Thermal Properties and Ionic Conductivity of Tetra-n-Butylammonium Perchlorate

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Abstract: The thermal parameters of the phase transitions and transport properties of tetra-n-butylammonium (TBA) perchlorate (n-C4H9)4NClO4 (TBAClO4) were investigated. TBAClO4 has a polymorphic transition at 330 K and melts at 487 K. The structure of the high-temperature (HT) phase belongs to cubic symmetry and is similar to the HT phases of TBABF4 and TBAI salts. The conductivity parameters of the low-temperature and HT phases of TBAClO4 were determined from the Arrhenius plots. The thermodynamic parameters and transport properties of TBAClO4 were compared with those of other TBA salts having isostructural HT phases. The polymorphous phase transition entropy was found to correlate with the conductivity of HT phases of TBA salts; TBAClO4 has the lowest conductivity compared to TBABF4 and TBAI salts.

Keywords: tetra-n-butylammonium perchlorate; polymorphous phase transition and melting; high-temperature phase; ionic conductivity

1. Introduction

Organic salts comprise a broad class of solids characterized by a great diversity of physical properties, which can be changed by variation of cations or anions with simple or more complicated structures. Many properties of organic salts, especially in high-temperature (HT) plastic phases, are caused by easy reorientations of organic groups. In particular, diffusion processes and ionic conductivity may be strongly enhanced by the reorientational motion of organic groups in the crystal structure [1–3]. It has been shown that HT phases of substituted ammonium salts with various cations and anions [4–12], piperidinium salts [C3H11]NX (X = ClO4−, PF6−, NO3−) [13,14], substituted pyrrolidinium [1,15,16] and imidazolium [1–3,17] salts, have a high ionic conductivity. Organic tetrabutylammonium (TBA) salts comprise a suitable model system for investigation of correlations between the transport, thermodynamic, and structural properties of plastic phases as a function of the anion size and shape. Unlike tetra-alkyl-ammonium salts with short aliphatic radicals, TBA salts have relatively low melting temperatures; they are stable in the molten state, being a typical ionic liquid, not hygroscopic, and may be easily compacted giving dense transparent pellets. As for the practical applications of these materials, molten quaternary ammonium salts are typical ionic liquids with a wide electrochemical window. In solid state, these salts are also expected to have good electrochemical stability and may be used as basic substances for preparation of solid electrolytes. To find appropriate ionic conductors, one should investigate the influence of the salts’ composition and basic physical properties on their conductivity. A relatively high ionic conductivity was earlier observed in HT phases of TBA salts (n-C4H9)4NI [11,18], (n-C4H9)4NBr [19], and (n-C4H9)4NBF4 [20,21]. Despite extensive research on the plastic phases of ionic salts, the correlation between the chemical structure and transport properties is still not completely understood, and the mechanism of
ionic conductivity in these salts remains obscure. HT phases of these salts are disordered, and thermodynamic properties of these phases should be related to the ionic conductivity. In particular, the melting entropy of such salts is comparable with the entropy change due to the phase transition to the high-temperature plastic phases. It would be of interest to find interrelations between the thermodynamic and transport properties of TBA salts.

In the present work, the thermodynamic and transport properties of tetra-n-butylammonium perchlorate (TBAClO₄), a typical representative of TBA salts, were studied by methods of X-ray diffraction, differential scanning calorimetry, dilatometry, and impedance spectroscopy. As shown below, the HT phase of this compound has a structure similar to TBAI and TBABF₄ salts. Therefore, comparative analysis of the properties of TBA salts with different anions enables elucidating the relations between the thermodynamic and transport properties in a series of TBA salts.

