STUDIES ON THE SYNTHESIS AND CHARACTERISATION OF ZINC ALKYL XANTHATES

3.1 INTRODUCTION

Xanthates are one of the important organosulphur compounds used in mining and rubber industry. They are derivative of xanthic acid. They are also known as xanthogenates, carbon dithioates and salts of xanthic (dithiocarbonic) acids. They have the general structure

\[
\left[ \begin{array}{c}
\text{R} \quad \text{O} \\
\text{S} \\
\text{M}^{n+}
\end{array} \right]_n 
\]

\( R = \text{alkyl group and } M^{n+} = \text{Na}^+, \text{K}^+, \text{Zn}^{2+} \)

Xanthates have a heteropolar molecular structure with a nonpolar hydrocarbon group and a polar sulphide group.

They are prepared by reacting an alcohol with CS\(_2\) and an alkali such as sodium hydroxide (NaOH) or KOH. The alcohols employed are not unique.\(^{246-250}\) The commonly used alcohols are methyl, ethyl, propyl (normal propyl, isopropyl), butyl (normal, isobutyl, secondary butyl) and amyl (normal amyl, isoamyl, secondary amyl) alcohols.

Xanthates were first discovered by Zeise in 1822.\(^{251}\) Xanthates were primarily used in mining industry for the extraction of minerals from the ores till the 20\(^{th}\) century. They are used in the mining industry as flotation agent in the recovery of metal sulphides. They were mainly used in the flotation of bases and precious metals, which is the standard method for separating valuable metals, such as gold, copper, lead. Also, they are used for separating zinc minerals (often referred to as “values”), from non-valuable minerals, such as lime stone or quartz.\(^{252-257}\) To extract values, conditioned ores are mixed in a solution of water and xanthates and then agitated in flotation cells. Xanthates may be added
in liquid or solid form. The xanthates cause the minerals to attach themselves to air bubbles and then float to the top of the flotation cell. As values reach the surface, the bubbles form a froth that overflows into a trough for collection. The residual may be reused for additional recovery or removed for disposal. Most of the xanthate is consumed in the process.

Different xanthates have different strengths. The strength of xanthate as a collector is based on the alcohol chain attached to the xanthate molecule with ethyl being the weakest and amyl being the strongest. Potassium ethyl xanthate is very selective in nature and cost effective. But potassium N-amyl xanthate is a non selective collector and used to produce high-grade concentrates or to promote the flotation of difficult-to-float minerals.

Long-chain alkyl xanthates are used for the capping of silver, copper and gold nano colloids. Unlike non-capped and oleate-capped colloids they are temperature sensitive, as a result of the thermal decomposition of the xanthate molecule itself and can be applied as thermally decomposable colloids.258-260 Xanthates are also used as defoliants, herbicides, insecticides and fungicides in agricultural production and as high-pressure lubricant additives.

Xanthates are also used for the production of transparent cellulose film, cellophane and related polymers.261,262 They are also versatile intermediates in organic synthesis. Xanthates are intermediates in the Chugaev elimination, which is the pyrolysis of xanthate to give an alkene. The most commonly used xanthate in Chugaev elimination is methyl xanthate.263,264 Xanthates are also used to control radical polymerization under the Reversible Addition-Fragmentation chain Transfer (RAFT) process, also termed Macromolecular design via the interchange of xanthates (MADIX).265-272

Other possible applications of xanthates include as chemical sensitizer for photographic film, synthetic precursors for the generation of metal sulphide nanoparticles, as therapeutic agent, as inhibitor for fertilizer nitrogen transformation and colour development for image recording materials.
Xanthates are also used in a froth flotation process of soils contaminated with mercury. The soil to be treated is run through hydrocyclones, and the slurries are flocculated, dewatered and removed to a secure landfill. The effluent water is recycled. The process is suitable for treating industrial land sites contaminated with mercury droplets. Xanthates have been used widely as reagents for the separation and quantitative determination of a large number of cations. The trifluoro ethyl xanthate has been used as a reagent for the analytical determination of gold.\textsuperscript{273,274}

