Electrochemical behaviour of mixed complexes of ethylenediamine and trimethylenediamine with Cd(II) and their thermodynamic parameters

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Ethylenediamine and Trimethylenediamine have been found to complex with Cd (II), forming three mixed complexes having stoichiometry 1:1:1, 1:1:2 and 1:2:1. The overall formation constants of these mixed complexes have been evaluated using Schaap and McMaster's method. The thermodynamic parameters of the mixed complexes have been calculated. The relative tendencies of the simple and mixed complexes to add and substitute another ligand have been discussed.

Literature reveals that Cd(II) forms complexes with ethylenediamine[1] (EDA) and trimethylenediamine[2] (TMDA) separately. The DeFord and Hume's[3] method for the determination of stability constants of simple complexes was extended by Schaap and McMasters[4] to determine the stability constants of mixed complexes. The method of Schaap and McMasters has been extensively used by several workers[5—8]. The mixed complexes of amines with metal ions have not been studied polarographically till now and also the literature lacks the data on thermodynamics of mixed complexes. Keeping this idea in mind the present investigations were carried out.

For the theory of Schaap and McMasters method reference may be made to our previous publication[5].

EXPERIMENTAL

All the solutions contained 1×10^{-3}M Cd^{2+}. The ionic strength was maintained constant at 1 by using KNO_3 as supporting electrolyte. The solutions were prepared in double distilled water. 0.001 per cent Triton X-100 was used to suppress maximum in each solution. For mixed complexes the two fixed concentrations of TMDA were 0.02M and 0.04M. All the measurements were carried out at 300°K and repeated at 310°K. The temperatures were maintained constant using a thermostat within ±0.10K variation. The capillary of the d.m.e. used had the following Characteristics, m = 2.4 gm/sec, t = 4.6 sec. (in open circuit)

RESULTS

Simple Complexes — The reduction of Cd^{2+} in the medium of EDA and TMDA was found reversible and diffusion controlled. The slope of the straight line plots of $\log \frac{i}{(i_d - i)}$ vs E_{de} were 30 to 32 mV and the plot of i_d vs $h_{eff}^{1/2}$ of mercury column was a straight line passing through origin.

Overall formation constants of the simple complexes were determined by DeFord and Hume's method using polarographic measurements. The results are summarised below:

Complex species		Overall formation constant at 300°K	310°K
$[Cd(TMDA)]^{2+}$,	$\log \beta_{01}$	5.380	5.000
$[Cd(TMDA)_2]^{2+}$,	$\log \beta_{02}$	7.447	7.168
$[Cd(TMDA)_3]^{2+}$,	$\log \beta_{03}$	8.954	8.245
$[Cd(en)]^{2+}$,	$\log \beta_{10}$	9.602	7.301
$[Cd(en)_2]^{2+}$,	$\log \beta_{20}$	10.000	9.000
$[Cd(en)_3]^{2+}$,	$\log \beta_{30}$	12.000	11.477

Mixed Complexes — The nature of reduction of Cd^{2+} in the mixed medium was the same as in individual media. The Schaap and McMasters function F_{oo} was calculated over the given range of variable concentration of EDA at two fixed concentrations of TMDA. F_{oo} function and other function values along with the polarographic measurements are recorded in Tables 1 and 2 at 300°K and in Table 3 and 4 at 310°K. The values of B, C and D obtained as a result of graphical extrapolation are also mentioned in the respective tables. The values of A were calculated as indicated in the theory[5].

Using the values of B at two fixed concentrations of TMDA, the values of β_{11} and β_{12} were calculated which are summarised below —

	Temperature 300K	310K
$\log \beta_{11}$	10.301	9.000
$\log \beta_{12}$	11.398	11.176

And the value of C resulted the following value of β_{21} $\log \beta_{21} = 11.699$ at 300° and 11.677 at 3 0°C. The thermodynamic parameters of the mixed complexes calculated using the following relations are recorded in Table 5.

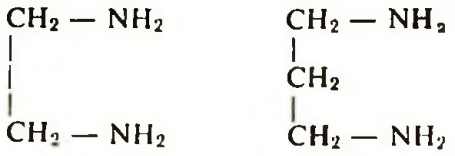
$$\Delta F^\circ = -2.303\ RT \log (\beta_j)_T \quad \text{... (i)}$$

