Semi-empirical calculations and potentiometric studies on complexation equilibria of 2,2'-Bipyridyl in SDS and TBAB micellar media

Chakravarthi P.S.S.¹, Shyamala P.^{1*}, Nageswara Rao G.¹ and Srikanth V.² 1. Department of Chemistry, Andhra University, Visakhapatnam, 530003, INDIA 2. Vignan's Institute of Engineering for Women, Kapujaggaraju peta, Visakhapatnam 530049, INDIA *shyamalapulipaka06@gmail.com

Abstract

Chemical speciation of Cu(II) complexes of 2,2-Bipyridyl in the of the presence of different- surfactant media (TBAB and SDS) has been studied pH metrically. The models containing different kinds of species were refined using the computer program, MINIQUAD75 and formation constants were determined. The predominant species detected were Cu(bipyH) and $Cu(bipy)_2$ in both surfactant media. It was found that the formation constant is more in SDS compared to TBAB and aqueous media because the proton association is more in the anionic micellar medium.

Binding energies and HOMO-LUMO energy gaps were calculated from semi-empirical studies based on PM6 method. It was found that $Cu(bipy)_2$ is more stable than Cu(bipy) and $Cu(bipyH^+)$.

Keywords: Complex equilibria, Chemical speciation, 2,2-Bipyridyl, copper, TBAB, SDS, Binding energy, HOMO, LUMO.

Introduction

Green analytical chemistry requires the development of environmentally friendly methods characterized by low if not zero use of pollutants. The unique features of surfactant aggregate (micelles) have been recognized as being very helpful to overcome a lot of problems associated with the use of organic solvents in molecular absorption/ luminescence spectroscopy⁵. An important property of micelles is that they solubilize different kinds of compounds which are polar and non-polar. The purpose of the present work was to study the complexation equilibria in the presence of surfactants which act as solubilizing agents. The incorporation of a solute into a micellar system can lead to important changes in its molecular properties^{3,6,8}.

Micelles can affect both the acid-base and metal-ligand equilibria of the reagents due to combination of electrostatic and microenvironmental factors. Knowledge on the distribution of various protonated species of a ligand and its metal-ligand complexes against pH is required for further studies in a solution. Hence, we have taken up a study on the protonation equilibria of in aqueous micellar media of anionic and cationic surfactants^{4,16-19}. 2,2'-Bipyridyl (bipy) complexes are used in studies of electron transfer, catalysis and supramolecular materials chemistry¹. It is widely used as a metal chelating ligand due to its redox stability and ease of functionalization. 2,2'-bipyridyl, a natural bidentate chelating ligand, first prepared by Fritz Blaw is the most commonly used and most easily identified ligand in coordination chemistry⁵.

Material and Methods

The method used for the study of protonation equilibria of bipy in aqueous-surfactant (TBAB and SDS) media was according to Calvin-Wilson. Required volumes of reagents to get a total volume of 50 cm³ were added as follows; 0.02 -0.05 mol. dm⁻³ concentration of hydrochloric acid, 0.16 mol. dm⁻³ oncentration of NaCl, 10% (w/v) solution of sodiumdodecylsulphate (SDS) and tertabutylammoniumbromide (TBAB). Bipy and water in the presence and absence of metal were titrated with ~0.4 mol dm⁻³ sodium hydroxide. The concentration of surfactant was varied between 0.5 to 2.5 % w/v and bipy concentration was changed between 0.004 to 0.01 mol dm⁻³ in various experiments. After the addition of each portion (0.1 ml) of sodium hydroxide, the pH meter reading was recorded at regular intervals of time.

The SCPHD computer program was used to analyze the data obtained from the experiments¹⁵. The Gran method^{2,10,15} was used to calculate pH correction factor. The formation constants obtained from SCPHD program were given as input to the MINIQUAD75 program for refinement taken as initial estimates for refinement by the MINIQUAD75 program¹⁴. The refined models obtained using the MINIQUAD75 program in aqueous and aqueous-surfactant (TBAB and SDS) media (Tables 1 and 2) contained protonation constant K₁ corresponding to the formation of bipyH⁺. [bipyH₂]²⁺ form does not exist in the pH range of our study.

