STUDIES OF CMC, SOLUTE – SOLVENT AND SOLUTE – SOLUTE INTERACTIONS OF COPPER (II) SOAPS DERIVED FROM EDIBLE OILS IN METHANOL – BENZENE SYSTEM AT 303 K

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ABSTRACT

Copper soaps prepared from various edible oils have been analyzed for their micellar characteristics in non-aqueous media with different polarities. The present work deals with the study of copper (II) mustard (CM) and soyabean (CSo) soap in 20% and 40% methanol – benzene system. Density of soap solutions of various concentrations has been measured and by using density data, molar volume and apparent molar volume has been evaluated in order to determine the critical micelle concentration (cmc) in different solvent compositions, nature and size of the micelles formed and to test the validity of Masson equation, which provides a plausible explanation for solute – solvent and solute – solute interactions with the variation in the polarity of the solvent. The cmc values have been found to be greater in higher volume percent of methanol than those in higher volume percent of benzene.

It has been observed that apparent molar volume decreases with the increase in the polar content in the solvent mixture for both the soaps ϕ_v (20%) > ϕ_v (40%). The apparent molar volume for CM soap is found to be higher than that of CSo soap for both the solvent compositions. Further, it has been observed that as the number of ionic polar heads increases in the soap content, the solute – solvent interaction also increases in both solvent mixtures i.e. $\phi^0 v_2$ (CSo) > $\phi^0 v_2$ (CM)

Key words: Critical micelle concentration (CMC), Copper (II), Edible oil, Soaps

INTRODUCTION

Anionic surfactants containing copper ions are vital components in biological systems and play an important role as an useful agent in many industries like paints, varnishes, water proofing and repellency, protection of crops, preservation of wood,

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lubrication etc.[1-4]

The colloido–chemical behavior of Cu (II) surfactants are gaining popularity on account of their utilitarian effect such as foaming, emulsification and fungicidal activities[5-8].

Colloidal behavior of copper (II) soaps in non-aqueous solvent has been investigated by Mehrotra et al.[9] Inspite of all these applications, copper surfactants have not been explored thoroughly. All these important applications led us to investigate the micellar features of copper (II) soaps derived from various edible oils in different solvents. These oils have been specially chosen, as they are easily available in the market and may be used in various fields as a biodegradable product.

EXPERIMENTAL

All the chemicals used were of LR/AR grade. Copper soaps were prepared by refluxing the mustard seed oil extracted directly through cold pressing technique and refined soyabean oil of reputed brand available in the Indian Market, with 2N KOH solution and alcohol for about 3 hours. The excess of KOH was neutralized using 1N HCl. The saturated solution of copper sulphate was added to it. The copper soap so obtained was filtered, dried at 50^0C and recrystallised from hot benzene. The formation of copper soap was confirmed by using UV, IR techniques and elemental analysis[10]. The purity of the soap was confirmed by T.L.C.

Purification of benzene 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 80^0C.

Methanol was purified by keeping over potassium hydroxide for twenty four hours and then distilled. The distillate was refluxed with 1% of calcium metal for about eight hours and then again distilled. The fraction at 60^0C was collected for experimental purpose.

The calculated amount of the soap was weighed in a volumetric flask and the solutions containing different concentrations of copper soap in methanol – benzene mixtures of varying compositions were prepared. Ostwald's modification of the Springel pyknometer with a volume of about 15 mL, which allowed an accuracy of about one unit in the fourth place of decimal was used for measuring the density of the soap solution in a thermostated water bath at 303 K ($\pm$ 0.1% accuracy).

Average molecular weight of the soap was calculated by saponification equivalent value of the oil (Table 1) and has been reported earlier[11,12].

Fatty acid compositions of both oils used are given in Table 2. The quantitative estimations of methyl esters were carried out using two different GLC units ; (a) F & M Model 720 and (b) Perkin–Elmer Model 154 equipped with thermal conductivity detectors.

Evaluation of molar volume and apparent molar volume

The molar volume of the soap solution, V has been calculated by the relationship:

$$V = (X_1 M_1 + X_2 M_2 + X_3 M_3) / \rho \qquad \ldots (1)$$

Where X_1 is the mole fraction of the soap of molecular weight, M_1 where as X_2 and X_3 are the mole fractions of the solvent of molecular weight M_2 and M_3, respectively and ρ is the density of the solution.

The apparent molar volume has been calculated with the error limit of ±0.2% from the density data by using the following equation[13,14] –

$$\phi_v = M/\rho_0 + 1000(\rho_0 - \rho) / C. \rho_0 \qquad \ldots (2)$$

Where ρ_0, ρ, M and C are density of solvent and solution, molecular weight of the soap and concentration of solution in g mol L^{-1}, respectively.

