Micellar Studies of Some New Biomedical Agents in Propanol – Benzene System

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Abstract

Coordination chemistry is a rapidly developing field having versatile applications. A great deal of attention has been focused on the complexes formed by 3d metals with nitrogen donar ligands. The azole and azine ring compounds are very good pharmacological agents and can be used as antimalarial, antimotion sickness, antihistaminic and analgesic. Combination of copper(II) soap and N-donor ligands makes complexes which are highly biodegrable. The copper(II) soaps in polar and non-polar solvents find their uses in various fields of applications like foaming wetting, emulsification and lubrication. Taking in view the applicability of heterocyclic compounds, in the present work several entities having heterocyclic nucleus have been selected. Complexes of copper(II) soap with N donor ligands were synthesized and characterized by their elemental analysis, molecular weight, m.pt, IR and NMR spectral studies. Copper soaps due to their surface active properties play a vital role in various fields. In the present work benzene and propanol have been chosen as mixed solvents which have tendency to interact with complex molecules and affect the aggregation of complex molecules. Viscometric measurements have been used to study the colloid chemical behavior of these complexes in benzene propanol mixture of varying composition. In the present study the solute-solvent interaction was investigated by viscosity measurement of different copper soap complexes non-aqueous binary solvent mixture.

Keywords: Nitrogen donor ligands, biodegradable, emulsification, colloid-chemical, viscometric.

Introduction

Organometallic surfactants are materials based on metal-organic frame works. They are generally considered to have dispersant characteristics. Studies have indicated that these surface active species have the ability to undergo self-assembly in certain solvents into various structures.

Metal surfactants are used today in every field of life. Their utility in day to day reutine can not be underestimated. They show noticeable industrial, medicinal and analytical applications due to their physico-chemical behaviour. This high surface active nature makes them so important as their presence changes the properties of surface[1-5].

Metallic surfactants especially of copper, play a vital role in many fields such as paints, varnishes, rubber industries, water proofing and repellence, emulsifications, protection of crops, stabilization of nylon threads, preservation of wood, lubrications etc. Calloido chemical behaviour of copper surfactants in non aqueous solvents make them more significant.

There is remarkable utility of copper surfactants to enhance the herbicidal, pesticidal, fungicidal and bacteriocidal activities in the field of wood preservation. Among the metal surfactants copper(II) soap complexes show significant interest in polar and non polar solvents and show great importance in aforesaid sectors. In biological systems these agents are vital components[6-8].

These wide range of applications led us to synthesize complexes of copper palmitate with nitrogen and

sulphur donor ligands. Complexes were characterized by elemental analysis, melting points, IR, NMR and ESR spectral studies. Benzene and propanol has been selected as co-solvents as mixed solvents show tendency to interact with complex molecules and thus affecting the aggregation of complex molecules.

Various physical properties i.e. density, viscosity and fluidity of soap solution, pure ligands and complexes of soap with nitrogen and sulphur donor ligand has been studied in varying composition of benzene + propanol solvent system. The data obtained helped us to understand the micellization process indepth.

Experimental

All the chemical used for the preparation of soap, ligands and complexes were of A-R grade.

i. Preparation of copper(II) soap

ii. Preparation of ligands

iii. preparation of complexes of soap and ligand

Stage – I

Preparation of copper soap

Copper soap 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 color appears. Meanwhile in another beaker prepare a saturated solution of $CuSO_4$ (approx 3-4 gms in 5 ml H_2O) and mix it into the above solution with constant 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.

Stage II

(A) Preparation of substituted benzothiazole:

Thiocynogenation method was used for the preparation of substituted-2-amino benzothiazoles. In this method, 12.3gm p-methoxy aniline (0.1 mole) 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 an hour[9-11].

