

Cyclic Square Wave Polarographic Studies of Tin (IV) in the Presence of Picolinic Acid

W. T. Tan

Department of Chemistry, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia.

email: wttan@science.upm.edu.my

Abstract : The irreversible reaction of stannic-tin, Sn(IV), in noncomplexing supporting electrolyte was found to be reversible in the presence of picolinic acid (PA). Experimental evidences obtained from Tast polarography, electrocapillarity studies and cyclic square wave polarography indicated that Sn(II)-PA complex was adsorbable at the electrode surface but not Sn(IV)-PA complex. The adsorption effect has caused some degree of current enhancement. The enhancement and reversibility of the electrode reaction was dependence on pH, electrolyte, sweep rate, initial potential and presence of interference such as triton X-100.

Key words: cyclic square wave polarography, Sn(IV), Sn(II), picolinic acid, adsorption.

Received : 30.06.08; accepted : 23.12.08

Introduction

The voltammetry of stannic-tin (Sn(IV)) and stannous-tin (Sn(II)) has been studied by various workers using different techniques [1-9]. The electrode processes of Sn(II)/Sn(IV) were mainly studied by direct current [1,2], alternating current[3,4], cyclic voltammetry [5], and square wave [6,7], while stripping voltammetry [8,9] found good applications in tin analysis at trace level. Thus far there is no report on the use of cyclic method of square wave polarographic studies of electrode processes of tin complexes. Tin (IV) is highly irreversible in most media such as nitrate, perchlorate and sulphate. It is however reversible in strongly acidic halide media [1] or in the presence of ligands such as pyrogallol[2], catechol[10], chloranilic acid [11] and 8-hydroxyquinone[12]. These ligands are some of the many reagents reported to form analytically useful tin complexes. The electrode reactions of Tin(IV) complexes usually associated with a two step reduction of Sn(IV) to Sn(II) and of Sn(II) to Sn(0). In our previous studies, the Cd(II)-Picolinic Acid system (Picolinic Acid (PA) is pyridine-2-carboxylic acid) has shown that the presence of PA causes reduction current of Cd(II) to be considerably increased and is probably due to the adsorption of Cd(II)-PA complex possibly uncharged Cd(Picolinate)₂.2H₂O complex onto the Hg electrode surface [13]. During the course of similar studies using Sn(IV), it was observed that PA was also capable of making electroinactive Sn(IV) to become electro active in non complexing media such as sulphate and nitrate. Since the report was made on

the theories of single drop square wave polarography (SDSWP) [14] and cyclic method of single drop square wave polarography (Cyclic SDSWP) [15], there was no write up on the use of Cyclic SDSWP in the study of metal ion complexes. It is therefore our intention to report the electrode processes of Sn(IV) in the presence of PA using Cyclic SDSWP.

Experimental

Single Drop Square Wave Polarography (SDSWP), Cyclic SDSWP and Cyclic Staircase Voltammetry (CSV).

The techniques and theories of SDSWP have been reported [14, 15]. In SDSWP, a Square wave of half-period (τ) with amplitude (ΔE) was superimposed onto a staircase potential of period 2τ and E step of 2 mV. The resultant waveform was used to a dropping mercury electrode (dme). Each period of the resultant square wave is subdivided into eight equally spaced segments of 8β 's. Each β is equal to 0.127τ current can be sampled at selected interval when the double layer charging current is negligible and for as long an integration as desired. The theoretical derivation of average current (or integrated current) for diffusion controlled reversible reaction has been reported¹⁶.

During the anodic and cathodic half-cycles of the resultant square wave, anodic and cathodic components of the average current are produced. The differential average current, $(i_p)_{\text{dif}}$ or i_p in short is obtained by subtracting the anodic component of the

average current from that of the cathodic component. Cyclic SDSWP is similar to other cyclic method (eg. Cyclic Voltammetry) in which the forward (cathodic) and reverse (anodic) scans are involved. The combined sweep of SDSWP is used in these two opposing polarization directions. In Cyclic SDSWP individual current components can be subtracted like that above to produce $(i_p)_{\text{dif}}$ or can be added to produce additive current $(i_p)_{\text{add}}$.

Apparatus

The computer-controlled potentiostat and cell system employed in this work have been previously described [14]. Switching circuit was employed to enable the instrument perform Cyclic SDSWP [15]. The potentials were measured versus the saturated calomel reference electrode. The experiments were carried out between 23 and 25°C using staircase step height of 2mV and square wave amplitude of 10mV. Unless otherwise stated, a delay time of 5 s, a scan rate of 0.781V/s and a mercury flow rate of 1.5mg⁻¹ were used.

