Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Thermal, Dielectric and Polarized Microscopy Studies of 1-Octadecylamine

Naotake Nakamura [a] , Masao Okada [a] , Yutaka Okada [a] & Kaichiro Sugita [a]

[a] Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Tojiin-kitamachi, Kita-ku, Kyoto, 603, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Naotake Nakamura , Masao Okada , Yutaka Okada & Kaichiro Sugita (1985): Thermal, Dielectric and Polarized Microscopy Studies of 1-Octadecylamine, Molecular Crystals and Liquid Crystals, 116:3-4, 181-186

To link to this article: http://dx.doi.org/10.1080/00268948508074571

Mol. Cryst. Liq. Cryst., 1985, Vol. 116, pp. 181–186
0026-8941/85/1164–0181/$15.00/0

Thermal, Dielectric and Polarized Microscopy Studies of 1-Octadecylamine

NAOTAKE NAKAMURA, MASAO OKADA, YUTAKA OKADA and KAICHIRO SUGITA

Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Tojiin-kitamachi, Kita-ku, Kyoto 603, Japan

(*Received May 23, 1984; in final form September 17, 1984*)

Measurements of the physical properties of 1-octadecylamine were carried out in a temperature range of 30 to 120°C. The melting point of the compound was observed at 55°C and no liquid crystalline phase was found within this temperature range. The decomposition point of the carbonate of this amine was found to be a little higher than the melting point. A mixture of the amine with a small amount of its carbonate gave DSC curve similar to that of typical liquid crystalline materials.

INTRODUCTION

Investigations of the phase transition phenomena of normal higher primary amines have been done by many workers.[1,2,3] In a recent study using X-ray powder diffraction experiments, it was reported that there was no solid state phase transition phenomena in an amine series in which carbon numbers from 12 through 20 were studied.[2] Other workers reported the existence of liquid crystalline phases in the four primary amines: 1-dodecylamine, 1-tetradecylamine, 1-hexadecylamine and 1-octadecylamine.[3] In 1-octadecylamine, a mesophase was reported to occur in a temperature range of 55 to 89°.

The purpose of this work is to study more thoroughly the physical properties of 1-octadecylamine with an awareness of its chemical properties and to determine if the previously observed liquid crystalline phase is due to the presence of impurities.

EXPERIMENTAL

The sample, 1-octadecylamine was synthesized in our laboratory from octadecanoic acid. The reaction is shown in the following equations.

$$C_{17}H_{35}COOH \xrightarrow{SOCl_2} C_{17}H_{35}COCl \xrightarrow{NH_3}$$

$$C_{17}H_{35}CONH_2 \xrightarrow[\text{(in THF)}]{LiAlH_4} C_{18}H_{37}NH_2$$

Final product was purified by vacuum distillations twice. The amine was converted into N-acetylamine in order to avoid an absorption of carbon dioxide in the air. The N-acetylamine was judged thoroughly pure by gas chromatography, elementary analysis and melting point measurement. Table 1 shows that the elementary analysis of the N-acetylamine was within experimental error. Preparation of the sample for the physical measurements was done in a dry N_2 atmosphere in a sealed box containing Ascarite to avoid the absorption of carbon dioxide by the amine.

Thermal analyses were carried out by differential scanning calorimeter (Perkin Elmer, DSC-1B) and by thermogravimeter (Shimadzu, DT-30TG). Dielectric measurements were performed using multi-frequency LCR meter (Yokogawa Hewlett Packard, 4274A) at 1, 10 and 100kHz. Polarizing microscopic observations were made using a Nikon XTP-11 microscope equipped with a heating stage system (Mettler, FP-800). These measurements were done in a temperature range of 30 to 120°.

RESULTS AND DISCUSSION

The DSC thermogram for 1-octadecylamine is shown in Fig. 1. An endothermic peak (A) is observed on heating at 55° and it corresponds

TABLE 1

Elementary analysis data of N-acetyloctadecylamine.

Element		C	H	N	O
Calcd.	(%)	77.10	13.27	4.50	5.14
Found	(%)	77.12	13.56	4.33	5.04

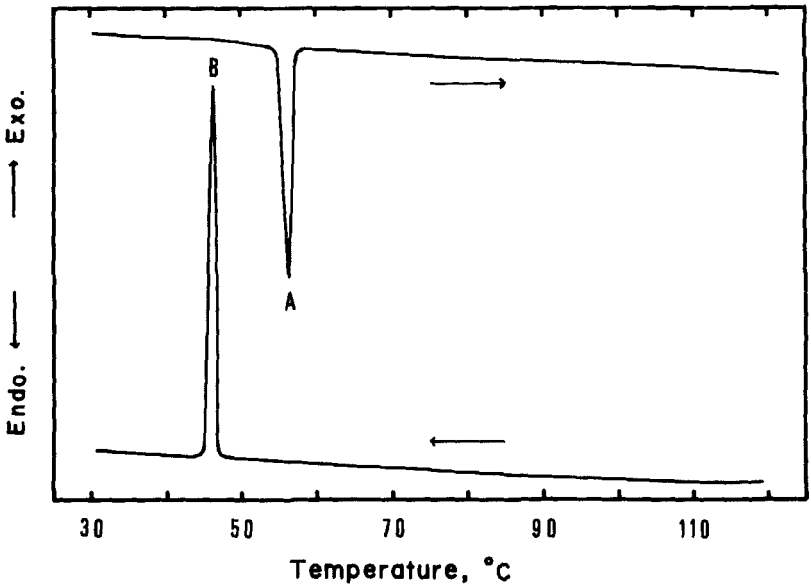

FIGURE 1 DSC thermogram for 1-octadecylamine. Arrows indicate direction of temperature change.
Scanning rate : 2.5°C/min.

