Journal of Current Chemical & Pharmaceutical Sciences

J. Curr. Chem. Pharm. Sc.: 1(1), 2011, 37-51
ISSN 2277-2871

STUDIES OF SOLUTE-SOLVENT INTERACTIONS AND APPLICATIONS OF GREEN AND BLUE COMPLEXES OF COPPER (II) PALMITATE WITH 2-AMINO BENZOTHIAZOLES

NEHA MATHUR*

Govt. P.G. College Dausa, JAIPUR (Raj.) INDIA

(*Received : 06.10.2011, Revised : 18.10.2011, Accepted : 20.10.2011*)

ABSTRACT

In the applied areas of research and many industrial process the complexes of copper metal with some aromatic ligands are very useful, to study the density data of above complexes in mixed solvent systems these complexes are derived from copper (II) palmitate with substituted 2-amino benzothiazoles and analyzed for their micellar characteristics in non-aqueous media with different polarities. The synthesized complexes were characterized by elemental analysis, melting points and their IR, NMR and ESR spectral studies. In the present work, benzene and methanol have been chosen as the co-solvent as mixed solvents have tendency to interact with complex molecules and result affecting the aggregation of complex molecules. Density of complexes have been measured in various concentrations and by using density data, the molar volume and apparent molar volume have been evaluated in order to determine the critical micelle concentration (CMC). The CMC values are found to decrease with increase in average molecular weight of the soap complexes. The apparent molar volume has been examined in terms of Masson equation, and the limiting apparent molar volume has been interpreted in terms of solute-solvent interaction. The detailed study of aforesaid compounds clearly indicates that the solute-solvent interaction decreases with the increase in ring strain and size of the synthesized complexes.

Key words: 2-Amino benzothiazole, Copper (II) palmitate, Density, Molar volume, Apparent molar volume, Critical micelle concentration (CMC).

INTRODUCTION

Many nitrogen and sulphur containing heterocycles were synthesized and investigated for a wide range of pharmacological[1-2] and biological activities[3-4]. They have been used as tranquilizers[5], anti-heliminthics[6], antiinflammatory[7], neuroleptics[8], anti-histamines[9], sedatives[10], antipsychotics[11], anti-viral[11], diuretics[13], fungicides[14-15], anesthetics[16], bacteriocides[17], antimalarials[18], etc. along with their activities. The copper (II) soap in polar and non-polar solvents having remarkable interest and find their uses in various fields of applications like foaming, wetting, emulsification and lubrication etc. due to the surface active properties of soaps[19,20]. Aniline and its derivatives are used as colorants, agrochemicals, pharmaceuticals, etc[21]. It has been found to be widely distributed in an aqueous environment and cause tetratosis in aquatic species[22].

Colloidal behavior of these copper (II) soap complexes play a significant role in their selection in various fields like preservatives, herbicidal, pesticidal activities, detergency paints, lubrication etc[23-24]. In

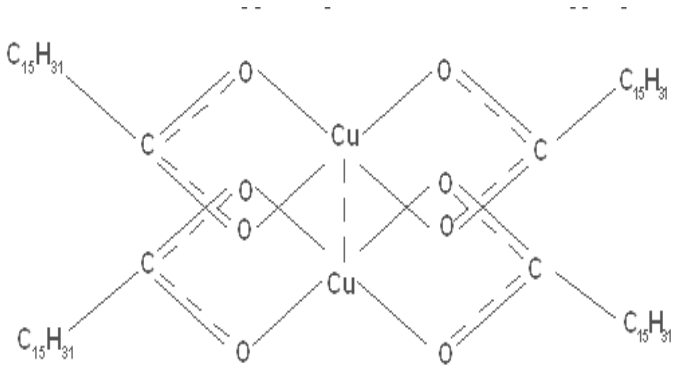
---

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

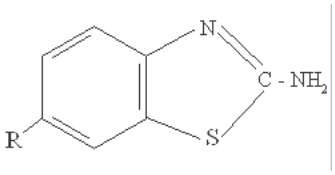
biological systems, these agents are vital components and useful in many industrial process like stabilizers, printing, fabrics, photo sensitizers and Indicator[25-27].

All the above applications led us to study micellar features of various copper (II) surfactants with the complex formation of aromatic ligands.

The purity of the synthesized complexes has been checked by thin layer chromatographic studies. The density of soap solution has been investigated with a view to under stand the nature, critical micelle concentration (CMC) of the complexes.

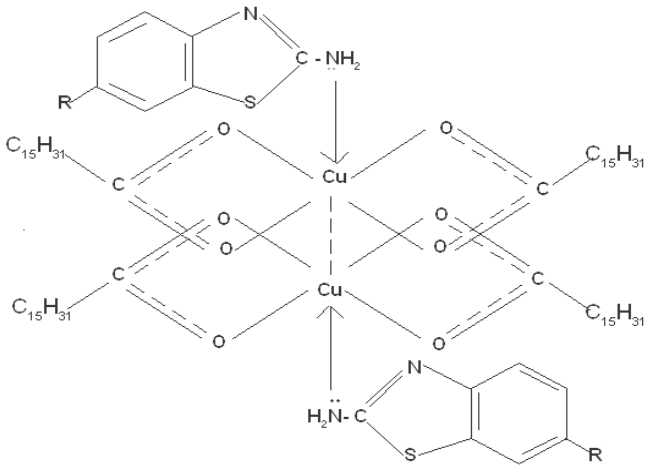


Structure of copper (II) palmitate



Structure of ligands

Where R = CH_3, Cl



Structure of complexes

Where R=CH_3, Cl

Abbreviation:

