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A DSC study of the phase transitions in $(CH_3)_3NH[CdCl_3]$

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Abstract

Three phase transitions are seen at 333, 365 and 408 K when $(CH_3)_3NH[CdCl_3]$ is heated in DSC. Only the transition at 333 K is reversible, although it shows considerable thermal hysteresis. That transition appears to have a ΔH value of 150 J mol^{-1} and a ΔS value of 0.45 J mol^{-1} K^{-1}. The transitions at 365 K and 408 K have ΔH values of 420 J mol^{-1} and 35 J mol^{-1} respectively, which give rise to ΔS values of 1.15 J mol^{-1} K^{-1} and 0.086 J mol^{-1} K^{-1} respectively.

INTRODUCTION

There have been several structural studies on the phase transitions that occur upon heating $(CH_3)_3NH[CdCl_3]$. In the first of these studies, Walther et al. reported that phase transitions occur around 342, 374 and 415 K [1]. From DTA measurements, the corresponding values of ΔH (J mol^{-1}) and ΔS (J mol^{-1} K^{-1}) are 140 and 0.4, 270 and 0.7, and 20 and 0.05 respectively. It was also reported that repeated cyclic heating and cooling brings about changes (blurring or complete disappearance of the peaks) in the DTA curve [1]. Accordingly, there is some question about the reversibility of the phase transitions. The structure of $(CH_3)_3NH[CdCl_3]$ contains a hexagonal arrangement of $CdCl_3$ chains with the $(CH_3)_3NH^+$ cations between them [2]. Reorientation of the $(CH_3)_3NH^+$ ions, which are hydrogen bonded to Cl^- in the $CdCl_3$ units, leads to the phase transitions [2]. The crystal structures of these phases have been determined [3-5]. Although the structures of some of the phases are known, there appear to be no definitive thermal data for the phase transitions. Accordingly, we have studied the thermal behavior of $(CH_3)_3NH[CdCl_3]$ using differential scanning calorimetry (DSC), and this report presents the results of that study.

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EXPERIMENTAL

Trimethylammonium trichlorocadmium(II) was synthesized from trimethylammonium chloride and cadmium chloride. The trimethylammonium chloride was prepared by the reaction of an aqueous solution of trimethylamine with concentrated HCl. Crystals of $(CH_3)_3NHCl$ were allowed to separate and were removed by filtration. The $(CH_3)_3NHCl$ was recrystallized from water three times prior to the reaction with $CdCl_2$. To prepare $(CH_3)_3NH[CdCl_3]$, $(CH_3)_3NHCl$ was dissolved in absolute ethanol and $CdCl_2$ was dissolved in hot water. The solutions were mixed and heated on a hot plate. As soon as crystal formation began, the mixture was removed from the hot plate and cooled in a cold bath. After a considerable extent of crystallization, the crystals were removed by filtration and recrystallized twice from water. The crystals were allowed to dry in air and were placed in a desiccator over $CaCl_2$. Analysis: Calc. for $(CH_3)NH[CdCl_3]$: C, 12.90%; H, 3.23%. Found: C, 12.84%; H, 3.44%.

Thermal studies were carried out using a Perkin-Elmer differential scanning calorimeter Model DSC-7. The procedures employed were similar to those previously described [6]. Heating and cooling rates of 1.2, 2.5, 5.0 and 10.0 °C min^{-1} were used. Several runs were made at each scanning rate and average values for the thermal parameters were determined.

