

Viscometric Behaviour and Micellization of Copper Surfactants Derived from Sesame (*Sesamum Indicum*) and Soyabean (*Glycine max*) Oils in Non-aqueous Solvent

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The viscosity, specific viscosity, and fluidity of complexes of Cu (II) surfactant derived from sesame and soyabean oils (fresh untreated and treated) in non-aqueous solvent were determined at constant temperature 303.15 K to study the micellar features and critical micelle concentration (CMC). The results were used to determine the CMC, soap complex-solvent interactions and the effect of chain length of the surfactant molecule on various parameters. The conclusions concerning solute-solute and solute-solvent interaction were discussed regarding well-known Moulik's and Jones-Dole equations. The effect of surfactant concentration on viscosity of the solution in the non-polar solvent was also discussed. The observations suggested that the structure breaking effect by the solute on the solvent molecules was more prominent above CMC as compared to below CMC after the formation of the micelles.

Key words: Cu(II) surfactant; sesame oil; soyabean oil; soap- solvent interaction; CMC; viscosity

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The knowledge of various interactions responsible for stabilizing the native state of a surfactant is essential to understand the structure and function of surfactant. In aqueous surfactant solution, the different residues of interacts through non-covalent interactions with each other and with surrounding water molecules [1-2]. Investigations of the physiochemical properties of the denatured states of the surfactants are required to identify and characterize the contribution of various non-bonding interactions between different functional groups of surfactant and surfactant-solvent interactions which are the driving forces for a biological process [3]. As the surfactants are the complex molecules, the task of direct interpretation from the studies of surfactants becomes difficult. Hence, the approach to study model compounds and their derivatives, which mimic some of their structural aspects, is pre-requisite which provides the means to understand these intermolecular interactions involved in the complex surfactant systems [4-5]. The colloidal-chemical behaviour

of Cu (II) surfactants are gaining popularity on account of their utilitarian effects such as foaming, emulsification and fungicidal activities [6-8]. Colloidal behaviour of copper (II) soaps in the non-aqueous solvent have been studied in many reported papers [9-10]. In spite 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 [11]. These oils have been specially chosen, as they are easily available in the market and these heated, treated and degraded waste oils may be used in various fields as a biodegradable product [12]. Therefore we report in this paper the viscosity measurements for the study of molecular interactions of Cu (II) surfactants derived from sesame and soyabean oils (fresh untreated and treated) in non-aqueous solvent at 303.15 K to understand the interpretation of solute-solvent interactions, the structural insight