Table 1. Analytical and physical data for copper soaps derived from edible oils

Name of copper soap	Colour	Melting Point (^{0}C)	Yield (%)	% Metal content		S.V.	S.E.	Average Mol. wt.
				Obse.	Calc.			
CM	Green	91	80	9.58	9.11	175.80	319.10	699.724
CSo	Green	110	90	10.80	10.303	194.90	287.83	637.17

Table 2. Fatty acid composition of oils used for copper soap synthesis

Name of oil	% Fatty Acids					
	16:0	18:0	18:1	18:2	18:3	Other acids
Mustard oil	2	1	25	18	10	C_{20}- C_{24} − 41%
Soyabean oil	12	4	24	51	9	-

RESULTS AND DISCUSSION

In continuation of our previous studies[12], it has been found that the density of copper–mustard and copper–soyabean soap solutions in 20% and 40% methanol – benzene mixture initially increases with the increase in soap concentration and then decreases at a particular concentration corresponding to the critical micelle concentration (cmc)[12]. After this, density again increases. The value of density for copper (II) soap in 20% Methanol – benzene mixture is higher than that of 40% methanol – benzene mixture. These differences may due to the varying influence of the polar group at the end of long hydrocarbon chain on the packing density in liquid state. [15]
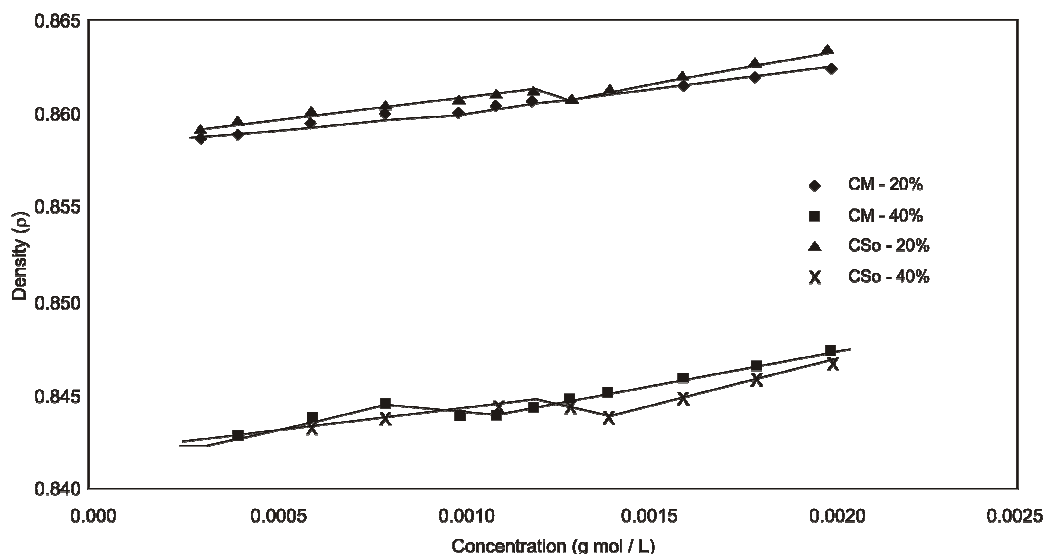

Fig. 1: Plots of density v/s concentration for copper soaps derived from edible oils in methanol-benzene mixtures

The plots of density 'ρ' versus 'c' g mol L^{-1} are characterized by an intersection of

a straight line followed by a slight concave curve (with respect to x-axis) and a straight line (Fig. 1) at a definite soap concentration, which corresponds to the cmc of the soap. It indicates that aggregation of soap molecules occurs at this point. Of course, this is the maximum concentration of molecular dispersion at which there is a balancing of internal forces causing the formation of micelles. The density and cmc of the soap follows the order

$$CSo > CM.$$

A perusal of Table 2 suggests that the density increases with the increase in shorter fatty acid content in the corresponding oil composition. The above trend clearly demonstrates that association of soap molecules occur at low concentration in mustard as compared to soyabean soap. The value of cmc of Copper (II) soaps derived from both edible oils in 40% methanol–benzene mixture is higher than 20% methanol – benzene mixture

