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DOI: 10.2174/1874842201805010119, 2018, *5*, 119-133

RESEARCH ARTICLE

Surface Active Properties and Micellar Features of Copper Soaps Derived from Various Edible Oils

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Received: August 11, 2018 Revised: September 20, 2018 Accepted: November 6, 2018

Abstract:

Introduction:

The molar volume, viscosity, specific viscosity, and fluidity of copper surfactant derived from various edible oils in methanol - benzene solvent have been determined at a constant temperature 303 K.

Methods / Results:

The results were used to calculate (CMC), soap complex-solvent interactions and the effect of chain length of the surfactant molecule on various parameters.

The conclusions with regard to soap-soap and soap- methanol -benzene interaction have been discussed in terms of well-known Moulik's and Jones- Dole equations. The effect of surfactant concentration on viscosity of the solution in solvent mixture has been discussed.

Conclusion:

The observations suggested that the structure breaking effect by the solute on the solvent molecules is more prominent above CMC as compared to below CMC after the formation of the micelles. The vital information plays an important role in various industrial process as well as biological applications.

Keywords: Cu(II) surfactant, Edible oils, Soap- solvent interaction, CMC, Viscosity.

1. INTRODUCTION

Surface-active agents are vital components in biological systems and play an important role in many industrial processes because of their ability to lower interfacial tension [1, 2]. Although the use of surfactants in preservation of wood, water proofing and repellency, protection of crops, stabilization of nylon threads, lubrication etc. is relatively a newer applications [3, 4]. Physical properties and biological application in terms of CMC, solvent- solute interactions and fungicidal effect of copper soaps in various organic solvents have been studied by Sharma *et al.* [5 - 10]. Sharma *et al.* have evaluated various parameters pertaining to micellar characteristics *i.e.* density, apparent molar volume for copper soaps derived from various edible oils [11, 12]. A perusal of literature survey reveals that a number of transition metal soaps and their complexes have been studied due to their wide applications, however scanty references are available as to the investigation of copper soap and their complexes in various organic solvents. In our previous

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communication we report various physical parameters (density, MV, AMV, ultrasound, surface tension) in benzene-methanol mixture (40% and 80%) of copper surfactant complexes of (caprylate, caprate and laurate) with 2-amino, 6-R benzothiazole (R = -Cl, -CH_3) [13], and other physical properties (density, MV, AMV, ultrasound, viscosity)in benzene-methanol mixture (60% and 80%) of copper surfactants derived from neem and karanj oils [14]. Mehrotra *et al.* studied various physical properties of metallic soaps such as Barium soap [15], samarium soaps [16], chromium soaps [17], Barium caproate [18], manganese Caprylate [19], copper soaps [20], and Millard studied Surface Tension parameters of alkaline soap solutions [21]. Mathur *et al.* studied viscometric behaviour of macromolecular complexes of copper soaps [22]. The colloidal chemical behaviour of Copper(II) soaps in the non- aqueous mixture of varying composition has been investigated by Mehta *et al.* using viscometric and allied parameters [23]. Mehrotra *et al.* carried out versility of colometric and polarographic method for the determination of metal content in copper soaps [24]. Malik *et al.* reported the polarographic behaviour of copper soaps in pyridine, o-toludine and dioxane and the effects of temperature and electrolytes on the solubilization and CMC have been reported [25]. The present work has been initiated with a view to obtain a profile about micellar characterization and aggregation of copper soaps derived from various edible oils in methanol -benzene mixture of 20% and 40% maximum effect of polarity on CMC and other parameters. The physical properties (viz. molar volume, viscosity, specific viscosity, and fluidity) of the copper soaps in “methanol -benzene mixture” have been investigated in order to find out the CMC, nature and size of the micelles formed as well as to test the validity of various equations under different conditions.

2. EXPERIMENTAL

Oils were procured directly from the seeds of Mustard, Groundnut, and Sesame. Soyabean (pure) oil was taken from the market of a reputed brand. The fatty acid composition of oils was confirmed by sending their methyl esters to RSIC, CDRI Lucknow U.P. India (Table **1**). Copper soaps were prepared by direct metathesis of the corresponding potassium soap with a slight excess of 50 ml of saturated solution of copper sulphate at 50-55C. After washing with hot water and alcohol, the samples were dried at 100-105C. Finally under reduced pressure, they were recrystallized twice from hot benzene [26]. The synthesized copper soaps shows maximum solubility in benzene and in some organic solvents, the methanol solvent was taken to study the effect of polarity on micellar features and CMC with non -polar benzene. In general, all the four copper soaps green in colour was obtained. Molecular weights of copper soaps was determined from saponification equivalent. The saponification equivalent or saponification value is a measure of the average chain length of the fatty acid which makes up fat. The Saponification Equivalent (S.E) is the amount of potassium hydroxide whilst the Saponification Value (S.V) is the number of milligrams of KOH required to saponify one gram of the oil, the two being related by the expression:

$$S.E = 56100/S.V$$

S.E may be taken as an average molecular weight of oil. Value of S.E is determined by experiment, the ratio taken for saponification of oil with 2N KOH was 1:10 and from this value, average molecular weight of the copper soap was calculated. According to their molecular formula $(RCOO^-)_2Cu$ where S.E is taken as average molecular weight of the fatty acid R-COOH which is converting into a soap. The values of S.V., molecular weights and other analytical data are recorded in Table **2**.