2. Materials and Methods

Before investigation, the commercial product (n-C₄H₉)₄NClO₄ (Merck CAS Number 1923-70-2, 99% pure) was purified by recrystallization several times in pure ethanol. The obtained TBA powder consisted of crystallites 2–6 mm in size. The heat effects associated with the polymorphous phase transition and melting were studied using a Netzsch DSC-200 F3 Maia Calorimeter with Al pans in an argon atmosphere. X-ray diffraction studies were carried out with a Bruker D8 Advance Diffractometer on CuKα radiation. Topas 4.2 software was applied to determine the symmetry of the crystal lattice and a full-profile analysis of the diffraction patterns. Dilatometric measurements were carried out on a Netzsch DIL402 C/7/1 Dilatometer on dense TBAClO₄ pellets (5 mm in thickness and 5 mm in diameter) compacted at 500 MPa. The powder can be easily compacted to transparent pellets with a density of 1.04 g/cm³, which seems to be close to theoretical density of the substance. The conductivity was measured on pellets obtained at a pressure of 500 MPa with Ni powder electrodes. The conductivity was measured in a vacuum of 2–4 Pa in the temperature range of 303–423 K in the isotherm stepwise mode with a step of 5 K and the exposure time of 15 min at each temperature before measurements. An E7-25 Immittance Analyzer, MNIPi Co., was used for measurements in the ac- frequency range of 25 Hz to 1 MHz. The values of conductivity were calculated at each temperature by the relation $\sigma = \frac{d}{S \cdot R^{-1}}$, where $d$ and $S$ are the pellet thickness and electrode, respectively, and $R$ is the sample resistance determined from the analysis of $Z'' = f (Z')$ impedance plots.

3. Results and Discussion

According to the data reported earlier [22], the decomposition temperatures of tetra-n-butylammonium salts exceed 300 °C. In the present work, all experiments were carried out at temperatures below 240 °C to avoid decomposition. The results of the thermal analysis are displayed in Figure 1.

Two peaks were seen on the differential thermal analysis (DTA) curve corresponding to the polymorphous transition at $T_t = 330$ K and melting at $T_m = 487$ K. The values of the phase transition enthalpy and the melting enthalpy, 2.90 and 13.4 kJ/mol, respectively, were determined by integration of the peaks. The dilatometric curve obtained for the compacted pellet is shown in Figure 1. An abrupt change on the curve was attributed to a polymorph transition, which was accompanied by a slight volume increase of nearly 2%. The volume thermal expansion coefficient (TEC) value for the low-temperature (LT) phase of TBAClO₄ determined from the dilatometric data was roughly estimated as 270–570 $\cdot 10^{-6}$ K$^{-1}$. This value exceeded typical TEC values for organic compounds, 80–240 $\cdot 10^{-6}$ K$^{-1}$ [23]. However, accurate determination of both TEC and volume change at the phase transition was not possible due to the plastic flow of the substance leading to a systematic irreversible deformation of the pellet at elevated temperatures.
X-ray diffraction patterns of low-temperature (LT) and high-temperature (HT) phases of TBAClO\(_4\) are presented in Figure 2. The LT phase stable at room temperature had an unknown structure. The peak positions were fitted using the Pawley method for several variants of the space group of the crystal lattice. The best fit was obtained for the space group P2\(/c\) with the lattice parameters of a = 10.539 Å, b = 12.397 Å, c = 18.270 Å, and β = 88.9°. However, a more precise refinement of powder diffraction pattern could be carried out using atomic coordinates. This problem could be solved using the diffraction study on a TBAClO\(_4\) single crystal. Such work is in progress now. The powder X-ray diffraction pattern of the HT phase is shown in Figure 2. The full-profile analysis using a Pawley method showed that the HT phase had a structure with a cubic elementary lattice belonging to the symmetry space group P4\(_3\)3\(n\) with the lattice parameter of a = 14.866 Å at 353 K. A similar structure was observed earlier for the HT phases of TBAI [11,18] and TBABF\(_4\) [20,22]. The Pawley method may be regarded as an initial approach for further full-profile refinement by the Rietveld method, which requires information on atom coordinates. In the literature, there was only one paper [22] where the structures of the HT phases of (C\(_4\)H\(_9\))\(_4\)NBF\(_4\) (TBABF\(_4\)) and (C\(_4\)H\(_9\))\(_4\)PBF\(_4\) salts (both are isostructural to the HT phase of TBAClO\(_4\)) were analyzed. The authors proposed only the coordinates of the centers of cations and anions. The location of the relatively long alkyl-radicals of cations and fluorine atoms of BF\(_4^–\) anions remained undetermined due to the reorientational disordering of cations and anions. Therefore, HT polymorphs of TBA salts may be regarded as plastic phases with the orientational disorder in the cationic sublattice.