Aryl amine undergoes thiocynogenation in the presence of the thiocyanogen gas, which is generated in situ by the reaction of cupric chloride and ammonium thiocyanate. After cooling the reaction mixture, add 100 ml conc. HCl and heat it again for half an hour, then cool it and saturated solution of sodium carbonate (Na_2CO_3) 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.

B. Preparation of substituted phenylthiourea

In this method aryl amine was treated with ammonium thiocyanate to prepare phenylthiourea. For this purpose 12.3 gm (0.1 mole) / p-methoxy aniline was heated in a 250 ml three necked flask with stirrer, dropping funnel and reflux condenser with a mixture of 9 ml (6NHCl) and 25 ml water at a temperature of 32°C on water bath till the aniline hydrochloride was formed (the solution now obtained is allowed to cool at room temperature and then 7.6 gm (1 mole) ammonium thiocyanate was added to it[12-14].

The reaction mixture was refluxed for about four hours on water bath. After cooling the solid separated out was filtered, washed with cold water, dried and then recrystallized with ethanol[15-17].

Stage-III

Preparation of complex using soap and ligand

Complexation of purified copper soap obtained from palmitic acid and substituted benzothiazole / substituted phenylthiourea was done by adding 0.001 mole copper palmitate with 0.002 mole benzothiazole / 0.002 mole phenylthiourea in 25-30 ml ethyl alcohol and mixture was refluxed for about two hours with constant stirring. After cooling the solid separated out was filtered, dried and recrystallized with hot benzene.

IR, NMR techniques were used to confirm the formation of complex. Thin layer chromatography was done to check the purity of the prepared complexes.

All the synthesized complexes were coloured and solid in nature. These are moderately soluble in organic solvents like methanol, ethanol, propanol, benzene and DMSO but insoluble in water. These complexes are highly soluble in binary solvent solvent mixture e.g. propanol + benzene mixture. Binuclear nature and 1:1 composition of metal ligand was revealed through elemental analysis. The physical data of ligands and complexes are given in Tables (1-5) to all the ligands and complexes are stable at room temperature.

Purity of the synthesized complexes were checked by TLCand respective R_f values of the synthesized compounds were obtained to check their purity.

Table-1
Rf Values of Copper soap

S.No.	Molecular Formula	Solvent			Color of Spot
		A	B	C	
1.	$C_{32}H_{62}O_4Cu$	54.3	52.1	51.7	Blue

A = acetone = carbontetrachloride
B = Acetone = Petroleum ether
C = Benzene = Acetone = Petroleum ether

Table-2
R_f Values of ligands [BTA]A and [PTU]A

S.No.	Molecular Formula	Solvent			Color of Spot
		A	B	C	
1.	[BTA]A	80.2	76.5	75.4	Purple
2.	[PTU]A	79.2	76.0	74.2	Mustard yellow

A = Acetone = carbon tetrachloride
B = Acetone = Petroleum ether
C = Benzene = Acetone = Petroleum ether

Table-3
R_f Values of copper complexes

S.No.	Complex	Solvent			Color of Spot
		A	B	C	
1.	CP[BTA]A	88.0	85.7	83.9	Dark purple
2.	CP[PTU]A	88.1	86.7	85.5	Mustard yellow

A = Acetone = carbon tetrachloride
B = Acetone = Petroleum ether
C = Benzene = Acetone = Petroleum ether

RESULTS AND DISCUSSION

To understand the micellar characteristic of the complexes prepared investigation of various physical properties like density, viscosity and fluidity was done.Literature survey show that the c.m.c is the concentration of surfactant solute at which the concentration of micelles becomes zero. By this definition, c.m.c. is the concentration at which two straight lines of solution properties below and above c.m.c intersects each other.

The solutes which are being studied i.e. CP[BTA]A and CP[PTU]A have both hydrophilic and hydrophobic characteristics i.e. $COO^-$of palmitic acid and aromatic $NH_2$of benzothiazole ligandas well as $CSNH_2$ of phenylthiourea are hydrophilic in nature and long alkyl chain is hydrophobic in nature.Solvent has mixed nature. Thus various types of interactions are assumed to occur between solute- solute and between solute- solvent molecules.

