Studies on Mixed Ligand Complexes in Aqueous Medium by the Polarographic Method.
Cadmium–Thiocyanate–Thioacetamide and Cadmium–Thioacetamide–Nicotinamide Systems

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The nature of mixed ligand complexes of thiocyanate (SCN), thioacetamide (TAA) and nicotinamide (nico) with Cd(II) was studied polarographically in aqueous medium at 25 ± 0.5 °C. The mixed complexes $[Cd(SCN)(TAA)]^+$ (2.05), $[Cd(SCN)(TAA)_2]^+$ (1.17), $[Cd(SCN)_2(TAA)]$ (2.15), $[Cd(TAA)_2(nico)]^{++}$ (1.61), $[Cd(TAA)(nico)_2]^{++}$ (1.36) and $[Cd(TAA)_2(nico)]^{++}$ (1.68) were detected (the values in parentheses are log stability constants). The positive values of mixing constant and stabilization constant reveal that the mixed complexes [Cd(SCN)(TAA)]$^+$ and [Cd(TAA)(nico)]$^{++}$ are more stable than their parent binary complexes. The observed enhancements of the complexation constants of the mixed complex species were attributed to the possibilities of some weak bonding between the unlike bound ligands, simultaneous π-bonding between Cd(II) and both the ligands and cooperative effects of electrostatic forces between the ligands.

Introduction

Polarographic studies of mixed ligands complexes of Cd(II) with many organic and inorganic anions have been reported from our laboratory [1–4]. In a previous report it has been shown that Cd(II) forms mixed ligand complexes with thiourea and glycine/β-alanine [4]. The present paper deals with the polarographic behaviour of cadmium(II) in thiocyanate, thioacetamide and nicotinamide media, as well as in mixed ligand media at 25 ± 0.5 °C. In all the cases the reduction of Cd(II) was found to be reversible.

Experimental

All the reagents used were of *Analar* grade and used as such. The ionic strength of all the experi-

mental solutions was kept constant at 1.0 M with potassium nitrate.

A Cambridge automatic recording polarograph was used for recording polarograms. Deoxygenation of the solutions was achieved by purified nitrogen gas. Half-wave potentials refer to saturated calomel electrode (SCE) and were obtained from log plots. The dropping mercury electrode had the following characteristics: t = 3.0 sec in 0.1 M KNO$_3$ (open circuit), m = 1.96 mg sec^{-1}. The cell resistance was found to be low in all cases.

Results and Discussion

Simple systems, namely Cd(II)–thiocyanate, Cd(II)–thioacetamide and Cd(II)–nicotinamide, were investigated in order to obtain their stabilities of simple complexes under identical experimental conditions maintained for the mixed systems.

For the Cd(II)–thiocyanate system the polarograms were recorded of the experimental solutions containing 1 mM Cd(II), ionic strength 1.0 M and varying concentration (0.08–0.88 M) of thiocyanate. The relationship between $-(E_{1/2})_c$ and log C_L was not linear but gave a smooth curve. The data were subjected to the DeFord–Hume method [5] which indicated the existence of 1:1, 1:2 and 1:3 complex species with their respective stabilities as log β_1 = 1.50, logβ_2 = 0.90 and log β_3 = 2.11. These values are in good agreement with the previously reported values [6] observed at an ionic strength of 1.5 M (KNO$_3$). The bonding of Cd(II) with thiocyanate occurs through S and not through N, as may be inferred from the attraction between soft base S and soft acid Cd(II) [7].

In the Cd(II)–thiocyanate system the concentration of the ligand was varied from 0.08 to 0.96 M. Other conditions were identical to those maintained in the above system. Three complex species

1:1, 1:2 and 1:3 were detected, with their stability constants: log β_1 = 0.81, log β_2 = 0.20 and log β_3 = 1.46. Thioacetamide exhibits thione–thiol tautomerism [8]. Since no sulphydryl vibration has been observed in the Raman spectrum [9] thioacetamide probably has the amide structure. It is shown [10] that the carbon–sulphur bond has a negligible single bond character and the carbon–nitrogen has a negligible double bound character so that thioacetamide may not have zwitterion character [11]. Most of the physical evidence indicates that acyclic thioamides exist primarily in the thione form [3,8]. In most of the transition metal complexes it has been noted [12–15] that the thioacetamide coordinates through sulphur. It was inferred therefore that Cd(II) may also bind through sulphur.

