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New structural phase transitions in potassium and sodium amidosulfonates

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Abstract

New structural transformations in K and Na amidosulfonates are detected and studied by means of DSC and in situ optical microscopy. The enantiotropic transformation in K amidosulfonate has a transition temperature of 437.9 K and a heat of transformation ΔH=4878 J mol^{-1}. The corresponding values for the weak first-order phase transition in $NaNH_2SO_3$ are 456.0 K and ΔH=1905 J mol^{-1}, respectively. © 1997 Published by Elsevier Science B.V.

Keywords: Amidosulfonates; DSC; Phase transitions; Thermal analysis

1. Introduction

Structural phase transformations in salts of amidosulfonic acid with monovalent cations have been detected by Rapp [1]. Recently, one of the phase transitions in $CsNH_2SO_3$ have been studied by Haussühl and Haussühl [2]. The aim of the present study is to detect and investigate phase transitions in K and Na amidosulfonate.

It is well-established, that the KNH_2SO_3 crystallizes at room temperature waterfree in the orthorhombic space group Pbcm with lattice parameters a=5.9107; b=8.333; c=8.302×10^{-10} m [3]. Manickkavagam et al. [4] reported the room temperature structure of $NaNH_2SO_3$ which belongs to the space $P2_12_12_1$ of the orthorhombic system with lattice parameters: a=5.506(2); b=12.449(3); c=15.672× 10^{-10} m.

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2. Experimental

The K and Na amidosulfonates were obtained by neutralization of aqueous solution of amidosulfonic acid HNH_2SO_3 with K_2CO_3 and Na_2CO_3, respectively. Preventing a decomposition of the salts during their preparation needs that the temperature is not substantially higher than room temperature.

Large single crystals of optical quality were grown from aqueous solutions at the University of Cologne.

3. DSC investigations

DSC investigations were carried out by means of a Perkin–Elmer calorimeter DSC-2C at scanning rates from 1.25 to 80 K min^{-1}. Temperature and enthalpy calibration of the device were performed for every scanning rate. The main experimental results were obtained at a scanning rate of 40 K min^{-1}.

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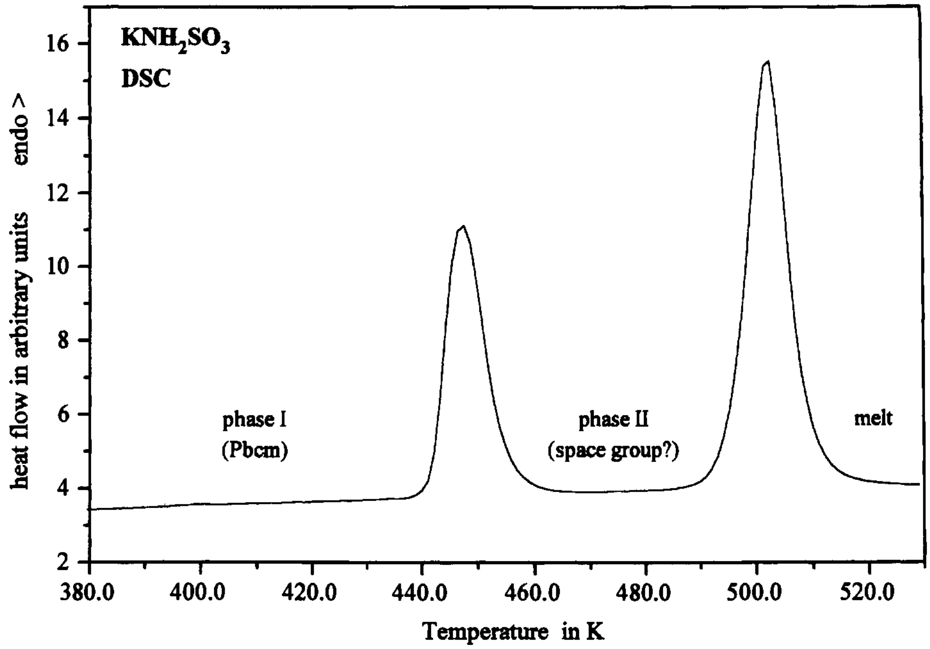

Fig. 1. DSC curve of KSO_3NH_2, obtained at a heating rate of 80 K/min, showing the phase transformation at 440–460 K and the melting peak.