The systems are abbreviated as follows:

Soap	Fraction of Methanol with benzene in solvent mixture	
	20%	**40%**
1. Copper soap of Mustard oil	CM_{20}	CM_{40}
2. Copper soap of Groundnut oil	CG_{20}	CG_{40}
3. Copper soap of Sesame oil	CSe_{20}	CSe_{40}
4.Copper soap of Soyabean oil	CSo_{20}	CSo_{40}

Total 25 ml solution containing different concentrations of solute was prepared in a clean volumetric flask at constant temperature for each study. The densities of pure methanol, benzene was 20% (5ml+20ml) and 40% (10ml+15ml) methanol- benzene solvent mixture. Ubbelohde type viscometer was used for measuring the viscosity of the solutions of varying concentrations of the soap. The densities were determined by means of a *Sprengel's* pyknometer. The viscosity of the soap solutions was calculated by the following relationship [27].

Table 1. 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
Groundnut Oil	10	4	61	18	-	C20-C24 7%
Mustard Oil	2	1	25	18	10	C20-C22 41%
Sesame Oil	8	4	45	41	-	-
Soyabean Oil	12	4	24	51	9	-

Table 2. Analytical and physical data of copper soaps derived from Various edible oils.

Name of Copper Soap	Color	M.P. (0C)	Yield %	Metal %		S.V.	S.E.	Average Mol. Wt.
				Found	Calculated			
CM	Green	91	80	10.15	9.72	175.80	319.10	699.72
CG	Green	97	75	9.58	9.60	188.70	297.29	656.08
CSe	Green	100	85	10.05	9.81	191.70	292.64	646.78
CSo	Green	110	90	10.80	9.96	194.90	287.83	637.17

$$S.E. = \frac{56100}{S.V.} \quad (1)$$

Where η,η,ρρ, t and 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 below 0.3%. All measurements were made at a constant temperature in thermostatic water bath (30± 0.1C=303K) in a thermostat. The viscosity date was reproducible within ± 0.02 milipoise.

The molar volume of the complex solution $\bar{V}$ has been calculated by the relationship [28].

$$\nabla = \frac{M_1X_1 + M_2X_2 + M_3X_3}{\rho} \quad (2)$$

Where X_1 is the mole fraction of the soap of molecular weight M_1 whereas X_2 is the mole fraction of benzene of molecular weight M_2 and X_3 is the mole fraction of Methanol of Molecular weight M_3 while p stands for density of the solution.The molar volume ∇ was reproducible within ± m^3mol^{-1}

3. RESULTS AND DISCUSSION

3.1. Copper Soaps Derived from Various Edible Oils in 20% Methanol-Benzene Mixture

3.1.1. Molar Volume:

The molar volume ∇ of copper soaps derived from various edible oils in 20% methanol-benzene mixture was calculated from density data and is recorded in Table **3**. It has been revealed from Table **3** that the values of molar volume ∇ first decreased then there was a slight increase followed by a decrease in a linear manner showing straight line. This may be attributed to the fact that above CMC and in the higher soap concentration region, the degree of aggregation of molecules became dissimilar to that of below CMC. The plots of molar volume, against the soap concentration c are characterized by an intersection of convex curve and a straight line at a definite soap concentration which corresponds to the CMC of the soap. At the CMC, hydrocarbon chain structure of soap molecules allows extensive contact between adjacent chains of fatty acids of varying composition, 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. The molar volume of copper soaps derived from various edible oils in 20% methanol-benzene mixture follows the order:

CM > CG≅ CSe>CSo

Table 3. molar volume of copper soaps derived from various edible oils in 20% and 40% methanol-benzene mixture.

Conc. of Soap g mole l^{-1}	Molar volume, m^3mol^{-1}							
	CM_{20}	CG_{20}	CSe_{20}	CSo_{20}	CM_{40}	CG_{40}	CSe_{40}	CSo_{40}
0.0000	72.048	72.048	72.048	72.048	60.384	60.384	60.384	60.384
0.0003	72.005	71.996	71.987	71.970	60.312	60.304	60.297	60.290
0.0004	71.986	71.984	71.959	71.946	60.274	60.280	60.287	60.272
0.0006	71.955	71.952	71.910	71.903	60.213	60.239	60.253	60.245
0.0008	71.923	71.929	71.853	71.882	60.172	60.205	60.218	60.225
0.0010	71.917	71.926	71.799	71.862	60.209	60.184	60.177	60.205
0.0011	71.904	71.947	71.771	71.850	60.221	60.221	60.160	60.188
0.0012	71.891	71.941	71.742	71.838	60.197	60.244	60.150	60.178
0.0013	71.875	71.920	71.744	71.877	60.181	60.219	60.137	60.203
0.0014	71.861	71.900	71.741	71.840	60.157	60.202	60.130	60.243
0.0016	71.834	71.877	71.734	71.799	60.109	60.161	60.118	60.173
0.0018	71.807	71.845	71.719	71.743	60.069	60.120	60.105	60.104
0.0020	71.776	71.814	71.687	71.702	60.022	60.086	60.092	60.055

The comparison of the results indicates that the values of the molar volume for CM are higher than that of CSo which is due to the presence of longer fatty acid content present in the system.