to the melting point of the amine observed using the capillary melting point method. No other peaks were observed on increasing the temperature to 120°. On cooling, only one exothermic peak (B) was observed at 47° and it corresponded to the freezing point of the sample. The absence of a clearing point shows that no liquid crystalline phases occur in the temperature range of 30 to 120°.

Figure 2 shows the temperature dependence of the dielectric constant for 1-octadecylamine. The dielectric constant ϵ' is about 2.2 at 30° and increases slightly with increasing temperature. At about 50°, ϵ' increases gradually to about 2.5, and exhibits a maximum value of 2.56 at 55°. This temperature corresponds to the melting point of the sample. Above the melting point, ϵ' decreases very gradually with rising temperature. This may be caused by an increase of a thermal motion and a decrease of sample density. The existence of a mesophase was not found in this ϵ' -temperature plot.

During these measurements careful treatment of a sample was necessary because the amine easily converts to its carbonate by absorption of carbon dioxide from the air. Further thermal behavior experiments were made on the amine carbonate, and the DSC ther-

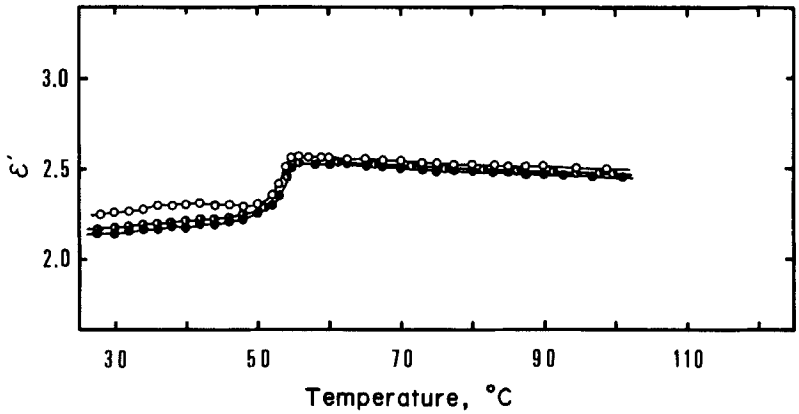

FIGURE 2 Temperature dependence of dielectric constant for 1-octadecylamine obtained at a heating rate of 0.5°C/min.
○ : 1 kHz ; ◑ : 10kHz ; ● : 100kHz.

mogram for the carbonate of 1-octadecylamine is shown in Fig. 3. One endothermic peak (C) on heating and one exothermic peak (D) on cooling were observed at 87 and 47°, respectively. Although the former was near the temperature previously reported for the clearing point of 1-octadecylamine,[3] the peak (C) can be identified as the decomposition point of the carbonate from the thermogravimetric measurement described later.

A mixture of the amine with its carbonate was prepared by an addition of the carbonate. In the DSC measurement for the mixture containing about 50% carbonate, two endothermic peaks were clearly observed at 52 and 85° on heating. The former corresponds to the melting point of the amine and the latter decomposition point of the carbonate described below. Figure 4 shows the result of the thermogravimetric measurement for this mixture. A distinct weight change of the sample was observed at about 85°, although no decrease in the sample weight was observed around the melting point of the amine. Namely, the distinct change was explained as an isolation of the carbon dioxide on the decomposition of the carbonate.

On the DSC scans for the mixtures of the amine and its carbonate, the decomposition peak of the carbonate became smaller with decreasing the concentration of the carbonate present. Figure 5 shows the thermogram for the sample of 1-octadecylamine containing a small amount of the carbonate. The percentage of the carbonate in this sample was difficult to determine. Two endothermic peaks (E) and (F) were observed and this scan is quite similar to those observed for

