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Binary Complex Equilibria of 1,10-Phenanthroline with Co(II), Ni(II) and Cu(II) in Non-Ionic Surfactant Media

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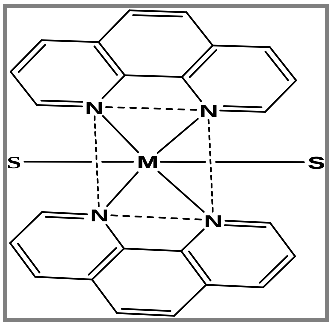
ABSTRACT

Complex formation of 1,10-Phenanthrolinre (phen) with Co(II), Ni(II) and Cu(II) in micellar media: polyethylene glycol 400 (PEG-400, a neutral surfactant) (v/v 0.5-2.5) % has been carried out pH metrically at constant temperature of 298℃ and 0.16 mol dm^{-3} ionic strength. Magnitude of stability constants and best fit model for metal complexes obtained from MINIQUAD75 computer program along with statistical parameters are presented. The plot of relative concentration of model species versus pH values has been developed from SIM refined data using origin85. Accordingly, ML_2 and ML_3 for Co(II) and Ni(II), ML, ML_2 and ML_3 for Cu(II) chemical models were obtained. The position of equilibria of the metal ligand binary system with percentage of surfactants at constant ionic strength and temperature could be attributed to low dielectric constant of the medium in the presence of PEG-400.

Graphical Abstract



Proposed Structures of M(II) phen complexes where M is
ether Ni(II) and S is either surfactant or water molecule.

Keywords: Complex equilibria, Metal ions, Phen, PEG-400, MINIQUAD75.

INTRODUCTION

Chemical speciation analysis has been remained an innovative theme for an extended period of time to researchers. Information about the total amount of an element in the environment is important but not sufficient to assess its toxicity, mobility, bioavailability and bioaccumulation in different environmental matrices including the human body [**1-6**]. It is useful to understand the bonding behavior of bioligands with the metal ion and the role of active site cavities in biological molecules [**5-6**]. The pH-metric approach for chemical speciation study has been widely applicable in a number of fields as it is simple, low cost, and potentially ideal for routine analysis [**3**], it is useful in: designing of successful clean-up strategies [**4**], identifying potential harmful or beneficial elements, promoting the development of appropriate safety regulations [**3, 4**], identifying the variety of chemical transformations once elements entered in to the organism [**4**]. Thus, speciation analysis of chemical species is still rising, and offers a promising area of research [**4-7**].

1,10-phenanthroline (phen) is a bidentate hetero cyclic ligand [**8**]. It has high ability to chelate with many metals [**10, 11**] in variety of organic-water mixtures with different degree of solubility. Several reports demonstrated that phen strongly interact with a number of metal ions to form stable complexes that are soluble in water but insoluble in organic solvents [**12, 13**]. It form a number of stable chelated complexes with rigid framework at 1 and 10 positions differing in the nature and solubility in variety of media like complexes of Co(II), Ni(II) and Cu(II) in low dielectric media [**14**], Cr(VI)-phen complex plays active role in the oxidation of ethanol and as good metal chelator used in metallocene industry [**15, 16**].

A number of complex formation reaction between ligands (Lewis bases) and Co(II), Ni(II) and Cu(II) (Lewis acids) have been reported by different researchers [**16-24**]. The stabilization/destabilization of the complexes is a function of the magnitude of stability constants. The values of the stability constants change with solvents and surfactant media [**22**]. Thus, the authors have taken up neutral surfactant media, PEG-400 to study the speciation of Co(II), Ni(II) and Cu(II) complexes with 1,10-phenanthroline.