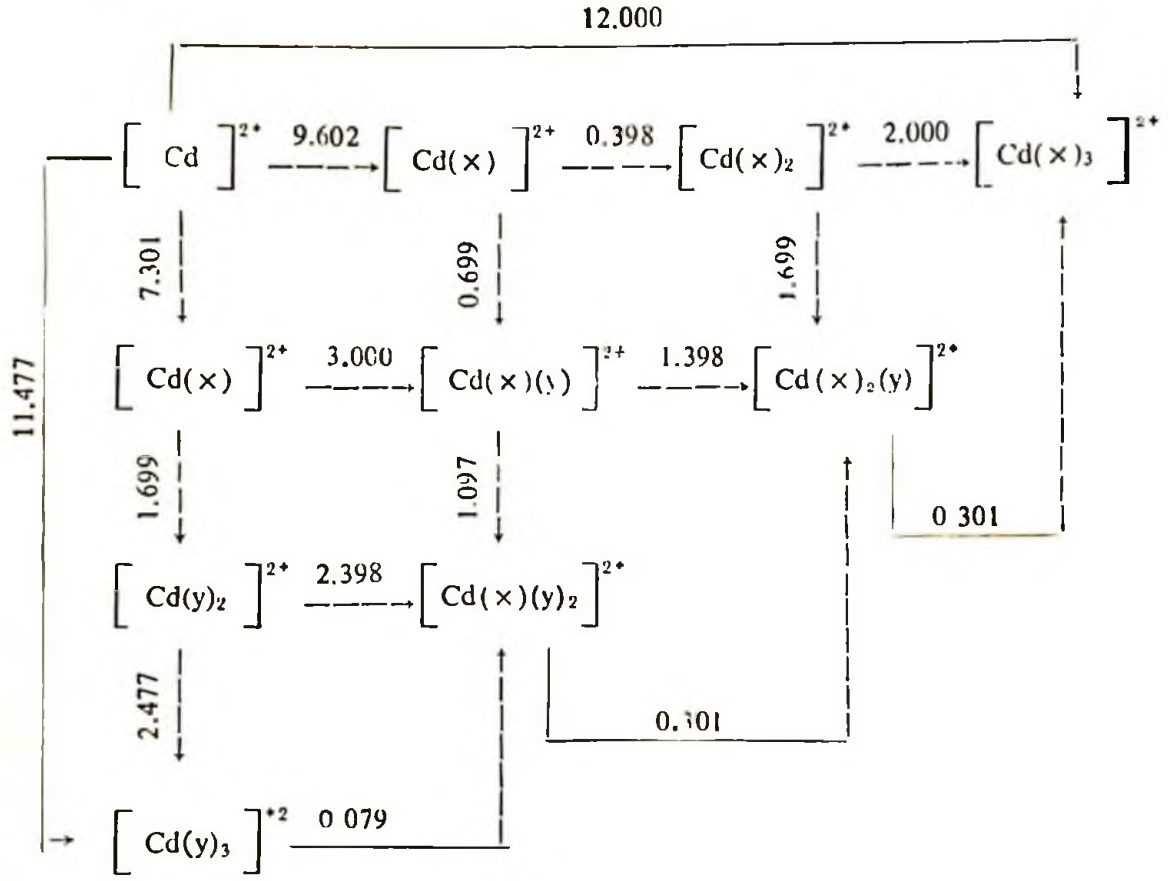
$$\Delta H^\circ = \left\{ 2.303\ RT_1T_2 \log \frac{\beta_j T_1}{\beta_j T_2} \right\} (T_2 - T_1) \quad \text{... (ii)}$$

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{... (iii)}$$

DISCUSSION

The structures of ethylenediamine (EDA or X) and trimethylenediamine (TMDA or Y) are





Both these ligands form hexacoordinated complexes with cadmium as seen from our observations. From the structures it is seen that EDA (= X) is a stronger ligand than TMDA (= Y) which is also observed in our results and supported by mixed complexation. The equilibria at 300°K among various complexes in solution are schematically shown below :

In the above scheme the numerical values are log K values where K is the equilibrium constant of the corresponding step. It is seen from the above scheme that $[Cd(Y)]^{2+}$ can add to X more easily than $[Cd(X)]^{2+}$ to Y and also that the tendency of $[Cd(Y)]^{2+}$ to add x is more than to add Y. In the same way $[Cd(X)(Y)]^{2+}$ can add X more easily than Y. It is also seen that $[Cd\ (X)\ (Y)_2]^{2+}$ can add X as well as Y but from the values of step constants it is seen that it is easier for X than Y to add to $[Cd(X)(Y)_2]^{2+}$. $[Cd(X)_2(Y)]^{2+}$ can add only X and not Y. All the above results show that the approach of X to the metal ion is less hindered than the approach of Y, and X forms stronger complexes than Y with Cd(II).

Since the complexes of Cd(II) with EDA and TMDA are very much stable they can affect the system wherever they are likely to be formed. Cadmium is reduced with controlled diffusion and can be estimated in such media polarographically.

Table 1 Polarographic measurements and F_{ij} functions of Cd EDA—TMDA mixed system at 300°K [TMDA] = 0.03M fixed; i_d of simple metal ion = 65 div; $E_{1/2}$ of simple metal ion = 0.6030 vs SCE.

