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   (Ms). M.P.Yashoda, B.S.Sherigara, V.P.Vaidya and J.Manjanna (Communicated)
Titanium (III) reduction of dimethyl-glyoxime: Electrochemical and kinetic studies

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Titanium (III) mediated electroreduction of dimethyl glyoxime has been carried out in aqueous sulphuric acid medium and the reduction product has been isolated and characterised. The kinetic investigations have been carried out under stoichiometric and non-stoichiometric conditions at 306K. It has been found that the reaction follows overall second order kinetics, first order in [Ti(III)] and [DMG] and fractional order in sulphuric acid. The effect of varying concentrations of Ti(III), DMG, H2SO4, ionic strength, and solvent composition has been studied. Effect of temperature has also been studied and activation parameters have been computed from Arrhenius and Eyring plots.

Titanium (III) in aqueous acid media has been found to be an efficient reducing agent for a variety of organic as well as inorganic compounds. The kinetics of reduction of nitro, nitroso, azo and azoxy compounds and its substituted products by titanium(III) chloride was studied by Hinshelwood and co-workers. Titanium(III)-mediated electro-reduction of nitro compounds has been reported earlier. Dimethyl glyoxime is mainly used in quantitative analysis as a complexing agent. On reduction, dimethyl glyoxime is expected to give the corresponding diamine. In recent years the production of diamines by reduction methods has become increasingly important due to their importance in organic synthesis. To understand the reductive capability of titanium(III), we have studied the kinetics of reduction of dimethyl glyoxime in aqueous sulphuric acid medium.

Experimental

All chemicals used were of analytical grade. Doubly distilled water was used throughout. The stock solution of titanium(IV) was prepared as reported elsewhere. Standard solutions of ferric ammonium sulphate (0.1 mol dm⁻³), 1,10-phenanthroline (0.25%), sodium acetate-acetic acid buffer, dimethyl glyoxime (0.1 mol dm⁻³) in ethanol and sodium sulphate (1.5 mol dm⁻³) were prepared.

The electrolytic cell consisted of a divided cell, comprising cationic exchange membrane. Catholyte was sulphuric acid (0.75 mol dm⁻³) containing titanium(IV) sulphate (0.20 mol dm⁻³) and dimethyl glyoxime (1.0 g). Copper and lead were used as cathode and anode respectively at a distance of 2.0 cm. The electrolysis was monitored with the help of an electrolytically stabilised dc power supply. The electrolytic cell was mounted on a magnetic stirrer and the medium was adequately stirred. The electrolysis was carried out under galvanostatic conditions using current 10% higher than that theoretically required. Completion of reduction was indicated by the appearance of permanent violet colour of titanium(III) species. Time taken for the complete reduction was noted and accordingly percentage current efficiency (% CE) was calculated using Eq. (1).

\[
\% \text{CE} = \left( \frac{\text{Theoretical time required for complete reduction}}{\text{Actual time taken for complete reduction}} \right) \times 100 \tag{1}
\]

where W is the weight of dimethyl glyoxime.

Effect of concentrations of titanium(IV) sulphate, sulphuric acid and temperature on the current efficiency was also studied. Repeated attempts by various method to isolate the corresponding diamine were not successful, therefore the product, 2,3-butane diamine, was isolated as Schiiff's base of salicylaldehyde and characterised by its melting point (182°C) and IR spectra. IR spectrum showed absorption frequencies at 1640 cm⁻¹ (C=N stretching), 1460 cm⁻¹ (C–H bending in CH₃), 1150 cm⁻¹ (C–O stretching and O–H bending of the phenol group) and 760 cm⁻¹ (aromatic ring with four adjacent hydrogen atoms).

Kinetic procedure

Kinetics of titanium(III) reduction of dimethyl glyoxime was studied under stoichiometric and non-stoichiometric conditions. The reaction mixture consisted
of organic substrate, sulphuric acid (to maintain acid concentration), titanium(IV) sulphate (to nullify the product effect), sodium sulphate solution (to maintain ionic strength), ethyl alcohol (to keep the organic substrate in homogeneous phase) and water (to keep the overall volume constant).

Kinetic runs were initiated by mixing the previously thermostated reactant solutions. A stream of nitrogen was passed over the reaction mixture. A known amount of titanium(III)sulphate solution, maintained at the same temperature under deaerated conditions, was added and homogenised. The progress of the reaction was monitored spectrophotometrically as follows:

At regular intervals of time, a known amount of reaction mixture was pipetted out into known excess of previously deaerated ammonium iron(III)sulphate solution in a 50.0 cm$^3$ standard flask. The volume was made up to the mark. Titanium(III) present in the reaction mixture quantitatively reduces iron(III) to iron(II). From this, 1.0 cm$^3$ of the solution was added to 4.0 cm$^3$ of 1,10-phenanthroline indicator (0.25%) and 12.0 cm$^3$ of sodium acetate-acetic acid buffer (to maintain the pH) taken in a 50.0 cm$^3$ standard flask. The solution was made up to the mark and the absorbance of the iron(II)-1,10-phenanthroline complex was measured at 515 nm using Shimadzu UV-vis spectrophotometer provided with 1.0 cm quartz cell. Concentration of iron(II) obtained from the calibration plot was used to compute the concentration of titanium(III). Separate calibration plots were obtained for variation of [Ti(III)], [DMG], [H$_2$SO$_4$], ionic strength and solvent composition.

