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Viscometric Behaviour and Miceller Studies of Some Biodegradable Organometallic Complexes in Binary Solvent System.

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ABSTRACT

Some nitrogen and sulphur containing aromatic ligands are ubiquitous components both for physiologically active products and important pharmaceuticals. The study of binuclear complexes of these ligands with transition metal Copper (II) is highly interesting due to their significance in physical and bioinorganic chemistry, material science and multi-electron redox chemistry. Likewise novel complexes of Copper(II) palmitate with N and S donor ligands were synthesized and viscometric behavior of these complexes was studied in non aqueous benzene – methanol solvent mixture. Their study helps in interpretation of solute-solvent interactions, structural insight of micelle and colloidal chemical behavior in binary systems. Study of these factors is essential as it indirectly makes them responsible for their immense applicability in wide areas of field.

KEYWORD: Substituted Benzothiazole, p- substituted Phenylthiourea, Copper (II) Palmitate, Viscosity

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INTRODUCTION

A great deal of attention has been focused on the complexes formed by 3d metals with bidented ligands using both sulphur and nitrogen. The interaction of Cu (II) palmitate with these ligands makes complexes of different geometries which are found to be potentially biologically active. These complexes are highly biodegradable and play important role in biological systems. The role of above complexes is of paramount importance. They show moderate antimicrobial activity [1-6] against gram positive bacteria and fungi. The combinations have also found to posses fungicidal, insecticidal, pesticidal and nematocidal [7-28].

Bez - fused compounds are primitive source of above said classes of complexes. They have been employed in the synthesis of pharmaceutical compounds because of significant activities possessed by them. Literature survey reveals that the nitrogen donor ligands like Phenylthiourea and 2- amino benzothiazole are well known compounds with multifaceted nucleus with privileged bicyclic ring system and bear N-C=S linkage making them suitable for coloring various substances like paper, cellulose, wool and nylon [29]. The exact information of the nature and structure of these aromatic compounds are of great significance for explaining their characteristics under different conditions [30]. Making them endowed with multiple applications like anti-inflammatory, antifungal, antimicrobial, anticancer, antitumor, anticonvulsant etc. They show increased potency upon complexation with copper soap, which is worth to be studied.

Coming onto copper surfactants applicability in our day to day life. They have sufficient pharmaceutical, industrial and analytical application due to special physico - chemical behavior. Due to their ability to lower surface tension surfactants are used as emulsifiers, detergents, dispersing agents foaming agents, wetting and penetrating agents and so forth. Use of surfactants as wood preservatives, water proofing, repellency agents in various industries of rubber and paints are well known.

So, here we synthesized complexes based upon their widest applicability Performa. Complexes were characterized by elemental analysis, melting points, IR, NMR, ESR spectral studies. Benzene-methanol has been selected as co- solvents since mixed solvents show tendency to interact with complex molecules and result in affecting the aggregation of complex molecule.
Viscosity of soap solution, pure ligands and complexes of soap with nitrogen and sulphur donor ligands has been deeply investigated in order to understand the nature of critical micelle concentration and miceller characterization.

EXPERIMENTAL SECTION

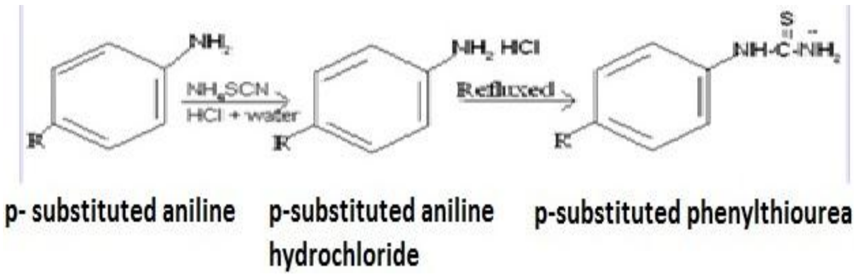
MATERIALS AND METHOD

All chemical used were of A.R. Grade. All solvents were purified by standard procedures. Purity of compounds was checked by T.L.C. The melting points were determined by electric melting point apparatus and in corrected. Complexes of Copper

Palmitate with Benzothiazole and Phenylthiourea as nitrogen and sulphur donor ligands were synthesized by following methods:

PREPARATION OF P-SUBSTITUTED PHENYLTHIOUREA:

Acc. to figure 1. (0.1 mole) of P-Substitutes aniline was heated in a 250 ml three necked flask with stirrer, dropping funnel, reflux condenser with a mixture of 9 ml(6N HCl) and 25 ml water at temperature 32˚C on water bath till aniline hydrochloride is formed. Resulting solution is now cooled to room temperature and 7.6 gm (0.1 mole) of NH_4SCN is added to it. Now, the reaction is refluxed for four hours on water bath. After cooling the solid separated out was filtered, washed with cold water dried and recrystallized with ethanol.

