CHAPTER-II

Chemistry of Xanthates
Xanthates are organic reagents of significant practical value. These are first synthesized in 1822 by Zeise. The chemical reactions of xanthates and the kinetics of these reactions were studied between 1920 and 1960.

Xanthates are salts of xanthic acid, which is essentially alkylthiocarbonic acid with two oxygen atoms in carbonic acid replaced by sulfur and one hydrogen atom replaced by an alkyl group.

\[
\begin{align*}
S &= C\text{OR} \\
\text{Xanthic acid} \\
S &= C\text{SH} \\
\text{Trithio carbonic acid}
\end{align*}
\]

In xanthic acid hydrogen atom can be easily replaced by the metal ion. Xanthic acid is also called alkyl dithiocarboxonic acid and the corresponding salts are called as alkylthiocarbonates.

**Preparation**

Xanthates are the reaction products of carbondisulfide, an alcohol and an alkali. They are formed by combination of the three reactants in the stoichiometric ratio 1:1:1, with the elimination of water.

The general reaction is

\[
\text{ROH} + \text{CS}_2 + \text{MOH} \rightarrow \text{ROC-}\text{SM} + \text{H}_2\text{O}
\]

Where \( R \) stands for an alkyl hydrocarbon radical and \( M \) denotes a monovalent metal such as sodium or potassium.

Preparation of potassium ethyl xanthate was described by Foster. In this method a specified amount of alcohol is measured into a wide mouth conical flask. A slight excess of potassium hydroxide is introduced into the flask in the form of a saturated solution. The flask is cooled in an ice bath to maintain the temperature below 20°C. An excess of \( \text{CS}_2 \) is
added gradually while the mixture is simultaneously stirred by a mechanical stirrer. Under these conditions a thick reddish brown mass is formed.

The reddish color results by a side reaction between alkali metal hydroxide and carbondisulfide. The solid is separated by filtration. The solid is then dissolved in minimum amount of pure acetone. The polysulfides form a separate red layer. The xanthate also dissolves, giving a pure yellow solution. The two layers, red and yellow, are separated using a separating funnel. To the xanthate solution, petroleum ether is added which acts as a desolvent, and the xanthate is precipitated as a fine faint yellow solid. It is filtered, washed with petroleum ether and dried in a vacuum desiccator. The equation corresponding to the formation of xanthate, is

\[
\text{CS}_2 + \text{KOH} \rightarrow \text{S} = \text{C} - \text{SK} - \text{OH}
\]

\[
\text{S} = \text{C} - \text{SK} + \text{EtOH} \rightarrow \text{S} = \text{C} - \text{SK} - \text{OEt} + \text{H}_2\text{O}
\]

A method for the preparation of the isoamyl xanthate of potassium was described by Gomez.

Keskyula described a comparative study of the preparation of alkali metal xanthates of various alcohols. In general method of preparation, 1.2 to 1.5 parts carbondisulfide are added to 1 part potassium hydroxide and 1 part alcohol. The xanthate that separates at once is designated as fraction I, the another part was cooled and separated as fraction II. The yield of fraction I depends upon the concentration of alcohol, potassium hydroxide and the water content. The highest yield is obtained with a concentration of 1 part potassium hydroxide to 1.5 parts rectified spirit. The percentage yields of xanthates of a large number of higher alcohols was given by Keskyula.
Structure of xanthate

Basing on the characteristic frequencies of C=S and C-O groups in the IR region the xanthate ion can be represented in the following three forms.

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} \\
\text{R-O-S-C-S}^- & \quad \text{R-O-C=S}^- & \quad \text{R-O-C=S}^-
\end{align*}
\]

In ionic compounds the xanthate is represented by the canonical structure I, whereas the resonating structures II & III represent the covalent xanthate in transition metal compounds.

Properties of xanthates

Alkali metal xanthates are pale yellow solids in the pure form and have a very faint odour. When kept in the atmosphere a deeper yellow color and a rather unpleasant odour, resembling that of carbondisulfide is seen. This is due to the slow decomposition of xanthate in the atmosphere and the products of decomposition, especially organosulfur compounds cause the disagreeable odor even when present in low concentrations.

