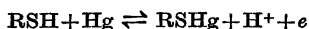


Polarography of β -Mercapto-Propionic Acid at the Dropping Mercury Electrode

R. S. Saxena and K. C. Gupta

The polarographic behaviour of β -Mercapto-propionic acid (RSH) at d.m.e. has been investigated in the presence of 0.1M KCl and 0.005% Triton X-100. The effect of pH, concentration of RSH, temperature and drop time on the wave characteristics and the mechanism of the reaction occurring at the surface of the mercury drop have been studied in detail. Variation in the H^+ ion concentration of the medium (between pH 2.50 to 7.90) had a negligible effect on the well defined reversible anodic wave of RSH; at lower (< 2.5) and higher (> 7.90) pH values, ill defined waves were obtained. The proportionality of wave height with RSH concentration, $\sqrt{h_{eff}}$, and temperature, and a linear plot of $E_{d.e.}$ Vs. $\log i_d - i/i$ with slope 0.061 indicate that the wave produced by RSH at d.m.e. is strictly diffusion controlled and reversible involving one electron transfer process. The current voltage curves over the pH range 1.30-7.90 have been found to obey the equation



Mathematical and experimental evidences are obtained to show that the anodic wave of RSH at d.m.e. does not correspond to the formation of di-mercapto-propionic acid (RSSR) but rather to the formation of a mercury compound RSHg in accordance with the above equation. The diffusion coefficient and the temperature coefficient of i_d for temperature range 30-60° at pH = 5.80, have been found to be 4.537×10^{-8} cm²/sec. and 1.04% per degree respectively. The linearity of ' i_d ' with RSH concentrations provides a rapid and precise method for the determination of RSH down to 0.20 mM.

Mercapto-acids and other sulphur containing compounds have a wide variety of applications varying from biological-pharmaceutical activity to analytical and other chemical uses, and therefore, the importance of this group of compounds has grown. The electro-chemical behaviour of number of such compounds like Cysteine⁽¹⁾, Cystine⁽²⁾, thioglycolic acid⁽³⁾, glutathione⁽⁴⁾, thiomalic acid⁽⁵⁾, diethyl dithiocarbamate⁽⁶⁾, etc., at the dropping mercury electrode, has been the subject of considerable investigations. There is hardly any reference in the literature regarding the study of the polarographic behaviour of β -mercapto-propionic acid (referred to herein as RSH) at the d.m.e. and hence the current study has been initiated. In the present communication, the interest has been focussed mainly on the mechanism of the reaction at d.m.e. and on the effect of the pH, temperature, drop time and concentration of RSH on the nature of the wave.

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E X P E R I M E N T A L

β -Mercapto-propionic acid (99.1%, Evan's Chemetics, Inc. N.Y.) and Anal-R (B.D.H.) reagents KCl, NaOH, HCl, Triton X-100, etc., were used and their solutions prepared in air-free conductivity water.

Polarographic curves were recorded manually by a Cambridge (general purpose) polarograph using a thermostated polarographic H cell. An external saturated calomel electrode connected to the cell by means of an agar bridge, served as a reference electrode. The capillary characteristics measured in 0.1M KCl at $E_{d.e} = -0.1$ volt and at a mercury height 75.0 cm., were $m = 1.4666$ mg/sec., $t = 3.87$ sec. and $m^{2/3}t^{1/6} = 1.616$ mg^{2/3} sec^{-1/2}. Dissolved air was removed from the solution by bubbling oxygen free nitrogen through the cell for 10 min. and passing it over the solution during electrolysis. The necessary correction was made for residual current in determining diffusion current data. 0.005% Triton X-100 was used as maximum suppressor and 0.1M KCl as supporting electrolyte.

The pH measurements were made on Cambridge bench pattern (null deflection type) pH meter. A general purpose glass electrode was used in conjunction with saturated calomel electrode.

R E S U L T S A N D D I S C U S S I O N

Preliminary experiments showed that RSH produces an anodic wave at all pH values in the region 1.30–11.30. The effect of the variation of pH, temperature, concentration of RSH and drop time has been studied with a view to establishing the characteristics of the wave. In order to determine the mechanism of the reaction taking place at the drop surface, the experiments consisting of electrolysis of RSH in well buffered medium and the polarographic analysis of the electrolysed solution were carried out.

