Dielectric Spectroscopy of (bis)Thiourea Pyridinium Bromide

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Policrystalline (bis)thiourea pyridinium bromide has been studied with dielectric spectroscopy and DSC method. New information about phase transitions in (bis)thiourea pyridinium bromide has been obtained and discussed. Two solid–solid phase transitions (at $T_2 = 150$ K – first order transition of order–disorder type, and $T_1 = 180$ K – second order) have been revealed. A change of the ion dynamics is observed at T_2.

Key words: Dielectric Spectroscopy; Inclusion Compounds; Thiourea; DSC Calorimetry; Pyridinium Salts.

1. Introduction

Urea and thiourea are known to form many host–guest inclusion compounds with the host lattice forming hexagonal or rhombohedrical channels of hydrogen–bonded urea/thiourea molecules. Usually the guest molecules are polymers and create incommensurate structures (mostly in urea compounds) [1].

Thiourea forms larger channels than urea, so it can accomodate a greater diversity of guest molecules. But the thiourea lattice forms not a simple channel. According to George and Harris, this channel shows periodical changes of the diameter (between about 5.5 and 5.8 Å for urea and between about 5.8 and 7.1 Å for thiourea) [2], and so it can have specific location sites for the guest molecules.

Interesting thiourea inclusion compounds are thiourea pyridinium halides, such as thiourea pyridinium bromide. In this compound the guest molecules are dissociated salts of pyridine. The pyridine molecule is placed in rhombohedral thiourea channels and the bromine anion between these channels (Fig. 1).

It is well known that the pyridine molecule makes 60° reorientational jumps about its pseudohexagonal axis. This motion has been observed and characterized in pyridinium salts such as $PyBF_4$, $PyClO_4$, and others [3]. We presume a similar behavior in the material studied.

The structure of thiourea pyridinium bromide has recently been determined by Prout et al. [4] and earlier by Truter and Vickery [5]. Unfortunatelly they have not determined the temperatures of phase the transitions and their character, but have just indicated the existence of three possible phases.

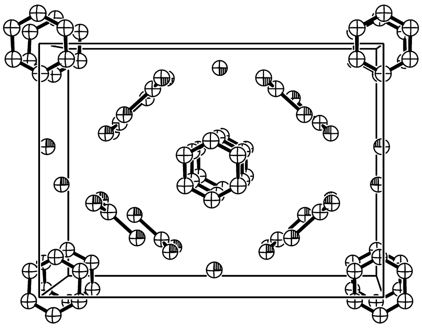

Fig. 1. Unit cell of thiourea pyridinium bromide at room temperature.

In this paper we present results of dielectric spectroscopy and DSC measurement of thiourea pyridinium bromide. The two different motions revealed in this compound are discussed.

2. Experimental

Thiourea pyridinium bromide (abbreviated as TPyBr) was prepared in a few steps. First we obtained pyridinium bromide $[C_5H_6]^+Br^-$ by crystalisation of the stoichiometric mixture of pyridine and bromide acid. The reaction product was mixed with thiourea, and the mixture was dissolved in ethanol. Single crystals were grown by cooling the solution and recrystalisation of the product. The crystals obtained had a needle–like shape. Their length was about 1 – 2 cm.

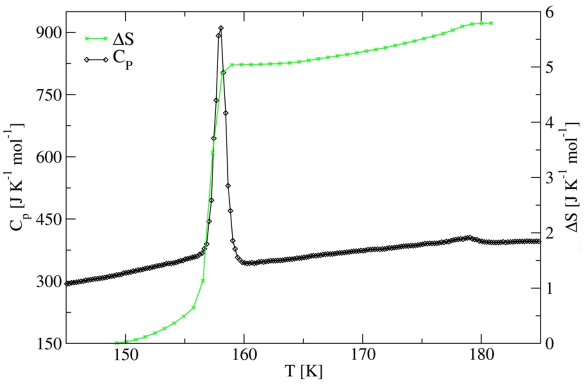

Fig. 2. DSC results of TPyBr.

The dielectric spectroscopy was performed with two computer-controled sets: first with an HP 4192A impedance analyser up to 10 MHz, and second with an HP 4291A up to about 500 MHz. Temperature was measured with a copper-constantan thermocouple and with a special semiconductor diode. The sample was prepared as a policrystalline pellet with silver electrodes. All measurements were made on the same sample. Because of the shape of the monocrystalline sample it was very difficult to perform dielectric measurements with this sample.

