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Thermodynamics Studies of Zinc Ethylenediamine Complexes in Aqueous-Non-Aqueous Media by Polarography

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Behavior of the complex Zinc (II) Ethylenediamine in Dimethylformamide-Water and Isopropanol-Water mixture studied by direct current polarography. The reduction of complex in both the mixtures was found to be diffusion controlled as revealed by constant value of $id/h^{½}eff$, and quassi-reversible also as the slope value varies from 51mV to 54mV. The $E^{r}_{½}$ values were determined using Gellings graphical methods and the shifting of $E^{r}_{½}$ towards more negative side with successive addition of the ligand to the metal and decreased diffusion current in all the mixture of the solvent [20%, 40% and 60% (by volume) DMF- water and isopropanol-water mixtures] confirm complexation between metal and ligand in them.

Key words : Direct current polarography, Complexation, Znic (II) Ethylenediamine, Aqueous-non-aqueous media.

Introduction

Polarographic investigations of chemical substances are not restricted to the measurements in aqueous solution. More recently inorganic polarography in non-aqueous solvents has received increasing attention. Polarographic study of metal ions viz. cobalt, lithium, lead, cadmium etc. in various organic solvents have been carried out by many research groups. (Sartori. and Giacomello, 1940, 1941; Zanko and Manusova, 1940; Arthur and Lyons, 1952; Kolthoff and Coetzee, 1957).

The study of the metal complexes in non-aqueous solvents by polarographic methods has attracted much attention in recent years. Nature of the solvent has a considerable influence on the composition and stability of complexes formed (Turyan and Chebotar, 1959). Lane and co-workers (Lane, 1960) made a polarographic study of the complexes of lead, cadmium and copper with thiourea and its alkyl derivatives. Turyan and his collaborators (Turyan, 1959; Turyan and Zhentlai, 1960; Turyan and Molyanesky, 1960) studied halides and thiocyanato complexes of lead and cadmium ion in various solvents and observed a linear relationship between values of pK for the complex and the inverse of the dielectric constants. Recent polarographic studies of complexes in methanol and ethanol by Migal *et al.* (Migal and

Grimbery, 1962; Migal and Serova, 1962, 1964; Migal and Taypyskova, 1963, 1964; Migal and Chebotar, 1967; Migal and Plooe, 1965) and others (Chandra and Kumar, 1974; Shaldybeav *et al*., 1975; Arevalo Arozena *et al*. 1973) have shown that there is a sharp increase in the stability of complexes above 20% concentration which they attributed to the solvation effect. Recently polarographic investigations of lead, cadmium and zinc in dimethylformamide are done by many workers (Fujinaga and Puri, 1974; Sharma *et al*., 1975; Sharma *et al*., 1975).

Different workers in this field have obtained different results. Thus it is a need for systematic study of the influence of aqueous organic solvent mixtures on complex formation. For the purpose we investigated zinc ethylenediamine [Zn (II) EDA] complexes in aqueous mixture of dimethylformamide (DMF) and iso-propanol and this paper deals with the peculiar polarographic behavior of the Zn (II) EDA in DMF-Water and isopropanol-Water mixture.

Experimental

All chemicals used were of analytical reagent grade. Triply distilled water (TDW) was used throughout. The solvents taken for study were purified by standard methods wherever necessary.

Solution of Zinc having concentration 5×10^{-4} M was prepared by dissolving appropriate amount of zinc sulphate in TDW. Triton X -100 (.002%) was used in both case to suppress maxima. Sodium perchlorate was used as supporting electrolyte and constant ionic strength (μ=0.5M) was also maintained with its help. Nitrogen for polarographic measurement was deoxygenized by passing through vanadium (II) chloride solution containing granulated zinc. Constant temperature 298 K and 398 K was maintained using U_3Ger.Ner 8354 type thermostat.

Result and Discussion

The reduction of Zn(II) EDA in DMF-Water and isopropanol-Water mixtures was found to be diffusion controlled as revealed by constant value of $i_d/h^{1/2}$eff, and it is quassireversible also as the slope value varies from 51mV to 54mV. The successive addition of the ligand shifts $E^r_{½}$ of the metal towards more negative side and decreased diffusion current in all the mixture of the solvent i.e. 20%, 40% and 60% (by volume) DMF- water and isopropanol-

water mixtures. These results confirmed complexation between metal and ligand in them.

