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Polarographic Studies on Interaction of 2-Aminoquinoxaline with Cd(II) in Alkanols, Formamide, Dimethyl Formamide and Dimethyl Sulphoxide Solvent Mixture

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The present study deals with the determination of composition and stability constants of Cd(II)-2-aminoquinoxaline complexes in 25, 50 and 75% (by volume) aqueous methanol solution. In each case, the single well defined reduction wave appeared. The plots of i_d *vs.* $\sqrt{h_{eff.}}$ confirmed that the reduction was of diffusion control. The reversible nature of the electrode reaction was evident from the slopes of the $E_{d.e.}$ *vs.* log $i/i_d - i$ curves which were of the order of 31 ± 2 mV. The indication of the formation of Cd(II) complexes with 2-aminoquinoxaline was provided by the shift in the $E_{1/2}$ values to more negative potentials and decrease in the diffusion currents with the increasing concentration of the ligand. The complexes formed by 2-aminoquinoxaline are very weak which confirm the validity of DeFord and Hume's method to calculate the consecutive formation constants of very weak complexes, which may not be detected by other techniques. The low stabilities of the complexes of 2-aminoquinoxaline may be due to the less tendency of the amino-group to donate electrons because of delocalisation of electrons in the heterocyclic ring. Thus it is obvious that the nature and concentration of the solvent not only affects the stability, but the composition of complexes formed also.

INTRODUCTION

Polarography in aqueous organic solvent mixtures and in non-aqueous media has become an excellent method for various types of measurements for both organic and inorganic substances.[1–6] The different number of water insoluble compounds initiated the search for organic solvents. The pioneers in the field were Sartori and Gaicomello,[7] who investigated the reduction of Co(II) and Li(I) in methanol-benzene mixtures. Zanko and Manusova[8] studied a number of common metal ions in several organic solvents including methanol, ethanol and glycerol. Kolthoff and Coetzee[9] have made a comprehensive study of the waves of many metal ions in acetonitrile. Larson and Iwamoto[10] have studied a number of inorganic depolarisers in benzonitrile, phenyl acetonitrile and propiononitrile. Formamide and N,N-dimethyl formamide have also been used by many workers.[11]

A wide variety of other solvents like acetic anhydride, dimethyl sulphoxide, dioxane, methanol, sulphonic acid[17] and n-methyl acetamide have been employed to study the polarographic behaviour of several cations. It seems, on the whole, that the organic solvents used in non-aqueous polarography are generally limited to a few favoured solvents such as acetonitrile, formamide and N,N-dimethyl formamide, although the efforts to discover the new solvents are still going on.

In general, the diffusion coefficients of most of the metals are relatively smaller in non-aqueous solvents than in aqueous media. This decrease may result either from increased viscosity or change in the size of the solvated species. The value of half wave potentials has been found to vary with change in the dielectric constants of the solvent. Pinfold and Scheba[12] have drawn attention to the fact that relationship between the values of pK for the complex and inverse of the value of half wave potentials is often more positive than those in aqueous solutions. This is attributed to the effect of hydration in aqueous solutions. Many metal ions which form stable complexes in aqueous media are so strongly solvated in some organic solvents such as ethylene diamine, some formamides, acetonitrile and dimethyl sulphoxide so as to influence other types of complex formations. In fact, a number of properties of the metal ions and the ligand and the nature of the solvent are operative in affecting the composition and stability of the complex ions. In view of the conflicting reports from different workers it is difficult to generalise the results obtained.

