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A DSC study of the phase transition in potassium thiocyanate

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Abstract

The phase transition that occurs at 413 K in potassium thiocyanate has been studied using differential scanning calorimetry. The transition was found to be reversible and the apparent ΔH value is dependent on heating/cooling rate. The transition displays a thermal hysteresis that also depends on rate of heating and cooling.

INTRODUCTION

The phase transition in potassium thiocyanate has been studied by various methods. Sakiyama et al. determined the mechanism of transition to be of the order–disorder type by thermal and infrared absorption data [1]. Yamada and Watanabe have also studied this transition using X-ray diffraction [2]. In both of these studies the transition was discovered to involve the rotational disordering of the thiocyanate ions as the material is heated past the transition temperature. In the low temperature phase the direction of the thiocyanate ion is aligned in a regular pattern. In the high temperature phase the direction of the thiocyanate ion is scrambled. That is, the probability of the anion's being oriented as SCN^- is the same as its being NCS^-. The transition mechanism has also been described using group theoretical parameters by Schranz et al. [3].

The temperature at which the structural phase transition occurs in potassium thiocyanate, according to each of the previous studies referenced, is about 413 K. However, the enthalpy of transition reported in these earlier studies varies from 1660 J mol^{-1} [4] to 2530 J mol^{-1} [5]. Because no studies have been conducted to determine the effect of heating rate and the nature of thermal hysteresis, we have conducted thermal studies on the phase transition in potassium thiocyanate using differential scanning calorimetry (DSC).

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EXPERIMENTAL

Reagent grade potassium thiocyanate was recrystallized from water and dried by heating at approximately 90°C for three days. The material was then ground into a fine powder and stored over desiccant. Enthalpy determinations were carried out using a Perkin-Elmer DSC 7 differential scanning calorimeter. The instrument was calibrated by means of the heats of fusion of indium and zinc.

Heating and cooling rates of 0.5, 1.0, 2.0, and 4.0°C min^{-1} were used. Samples were studied under a dry nitrogen atmosphere at a flow rate of 40 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Sample sizes ranged from 2 to 5 mg. Four to five samples at each heating/cooling rate were used to determine mean value and standard deviations for the enthalpy of transition.

In order to study the thermal hysteresis occurring between heating and cooling, the fraction of the sample converted was determined as a function of temperature at each heating and cooling rate. This was done by comparing the area of the peak up to the temperature in question with the area for the conversion of the entire sample.

RESULTS AND DISCUSSION

The DSC curves for potassium thiocyanate show a single reversible phase transition between ambient temperature and the melting point. A

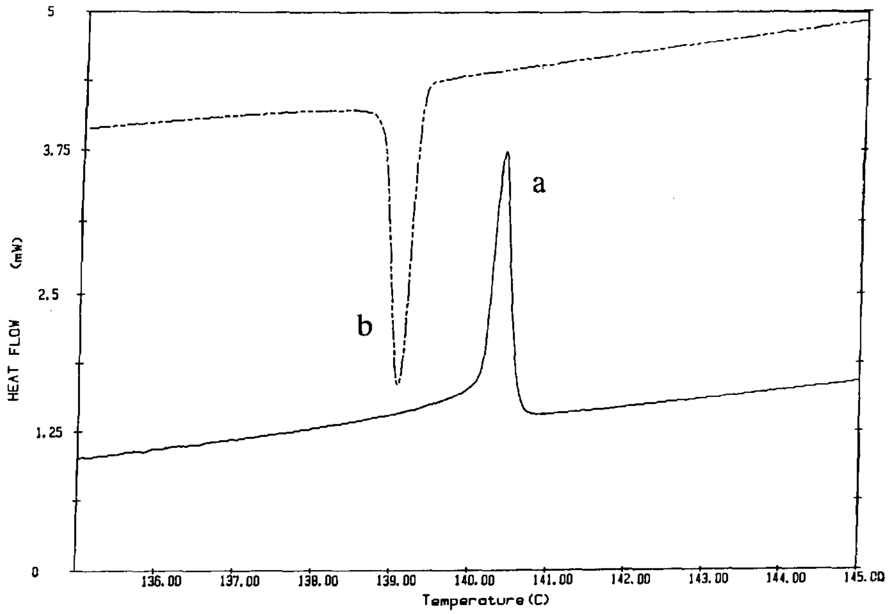

Fig. 1. DSC curve for potassium thiocyanate at heating and cooling rates of 2.0 min^{-1}: (a) heating endotherm; (b) cooling exotherm.