The $E^{r}_{½}$ values were determined using Gellings graphical methods which were then used for calculating $F_o(X)$ function of Deford Hume at various ligand concentrations. The $F_o(X)$ values and other derived function resulted from graphical extrapolation are recorded in Table-1 and Table-2 for 20% isopropanol-water and 20% DMF-water mixtures respectively at 298 K, Table-3 records only the polarographic measurements i.e. ($C_xE_{½}$ and i_d) for other cases of isopropanol-water mixture, Table-4 records polarographic measurements for all the cases in DMF-water mixture at 298 K and 398K temprature. Knowing the highest stoichiometric number of the ligand bound to the metal ion, the Mihailov's mathematical method could also be applied and Mihailov's constants 'a' and 'A' are calculated and recorded in Table-5 and Table-6 in isopropanol-water and DMF-water mixtures respectively. The overall formation constant of the resulting complexes were calculated using calculated average values of 'a' and 'A'

Temprature	**log β_1**	**log β_2**	**log β_3**
298 K	11.204	12.302	14.748
398 K	10.255	11.477	13.792

$$n = A.a^{n}/n'$$

The two methods resulted in the following values of overall formation constants in isopropanol-water mixture (Table-7) and in DMF-water mixture (Table-8). Table-9 records the thermodynamics parameters in DMF-water mixture.

The values of overall formation constants of Zn (II) Ethylenediamine system in water are given below:

The values of overall formation constants are more in case of DMF-water Table-8 than in pure aqueous medium. Since the dipole moment of dimethylformamide is less than water so the solvation of Zn (II) will be less in dimethylformamide than in water, and hence the complexes formed in DMF-water mixture will be more stable than in pure aqueous medium. Its clear from the Table-8 that with increasing percentage of dimethylformamide in DMF-water mixture the value of stability constant decreases except β_1

value which is more in 40% DMF-water mixture and the same time the steric hindrance factor, due to bigger dimethylformamide molecule, predominant over the solvation effect so the further addition of ligand to metal ion is just impossible and hence only two complexes are formed in higher concentration of dimethylformamide.

The values of overall formation constants are less in case of isopropanol-water mixture Table-7 than in pure aqueous medium. This is attributed to less dielectric constants of isopropanol than of water. The values of overall formation constants increase with the increase of isopropanol percentage in isopropanol-water mixtures. This may be due to the change in viscosity, density etc. The decreasing order of overall formation constants-

DMF > Water > Isopropanol

shows that the most responsible factor for this is solvation as the solvating power of these solvents is just of reverse order.

The negative values for enthalpy during the complex formation show the exothermic nature of overall reactions. But in stepwise replacement of solvent molecule by ligand, heat is evolved in first step. The reaction is that the metal ligand bond is stronger than metal-dimethylformamide bond assuming no change in stereochemistry of the metal ion. Second step is accompanied with absorption of heat i.e. $\Delta H^\circ_2 < \Delta H^\circ_1$. It may be due to the fact that Zn (II) changes its octahedral geometry to tetrahedral.

$$EDA + [Zn(H_2O)_4EDA]^{+2} \longrightarrow [Zn(EDA)_2]^{+2} + 2\,H_2O + 2H_2O$$

Now the further addition of ligand to the $[Zn(EDA)_2]^{+2}$ complex will naturally release heat and $\Delta H^\circ_3 > \Delta H^\circ_2$. The ΔH° values increases as we increase the percentage of dimethylformamide from 20 to 40 %. It is due to the weakness of Zn-DMF bond than Zn-H_2O bond.

Exceptional values are observed in 60 % dimethylformamide where the ΔH° values are lower than those in 40 % Dimethylformamide which may be due to the statistical, steric or electrostatic factors.

