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Polarographic Studies on o-Aminobenzenethiol

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With 4 Figures

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Polarographic behaviour of o-aminobenzenethiol (RSH) is studied at dme in 0.1*M*-$HClO_4$, 0.1*M*-NaOH, *Britton—Robinson* buffers of different pH values and aqueous acetic acid. A well defined single wave is obtained in 0.1*M*-$HClO_4$ and buffers of pH 2.0 at all concentrations of the depolarizer whereas in all the other buffers, a well defined single wave is obtained only if the concentration is less than $2 \times 10^{-4}M$. In other cases, two waves are observed. With the increase in pH, the $E_{1/2}$ becomes more negative and finally attains a constant value. Thus the dissociation constant of sulphydryl group under the experimental conditions is 5.14. The diffusion coefficient in buffer of pH 2.0 is calculated to be 5.76×10^{-6} using *Ilkovič* equation.

The reaction is reversible and the oxidation product is a mercurous compound (RSHg) which converts quickly to $(RS)_2Hg$. Even in acetic acid media, well defined reversible anodic wave is obtained in all proportions of acetic acid and water.

In continuation of the electrochemical investigations of mercaptans[1], the polarographic behaviour of o-aminobenzenethiol was studied at the dropping mercury electrode in aqueous and 10–100% acetic acid media.

Experimental Procedure

o-Aminobenzenethiol (Koch-Light, England) was purified by distillation at 125–127 °C/6 Torr. All the other chemicals used were of guaranted purity.

The solutions were prepared in air-free conductivity water. Fresh solution of o-aminobenzenethiol was used everyday and standardized as reported earlier[2]. Double strength *Britton—Robinson* buffers of different pH values were used.

Polarograms were recorded with Radelkis Polarograph Type OH 102 No. 3558 using a thermostated H type cell. The temperature was maintained at 25 ± 0.5 °C, except to study the effect of temperature. The pH measurements were made on Radelkis pH meter type OP 205 No. 3982 using glass and calomel electrodes. The capillary characteristics measured in $0.1M$-KNO_3 at $E_{d.e.} = 0.1$ V (vs. *SCE*) and at a mercury height of 66.0 cm were $m = 1.993$ mg sec^{-1}, $t = 4.40$ sec and $m^{2/3} t^{1/6} = 2.027$ mg$^{2/3}$ sec$^{-1/2}$.

Purified N_2 presaturated with the background solution to be polarographed was used for deaeration and an inert atmosphere was maintained over the solution during electrolysis. Necessary corrections were made in processing the diffusion current data.

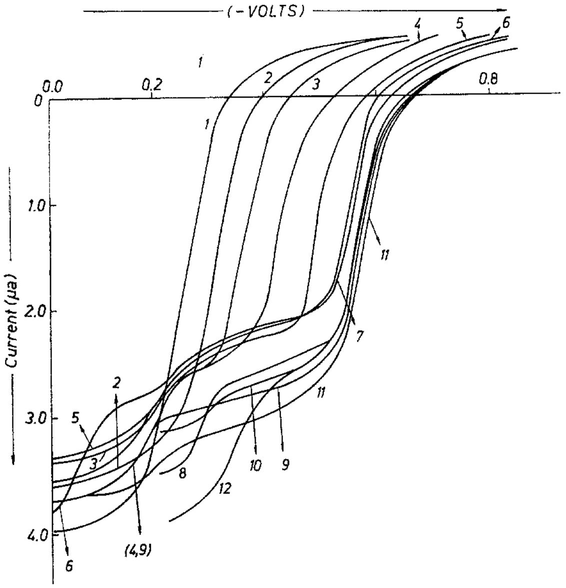

Fig. 1. Polarograms of $10^{-3}M$ o-aminobenzenethiol in different buffers. *1* $0.1M$-$HClO_4$, *2* pH 2.0, *3* pH 3.0, *4* pH 4.0, *5* pH 5.0, *6* pH 6.04, *7* pH 7.0, *8* pH 8.01, *9* pH 9.0, *10* pH 10.0, *11* pH 11.0, *12* pH 12.01

Potentiostatic electrolysis of a solution of RSH ($10^{-3}M$) in a buffer of pH 2.0 was carried out at a large Hg pool electrode using a large surface Pt electrode. In order to save time, a very slow stream of N_2 was passed through the solution so as to increase the rate of mass transfer of the depolarizer to the Hg electrode. Thus complete electrolysis was achieved in four hours.

