



Potentiometric studies of complex equilibria of Ca^{II} , Mg^{II} and Zn^{II} with 5-sulphosalicylic acid in cationic micelles of CTAB



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ABSTRACT

Formation of metal ligand complex species of 5-sulphosalicylic acid with Ca^{II} , Mg^{II} and Zn^{II} metal ions have been studied potentiometrically in various composition (0.0, 0.5, 1.0, 1.5, 2.0, and 2.5% w/v) of cetyltrimethylammonium bromide (CTAB). The study has been carried out at 303 K temperature and maintaining 0.16 mol dm⁻³ ionic strength using NaCl. The dynamic species belongs to 5-sulphosalicylic acid are LH_2 and LH^{2-} . The best fit of complex speciation has been preferred on basis of statistical parameters like skewness, χ^2 , Kurtosis and crystallographic R-factor. ML_2H , ML_2H_2 and ML_3H_3 type complex were formed by the complexation of 5-sulphosalicylic acid with the metal ions. The change in stability of complex species with composition of the surfactant has been illustrated on the basis electrostatic grounds. Distribution of chemical species with respect to pH and various compositions medium and probable complex equilibria are also studied.

1. Introduction

Estimation of concentration of chemical compound is not important in studies like nutrition, toxicology, human biology and in clinical practice. Speciation study involves determination of concentration of different forms of element is useful in the above studies. Toxicity and bioavailability of an element are strongly influenced by speciation of the element. Nature and form of the chemical species influence the toxicity, bioavailability, bioaccumulation, solubility, extractability and many other critical properties [1, 2, 3]. Complexation behavior of metals and binding state depends on various parameters like change in ionic strength, pH and temperature and complexation shows the bioavailability of the metal ions in various biosystems [4, 5]. In speciation study, concentrations of separate and unique atomic and molecular forms of an element are important in nutrition, toxicology and in clinical practice [6, 7]. Speciation may also exploit certain issues in medical sciences such as therapeutic, diagnostic, and investigative uses of trace metals. Some examples could be portrayed at each level of structure, affecting bioavailability, toxicity, and clinical usage [8, 9].

The majority of the complex speciation investigations are carried out in aqueous environment and the studies are subjected to biosystems. These studies applied to the biofluids and water. However biofluids

existing with low dielectric conditions with various magnitude. In biosystems, metabolic reactions are performed under rigorously compartmentalized environment. Few studies were carried out in organic-water media to take off this environment but very less work was made to explanation for the compartmentalization conditions.

This Cetyltrimethylammonium bromide (CTAB) is cationic micelles and these likely to change the nature of proteins and intensely affects the many biosystems properties. Molecules, ions and chemical species are solubilise, concentrate, and compartmentalized by the surfactants [10]. Cationic micelles could alter the acid-base equilibria. It is due to dissimilarity among the bulk solvent properties and perturbation of the charged interface electrostatic field effect on chemical equilibria of acid-base and of the interfacial region. Previously substituted benzoic acids dissociation equilibria in anionic and cationic surfactants have been studied potentiometrically and reported that the pK_a values substituted benzoic acids altered in the range of 0.5–3.0 in micelles of anionic nature [11].

So many phenols, carboxylic acids and amines acid-base equilibria in micellar media are reported earlier [12]. In view of this, the present investigation, the author attempt to study the complexes equilibria of 5-sulphosalicylic acid with Ca^{II} , Mg^{II} and Zn^{II} ions in cationic micelles of CTAB to stabilize the complex species.

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2. Experimental

2.1. Materials

0.05 M 5-sulphosalicylic acid (TCl, India) solution was prepared using deionised water. Hydrochloric acid is used to maintain the 0.05 M acid concentration in ligand and also increase the solubility of 5-sulphosalicylic acid. CTAB (Merck, India) used as cationic micelles. Sodium chloride (Qualigens, India) was prepared in deionised water used to maintain the ionic strength of system under study. All the metal ion (Ca^{II} , Mg^{II} and Zn^{II}) solutions were made by dissolving their chlorides (E-Merck, Germany) in deionised water. 0.05 M HCl is used to enhance the solubility and also inhibit the hydrolysis of metal salts. Standard methods used to standardize all solutions. The data were analyzed by one way classification [13] to evaluate errors in concentration of the solutions. Gran plot method [14, 15] is used to determine the concentration acid and alkali.