Effect of pH: Figure 1 illustrates the polarograms of the solution 1.0 mM in RSH in Clark and Lubs⁽⁷⁾ buffer solutions of different pH values. It may be seen from Fig. 1, curve 1, that the reaction begins at a potential of about -0.15 volt and that no diffusion current region was established. However, as the pH increases, the diffusion current plateau becomes more defined (curves, 2–4) within the negative potentials and a very well defined anodic wave is obtained at pH 5.80 (curve 5). All subsequent studies were therefore, made at pH 5.80 in Clark and Lubs buffer. It is observed that with the increase in pH, the anodic waves start at more negative potentials and level off to give almost constant diffusion current upto pH = 5.80. Above this pH, the wave height decreases with the increase in pH upto 7.90 and almost vanishes at higher pH. The half wave potential of the wave shifts to more negative values with the increase in pH. It may be noted that beyond pH 7.90, the waves show an irregular behaviour (curves 8–10) which can be attributed to the formation of a film of mercury compound of RSH around the drop which prevents further interaction of RSH and the drop. The behaviour of the wave below pH 7.90 is normal which may be ascribed to the fact that the film of the mercury compound of RSH may be soluble in this pH range. The reversibility of the electrode reaction was tested by plotting $\log i_d - i/i$ Vs $-E_{d.e}$. The plot yielded a straight line with the slope 0.060 ± 0.004 over the pH range 1.30–7.90, indicating one electron transfer process.

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Electrocapillary curves : Electrocapillary curves (drop time against applied potential) were obtained in Clark and Lubs buffer of pH 8.40 and in $0.1M$ KCl in the absence and presence of RSH (Fig. 4). A comparison of the curves 1 and 2 indicates that in the presence of $10^{-3}M$ RSH, there is a decrease in drop time of the d.m.e. The depression occurs at a potential range where the anodic RSH wave is observed, indicating that the product of anodic reaction is adsorbed on the drop surface resulting in the decrease in droptime. The electrocapillary curves obtained in 75% ethyl-alcohol were almost similar in shape to those obtained in aqueous solution (curves 3 and 4, Fig. 4). Electrocapillary curves of diethyl dithiocarbamate solution reported by Strick's and Coworker⁽⁶⁾ exhibit similar behaviour, although in the present case, the effect of suppressing the surface tension at the mercury drop is smaller than that observed with diethyl dithiocarbamate. Apparently, the suppression of surface tension at the drop surface indicates that the reaction product is adsorbed in the form of a thin film but the adsorption is not strong enough to give a pre-wave⁽⁶⁾.

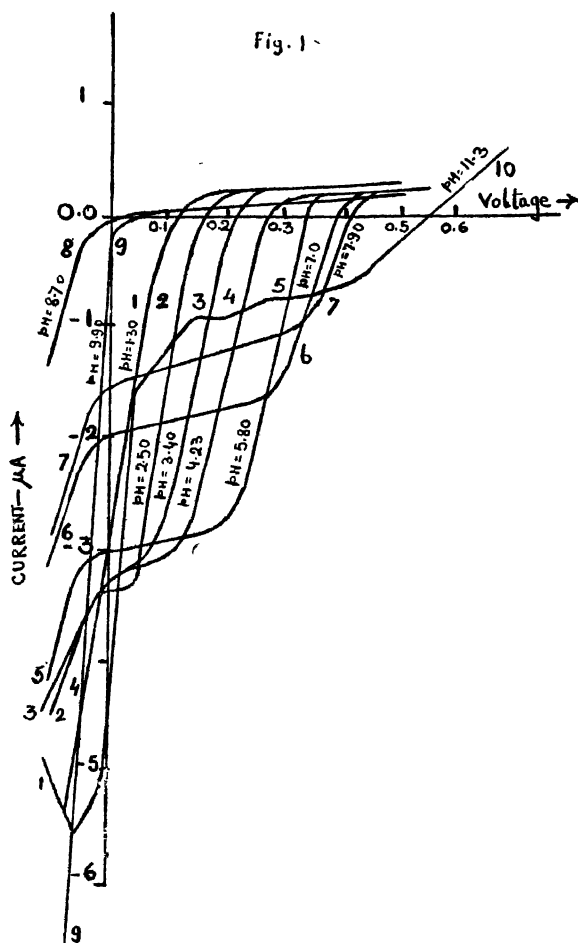


Figure-1. Polarograms of 1.0 mM RSH at different pH values.

Effect of RSH concentration: Polarograms of solutions containing different concentrations of RSH (0.2–2.0 mM) at pH 5.80 were drawn and the values of diffusion current constant were calculated (Table I). The diffusion coefficient at pH 5.80 and at 30° calculated by Ilkovic equation was found to be 4.537×10^{-6} cm²/sec.