$$CSo (40\%) > CSo (20\%)$$

This may be attributed to the fact that aggregation of the soap molecules is delayed in the dominance of polar solvent in the solution mixture as compared to the predominance of non-polar solvent in solution mixture. The cmc is further confirmed by viscometric and ultrasonic studies for the referred system.
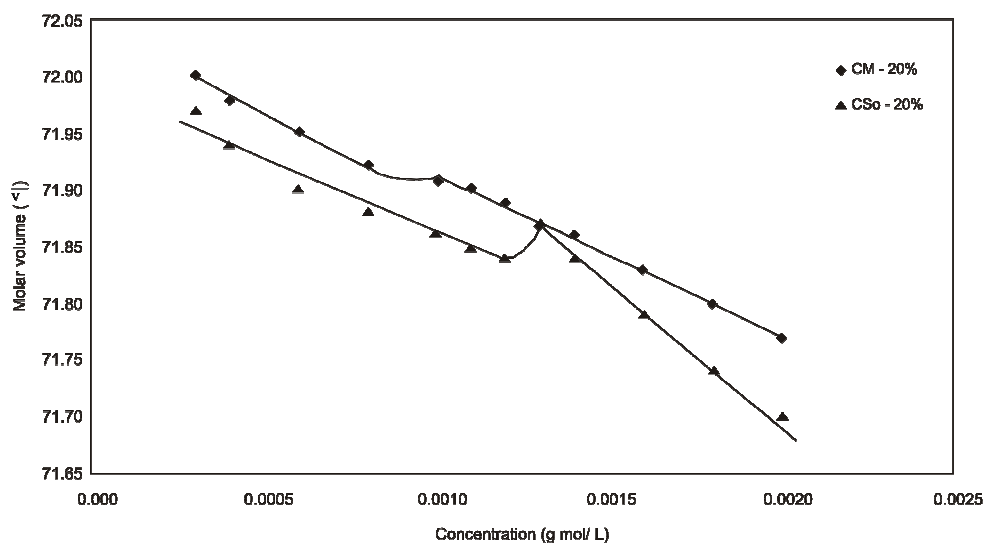

Fig. 2: Plots of molar volume v/s concentration for copper soaps derived from edible oils in methanol-benzene mixtures

The molar volume V was calculated from density data and the comparison of the results indicates that values are higher for copper (II) mustard soap than copper (II) soyabean soap in both 20% and 40% methanol – benzene mixture.

The plots of V versus C are characterized by an intersection of a convex curve (with respect to x – axis) and a straight line (Fig. 2). It is revealed from the data that the values of V for the soap solution decreases with the increase in the concentration of soap.

Below cmc, a straight line followed by a convex curve was increasing trend is observed, and after cmc there is a sharp decrease in the molar volume. The values of molar volume V for 40% methanol – benzene mixture are lower than that of 20% methanol – benzene mixture. It is, therefore, concluded that the nature of solvent plays a significant role in ordering and compacting the scattered micellar units.

The cmc of soaps obtained from molar volume V vs C plots follow the order

$$CSo > CM$$

This observation is in agreement with the fact that there is a decrease in the cmc value with the increase of the molecular weight of the soap.[16-18]

It is also known that the cmc decreases by about one third per methylene group in aqueous solution, but this change is smaller in aqueous solutions because the energy required to transfer a methylene group from micelle to bulk is small because intermolecular forces are stronger in polar solvents like water and methanol where as intermolecular forces are weaker in non-polar solvents like benzene.[19]

The apparent molar volume of copper (II) soap solution in non-aqueous media is calculated by using equation (2).

