

ELECTROCHEMICAL REDUCTION OF Tl^+ FROM MOLTEN $Ca(NO_3)_2 \cdot 4H_2O$ AT 60 °C

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(Received 16 November 1981)

The reduction of Tl^+ at a mercury electrode (d.m.e. and h.m.d.e.) has been followed by D. C. and A. C. Polarography, Cyclicvoltammetry, Chronopotentiometry and Chronoamperometry. The reduction is found to be a one electron reversible diffusion controlled process. The reduction is also characterised by a polarographic maximum with Tl^+ ions exceeding 0.26 millimolar concentration. The post maximum current is diffusion limited. Two transitions with an intervening potential maximum are observed in chronopotentiogram and a current maximum in $i-t$ curves obtained with a h.m.d.e. and with a high concentration of Tl^+ ions. There are marked similarities of this reduction with those of Cd^{2+} ions in the presence of Br^- ion and thiourea. The observations are accounted for in terms of reduction of an adsorbed thallium species. Bromide ion and thiourea addition effects on the polarographic maximum are discussed.

Keywords : Electrochemical Reduction; Tl^+ ; Molten $Ca(NO_3)_2 \cdot 4H_2O$; D.C. & A.C. Polarography; Cyclicvoltammetry; Chronopotentiometry; Chronoamperometry; Chronopotentiogram

INTRODUCTION

THE half-wave potential and diffusion coefficient (Moynihan & Angell, 1970; Lovering, 1972; Bansal & Plambeck, 1977; and Nanjundiah, 1979) of Tl^+ in $Ca(NO_3)_2 \cdot 4H_2O$ were reported by earlier workers. Bansal & Plambeck (1977) studied the reduction of Tl^+ at the mercury electrode from $Ca(NO_3)_2 \cdot 4H_2O$ at 50 °C. Their D.C. polarograms were constructed from $i-t$ curves. These polarograms show a maximum. They have suggested that Tl^+ ion reduction is controlled by a rate-determining nucleation step during the initial stages of reduction and this could be responsible for the occurrence of the maximum. They have attempted to support this hypothesis with the results of cyclic voltammetric and chronopotentiometric experiments. However, their hypothesis does not explain several other observations including some of their own. An investigation of Tl^+ ion reduction was undertaken in connection with our studies on the effects of anion adsorption on metal ion reduction.

EXPERIMENTAL

Techniques used are D. C. and A. C. polarography, cyclic voltammetry, chronopotentiometry and chronoamperometry. Both d.m.e. and h.m.d.e. are employed.

A Ag, AgCl/Cl_(satd.)⁻ electrode, with the materials enclosed in a glass bulb, is used as the reference electrode. A large platinum foil served as the counter electrode. Analar Ca(NO₃)₂·4H₂O, TiNO₃, KBr and thiourea are used. Ca(NO₃)₂·4H₂O, is dried under vacuum for 24 hours. 50gm of the salt is melted and thermostated at 60 °C. Deaeration when necessary was carried out using purified nitrogen.

RESULTS AND DISCUSSION

Thalious ion reduction from Ca(NO₃)₂·4H₂O at 60 °C produces a single well defined wave in d. c. polarography when TI⁺ is present in concentrations less than or equal to 0.26mM (Fig. 1). Above this concentration a maximum appears with a post limiting current (Fig. 1). The limiting currents are proportional to TI⁺ ion concentrations. Log (*id* - *I*)/*I* vs. -*E* is a linear plot with slope corresponding to a one electron process. *I_a* is proportional to *h*^{1/2} for all concentrations. These results indicate that the reduction of TI⁺ is a diffusion controlled and reversible one electron transfer process.

E_p (66mV) in cyclic voltammetry corresponds to a one electron transfer (Fig. 2). *I_p* vs. *v*^{1/2} (all sweep rates if the concentration of TI⁺ is < 1.2mM and sweep rates > 60mV/sec if the concentration of TI⁺ exceeds 3.2mM) is a straight line passing