Turyan[13] studied halide and thiocyanato complexes of Pb(II) and Cd(II) in various solvents and observed a linear dielectric constant, but no such linear relationship was found by Babko and co-workers[14]. Khotsyanoki and Kundra[15] observed an increase in the value of the stability constants for halide complexes of Cd(II) in methanol water solvents. Polargraphic studies of the complexes in methanol and ethanol by Migal *et al.*[16, 17] have shown that there is a sharp increase in the stability of complexes above 80 per cent alcohol concentration, which they attribute to the solvent effect. Nazarova[18] studied the pyridine complexes of Ag(I) and Cd(II) in aqueous ethanol solutions and reported that when the non-aqueous solvent is added, the stability at first decreases relative to that for aqueous solutions. The same result was noted by Larson.[19]

Thus, it is interesting to see what happens to the stability and the composition of complex ions when a purely aqueous medium is replaced by an aqueous organic mixture. Different results have been obtained by different workers in this field and hence there is a need for systematic study of the influence of aqueous organic solvent mixtures on complex formation. In this paper, an attempt has been made to study the Cd(II)-2-aminoquinoxaline complexes in aqueous mixture of methanol, ethanol, propanol-1, formamide, dimethyl formamide and dimethyl sulphoxide.

EXPERIMENTAL

A manual polarograph was used for obtaining C-V curves. The dropping mercury electrode having m = 1.65 mg/s and t = 2.98 s (in open circuit) was used.

Reagent grade chemicals were used. Solutions containing 0.5 mM Cd(II) and different concentrations of 2-aminoquinoxaline (0.10 M to 0.80 M) were prepared. Sodium perchlorate was used to maintain ionic strength constant (0.1). The IR drop correction was applied wherever needed. For this purpose Systronics conductivity bridge was used. Purified nitrogen, presaturated with the solution to be polarographed, was used for removing dissolved oxygen from the solution. The nitrogen gas was passed over the solution during actual measurement. The various organic solvents used were purified as described below:

(i) Alkanols (methanol, ethanol and propanol-1) were refluxed with excess of quicklime and then fractionated.

(ii) Formamide: E. Merck formamide was dried over anhydrous sodium sulphate and then distilled under reduced pressure.

(iii) Dimethyl formamide: AR grade dimethyl formamide was purified by allowing it to stand over anhydrous solid sodium carbonate for several hours followed by fractionation under reduced pressure.

(iv) Dimethyl sulphoxide: This was purified by shaking it overnight in contact with ignited chromatographic grade alumina. The liquid was decanted from the solid, with care to avoid contamination by the atmosphere, and vacuum distilled.

The suitability of these solvents after purification for polarographic work was tested by taking the blank polarograms.

RESULTS AND DISCUSSION

(i) Cd(II)-2-Aminoquinoxaline complexes in aqueous methanol mixtures: The present study deals with the determination of composition and stability constants of Cd(II)-2-aminoquinoxaline complexes in 25%, 50% and 75% (by volume) aqueous methanol solution. In each case, the single well defined reduction wave appeared. The plots of i_d *vs.* $\sqrt{h_{eff.}}$ confirmed that the reduction was of diffusion control. The reversible nature of the electrode reaction was evident from the slopes of the $E_{d.e.}$ *vs.* $\log i/i_d - i$ curves which were of the order of 31 ± 2 mV. The indication of the formation of Cd(II) complexes with 2-aminoquinoxaline was provided by the shift in the $E_{1/2}$ values to more negative potentials and decrease in the diffusion currents with the increasing concentrations of the ligand.

The $E_{1/2}$ *vs.* $-\log C_x$ plots were found to be smooth curves in all the cases suggesting the existence of more than one complex in equilibrium. The modified Deford-Hume method was applied for determination of composition and stability constants.

The $F_j([X])$ *vs.* C_x (C_x is concentration of 2-aminoquinoxaline) plots for the system in 25% methanol (Fig. 1) showed the presence of only two complex species with the composition $[Cd(2\text{-}AQ)]^{2+}$ and $[Cd(2\text{-}AQ)_2]^{2+}$. The analysis of $F_j([X])$ functions for the system (in 25%, 50% and 75% aqueous methanol) have been incorporated in Table-1. The overall formation constants have been summarised below:

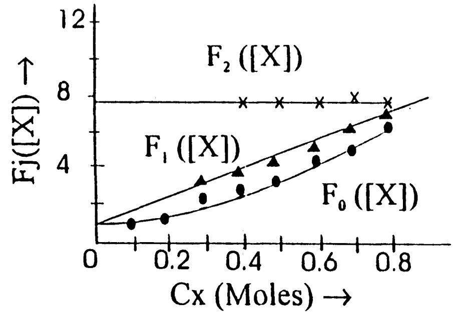


Fig. 1. Plots of $F_j([X])$ *vs.* C_x in 25% methanol

Percentage of methanol (by volume)	Stability constants	
	β_1	β_2
25	0.9	7.3
50	1.8	6.2
75	2.0	3.5

TABLE-1

POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR Cd(II)-2-AMINOQUINOXALINE SYSTEM IN 25% METHANOL AT M = 0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$
0.00	95.0	0.5642	–	–	–
0.10	90.0	0.5679	1.120	–	–
0.20	78.0	0.5689	1.342	–	–
0.30	75.0	0.5720	1.963	3.210	–
0.40	71.5	0.5750	2.528	3.820	7.30
0.50	69.0	0.5775	3.210	4.420	7.04
0.60	68.0	0.5801	4.052	5.088	6.98
0.70	67.0	0.5826	5.211	6.017	7.31
0.80	67.0	0.5872	6.392	6.740	7.30

It is clear from the above results that the half-wave potentials shifted towards more negative values with the increase in the percentage of methanol. This is also evident from the plots of $E_{1/2}$ *vs.* $-\log C_x$ shown in Fig. 2. The number of complexes remain two irrespective of the concentration of the solvent, but the stability of the first complex species (1 : 1) goes on increasing, whereas that of the second (1 : 2) goes on decreasing with increasing the methanol percentage suggesting that methanol affects that stability.

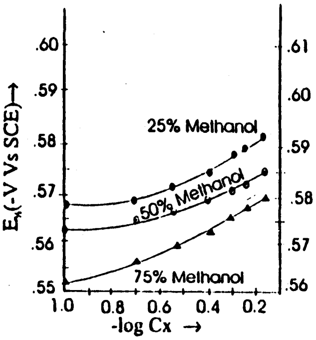


Fig. 2. Plots of $E_{1/2}$ *vs.* – log C_x

Cd(II)-2-Aminoquinoxaline complexes in aqueous ethanol mixtures: The measurements were made in 25%, 50% and 75% (by volume) of ethanol. The experimmental details were same as described earlier.

A regular shift in the $E_{1/2}$ values towards more negative potentials with the increasing percentage of ethanol was observed, *i.e.*, the $E_{1/2}$ values increased with increase in the ethanol percentage. The values of stability constants obtained in different concentrations of ethanol are summarised below:

Percentage of ethanol (by volume)	Stability constants		
	β_1	β_2	β_3
25	1.1	2.60	4.8
50	1.2	6.50	–
75	0.9	9.02	–

Table-2 incorporates the results and Fig. 3 shows the plots of $F_j([X])$ *vs.* C_x for 75 per cent ethanol. Again it has been noticed that ethanol not only affects the stability of the metal complexes but also changes the composition of the complexes.

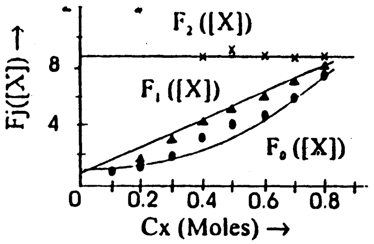


Fig. 3. Plots of $F_j([X])$ *vs.* C_x in 75% ethanol

TABLE-2
POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR Cd(II)-2-AMINOQUINOXALINE SYSTEM IN 75% ETHANOL AT M=0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$
0.00	50.0	0.5545	–	–	–
0.10	49.0	0.5585	1.090	–	–
0.20	45.5	0.5595	1.420	2.10	–
0.30	44.0	0.5630	1.930	3.10	–
0.40	40.0	0.5665	2.800	4.50	9.02
0.50	39.0	0.5685	3.815	5.63	9.46
0.60	37.0	0.5705	4.768	6.28	8.98
0.70	35.5	0.5728	6.047	7.21	9.02
0.80	34.5	0.5741	7.616	8.27	9.22