Results and discussion

The effect of variation in concentrations of titanium(IV) sulphate, sulphuric acid and temperature on the percentage of current efficiency (%CE) was studied at 298K. It was found that the %CE steadily increased from 47.0-75.0 as the concentration of titanium(IV)sulphate was varied from 0.40-0.05 mol dm$^{-3}$ at 0.75 mol dm$^{-3}$ [H$_2$SO$_4$]. Similarly, as [H$_2$SO$_4$] was varied from 0.50-2.25 mol dm$^{-3}$, %CE increased steadily from 47.0-82.0 at 0.20 mol dm$^{-3}$ titanium(IV)sulphate. Also, the %CE increased from 60.0-75.0 with rise in temperature from 298.313K at 0.20 mol dm$^{-3}$ (titanium(IV)sulphate) and 0.75 mol dm$^{-3}$ [H$_2$SO$_4$]. In all the above cases the amount of dimethyl glyoxime (1.0 g) and cathode current (200 mA) was kept constant.

Stoichiometry for the reduction of dimethyl glyoxime by titanium(III) was established by back-titration method. To a known volume ($v_1$) of substrate in aqueous ethanol (5.0 cm$^3$, 0.001 mol dm$^{-3}$), titanium(III)sulphate (5.0 cm$^3$, 0.01 mol dm$^{-3}$) solution ($v_2$) was added under deaerated condition. To this, ammonium iron(III)sulphate solution (5 cm$^3$, 0.025 mol dm$^{-3}$) was added. The resulting solution was back-titrated against standard titanium(III)sulphate (0.05 mol dm$^{-3}$) stored under nitrogen atmosphere using 10% ammonium thiocyanate as indicator ($v_3$). A blank titration was carried out by taking the same amounts of titanium(III)sulphate and ammonium iron(III)sulphate solutions. Titration volume was $v_4$.

The number of electrons is given by the Eq. (2).

$$n = [v_2 - (v_4 - v_3)] \times M_2 / v_1 \times M_1 \ldots (2)$$

where $M_1$ and $M_2$ are the molarities of sample solution and titanium(III)sulphate solution respectively.

Stoichiometry of reduction of dimethyl glyoxime by titanium(III) was found to be 1:8 as shown below,

$$C_4H_8N_2O_2 + 8 \text{Ti}^{3+} + 8 \text{H}^+ \rightarrow C_4H_6N_2 + 8 \text{Ti}^{4+} + 2 \text{H}_2\text{O} \ldots (3)$$

The initial rates were obtained from the slopes of concentration versus time curves at the initial stages of the reaction by the plane mirror method$^6$ reproducible to ±5%.

The order of the reaction was found by log[rate] versus log[concentration] plots. The order was found by varying the concentration of oxidant, reductant, sulphuric acid in turn, while keeping others constant (Table 1). The order with respect to oxidant and reductant was nearly unity and the order with respect to sulphuric acid was about 0.5 (Eq. 4).

$$\text{Rate} = k \left[\text{Ti}^{(III)}\right]^{1.0} \left[\text{DMG}\right]^{0.5} \ldots (4)$$

In a standard run, kinetics were studied at [Ti(III)]=0.05 mol dm$^{-3}$; [DMG]=0.00625 mol dm$^{-3}$, [H$_2$SO$_4$]=0.4 mol dm$^{-3}$; ionic strength of 3.0 mol dm$^{-3}$ and temp.=306K in 25% ethanol-water medium.

The mechanism as shown in Scheme 1 for the observed kinetics:

The rate law was derived by applying steady state approximation to the intermediate SH$^+$,

$$d[\text{SH}^+] / dt = k_1 \left([\text{S}]_0 - [\text{SH}^+]\right) [\text{H}^+] - k_2 [\text{SH}^+] = 0 \ldots (5)$$
Table 1—Effect of varying concentration of Ti(III), DMG and H$_2$SO$_4$ on initial rate of the reaction. [Temp.=306K, $\tau$=3.0 mol dm$^{-3}$]

<table>
<thead>
<tr>
<th>[Ti(III)]x10$^2$ (mol dm$^{-3}$)</th>
<th>[DMG]x10$^3$ (mol dm$^{-3}$)</th>
<th>[H$_2$SO$_4$]x10$^1$ (mol dm$^{-3}$)</th>
<th>10$^6$xInitial rate (mol dm$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.15</td>
<td>6.25</td>
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<td>6.25</td>
<td>4.0</td>
<td>7.50</td>
</tr>
<tr>
<td>5.00</td>
<td>6.25</td>
<td>4.0</td>
<td>7.94</td>
</tr>
<tr>
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<td>3.95</td>
</tr>
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<td>4.25</td>
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</tr>
<tr>
<td>5.00</td>
<td>6.25</td>
<td>2.0</td>
<td>5.59</td>
</tr>
<tr>
<td>6.00</td>
<td>6.25</td>
<td>7.5</td>
<td>10.00</td>
</tr>
</tbody>
</table>

\[
K_1
\]