The same procedure was adopted for the Cd(II)–nicotinamide system within the same concentration range of the ligand. Two complex species were detected with their stability constants log β_1 = 0.67 and log β_2 = 0.76. The existence of such weak complex species of nicotinamide with Cd(II) in aqueous as well as in mixed solvents was observed by other workers [16]. The coordination of nicotinamide with Cd(II) was shown to occur through the pyridine ring nitrogen [17]. Nicotinamide contains an electron attracting group which is expected to decrease the electron density in the pyridine ring. Murman and Basolo [18] have studied the effect of substitution in the pyridine ring in silver complexes. They observed that groups in the 4-position tend to pull electrons from Ag(I) ion into the ring, i.e., increase the tendency of forming a double bond. It was also noted that the group in the 3-position, as in nicotinamide, did not contribute to this type of resonance and hence the stabilities of these complexes were expected to correlate largely with the base strength of pyridine and hence the stabilities of metal–nicotinamide complexes ought to be low.
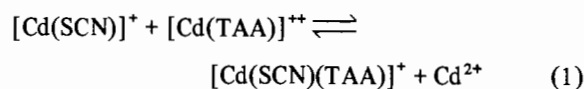
Mixed Systems

For Cd(II)–thiocyanate–thioacetamide and Cd-(II)–thiocyanate–nicotinamide systems polarograms were recorded with solutions containing 1 mM Cd(II), constant thioacetamide and varying thiocyanate and constant nicotinamide with varying thioacetamide at 1.0 M (KNO$_3$) ionic strength. The two constant concentrations 0.24 M and 0.56 M of TAA and 0.32 M and 0.80 M of nico at which 1:1 and 1:2 complex species predominated in the simple systems were chosen for the study of mixed systems. In all the sets of the mixed ligand systems the reduction waves were found to be well defined and reversible, both in the presence and absence of ligand (slope of log plots 32 ± 2mV), and to be diffusion controlled, as indicated by the linear plot of i_d *vs.* $\sqrt{h}$ (effective) which passed through the origin.

On increasing the concentration of thiocyanate in the former and thioacetamide in the latter system, the half-wave potential of Cd(II) shifted towards more negative values and the shift was found to be more marked than in the simple systems. Similar observations were recorded at higher concentration of TAA and nico (kept constant) in the respective systems. Schaap and McMasters [19] method was applied to determine the overall stability constants of the mixed ligand complexes. The values of the constants A, B, C and D (having their usual significances) obtained for both the systems are given in Table I.

The average log D values for Cd(II)–SCN–TAA and Cd(II)–TAA–nico systems are 2.36 and 1.85 respectively, nearly identical with the stability constant of the parent species [Cd(SCN)$_3$]$^-$ and [Cd-(TAA)$_3$]$^{++}$ respectively. Slightly higher values of log D may be due to the incomplete dissociation of [Cd(SCN)$_2$(TAA)] and [Cd(TAA$_2$)(nico)]$^{++}$ complexes in aqueous medium.

The stability of mixed ligand complexes can be compared with those of simple complexes. The equilibrium constant K for the reactions:

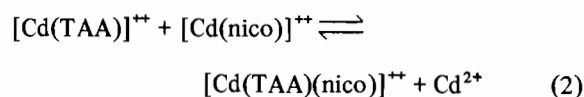$$[Cd(SCN)]^+ + [Cd(TAA)]^{++} \rightleftharpoons$$
$$[Cd(SCN)(TAA)]^+ + Cd^{2+} \quad (1)$$

and

$$[Cd(TAA)]^{++} + [Cd(nico)]^{++} \rightleftharpoons$$
$$[Cd(TAA)(nico)]^{++} + Cd^{2+} \quad (2)$$

TABLE I.