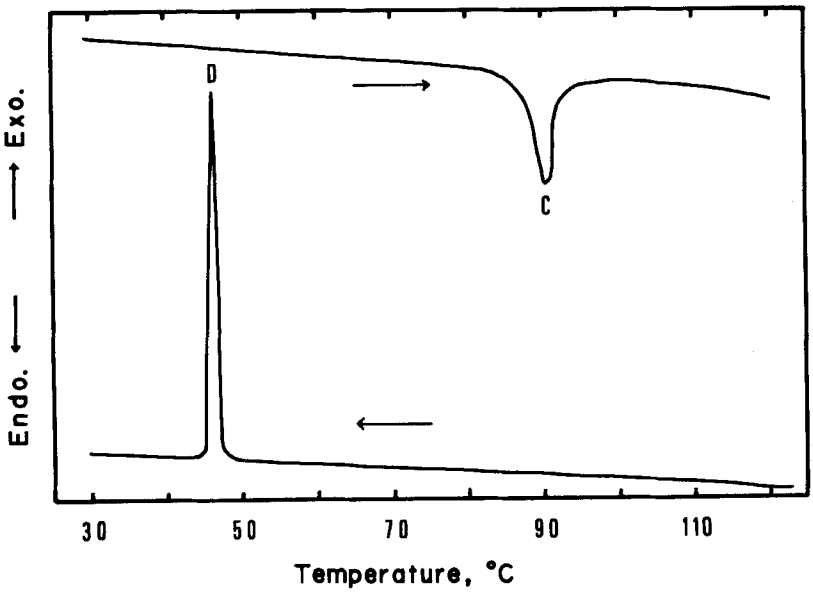

FIGURE 3 DSC thermogram for carbonate of 1-octadecylamine. Arrows indicate direction of temperature change. Scanning rate : 2.5°C/min.

typical liquid crystalline materials. But, the former peak at 52° is the melting point of the amine, and the latter, 84° was identified as the decomposition point of the carbonate as described above. These temperatures are somewhat lower because of the existence of the carbonate as an impurity in the sample. On cooling, one exothermic

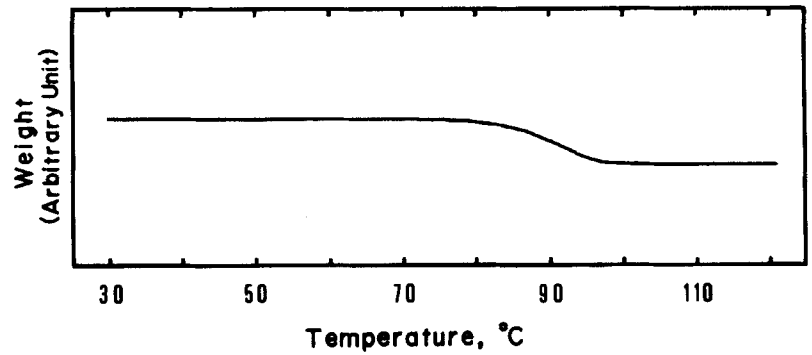

FIGURE 4 Thermogravimetric curve for a mixture of the 1-octadecylamine with its carbonate obtained at a heating rate of 1°C/min.

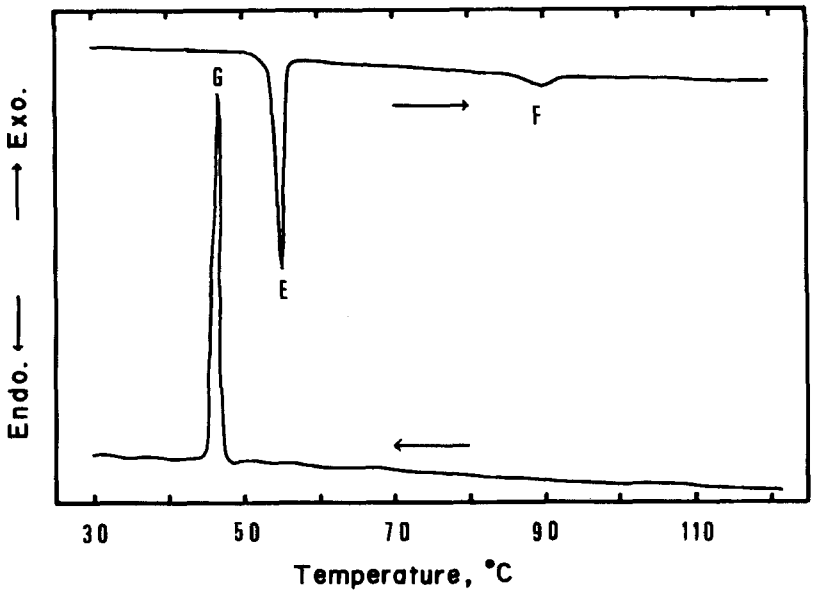

FIGURE 5 DSC thermogram for 1-octadecylamine containing a small amount of its carbonate.
Arrows indicate direction of temperature change.
Scanning rate : 2.5°C/min.

peak (G) was observed which corresponded to the freezing point of the free amine.

Optical microscopic observations with polarized light were performed on 1-octadecylamine in the same temperature range. There was no evidence of the existence any liquid crystal textures.

It is concluded that pure 1-octadecylamine has no liquid crystalline phase in both heating and cooling processes in the temperature range of 30 to 120°.

Acknowledgment

The authors wish to express their thanks to Emeritus Professor A. Watanabe of Ritsumeikan University for valuable discussion and encouragement.

References

1. J. D. Hoffman and C. P. Smyth, *J. Am. Chem. Soc.*, **71**, 3591 (1949).
2. A. Watanabe, A. Ishizawa, M. Kosaka and R. Goto, *Bull. Chem. Soc. Jpn.*, **42**, 1360 (1969).
3. M. Nishida, S. Miyagishi, T. Tarutani and M. Okano, *Yukagaku*, **24**, 687 (1975).