RESULTS AND DISCUSSION

A typical DSC curve showing the endothermic peaks observed under heating conditions is shown in Fig. 1. Clearly, three phase transitions are indicated at temperatures of about 333, 370 and 410 K. However, upon

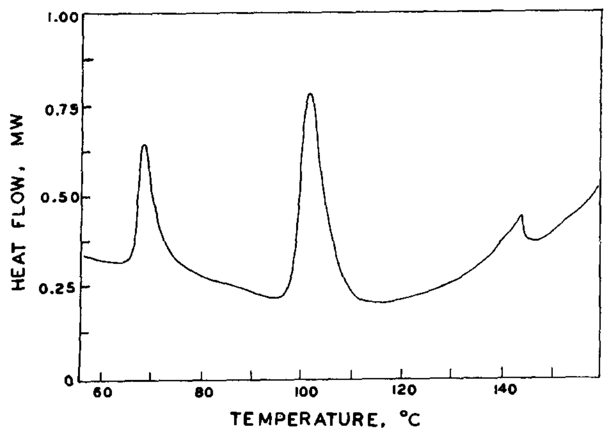

Fig. 1. DSC curve for $(CH_3)_3NH[CdCl_3]$ showing three phase transitions: sample mass, 10.560 mg; heating rate, 10 °C min^{-1}.

cooling, exothermic peaks for the transitions at 370 and 410 K are usually not seen. Only when relatively large samples (10–15 mg) were cooled slowly were these peaks seen. Even then the first derivative curve had to be examined in order to see the peaks with any degree of certainty. The instrument noise was essentially as great as the signal. Consequently, the last two peaks were studied only under heating conditions because for all practical purposes the two transitions at higher temperatures are essentially non-reversible, in accordance with earlier observations [1].

The lowest temperature transition was found to be fully reversible, although it does seem for some runs to be somewhat non-reproducible. The exothermic peak seen upon cooling was observed to be much broader than the endothermic peak seen upon heating. Also, as will be discussed later, the exothermic peak seen during cooling was observed at a lower temperature than that at which the transition was seen during heating, giving rise to considerable thermal hysteresis.

Table 1 shows the thermal data for the phase transition occurring at 333 K. It can be seen that the lack of uniformity of the transition during cooling is reflected in the large fluctuation in the ΔH values obtained. The apparent ΔH obtained during heating is seen to vary with heating rate, as has been observed for the phase transitions in sodium acetate [6] and potassium acetate [7]. The transition temperature itself varies slightly with the heating rate also. However, under cooling conditions, the transition was seen at about 325 K, with supercooling resulting in a slightly lower observed transition temperature the higher the cooling rate. Even at a heating/cooling rate of 1.2 K min^{-1}, the width of the hysteresis loop is 13.6 K. Figure 2 shows a typical thermal hysteresis loop obtained for a heating/cooling rate of 5 K min^{-1}. However, the extent of thermal hysteresis varies with heating/cooling rate, and Fig. 3 shows the variation in the width of the thermal hysteresis loop as a function of the rate of temperature change. Whereas phase transitions in some materials show little thermal hysteresis at low heating/cooling rates, the first phase transition in $(CH_3)_3NH[CdCl_3]$ exhibits rather extreme behavior. This may be related to the fact that this transition behaved somewhat erratically with regard to reversibility. Considering the results obtained in this work, it is unlikely that the phase transition at 333 K could be cycled without some hysteresis regardless of the heating/cooling rate used.

The observed transition temperature varies somewhat with heating rate. It appears that the temperature obtained by extrapolation to a heating rate of 0 K min^{-1} is about 333 K. Failure to consider the effect of heating rate probably accounts for some of the variation in the temperatures reported for this transition [1–5]. Although the phase transition which occurs at 333 K appears to be reversible, the ΔH values obtained appear to lack agreement when different cooling rates are used. Accordingly, we have used only values of ΔH obtained under heating conditions in the calcula-

TABLE 1

Thermal data for the lowest temperature (about 333 K) phase transition in $(CH_3)_3NH[CdCl_3]$

