

Full Length Research Article

INTERPRETATION OF RELATIONSHIP BETWEEN DENSITY AND MICELLIZATION OF COPPER (II) SOAP COMPLEXES IN BINARY SOLVENT MIXTURE

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Co-ordination chemistry is undoubtedly the most active research area in inorganic chemistry. Investigations about the transition metal cations interacting with the heterocyclic molecules are essential for a better assessment of the role and effects of metal ions in biological systems. Heterocyclic compound is one which possesses a cyclic structure with at least two different kinds of heteroatoms in the ring. Nitrogen, oxygen and sulphur are the most important heteroatoms. Azoles played a significant role in the history of heterocyclic chemistry and also been used as remarkable synthons in organic reactions. The presence of $-NH_2$ group at 2-position of the azole and azine ring compounds make them more efficient in pharmacological field. Substituted benzothiazoles have been studied and found to have various chemical reactivity and biological activities. Its aromaticity makes it stable, although as a heterocycle, it has reactive sites which allow for functionalization. Thiourea derivatives and their structures can be considered as good chelating agents due to their ability to encapsulate metal ions into their co-ordination moiety. Various thiourea derivatives are well known for their complexation capacity. These ligands are of interest because they have two potential co-ordination sites i.e. sulphur and nitrogen atoms. The interaction of these donor ligands and copper soap (copper palmitate) gives complexes of different geometries. These complexes are potentially more biologically active. Owing to their multifold applications we synthesized complexes of copper(II) palmitate having 4-nitrophenylthiourea and 2-amino-6-nitro-benzothiazole. Densities of these complexes in varying concentration in non-aqueous benzene-propanol solvent mixture were studied. Using density data, critical micelle concentration was elucidated. This study clearly indicates that solute-solvent interaction decreases with increase in ring strain and size of synthesized complexes.

Key words: 4-Nitro Phenylthiourea, 2-Amino-6-Nitro Benzothiazole, Copper (II) Palmitate, Density, Critical Micelle Concentration (c.m.c.).

INTRODUCTION

Thiazole a heterocyclic nucleus played influential role in the advancement of different medicinally important moiety (Sharma *et al.*, 2013). They are mainly intrinsically toxic to microorganism especially to fungi and bacteria. Substituted benzothiazoles and phenylthiourea constitute an important class of compounds. The basic structure of benzothiazole consist of benzene ring fused with 4,5 position of thiazole. The two rings together constitute the basic nucleus. The molecule has a conjugated $-(CH=CH)-$ group making itself a chromophore and excellent class of dyes for fibres. The aromaticity contribute in bathochromic shift and this contribution is greater in para substituted compounds. Both phenylthiourea and benzothiazole possesses N-C=S linkage making them suitable for coloring various substances like paper, cellulose, wool and nylon. N and S atoms are present at ortho position. The exact structures of both the ligands are shown in Fig.1. and Fig. 2. The presence of NO_2 group at para position increases the electron transfer in resonance and compounds show remarkable activity for S_NAr reaction.

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Consequently these derivatives possess biological activities such as antitumor, antimalarial, antimicrobial (Rai *et al.*, 2013 and Rai *et al.*, 2011), antihelminthic, antileishmanial, anticonvulsant, anti-inflammatory and analgesic. Pathogenic activity of these organic ligands is enhanced after complex formation with transition metal which are toxic in nature (Jevtovic *et al.*, 2009). Copper has efficiency to bind with fatty acids and oils to form copper soaps. Copper (II) soaps in polar and non polar solvents are used in emulsification, wetting, lubricating and foaming due to their surface active properties (Mathur, 2011). Combination of copper soaps with heterocyclic ligands play wonderful role in various fields. They show fungicidal, pesticidal, insecticidal and nematocidal activities (Jevtovic *et al.*, 2010 and Srivastava *et al.*, 2012).