A very low standard deviation (SD) in log K₁ indicates the precision of the parameter. The small values of U_{Corr} (the sum of the squares of deviations in concentrations of ligand and hydrogen ion at all experimental points), the value of skewness from -1.53 to 2.82 in TBAB and -2.04 to 2.78 in SDS for 2,2-bipyridyl show that the residuals of many systems form part of a normal distribution, hence least squares method can be applied to the present data. Bipy exists in three forms in aqueous solutions. Acid solutions (pH < 1) contain the protonated [bipyH₂]²⁺ ion. Between pH 2 and 11, bipy occurs as the bipyH⁺ molecule.

Table 1
Refined chemical model obtained from MINIQUAD75 for acid-base equilibria of bipy in TBAB medium.
T = 30.0 \pm 0.1°C and ionic strength, I = 0.16 mol.dm ⁻³

% of			UCorr X	Skewness	Kurtosis	2	R- Factor
TBAB	log K	NP	10 ⁸			χ-	
			pH Rang	e – 2.2 –9.5			
0.0	4.2831	54	1.30	-1.11	4.03	8.50	0.0070
0.5	4.2790	59	3.09	-1.53	3.74	2.55	0.0429
1.0	4.2550	47	1.27	-0.02	1.82	3.65	0.0199
1.5	4.2411	53	6.43	0.42	3.20	6.06	0.0094
2.0	4.2394	39	5.61	2.82	17.10	18.48	0.0115
2.5	4.2236	41	1.30	-1.11	4.03	8.50	0.0070

Table 2Refined chemical model obtained from MINIQUAD75 for acid-base equilibria of bipy in SDS medium. $T = 30.0 + 0.1^{\circ}C$ and jonic strength, I = 0.16 mol.dm⁻³

% of SDS	log K	NP	UCorr X 10 ⁸	Skewness	Kurtosis	χ ²	R- Factor	
	pH Range – 1.8 –8.85							
0.0	4.2831	43	3.94	-2.04	5.59	5.79	0.0154	
0.5	4.3444	56	1.35	-1.10	4.23	9.01	0.0074	
1.0	4.3624	51	3.20	-1.51	3.93	2.70	0.0451	
1.5	4.4015	63	1.32	-0.02	1.91	3.86	0.0209	
2.0	4.4326	42	6.67	0.41	3.35	6.42	0.0099	
2.5	4.4981	48	5.82	2.78	17.94	19.58	0.0121	

Results and Discussion

Effect of surfactant: The micellar effect on acid-basic equilibria of bipy can be explained on the basis of electrostatic and micro-environmental factors of the respective surfactants. In the case of first protonation of the most neutral form of bipy, (bipy+ H^+ bipy H^+), the K₁ in SDS medium is higher compared to that in TBAB and water. It indicates that anionic surfactants strongly enhance the proton association to bipy whereas the cationic surfactant retards the association. The negative charge of SDS micellar surface is favourable for the formation of the cationic bipyH⁺ form of bipy and association equilibrium is shifted to the right.

$$U^{2+} + \rightleftharpoons [Cu-bipy]^{2+} + H^{+}$$

$$\overset{`u-bipy]^{2+}}{\longrightarrow} + \overset{+}{\xrightarrow{bipyH^{+}}} \underbrace{[Cu(bipy)_{2}]^{2+}}_{[Cu(bipy)_{2}]^{2+}} + \underbrace{[Cu(bipy)_{2}]^{2+}}_{2H} + H^{+}$$

Metal-Ligand equilibria: In these studies, the ligand metal ratio is greater than unity and hence mono nuclear complexes like Cu(bipy), Cu(bipy)₂ binary forms can be expected to be present. The study was further carried out by changing metal-ligand ratio, the results were analyzed using MINIQUAD75 program.