MATERIALS AND METHODS

Reagents and Solutions: In this study, all chemicals used were of analytical reagent grade. Solutions of chemicals were prepared in triply distilled water free of dissolved oxygen or carbon dioxide via purging nitrogen gas in to it. Solutions of ~0.05 mol dm^{-3} phen {Sigma-Aldrich, India), ~ 0.4 mol dm^{-3} of sodium hydroxide and 0.2 mol dm^{-3} hydrochloric acid (both Merck, India) were prepared. Gran titration was carried out to remove carbonates from NaOH. NaOH was standardized against potassium hydrogen phthalate and used to standardize HCl solution before use. A ~ 0.1 mol dm^{-3} solutions of Cu(II), Co(II) and Ni(II) (all E-Merck, Germany) were prepared from the corresponding chloride salts and standardized by complexometric titration method. The ligand and metal solutions were maintained in 0.05 mol dm^{-3} HCl. Polyethylene glycol 400 (PEG-400) (Merck, India) was used as received and 0.0% - 2.5% were prepared. The ionic strength of the titration mixture was maintained to be 0.16 mol dm^{-3} sodium chloride (Merck, India).

Methods and equipment: Potentiometric titration has been carried out using Metrohm 877 titrino plus auto-titrator (Switzerland) (readability 0.001) in conjunction with combined glass electrode of 0-14 pH reading. Data acquisition was carried out under carefully designed experimental conditions at the temperature of 298 K and with constant slow stream of purified nitrogen atmosphere through the test solutions [**26**]. The electrode was calibrated to give stable and reproducible response. It was also equilibrated in well stirred PEG-400 with regular checking via initial titration of strong acid with alkali solution. After equilibration of the electrode, the data obtained by the three replicate titration measurements were reproducible and found to differ by not more than 0.02 units.

Data processing: The relative compositions of chemical models for metal ligand complexes and their corresponding free forms at the given set of experimental conditions (pH, temperature and ionic strength) have been studied using the modified [27] Calvin-Wilson titration technique.

A total volume of 50 dm^3 titration mixtures containing different percentage of PEG-400, ligands and fixed concentration of metal ions in an ionic strength of 0.16 mol dm^{-3} NaCl and 298 K has been carried out to study the formation of binary complexes (Table 1). Determination of metal ligand stability constants were performed by the titration of metal-ligand mixtures with 0.05 cm^3 sodium hydroxide (0.4 mol dm^{-3}) at regular intervals. For each experimental data point, volumes of the titration mixture were taken intending to achieve the metal to ligand ratios of 1:1, 1:2 and 1:3 (M:L). The titrimetric data generated were automatically saved in the instrument (Metrohm 877 titrino plus auto-titrator).

The effect of variations in liquid junction potential, asymmetry potential, dielectric constant, sodium ion error, dissolved carbon dioxide and activity coefficient on the response of the electrode were accounted for by correction factor which was calculated using SCPHD [28] program. The stability constants of the binary complexes were determined by MINIQUAD75 computer program [29, 30] using value of correction factor as initial imputes and fixed values of Kw and protonation constants of the ligands during refinement.

Table 1. Comparison with previously reported literature values of Co(II), Ni(II) and Cu(II)-Phen complexes in aqueous media and PEG-400 media

Metal ion	log β_{mlh}			Solvents	Instrumental method	Ref.
	ML	ML$_2$	ML$_3$			
Co(II)	5.95	11.58	17.43	Aqueous	Potentiometry	[31]
		14.38	19.32	Aqueous	Potentiometry	Current work
		12.22	17.93	PEG-400(2.5%)	Potentiometry	Current work
Ni(II)	6.30	10.24	14.15	Aqueous	Potentiometry	[31]
		13.19	18.64	Aqueous	Potentiometry	Current work
		12.26	17.68	PEG-400(2.5%)	Potentiometry	Current work
Cu(II)	6.28	12.06	----	Aqueous	Potentiometry	[31]
	7.64	14.36	19.04	Aqueous	Potentiometry	Current work
	5.74	12.08	17.78	PEG-400(2.5%)	Potentiometry	Current work

RESULTS AND DISCUSSION

Modeling of chemical species: The results of MINIQUAD75 computer program assisted calculated stability constants based on statistical parameters of plausible models of chemical species given in table 2. ML, ML$_2$ and ML$_3$ forms of metal ligand complexes were successfully refined. The validity and sufficiency of the chemical models to qualify the experimental data has also been checked based on sum of squares of residuals in mass balance equations ‘U’, the standard deviations in the refined complex stability constants, chi-square, skewness, crystallographic R-factor and kurtosis. These statistical parameters satisfy the requirements for the least square method to be applied to the data presented. As can be seen from table 2, the distribution error is skewed between -1.84 to 2.75 and thus it is part of the normal distribution curve. The distribution curve of the error was also found to show leptokurtic pattern (>3) for Co(II)-, Ni(II)- and Cu(II)-phen system. In the case of 1.0 and 2.5% PEG-400–water for Ni(II), it showed platykurtic pattern. The precision of the parameters was further ensured by the small values of the standard deviation in the calculated over all stability constants.

