Polarographic Behaviour of 3-Mercapto-1,2-propanediol at d.m.e.

R. S. Saxena and Pratap Singh

Chemistry Department, Malaviya Regional Engineering College, Jaipur, India


The polarographic behaviour of 3-mercapto-1,2-propanediol (TSH) at the d.m.e. has been investigated in presence of 0.1 M NaClO₄ and 0.001% Triton X-100 with respect to the effects of changes in pH, concentration of TSH, drop time and temperature on the wave characteristics. A single well defined irreversible anodic wave was obtained over the entire pH range (1.84—12.3) which was found to shift towards the more negative potential with the increase in pH. The $E_{1/2}$ values obtained at different pH were used to evaluate the dissociation constant of sulphydryl group; the pK value has been found to be 9.25.

The linearity of $i_d$ with TSH concentration provides a rapid and precise method for the determination of TSH to 0.1 nmole. The values of Kinetic parameters-formal rate constant ($K_{b,h}$) and transfer coefficient ($a$) have been evaluated by applying Koutecky’s theoretical treatment as extended by Meites and Israel and were found to be $1.738 \times 10^{-4}$ cm/sec and 0.277 respectively.

Mercapto acids and other sulphhydryl compounds are very useful from analytical, biological and pharmaceutical point of view and, hence, the importance of this group of compounds has grown during the past few years. The polarographic behaviour of a number of such compounds viz. cysteine¹, cystine², thioglycollic acid³ and glutathione⁴ have been reported by Kolthoff and co-workers. Saxena and Gupta have studied the polarographic behaviour of thiomalic acid⁵ and β-mercapto propionic acid⁶. The literature reported so far is, however, silent on the polarographic behaviour of 3-mercapto-1,2-propanediol (CH₂OH), CH(OH)CH₂SH (referred to herein as TSH).

In view of the interesting results obtained by the earlier workers on the polarography of organo-sulphur compounds, it was considered worthwhile to undertake a detailed investigation of the electrochemical behaviour of 3-mercapto-1,2-propanediol at the d.m.e.

The present contribution describes the effect of changes in pH, concentration of TSH, drop time and temperature on the characteristics of the wave. The values of dissociation constant of sulphhydryl group (pK) and Kinetic parameters $-a$ and $K_{b,h}$ have also been evaluated.

---

1 I. M. Kolthoff and C. Barnum, J. Amer. chem. Soc. 62, 3061 [1940].
2 I. M. Kolthoff and C. Barnum, J. Amer. chem. Soc. 63, 520 [1941].
4 W. Stricks and I. M. Kolthoff, J. Amer. chem. Soc. 74, 4646 [1952].
6 R. S. Saxena and K. C. Gupta, Presented at the 6th Annual Convention of Indian Chemical Society held at Gujarat University, Ahmedabad in October 1968.
ly mixed solution was then transferred to the cell and the polarograms were recorded. Unless otherwise stated, the average current was recorded throughout the investigation. Half wave potentials were determined by the conventional logarithmic plots.

**Kinetic parameters:** For the calculation of Kinetic parameters a solution containing 1.0 mmole TSH in 0.1 M NaClO₄ and 0.001% Triton X-100 at pH 6.45 was polarographed (Fig. 4, curve 1). In this case the current at the end of the drop life was recorded instead of the average current because the determination of Kinetic parameters are based on the Koutecky's calculations which are more accurately reproduced by measuring the maximum current. The values of t were measured at different potentials on the rising portion of the wave such that i lies between 10 to 95% of i₈ which are the approximate limits of the validity of the equations employed for calculations.

**Results and Discussion**

Preliminary experiments showed that TSH produces an anodic wave at all the pH values in the region 1.84 — 12.3. The effects of the variation of pH, temperature, concentration of TSH and drop time have been studied with a view to recognise the characteristic of the wave. Conventional log plots showed that the anodic wave corresponds to an irreversible process and hence, it was found expedient to apply Koutecky's theoretical treatment as extended by Meites and Israel for evaluating the Kinetic parameters (transfer coefficient, α and Kₒ,b,h the formal rate constant). The dissociation constant of the sulphydryl group was determined by plotting E₁/₂ against pH.

**Effect of pH:** Polarograms of 1.0 mm TSH were taken in 0.1 M NaClO₄ and 0.001% Triton X-100 in aqueous media at different pH values using Clark and Lubs buffer mixtures (Fig. 1). TSH gave an anodic wave at all the pH values studied (pH 1.84 — 12.3). It may be seen from Fig. 1, curve 1 that the reaction begins at a potential about 0.25 V and that no diffusion current region is established up to zero volt, although, a poorly defined diffusion current plateau is reached at positive potential. However, as the pH increases beyond pH 1.84, the diffusion current plateau becomes more defined even at negative potentials (Fig. 1, curve 1 — 6) and well defined regular waves were obtained between pH 6.45 — 12.3 (Fig. 1, curves 7 — 14). All the studies were, therefore, made at pH 6.45 on which TSH gave a very well defined anodic wave. The analysis of the waves at all pH values (1.84 — 12.3) showed that the plots of log (i₁ — i) as a function of Eₐ.d.e. are linear but the resulting slopes were not agreeing with the theoretical value indicating the irreversible nature of the electrode reaction. The half wave potential shifts to more negative values with the increase in pH and becomes constant beyond pH 9.25.