Table-4
Viscosity and fluidity of complex solutions of CP[BTA]A and CP[PTU]A in 20% propanol + 80% benzene mixture

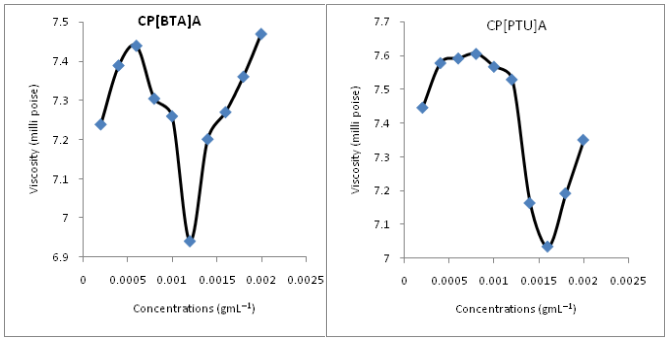
Concentration of complex in g mol L^{-1}	VISCOSITY		FLUIDITY	
	CP[BTA]A	CP[PTU]A	CP[BTA]A	CP[PTU]A
0.0002	7.2394	7.4463	0.1381	0.1343
0.0004	7.3898	7.5785	0.1353	0.1319
0.0006	7.4403	7.5922	0.1344	0.1317
0.0008	7.3053	7.6057	0.1369	0.1315
0.0010	7.2604	7.5677	0.1377	0.1321
0.0012	6.9408	7.5296	0.1441	0.1328
0.0014	7.2015	7.1638	0.1389	0.1396
0.0016	7.2706	7.0347	0.1375	0.1421
0.0018	7.3612	7.1922	0.1358	0.1390
0.0020	7.4705	7.3508	0.1338	0.1360

Table-5
Viscosity and fluidity of complex solutions of CP[BTA]A and CP[PTU]A in 40% propanol + 60% benzene mixture

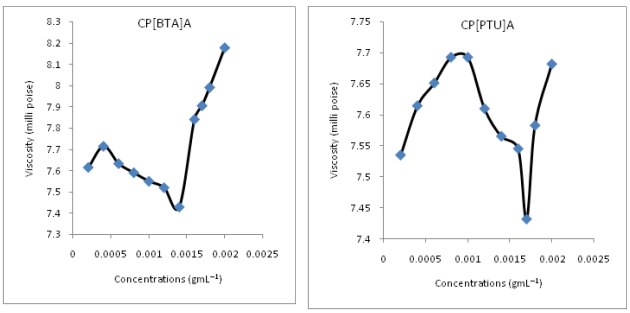
Concentration of complex in g mol L^{-1}	VISCOSITY		FLUIDITY	
	CP[BTA]A	CP[PTU]A	CP[BTA]A	CP[PTU]A
0.0002	7.6160	7.5348	0.1313	0.1327
0.0004	7.7148	7.6142	0.1296	0.1313
0.0006	7.6337	7.6509	0.1309	0.1307
0.0008	7.5912	7.6924	0.1317	0.1300
0.0010	7.5511	7.6924	0.1324	0.1300
0.0012	7.5210	7.6096	0.1329	0.1314

0.0014	7.4302	7.5650	0.1345	0.1321
0.0016	7.8408	7.5450	0.1275	0.1325
0.0017	7.9050	7.4315	0.1265	0.1345
0.0018	7.9905	7.5825	0.1251	0.1318
0.0020	8.1765	7.6815	0.1223	0.1302

