Polarographic Behaviour of n-Butyl Thioglycolate

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With 1 Figure

The polarographic behaviour of n-butyl thioglycolate, [$HSCH_2OOC(C_4H_9)$] has been studied in 25% ethanol, $0.1M$-KNO_3 and 0.002% Triton X-100 in the pH range 1.96—11.84 at the d.m.e. The polarograms consist of two waves, a pre-wave of constant height followed by a normal anodic wave. The electrode reaction is reversible and diffusion controlled involving one electron transfer process. The maximum number of moles adsorbed per unit area is 1.30×10^{-9} mole/cm^2, i.e. 7.82×10^{14} molecules/cm^2, which corresponds to an area 12.84 Å per adsorbed molecule. The adsorption coefficient and molar adsorption energy have been calculated to be 43.4×10^4 and 142.8 kcal/mole respectively. The dissociation constant (pK) of the sulphydryl group is found to be 9.4.

Introduction

On account of the increased significance of the sulphur containing organic compounds in pharmaceutical and industrial fields, considerable interest regarding their electrochemical behaviour has been shown in the past two decades. Thus the polarography of ethane-1,2-dithiol[1], diisopropylaminoethane-thiol—hydrochloride[2], glycoldimercaptoace-tate[3] and mercaptofuran[4] etc., has been studied in these laboratories by *Saxena* et al. The present communication reports the polarographic behaviour of n-butyl thioglycolate in different buffers, viz. *Britton—Robinson, Clark* and *Lub*'s, *Michaelis*-borate, acetate and NH_3—NH_4Cl; and supporting electrolytes, viz. NaCl, KNO_3, KCl, $KClO_4$, $NaClO_4$, Li_2SO_4 for which there is no reference in the literature.

Experimental

n-Butyl thioglycolate (referred to herein as RSH) was obtained from Evan's Chemetics Inc., New York, and all other chemicals were A. R. (B.D.H.) quality. A manual polarograph, with scalamp galvanometer and

a SCE as reference electrode, was used for recording the polarograms. The capillary had the following characteristics in 25% ethanol, $0.1M$-KNO$_3$ and 0.002% Triton X-100 at — 0.30 V vs. SCE with h_{Hg} value being 50 cm, $m = 4.126$ mg/sec., $t = 2.23$ seconds; $m^{2/3} t^{1/6} = 2.940$ mg$^{2/3}$ sec$^{-1/2}$. Polarograms were recorded in an inert atmosphere of nitrogen at 28 ± 0.1 °C.

Results and Discussions

Effect of pH

The polarograms for RSH (1.0 mM) in 25% ethanol containing $0.1M$-KNO$_3$ and 0.002% Triton X-100 at different pH values using *Clark* and *Lub*'s buffers showed an anodic wave followed by a prewave at all pH values.

The plots of Log $(i_d - i)/i$ vs. $-E._{d.e.}$ were linear with a slope 0.05210 indicating the reversible electrode reaction involving one electron transfer process. With increase in pH, the $E_{1/2}$ of the anodic wave as well as of the prewave shifted towards more negative potential, according to the following equation[5]

$$E_{1/2} = \text{Const.} - \frac{2 \cdot 3\, RT}{n\, F} \text{pH}$$

The point of intersection of two linear portions of the plots of $E_{1/2}$ vs. pH corresponds to the dissociation constant of the sulphydryl group[6] (pK) and is found to be 9.4.

Several polarograms of RSH were drawn in the pH range (5—11) using different buffers viz. *Britton-Robinson*, *Clark* and *Lub*'s, *Michaelis*-borate, NH$_3$—NH$_4$Cl and acetate buffer, but the nature of the wave remained unaffected by the constituents of the buffers.

Effect of ethanol concentration. It was observed that the diffusion current decreased with the increase in ethanol concentration up to 40% beyond which it showed an increase, the nature of the wave, however, remained unchanged. This may be due to the change in diffusion coefficient D which depends on the viscosity of the solution[7].

Effect of RSH Conc., Drop Time and Temperature
(Fig. 1, Table 1)

The height of the prewave (i_p) varies linearly with RSH up to 0.4 mM beyond which it remains almost constant. The value $i_l + i_p = i_d$ is proportional to [RSH] and the mean value of diffusion current constant (I) and diffusion coefficient ($D_{1/2}$) are found to be 5.98 μA/mM and 2.06 μA/mM mg$^{2/3}$ sec$^{-1/2}$ resp.