2.2. Instrumentation

Potentiometric titration was done using pH meter (ELICO, LI-120). 0.05 M potassium hydrogen phthalate and 0.01 M borax solutions were used to calibrated the instrument in acidic and basic pH. All the Potentiometric titrations were performed in various composition of Cetyltrimethylammonium bromide ranging from 0.0 to 2.5 % w/v at 303.0 \pm 0.1 K with maintaining ionic strength using NaCl. Correction factor [16, 17] is applied to account the effect of variation in the dissolved CO_2 , asymmetry potential, activity coefficient, liquid junction potential and sodium ion error due to use of glass electrode.

2.3. Analytical procedures

Strong acid-base titrations were regularly carried out before the experiential titrations to check the electrode equilibration with the media. In all the titrations total volume of the titrand is 50 ml which contain 1 mmol mineral acid. 1:2.5, 1:3.75, and 1:5.0 metal-ligand ratios of titrations were executed using 0.4 M NaOH. Additional details of experiments are reported previously [18, 19].

2.4. Modeling strategy

Correction factor was calculated using SCPHD [20] computer program. MINIQUAD75 [21] computer program is used to calculate the

stability constants of metal-ligand binary complexes by analyzing the titration data. MINIQUAD75 exploit the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. The correction factor and the protonation [22] constants of 5-sulphosalicylic acid were predetermined at the time of calculation of stability constants of binary metal-ligand complexes. The alteration of stability of complex species with the composition of the cationic surfactant was investigated on electrostatic grounds and interactions between solute and solvent.

3. Results and discussion

The data resulting from computer modeling study is given in Table 1. The parameters like less value of U_{corr} (deviations in concentrations of components), less value of standard deviation, small value of standard deviation, mean deviation, and mean validates the data through analysis of residuals [23, 24].

3.1. Residual analysis

Some statistical parameters like χ^2 , Skewness, Kurtosis and R -factor shows that the models reveal the metal-ligand species in CTAB-water system. The kurtosis value shows that the residuals are in leptokurtic pattern. Skewness values in the present study are from 0.18 to 1.32 for Ca^{II} , -0.01 to 0.20 for Mg^{II} and -0.16 to 0.53 for Zn^{II} . From this data we conclude that the residuals are in normal distribution and the least squares method has been applied for this data. Crystallographic R -values also validates the adequacy of the model. These statistical parameters show that the best fit models portray the metal-ligand species in CTAB-water mixtures, as discussed below.

3.2. χ^2 test

χ^2 (chi square) 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 the χ^2 calculated is less than the table value, the model is accepted.

3.3. Crystallographic R -test

Hamilton's R factor ratio test is applied in complex equilibria to

Table 1
Parameters of final model of Ca^{II} , Mg^{II} and Zn^{II} - 5-sulphosalicylic acid complexes in CTAB-aqueous system.

