Research Article

Viscometric Evaluation of Azole Derivatives in Non-Aqueous Solvent System

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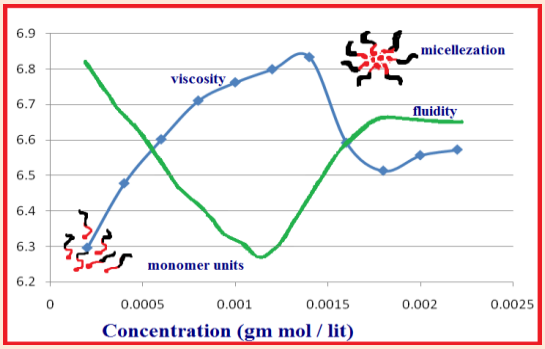
Abstract

Macrocyclic complexes of sulphur and nitrogen containing ligands have their great utility in biochemical and industrial fields. In relevance to aforesaid applications, the present communication deals with synthesis of such valuable heterocyclic. Among them transition metal complexes shares a significant place. For the same, surfactants derived from common fatty acid were complexes with bio-active ligands. The molar ratio of soap to ligands (1:2) respectively was used in reaction. Dull black coloured, powdered compounds were obtained with molecular formula 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 benzothiazole. Purity of complexes was checked by silica gel method. On the basis of elemental analysis, IR, NMR, ESR and Mass spectral studies interesting results relating to their molecular structures were obtained. Physico-chemical investigations were performed deeply. In this context, viscometric parameters were measured by Ostwald's viscometer and were thoroughly studied. All the experiments were performed in benzene-propanol solvent system of varying composition. Accordingly their fluidity and CMC values were co-related. CMC is the total surfactant concentration at which a small and constant number of surfactant molecules are in aggregated form.

Keywords: Viscosity, Critical Micelle Concentration, Fluidity, Benzothiazole, Copper Surfactants



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Introduction

Recently researchers' attentions have been focused on inter-disciplinary areas of co-ordination chemistry [1–2]. This has been partially a result of various synthesised valuable chemicals, their novel structures and physico-chemical colloidal properties. Surely, these properties can be important and informative for understanding the structural insight, miceller outlook, molecular structure, efficiency of a chemical regarding specific activity.

In the last decade, various hetero-atomic ligands have been extensively studied. Among them nitrogen and sulphur donor ligands containing azole ring systems are highly valuable [3–4]. Furthermore, complexation of these ligands with transition metal ions bears number of potential applications. The increased tendency of such moieties may be attributed to aromaticity, conjugated double bonds, electron density on donor atoms, presence of basic groups like amine, activeness of functional groups etc. On the other hand, sometimes it becomes difficult to differentiate the enhancement of property is due to solvent or due to structural effect.

Summarizing the literature survey, we can say that all the factors which directly or indirectly influence any physical characteristics of complexes are worth to be co-related and studied. Studies of immense importance relating

to above context are viscosity, density, surface tension, fluidity [5–9] etc. Surprisingly not much of the work has been done in this area.

As said before, physical properties of solution have proven to be a very useful tool in elucidating the structural interactions among components. Different factors may be dominant in different conditions influencing a part or whole of the property. Further, such colloidal aspects of liquid mixtures are of interest to chemical industries and chemical engineering [10].

Similarly, viscometric properties of mixed solvent systems of complexes containing nitrogen and sulphur and their dependence on different composition of solvent have found applications in many important chemical, industrial, and biological processes. Few workers have reported viscosities in binary [11–15] and ternary [16–18] liquid mixtures. The study of functions such as specific viscosity and fluidity etc. of binary mixture are useful in understanding of nature and strength of molecular interactions between the components molecules [19–20]. The importance of solute-solvent interaction and nature of solvation has been widely emphasised [21]. Since, most of the reactions of chemicals and biological interest occur in solution; understanding of solvation phenomenon demands extensive studies of physical properties of electrolyte and non electrolytes in aqueous, mixed and non aqueous solvents [22].

