Journal of Current Chemical & Pharmaceutical Sciences

J. Curr. Chem. Pharm. Sc.: 5(1), 2015, 39-46
ISSN 2277-2871

ESTIMATION OF SOME PHYSICO-CHEMICAL PARAMETERS OF NOVEL HETEROCYCLICS IN BINARY SOLVENT SYSTEM

NEHA MATHUR*, SONLATA BARGOTYA and IMRAN AHMED[a]

Department of Chemistry, Pt. N. K. S. Govt. P. G. College, Dausa, University of Rajasthan, DAUSA (Raj.) INDIA
[a]Department of Chemistry, University of South Korea, SOUTH KOREA

(*Received : 19.02.2015; Revised : 28.02.2015; Accepted : 02.03.2015*)

ABSTRACT

Few novel compounds of transition metals have been synthesized by complexing copper surfactants with bio-potent nitrogen and sulphur donor ligands. All the complexes were synthesized in refluxed reaction with (1:2, M: L ratio).The yield percentage of formed complex is ranging from 80-95%. The complexes are coloured solids and of the type $(Cu_2(C_{15}H_{31}COO)_4L_2$ and $Cu_2(C_7H_{15}COO)_4L_2$ where L is substituted 2-amino 6 bromo benzothiazole). They were characterized through elemental analyses and spectroscopy (IR, NMR, Mass and ESR). Their purity was confirmed by thin layer chromatography techniques. In special reference to the study of their physico-chemical parameters, "density" was deeply investigated in benzene-propanol mixtures. The measurements were done by springel pyknometer to understand the solute-solvent interactions of different copper soap complexes. Such investigations help us to understand the nature, critical micelle concentration (cmc) and micelle concentrations of complexes. The cmc was calculated and found to decrease with increase in molecular size and average molecular weight of the soap complex. The studies of aforesaid interactions suggest that solute-solvent interaction increases with the increase in carbon composition of fatty acid and lowering of molecular weight whereas solute-solute interaction decreases.

Key words: Copper surfactants, Density, Criticle micelle concentration, Benzothiazole.

INTRODUCTION

Metal surfactants like substances are used today in every field of usage. This may be either due to their high surface active properties or formation of micelles in solutions. These surface active agents not only accumulate at the surfaces but also by their presence change the properties of the surfaces. The colloidal chemical behaviour makes their properties more pronounced. Hence, they are widely used in multiple sectors like medicinal, agricultural, industrial, pharmaceutical[1,2] etc. Surfactants have valuable characteristics like emulsification, wetting, water proofing, repellence, protection of crops etc.

Among these metal surfactants copper (II) soaps complexes show remarkable interest in polar and non-polar solvents and find significant uses in aforesaid fields. Copper soaps have a tendency of complexation with 'nitrogen' and 'sulphur' containing ligands. Specifying such ligands azoles derivatives are worth mentioning. Literature survey reveals that copper metal is already toxic in nature and further on coordinating such moiety with bioactive ligands plays a significant role in biological activities such as antifungal[3,4], antimicrobial[5], anti-tumour[6], anti-inflammatory[7] anti-HIV and analgesics[8-12].

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: nehavmathur@yahoo.co.in, b.sonlata@gmail.com

Therefore, it is worth to study the significant physical properties[13-15] of such compounds due to which they show marked noticeable chemical nature. For the same, the chemical colloidal behaviour of soaps with nitrogen donor ligands in benzene-propanol mixtures of varying composition has been investigated by density measurements. Density evaluations are a good tool for finding cmc of complexes[16]. The cmc values depend upon the composition solvent mixtures. The general trends observed in density parameters with concentrations are different for different compositions.

In this paper, using substituted benzothiazoles as a ligand, complexation of synthesized soaps have been done to obtain their copper complexes. The following matter will explain the details of our research work.

EXPERIMENTAL

All the chemicals used were of LR/AR grade. Substituted aniline used purchased from Merck and were used as received. Solvents were purified according to standard procedures. Micro analytical data of the compounds was recorded at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow (RSIC, CDRI). Thin layer chromatography was used to access the purity of the synthesized compounds. The IR spectra of the complexes were obtained as KBR discs in the range 400-4000 cm^{-1} on Perkin Elmer spectrophotometer and ^1H NMR spectra were recorded at at Therachem laboratories, Jaipur using DMSO d6 as reference. ESR spectra of the complexes were recorded in liquid nitrogen.