TABLE 1

Enthalpy and hysteresis data for the phase transition of KSCN

Heating/cooling rate (°C $\min^{-1}$)	ΔH (J mol^{-1})			ΔS (J mol^{-1} K^{-1})	Hysteresis width (K)
	Heating	Cooling	Combined av.		
0.5	565 ± 22	−616 ± 16	590 ± 32	1.43 ± 0.08	0.54 ± 0.03
1.0	594 ± 21	−660 ± 25	627 ± 41	1.52 ± 0.10	0.87 ± 0.08
2.0	606 ± 11	−645 ± 18	625 ± 25	1.52 ± 0.06	1.25 ± 0.03
4.0	691 ± 24	−722 ± 23	707 ± 28	1.71 ± 0.07	2.25 ± 0.05

typical DSC curve is shown in Fig. 1. The sample begins to absorb heat at about 413 K. This value agreed well with the value for the transition temperature previously reported. The temperature of the transition was independent of heating rate in the range studied.

The apparent enthalpy of the transition was observed to increase as a function of heating/cooling rate. The results obtained are shown in Table 1. The apparent enthalpy increased from 590 to 707 kJ mol^{-1} when the heating rate was increased from 0.5 to 4.0°C $\min^{-1}$. Although the apparent ΔS value varies according to the heating rate used, the n_2/n_1 value from the equation

$$\Delta S = R \ln(n_2/n_1)$$

varies from 1.19 to 1.23. These values are lower than those previously reported [1]. Reported n_2/n_1 values for order–disorder processes generally range from approximately 1.20 up to 48 [6]. It is probable that the phase transition is an order–disorder process. This dependency on heating/cooling rate may be responsible for the discrepancy in the literature. Also, in 1963 Sakiyama et al. reported that no hysteresis phenomenon was observed [1]. However, in the present study a hysteresis phenomenon which depends on heating/cooling rate was observed. Figure 2 shows a typical hysteresis loop for the phase transition of KSCN. When the hysteresis width is

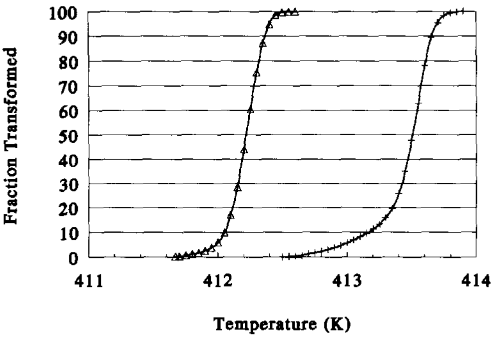

Fig. 2. Thermal hysteresis loop for the phase transition at 413 K. Fraction converted vs. temperature at a heating (+) and cooling (△) rate of 2°C $\min^{-1}$.

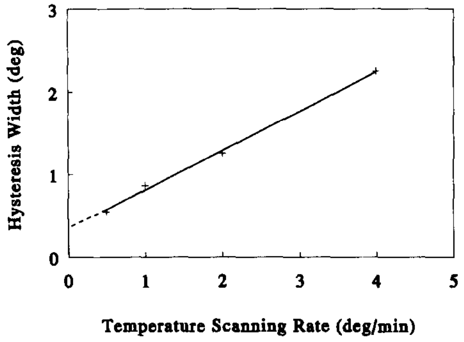

Fig. 3. Thermal hysteresis width as function of heating/cooling rate.

plotted against heating/cooling rate a nearly linear relationship is observed. This behavior is shown in Fig. 3.

CONCLUSIONS

The results obtained in this work show that the enthalpy of the phase transition is dependent on the heating/cooling rate. Also, a hysteresis phenomenon was observed for the transition. This was not previously reported in the literature.

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