For the same, we have synthesised copper complexes with nitrogen and sulphur donor ligands. All the characterization of complexes was done through standard procedures. Following pages will reveal our approach of investigation for profiling structural insight, physico-chemical colloidal evaluation and generalisation of compounds under study.

Experimental

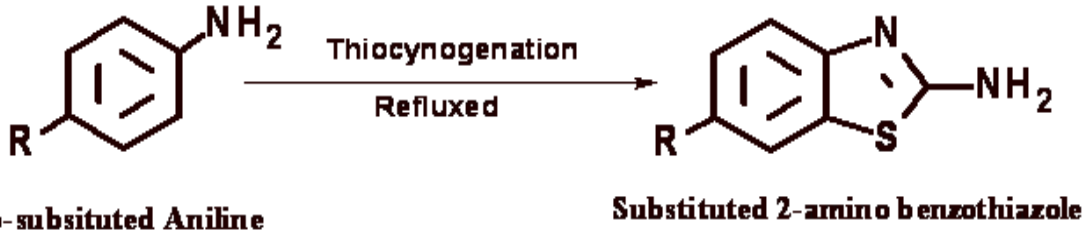
Materials and reagents

All chemical used were of A.R. Grade. Substituted aniline used purchased from Merck and were used as received. All solvents were purified by standard procedures [23]. Purity of compounds was checked by T.L.C. The melting points were determined by electric melting point apparatus and in corrected.

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 gm 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 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 recrystallized with ethanol.



Here, R = Br

Scheme 1 Synthesis of p- Bromo Benzothiazole

Synthesis of Copper Surfactants

Copper palmitate/Copper Caprylate was prepared by mixing one gm 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 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 colour soap is formed. Filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene.

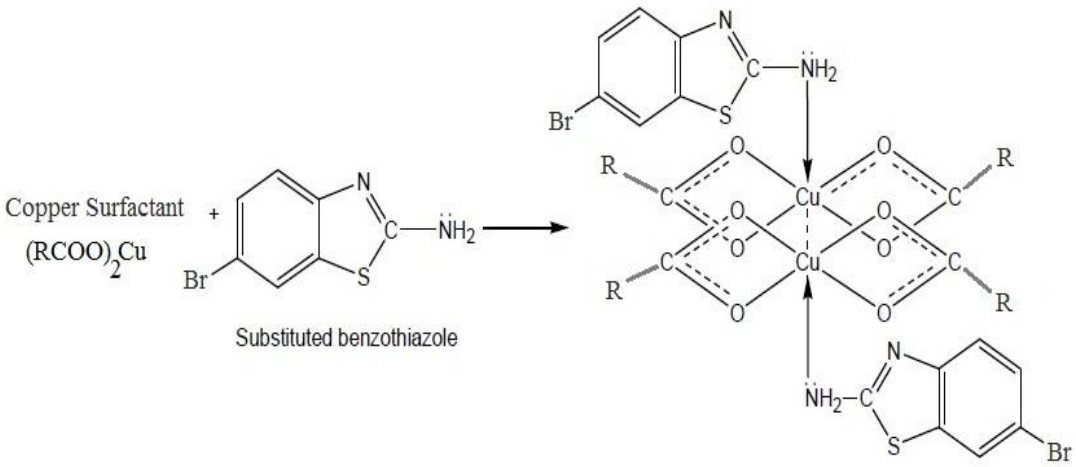
$C_{15}H_{31}COOH$ + C_2H_5OH + $CuSO_4$ ⟶ $(C_{15}H_{31}COO)_2Cu$
Palmitic Acid Ethanol Copper Sulphate Copper palmitate

$C_7H_{15}COOH$ + C_2H_5OH + $CuSO_4$ ⟶ $(C_7H_{15}COO)_2Cu$
Caprylic Acid Ethanol Copper Sulphate Copper caprylate

Scheme 2 Synthesis of Copper Surfactants

Preparation of Copper 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 two hours with constant stirring. After cooling the precipitate were filtered, dried and recrystallized with hot benzene.