Fig. 2 shows the plot of pH vs. half wave potential obtained from the conventional log plots. It is seen that there are two linear portions in the plot whose intersection corresponds to pH 9.25. This indicates that under the condition of experiment, the H⁺ ion of sulphydryl group has pK = 9.25.

In unbuffered medium the wave due to TSH is very ill-defined (Fig. 3, curve 1). However, in 0.1 M HClO₄ and 0.1 M NaOH, TSH produces well defined irreversible anodic waves (Fig. 3, curves 2 — 3).

---

**Effect of TSH concentration**: Polarograms of solutions containing different concentrations of TSH (0.1 mM to 2.0 mM) at pH 6.45 were recorded and the diffusion current constant was calculated (Table 1).

<table>
<thead>
<tr>
<th>TSH concentration (mM)</th>
<th>$i_d$ after correction for $i_R$ ($\mu A$)</th>
<th>$i_d/C$</th>
<th>$I = i_d/C \cdot m^{1/3} \cdot t^{-1/3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>2.50</td>
<td>1.55</td>
</tr>
<tr>
<td>1.0</td>
<td>2.52</td>
<td>2.52</td>
<td>1.56</td>
</tr>
<tr>
<td>0.5</td>
<td>1.25</td>
<td>2.50</td>
<td>1.55</td>
</tr>
<tr>
<td>0.4</td>
<td>1.01</td>
<td>2.52</td>
<td>1.56</td>
</tr>
<tr>
<td>0.2</td>
<td>0.51</td>
<td>2.55</td>
<td>1.58</td>
</tr>
<tr>
<td>0.1</td>
<td>0.26</td>
<td>2.60</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Table 1. Test of linearity of wave height with TSH concentration.

It is evident from Table 1 that $i_d/C$ and $I$ are constant within experimental errors, which shows that $i_d$ varies linearly with TSH concentration. TSH can thus be determined polarographically in 0.1 mM NaClO$_4$ and 0.001% Triton X-100 at pH 6.45 down to 0.1 mMole.

**Effect of Hg pressure**: A solution of 1.0 mMole in TSH, pH 6.45 was polarographed at different heights of Hg column. Well defined anodic waves were obtained over the whole range (Table 2). The height of the waves decreases with increase in Hg pressure. The increase in $i_d/C$ and $I$ is due to decrease in the height of Hg reservoir.

<table>
<thead>
<tr>
<th>Hg pressure (cm)</th>
<th>$m$ (mg)</th>
<th>$t$ (s)</th>
<th>$m_t$ (mg)</th>
<th>$h_{ef}$ (cm)</th>
<th>$\sqrt{h_{ef}}$ (cm)</th>
<th>$i_d$ ($\mu A$)</th>
<th>$i_d$/$h_{ef}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1.104</td>
<td>3.94</td>
<td>4.349</td>
<td>42.023</td>
<td>6.528</td>
<td>2.32</td>
<td>0.355</td>
</tr>
<tr>
<td>50</td>
<td>1.232</td>
<td>3.53</td>
<td>4.348</td>
<td>47.623</td>
<td>6.901</td>
<td>2.42</td>
<td>0.350</td>
</tr>
<tr>
<td>55</td>
<td>1.338</td>
<td>3.25</td>
<td>4.347</td>
<td>52.623</td>
<td>7.254</td>
<td>2.53</td>
<td>0.348</td>
</tr>
<tr>
<td>60</td>
<td>1.450</td>
<td>2.98</td>
<td>4.348</td>
<td>57.623</td>
<td>7.591</td>
<td>2.61</td>
<td>0.344</td>
</tr>
<tr>
<td>65</td>
<td>1.587</td>
<td>2.74</td>
<td>4.348</td>
<td>62.623</td>
<td>7.912</td>
<td>2.69</td>
<td>0.341</td>
</tr>
</tbody>
</table>

Table 2. Effect of Hg pressure $h_{so}{cm}=6.5$ cm (= 0.477 cm of Hg). Back pressure = $3.1/(4.348)^{1/3}=1.90$.