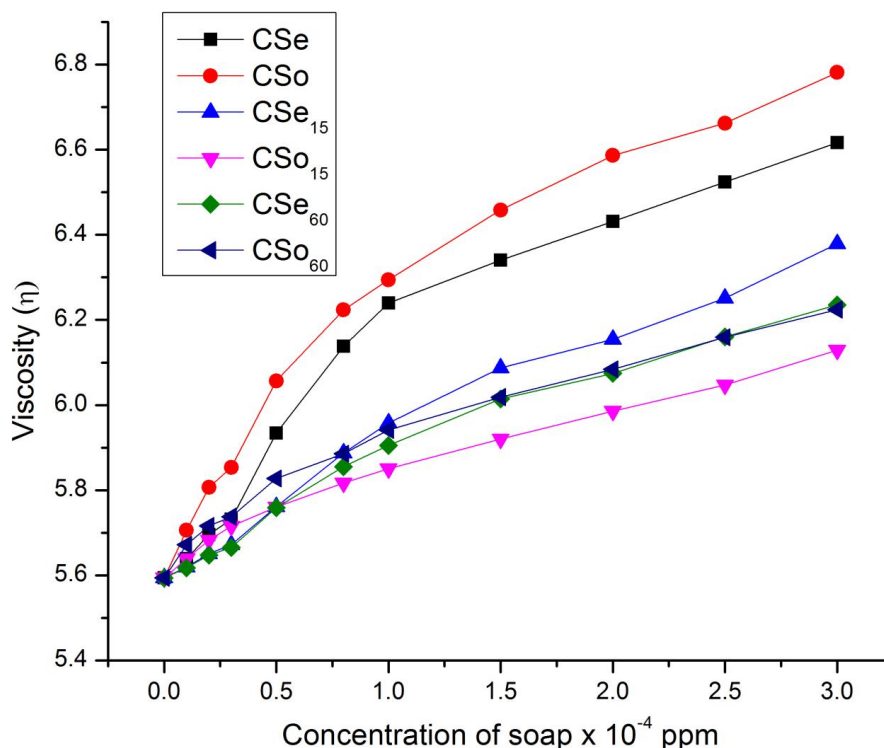


Figure 1. A plot shows between concentration and viscosity for sesame and soyabean oils (untreated and treated) in benzene.

of micelle and colloidal chemical behaviour in binary systems. Study of these factors is essential as it indirectly makes them responsible for their immense applicability in wide areas of the field.

EXPERIMENTAL

All the chemicals used were of LR/AR grade with 99.99% purity from Merck chemicals India. Copper soap was prepared by refluxing the sesame and soyabean oils (extracted from kernels and purified) with ethyl alcohol and 2N KOH solutions for 3-4 hours (direct metathesis), copper soap so obtained was then washed with warm distilled water and 10% alcohol at 50°C and recrystallized using hot benzene (50°C). The molecular weight of copper soap was determined from saponification value [13]. The copper soaps are abbreviated as copper-soyabean (CSo) and copper-sesame(CSe) treated for 15 and 60 min are as CSe₁₅, CSo₁₅, CSe₆₀, and CSo₆₀. We studied many other parameters related with thermal abuse and effect of temperature, and air on edible oils, so to analyze the solution behaviour and micellar features these

studies have been done on oils treated at different temperature and time.

Ostwald type viscometer of a definite volume of 25 ml was used for measuring the viscosity of the solutions of varying concentrations of the soaps supplied by Fusion's Glasswork's Jodhpur, Rajasthan India. Means of a pycnometer determined the densities at 303.15 K in the thermostat. The viscosity of the soap solutions was calculated by the following relationship-[14]:

$$\frac{\eta_0}{\eta} = \frac{\rho_0 \cdot t_0}{\rho \cdot t} \quad (1)$$

where, η_0 , η , ρ_0 , ρ , t_0 and t are the viscosity, density and time of flow for the solvent and solution 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 below 0.3%. All the measurements were made at a constant temperature 303.15 K in a thermostat. The viscosity results are expressed in millipoise.

RESULTS AND DISCUSSION

Viscosity

Flow characterization of solutions of complexes regarding viscometric measurement has been employed as a tool for finding out the CMC of copper soaps in benzene.

The viscosity η of the copper soaps, derived from fresh untreated and treated oils in benzene increases with the increase in the soap concentration. The increase in viscosity with the increase of soap concentration may be due to the increasing tendency of soap molecules to associate in the form of micelles. The existences of micelles of surfactants in organic solvents and mixed solvents have been reported by the number of workers [15]. The plots of viscosity η against the soap concentration, c (mol l^{-1}) are characterized by an intersection of two straight lines corresponding to CMC of the soap (Figure 1). Of course, this is the maximum concentration of molecular dispersion, at which there is balancing of internal forces causing the formation of micelles. The values of CMC follow the order:

$$\text{CSe} < \text{CSo}$$

It was found that the extrapolated values of viscosity in the plots of η v/s c for copper soaps were in close agreement with the experimental values of solvent (benzene) and were independent of the nature of the soap. This showed that soap molecules did not aggregate below CMC. The viscosity of these copper soaps followed the order:

$$\text{CSo} > \text{CSo}$$

The CMC of treated oils for 15 min is as follows:

$$\text{CSe}_{15} < \text{CSO}_{15}$$

This was in agreement with the fact that there was a decrease in the CMC values with the increase in the average molecular weight {A.M.W.} of the soap. The viscosity of various copper soaps derived from treated oils for 15 min followed the order:

$$\text{CSe}_{15} > \text{CSO}_{15}$$

The above trend demonstrated that the viscosity of the soap solutions increased with an increase in the average molecular weight of the soap. This might be due to an increase in the size of the micelles with the increase in the average molecular weight. It was observed that the viscosity of CSe_{60} was lower than CSe_{15} respectively but the viscosity of CSO_{60} was higher than CSO_{15} .