3. Results and Discussion

The temperature dependence of the specific heat is presented in Figure 2. It reveals two anomalies related to the phase transitions at $T_1 = 180$ K and $T_2 = 155$ K. The heating and cooling runs show a thermal hysteresis of T_2, whose value is about 8 K. There is no hysteresis of T_1. The phase transition at T_2 is of first order. The lack of the hysteresis at T_1 suggests its continuous character.

To characterise the type of the phase transitions we have calculated the anomalous part of the entropy from the DSC measurements. The base line $C_p^b(T)$ has been obtained by approximating $C_p(T)$ from beyond the phase transitions region. The anomalous part of the entropy was found using the relation

$$\Delta S(T) = \int \frac{C_p(T) - C_p^b(T)}{T} \mathrm{d}T,$$

where C_p^b(T) is the base line.

The total entropy change accompanying the phase transitions indicates a change in the number of inequivalent positions of molecules. According to the results of the structural and NMR investigation [4] the pyridinium cation is strongly disordered in the room temperature phase and has more than one inequivalent position. Knowing the change of the entropy ΔS, the change in the number of inequivalent positions can be estimated from the relation

$$\Delta S(T) = R \ln \frac{N_1}{N_2},$$

where N_1 and N_2 are the numbers of inequivalent positions in the high- and low-temperature phase, and R is the gas constant.

The number N_1 of pyridinium ring positions can in first approximation be equal to the number of nitrogen atoms in the ring. The site symmetry of the pyridinium cation at room temperature is 2/m [4], so the inequivalent positions N_1 of the cation can be $N_1 = 4$ or $N_1 = 2$.

The small entropy decrease at T_1 is consistent with the claim that both the dynamics and N_1 parameter of the cation are practically unchanged at this phase transition. The change of the entropy at T_2 is equal $\Delta S = 5.2$ [J K^{-1} mol^{-1}] which is close to the value $R \ln 2 = 5.7$ [J K^{-1} mol^{-1}], so $\frac{N_1}{N_2}$ is about 2. In the ordered low temperature phase the number of inequivalent positions of the cation $N_1 = 2$ [4], so we conclude that the number of inequivalent positions of the pyridinium cation at the room temperature is $N_1 = 4$.

Results of the dielectric spectroscopy (DS) measurements of the policrystalline sample are shown in Figure 3. These curves provide information about the molecular motion and imply that in the lowest-temperature phase the molecules are ordered and frozen. We can clearly see the evidence of the first phase transition detected at $T_1 = 150$ K, but the second one is practically imperceptible. This transition is observed in the DSC results.

Above T_1, in the real part of the permittivity the dielectric dispersion appears (Fig. 3, left). The temperature dependence of the loss tangent reveals two maxima (Fig. 3, right) above T_1. The presence of the two maxima, as well as the dispersion, implies the existence of relaxation processes. The maxima are frequency dependent and allow a determination of the relaxation time, using the formula $\omega\tau = 1$.

The maxima of the dielectric loss at two temperatures (Fig. 3) indicate the occurrence of two different relaxation processes. Their occurrence suggests that the reorientation of the pyridinium cation is more complex than that in simple pyridinium salts [6–8]. Two relaxation processes can be caused by reorientation of

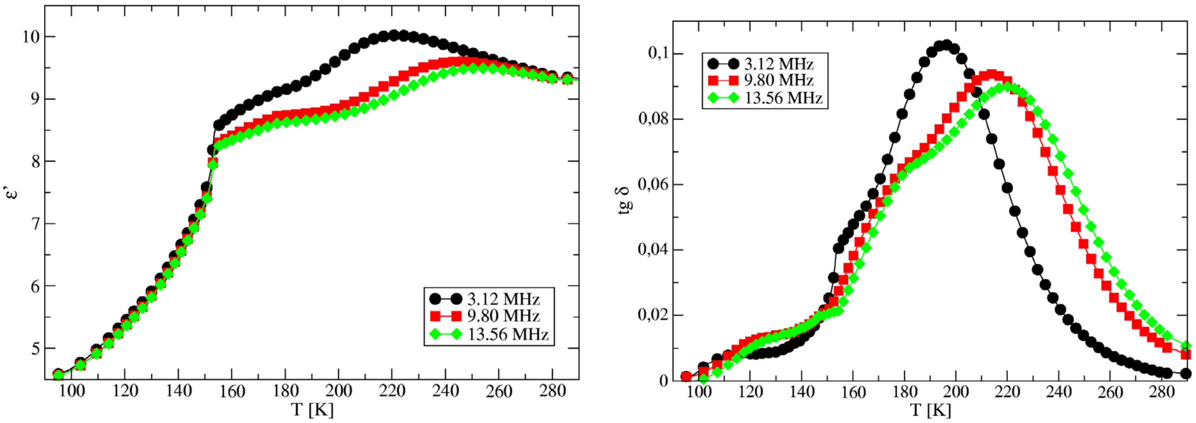

Fig. 3. DS measurement results of TPyBr policrystal.