Chemical speciation and species distribution plots: 1,10-phenanthroline (phen) is a bidentate hetero cyclic ligand with two associable protons. It has high ability to chelate with many metals in its active forms like LH_2^{2+}, LH^+ and L in a variety of surfactant-water mixed solvent with different degree of solubility. In the present study, the most likely complex model species of phen formed in the metal-ligand system are ML_3, ML_2 for Co(II) and Ni(II) and ML_3, ML_2 and ML for Cu(II) in PEG-400-water mixture where M = Co(II), Ni(II) and Cu(II); L = Phen.

Table 2. Parameters of best fit chemical models of Co(II), Ni(II) and Cu(II)-Phen complexes in PEG-400–water mixtures

% V/v PEG-400	log β_{mlh} (SD)			pH-Range	NP	$U_{corr\times10^8}$	χ^2	Skewness	Kurtosis	R-factor
	ML	ML_2	ML_3							
					Co(II)					
0.0	---	14.38(4)	19.32(7)	1.4-4.5	284	2.13	30.20	0.19	3.57	0.0063
0.5	---	13.08(4)	19.21(2)	1.4-5.0	231	1.86	61.25	-0.89	6.87	0.0049
1.0	---	13.70(33)	18.14(34)	1.55-5.0	46	2.09	2.52	0.12	3.17	0.0077
1.5	---	13.05(10)	18.75(7)	1.5-7.0	119	6.08	9.68	-0.15	3.65	0.0084
2.0	---	12.66(10)	18.70(3)	1.4-5.0	162	5.56	44.40	-1.84	8.49	0.0082
2.5	---	12.22(5)	17.93(3)	1.5-4.0	192	3.71	69.78	-0.92	7.85	0 .0071
					Ni(II)					
0.0	---	13.19(8)	18.64 (8)	1.5-4.0	111	5.19	183.35	2.75	16.99	0.0099
0.5	---	12.71(6)	18.62(3)	1.8-3.5	68	1.62	155.64	2.37	11.17	0.0086
1.0	---	12.31(21)	18.01(12)	1.63-4.0	115	5.19	33.04	0.02	2.88	0.0108
1.5	---	12.16(16)	17.71(11)	1.67-4.0	68	15	34.43	-2.10	9.14	0.0186
2.0	---	12.52(7)	17.72(10)	1.54-4.2	101	8.98	25.16	-0.57	7.65	0.0115
2.5	---	12.26(17)	17.68(12)	1.5-4.0	42	9.21	2.50	-0.32	2.74	0 .0231
					Cu(II)					
0.0	7.64(14)	14.36(11)	19.04(15)	1.47-5.0	244	1.16	93.92	-0.06	7.04	0.0049
0.5	7.11(12)	13.92(8)	18.80(11)	1.55-5.0	218	1.43	31.46	-0.01	4.65	0.0063
1.0	6.60(11)	12.75(4)	18.14(11)	1.42-4.0	202	1.67	121.18	-0.20	6.01	0.0046
1.5	6.25(11)	12.44(3)	17.98(9)	1.5-4.0	170	1.10	38.52	0.25	6.31	0.0042
2.0	5.85(35)	12.22(3)	17.97(11)	1.67-5.0	89	0.30	72.09	2.40	13.03	0.0031
2.5	5.74(48)	12.08(4)	17.78(15)	1.7-5.0	67	0.28	26.62	1.84	9.33	0.0029