The plots of ϕ_v versus $\sqrt{c}$ are characterized by an intersection of two straight lines at a point, which corresponds to the cmc of CSo soap (Fig. 3). The value of ϕ_v increases sharply below cmc, and after cmc a straight line in a decreasing trend is observed in CSo soap for 20% methanol-benzene solvent mixture, whereas for CSo (40%), the plot follows a slightly different trend in which an intersection is observed at cmc between a straight line followed by a curvature nature with increasing trend and a straight line with decreasing trend. The plots of ϕ_v versus $\sqrt{c}$ for CM soaps are characterised by an intersection of convex curve and a straight line in both 20% and 40% methanol–benzene solvent mixtures
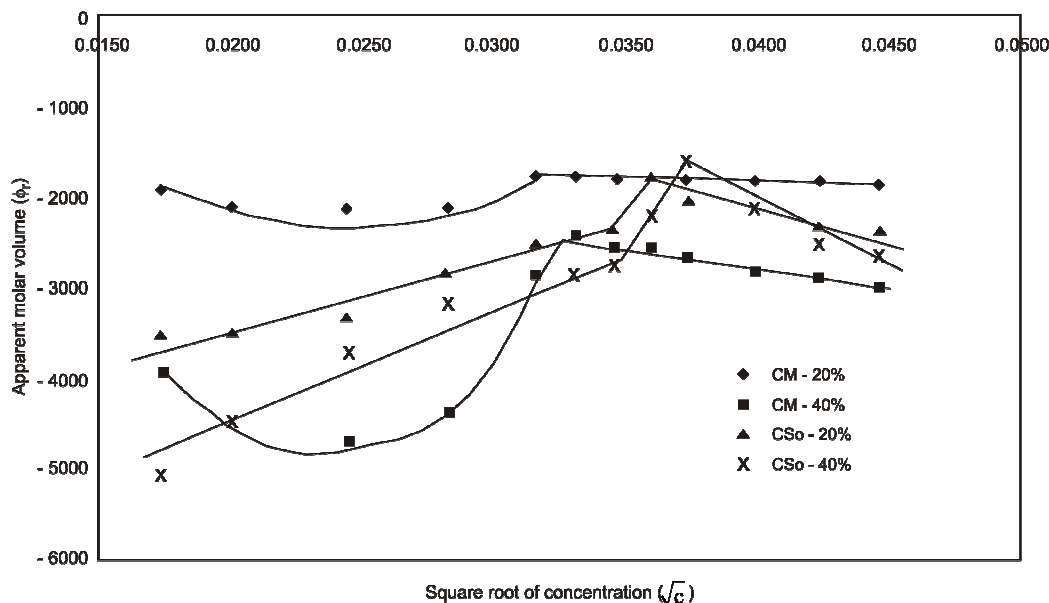
(Fig. 3).

Fig. 3: Plots of apparent molar volume v/s square root of concentration for copper soaps derived from edible oils in methanol-benzene mixtures

Various factors such as solvation of amphiphilic solutes, electrostriction of methanol molecules by charged moieties, nature of ionic head group and length of non-polar portion of amphiphilic molecules contribute to apparent molar volume. It has been also observed that apparent molar volume decreases with the increase in methanol percentage and follows the following order in dilute solutions: ϕ_v (CM) > ϕ_v (CSo) . This may be due to counter ion binding, which in general increases with the increasing alkyl chain length for ionic surfactants and is decreased by addition of alcohols.[20]

The cmc obtained from plots of ϕ_v versus $\sqrt{c}$ also follow the same order as observed for density and molar volume. The values of cmc obtained in this study is also confirmed by other physical properties studied like ultrasonic velocity and viscosity and follows the order

CSo > CM

This is in agreement with the fact that there is a decrease in cmc values with the increase in the average molecular weight of the soap. This may be attributed to the fact that

increasing the size of the alkyl group will decrease cmc. (Table 4)[21].

Table 3.

Methanol % in the solvent mixture	Soap derived from	$\phi^0_{v1} \times 10^{-2}$	$\phi^0_{v2} \times 10^{-2}$	S_{v1}	S_{v2}
20%	Mustard oil	~	-16.4	~	-0.1051
	Soyabean oil	-38.50	+2.0	+1.5398	-1.6003
40%	Mustard oil	~	-13.2	~	-0.4244
	Soyabean oil	-51.50	+25.0	+1.4281	-1.8040

The data has been analysed in terms of Masson equation. This equation fits well for above cmc in CM and CSo, while in CM below cmc, due to presence of curvature nature it is applied only at the initial part of the plot consisting dilute concentration range and having straight line trend.

Computed parameters ϕ_v, S_v of Masson equation for copper (II) mustard and soyabean soap in methanol – benzene mixture at 303 K.

Table 4. CMC of copper (II) mustard and copper (II) soyabean soap in methanol – benzene at 303 K

Physical parameter	Soap–Solvent			
	20% Methanol–benzene mixture		40% Methanol–benzene mixture	
	CM	CSo	CM	CSo
Density	0.0010	0.0013	0.0011	0.0014
Molar volume	0.0010	0.0013	0.0011	0.0014
Apparent molar volume	0.0010	0.0013	0.0011	0.0014

The value of limiting apparent molar volume (ϕ^0_v) for both the soap solutions is obtained from extrapolation of ϕ_v versus $\sqrt{c}$ plots to $c \rightarrow o$ and there are two values of ϕ^0_v referred to as ϕ^0_{v1} (below cmc) and ϕ^0_{v2} (above cmc) (Table 3).

It is obvious from the table that solute – solvent interaction for both the solutes follows the order

$$\phi^0_{v1} < \phi^0_{v2}$$

This shows that soap – solvent interaction is more pronounced in concentrated solution. This may be ascribed due to the favorable interaction between soap and solvent molecules at the post–micellar concentration.

