Chemical Speciation of Binary Complexes of Co(II), Ni(II) and Cu(II) with 1,10 Phenanthroline in Acetonitrile-Water and DMF Water Mixtures

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Abstract: **A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with 1,10-Phenanthroline. The titrations were performed in the presence of different relative concentrations with sodium hydroxide in varying concentrations (0–60% v/v) of acetonitrile–water mixtures and DMF-water mixtures at an ionic strength of 0.16 mol L-1 and at a temperature of 303.0 K. Stability constants of the binary complexes were refined using MINIQUAD75. The best-fit chemical models were selected based on various statistical parameters. The models for binary complex systems contain the chemical species ML2, ML3 and ML2H for Co(II), Ni(II) and Cu(II) in acetonitrile-water and DMF-water mixtures. The trend in the variation of stability constants with change in the mole fraction of the medium was explained based on electrostatic and non-electrostatic forces. Distribution of the species with pH at different compositions of acetonitrile-water and DMF-water mixtures was also presented.**

Keywords: **1, 10-Phenanthroline, Acetonitrile, Distribution diagrams, Dielectric constant, MINIQUAD75**

1. Introduction

One of the major applications of the transition metal complexes is their medical testing as antibacterial and antitumor agents aiming toward the discovery of an effective and safe therapeutic procedure for the treatment of several bacterial infections and cancers. Research in medicinal inorganic chemistry has prolonged in current years by exploiting a variety of chelating ligands to modify and control the properties of metal ions in biological systems [1–3]. In chemotherapy, the extensive applications have been found to be transition metal ions coordinated to a nitrogen containing ligands, such as 1,10–Phenanthroline. There are several biologically active molecules which contain various hetero atoms such as nitrogen, sulphur and oxygen, for perpetuity drawn the attention of chemist over the years mainly because of their biological consequence.

The ligand 1,10–Phenanthroline is sturdy field bidentate ligand that form very stable chelates with many first-row transition metals [4]. 1,10 Phenonthroline (Phen) or 4,5-diazaPhenanthrene is a tricyclic compound. Phen is a metal chelator. As a bidentate ligand in coordination chemistry, it forms strong Complexes with many metal ions through N-atoms [5-11]. Due to hydrophobicity of aromatic rings of Phen, the solubility of the neutral species is low in water which remarkably increases in organic solvents and also in aqua-organic mixtures.

Due to its superb ability to coordinate many metal ions, Phen and its derivatives are frequently used in many processes involving metal complexes, in which they can be featured in many roles; for example, as ligand for catalysis [12] or as stabilizing agents for nano particle synthesis [13].Phen has been used as important heterocyclic ligand for a large number of metal complexes that play an important role in a variety of important technological and medicinal applications; for example, promising applications in the field of electroluminescent materials [14-17], organic light-emitting devices (OLED) [18], organic semiconductors [19] or as chemical nucleases and therapeutic agents, due to their ability to bind or interact with the DNA bio macromolecule [20-23].

Metals by themselves and in proper balance to one another have important biochemical and nutritional functions [24-25]. The bioavailability of these minerals is also a very important factor, depending on the food source and also upon the pH of intestine [26-27]. Co(II), Cu(II) and Ni(II) are associated with several enzymes [28-29] and any variation in their concentration leads to metabolic disorders [30]. Hence speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ions. In biological fluids, metal ions exist in non-exchangeable form as in metallo-proteins or loosely bound to some bioligands as in metal-activated proteins.

The loosely bound metal ions are in equilibrium with simple metal ions present in the bio-fluids. These simultaneous equilibria involving a variety of metal ions and ligands are important in bio-fluids [31].