Reagents

All chemical used were of reagent grade. picolinic acid (pyridine-2-carboxylic acid) from J.T. Barker was used as received. Stannic tin was prepared by dissolving tin metal in a HCL-HNO₃ mixture and boiling to remove oxides of nitrogen. The final stock contains 50mM Sn(IV) in 2M HCl. Laboratory distilled water was passed through activated charcoal and distilled once more from an all glass still before use.

Results and Discussion

Cyclic SDSWP of Sn(IV)/Sn(II) in the presence of PA

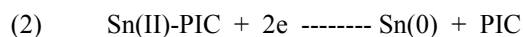
For a complete square wave polarogram of Sn(IV)/Sn(II) to be constructed, it is necessary to use Cyclic SDSWP. The following studies have been conducted using this technique. When Sn(IV) in strongly acidic halide media such as 4M NH₄Cl/1 M HCl was analysed by Cyclic SDSWP, it yields polarogram with redox potential similar to those

reported earlier[5,13]. In non complexing media such as sulphate, perchlorate, nitrate and weakly acidic media such as 1M KCl with acetate buffer at pH 4.6, Sn(IV) produces no reversible waves. However on the addition of picolinic acid i.e. pyridine-2-carboxylic acid (PA) to the above media at weakly acidic conditions distinct waveforms were observed. PA dissociates in accordance to the following equilibria with $pK_1 = 1.03$ and $pK_2 = 5.21$ (Scheme 1). At $pH > 5.21$, picolinate ion (PIC) predominants which is expected to chelate with metal ion such as Sn(II) and Sn(IV) to form a neutral Sn(II) / Sn(IV) - PIC complex species forming 5-membered ring via interaction of carboxylate anion and lone pair electrons bearing heterocyclic N with Sn(II) or Sn(IV) ion.

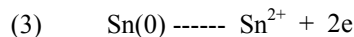
Fig.1 is a typical Cyclic SDSWP polarogram of Sn(IV) in the presence of PA. It constitutes the reduction and oxidation waves corresponding to the Sn(IV)/Sn(II) and Sn(II)/Sn(0) couples during the cathodic(forward) sweep and anodic(reverse) sweep of Cyclic SDSWP respectively. The forward sweep gives rise to an ill-defined wave with peak potential, E_p at -0.5V which is due to the following electrode reaction:



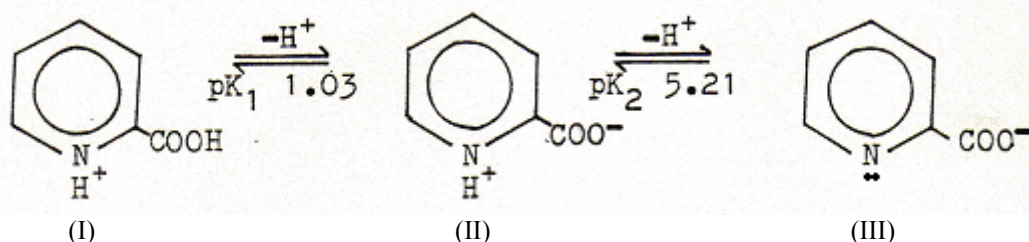
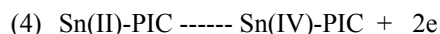
The well defined and enhanced adsorption like peak observed at E_p of -0.7 (peak a) is produced by the electrode reaction:



During the reverse sweep, the wave at E_p of -0.7V (peak b) is due to the electrode reaction:



The oxidized Sn²⁺ probably complexes with PIC again and readsorbs onto the electrode surface. The following electrode reaction:



