POLAROGRAPHIC STUDIES ON ELECTRODE KINETICS OF ANTIMONY IN FIVE DIFFERENT SUPPORTING ELECTROLYTES

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The reduction of trivalent antimony at the d.m.e. in (1) disodium tartrate + sodium hydroxide, (2) acetic acid + sodium acetate, (3) ammonium hydroxide + triammonium citrate, (4) disodium salt of EDTA, and (5) disodium tartrate solutions has been studied. The reduction is diffusion controlled and irreversible. The kinetic parameters have been calculated by Koutecky—Weber, Koutecky—Cizek, Delahay, and Oldham—Parry methods employed for average current. The effect of temperature on the kinetic parameters have been investigated. With the increase of temperature, irreversibility decreases. Solvation phenomena predicted on the basis of decreases in the value of radius, were calculated on the basis of Stoke's—Einstein relation, with the increase of temperature.

From the survey of literature[1–3] it was found that very little attention has been paid towards the electrode kinetics viz. heterogeneous rate constant ($k_{f,h}$) of the electrode process using various treatments for the determination of transfer coefficient (α) and energy of activation (ΔH^*) of antimony.

In the present investigation an attempt is made to determine (a) the nature of the waves (b) the formal rate constants at the SCE and (c) other thermodynamic functions of Sb^{3+} reduction in presence of (1) 0.25M disodium tartrate + 0.1M sodium hydroxide (pH = 11.5), (2) 0.85M acetic acid + 0.85M sodium acetate (pH = 4.4), (3) 1M ammonium hydroxide + 0.1M triammonium citrate (pH = 10), (4) 0.1M disodium salt of EDTA (pH = 6.2) and (5) 0.5M disodium tartrate (pH = 4) media at three different temperatures. In evaluation of formal rate constants, various treatments viz. Koutecky—Weber[4], Koutecky – Cizek[5], Delahay[6] and Oldham – Parry[7] employed for average currents, were used in order to decide appropriateness of any one treatment over the other and to show the validity of the values derived for formal rate constants of the systems in study. Thermodynamic parameters viz. enthalpy of activation (ΔHp^*), transfer coefficients (α), diffusion coefficients (D), and viscosity coefficients (η) are determined in order to throw some light on the size of the reduced species of Sb^{3+}.

Experimental

Chemicals, viz. antimony trichloride, disodium tartrate, sodium hydroxide, acetic acid, sodium acetate, ammonium hydroxide, triammonium citrate, disodium salt of EDTA and gelatin used in the work were of A.R. or G.R make. All polarographic solutions were prepared in doubly distilled air-free water.

Polarographic solutions viz. (1) 1.44 mM Sb^{3+} + 0.25M Na_2 tartrate + 0.1M NaOH (pH = 11.5), (2) 1.15 mM Sb^{3+} + 0.85M acetic acid + 0.85M sodium acetate (pH = 4.4), (3) 1.27 mM Sb^{3+} + 1M ammonium hydroxide + 0.1M ammonium citrate (pH = 10), (4) 1.62 mM Sb^{3+} + 0.1M disodium salt of EDTA (pH = 6.2) and (5) 1.49 mM Sb^{3+} + 0.5M disodium tartrate (pH = 4.0) were prepared for the investigation. In all the polarographic solutions 0.01% gelatin was added as supressor. Each solution was taken one after the other in clean dry H type cell. The current–voltage measurements of each solution was made (vs S.C.E.) after deaerating with oxygen-free nitrogen. The capillary constant of individual system is reported on the respective tables.

Average currents (i) vs applied votage (E) of the solution were noted for different heights of mercury head (h) in order to decide the type of the current. The current measurements of the solutions were also noted at the interval of 10°C. in the temperature range of 30° to 50°C. at some definite value of "h" when capillary constant $m^{2/3}\ t_1^{1/6}$ had the values as reported on the respective tables.

The number of electrons involved in the process of trivalent antimony in system 1 was determined as three by comparing i_d under identical conditions[8] with Pb^{2+} for which number of electrons involved in the electrode process is known[9]. Further, this is

also verified from the information available in the literature [10,11]. In systems 2, 3 and 4 the number of electrons involved in the electrode process was approximated as three taking into account the relation[12] $I/_{1\cdot6} = n$. In system 5, the number of electrons involved in the electrode process was found as three by comparing i_d of the system consisting of Bi^{3+}, for which number of electrons involved in the electrode process is known[13].