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Cobalt is an essential trace element that is an integral part of vitamin B12, which is essential in the metabolism of folic acid and fatty acids. Cobalt is essential for the production of red blood cells and cobalamin and it acts as the substrate for the final enzymatic reaction that yields the active coenzyme derivatives of cyanocobalamin and aqua cobalamin. Although cobalt is an essential element for life in minute amounts (10 mg/day), at higher levels of exposure it shows mutagenic and carcinogenic effects [32]. Trace amounts of vitamin B12 are essential for the synthesis of hemoglobin. Its deficiency causes anemia. . Besides cobalt is involved in the production of red blood cells and is important for the proper functioning of the nervous system as it can help in creating a myelin sheath. Nickel plays numerous roles in the biology of microorganisms and plants [33-34]. Nickel is found in enzymes, such as urease, which is a dinuclear Ni(II)-containing metalloenzyme [35-37]. This enzyme catalyses the hydrolysis of urea to yield ammonia and arbamate. Other nickel-containing enzymes include a class of superoxide dismutase [38] and a glyoxalase [39]. Copper is essential in all plants and animals. Copper is distributed widely in the body and occurs in liver, muscle and bone. In humans, the symptoms of Wilson's disease are caused by an accumulation of copper in body tissues. The copper-containing enzymes and proteins constitute an important class of biologically active compounds. The biological functions include electron transfer, dioxygen transport, oxygenation, oxidation, reduction and disproportionation [40-41].

Hence, speciation studies of the title systems have been undertaken based on their involvement in various physiological reactions. Protonation equlibria of Phen in acetonitrile-water and DMF-water mixtures have already been reported from this laboratory [42]. Speciation analysis is important in human biology, nutrition, toxicology and in clinical practice. The speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ion. The species refined and their relative concentrations under the experimental conditions represent the possible forms of amino acids in bio-fluids

Since the dielectric constant at the active site cavities is very small compared to that at biofluids, low dielectric constant is mimicked by using a water soluble organic solvent like acetonitrile (AN) and dimethylformamide (DMF). Very few studies have been reported in the literature on effect of dielectric constants in organic solvent- water mixtures [43-44]. Hence, speciation studies of the title systems have been undertaken based on their involvement in various physiological reactions.

2. Materials and methods

Solution (0.05 mol L^{-1}1) of Phen (Himedia, India) is prepared in triple-distilled deionised water by maintaining 0.05 mol L^{-1} hydrochloric acid concentration to increase the solubility. Acetonitrile (Merck, India) and Dimethylformamide (Merck, India) were used as received. 2 mol L^{-1} Sodium Chloride

(Merck, India) was prepared to maintain the ionic strength in the titrand. Sodium hydroxide (Merck, India) of 0.4 mol L^{-1} and Hydrochloric acid (Merck, India) of 0.2 mol L^{-1} were prepared. Solutions of Co(II), Cu(II) and Ni(II) chlorides (0.05 mol L^{-1}) were prepared by dissolving G.R. Grade (Merck, India) salts in triple distilled water maintaining 0.05 mol L^{-1}acid (HCl) to suppresses the hydrolysis of metal salts. All the solutions were standardized by standard methods. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification [45]. The strengths of alkali and mineral acid were determined using the Gran plot method [46-47].

A. Procedure

The titrimetric data were obtained by using calibrated digital auto titrating pH meter Metrohlm 877 titrino plus (readability 0.001) with mechanical stirring carried by a teflon stirrer. The glass electrode was equilibrated in a well stirred AN-water and DMF-water mixtures (0–60% v/v) containing inert electrolyte for several days. The effect of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor [48]. For the determination of stability constants of binary species, initially, titration of strong acid was titrated against alkali at regular intervals to check the complete equilibration of the glass electrode. Then, the glass electrode was refilled with AN-water or DMF-water mixtures of equivalent composition as that of the titrand. All the titrations were performed in medium containing varying concentrations of AN-water and DMF-water mixtures (0–60% v/v) pH metrically at 303+0.1K. In each of the titrations, the titrand consisted of approximately 1m mol mineral acid in a total volume of 50 cm^3. Titrations with different metal-to-ligand ratios (1 : 2.5, 1 : 3.75 and 1 : 5) were carried out with 0.4 mol L^{-1} sodium hydroxide [49].