Experimental Results and Discussion

o-Aminobenzenethiol (RSH) gives anodic waves in buffers of various pH values. The effect of pH, depolarizer concentration, mercury height (*h*), temperature and composition of the solvent on the wave are studied with a view to understanding the mechanism of anodic reaction at the electrode surface.

Effect of pH

Anodic waves of RSH ($10^{-3}M$) recorded in $0.1M$-$HClO_4$, $0.1M$-NaOH and *Britton—Robinson* buffers of different pH values (2.00–12.00), all containing $0.1M$-KNO_3, are shown in Fig. 1. Well defined single wave is obtained only in $0.1M$-$HClO_4$ and in a buffer of pH 2.0. With increase in pH, the anodic wave shifts to more negative potential indicating that the hydrogen ions are involved in the electrode reaction. The wave splits up into two waves at pH higher than 2.0. Polarograms of $10^{-3}M$-RSH recorded in *Lubs* and *McIlvaine* buffers of pH 2.0 and 6.0 show that the nature and the shape of the polarograms is dependent on the pH value but is independent of the constituents of the buffer. The concentration of KNO_3 (0.05 — $1M$) does not have any effect on the shape of the polarogram.

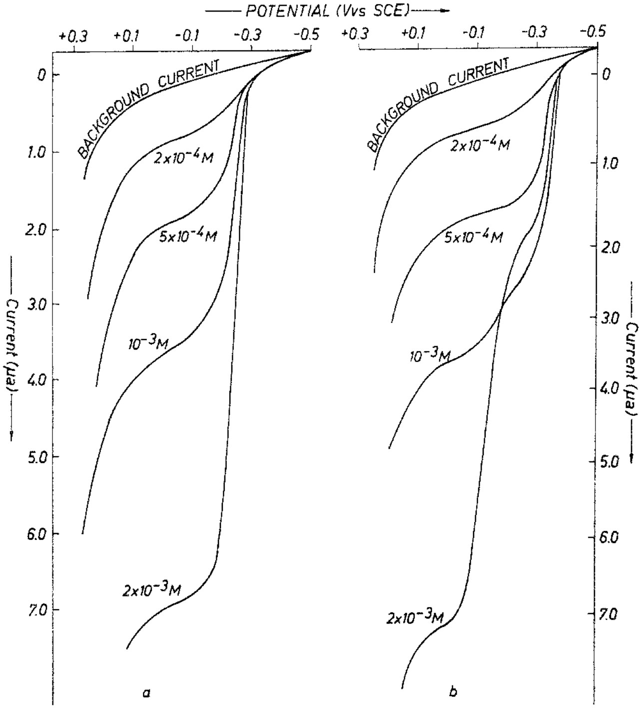

Fig. 2. Polarograms obtained for different concentrations of o-aminobenzenethiol in buffer of (*a*) pH 2.0, (*b*) pH 8.0

Effect of RSH Concentration

Polarograms of RSH in the concentration range from 2×10^{-5} to $2 \times 10^{-3}M$ are recorded in $0.1M$-$HClO_4$, $0.1M$-NaOH and *Britton—Robinson* buffers of different pH values. In $0.1M$-$HClO_4$ and in buffer of pH 2.0, only a single wave is observed at all concentrations of the depolarizer. The wave is well defined with well defined limiting diffusion current plateau followed by steep current rise (Fig. 2*a*) due to the dissolution of Hg at more positive potentials. The limiting height of the anodic wave varies directly with the concentration of the depolarizer. The half-wave potential is independent of the concentration indicating thereby the solubility of the reaction product and the reversibility of the electrode reaction.