The above mentioned applications give us the reason to synthesize the complexes of copper soap with N-donor ligands. With the help of elemental analysis, melting points, IR, NMR and ESR spectroscopy; characterization of these complexes were done. Mixed solvent system containing benzene and propanol has been selected to study the micelle behaviour of these complexes. Density (Heda *et al.*, 2009) is employed as a tool to find out critical micelle concentrations (c.m.c.) of complexes and this study provides satisfactory information about solute solvent interaction and structural analysis of micelles.

The complexes are abbreviated as follows:

- CP [PTU] NA: Complex of copper palmitate with 4 nitro phenylthiourea.
- CP [BTA] NA: Complex of copper palmitate with 2-amino-6-nitro-benzothiazole.

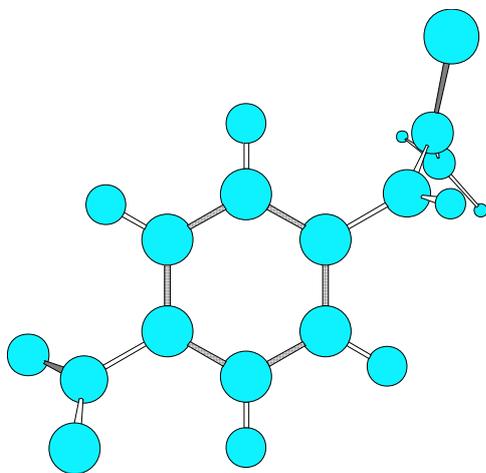


Fig. 1. Nitro-phenylthiourea

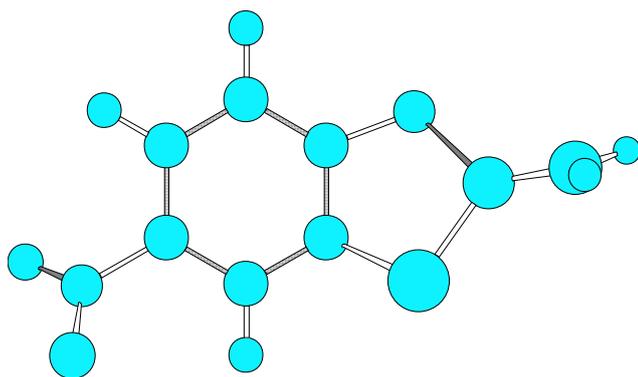


Fig. 2. Amino-6-nitro-benzothiazole

MATERIALS AND METHODS

All chemical used were of A.R. grade. All the solvents were purified by standard procedures. Purity of the compounds was checked by T.L.C. The melting points were determined on an electrical melting point apparatus and are in corrected. Complexes of copper palmitate with substituted phenylthiourea and substituted benzothiazole were synthesized by the following method.

Preparation of Phenylthiourea of p-nitroaniline (Sahail Saeed *et al.*, 2010 and More and Bhalvankar, 2004)

According to scheme 1. 13.89 (0.1 mole) of p-nitro aniline was heated in a 250 ml three necked flask with stirrer, dropping funnels, and reflux condenser with a mixture of 9 ml (6 N HCl) and 25 ml water at a temperature of 32°C on water bath till the aniline hydrochloride is formed. The resultant solution is now allowed to cool at room temperature and then 7.6 g (1 mole) ammonium thiocyanate was added to it. The reaction mixture was refluxed about for four hours on water bath. After cooling the solid separated out was filtered, washed with cold water, dried and then recrystallised with ethanol.

Preparation of benzothiazole of p-nitroaniline (Zhang *et al.*, 2004)