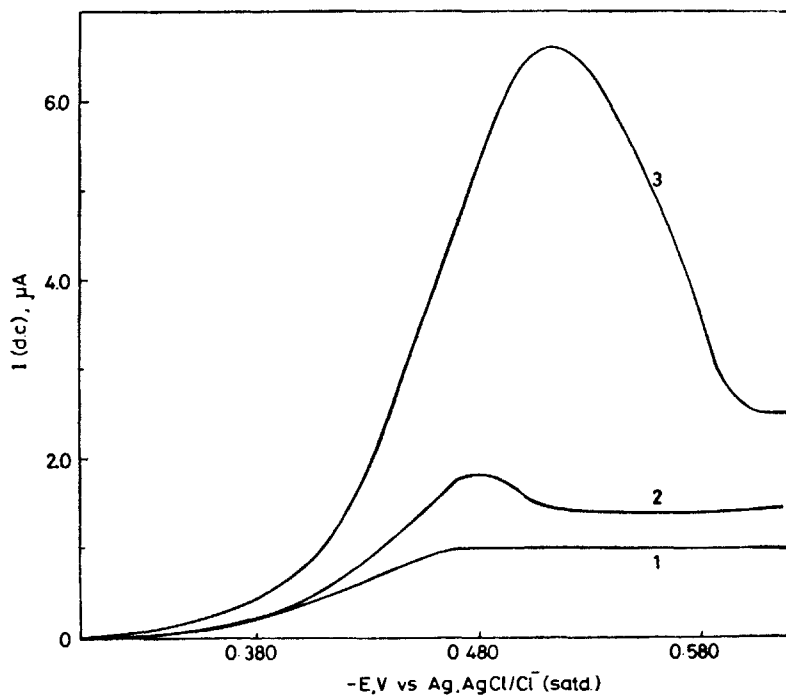


FIG. 1. D.C. polarograms of TI⁺ reduction.

- (1) 0.26mM of TI⁺ Y-axis 1 div = 0.3μA
- (2) 0.75mM of TI⁺ Y-axis 1 div = 0.6μA
- (3) 3.2mM of TI⁺ Y-axis 1 div = 1.5μA.

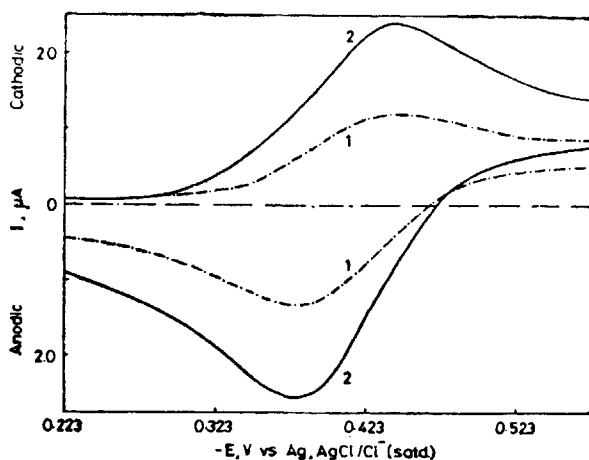


FIG. 2. Cyclic voltammograms. (1) 0.75mM of Tl^+ . (2) 1.2mM of Tl^+ . $V = 40\text{mV/sec}$.

through the origin $I t^{1/2}$ (chronopotentiometry) is independent of current density and is proportional to concentration upto 1.2mM of Tl^+ . The diffusion coefficient of Tl^+ using different techniques is reported in Table I. Values reported by other workers are also included in the table.

TABLE I

Diffusion coefficient of Tl^+ in molten $Ca(NO_3)_2 \cdot 4H_2O$ at 60 °C

Technique	D values in $\text{cm}^2 \text{sec}$ at 60 °C
Polarography	$5.45 \times 10^{-7} \pm 0.5 \times 10^{-7}$
Linear-sweep voltammetry	$5.50 \times 10^{-7} \pm 0.6 \times 10^{-7}$
Chronopotentiometry	$5.02 \times 10^{-7} \pm 1.0 \times 10^{-7}$

The polarographic maximum observed with higher concentrations of Tl^+ ion has unusual characteristics. Both I_d and I_p increase with the height of mercury column. Bauer reported that I_p (d. c.) in the case of first kind of polarographic maximum will not change with the height of the mercury column although I_d will increase with the height. According to Bauer*, I_p (a. c.) is not expected to be affected if the d. c. maximum is of the first kind or second kind. In the present case whenever d. c. maximum is present, I_p (a. c.) does not vary linearly with concentration but more than to be expected (Fig. 3). Hence, this maximum is not of the first kind. The capillaries used are not of the fast dropping variety, which cause

*Vide his book, *Electroanalytical Chemistry* (Ed. A. J. Bard), Vol. 8. Marcel Dekker, New York.

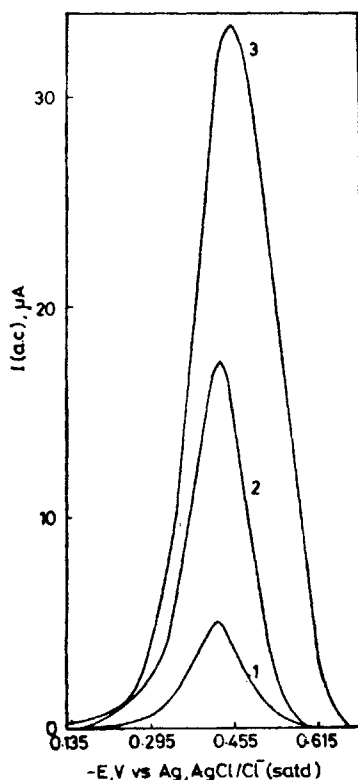


FIG. 3. A. C. polarograms.

