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CHARACTERIZATION OF SOLID–SOLID PHASE TRANSITIONS: DIFFERENTIAL SCANNING CALORIMETRY VS. ADIABATIC CALORIMETRY

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ABSTRACT

Results for the characterization of solid–solid phase transitions by adiabatic calorimetry and differential scanning calorimetry are compared for the compound $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$. While the former method was able to resolve and fully characterize transition temperatures, enthalpies and entropies for each of four transitions in the temperature range $T = 349.6\text{–}365.6$ K, DSC was unable to fully resolve the transitions and gave only limited information concerning T_{trans}, ΔH_{trans} and ΔS_{trans} for this compound.

INTRODUCTION

Very often the thermal characterization of solid–solid phase transitions can lend insight into the changes in ordering within the solid state that are the source of such transformations. For example, it is well known that simple structural transformations give sharp anomalies in the C_p vs. T curve, with relatively small transition entropies, whereas order–disorder transitions have C_p values that may be anomalously high over a large temperature range and correspondingly large ΔS_{trans} values. (See ref. 1 for examples of order–disorder transitions.)

The detection of solid–solid phase transitions and the determination of the temperature, enthalpy and entropy of such transformations can, in principle, be carried out by two types of calorimetric methods: differential calorimetry (differential scanning calorimetry or differential thermal analysis) and adiabatic calorimetry.

The purpose of this report is the comparison of the use of differential scanning calorimetry and adiabatic calorimetry in the detection and characterization of solid–solid phase transitions in the compound $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$. This compound was chosen for this study both for its

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multiplicity of solid–solid phase transitions and because compounds of the same general formula have recently been studied extensively using DSC [2–5].

EXPERIMENTAL

The adiabatic calorimetric results were obtained using a heat pulse technique. The cylindrical copper calorimetric vessel (volume ~ 30 cm^3, wall thickness ~ 0.5 mm) was constructed with a central thermometer well that was fitted with a calibrated Pt resistance thermometer [Leeds and Northrup Model 8163, R (25°C) ~ 25 Ω] and heat was applied to the vessel through the Joule heating of 8 m of 32 SWG manganin wire ($R \sim 50$ Ω), bifilarly wound on the outside of the vessel. The vessel was surrounded by a cylindrical copper shield, which was kept at a temperature close to that of the calorimetric vessel, in order to maintain adiabatic conditions. The calorimetric experiment was suspended in a vacuum to further reduce heat exchange with the surroundings and the entire set-up was immersed in a cryogenic fluid to allow measurements below room temperature. The temperature range of the experiment was from $T \sim 10$ to ~ 400 K, limited at the low end by the relative insensitivity of the Pt thermometer to further reductions in temperature, and at the high end by the melting point of the soldered connections on the sample inlet port. In order to minimize the contributions due to thermally-generated voltages, all electrical connections were made with Leeds and Northrup thermal free solder. Temperature (resistance) and heat input (voltage, resistance) measurements were made with a Hewlett-Packard 3456A digital multi-meter. This was coupled to a Hewlett-Packard 87A personal computer that was used for data acquisition and analysis.

In a typical calorimetric investigation using the above apparatus, a 10–20 g sample was sealed in the vessel, under an atmosphere of ~ 10^{-6} atm He exchange gas. Except for the transition region, where it was considerably greater, the heat capacity of the sample comprised ~ 50% of the total heat capacity of the filled assembled calorimeter.

In order to test the adiabatic calorimeter, the heat capacity of a sample of Calorimetry Conference benzoic acid was measured for $T = 10–350$ K. The results agreed with the published values [6] to better than 1%, with a scatter of ±0.5%.

The differential scanning calorimetric measurements were made in two different calorimeters; a DuPont 1090 Thermal Analyser (operated in the DSC mode) and a Perkin–Elmer DSC 4.

$(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ was made from the reaction of stoichiometric amounts of $n\text{-}C_{18}H_{37}NH_2$ (Aldrich Chemical Company) with HCl and $CdCl_2$ (BDH Chemicals) in ethanol at 90°C [7]. Chemical analysis gave the following results (theoretical mass % in brackets): C, 55.3 (54.4); H, 10.9 (10.1); N, 3.59 (3.52); Cl, 17.9 (17.8).