% w/v CTAB	$\log \beta_{\text{mlh}}$ (SD)			pH-Range	NP	$U_{\text{corr}} \times \frac{8}{10}$	χ^2	Skewness	Kurtosis	R -factor
	ML_2H	ML_2H_2	ML_3H_3							
Ca^{II}										
0.0	21.80 (30)	32.29 (23)	45.43 (30)	1.8–11.3	98	13.02	91.03	1.32	5.20	0.0422
0.5	20.63 (39)	30.68 (43)	44.86 (39)	1.9–11.2	84	37.80	21.38	1.09	3.03	0.0314
1.0	20.32 (39)	30.37 (43)	44.56 (39)	1.9–11.1	82	38.60	21.58	1.19	5.15	0.0415
1.5	19.70 (24)	30.43 (23)	44.26 (26)	1.8–11.4	104	26.37	21.69	0.44	4.02	0.0302
2.0	19.71 (27)	29.91 (30)	43.95 (28)	1.8–11.1	84	15.97	30.78	0.20	3.80	0.0251
2.5	17.60 (23)	27.87 (39)	41.34 (28)	1.9–11.1	85	35.90	6.93	0.18	4.11	0.0344
Mg^{II}										
0.0	18.85 (38)	28.96 (55)	42.95 (31)	2.0–11.0	69	22.98	32.81	0.20	3.14	0.0333
0.5	18.39 (34)	28.65 (57)	42.60 (28)	2.0–11.0	64	25.16	15.25	0.19	3.41	0.0363
1.0	17.01 (38)	27.23 (77)	40.56 (29)	1.9–11.0	91	68.65	36.60	-0.01	4.34	0.0478
1.5	16.67 (32)	27.08 (25)	40.18 (21)	1.9–11.0	82	32.75	68.67	0.01	4.12	0.0339
2.0	17.00 (39)	26.14 (25)	39.56 (58)	1.9–10.9	72	19.85	65.11	0.11	4.01	0.0292
2.5	16.70 (52)	26.71 (73)	39.94 (49)	2.5–11.0	37	47.71	39.13	0.01	3.93	0.0602
Zn^{II}										
0.0	17.62 (62)	26.86 (51)	40.17 (50)	2.0–10.8	81	77.97	60.31	0.16	3.61	0.1818
0.5	19.55 (72)	26.85 (63)	40.40 (90)	2.5–10.7	31	69.31	17.19	0.02	5.14	0.0528
1.0	20.01 (52)	26.89 (49)	40.13 (42)	2.6–10.8	35	46.96	39.28	-0.16	3.71	0.0473
1.5	20.55 (50)	27.30 (62)	40.19 (55)	1.8–10.9	85	33.61	68.67	0.53	4.26	0.0360
2.0	21.52 (63)	28.65 (90)	42.35 (51)	2.2–10.8	48	36.95	5.22	0.13	3.19	0.0475
2.5	21.47 (66)	28.87 (80)	42.97 (56)	2.2–10.8	43	66.34	14.81	0.09	3.49	0.0662

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.

3.4. 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. These data evince that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

3.5. 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). These statistical parameters thus show that the best-fit models portray the metal-ligand species in CTAB media.

3.6. Effect of errors on accepted model

To validate the final and accepted model, the errors in the influenced components have been introduced and the details are given in Table 2. Due to introducing the errors in influenced components some complex species have been discarded and standard deviation of stability constants

Table 2

Results of errors in the influenced components on Ca^{II} - 5-sulphosalicylic acid complexes in 2% w/v CTAB- aqueous system.

Component	% Error	$\log \beta_{\text{mlh}}$ (SD)		
		ML_2H	ML_2H_2	ML_3H_3
Acid	0	19.71 (27)	29.91 (30)	43.95 (28)
	-5	Rejected	Rejected	Rejected
	-2	Rejected	Rejected	Rejected
	+2	Rejected	27.45 (45)	Rejected
	+5	Rejected	27.28 (59)	Rejected
Alkali	-5	Rejected	31.75 (99)	Rejected
	-2	Rejected	27.76 (44)	Rejected
	+2	Rejected	Rejected	Rejected
	+5	Rejected	Rejected	Rejected
	-5	Rejected	Rejected	Rejected
Ligand	-5	Rejected	Rejected	Rejected
	-2	21.08 (30)	30.26 (53)	45.12 (35)
	+2	16.61 (67)	27.86 (60)	40.74 (84)
	+5	Rejected	27.64 (69)	Rejected
	-5	19.70 (57)	29.91 (51)	43.95 (48)
Metal	-2	19.70 (47)	29.91 (46)	43.95 (40)
	+2	19.71 (55)	29.91 (45)	43.95 (44)
	+5	19.71 (67)	29.91 (50)	43.95 (58)
	-5	19.71 (47)	29.91 (46)	43.95 (46)
	-2	19.71 (35)	29.91 (39)	43.95 (38)
Volume	+2	19.71 (33)	29.91 (37)	43.95 (36)
	+5	19.71 (49)	29.91 (48)	43.95 (47)
	-5	19.71 (40)	29.91 (42)	43.95 (40)
	-2	19.71 (31)	29.91 (32)	43.95 (33)
	+2	19.71 (30)	29.91 (33)	43.95 (31)
Log F	+5	19.71 (43)	29.91 (44)	43.95 (42)

have been increased. This indicates the model have been final and accepted model. The order of components has been influenced in the errors is $\log F < \text{total volume} < \text{metal} < \text{ligand} < \text{acid} < \text{alkali}$.