$S + H^+ \rightarrow SH^+$  \hspace{1cm} \ldots \text{(fast)}

(DMG)

$SH^+ + Ti^{3+} \rightarrow SH + Ti^{4+}$  \hspace{1cm} \ldots \text{(slow and rds)}

$SH + 7Ti^{3+} + 7H^+ \rightarrow \text{Diamine product} + 2H_2O + 7Ti^{2+}$  \hspace{1cm} \ldots \text{(fast)}

Scheme 1

\[
\text{here, } [S] = ([S]_0 - [SH^+])
\]

\[
[SH^+] = \frac{k_1 [S]_0 [H^+]}{k_{-1} + k_1 [H^+] + k_2 [Ti^{3+}]} \quad \ldots \text{(6)}
\]

Overall rate of the reaction $= k_2 [SH^+] [Ti^{3+}]$  \hspace{1cm} \ldots \text{(7)}

Rate $= \frac{k_1 k_2 [S]_0 [Ti^{3+}] [H^+]}{k_{-1} + k_1 [H^+] + k_2 [Ti^{3+}]}$  \hspace{1cm} \ldots \text{(8)}

Assuming that $k_2$ is negligible as compared to other terms in the denominator,

Rate $= \frac{K_1 k_2 [S]_0 [Ti^{3+}] [H^+]}{1 + K_1 [H^+]}$  \hspace{1cm} \ldots \text{(9)}

where $K_1 = \frac{k_1}{k_{-1}}$. Rate law (9) also takes the form,

$1/\text{Rate} = 1/K_1 k_2 [S]_0 [Ti^{3+}] [H^+] + 1/k_2 [S]_0 [Ti^{3+}]$  \hspace{1cm} \ldots \text{(10)}

The plots of $1/\text{Rate}$ versus $1/[H^+]$ were linear with intercept on the ordinate in accordance with rate law (10) and Scheme 1. The second order rate constant $k_2$ (4.00 mol$^{-1}$ dm$^{-3}$ s$^{-1}$) of the reduction process and the formation equilibrium constant $K_1$ (4.80 mol$^{-1}$ dm$^{-3}$) were calculated from the intercept and slopes of the double reciprocal plot. The detailed mechanism of reduction is shown in Scheme 2.

The protonated substrate, $SH^+$ reacts with $Ti^{3+}$ in the slow step to give a free radical. The free radical further reacts with additional $Ti^{3+}$ ions in fast steps to give the products. The observed decrease in rate (Table 2) with decrease in dielectric constant of the medium is in accordance with Laidler and Eyring equation$^1$ as applicable to reaction between ions of equal charge. Decrease in rate of the reaction with increase in ionic strength due to the added $SO_4^{2-}$ could be due to the equilibria,

$\text{H}^+ + SO_4^{2-} \rightarrow \text{HSO}_4^-$

resulting in lowering of $\text{H}^+$ and hence decrease in rate.

It was found that the reaction mixtures initiate polymerisation of monomers like acrylonitrile or methyl methacrylate in an hour. As neither of the reacting species, Ti(III) or DMG, initiate polymerisation when added separately to an aqueous mixture of the two monomers, it can be assumed that the reduction steps produce free radicals which induce polymerisation. The IR spectrum of the polymer product shows absorption frequencies at 3468 cm$^{-1}$ (–N–H and O–H stretching), 2939 cm$^{-1}$ (–C–H stretching), 2250 cm$^{-1}$ (–C≡N stretching) and 1650 cm$^{-1}$ (–N–H bending and –C≡N stretching),

Table 2—Effect of ionic strength and solvent composition on the initial rate of the reaction

<table>
<thead>
<tr>
<th>Ionic strength (mol dm$^{-3}$)</th>
<th>Alcoholic (mol dm$^{-3}$ s$^{-1}$)</th>
<th>Alcohol (%)</th>
<th>Initial rate (mol dm$^{-3}$ s$^{-1}$ x 10$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>11.75</td>
<td>22</td>
<td>9.00</td>
</tr>
<tr>
<td>2.75</td>
<td>10.50</td>
<td>25</td>
<td>7.94</td>
</tr>
<tr>
<td>3.00</td>
<td>7.94</td>
<td>30</td>
<td>6.36</td>
</tr>
<tr>
<td>3.50</td>
<td>5.44</td>
<td>35</td>
<td>5.65</td>
</tr>
</tbody>
</table>

\[
\text{here, } [SH'] = ([S]_0 - [SH^+])
\]

Overall rate of the reaction $= k_2 [SH'] [Ti^{3+}]$  \hspace{1cm} \ldots \text{(7)}

Rate $= \frac{k_1 k_2 [S]_0 [Ti^{3+}] [H^+]}{k_{-1} + k_1 [H^+] + k_2 [Ti^{3+}]}$  \hspace{1cm} \ldots \text{(8)}

Assuming that $k_2$ is negligible as compared to other terms in the denominator,

Rate $= \frac{K_1 k_2 [S]_0 [Ti^{3+}] [H^+]}{1 + K_1 [H^+]}$  \hspace{1cm} \ldots \text{(9)}

where $K_1 = \frac{k_1}{k_{-1}}$. Rate law (9) also takes the form,

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The plots of $1/\text{Rate}$ versus $1/[H^+]$ were linear with intercept on the ordinate in accordance with rate law (10) and Scheme 1. The second order rate constant $k_2$ (4.00 mol$^{-1}$ dm$^{-3}$ s$^{-1}$) of the reduction process and the formation equilibrium constant $K_1$ (4.80 mol$^{-1}$ dm$^{-3}$) were calculated from the intercept and slopes of the double reciprocal plot. The detailed mechanism of reduction is shown in Scheme 2.