The best fit model based on statistical parameters is given in tables 3 and 4. The statistical parameters taken into

consideration are skewness, kurtosis, crystallographic R values and slandered deviation. The residuals are closer to zero mean with little dispersion indicating that the model is said to be adequate. For an ideal normal distribution, the values of skewness and kurtosis should be 0 and 3 respectively. The values of skewness lie between -1.94 to 0.25 in TBAB and -1.94 to 2.64 in SDS [Tables 3 and 4] suggesting that the residual forms a part of normal distribution, hence least square method can be applied to the present data.

Species distribution diagrams

Proton-ligand systems: The species distribution diagram obtained using Origin 8.5 software for acid- base equilibria of bipy in TBAB micellar medium indicates that only the bipyH⁺ form of bipy exists around at pH 3.5. The formation of bipyH⁺ species (Figs. 1 and 2) decreases from pH 3.5.

It may be due to the deprotonation of the ligand at the pyridine nitrogen atom. The extent of its formation is 50% at pH 5. Above pH of 6, the extent of formation of bipy species reaches 93% in the pH region (~6.0).

Similar pattern was observed in the cased of SDS. In SDS micellar media, bipyH⁺ form of bipy nearly 94% of the ligand is observed at a pH of 2.0. It totally deprotonates above 5.0 pH and the entire ligand is in the bipyH⁺ form between 2.0 and 5.5 pH.

Table	3
75 fam	~

Refined chemical model obtained from MINIQUAD75 for copper ion-bipy systems in aqueous-TBAB surfactant medium Temp. 30.0+-0.1 ionic strength=0.16 mol.dm⁻³

ĺ		log	B _{MLH}	NP	UCorr X	Skewness	Kurtosis	γ ²	R-
	%of				108			~	Factor
	TBAB	110	120		10				
	Cu(II) pH Range –2.0 –8.5								
	0.0	8.82	15.62	95	3.36	-1.94	4.38	3.48	0.0121
	0.5	8.77	15.55	104	5.46	0.54	5.21	3.18	0.0121
	1.0	8.72	15.48	108	4.79	0.56	4.64	2.42	0.0142
	1.5	8.68	15.41	96	2.82	-0.86	3.86	4.54	0.0184
	2.0	8.63	15.34	102	5.81	-0.31	2.18	2.69	0.0318
ĺ	2.5	8.58	15.27	99	9.06	0.25	3.23	3.89	0.016

Table 4

Refined chemical model obtained from MINIQUAD75 for copper ion-Bipy systems in aqueous-SDS surfactant medium Temp. 30.0±0.1 ionic strength=0.16 mol.dm⁻³

% of SDS	log f	B _{MLH}	NP	UCorr X	Skewness	Kurtosis	χ ²	R- Factor
505	110	120		10 ^o				Factor
	Cu(II) pH Range –2.0 –8.5							
0.0	8.82	15.62	95	3.36	-1.94	4.38	3.48	0.0121
0.5	8.89	15.86	78	1.15	-1.04	3.31	5.41	0.0058
1.0	8.91	16.11	67	2.73	-1.43	3.07	1.62	0.0354
1.5	8.93	16.36	79	1.13	-0.02	1.50	2.32	0.0164
2.0	8.97	16.62	85	5.69	0.39	2.63	3.86	0.0078
2.5	8.98	16.87	86	4.96	2.64	14.05	11.75	0.0095



Fig. 1: Species distribution of bipy in TBAB



Fig. 2: Species distribution of bipy

Metal-ligand complexes: Using the values of % species and pH, the species distribution diagrams were drawn in presence of TBAB using Origin 8.5 (Fig. 3). It was found that Cubipy and Cu(bipy)₂ exist in the pH range 2.0 -10.0. The species Cu(bipy) starts at pH 2 and increases in the range of pH 2.0-4.0. It remains constant up to pH 7.0 and thereafter decreases. Cu((bipy)₂ species is formed at a pH 8.0 and increases up to pH 9.0 and remains constant. In case of SDS, the species distribution diagram shows that Cu(II)bipy increased up to pH 4.0, then decreases up to pH 7.0 unlike in the presence of TBAB. By increasing the pH, the formation of Cubipy species in SDS was found to be similar in TBAB.