1. Copper (II) palmitate = CP
2. 2-amino-6-methyl benzothiazole = $(BTA)_T$
3. 2-amino-6-chloro benzothiazole = $(BTA)_C$
4. Complex of 2-amino-6-methyl benzothiazole = CP $(BTA)_T$
5. Complex of 2-amino-6-chloro benzothiazole = CP $(BTA)_C$

RESULTS AND DISCUSSION

The density of a series of CP (BTA) solutions initially increase slightly with the increase in complex concentration and then it decrease after a particular concentration corresponding to critical micellar concentration[28] and after this concentration the density again increases with increase in concentration of CP (BTA) solution. The plot of density 'd' against complex concentration of 'C' ($g.mol.l^{-1}$) is characterized by an intersection of convex curve with respect to X-axis and straight line Fig. 1, 2, 3 and 4, 5, 6 at a definite complex concentration which corresponds to the CMC of the complex. It is clear from the plot that after CMC the density values sharply increase with a definite straight line. The CMC decreases by about one third per methyl group in aqueous solution because the energy required to transfer a methylene group form micelle to bulk is small as intermolecular forces are stronger in polar solvent like methanol and water, whereas in nonpolar solvent like benzene, these intermolecular forces are weaker, the value of CMC order as follows.

$$(BTA)_T > (BTA)_C$$

$$CP\ (BTA)_T > CP\ (BTA)_C$$

The above order shows that the CMC values are of $(BTA)_T$, CP $(BTA)_T$ higher as compared to $(BTA)_C$ and CP $(BTA)_C$, because the average molecular weight of CP $(BTA)_T$ is lower as compared to CP $(BTA)_C$, so the interaction is lower and the formation of micelle is slower due to this the CMC obtain later.

Secondly the presence of methyl group at para position produces + I effect, hence the formation of micelle takes place slowly as compare to CP $(BTA)_C$. The value of density of (BTA) and CP (BTA) in 20% methanol-benzene mixture is higher then that of 40% methanol (i.e 20% methanol-benzene). This difference clearly demonstrates that agglomeration of complex molecules initiates earlier in the predominance of non-polar solvent (benzene) as compared to polar solvent (methanol). According to the average molecular weight of the complex the CMC value follows the order.

$$(BTA)_T > (BTA)_C$$

$$CP\ (BTA)_T > CP\ (BTA)_C$$

Table 1: Physical data for Copper soap and ligands in 20% methanol-benzene system

Conc. ($g.mol.l^{-1}$)	Density			Molar volume			Apparent molar volume		
	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$
0.0004	0.8861	0.9061	0.9060	67.67	68.12	68.13	228758	177927	178162
0.0006	0.8363	0.9063	0.9063	69.66	68.10	68.11	151967	118220	118199
0.0008	0.8864	0.9064	0.9063	69.66	68.09	68.11	113700	88495	88602

Cont…

Conc. (g.mol.l^{-1})	Density			Molar volume			Apparent molar volume		
	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$
0.0010	0.8864	0.9064	0.9061	69.67	68.09	68.13	90843	70762	71049
0.0011	0.8863	0.9063	0.9062	69.68	68.11	68.12	82624	59025	64479
0.0012	0.8861	0.9061	0.9063	69.70	68.12	68.11	75860	59197	59195
0.0013	0.8862	0.9062	0.9064	69.69	68.12	68.10	69901	54551	54372
0.0014	0.8863	0.9063	0.9065	69.68	68.11	68.10	64793	17744	50402
0.0015	0.8864	0.9064	0.9066	69.67	68.10	68.09	60366	47119	46961
0.0016	0.8865	0.9066	0.9067	69.66	68.09	68.08	56492	44035	43950
0.0018	0.8867	0.9067	0.9069	69.65	68.06	68.07	50037	39067	38932
0.0020	0.8869	0.9069	0.9071	69.64	68.04	68.06	44871	35041	34917

Table 2: Physical data for Copper soap and ligands in 40% methanol-benzene system

Conc. (g.mol.l^{-1})	Density			Molar volume			Apparent molar volume		
	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$	CP	$(BTA)_T$	$(BTA)_C$
0.0004	0.8837	0.9037	0.9039	57.38	56.09	56.08	230256	179320	17875
0.0006	0.8839	0.9039	0.9041	57.37	56.08	56.07	152965	119148	118784
0.0008	0.8841	0.9041	0.9042	57.36	56.07	56.06	114320	89062	88912
0.0010	0.8842	0.9041	0.9042	57.36	56.07	56.07	91236	71384	71092
0.0011	0.8842	0.9040	0.9038	57.37	56.08	56.10	82888	64819	83660
0.0012	0.8840	0.9039	0.9040	57.38	56.09	56.08	76103	59489	59382
0.0013	0.8838	0.9038	0.9042	57.40	56.10	56.07	70362	57979	54642
0.0014	0.8840	0.9041	0.9044	57.39	56.08	56.06	65147	50820	50579
0.0015	0.8842	0.9043	0.9046	57.38	56.07	56.05	60628	47284	47057
0.0016	0.8844	0.9045	0.9048	57.37	56.06	56.04	56673	44190	43976
0.0018	0.8848	0.9049	0.9051	57.36	56.03	56.02	50083	39033	38897
0.0020	0.8851	0.9052	0.9054	57.34	56.02	56.01	44861	34958	34835

Table 3: Physical data for complexes of Copper (II) palmitate with substituted 2-amino benzothiazole in 20% methanol-benzene system

Conc. (g.mol.l^{-1})	Density		Molar volume		Apparent molar volume	
	$CP(BTA)_T$	$CP(BTA)_C$	$CP(BTA)_T$	$CP(BTA)_C$	$CP(BTA)_T$	$CP(BTA)_C$
0.0004	0.9761	0.9761	63.37	63.37	486	272
0.0006	0.9763	0.9762	63.38	63.38	316	358
0.0008	0.9764	0.9763	63.40	63.40	486	657
0.0010	0.9764	0.9763	63.42	63.44	691	1041
0.0011	0.9763	0.9762	63.42	63.44	673	994