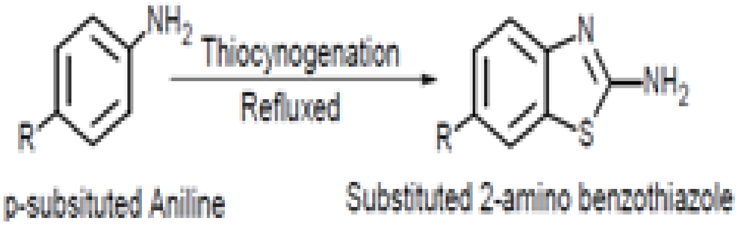


R = CH_3, Cl

Figure 1.

SYNTHESIS OF SUBSTITUTED 2-AMINO BENZOTHIAZOLE

Substituted 2-amino benzothiazoles were synthesized using thiocyanation method. . In this method (0.1 mol) p- nitro aniline was treated with a mixture of 7.6 gm 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 insitu 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 then 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 (Figure 2).



R = CH_3, Cl

Figure 2.

SYNTHESIS OF COPPER SURFACTANTS

Copper palmitate was prepared by mixing one gm of palmitic 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 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 (Figure 3).

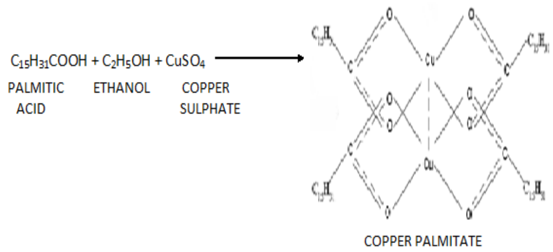
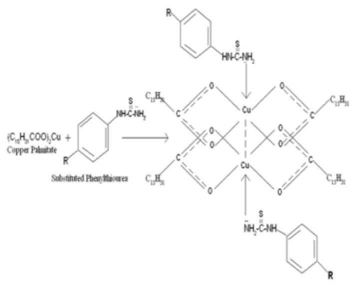


Figure 3.

COMPLEXATION OF COPPER SURFACTANTS WITH SUBSTITUTED N-DONOR LIGANDS:

The purified copper palmitate derived from palmitic acid was refluxed with the ligands, substituted Benzothiazole and substituted phenylthiourea 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. They are insoluble in water but soluble in organic solvent.



R = CH_3, Cl

Figure 4.

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 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 thermostate water bath at 301 K (± 0.1) (Figure 4).

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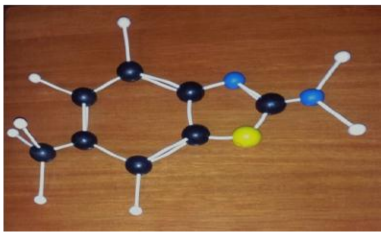
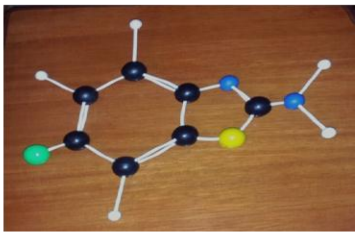
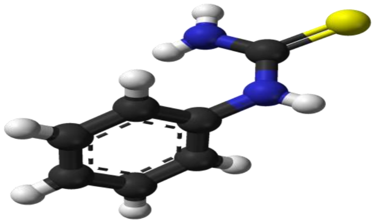
Ball and Stick Diagrams of Synthesised Structures



2-amino 6-methyl Benzothiazole



2-amino 6- chloro Benzothiazole



Phenylthiourea

ABBREVIATIONS USED:

Copper Palmitate – CP, Phenylthiourea – PTU, Benzothiazole – BTA, Complex of 4- methyl phenylthiourea and copper palmitate – CP $(PTU)_{T,}$ Complex of 2-amino 6-methyl benzothiazole and copper palmitate – CP($BTA)_T$ Complex of 4- chloro phenylthiourea and copper palmitate - CP $(PTU)_{C,}$ Complex of 2-amino 6-chloro benzothiazole and copper palmitate – CP $(BTA)_C$

RESULT AND DISCUSSION

The colloidal behavior of anionic surfactants containing copper ions is worth to be studies as they contain multiple valuable characteristics. The viscous behaviour of complex molecule in solution is important in understanding the mechanism of transport process. The study shows that viscosity of soap solution as well as complexes with phenylthiourea and benzothiazole in benzene and methanol mixtures first increases then decreases with the increase in the concentration. This trend of variation of viscosity with increasing concentration may be due to increasing tendency of soap molecule to form micelle.