C_X	$-E_{1/2}$	i_d (div)	F_{00} ($\times 10^5$)	F_{10} ($\times 10^9$)	F_{20} ($\times 10^{10}$)	F_{30} (10^{10})
0.00	0.603	65	—	—	—	—
0.01	0.834	59	505	5.25	7.5	—
0.02	0.846	58	1387	0.93	12.1	507
0.03	0.855	57	2815	9.38	16.3	475
0.04	0.862	56	5006	12 51	20.0	450
0.05	0.870	56	9057	18.11	27.2	504
0.06	0.875	55	14060	23.43	31.5	492
0.07	0.880	55	20640	29.48	35.7	481
0.08	0.885	55	29610	37.01	40.6	481

$A = 2.4 \times 10^5$; $B = 4.5 \times 10.^9$; $C = 2.0 \times 10^{1\,0}$; $D_{av} = 4.84 \times 10^{10}$

Table 2. Polarographic measurement and F_{ij} functions of Cd EDA–TMDA mixed system at 300°K [TMDA] = 0.04M fixed ; i_d of simple metal ion = 65 $_{div}$; $-E_{1/2}$ of simple metal ion = 0.603 vs SCE.

C_x	$E_{1/2}$	i_d	F_{00} ($\times 10^5$)	F_{10} ($\times 10^9$)	F_{20} ($\times 0^{10}$)	F_{30} ($\times 10^{10}$)
0.00	0.603	65	—	—	—	—
0.01	0.835	59	596	5.96	7.60	—
0.02	0.847	58	1583	7.91	13.55	—
0.03	0.847	58	3469	11.56	21.20	606
0.04	0.865	57	6621	16.55	28.37	534
0.05	0.872	56	10750	21.50	32.60	592
0.06	0.872	56	17680	29.46	40.43	623
0.07	0.884	55	25710	36.80	48.00	657
0.08	0.885	55	35800	45.50	51.60	600

$A = 3 \times 10^5$; $B = 5.2 \times 10^9$; $C = 3 \times 10^{10}$;
$D_{av} = 6.18 \times 10^{12}$

Table 3. Polarographic measurements and F_{ij} functions of Cd EDA–TMDA mixed system at 310°K. [TMDA] = 0.02M fixed ; i_d = 67 div of simple metal ion ; $-E_{1/2}$ of simple metal ion = 0.600 (vs SCE)

C_x	$-E_{1/2}$	i_d div	F_{00} ($\times 10^4$)	F_{10} ($\times 10^8$)	F_{20} ($\times 10^{10}$)	F_{30} ($\times 10^{10}$)
0.00	0.600	67	—	—	—	—
0.01	0.795	65	260	2.6	1.6	—
0.02	0.812	63	960	4.8	1.9	15.0
0.03	0.822	60	2100	7.0	2.9	16.0
0.04	0.830	59	4080	10.2	2.3	17.5
0.05	0.836	58	6500	13.0	2.5	18.3
0.06	0.842	58	9960	16.6	2.6	16.6
0.07	0.846	57	14420	20.6	2.8	17.0
0.08	0.851	56	20000	25.0	3.0	17.5

$A = 1.7 \times 10^4$; $B = 1.0 \times 10^8$; $C = 1.6 \times 10^{10}$;
$D = 1.68 \times 10^{11}$

Table 4 Polarographic measurements and F_{ij} function of Cd EDA–TMDA mixed system at 310°K. [TMDA] = 0.04M fixed ; i_d of simple metal ion = 67 div ; $-E_{1/2}$ of simple metal ion = 0.600 (vs SCE)

C_x	$-E_{1/2}$	i_d	F_{00} ($\times 10^4$)	F_{10} ($\times 10^8$)	F_{20} ($\times 10^{10}$)	F_{30} (10^{10})
0.00	0.603	67	—	—	—	—
0.01	0.805	65	591	5.90	2,90	—
0.02	0.821	63	1874	9.37	3.18	—
0.03	0,831	61	4345	14.48	3.82	60.0
0,04	0 839	60	8083	20.20	4.30	57.5
0.05	0,846	59	13440	26.88	4.77	55.4
0.06	0.852	58	21950	36.58	5.59	59,8
0.07	0.857	57	30570	43.67	5.80	59.0
0 08	0.862	56	45750	57.18	6.77	59.6

$A = 6.6 \times 10^4$; $B = 3.00 \times 10^{18}$; $C = 2.00 \times 10^{10}$;
$D = _{av}$ 5.85×10^{11}

Table 5. Thermodynamic Parameters

Complex species	ΔH° (Kcal)	ΔG° (Kcal)	ΔS° (cal)
$[Cd(ETA)(TMDA)]^{2+}$	— 55.7	— 14.23	+ 138.0
$[Cd(EDA)(TMDA)_2]^{2+}$	— 9.5	— 15.7	— 20.6
$[Cd(EDA)(TMDA)]^{2+}$	— 0.955	— 16.16	— 50 6

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