RESULTS AND DISCUSSION

Figure 1 illustrates the heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ for T = 10–370 K, as determined in the adiabatic calorimeter described above. The general shape of the C_p curve, in comparison with that of similar compounds [8,9], indicates an additional contribution to C_p due to the phase transitions

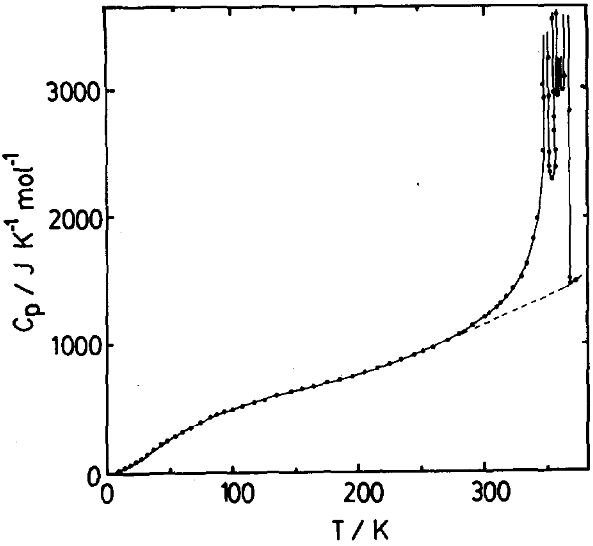

Fig. 1. The heat capacity, C_p, of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ as a function of temperature, as determined in the adiabatic calorimeter. - - - - - -, non-transition or baseline heat capacity.

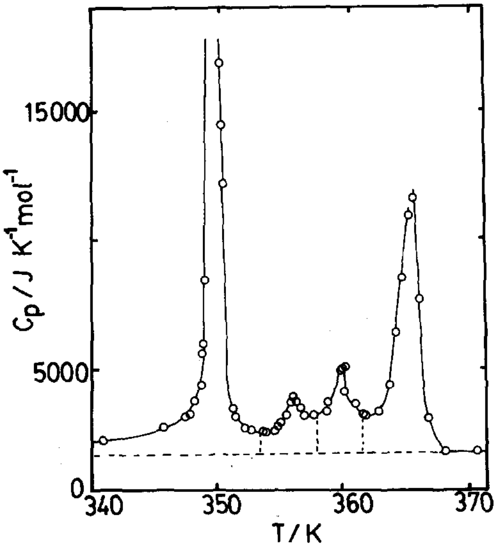

Fig. 2. C_p as a function of temperature T for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ in the region of the phase transitions, as determined by adiabatic calorimetry.

TABLE 1

Transition parameters for transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, as determined by adiabatic calorimetry

T(K)	ΔH_{trans}(J mol^{-1})	ΔS_{trans}(J K^{-1} mol^{-1})
349.6 ± 0.1	49500 ± 500	132 ± 1
356.0 ± 0.1	2300 ± 100	6.5 ± 0.3
359.5 ± 0.3	3500 ± 100	9.6 ± 0.3
365.6 ± 0.3	34300 ± 300	95 ± 1

throughout the range $280 \leqslant T \leqslant 368$ K. The "non-transition" (baseline) heat capacity curve for this compound, as determined by analogy with C_p values for $(n\text{-}C_7H_{15}NH_3)_2CdCl_4$ [9] is given by the dashed line in Fig. 1.

In Fig. 2 the heat capacity in the region of the phase transitions is shown in detail and from this figure $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ can be seen to have five solid phases in the temperature range of the experiment. The enthalpies (as determined by the long-heat method [10]), entropies and temperatures of the transitions are given in Table 1, and a detailed discussion of the nature of the phase transitions is given elsewhere [11].

While there are many reports of the detection and characterization of phase transitions in compounds of the general formula $(RNH_3)_2MX_4$, where R = long-chain alkyl, M = divalent metal, X = Cl or Br [2–5], it appears that the previous investigations found only two stable transitions between room temperature and the melting point in each compound. However, since $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ would not be expected to be so different from its homologues, and since all the previous studies had been done with DSC, a DSC investigation of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ was also carried out.