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Table 1 : Polarographic measurement and Fj (x) function value of Zn- (Ethylenediamine) system in 20% isopropanol at 298 K, ionic strength (μ)= 0.5M

C_x (Moles)	I_d (div.)	$E^r_{½}$ (-Volt Vs S.C.E.)	F_o (x)	F_1 (x)	F_2 (x)	F_3 (x)
0·000	73	1·0150	-	-	-	-
0·008	73	1·1455	$0·0022 \times 10^{-7}$	$0·2800 \times 10^{-7}$	-	-
0·020	72	1·1685	$0·0133 \times 10^{-7}$	$0·6630 \times 10^{-7}$	0.8150×10^{-8}	15.75×10^{-8}
0·080	70	1·2005	$0·1591 \times 10^{-7}$	$1·9877 \times 10^{-7}$	1.8600×10^{-8}	17.00×10^{-8}
0·120	70	1·2135	$0·4314 \times 10^{-7}$	$3·5950 \times 10^{-7}$	2.5791×10^{-8}	17.32×10^{-8}
0·160	71	1·2235	$0·9160 \times 10^{-7}$	$5·7250 \times 10^{-7}$	3.2656×10^{-8}	17.28×10^{-8}
0·200	71	1·2305	$1·5680 \times 10^{-7}$	$7·8400 \times 10^{-7}$	3.6700×10^{-8}	15.85×10^{-8}
0·250	70	1·2355	$2·9390 \times 10^{-7}$	$11·7200 \times 10^{-7}$	4.4880×10^{-8}	15.95×10^{-8}

Table 2 : Polarographic measurement and Fj (x) function value of Zn- (Ethylenediamine) system in 20% Dimethylformamide at 298 K, ionic strength (μ)= 0·5M

C_x (Moles)	I_d (div.)	$E^r_{½}$ (-Volt Vs S.C.E.)	F_o (x)	F_1 (x)	F_2 (x)	F_3 (x)
0·000	73	1·0150	-	-	-	-
0×00	68	1×0175	-	-	-	-
0×02	66	1×3325	0.0325×10^{-12}	1.6250×10^{-12}	3.1250×10^{-13}	-
0×04	64	1×3560	0.2040×10^{-12}	5.0999×10^{-12}	0.8150×10^{-13}	156.24×10^{-13}
0×06	63	1×3690	0.5620×10^{-12}	9.3666×10^{-12}	1.8600×10^{-13}	165.73×10^{-13}
0×08	62	1×3785	1.1842×10^{-12}	14.8023×10^{-12}	2.5791×10^{-13}	165.66×10^{-13}
0×10	62	1×3965	2.1877×10^{-12}	21.8770×10^{-12}	3.2656×10^{-13}	168.77×10^{-13}
0×12	60	1×3925	3.5826×10^{-12}	29.8550×10^{-12}	3.6700×10^{-13}	167.05×10^{-13}
0×14	59	1×3975	5.3481×10^{-12}	38.2007×10^{-12}	4.4880×10^{-13}	161.23×10^{-13}
0×16	59	1×4025	7.8509×10^{-12}	49.0681×10^{-12}	30.0425×10^{-13}	162.76×10^{-13}

Table 3 : Polarographic measurement of Zn (II) Ethylenediamine system in Isopropanol-water mixture at 298 K temperature. Ionic Strength (μ) = 0·5M

C_x in moles	20% Isopropanol		40% Isopropanol		60% Isopropanol	
	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.
0·000	1·0150	73	1·0135	54	1·0100	85
0·008	1·1455	73	1·2345	53	-	-
0·020	1·1685	72	1·2605	53	1·2510	83
0·040	-	-	1·2755	54	1·2695	83
0·080	1·2005	70	1·2930	54	1·2895	81
0·120	1·2135	70	1·3060	52	1·3020	81
0·160	1·2235	71	1·3140	51	1·3115	80
0·200	1·2305	71	1·3210	50	1·3085	78
0·250	1·2355	70	1·3295	54	1·3255	76

Table 4 : Polarographic measurement of Zn (II) Ethylenediamine system in Dimethylfor- mamide-water mixture. Ionic Strength (μ) = 0·5