Scheme 1 : Chemical equilibria of picolinic acid

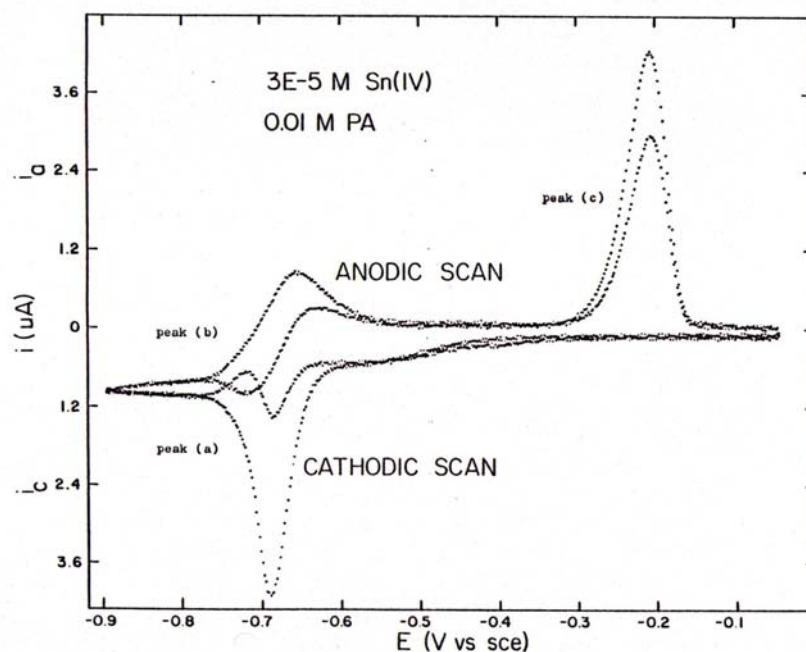


Figure 1 : Cyclic square wave polarograms of $3.0 \times 10^{-5} \text{ M Sn(IV)}$ with $1.0 \times 10^{-2} \text{ M PIC}$, 1.0 M KNO_3 and $1.0 \times 10^{-2} \text{ M Acetate buffer}$; $\text{pH} = 5.0$, sweep rate = 0.781 V/s

yields the polarographic wave at E_p of -0.2 V (peak c). The reaction evidently is irreversible in behavior although the peaks appear to be more symmetrical and enhanced but no similar peak was observed on the reverse scan indicating that Sn(IV)-PIC formed by the oxidation of Sn(II)-PIC is not reversible. The behaviors of the redox waves corresponding to Sn(IV)/Sn(II) and Sn(II)/Sn(0) couples during Cyclic SDSWP can be further substantiated by the following studies.

Optimum conditions for the observed current enhancement

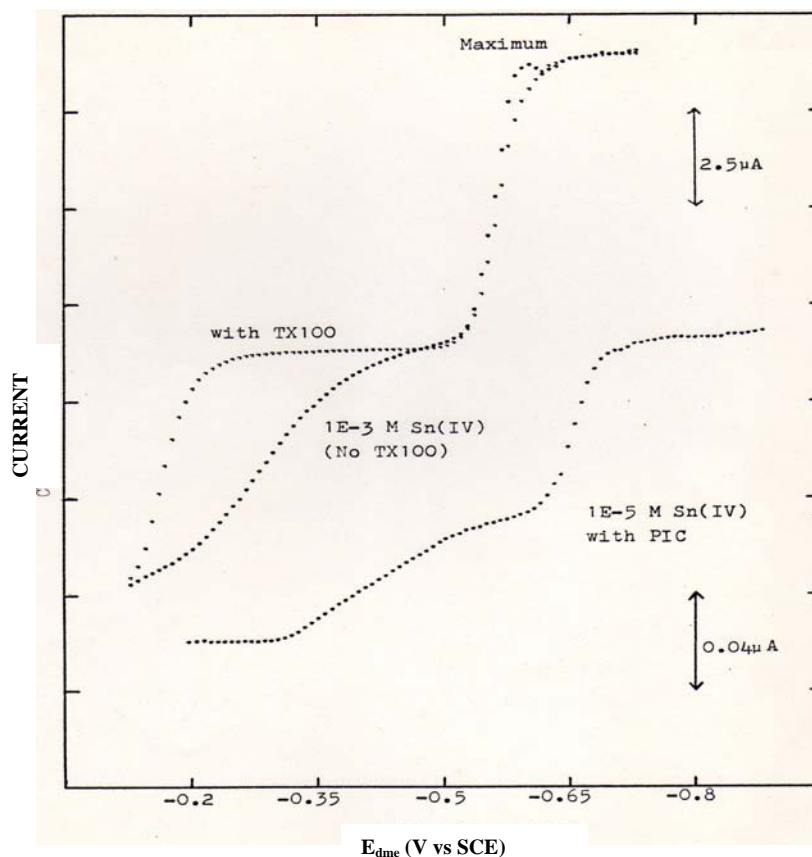
Initial studies show that in the absence of PA, all the polarographic waves of Sn(IV) were not detected in sulphate or nitrate media at $\text{pH} 5$. However, the addition of 0.02 mM PA enables the electroinactive Sn(IV) ions to be electroactive producing peaks smaller than but similar to Fig.1. Its $(i_p)_{\text{dif}}$ gradually increases as PA concentration increases to 10 mM (Table 1). pH study shows that the optimum pH range for greater current output was 3 to 5 (Table 2). Hydrolysis of Sn(IV) was responsible for the low i_p at $\text{pH} > 6$. Hence, $1\text{-}5 \text{ mM PA}$ at $\text{pH} 5$ was employed in most of the following studies.