3. Modelling strategy

The computer program SCPHD [50] was used to calculate the correction factor. By using pH metric titration data, the binary stability constants were calculated with the computer program MINIQUAD75 [51] which exploit the advantage of constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor and protonation constants of Phen were fixed. The variation of stability constants with the mole fraction of the medium was analyzed on the basis of electrostatic, non- electrostatic, solute–solute and solute– solvent interactions.

4. Results and discussion

Alkalimetric titration curves in AN-water and DMF-water mixtures revealed that the acido-basic equilibria of Phen were active in the pH range 1.6-11.5. Based on the active forms of the ligand in this pH range, models containing various numbers

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Table 1
Exhaustive modeling of Cu(II) –Phen complexes in 30% v/v DMF-water mixtures

Model Number	Log β$_{mlh}$			U$_{Corr}$ x10^8	Skewness	Kurtosis	χ^2	R-Factor
	120	130	121					
1	14.31(02)	----------	----------	8.57	0.35	4.32	61.8	0.1632
2	----------	19.33(13)	----------	8.40	-0.28	2.69	18.16	0.1449
3	----------	----------	12.36(07)	3.76	-0.24	3.05	17.04	0.2941
4	14.79(03)	19.18(13)	----------	1.66	0.55	3.47	59.20	0.1851
5	14.86(03)	----------	12.81(10)	1.42	1.14	3.38	39.67	0.2471
6	----------	19.64(13)	13.01(06)	2.19	-0.09	3.24	14.32	0.1934
7	14.29(03)	18.92(19)	12.05(08)	8.52	0.67	4.52	42.66	0.1742

and combinations of complex species were fed to MINIQUAD75 along with the alkalimetric titration data. Exhaustive modelling was performed for a typical system and given in Table 1.

The results of the best fit models that contain the stoichiometry of the complex species and their overall formation constants along with some of the important statistical parameters are given in Table 2(a) for AN-water and Table 2(b) for DMF-water mixtures. Very low standard deviation in overall stability constants (log β) signifies the precision of these constants. The small values of U (sum of squares of deviations in concentrations of ligand and hydrogen ion at all experimental points) corrected for degrees of freedom, small values of mean, standard deviation and mean deviation for the systems are validated by the residual analysis. Residual analysis in data analysis with least squares methods, the residuals (the differences between the experimental data and the data simulated based on model parameters) are assumed to follow Gaussian or normal distribution. When the data are fit into the models, the residuals should ideally be equal to zero. If statistical measures of the residuals and the errors assumed in the models are not significantly different from each other, the model is said to be adequate. Further, a model is considered adequate only if the residuals do not show any trend.

Respecting the hypothesis that the errors are random following normal distribution in the least squares analysis, the residuals are tested for normal distribution. Such tests are skewness, kurtosis, χ^2 and R factor. These statistical parameters show that the best fit models portray the metal– ligand species in An-water and DMF-water mixtures, as discussed below.

A. χ^2 test

χ^2 (chi square) is a special case of gamma distribution whose probability density function is a symmetrical function. This distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation. If the χ^2 calculated is less than the table value, the model is accepted.

B. Crystallographic R-test

Hamilton's R factor ratio test is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not. In pH metric method, the readability of pH meter is taken as the R limit which represents the upper boundary of R beyond which the model bears no significance.

When these are different numbers of species the models whose values are greater than R-table are rejected. The low crystallographic R-values given in Table 1 indicate the sufficiency of the model.

C. Skewness

It is a dimensionless quantity indicating the shape of the error distribution profile. A value of zero for skewness indicates that the underlying distribution is symmetrical.

If the skewness is greater than zero, the peak of the error distribution curve is to the left of the mean and the peak is to the right of the mean if skewness is less than zero. The values of skewness recorded in Table 1 are between 0.08 and 2.83 for Co(II), 0.32 and 2.49 for Cu(II) and -2.81 and 2.29 for Ni(II). These data suggest that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

D. Kurtosis

It is a measure of the peak nature of the error distribution near a model value. For an ideal normal distribution kurtosis value should be three (mesokurtic). If the calculated kurtosis is less than three, the peak of the error distribution curve is flat (platykurtic) and if the kurtosis is greater than three, the distribution shall have sharp peak (leptokurtic). The kurtosis values in the present study indicate that the residuals form leptokurtic pattern.

