

trimethylammonium halide compounds with a differential scanning calorimeter, and found an endothermic change in the temperature range 350 ~ 400 K during the heating scan. The observation by an optical microscope and a thermobalance reveals that this transition is neither a totally melting nor a decomposing process.

As stated before, the compounds used in the present investigation have a common structural feature; that is, these compounds are constructed of polar and apolar groups, resulting in crystalline structures with the polar layers separated by a pair of apolar layers. It would be suggested from structural considerations that the transitions observed here correspond to the melting process in the layer of apolar carbon chains. We will discuss this problem by the comparison with the phase transition behavior of related *n*-alkane compounds.

EXPERIMENTAL

The long-chain *n*-alkyltrimethylammonium halides were prepared by the method described by Scott and Tartar.[7] These compounds were modified to the required forms and recrystallized three or four times from dry ethanol-ether solutions.

The thermograms of the compounds were recorded in the temperature range from 350 to 400 K on a differential scanning calorimeter, Perkin-Elmer DSC-2, at a scanning rate of 1.25 K/min in N_2 atmosphere; the values of transition enthalpy were calibrated to the reference of a standard sample of indium ($\Delta H = 2.85 \times 10^4$ J/g). The reported values are the mean of several measurements on different samples; under the described conditions the precision is of the order of ±5%. The X-ray powder spectra of all the compounds at various temperatures were taken with an X-ray diffractometer, Rigaku Denki, Geigerflex, equipped with a high temperature attachment using the CuKα radiation. Microscopic observations at higher temperatures were made on a Plympus POM microscope with an attachment devised for this purpose.

RESULTS AND DISCUSSION

All the compounds appear as white platelets after recrystallizations, and decompose if heated at a temperature around 520 K. The typical thermograms of the compounds recorded in the temperature range 350 ~ 400 K on a DSC apparatus are shown in Figure 1. Endothermic and exothermic peaks appear in the heating and cooling scans respectively, and the enthalpy changes calculated from these peak areas are practically equal; that is, these changes are regarded to be a phase transition of first order. The examination on a hot plate under a microscope shows that the changes at these temperatures are not

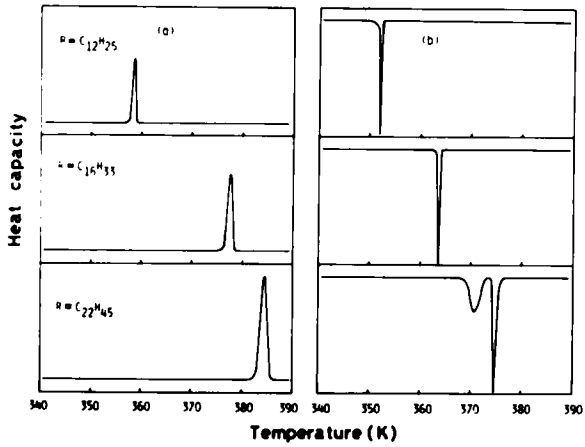

FIGURE 1 Thermograms of $RN^+(CH_3)_3Br^-$ obtained by a differential scanning calorimeter during (a) heating and (b) cooling scans.

owing to the melting process. Moreover, the lack of any weight loss, confirmed by measurements using a thermobalance (Shimadzu, TGA-20), implies that the endothermic peaks are not to be attributed to any thermal decomposition process. These observations lead us to the conclusion that the phenomenon occurring in the temperature range 350 ~ 400 K for the long *n*-alkyltrimethylammonium halides is a kind of solid-solid phase transition.

Table I shows the transition temperatures and, the enthalpy and entropy

TABLE I

Transition temperatures, enthalpies and entropies for various $R—N^+(CH_3)_3X^-$ compounds observed by DSC measurements.