3.1.2. Viscosity

Flow characterization of solution of soap solutions in terms of viscometric measurements has been employed as a tool to find out CMC of copper soaps. The viscosity, η of copper soaps in non-aqueous solvents of varying composition has been determined at a constant temperature *i.e.* 30 ±0.1C. The value of viscosity η for all the copper soaps (*i.e.*CM_{20}, CG_{20}, CSe_{20}, and CSo_{20}) was found to increase with the increase in 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 existence of micelles of surfactants in organic solvents and mixed solvents has been reported by number of workers [29, 30].The plots of viscosity η against the soap concentration c are characterized by an intersection of two straight lines corresponding to the CMC of the soap Fig. (**1**). The change in the slope of the curve below and above CMC, however, suggests that there is a phenomenal change in the micellar agglomeration below and above CMC. At the CMC, hydrocarbon chain structure of soap molecules allows extensive contact between adjacent chains possibly accompanied by the change in vibration and rotational degree of freedom of methylene group. CMC follows the order:

$$CSo > CSe > CG > CM$$

The above trend clearly demonstrates that the association of soap molecules occurs at lower concentration in copper soaps of mustard and groundnut soaps in methanol-benzene as compared to sesame and soyabean soaps. It may also be pointed out that the viscosity of the soap solutions decreases with an increase in the chain length of the acid in the soap. This may be due to an increase in the size of the micelles with an increase in the number of carbon atoms in the soap. The viscosity of the soap has been found in the order:

$$CM < CG < CSe < CSo$$

The difference in the viscosities of copper soap solutions, in varying composition of methanol-benzene mixture is mainly due to difference in the viscosities of solvent mixture. Thus, with the increase in the number of carbon atoms in the hydrophobic chain, viscosity, η and CMC increased and then decreased. The viscosity results confirm that there is no appreciable aggregation of the soap molecules below the CMC whereas there is a marked change in the aggregation at this soap concentration.

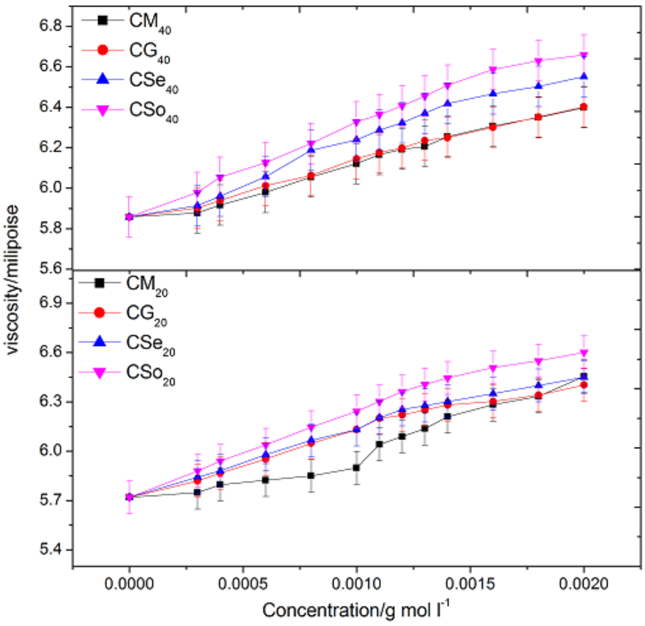

Fig. (1). Plots of viscosity v/s concentration of copper soaps derived from various edible oils in 20 and 40 % methanol- benzene mixture.

3.1.3. Specific Viscosity

The ratio of change in viscosity to the original viscosity of the solvent is called the specific viscosity η_{sp} [31]

$$\frac{\eta_0}{\eta} = \frac{\rho_0 \, . \, t_0}{\rho \, . \, t} \tag{3}$$

Where η and η are the viscosities of solution and solvent, respectively.

The value of specific viscosity η_{sp} of copper soaps derived from various edible oils in 20% methanol-benzene mixture was recorded as shown in Table **4**. The results show that specific viscosity η_{sp} of the soap solution increases with the increase in soap concentration. This increase may be due to the increasing tendency of the soap molecules to form aggregates with increasing soap concentration. The values of the CMC so obtained are in good agreement with the values obtained from the plots of viscosity ηagainst the soap concentration c.