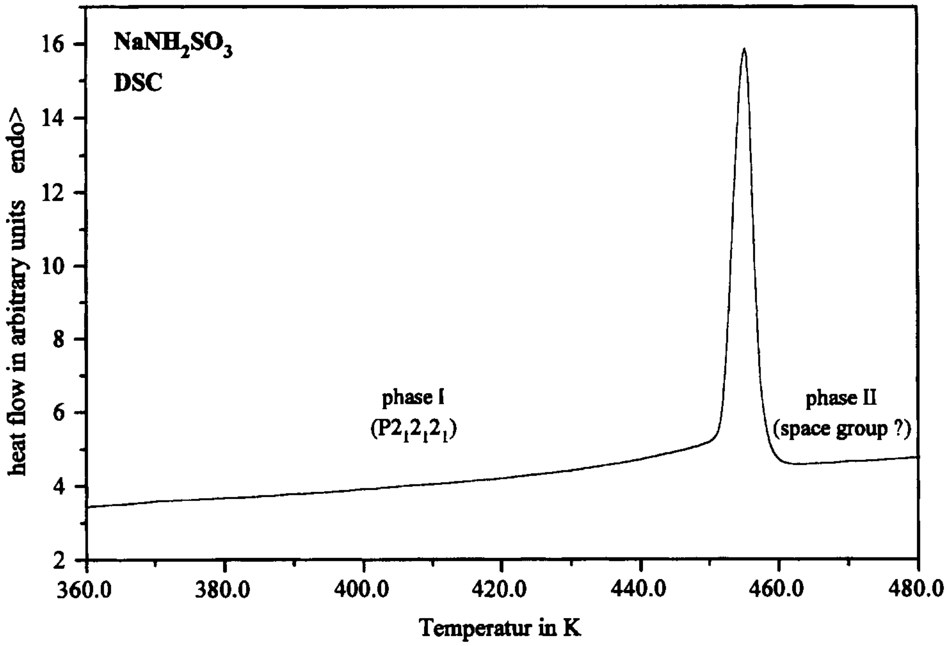

Fig. 2. DSC curve of $NaSO_3NH_2$, obtained at a heating rate of 20 K/min.

Figs. 1 and 2 show DSC curves of KNH_2SO_3, and $NaNH_2SO_3$, respectively. As it is obvious, on the thermoanalytical curves of both salts an endothermic peak due to a polymorphous transformation appears. The thermal peak of the KNH_2SO_3 has approximately a symmetrical shape. On the contrary, in the DSC-

Table 1
Characteristic data of phase transitions (DSC measurements, 40 K/min)

	T_{onset} (K)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
KNH_2SO_3	437.9	4878	11.14
$NaNH_2SO_3$	456.0	1905	4.18

trace of $NaNH_2SO_3$ a smooth curvature starts at about 40 K below the peak, giving the DSC curve the shape of a λ-transformation (Fig. 2). The phase transition characteristics of K and Na amidosulfonates (transformation temperature T_{onset}, changes of enthalpy and entropy) determined by DSC at a heating rate of 40 K/min are listed in Table 1. It can be seen, that the transition enthalpy and the entropy of K salt is considerably higher than those of $NaNH_2SO_3$. The entropy and the enthalpy of the phase transition in KNH_2SO_3 is very close to the melting entropy and enthalpy in contrast to the corresponding values in $NaNH_2SO_3$ (Table 3).

A DSC curve of a cooling experiment of the high-temperature $NaNH_2SO_3$ modification is shown in Fig. 3. A hysteresis of ΔT=12 K of the transition in cooling, compared to a heating experiment, is observed. In similar cooling–heating experiments the phase transition in KNH_2SO_3 shows a 20 K hysteresis.

Using Kissinger's [5] and Ozawa's [6] methods the activation energy of the polymorphous transformation of K and Na amidosulfonates was determined. The dependence of the temperature of the thermal peak's maximum (T_{max}) on the heating rate β=dT/dt, where T is the temperature and t the time, was determined. Figs. 4(a) and (b) Fig. 5(a) and (b) show the experimental data for K and Na amidosulfonates, respectively, in the linearizing coordinates of Kissinger's ($\ln(\beta/T^2_{max})$ vs. 1000/T_{max} and Ozawa's ($\ln(\beta)$ vs. 1000/T_{max}) equations. The values of activation energy of polymorphous transition, determined from the slope of the obtained straight lines, are given in Table 2.

