



MICELLAR BEHAVIOUR AND SOLUTE-SOLVENT INTERACTIONS OF COPPER SOAPS (DERIVED FROM TREATED VEGETABLE OILS) IN NON-AQUEOUS SOLVENT

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ABSTRACT

copper soaps prepared from treated oils have been analysed for their micellar characteristics. Mustard and soyabean oils have been treated for 15 and 60 minutes. Densities of copper soap solutions of various concentrations have been measured and using density data, molar volume and apparent molar volumes have been evaluated. These parameters show a change at cmc, which suggests the micellar behaviour of the soaps. The critical micelle concentrations are found to decrease with increase in average molecular weight of the soap. The results of apparent molar volume have been explained on the basis of Masson's equation. The plots of apparent molar volume against \sqrt{c} are characterised by an intersection of two straight lines at the cmc of the soap. It has been observed that the solute-solvent interaction is more pronounced in dilute solutions while in concentrated solutions, solute-solute interaction becomes prominent. The cmc has been further confirmed by viscosity and acoustic parameters.

Key words: Micellar, Solute-solvent interaction, Copper soap.

INTRODUCTION

In our previous communication¹, the critical micelle concentration (cmc), solute-solvent and solute-solute interactions of copper soaps of untreated mustard and soyabean oils were analysed and discussed for various physical properties like density, molar volume and apparent molar volume. In the present work, the oils have been treated for 15 and 60 minutes and from them, copper soaps have been synthesized. Densities, molar volumes and apparent molar volumes have been measured and calculated as surfactants possess valuable characteristics such as wetting, emulsification, lubrications, wood preservation etc. and play a vital role in various fields like rubber industries, paints, water proofing etc²⁻⁵.

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Further the work has been elaborated to enumerate qualitatively the effect of the nature of solute on the micellar aggregate and to gain insight of the chain length compatibility in the midst of lucid micellar profile prevailing in such systems. These oils have been chosen specially as they are easily available in the market as a waste product after deep frying and they may be reused in various fields as a biodegradable products. To understand their micellar characterization, our studies will provide very significant and fundamental information.

EXPERIMENTAL

Mustard and soyabean oils available in the Indian market of reputed brand were chosen for the investigation. The oils in their purest form were taken. Their compositions have been confirmed by GLC methods. 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.

Oils were treated in the similar manner in the laboratory. They were treated for 15 and 60 minutes separately.

For preparation of treated oils, about 500 g oil was taken in an iron pan. The oil was heated to the highest temperature and 5 g potato chips were deep fried while maintaining the frying temperature between 180-200° C. The oil was heated for 15 and 60 minutes in the open air and sunlight in iron pan at 180-200° C. The volume of the oil was not replenished to the original volume after frying operations.

All chemicals used were of LR/AR grade. copper soaps from treated oils are prepared by direct metathesis. Oil was refluxed with 2 N KOH solution and alcohol for about 3 hours. The excess of KOH was neutralized using 1N HCl. Saturated solution of copper sulphate was added to it. The copper soap obtained was filtered, washed with hot water followed by alcohol, dried at 50°C and recrystallised from hot benzene. The purity of soaps was checked by elemental analysis and the results were in agreement with the theoretically calculated values (Table 1). The reproducibility of the results was checked by preparing the samples of the same soap under similar conditions.

The copper soaps synthesized are abbreviated as follows:

Copper soap derived from mustard oil treated for 15 minutes- CM₁₅

Copper soap derived from soyabean oil treated for 15 minutes- CS₁₅

Copper soap derived from mustard oil treated for 60 minutes- CM₆₀

Copper soap derived from mustard oil treated for 60 minutes- CS₆₀

Table 1. Analytical and physical data of copper soaps derived from various oils

Name of the soap	Melting point (°C)	Metal (%)		S. V.	S. E.	Average mol. wt.
		Found	Calculated			
CM	92	9.58	9.110	175.80	319.10	699.72
CS ₀	108	10.80	10.303	194.90	287.83	637.17
CM ₁₅	84	12.48	12.549	266.47	210.53	482.56
CS ₁₅	101	15.98	16.116	336.60	166.66	394.82
CM ₆₀	61	12.96	13.138	260.00	215.76	493.03
CS ₆₀	70	10.52	10.672	210.38	266.66	594.82

The formation of copper soaps was confirmed by IR and UV spectral analysis. The electronic absorption spectra of all copper soaps show one broad band at about 670-680 nm (14925- 14706 cm⁻¹) and a sharp band at about 280 nm (35714 cm⁻¹). One broad band may be attributed to 2E_g → 2T_{2g} transitions arising from MLCT (metal-ligand charge transfer) absorption bands, which confirms the formation of copper soaps.