For 1.0 mM-RSH, i_d is found to be proportional to $h_{\mathrm{eff}}^{1/2}$ while i_p varied linearly with h_{eff}. The values of $i_d/h_{\mathrm{eff}}^{1/2}$ are given in Table 1. The temperature coefficient for i_d is 0.8035% per degree. These observations substantiate the diffusion controlled nature of the wave.
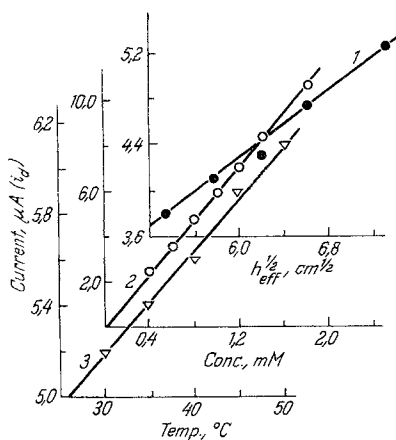

Fig. 1. Curve 1. Plot of i_d vs. $h_{\mathrm{eff}}^{1/2}$; Curve 2. Plot of i_d vs. RSH concentration; Curve 3. Plot of i_d vs. Temp.

Table 1. *Effect of Varying* [RSH], *Temperature and* Hg *Pressure on the Polarography of n-Butyl-Thioglycolate*

RSH mM/l	i_d/c	I	h_{Hg}, cm	h_{eff}, cm	i_d, μ A	$i_d/h_{\mathrm{eff}}^{1/2}$	Temp., °C	i_d	i_d(ambient)/ i_d (30 °C)	Temp. coeff., % per degree
0.2	8.5	2.892	25	23.43	3.6	0.7439	30	5.19	1.00	—
0.4	6.0	2.212	30	28.43	3.8	0.7131	35	5.40	1.04	0.7921
0.6	6.16	2.098	35	33.43	4.1	0.7094	40	5.60	1.07	0.760
0.8	6.12	2.084	40	38.43	4.3	0.6947	45	5.90	1.137	0.850
1.0	6.00	2.042	45	43.43	4.75	0.7197	50	6.10	1.175	0.8072
1.2	5.83	1.985	50	48.43	4.95	0.725	—	—	—	—
1.4	5.92	2.0180	55	53.43	5.25	0.7360	—	—	—	—

h_{soln} = 1.2 cm; back pressure = $3.1/(mt)^{1/3}$ = 1.480 cm of Hg

Effect of Supporting Electrolytes

i_d for 1.0 mM-RSH in 25% ethanol and 0.002% triton X-100 was measured at pH 4.28 using different supporting electrolytes of the concentration 0.1M. A well defined reversible anodic wave associated

with a prewave was observed in each case. The diffusion current constant (I) was found to increase in the following order.

$$KNO_3 > KCl > KClO_4 > NaClO_4 > NaCl > Li_2SO_4.$$

The values of I and $-E_{1/2}$ have been summarised in Table 2.

Table 2. *Effect of Supporting Electrolytes*

Supporting electrolyte	I	$-E_{1/2}$	Supporting electrolyte	I	$-E_{1/2}$
KNO$_3$	1.40	0.245	NaClO$_4$	1.279	0.240
KCl	1.347	0.250	NaCl	1.06	0.246
KClO$_4$	1.313	0.251	Li$_2$SO$_4$	0.976	0.250

Controlled-Potential Electrolysis

A solution of RSH (1.00 mM) containing 0.1M-KNO$_3$ and 0.002% Triton X-100 in 25% ethanol at pH 4.28 was electrolysed in an inert atmosphere for 5 hours at potential -0.10 V (corresponding to the limiting current). A portion of electrolysed solution was polarographed under identical conditions when it exhibited an anodic wave with decreased wave height. Absence of a composite wave indicates that the electrode reaction product is an insoluble compound of mercury. The $E_{1/2}$ of the main wave before electrolysis did not change after electrolysis for 2 hours, thereby indicating reversible nature of the wave[8].

Adsorption Prewave

A steep depression in E vs. t curves was obtained for 1.0 mM-RSH containing 0.1M-KNO$_3$ at pH 4.28 in the potential range where the prewave appeared, showing a strong adsorption of the electrolysis product at the d.m.e. *Brdička* gave the expression for the average limiting current, i_p, of the adsorption wave[5]

$$i_p = 0.85 \, nFZm^{2/3} t^{-1/3} \tag{1}$$

where i_p is expressed in amperes, Z is the maximum number of moles adsorbed per cm^2, m is the rate of mercury flow in mg/sec^{-1}, t is the drop time in seconds, and n and F have their usual notations. From eq. (1) the value of Z was calculated to be 1.30×10^{-9} or 7.82×10^{14} molecules/cm^2 which corresponds to an area 12.84 Å per adsorbed molecule.

Adsorption coefficient (ω) and molar adsorption energy (ϕ) were 43.4×10^4 and 142.8 kcal/mole resp. as evaluated from eqs. (2) and (3).

$$\omega = \frac{2}{C_a} \exp \frac{n \, \Delta \, E \, F}{RT} \tag{2}$$

$$\phi = n \, \Delta \, E \, F + RT \ln \frac{2}{C_a V} \tag{3}$$

where ΔE stands for the difference in $E_{\frac{1}{2}}$ of the prewave and main wave at the concentration C_a at which adsorption and diffusion currents are equal and V is the molar volume of the particles.

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