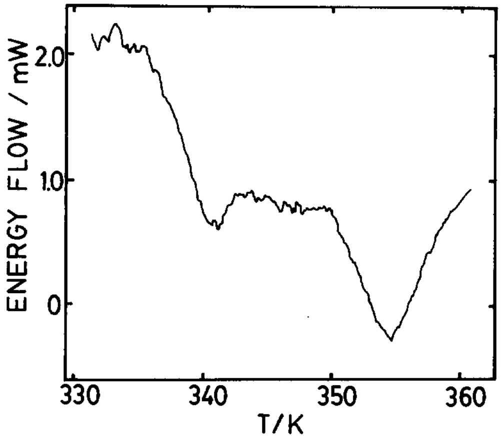

Fig. 3. DSC results for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, at a heating rate of 0.5 K min^{-1}, as determined in a DuPont 1090 Thermal Analyser.

The DSC trace for a 4.20 mg sample of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ on a DuPont 1090 Thermal Analyser is shown in Fig. 3. The heating rate was 0.5 K $\min^{-1}$, optimized to give the best resolution of the transitions with the highest signal-to-noise ratio. (Lower heating rates can, in principle, give higher resolution, but in practise also give more noise.) It is apparent from Fig. 3 that the DuPont 1090 DSC experiment was unable to resolve the four transitions, although it clearly indicated that more than two transitions occurred in the temperature range of the experiment.

From this DSC experiment, the temperatures of the highest and lowest transitions can be determined from the intersections of the baseline and the low temperature sides of the peaks. The transition temperatures thus determined are 336 K and 345 K, very much lower than those determined by adiabatic calorimetry (Table 1). The difference is probably attributable to the non-equilibrium, scanning nature of the DSC experiment, probably accentuated by the fact that the observed transitions involved very large enthalpy changes. It is interesting to note that the transition temperatures were not significantly changed when much faster DSC heating rates (10 K $\min^{-1}$) were used.

While it is not possible to resolve the enthalpies of the individual transitions from the DSC experiment, the total transition enthalpy can be calculated. Using the baseline shown in Fig. 4, $\Delta H_{trans}(\text{total}) = 9.28 \times 10^4$ J mol^{-1}, which is greater than the value from the adiabatic calorimetry experiment $[(9.0 \pm 0.1) \times 10^4$ J $\text{mol}^{-1}]$. This is surprising in light of the fact that the DSC experiment is unable to detect, and therefore omits, the contribution due to the gradual start-up of the transition. However, in this case this contribution is small (1.3×10^3 J mol^{-1} from $T = 280\text{–}315$ K) relative to the total ΔH_{trans}.

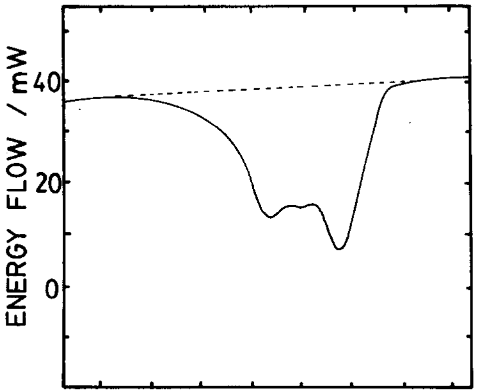

Fig. 4. DSC results for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, at a heating rate of 10 K $\min^{-1}$ in a DuPont 1090 Thermal Analyser. - - - - - -, baseline chosen for the calculation of ΔH_{trans}.

One of the most important parameters in the interpretation of phase transitions is $\Delta S_{\mathrm{trans}}$. While the most accurate values of $\Delta S_{\mathrm{trans}}$ are determined from the experimental and baseline heat capacity values

$$\Delta S_{\mathrm{trans}} = \int_{\mathrm{expt}} \frac{C_{\mathrm{p}}}{T}\mathrm{d}T - \int_{\mathrm{baseline}} \frac{C_{\mathrm{p}}}{T}\mathrm{d}T \tag{1}$$

if the transition is primarily isothermal, then

$$\Delta S_{\mathrm{trans}} = \frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}} \tag{2}$$