Here R= $C_{15}H_{31}$ for Copper Palmitate and R= C_7H_{15} for Copper Caprylate

Scheme 3 Synthesis of Complex

Results and Discussion

Viscosity of a substance is it's resistance to flow. Ostwald's type viscometer was used for measuring the viscosity of the solutions of varying concentrations of complexes. The viscosities were calculated thermostatically by relationship:

$$\frac{\eta_o = d_o\, t_o}{\eta = d\, t}$$

Where η_o, η, d_o, d, t_o, t are the viscosity, density and time of flow for the known and unknown solutions respectively. The accuracy of the results was checked by determining the viscosity of known solutions and the agreement was found to be good and the difference was 0.3%. All measurements were made at constant temperature (303 K) in thermostat. The viscosity results are expressed in millipoise.

All the viscometric measurements of synthesized complexes in benzene plus propanol solvent system of varying compositions provide a useful information regarding critical micelle concentration (cmc) and clustering phenomenon present in between solute-solute or solute-solvent molecules.

Also "fluidity" of complexes under study was deeply investigated. It is defined as the ease of the substance to flow smoothly. It is reciprocal coefficient of viscosity.

$$\Phi = 1/\eta$$

The trends of fluidity were inverse to that of viscosity. Fluidity of complexes first decreases than increases showing a concave nature of curve upto the cmc. After the cmc the graph shows decreasing trend.

Table 1 Viscometric parameters for synthesized complexes in 20-80 propanol-benzene solvent system

CONCENTRATIONS (gm mol/ lit)	CP(BTA)	CC(BTA)
0.0002	5.3391	5.9664
0.0004	5.397	6.1317
0.0006	5.4871	6.2367
0.0008	5.5978	6.3002
0.0010	5.6531	6.3785
0.0012	5.4732	6.4100
0.0014	5.3755	6.0179
0.0016	5.5779	6.0003
0.0018	5.7691	6.2844
0.0020	5.8887	6.3950

Table 2 Viscometric parameters for synthesized complexes in 40-60 propanol-benzene solvent system

CONCENTRATIONS (gm mol/ lit)	CP(BTA)	CC(BTA)
0.0002	5.6261	6.2962
0.0004	5.7372	6.4778
0.0006	5.8559	6.6019
0.0008	6.0348	6.7108
0.0010	6.1210	6.7623
0.0012	6.2117	6.7993
0.0014	6.0041	6.8335
0.0016	5.9117	6.5921
0.0017	6.1265	6.2010
0.0018	6.4972	6.5134
0.0020	6.5372	6.5569

Table 3 Fluidity parameters for synthesized complexes in 20-80 propanol-benzene solvent system

CONCENTRATIONS (gm mol/ lit)	CP(BTA)	CC(BTA)
0.0002	0.1873	0.1676
0.0004	0.1852	0.1630
0.0006	0.1822	0.1603
0.0008	0.1587	0.1786
0.0010	0.1768	0.1567
0.0012	0.1827	0.1560
0.0014	0.1860	0.1661
0.0016	0.1666	0.1792
0.0018	0.1733	0.1591
0.0020	0.1698	0.1563

Table 4 Fluidity parameters for synthesized complexes in 40-60 propanol-benzene solvent system

CONCENTRATIONS (gm mol/ lit)	CP(BTA)	CC(BTA)
0.0002	0.1772	0.1588
0.0004	0.1743	0.1543
0.0006	0.1707	0.1514
0.0008	0.1657	0.1490
0.0010	0.1633	0.1478
0.0012	0.1609	0.1470
0.0014	0.1665	0.1463
0.0016	0.1691	0.1517
0.0017	0.1632	0.1612
0.0018	0.1539	0.1535
0.0020	0.1529	0.1525

Graphical interpretations:

The graphical forms of tables can be presented as follows

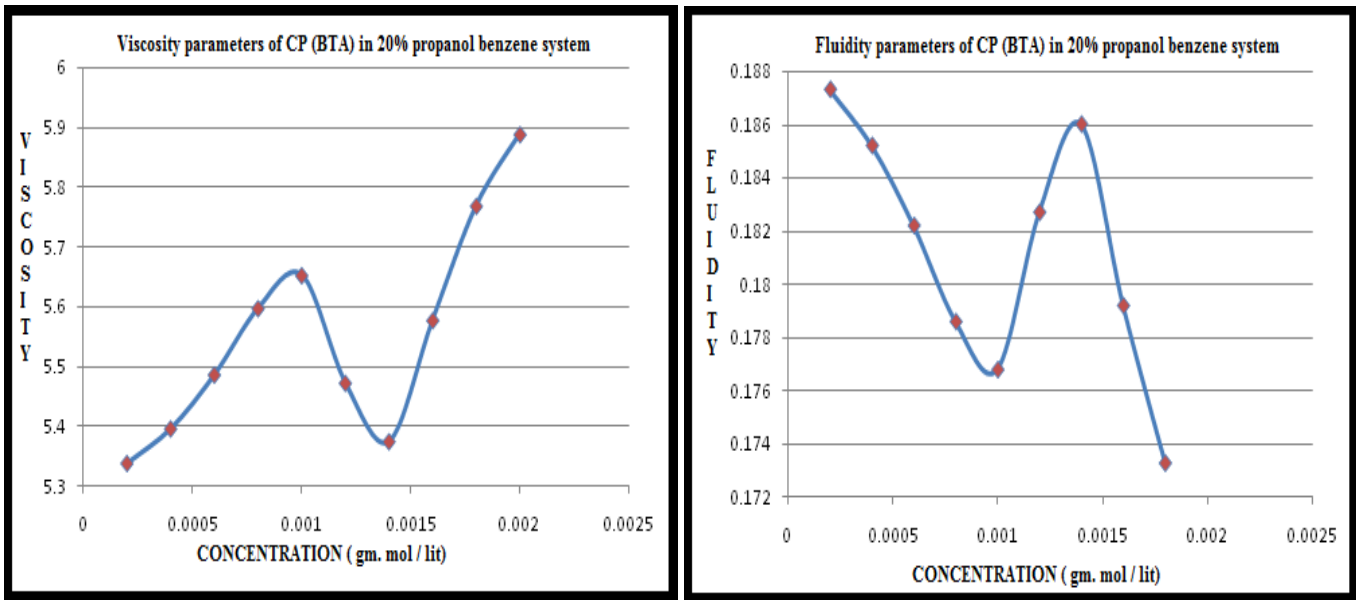


Figure 1 Viscometric and fluidity plots for CP(BTA) in 20-80 propanol-benzene system