The CMC values were in good agreement with the values of CMC obtained from other physical properties and followed the order:

$$\text{CSO}_{60} < \text{CSe}_{60}$$

This is in agreement with the fact that there was a decrease in the CMC values with the increase of the average molecular weight of the soap. The extrapolated values of the viscosity for zero soap concentration, evaluated from the plots of the viscosity against the soap concentration was in close agreement with the experimental value of the viscosity of the solvent and independent of the nature of the soap.

The values of viscosity and specific viscosity for differently treated oils were in the following order:

$$\text{CSe} > \text{CSe}_{15} > \text{CSe}_{60}$$

$$\text{CSO} > \text{CSO}_{60} > \text{CSO}_{15}$$

From the above trends, this inference could be drawn that with the increase of average molecular weight, viscosity increases.

Specific Viscosity

The ratio of change in viscosity to the original viscosity of the solvent is called the specific viscosity η_{sp} .

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \quad (2)$$

where, η and η_0 are the viscosities of solution and solvent respectively.

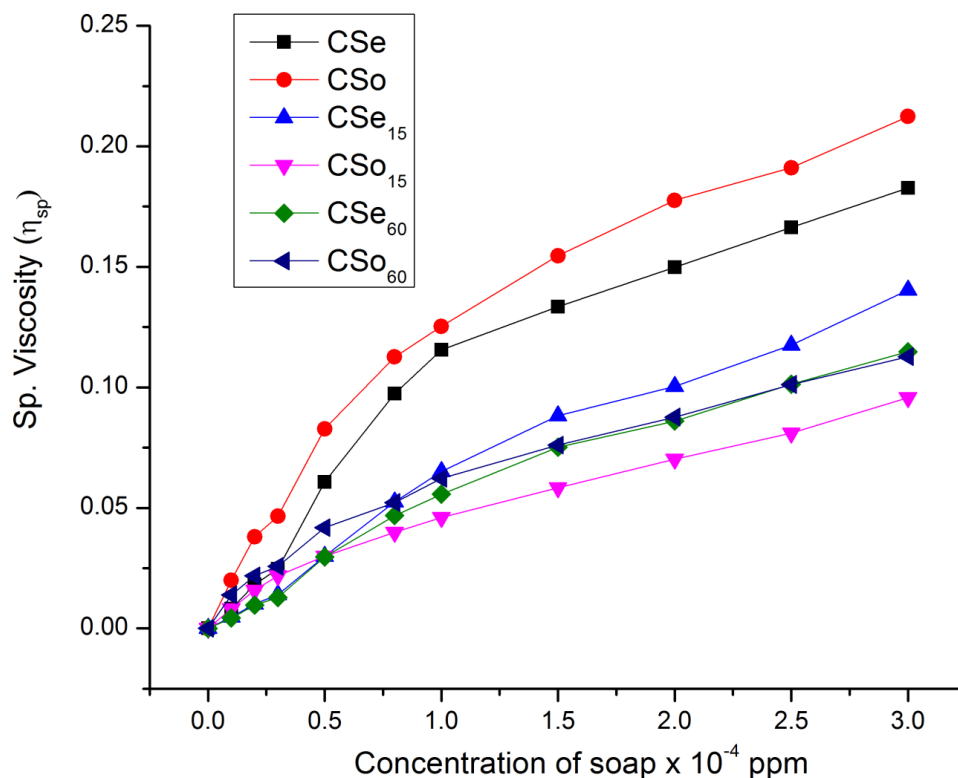


Figure 2. A plot shows between concentration and sp. viscosity for sesame and soyabean oils (untreated and treated) in benzene.

The results shows that specific viscosity η_{sp} increased with the increase in soap concentration.