R	X	T_{tr}/K		ΔH_{tr}/kJ mol^{-1}[a]		ΔS_{tr}/J K^{-1} mol^{-1}[a]	
		heating	cooling	heating	cooling	heating	cooling
$C_{10}H_{21}$	Br	369.5	361.7	32.4	33.1	88	92
$C_{12}H_{25}$	Br	370.4	360.0	42.3	46.4	114	129
$C_{14}H_{29}$	Br	372.3	358.8	46.9	48.1	126	134
$C_{16}H_{33}$	Br	376.1	362.2	51.5	53.6	138	148
$C_{18}H_{37}$	Br	378.3	368.3	64.9	64.4	172	175
$C_{22}H_{45}$	Br	382.6	{372.7 375.3	78.7	{35.3 40.0	218	{95 107
$C_{12}H_{25}$	Cl	357.2	350.5	29.6	29.7	83	85
$C_{14}H_{29}$	Cl	364.5	354.0	37.4	38.5	103	108
$C_{16}H_{33}$	Cl	368.4	360.6	41.8	40.8	113	113
$C_{18}H_{37}$	Cl	374.7	366.7	42.7	40.2	114	110
$C_{18}H_{37}$	I	393.9	386.4	46.9	49.7	119	128

[a] Precision of these data is of the order of ±5%.

changes of the transition of these compounds. The heating and cooling scanning rates are 1.25 K/min. The transition temperature in the cooling scans are lower by about 10 degrees than those in the heating scans. This implies the existence of a supercooled state in these temperature ranges.

Figure 2 shows plots of the transition enthalpy and entropy changes against the number of carbon atoms in the alkyl chains of the ammonium salts. Both quantities increase almost linearly with the number of carbon atoms. In the same figure, the enthalpy changes on melting of the corresponding *n*-alkanes are also shown. It is worthy of note that the enthalpy changes of melting of *n*-alkanes are very close to those of the transition of the corresponding *n*-alkyltrimethylammonium halides. This result indicates that the hydrocarbon chains of the long-chain alkylammonium take an ordered arrangement at temperatures lower than the transition point, and at this point they change into a disordered form, resulting mainly from the thermal liberation of the rotational freedom around the carbon-carbon bonds. Thus, the hydrocarbon chains take a "quasi-liquid" structure at the temperatures higher than the transition point.

The crystalline structure of hexadecyltrimethylammonium bromide was already reported and it belongs to the monoclinic form, space group $P2_1$, with $a = 5.66 \pm 0.01$ Å, $b = 7.26 \pm 0.01$ Å, $c = 51.9 \pm 0.1$ Å, and $\beta = 94°$.[8] According to these values, the molecular arrangement is schematically shown in Figure 3. In the case of hexadecyl group, the calculated length of the hydrocarbon chain is about 22 Å and, as the distance between two adjacent ionic

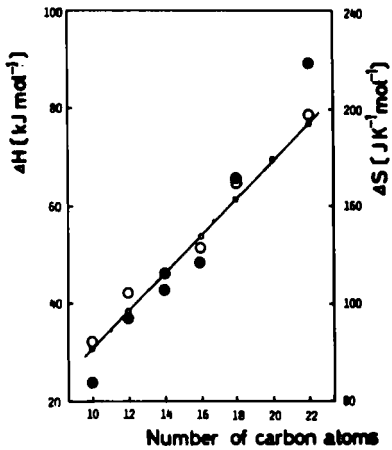

FIGURE 2 Plots of transition enthalpy and entropy changes against the number of carbon atoms. Large open and closed circles represent enthalpy and entropy changes of the transition, respectively. Small open circles represent enthalpy changes of melting for the corresponding *n*-alkanes.

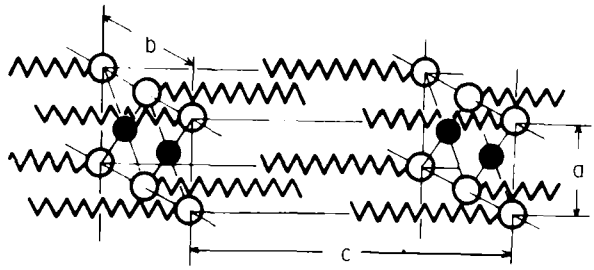

FIGURE 3 Schematic representation of the crystalline structure of hexadecyltrimethylammonium bromide. $a = 5.66 \pm 0.01$ Å, $b = 7.26 \pm 0.01$ Å, $c = 51.9 \pm 0.1$ Å, and $\beta = 94°$. Closed circles represent bromide anions and open circles represent $N^+(CH_3)_3$ cations.

layers is about 52 Å, there is no overlapping among the hydrocarbon chains. In this case, the distances between neighboring carbon chains are 5.66 Å and 7.26 Å, and these values are almost equal to those of *n*-alkane crystals,[9] which are held together primarily by van der Waals forces. Ammonium cations and halide anions extend bidimensionally to form an ionic layer, which is sandwiched between the hydrocarbon chain layers. The ionic bonding in the ionic layer is very strong compared to van der Waals forces in the hydrocarbon layer.