Polarograms recorded in higher pH solutions show that a single anodic wave is obtained only at concentrations lower than $2 \times 10^{-4} M$, and its $E_{1/2}$ is independent of the concentration. At higher concentrations, the anodic wave splits up into more than one wave (Fig. 2*b*). The total limiting current in all the buffers is proportional to concentration in the range 10^{-5} to $10^{-3} M$. At higher concentrations, the limiting diffusion current is less than that expected for the linear relation. The non-linearity at higher concentrations and the splitting up of the waves may be caused by the partial insolubility of RSH in higher pH buffers. RSH gives a turbidity on addition to the different buffers if its concentration exceeds $2 \times 10^{-3} M$. Even at lower concentrations, the presence of undissolved RSH in the colloidal form cannot be ruled out. The half-wave potentials for all the steps in the split up waves increase with the concentration indicating the possible insolubility of the reaction product in these media. RSH can thus be conveniently estimated in $0.1 M$-KNO_3. The diffusion coefficient of RSH in a buffer of pH 2.0 calculated from *Ilkovič* equation is 5.76×10^{-6} cm^2 sec^{-1}.

Effect of Mercury Height (h_{corr})

The limiting height of the anodic wave (i_d) is proportional to $\sqrt{h_{\text{corr}}}$ (Table 1) indicating the diffusion controlled nature of the wave. The $E_{1/2}$ of the anodic wave is independent of the Hg height suggesting thereby, the reversibility of the reaction. At pH value higher than 2.0, the total limiting diffusion current (i_d') is proportional to $\sqrt{h_{\text{corr}}}$ (Table 1). It suggests the diffusion controlled nature of the overall anodic reaction. However, neither of the individual wave heights is proportional to the Hg height and thus none of these waves is an adsorption wave.

Effect of Temperature

Polarograms of $10^{-3} M$-RSH in a buffer of pH 2.0 are recorded at different temperatures (Table 2). It is observed that the average value of the temperature coefficient for RSH is 1.2% per °C. That the half-wave potential remains independent of the temperature is in keeping with the reversible nature of the electrode process.

Logarithmic Analysis of Waves

Plots of $-E_{d.e.}$ vs. $\log \frac{i_d - i}{i}$ and $\log \frac{(i_d - i)^2}{i}$ are plotted for the single wave obtained in $0.1 M$-$HClO_4$ and in pH 2.0 (Fig. 3). The plot of $-E_{d.e.}$ vs. $\log \frac{(i_d - i)^2}{i}$ does not yield a straight line but that of $-E_{d.e.}$

vs. log $\frac{i_d - i}{i}$ is a straight line with a slope of 60 mV, a value very close to the theoretical value of 59 mV for one electron reversible charge transfer at 25 °C. The electrode process is, therefore, reversible and involves only one electron change in these media. Similar plots for the single waves obtained in all the other buffers containing $2 \times 10^{-4} M$-RSH give straight lines with slope of 58–60 mV. Thus it is concluded that the electrode process is reversible and involves one electron change under these conditions. At higher concentrations of RSH in these buffers, $E_{d.e.}$ is not plotted against log $\frac{i_d - i}{i}$ since the multiple waves appear in these cases, where $E_{1/2}$ is a function of pH.