Table 2
Activation energies of polymorphous transitions

	E_a (Kissinger) (kJ mol^{-1})	E_a (Ozawa) (kJ mol^{-1})
KNH_2SO_3	467±50	474±50
$NaNH_2SO_3$	450±73	458±73

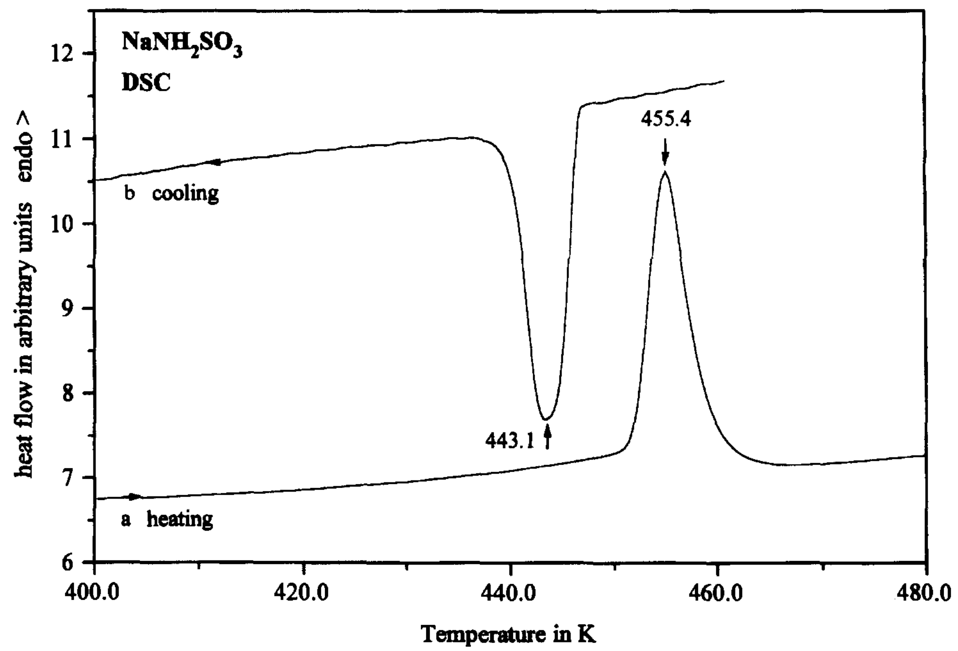

Fig. 3. DSC curve of $NaSO_3NH_2$, obtained at (a) a heating rate of 20 K/min and (b) a cooling rate of 20 K/min.