Computational analysis: To understand the stability of the different species $(Cu(bipy)_2, Cu(bipy) \text{ and } Cu(bipyH^+),$

calculations on HOMO – LUMO energy gap using the semiempirical PM6 (solvent = methanol) method (Figs. 6 a, b and c) were made. Two files are generated during these calculations, one is checkpoint file and other one is log file. The log files are used to determine the binding energies and check point files are used to identify the HOMO and LUMO energies.

Binding energies (BE) were calculated for the complexes Cu(bipy)₂, Cu(bipy) and Cu(bipyH⁺), BE values for the complexes were determined by adding the energies of the monomers and the sum was subtracted from the energy of the complex. BEs of the Cu(bipy), Cu(bipyH⁺) and Cu(bipy)₂ complexes have been found to be -107.5 kcal/mol, -93.8 kcal/mol and -149.2 kcal/mol, respectively (Table 5). The BE values indicate that the Cu(bipy)₂ is more stable and Cu(bipyH⁺) is less stable among the complexes.



Fig. 3: Species distribution of Cu-bipy in TBAB



Fig. 4: Species distribution of Cu-bipy in TBAB



Fig. 5: Semi-empirical/ PM6 method

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecule are well known as the frontier molecular orbitals and according to Fukui et al¹² HOMO and LUMO energy gap (HLEG) is responsible for chemical reactivity (table 5). The HLEG analyses for the complexes Cu(bipy), Cu(bipyH⁺) and Cu(bipy)₂. Fig. 5 shows semi-empirical/ PM6 method (solvent = methanol) level study.

This can be calculated by the subtraction of LUMO and HOMO energy values which were obtained from the checkpoint file of the calculations. The positive lobes are represented by the green colour scheme and the negative lobes are indicated by the red color scheme (Fig. 5). The HLEGs of the Cu(bipyH⁺) (Fig. 6a), Cu-bipy(Fig 6b) and

https://doi.org/10.25303/2706rjce080087

Cu(bipy)₂(Fig 6c) values are 194.9, 169.1 and 187.4 kcal/mol respectively (Table 5).

In the case of Cu-bipy and Cu-(bipy)₂ molecules, both HOMO and LUMO lobes were found to be distributed through benzene rings of bipy molecules and the transition is more likely to show π to π^* transition. While in the case of Cu(bipyH⁺), LUMO lobes were found to be distributed among the benzene ring of bipy moiety and HOMO lobes distributed among Cu atoms attach to one benzene ring of bipyH⁺ which shows likely n to π^* transitions. Because of these transitions, Cu(bipyH⁺) shows a small band gap among others and high reactivity. The stability order of species from the table was found to be Cu(bipy)₂>Cu(bipy)>Cu(bipyH⁺) (Table 5).

Computational calculations using PM6 Method							
Complex	Binding	Band Gap					
	Energy	Kcal/mol					
	Kcal/mol						
H-bipy	-106.1	202.0					
H ₂ -bipy	-206.1	219.4					
Cu-bipy	-107.5	194.9					
Cu-Hbipy	-41.7	169.1					
Cu-(bipy) ₂	-149.2	187.4					

Table 5						
Computational calculations using PM6 Method						
~						

ML= Cu(II)bipy, ML_2 = Cu (II)(bipy)₂, FL= Free ligand, FM = Free metal LH= Protonated ligand



Fig. 6a: Cu(bipy) molecule



Fig. 6b: Cu(bipyH⁺) molecule



Fig. 6(c): Cu(bipy)₂ moicule

Conclusion

- The micellar effect of TBAB and SDS on the complexation equilibrium of Cu-bipy complexes was studied. It was found that the formation constant is more in SDS compared to TBAB and aqueous medium because the proton association is more in the anionic micelles.
- Binding energies and HOMO-LUMO energy gaps obtained from semi empirical calculations based on PM6 method were used to study the relative stabilities of Cubipy complexes and it was found that Cu(bipy)₂ is most stable species among Cu(bipyH⁺), Cu(bipy) and Cu(bipy)₂.