5. Effect of systematic errors on best fit model

Effect of systematic errors on best fit model In order to obtain the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was undertaken by introducing pessimistic errors in the influential parameters like concentrations of alkali, mineral acid, ligand and metal [Table 3].

The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali>acid>ligand>metal. Some species were even rejected when errors are introduced in the concentrations. The rejection of some species and increased standard deviations in the stability constants on introduction of errors confirm the suitability of the experimental conditions (concentrations of ingredients) and choice of the best fit models.

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Table 2(a)
Parameters of best-fit chemical models of Co(II), Ni(II) and Cu(II) –Phen complexes in AN-water mixture

%v/v	log β_MLH (SD)			NP	U_{Corr} x10⁻⁸	Skewness	Kurtosis	χ^2	R-Factor	pH Range
	120	130	121							
				Co(II)						
0.0	8.14(25)	10.57(19)	11.24(09)	163	7.4	2.83	16.84	92	0.035	3.0-11.2
10.0	9.02(02)	11.94(04)	12.88(07)	160	7.50	0.08	3.22	112.2	0.097	2.0-10.0
20.0	9.56(08)	11.59(04)	13.73(04)	182	1.55	1.59	3.93	180.8	0.2541	3.0-11.5
30.0	10.31(10)	12.27(05)	13.50(08)	152	1.06	0.99	3.10	114	0.2207	2.9-11.5
40.0	10.12(16)	12.44(08)	11.61(32)	156	1.77	1.3	3.37	23	0.2829	2.9-11.5
50.0	11.53(19)	13.77(06)	14.91(06)	148	1.90	0.72	1.81	61.22	0.2935	2.5-11.5
60.0	11.84(06)	14.20(13)	15.80(03)	157	1.97	0.66	1.92	31.33	0.1738	3.5-10.5
				Ni(II)						
0.0	20.25(32)	23.24(21)	15.21(14)	158	3.97	2.05	13.23	101	0.012	2.1-11.2
10.0	18.24(18)	22.05(25)	14.46(35)	150	1.05	1.26	3.38	173.63	0.2084	2.5-11.6
20.0	17.68(03)	20.88(16)	14.31(05)	170	2.14	1.67	3.92	106.2	0.3246	2.5-11.6
30.0	16.54(04)	20.60(10)	14.10(06)	154	1.52	0.99	3.14	103.09	0.2629	2.8-11.5
40.0	16.14(09)	19.02(36)	17.75(20)	149	1.32	0.67	2.86	30.83	0.1168	1.7-11.5
50.0	15.81(24)	19.72(07)	18.87(11)	145	2.11	0.72	1.83	41.65	0.3067	2.5-11.5
60.0	14.84(11)	18.56(07)	19.22(22)	176	1.95	2.29	9.17	183	0.4491	2.2-11.5
				Cu(II)						
0.0	17.67(25)	20.25(14)	11.95(16)	143	6.41	0.32	4.50	93	0.0049	3.0-11.6
10.0	16.91(29)	18.88(31)	14.90(27)	146	2.08	2.49	9.09	155.2	0.1634	2.4-11.6
20.0	16.22(13)	18.48(27)	13.46(04)	92	2.15	1.69	3.96	123.9	0.2923	3.0-11.5
30.0	15.02(14)	19.53(06)	14.26(39)	135	1.42	0.70	1.67	53.24	0.2114	2.0-8.5
40.0	15.34(07)	17.37(03)	15.31(30)	130	1.9	0.74	62.90	2.64	0.3008	3.8-10.5
50.0	14.04(05)	17.39(21)	14.08(08)	119	1.59	0.82	2.37	25.75	0.2735	2.9-11.5
60.0	13.14(15)	16.94(13)	16.08(06)	123	7.40	0.78	2.23	65.65	0.1747	1.9-11.5

Table 2(b)
Parameters of best-fit chemical models of Co(II), Ni(II) and Cu(II) –Phen complexes in DMF-water mixture.