In the IR spectra of these copper soaps, there is complete disappearance of the characteristic bands of esters and appearance of two new absorption bands in the region 1580-1610 cm⁻¹ and 1380-1400 cm⁻¹. These bands may be assigned to a symmetric and antisymmetric vibration of carboxylate ion. The disappearance of the characteristic bands of esters and appearance of the bands of carboxylate ion indicate the formation of copper soaps.

Comparing IR spectra of copper soaps of untreated oils and copper soaps of treated oils, it is found that there is absence of band in 3200-3600 cm⁻¹ region in copper soaps derived from untreated oils where as in the IR spectra of copper soaps derived from treated oils, the bands are present at about 3400-3500 cm⁻¹, 1750 cm⁻¹, 1625 cm⁻¹ and 1100 cm⁻¹. These bands may be due to formation of various autoxidised products such as enediol,

keto-hydroxide or carbonyl degradation products during heating the oil.

Determination of average molecular weight

Average molecular weight of soaps has been determined from saponification equivalent (S.E.) of the oil. The saponification equivalent (S.E) is the amount of material saponified by one gram equivalent of potassium hydroxide whilst the saponification value (S.V) is the number of milligrams of KOH required to hydrolyse one gram of material. The two being related by the expression:

$$S.E = 56100/S.V \quad \dots(1)$$

S.E may be taken as average molecular weight of the fatty acid, which forms the soap^{6,7}. Values of S.E are determined by experiments and from these values, average molecular weight of copper soaps was calculated.

The calculated amount of the soap was weighed in a standard flask and the solutions containing different concentration of soap in benzene were prepared. Ostwald's modification of the Springel Pyknometer was used for measuring the density of the soap solutions. The density of the solutions ' ρ ' was calculated by the relationship:

$$\rho = \frac{w}{w_0} \quad \dots(2)$$

Where w and w_0 are the weights of the same volume of the solution and water respectively.

The volume of pyknometer was taken as 15 mL, which allowed an accuracy of one unit in the fourth place of decimal. All the measurements were made at a constant temperature ($30 \pm 1^\circ\text{C}$) in the thermostat.

The molar volume of the soap solution \bar{V} has been calculated by the relationship;

$$\bar{V} = \frac{X_1M_1 + X_2M_2}{\rho} \quad \dots(3)$$

Where X_1 is the mole fraction of the soap of molecular weight M_1 and X_2 is the mole fraction of solvent of molecular weight M_2 . ' ρ ' stands for density of the solution.

The apparent molar volume ϕ_v has been calculated with the error limit of $\pm 0.2\%$

from the density using equation⁸.

$$\phi_v = \frac{M}{\rho_0} + \frac{1000(\rho - \rho_0)}{c \cdot \rho_0} \quad \dots(4)$$

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

RESULTS AND DISCUSSION

The density of copper soaps derived from treated oils for 15 and 60 minutes increases with increase in soap concentration. The plots of density with soap concentration are characterised by an intersection of two straight lines at definite soap concentration, which corresponds to the cmc of the soap (Fig. 1).