Table 1 : Effect of varying $[\text{PIC}]$ on $1 \times 10^{-5} \text{ M Sn(IV)}$ in $0.50 \text{ M (NH}_4)_2\text{SO}_4$, $\text{pH} 5.03$ during cyclic SDSWP; sweep rate = 0.781 V/s

| PIC (mM) | $E_p(\text{V})$ (peak (a)) | $(i_p)_{\text{dif}}(\mu\text{A})$ |
|----------|----------------------------|-----------------------------------|
| 0.02 | -0.579 | 0.15 |
| 0.05 | -0.591 | 0.31 |
| 0.20 | -0.613 | 0.53 |
| 0.50 | -0.633 | 0.68 |
| 1.0 | -0.650 | 0.82 |
| 2.0 | -0.667 | 1.04 |
| 5.0 | -0.688 | 1.15 |
| 10.0 | -0.699 | 1.11 |
| 20.0 | -0.709 | 0.94 |
| 50.0 | -0.720 | 0.62 |

Table 2 : Effect of pH on cyclic square wave polarographic parameters for 1.0×10^{-5} M Sn(IV) in 0.50M $(\text{NH}_4)_2\text{SO}_4$ with 4.5×10^{-3} M PIC, sweep rate= 0.781V/s .

| pH | Sn(IV)-PIC | |
|-----|-------------------------------|------------------------------------|
| | $E_p(\text{V})$ (peak (a)) | $(i_p)_{\text{diff}}(\mu\text{A})$ |
| 2.0 | -0.512 | 0.83 |
| 2.4 | - | - |
| 3.0 | -0.562 | 1.58 |
| 3.3 | - | - |
| 5.0 | -0.703 | 1.37 |
| 7.3 | -0.734 | 0.19 |

**Figure 2 :** Tast polarogram of (a) 1.0×10^{-3} M Sn(IV) in 1.0M KCl, 4.0M NH_4Cl (b) solution (a) with added 0.0020% Triton X-100 (c) 1.0×10^{-5} M Sn(IV) with 5.0×10^{-3} M PIC, 0.50M $(\text{NH}_4)_2\text{SO}_4$, 1.0×10^{-2} M acetate buffer, pH=5.0

Tast DC Polarogram

Fig.2 depicts the tast polarographic dc response of Sn(IV) towards PA. Behavior of Sn(IV) in a strongly acidic chloride medium of 4M NH₄CL/1 M HCL was carried out for comparison. In this acidic chloride media, the first wave with half-wave potential ($E_{1/2}$) of -0.284V is a well defied but irreversible wave ($n = 0.4$) and is due to the reduction of Sn(IV) to Sn(II), while the second wave with a maximum ($E_{1/2} = -0.561V$, $n = 2.1$) corresponds to the reversible reduction of Sn(II) to Sn(0). As expected in the presence of 5mM PA, 10 μ M Sn(IV) in SO₄²⁻ medium produced two similar waves but with cathodically shifted peak indicating complexation of Sn(IV)-PA system. It follows that the first wave corresponds to the reduction of Sn(IV)-PIC to Sn(II)-PIC ($E_{1/2} = -0.430V$) which still appears irreversible since $n = 0.4$ while the second wave with

$E_{1/2} = -0.654V$ corresponds to the reduction of Sn(II)-PIC to Sn(0) which is reversible since $n=1.7$.

Effect of Triton X100

Similar to the studies of Cd(II)-PIC system reported previously⁶, peak current in Cyclic SDSWP polarogram of Sn-PA system were suppressed by the presence of a strong surfactant and adsorbate, Triton X100. In the presence of 0.0005% (V/V) Triton X100 of peak (a) was found to decrease by 19% and an addition of 0.001% of surfactant caused a 58% decrease in peak current. 0.018% Triton X100 was found sufficient to suppress the cathodic and anodic peak currents completely. In general, peak (a) of Sn(II)/Sn(0) was found to be more sensitive to the surfactant indicating its adsorption behavior. Fig.3 shows that the electrode reaction esp. Sn(II)/Sn(0) couple tends towards irreversibility with the addition of increasing amount of Triton X100.

