Monatshefte für Chemie 115, 1293—1298 (1984)

**Monatshefte für Chemie**
**Chemical Monthly**

# Electrochemical Studies on the Composition, Stability Constants and Thermodynamics of Tl(I) Complexes with Dithiodipropionic Acid

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*(Received 4 August 1983. Accepted 2 February 1984)*

The composition and stability constants of Tl(I) complexes with dithiodipropionic acid have been studied employing *Lingane's* polarographic method, *Calvin-Melchior's* *pH*-metric technique, and conductance measurements. The thermodynamic functions $\Delta G$, $\Delta H$ and $\Delta S$ involved in complex formation are also determined at 30 °C.

*[Keywords: Dithiopropionic acid complexes; Electrochemistry; Thallium(I) complexes]*

*Elektrochemische Untersuchungen von Zusammensetzung, Stabilitätskonstanten und Thermodynamic von* Tl(I)-*Komplexen mit Dithiodipropionsäure*

Die Zusammensetzung und die Stabilitätskonstanten von Tl(I)-Komplexen mit Dithiodipropionsäure wurde mittels polarographischer Methoden (nach *Lingane*), *pH*-metrischer Titration (nach *Calvin-Melchior*) und Leitfähigkeitsmessungen untersucht. Die thermodynamischen Funktionen der Komplexbildung ($\Delta G$, $\Delta H$ und $\Delta S$) wurden bei 30 °C bestimmt.

## Introduction

In continuation of the earlier work by *Saxena* and coworkers[1–5] on the electrochemical behaviour of several organo-sulphur compounds and their metal complexes, this communication reports the formation, composition and stability constants of Tl(I) with dithiodipropionic acid.

## Experimental

Dithiodipropionic acid (referred herein as DTDPA) of 99% purity was supplied by Evan's Chemetics, Inc. New York. All other chemicals used were of reagent grade and their solutions were prepared in doubly distilled water. Triton-X-100 (0.002%) was used as maximum suppressor.

Polarographic measurements were made on a Toshniwal polarograph equipped with thermostated H-cell and saturated calomel electrode. The capillary had the following characteristics: $m = 1.862$ mg/s; $t = 3.66$ s, $m^{2/3}t^{1/6} = 1.878$ mg$^{2/3}$ s$^{-1/2}$ at $h_{Hg} = 50$ cms.

*pH* measurements were made on a Toshniwal digital *pH* meter (accuracy ± 0.01 *pH*) with glass calomel electrode assembly in nitrogen atmosphere. Conductance measurements were carried out with an electronic eye type conductometer (L.B.R.; W.T.W. Germany).

## Results and Discussion

### *Polarographic Studies*

The current voltage curve of $Tl^{+1}$ in presence of different concentrations of dithiodipropionic acid are plotted at 30 °C. A single well defined cathodic wave appeared. The plots of $\log i/i_d - i$ vs. $E_{d.e.}$ yielded straight lines with slopes which agreed with theoretical values; the mean slope for the series was 0.061, showing the reversibility of the reduction. The value of $n$ – number of electrons involved – was also determined by the millicoulometric method of *DeVries* and *Kroon*[6]. The cathodic shift of $E_{1/2}$ coupled with decrease in diffusion current on increasing ligand concentration shows the complex formation. The plots $i_d$ vs. $\sqrt{h}$ were found to be linear, indicating the diffusion controlled nature of the reduction.

The plot of $-\Delta E_{1/2}$ vs. $-\log C_X$ yielded a straight line (Fig. 1), indicating the formation of one complex species and hence the method of *Lingane*[7] was adopted for the evaluation of stability constants and the co-ordination number.

*Lingane* found that at 25 °C

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{MX_j} + j\frac{0.0951}{n} \log C_X \qquad (1)$$

Where $\beta_{MX_j}$ is the stability constant, '$j$' is the number of coordinated ligand(s) and $C_X$ is the ligand concentration.

The rate of change of half wave potential with ligand concentration may be expressed as

$$\Delta E_{1/2} = -j\frac{0.0591}{n} \log C_X \ (25\,°\mathrm{C}) \qquad (2)$$

Thus a plot of $-\Delta E_{1/2}$ vs. $-\log C_X$ (Eq. 2) yields a straight line of slope $-j\ 0.0591/n$ from which the co-ordination number $j$ of the complex species is determined and found to be 2.15 revealing the formation of a 1 : 2

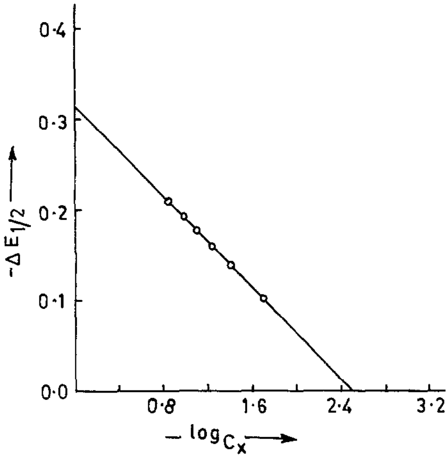

Fig. 1. Plot of $-\Delta E_{1/2}$ vs. $-\log C_X$ for the $Tl^{+1}$ – dithiodipropionic acid system

complex. Now, from the known value of '$j$' the value of $\log\beta$ is calculated using eq. (1) and found to be 5.40 at 30 °C which is in close proximity with the value obtained from the *pH*-metric titration technique.