Table 4. Specific viscosity ηsp of copper soaps derivedfrom various edible oils (in methanol-benzene mixture).

Conc. of Soap g mole l^{-1}	Specific Viscosity, milipoise							
	CM_{20}	CG_{20}	CSe_{20}	CSo_{20}	CM_{20}	CG_{20}	CSe_{20}	CSo_{20}
0.0003	0.00490	0.01730	0.02150	0.02785	0.00340	0.00741	0.00949	0.02057
0.0004	0.01342	0.02570	0.02810	0.03849	0.01000	0.01376	0.01756	0.03346
0.0006	0.01810	0.04060	0.04530	0.05561	0.02080	0.02636	0.03395	0.04582
0.0008	0.02279	0.05740	0.06060	0.07449	0.03360	0.03493	0.05624	0.06199
0.0010	0.03121	0.07190	0.07180	0.09130	0.04490	0.04917	0.06496	0.08014
0.0011	0.05603	0.08400	0.08460	0.10180	0.05260	0.05447	0.07319	0.08640
0.0012	0.06450	0.08740	0.09330	0.11230	0.05700	0.05807	0.07933	0.09372
0.0013	0.07300	0.09270	0.09740	0.11997	0.05930	0.06446	0.08747	0.10196
0.0014	0.08558	0.09800	0.10170	0.12677	0.06770	0.06679	0.09554	0.11111
0.0016	0.09845	0.10180	0.11010	0.13780	0.07650	0.07553	0.10379	0.12433
0.0018	0.10723	0.10860	0.11870	0.14501	0.08390	0.08428	0.11008	0.13169
0.0020	0.12839	0.11950	0.12760	0.15402	0.09220	0.09291	0.11833	0.13669

3.1.4. Fluidity

The reciprocal of co-efficient of viscosity is called fluidity [32].

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \tag{4}$$

The fluidityϕ of copper soap solution in 20% methanol-benzene mixture decreases with an increase in soap concentration. The plots of fluidity ϕ against soap concentration (c) show an abrupt change at a point corresponding to the CMC of the soap Fig. (**2**). A perusal of the CMC data shows that it is dependent on the solvent composition and values are in good agreement with the values obtained from η v/s c, and η_{sp} v/s c plots.

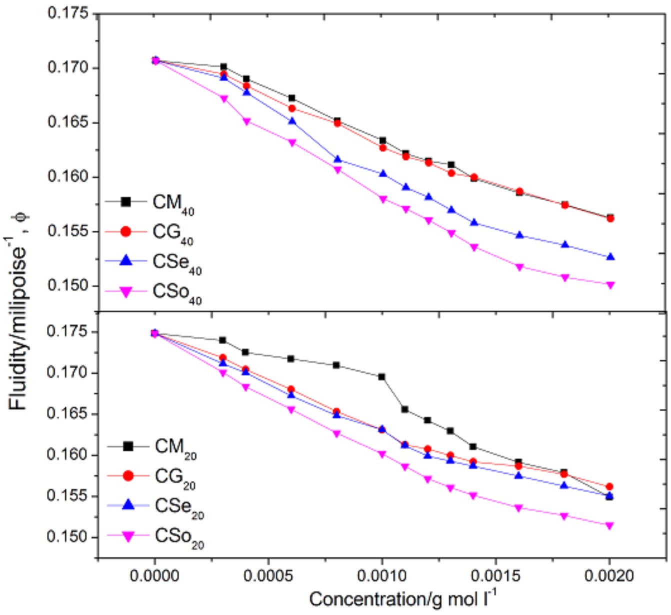

Fig. (2). Plots of fluidity *v/s* concentration of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture.

3.1.5. Important Equations

The results of the viscosity of the solutions of copper soaps in 20% methanol-benzene mixture have been interpreted in the light of equations proposed by Einstein, Thomas and Vand.

Einstein Equation [33]:

$$\phi = \frac{1}{\eta} \tag{5}$$

Thomas equation [34]:

$$\eta_{sp} = 2.5\ \nabla .\ c \tag{6}$$

Vand equation [35]

$$\frac{(\frac{\eta}{\eta_0} - 1)}{c} = 2.5\ \nabla + (10.05\ \nabla)^2 .\ c \tag{7}$$

Where V, c, Q, η,η $_0$ and η_{sp} are the molar volume of the soap, concentration of the soap, interaction coefficient, viscosity of the solution and viscosity of the solvent, respectively. The values of molar volume V evaluated from the plots of η_{sp} v/s c (Einstein equation), η_{sp}/c η v/s c (Thomas Equation) and 1/c v/s 1/ log η/η (Vand equations) was below and above CMC. For our referred system, the plots corresponding to Einstein, Thomas and Vand equation was obtained as an intersection of two straight lines Figs. (**3** and **5**). Therefore the value of molar volume enumerated from these equations show a slight difference but the trend remains unaltered irrespective of the type of equation applied. Due to irregular trend, Thomas equation is not fit for copper soap for both the solvents *i.e.*20% methanol and 40% methanol-benzene mixture.