(1) 0.75mM of Tl^+

(2) 2.00mM of Tl^+

(3) 4.00mM of Tl^+

mt = 4.66mg

a.v. = 30mV (r.m.s.).

hydrodynamic effects. ' m ' is always lesser than 1.0mg/sec and drop-times vary from 3 to 9 seconds. Bauer had pointed out that these second kind of maximum currents show a dependence on $m^{7/6} t^{1/6}$. This is not found to be true in the present case. Hence, the maximum is not of the second kind.

Bansal and Plambeck (1977) attempted to explain the maximum on the basis of nucleation theory following the suggestion of Hills and others (1974*a, b*). If there is nucleation in the initial stages of reduction the thickness of the diffusion layer is lesser than what would have been if the initial stages of reduction had been totally diffusion controlled. The concentration gradient is hence higher and an increase in current over the normal diffusion limited current is observed. According to Bansal and Plambeck (1977), additional evidence for the nucleation theory are (i) shift of cathodic peak potentials to anodic values on successive cycling in cyclic voltammetry; (ii) occurrence of a potential maximum in chronopotentiometry; and (iii) occurrence of a current maximum in chronoamperometry. However, the following observations are not supported by the nucleation hypothesis.

1. Thallium forms amalgams easily with mercury to the extent of 40 mole per cent.
2. Log analysis at the foot of the polarogram with a d.m.e. (i.e.) $-E$ vs. $\log(I_a - I)/I$ gives an 'n' value equal to one whereas $-E$ vs. $\log(I_a - I)$ (relation for an insoluble product being formed) gives an 'n' value equal to 0.1. If nucleation is operative, a second phase should form and $-E$ vs. $\log(I_a - I)$ plot is expected to be obeyed.
3. If nucleation is operative I_p vs. $v^{1/2}$ is not expected to be a straight line passing through the origin. But all reported work and the present work show that I_p vs. $v^{1/2}$ is a straight line passing through the origin.
4. 'D' values calculated by these authors from cyclic voltammetry and polarography are in close agreement. This is not expected if slow nucleation is operative (Hills *et al.*, 1974a). 'D' from lsv is expected to be higher than the 'D' from polarography.
5. Further our results show a constancy of $I_p V^{1/2} C^{-1} A^{-1}$ for all concentrations of Tl^+ (Table II).

TABLE II

Dependence of peak currents on sweep rates

I_p (lsv) in μA . Concentration in millimoles/litre V in volt/sec. A in cm^2 . Polarographic 'D' value = $5.45 \times 10^{-7} cm^2/sec$

Conc. of Tl^+	Experimental $I_p V^{-1/2} C^{-1} A^{-1}$	Theoretical $I_p V^{-1/2} C^{-1} A^{-1}$
0.26	322.0	322
0.75	335.3	
1.20	328.3	
3.20	325.3	

6. If nucleation is operative the current in linear-sweep voltammetry will rise very much faster than that for the normal diffusion wave. This is supported by the results of Hills and others for Ag^+ ion reduction on platinum in $NaNO_3 + KNO_3$ eutectic. Present observations with Ag^+ ion deposition on to a platinum surface from $Ca(NO_3)_2 \cdot 4H_2O$ confirms this (Fig. 4). But the linear-sweep voltammograms for the reduction of Tl^+ ion at mercury electrode has generally the appearance of a normal diffusion controlled wave (Fig. 2).
7. Bansal and Plambeck also quote the occurrence of the maxima in chronopotentiometry as evidence for nucleation. If nucleation is operative the potential maximum in chronopotentiometry is expected to occur in the beginning of transition and not in the middle of the transition ($> 1-2$ secs) as observed with Tl^+ ion reduction (Fig. 7).
8. Bansal and Plambeck did not explain why E_p (cathodic) shifts to positive values on successive cycling and the appearance of a second peak in lsv (Fig. 5).