The synthesis of complexes was conducted in three steps, which are as follows:

Synthesis of metal surfactants

Copper palmitate/copper caprylate was prepared by mixing 1.0 g of palmitic acid/caprylic acid into 25 mL ethyl alcohol, shake the mixture in hot water bath and then add one drop of phenolphthalein. A saturated solution of KOH in another beaker was prepared then it was added into palmitic acid/caprylic acid solution drop by drop until the light pink colour appears. Now in another beaker prepare a saturated solution of $CuSO_4$ (about 2-3 g in 5 mL H_2O) and mix it into above solution with stirring till the blue colour soap is formed. It was filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene.

Synthesis of ligands

2-amino 6-bromo benzothiazole was synthesized using thiocyanogenation method. In this method (0.1 mol) p-bromo aniline was treated with a mixture of 7.6 g ammonium thiocyanate, (0.1 mole) cupric chloride and 80 mL glacial acetic acid in a 250 mL three necked round bottom flask, with stirrer, dropping funnel and reflux condenser at room temperature for 1.5 hr. The thiocyanogenation of aryl amine takes place in the presence of thiocynogen gas, which is generated insitu by the reaction of cupric chloride and ammonium thiocynate.

After cooling the reaction mixture, add 100 mL concentrated HCl, and heat again for 0.5 hr, then cool it and then saturated solution of sodium carbonate (Na_2CO_3) is added to neutralize it, till the solid was formed.

Synthesis of complexes

The complexes of copper palmitate/copper caprylate and benzothiazole were prepared by adding (0.001 mole) copper palmitate/copper caprylate with 0.002 mole benzothiazoles in 25-30 mL ethyl alcohol and the mixtures were refluxed for about 2 hrs with constant stirring. After cooling the precipitate were filtered, dried and recrystallized with hot benzene.

The purity of the complexes was confirmed by thin layer chromatographic technique and the formation of complexes was confirmed by IR, NMR ESR and mass spectral studies.

RESULTS AND DISCUSSION

In the present study the synthesised complexes are abbreviated as follows.

- Complex of copper palmitate with 2-amino-6-bromobenzothiazole CP (BTA)
- Complex of copper caprylate with 2-amino-6-bromobenzothiazole CC (BTA)

Table 1: Analytical and physical data of the complexes

Complex	Molecular formula	Mol. wt.	Colour	% Composition Found (Cal.)						
				C	H	N	O	S	Br	Cu
CP (BTA)	$C_{78}H_{134}O_8N_4S_2Br_2Cu_2$	1604.88	Dull black	58.30 (58.33)	8.30 (8.36)	3.42 (3.49)	7.95 (7.97)	3.92 (3.98)	9.94 (9.96)	7.88 (7.91)
CC (BTA)	$C_{46}H_{70}O_8N_4S_2Br_2Cu_2$	1156.88	Dull black	47.66 (47.71)	6.03 (6.06)	4.81 (4.85)	11.05 (11.06)	5.52 (5.53)	13.79 (13.82)	10.90 (10.97)

NMR Spectra

Aliphatic $–CH_3$ and $–CH_2$ proton attached to $–CH_2$-R group show signal around δ 0.84 and δ 1.25, respectively. A broadened peak is observed at δ 3.12-3.99 corresponding to $–NH_2$ proton. This peak indicates the coordination through $–NH_2$ group of benzothiazole segment to the metal. Broadening of the observed peak is suggestive to be a slow exchange because the electrical quadripole moment of nitrogen nucleus induces a moderately efficient spin relaxation.

Table 2: NMR spectral data for copper (II) complexes

Signal	CP (BTA)	CC (BTA)
$-CH_3-CH_2$-R	0.84	0.96
$-CH_2-CH_2$-R	1.22	1.53
$-NH_2$	3.12-3.95	3.15-3.99
Tautomeric $–NH_2$	7.83	7.82

ESR spectral analysis

The g-tensor value of the copper complex can be used to derive the ground state. In octahedral complexes, the unpaired electron may lie in the $d_{x^2-y^2}$ or d_{z^2} orbital. The spin Hamiltonian parameters for the copper complexes are calculated from the spectra. g-tensor values (for both complexes) are **g|| > g| > g0** suggest that complexes has distorted octahedral geometry with unpaired electron lying in $d_{x^2-y^2}$ orbital. The ESR parameters of the complexes coincide well with the related systems, which suggest that the complexes have octahedral geometry and the systems are axially symmetric. In the axial spectra, the g-values are related with exchange interaction coupling constant (G) by the expression,

$$G = g||-2/\ g1-2$$

Mass spectra

The following mass spectra were obtained for synthesised complexes. The disintegration m/z peaks of complexes are in agreement proposed structure of compounds.