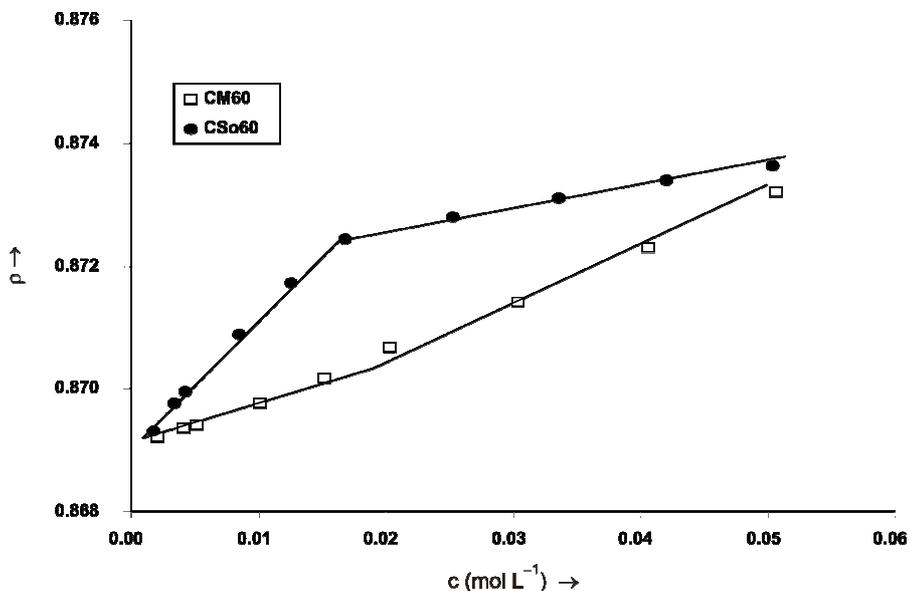


Fig. 1: Plots of density v/s soap concentration of copper soaps derived from treated oils for 60 minutes

At the cmc, there is a sudden change in the aggregation of the soap molecules. It is therefore concluded that the soap molecules do not aggregate adequately below cmc whereas at this definite soap concentration, there is a marked enhancement in the degree of aggregation of the soap molecules. The values of cmc are recorded in Table 2. The values

of cmc are further confirmed by viscometric and acoustic studies carried out by us for the same system (and are also given in the Table 2) by plots of viscosity and ultrasonic velocity against concentration. A perusal of Table 2 shows that cmc values are found higher for CSo₁₅ and CM₆₀ in comparison to CM₁₅ and CSo₆₀, respectively. This observation is in agreement with the fact that there is increase in cmc values with the decrease of the average molecular weight of the soap⁹⁻¹¹. It is evident that in the same solvent, the cmc value is found to be a function of number of carbon atoms present in soap molecule and it increases as the molecular weight or carbon chain length decreases¹². On comparing the cmc of untreated oil soaps with treated oil soaps, it has been observed that cmc increases as average molecular weight decreases on treatment due to thermal abuse.

The molar volume of referred system has been calculated from equation (3). It has been found that molar volume increases with the increase in concentration of soap solutions. The plots of molar volume against soap concentration are characterised by an intersection of two straight lines at a definite soap concentration corresponding to cmc of the soap. At the cmc, hydrocarbon chain structure of complex molecule allows extensive contact between adjacent chains, possibly accompanied by changes in the vibrational and rotational degree of freedom of methylene group. The values of cmc, so determined, are in good agreement with the values obtained from the density measurements (Table 2).

Table 2. Values of cmc of copper soaps derived from various oils

Name of the soap	Parameter				
	Density	Molar volume	Apparent molar volume	Viscosity	Ultrasonic velocity
CM	0.0105	0.0105	0.0108	0.0110	0.0105
CSo	0.0155	0.0155	0.0158	0.0150	0.0155
CM ₁₅	0.0155	0.0155	0.0149	0.0155	0.0155
CSo ₁₅	0.0190	0.0190	0.0190	0.0190	0.0185
CM ₆₀	0.0155	0.0155	0.0154	0.0155	0.0150
CSo ₆₀	0.0147	0.0150	0.0144	0.0150	0.0140

The apparent molar volume (ϕ_v) of copper soap solutions is calculated by using equation (4). The values of apparent molar volume (ϕ_v) for CM₁₅ and CSo₁₅ decreases with the increase in soap concentration and after cmc the values of ϕ_v remain almost constant

while the values of ϕ_v for CM_{60} and CSO_{60} decrease continuously with the increase in concentration (Fig. 2 and 3).

Table 3. Computed parameters of masson's equation for copper soaps derived from various oils

Name of the soap	ϕ_{v1}°	ϕ_{v2}°	S_{v1}	S_{v2}
CM	1070	931	-1.4000	-0.0875
CSO	1293	810	-3.3700	+0.2686
CM_{15}	740	665	-0.2679	-0.0175
CSO_{15}	635	565	-0.2586	-0.0699
CM_{60}	882	785	-0.5317	-0.2493
CSO_{60}	1185	970	-0.9823	-0.3346