The viscosity coefficients of the solutions were determined. The heterogeneous rate constants ($k_{f,h}$) were calculated for each system at various temperatures using Koutecky—Weber[4], Koutecky—Cizek[5], Delahay[6] and Oldham—Parry[7] treatments. The values of formal rate constant, $k^\circ_{f,h}$ were determined for all the systems at the temperatures from log $k_{f,h}$ vs E plots extrapolated to potential of S.C.E. The enthalpy of activation ($\triangle H^*$) was calculated from the slope of the plots of log $k^\circ_{f,h}$ vs T^{-1} (i.e. $\triangle H^*_p$) and of log D vs T^{-1} (i.e. $\triangle H^*_D$)[13]. The heat of activation at constant volume was determined using the relation : $\triangle H^*_p = \triangle H^*_v + RT$. The activation free energy change $\triangle G^*$ was determined using relation

$$k^\circ_{f,h} = \frac{kT}{h}\,\gamma_o \exp\frac{-\triangle G^*}{RT},$$

where γ_o represents mean distance between two depolariser ions in the bulk solution and its value generally considered as 2×10^{-8}cm. The activation entropy was calculated using Helmholtz relation

$$\triangle S^* = \frac{\triangle H^*_v - \triangle G^*}{T}.$$

Transfer coefficients (α) of Sb^{3+} present in different systems were determined from traditional log plot, Oldham-Parry log plot and from the slope values of log $k_{f,h}$ vs E for all the temperatures. Assuming Stokes-Einstein law is obeyed for the systems studied, the approximate radius of the reduced species was calculated.

Results and Discussions

Plot of i_d vs $h^{1/2}$ is linear for each system. Temperature coefficients of i_d expressed in percent per degree are far below the value of 2% per degree. Both these results are indicative of diffusion controlled nature of the wave[14,15]. The values of diffusion coefficients and their temperature coefficients expressed in cm^2/sec and percent per degree of reducible species present in systems 1 to 5 are varying respectively from [4.20 to 7.78] $\times 10^{-6}$ and 2.86 to 2.56; [7.69 to 12.86] $\times 10^{-6}$ and 2.88 to 2.98; [6.52 to 10.39] $\times 10^{-6}$ and 2.69 to 2.55; [7.36 to 11.15] $\times 10^{-6}$ and 2.40 to 2.22; and [3.03 to 4 59] $\times 10^{-6}$ and 2.26 to 2.35 in the temperature range studied.

For all the systems polarograms were found of drawn out nature with a large slope value of the linear log plot than the value expected for reversible wave of three electron system. The values of α determined from traditional log plots in the temperature range studied are varying respectively from systems 1 to 5 as (1) 0 207 to 0 233, (2) 0.205 to 0 217, (3) 0.137 to 0.149, (4) 0.206 to 0.224, (5) 0.190 to 0.206 while in case of Oldham-Parry log plots they are varying as (1) 0.206 to 0.217 (2) 0.203 to 0.217, (3) 0.135 to 0.144, (4) 0.205 to 0.216, (5) 0.184 to 0.200.

The values of α determined from the slope of log $k_{f,h}$ vs E plots of different treatments for various systems are also within the range of the values derived from traditional log plots or from Oldham-Parry log plots. All these results suggest irreversible nature of the wave Further, it is concluded from the value of α that irreversibility decreases with rise in temperature and the irreversible nature is pronounced in systems (3) and (5) than the others. The values of $k^\circ_{f,h}$ and the thermodynamic functions viz. $\triangle H^*_p$, $\triangle H^*_v$, $\triangle G^*$, $\triangle S^*$, determined in different treatments for the systems in study consisting of Sb^{3+} are shown in tables 1—5. The values of $\triangle H^*_D$ are found respectively from system (1) to (5) as 4.70, 4.92, 4.72, 4.05 and 3.97. The diffusion current constants, the viscosity coefficients and the radious of the reduced species in the temp. range studied are found as under in the respective system.