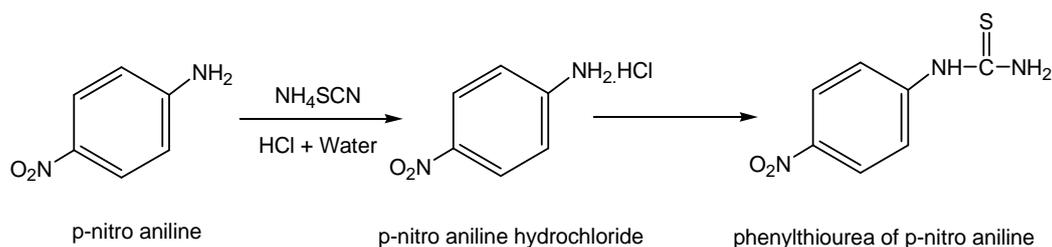
In the thiocynogenation method 13.8 g. p-nitro aniline (0.1 mole) was treated with a mixture of 7.6 gm NH_4SCN and 80 ml glacial acetic acid in a 250 ml three necked round bottom flask, with stirrer, dropping funnel and reflux condenser at room temperature for one and half hour. The thiocynogenation of aryl amine takes place in 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 saturated solution of sodium carbonate is added to neutralize it, till the solid was formed. The solid separated out was filtered, washed with cold water dried and recrystallized with ethanol (Scheme 2).

Synthesis of Copper Palmitate (Sabrina *et al.*, 2004 and Pugazhuadiva and Jeyachaudra, 2005)

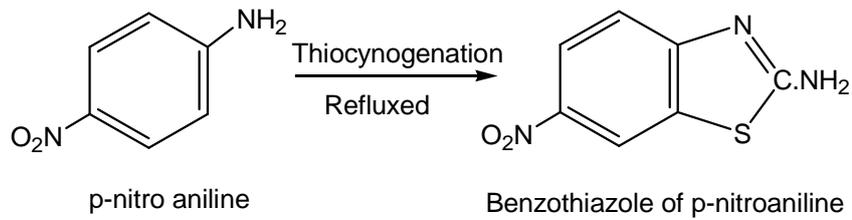
Palmitate was prepared by mixing one gram of palmitic acid into 25 ml ethyl alcohol, shake the mixture in hot water bath at about 50°C and then add one drop of phenolphthalein. Prepare a saturated solution of KOH in another beaker and add it drop by drop into the first beaker until the light pink colour appears. Now again in another beaker prepare a saturated solution of CuSO_4 (about 3-4 gm in 5 ml H_2O) and mix it into the above solution with stirring till the blue coloured soap is formed. Filtered it and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene.

Complexation of Soap and Ligand (Berhanu *et al.*, 2013 and Thummarok Suksrichavalit Supaluk, 2009)

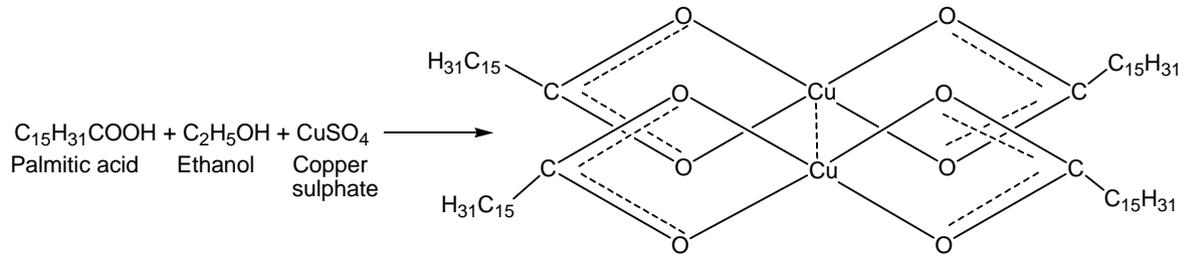
The purified copper palmitate derived from palmitic acid was refluxed with the ligands, substituted phenylthiourea and substituted benzothiazole in 1:2 molar ratio using ethyl alcohol for one and half an hour.