TABLE I

Test for the linearity of wave height with RSH concentration

Concentration of RSH (mM)	' i_a ' after correction for ' i_r ' (μA)	i_a/C	$I = i_a/C.m^{2/3}t^{1/6}$
2.00	4.30	2.15	1.330
1.33	2.80	2.105	1.302
1.00	2.10	2.10	1.297
0.66	1.39	2.10	1.297
0.50	1.05	2.10	1.297
0.20	0.40	2.00	1.237

$$D = 4.537 \times 10^{-6} \text{ cm}^2/\text{sec.} \quad \text{Mean } I = 1.293$$

It is evident from the above table that the values of ' i_a/C ' and ' I ' are constant within the experimental errors, which clearly show that ' i_a ' is strictly proportional to the RSH concentration. RSH can, therefore, be determined polarographically in 0.1M KCl and 0.005% Triton X-100 at pH 5.80.

Effect of drop time: A series of polarograms of the solution 1.0 mM in RSH (pH = 5.80) were drawn at different heights of the mercury column. Well defined anodic waves were obtained over the whole range of the heights investigated. Table II shows the data secured:

TABLE II

Effect of drop time—

$$h_{s,m.} = 2.5 \text{ cm (} = 0.184 \text{ cm. of Hg)}$$

$$\text{Back pressure} = \frac{3.1}{(mt)^{1/3}} = \frac{3.1}{(5.636)^{1/3}} = 1.742$$

h Hg. cm.	m mg/sec.	t sec.	mt mg	h_{eff} cm.	$\sqrt{h_{eff}}$ cm.	i_a	$i_a/\sqrt{h_{eff}}$
55.0	0.9837	5.37	5.640	53.074	7.285	1.95	0.268
60.0	1.116	5.05	5.639	58.074	7.619	2.06	0.270
65.0	1.2404	4.54	5.637	63.074	7.941	2.16	0.272
70.0	1.350	4.17	5.631	68.074	8.249	2.26	0.274
75.0	1.466	3.87	5.633	73.074	8.545	2.35	0.275
80.0	1.57	3.59	5.636	78.074	8.833	2.44	0.276

$$\text{Mean} = 5.636$$

$$\text{Mean} = 0.272$$

which depicts the constancy of $i_a/\sqrt{h_{eff}}$ and hence the diffusion controlled nature of the anodic wave.

Effect of temperature : A solution 1.0 mM in RSH ($pH = 5.80$) was polarographed at various temperatures ranging from 30.0–60.0°. The values of the temperature coefficients of ' i_d ' for each temperature interval was calculated by using Nejedly's method⁽⁸⁾ and are tabulated below.

TABLE III

Effect of the variation of temperature on the wave characteristics

Temperature (°C)	i_d	Ratios of i_d at the indicated temperature to i_d at 30°C.	Temperature coefficient (% per °C)	$E_{1/2}$
30.0	1.98	1.0	—	0.28
35.0	2.09	1.055	1.10	0.28
40.0	2.18	1.101	1.01	0.28
45.0	2.29	1.156	1.04	0.28
50.0	2.38	1.201	1.005	0.28
55.0	2.50	1.263	1.052	0.28
60.0	2.60	1.313	1.043	0.28
Mean =			1.041	

The linearity of ' i_d ' with temperature and constancy of temperature coefficient of i_d at all temperature levels reveal that the height of the anodic wave is solely controlled by the diffusion factor. The constant value of $E_{1/2}$ at all temperatures indicates that the reaction taking place at the drop surface is thermodynamically reversible.

Mechanism of the anodic reaction : It is evident from the experimental data that the anodic wave produced by RSH is due to a reversible, diffusion controlled and one electron transfer process at the drop surface. From the mathematical analysis of the waves at d.m.e., it should be possible to get an indication of the mechanism of the anodic reaction. If the reaction at d.m.e. is due to the oxidation of RSH to di-mercapto-propionic acid (RSSR) and reaction was reversible



then the potential at every point on the wave should be given by the equation

$$E_{d.e.} = \text{Const.} + \frac{RT}{F} \ln [\text{H}^+]_0 + \frac{RT}{2F} \ln \frac{[\text{RSSR}]_0}{[\text{RSH}]_0^2} \quad \dots (2)$$

which can be written as

$$E_{d.e.} = \text{Const.} + \frac{RT}{F} \ln [\text{H}^+]_0 + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^2} \quad \dots (3)$$