The decomposition of solid xanthate is enhanced by the action of heat. Thermal decomposition of xanthates was described by Hebert in 1911. A detailed investigation of the thermal decomposition of potassium xanthates by gas chromatographic study and differential thermal analysis has been described by Tyden.

The decomposition of solid xanthates in aqueous solution is of much greater interest largely because of its importance in mineral flotation. On dissolution xanthates dissociate, forming cations of alkali metals and xanthate anions. They are strong electrolytes, and xanthic acid is a fairly

\[\text{RS}S\text{O}_2\text{H}\]

\[\text{D 535}\]

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strong acid. The solution undergoes slow hydrolysis giving rise to xanthic acid which further decomposes into carbondisulfide and alcohol.

\[
R\text{-}O\text{-}C\equiv S^- + H_2O \rightarrow R\text{-}O\text{-}C\equiv S^- + OH^- \\
R\text{-}O\text{-}C\equiv S^- \rightarrow CS_2 + ROH
\]

The decomposition of xanthate is enhanced by covering the pH of the solution to neutralise the OH\(^-\) ions produced. In the presence of oxygen xanthate is oxidized to dixanthogen according to the reaction:

\[
2S\equiv C\text{-}S^- + \frac{1}{2} O_2 + H_2O \rightarrow S\equiv C\equiv S\equiv C\equiv S + 2OH^- \\
\text{OR} \quad \text{OR}
\]

The resulting dixanthogen causes turbidity in a xanthate solution when kept in the atmosphere. In neutral and alkaline media, xanthates decompose as hydrolytic decomposition. This mechanism was described by Klauditz\(^9\). In strong alkaline solutions, Klauditz\(^9\) identified the following main reaction, in strong alkaline solution.

\[
6S\equiv C\text{-}S^- + 3H_2O \rightarrow 6ROH + CO_3^{2-} + 3CS_2 + 2CS_3^{2-}
\]

The effects of medium pH, concentration of solutions and temperature on the decomposition of aqueous solutions of ethyl and isoamyl xanthates were first reported by Homylev\(^10\).

The general formula

\[
\text{pH} = KT_a \\
T \quad = \quad \text{half-life of decomposition of xanthates in minutes.} \\
K \text{ and } a \quad = \quad \text{constants for a given temperature and a specific hydrocarbon chain.}
\]
The decomposition of xanthates in an alkaline medium is very slow. Homylev\textsuperscript{10} showed that higher the concentration and temperature of the solution the more intense the decomposition of the xanthate.

Schaum and co-workers\textsuperscript{11} showed that the rate of decomposition of xanthate is also influenced by the length of the hydrocarbon chain. Wronski\textsuperscript{12} studied the kinetics of the decomposition of xanthates in sodium hydroxide solutions.

\[
\text{ROCS}_{2}^- = \text{RO}^- + \text{CS}_2 \text{ and}
\]
\[
\text{ROCS}_{2}^- + \text{OH}^- = \text{ROH} + \text{CS}_2\text{O}^- -
\]

and the kinetic equation is given as

\[
- \frac{dx}{dt} = K_1 + K_2C^n
\]

where

\[
x \quad \text{= xanthate concentration}
\]
\[
C \quad \text{= sodium hydroxide concentration}
\]

An extensive study of the kinetics of decomposition of ethyl, isopropyl, n-butyl and iso-amyl xanthates of potassium in aqueous solution in the presence of different gaseous systems such as oxygen, carbondioxide and a mixture of oxygen and carbondioxide was carried out by Rao and Patel\textsuperscript{13}.

The stability of xanthate solution depends on the acidity of the solution. The rate of decomposition increases greatly with decrease of pH and is attributable to the formation of xanthic acid\textsuperscript{14}.

**Determination of xanthates**

The quantitative determination of xanthates in solutions is often required in flotation techniques. The oldest method for the quantitative
determination of xanthate is based on the quantitative oxidation of xanthate to diaxanthogen by iodine:

\[2S\equiv C\overset{SK}{\underset{OR}{\text{OR}}} + I_2 \rightarrow S\equiv C\underset{OR}{\text{S}}\underset{OR}{\text{S}}C\equiv S + 2KI\]

The analysis is done in aqueous medium.