The plots of specific viscosity η_{sp} against soap concentration were characterized by an intersection of two straight lines at a definite soap concentration corresponding to the CMC of the soap (Figure 2). The values of the CMC obtained were in good agreement with the values obtained from the plots of the viscosity against the soap concentration. The change in the slope of the curve below and above CMC suggested that there was a phenomenal change in the micellar agglomeration below and above CMC. At the CMC, hydrocarbon chain of soap molecules allowed extensive contact between adjacent chains possibly accompanied by a change in the vibrational and rotational degree of freedom of methylene group.

Fluidity

$$\phi = \frac{1}{\eta}$$

(3)

The fluidity ϕ which is defined as the reciprocal of viscosity. The fluidity of soap solutions in benzene decreased with the increase in the soap concentration. The plots of the fluidity ϕ against soap concentration 'c' shows an abrupt change at a point corresponding to the CMC of the soap (Figure 3). A perusal of results shows that CMC values obtained from the plots of ϕ against soap concentration were in good agreement with the values obtained from η v/s c, and η_{sp} v/s c plots.

Important Equations

The results of the viscosities of the solutions of CMU in benzene could be satisfactorily explained when applied to the various equations discussed below.

Einstein Equation [16]:

$$\eta_{sp} = 2.5 \nabla \cdot c \quad (4)$$

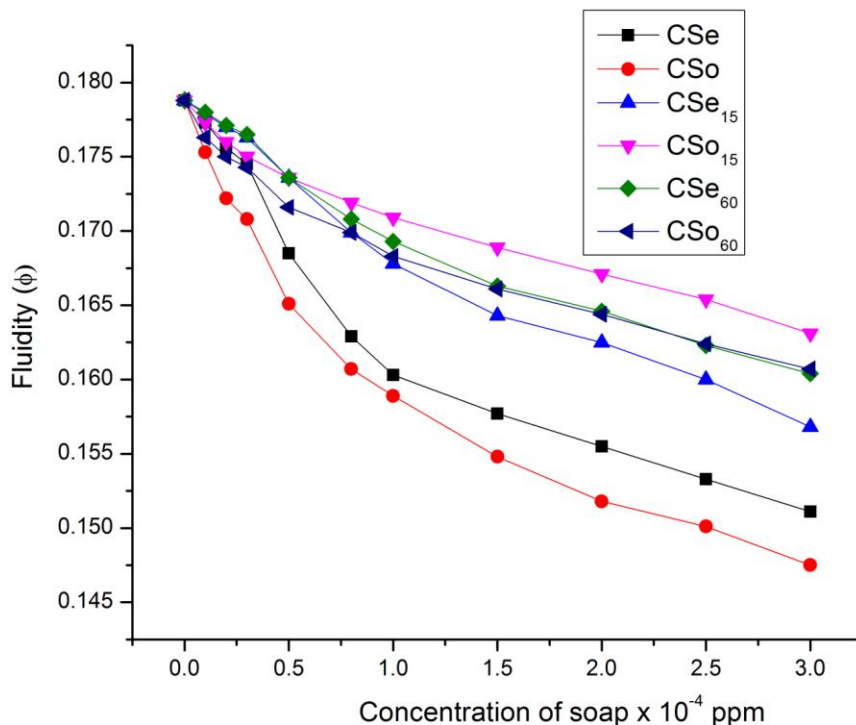


Figure 3. A plot shows between concentration and fluidity for sesame and soyabean oils (untreated and treated) in benzene.

Thomas equation[17]:

$$\frac{(\frac{\eta}{\eta_0} - 1)}{c} = 2.5 \bar{V} + (10.05 \bar{V})^2 \cdot c \quad (5)$$

V and equation [18]:

$$\frac{1}{c} = \left(\frac{0.921}{\bar{V}}\right)^{-1} \frac{1}{\log\left(\frac{\eta}{\eta_0}\right)} + Q \bar{V} \quad (6)$$

where, \bar{V} , C , Q , η and η_0 are the molar volume of the soap solution, the concentration of the soap solution, the interaction coefficient, viscosity of the solution and solvent respectively.