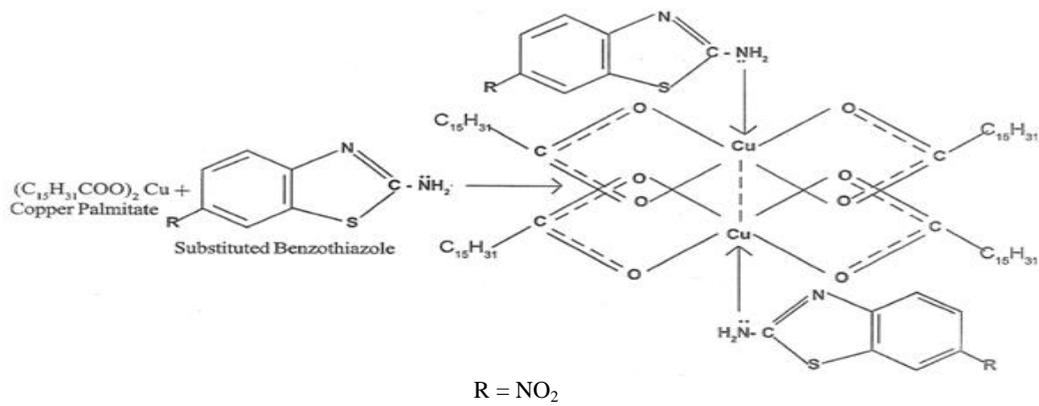
Scheme 1. Phenylthiourea of p-nitroaniline



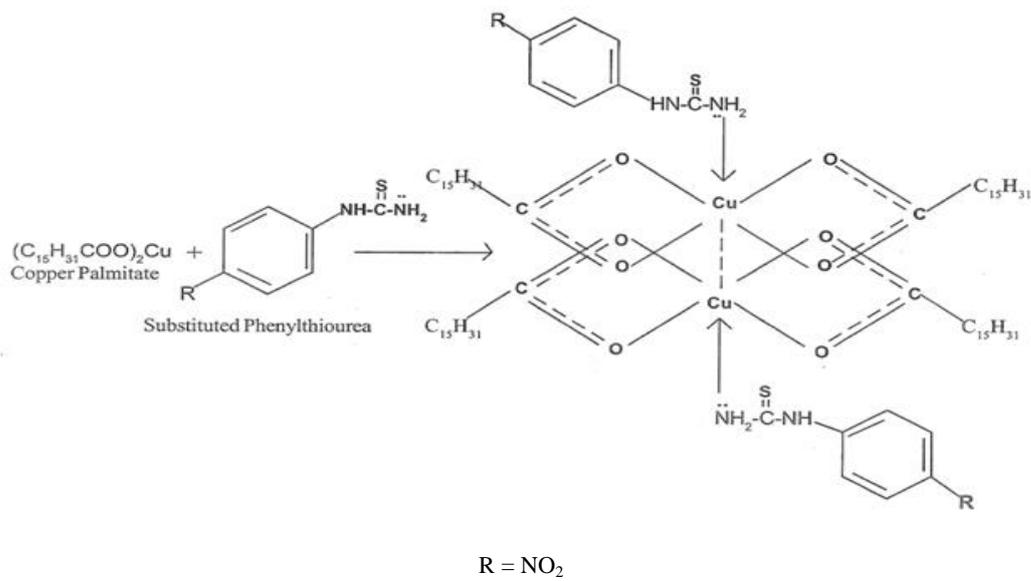
Scheme 2. Benzothiazole of p-nitroaniline



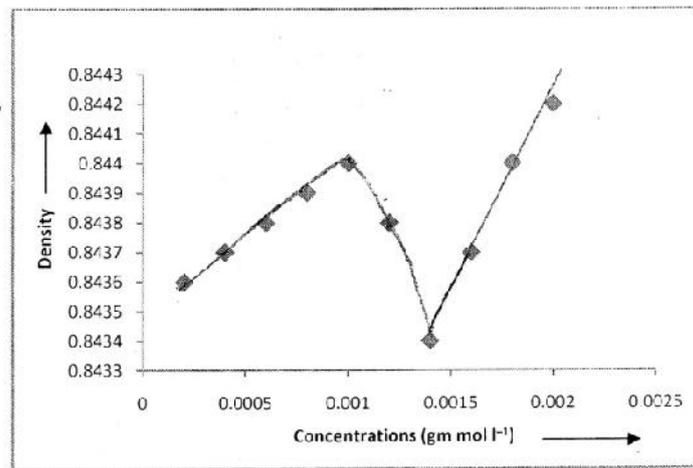
Scheme 3.