### *Potentiometric and Conductometric Studies*

The stoichiometry of the reaction between $Tl^{+1}$ and dithiodipropionic acid was determined by *pH* metric and conductometric titrations of mixtures of reactants in various ratios against standard NaOH (Fig. 2).

The neutralisation curve of free dithiodipropionic acid denoted as $H_2A$ ($A = {}^{-}OOC-CH_2-CH_2-S-S-CH_2-CH_2-COO^{-}$) against standard alkali showed an inflection at two moles of base per mole of ligand according to the following equation:

$$H_2A + 2\,OH^- \rightarrow A^{-2} + 2\,H_2O \qquad (3)$$

Addition of an equimolar concentration of $Tl^{+1}$ ion (Fig. 2, curve 4) alters the shape of the titration curve. The resulting inflection at 2.5 and 3 moles of alkali per mole of ligand may be attributed to the formation of the 1 : 2 chelate and its decomposition to disodium salt of ligand and metal hydroxide according to the following equations:

$$Tl^{+1} + H_2A + 2\,OH^- \rightleftharpoons TlA^- + 2\,H_2O \qquad (4)$$

$$TlA^- + \frac{1}{2}OH^- \rightleftharpoons \frac{1}{2}[Tl(A)_2]^{-3} + \frac{1}{2}TlOH \qquad (5)$$

$$\frac{1}{2}[Tl(A)_2]^{-3} + \frac{1}{2}OH^- \rightleftharpoons A^{-2} + \frac{1}{2}TlOH \qquad (6)$$

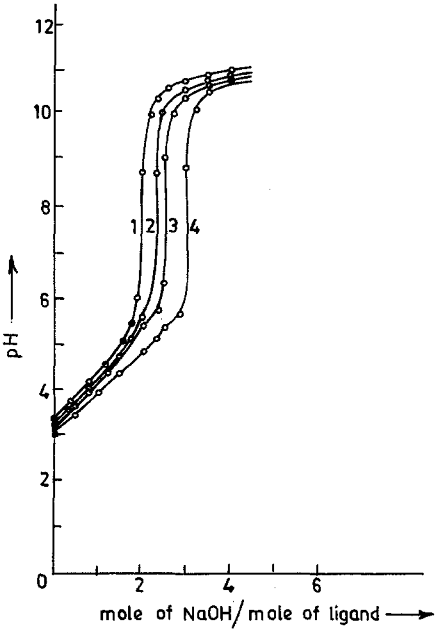

Fig. 2. *pH* metric titration of the solutions. *1* $4\cdot10^{-3}$ *M DTDPA*; *2* $4\cdot10^{-3}$ *M DTDPA* + $1.33\cdot10^{-3}$ *M* $\mathrm{Tl}^+$; *3* $4\cdot10^{-3}$ *M DTDPA* + $2\cdot10^{-3}$ *M* $\mathrm{Tl}^+$; *4* $4\cdot10^{-3}$ *M DTDPA* + $4\cdot10^{3}$ *M* $\mathrm{Tl}^+$

When two moles of ligand are added to $\mathrm{Tl}^{+1}$ (Fig. 2, curve 3), the curve shows two inflections at 2 and 2.5 moles of alkali per mole of ligand which correspond to decomposition of 1 : 2 chelate into its disodium salt of acid and metal hydroxide according to following equations:

$$\frac{1}{2}\mathrm{Tl}^+ + \mathrm{H}_2A + 2\,\mathrm{OH}^- \rightleftharpoons \frac{1}{2}[\mathrm{Tl}(A)_2]^{-3} + 2\,\mathrm{H_2O} \tag{7}$$

$$\frac{1}{2}[\mathrm{Tl}(A)_2]^{-3} + \frac{1}{2}\mathrm{OH}^- \rightleftharpoons A^{-2} + \frac{1}{2}\mathrm{TlOH} \tag{8}$$

This has been further confirmed by the inflection at 2 and 2.33 moles of alkali per mole of ligand (Fig. 1, curve 2) when the ratio of metal to ligand has decreased to 1 : 3.

The stoichiometry was further determined by conductometric titrations of the solutions containing Tl(I) ions and the dithiodipropionic acid mixed in different ratios against standard 0.1 NaOH. The breaks in the titration curves reveal the formation of an 1 : 2 complex as obtained from *pH* titration curves.