The role of xanthates in the vulcanization of rubber as an ultrafast accelerator has been under study by researchers for quite some time. The activity of xanthates is so high that they can bring about vulcanization even at room temperature.\textsuperscript{275} Xanthates prepared as their sodium and potassium salts are water soluble and are used in latex compounds, while their zinc salts being water insoluble are used in dry rubber compounds.\textsuperscript{276} Although xanthates are known to act as accelerators for low temperature vulcanization, a systematic study on the mechanism of vulcanization, the mechanical properties of the vulcanisates at varying temperatures of vulcanization, cure characteristics etc. are not reported until 2000. At present, xanthates were known to be effective for the low temperature vulcanization of dry NR and NBR compounds.\textsuperscript{277-285} Xanthates in combination with another ultrafast accelerator such as dithiocarbamate can be used for the fast curing of rubber compounds. Zinc alkyl xanthate/ZDC accelerator combination has a positive synergistic effect on the mechanical properties of carbon black filled NR compounds. This accelerator system can also be used for the curing of short isora fiber reinforced natural rubber compounds. \textbf{The work presented in this thesis is about the use of xanthate accelerator in combination with ZDC for low temperature prevulcanisation of NRL.}

This chapter includes two parts. The first part describes the preparation and characterization of zinc isopropyl xanthate and zinc butyl xanthate. The second part deals with the optimization of preparation method of Zn(bxt)\textsubscript{2}. 

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Part I

3.2 SYNTHESIS AND CHARACTERISATION OF ZINC ALKYL XANTHATES

This part describes the synthesis and characterization of Zn(ipxt)₂ and Zn(bxt)₂.

EXPERIMENTAL

- **Materials**

  Isopropyl alcohol, n-butyl alcohol (n-BuOH), KOH, CS₂ and ZnCl₂ (supplied by E.Merck Ltd, Mumbai, India) used for the preparation of Zn(ipxt)₂ and Zn(bxt)₂ were analytical grade.

- **Instruments**

  The Instruments used in this study include Thermo Nicolet Avatar 370 FTIR Spectrometer using KBr pellet technique in the wave length range 400-4000 cm⁻¹, Bruker-Avance III 400 MHz Spectrometer and Perkin Elmer Diamond TG/DTA.

- **Experimental Procedure**

  Zn(ipxt)₂ and Zn(bxt)₂ were prepared by reacting equimolar amounts of corresponding alcohols (isopropyl alcohol and n-butyl alcohol) with CS₂, KOH and ZnCl₂. The prepared xanthates were characterized using FTIR, ¹H-NMR, TGA and DTA techniques.

  The FTIR spectra of xanthates were recorded using Thermo Nicolet Avatar 370 FTIR spectrometer using KBr pellet technique in the wave length range 400-4000 cm⁻¹. The results are reported in Figures 3.1 and 3.2. The ¹H-NMR spectra of Zn(ipxt)₂ and Zn(bxt)₂ was recorded from a solution of CDCl₃ containing tetra methyl silane as an internal standard using Bruker-Avance III 400 MHz Spectrometer. The results are reported in Figures 3.3 and 3.4.
The TGA was carried out in the temperature range of 30°C to 1000°C at a heating rate of 10°C per minute in an atmosphere of nitrogen using Perkin Elmer Diamond TG/DTA. Sample weight is between 5-10 mg. The TGA curves are given in Figures 3.5 and 3.6. DTA curves show parallel peaks corresponding to weight losses in the TGA curves and Figures 3.7 and 3.8 represent the DTA curves of Zn(ipx)2 and Zn(btx)2 respectively.