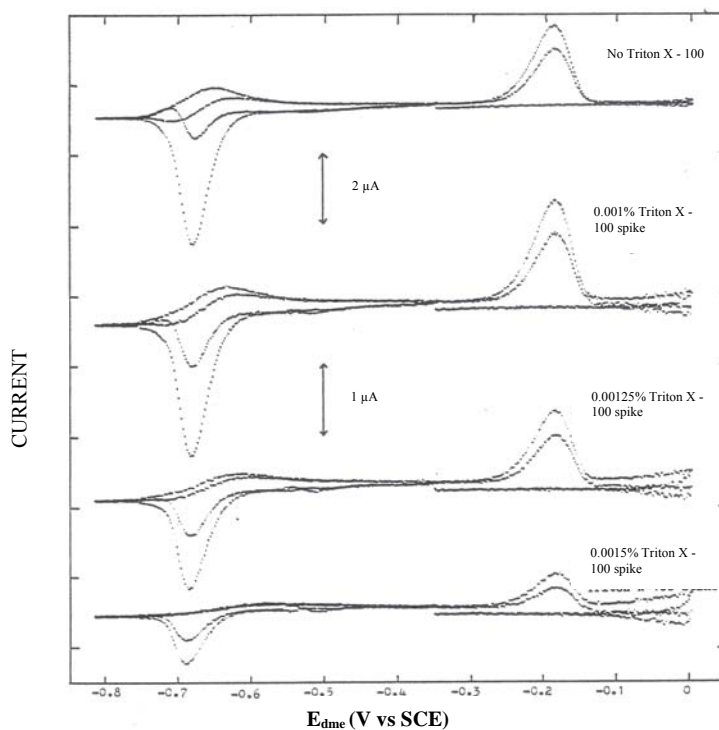


Figure 3 : Effect of Triton X-100 on cyclic square wave polarogram for $1.0 \times 10^{-5}M$ Sn(IV), $1.0 \times 10^{-2}M$ PIC, $0.50M$ (NH₄)₂SO₄, $1.0 \times 10^{-2}M$ acetate buffer; pH = 5.0, sweep rate = 0.781 V/s

Delay Time study

It has been shown previously that for a reversible reaction diffusion controlled SDSWP experiment [14,15] with all parameters except electrode area held constant, $i_p = k_1 t_p^{2/3}$ where t_p is peak time. For a system in which the reactant is adsorbed strongly and provides major contribution to reduction current, it can be shown that $i_p = k_2 t_p^{7/6}$, based on Koryta's equation for strong adsorption [14,16]. Experimentally, variation of peak time (t_p) was done by varying the delay time (t_d) while keeping all the other parameters constant, t_d is the time allowed for the dme to grow and dme is held at constant potential (E_i) before potential sweep begins and t_p is given by $(E_p - E_i) / \nu + t_d$ where ν is a sweep rate. Hence by a plot of $\ln(i_p)$ vs $\ln(t_p)$ should have a slope of 0.67 for diffusion controlled process and 1.17 for strong adsorption controlled process.

When Sn-PA was subjected to the delay time study, adsorption behavior of Sn(II)-PIC (peak a) was demonstrated. For a cyclic SDSWP experiment of Sn(IV)-PIC, which commenced sweeping cathodically (negatively) at an initial potential close to Sn(II)/Sn(0) peak (peak a) and then sweep anodically to E_i , a slope of 1 was obtained from a least square plot of $\ln(i_p)$ vs $\ln(t_p)$. This value is close

to the theoretical value of 1.17 for strong adsorption. However when E_i was held at zero volt further away from peak (a), a slope of 0.77 was obtained which is smaller than the slope for strong adsorption but was larger than the theoretical value for diffusion controlled process indicating weak adsorption of reactant. These results show that the extent of adsorption of Sn(II)-PIC (peak (a)) is E_i dependent.

Effect of Initial Potential

Further studies on the effect of E_i are summarized in Tables 3 and 4. The results show that the more cathodic the E_i , the larger is the reduction current of Sn(II)-PIC. Assuming Sn(IV) complexes do not adsorb while those of Sn(II) do, thus if E_i is held in a region in which Sn(IV) is not reduced to Sn(II), no adsorption occur prior to the beginning of the sweep. As E_i moves cathodically into a region where Sn(IV) is reduced to Sn(II), adsorption of Sn(II) occurs during the entire drop growth, giving rise to an increase in the adsorption peak for the reduction of Sn(II)-PIC (peak a). The strongly irreversible nature of the reduction curve of Sn(IV) makes the region of E over which this phenomenon occurs quite broad. Peaks b, c are affected in the same way for the same reason as peak a.

Table 3 : Effect of initial potential on cyclic square wave polarographic parameters for 1.0×10^{-5} M Sn(IV), 1.0×10^{-2} M PIC, 0.50 M $(\text{NH}_4)_2\text{SO}_4$, 0.01 M acetate buffer, pH = 5.0, sweep rate = 0.781 V/s

| E_i | $E_p(\text{V})$ (peak (a)) | $(i_p)^*_{\text{dif}}$ (μA) | $E_p(\text{V})$ (peak (c)) | $(i_p)^{**}_{\text{add}}$ (μA) |
|-------|-------------------------------|---|-------------------------------|--|
| 0 | -0.704 | 1.70 | - | - |
| -0.30 | - | - | -0.192 | 0.16 |
| -0.35 | -0.702 | 2.60 | -0.190 | 0.74 |
| -0.40 | - | - | -0.192 | 3.04 |
| -0.45 | -0.702 | 4.41 | -0.192 | 4.40 |
| -0.55 | -0.703 | 5.69 | -0.191 | 5.60 |

* results obtained from sweeping the potential cathodically.

