pH Metric Investigation on Speciation Studies of 5-Sulfosalicylic acid complexes of Co(II), Ni(II) and Cu(II) in DMF-Water Mixtures

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ABSTRACT

Speciation of Co(II), Ni(II) and Cu(II) complexes with 5-Sulfosalicylic acid (5-SSA) in the presence of N, N'-Dimethyl formamide-water mixtures(0.0-60% v/v) at an ionic strength of 0.16 mol dm^{-3} and temperature 303 K were investigated pH metrically. The existence of different binary complex species was established from modeling studies using the computer program MINIQUAD75. The increased stability of the complexes with increasing DMF was explained by electrostatic forces. The influence of the DMF on the chemical speciation is discussed based on the dielectric constant of the medium. Distribution diagrams of various species of the complexes in relation to pH are presented.

Keywords: 5-Sulfo salicylic acid; Speciation; DMF-Water; Binary complexes; Dielectric constant.
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INTRODUCTION

The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility, solubility, extractability and many other critical properties depend on the form and nature of the chemical species [1-3]. Bioavailability of metal ions depends on either in Free State or in binding state or in complexation state with various constituents present in the requisite amounts during biological reactions. The changes in various constraints like change in pH, temperature and ionic strength cause change in complexation behavior of metals and binding state. So complexation can signify the bioavailability of the metal ions in various biosystems [4, 5].

Speciation analysis, the determination of the concentrations of separate and unique atomic and molecular forms of an element instead of its total concentration in a sample is important in human biology, nutrition, toxicology and in clinical practice [6-8]. On the other hand, speciation profoundly influences both the toxicity and bioavailability of an element. The speciation study of toxic and essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of drug residues with the metal ion [9, 10]. The species refined and their relative concentrations under the experimental conditions represent the possible forms of drugs in bio-fluids.

Cobalt is essential for the production of red blood cells. It acts as coenzyme in several biochemical processes. Cobalt in the form of vitamin B12 is essential for animals. Vitamin B12 is synthesized only by microorganisms, in

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particular anaerobic bacteria. Nickel is associated with several enzymes [11-13] and any variation in its concentration leads to metabolic disorders [14]. Copper is largely rejected from cells but outside the cell, it is essential for the metabolism of many hormones and connective tissue. The biological functions include electron transfer, dioxygen transport, oxygenation, oxidation, reduction and disproportionation [15, 16].

The aim of the present study is to understand the role of metal ions at active site cavities in bioactive molecules like drugs, enzymes and proteins to know the effect of dielectric constant of the medium on the chemical speciation of the title systems. 5-SSA has been taken as a model compound for drug residues, since the dielectric constant at the active site cavities is very small compared to that at bio-fluids, low dielectric constant is mimicked by using a water soluble organic solvent like N,N' Dimethyl Formamide (DMF).

Among the different solvents, the H-bonded structures of amides and their mixtures, especially with water and aliphatic alcohols have an important role in biological systems, because the hydrogen bonds are important as a force governing the structure and the dynamics of chemical and biological system. In the case of amides, the dipolar aprotic solvent, DMF is unable to engage in N-H···O=C hydrogen bonding with dialkyl substitution at nitrogen. However, with water and alcohols DMF forms the C-H···O and C=O···H type H-bond interactions, which result in the complex H-bonded network structures of these systems.

MATERIALS AND METHODS

Materials
5-SSA (TCI, India) solution (0.05 mol L^{-1}) was prepared in triple-distilled deionised water by maintaining 0.05 mol L^{-1} hydrochloric acid concentration to increase the solubility. DMF (Qualigens, India) was used as received. 2 mol L^{-1} sodium chloride (Qualigens, India) was prepared to maintain the ionic strength in the titrand. 0.1 mol L^{-1} aqueous solutions of Co(II), Ni(II) and Cu(II) chlorides were prepared by dissolving G.R. Grade (E-Merck, India) salts in triple-distilled water maintaining 0.05 mol L^{-1} hydrochloric acid to suppress 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 [17, 18]. The strengths of alkali and mineral acid were determined using the Gran plot method [19, 20]