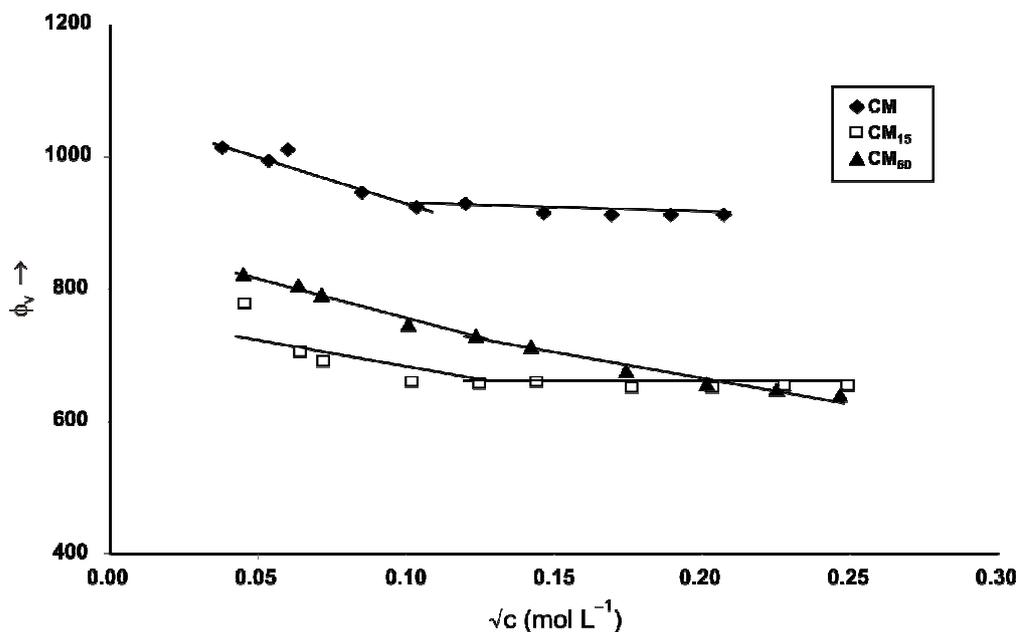


Fig. 2: Plots of apparent molar volume v/s square root of concentration of copper soaps derived from differently treated mustard oils

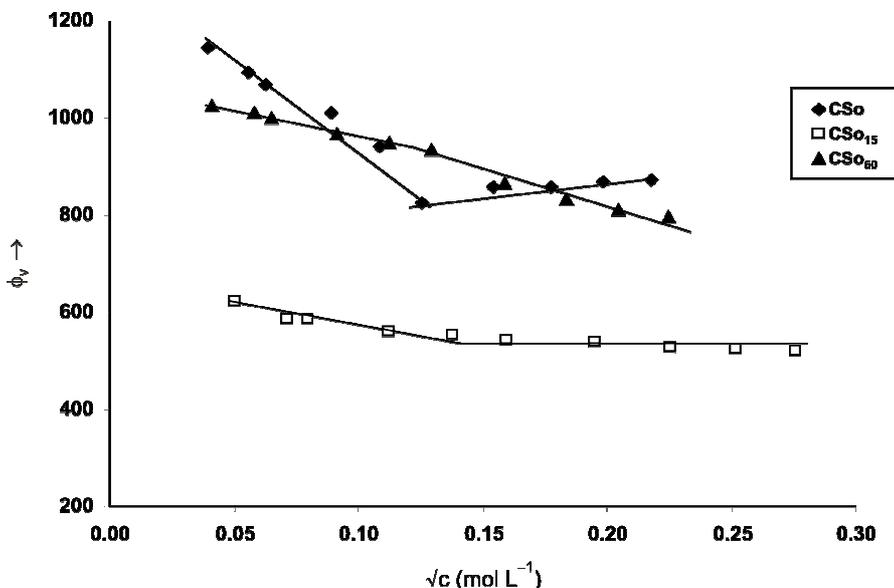


Fig. 3: Plots of apparent molar volume v/s square root of concentration of copper soaps derived from differently treated soyabean oils

The data have been analysed in terms of Masson Equation ($\phi_v = \phi_{v0} + S_v \sqrt{c}$). The plots of ϕ_v vs \sqrt{c} show an intersection of two straight lines at a definite soap concentration, which corresponds to the cmc of the soap. As Masson equation is applicable to both straight lines, it is reasonable to stipulate two values of parameters below and above cmc designated as ϕ_{v1}^0 , S_{v1} and ϕ_{v2}^0 , S_{v2} . The values of these parameters are recorded in Table 3. The value of limiting apparent molar volume for these soaps is obtained from extrapolation of ϕ_v vs \sqrt{c} plots to $c \rightarrow 0$. The change in the value of ϕ_v^0 and S_v below and above cmc suggests that there is a phenomenal change in the micellar agglomeration below and above cmc.