Table 1. *Effect of Mercury Height on the Wave Height of o-Aminobenzenethiol ($10^{-3}M$) in pH 2.0 and pH 5.0*
[$h_{\mathrm{soln}} = 3.00$ cm ($= 0.220$ cm of Hg);
back pressure $= \frac{3.1}{(1.993 \times 4.40)^{1/3}} = 1.503$]

h_{Hg}	h_{corr}	pH 2.0			pH 5.0	
		i_d	$\frac{i_d}{\sqrt{h_{\mathrm{corr}}}}$	$-E_{1/2}$ V(vs. SCE)	i_d	$\frac{i_d}{\sqrt{h_{\mathrm{corr}}}}$
76	74.277	3.02	0.350	0.295	2.74	0.318
70	68.277	2.91	0.352	0.295	2.66	0.322
65	63.277	2.79	0.350	0.295	2.55	0.318
60	58.277	2.66	0.346	0.295	2.44	0.320
55	53.277	2.56	0.351	0.295	2.34	0.320
50	48.277	2.42	0.348	0.295	2.22	0.319
45	43.277	2.29	0.348	0.295	2.12	0.322

Table 2. *Effect of Temperature on the Wave Characteristics of o-Aminobenzenethiol ($10^{-3}M$) in pH 2.0*

Temp., °C	i_d	Temp. coefficient, % per °C	$-E_{1/2}$ V (vs. SCE)
25	3.02	—	0.295
30	3.13	1.220	0.295
35	3.22	1.222	0.295
40	3.35	1.218	0.295
45	3.46	1.226	0.295
		Mean = 1.2215	

Mechanism of Anodic Reaction

The oxidation of RSH may be proposed to proceed according to one of the following equations:

$$2\,\mathrm{RSH} \rightarrow \mathrm{RSSR} + 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \qquad (1)$$

$$2\,\mathrm{RSH} \rightarrow \underset{\substack{\downarrow\\ \mathrm{RSSR}}}{2\,\mathrm{RS}} + 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \qquad (2)$$

$$\mathrm{RSH} + \mathrm{Hg} \rightleftharpoons \mathrm{RSHg} + \mathrm{H}^+ + \mathrm{e}^- \qquad (3)$$

Since a plot of $-E_{d.e.}$ vs. $\log \frac{(i_d - i)^2}{i}$ for polarograms in buffers of pH 2.0 and in $0.1M$-$HClO_4$ at all concentrations of RSH and in all other buffers at a concentration of $2 \times 10^{-4}M$ does not yield a straight line with a slope of 59/2 mV, it may be concluded that the reaction does not proceed through Eq. (1). That $E_{1/2}$ is independent of RSH concentration in a buffer of pH 2.0 and in $0.1M$-$HClO_4$ further rules out the possibility of reaction (1). On the other hand, a plot of $-E_{d.e.}$ vs. $\log \frac{i_d - i}{i}$ yields a straight line with a slope of 60 mV suggesting that the reaction proceeds through either Eq. (2) or (3).

In order to arrive at a definite reaction mechanism, a solution of RSH ($10^{-3}M$) in pH 2.0 is electrolyzed to completion at a large Hg pool electrode at a controlled potential of 0.0 V. The electrolysed solution gives only a single cathodic wave under similar conditions (Fig. 4ii) and corresponds to a reversible one electron process. A part of this solution gives black turbidity with hydrogen sulphide gas showing the presence of soluble Hg in the solution. To the other part, stock solution of the depolarizer is added so as to give approximately $2 \times 10^{-3}M$ concentration with respect to it and the resulting solution on being polarographed gives a composite wave (Fig. 4iii); the cathodic part due to the reduction of the oxidation product at the large Hg electrode and the anodic part because of the oxidation of RSH. The observations show that the reaction proceeds through the Eq. (3) since the product of oxidation at Hg pool is a soluble compound of Hg. The solubility of the reaction product is inferred from the observation that $E_{1/2}$ is independent of RSH concentration. The formation of a composite wave also supports the reversible nature of the electrode reaction.

With a view to obtain a conclusive evidence, solutions containing (a) $10^{-3}M$-RSH, (b) $10^{-3}M$-RSH, and $5 \times 10^{-4}M$-$HgCl_2$ as well as (c) $2 \times 10^{-3}M$-RSH and $5 \times 10^{-4}M$-$HgCl_2$ are polarographed under identical conditions. The solution (b) yields a well defined cathodic wave having the same characteristics as that obtained for the reduction of the oxidised product at *dme* (Fig. 4ii) and the solution (c) yields a composite wave similar to that in Fig. 4iii. This shows that the product of electrode reaction is a mercuric compound, and the Hg and RSH combine in the ratio 1 : 2 so that the ultimate product is $(RS)_2Hg$.