%v/v	log β_MLH (SD)			NP	U_{Corr} x10⁻⁸	Skewness	Kurtosis	χ^2	R-Factor	pH Range
	120	130	121							
				Co(II)						
0.0	8.14(25)	10.57(19)	11.24(09)	163	7.4	2.83	16.84	92	0.035	3.0-11.2
10.0	9.16(21)	12.25(14)	12.49(12)	86	9.13	0.49	5.12	15.98	0.034	1.8-8.6
20.0	10.55(26)	12.83(33)	13.69(04)	123	4.99	0.96	2.80	29.33	0.074	1.5-11.6
30.0	10.79(14)	13.37(13)	12.26(13)	43	1.30	1.22	2.62	126.07	0.2407	3.0-11.6
40.0	11.37(23)	13.96(21)	13.66(29)	112	5.39	0.12	2.76	6	0.0755	1.5-9.6
50.0	11.60(16)	14.72(15)	14.73(19)	108	7.98	1.11	7.14	76.40	0.0268	1.5-8.5
60.0	12.75(09)	15.97(09)	16.02(11)	82	6.86	2.46	6.59	166	0.409	2.9-11.6
				Ni(II)						
0.0	20.25(32)	23.24(21)	15.21(14)	158	3.97	2.05	13.23	101	0.012	2.1-11.2
10.0	19.76(04)	22.19(22)	13.66(36)	132	9.14	1.08	2.85	84.32	0.1033	1.5-11.6
20.0	19.86(37)	23.87(37)	14.10(11)	138	1.38	1.07	2.13	96.76	0.2073	1.8-11.5
30.0	18.08(04)	22.59(17)	11.89(08)	80	4.77	-1.44	3.12	61.87	0.3704	2.0-11.0
40.0	17.57(16)	21.70(16)	14.38(07)	132	1.22	0.98	2.55	91.83	0.1917	1.8-10.5
50.0	16.33(10)	21.40(08)	13.98(34)	137	1.32	-2.81	19.94	77.90	0.072	2.7-11.6
60.0	16.01(05)	20.48(02)	13.44(09)	76	7.19	2.18	5.47	162.30	0.4475	2.5-11.6
				Cu(II)						
0.0	17.67(25)	20.25(14)	8.82(24)	143	6.41	0.32	4.50	93	0.0049	3.0-11.6
10.0	16.76(05)	19.01(05)	9.57(11)	85	8.93	1.03	2.99	16.33	0.1925	3.2-8.6
20.0	16.11(11)	19.28(06)	13.94(09)	42	1.94	1.55	3.68	84.29	0.1794	1.5-11.5
30.0	14.29(16)	18.92(8)	12.05(12)	51	2.73	1.45	2.95	141.54	0.3430	2.8-11.5
40.0	14.28(11)	17.32(16)	13.91(18)	117	3.00	0.71	6.45	71.54	0.06137	1.8-11.6
50.0	13.55(08)	16.55(12)	13.21(18)	115	3.55	0.69	4.68	94.03	0.058	1.5-10.0
60.0	13.34(15)	15.95(39)	13.81(05)	76	5.46	2.03	5.8	144.19	0.4205	2.2-11.5

Ucorr =U/(NP-m)*10⁸, m –number of species: NP= number of experimental points

6. Effect of solvent

Both AN and DMF are polar aprotic solvents. The dielectric constant of AN-water and DMF-water mixtures decrease with increasing concentration of AN and DMF respectively. These solutions are expected to mimic physiological conditions where the concept of equivalent solution dielectric constant for protein cavities is applicable [52]. The dielectric constants of AN and DMF at different percentages (0.0-60.0 vol%) of water were taken from literature [53].