**Kinetic parameters for TSH**: It has been discussed earlier that the wave due to TSH over the pH range (1.84 — 12.3) is irreversible in nature, since the plots of $E_{d.e.}$ as a function of $log i_d/i$ yielded straight lines but the resulting slopes were not agreeing with the theoretical values. KOUTECKY has given a rigorous theoretical treatment for such irreversible waves. It was, therefore, considered of interest to apply KOUTECKY’s treatment in a modified form to determine the Kinetic parameters.

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

$$\frac{i/i_d}{F(X)}, \quad (1)$$

where $X = \left( \frac{12}{7} \right)^{1/3} K_{f,h} D_5^{1/5}$, (2)

in which $t$ is droptime, $D$ is diffusion coefficient of electroactive substance, $K_{f,h}$ is the potential dependent on the heterogeneous rate constant described by

$$K_{f,h} = K_0 f_h \exp[-a nF(E-0.2412)/RT], \quad (3)$$

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

From the values of $i/i_d$ at various selected potentials, the corresponding values of function $X$ may be obtained from the original tables of KOUTECKY. Plotting $log X$ vs $E_{d.e.}$, then permits values for both
\( K^{0\text{f}, h} \) and \( a_n \) to be secured. For this purpose it is convenient to combine preceeding equations into

\[
\log_{10} X = \log_{10} \left( \frac{12}{7} \right)^{\frac{1}{2}} \frac{K^{0\text{f}, h} i^{1/2}}{D^2_n} - \frac{a_n F}{2\cdot303 RT} . \tag{4}
\]

Thus a plot of \( \log X \) vs \( E_{\text{d.e.}} \) shall be linear, by extrapolating it to \( E = 0 \) (vs. S.C.E.), the value of \( K^{0\text{f}, h} \) can be obtained. Meanwhile \( a_n \) is obtained from the slope of the line.

The amount of labour involved in this process is excessive. Mettes and Israel \(^9\) have shown that the labour can be considerably decreased by taking advantage of the fact that, for values of \( i/i_d \) between 0.1 to 0.95, Koutecky’s values for \( X \) and \( i/i_d \) corresponded to a linear relationship between \( \log X \) and \( i/i_d \). In this way the equation of a totally irreversible wave becomes at 25°C:

\[
E_{\text{d.e.}} + 0.2412 = \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{f}, h} i^{1/2}}{D^2_n} - \frac{0.0542}{a_n} \log i \tag{5}
\]

which may be written as:

\[
E_{\text{d.e.}} = E_{1/2} - \frac{0.0542}{a_n} \log i \tag{6}
\]

with

\[
E_{1/2} = -0.2412 + \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{f}, h} i^{1/2}}{D^2_n} . \tag{7}
\]

In this equation both \( E_{\text{d.e.}} \) and \( E_{1/2} \) are referred to S.C.E.

The variation of \( t \) with potential sometimes poses a problem in the use of these equations. For the waves in which \( t \) varies appreciably over the range of potentials covered by the rising part of the wave, the equation (5) has been written as:

\[
E_{\text{d.e.}} + 0.2412 = \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{f}, h} i^{1/2}}{D^2_n} - \frac{0.0542}{a_n} \log \frac{i}{i_d} - 0.546 \log t . \tag{8}
\]

It is clear from the above equation that plot of \( E_{\text{d.e.}} \) vs. \( \log \frac{i}{i_d} \) - 0.546 \( \log t \) has a slope of

\[
- \frac{0.0542}{a_n} \tag{9}
\]

and an intercept, where the quantity being plotted as abcissa is zero, which is equal to the parameter \( E^{0\text{f}, h} \), defined by the equation:

\[
E^{0\text{f}, h} = -0.2412 + \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{f}, h} i^{1/2}}{D^2_n} . \tag{9}
\]

The anodic wave obeys essentially identical equations which may be obtained from those given above by replacing \( a_n \) by \( -(1-a)n \) and \( K^{0\text{f}, h} \) by \( K^{0\text{b}, h} \). Hence for anodic waves, equations (8) and (9) can be written as:

\[
E_{\text{d.e.}} + 0.2412 = \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{b}, h} i^{1/2}}{D^2_n} - \frac{0.0542}{a_n} \log \frac{i}{i_d} - 0.546 \log t , \tag{10}
\]

and

\[
E^{0\text{f}, h} = -0.2412 - \frac{0.05915}{a_n} \log \frac{1.349 K^{0\text{b}, h} i^{1/2}}{D^2_n} . \tag{11}
\]

The Kinetic parameters have thus been calculated by employing the general equations (10) and (11). The value of \( (1-a)n \) was obtained by equating the slope 0.075 of the straight line plot \( E_{\text{d.e.}} \) vs \( \log \frac{i}{i_d} - 0.546 \log t \) (Fig. 4, curve 2) with

\[
\frac{0.0542}{(1-a)n} . \tag{12}
\]

The same plot gave the intercept \( E^{0\text{f}, h} = -0.324 \) which was used to calculate \( K^{0\text{b}, h} \).