Apparatus
The titrimetric data were obtained using EQUIPTRONICS (Model EQ 614 A) pH meter (readability 0.01), which was calibrated with 0.05 mol L^{-1} potassium hydrogen phthalate in acidic region and 0.01 mol L^{-1} borax solution in basic region. The glass electrode was equilibrated in a well stirred DMF-water mixture containing the inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of DMF-water mixtures (0.0-60% v/v) by maintaining an ionic strength 0.16 mol L^{-1} with sodium chloride at 303.0 ± 0.1 K. The effect of variation in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode was accounted for in the form of correction factor [21].

Procedure
For the determination of stability constants of metal-ligand binary species, initially titrations of strong acid with alkali were carried out at regular intervals to check whether complete equilibration was achieved. In each of the titrations, the titrand consisted of approximately 1 mmol mineral acid in a total volume of 50 mL. Titrations with different ratios (1:2.5, 1:3.75 and 1:5.0) of metal-to-ligand were carried out using 0.4 mol L^{-1} Sodium hydroxide. Other experimental details are given elsewhere [22, 23].

Modeling Strategy
The computer program SCPHD [24, 25] was used to calculate the correction factor. By using the pH-metric titration data, the binary stability constants were calculated with the computer program MINIQUAD75 [26, 27], which exploit the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor and the protonation constants of 5-SSA were fixed. The variation of stability constants with the dielectric constant of the medium was analyzed on electrostatic grounds on the basis of solute-solute and solute-solvent interactions.

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RESULTS AND DISCUSSION

The results of the final 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 1. Very low-standard deviation in overall stability constants (log β) signifies the precision of these constants. The small values of U_{corr} (sum of squares of deviations in concentrations of ingredients 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 [28].

Table 1. Parameters of best fit chemical models of Co(II), Ni(II) and Cu(II) – 5-SSA complexes in DMF-water mixtures. Temp= 303 K, Ionic strength=0.16 mol dm^{-3}

% v/v DMF	log β_{mlh} (SD)			pH-Range	NP	U_{corr}	χ^2	Skewness	Kurtosis	R-factor
	ML	MLH	ML$_2$							
Co (II)										
0.0	4.03(90)	13.93(32)	7.52(96)	1.80-9.80	81	53.38	44.24	0.25	4.14	0.03885
10	4.16(43)	13.81(44)	7.80(59)	2.00-10.30	58	54.61	54.51	0.11	3.59	0.05933
20	4.38(76)	13.65(55)	8.02(61)	3.40-10.30	17	26.54	30.41	0.07	4.11	0.09611
30	4.55(65)	13.48(49)	8.32(63)	3.60-10.40	21	41.29	47.35	0.07	4.81	0.09532
40	4.78(78)	13.36(81)	8.57(90)	3.80-10.20	34	52.36	58.76	0.06	5.11	0.06881
50	4.97(76)	13.20(61)	8.80(55)	3.90-10.20	40	55.06	60.73	0.04	4.43	0.07340
60	5.15(52)	12.98(42)	8.93(60)	4.00-10.30	53	44.51	45.43	0.08	4.13	0.08425
Ni (II)										
0.0	4.12(49)	13.57(32)	7.25(94)	1.90-10.10	73	30.36	16.80	0.25	3.86	0.11338
10	4.34(98)	13.69(42)	7.54(59)	2.00-10.50	71	41.03	66.23	0.41	3.53	0.06891
20	4.48(88)	13.47(44)	7.71(45)	2.20-10.30	64	31.86	53.08	0.46	2.66	0.09246
30	4.69(54)	13.62(52)	7.84(67)	2.50-10.00	67	41.13	59.11	0.42	2.72	0.06457
40	4.86(35)	13.38(41)	7.96(67)	2.20-10.00	85	21.22	67.24	0.56	2.44	0.08177
50	4.98(82)	13.22(77)	8.12(63)	3.20-10.00	46	53.89	67.19	0.14	3.36	0.07718
60	5.15(67)	13.01(52)	8.33(47)	3.30-10.00	53	52.79	54.12	0.18	3.56	0.08472
Cu (II)										
0.0	4.74(91)	13.97(30)	7.70(42)	1.80-9.90	58	44.02	27.56	0.23	3.84	0.32120
10	4.86(35)	13.79(92)	7.89(85)	2.30-11.00	53	50.21	33.35	0.22	3.43	0.05942
20	4.94(53)	13.66(63)	8.03(90)	2.30-11.00	67	49.11	52.73	0.45	3.18	0.09727
30	5.17(44)	13.47(64)	8.21(66)	3.00-10.00	37	55.13	52.68	0.05	5.20	0.08628
40	5.43(74)	13.20(77)	8.45(58)	3.30-10.00	34	45.81	32.27	0.01	5.57	0.09712
50	5.68(42)	13.07(45)	8.61(65)	3.50-10.00	23	55.44	21.32	0.01	5.11	0.08564
60	5.82(50)	12.93(37)	8.78(75)	3.70-10.10	36	54.22	25.14	0.03	4.46	0.09752