** results obtained from sweeping the potential anodically.

Table 4 : Effect of initial potential on cyclic square wave polarographic parameters for 1.0×10^{-5} M Sn(II), 1.0×10^{-2} M PIC, 0.50 M $(\text{NH}_4)_2\text{SO}_4$, 0.01 M acetate buffer, pH = 5.0, sweep rate = 0.781 V/s.

| E_i | $E_p(\text{V})$ (peak (a)) | $(i_p)^*_{\text{dif}}$ (μA) | $E_p(\text{V})$ (peak (c)) | $(i_p)^{**}_{\text{add}}$ (μA) |
|-------|-------------------------------|---|-------------------------------|--|
| 0 | -0.703 | 1.70 | - | - |
| -0.30 | -0.703 | 1.85 | -0.223 | 0.56 |
| -0.35 | - | - | -0.223 | 1.56 |
| -0.40 | -0.70 | 4.01 | - | - |
| -0.50 | -0.70 | 6.45 | - | - |
| -0.60 | -0.70 | 7.05 | -0.223 | 12.0 |

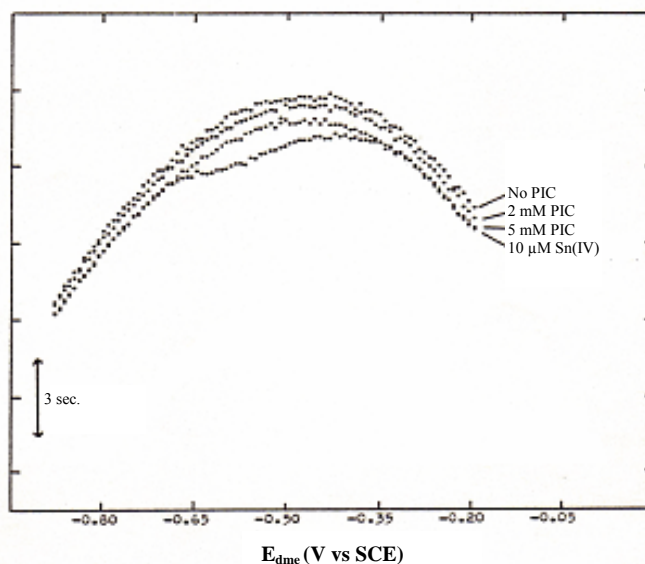
* results obtained from sweeping the potential cathodically

** results obtained from sweeping the potential anodically

Electrocapillarity curves

Electrocapillarity studies on Sn(IV)-PIC have further shown that the adsorption of Sn(II)-PIC complex at the electrode surface and indicated that Sn(IV)-PIC species are not adsorbable. Fig.4 shows that the lowering of the drop time and hence the lowering of surface tension was observed as PA was spiked into the supporting electrolyte. The lowering of drop time seems to confine only at the region around the electrocapillary maximum and there was no lowering of drop time on the anodic portion of the

curve. The latter can be attributed to the reason that Sn(IV)-PIC species are not adsorbable as no lowering of drop time was observed over its reduction potential of about -0.2 V. The lowering of drop time in the region around ECM can be accounted for by the adsorption of a reduced Sn(II)-PIC complex which is formed in this region. On the more cathodic region of the curves the desorption of adsorbed species by the reduction of the Sn(II) complex takes place.

**Figure 4 :** Variation of drop time with potential in fast polarography of 0.50 M $(\text{NH}_4)_2\text{SO}_4$ with added PIC and 1.0×10^{-5} M Sn(IV)