Cd(II)-2-Aminoquinoxaline complexes in aqueous propanol-1-mixture: A similar trend in the shift of the half-wave potentials towards more negative values, as in methanol and ethanol, was also observed for propanol-1, which is quite obvious from $E_{1/2}$ *vs.* $-\log C_x$ plots. $F_j([X])$ values *vs.* C_x plots (Fig. 4) show the presence of two complexes having the stability constants as recorded below:

Percentage of propanol-1 (by volume)	Stability constants	
	β_1	β_2
25	1.10	5.80
50	1.60	8.30
75	1.50	14.30

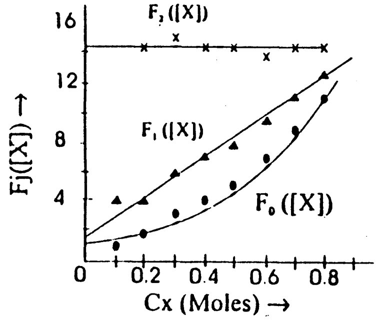


Fig. 4. Plots of $F_j([X])$ *vs.* C_x in 75% propanol-1

It is clear from these results that as the water content of the solvent decreases, the stability of the complexes increases. Thus stability of the complexes formed increases with increase of propanol-1 percentage.

The polarographic characteristics and $F_j([X])$ function have been incorporated in Table-3.

TABLE-3
POLAROGRAPHICH CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR Cd(II)-2-AMINOQUINOXALINE SYSTEM IN 75% PROPANOL AT M = 0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$
0.00	49.0	0.5489	–	–	–
0.10	44.0	0.5542	1.410	4.10	–
0.20	42.0	0.5583	1.864	4.32	14.10
0.30	39.5	0.5630	2.791	5.97	14.92
0.40	38.0	0.5675	3.904	7.26	14.40
0.50	36.0	0.5720	5.325	8.65	14.30
0.60	33.5	0.5752	6.850	9.75	13.75
0.70	32.9	0.5800	9.057	11.51	14.30
0.80	30.0	0.5823	11.352	12.94	14.30

Cd(II)-2-aminoquinoxaline complexes in aqueous formamide mixture: The plots of $E_{1/2}$ *vs.* $-\log C_x$ (Fig. 5) for different concentrations of formamide in water indicated that the $E_{1/2}$ values shift towards more negative potentials as the formamide percentage increases from 25 to 75% on extrapolation of $F_j([X])$ values to zero ligand concentration. The overall stability constants were found to be as follows:

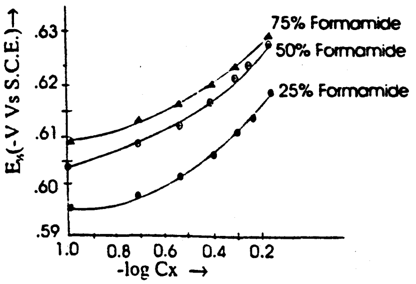


Fig. 5. Plots of $E_{1/2}$ *vs.* $-\log C_x$

Percentage of fomamide (by volume)	Stability constants	
	β_1	β_2
25	1.00	1.90
50	0.75	1.75
75	0.32	2.46

The $F_j([X])$ values and polarographic characteristics are presented in Table-4. The plots of $F_j([X])$ values *vs.* C_x are represented in Fig. 6.