$U_{corr} = U/ (NP – m)$; m = number of species; NP = number of experimental points; SD = standard Deviation.

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, the residuals are tested for normal distribution. Such tests are χ^2, Skewness, Kurtosis and R-factor [29]. These statistical parameters show that the best-fit models portray the metal-ligand species in DMF-water mixtures, as discussed below.

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

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 different values are obtained for models containing different number of species, 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.

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Table 2. Effect of errors in influential parameters on Co(II) and 5-SSA complex stability constants in 10 % v/v DMF-water mixture

Ingredient	% Error	Log β_{mlh}(SD)		
		110	111	120
Acid	0	4.16(43)	13.81(44)	7.80(59)
	-4	4.31(65)	13.99(68)	7.90(75)
	-2	4.40(99)	13.71(85)	7.60(98)
	+2	4.15(76)	Rejected	7.81(66)
	+4	4.24(76)	13.56(62)	Rejected
Alkali	-4	Rejected	13.32(61)	8.00(62)
	-2	4.34(89)	13.66(82)	7.60(93)
	+2	4.25(87)	13.72(90)	Rejected
	+4	4.03(95)	14.12(72)	7.99(77)
Ligand	-4	4.50(58)	13.50(75)	7.39(46)
	-2	4.18(96)	13.65(78)	7.72(82)
	+2	4.33(85)	13.41(46)	8.10(43)
	+4	4.48(34)	13.50(42)	8.03(35)
Metal	-4	4.25(52)	13.65(59)	7.89(38)
	-2	4.35(28)	13.55(55)	7.65(66)
	+2	4.10(90)	13.80(72)	7.58(56)
	+4	4.12(52)	13.60(65)	7.60(81)
Volume	-4	4.13(45)	13.64(47)	7.66(39)
	-2	4.28(59)	13.66(42)	7.72(92)
	+2	4.31(65)	13.92(62)	7.60(56)
	+4	4.43(63)	13.96(52)	7.63(94)
Log F	-4	4.16(44)	13.64(60)	8.00(61)
	-2	4.25(66)	13.82(75)	7.62(39)
	+2	4.15(45)	13.55(51)	7.55(39)
	+4	4.18(76)	13.90(81)	7.61(99)

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 0.04 and 0.25 for Co(II), 0.14 and 0.56 for Ni(II) and 0.01and 0.45 for Cu(II). These data evince that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

Kurtosis
It is a measure of the peakedness 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.

Effect of Systematic Errors on Best Fit Model
In order to rely upon the best-fit 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, metal, log F and volume in Table 2. The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > metal > ligand > volume > log F. Some species were even rejected when errors were 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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Effect of Solvent

The dielectric constant is one of the characteristics of liquid. The metal-ligand stability constants are strongly affected by the dielectric constant of the medium because of the fact that at least one of the constituents is charged and other is either changed or has a dipole. Variations in the relative strengths of acids and bases with changing solvents should be a function of the charge, the radius of the ion and the dielectric constants of the medium [30].