RESULTS AND DISCUSSION

3.2.1 Synthesis

The preparation of Zn(ipx)2 and Zn(btx)2 takes place according to the following equations.

\[
\text{CH}_2\text{OH} + \text{KOH} + \text{CS}_2 \rightarrow \text{CH}_2\text{OCS}_2\text{S-K}
\]

Isopropyl alcohol

Potassium isopropyl xanthate (water soluble)

\[
\text{CH}_2\text{OH} + \text{KOH} + \text{CS}_2 \rightarrow \text{CH}_2\text{OCS}_2\text{S-S-Zn}
\]

Zinc isopropyl xanthate (water insoluble)

\[
\text{CH}_2\text{OH} + \text{KOH} + \text{CS}_2 \rightarrow \text{CH}_2\text{OCS}_2\text{S-K}
\]

Potassium butyl xanthate (water soluble)

\[
\text{CH}_2\text{OCS}_2\text{S-S-Zn}
\]

Zinc butyl xanthate (water insoluble)

The molecular formula, molecular weight, reaction temperature, reaction time and yield of xanthates were reported in Table 3.1.
Table 3.1: Reaction temperature, reaction time and yield of zinc alkyl xanthates

<table>
<thead>
<tr>
<th>Xanthates</th>
<th>Molecular Formula</th>
<th>Molecular Weight(g)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (Minutes)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(ipxt)₂</td>
<td>C₈H₁₄O₂S₄Zn</td>
<td>336.153</td>
<td>300°C</td>
<td>150</td>
<td>20.2</td>
</tr>
<tr>
<td>Zn(bxt)₂</td>
<td>C₁₀H₁₈O₂S₄Zn</td>
<td>364.206</td>
<td>300°C</td>
<td>27</td>
<td>29.9</td>
</tr>
</tbody>
</table>

3.2.2 Characterisation

3.2.2.1 FTIR Spectroscopy

Figure 3.1 shows the FTIR spectrum of Zn(ipxt)₂. The peaks at 2978.00 cm⁻¹ and 2868.10 cm⁻¹ correspond to asymmetric and symmetric stretching of C-H bond in terminal CH₃ group, 2931.40 cm⁻¹ corresponds to aliphatic C-H stretching. The C-H bending vibration of the CH₃ group gives a band around 1370 cm⁻¹. This band is split into a doublet at 1385.73 cm⁻¹ and 1372.01 cm⁻¹ which indicate the presence of more than one methyl group on the same carbon atom. The peaks at 1233.09 cm⁻¹ and 1032.07 cm⁻¹ corresponds to asymmetric and symmetric C-O-C stretching vibrations. The peaks at 1144.06 cm⁻¹ and 650.95 cm⁻¹ correspond to –C=S and –C-S stretching vibrations.
Figure 3.1: FTIR spectrum of Zn(ipxt)₂

Figure 3.2 shows the FTIR spectrum of Zn(bxt)₂. The peak at 2952.48 cm⁻¹ and 2867.40 cm⁻¹ correspond to asymmetric and symmetric stretching of C-H bond in terminal CH₃ group, the peaks at 1463.18 cm⁻¹ and 1371.30 cm⁻¹ correspond to asymmetric and symmetric deformation of C-H bond in terminal CH₃ group. The peak at 2929.40 cm⁻¹ corresponds to asymmetric C-H stretching in -CH₂ groups. The peaks at 1205.83 cm⁻¹ and 1042.60 cm⁻¹ correspond to asymmetric and symmetric C-O-C stretching vibrations. The peaks at 1130.94 cm⁻¹ and 662.66 cm⁻¹ correspond to -C=S and -C-S stretching vibrations.

Figure 3.2: FTIR spectrum of Zn(bxt)₂
3.2.2.2 $^1$H-NMR Spectroscopy

Figure 3.3 shows the $^1$H-NMR spectrum of Zn(ipxt)$_2$. There is a six proton doublet at $\delta = 1.2$, and a one proton septet at $\delta = 5.5$ ppm showing the presence of the following isopropyl group in Zn(ipxt)$_2$.