Cont…

Conc. ($g.mol.l^{-1}$)	Density		Molar volume		Apparent molar volume	
	$CP(BTA)_T$	$CP(BTA)_C$	$CP(BTA)_T$	$CP(BTA)_C$	$CP(BTA)_T$	$CP(BTA)_C$
0.0012	0.9765	0.9760	63.44	63.44	913	955
0.0013	0.9763	0.9762	63.43	63.45	802	844
0.0014	0.9762	0.9764	63.45	63.45	779	894
0.0015	0.9763	0.9765	63.44	63.46	691	870
0.0016	0.9764	0.9767	63.45	63.47	679	849
0.0018	0.9766	0.9768	63.45	63.48	600	813
0.0020	0.9769	0.9771	63.45	63.48	538	836

Table 4: Physical data for complexes of Copper (II) palmitate with substituted 2-amino benzothiazole in 40% methanol-benzene system

Conc. ($g.mol.l^{-1}$)	Density		Molar Volume		Apparent molar volume	
	$CP(BTA)_T$	$CP(BTA)_C$	$(BTA)_T$	$CP(BTA)_C$	$CP(BTA)_T$	$CP(BTA)_C$
0.0004	0.9738	0.9737	52.18	52.19	1001	1043
0.0006	0.9740	0.9738	52.19	52.20	830	1215
0.0008	0.9741	0.9740	52.20	52.21	873	1043
0.0010	0.9740	0.9740	52.22	52.23	1104	1146
0.0011	0.9741	0.9738	52.22	52.25	1048	1370
0.0012	0.9739	0.9739	52.25	52.25	1258	1300
0.0013	0.9738	0.9741	52.26	52.25	1356	1162
0.0014	0.9740	0.9743	52.26	52.25	1221	1043
0.0015	0.9742	0.9744	52.25	52.25	1104	1009
0.0016	0.9743	0.9746	52.26	52.25	1065	915
0.0018	0.9746	0.9749	52.26	52.25	944	815
0.0020	0.9749	0.9751	52.26	52.26	847	786

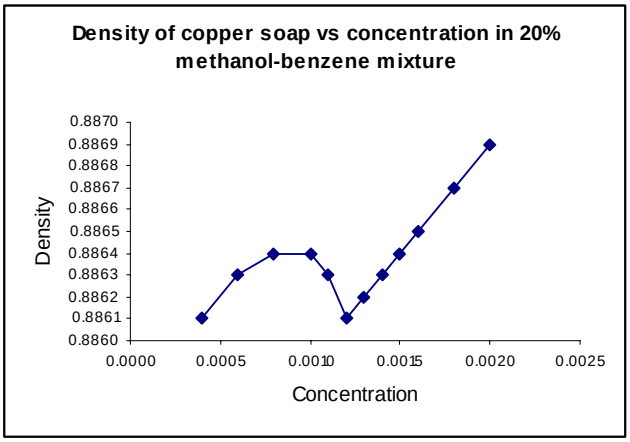


Fig. 1

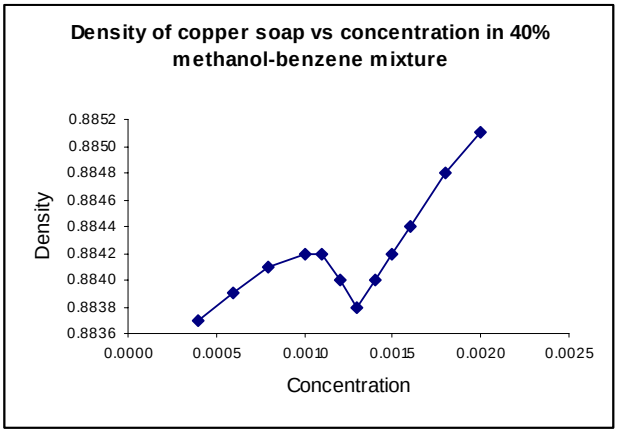


Fig. 2

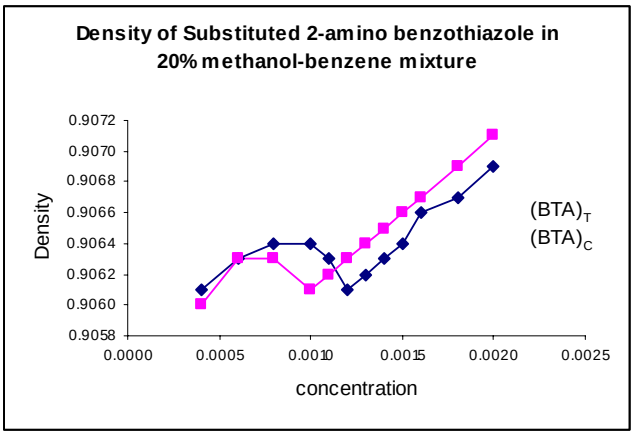


Fig. 3

$(BTA)_T$ = Benzothiazole of toludine

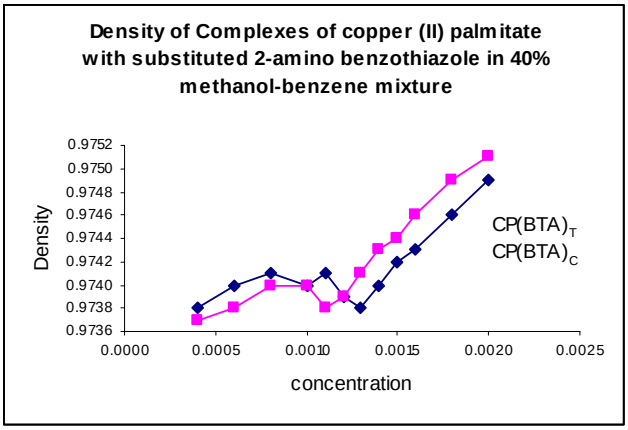


Fig. 4

$(BTA)_C$ = Benzothiazole of chloro aniline

The molar volume of the soap complex solution V has been calculated by the relationship.

$$V = \frac{X_1M_1 + X_2M_2 + X_3M_3}{d} \qquad \ldots(1)$$

Where X_1 is the mole fraction of the complex of molecular weight M_1, whereas X_2 and X_3 are the mole fraction of benzene and methanol of molecular weight M_2 and M_3 and 'd' stands for density of the solution.