Heating/cooling rate (°C min^{-1})	Transition temp. (K)		ΔH (J mol^{-1})		ΔS (J mol^{-1} K^{-1})		Hysteresis width (K) [a]
	Heating	Cooling	Heating	Cooling	Heating	Cooling	
1.2	333.5 ± 1.6	326.0 ± 0.9	157.0 ± 17.6	−145.0 ± 3.9	0.47 ± 0.08	−0.46 ± 0.01	13.6 ± 2.1
2.5	334.6 ± 2.1	325.2 ± 0.9	167.3 ± 6.5	−137.8 ± 3.8	0.51 ± 0.02	−0.43 ± 0.01	17.2 ± 1.7
5.0	335.3 ± 2.2	325.8 ± 0.6	179.8 ± 5.3	−188.5 ± 4.7	0.53 ± 0.02	−0.59 ± 0.02	19.9 ± 0.8
10.0 [b]	335.7 ± 3.2	324.2 ± 1.3	171.5 ± 5.3	−223.1 ± 27.6	0.52 ± 0.02	−0.71 ± 0.09	21.4 ± 6.2

[a] Width of the hysteresis loop when one-half of the material is converted.

[b] Only two runs were made on the cooling part of the cycle.

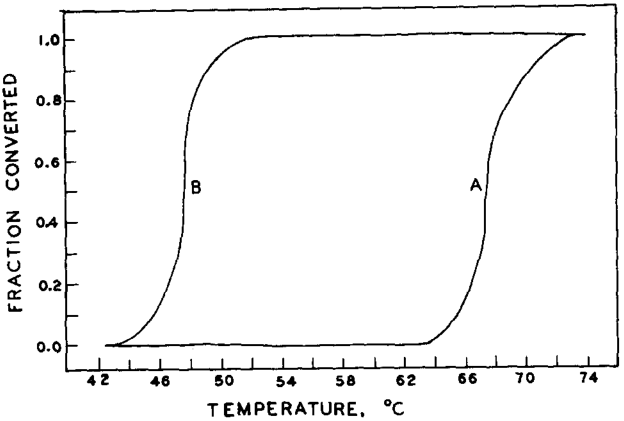

Fig. 2. Hysteresis loop for the phase transition at 333 K at a heating/cooling rate of 5 K $\min^{-1}$. Curve A is for heating and curve B is for cooling.

tions. Since the apparent value of ΔH varies with heating rate, it is necessary to determine the lowest value, determined at a hypothetical heating rate of 0 K $\min^{-1}$. Figure 4 shows the apparent ΔH value as a function of heating rate. It appears that the correct value for ΔH at a heating rate of 0 K $\min^{-1}$ is about 150 J mol^{-1}. This value is in reasonable agreement with the value of 140 J mol^{-1} reported by Walther et al., which was determined at an unreported heating rate [1]. The value for ΔS is therefore 0.45 J mol^{-1} K^{-1}, in good agreement with the value of 0.40 J mol^{-1} K^{-1} previously reported [1]. For a phase transition, ΔS is related to the number of orientations in the two phases by

$$\Delta S = R \ln(n_2/n_1) \tag{1}$$

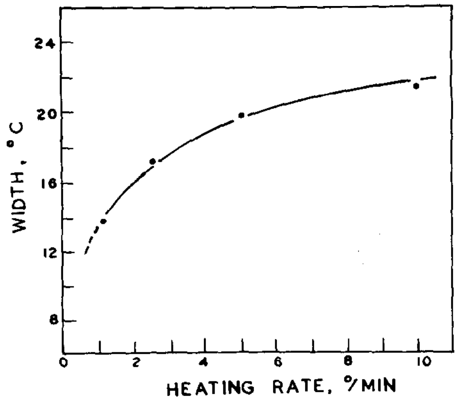

Fig. 3. Variation of the width of the hysteresis loop for the phase transition occurring in $(CH_3)_3NH[CdCl_3]$ at 333 K as a function of heating/cooling rate.