References

1. Bhargavi K., Shyamala P. and Nageswara Rao G., Determination of Protonation Constants of Viral Inhibitor, Aurintricarboxylic Acid in SDS and CTAB Micellar Media: Potentiometric Study, *Asian J. Chem.*, **33**, 2301 (**2021**)

2. Born M., Volumen und Hydratationsw~rme der Ionen, Z. Phys., 1, 45 (1920)

3. Buurma N., Kinetic medium effects on organic reactions in aqueous colloidal solutions, J. Adv. Phys. Org. Chem., 43, 1–37 (2009)

4. Chaimovich H. et al, Ion exchange in micellar solutions. 2. Binding of hydroxide ion to positive micelles, *J. Phys. Chem.*, **83**, 1951 (**1979**)

5. Cho H. et al, Aurintricarboxylic Acid Translocates across the Plasma Membrane, Inhibits Protein Tyrosine Phosphatase and Prevents Apoptosis in PC12 Cells, *J. Mol. Cell.*, **18**, 46 (**2004**)

6. De Lemos Cristovao and Robert Arnaud Roland Alain, Crosslinking and physical properties of poly (ethylene-co-vinyl

acetate) produced by autoclave and tubular reactors, *Res. J. Chem. Environ.*, **25**(4), 1–11 (**2021**)

7. Devi K.V.S., Ramaraju B. and Rao G., Effect of Dielectric Constant on Protonation Equilibria of L-Dopa and 1, 10 – Phenanthroline in Dioxan-Water Mixtures, *Acta Chim. Slovenica*, **57**, 398 (**2010**)

8. Dwars T., Paetzold E. and Oehme G., Angew. Reaction in micellar systems Chem., Int. Ed., 44, 7174–7199 (2005)

9. Edwin C., Constable E.C. and Housecroft C.E., The early years of 2,2'-Bipyridine A Ligand in Its Own Lifetime, 1-38 (**2019**)

10. Ezio Pelizzetti and Edmondo Pramauro, Analytical applications of organized molecular assemblies, *Analytica Chimica Acta*, **169**, 1–29 (**1985**)

11. Feakins D. et al, J. Chem. Soc. Faraday Trans., 79, 2289 (1983)

12. Fukui K., Yomezawa T. and Shingu H., J. Chem. Phys., 20, 722 (1952)

13. Gans P., Sabatini A. and Vacca A., *Inorg. Chim. Acta*, **18**, 237 (**1976**)

14. Gran G., Anal. Equivalence volumes in potentiometric titrations, *Analytica Chimica Acta*, **206**, 111 (**1988**)

15. Gran G., Determination of the equivalence point in potentiometric titrations, Part II, *Analyst*, **77**, 661 (**1952**)

16. Manaiah M., Gouthamsri S. and Sailaja B.B.V., Stability of binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid in TX100-water mixtures, *Bull. Chem. Soc. Ethiop*, **28**, 383 (**2014**)

17. Pelizzetti E. and Pramauro E., Analytical applications of organized molecular assemblies, *Analytica Chimica Acta*, **169**, 1-29 (**1985**)

18. Ramanaih and Sailaja B.B.V., Protonation equilibria of Lphenylalanine and maleic acid in cationic micellar media, *Chem. Speciat. Bioavail.*, **26**, 119 (**2014**)

19. Ramanaiah M., Seetharam P. and Sailaja B.B.V., Chemical speciation of ternary complexes of Pb-II, Cd-II and Hg-II with L-

phenylalanine and maleic acid in TX100-water mixtures, *J. Indian Chem. Soc.*, **91**, 1011 (**2014**).

(Received 31st March 2023, accepted 01st May 2023)