At constant pH and at 25°

$$E_{d.e.} = \text{Const.} - \frac{0.059}{2} \log \frac{(i_d - i)^2}{i} \quad \dots (4)$$

The other possible explanation for the mechanism of the anodic wave produced by RSH at d.m.e., may be the oxidation of RSH with intermediate formation of a free radical and the anodic dissolution of mercury resulting into the formation of mercury-RSH complex, expressed as follows



and



Both the reactions (5) and (7) involve one electron transfer process. Potential at any point on the wave occurring as a result of these reactions is given by

$$E_{d.e.} = E_{1/2} - 0.059 \log (i_d - i/i) \quad \dots (8)$$

Now if equation (4) describes the wave, then a plot of $E_{d.e.}$ Vs $\log (i_d - i)^2/i$ should yield a straight line with a slope of $0.059/2$, which is not found in the present case (Fig. 2, curve 2). On the other hand, if equation (8) determines the wave, the plot of $E_{d.e.}$ vs. $\log i_d - i/i$ should yield a straight line with a slope 0.059 , which has been found to be true (see fig. 2, curve 1). The calculated slope value is 0.060 . Further more it was found that the half wave potentials were independent of RSH concentrations. This constancy of half wave potential is the characteristic of eq. (8) and not that of equation (4). These analyses indicate that the anodic reaction of RSH at d.m.e. occurs either according to equation (5) and (6) or by the formation of mercury-RSH_g compound (equation 7).

Fig. 2

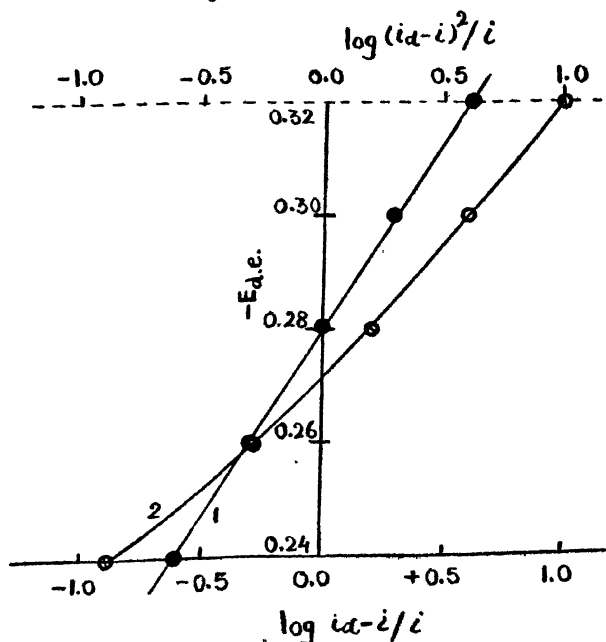


Figure-2. Plots of $-E_{d.e.}$ Vs. $\log i_d - i/i$ (curve-1) and $-E_{d.e.}$ Vs. $\log (i_d - i)^2/i$ (curve-2).

In order to arrive at a definite reaction mechanism, a solution of RSH (1.0 mM at pH 5.80) was electrolysed at +0.2 volts (Vs. pool dectrode) on a large mercury pool electrode in complete inert atmosphere for seven hours. A portion of electrolysed solution was then polarographed under identical conditions; a cathodic wave was obtained (Fig. 2, curve 1) which corresponds to the reversible one electron reduction process. On passing H_2S through another portion of the electrolysed solution, a slight black precipitate occurred showing the presence of mercury in the solution. Further when stationery platinum microelectrode was used, no anodic or cathodic wave was produced by RSH. This also shows that the mercury takes part in the electrode reaction. On the basis of these observations, the reaction mechanism indicated by equations 4, and 5 and 6 can be discarded. From the evidences obtained it can be concluded that the product of the anodic reaction of RSH at d.m.e. is a mercury compound of RSH.