As the hydrocarbon chains take an ordered arrangement by weak intermolecular forces of van der Waals type, the thermal liberation of rotational freedom around the chain occurs at a comparatively low temperature, while the ionic layers remain unchanged. Therefore, the solid state continues to exist even above the transition temperature. This is the transition observed in the temperature range 350 ~ 400 K for these compounds.

While the enthalpy changes of transition of the ammonium salts are comparable to the enthalpy changes of melting of the corresponding *n*-alkanes, the temperatures and the entropy changes of the former are greatly different from those of the latter. This is due to the rigid structure of the ionic layers remaining above the transition temperature; that is, completely free motions of alkyltrimethylammonium halide molecules are not allowed owing to the rigid ionic layers. This reflects a small entropy change on transition compared to that of melting. As the transition temperature T_{tr} is governed by $T_{tr} = \Delta H_{tr}/\Delta S_{tr}$, it becomes large compared to the melting temperature of *n*-alkanes.

In order to obtain further information about the solid-solid phase transitions, X-ray reflections were measured by the powder method at various temperatures. Figure 4a shows the pattern at 293 K, indicating a series of small peaks in the region of higher angles than $2\theta = 30°$ which are assigned to the frozen hydrocarbon chains.[10] These peaks remain practically unchanged with increasing temperature though they shift a little to smaller angle owing to thermal expansion (Figure 4b). Figure 4c shows the pattern of powders at 383

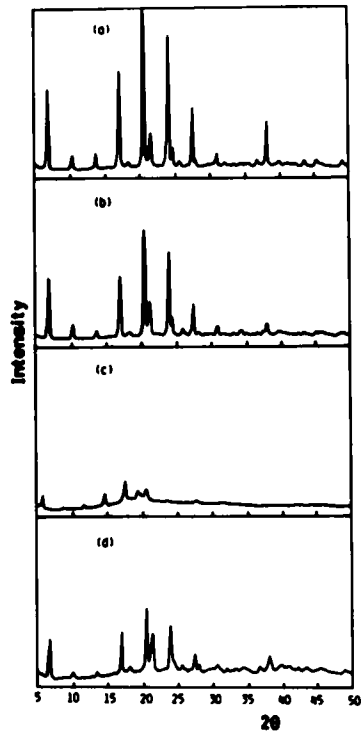

FIGURE 4 X-ray reflection pattern of hexadecyltrimethylammonium bromide at various temperatures. (a) 293 K, (b) 353 K, (c) 383 K, and (d) 293 K.

K, higher than the transition point. The peaks due to the hydrocarbon chains disappear, and alternatively a diffuse band appears around $2\theta = 20°$. This diffuse band is due to an amorphous phase of molten hydrocarbon chains. In the low angle region, there remain some peaks even at temperatures above the transition. These peaks are attributed to the ionic layers remaining at these temperatures. Although these peaks are not assigned exactly, there is a one-to-one correspondence between the spectra above (Figure 4c) and below (Figure 4b) the transition point with a shift to the lower angle side above the transition temperature. This implies expansion of the lattice spacing at the transition temperature. Figure 4d shows the X-ray reflection pattern of the sample powder cooled again to the starting temperature of 293 K from 383 K. The measurement was done one hour after the start of cooling. The peaks due to the crystalline hydrocarbon chains reappear and the diffuse band due to the amorphous phase almost disappears. But the intensity of each peak does not completely recover and this means that the solid–solid phase transition is a rather slow process. The position of each peak is the same as that in the origi-

nal sample. These results show that the recooled compound recovers the original crystalline structure, although a small portion of disordered phase remains.

For a long hydrocarbon chain, like the $C_{16}H_{33}$ group, it may be difficult to recover the original regularly ordered orientation from the disordered state. Thus, a supercooled state appears in the cooling scan; as shown in Table I, the transition temperature in the cooling scan is lower by about 10 degrees than that in the heating scan. A supercooled state is metastable, and the crystallizing process from a supercooled state is a strongly cooperative phenomenon.[11] This explains the fact that the peak in the cooling scan is sharper than that in the heating scan.