The iodimetric method of analysis has some serious limitations. It cannot be used for the determination of xanthate in the presence of reducing ions such as sulfite, sulfide or thiosulfate. It is currently used in laboratories mainly as a check to ascertain the purity of freshly prepared xanthates.

The various methods for the determination of xanthates that appeared in the literature after 1970 are included here since the monograph\(^{16}\) on "xanthates and related compounds" reviewed all the references up to 1970.

Maganyuk et al.\(^{16}\) reported pulse polarographic determination of xanthate on a copper or graphite electrode. Identification and determination of xanthate, diaxanthogen and sulfur xanthates by fast-sweep differential polarography, a.c. polarography and cyclic voltammetry were studied by Bond et al.\(^{17}\). Gorodetskii et al.\(^{18,19}\) have suggested a mechanism for a number of xanthates in KNO\(_3\) supporting electrolyte at HMDE, Pt and Au electrodes and determined small amounts of xanthates in ammonium chloride-ammonium hydroxide supporting electrolyte.

A photometric method for the estimation of xanthates after complexation with nickel and extraction into Me\(_2\)CO was established by Rao and Singh\(^{20}\). The titrimetric method of estimation of xanthates by titrating with iodine cyanide or bromo cyanide in aqueous solution was reported by Ramchand and his coworkers\(^{21}\).
Polarography of potassium ethyl xanthate and its applications as titrant in amperometry was given in detail by Saraswathi\textsuperscript{22}. She reported a prewave due to strong adsorption of the product on DME.

**Application of xanthates**

Xanthates are of potential importance, in agricultural, industrial and related fields of technology and are important analytical reagents known for their reactivity, selectivity, sensitivity, versatility and ability to form strong complexes with most of the metal ions.

In addition, their applications in separation and detection of alcohols, in agriculture as weed killers, in rubber industry, in waste water treatment to reduce heavy metal contamination, as catalysts in the polymerization of olefins, in lubricating oil additives, fire proof agent for self extinguishing resins, as corrosion inhibitors for steel in acid solutions and in floatation technique in number of ores are worth mentioning\textsuperscript{23}.

Xanthates have therefore attracted the attention of analytical chemists to use them as reagents in the extraction, determination and estimation of metals in trace quantities and extensive literature in this regard is available\textsuperscript{15}. In addition, the complexes of transition metal ions with thio compounds are known to serve as catalysts or to accelerate the catalytic activity of organic compounds containing – SH groups due to high adsorptivity\textsuperscript{23,24}.

**Separation and detection of alcohols**

Xanthates and their derivatives were utilized in the identification of alcohols based on their definite melting points and easily determinable iodine equivalents\textsuperscript{26}. A thin layer chromatographic method for the separation of lower alcohols by converting them into xanthates were developed by Roehr and Chiari\textsuperscript{28}. Paper chromatography of alcohols as potassium xanthates was recommended by Kariyone and coworkers\textsuperscript{27}. Spanyer and Phillips\textsuperscript{29} adopted a chromatographic method for the
separation of alcohols using a cellulose column. A method for the identification of alcohols by the X-ray diffraction pattern of their xanthate derivatives has been described by Warren and Matthews\textsuperscript{30}.

**Rubber industry**

Zinc butyl xanthate has been used as an accelerator in the vulcanization of rubber\textsuperscript{30,31}. Another use is in the protection of rubber against atmospheric gases, especially oxygen and ozone\textsuperscript{32,33}.

**Polymerization of olefins**

Zinc isopropyl xanthate is used as a catalyst in the polymerization of olefins to high molecular weight polymers\textsuperscript{34,35}. Vinyl monomers were polymerized in aprotic polar solvents at 0°C using heptyl, isooctyl xanthates as catalysts\textsuperscript{36}.

**Waste water treatment**

The lead content in waste water was decreased by treatment with propyl xanthate\textsuperscript{37}.

**Floatation technique**

Propyl xanthate was used in flotation techniques to produce high recovery of sulfide ores\textsuperscript{38}. Abramov and Airapetov\textsuperscript{39} have mentioned the usefulness of potassium butyl xanthate in optimization and automatic control of zinc-pyrite ore floatation.