C_x in moles	20% Dimethylformamide				20% Dimethylformamide				20% Dimethylformamide			
	At 298 K		At 308 K		At 298 K		At 308 K		At 298 K		At 308 K	
	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.	$-E^r_{½}$ in Volts V_s SCE	I_d in div.
0·000	1·0175	68	1·0010	86	1·0160	56	1·0050	78	1·0150	50	1·0045	63
0·002	-	-	-	-	-	-	-	78	1·2860	48	1·2655	62
0·004	-	-	-	-	1·3190	·54	1·2990	78	1·2965	47	1·2770	61
0·008	-	-	-	-	1·3215	53	1·3015	-	-	-	-	-
0·020	1·3325	66	1·3100	85	-	-	-	-	1·3590	44	1·3375	58
0·040	1·3560	64	1·3350	83	-	-	-	77	1·3740	45	1·3530	57
0·060	1·3690	63	1·3470	81	1·3690	52	1·3480	76	1·3840	44	1·3625	55
0·080	1·3785	62	1·3570	81	1·3755	52	1·3550	74	-	-	-	-
0·100	1·3965	62	1·3655	80	1·3825	56	1·3610	72	-	-	-	-
0·120	1·3925	60	1·3715	79	1·3860	51	1·3650	70	-	-	-	-
0·140	1·3975	59	1·3760	77	1·3905	50	1·3705	-	-	-	-	-
0·160	1·4025	59	1·3815	77	-	-	-	65	-	-	-	-
0·180	-	-	-	-	1·3980	50	1·3780	-	-	-	-	-

Table: 5 Mihailov constant 'a' for various combinations of Ethylenediamine concent- rations and 'A' at various Ethylenediamine concentration in Isopropanol at 298ºK

Combination of Ethylene diamine concentra-tion	"a"			Concen-tration of Ethylene diamine	"A"		
	20% Isopropanol	40% Isopropanol	60% Isopropanol		20% Isopropanol	40% Isopropanol	60% Isopropanol
0·02-0·04	-	46·34	93·72	0·02	9·28 × 104	12·91 × 107	6·78 × 107
0·02-0·08	42·61	42·21	-	0·04	-	13·22 × 107	8·81 × 107
0·02-0·12	45·18	-	-	0·08	8·90 × 104	12·66 × 107	9·92 × 107
0·04-0·08	-	39·06	31·35	0·12	9·35 × 104	13·86 × 107	9·81 × 107
0·04-0·12	-	46·61	58·71	0·16	9·63 × 104	12·71 × 107	9·87 × 107
0·08-0·12	30·34	-	46·72	0·20	9·19 × 104	12·46 × 107	9·59 × 107
0·08-0·16	57·02	43·75	48·53	0·25	9·44 × 104	12·18 × 107	9·19 × 107
0·08-0·20	48·35	41·69	45·38	Average value of 'a' and 'A' in Isopropanol-water mixture			
0·08-0·25	50·79	-	-				
0·12-0·16	-	-	52·37		20%	40%	60%
0·12-0·20	41·43	-	43·94				
0·12-0·25	46·66	-	-	a	44·96	43·27	49·27
0·16-0·20	-	34·72	35·31				
0·16-0·25	39·74	33·55	-	A	9·30 × 10^4	12·69 × 10^4	9·53 × 10^4

Table 6 : Mihailov constant 'a' for various combination of Ethylenediamine concentration and 'A' at various Ethylenediamine concentration in Dimethylformamide (DMF) at 298 K

Combination of Ethylene diamine concentration	"a"			Concen-tration of Ethylene diamine	"A"		
	20% DMF	40% DMF	60% DMF		20% DMF	40% DMF	60% DMF
0.002 0.004	_	_	172.77	0.002	_	_	$23.68 \times 10^{8*}$
0.004 0.100	_	_	227.90	0.004	_	_	$23.32 \times 10^{8*}$
0.010 0.020	42.61	_	288.20*	0.007	_	_	265.8×10^{8}
0.010 0.040	45.18	_	193.72	0.010	_	_	266×10^{8}
0.010 0.060	_	_	218.79	0.020	_	_	283×10^{8}
0.020 0.040	_	_	125.71*	0.040	7.22×10^{9}	_	264×10^{8}
0.020 0.060	_	_	174.47	0.060	7.37×10^{9}	16.09×10^{10}	276×10^{8}
0.040 0.060	122.92	_	557.03*	0.080	7.36×10^{9}	15.52×10^{10}	_
0.060 0.080	108.83	31.78	_	0.10	7.46×10^{9}	15.73×10^{10}	_
0.060 0.100	118.24	30.12	_	0.12	7.41×10^{9}	15.29×10^{10}	_
0.060 0.120	112.82	_	_	0.14	7.21×10^{9}	15.60×10^{10}	_

Table Contd...