Effect of solvent on stability constant of chemical speciation depends upon electrostatic and non-electrostatic factors. Born's classical treatment holds good in accounting for the electrostatic contribution [54] which is related to dielectric constant. The linear variation (Fig. 1) of stability constants of

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Phen complexes of Co(II), Ni(II) and Cu(II) in AN-water and DMF-water mixtures with $1/D$ (where D is dielectric constant of the medium) indicates that electrostatic forces dominate the equilibrium process under the present experimental conditions.
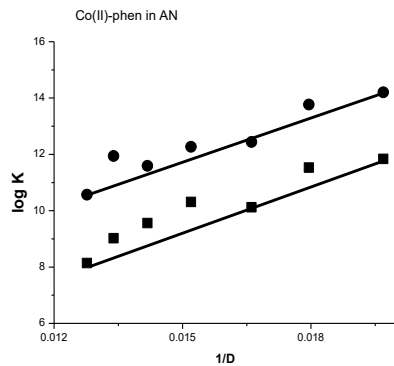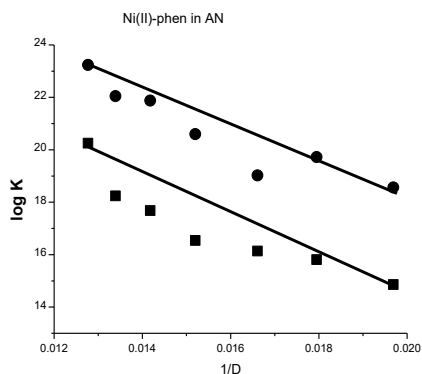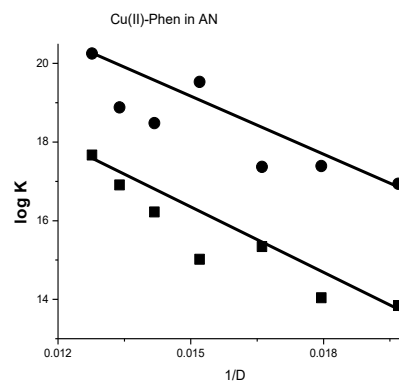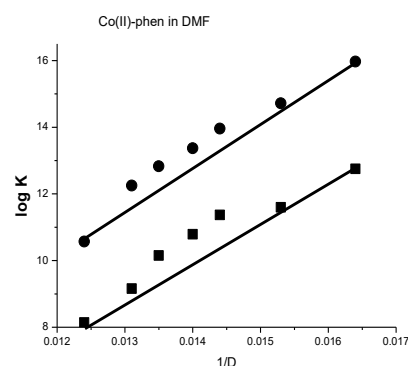

1(a)

Fig. 1(b)

Fig. 1(c)

Fig. 1(d)

Table 3
Effect of errors in concentrations of ingredients on stability constants of Cu(II)-Phen complexes in 30% v/v DMF-water mixtures

Ingredient	% of error	log β_{MLH}		
		120	**130**	**121**
Alkali	-5	Rejected	19.88(04)	12.34(22)
	-2	14.87(04)	20.14(27)	13.04(13)
	0	14.29(03)	18.92(08)	12.05(08)
	+2	14.52(02)	18.99(13)	12.33(05)
	+5	15.14(02)	Rejected	12.89(05)
Acid	-5	15.75(02)	19.75(02)	Rejected
	-2	15.15(02)	19.55(02)	12.55(05)
	0	14.29(03)	18.92(04)	12.05(08)
	+2	14.84(04)	19.34(04)	12.32(13)
	+5	Rejected	19.18(07)	Rejected
Ligand	-5	14.41(03)	19.01(03)	12.22(09)
	-2	14.43(03)	18.91(03)	12.08(09)
	0	14.29(03)	18.92(04)	12.05(08)
	+2	14.45(03)	18.94(03)	12.02(08)
	+5	14.47(03)	18.98(03)	12.17(08)
Metal	-5	14.48(03)	18.81(19)	11.98(08)
	-2	14.32(03)	18.88(19)	12.00(08)
	0	14.29(03)	18.92(04)	12.05(08)
	+2	14.36(03)	19.01(02)	12.12(09)
	+5	14.65(03)	19.24(20)	12.29(09)

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Ni(II)-phen in DMF

Fig. 1(e)