Analytical application

The effect of adsorption enhancement of Sn(II)/Sn(IV) in the presence of PA may successfully be employed in analytical routine of tin determination esp. in such technique as SDSWP. The use of Cyclic SDSWP would further enhance the usefulness of PA as complexing agent for tin analyses. This is because Cyclic SDSWP offer certain merit when it's operated at differential and additional modes as illustrated in Fig.5. Fig.5 shows that for a Cyclic SDSWP polarogram where a potential sweep initiates at a potential as anodic as possible, the oxidation peak of Sn(II) to Sn(IV) (peak c) is the peak of choice for analysis if the individual current components are added together (addition mode). On the other hand for Cyclic SDSWP of Sn(IV)/Sn(II) where the E_i starts near the reduction peak of the Sn(II)/Sn(0) couple, the best analytical peak is the peak current

due to the Sn(II)/Sn(0) reduction couple (peak a) if the differential mode is used. Since in the addition mode peak c appears to be of comparable magnitude, it follows that it can be used especially in cases where metal ions such as Cd(II) or In(III) interfered in the tin analysis. Peak current increases with an increase in Sn(IV) concentration for both the peak a and peak c during Cyclic SDSWV (Fig. 6), however, calibration curves for Sn-PA system is linear only at tin concentration below $20\mu\text{M}$. The reduction current of Sn(IV)-PA system was not only scan rate and initial potential dependent, it was also pH and ligand concentration dependent. The pH range 3 to 5 and picolinic acid concentration of 5-10mM should be employed for maximum current output. Based on the product of two times the standard deviation of the background noise, the detection limit for Tin is estimated to be of the order of 10^{-9}M .

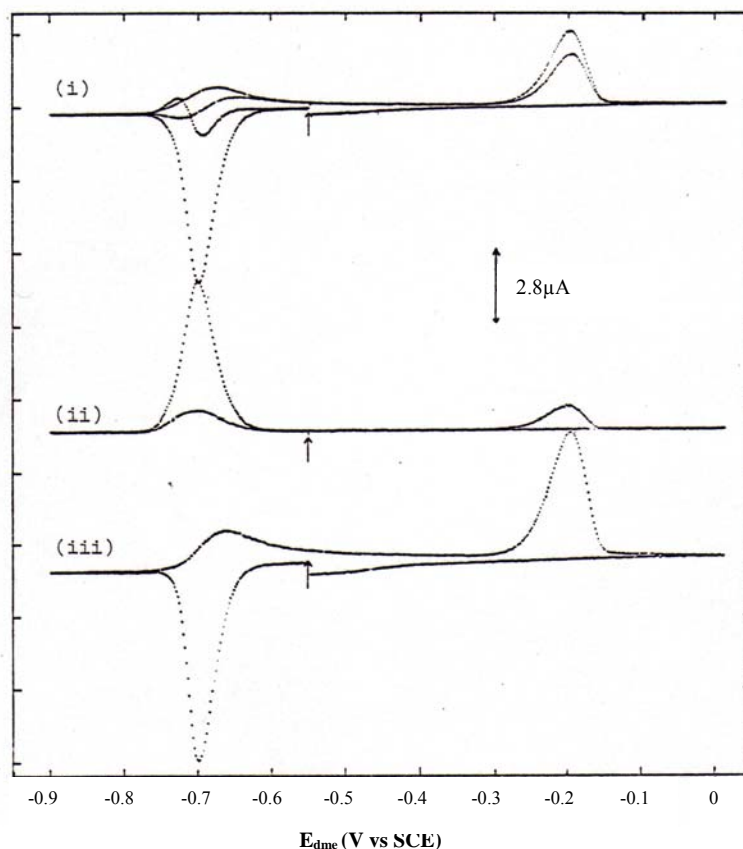


Figure 5 : Comparison of cyclic square wave polarogram of:
 (i) actual (individual) currents curves
 (ii) differential average currents curves
 (iii) currents curves from the addition of those from cathodic and anodic scans for $1.0 \times 10^{-5}\text{ M Sn(IV)}$ with $1.0 \times 10^{-2}\text{ M PIC}$, $0.50\text{M (NH}_4)_2\text{SO}_4$, $1.0 \times 10^{-2}\text{ M Acetate buffer}$; pH = 5.0, sweep rate = 0.781 V/s , $E_i = -0.55\text{ V}$.