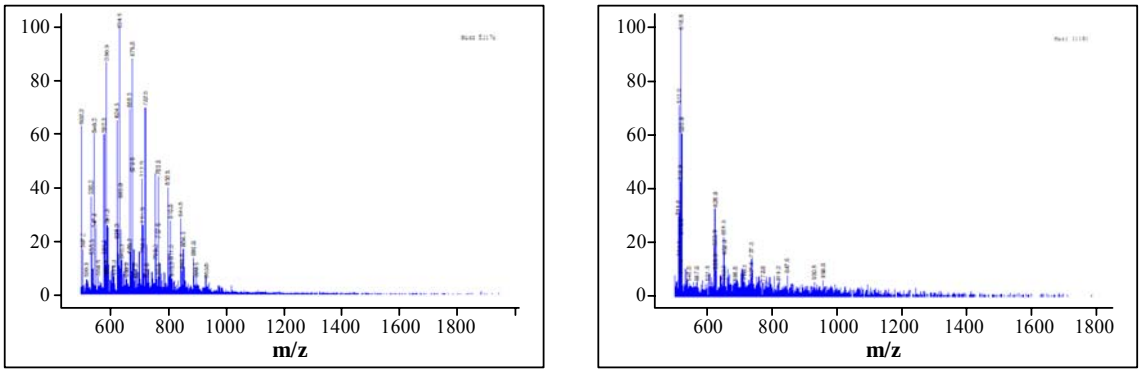

Fig. 1: (a) Mass spectra of CP (BTA) complex (b) Mass spectra of CC (BTA) complex

IR Spectra

The IR spectra provide valuable information regarding coordination site of the ligand attached to the metal ion. From IR spectral data, it is evident that ligand acts as a monodentate, bonded to copper ion through primary nitrogen atom of NH_2. The strong band at 1602 cm^{-1} was observed due to the N-H bending vibration of NH_2 group in free ligands but in the complexes it is shifted to lower frequency at 1600 and 1580 cm^{-1} indicating that the primary nitrogen is the coordinating site in the complexes. This is further supported by the formation of new band at 560 cm^{-1} and 500 cm^{-1}, which are due to υ M-N band in both the complexes. C-O stretching bond is observed at 490 and 497 cm^{-1}. Hence, the IR data suggest that the copper is bound to its ligand through the nitrogen of NH_2 group.

Table 3: IR Spectral data for copper (II) complexes (in cm^{-1})

Absorbption bands	CP (BTA)	CC (BTA)
CH_3 & CH_2, C-H Antisym. stretching	2910	2919.0
CH_3 and CH_2 C-H Sym. stretching	2850	2830
N-H bending	1600	1580
COO^-, C-O Antisym. stretching	1509	1558
COO^-, C-O sym. stretching	1460	1490
CH_2, C-H Bending (δ) (twisting and wagging)	1300	1320
CH_3, C-H rocking	1110	1120
CH_2, C-H rocking	740	749
Cu-N stretching	560	500
Cu-O stretching	490	497

Cont…

Absorbption bands	CP (BTA)	CC (BTA)
NH_2, N-H stretching	3450	3448
N-C=S stretching	1301	1306
C=S stretching	1180	1182
C-H, Deformation ("oop")	832	840

Estimation of density

Ostwald's modification of the densimeter[17-19] was used for measuring the density of complex solutions. The density of solution "d" was calculated by relationship-

$$d = w/w_o$$

where, w and w_o are the weights of the same volume of solution and water resp. Accurate density of water was taken from literature[20]. Volume of pyknometer was taken about 15 mL that allowed an accuracy of about one unit in the fourth place of decimal. All the measurements were made at constant temperature (303 K) in the thermostate.

It was seen from the performed experiments that density of a series of synthesised solutions in non aqueous solvent system at various concentrations initially increase with the increase in complex concentration and then it decrease after a particular concentration corresponding to critical miceller concentration. After this concentration the density again increases with increase in concentration.

The following tables' shows pattern obtained during the experiments. Table 4 gives physical data for (20-80) propanol-benzene mixture while Table 5 shows data for (40-60) propanol-benzene mixture.

Table 4: Physical data for synthesized complexes in 20% propanol-benzene system

Concentration (g. mol/L)	CP (BTA)	CC (BTA)
0.0002	0.8521	0.8522
0.0004	0.8530	0.8530
0.0006	0.8545	0.8543
0.0008	0.8561	0.8547
0.0010	0.8573	0.8557
0.0012	0.8542	0.8568
0.0014	0.8528	0.8552
0.0016	0.8537	0.8531
0.0018	0.8549	0.8548
0.0020	0.8553	0.8559

The value of density of CP (BTA) and CC (BTA) in 20% propanol-benzene mixture is higher than that of 40% methanol-benzene mixture. This difference clearly demonstrates that agglomeration of complex molecules initiates earlier in the predominance of non-polar solvent (benzene) as compared to polar solvent (propanol). According to the average molecular weight of the complex the CMC value follows the order.