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{CH} \\
\end{array}
\]

**Figure 3.3: $^1$H-NMR spectrum of Zn(ipxt)$_2$**

Hence the structure of Zn(ipxt)$_2$ is

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH-O-S-Zn-S-O-CH}_3 \\
\text{H}_3\text{C} \\
\end{array}
\]

Figure 3.4 shows the $^1$H-NMR spectrum of Zn(bxt)$_2$. There is a three proton triplet at $\delta = 0.9$, a two proton sextet at $\delta = 1.8$, a two proton pentet at $\delta = 1.5$ and a two proton triplet at $\delta = 4.5$ showing the presence of CH$_3$-CH$_2$-CH$_2$-CH$_2$ group in Zn(bxt)$_2$.
So the structure of Zn(bxt)$_2$ is

\[
\text{H}_3\text{C}--\text{CH}_2--\text{CH}_2--\text{CH}_2--\overset{\text{S}}{\text{O}}--\overset{\text{S}}{\text{C}}--\text{Zn}--\overset{\text{S}}{\text{C}}--\overset{\text{S}}{\text{O}}--\text{CH}_2--\text{CH}_2--\text{CH}_2--\text{CH}_3
\]

### 3.2.2.3 Thermal Decomposition Study Using TGA/DTA Techniques

From the TGA curve of Zn(ipxt)$_2$ given in Figure 3.5 it is clear that the first stage of decomposition begins at 123.23°C. The net weight loss of 75.69% corresponds to decomposition of Zn(ipxt)$_2$ to the corresponding dixanthogen [(CH$_3$)$_2$CHOCS$_2$]$_2$ which is stable upto 550°C. The second stage of decomposition sets in the sample at about 550°C. The net weight loss is about 50% which corresponds to the decomposition of Zn(ipxt)$_2$ to ZnSO$_4$. 
From the TGA curve of Zn(bxt)$_2$ given in Figure 3.6 it is clear that the first stage of decomposition begins at 130$^\circ$C and terminates at 160$^\circ$C. The net weight loss of 44.45% corresponds to decomposition of Zn(bxt)$_2$ into ZnSO$_4$ which is stable up to 270$^\circ$C. The second stage of decomposition sets in the sample at about 270$^\circ$C and is completed at 350$^\circ$C. The net weight loss is 40.03%, resulting in the formation of ZnSO$_3$. 

Figure 3.5: TGA curve of Zn(ipxt)$_2$

Figure 3.6: TGA curve of Zn(bxt)$_2$
Figure 3.7 illustrates the DTA curves recorded for 4.894 mg of 
Zn(ipxt)₂ sample. The curve shows two endothermic peaks at about 125°C and 
550°C corresponding to the thermal decomposition of Zn(ipxt)₂ to the 
corresponding dixanthogen and ZnSO₄ respectively.

![Figure 3.7: DTA curve of Zn(ipxt)₂](image)

Figure 3.8 illustrates DTA curves recorded for 5.257 mg of Zn(bxt)₂ 
powder. The curve shows an endothermic peak at 130°C corresponding to the 
decomposition of Zn(bxt)₂ to ZnSO₄. Thermal decomposition reactions are 
usually endothermic. Here, one of the DTA peaks is exothermic. This is due to 
the concomitant oxidation reaction taking place along with decomposition.

Figure 3.8: DTA curves recorded for 5.257 mg of Zn(bxt)₂ powder. The curve shows an endothermic peak at 130°C corresponding to the decomposition of Zn(bxt)₂ to ZnSO₄. Thermal decomposition reactions are usually endothermic. Here, one of the DTA peaks is exothermic. This is due to the concomitant oxidation reaction taking place along with decomposition.
Figure 3.8: DTA curve of Zn(bxt)$_2$

Reaction time required is less for Zn(bxt)$_2$ compared to Zn(ipxt)$_2$. Also, high yield is obtained for Zn(bxt)$_2$ and hence it is selected for further studies.

Part II

3.3 OPTIMISATION OF PREPARATION METHOD OF ZINC BUTYL XANTHATE

This part describes the optimization of preparation method of Zn(bxt)$_2$.

EXPERIMENTAL

- Materials

  Both A.R. and commercial grade KOH, n-BuOH, CS$_2$ and ZnCl$_2$ were used for the preparation of Zn(bxt)$_2$. 