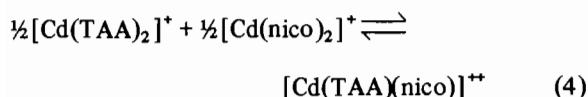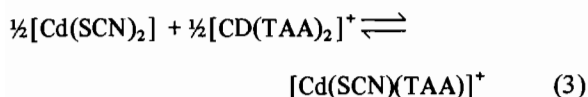| Constant conc. of the ligand	Values of the constant				Overall stability constants (log values)
	A	B	C	D	
[TAA] = 0.24 M	5	60	20	165	β_{11} = 2.05, β_{12} = 1.17 and β_{21} = 2.15
[TAA] = 0.56 M	12	100	140	300	
[nico] = 0.32 M	5	16	8	55	β_{11} = 1.21, β_{12} = 1.56 and β_{21} = 1.33
[nico] = 0.80 M	8	44	20	87	

TABLE II.

Species	Observed	Predicted	Enhancements
$[Cd(SCN)_2(TAA)]$	$10^{2.15}$	$10^{0.68}$	$10^{1.37}$
$[Cd(SCN)(TAA)_2]^+$	$10^{1.17}$	$10^{2.15}$	$10^{-0.98}$
$[Cd(SCN)(TAA)]^+$	$10^{2.05}$	$10^{2.37}$	$10^{-0.22}$
$[Cd(TAA)(nico)_2]^{++}$	$10^{1.68}$	$10^{1.45}$	$10^{0.23}$
$[Cd(TAA)_2(nico)]^{++}$	$10^{1.36}$	$10^{0.96}$	$10^{0.40}$
$[Cd(TAA)(nico)]^{++}$	$10^{1.61}$	$10^{0.61}$	$10^{1.00}$

is given by the relation

$$\Delta\log K = \log \beta_{11} - \log \beta_{10} - \log \beta_{01}.$$

The $\Delta\log K$ values for reactions 1 and 2 have been estimated as -0.26 and -0.27 respectively. These negative values suggest that the mixed complex species are less stable than the parent mono-complexes. The mixing constant K_m (equilibrium constant) for the reactions 3 and 4:

$$\tfrac{1}{2}[Cd(SCN)_2] + \tfrac{1}{2}[CD(TAA)_2]^+ \rightleftharpoons$$

$$[Cd(SCN)(TAA)]^+ \qquad (3)$$

$$\tfrac{1}{2}[Cd(TAA)_2]^+ + \tfrac{1}{2}[Cd(nico)_2]^+ \rightleftharpoons$$

$$[Cd(TAA)(nico)]^{++} \qquad (4)$$

indicate the relative stability of the respective mixed complexes in solution as compared to the parent binary complexes. This is given by the relation

$$K_m = \beta_{11}/\sqrt{\beta_{20} \cdot \beta_{02}}$$

The values of $\log K_m$ for the reactions 3 and 4 are 1.50 and 0.73 respectively. The stabilization constant K_s [20] is expressed as: $\log K_s = \log \beta_{11} - \tfrac{1}{2} (\log\beta_{20} + \log \beta_{02} + \log 4)$. The $\log K_s$ values for both the systems were found to be 1.20 and 0.43 respectively.

The positive value of mixing constant and stabilization constants show that the respective mixed complexes are somewhat more stable than the concerned simple bis complexes. Such positive values of stabilization constant have also been observed by Brooks and Pettit [21], Gergely and Sovago [22], Ting and Nancolas [23] and recently by Jain and Kapoor [24].

Statistical Calculations

Bjerrum [25] has used the logarithm of the N'th root of N' for a simple complex — $\log N'$ — as a measure of the complex formation tendency of a ligand. It has been deduced [26, 27] that for a mixed ligand system in which three mixed complexes are

formed, it is possible to predict on a statistical basis that the value of the formation constant, $\beta_{21} = 3 \times \beta_{30}^{2/3} \times \beta_{03}^{1/3}$, $\beta_{11} = 2(4/9 \beta_{02} \times \beta_{20})^{1/2}$ and $\beta_{12} = 3 \times \beta_{30}^{1/3} \times \beta_{03}^{2/3}$.

The observed values of stability constants of mixed ligand complexes with the predicted values obtained from the above equations for the various mixed complexes are presented in Table II.

It is also observed that the mixed ligand complexes have higher stabilities than would be predicted on statistical considerations, except for $[Cd(SCN)(TAA)_2]^+$ and $[Cd(SCN)(TAA)]^+$. Such enhancements may be due to some weak bonding between unlike bound ligands, simultaneous π-bonding between Cd(II) and both the ligands. The inverse enhancement in some cases may be ascribed to inter-ligand repulsion.

Acknowledgements

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