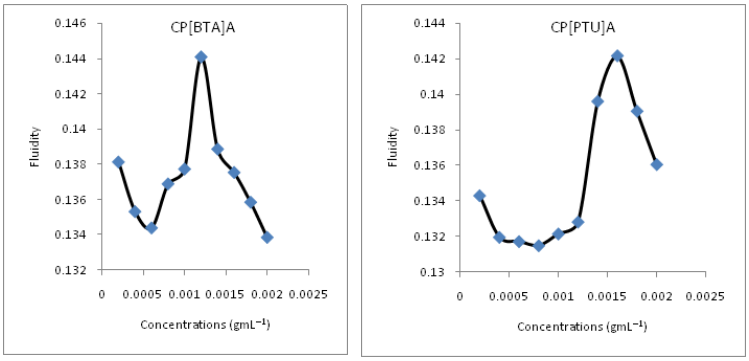
Plots of Viscosity vs. Concentration for CP[BTA]A and CP[PTU]A in 20% propanol – 80% benzene system



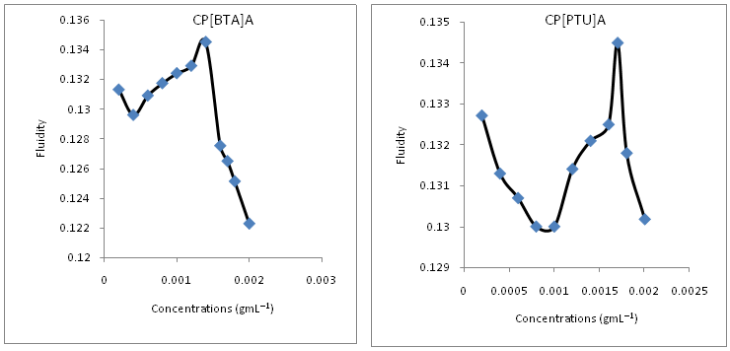
Plot of Viscosity vs. Concentration for CP[BTA]A and CP[PTU]A in 40% propanol – 60% benzene system



Plots of Fluidity vs. Concentration for CP[BTA]A and CP[PTU]A in 20% propanol – 80% benzene system



Plots of Fluidity vs. Concentration for CP[BTA]A and CP[PTU]A in 40% propanol – 60% benzene system



The data reveals that solute-solute interaction are greater before cmc as compared to after cmc.

Viscometric measurements of CP[BTA]A and CP[PTU]A complex in benzene + propanol solvent mixture of varying composition provide a useful information regarding cmc (critical micelle concentration) and clustering phenomenon present in between solute-solute or solute-solvent molecules.

The viscosity of these complexes in non-aqueous solvent mixture of benzene and propanol initially increase with complex concentration and then decreases at a particular concentration corresponding to cmc and after this viscosity again increases with the increase in complex concentration. The plot of viscosity vs concentration are characterized by an interaction of convex curve (wr. to X axis) and straight line at a point correspond to cmc of the complex solution. The value of cmc follow the order:

CP[PTU]A > CP[BTA]A.

This observation supports the fact that cmc decreases with the increase of average molecular weight of the complex. It is noticed that cmc values are dependent on the composition solvent mixture when the concentration of non polar solvent (benzene) predominates the early micelles formation takes place. Propanol takes quite different position in the mecille formation and the complexes exhibit different degree of aggregation in the mixed solvent system of varying compositions.

It is observed that viscosity and fluidity is not only dependent upon the solute complex concentration but on propanol composition also. This changes is attributed due to the change in agglomeration of solute entity both below and above cmc at different propanol composition.The value of cmc obtained from the plots of viscosity (h) vs concentration (C) in different compositions of solvent mixture follows the order

CP[BTA]A (40% propanol) > CP[BTA]A (20% propanol)

CP[PTU]A (40% propanol) > CP[BTA]A (20% propanol)

Conclusion

We can conclude that cmc values increase with increasing volume percent of propanol suggesting that there is an increase in the interactions between polar solvent and complex molecules which reduces the tendency of micellizaiton and cmc (becomes higher) increases. Aggregation of the complex molecule is delayed in the predominance of polar solvent in benzene-propanol mixture.

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