3.7. Effect of solvent

Effect of composition of surfactant on stability of complex species of

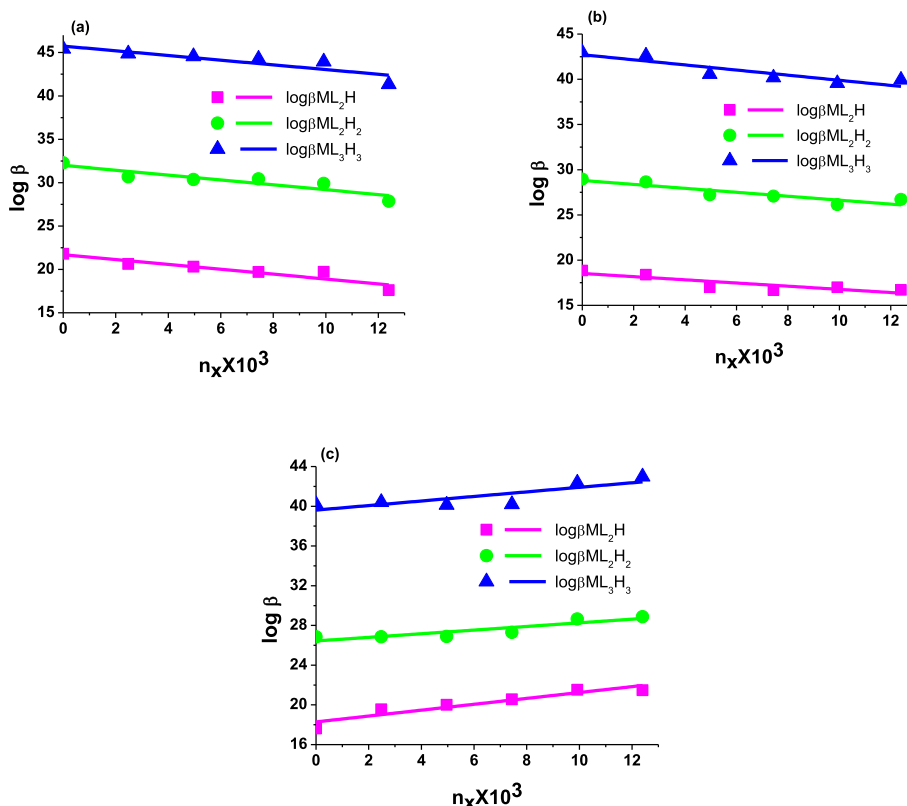
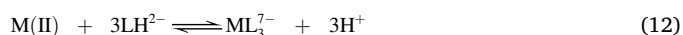
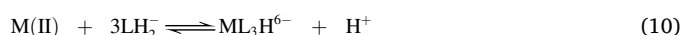
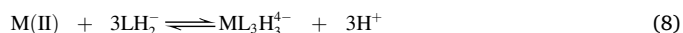
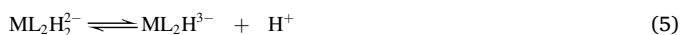
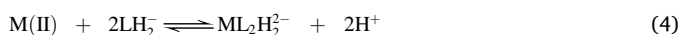
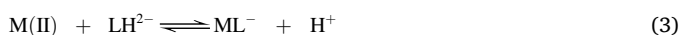


Fig. 1. Change in stability of metal-5-sulphosalicylic acid complexes in CTAB-water system: (a) Ca^{II} , (b) Mg^{II} and (c) Zn^{II} .