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indicating the dimethyl glyoxime moiety as end group of the polyacrylonitrile macromolecule. The investigation on kinetics of titanium(III)-dimethyl glyoxime mediated electro-polymerisation of acrylonitrile is under progress.

The effect of temperature on the initial rate of the reaction was also studied at 296, 301, 306 and 311 K, and 10⁶ x initial rate obtained were 3.75, 5.00, 7.04 and 10.29 mol dm⁻³ s⁻¹ respectively giving the activation parameters $E_a = 46.70 \pm 5$ kJ mol⁻¹, $\Delta H^\circ = 44.18 \pm 5$ kJ mol⁻¹, $\Delta G^\circ = 92.78 \pm 9$ kJ mol⁻¹, $\Delta S^\circ = -160.10 \pm 16$ JK⁻¹ mol⁻¹ and $\log A = 4.83 \pm 0.8$.

The relatively low energy of activation energy or enthalpy of activation for the overall reaction support the free radical mechanism. Large negative entropies of activation and high positive free energy of activation suggest the role of bond breaking in the formation of reduction product.

Acknowledgement

The authors thank the Department of Atomic Energy, Government of India, for financial assistance on a Research Project.

References

Kinetics of electroinitiated polymerization of acrylonitrile mediated by titanium (III)–dimethylglyoxime redox system

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²Manipal Institute of Technology, Manipal 576 119, India

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ABSTRACT: Acrylonitrile was polymerized in an aqueous sulphuric acid–methanol medium by an electrolytically generated mediator species, titanium(III). Titanium(III)–dimethylglyoxime was used as the initiator redox system. The reaction was confined to the cathode compartment and was found to proceed via a free radical mechanism. The kinetics of polymerization were investigated for different initial monomer concentrations, acid concentrations, electric currents, dielectric constants of the solvent and electrode materials. A suitable mechanism for titanium(III)–dimethylglyoxime-mediated indirect electropolymerization of acrylonitrile is proposed. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: acrylonitrile polymerization; electroinitiated polymerization; titanium(III)–dimethylglyoxime redox system; kinetics

INTRODUCTION

The kinetics of electrochemical polymerization have received great attention by various researchers,¹–⁴ as they play a unique role in predicting the mechanism of polymerization. Previous studies have established that Ti(III)–NH₂OH is a potential initiator for the polymerization of vinyl monomers.⁵ As a part of our mechanistic studies on redox polymerization,⁶–⁸ we present here the results of a kinetic study of titanium(III)–dimethylglyoxime-mediated electropolymerization of acrylonitrile in aqueous sulphuric acid–methanol medium.

EXPERIMENTAL

All chemicals were of analytical grade unless indicated otherwise and doubly distilled water was used throughout. A stock solution of titanium(IV) was prepared by the gradual addition of TiO₂ (Glaxo, special quality) to hot concentrated sulphuric acid. The yellowish green solid of titanium(IV) sulphate thus produced was dissolved in distilled water, boiled well and filtered to give a clear solution.⁹ The titanium(IV) concentration was determined by spectrophotometry.

Acrylonitrile (SRL) was washed with 5% sodium hydroxide followed by dilute orthophosphoric acid and finally with distilled water. It was dried over anhydrous calcium chloride and again distilled under reduced pressure in a nitrogen atmosphere. The middle fraction was collected and stored at 5 °C. A standard solution of 0.1 mol dm⁻³ dimethylglyoxime was prepared in methanol.

Polymerization method. Polymerization was carried out in a simple H-shaped cell consisting of two cylindrical glass tubes fused to two halves of square-shaped steel frames, having a circular opening at the centre. These steel frames were tightened together with the help of screws provided for this purpose by placing a cation-exchange membrane in between to act as a diaphragm. One glass tube was used as the anodic compartment and the other as the cathodic compartment.

The catholyte was an electrolytic solution containing titanium(IV) sulphate (3.0 cm⁻³ of 0.25 mol dm⁻³), dimethylglyoxime (2.5 cm⁻³ of 0.1 mol dm⁻³), sulphuric acid (to maintain a constant acid concentration of 0.5 mol dm⁻³), methanol (to keep the organic substrate in a homogeneous phase), 1.21 mol dm⁻³ acrylonitrile and water (to keep the overall volume to 25.0 cm⁻³). The anolyte was 25.0 cm⁻³ of 0.5 mol dm⁻³ sulphuric acid. A thin, bright platinum foil was used as the anode and a rectangular copper plate (1.0 × 9.0 cm) as the cathode. A stream of pure nitrogen was slowly bubbled over the catholyte. The electrolytic cell was mounted on a
magnetic stirrer and the medium was adequately stirred. A constant current was obtained from a stabilized d.c. power supply of 0–150 V, which gave currents of 0–1000 mA.