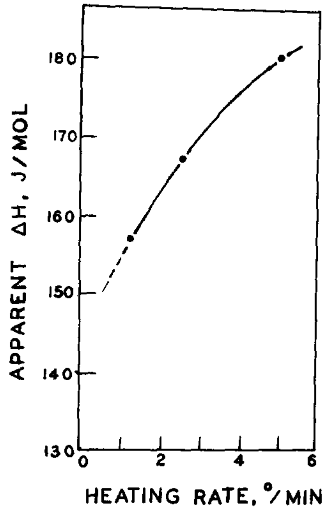

Fig. 4. Variation in apparent ΔH for the phase transition at 333 K as a function of heating rate.

where n_2 and n_1 are the number of orientations in the higher and lower temperature phases respectively [8]. For a ΔS value of 0.45 J mol^{-1} K^{-1}, the corresponding value of n_2/n_1 is 1.06. Since this value is so close to 1.00, it appears that the number of orientations is the same in the two phases (the phase stable at room temperature and the phase stable above 333 K). If this is the case, the phase transition may, in fact, represent a reorientation of $(CH_3)_3NH^+$ ions as has been previously described [2], but involving no increase in overall disorder.

As described earlier, the two phase transitions at temperatures of 365 and 408 K were found to be essentially non-reversible under cooling conditions. Under heating conditions, the two transitions appear to behave normally, although there is only a slight variation in transition temperature with heating rate for both transitions. In fact, there was a much greater variation in observed temperature between runs at the same heating rate than was observed at different heating rates. Table 2 shows the data obtained for these two phase transitions. For the phase transition at 365 K, extrapolation of the apparent ΔH values to a heating rate of 0 K min^{-1} yields a value of about 420 J mol^{-1} for this transition. The corresponding value for ΔS is 1.15 J mol^{-1} K^{-1}. These values are greatly different from the $\Delta H = 270$ J mol^{-1} and $\Delta S = 0.7$ J mol^{-1} K^{-1} previously reported [1]. For the phase transition at 408 K, the value for ΔH obtained by extrapolation of the apparent values to a heating rate of 0 K min^{-1} is 35 J mol^{-1}. Using this value for ΔH, a value of 0.086 J mol^{-1} K^{-1} is obtained for ΔS. Previously reported ΔH and ΔS values for this transition are 20 J mol^{-1} and 0.05 J mol^{-1} K^{-1} respectively [1].

TABLE 2

Thermal data for the phase transitions at 365 and 408 K

Heating/cooling rate (K $\min^{-1}$)	Transition temp. (K)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
365 K transition			
2.5	365.2 ± 8.8	450.9 ± 9.8	1.23 ± 0.03
5.0	363.7 ± 11.9	474.1 ± 26.6	1.30 ± 0.07
10.0	365.9 ± 12.5	481.9 ± 23.9	1.46 ± 0.06
408 K transition			
2.5	408.7 ± 7.4	38.1 ± 8.0	0.09 ± 0.02
5.0	407.7 ± 5.7	41.8 ± 2.8	0.10 ± 0.06
10.0	408.4 ± 8.6	48.5 ± 7.8	0.12 ± 0.02

Reported n_2/n_1 values for order–disorder processes generally range from about 1.20 to 48 [8]. A value of 1.15 is obtained for n_2/n_1 from the ΔS of 1.15 J mol^{-1} K^{-1} for the phase transition at 365 K. The exact nature of this transition is not known [5]; however, it appears to involve a reorientation of $(CH_3)_3NH^+$ ions. It has been stated that this leads to an increase in disorder [5], but it is not sufficiently described in a microscopic way. The transition at 408 K has been said to involve a change in stoichiometry [5]. This may explain the lack of reversibility of this transition. Certainly a ΔS value of 0.086 J mol^{-1} K^{-1}, which leads to an n_2/n_1 value of 1.01, is too low to indicate an order–disorder type of transition. Accordingly, the statement that "... in order to clarify the nature of these transitions, further microscopic investigations in theory and experiment are necessary" [5] seems appropriate.

In this work, we have shown that earlier thermal studies on the phase transitions in $(CH_3)_3NH[CdCl_3]$ provided thermodynamic parameters that are substantially in error. Although the present study has yielded more reliable thermal data, the exact nature of the transitions remains unclear.

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