Polarographic Reduction of Zinc and Thorium in Furfuryl Mercaptan Media

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Polarographic reduction, furfuryl mercaptan, zinc, thorium

The reduction of Zn and Th in furfuryl mercaptan has been found to be irreversible and diffusion-controlled in 50% ethanolic media and 0.1 m NaClO₄. The values of kinetic parameters – transfer coefficient (α), formal rate constant (kφ), – for the electrode reactions were determined by Koutecky’s method as extended by Meites and Israeli. The values of ΔH, ΔG and ΔS have also been reported.

Experimental

Furfuryl mercaptan belongs to an important class of mercapto-compounds which have applications in biological, pharmaceutical and industrial fields. In these laboratories considerable work has been done on the polarographic behaviour of organosulphur compounds and their metal complexes. This investigation reports the polarographic reduction of zinc and thorium in presence of furfuryl mercaptan for which no reference could be traced in the literature.

Results and Discussion

The conventional log plots of the reduction waves of Zn(II) and Th(IV) in furfuryl mercaptan media were straight lines but their slopes were not agreeing with the theoretical values indicating the irreversible nature of the waves in both systems.

Effects of Hg-pressure, temperature, concentrations of FSH and metal ions

The constancy of iₕ/½ in each case and the values of temperature coefficients of iₕ (2.1 and 1.99% per degree for Zn and Th respectively) indicate the diffusion-controlled nature of the waves. The plots of iₕ versus temperature and h¹/₂ are shown in Figs 2, 3, 5, 6. The value of iₕ changes linearly with concentration of metal ion (0.2—2.0 mM for Zn and 0.08—0.6 mM for Th) (Figs 1 and 4) in presence of 8.0 mM FSH. With increase in [FSH], the E½ shifts towards more negative potential showing the complex formation between metal ions and ligand, whereas iₕ decreases indicating that the aquo-zinc and aquo-thorium ions differ in size from their complexes of FSH.

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Kinetic parameters

Since zinc and thorium reduce irreversibly in presence of FSH, it is considered expedient to determine the values of kinetic parameters—transfer coefficient (α) and formal rate constant ($K_{f,h}$)—for the electrode reaction by applying Koutecky’s theoretical treatment as extended by Meites and Israel which is based on the plot of $E_{d.e.}$ vs log $i/i_d$ and can be constructed as for a reversible wave.

The mathematical solution for an electrode reaction at d.m.e. controlled by the kinetics of the electron transfer is given by

$$\frac{i}{i_d} = F(X)$$  \hspace{1cm} (1)

where

$$X = \left(\frac{12}{7}\right)^{1/2} K_{f,h} \left(\frac{t}{D_0}\right)^{1/2}$$  \hspace{1cm} (2)

in which $t$ is the drop time, $D_0$ is the diffusion coefficient of electroactive substance, $K_{f,h}$ is the potential-dependent heterogeneous rate constant described by

$$K_{f,h} = K_{o,f,h} \exp \left(-\alpha n F E + 0.2412 \right)$$  \hspace{1cm} (3)

where $E$ is referred to S.C.E., $i$ and $i_d$ are the currents that actually flow at the end of the drop life at potential $E$ and on the plateau of the wave respectively.

From the values of $X$ and $F(X)$ given by Koutecky, Meites, and Israel found that log $X$ varied linearly with log $\frac{F(X)}{1-F(X)}$ explicitly,
\[
\log X = -0.0130 + 0.9163 \log \frac{F(X)}{1 - F(X)} \tag{4}
\]

Combination of Eqns (1) – (4) gives

\[
E_{d.e.} = 0.05915 \log \frac{1.349 K^o_{f,h} \theta}{D_0^{1/2}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i}
\]

which may be written as

\[
E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \tag{5}
\]

with

\[
E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349 K^o_{f,h} \theta}{D_0^{1/2}} \tag{6}
\]

The values of kinetic parameters for the present systems were calculated with the help of Eqns (5) and (6). The value of \(\alpha n\) was obtained by equating the slope of \(E_{d.e.}\) vs \(\log \frac{i}{i_d - i}\) plot to \(-\frac{0.0542}{\alpha n}\) and the intercept of the same plot (\(E_{1/2}\)) was used to calculate \(K^o_{f,h}\). The values of \(D_0^{1/2}\) were determined from Ilkovic equation. Since \(i_d\) does not vary appreciably over the range of potential covered by the rising part of the wave, it was considered unnecessary to apply the correction for drop-time 7.

Table I shows that the values of \(\alpha n\) and \(K^o_{f,h}\) are affected by the concentration of the ligand because of the change in \(E_{1/2}\) and \(i_d\). Increase in \(K^o_{f,h}\) with temperature indicates that the rate of electrode process for Zn–FSH and Th–FSH systems increases with temperature (Table II). Shift in halfwave potential towards more positive value shows the easier reduction of the complexes at higher temperatures and is in accordance with the irreversible nature of the electrode processes.

**Thermodynamic functions**

The enthalpy of activation (\(\Delta H\)) for the electrode reaction has been calculated by equating the slope of \(\log K^o_{f,h}\) vs \(1/H\) plot to \(\Delta H\) and found to be 30.40 and 42.62 kcal/mole for Zn and Th systems respectively.

The free energy of activation (\(\Delta G\)) can be determined by expliciting the value of \(K^o_{f,h}\) on the basis of general principles of the absolute rate theory according to which

\[
K^o_{f,h} = \frac{kT}{h} \varphi \exp \left[ -\frac{\Delta G}{RT} \right] \tag{7}
\]

where \(k =\) Boltzmann constant, \(h =\) Plank's constant, \(\varphi = 2.0 \cdot 10^{-8}\) cm and other terms have their usual meanings. From Eqn (7), the values of \(\Delta G\) for Zn and Th systems are found to be 22.24 and 34.00 kcal/mole respectively.

The entropy of activation (\(\Delta S\)) calculated from the relation

\[
\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}
\]

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<tr>
<th>[FSH] [mM]</th>
<th>(i_d [\mu A])</th>
<th>(-E_{1/2} [V])</th>
<th>(\alpha n)</th>
<th>(K^o_{f,h} [\text{cm/sec}])</th>
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<th>Temp [°C]</th>
<th>(i_d [\mu A])</th>
<th>(-E_{1/2} [V])</th>
<th>(\alpha n)</th>
<th>(K^o_{f,h} [\text{cm/sec}])</th>
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is 26.49 and 28.00 cal/mole/degree for Zn and Th respectively.

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