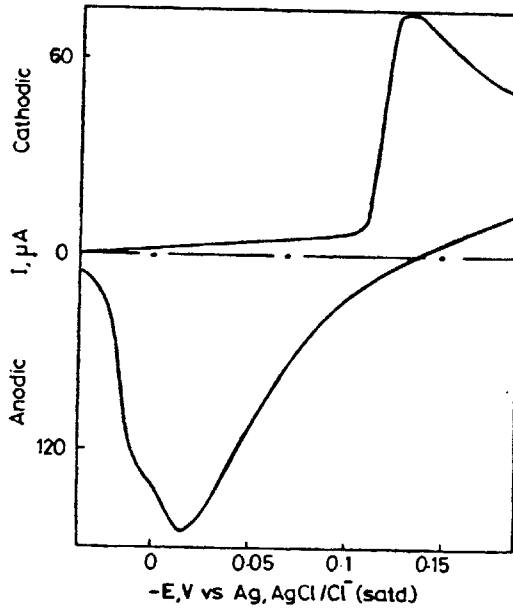


FIG. 4. Cyclic voltammogram for reduction of 1.9mM of Ag^+ from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 60°C Pt electrode $A = 0.479\text{cm}^2$ $V = 40\text{mV sec}^{-1}$.

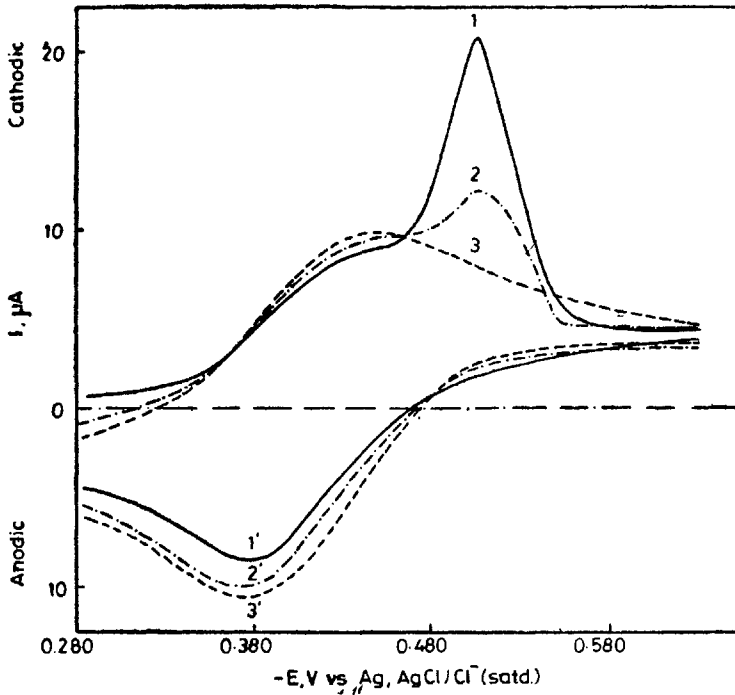


FIG. 5. Repetitive cyclic voltammograms. 3.2mM of Tl^+ $V = 60\text{mV/sec}$ $A = 0.036\text{cm}^2$
1,1' First cycle; 2,2' Second cycle; 3,3' Third cycle.

An alternative explanation for the appearance of a polarographic maximum is based on the adsorption of thallos ions at the $Hg/Ca(NO_3)_2 \cdot 4H_2O$ interface. Adsorption of thallos ions at $Hg/aqueous$ solution interface has been reported and proved by Sluyters and others (Sluyters-Rehback *et al.*, 1963; and Timmer *et al.*, 1967) using impedance measurement. This adsorption was also reflected in the earlier polarographic studies as a polarographic maximum (Heyrovsky & Kuta—Principles of Polarography, p. 437). If thallos ion adsorption can also occur from the aqueous melts, then the reduction of the adsorbed thallos ion at potentials a little more negative than that of the diffusing species can lead to the polarographic maximum. This explanation is similar to that offered for the occurrence of maximum during the reduction of Cd^{2+} and In^{3+} in the presence of Br^- (Nanjundiah, 1979). There are several other characteristic features which are common to both the cadmium bromide system and Tl^+ ion systems.

At low sweep rates in lsv ($< 60mV/sec$) apart from the usual diffusion controlled peak, there is a more cathodic peak. The current beyond this peak decays much more rapidly than expected from the $t^{1/2}$ diffusion law (Fig. 5). This peak becomes smaller progressively with cycling (Fig. 5). No anodic peak is observed corresponding to the additional sharp cathodic peak; but a sharp cathodic peak makes its appearance during the anodic sweep at slow rates (ca. $10mV sec^{-1}$) (Fig. 6). This is similar to the observation made with cadmium-bromide system