Initially conditions were established to obtain a maximum yield of polymers. This was done by carrying out the electrolysis at a specified current for 60 min. The polymer yield was determined gravimetrically. The results are given in Tables 1 and 2.

**Kinetic procedure.** The kinetic measurements were performed under an inert atmosphere. In a typical kinetic run, a mixture of solutions containing the requisite amounts of the acrylonitrile monomer (M), dimethylglyoxime (DMG), titanium(IV) ions, sulphuric acid, methanol and water was thermally equilibrated in a water-bath at the desired temperature. A wash-bottle containing an aqueous solution of acrylonitrile and methanol of the same concentration as in the electrolytic cell was interposed between the nitrogen train and the electrolytic cell to avoid any loss due to deaeration. Electrolysis was carried out for a desired time. The percentage yield of polymerisation was determined gravimetrically at 300 K. The initial rate of polymerization (\(R_p\)) was determined from the initial slope of the curve of percentage conversion versus time plot by the plane mirror method, reproducible to ±6%. The order of the reaction was found from log (rate) versus log (concentration) plots.

The effect of variation of the concentration of monomer, cathode current, solvent, sulphuric acid, dimethylglyoxime, titanium(IV) and cathode materials was studied. The effect of temperature on the polymer yield was also examined (Table 3) and activation parameters were calculated using Arrhenius and Eyring plots. The gravimetric determination of the polymer produced is one of the most direct ways of obtaining conversion data for polymerization. Always a constant volume of the reaction mixture was taken in the cell. In order to determine the amount of polymer formed in a known interval of time, the electrolysis was terminated at the desired time and the polymer obtained was filtered through a previously weighed sintered glass crucible of the required specification, washed properly with methanol and dried in a vacuum oven at 343 K to a constant weight.

The intrinsic viscosity was measured in \(N, N\)-dimethylformamide at 300 K with an Ubbelhode viscometer. The limiting viscosity values were converted into average molecular weights by the Mark–Houwink equation, \([\eta] = KM^n\), where \(K\) is the molecular weight of the polymer and \(n\) and \(m\) are constants, their values being \(K = 2.303 \times 10^{-4}\) and \(n = 0.75\).

### RESULTS AND DISCUSSION

**Blank experiments**

Electrochemical polymerization did not occur when acrylonitrile was added separately to either of the reagents, titanium(IV) or dimethylglyoxime, in aqueous sulphuric acid–methanol medium. However, the addition of acrylonitrile was found to initiate the polymerization in the presence of a mixture of titanium(IV) and dimethylglyoxime in aqueous sulphuric acid–methanol medium only when subjected to electrolysis.

---

**Table 1. Effect of titanium (IV) and dimethylglyoxime concentration on polymer yield for the cathodic polymerization of acrylonitrile**

<table>
<thead>
<tr>
<th>[Ti(IV)] × 10^2 (mol dm^-3)</th>
<th>Polymer yield (%)</th>
<th>[DMG] × 10^2 (mol dm^-3)</th>
<th>Polymer yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60.38</td>
<td>0.6</td>
<td>86.26</td>
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<td>3.0</td>
<td>78.95</td>
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<td>5.0</td>
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</tr>
<tr>
<td>6.0</td>
<td>83.20</td>
<td>1.8</td>
<td>44.63</td>
</tr>
</tbody>
</table>

* Conditions: temperature, 300 K; current, 200 mA; [AN], 1.21 mol dm^-3; [H_2SO_4], 0.5 mol dm^-3; [methanol], 18% (v/v); electrolysis time, 60 min.

**Table 2. Effect of sulphuric acid concentration and solvent composition on polymer yield for the cathodic polymerization of acrylonitrile**

<table>
<thead>
<tr>
<th>[H_2SO_4] × 10^-1 (mol dm^-3)</th>
<th>Polymer yield (%)</th>
<th>[methanol] (mol dm^-3)</th>
<th>Polymer yield (%)</th>
</tr>
</thead>
<tbody>
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<td>82.90</td>
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</tbody>
</table>

* Conditions: temperature, 300 K; current, 200 mA; [AN], 1.214 mol dm^-3; [DMG], 0.01 mol dm^-3; [Ti(IV)], 0.03 mol dm^-3; electrolysis time, 60 min.

**Table 3. Effect of temperature on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile**

| Temperature (K) | Polymer yield (%) | Average molecular weight
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>33.00^a</td>
<td>4.0 × 10^4</td>
</tr>
<tr>
<td>298</td>
<td>64.54</td>
<td>4.0 × 10^4</td>
</tr>
<tr>
<td>300</td>
<td>78.95</td>
<td>4.0 × 10^4</td>
</tr>
<tr>
<td>305</td>
<td>92.48</td>
<td>3.6 × 10^4</td>
</tr>
</tbody>
</table>

* Conditions: current, 200 mA; [AN], 1.21 mol dm^-3; [H_2SO_4], 0.5 mol dm^-3; [DMG], 0.01 mol dm^-3; [methanol] 18% (v/v); electrolysis time, 60 min.
Kinetics of polymerization

The polymerization kinetic studies were carried out with different currents, monomer concentrations and solvents at 300 K and the results are presented in Figs 1–3 and Tables 4–6.