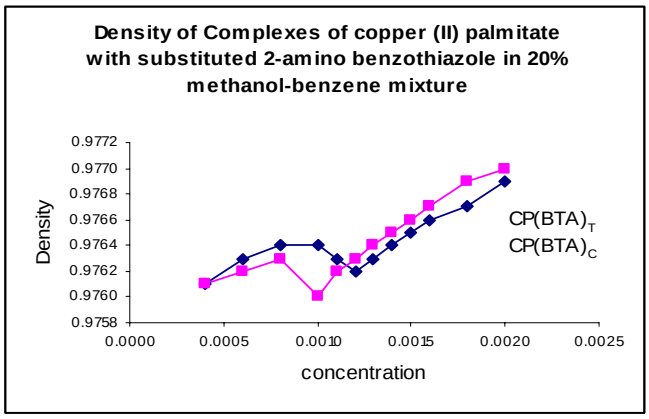


Fig. 5

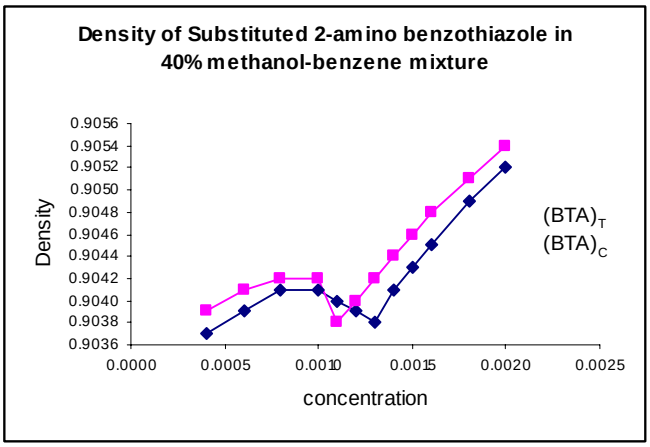


Fig. 6

$CP\ (BTA)_T$ = Complex of copper (II) palmitate with 2-amino-6-methyl benzothiazole

$CP\ (BTA)_C$ = Complex of copper (II) palmitate with 2-amino-6-chloro benzothiazole

The apparent molar volume has been calculated with the error limit of +0.02% from the density using the following equation[28].

$$\Phi_V = \frac{M + 1000\ (d_0\text{-}d)}{d \quad Cd_0} \qquad \ldots(2)$$

Where d_0, d, M and C are density of solvent and solution, molecular weight of the complex and concentration of solution in ($g.mol.l^{-1}$) respectively. The molar volume was calculated from density data and the comparisons of results indicate date the value V follows the order.

$$CP\ (BTA)_T > CP\ (BTA)_C$$

The plot of V against concentration shows a change at CMC Fig. 7, 8, 9 and 10, 11, 12. Below CMC the curve is concave, whereas a linear trend is obtained after CMC. This suggests that the environment such as micellar clustering, mobility is entirely different below and above CMC. The CMC of complex obtained from molar volume v/s concentration plots follow again the same order which is found by density v/s concentration plots.