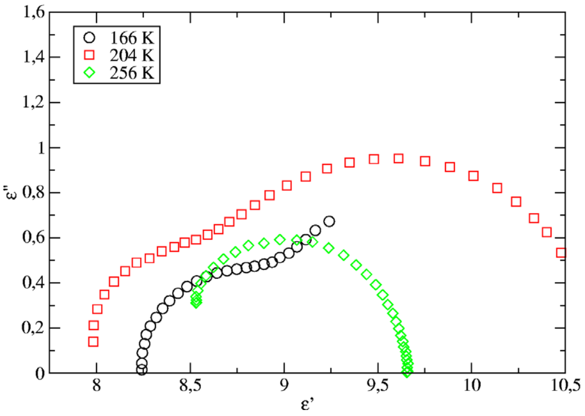

Fig. 4. Cole–Cole plot of TPyBr.

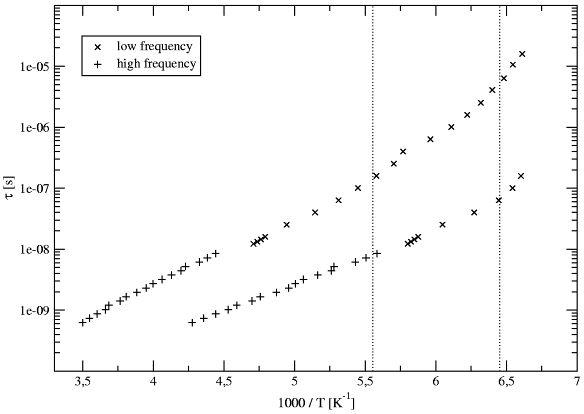

Fig. 5. Temperature dependence of the relaxation time of TPyBr. The dotted–lines show the phase transition temperatures.

the dipole of the pyridinium cations or the dipole of the thiourea host molecules. We suppose that the reorientation of the rigid thiourea host is only possible at higher temperatures [9], so the two processes are caused by reorientation of the pyridinium cation. The site symmetry of the cation allows the existence of two types of inequivalent energy barriers. The activation energy of the two processes is similar, which means that the difference in the two types of energy barriers is small. The existance of the two processes can clearly be seen in the Cole–Cole diagram presented in Figure 4. The relaxation times of these motions are similar (see Fig. 5). The activation energy obtained from the Arrhenius is about 23 kJ mol^{-1} for the first, and about 20 kJ mol^{-1} for the second process. These values are close to those obtained in [3] for the pyridinium cation reorientation. This suggests that mostly the pyridinium cation contributes to the molecular dynamics in the compound.

The host lattice (thiourea channels) is rather inflexible from the DS point of view. It is suggested by many researchers [9, 10] that the thiourea molecule performs specific pendulum–like motions about the C=S axis with an activation energy of about 40 kJ mol^{-1}. These motions have not been detected in our studies despite of the dipole moment in the thiourea molecule along the C=S bond (see [11]).

4. Conclusions

The dielectric permittivity and losses of (bis)thiourea pyridinium bromide imply the occurrence of two phase transitions of first and second–order, respectively. The low-temperature phase is ordered and supposedly ferroelectric, as suggested by the crystallographic data from [4]. The intermediate phase is probably also ferroelectric. In this phase some cations behave like those at room temperature, while most cations behave as those in the low-temperature phase, which makes this phase non-centrosymmetric. However the polarisation is too weak to be detectable by dielectric spectroscopy.

The main contribution to the molecular motions comes from the pyridinium cation: jumps about the pseudohexal axis and another motion, which is probably wobbling of the cation plane or in-plane libration of the molecule (as proposed in [4]). From the dielectric spectroscopy point of view, the host lattice (thiourea molecules) is rather rigid, but this is no evidence for the absence of motion in the host lattice since it can be detected by other measurement techniques [9].

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