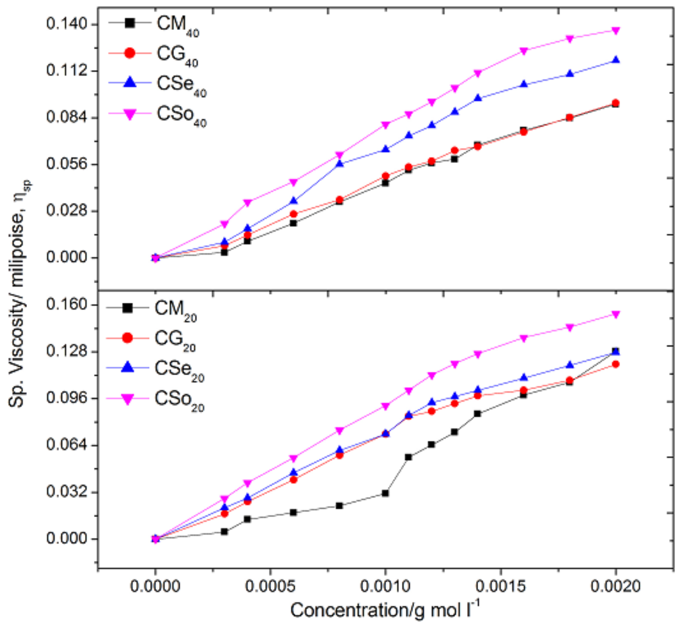

Fig. (3). Plots of η_{sp}*v/s* concentration of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Einstein Equation).

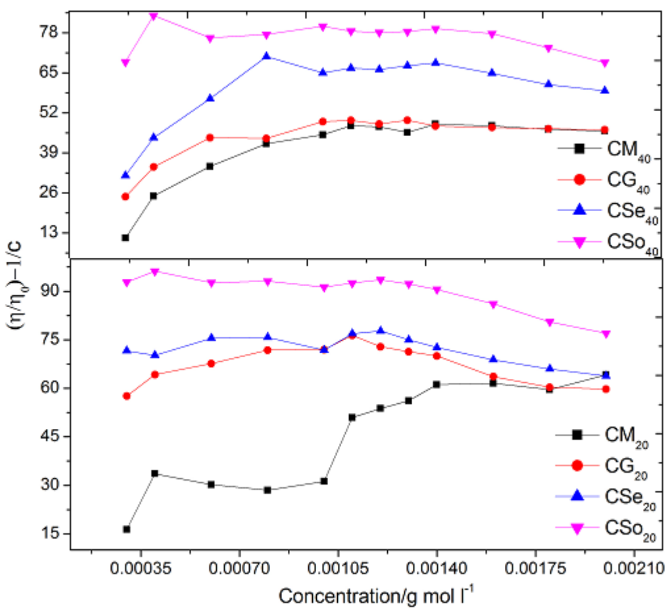

Fig. (4). Plots of {(η/η)-1}/c *v/s* concentration of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Thomas Equation).

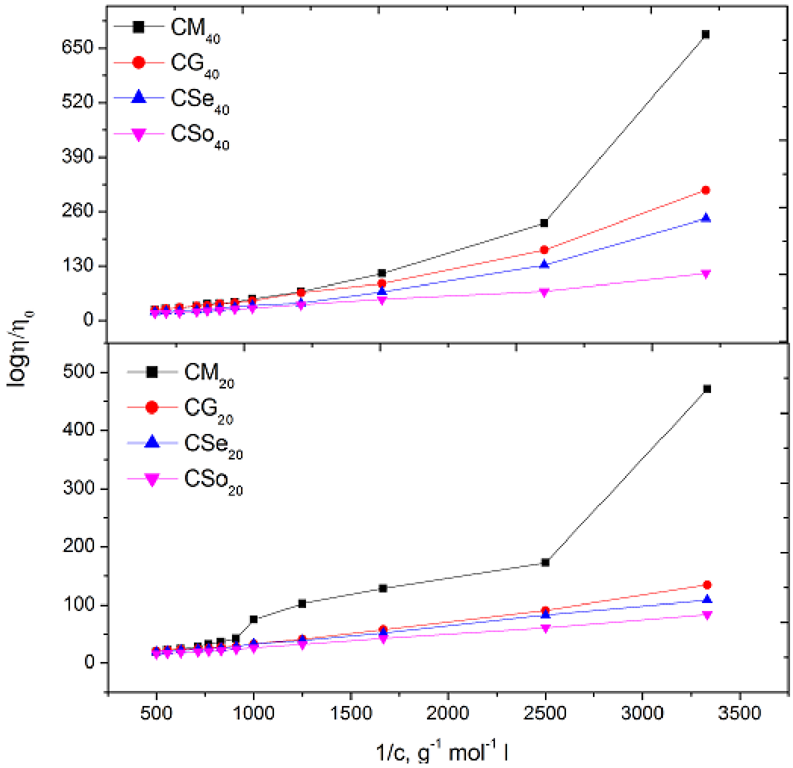

Fig. (5). Plots of 1/ {log (η/η)} *v/s* 1/c of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Vand Equation).