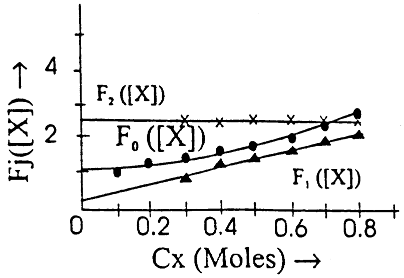


Fig. 6. Plots of $F_j([X])$ *vs.* C_x in 75% formamide

TABLE-4
POLAROGRAPHIC CHARACTERISTICS $F_j([X])$ FUNCTIONS FOR Cd(II)-2-AMINO-QUINOXALINE SYSTEM IN 75% FORMAMIDE AT M = 0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$
0.00	49.0	0.6045	–	–	–
0.10	47.0	0.6088	1.000	–	–
0.20	45.5	0.6130	1.215	–	–
0.30	44.5	0.6171	1.321	1.073	2.51
0.40	42.5	0.6211	1.601	1.504	2.96
0.50	40.0	0.6245	1.775	1.550	2.46
0.60	39.5	0.6275	2.095	1.826	2.51
0.70	39.5	0.6300	2.419	2.028	2.44
0.80	36.0	0.6325	2.830	2.288	2.46

This is obvious from the results that the stability of metal complexes is not affected much by increasing the percentage of formamide.

Cd(II)-2-aminoquinoxaline complexes in aqueous N,N-dimethyl formamide mixture: It is evident from the $E_{1/2}$ *vs.* $-\log C_x$ plots (Fig. 7) that the values of the half wave potentials became more and more negative as the concentration of dimethyl formamide was increased from 25 to 75%. The overall formation constants calculated from the $F_j([X])$ *vs.* C_x plots in various concentrations of dimethyl formamide are given as under:

Percentage of N,N-dimethyl formamide (by volume)	Stability constants	
	β_1	β_2
25	1.02	2.10
50	1.00	2.80
75	0.75	10.40

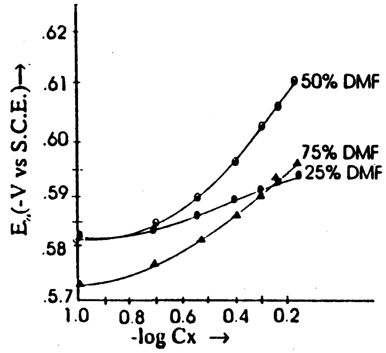


Fig. 7. Plots of $E_{1/2}$ vs. -log C_x

Fig. 8 depicts the $F_j([X])$ values as the formation of 2-aminoquinoxaline concentrations and Fig. 9 the percentage composition in 75% dimethyl formamide. The polarographic characteristics and $F_j([X])$ functions for 75% N,N-dimethyl formamide solutions are presented in Table-5.

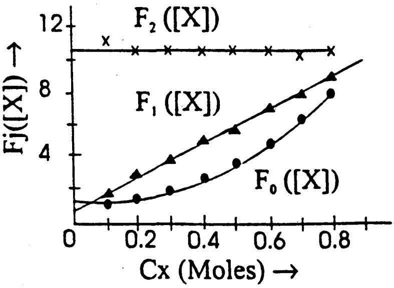


Fig. 8. Plots of $F_j([X])$ vs. C_x in 75% DMF

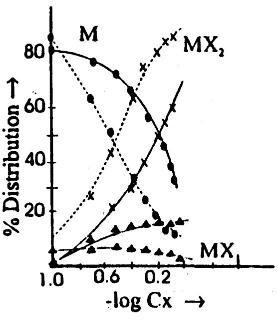


Fig. 9. % Distribution in 25% DMF (_____) and 75% DMF (– – – – –)

TABLE-5
POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR Cd(II)-2-AMINOQUINOXALINE SYSTEM IN 75% DIMETHYL FORMAMIDE AT M = 0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$
0.00	36.0	0.5712	–	–	–
0.10	33.0	0.5732	1.184	1.84	10.96
0.20	31.0	0.5772	1.568	2.84	10.49
0.30	30.5	0.5840	2.161	3.87	10.42
0.40	30.2	0.5865	2.964	4.91	10.40
0.50	30.2	0.5905	3.985	5.97	10.44
0.60	30.2	0.5932	5.188	6.98	10.39
0.70	30.2	0.5972	6.600	8.00	10.36
0.80	30.0	0.5997	8.256	9.07	10.40

The stability of first complex species is found to decrease very little whereas that of the second complex increases with increasing amount of N,N-dimethyl formamide.