Table 4. Effect of current on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>Polymer yield (%)</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>61.95</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>200</td>
<td>78.95</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>250</td>
<td>91.86</td>
<td>$3.8 \times 10^6$</td>
</tr>
<tr>
<td>300</td>
<td>71.46</td>
<td>$3.2 \times 10^6$</td>
</tr>
<tr>
<td>400</td>
<td>63.95</td>
<td>$2.5 \times 10^6$</td>
</tr>
</tbody>
</table>

*Conditions: temperature, 300 K; [AN], 1.21 mol dm$^{-3}$; [H$_2$SO$_4$], 0.5 mol dm$^{-3}$; [DMG], 0.01 mol dm$^{-3}$; [Ti(IV)], 0.03 mol dm$^{-3}$; [methanol], 18% (v/v); electrolysis time, 60 min.

Table 5. Effect of acrylonitrile concentration on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile

<table>
<thead>
<tr>
<th>[AN] (mol dm$^{-3}$)</th>
<th>Polymer yield (%)</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>43.46</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>1.21</td>
<td>78.95</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>1.52</td>
<td>89.05</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>1.82</td>
<td>92.28</td>
<td>$4.0 \times 10^6$</td>
</tr>
<tr>
<td>2.12</td>
<td>74.82</td>
<td>$3.8 \times 10^6$</td>
</tr>
<tr>
<td>2.42</td>
<td>59.89</td>
<td>$3.7 \times 10^6$</td>
</tr>
</tbody>
</table>

*Conditions: temperature, 300 K; current, 200 mA; [H$_2$SO$_4$], 0.5 mol dm$^{-3}$; [DMG], 0.01 mol dm$^{-3}$; [Ti(IV)], 0.03 mol dm$^{-3}$; [methanol], 18% (v/v); electrolysis time, 60 min.
Table 6. Effect of solvent on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polymer yield (%)</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>78.95</td>
<td>4.0 x 10^6</td>
</tr>
<tr>
<td>Dimethyl sulphoxide</td>
<td>68.30</td>
<td>3.6 x 10^6</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>83.21</td>
<td>4.7 x 10^6</td>
</tr>
<tr>
<td>Mixture of methanol and carbon tetrachloride</td>
<td>30.30</td>
<td>2.0 x 10^5</td>
</tr>
</tbody>
</table>

*Conditions: temperature, 300 K; current, 200mA; [H_2SO_4], 0.5 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; (methanol), 18% (v/v); electrolysis time, 60 min.

Factors influencing polymer yield

**Effect of cathode current.** The effect of variations in titanium(IV) sulphate concentration, electric current, temperature and sulphuric acid concentration on the current efficiency for the generation of titanium(III) was studied by Narasimhan et al. The current efficiency was found to decrease with increase in current or concentration of titanium(IV) sulphate. Also, the current efficiency was found to increase with increase in sulphuric acid concentration or temperature.

It was found that the polymer yield increases with increase in cathode current in the range 150-250 mA. However, when the cathode current exceeds 250 mA, the polymer yield decreases (Fig. 1). This can be explained as follows. As already stated, the current efficiency for the generation of titanium(III) decreases with increase in current. Consequently, the reduction of dimethylglyoxime becomes slower and there will be a slow and steady generation of free radicals. Hence the polymer yield increases.

However, at higher current levels (250-400 mA), the apparent decrease in current efficiency can be due to the depletion of the monomer at the cathode-catholyte interface, and also due to hydrogen production, as shown in some early studies.

**Effect of monomer concentration.** The polymer yield increases with increase in monomer concentration in the range 0.91-1.82 mol dm^{-3}. However, it decreases when the monomer concentration exceeds 1.82 mol dm^{-3}. This deviation may be due to an increase in the viscosity of the medium and a consequent decrease in the mobility of the propagating species.

**Effect of dimethylglyoxime concentration.** The polymer yield decreases with an increase in the concentration of dimethylglyoxime. This is because an increase in dimethylglyoxime concentration results in an increase in the rate of its reduction and there will be a local over-concentration of the free radicals in the vicinity of the electrode surface. This situation favours chain initiation and chain termination. Consequently, the polymer yield decreases.

**Effect of titanium(IV) sulphate concentration.** The polymer yield increases with increase in titanium(IV) sulphate concentration in the range 0.015-0.04 mol dm^{-3}. However, the yield decreases if the titanium(IV)sulphate concentration exceeds 0.04 mol dm^{-3}. This may be due to the steady generation of free radicals in the range 0.015-0.04 mol dm^{-3}. This situation favours chain propagation and hence the polymer yield gradually increases. However, beyond a certain optimum concentration of titanium(IV) sulphate (>0.04 mol dm^{-3}) the titanium(III) generated will be of low concentration and the free radicals generated by the reduction of dimethylglyoxime will also be of lower concentration. Consequently, the polymer yield gradually decreases.

**Effect of temperature.** The current efficiency for the generation of titanium(III) increases with increase in temperature. Also, the reaction rate of titanium(III) reduction of dimethylglyoxime has been shown to be temperature dependent. There will be slow and steady generation of free radicals, hence the polymer yield gradually increases in the temperature range 293-305 K. However, above 305 K, the reduction reaction becomes very fast, resulting in a local over-concentration of free radicals near the electrode surface. This situation favours chain initiation and chain termination at the expense of chain propagation, hence the polymer yield decreases.