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- **Instruments**

The Instruments used in this study include Thermo Nicolet Avatar 370 FTIR Spectrometer using KBr pellet technique in the wave length range 400-4000 cm$^{-1}$.

- **Experimental Procedure**

Zn(bxt)$_2$ was prepared by mixing equimolar amounts of A.R grades of n-BuOH, KOH, CS$_2$ and ZnCl$_2$. The product is named as S$_1$. Colour, smell, reaction time and yield of the product were noted and reported in Table 3.4.

Zn(bxt)$_2$ was also prepared using commercial grade reagents as per the above mentioned procedure. To study the effect of order of mixing the reactants on reaction time, six combinations were taken as given in Table 3.2. The reaction time and yield of the xanthate prepared are given in Table 3.5.

**Table 3.2**: Different order of mixing of reactants for the preparation of Zn(bxt)$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Order of mixing of reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_2$</td>
<td>BuOH+CS$_2$+KOH + ZnCl$_2$</td>
</tr>
<tr>
<td>S$_3$</td>
<td>BuOH+ KOH+CS$_2$+ ZnCl$_2$</td>
</tr>
<tr>
<td>S$_4$</td>
<td>CS$_2$+ BuOH+ KOH + ZnCl$_2$</td>
</tr>
<tr>
<td>S$_5$</td>
<td>CS$_2$+ KOH+ BuOH + ZnCl$_2$</td>
</tr>
<tr>
<td>S$_6$</td>
<td>KOH+CS$_2$+ BuOH + ZnCl$_2$</td>
</tr>
<tr>
<td>S$_7$</td>
<td>KOH+ BuOH+CS$_2$+ ZnCl$_2$</td>
</tr>
</tbody>
</table>

To study the effect of stirring time on the yield of Zn(bxt)$_2$ produced, S$_3$ was prepared under different stirring time and the results are reported in Table 3.6. Effect of the amount of ZnCl$_2$ used for precipitation on the yield of the
product was studied by varying the amount of ZnCl₂ as given in Table 3.3 and the results are reported in Table 3.7.

**Table 3.3:** Variation in the amount of ZnCl₂ used for the precipitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reactants taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₈</td>
<td>BuOH+ KOH+CS₂ + 136g ZnCl₂</td>
</tr>
<tr>
<td>S₉</td>
<td>BuOH+ KOH+CS₂ + 120g ZnCl₂</td>
</tr>
<tr>
<td>S₁₀</td>
<td>BuOH+ KOH+CS₂ + 108g ZnCl₂</td>
</tr>
<tr>
<td>S₁₁</td>
<td>BuOH+ KOH+CS₂ + 96g ZnCl₂</td>
</tr>
</tbody>
</table>

In all the above preparations, the reaction mixture was stirred using a magnetic stirrer rotating at a speed of 500 rpm. Zn(bxt)₂ (S₈) was also prepared using a mechanical stirrer rotating at a speed of 3000 rpm and the product is named S₁₂. The reaction time and yield of S₁₂ are given in Table 3.8 and are compared with that of S₈ prepared using a magnetic stirrer. Preparation of Zn(bxt)₂ was also done at 0°C. The FTIR of spectrum S₁₂ was recorded (Figure 3.9) and compared with that of S₁ (Figure 3.2).

### 3.4 Cytotoxicity Study

There are many biocompatibility tests utilized by industry, government and academia. Among the most sensitive biocompatibility tests, the cytotoxicity tests are important. One of the most common tests in this area is the *in vitro* cytotoxicity test. The testing presented in this chapter was conducted in the tissue culture laboratory at Sree Chitra Tirunal Institute for Medical Sciences and Technology, Biomedical Technology wing, Thiruvananthapuram.