At low pH region, (pH 1.0-3.0), both ML_3 and ML_2 exists simultaneously as indicated by the simultaneous increase in percentage of both species. In this pH range (pH 1.0-3.0), ML_3 was formed by the interaction of LH with the metal ion and ML [Equil. 7 and 8) and LH_2 with the metal ion [Equil. 9]. The ML_2 model was also formed by the interaction of LH with the metal ion and ML [Equil. 3 and 4) and LH_2 with the metal in the same pH range [Equil. 5]. Above pH 3, ML_3 is the predominant species since the relative percentage of ML_3 kept on increasing while that of ML_2 decreases. This confirms the contribution of equilibrium 10 in the formation of ML_3 from the interaction of LH_2 and ML_2 at higher pH [Equil. 10]. The extra stability as indicated by relatively high percentage of ML_3 in almost all the determinations could be accounted for by the formation of rigid and chelated metal-ligand complexes at high concentration of the ligand. As the metal to ligand ratio (1:1 in ML, 1:2 in ML_2, 1:3 in ML_3) got smaller and smaller, the possible formation of complex species with higher coordination number increases. Moreover, the competition between metal ion and hydrogen ion for the binding site of the ligand decreases with increasing pH resulting lone pair of the electron available to readily donate to metal ions. Thus, at higher pH, ML_3 is formed in preference to ML_2.

In the case of copper complexes of 1,10-phenanthroline, ML was found to exist in quantitative amount (~15-45%) in addition to ML_3 and ML_2 below pH 2.5 in PEG-400-water mixture. The lower percentage of ML in Cu(II)-Phen system in PEG-400-water media at higher pH or its complete absence in Co(II)- and Ni(II)-1,10-Phen system at all pH range indicates the contribution to M-L equilibria of [Equil. (1) and (2)] is less compared to other equilibria positions. At low pH (<1), the competition between the metal ion and hydrogen ion for the ligand is very high making the binding site in the ligand less available for coordination. The high participation of the metal ion in the formation of metal ligand equilibria is indicated by the lower percentage of the metal ion in the distribution diagram with increasing pH. Similar argument could be extended to the lower percentage composition and/or the disappearance of free ligand in the chemical model distribution diagram of the complex equilibria. The typical concentration distribution diagrams of M-L system in PEG-400-water mixtures plotted as a function of pH are given elsewhere (Figure 1) and the dynamic metal ligand complex formation equilibria are also presented below.

$$M + LH \rightleftharpoons ML + H^+ \quad (1)$$

$$M(II) + LH_2 \rightleftharpoons ML + 2H^+ \quad (2)$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \quad (3)$$

$$M(II) + 2LH \rightleftharpoons ML_2 + 2H^+ \quad (4)$$

$$M(II) + 2LH_2 \rightleftharpoons ML_2 + 4H^+ \quad (5)$$

$$ML_2 + LH \rightleftharpoons ML_3 + H^+ \quad (6)$$

$$ML + 2LH \rightleftharpoons ML_3 + 2H^+ \quad (7)$$

$$M(II) + 3LH \rightleftharpoons ML_3 + 3H^+ \quad (8)$$

$$M(II) + 3LH_2 \rightleftharpoons ML_3 + 6H^+ \quad (9)$$

$$ML_2 + LH_2 \rightleftharpoons ML_3 + 2H^+ \quad (10)$$

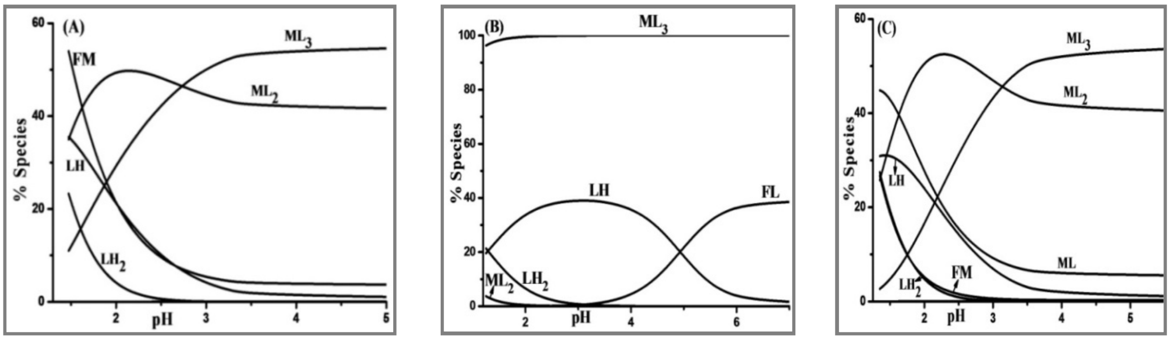


Figure 1. Concentration distribution diagrams of Phen complexes in 2.0% v/v PEG 400–water solvent. (A) Co(II) (B) Cu(II) and (C) Ni(II). The analytical concentrations of metal and ligand are: M(II): ~0.1 and Phen: 0.05.mol L^{-1} respectively.