The activation energy (E_a) calculated from the Arrhenius plot of log(rate) vs 1/T in the temperature range 293-305 K was 36.35 ± 2 kJ mol^{-1}. The other activation parameters calculated from the Eyring plot are ΔH^* = 33.86 ± 2 kJ mol^{-1}, ΔG^* = 71.31 ± 0.6 kJ mol^{-1} and ΔS^* = -125.18 ± 6 J K^{-1} mol^{-1}. The relatively low energy of activation or enthalpy of activation and high negative entropy of activation observed are characteristic of a free radical polymerization process.

**Effect of sulphuric acid concentration.** The current efficiency for the generation of titanium(III) sulphate and also the rate of titanium(III) reduction of dimethylglyoxime increase with increase in sulphuric acid concentration. This situation favours chain propagation. Hence the polymer yield increases in the range 0.3-0.6 mol dm^{-3} sulphuric acid. However, when the sulphuric acid concentration exceeds 0.6 mol dm^{-3}, the reduction reaction becomes so fast as to increase the production of free radicals to favour chain initiation and chain termination against chain propagation. Hence the polymer yield decreases at higher acid concentrations.

**Effect of solvent composition.** It was found that the polymer yield decreases when the percentage of methanol increases. This is due to retardation of the
Table 7. Effect of electrode material on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Polymer yield (%)</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>78.95</td>
<td>$4.0 \times 10^4$</td>
</tr>
<tr>
<td>Lead</td>
<td>70.38</td>
<td>$3.8 \times 10^4$</td>
</tr>
<tr>
<td>Graphite</td>
<td>62.06</td>
<td>$3.6 \times 10^4$</td>
</tr>
<tr>
<td>Platinum</td>
<td>59.29</td>
<td>$3.3 \times 10^4$</td>
</tr>
</tbody>
</table>

*Conditions: temperature, 300 K; current, 200 mA; $[\text{H}_2\text{SO}_4]$, 0.5 mol dm$^{-3}$; $[\text{Ti}^{IV}]$, 0.03 mol dm$^{-3}$; $[\text{DMG}]$, 0.01 mol dm$^{-3}$; [methanol], 18% (v/v); electrolysis time, 60 min.

The kinetics of the reduction of dimethylglyoxime by titanium(III) in aqueous sulphuric acid medium has recently been studied. The stoichiometry of the reduction of dimethylglyoxime by titanium(III) was found to be 1:8 according to

$$\text{C}_4\text{H}_4\text{N}_2\text{O}_2 + 8\text{Ti}^{3+} + 8\text{H}^+ \rightarrow \text{C}_4\text{H}_12\text{N}_2 + 8\text{Ti}^{4+} + 2\text{H}_2\text{O}$$

(1)

(butane-2,3-diamine)

The kinetic orders of the reactants were found from log (rate) versus log (concentration) plots. The order was found by varying the concentrations of dimethylglyoxime, titanium(III), sulphuric acid in turn while keeping the others constant. The kinetic orders with respect to dimethylglyoxime and titanium(III) was nearly unity and the order with respect to sulphuric acid was about 0.5.

In the absence of a free radical scavenger in the system, the titanium(III) reduction of dimethylglyoxime has been shown to follow Scheme 1.

Scheme 1

The protonated substrate SH$^+$ reacts with Ti$^{3+}$ in the slow step to give a free radical, R. This free radical further reacts with additional Ti$^{3+}$ ions in a fast step to give the product. By applying the steady-state approximation to the intermediate SH$^+$, the rate law was derived:

$$\text{rate} = \frac{K[S][\text{Ti}^{3+}][\text{H}^+]}{1 + K'[\text{H}^+]}$$

(2)
where the resultant substrate concentration, [S], is the difference between the initial, [S]₀, and protonated, [SH⁺], substrate concentration values, K is the equilibrium constant for the protonation step and k is the rate constant for the rate-determining step.

The kinetic scheme which accounts for the results obtained in the electrioinitiated polymerization system can be described by Scheme 2.

In Scheme 2, M is the monomer, acrylonitrile, \( k_e, k_d, k_i \)

\[
\text{Ti}^{3+} + \text{H} \rightarrow \text{Ti}^{4+} + \text{H}^+ \quad \text{(at the cathode)}
\]

\[ \text{Ti}^{3+} + \text{SH}^+ \rightarrow \text{Ti}^{4+} + \text{R}^* \]

\[ \text{R}^* + \text{M} \rightarrow \text{RM}^* \]

\[ \text{RM}^*_{(m-1)} + \text{M} \rightarrow \text{RM}^*_m \]

\[ \text{RM}^*_m + \text{RM}^*_n \rightarrow \text{RM}^*_{m+n} \]

\[ \text{RM}^*_m + \text{H} \rightarrow \text{RM}^*_m \text{H} \]

\[ \text{RM}^*_m + \text{XH} \rightarrow \text{RM}^*_m \text{H} + \text{X}^* \]

\[ \text{Scheme 2} \]

\( k_p, k_i, k_{tr} \) are the rate constants for the electrolysis, decomposition, initiation, propagation, termination and chain transfer steps, respectively, and \( \text{XH} \) is the chain transfer agent.