The values of molar volume \bar{V} were evaluated from the plot of η_{sp}/s v/s c , and $1/c$ v/s $1/[\log(\eta/\eta_0)]$ corresponding to Einstein and Thomas equations as depicted in Figure 4-5 respectively. For our referred system, the plots corresponding to Einstein and Thomas equation

were obtained as an intersection of two straight lines; therefore, the molar volume values were evaluated only below CMC for the above-mentioned equations. The values of molar volume enumerated from these equations shows some difference but the trend remained unaltered irrespective of the type of the equation applied. Similar work have been reported by various workers [19]. The evaluated values of molar volume \bar{V} were recorded in Table 1.

Interestingly Moulik's equation [20] also fitted equally well to our referred system. The equation was:

$$\left(\frac{\eta}{\eta_0}\right)^2 = M + K c^2 \quad (7)$$

where, M and K were constants. The values of M and K were evaluated from the plot of (η / η_0) v/s c^2 which were recorded in Table 2. The plot of $(\eta / \eta_0)^2$ v/s c^2 was characterized by an intersection of a straight line and a curve (Figure 6). Thus the values of M and K could be evaluated only below CMC.

Table 1. Values of molar volume obtained from different equations for copper soaps derived from untreated and treated oils.

Name of the soap	Einstein equation		Thomas equation	
	v_1	v_2	V1	V ₂
CSe	0.9199	0.2172	1.94	4.04
CS _o	0.8777	0.2403	5.18	3.64
CSe ₁₅	0.3665	0.1994	0.88	1.60
CS _{o15}	0.1781	0.0960	1.37	0.82
CSe ₆₀	0.2082	0.0960	0.52	0.94
CS _{o60}	0.3014	0.1495	2.94	1.50

Table 2. Values of viscometric parameters obtained from different equations of copper soaps derived from untreated and treated oils.

Name of the soap	Moulik's equation				Jones-Dole equation			
	M ₁	M ₂	K ₁	K ₂	A ₁	A ₂	B ₁	B ₂
CSe	1.0275	1.2412	14.300	0.7813	-0.3450	1.6750	4.7046	-0.4877
CS _o	1.0900	1.3040	10.390	0.7400	0.3650	1.2700	2.4750	-0.6370
CSe ₁₅	1.0150	1.1150	4.3315	0.5206	-0.1250	0.2900	1.8040	0.4452
CS _{o15}	1.0300	1.0825	1.3764	0.2126	0.0850	0.2550	0.5890	0.1139
CSe ₆₀	1.0125	1.0925	1.4826	0.2126	-0.0550	0.2350	0.9004	0.1853
CS _{o60}	1.0425	1.1325	7.1154	0.4142	0.2800	0.4400	0.7002	0.1317