The DSC measurements on long-chain *n*-alkanes,[12] *n*-alkylhalides,[13] and *n*-alkyl alcohols[14] show small endothermic peaks at temperatures a little below the melting points in the heating scans. These phenomena are called premelting where the rotation around the principal rotational axes of the alkyl chain is liberated. In our measurements, $n\text{-}C_{22}H_{45}N^{+}(CH_3)_3Br^{-}$ shows a small exothermic peak a little below the transition temperature in the cooling scan (See Figure 1). A similar peak is not observed in the heating scan. This phenomenon is considered to be similar to premelting.

Figure 5 shows plots of the transition temperature and the melting point against the carbon number of the hydrocarbon chains. The mesophase above the transition temperature exists as a stable phase over 100 K. This is owing to the strong binding in the ionic layer. At the melting point, the compound changes to a transparent liquid and then to a black solid; that is, the compound decomposes after melting.

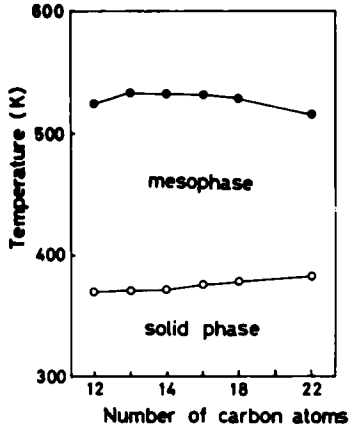

FIGURE 5 Plots of the transition temperatures and the melting points against the number of carbon atoms. Closed and open circles represent melting points and transition temperatures, respectively.

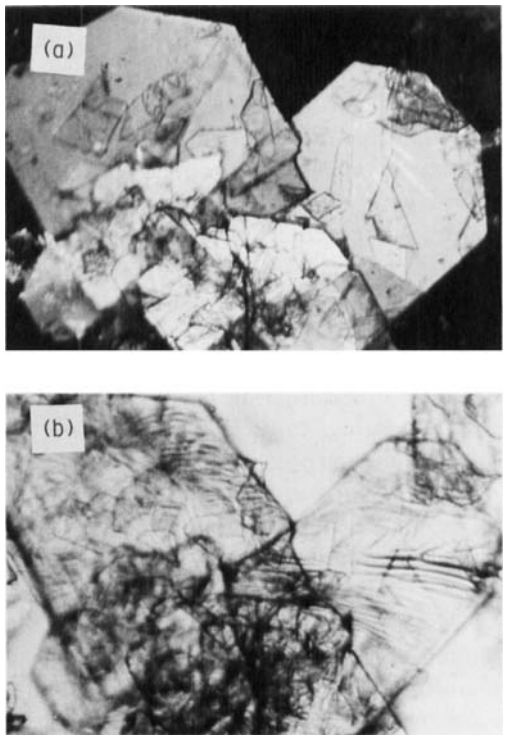

FIGURE 6 Optical photographs of crystals of hexadecyltrimethylammonium bromide. (a) 293 K and (b) 383 K. Crossed polaroids were used for observation at 293 K.

The properties of the mesophase reflect the existence of the disordered hydrocarbon layer. In fact, the hardness of the compounds varies drastically at the transition temperature. At temperatures above the transition point, the compounds are easily deformed by applying external forces, but they are scarcely deformed and broken by a certain strength of forces below the transition temperature. Microscopic photographs of single crystals of hexadecyltrimethylammonium bromide are shown in Figure 6. The crystals are anisotropic below the transition temperature, and above the transition point many wrinkles are observed in the crystals, which are almost isotropic; the plate-like crystals extinguish light for practically all orientations at crossed polaroids. This is explained by the existence of amorphous layers, which occupy a large part of the compound. When the crystals were cooled below the transition temperature, they become again anisotropic but the wrinkles remain.

The results of the present investigations are summarized as follows. (1) Long-chain *n*-alkyltrimethylammonium halides show an endothermic solid–solid phase transition in the range of temperature 350 ~ 400 K. (2) This tran-

sition is owing to the melting of the hydrocarbon layers, while the ionic layers are practically unaffected during this transition. (3) A supercooled state is observed in the cooling process and complete recovery to the original state is practically difficult.

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