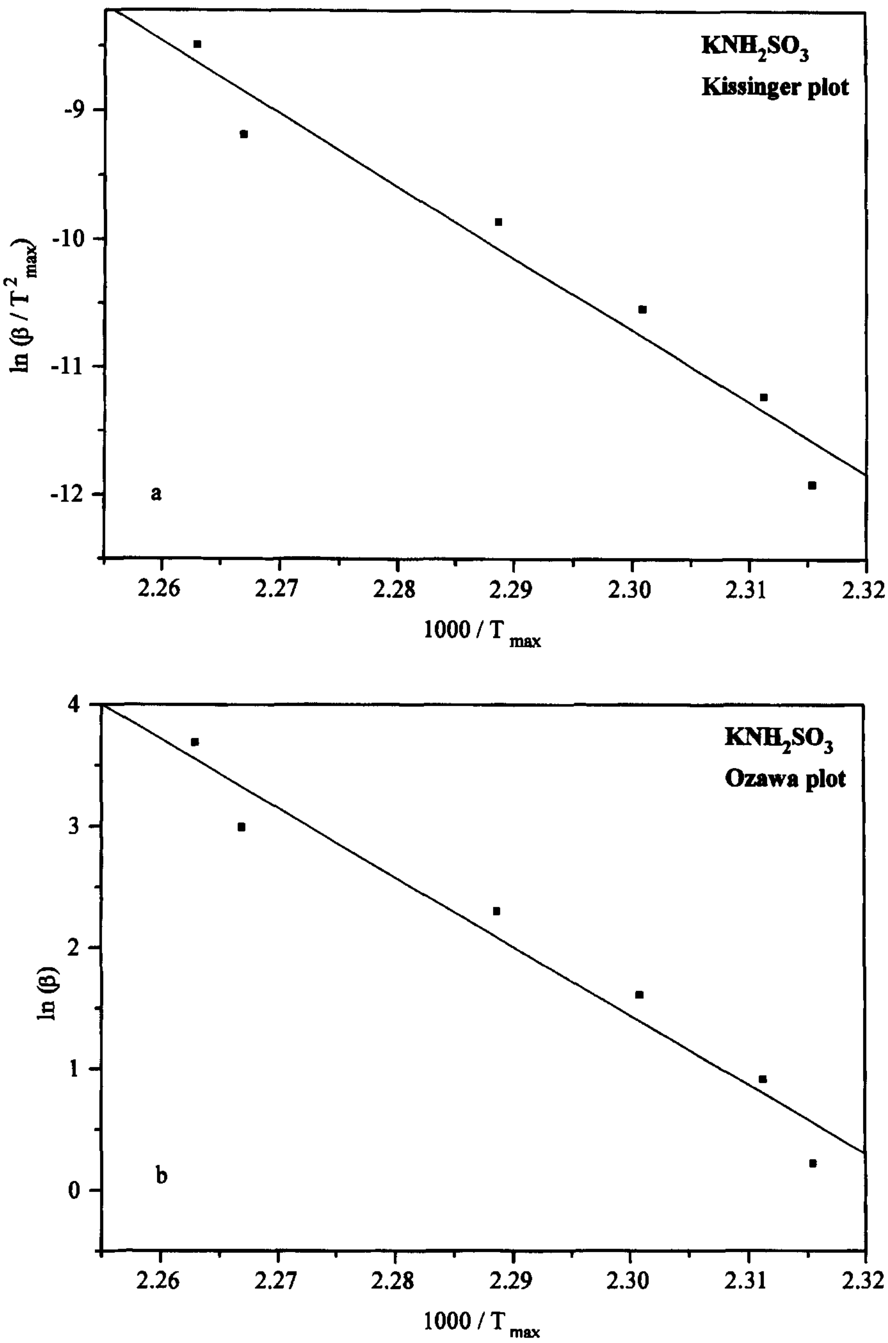

Fig. 4. Dependence of the temperature of the maximum in the KSO_3NH_2 DSC curves (T_{max}) on the heating rate (β) in the coordinates of (a) Kissinger's and (b) Ozawa's equations (Temperature in K).

Investigation of the melting of KNH_2SO_3 and $NaNH_2SO_3$ is hindered by the beginning of decomposition of these salts. In spite of all, the temperature and enthalpy of melting of both salts were determined by DSC-experiments (Table 3). For every melting experiment a new