**Analytical applications**

The solvent extraction of thallium(II) xanthates with number of organic solvents, in sodium perchlorate medium was evaluated by Schweitzer and Davidson\textsuperscript{40}. Paria and Majumdar\textsuperscript{41} described the spectrophotometric determination of palladium – Khenxan in chloroform. A sensitive atomic absorption spectrophotometric (AAS) method was
recommended by Masato and Mitsio for chromium (VI) up to 10 µg / ml with Kbenxan in MIBK. The method was used for the determination of Cr(VI) in waste water. The same authors also developed an AAS method for Au(III) using Kbenxan after extraction into MIBK and was applied for the determination of Au in human organs.

Hayashi et al. reported the spectrophotometric determination of iron(II) and (III) with Kbenxan and water soluble brown complexes were extracted into chloroform. Bond and his coworkers studied the polarographic behaviour of Vanadium(V) - Kpxan and Kbxan complexes in acetone medium and general mechanism for electrode processes was suggested.

Nickel(II) was found to react with three xanthates to form insoluble yellowish brown complexes extractable into chloroform. The absorbance was measured spectrophotometrically and the formation constants, distribution constants and molar absorptivity values were calculated by Hayashi and Sasaki. Sasaki adopted the extraction - spectrophotometric method for manganese(II) xanthate in chloroform.

A spectrophotometric method for nickel and palladium using various xanthates and extracting the complexes into chloroform was deduced by Paria and Majumdar. Thokdar et al. developed an extractive spectrophotometric method for traces of cobalt with various xanthates extractable into chloroform.

Nanogram amount of molybdenum in silicate rocks as xanthate complexes was detected by inductively coupled plasma atomic emission spectrometry (ICP-AES) after extraction into xylene by Hideo and his associates. The same authors developed ICP-AES method for the determination of iridium in catalysts using iridium-xanthate complexes. Trace amount of copper in aluminium alloys by ICP-AES after solvent extraction with potassium xanthates was determined by Tadani et al.
The work reported so far include insoluble xanthate complexes with metal ions extractable into organic solvents. Under controlled experimental conditions xanthates also give soluble complexes with few transition metal ions which are known to give catalytic hydrogen currents at DME.

Bundnikov et al. studied the polarographic behaviour of cobalt(II) and (III), nickel(II), zinc(II) and cadmium in presence of pxan and bxan in DMF and EtOH-H₂O solution with EtNCIO₄ as supporting electrolyte and reported that Zn(II) and Cd(II) give simple cathodic currents, whereas Co(II) and (III) and Ni(II) produce catalytic hydrogen waves.

In the field of catalytic hydrogen waves with thio compounds, a few thio compound complexes of Cr(VI) & (III), Fe(II), Co(II), Ni(II), Mn(II) and Cu(II) in ammonium chloride-ammonia buffer have been extensively studied and developed sensitive and selective methods for their estimation in environmental samples in these laboratories.

Keeping in view, the importance of xanthates in various fields and also their activity in giving catalytic hydrogen waves at DME the present study utilized two xanthates, potassium heptylxanthate (Khxan) and potassium isoctyl xanthate (Kocxan), for trace quantities of Fe(II), Co(II), Ni(II), Cu(II) & Cr(VI) in aqueous medium and to compare the sensitivity of the ligands towards these metal ions. The methods developed have been applied for the determination of these metal ions in various environmental samples such as water, industrial effluents, agricultural samples, pharmaceuticals and in synthetic mixtures of metal ions commonly associated in ores and alloys.
Structures of xanthates used:

1) Potassium heptyl xanthate

\[
\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{O-C-}\text{S}_{\text{SK}}
\]

2) Potassium isooctyl xanthate

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

(or)

\[
\text{CH}_3(\text{CH}_2)_3\text{CH(CH}_2\text{C}_2\text{H}_3)\text{CH}_2\text{O-C-}\text{S}_{\text{SK}}
\]
References

36. Yamaguchi, K., Sonoda, O. and Minoura, Y. Ibid., 1972, 10, 63.


50. Ibid., Chem. Express. 1990, 5, 357.