The rate of initiation is

\[ R_i = f_k d [\text{Ti}^{3+}][\text{SH}^+] \quad (3) \]

Substituting for \( [\text{Ti}^{3+}] \) with the product, \( k_e [\text{I}] \), leads to

\[ R_i = f_k d k_e [\text{I}][\text{SH}^+] \quad (4) \]

where \( [\text{I}] \) is the current in faraday per unit volume and \( f \) is the factor representing the fraction of the current which initiates chains.

Under steady-state conditions,

\[ R_i = R_t \quad (5) \]

If termination takes place by coupling,

\[ f_k d k_e [\text{I}][\text{SH}^+] = k_t [\text{M}]^2 \quad (6) \]

Rearrangement of Eqn. (6) gives

\[ [\text{M}] = \left( \frac{(f_k d k_e [\text{I}][\text{SH}^+])}{k_t} \right)^{1/2} \quad (7) \]

The rate of polymerization is given by

\[ R_p = k_p [\text{M}][\text{M}] \quad (8) \]

Substituting for \( [\text{M}] \) in Eqn. (8) gives

\[ R_p = k_p (f_k d k_e / k_t)^{1/2} [\text{I}]^{1/2} [\text{SH}^+]^{1/2} [\text{M}] \quad (9) \]

Replacing \( [\text{SH}^+] \) by \( K [\text{S}][\text{H}^+] \) leads to

\[ R_p = k^{1/2} k_p (f_k d k_e / k_t)^{1/2} [\text{I}]^{1/2} [\text{S}]^{1/2} [\text{H}^+]^{1/2} [\text{M}] \quad (10) \]

The dependence of the initial rate of polymerization \( R_p \) on \( [\text{I}]^{1/2}, [\text{S}]^{1/2}, [\text{H}^+]^{1/2} \) and \( [\text{M}] \), which was experimentally observed, is consistent with Scheme 2.

The kinetic chain length, \( \nu \), has the following dependence on the current and monomer concentration:

\[ \nu = R_p / R_i = k_p[M^*][M]/k_t[M^*]^2 \quad (11) \]

Substituting for \( R_p \) and \( R_i \) and on simplification, Eqn. (11) gives

\[ \nu = k_p[M]k_i/(f_k d k_e)^{1/2}[\text{I}]^{1/2}[\text{SH}^+]^{1/2} \quad (12) \]

**CONCLUSIONS**

This is a clear case of indirect electrochemical polymerization. It involves the electrolytic generation of a reactive species, \( \text{Ti}^{3+} \), which in turn reacts with a chemical initiator, dimethylglyoxime, present in the bulk of the solution to produce free radicals. Chain termination of the polymer is essentially by coupling. This provides an excellent means for the controlled initiation of polymerization reactions.

**Acknowledgements**

The authors thank the Department of Atomic Energy, Government of India, for the financial assistance.

**REFERENCES**


AQUEOUS POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY TITANIUM(III) – SALICYLALDOXIME REDOX SYSTEM: A KINETIC STUDY

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Key Words: Aqueous Polymerization, Kinetics, Cyclic Voltammetry, Methyl methacrylate, Titanium(III)-Salicylaldoxime Redox system.

ABSTRACT

The polymerization of methyl methacrylate initiated by the titanium(III) – salicylaldoxime redox system was studied in an aqueous sulfuric acid -ethanol medium in the temperature range of 20-30°C. The rates of polymerization were investigated at various concentrations of reductant, oxidant, ethanol, sulfuric acid and monomer. Cyclic voltammetric sensing of salicylaldoxime under the kinetic conditions demonstrated its reduction behavior. From the results obtained it was inferred that the polymerization reaction was initiated by an organic free radical arising from the titanium(III)-salicylaldoxime redox system and termination took place predominantly by mutual coupling and small fraction by chain transfer mechanism involving solvent molecules. The effects of some water–miscible organic solvents and surfactants on the rate of polymerization were investigated. The temperature dependence of the rate was studied and the activation parameters were computed using Arrhenius and Eyring plots. A suitable kinetic scheme has been proposed on the basis of experimental observations.

*Author to whom correspondence to be sent.
ELECTROINITIATED POLYMERISATION OF METHYL METHACRYLATE MEDIATED BY TITANIUM(III) - HYDROXYLAMINE REDOX SYSTEM: A KINETIC STUDY.

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ABSTRACT

Methyl methacrylate was polymerised in an aqueous sulphuric acid – methanol medium in a divided cell by an electrolytically generated mediator species titanium(III). Titanium(III)-hydroxylamine sulphate was used as the initiator redox system. The reaction was confined to the cathode compartment and was found to proceed via a free radical mechanism. Kinetics of polymerisation were investigated for different initial monomer concentrations, acid concentrations, electrical currents, dielectric constants of the solvent and electrode materials. Chain termination of the polymer was due to coupling of growing macroradicals, also a fraction of the termination took place by chain transfer mechanism involving the organic solvent molecules. A suitable mechanism for titanium(III) – hydroxylamine sulphate mediated indirect electropolymerisation of methyl methacrylate is proposed.

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