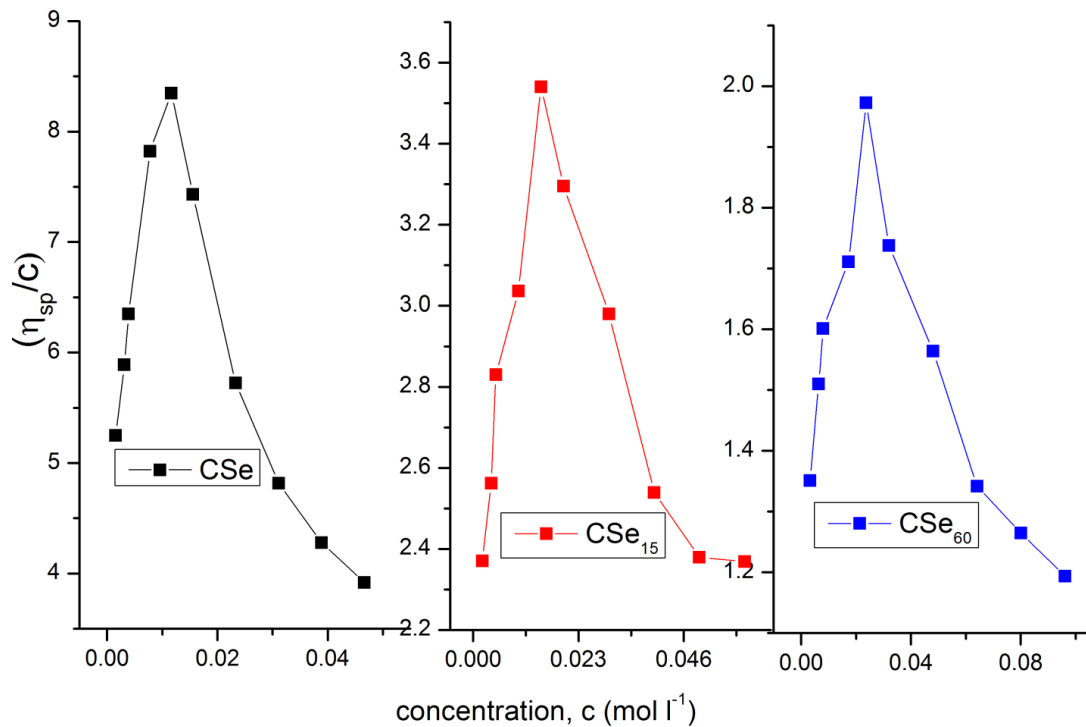


Figure 4. Plots of η_{sp}/c v/s c of copper soaps derived from sesame oil (Fresh and treated) - Thomas equation.

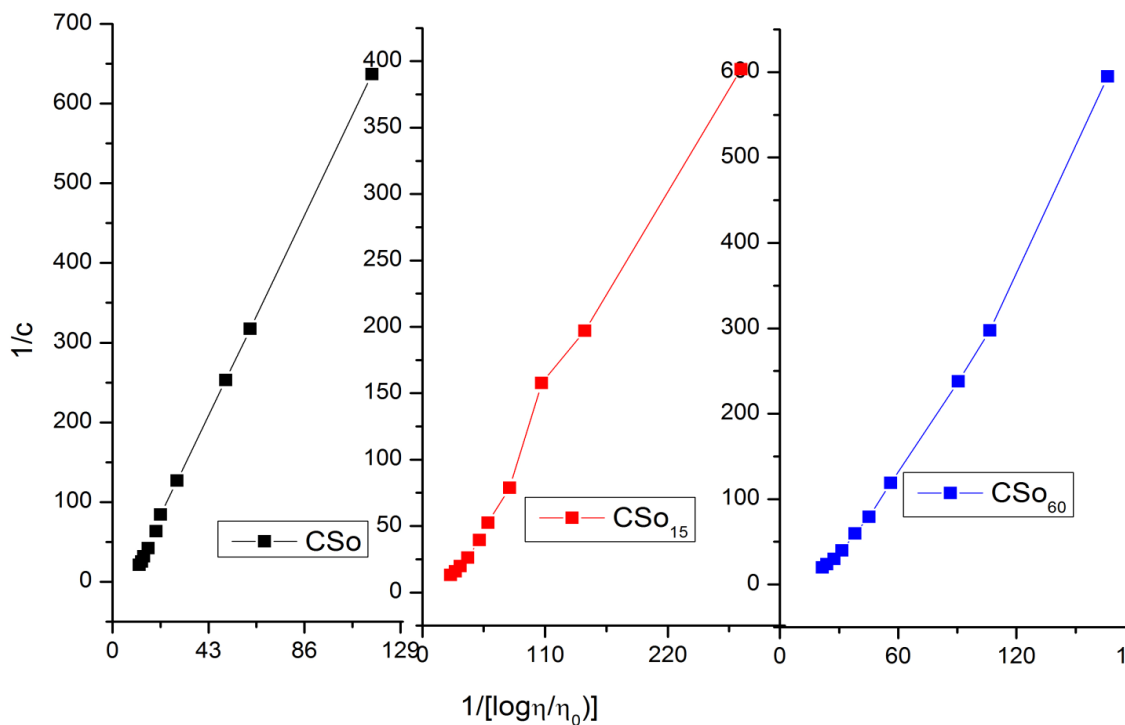


Figure 5. Plots of $1/c$ v/s $1/[\log(\eta/\eta_0)]$ of copper soaps derived from soyabean oil (Fresh and treated) - Vand equation.