Cd(II)-2-aminoquinoxaline complexes in aqueous dimethyl sulphoxide mixture: The plots of $E_{1/2}$ *vs.* $-\log C_x$ were found to be smooth curves in every case with the increasing percentage of dimethyl sulphoxide and a shift in the $E_{1/2}$ values towards more negative side was noted. From graphical extrapolation of $F_j([X])$ functions to zero ligand concentration, the stability constants have been calculated in different concentrations of dimethyl sulphoxide. The value of 'p' was found to be two in 25% and 50% but was found to be three in 75% dimethyl sulphoxide mixture. The values of stability constants obtained in different percentages of dimethyl sulphoxide are given below.

Percentage of dimethyl sulphoxide (by volume)	Stability constants		
	β_1	β_2	β_3
25	0.71	2.55	–
50	0.60	2.40	–
75	1.85	0.86	1.99

The results of $F_j([X])$ values for the various concentrations of dimethyl sulphoxide are summarised in Table-6 and indicated graphically in Fig. 10 for 75% dimethyl sulphoxide solutions.

It is obvious that dimethyl sulhoxide not only affects the stability of the complexes formed but also changes the composition of the metal complexes.

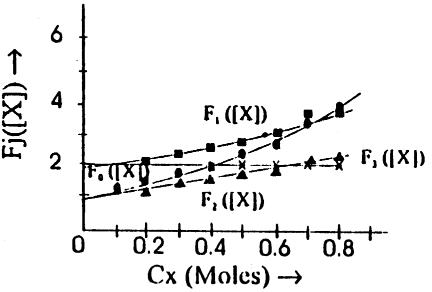


Fig. 10. Plots of $F_j([X])$ *vs.* C_x in 75% dimethyl sulphoxide

TABLE-6
POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR
Cd(II)-2-AMINOQUINOXALINE SYSTEM IN 75% DIMETHYL SULPHOXIDE
AT M = 0.10 ($NaClO_4$) WITH 30°C

C_x (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$	$F_1([X])$	$F_2([X])$	$F_3([X])$
0.00	30.0	0.5933	–	–	–	–
0.10	28.0	0.5968	1.230	–	–	–
0.20	27.0	0.5990	1.418	2.09	1.20	–
0.30	24.0	0.6035	1.690	2.30	1.50	–
0.40	23.0	0.6075	2.004	2.51	1.65	1.99
0.50	22.0	0.6118	2.370	2.74	1.79	1.99
0.60	21.5	0.6149	2.848	3.08	2.05	1.99
0.70	21.5	0.6185	3.443	3.49	2.35	2.14
0.80	20.5	0.6178	4.048	3.81	2.45	1.99

With a view to investigate the effect of some solvent on complexation, the complexes formed by Cd(II) with 2-aminoquinoxaline have been studied (under identical conditions) and by varying the percentage (by volume) of methanol, ethanol, n-propanol, formamide, dimethyl formamide and dimethyl sulphoxide in aqueous solvent mixtures. The results show that the half-wave potential shifted towards more negative values with the increase in the percentage of methanol. The number of complexes remains two, irrespective of the concentration of the solvent, but the stability of first complex (1 : 1) goes on increasing whereas that of the second *i.e.*, (1 : 2) decreases with increase in the methanol percentage.

In ethanol-aqueous mixture, the stability of the complexes is found to increase with the increase in the percentage of ethanol. Moreover, three complexes are formed in 25% ethanol concentration, whereas in 50% and 75% concentrations, the usual two complexes are formed. A similar trend in the values has been observed in case of n-propanol-aqueous mixture. Among the alkanols, methanol behaves in a slightly different manner. The stability of the complexes formed decreases with increase of methanol percentage, whereas it increases in case of ethanol and propanol-1.