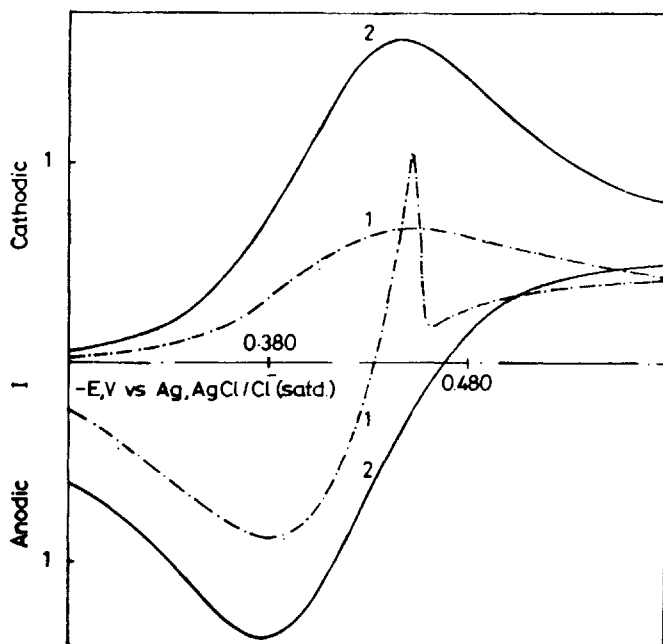


FIG. 6. Cyclic voltammograms for reduction of 3.2mM of Tl^+

- (1) $V = 10mV sec^{-1}$ Y-axis 1 div = $5\mu A$
 (2) $V = 200 A$ " " = $10\mu A$
 h.m.d.e. A = $0.036cm^2$

(Nanjundiah, 1979) but with a difference. The peak is observed only if the additional sharp cathodic peak is not present in the forward sweep. As the sweep rate is increased, the reverse cathodic peak disappears. If the sweep is reversed after a short stay at negative potentials, the reverse cathodic peak is not observed. These observations can be explained as follows. If the reduction of the adsorbed thallium is very much slower compared to the reduction rate of the diffusion species, the reduction of the former will be observed only with slow sweep rates. At high sweep rates, the waves will have the form of diffusion controlled reduction. If the reduction of the adsorbed species does not occur or is not completed in the forward sweep the reduction takes place during the reversal and the peculiar cathodic peak is observed (Nanjundiah & Narayan, 1979).

The reduction of the adsorbed Tl^+ ion as being a slow process is also confirmed by the observation of a potential hump in chronopotentiometry with low currents (Fig. 7) and well-defined single transitions with higher currents. The $I\tau^{1/2}$ reaches the value expected at high currents yielding a ' D ' value close to that of the polarographic ' D ' value. τ_f/Cr is then 3.0. The small potential maximum observed in the middle of the chronopotentiometric potential-time variations can be explained as follows. As the reduction of Tl^+ ion diffusing towards the electrode progresses, potential becomes increasingly negative and the concentration of Tl^+ at $x = 0$ tends to zero. If the adsorbed Tl^+ ions do not get reduced when the concentration of Tl^+ ion at $x = 0$ has fallen to a very small values then desorption will have to take place thus increasing the concentrations of Tl^+ ion at $x = 0$. The potential of the electrode will thus become positive. This opposing effect results in a small maximum. Alternatively, the maximum can be the result of a higher potential necessary to initiate the reduction of a tenaciously bound adsorbed species.

Surface excess cannot be evaluated in the present system from lsv as was done with the cadmium-bromide and indium bromide system (Nanjundiah, 1979) since the reduction of the adsorbed species is reflected to varying extents with the sweep

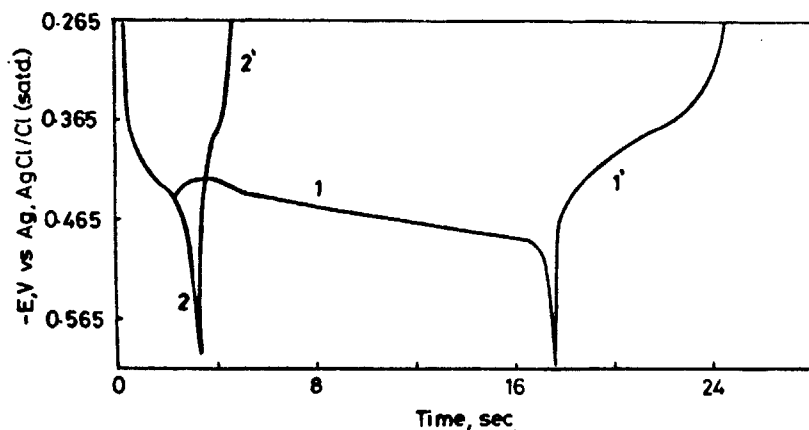


FIG. 7. Chronopotentiograms 1, 1' 3.2mM of Tl^+ 1 = $7.25\mu A$ 2, 2' 3.2mM of Tl^+ + 30mM of thiourea $A = 0.036cm^2$.

rates and that too only when the concentrations of Tl⁺ exceed 3.2mM. An approximate evaluation of the surface excess has therefore been attempted as follows : (for the concentration of Tl⁺ = 3.2mM). The rising region upto the shoulder preceding the cathodic peak has all the characteristics of a diffusion-controlled process. The reduction starts as a diffusion-controlled process and then a surface reduction process sets in when the diffusion controlled current is decaying. This decaying portion is constructed from the theoretical expression using the polarographic diffusion coefficient upto that potential where the theoretical current merges with the experimental curve. The charge contribution due to the diffusion controlled reduction process is subtracted from the total charge due to the reduction (computed upto the potential where experimental and extrapolated curves merge), and the remainder equated to the charge contribution due to the reduction of the adsorbed species. The surface excess evaluated (Table III) will only give the order of the magnitude as it is obvious from the dependence of the excess charge on the sweep rate.