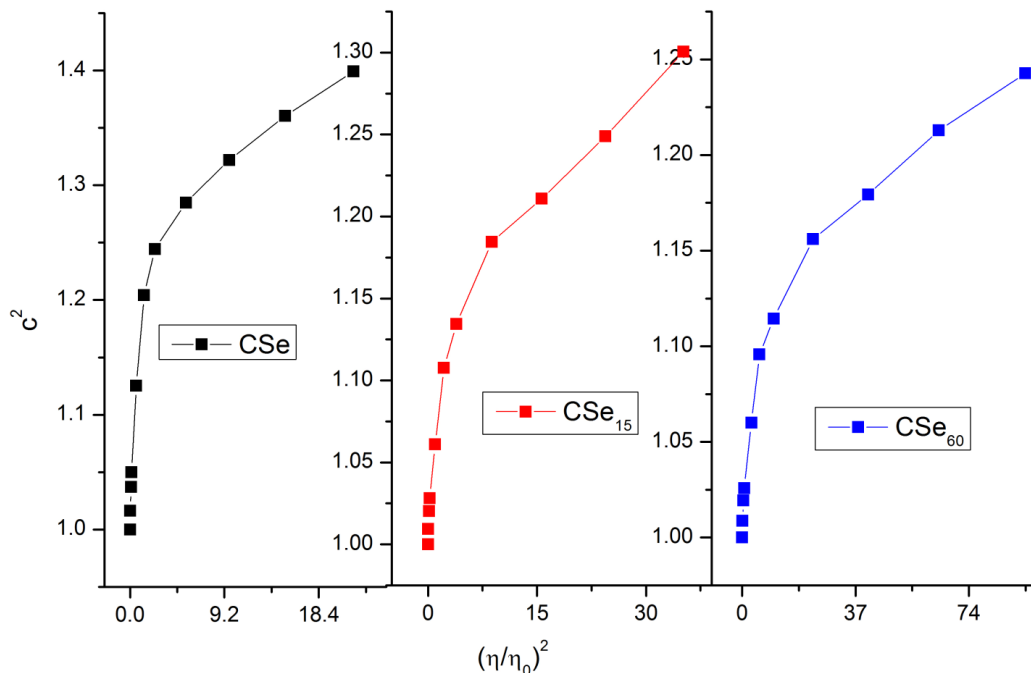


Figure 6. Plots of $(\eta / \eta_0)^2$ v/s c^2 of copper soaps derived from sesame oil (Fresh and treated)- Moulik’s equation.

The viscosity data was also been interpreted in the light of Jones–Dole equation [21].

$$\frac{\left(\frac{\eta}{\eta_0}\right)^2 - 1}{\sqrt{c}} = A + B \sqrt{c} \quad (8)$$

For convenience, the equation might be expressed as:

$$\frac{\psi}{\sqrt{c}} = A + B \sqrt{c} \quad (9)$$

where, the coefficient A and B refer to the solute-solute and solute-solvent interaction, respectively. The values of A and B were evaluated from the plot of $\frac{\psi}{\sqrt{c}}$ v/s \sqrt{c} which was characterized by an intersection of a straight line and a curvature (Figure 7). Thus Jones–Dole equation fitted well only below CMC. The value of CMC so obtained was in close agreement with the CMC values obtained from η v/s c , η_{sp} v/s c and ϕ v/s c plots. Given the two intersecting straight lines for $\frac{\psi}{\sqrt{c}}$ v/s \sqrt{c} , it was reasonable to evaluate two values of A and B . From this trend, it was clear that soap-

solvent interaction was larger than the soap-soap interaction in dilute solution i.e. below CMC [22–25]. The trend of these coefficients might be summed up as under:

$$A_1 < A_2 \text{ \& } B_2 < B_1$$

From this trend, it might be concluded that soap-solvent interaction was more pronounced below CMC. This might be ascribed to the favourable interaction between soap and solvent molecules at the premicellar concentration.