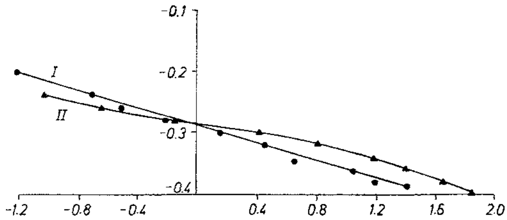

Fig. 3. Plots of $-E_{d.e.}$ vs. $\log (i - i_d)/i$ (Curve I) and $-E_{d.e.}$ vs. $\log (i_d - i)^2/i$ (Curve II)

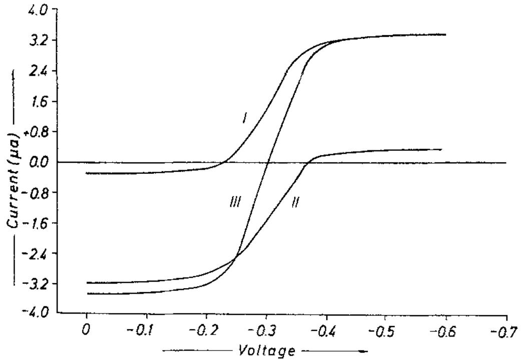

Fig. 4. Comparative anodic cathodic C—V curves of RSH and its oxidation product at mercury electrode in buffer of pH 2.0. Curve I: 1.0 mM RSH; electrolysed solution at large mercury pool electrode. Curve II: 1.0 mM RSH. Curve III: Solution of Curve I + 1.0 mM RSH

A $10^{-3}M$ solution of RSH is prepared in a buffer of pH 2.0 presaturated with Hg_2Cl_2. This solution on being polarographed after addition of required amount of KNO_3, gives a wave similar to the one given by solution (b), indicating that the species being reduced in both the cases is the same i.e. RSHg. The stable species of mercury and RSH complex is, therefore, $(RS)_2Hg$. However, the cathodic

Table 3. *Polarographic Data of Anodic Waves of o-Aminobenzenethiol in Aqueous Acetic Acid Mixtures*