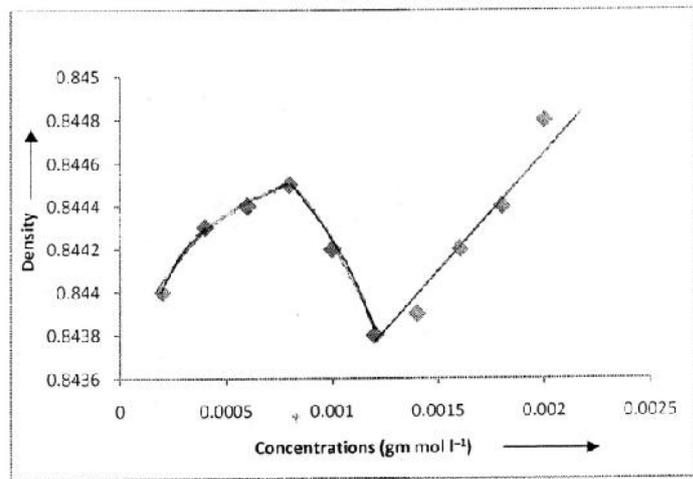
Scheme 4.



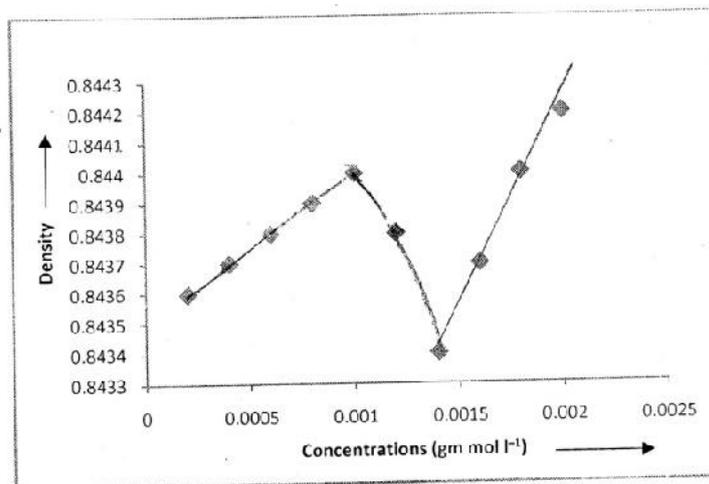
Scheme 5.



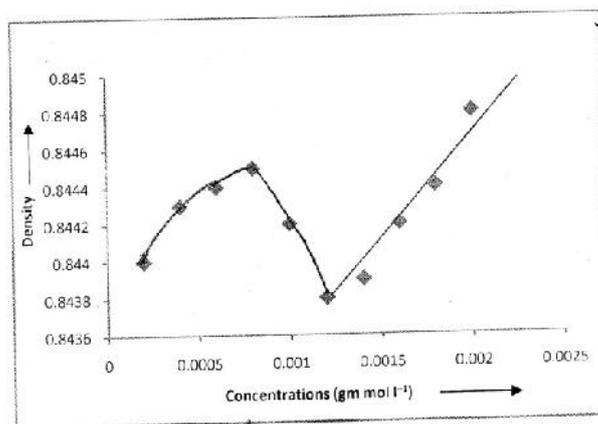
Polt of Density vs. Concentration of CP [PTU] NA in 20% Propanol-80% Benzene System



Polt of Density vs. Concentration of CP [BTA] NA in 20% Propanol-80% Benzene System



Polt of Density vs. Concentration of CP [PTU] NA in 20% Propanol-80% Benzene System



Plot of Density vs. Concentration of CP [BTA] NA in 20% Propanol-80% Benzene System

It was then filtered hot, dried, recrystallized and purified in hot benzene. In general all the complexes are solid, powdered in nature. They are insoluble in water but soluble in organic solvent.