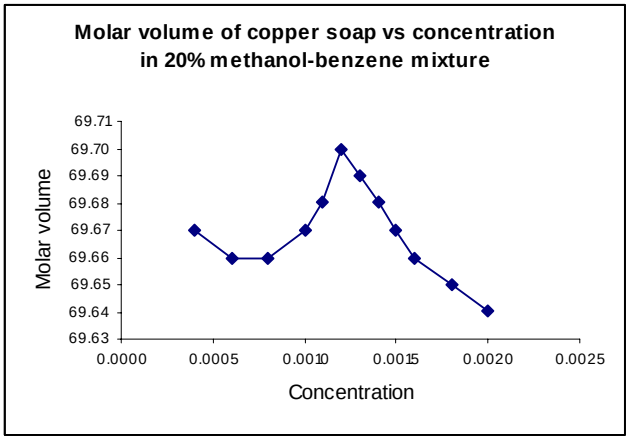


Fig. 7

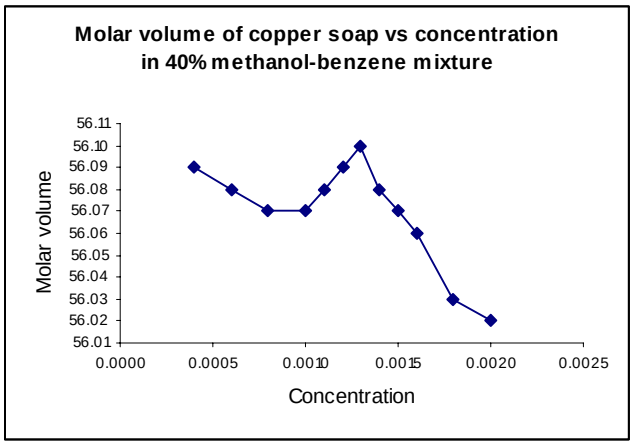


Fig. 8

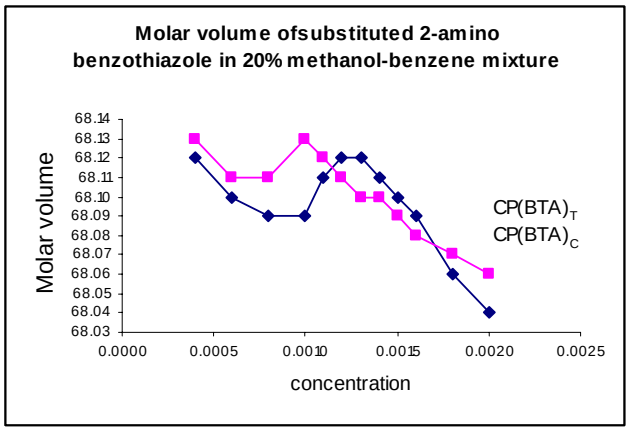


Fig. 9

$(BTA)_T$ = Benzothiazole of toludine

This observation is in agreement with the fact that there is decrease in CMC value with the increase of the molecular weight of the soap[29-31].

The apparent molar volume of copper soap complex of palmitic acid is calculated using Eq. (3) the plots of Φ v/s √C are characterized by an intersection of two straight lines at a point corresponding to the

CMC of the complex Fig. 13,14,15 and 16,17,18. The value of Φv shows a sharp increase below CMC. The CMC obtained from plots of Φ_v v/s √C also follows the same order as for density and molar volume. CMC so obtained in this study is also confirmed by other physical properties studies like surface tension, parachore and viscosity[32-33].

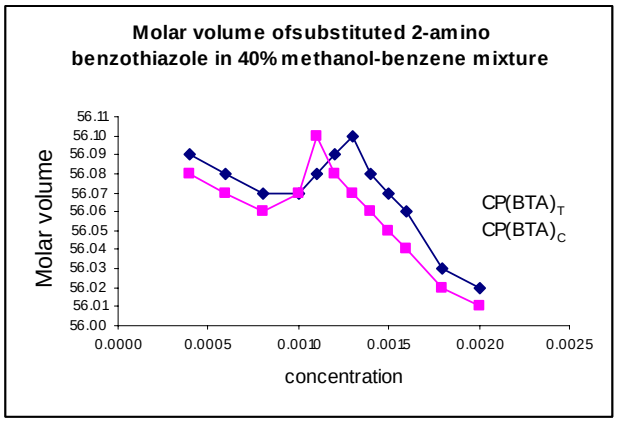


Fig. 10

$(BTA)_C$ = Benzothiazole of chloro aniline

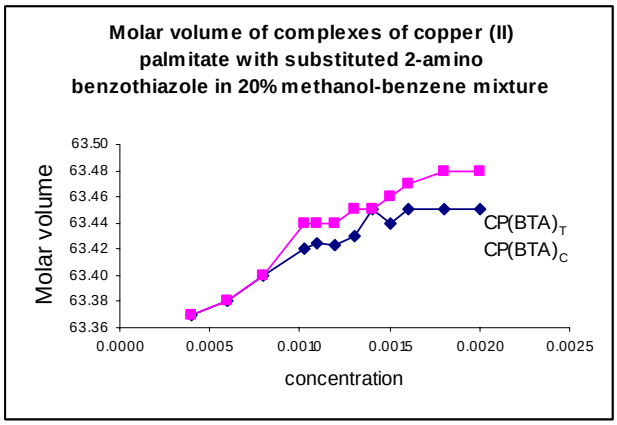


Fig. 11

$CP(BTA)_T$ = Complex of copper (II) palmitate with 2-amino-6-methyl Benzothiazole

$CP(BTA)_C$ = Complex of copper (II) palmitate with 2-amino-6-chloro Benzothiazole