Since ϕ_v^0 has been regarded as a measure of solute- solvent interaction by earlier workers^{13, 14}, it is reasonable that greater magnitude of ϕ_v^0 may be regarded as a greater soap-solvent interaction. It is obvious from Table 3 that for all the referred systems, the order is as follows:

$$\phi_{v1}^0 > \phi_{v2}^0 \quad \text{and} \quad S_{v2} > S_{v1}$$

From above trend, it is obvious that soap-solvent interaction is more pronounced in

dilute solution. This may be ascribed due to the favourable interaction between soap and solvent molecules at the premicellar concentration. This observation suggests that solvent-solute interaction is greater below cmc due to the fact that soap molecules do not aggregate adequately below cmc. After cmc, the solute molecules come closer to form micelles and solute-solvent interaction decreases where as solute-solute interaction increases. Above cmc, solute-solute interaction becomes more prominent.

A perusal of Table 3 suggests that the soap-solvent interaction below cmc (ϕ_{v1}^0) follows the order:

$$\begin{aligned} \text{CM}_{15} &> \text{CSO}_{15} \\ \text{CSO}_{60} &> \text{CM}_{60} \\ \text{CM} &> \text{CM}_{15} < \text{CM}_{60} \\ \text{CSO} &> \text{CSO}_{15} < \text{CSO}_{60} \end{aligned}$$

These trends reveal that there is a decrease in soap-solvent interaction ϕ_{v1}^0 (below cmc) with the decrease in average molecular weight of copper soap (Tables 1 and 3). Our observations are supported by the literature that in organic molecules, the bond length C-X between carbon atom and X atom varies with the nature of X and therefore, as in the referred system, where X = $-\text{CH}_2-\text{CH}_2$ or $-\text{CH}=\text{CH}-$ in the fatty acid component of the soap molecule exhibit a different volume in different soaps according to their composition of the fatty acid content present in the structure¹⁵. The volume contribution of the polar group COO^- present in the soaps remains same for all the soaps due to its similar site and structure in all the moieties studied. It may be concluded that the difference in the volumes are mainly due to change in the fatty acid content and composition present in the mustard and soyabean oils. Further it has been observed that values of apparent molar volumes are found higher for CM_{15} and CSO_{60} and highest for CSO and CM . These results are in conformity with the fact that apparent molar volume for linear hydrocarbons varies and affected by size, shape, packing densities and other factors present in the similar type of the systems.

The parameter S_v in Masson equation represents the limiting apparent slope and indicates the existence of soap-soap interactions. Enumerated values have been summarised in Table and it is found that values of S_{v1} follows the order just reverse of ϕ_{v1}^0 . The results suggest that the solute-solute interaction increases above cmc ($S_{v2} > S_{v1}$), which indicates that aggregation of soap molecules is enhanced and there is appreciable solute-solvent interactions present in the system.

The cmc values obtained from ϕ_v vs \sqrt{c} plots are recorded in Table 2 and follow the order:

$$\begin{aligned} \text{CSO}_{15} &> \text{CM}_{15} \\ \text{CM}_{60} &> \text{CSO}_{60} \\ \text{CM}_{60} &\approx \text{CM}_{15} > \text{CM} \\ \text{CSO}_{15} &> \text{CSO} > \text{CSO}_{60} \end{aligned}$$

These values are in agreement with the values of cmc obtained from other physical properties and according to the fact that there is an increase in value of cmc with the decrease in average molecular weight of the soap (Table 2).

A perusal of Table 2 shows that there is a greater change in the values of cmc for CSO₁₅ and CSO₆₀ in comparison to CM₁₅ and CM₆₀ due to greater change in the average molecular weight or more thermal abuse in the case of soyabean oil (Tables 1 and 2). This may be attributed to the fact that higher amount of polyunsaturated fatty acids present in soyabean oil makes this oil more susceptible to oxidative polymerisation under frying conditions¹⁶. Auto-oxidation also occurs more rapidly at higher temperature in soyabean oil, which is responsible for the increase in the average molecular weight⁵ (Table 1).

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