RESULTS AND DISCUSSION

In the present work complexes of copper palmitate with 4-nitro phenylthiourea and 2-amino-6-nitro benzothiazole were examined in binary solvent mixture. Composition of the solvent mixture taken was 20% propanol + 80% benzene and 40% propanol + 60% benzene. Complex solutions of varying concentrations (g mol^{-1}) were prepared by using 20% propanol + 80% benzene and 40% propanol and 60% benzene. The values of density of CP [PTU]NA and CP[BTA]NA are recorded in Table 1 and Table 2.

Table 1. Physical data for complex of copper palmitate with 4-nitro phenylthiourea and 2-Amino-6-nitro-benzothiazole in 20% propanol + 80% benzene mixture

Concentration (gm mol^{-1})	Density of complex CP[PTU]NA	Density of complex CP[BTA]NA
0.0002	0.8436	0.8440
0.0004	0.8437	0.8443
0.0006	0.8438	0.8444
0.0008	0.8439	0.8445
0.0010	0.8440	0.8442
0.0012	0.8438	0.8438
0.0014	0.8434	0.8439
0.0016	0.8437	0.8442
0.0018	0.8440	0.8444
0.0020	0.8442	0.8448

Table 2. Physical data for complex of copper palmitate with 4-nitro phenylthiourea and 2-Amino-6-nitro-benzothiazole in 40% propanol + 60% benzene mixture

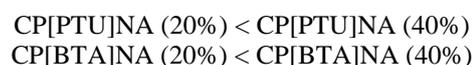
Concentration (gm mol^{-1})	Density of complex CP[PTU]NA	Density of complex CP[BTA]NA
0.0002	0.8412	0.8384
0.0004	0.8414	0.8385
0.0006	0.8415	0.8386
0.0008	0.8416	0.8385
0.0010	0.8417	0.8383
0.0012	0.8414	0.8379
0.0014	0.8412	0.8382
0.0016	0.8410	0.8386
0.0018	0.8416	0.8389
0.0020	0.8420	0.8392

Table 3. Value of c.m.c. (in gm mol^{-1}) for synthesized complexes in propanol benzene mixture

Name of complex	Study	c.m.c (in gm mol^{-1})	
		20% Propanol	40% Propanol
CP[PTU]NA	Density	0.0014	0.0016
CP[BTA]NA	Density	0.0012	0.0012

The interpretation of the data shows that density for both of the complex solutions increases with increasing concentration then there is a decrease with linear increase. The shape of plot of density 'd' vs concentration is convex below c.m.c., thereafter it becomes linear. The intersection point of convex curve and a straight line corresponds to c.m.c. of the complex. Aggregation of the molecules results in critical array. It can be concluded that below c.m.c. there is no adequate aggregation of molecules.

There is appreciable increase in aggregation of surfactant molecules at a definite concentration i.e. c.m.c. Environment, such as micellar clustering, solvation of soap molecules and diminution mobility is entirely different below and above c.m.c. Since density parameter shows a change at c.m.c, it indicates the micellar behaviour of the complex. The values of c.m.c. obtained from the plots follow the order. CP [PTU]NA > CP[BTA]NA. This observation is in agreement with the fact that there is a decrease in c.m.c. values with the increase in average molecular weight of the complex. It is clear from c.m.c. data that it is also dependent on solvent composition and follow the order-



Conclusion

The present study clearly demonstrates that association of complex molecules occur at lower concentration in CP[BTA]NA as compared to CP[PTU]NA. This may be due to the larger size and higher average molecular weight of the former complex. Which is responsible for its early micelle formation at lower concentration. Average molecular weight and nature of solvent play an important role in determination of density of the complex. Due to larger size of 2-amino-6-nitro benzothiazole less number of molecules are required to form micelles. Substituted benzothiazole has more conjugation as compared to substituted phenylthiourea, this factor contributes in decreased aggregation.

Inspite of higher molecular weight and size, ring strain and aromaticity are other factors responsible for lower c.m.c. value for CP [BTA]NA.

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