When the ionization of an acid gives a net increase of ions, a decrease in the dielectric constant of the solvent should be accompanied by an increase in the stability constant of a weak acid dissolved in it. The variation of stability constant or change in free energy with co-solvent content depends upon two factors, viz, electrostatic and non-electrostatic forces. Born's classical treatment holds good in accounting for the electrostatic contribution to the free energy change [31]. According to this treatment, the energy of electrostatic interaction or stability constants should vary linearly as a function of the reciprocal of the dielectric constant (1/D) of the medium. Such linear variation of stability constants of 5-SSA in DMF-water mixtures shows the dominance of electrostatic interactions and the trend is showed in Figure 1.

A plot of log β versus 1/D (D is dielectric constant) should be linear if Born's classical treatment holds good indicating that electrostatic forces alone operate. The values of Co(II), Ni(II) and Cu(II) complexes of 5-SSA with 1/D reveals that the electrostatic forces are dominating the equilibrium process under the present experimental conditions. The solute-solvent interactions, relative thermodynamic stabilities and kinetic liabilities are also expected to play an important role.
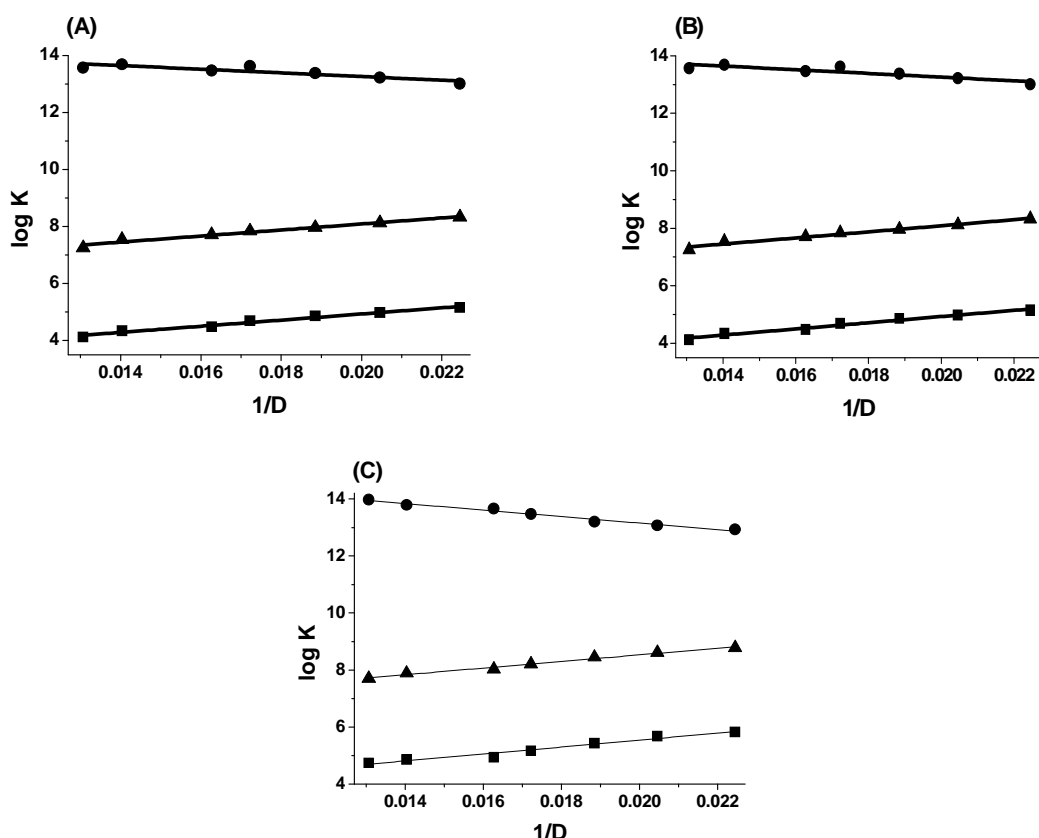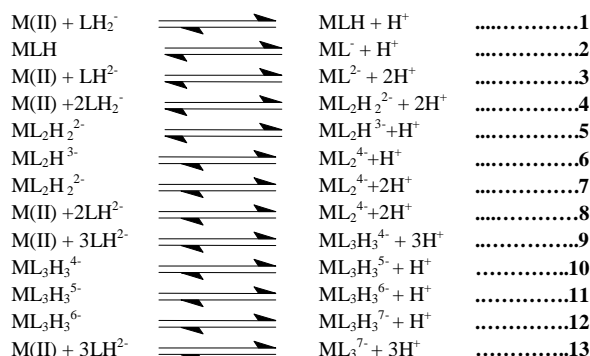