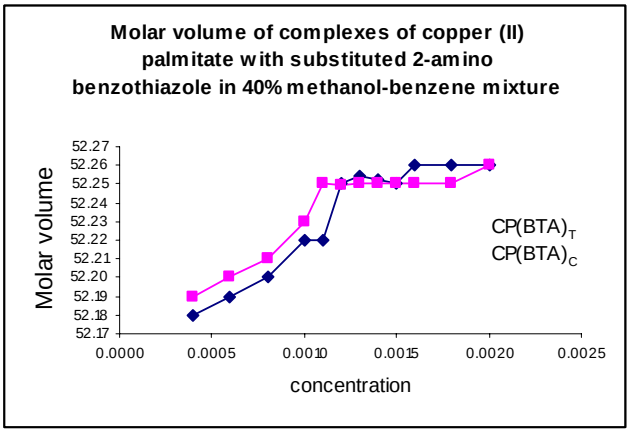


Fig. 12

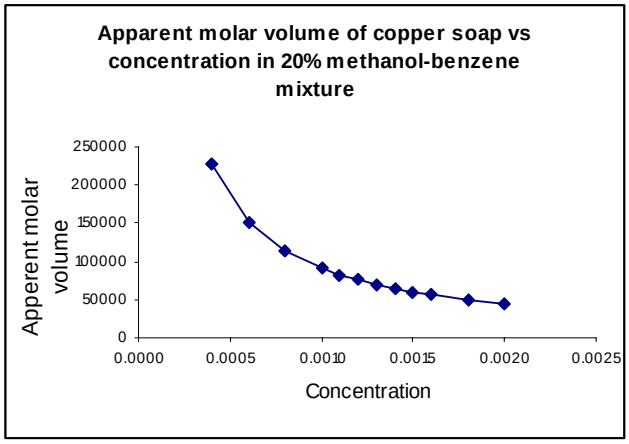


Fig. 13

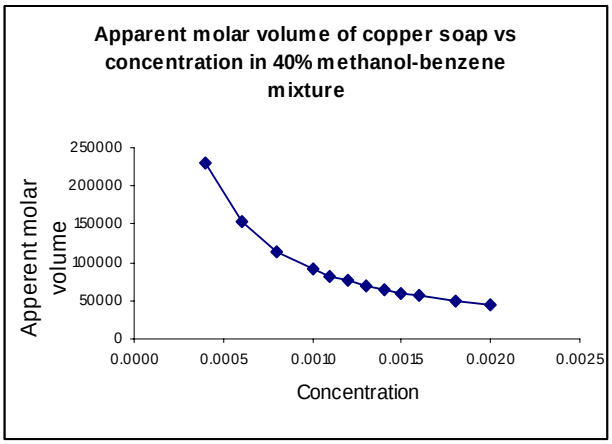


Fig. 14

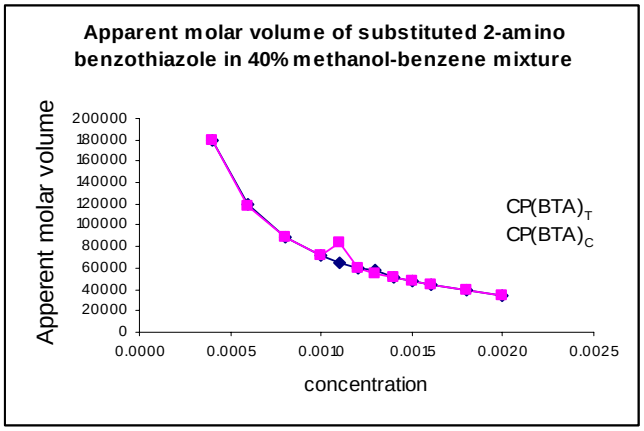


Fig. 15

$(BTA)_T$ = Benzothiazole of toludine

The data has been analyzed in terms of Masson equation [34].

$$\Phi_V = \sqrt{\Phi^0_V + \delta_V \sqrt{C}} \qquad ...(3)$$

The above equation fits well both below and above CMC. The value of limiting apparent molar volume (Φ_V) for these complexes is obtained by the extrapolation of Φ_V v/s $\sqrt{C}$ plots to C→0. The two value of Φ_V have been obtained and are regarded to as a Φ_{V1} (below CMC) and Φ_{V2} (above CMC). Since Φ_V has been regarded as a measure of solute solvent interaction[35], it is reasonable to assume that greater magnitude of Φ_V shall quantitatively be referred to as greater solute-solvent interaction are more pronounced after CMC as compared to before CMC.

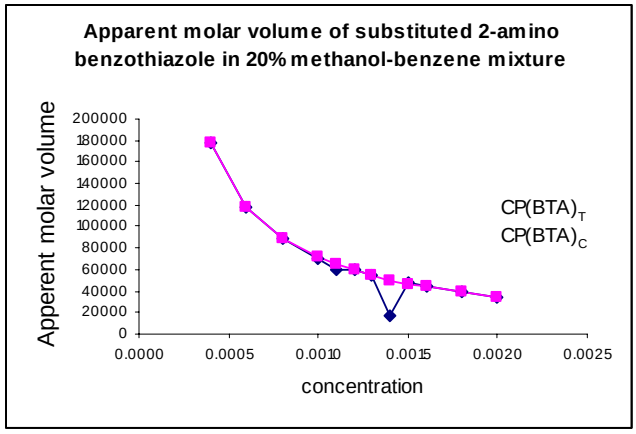


Fig. 16

$(BTA)_C$ = Benzothiazole of chloro aniline

Table 5: Computed parameters of Masson's equation for complexes of Copper (II) palmitate with 2-amino benzothiazole in 20% Methanol-Benzene Mixture

Name of complex	Volume of methanol			
	Φ_{v1}	Φ_{v2}	δ_{v1}	δ_{v2}
$CP(BTA)_T$	-490	1475	55000	46666
$CP(BTA)_C$	-960	1600	86000	25000

$CP(BTA)_T$: Copper (II) palmitate complex 2-amino-6-mithyl-benzothiazole

$CP(BTA)_C$: Copper (II) palmitate complex 2-amino-6-chloro-benzothiazole

Table 6: Computed parameters of Masson's equation for complexes of copper (II) palmitate with 2-amino benzothiazole in 40% Methanol-Benzene Mixture

Name of complex	Volume of methanol			
	Φ_{v1}	Φ_{v2}	δ_{v1}	δ_{v2}
$CP(BTA)_T$	-220	3300	65000	64000
$CP(BTA)_C$	-150	2900	68000	65000

$CP(BTA)_T$: Copper (II) palmitate complex 2-amino-6-mithyl-benzothiazole

$CP(BTA)_C$: Copper (II) palmitate complex 2-amino-6-chloro-benzothiazole

The solute-solvent interaction follows the order for both of the complexes.

$$\Phi_v \text{ 40\%} > \Phi_V \text{ 20\%}$$

From the above observation it is clear that the solvent-solute interactions are found higher in the dominance of polar the solvent constant in the solvent mixture. The parameter δ_v in Masson's equation represents the limiting apparent slope and is indicative of existence of solute-solute interaction. It is again reasonable to determine two Value of parameter δ_v one below CMC and another above CMC designated as δ_{v1} and δ_{v2} respectively. The data reveal that $\delta_{v1} > \delta_{v2}$ for $CP(BTA)_T$ $CP(BTA)_C$ complex thus it is obvious that solute-solute interactions are more pronounced below CMC in both of the complexes.