It was observed that the values of molar volume below and above CMC(*i.e.* V_1& V_2) enumerated from Einstein equation follow the order Table **5**.

$$M_2 \text{ (above CMC) } > M_1 \text{ (below CMC)}$$

Table 5. values of molar volume obtained from different equations for copper soaps derivedfrom various edible oils in 20% and 40% methanol-benzene mixture.

Name of the Soap	Einstein Equation		Vand's Equation	
	V_1	V_2	V_1	V_2
CM_{20}	0.1222	0.2698	1.0976	1.3664
CG_{20}	0.3125	0.1616	1.1788	2.2795
CSe_{20}	0.3914	0.1455	1.3654	1.9750
CSo_{20}	0.3356	0.1865	3.4372	7.5009
CM_{40}	0.2217	0.1780	0.9876	1.7321
CG_{40}	0.2217	0.1697	1.5952	2.0200
CSe_{40}	0.2800	0.1865	1.8075	5.2232
CSo_{40}	0.3014	0.1950	2.2795	5.2232

Interestingly Moulik's equation fits equally well to the soap solutions both below and above CMC. The equation is [36]:

$$\frac{1}{c} = \left(\frac{0.921}{\nabla}\right)^{-1} \frac{1}{\log\left(\dfrac{\eta}{\eta_0}\right)} + Q\,\nabla \qquad \textbf{(8)}$$

Where M and K are constants. Evaluated values of M and K from the plots of $(\eta/\eta_0)^2$ v/s $c^2$are shown in Table **6**.

Table 6. values of viscometric parameters obtained from different equations of copper soaps derived from various edible oils in 20% and 40% methanol-benzene mixture.

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
CM_{20}	1.0140	1.0301	0.3639	0.6248	0.42		0.5773	2.3558
CG_{20}	1.0300	1.1340	1.0355	0.2679	0.72	2.200	1.7320	0.3249
CSe_{20}	1.0520	1.1420	0.9004	0.2867	1.16	2.380	1.4825	0.3443
CSo_{20}	1.0780	1.2000	0.9325	0.3249	1.54	3.000	1.7320	0.3639
CM_{40}	1.0150	1.0610	1.3270	0.6618	0.12	0.700	1.7320	0.8390
CG_{40}	1.0340	1.0820	1.3032	0.5095	0.22	0.980	0.6248	0.3443
CSe_{40}	1.0400	1.1400	0.7812	0.2493	0.38	1.870	1.9626	0.4877
CSo_{40}	1.0620	1.1106	1.1106	0.3443	0.94	2.000	0.8390	0.4040

The plots of $(\eta/\eta_0)^2$ *v/s* c^2show a break at a definite soap concentration corresponding to the CMC of the soap Fig. (**6**). The values of Moulik's constant M and K have been obtained from the intercept and slope of these plots follows the order:

$$M_2 \text{ (above CMC)} > M_1 \text{ (below CMC)}$$

Unlike 'M', the stipulated values of 'K' follow the order:

$$K_1 \text{ (below CMC)} > K_2 \text{ (above CMC)}$$

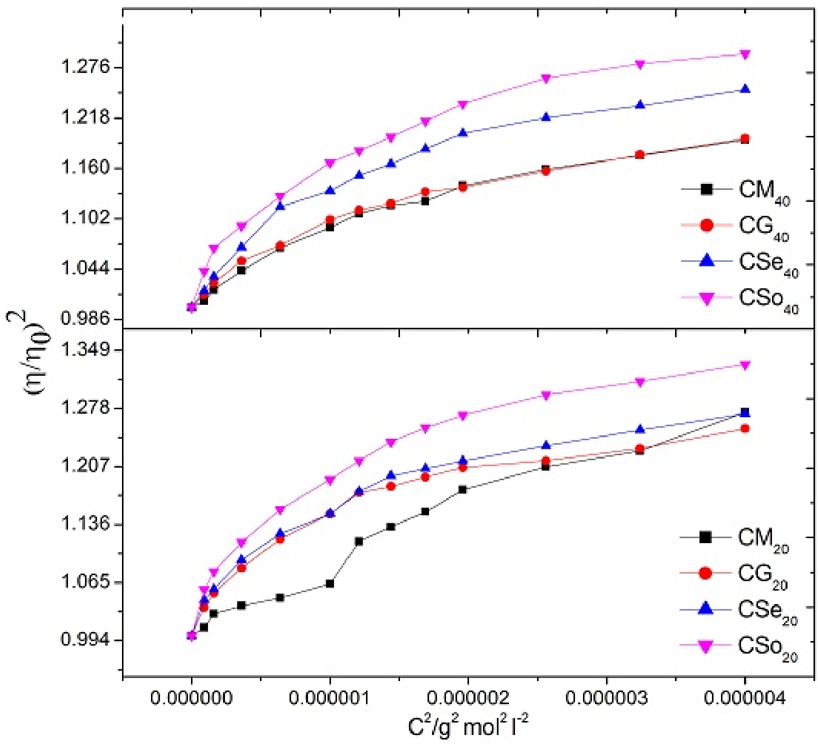

Fig. (6). Plots of $(\eta/\eta_0)^2$ *v/s* c^2 of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Moulik's equation).