5-sulphosalicylic acid is exposed in Fig. 1. The predictable change of stability of complex species with concentration of micelles is due to lowering the system dielectric constant and the growing of micelles concentration. The previous studies [25, 26] and Born's [27] equation suggests that electrostatic interaction are influences the system dielectric constant. The change in stability of metal-5-sulphosalicylic acid complexes in CTAB-water system signifies predomination of electrostatic forces more than non electrostatic. Some divergence in linear change of stability of metal complexes with composition of the CTAB is may be due to co-solvent actions like interaction with water, anionic stabilizing nature, and specific interactions. Effect of co-solvent at the molecular level is understands by this investigation [28, 29, 30].

3.8. Distribution diagrams

Carboxyl groups and hydroxyl group protons in 5-sulphosalicylic acid (LH_2) are ionizable. Sulfonic acid group proton is released at lower pH which is unreliable to detect using glass electrode and unpredictable in determining the particular constant. LH_2 , LH^{2-} , and L^3 are the active forms of 5-sulphosalicylic acid in the pH range <4, 2–11 and >10 respectively. In this study ML_2H , ML_2H_2 , ML_3H_3 complexes are predicted for all the three metal ions. The feasible complex equilibria of 5-sulphosalicylic acid with Ca^{II} , Mg^{II} , and Zn^{II} ions given below.



The distribution diagrams various species of 5-sulphosalicylic acid with Ca^{II} , Mg^{II} and Zn^{II} given in Fig. 2. The diagrams reveals that Ca^{II} , Mg^{II} and Zn^{II} complexes with the 5-sulphosalicylic acid produced in 2.0–11.5 pH. The type of species developed in the pH range is ML_2H , ML_2H_2 and ML_3H_3 .

ML_2H_2 and ML_3H_3 [Equilibria (4) and (8)] complexes are observed at low pH when compared to ML_2H . ML_2H is developed by the deprotonation of ML_2H_2 species. The concentration of ML_3H_3 complexes increase along with the pH up to 11. The concentration of ML_2H_2 and ML_3H_3 species decreased and the concentration of ML_2H increased in the pH range 7.5–11.0 for Ca^{II} and Mg^{II} . In case of Zn^{II} , the concentration of ML_2H developed in the pH range 4.5–11.0.

3.9. Structures of metal complexes

Two oxygen sites in the 5-sulphosalicylic acid are involved in the formation of binary metal complexes which results the more stable six membered rings. Proposed structures for all the metal ions investigated in the study is Octahedral in shape. With the knowledge of valence shell

