

## S Y N O P S I S

During recent years a considerable attention has been paid to the quantitative characteristics of complex compounds and complex formation in solution. Stability constants quantitatively characterise the equilibria in solution and in this connection are widely used by chemists working in different fields for appropriate calculations. In order to have the most accurate approach for an investigation of the nature of forces acting within the complexes when these are formed in solution, it is necessary to have a knowledge of the enthalpy and entropy changes accompanying such reactions, as the former are more closely related to the metal-ligand bond strength than are the stability constants and the latter include the probability factors controlling the stability of complexes in solution.

Although an abundance of such data is available for ligands containing nitrogen and oxygen, the data for sulphur containing ligands is very meager and even the data available are of doubtful validity. In order, therefore, to throw some light on the bonding characteristics of sulphur containing ligands, it would be highly desirable to carry out accurate investigations on complex formation with such ligands.

Thiourea is an important sulphur containing ligand, and though its complexes have found important applications in analytical chemistry, accurate data on the thermodynamic characteristics of its complex formation in solution is lacking.

and the corresponding overall enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes have been evaluated.

Complex formation between Tl(I) and thiourea has been studied at 30°C. Since the higher complexes of this metal with thiourea are highly insoluble, it was found necessary to work in a small range of thiourea concentrations. Treatment of the data by DeFord and Hume's method of analysis reveals that the only predominating species in the range of thiourea concentrations from 0.05 to 0.23M are  $[\text{Tl}(\text{Tu})]^+$  and  $[\text{Tl}(\text{Tu})_2]^+$ . Their formation constants have also been determined.

Since the evaluation of the stability constants from the DeFord and Hume's functions by the graphical extrapolation is subject to errors, the 'least squares' procedure has been recommended by several authors. The polarographic data for Cd(II), Pb(II) and Tl(I) at 30°C has been treated by this procedure and the values of the constants obtained by this method are found to differ substantially from the values obtained by the graphical procedure. Probable reasons for these discrepancies have been suggested.

#### Chapter - IV. Potentiometric studies on complex formation:

This chapter deals with the potentiometric studies on complex formation. Potentiometric studies have been carried out for the Cd(II) and Pb(II) thiourea systems, in order to corroborate the results of the polarographic measurements. Initial

"resistance-potentiometer polarograph" described by Meites and Thomas has been assembled and highly refined polarographic measurements of the half-wave potential  $E_{1/2}$ , have been carried out for the cadmium(II)-, lead(II)- and thallium(I)-thiourea system in cells of the following type,

Hg	Hg <sub>2</sub> Cl <sub>2</sub>		NaClO <sub>4</sub> ..... 0.899M	NaClO <sub>4</sub> ..... 0.998M	D.M.E.
			NaCl ..... 0.100M	M(ClO <sub>4</sub> ) <sub>2</sub> .... 0.0005M	
			HClO <sub>4</sub> ..... 0.001M	HClO <sub>4</sub> ..... 0.001M	
				gelatin ..... 0.002%	
				thiourea .... ~	

making full allowance for all sources of potential errors which are known to cause deviation in the measured  $E_{1/2}$  values. The  $E_{1/2}$  values have been evaluated to 0.05 mv. and the reproducibility of the measurements in duplicate experiments is of the order of 0.2 mv.

Complex formation between Cd(II) and Pb(II) with thiourea has been studied polarographically at different temperatures between 25°C and 50°C and a series of measurements have been carried out at each temperature in the range of thiourea concentrations from 0.01 to 1M. The data obtained has been treated according to DeFord and Hume's method of analysis. The results reveal the existence of mono-, bis-, tris- and tetrakis- coordinated species for both cadmium(II)- and lead(II)-thiourea systems at all the temperatures studied. The overall formation constants ( $\beta_1$ 's) have also been determined at the different temperatures,

In the work described in the present thesis, an attempt has been made to study the complete thermodynamic characteristics including the free energy change  $\Delta F^\circ$ , enthalpy change  $\Delta H^\circ$  and entropy change  $\Delta S^\circ$ , accompanying the formation of cadmium(II)-, lead(II)- and thallium(I)-thiourea complexes in solution. The thesis comprises six chapters and one appendix.

Chapter - I. Introduction and literature survey:

This chapter includes the literature survey of the analytical applications of thiourea and of the physico-chemical studies on metal-thiourea complexes. The solution equilibria studies reported in the literature for the metal-thiourea systems have been critically reviewed and their limitations pointed out.

Chapter - II. Fundamental principles characterizing complex formation in solution:

This chapter deals with the theoretical aspects of stepwise equilibria of complexes in solution. The various functions used to characterise complex formation in solution have been derived and the methods used for evaluating stepwise stability constants in solution, and the enthalpy and entropy changes involved in the complex formation reactions have been discussed.

Chapter - III. Polarographic studies on complex formation:

In this chapter the polarographic studies on complex formation have been described. A modified version of the

"resistance-potentiometer polarograph" described by Meites and Thomas has been assembled and highly refined polarographic measurements of the half-wave potential  $E_{1/2}$ , have been carried out for the cadmium(II)-, lead(II)- and thallium(I)-thiourea system in cells of the following type,

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