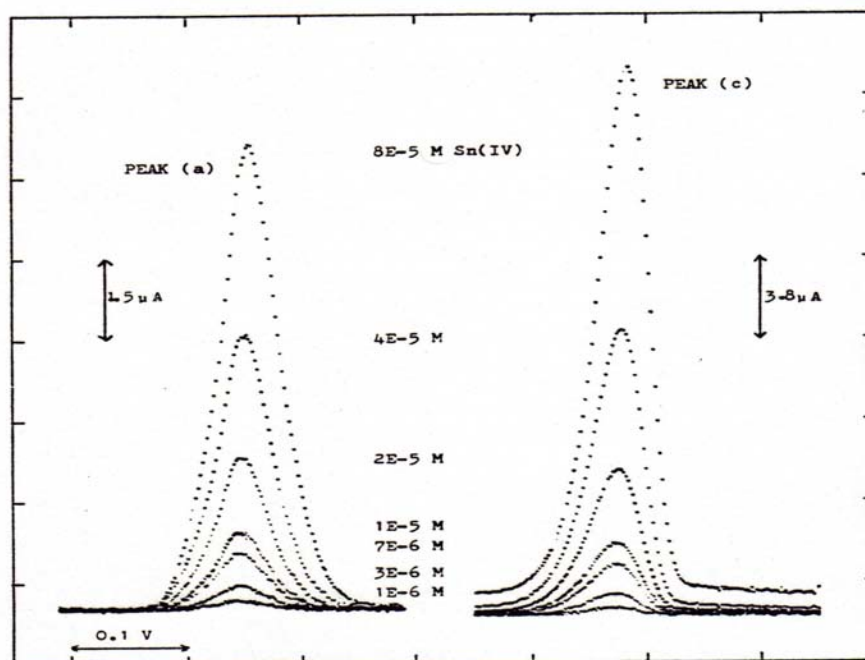


Figure 6 : Variation of differential peak current curves (peak (a)) and additive i_p curves (peak (c)) of cyclic square wave polarogram with Sn(IV) concentration in 10.0 mM PIC, 0.50 M $(\text{NH}_4)_2\text{SO}_4$ 10.0 mM acetate buffer; pH = 5.0, sweep rate = 0.781 V/s.

Conclusion

Cyclic single drop square wave polarography has been demonstrated to be able to construct cyclic polarogram of Sn(IV) based on SDSWP using a single drop of dropping mercury electrode, allowing both the forward and reverse steps of the redox reaction to be monitored. The reduction of Sn(IV) ions is still rather irreversible in noncomplexing media during Cyclic SDSWP. However, the presence of picolinic acid renders the rather irreversible electrode reactions of Sn(IV) ions to be more reversible, and also produces enhanced peaks of close to 3 folds. The polarographic waves due to Sn(IV)-PIC/Sn(II)-PIC and Sn(II)-PIC/Sn(0) redox couples are readily observed during Cyclic SDSWP. The conditions for maximum current enhancement have been optimized. Evidences obtained from delay time, electrocapillarity curves and Triton-X studies have shown that the observed enhancement effect is due to the adsorption of metal-picolinate complex species on the Hg electrode surface. Sn(II)-PIC and not Sn(IV)-PIC complex species is adsorbable and more reversible. The versatility of Cyclic SDSWP modes enabling differential and additional modes to be used depending on analytical needs such as that of tin(II)/(IV) ions analysis is demonstrated.

Aknowledgement

The author wishes to thank Universiti Putra Malaysia for granting the study leave and Trace Analysis Research Centre, TARC, Department of Chemistry, Dalhousie University, Canada for the use of a Lab.built Polarographic Workstation constructed by Prof. Dr L.Ramaley and his group during the leave.

References

1. Lingane J. J. (1945) *J. Am. Chem Soc.*, **67**:919
2. Bard, A. J. (1962) *Anal. Chem.*, **34**: 266
3. Bond, A. M. (1970) *Anal Chem.*, **42**: 1165
4. Bond, A. M. and Taylor, R. J. (1970) *J. Electroanal. Chem.*, **28**, 207
5. Kadish, K. M., Stamp J., Chemla, M. and Fatouros, N. (1973) *Anal. Lett.*, **6(10)**: 909
6. Borus-Boszormenyi N., Nahrung (1980) *Anal. Abstr.*, **2413**: 295, 39(4): 441 (1980); 4F6
7. Darja Benne, Ralf Keding, Christian Russel, (2005) *J. of Non-crystalline Solids*, **351**, 2987-2994.
8. Yi-Heng Li, Hui Long, Fang-Qin Zhou (2005) *Anal. Chim. Acta*, **554**, 86-91
9. Samuel B. O. Adeloju and Fleurdelis Pablo (1992) *Anal. Chim. Acta*, **270**, 143-152

10. S. B. Adeloju (1991) *Anal. Sci.*, **7**, 1099
11. F. Heppeler, S. Sander, G. Henze (1996) *Anal. Chim. Acta*, **319**, 19
12. Z. Q. Gao, K. S. Siow (1996) *Anal. Sci.*, **12**, 267
13. Ramaley, L.; Dalziel, J. A. and Tan. W. T. (1981) *Can. J. Chem.*, **59**:3334
14. Ramaley, L. and Tan, W. T. (1981) *Can. J. Chem.*, **59**:3326
15. Ramaley, L. and Tan, W. T. (1987) *Can. J. Chem.*, **65**:1025.
16. Koryta, J. (1953) *Collt. Czech. Chem. Commun.*, **18** : 206.