Perturbation in stability constants due to systematic errors: The goal of refinements of the stability constants by computer program setting statistical parameters as criteria of selection was intended for minimizing errors in the concentration of the titrand components like alkali, mineral acid, ligand and metal ions. The availed random error if it existed, would affect both the β values and species to be included in the model. Even some of the species actual exist may be rejected due to such errors. MINIQUAD75 has no stipulation to vary the influential parameters. In order to test the effects of errors in concentrations of ingredients on the magnitude of stability constants and refinement status of the species for mononuclear binary metal ligand system, the author has carried out deliberate incorporation of 0%, ±2%, ±5% errors in concentration of the ingredients. The variation in magnitude of the stability constants and standard deviations corresponding to stability constants; rejection of some of the models which could have been existed at normal condition otherwise all indicate the effect of these influential parameters on the stability of species and on the values of the stability constants. The results are given in table 3. An overall observation of the results clear show that the effect of alkali and mineral acid on the magnitudes of stability constants was found to be more severe than the ligand or metal ion each does. The increased in standard deviation in the calculated stability constants and rejection of some species owning to purposive inclusion of errors confirms the validity and sufficiency of the proposed models for plausible chemical species. Such study has paramount importance to explain reproducibility of the experimental data to ensure method precision and accuracies under varied experimental designs.

Table 3. Effect of errors in concentrations of ingredients on stability constants of Cu(II)-Phen complexes in 1.5% v/v PEG-400-water mixtures

Ingredient	**% Error**	**Log β_{mlh}(SD)**		
		ML_1	**ML_2**	**ML_3**
			Cu(II)-1,10-phen	
	0	6.25(11)	12.44(3)	17.98(9)
Acid	-5	Rejected	Rejected	Rejected
	-2	7.61(18)	Rejected	19.98(16)
	+2	6.04(3)	11.90(1)	12.78(40)
	+5	5.64(2)	Rejected	19.01(8)
Alkali	-5	6.89(2)	Rejected	Rejected
	-2	6.35(3)	12.37(13)	15.98(9)
	+2	6.59(8)	Rejected	18.81(4)
	+5	Rejected	Rejected	19.15(5)
Ligand	-5	6.10(11)	12.42(2)	17.42(14)
	-2	6.40(11)	12.43(3)	17.80(10)
	+2	6.32(11)	12.44(4)	18.13(8)
	+5	6.42(11)	12.41(7)	18.34(8)
Metal	-5	6.19(11)	12.45(3)	17.85(9)
	-2	6.31(11)	12.44(4)	18.07(8)
	+2	6.09(12)	12.44(3)	17.99(10)
	+5	6.40(10)	12.43(5)	18.21(8)

Effects of PEG-400: The stability constants of complexes of metal ligand couples in the presence and absence of surfactants have been determined to measure the degree of stability of the complexes. The results of the stability constants depicted in table 2 and figure 2 were found to decrease linearly with increasing percentage of PEG-400.