Cu(II)-phen in DMF
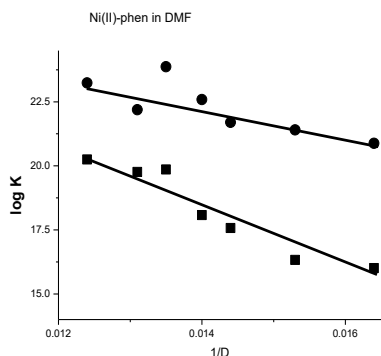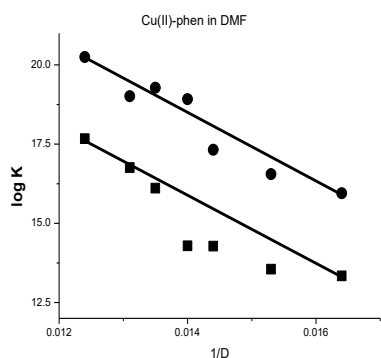
Fig. 1(f)

Fig. 1. Variation of stability constant values of metal-Phen complexes with reciprocal of dielectric constants (1/D) in AN-water[1(a), 1(b), 1(c)] and DMF-water[1(d), 1(e), 1(f)] mixtures at temperature = 303 K, ionic strength = 0.16 M respectively; (a) Co(II), (b) Ni(II), (c) Cu(II) , (d) Co(II), (e) Ni(II), (f) Cu(II). log 120(■), log 130(●)

7. Distribution diagrams

Phen, a neutral base, has only one proton attached to the nitrogen atom under the present experimental conditions. The form of Phen that exist in the pH region of 3.0-6.0 is LH^+. The possible species are ML, ML_2 and ML_3, as the two imine nitrogen atoms of Phen are the potential sites for coordination of metal ligands. The species formed in the present study for different metals, as given in Table 1[(a) & (b)] are ML_2 and ML_3 for Co(II), Ni(II) and Cu(II). The formation equilibria based on the distribution of species with pH are represented below [Fig. 2].

Distribution diagram were drawn for various complex species using the formation constants of the best-fit models for AN-water and DMF-water are shown in Fig. 3[(a), (b) & 3(c)], Fig. 3[(d), (e) & (f)] respectively. Fig. 3[(a) & (d)] represents the formation of Co(II)-Phen complexes. The species ML_2, ML_3 and ML_2H are formed in the pH range of 1.8-11.6. Fig. 3[(b) & (e)] represents the formation of Ni(II)-Phen complexes. The concentration of ML_2H and ML_2 decreased, while the concentration of ML_3 increased in the pH range 2.5-11.6. Fig. 3[(c) & (f)] represents the formation of Cu(II)-Phen complexes. The concentration of ML_2H, and ML_2 are decreased, while the concentration of ML_3 is increased in the pH range 1.5-11.5.
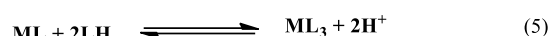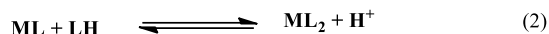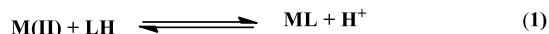
$$M(II) + LH \rightleftharpoons ML + H^+ \qquad (1)$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \qquad (2)$$

$$M(II) + 2LH \rightleftharpoons ML_2 + 2H^+ \qquad (3)$$

$$ML_2 + LH \rightleftharpoons ML_3 + H^+ \qquad (4)$$

$$ML + 2LH \rightleftharpoons ML_3 + 2H^+ \qquad (5)$$

Fig. 2. The formation of various Phen complex species

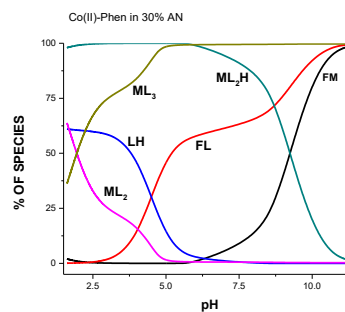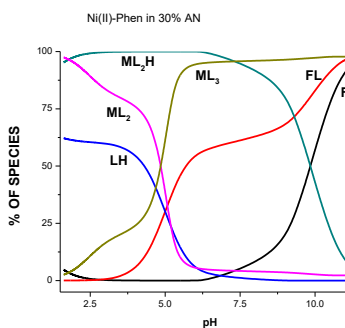Co(II)-Phen in 30% AN