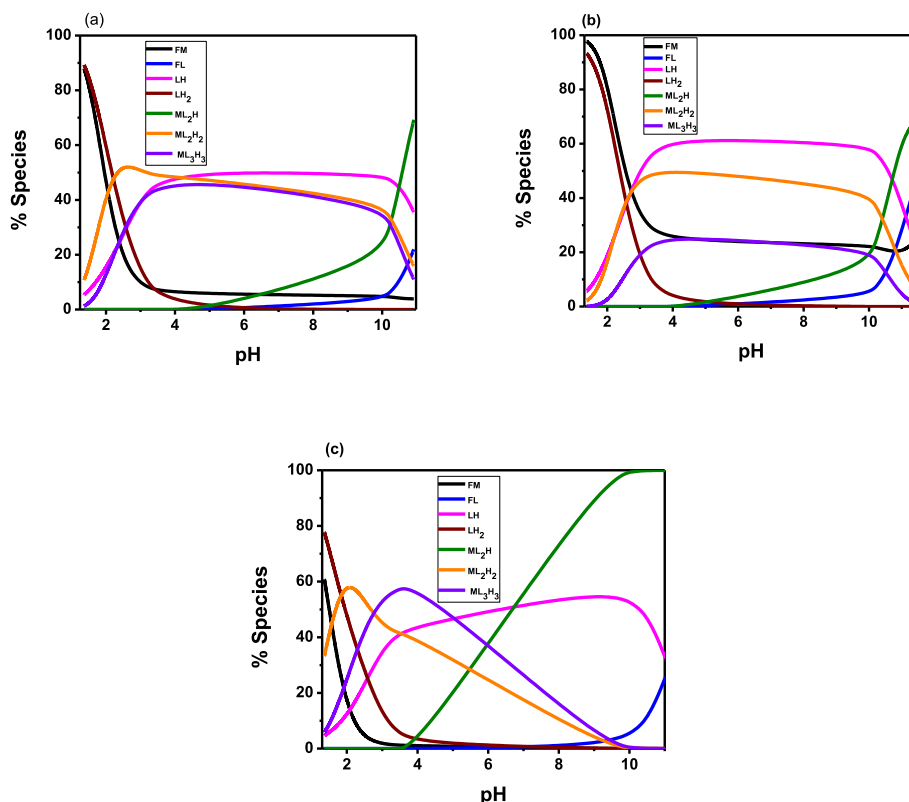


Fig. 2. % Species of 5-sulphosalicylic acid complexes in 2.0% w/v CTAB: (a) Ca^{II} , (b) Mg^{II} and (c) Zn^{II} .

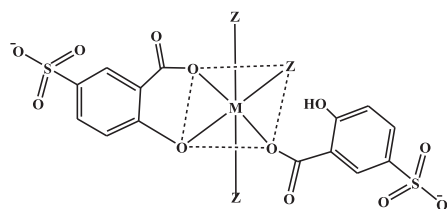
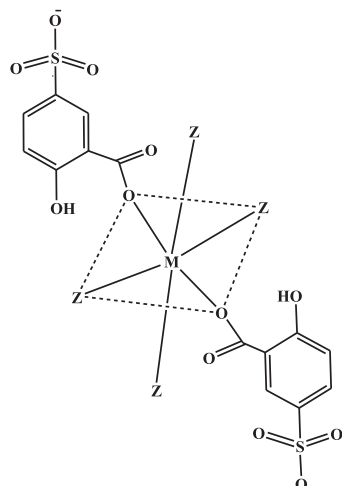
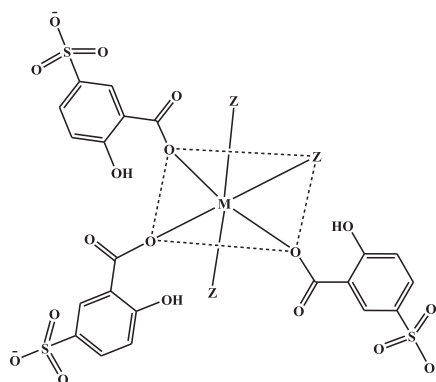
ML₂HML₂H₂ML₃H₃

Fig. 3. Structure of 5-sulphosalicylic acid complexes where Z is either solvent or water molecules.

electron pair repulsion theory Ca^{II}, Mg^{II} and Zn^{II} complexes should be octahedral in shape due to availability of six electron pairs, which suggests proposed structures in Fig. 3.

4. Conclusions

5-sulphosalicylic acid form complex with Ca^{II}, Mg^{II} and Zn^{II} species in 2.0–11.5 pH range. CaL₂H, CaL₂H₂, CaL₃H₃, MgL₂H, MgL₂H₂, MgL₃H₃, ZnL₂H, ZnL₂H₂ and ZnL₃H₃ species produced by the reaction metal ions (Ca^{II}, Mg^{II} and Zn^{II}) with 5-sulphosalicylic acid. The change in stability of metal complexes as a function of composition of CTAB shows the predomination of electrostatic forces. The values of log β_{mlh} of Ca^{II}, Mg^{II} complexes decreased with the increasing composition of CTAB and increased in the case of Zn^{II} complexes this might be due to complexation was different in alkaline earth metals and/or transition metals with respect to surfactant concentration. Electrostatic interactions and decreasing dielectric constant is responsible for stabilization and destabilization of species. Stability of complexes affected by the reactants due introducing errors in their strength is follows in the order log F < total volume < metal < ligand < acid < alkali. Speciation study of 5-sulphosalicylic acid with metal ions in the binary solvent medium could be

important information for biochemists. This study helps to understand the metal-ligand interactions in aqueous-organic solvent mixtures and could be quite informative for the study of the pharmaceutical applications.

Declarations

Author contribution statement

M. Ramanaiah: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

P. Seetharam: Conceived and designed the experiments; Performed the experiments.

M. Balakrishna, B. Rama Raju: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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