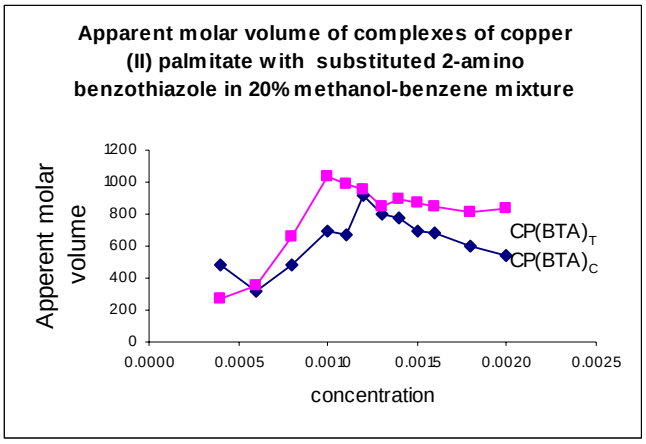


Fig. 17

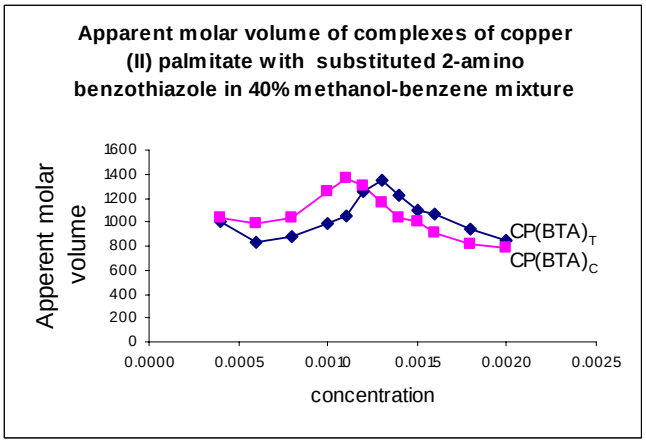


Fig. 18

$CP\ (BTA)_T$ = Complex of copper (II) palmitate with 2-amino-6-methyl Benzothiazole

$CP\ (BTA)_C$ = Complex of copper (II) palmitate with 2-amino-6-chloro Benzothiazole

Methodology of envirochemical biological synthesis

Standard solutions of standard chemicals (A.R., B.D.H., G.R. or E.merck) benzene, methanol, copper sulphate and palmtic acid and anilines were used. All the reagents were distilled, purified and dried according to the standard procedure.

Complexes of substituted 2-amino benzothiazoles with copper surfactants were prepared by the following method. The synthesized complexes were purified by washing with distilled water and ethanol, and than recrystallised and dried.

A calculated amount of surfactant, ligands and complexes were separately weighted in volumetric flask and the separate solutions were made up.

Synthesis of substituted 2-amino benzothiazole[36-40]

Substituted 2-amino benzothiazoles were synthesized using thiocyanation method. In this method (0.1 mol) para substituted aniline was treated with a mixture of (0.1 mol) ammonium thiocyanate 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 one and half hour.

The thiocyanogenation of aryl amine takes place in the presence of thiocynogen gas which is generated in situ by the reaction of cupric chloride and ammonium thiocynate. After cooling the reaction mixture, add 100 mL concentrated HCl, and heat again for half an hour, then cool it and than saturated solution of sodium carbonate (Na_2CO_3) is added to neutralize it, till the solid was formed. The solid separated out was filtered and washed with cold water, dried and recrystallised with ethanol.

Synthesis of copper surfactants[41-43]

Copper palmitate was prepare by mixing one gm of palmitic acid into 25 mL ethyl alcohol, shake the mixture in hot water bath at about 60-65^{0}C and than add one drop of phenolphthalein. A saturated solution of KOH in another beaker was prepared then it was added into palmitic acid solution drop by drop until the light pink color appears. Now again 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 colored soap is formed. Filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene.

Copper surfactants with substituted N-donor ligands[43-46]

The purified copper palmitate derived from palmitic acid was refluxed with the ligands. 2-amino benzothiazoles in 1:2 ratio using ethyl alcohol as a solvent for one and half hour, it was than filtered hot, dried, recrystallised and purified in hot benzene.

In general all the complexes are solid, powdered in nature and rare green bluish black in colour. They are insoluble in water but soluble in organic solvent.

Purification of benzene-methanol was done by keeping over sodium wire for a couple of days and then distilled. The distillate was refluxed over sodium metal and again distilled. The fraction was collected at 80^{0}C. The calculated amount of the soap, ligand and complexes was weighted in a volumetric flask and solution made up to mark by adding the required amount of benzene-methanol. Ostwald modification of the Springel pyknometer with a volume of about 10 mL which allowed an accuracy of about one unit in the fourth place of decimal was used for measuring the density of the soap, ligand and complex solution in a thermostated water bath at 301 K (± 0.1).

Table 7: Physical data of the synthesized complexed

Name of the complex	Colour	MP (^{0}C)	Yield (%)	Average m.w.
CP	Blue	80	98	573.54
$(BTA)_T$	Bluish black	130	97	164
$(BTA)_C$	Bluish black	135	95	184.5
$CP(BTA)_T$	Green black	270	94	1520
$CP(BTA)_C$	Green black	285	195	1516

ACKNOWLEDGEMENT

The authors are grateful to the Principal and Head, Department of Chemistry, S.D. Govt. College Beawar and Govt. P.G. College Dausa for providing all the necessary facilities, support and infra structure for carrying out this research work.