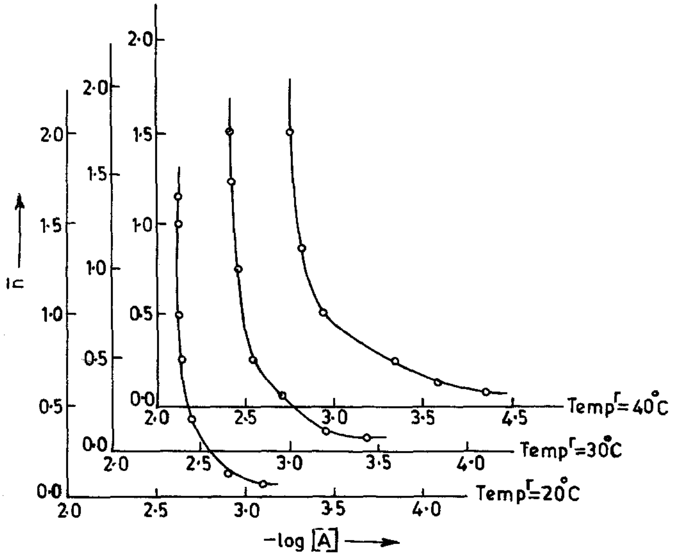

Fig. 3. Formation curves of $Tl^+$ complexes of dithiodipropionic acid at 20°, 30° and 40 °C

Table 1. *Values of stability constants at 20, 30, and 40 °C by potentiometric method, and at 30 °C by Lingane's polarographic method*

| Methods | 20 °C | | | 30 °C | | | 40 °C | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\log K_1$ | $\log K_2$ | $\log \beta$ | $\log K_1$ | $\log K_2$ | $\log \beta$ | $\log K_1$ | $\log K_2$ | $\log \beta$ |
| *Potentiometric* | | | | | | | | | |
| Extension of *Bjerrum*'s method | 2.66 | 2.63 | 5.29 | 2.76 | 2.67 | 5.43 | 2.92 | 2.75 | 5.67 |
| Least square | 2.67 | 2.63 | 5.30 | 2.77 | 2.67 | 5.44 | 2.97 | 2.80 | 5.77 |
| Correction term | 2.68 | 2.64 | 5.32 | 2.77 | 2.68 | 5.45 | 2.93 | 2.77 | 5.70 |
| Convergence formulas | 2.66 | 2.62 | 5.28 | 2.75 | 2.67 | 5.42 | 2.92 | 2.74 | 5.66 |
| *Polarographic* | – | – | – | – | – | 5.40 | – | – | – |

Formation curves for *pH*-metric titrations were obtained by plotting $\bar{n}$ against $-\log[A]$ at 20°, 30° and 40 °C (Fig. 3). The values of stability constants were obtained at $\bar{n} = 0.5$ and $\bar{n} = 1.5$, respectively, employing *Calvin-Bjerrum*'s method[8,9] and further refined by least square treatment[10] (correction term[10] and convergence formulas[11] are recorded in Table 1). From the nature of the formation curves and Table 1 it is observed that the values of $\log K_1$ and $\log K_2$ are not much different and that $\log K_{stab}$ values increase with rising temperature indicating that the complexes become more stable with increase in temperature.

## Thermodynamic Functions

The values of $\Delta G$, $\Delta H$ and $\Delta S$ have been evaluated accompanying the complexation reaction at 30 °C by employing the standard equations[12] and found to be − 7.53 K cal/mol, − 7.76 K cal/mol and − 0.788 cal/(deg mol), respectively.

## References

[1] *Saxena R. S., Gupta K. C.,* J. Indian Chem. Soc. **46**, 303 (1969).
[2] *Saxena R. S., Singh P., Mittal M. L.,* Indian J. Chem. **7**, 1149 (1969).
[3] *Saxena R. S., Gupta K. C., Mittal M. L.,* Can. J. Chem. **46**, 311 (1968).
[4] *Saxena R. S., Gupta K. C., Mittal M. L.,* J. Inorg. Nucl. Chem. **30**, 189 (1968).
[5] *Saxena R. S., Gupta K. C., Mittal M. L.,* Aust. J. Chem. **21**, 641 (1968).
[6] *DeVries T., Kroon J. L.,* J. Amer. Chem. Soc. **75**, 2484 (1953).
[7] *Lingane J. J.,* Chem. Rev. **29**, 1 (1941).
[8] *Calvin M., Melchior N. C.,* J. Amer. Chem. Soc. **70**, 3270 (1948).
[9] *Bjerrum J.,* Metal Amine Formation in Aqueous Solutions. Copenhagen: P. Hasse and Sons. 1941.
[10] *Irving H., Rosotti H. S.,* J. Chem. Soc. **1953**, 3397.
[11] *Schroder K. N.,* Acta Chem. Scand. **20**, 1401 (1966).
[12] *Yatsimirskii K. B., Vasil'ev V. P.,* Instability Constants of Complex Compound. Oxford: Pergamon. 1960.