With a view to obtain more conclusive evidences, the solutions containing (1) 1.0 mM RSH, (2) 1.0 mM RSH+0.5 mM $HgCl_2$, (3) 2.0 mM RSH+0.5 mM $HgCl_2$ (all at pH 5.80), were polarographed under identical conditions (Figure 3). It may be noted that the solution (2) yielded a well defined cathodic wave (Fig. 3, curve 3) corresponding to one electron reduction having $E_{1/2}$ similar to the anodic wave of RSH (Fig. 3, curve 2). The solution (3) produced a composite wave (Fig. 3, curve 4) which was found to have the same characteristics

Fig. 3

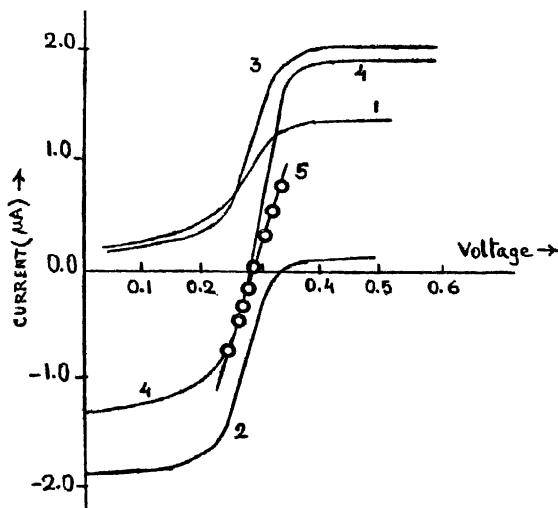


Figure-3. Comparative anodic-cathodic c-v curves of RSH and mercury-RSH compound at pH 5.80.

Curve-1. 1.0 mM in RSH. Electrolysed solution at large mercury pool electrode.

Curve-2. 1.0 mM in RSH.

Curve-3. 2.0 mM in RSH+0.5 mM in $HgCl_2$.

Curve-4. 2.0 mM in RSH+0.5 mM in $HgCl_2$.

Curve-5. Plot of $-E_{a.e.}$ Vs. $\log \frac{i-(i_d)_a}{(i_d)_c-i}$ for C-V curve no. 4.

as the anodic wave of solution (1) and cathodic wave of solution (2). The plot of $i-(i_d)_a/(i_d)_c-i$ for the composite wave yielded a straight line with a slope 0.059 (Fig. 3, curve 5).

These observations clearly indicate that the anodic reaction occurring at d.m.e. is solely due to the anodic dissolution of Hg compound with RSH.

The solution containing (1) HgCl_2 and RSH in equimolar ratio and (2) RSH solution saturated with Hg_2Cl_2 were also polarographed under similar conditions. It was striking to note that the $c-v$ curves for the first solution showed large diffusion current at zero applied potential, but the same value of slope and half-wave potential as that given by polarogram of solution (2), and thus indicating the reduction of same compound RSHg and the presence of free mercuric ions. These observations clearly reveal that the stable species of the mercury and RSH complex is $(\text{RS})_2\text{Hg}$, but the cathodic wave given by the complex is due to reduction of RSHg —an unstable compound.

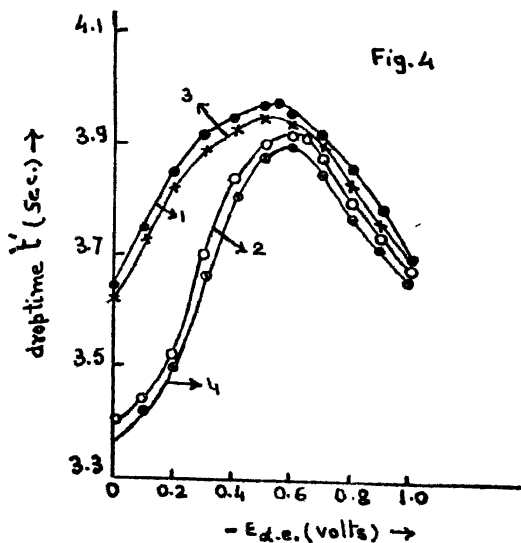


Figure-4. Electrocapillary curves in Clark and Lubs buffer of $\text{pH} = 8.40$.

- Curve-1. $0.1M$ in KNO_3 .
 Curve-2. $0.1M$ in $\text{KNO}_3 + 1.0 \text{ mM}$ in RSH.
 Curve-3. $0.1M$ in KNO_3 .
 Curve-4. $0.1M$ in $\text{KNO}_3 + 1.0 \text{ mM}$ in RSH.] in 75% ethanol.

The results of these investigations allow the conclusion that RSH is not being oxidised to RSSR at the d.m.e., but that it depolarises Hg with the formation of unstable RSHg . The reduction wave of $(\text{RS})_2\text{Hg}$ corresponds to the reduction of univalent cation. Hence the reaction can be best represented by the following mechanism



Apparently the reaction (10) is very rapid, the RSHg being the compound which is reduced.

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