Fig. 3(a)

Ni(II)-Phen in 30% AN

Fig. 3(b)

Cu(II)-Phen in 30% AN

Fig. 3(c)

Co(II)-Phen in 30% DMF

Fig. 3(d)

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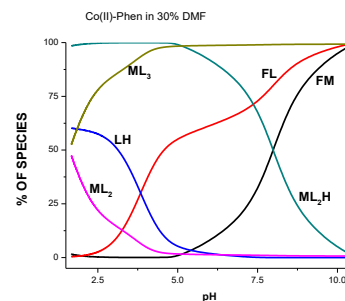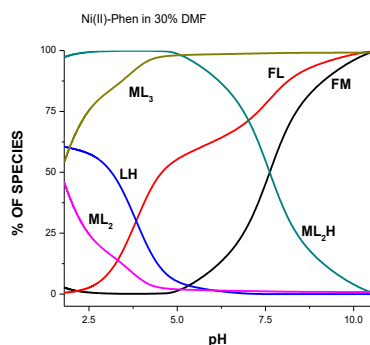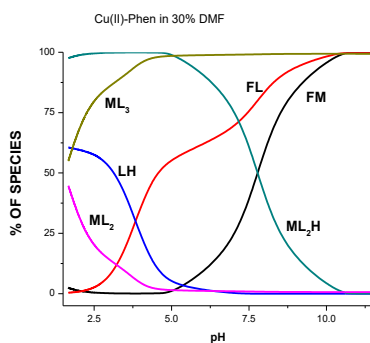**www.ijresm.com | ISSN (Online): 2581-5792**

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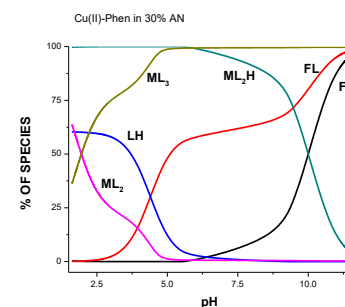
Fig. 3(e)

Fig. 3(f)

Fig. 3. Distribution diagrams of binary complexes of Phen in 30% AN-water and DMF-water mixtures respectively (a) & (d) Co(II), (b) & (e) Ni(II) and (c) & (f) Cu(II).

8. Structures of complexes

Depending on the active sites in ligand and the nature of the metal ions, the structures were proposed for the species detected as shown in Fig. 4.
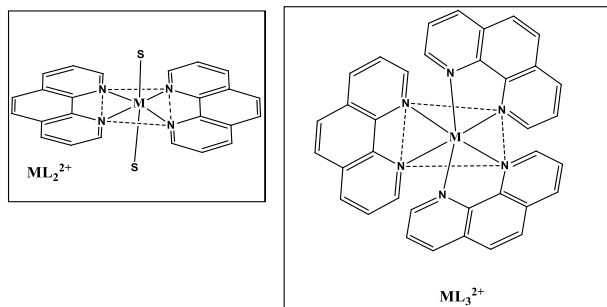

Fig. 4. Structures of Metal-Phen complexes where M is Co(II), Cu(II) or Ni(II), L is Phen and S is either solvent or water molecules

9. Conclusions

The following conclusions have been drawn from the modeling studies of the speciation of binary complexes of Co(II), Cu(II), and Ni(II) with Phen in AN-water and DMF-water mixtures:

1) Due to the interaction of Phen with metals Co(II), Ni(II) and Cu(II), the binary species ML2, ML3 and ML2H are formed. These models are validated by using statistical treatment of the data.

2) The log β values linearly increased with 1/D of the medium in the case of Co(II), indicating the dominance of electrostatic forces over non-electrostatic forces and linearly decreased in the case of Ni(II) and Cu(II) indicating the dominance of non-electrostatic forces of electrostatic forces.

3) The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal.

4) At higher pH values, the high concentrations of chemical species indicate that the metals are more amenable for transportation at higher pH values.

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