Table 5: Physical data for synthesised complexes in 40% propanol-benzene system

Concentration (g.mol/L)	CP (BTA)	CC (BTA)
0.0002	0.8410	0.8411
0.0004	0.8415	0.8416
0.0006	0.8419	0.8423
0.0008	0.8428	0.8425
0.0010	0.8434	0.8431
0.0012	0.8436	0.8437
0.0013	0.8439	0.8439
0.0014	0.8442	0.8427
0.0016	0.8413	0.8425
0.0017	0.8415	0.8421
0.0018	0.8418	0.8433
0.0020	0.8425	0.8441

The plot of density 'd' against complex concentration of 'C' (g.mol.l^{-1}) was characterized by an intersection of convex curve with respect to X-axis and straight line Fig. 2, 3, 4 and 5 at a definite complex concentration which corresponds to the CMC of the complex.

The plots above clearly shows that after CMC the density values sharply increase with a definite straight line. The above order shows that the CMC values are so because the average molecular weight of CC (BTA) is lower as compared to CP (BTA), so the interaction is lower and the formation of micelle is slower due to this the CMC obtain later. The observations are in accordance with the cmc values, decreases with increase in size and molecular weight of moiety.

Also in our complexes, we found that the solute solute interactions are greater before cmc whereas solute solvent interactions are greater after cmc. By increasing the polarity of solvent, we found that the critical micelle concentration was also increased.