TABLE III
Surface excess values from lsv for 3.2mM of Tl⁺
(Sweep rate in mV/sec. Γ in mole/cm²)

Sweep rate	10	20	40	60
$\Gamma \times 10^{-9}$	13.4	6.63	3.0	1.36

Analysis of the chronopotentiometric transition times by the APSR model and SAR model of chronopotentiometry lead to negative surface excess values. SPAR model analysis leads to positive surface excess values but vary with current densities which is to be expected (Table IV). The surface excess values are compiled only from the total transition times obtained with the low currents when potential humps are present.

TABLE IV
Surface excess values from chronopotentiometry
(I in μ A, τ in sec. Γ in mole cm⁻² Concentration of Tl⁺ = 3.2mM)

I	$\tau_{f,1}$	$\tau_{f,2}$	Surface excess
7.3	2.1	15.1	1.76×10^{-8}
9.1	1.1	7.7	1.01×10^{-8}
10.4	0.8	5.9	0.86×10^{-8}
12.1	0.7	4.0	0.68×10^{-8}

$I-t$ curves, recorded with a h.m.d.e. at potentials in the limiting region, obey $I \propto t^{-1/2}$ law for diffusion. But $I-t$ curves shows a sharp maximum when recorded

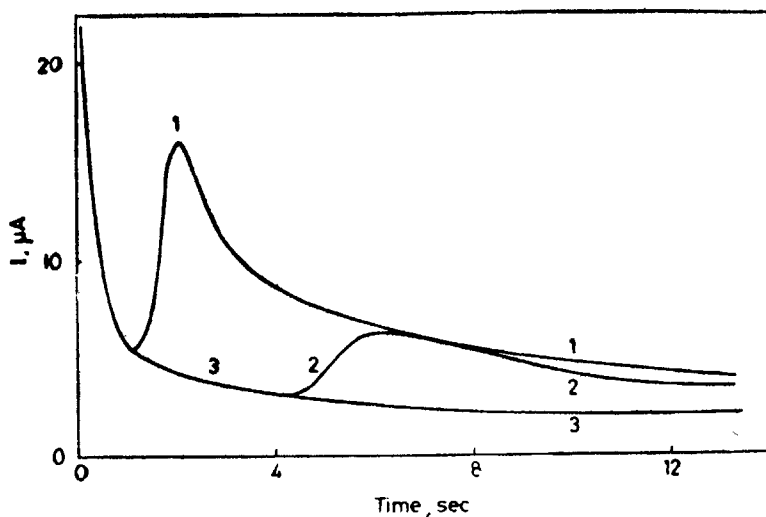


FIG. 8. I vs. t curves (h.m.d.e.)

- (1) 3.2mM of Tl^+ Potential of the polarographic maximum, $-E = 0.514V$ vs. Ag, AgCl/ Cl^- (satd).
- (2) 3.2mM of Tl^+ + 30mM of thiourea Potential of the polarographic maximum, $-E = 0.504V$ vs. Ag, AgCl/ Cl^- (satd).
- (3) 3.2mM of Tl^+ + 30mM of thiourea potential of the limiting current, $-E = 0.610V$ vs. Ag, AgCl/ Cl^- (satd).

at other potentials close to that of the polarographic maximum (Fig. 8). The $i-t$ curves obtained at the potentials of limiting current region of the polarogram are integrated. This charge is then subtracted from the charge obtained from the $i-t$ curves at the potential of the polarographic maximum current. The excess charge is equated to the charge contributed from the surface reduction. Values calculated from lsv with the low sweep rates, from chronopotentiometry with low currents and from $i-t$ curves on h.m.d.e. are compared (Table V).