System	I	(cP)	r(A°)
1.	3.73 to 4 74	0.925 to 0 650	5.74 to 5.36
2.	5 05 to 6 53	1.045 to 0.720	2.76 to 2.55
3.	4 65 to 5.67	0.876 to 0.590	3.88 to 3.87
4.	4.94 to 6.08	0.860 to 0 610	3.50 to 3.48
5.	3.17 to 3.90	0.980 to 0.710	7.47 to 7.25

Table 1 : Values of thermodynamic parameters of Sb^{3+} reduction in various treatments : $[Sb^{3+}]$: 1.44 mM : Supporting electrolyte : 0.25M Na_2 tartrate + 0.1M NaOH (pH = 11.5) Capillary constant, $m^{2/3} t_1^{1/6*} = 2.02\ mg^{2/3}\ sec^{-1/2}$.

Parameters	30°C.	40°C.	50°C.
Koutecky—Weber			
$k^\circ_{f,h} \times 10^{14}$	2.00	4.37	9.33
ΔH^*_p	.....	14.72	.....
ΔH^*_v	14.11	14.09	14.07
ΔG^*	26.24	26.64	27.02
ΔS^*	—40.01	—40.07	—40.07
Koutecky—Cizek			
$k^\circ_{f,h} \times 10^{14}$	1.74	3.75	7.94
ΔH^*_p	.....	15.10	.....
ΔH^*_v	14.49	14.47	14.45
ΔG^*	26.32	26.73	27.12
ΔS^*	—39.04	—39.16	—39.21
Delahay			
$k^\circ_{f,h} \times 10^{14}$	1.59	3.39	7.24
ΔH^*_p	.....	14.90	.....
ΔH^*_v	14.29	14.27	14.25
ΔG^*	26.38	26.79	27.18
ΔS^*	—39.88	—40.00	—40.02
Oldham—Parry			
$k^\circ_{f,h} \times 10^{14}$	1.82	3.98	8.71
ΔH^*_p	.....	15.27	.....
ΔH^*_v	14.66	14.64	14.62
ΔG^*	26.30	26.69	27.06
ΔS^*	—38.39	—38.50	—38.54

$E_{0.5}$ (From traditional log plots) — 1.310 — 1.290 — 1.270 V $E_{0.5}$ (From Oldham—Parry log plots) — 1.307 — 1.288 — 1.271 V. $*t_1$ = average drop time; $k^\circ_{f,h}$ in cm/sec; ΔH^*_p, ΔH^*_v and ΔG^* in k cal/mole; ΔS^* in e.v.

Table : 2 Values of thermodynamic parameters of Sb^{3+} reduction in various studied treatments; $[Sb^{3+}]$: 1.15 mM; Spporting electrolyte : 0.85M CH_3COOH + 0.85M CH_3COONa (pH = 4.4). Capillary constant = 2.05; units as in Table 1.

Parameters	30°C.	40°C.	50°C.
Koutecky - Weber			
$k^\circ_{f,h} \times 10^{7}$	12.59	21.38	36.31
ΔH^*_p	.....	10.30	.....
ΔH^*_v	9.69	9.67	9.65
ΔG^*	15.36	15.55	15.72
ΔS^* (e.u.)	—18.78	—18.79	—18.79
Koutecky—Cizek			
$k^\circ_{f,h} \times 10^{7}$	10.47	17.38	28.84
ΔH^*_p	.....	11'22	.....
ΔH^*_v	10.61	10.59	10.57
ΔG^*	15.47	15.68	15.87
ΔS^*	—16.95	—17.14	—17.26
Delahay			
$k^\circ_{f,h} \times 10^{7}$	7.94	13.80	23.99
ΔH^*_p	.....	10.67	.....
ΔH^*_v	10.06	10.04	10.02
ΔG^*	15.63	15.82	15.99
ΔS^*	—18.37	—18.45	—18.47
Oldham—Parry			
$k^\circ_{f,h} \times 10^{7}$	10.96	18.20	30.20
ΔH^*_p	.....	10.94	.....
ΔH^*_v	10.33	10.31	10 29
ΔG^*	15.44	15.65	15.84
ΔS^*	—16 87	—17.06	—17.18

$E_{0.5}$ (From traditional log plots) — 0.547 — 0.525 — 0.506 V. $E_{0.5}$ (From Oldham—Parry log plots) — 0.547 — 0.525 — 0.506 V.

Table 3 : Values of thermodynamic parameters of Sb^{3+} reduction in various studied treatments; [Sb^{+3}] : 1.27 mM; Supporting electrolyte : 1.0M NH_4OH + 0.1M $(NH_4)_3$ citrate (pH = 10). Capillary constant, = 2.00; units as in Table 1.