Impedance plots and Arrhenius dependences for the conductivity of TBAClO\(_4\) are presented in Figure 3. The equivalent circuit including the bulk resistance (R), the constant phase element (CPE), and the capacitance (C), connected in parallel, and the Warburg impedance (W) connected in series, was used for the data description. It was shown that at high temperatures, an electrode polarization, W, makes an appreciable contribution to the total impedance of the sample. It is a clear indication of the ionic character of the conductivity of TBAClO\(_4\). As the data obtained on heating and cooling were close, no irreversible processes took place during the experiment, and the conductivity related to the equilibrium state of the salt.
Figure 2. X-ray powder diffraction patterns of the LT and HT phases of TBAClO$_4$ recorded at 298 K and 353 K, lower and upper plots, respectively. The fitting curves and residual plots are also shown.

Figure 3. (a) Impedance plots obtained at different temperatures and the equivalent circuit used for the data fitting; points are experimental data and lines are fitting curves; (b) Arrhenius dependence of conductivity for TBAClO$_4$ sample.

According to the results of electrical measurements, there were two temperature regions corresponding to the LT and HT phases of TBAClO$_4$. In both the LT and HT regions the conductivity ($\sigma$) obeyed Arrhenius dependence $\sigma = (A/T) \cdot \exp(-E_a/kT)$, where $A$ is the pre-exponential factor, and $E_a$ is the activation energy. The conductivity parameters for both phases are listed in Table 1. At the temperature of phase transition, there was a slight conductivity change of 1.5 times.

Available data concerning the mechanism of the ionic conductivity of TBA salts are contradictory. The authors of paper [11] proposed that conductivity of TBAI is caused by the plastic domains in the cationic sublattice. In our previous papers [18–20], we proposed...
that the dominant charge carriers in isostructural HT phases of TBA salts were anions. The particular type of the defects (Schottky or Frenkel) responsible for ionic transport is yet to be elucidated. To solve this problem, doping of the salts with heterovalent impurities and theoretical estimations should be conducted. This work is planned for the future.

The thermodynamic parameters of the phase transition, melting, and transport properties of TBA salts (which have high-temperature phases with similar cubic elementary cells) are presented in Table 1. The theoretical values of the melting entropy, $S_m^*$ for organic compounds may be roughly estimated using the semiempirical equation of Dannenfalser and Yalkowsky [24]:

$$S_m^* = C - R \ln \sigma + R \ln \Phi$$

(1)

where $C = 50 \text{ J mol}^{-1} \text{ K}^{-1}$, $\sigma$ is the rotational symmetry number and $\Phi$ is the flexibility number [25]. Equation (1) is applicable to a wide range of organic compounds and takes into account contributions of positional, rotational, and conformational components in the total entropy of melting. These data may be used as reference values for a qualitative comparison. Taking $\sigma = 12$ (for tetrahedral cations) and $\Phi = 2.345n^{-1}$ ($n = 12$ is the number of nonterminal groups in $\text{(C}_4\text{H}_9)_4\text{N}^+$ cations), one can find that $S_m^* = 13.3R$. This value is considerably higher than the experimentally observed melting entropy of $\text{TBAClO}_4$ $S_m = 3.31R$. The difference may be explained by a strong disordering of the $\text{TBAClO}_4$ crystal lattice in the high-temperature phase. The melting ability values of TBA salts are close to a limiting Timmermanns value $S_m < 2.5R$ for plastic phases [26]. This means that the HT phases of TBA salts are strongly disordered and may be regarded as plastic phases.