Figure 1. Variation of overall stability constant values of metal-5-SSA complexes with 1/D of DMF-water mixtures (a) Co(II); (b) Ni(II); (c) Cu(II); (■)log β_{ML}; (●) log β_{MLH}; (▲) log β_{ML2}

Distribution Diagrams

5-SSA is a tridentate ligand, it has one carboxyl (–COOH), one hydroxyl (-OH) and one sulfo (–SO$_3$H) groups. The different forms of 5-SSA are LH$_2^-$, LH^{2-}, and L^{3-} in the pH range 1.5-8.5, 1.5-11.9 and 4.7-11.9 respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the

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existence of ML, MLH, and ML_2 for Co(II), Ni(II) and Cu(II). The formation of various 5-SSA complex species is shown in the following equilibria.

$$M(II) + LH_2^- \rightleftharpoons MLH + H^+ \quad ....1$$
$$MLH \rightleftharpoons ML^- + H^+ \quad ....2$$
$$M(II) + LH^{2-} \rightleftharpoons ML^{2-} + 2H^+ \quad ....3$$
$$M(II) + 2LH_2^- \rightleftharpoons ML_2H_2^{2-} + 2H^+ \quad ....4$$
$$ML_2H_2^{2-} \rightleftharpoons ML_2H^{3-} + H^+ \quad ....5$$
$$ML_2H^{3-} \rightleftharpoons ML_2^{4-} + H^+ \quad ....6$$
$$ML_2H_2^{2-} \rightleftharpoons ML_2^{4-} + 2H^+ \quad ....7$$
$$M(II) + 2LH^{2-} \rightleftharpoons ML_2^{4-} + 2H^+ \quad ....8$$
$$M(II) + 3LH^{2-} \rightleftharpoons ML_3H_3^{4-} + 3H^+ \quad ....9$$
$$ML_3H_3^{4-} \rightleftharpoons ML_3H_3^{5-} + H^+ \quad ....10$$
$$ML_3H_3^{5-} \rightleftharpoons ML_3H_3^{6-} + H^+ \quad ....11$$
$$ML_3H_3^{6-} \rightleftharpoons ML_3H_3^{7-} + H^+ \quad ....12$$
$$M(II) + 3LH^{2-} \rightleftharpoons ML_3^{7-} + 3H^+ \quad ....13$$