An *in vitro* cytotoxicity test using Test on Extract method was performed with test sample based on ISO 10993-5, 1999. Extract was prepared
by incubating test material with culture medium (MEM supplemented with Foetal Bovine Serum) containing serum at 37 ± 2°C for 24 – 26 hours at an extraction ratio of 0.1 g/mL. 100 % extracts were diluted to get concentrations of 50% and 25% with media. Ultra High Molecular Weight Polyethylene is used as the negative control and dilute phenol is used as the positive control. Different dilutions of extracts of test sample, negative control and positive control in triplicate were placed on subconfluent monolayer of L-929 cells (L-929 is an established and well characterized mammalian cell line that has demonstrated reproducible results). After incubation of cells with extracts of test sample and controls at 37 ± 2°C for 24 ± 2h, cell culture was examined microscopically for cellular response. Cellular responses were scored as 0, 1, 2, 3 and 4 according to none, slight, mild, moderate and severe. Extracts of negative control gave no cytotoxic response and positive control gave severe cytotoxic responses as expected. Table 3.9 shows cytotoxicity test results.

RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Table 3.4: Reaction time and yield of Zn(bxt)₂ produced using A.R grade reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>S₁</td>
</tr>
</tbody>
</table>

Table 3.4 shows the reaction time, yield, colour and smell of S₁. Sample S₁ prepared using A.R grade reagents has a foul and irritating smell. When commercial grade KOH, n-BuOH, CS₂ and ZnCl₂ were used for the preparation, the irritating smell of Zn(bxt)₂ was reduced considerably. So commercial grade reagents were used for further studies. The yield of S₁ was also low and the reaction time was high compared to Zn(bxt)₂ prepared using commercial grade reagents.
Table 3.5 shows the effect of order of mixing the reactants on reaction time and yield of Zn(bxt)$_2$ produced using commercial grade reagents. S$_3$ has maximum yield and we have selected this order of mixing of reactants for further studies.

**Table 3.5: Effect of order of mixing of reactants on reaction time and yield of Zn(bxt)$_2$**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (Minutes)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_2$</td>
<td>20</td>
<td>32.9</td>
</tr>
<tr>
<td>S$_3$</td>
<td>20</td>
<td>55.9</td>
</tr>
<tr>
<td>S$_4$</td>
<td>25</td>
<td>42.4</td>
</tr>
<tr>
<td>S$_5$</td>
<td>21</td>
<td>42.9</td>
</tr>
<tr>
<td>S$_6$</td>
<td>25</td>
<td>33.6</td>
</tr>
<tr>
<td>S$_7$</td>
<td>20</td>
<td>35.2</td>
</tr>
</tbody>
</table>

Table 3.6 shows the effect of stirring time on yield of Zn(bxt)$_2$ prepared. From the Table 3.6 it is clear that maximum yield is obtained when reaction time is 20 minutes and increasing the stirring time has no profound effect on the yield of the product.
Table 3.6: Effect of stirring time on yield of Zn(bxt)$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (Minutes)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_3$</td>
<td>20</td>
<td>55.9</td>
</tr>
<tr>
<td>S$_3$</td>
<td>25</td>
<td>45.4</td>
</tr>
<tr>
<td>S$_3$</td>
<td>30</td>
<td>45.5</td>
</tr>
</tbody>
</table>

Table 3.7 shows the effect of varying the amount of ZnCl$_2$ used for precipitation, on the yield of Zn(bxt)$_2$ produced. From the Table 3.7 it is evident that maximum yield was obtained when one molecular weight of ZnCl$_2$ was used.

Table 3.7: Effect of varying the amount of ZnCl$_2$ on yield of Zn(bxt)$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (Minutes)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_8$</td>
<td>20</td>
<td>55.9</td>
</tr>
<tr>
<td>S$_9$</td>
<td>20</td>
<td>52.9</td>
</tr>
<tr>
<td>S$_{10}$</td>
<td>20</td>
<td>38.2</td>
</tr>
<tr>
<td>S$_{11}$</td>
<td>20</td>
<td>38.4</td>
</tr>
</tbody>
</table>

Table 3.8 shows the reaction time and yield of the product when the preparation was done using magnetic stirrer (S$_8$) and mechanical stirrer (S$_{12}$) respectively.