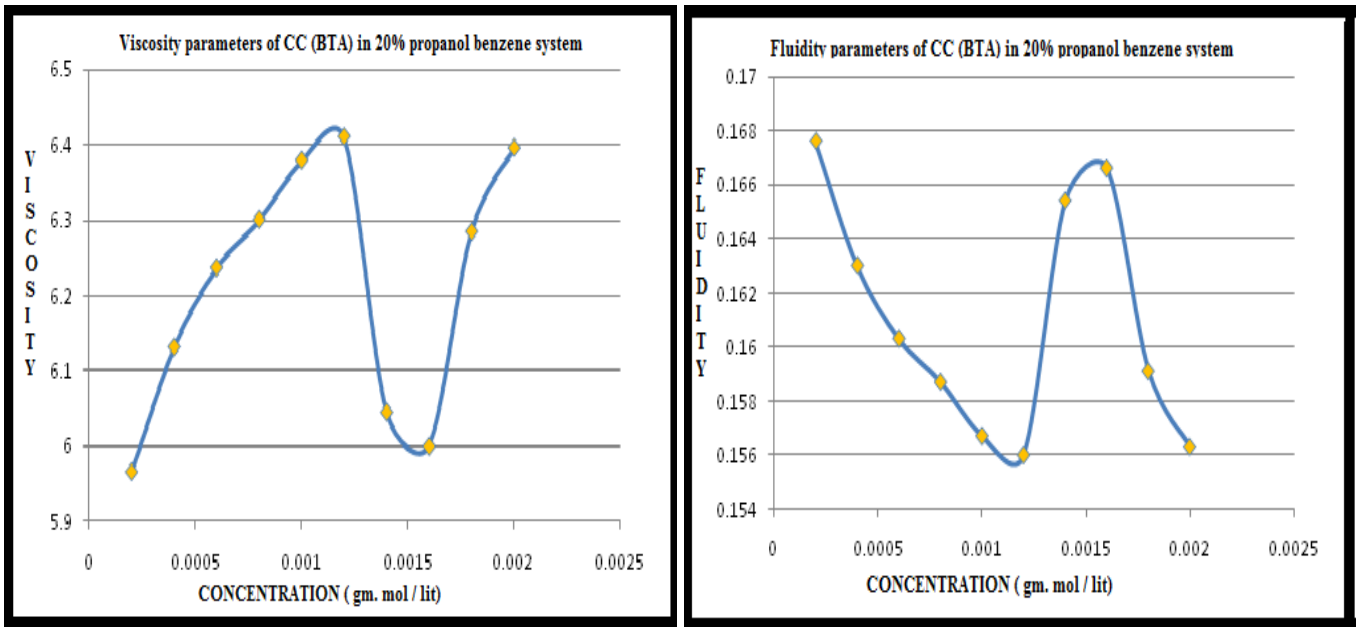


Figure 2 Viscometric plot for CC(BTA) in 20-80 propanol-benzene system

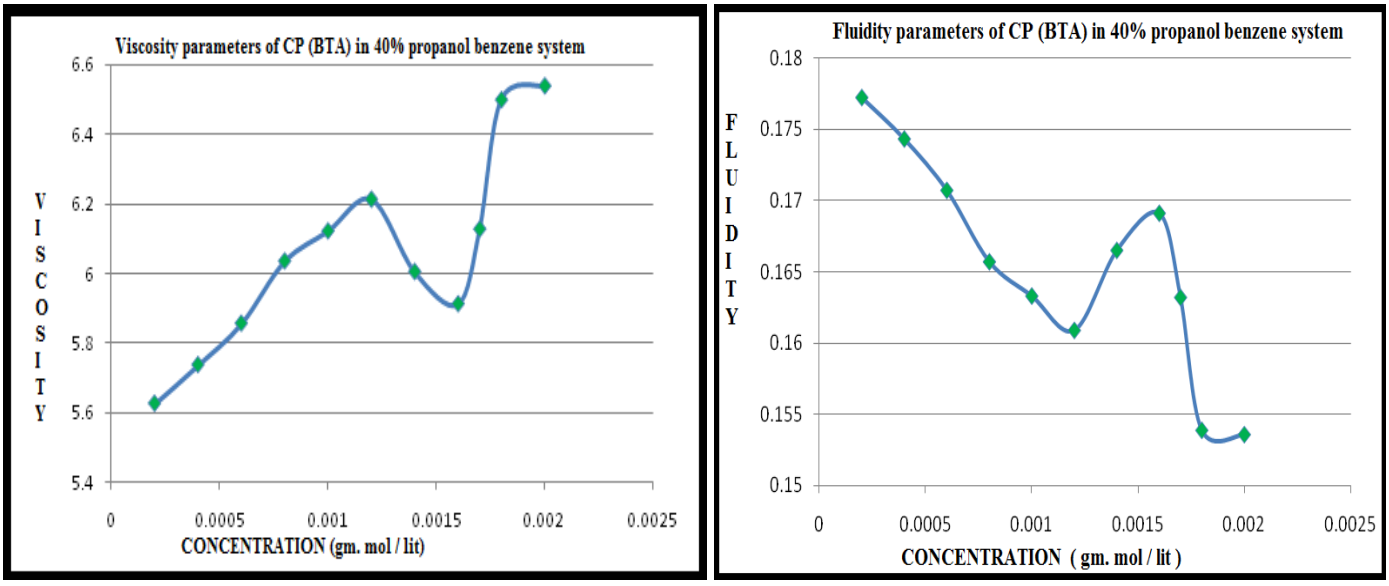


Figure 3 Viscometric and fluidity plots for CP(BTA) in 40-60 propanol-benzene system