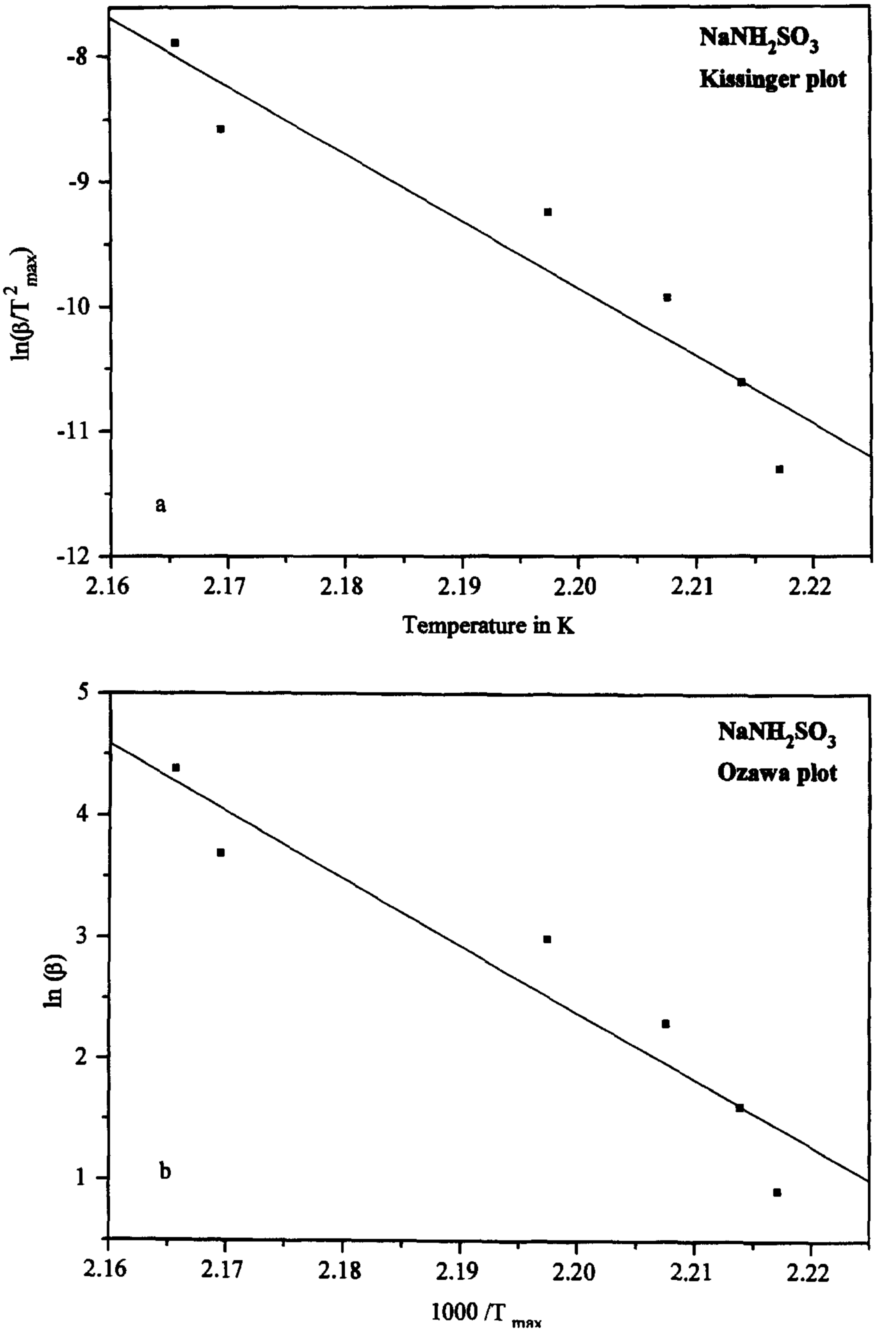

Fig. 5. Dependence of the temperature of the maximum in the $NaSO_3NH_2$ DSC curves (T_{max}) on the heating rate (β) in the coordinates of (a) Kissinger's and (b) Ozawa's equations (Temperature in K).

sample was used. The melting points of K and Na amidosulfonates are higher in comparison with the melting points of other amidosulfonates of monovalent cations ($TlNH_2SO_3$: 417.7 K, $RbNH_2SO_3$: 459.2 K, $NH_4NH_2SO_3$: 403 K and $CsNH_2SO_3$: 450.0 K).

Table 3
Temperature and enthalpy of melting (DSC measurements)

	T_{onset} (K)	ΔH ($J\,mol^{-1}$)	$\Delta S=\Delta H/T_{onset}$ ($J\,mol^{-1}\,K^{-1}$)
KNH_2SO_3	490.7	6106	12.45
$NaNH_2SO_3$	541.5	15177	28.03

DSC experiments below the room temperature (130–330 K) performed with the aid of the low-temperature equipment of Perkin–Elmer DSC (cooling fluid liquid nitrogen, dry gas argon) did not show any anomalies.

4. Optical microscopy

Optical observations of the phase transitions in oriented monocrystalline K and Na amidosulfonates slabs in a heating–cooling box of the firm 'Raczek–Linkham,' disposed on a polarizing microscope, were performed. A very good coincidence between the temperatures of polymorphous transformation, determined by microscopy and DSC, was found. After passing the phase transition the transparent monocrystalline $NaNH_2SO_3$ slabs become milky and the formation of a fiber texture was observed. On the contrary to the transition in $NaNH_2SO_3$, the polymorphous transformation in KNH_2SO_3 is coupled with a drastic change of the sample's volume, producing a cracking of the crystal samples and a popcorn-like structure.

Temperature dependent X-ray powder diffraction studies and measurements of dielectric properties are in progress. The preliminary results of these investigations concerning the phase transitions are in agreement with the thermoanalytical effects.

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