Parameters	30°C.	40°C.	50°C.
Koutecky - Weber			
$k^\circ_{f,h} \times 10^9$	4.57	9.12	17.00
ΔH^*_p	.....	12.42	.....
ΔH^*_v	11.81	11.79	11.77
ΔG^*	18.76	18.97	19.19
ΔS^*	—22.94	—22.94	—22.97
Koutecky—Cizek			
$k^\circ_{f,h} \times 10^9$	3.16	6.17	11.75
ΔH^*_p	.....	12.82	.....
ΔH^*_v	12.21	12.19	12.17
ΔG^*	18.98	19.21	19.43
ΔS^*	—22.34	—22.43	—22.48
Delahay			
$k^\circ_{f,h} \times 10^9$	2.19	4.20	7.90
ΔH^*_p	...	12.19	.....
ΔH^*_v	11.58	11.56	11.54
ΔG^*	19.21	19.45	19.69
ΔS^*	—25.18	—25.21	—25.23
Oldham—Parry			
$k^\circ_{f,h} \times 10^9$	3.72	7.08	13.80
ΔH^*_p	.....	12.88	.....
ΔH^*_v	12.27	12.25	12.23
ΔG^*	18.88	19.12	19.32
ΔS^*	—21.82	—21.95	—21.95

$E_{0.5}$ (From traditional log plots) — 1.040 — 1.015 — 0.980 V. $E_{0.5}$ (From Oldham—Parry log plots) — 1.040 — 1.014 — 0.980 V.

Table 4 Values of thermodynamic parameters of Sb^{3+} reduction in various studied treatments; [Sb^{3+}] : 1.62 mM; Supporting electrolyte : 0.1M Na_2EDTA (pH = 6.2). Capillarry constant, = 2.00; units as in Table 1.

Parameters	30°C.	40°C.	50°C.
Koutecky—Weber			
$k^\circ_{f,h} \times 10^{10}$	10.00	20.42	41.69
ΔH^*_p	.....	13.80	
ΔH^*_v	13.19	13.17	13.15
ΔG^*	19.68	19.90	20.10
ΔS^*	—21.42	—21.50	—21.52
Koutecky—Cizek			
$k^\circ_{f,h} \times 10^{10}$	8.32	17.38	36.31
ΔH^*_p	.....	14.33	.....
ΔH^*_v	13.74	13.72	13.70
ΔG^*	19.79	20.00	20.19
ΔS^*	—19.97	—20.06	—20.09
Delahay			
$k^\circ_{f,h} \times 10^{10}$	7.41	15.49	30.90
ΔH^*_p	.....	14.27	.....
ΔH^*_v	13.66	13.64	13.62
ΔG^*	19.86	20.08	20.29
ΔS^*	—20.46	—20.58	—20.65
Oldham—Parry			
$k^\circ_{f,h} \times 10^{10}$	9.12	19.05	38.90
ΔH^*_p	.....	13.98	.....
ΔH^*_v	13.37	13.35	13.33
ΔG^*	19.74	19.95	20.14
ΔS^*	—21.02	—21.09	—21.09

$E_{0.5}$ (From traditional log plots) — 0.849 — 0.825 — 0.801 V. $E_{0.5}$ (From Oldham—Parry log plots) — 0.848 — 0.824 — 0.802 V.

Table : 5 Values of thermodynamic parameters of Sb^{3+} reduction in various studied treatments; [Sb^{3+}] : 1.49 mM; Supporting electrolyte : 0.5M Na_2 tartrate (pH = 4). Capillary constant, = 2.20; units as in Table 1.

Parameters	30°C.	40°C.	50°C.
Koutecky—Weber			
$k^\circ_{f,h} \times 10^8$	9.55	18.62	34.64
ΔH^*_p	...	12.42	...
ΔH^*_v	11.81	11.79	11.77
ΔG^*	16.92	17.08	17.24
ΔS^*	—16.84	—16.88	—16.93
Koutecky—Cizek			
$k^\circ_{f,h} \times 10^8$	9.45	18.00	32.36
ΔH^*_p	.....	11.50	...
ΔH^*_v	10.89	10.87	10.85
ΔG^*	16.92	17.10	17.29
ΔS^*	—19.90	—19.90	—19.91
Delahay			
$k^\circ_{f,h} \times 10^8$	8.75	16.60	31.62
ΔH^*_p	...	11.96	...
ΔH^*_v	11.35	11.33	11.31
ΔG^*	16.97	17.14	17.30
ΔS^*	—18.54	—18.54	—18.54
Oldham—Parry			
$k^\circ_{f,h} \times 10^8$	9.12	16.98	30.20
ΔH^*_p	...	11.73	...
ΔH^*_v	11.12	11.10	11.08
ΔG^*	16.95	17.14	17.33
ΔS^*	—19.21	—19.27	—19.34

$E_{0.5}$ (From traditional log plots) — 0.6725 — 0.6475 — 0.6225 V. $E_{0.5}$ (From Oldham-Parry log plots) — 0.6725 — 0.6475 — 0.6225 V.