Some typical distribution diagrams in DMF-water mixtures are shown in Figure 2. They indicate that the binary complexes of Co(II), Ni(II) and Cu(II) are formed in the pH range1.5-12.5. MLH, ML and ML_2 are simultaneously formed with the increasing pH. ML, ML_2 species percentage successively increases with increasing pH. Successive deprotonation of MLH forms ML beyond a pH 5.0. The percentage of the ML_2 species increases successively with increasing in pH up to 11.5. The concentration of MLH species decreased, while the concentration of ML and ML_2 increased in the pH range 4.0-12.0. ML_2 formed at higher pH with high percentage in the case of Co(II), Ni(II) and Cu(II).
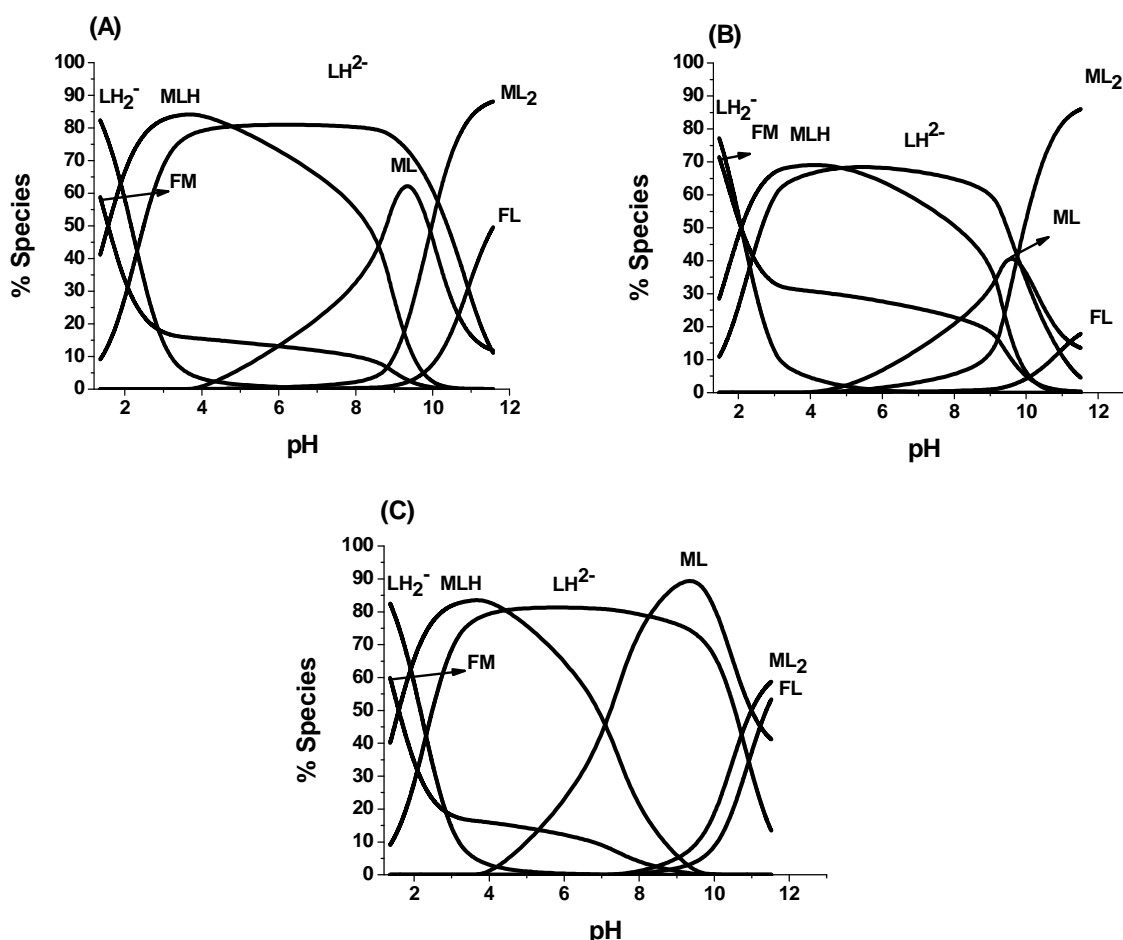

Figure 2: Distribution diagrams of binary complexes of 5-SSA in 10% v/v DMF-water mixture: (a) Co(II), (b) Ni(II) and (c) Cu(II)

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MLH species is formed at pH less than 2.0 (Equilibrium 1) by interacting LH_2^- with free metal, which might have been quickly deprotonated to ML (Equilibrium 2) or the Free metal interacts with LH^{2-} to form ML(Equilibrium 3) at pH more than 4.0. Free metal reacts with LH^{2-} to form ML_2 (Equilibrium 8) at a pH greater than 6.0. The deprotonation of ML_2H^{3-} and $ML_2H_2^{2-}$ results to form ML_2 at more pH (Equilibrium 6 and 7) in the case of Co(II), Ni(II) and Cu(II).