Table No: 1 Physical data for complex of Copper Palmitate with 2 amino 6- chloro Benzothiazole

Concentration of complex in (g mol/l)	Viscosity (η) in (milipoise)	η_o (milli poise)	Specific Viscosity	Fluidity
0.0004	6.1559	5.1390	0.0202	0.1624
0.0006	6.2995	5.1390	0.0559	0.1569
0.0008	6.3474	5.1390	0.0520	0.1575
0.0010	6.1797	5.1390	0.0242	0.1618
0.0011	6.2516	5.1390	0.0360	0.1599
0.0012	6.4187	5.1390	0.0638	0.1558
0.0013	6.4676	5.1390	0.0719	0.1546
0.0014	6.5627	5.1390	0.0758	0.1540
0.0015	6.6585	5.1390	0.1035	0.1502
0.0016	6.7543	5.1390	0.1194	0.1480
0.0018	6.7557	5.1390	0.1196	0.1196
0.0020	6.8515	5.1390	0.1355	0.1355

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Table No: 2 Physical data for complex of copper palmitate with 2-amino 6- methyl benzothiazole

Concentration of complex in (g mol/l)	Viscosity (η) in (milipoise)	$\eta_{\circ}$ (milli poise)	Specific Viscosity	Fluidity
0.0004	6.1078	5.1390	0.0122	0.1637
0.0006	6.2523	5.1390	0.0362	0.1599
0.0008	6.3718	5.1390	0.0560	0.1569
0.0010	6.3718	5.1390	0.0560	0.1569
0.0011	6.3487	5.1390	0.0522	0.1575
0.0012	6.1572	5.1390	0.0204	0.1624
0.0013	6.3011	5.1390	0.0443	0.1587
0.0014	6.3730	5.1390	0.0562	0.1569
0.0015	6.5409	5.1390	0.0840	0.1529
0.0016	6.5654	5.1390	0.0880	0.1523
0.0018	6.8767	5.1390	0.1397	0.1454
0.0020	6.8550	5.1390	0.1360	0.1459

Table No: 3 Physical data for complex of copper palmitate with 4- chloro phenylthiourea

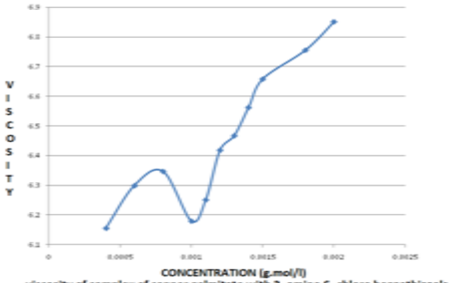
Concentration of complex in (g mol/l)	Viscosity (η) in (milipoise)	$\eta_{\circ}$ (milli poise)	Specific Viscosity	Fluidity
0.0004	6.0608	5.1390	0.0045	0.1649
0.0006	6.1590	5.1390	0.0125	0.1637
0.0008	6.2760	5.1390	0.0401	0.1593
0.0010	6.2523	5.1390	0.0362	0.1599
0.0011	6.1803	5.1390	0.0122	0.1618
0.0012	6.1078	5.1390	0.0122	0.1637
0.0013	6.1568	5.1390	0.0203	0.1624
0.0014	6.1816	5.1390	0.0245	0.1624
0.0015	6.3727	5.1390	0.0460	0.1569
0.0016	6.4689	5.1390	0.0720	0.1546
0.0018	6.7549	5.1390	0.1195	0.1480
0.0020	6.8522	5.1390	0.1356	0.1459

Table No: 4 Physical data for complex of copper palmitate with 4- methyl phenylthiourea

Concentration of complex in (g mol/l)	Viscosity (η) in (milipoise)	$\eta_{\circ}$ (milli poise)	Specific Viscosity	Fluidity
0.0004	6.1322	5.1390	0.0163	0.1630
0.0006	6.1572	5.1390	0.0204	0.1624
0.0008	6.2529	5.1390	0.0363	0.1599
0.0010	6.3718	5.1390	0.0560	0.1569
0.0011	6.3711	5.1390	0.0559	0.1569
0.0012	6.2536	5.1390	0.0364	0.1599
0.0013	6.1572	5.1390	0.0204	0.1624
0.0014	6.1327	5.1390	0.0164	0.1531
0.0015	6.1809	5.1390	0.0244	0.1618
0.0016	6.3005	5.1390	0.0441	0.1587
0.0018	6.3730	5.1390	0.0562	0.1569
0.0020	6.6605	5.1390	0.1038	0.1501

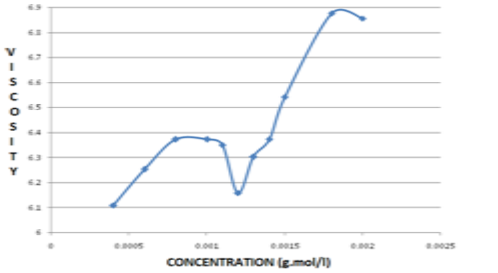
Therefore plots of viscosity ‘η’ v/s concentration ‘C’ (g moles/lit) are characterized by a convex nature of curve before c.m.c. and thereafter increasing trend. Thus, interaction in between the convex curve and straight line after c.m.c. as in shown by the following plots (1to 4).