The intrinsic viscosity $[\eta]$ = limit ($c\rightarrow 0$) $[\eta_{sp}]$ of the soap solution according to Gray and Alexander can be represented by the equation [37]:

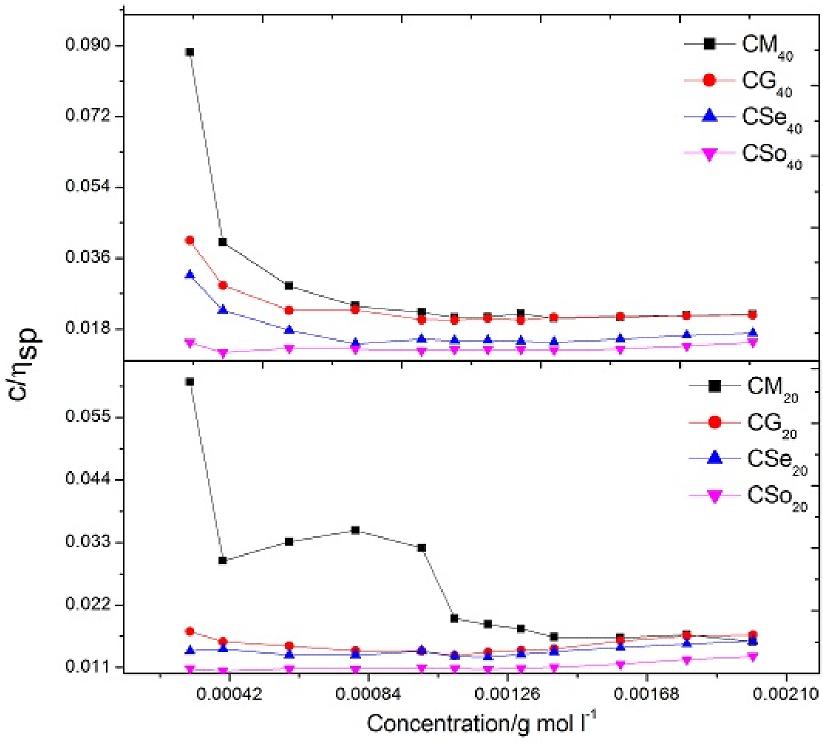

Fig. (7). Plots of (c/η_{sp}) *v/s* c of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Gray and Alexander equation).

$$\left(\frac{\eta}{\eta_0}\right)^2 = M + K\ c^2 \quad (9)$$

The values of intrinsic viscosity and coefficient K' are determined from the plot of reduced viscosity (c/η_{sp}) against the concentration c of the soap. The plot of (c/η_{sp}) v/s c is characterized by an intersection of two straight lines Fig. (**7**), thus Gray and Alexander equation fits well both below and above CMC. The sudden change in the trend of the plot at CMC clearly indicated that the change in the behaviour of the soap took place in the periphery of this concentration.

The viscosity data have also been interpreted in light of Jones-Dole Equation [38]:

$$\frac{c}{\eta_{sp}} = \frac{1}{\eta} - K.c \quad (10)$$

For convenience, the equation may be expressed as:

$$\frac{\left(\frac{\eta}{\eta_0}\right)^2 - 1}{\sqrt{c}} = A + B\ \sqrt{c} \quad (11)$$

$$\frac{\psi}{\sqrt{c}} = A + B\ \sqrt{c} \quad (12)$$

Where the coefficient A and B refer to the solute–solute and solute–solvent interaction, respectively.

The plots of ψ/√c *v/s* √c was characterized by an intersection of two straight lines at a point corresponding to the CMC of the soap Fig. (**8**). The values of CMC are in close agreement with the values obtained fromη *v/s* c, η_{sp} v/s c, ϕ v/s c plots.

In view of the two intersecting straight lines forψ/√c *v/s* √c plots, it is reasonable to evaluate two values of each coefficient below and above CMC designated as A_1, B_1 and A_2, B_2, respectively, that are given in Table **6**. The positive value of A suggests that there is a strong soap- soap interaction in this system and positive value of B indicates a strong alignment of solvent molecules with solute, which reveals the structure forming behaviour of the solvent.