TABLE V
Surface excess values in mole/cm²
(Concentration of Tl^+ = 3.2mM)

From lsv ($V = 10mV s^{-1}$)	From chrono. $I = 7.3\mu A$	From $I-t$ curves
1.34×10^{-8}	1.77×10^{-8}	1.97×10^{-8}

Surface excess values reported in literature are generally of the order of 10^{-10} mole/cm². The surface excess of adsorbed Tl^+ ions calculated when bulk concentration is 3.2mM, is even higher than that calculated for a complete monolayer

coverage which is 0.24×10^{-8} mole/cm². The value is based on an ionic radius of 1.47Å. The solvated ion will be even larger than this. The adsorbed Tl^+ ion is bound to be partially solvated in the melt. Hence, the number of Tl^+ ions required for a complete monolayer will work out to be even smaller than the above value. Further, since an appreciable diffusion current is always observed in d.c. polarography at the potential of the maximum it is obvious that Hg surface is only partly covered by the adsorbed species. Hence, the high coverage of the order of 10^{-8} mole/cm² can only be accounted for by a compact multilayered coverage. In the cadmium-bromide system when the Cd^{2+} ion concentration ($> 3mM$) and Br^- ion concentration ($> 50mM$) are high the surface excess worked out to be in the order of 10^{-8} mole/cm² (Nanjundiah, 1979).

A compact or multi-molecular layer is perhaps responsible for the slow stage in the reduction of the adsorbed species as seen earlier (Nanjundiah & Narayan, 1979).

Effect of Br^- on Tl^+ Reduction

Thalious ions apparently do not form complexes with Br^- ions in the melt since there is no appreciable shift of $E_{1/2}$, E_p (a.c.), E_p (lsv) and $E_{1/4}$ (chronopotentiometry) due to the additions of Br^- ions. However, Br^- additions in low concentrations induce a maximum when there is no maximum (Fig. 9) or enhance the maximum of Tl^+ if already present. The Br^- ion obviously increases the adsorption of Tl^+ . A single clear transition is observed for the reduction of Tl^+ ions upto 1.2mM of Tl^+ ions but in presence of Br^- , transition with a maximum are observed as with the reduction of Tl^+ ions present in high concentration ($\sim 3.2mM$). This indicates that Br^- ions are able to increase the surface excess of adsorbed Tl^+

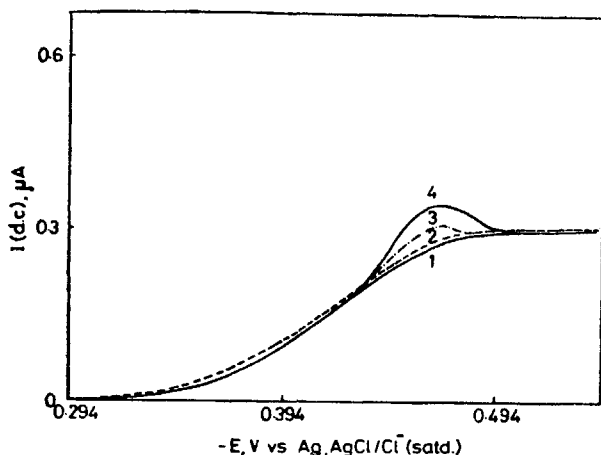


FIG. 9. D.C. Polarograms 0.26mM of Tl^+ in the presence of Br^-

- (1) 0mM of Br^-
- (2) 20mM of Br^-
- (3) 40mM of Br^-
- (4) 60mM of Br^-

ions enormously. The surface excess and excess charge are shown in the Table VI. Since the 1sv at higher sweep rates still shows only diffusion controlled characteristics and only at lower sweep rates ($< 60\text{mV/sec}$) the surface reduction characteristics can be observed, the kinetics of reduction of the adsorbed Tl^+ ion are not very much altered by the presence of Br^- ion.

TABLE VI

Surface excess of Tl^+ in presence of Br^-

Concentration in mM. Surface excess in mole/cm² (T) Q (excess) in microcoulombs

Conc. of Tl^+	Conc. of Br^-	Q from $i-t$ curves (d.m.e.)	Γ from $i-t$ curves (h.m.d.e.)	T from chrono (SR, AR) $I = 1.81\mu\text{A}$	T from 1sv $V = 10\text{mV/sec}$
1.2	0	0.75	—	—	—
1.2	40	7.1	9×10^{-9}	6.2×10^{-9}	7×10^{-9}

Since the interfacial forces responsible for the adsorption of Tl^+ are not understood, one can only guess that the adsorption is increased by additional coulombic forces coming into operation when Br^- ions are adsorbed.

Additions of Br^- ions at high concentrations ($> 20\text{mM}$) to Tl^+ ions (3.2mM) however, reduces the maximum and also bring down the I_d , I_p (ac), I_p (1sv) and $I^{1/2}$ values. This can only be explained on the basis that Tl^+ ion concentration is reduced even in the bulk of the solution. The Tl^+ ions are removed as TlBr precipitates appear when the melt containing Tl^+ and Br^- ions are left standing. The time required for precipitation depends both on the concentration of Tl^+ ions and Br^- ions. If the concentration of Tl^+ ca 10mM , precipitation occurs immediately.