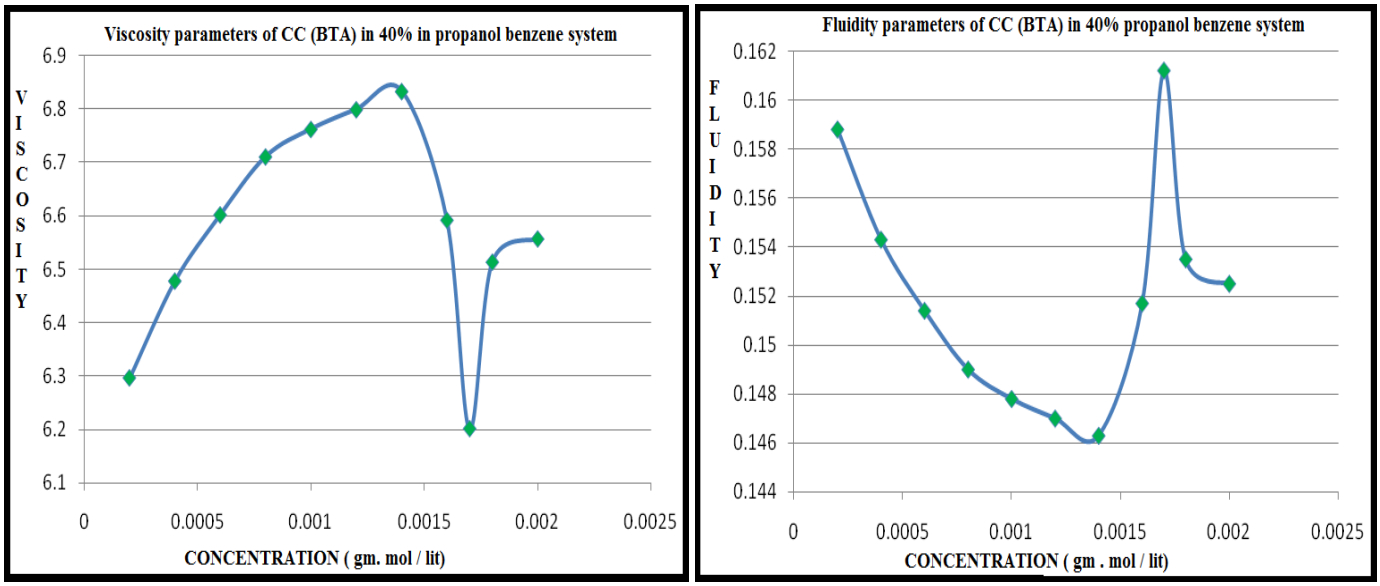


Figure 4 Viscometric and fluidity plots for CC(BTA) in 40-60 propanol-benzene system

From the plots, it is clear that the viscosity of synthesised complexes initially increases with increase in complex concentration and then decrease at particular concentration corresponding to the cmc. After this the viscosity again increases with the increase in complex concentration. This increase in viscosity may be due to the increasing tendency of solute molecules to associate in form of clustering entity in the complex solvent system.

The plot of viscosity (η) against complex concentration (C) are characterised by intersection of convex curve (w.r.t. x axis) and straight line at appoint corresponding to cmc of the complex solution. Indeed this is the utmost concentration of molecular dissemination where reconciliation of internal forces in inducing the establishment of complex conglomeration. At cmc, the hydrocarbon chain structure of complexes allows extensive contact between adjacent chains, possibly accompanied by changes in vibrational and rotational degree of freedom of methylene group.

The values of cmc follow order: CP (BTA) < CC (BTA)

This is agreement with the fact the there is a decrease in the cmc value with the increase of average molecular weight of the complex.

Conclusion

Colloidal behaviour of copper(II) soap complexes play a significant role in their selection in various fields like preservatives, herbicidal, pesticidal activities, detergency, paints, lubrication. In biological systems, these agents are vital components and useful in many industrial process. All these properties led us to study micellar features of various copper soap complexes for their possible uses and applications in agriculture and industries. The viscosity of soap solution has been investigated with a view to understand the nature, critical micelle concentration and micellar characteristics of the complexes.

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