Combination of Ethylene diamine concentra-tion	"a"			Concen-tration of Ethylene diamine	"A"		
	20% DMF	**40% DMF**	**60% DMF**		**20% DMF**	**40% DMF**	**60% DMF**
0.060 0.140	101.04	_	_	0.16	7.27×10^9	_	_
0.080 0.100	123.34	46.02*	_	0.18	_	15.36×10^{10}	_
0.080 0.120	_	26.49	_				
0.080 0.140	96.52	28.54	_				
0.080 0.160	82.98*	_	_				
0.100 0.120	95.88	27.03	_	Average value of 'a' and 'A' in Isopropanol-water mixture			
0.100 0.140	_	_	_		20%	40%	60%
0.100 0.160	87.66*	_	_	a	44·96	43·27	49·27
0.100 0.180	_	27.25	_	A	$9{\cdot}30 \times 10^4$	$12{\cdot}69 \times 10^4$	$9{\cdot}53 \times 10^4$
0.120 0.140	_	35.52*	_				
0.120 0.180	_	28.63	_				
0.140 0.180	_	25.05	_				

Table 7 : Overall formation constant of Zn(II) ethylenediamine system in isopropanol-water mixture at 298 K

Overall formation constant	DeForm Hume's Method			Mihailov's Method		
	20% isopropanol	40% isopropanol	60% isopropanol	20% isopropanol	40% isopropanol	60% isopropanol
$Log\beta_1$	8.699	9.69	9.000	8.621	9.739	9.671
$Log\beta_2$	10.699	11.204	11.301	10.973	11.075	11.060
$Log\beta_3$	11.218	12.153	12.185	11.148	12.234	12.278

Table 8 : Overall formation constant of Zn(II) ethylenediamine system in Dimethyl formamide-water mixture at 298 K

Overall formation constant	DeForm Hume's Method						Mihailov's Method					
	20%		40%		60%		20%		40%		60%	
	at 298K	at 308K	at 298K	at 308K	at 298K	at 308K	at 298K	at 308K	at 298K	at 308K	at 298K	at 308K
$Log\beta_1$	12.000	11.301	12.845	12.000	12.699	12.204	11.906	----	12.643	-----	12.729	----
$Log\beta_2$	13.602	12.954	13.398	12.875	14.740	14.162	13.643	----	13.789	----	14.724	----
$Log\beta_3$	15.217	14.415	14.816	14.150	----	----	15.210	----	14.761	----	----	----

Table 9 : Thermodynamic parameters of Zn-ethylenediamine system in dimethyl formamide water mixture

Percentage of dimethyl formamide	Complex Species	Thermodynamic parameters		
		Δ F° K cal deg^{-1} mole^{-1}	**Δ H° K cal deg^{-1} mole^{-1}**	**Δ S° K cal deg^{-1} mole^{-1}**
20%	[Zn (EDA)] $^{2+}$	-16.47	-29.51	-43.75
	[Zn (EDA)2] $^{2+}$	-18.67	-27.39	-29.26
	[Zn (EDA)3] $^{2+}$	-20.88	-33.90	-43.69
40%	[Zn (EDA)] $^{2+}$	-17.63	-35.72	-60.70
	[Zn (EDA)2] $^{2+}$	-18.39	-22.10	-12.47
	[Zn (EDA)3] $^{2+}$	-20.33	-27.73	-24.80
60%	[Zn (EDA)] $^{2+}$	-17.43	-20.92	-11.70
	[Zn (EDA)2] $^{2+}$	-20.23	-24.46	-14.19

(EDA)= Ethylenediamine