It is marked from tables 1—5 that the values of $k^\circ_{f,h}$ for each system in each treatment increase with temperature suggesting thereby decrease in irreversibility. The values of $k^\circ_{f,h}$ determined by various treatments have shown the same order thereby indicating the validity of the results derived Further, the values of $k^\circ_{f,h}$ determined by Koutecky-Cizek treatment are found in good agreement with the values derived from Oldham-Parry treatment which may be because of the reason that while placing the suitable criteria for reversibility and total irreversibility Oldham-Parry[7] might have considered curvature effect resulting from electrode sphericity, as considered by Koutecky-Cizek in introducing correction factor in Koutecky-Weber equation, and the influence of double layer structure on electrode kinetics. However, looking to the lengthy procedure of Koutecky Cizek treatment regarding use of standard tables and evaluation of Σ it seems to us that the Oldham-Parry treatment is more preferable over Koutecky-Cizek treatment.

The trend of $k^\circ_{f,h}$ of reduced species of trivalent antimony in various system is as follows : $2 > 5 > 3 > 4 > 1$ The trend suggests easier reduction in system 2 leading to difficult reductions in system 5.

The values of thermodynamic functions, follow the same trend as that of $k^\circ_{f,h}$. The positive values of ΔG^* for all the systems suggest difficult reduction of the reducible species. A little positive increase in the value of ΔG^*, in all the systems, with the rise in temperature may be because of inconstancy in the value of r_o with the change of temperature as the value of $k^\circ_{f,h}$ increases with temperature. The negative value of ΔS^* obtained in each system suggests that the activated state has more rigid structure than the initial state. The trend of the radius (r) and the diffusion coefficient of the reduced species present in different systems are found as follows : Radius (r) $5 > 1 > 3 > 4 > 2$; Diffusion Coefficient (D) $2 > 4 > 3 > 1 > 5$ which is in agreement with the expectation if Stoke's-Einstein relation is obeyed for the systems studied. Further, the decrease in the value of r with temperature clearly indicates that the reduced species are solvated; no doubt, decrease in the value of r is different in different system which may be because of different extent of salvation.

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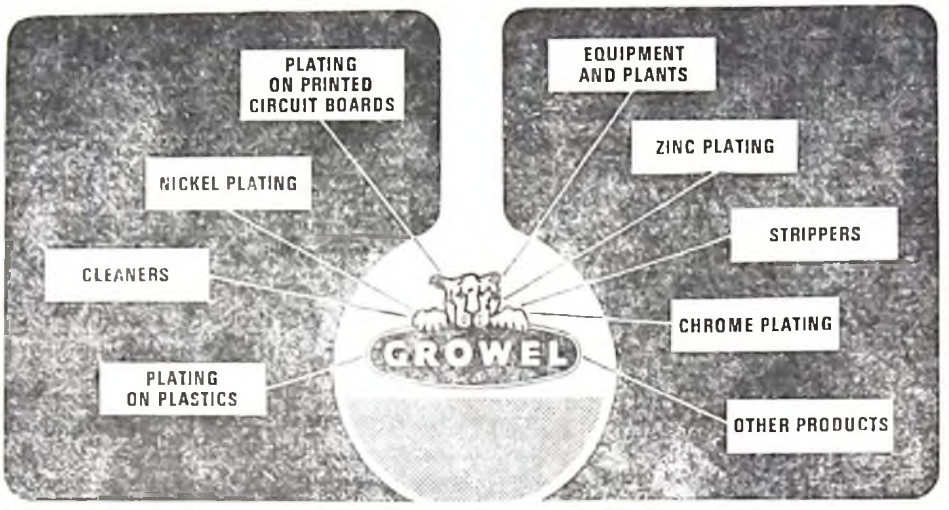
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