REFERENCES

1. K. G. Ojha, N. Jaisinghani and H. J. Tahiliani, Indian Chem. Soc., **79,** 191 (2002).
2. A. Gupta, R. Sharma and Prakash, J. Indian Chem. Soc., **74**, 635 (1994).
3. R. R. Gupta, Phenothiazines and 1,4-Benzothiazine, Chemical and Biomedical Aspects, Elsevier, Amsterdam, (1988).
4. G. Valli, S. Sivakolunthu, S. Muthusubramanian and S. Sivasubramanian, J. Indian Chem. Soc., **77,** 252 (2000).
5. K. G. Kulkarni and M. Fingerman, Gen. Pharmacol., **17(6),** 671 (1986).
6. Gour Har Singh Vishwavidhyalaya, Sunita Chaurasia and Savitri Shrivastava, Indian Drugs, **28,** 474 (1991); Chem. Abst., **116**, 15347f (1992).
7. S. S. Sawahney, S. S. Phindsa and D. Vir, J. Indian Chem. Soc., **65(9)**, 643 (1998).
8. E. A. Burach and Ayd. F.J. J. Clin. Psychiatry, **44**, 242 (1983); Chem. Abst., **95,** 133118 (1983).
9. F. Koland, P IRCS Med. Sci. Libr. Compound **9(6)**, 546 (1981); Chem. Abst., **95**, 9085 (1981).
10. F. P. Marvini, Mech. Ageing Dev., **36(3)**, 295 (1986).
11. C. Shukla, J. Inst. Chem., (India) **62(4),** 159 (1909); Chem. Abst., **114**, 1503075 (1991).
12. N. Raknew, Farmatsi (Sofia), **37(3)**, 10 (1987).
13. Y. V. Vorontsov, I. M. Lerner and E. L. Shchelkunov, Farmacol. Toksikol, **43(1),** 81(1980); Chem. Abst., **92,** 157547 (1980).
14. E. Schacht, J. Vandorpe, S. Dejardin and Y. Lemmouchi, L. Seymour, Biotechnology and Bioengineering, **52**, 102 (1996).
15. E. Chacht, S. Dejardin and Y. Lemmouchi, Bioactive and Compatible Polymers, **13**, 4 (1998).
16. R. J. Morgan, L. B. Eaddy, T. N. Solie and C. C. Turbes, Lab. Anim., **15**, 281 (1981); Chem. Abst., **95**, 214987 (1981).
17. A. M. Dave, K. N. Bhatt, N. K. Vndania and P. B. Trivedi, J. Indian Chem. Soc., **65(5)**, 365 (1988).
18. C. Pinto, R. S. Dasilva and R. A. Hollins, J. Heterocycles Chem., **16(5)**, 1085 (1979); Chem. Abst., **92**, 58705 (1980).
19. Hostynek and H. Maibach, Toxicol. Mechan. Methods, **16,** 245 (2006).
20. K. Czeslaw, Tribology Internat., **38**, 337 (2005).
21. S. Zok, G. George, W. Kalasch and R. Nagel, Sci. Total Environ., **411**, 109-110 (1991).
22. F. S. H. Abram and. I. R. Slims, Water Res., **16**, 1309 (1982); A. L. Walpole and M. H. C. S. Williams, Bull., **14**,141(1958).
23. R. N. Patel, S. Kumar and K. B. Pandeya, Indian J. Chem., **39A**, 1124 (2000).

24. J. L. Soyenz, Brighton Crop, Preotection Conference, Pest and Diseases, France, **Vol. 1,** (1992) pp. 451-456.

25. M. R. Sherwani, K. Sharma, R. A. Gangwal and. R. Bhutra, Indian J. Chem., **42A**, 2527 (2003).

26. S. N. Aminov, R. S. Iskandarov and Kh. T. Avezov, Chem. Natural Comp., **34**, 590 (1998).

27. K.N. Sharma, V. P. Mehta and T. N. Nagar, Cellulose Chem. Technol., **1**, 38 (1973).

28. V. P. Mehta, M. Hasan and. G. L. Rai, Tenside Detergent, **16**, 79 (1979).

29. S. Voywtsky, Colloid Chemistry, Mir Publication, Moscow (1978).

30. H. R. Kruyt, Colloid Science, Elsevier Publishing Company, New York (1969).

31. H. S. Harened and B. B. Dwen, Physical Chemistry of Electro kinetic Solutions, Reinhold (1958) p. 358.

32. V. P. Mehta, P. R. Talesara and R. Sharma, India J. Chem., **40A**, 399 (2001).

33. D. O. Masson, Phil. Mag., **8**, 218 (1929).

34. V. K. V. Unni and T. L. Ramachar, Corrosion, **22**, 153 (1966).

35. S. K. Jain, D. Chandra and R. L. Mittal, Chem. and Industry, **22**, 989 (1969).

36. Zhang Pei-Zhi, Wu Jan, J. Indian Chem. Soc., **81**, 501 (2004).

37. K. G. Ojha, N. Mathur, Asian J. Chem., **4**, 924 (1992).

38. G. Vasundhara, G. Jayshree and G. Kurup, Bulletin of Environmental Contamination and Toxicology, Springer Verly, New York, Inc., **72**, 1122 (2004).

39. Mathur, P. Adwani, K. G, Ojha, Die Pharmazie, **11H**, 47 (1992).

40. D. Kumar, A. Syaml and A. K. Singh, J. Indian Chem. Soc., **81**, 911 (2004).

41. L. S. Sabrina, V. Muresan, L. S. Sabrina and V. Muresan, C. I. Lepadatu, J. Indian Chem.Soc., **81**, 150 (2004).

42. V. P. Mehta, M. Hasan and S. P. Mathur, An Quim, **74**, 1016 (1978).

43. M. Pugazhuadiva, K. Jeyachaudra, Elsevier Ltd., **30**, 14 (2005).

44. Zhang Pei-Zhi, Wu Jan, J. Indian Chem. Soc., **81**, 501 (2004).

45. G. More and R. B. Bhalvankar, J. Indian Chem. Soc., **81**, 31(2004).

46. S. A. Javed, N. Siddiqui and S. Dradu, Indian J. Heterocycl. Chem., **13**, 287 (2004).