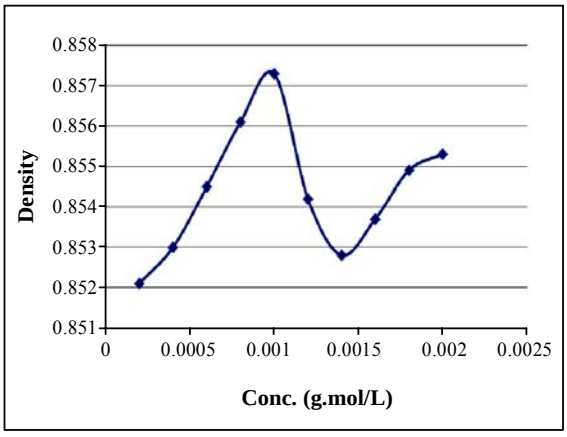

Fig. 2: Density parameter of CP (BTA) in 20% propane-benzene system

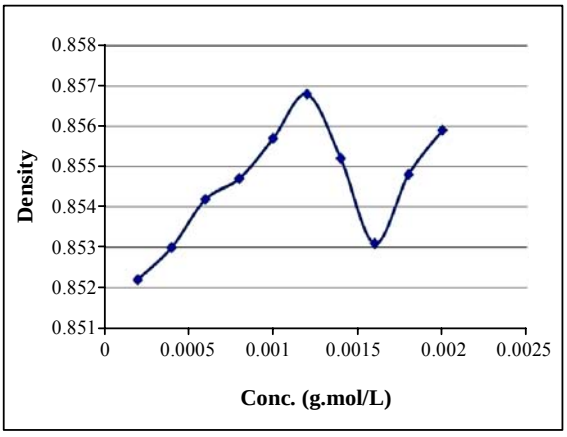

Fig. 3: Density parameter of CC (BTA) in 20% propane-benzene system

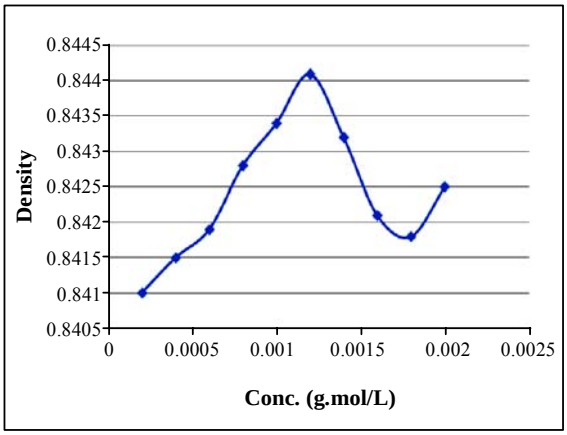

Fig. 4: Density parameter of CP (BTA) in 40% propane-benzene system

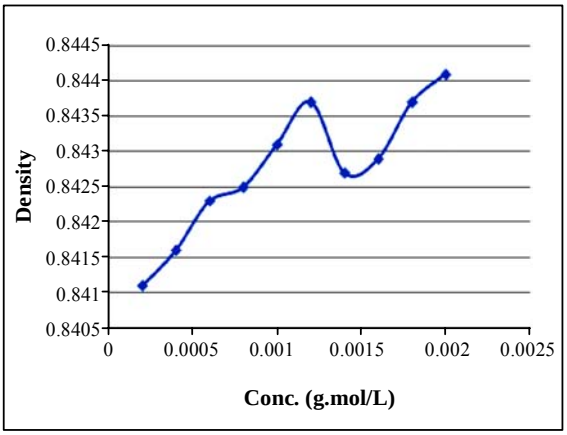

Fig. 5: Density parameter of CC (BTA) in 40% propane-benzene system

Table 6: Values of the CMC (in g. mol/lit) for synthesized complexes in propanol-benzene mixture

Name of complex	Volume percent of propanol in solvent mixture	
	20%	40%
CP (BTA)	0.0014	0.0016
CC (BTA)	0.0016	0.0017

CONCLUSION

This study reports the successful synthesis and characterization, through analytical and physicochemical techniques, of new complexes of Cu (II) with 2-amino 6-bromo benzothiazole as ligand. The density of soap solutions has been investigated with a view to understand the nature, critical micelle concentration and micellar characteristics of the complexes. Synthesised complexes contribute diverse therapeutically potent applications by being less economical, harmless, non toxic and eco-environmental friendly. Also these heterocycles play important and great potentials in the field of the organic chemistry, inorganic chemistry as well as medicinal chemistry.

ACKNOWLEDGEMENT

The authors express their sincere thanks to the Principal and Head of the Department of Chemistry of Govt. P.G. College, Dausa for providing laboratory facilities and CDRI Lucknow, IIT Mumbai, Therachem Laboratories, Jaipur for providing spectral data. One of the author Ms. Sonlata Bargotya is thankful to UGC, New Delhi for sanctioning Junior Research Fellowship for providing aid in this work.

REFERENCES

1. G. N. Mukherjee and P. K. Chakraborty, J. Indian Chem. Soc., **79**, 137 (2002).
2. R. N. Patel, K. Subhod and K. B. Pandeya, Indian J. Chem., **39A**, 1124 (2000).
3. Prakash and D. Adhikari, Int. J. Chem. Tech. Res., **3**, 1891 (2011).
4. N. Mathur and V. K. Mathur, Int. Conf. Biol. Envir. Chem., **24**, 133 (2011).

5. V. S. Premlata and G. Seth, J. Chem. Pharm. Res., **4**, 1327 (2012).
6. C. G. Mortimer, G. Wells and J. P. Crochard, J. Med. Chem., **49**, 179 (2006).
7. R. Paramashivappa, K. P. Phani, P. V. S. Rao and S. Rao, Bioorg. Med. Chem. Lett., **13**, 657 (2003).
8. J. Joseph and G. Boomadevi Janaki, J. Mater. Environ. Sci., **5(3)**, 693 (2014).
9. Begum, N. F. Khanum, Naveen, Gurupadaswamy, Prashanth and S. A. Khanum, Int. J. Sci. Res. Pub., **4(4)**, 1 (2014).
10. S. A. Olagboye and G. F. Hassan, Int. J. Appl. Sci. Biotechnol., **1(4)**, 258 (2013)
11. M. V. Angelusiu, G. L. Almajan, D. C. Ilies, T. Rosu and M. Negoiu, Chem. Bull., **53(67)**, 1, 78 (2008).
12. N. Raman, J. Joseph, A. Senthil, K. Velan and C. Pothiraj, Mycobiology., **34(4)**, 214 (2006).
13. R. Sharma, M. Saxena, S. Acharya, J. Indian Chem. Soc., **8**, 585 (2012).
14. N. Mathur, J. Curr. Chem. Pharm. Sci., **1(1)**, 37 (2011).
15. M. Khedr, H. M. Marwani, Int. J. Electrochem. Sci., 7, 10074 (2012).
16. L. C. Heda, N. Mathur, P. Saxena and I. Ahmed, Asian J. Chem., **21(1)**, 57 (2009).
17. P. S. Nikam, T. R. Mahale and M. Hasan, Acoustica., **84**, 579 (1998).
18. P. R. Naidu and V. R. Kishnan, Trans. Fraday Soc., **61**, 1347 (1965).
19. A. B. Sawant and P. S. Nikam, Bull. Chem. Soc. Jpn., **71**, 2055 (1998).
20. G. S. Kell, J. Chem. Eng. Data, **12**, 66 (1967).