Soln. of acetic acid	Concentration, c	i_d	$\frac{i_d}{c} \times 10^3$	$E_{1/2}$ V
10%	1×10^{-4}	0.301	3.01	— 0.390
	2×10^{-4}	0.600	3.00	— 0.390
	5×10^{-4}	1.510	3.01	— 0.390
	1×10^{-3}	3.000	3.00	— 0.390
	2×10^{-3}	5.960	2.98	— 0-390
20%	1×10^{-4}	0.28	2.80	— 0.395
	2×10^{-4}	0.56	2.80	— 0.395
	5×10^{-4}	1.39	2.78	— 0-390
	1×10^{-3}	2.78	2.78	— 0.390
	2×10^{-3}	5.56	2.78	— 0.390
30%	1×10^{-4}	0.26	2.61	— 0.405
	2×10^{-4}	0.52	2.60	— 0.400
	5×10^{-4}	1.30	2.60	— 0.400
	1×10^{-3}	2.60	2.60	— 0.400
	2×10^{-3}	5.16	2.58	— 0.400
40%	1×10^{-4}	0.252	2.52	— 0.415
	2×10^{-4}	0.500	2.50	— 0.410
	5×10^{-4}	1.250	2.50	— 0.410
	1×10^{-3}	2.500	2.50	— 0.410
	2×10^{-3}	5.000	2.50	— 0.410
50%	1×10^{-4}	0.248	2.48	— 0.415
	2×10^{-4}	0.598	2.49	— 0.415
	5×10^{-4}	1.240	2.48	— 0.415
	1×10^{-3}	2.480	2.48	— 0.415
	2×10^{-3}	4.920	2.46	— 0.415
60%	1×10^{-4}	0.233	2.33	— 0.390
	2×10^{-4}	0.462	2.31	— 0.395
	5×10^{-4}	1.150	2.30	— 0.390
	1×10^{-3}	2.300	2.30	— 0.390
	2×10^{-3}	4.600	2.30	— 0.390
70%	1×10^{-4}	0.226	2.26	— 0.384
	2×10^{-4}	0.448	2.24	— 0.385
	5×10^{-4}	1.126	2.25	— 0.385
	1×10^{-3}	2.240	2.24	— 0.380
	2×10^{-3}	4.480	2.24	— 0.385
80%	1×10^{-4}	0.210	2.10	— 0.375
	2×10^{-4}	0.424	2.12	— 0.370
	5×10^{-4}	1.050	2.10	— 0.370
	1×10^{-3}	2.100	2.10	— 0.370
	2×10^{-3}	4.180	2.09	— 0.370
90%	1×10^{-4}	0.201	2.01	— 0.370
	2×10^{-4}	0.402	2.01	— 0.375
	5×10^{-4}	1.000	2.00	— 0.375
	1×10^{-3}	2.000	2.00	— 0.375
	2×10^{-3}	3.960	1.98	— 0.370
100%	1×10^{-4}	0.180	1.80	— 0.370
	2×10^{-4}	0.360	1.80	— 0.375
	5×10^{-4}	0.900	1.80	— 0-375
	1×10^{-3}	1.800	1.80	— 0.370
	2×10^{-3}	3.600	1.80	— 0.370

wave is given by the reduction of RSHg, an unstable species which is immediately converted into $(RS)_2Hg$.

$$2\ \mathrm{RSHg} \rightleftharpoons (\mathrm{RS})_2\mathrm{Hg} + \mathrm{Hg} \qquad (4)$$

Apparently Eq. (4) is very rapid so that RSHg is the compound being reduced at the dropping mercury electrode.

Determination of the Polarographic Dissociation Constant

The half-wave potential of the single wave, obtained by plotting $-E_{d.e.}$ vs. $\log \frac{i_d - i}{i}$ for polarograms of $2 \times 10^{-4} M$ solutions in different buffers, on plotting against pH of the buffers gives two linear portions. The $E_{1/2}$ becomes more negative with increase in pH up to 5.15 indicating the formation of hydrogen ions in the electrode reaction. However, in more alkaline solutions than this, the $E_{1/2}$ remains constant indicating, thereby, that the hydrogen ions are no more evolved in electrode reaction in these media. The dissociation constant of SH group in RSH is, therefore, 5.14.

Polarographic Behaviour in Acetic Acid Media

Polarograms are recorded using different concentrations of RSH in aqueous mixtures of acetic acid containing $0.1 M$ sodium acetate as supporting electrolyte. Well defined single wave is obtained in all the media in the depolarizer concentration range from 10^{-5} to $2 \times 10^{-3} M$ (Table 3). In every solvent mixture the limiting current is proportional to the concentration of the depolarizer. The $E_{1/2}$ remains independent of the concentration. Any of the media containing $0.1 M$ sodium acetate may, therefore, be used for the estimation of RSH.

The $E_{1/2}$ of the anodic wave first increases with increase in acetic acid proportion until it is 50% after which a decrease is observed up to 80%. The $E_{1/2}$ is, however, independent of acetic acid concentration in media containing still higher proportions. That the i_d/c decreases with increase in acetic acid proportion may be attributed to the decrease in diffusion coefficient of RSH.

Plots of $E_{d.e.}$ vs. $\log \frac{i_d - i}{i}$ for the waves obtained in these media for $10^{-3} M$-RSH give straight lines with a slope of 58–62 mV indicating that the electrode process is reversible even in acetic acid media and involves one electron transfer.

Acknowledgement

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