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Literature survey revealed that the positive value of A suggested a strong solute-solute

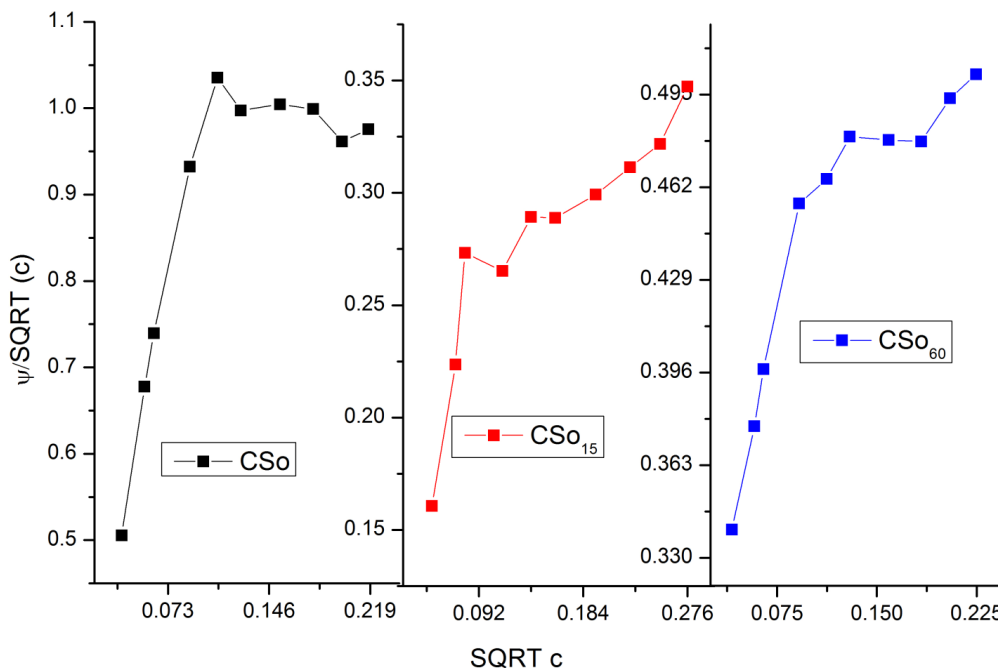


Figure 7. Plots of $\frac{\psi}{\sqrt{c}}$ vs \sqrt{c} of copper soaps derived from soyabean oil (Fresh and treated) - Jones Dole equation.

interaction and B values measure the structural modification induced by solute-solvent interaction [26-28]. Earlier studies done show that the increase in the concentration of solute in solution contributes positively to the viscosity of B coefficient [29-30]. On the other hand, the breaking of the solvent structures by solute caused a decrease in viscosity. This contributed negatively to the B coefficient. Thus B coefficient was the resultant of these two opposing forces. Therefore the systems/molecules exhibited negative B coefficient was assumed to exert a structure breaking effect by the solute on the solvent molecules. For all the three complexes, the values of A co-efficient are positive, which suggests strong solute-solute interactions [31-34]. At the same time, for all the complexes the B coefficient, which was a measure of the effective hydrodynamic volume of solute, which accounted for the solute-solvent interactions and is also known to be a measure of the order or disorder introduced by the solute into the solvent, were observed to be negative. Literature survey suggests that solutes with negative B coefficient were characterized as for structure breaking indicating weak solute-solvent interaction [35]. The CMC of the

complexes for all the parameters were observed and followed the given order:

$$CSe > CSe_{15} > CSe_{60}$$

$$CSo > CSo_{60} > CSo_{15}$$

CONCLUSION

The present research work was an attempt to prepare surface-active compounds from metal and natural oils. The viscosity parameters are important to understand the colloidal behavior, CMC characteristics, and nature of the complexes. These studies indirectly helped in identifying the structural insight, physical and micellar properties of surface active molecule. This might provide significant information regarding the solution behavior and would definitely help future researchers to apply these novel copper surfactants in multiple interlinked fields based on their widest applicability.

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