Thallium-Thiourea System

Thiourea additions do not appreciably shift the $E_{1/2}$, E_p (ac), E_p (1sv) and $E_{1/4}$ potentials. Tl^+ ions in solution do not form any strong complexes with thiourea. However, thiourea additions reduces the polarographic maximum of Tl^+ ion reduction without effecting the I_d . It is concluded that thiourea competes with Tl^+ for the same adsorption sites and reduces the extent of adsorption. This competition increases with the concentration of thiourea. In chronopotentiometry only a single well defined transition is observed in the presence of thiourea even with those concentrations of Tl^+ ions which had produced a transition with a potential maximum in the absence of thiourea (Fig. 7). $I\tau^{1/2}$ is nearly constant in the presence of thiourea and is $12.5\mu\text{A sec}^{1/2}$. The expected value of $I\tau^{1/2}$ for Tl^+ (3.2mM) on the basis of polarographic diffusion coefficient is $12.4\mu\text{A sec}^{1/2}$. In 1sv cathodic peak current due to surface reduction process are observed at low sweep rate ($< 20\text{mV/sec}$) and are such smaller than those observed for the surface reduction of Tl^+ ion in the

absence of thiourea at the same sweep rate. The surface reduction peaks are observed only at sweep rates smaller than 20mV/sec in the presence of thiourea while the surface reduction process can be observed even at a higher sweep rate (40mV/sec) in the case of pure Tl^+ ions. This again indicates a smaller surface excess of the adsorbed Tl^+ ion species in the presence of thiourea $I-t$ curves on h.m.d.e. also exhibit a smaller maximum than those observed in the absence of thiourea (Fig. 8).

A strong mercury-sulphur interaction which promotes the specific adsorption of thiourea seems to compete with a similar Hg- Tl^+ interaction causing adsorption of Tl^+ ion.

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Discussion

- K. BALAKRISHNAN (*Central Electrochemical Research Institute, Karaikudi*): 1. How far is thiourea stable under these conditions? 2. Is there any difference in the linear and repetitive sweeps?
- R. NARAYAN: 1. Thiourea and several other organic chemicals are quite stable in this melt at this temperature. 2. (a) In the absence of Br^- or (TU) practically unchanged in the cathodic half, while the stripping peak currents increase slightly (Please note, all these observations are at a h.m.d.e) (because with Pt in anhydrous nitrates, the first cycle is shifted to more cathodic potential). (b) With low concentration of the Cu^{2+} & In^{3+} metal ions (h1mM) the peak currents in the presence of Br^- & Tu vary somewhat during the first 3-4 cycles and then remain constant. (c) With higher concentration of metal ions and additives there is a drastic distortion of the lsv and with the appearance of reverse cathode peaks. The current due to the surface reduction process on successive cycling, becomes smaller and disappear after a few cycles. When the sweep rate is less than $60mV\ sec^{-1}$, surface processes do not even show up in the first cycle. (d) With Tl^+ ions, surface process show up in lsv, when the concentration of Tl^+ ion is high ($>1-2mM$) and sweep rates are less than $60mV\ sec^{-1}$. On cycling the surface processes disappear. These and other observations are explained on the basis of slow kinetics in the reduction of surface films which are multimolecular or highly condensed in nature.
- V. K. VENKATESAN (*Central Electrochemical Research Institute, Karaikudi*): (a) What is the mechanism by which thiourea suppresses the polarographic maximum of thallium? (b) Is any pretreatment to be given for the glass capillary used in the DME system in molten medium?
- R. NARAYAN: The forces that promote adsorption of Tl^+ and thiourea (TU) at the Hg-solution interface are probably the same. Hence, in the absence of complex formation, there will be competition for adsorption sites since it is the adsorbed Tl^+ which cause the maximum, TU competition will reduce the intensity of the maximum. (b) No special treatments are necessary.

- A. V. GORODYSKY (*Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, USSR*) : 1. In which way was determined electrode process reversibility? Is it on the basis of shift of peak? 2. Why is diffusion coefficient so small for Tl^+ ?
- R. NARAYAN : 1. All criteria were answered — log analysis of DC polarograms, coincidence of $E_{1/2}$ with E_p (ac), value of $\Delta E_{p\text{peak}}$ ($E_p^c - E_p^a$) in 1sv coincidence of $E_{1/2} + E_{1/4}$ potential etc.
2. D for Tl^+ was found to be $5 \pm 0.5 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$. The low value is mainly due to the viscosity of the medium. Presently, I do not know how the Tl^+ ion is coordinated with H_2O & NO_3^- . We only observe the D to be in the order $Tl^+ > Cd^{2+} > In^{3+}$.