Above cmc, solute – solvent interaction becomes more prominent than solute – solute interaction. The result also suggests that solute – solvent interaction follows the order

$$\phi^0_{v2} \text{ (CSo)} > \phi^0_{v2} \text{ (CM)}$$

Thus, the solute – solvent interaction increases with the increase in the shorter fatty acid content in the oil. This observation clearly indicates that as the number of ionic polar heads increases in the soap content, the solute – solvent interaction increases in both the solvent mixtures (20% methanol – benzene and 40% methanol – benzene). Solute – solvent interactions are also greater above cmc in the predominance of methanol in the solvent mixture as compared to hydrocarbons

$$\phi^0_{v2} \text{ (40\%)} > \phi^0_{v2} \text{ (20\%)}$$

This may be attributed to greater interaction between polar group of soap molecules and hydrogen bonded alcohols[22,23], which are responsible for greater partial molar volumes in the dominance of methanol. In general, copper (II) soyabean soap is more prone to solute – solvent interaction as compared to copper (II) mustard soap in mixture solvents.

The parameter S_v in Masson's equation represents the limiting apparent slope and indicates the existence of solute – solute interactions. It is reasonable to determine two values of parameters S_v below and above cmc designated as S_{v1} and S_{v2}, respectively. Enumerated values have been summarized in Table 3. With regards to chain length of the soap, the values of S_v follow the order –

$$S_{v2} \text{ (CSo)} > S_{v2} \text{ (CM)}$$

The data also revealed that within the micellar palisade layers, after cmc solute – solute interaction are lower for soyabean soap in comparison to mustard soap due to the presence of lower fatty acid content in the oil. For both the soaps, with respect to solvents

the observed order is – $S_{v1} > S_{v2}$ (20 % and 40%). It has also been observed that for CSo soap the solute–solute interaction is found higher below cmc in comparison to above cmc for both the solvent mixture compositions.

For CSo, the studies reveal that S_{v1} (20%) > S_{v1} (40%) and S_{v2} (20%) > S_{v2} (40%), indicating that below cmc solute – solute interaction is found lower in the dominance of methanol content in the solvent mixture, which indicates that solute – solute interaction below cmc decreases between hydrophobic long chain of the solute molecules with the increase in the polarity of the solvent mixture. After cmc, the solute – solute interaction is also found higher in predominance of non-polar hydrocarbon i.e. which indicates that solute – solute interaction becomes greater in less polar solvent mixture.

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REFERENCES

1. M. D. Goff, R. L. Shumack, K. M. Tilt and A. K. Hagan, J. Arboriculture, **22**, 201 (1996).

2. J. L. Soyez, Brighton Crop Protection Conference on Pests and Diseases, **1**, 451 (1992).

3. D. Conradie, P. Turner, W. E. Conradie, J. Pandle Gurry and T. Pizzi, Bibliographic Citation, Stockholm, Sweden, 22 (1995).

4. P. S. Nikam, H. R. Ansari and Hassan Mehdi, J. Indian Chem. Soc., **76**, 344 (1999).

5. V. Mark and J. Solbe, Chemosphere, **1**, 36 (1998).

6. J. H. Clint, Surfactant Aggregation, Chapman and Hall, New York, (1992).

7. M. R. J. Dack, K. T. Bird and J. Parker, Aust. J. Chem. , **26**, 955 (1975).

8. B. Jadrnicek and K. Vesely, Coll. Czech Chem. Commun. , 35, 358 (1970).

9. K. N. Mehrotra, V. P. Mehta and T. N. Nagar, J. Prakt. Chem. B., 312 (1970)

10. A. I. Vogel, A Text Book of Qualitative Inorganic Analysis, 4th Edition, Longman , London, (1985).

11.   An Introduction to the Chemistry of Fats and Fatty acids, F. D. Gunstone (Ed.), Chapman and Hall Ltd., London, (1958).

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

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

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

15.   B. R. Gaikwad and V. V. R. Subrahmanyam, J. Indian Chem. Soc., **65**, 266 (1988).

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

17.   S. Voyutsky, Colloid Chem., MIR Publication, Moscow (1978).

18.   H. R. Kruyt, Colloid Science, Elsevier Publication Company, New York (1969).

19.   V. P. Mehta, P. R. Talesara, and R. Sharma, Indian J. Chem., **39A**, 383 (2001)

20.   Y. Moroi, Micelles: Theoretical and Applied Aspects, Springer, International Edition (2005).

21.   L. Lepori and P. Gianni, J. Solution Chem. , **29**, 405 (2000).

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

23.   H. S. Harned and B. B. Dwen, Physical Chemistry of Electrokinetic Solutions, Reinhold (1958) p. 358.