Structures of complexes

5-SSA has three functional groups such as -OH, -COOH and SO_3H groups, and is helpful to form different complexes with Co(II), Ni(II) and Cu(II). Octahedral structures are proposed to the complexes of all the metal ions. The VSEPR theory suggests that Co(II), Ni(II) and Cu(II) complexes shall be octahedral because, there are six outer electron pairs. This argument supports the structures of complexes proposed in Figure 3.
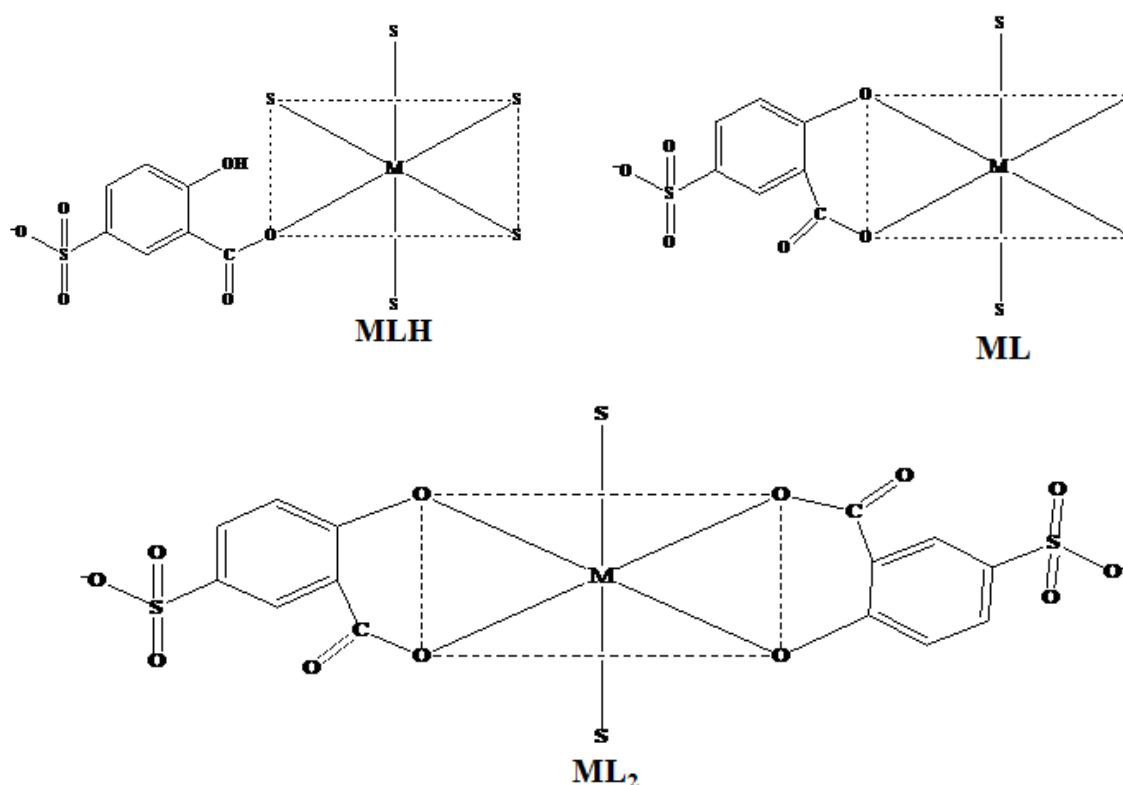

Figure 3: Structure of 5-SSA complexes, where S is either solvent or water molecules

CONCLUSION

The following conclusions have been drawn from the modeling studies of 5-SSA complexes of Co(II), Ni(II) and Cu(II) in DMF-water mixtures.

1. 5-SSA forms both protonated and unprotonated complexes under pH range 4.0–12.0
2. The complex species formed due to interaction of 5-SSA with the essential metals are ML, MLH and ML_2.
3. The linear variation of the stability constants with 1/D of the DMF indicates the dominance of electrostatic forces over non-electrostatic forces.
4. The order of the components in influencing the magnitudes of the stability constants due to incorporation of errors is alkali > acid > ligand > metal > volume > Log F.
5. Some species are stabilized due to electrostatic interactions and some are destabilized due to the decreased dielectric constant.

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