While it is possible to derive accurate values of C_{p} from some DSC experiments [12] the usual procedure is to obtain $\Delta S_{\mathrm{trans}}$ from DSC data through the use of eqn. (2). Because the transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ exist over an exceptionally wide temperature range (280–368 K), use of eqn. (2) with an "average" T_{trans} will have a large associated error. However, this method can be used to estimate the total transition entropy change and, using the DuPont DSC value of $\Delta H_{\mathrm{trans}}$ and $T_{\mathrm{trans}} = 360$ K, $\Delta S_{\mathrm{trans}}(\mathrm{total}) = 2.58 \times 10^2$ J K^{-1} mol^{-1}. This is somewhat larger than the adiabatic calorimetry value [$(2.43 \pm 0.03) \times 10^2$ J K^{-1} mol^{-1}] which was derived using the C_{p} values and eqn. (1). The DSC value of $\Delta S_{\mathrm{trans}}$ can be improved through the use of the adiabatic calorimetry value of $\Delta H_{\mathrm{trans}}$; with $T_{\mathrm{trans}} = 360$ K, eqn. (2) gives $\Delta S_{\mathrm{trans}} = 2.49 \times 10^2$ J K^{-1} mol^{-1}. The remaining difference can be attributed to the error in assessing the non-isothermal contributions to $\Delta S_{\mathrm{trans}}$.

The DSC trace for a 7.71 mg sample of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ on a Perkin–Elmer DSC-4 is shown in Fig. 5. In this case the heating rate was 2 K min^{-1}, as higher rates gave poorer resolution and lower rates washed the transition enthalpy into the background.

It is interesting to compare the results of the Perkin–Elmer DSC experiment with the others. While there is evidence for more than 3 phase transitions (Fig. 5) again complete resolution is lacking. Estimates of the

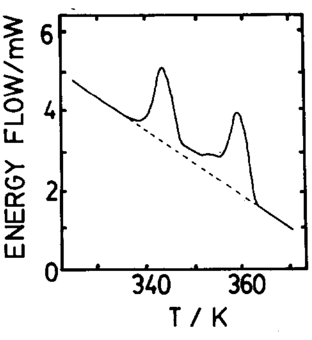

Fig. 5. DSC results for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, at a heating rate of 2 K min^{-1}, as determined in a Perkin–Elmer DSC-4.

transition temperatures of the highest and lowest transitions (341 K and 355 K as determined by the onset temperatures at 2 K min^{-1}) again are considerably lower than the values determined by adiabatic calorimetry (Table 1). It is interesting to note that the Perkin–Elmer DSC transition temperatures increased with increased heating rate, and were within a few degrees of the adiabatic calorimetry values at 20 K min^{-1}.

The transition enthalpies for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, as determined with the Perkin–Elmer DSC-4, also depend critically on the heating rate. At 20 K min^{-1}, the total ΔH_{trans} was determined to be 8.0×10^4 J mol^{-1}, and this value fell with lowered heating rates to 7.0×10^4 J mol^{-1} at 5 K min^{-1} and 5.9×10^4 J mol^{-1} at 2 K min^{-1}. (The adiabatic calorimetry value was 9.0×10^4 J mol^{-1}.) This heating rate effect, which was very reproducible, did not occur when calibration compounds with sharp transitions were examined, and is almost certainly due to the non-equilibrium nature of the DSC experiment.

As the transition enthalpy results from the Perkin–Elmer DSC experiment were so uncertain, no discussion of ΔS_{trans} from this method will be given.

CONCLUSIONS

A comparison of the characterization of solid–solid phase transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ by adiabatic calorimetry and differential scanning calorimetry has been made. For this particular compound, DSC is unable to fully resolve the four phase transitions. Of the important transition parameters (T_{trans}, ΔH_{trans}, ΔS_{trans}), only the enthalpy of the sum of the transitions is determined with fair accuracy by DSC, whereas adiabatic calorimetry gives the temperature, enthalpy and entropy of each of the transitions. In addition, because of the scanning nature of experiment, DSC cannot provide as accurate information as adiabatic calorimetry on the "shape" of the transition. However, an adiabatic calorimetry experiment such as the one described herein takes weeks to accomplish with apparatus that is not commercially available, whereas DSC is a much faster experiment and one that can be done with a minimum of technical knowledge. This paper shows by example that the DSC technique is useful for preliminary investigations of solid–solid phase transitions, that can be further characterized by adiabatic calorimetry.

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