Table 3.8: Reaction time and yield of S$_8$ and S$_{12}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (Minutes)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_8$</td>
<td>20</td>
<td>55.9</td>
</tr>
<tr>
<td>S$_{12}$</td>
<td>10</td>
<td>64.5</td>
</tr>
</tbody>
</table>
From the Table 3.8 it is clear that when stirring speed is increased, the reaction time could be reduced considerably. The yield of the product is also increased. When mechanical stirrer is used particle size of xanthate produced was highly reduced and the product is obtained as a fine powder. When the particle size of accelerator is reduced, it will be more uniformly distributed in the latex during compounding and this will improve the mechanical properties of the vulcanisate.

When the preparation of Zn(bxt)$_2$ was done at 0°C, we couldn’t complete the reaction, because potassium butyl xanthate started crystallizing during the reaction. Zn(bxt)$_2$ produced under all different conditions has a pale yellow colour. The odour of Zn(bxt)$_2$ produced could be reduced using commercial grade KOH, n-BuOH and CS$_2$.

The FTIR spectrum of Zn(bxt)$_2$ prepared using commercial grade regents is given in Figure 3.9.

![Figure 3.9: FTIR spectrum of Zn(bxt)$_2$ prepared using commercial grade regents](image)

From the Figure 3.9 it is clear that there is no difference in the position or intensity of peaks in the FTIR spectrum of Zn(bxt)$_2$ prepared using
commercial grade reagents and A.R grade reagents. The foul and irritating smell of Zn(bxt)₂ prepared using A.R grade reagent may be due to the presence of adsorbed CS₂ molecules on its surface.

Figure 3.10 shows the FTIR spectrum of Zn(bxt)₂ prepared using commercial grade reagents after one year of storage.

![FTIR spectrum of Zn(bxt)₂](image)

**Figure 3.10:** FTIR spectrum of Zn(bxt)₂ prepared using commercial grade reagents after one year of storage.

From the Figure 3.10 it is clear that there is no change in position or intensity of peaks in the spectrum suggesting that Zn(bxt)₂ is stable even after one year of storage.

Table 3.9 shows cytotoxicity test results of Zn(bxt)₂ and Figure 3.11 shows the fibroblast cells after contact with Zn(bxt)₂.

**Table 3.9:** Cytotoxicity test data of Zn(bxt)₂

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample</th>
<th>Cytotoxicity scale</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Negative control</td>
<td>0</td>
<td>None cytotoxic</td>
</tr>
<tr>
<td>2</td>
<td>Positive control</td>
<td>4</td>
<td>Severe cytotoxic</td>
</tr>
<tr>
<td>3</td>
<td>Sample</td>
<td>0</td>
<td>None cytotoxic</td>
</tr>
</tbody>
</table>
Figure 3.11: Fibroblast cells after contact with Zn(bxt)$_2$

The extract of Zn(bxt)$_2$ showed no cytotoxic response to fibroblast cells at an extraction ratio of 0.1 g/mL.

3.5 CONCLUSIONS

- Zn(ipxt)$_2$ and Zn(bxt)$_2$ were prepared in the laboratory. Characterization of xanthates was done using FTIR and $^1$H-NMR spectroscopy. Thermal decomposition behaviour of these xanthates was studied using TGA and DTA techniques.

- Reaction time required is less and yield is high for Zn(bxt)$_2$ compared to Zn(ipxt)$_2$. So Zn(bxt)$_2$ was selected for further studies. Preparation method of Zn(bxt)$_2$ was optimized. Zn(bxt)$_2$ could be prepared using both commercial grade and A.R grade n-Butanol, KOH, CS$_2$ and ZnCl$_2$. The irritating smell of Zn(bxt)$_2$ could be reduced when commercial grade reagents were used.

- The yield of the product could be increased and reaction time could be reduced by changing the stirring speed and also by changing the order of mixing of reactants. Zn(bxt)$_2$ showed no cytotoxic response to fibroblast cells in vitro cytotoxicity test.