GRAPHICAL SECTION



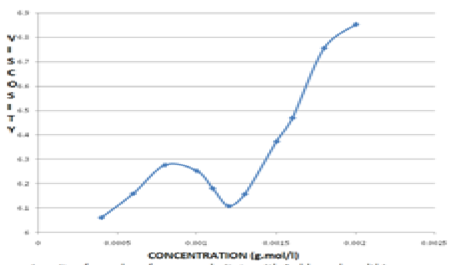
viscosity of complex of copper palmitate with 2- amino 6- chloro benzothiazole

GRAPH NO. 1



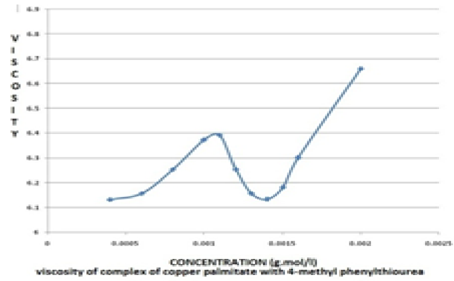
viscosity of complex of copper palmitate with 2-amino-6 methyl benzothiazole

GRAPH NO. 2



viscosity of complex of copper palmitate with 4-chloro phenylthiourea

GRAPH NO. 3



viscosity of complex of copper palmitate with 4-methyl phenylthiourea

GRAPH NO. 4

This shows that the c.m.c. values of soap complexes of phenylthiourea and soap complex of benzothioazole are in order-

$$CP(PTU) > CP(BTA)$$

This is in agreement with the fact the viscosity for both the complexes initially increases slightly then decreases upto c.m.c. and after it they show a same trend of increasing slightly then decrease upto c.m.c. and after it show a same trend of increasing order, as observed in the case of soap solution. . The observation suggests that the c.m.c. values increases with the decrease in molecular weight and the size of the molecule. This may be interpreted that the micelle formation takes place earlier in the case of benzothiazole ligand due the larger molecular structure so the less number of molecule are needed to form micelle.

The ligand benzothiazole has more conjugation(alternative double bonds) than the earlier one hence the later complex will also have more conjugation, which results in decrease of aggregation. Ring strain, more resonating structure and aromaticity are the factors inspite of higher molecular weight and size which affects the c.m.c. values.

$$\text{So, } CP(PTU)_T > CP(PTU)_C \quad \text{and} \quad CP(BTA)_T > CP(BTA)_C$$

Because the average molecular weight of $CP(PTU)_T$ and $CP(BTA)_T$ are lower therefore the value of C.M.C. is higher. Thus, the cmc value decreases with an increase in molecular weight of complex as well as ligands.

Table No: 5 Values of C.M.C. for synthesized complexes:

PLOTS → / COMPLEXES↓	η V/S C	η_{SP} V/S C	Φ V/S C
$CP(BTA)_T$	0.0012	0.0012	0.0012
$CP(BTA)_C$	0.0010	0.0010	0.0010
$CP(PTU)_T$	0.0014	0.0014	0.0014
$CP(PTU)_C$	0.0012	0.0012	0.0012

The viscometric data below and above c.m.c. are interpreted in terms of Moulik equation:

$$(\eta/\eta_{\circ})^2 = M + KC^2$$

The values of Moulik's constant M and K are obtained from the intercept and slope of the plots of $(\eta/\eta_{\circ})^2$ v/s C^2. The value of M below c.m.c. is higher than that of after c.m.c. explaining much interaction of complex molecule with each other below c.m.c. the value of K for Benzothiazole complexes are much higher as compared to phenylthiourea complexes and suggest that bigger size molecule will have strong interaction with solvent and hence the value for c.m.c. is lowered.

CONCLUSION

The present research work makes an attempt to prepare macrocyclics from metal and azole/azine ring compounds and it is found that the beneficial effects of the synthesized pharmaceuticals are much more then narrowly mentioned. Azoles and azines compounds are themselves very good pharmalogical agent and can be used as antimalarial, antimotion sickness, antihistaminic and analgesics. The current topic will not only strengthen relation b/w industries, private sectors and research laboratories on the focal theme of biology, physics, and environment but also will also play a significant role in forth coming scientific development.

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