In the presence of formamide, the stability of the complexes is not affected much by changing the percentage of formamide in aqueous mixture. The stability of the first complex species is found to decrease very little, whereas that of the second complex increases with increasing amount of dimethyl formamide. With dimethyl sulphoxide the stability of the first complex species is found to increase and that of the second is found to decrease with increase in the percentage of dimethyl sulphoxide in solution. Moreover, with 75% DMSO in solution the number of complex species formed is three and not two as in 25% and 50% concentrations of dimethyl sulphoxide.

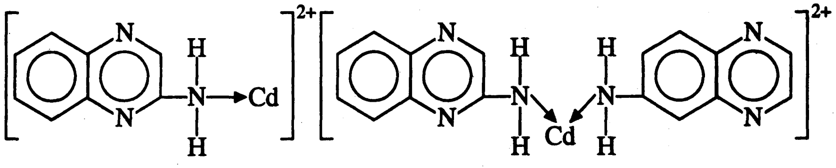
Thus from our studies it is obvious that the nature and concentration of solvent not only affects the stability, but the composition of complexes formed also. While discussing the effect of solvent on complex formation, the physical as well as the chemical properties of the solvent are taken into consideration. The dielectric constant of methanol (32.6), ethanol (24.3), propanol-1 (20.1), formamide (109.5), dimethyl formamide (36.3) and dimethyl sulphoxide (46.7) are very much different as compared to that of water (78.3), but in some cases the stability of the complexes is found to increase and in some other cases it decreases when the percentage of organic solvent increases. Except methanol, our results in aqueous alkanol mixtures show that the stability of the complexes increases by increasing the concentration of alkanols. These results are in close agreement with the results of Vleck[20], Turyan and coworkers[21] who studied the effect of alcohols on halide and thiocyanato complexes of Cd(II), showing that the dielectric constant is not playing any important role.

Golub and Samorlendo[22] have studied the thiocyanato complexes of Cd(II) in methanol, dimethyl formamide and acetonitrile by conductometric and potentiometric methods. They also feel that the chief factor determining the composition and stability of complexes is the chemical nature of the solvent and not the dielectric constant of the solvent. The important chemical properties which are operative in affecting the composition and stability of complexes are the acidic or basic nature of the solvent and solvation of the metal ion in the presence of increasing concentration of organic solvents. Neutral solvents like formamide, dimethyl formamide and acetonitrile have neither strong proton donor tendencies nor strong proton accepting tendencies. Such solvents serve practically as the suspending media for the solute species and participate in the chemical reactions itself to a minor extent. Thus solvation[23] is the most important factor in affecting complex formation in aqueous organic solvents.

Solvation of metal ions occurs either through ion dipole interaction between the positive cation and the negative end of the ion dipole, or through coordinate covalent bonds in which the solvent molecules share a pair of electrons with the cation. Increase in the stability with increase in solvent concentration may be due to a change in the hydrated sheath of metal ion. When the metal forms the complex with the ligand (2-aminoquinoxaline), the latter displaces either water or solvent molecules. Thus the effect of the solvent on the formation of complexes can satisfactorily be explained in terms of solvation, because it preferentially displaces water molecules from the solvate sheath of ions. The ligands can be used to demonstrate the change in their solvate environment as the composition of the solvation is varied.

Solvation may also take place through coordinate covalent bonds. In such cases the solvent molecules will be held more rigidly by the metal ion, thus hindering coordination with the ligand with the result that the stability decreases with increase in concentration of the solvent. This seems to be a possible explanation to our results in formamide, dimethyl sulphoxide and methanol-aqueous solutions.

The probable structures of the complexes with a cadmium metal, may be shown as in Fig. 11.



MX_1 MX_2

Fig. 11

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