Table 1. The thermodynamic parameters of phase transitions and conductivity data for TBA salts having isostructural HT phases.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$T_t$, K</th>
<th>$S_t/R$</th>
<th>$T_m$, K</th>
<th>$S_m/R$</th>
<th>$\log (A, \text{ S K/cm})$</th>
<th>$E_a$, eV at 373 K, S/cm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TBAClO}_4$</td>
<td>330</td>
<td>1.04 ± 0.03</td>
<td>487</td>
<td>3.31 ± 0.03</td>
<td>7.22 ± 0.04 *</td>
<td>0.98 ± 0.02 *</td>
<td>4 × 10^{-5}</td>
</tr>
<tr>
<td>$\text{TBABF}_4$</td>
<td>335</td>
<td>2.27</td>
<td>434</td>
<td>2.65</td>
<td>6.42 ± 0.02 **</td>
<td>0.91 ± 0.01 **</td>
<td>6 × 10^{-8}</td>
</tr>
<tr>
<td>341</td>
<td>2.37</td>
<td>439</td>
<td>2.92</td>
<td>8.47 ± 0.03 **</td>
<td>0.96 ± 0.03 **</td>
<td>6 × 10^{-8}</td>
<td>[27]</td>
</tr>
<tr>
<td>335</td>
<td>2.84</td>
<td>429</td>
<td>3.39</td>
<td></td>
<td></td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>$\text{TBAI}$</td>
<td>389</td>
<td>8.75</td>
<td>418</td>
<td>2.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>392</td>
<td>8.60</td>
<td>419</td>
<td>2.76</td>
<td></td>
<td></td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>392</td>
<td>8.60</td>
<td>418</td>
<td>2.62</td>
<td></td>
<td></td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>394</td>
<td>8.56</td>
<td>421</td>
<td>2.56</td>
<td></td>
<td></td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>392</td>
<td>8.39</td>
<td>419</td>
<td>2.58</td>
<td></td>
<td></td>
<td></td>
<td>[31]</td>
</tr>
</tbody>
</table>

* LT phase; ** HT phase.

From the comparison of the thermodynamic data for TBA salts presented in Table 1, it is seen that there was no appreciable decrease in the melting entropy in a series $\text{TBAClO}_4$-$\text{TBABF}_4$-$\text{TBAI}$. In contrast to the melting entropy, the phase transition entropy ($S_t$) changes were much stronger in the same series of the salts. As seen from Figure 4, there was a clear correlation between $S_t$ and ionic conductivity. This suggests that the phase transition entropy may be used as a good indicator of the disordering of the crystal lattice at the phase transition, which, in turn, causes change in the transport properties. The conductivity of the HT phase increased with the diminishing of the anionic radius in a series of $\text{TBAClO}_4$-$\text{TBABF}_4$-$\text{TBAI}$ This tendency may be explained assuming that anions are dominant charge carriers, and the ionic migration is limited by steric factors.
The correlations between the thermodynamic parameters of the phase transitions and the ionic conductivity are known for inorganic salts [32–34]. For instance, there is a correlation between the Schottky defect formation, the activation energy for conductivity, and the melting enthalpy in alkali halides [34]. The disordering of the crystal lattice at the phase transition has a great influence on ionic transport. In particular, the phase transition to the HT superionic phases may be regarded as a melting of one sublattice in the crystal and is accompanied by a strong increase in the conductivity [32,33]. In the present study, a similar correlation was shown to hold in organic TBA salts for a phase transition to the plastic phase.

4. Conclusions

The physical properties of solid organic salt TBAClO$_4$ were investigated by the methods of X-ray diffraction, thermal analysis, dilatometry, and conductivity measurements. It was found that two phase transitions took place in TBAClO$_4$: a polymorphous transition at 330 K and melting at 487 K. The structure of the HT phase belonged to cubic symmetry and was similar to the HT phases of TBABF$_4$ and TBAI salts. The conductivity parameters were determined from the Arrhenius plots obtained for the LT and HT phases. The thermodynamic parameters and transport properties of TBAClO$_4$ were compared with salts TBAI and TBABF$_4$ having isostructural HT phases. It was found that there was a correlation between the polymorphous phase transition entropy $S_t$ and the ionic conductivity, $s$, of the HT phases of TBA salts.

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References