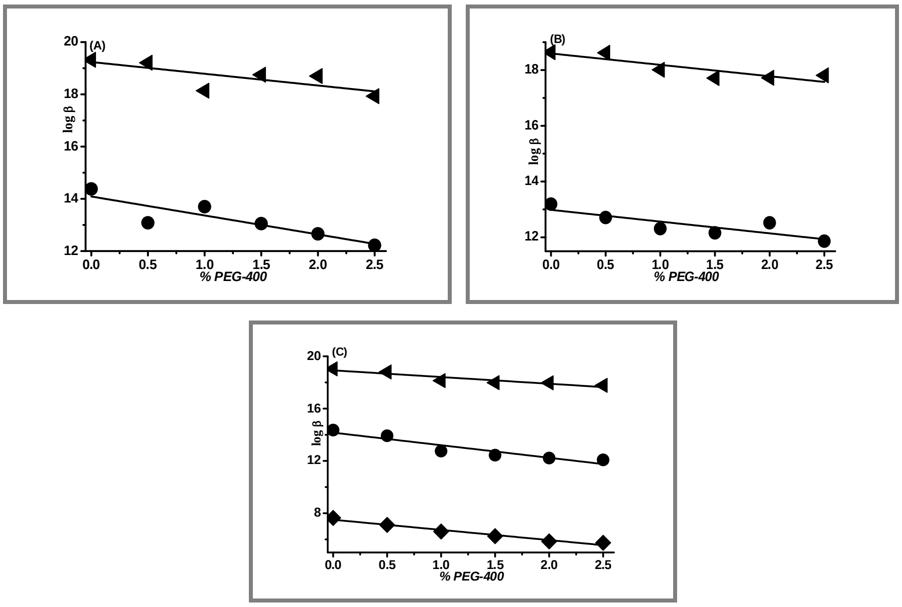


Figure 2. Variation of stability constants of Phen complexes of (A) Co(II), (B) Ni(II), (C) Cu(II) with percentage of surfactants in PEG-400-water mixture: (■) log β_{110}, (●) log $\beta_{120}$and (▲) log β_{130}.

Structure: Phen is bidentate complexing agent with two N electron donor atoms. The electrons on the nitrogen atoms at 1 and 10 positions of one ligand could be coordinated to the central metal ion thereby minimizing repulsive forces with the second ligand molecules. Based on previous suggested structures [33], the net influences of repulsive forces, steric hindrance and other micro-environmental factors between bonding pairs, the following plausible chemical structures for M(II)-L complex are proposed (Figure 3).

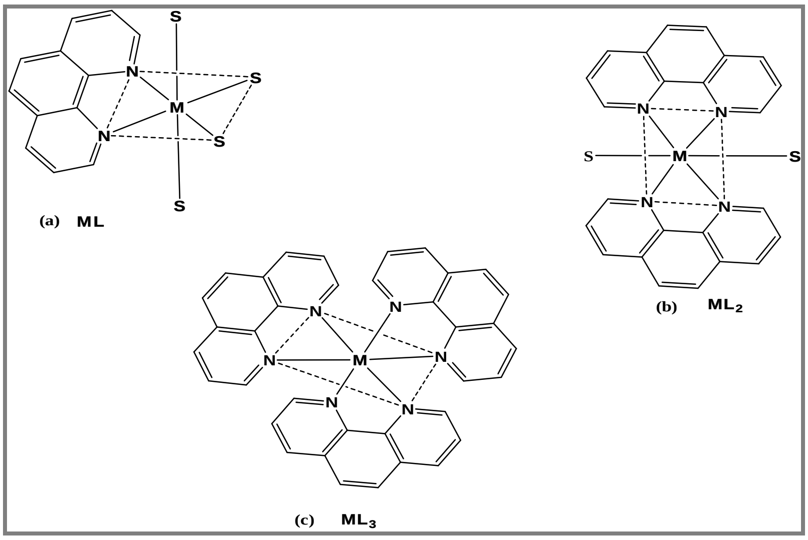


Figure 3. Proposed Structures of M(II)- phen complexes where M is ether Co(II), Ni(II) or Cu(II) and S is either surfactant or water molecule.

APPLICATION

Chemical speciation study of metal-ligand complexes throw light to understand the role played by the active site cavities in biological molecules and their bonding behavior.

CONCLUSION

- In the present study, the stability constants of the M(II)-Phen complexes in PEG-400 micellar media has been studied.
- ML, ML_2 and ML_3 best fit models for plausible chemical species were converged using MINIQUAD75 computer program for M(II)-Phen complexes where M= Co, Ni and Cu.
- The magnitude of the stability constants was found to decrease linearly in PEG-400-water solvent more significantly in aqueous media due to low dielectric constant of the medium.
- The effect of change in concentrations of influential parameters were also converged by deliberate incorporation of 0%, ±2%, ±5% errors in concentration of the ingredients.
- The stability constants and stability of complexes were significantly affected by change in concentration of acids and alkali compared to other parameters. This has been seen from the large SD in stability constants and some of rejection of refined species after the incorporation of errors.

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