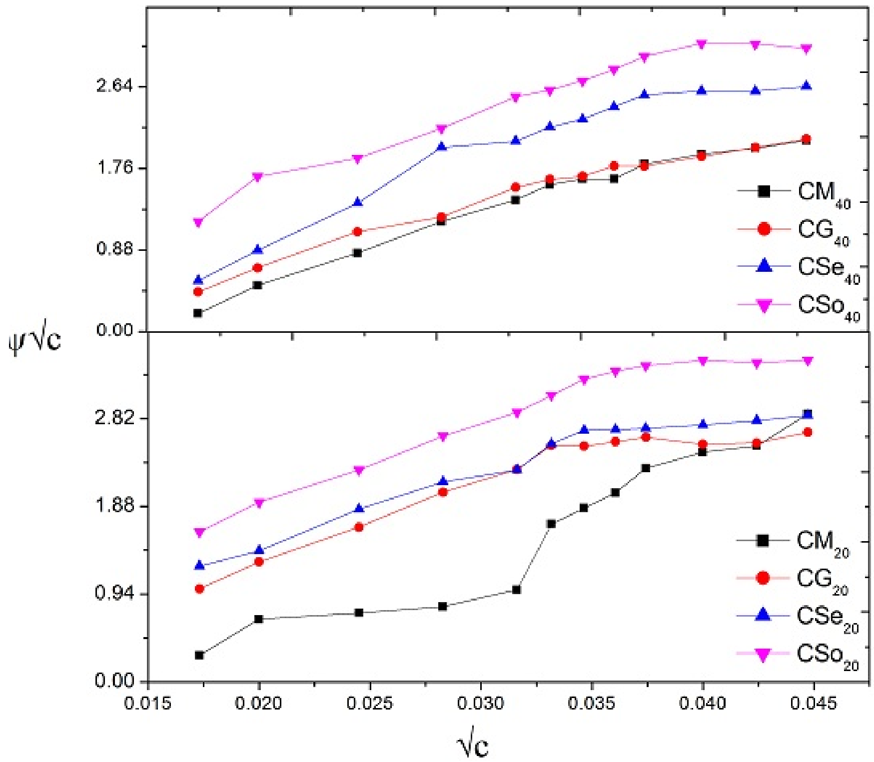

Fig. (8). Plots of (ψ/√c) *v/s* √c of copper soaps derived from various edible oils in 20 and 40% methanol- benzene mixture (Jones – Dole equation).

From the data collected it is obvious that below the CMC, the values of coefficient B_1 (soap-solvent interaction) are larger than the values of coefficient A_1 (soap-soap interaction) which confirms that the molecules of the soap do not aggregate appreciably below the CMC and there is sudden change in the aggregation above the CMC. From this trend, it is clear that soap-solvent interaction is larger than the soap-soap interaction in dilute solution. The trend of these coefficients may be as follows:

$$A_1 < A_2 \& \quad B_2 < B_1$$

From this trend it may be concluded that soap-solvent interaction is more pronounced below CMC. This may be ascribed to the favorable interaction between soap and solvent molecules at the premicellar concentration.

3.2. Copper Soaps Derived from Various Edible Oils in 40% Methanol-Benzene Mixture

3.2.1. Molar Volume

The value of molar volume forcopper soaps derived from various edible oils in 40% methanol-benzene mixture were calculated and recorded. The results show that the effect of soap concentration on the molar volume of copper soap solutions in 40% methanol-benzene mixture is almost similar to that of molar volume of copper soap solutions in

20% methanol-benzene mixture.

The plots of molar volume, V against the soap concentration is characterized by an intersection of convex curve and a straight line. Below CMC, a straight line followed by a convex curve in increasing trend is observed, and after CMC, there is a sharp decrease in molar volume.

The values of CMC determined are in good agreement with the values obtained from density measurements. The values of molar volume V for 40% methanol-benzene mixture was observed lower than that of 20% methanol-benzene mixture which is due to the fact that the nature of solvent plays a significant role in ordering and compacting the scattered micellar units. It is further suggested that methanol occupies quite a different position in the palisade layers of soap anion exhibiting a different degree of aggregation in the mixed solvent of varying composition.

3.2.2. Viscosity, Specific Viscosity, and Fluidity

The effect of the soap concentration on the viscosity, specific viscosity and fluidity of copper soap in 40% methanol-benzene mixture of varying composition similar to that of 20% methanol-benzene mixture. It observed that the viscosity of copper soap in 40% methanol-benzene mixture slightly higher than 20% methanol-benzene mixture which is due to the difference in the viscosities of solvent mixtures. The values of the CMC for the above referred system are recorded in Table **7**. It can be easily seen from the table that the CMC of these soap follows the order:

$$CSo > CSe > CG > CM.$$

Table 7. Values of viscometric parameters obtained from different equations of copper soaps derived from various edible oils in 20% and 40% methanol-benzene mixture

Plot	CMC, g mol l^{-1}							
	CM_{20}	CG_{20}	CSe_{20}	CSo_{20}	CM_{40}	CG_{40}	CSe_{40}	CSo_{40}
η *v/s* c	0.0010	0.0011	0.0012	0.0013	0.0011	0.0012	0.0013	0.0014
η_{sp} *v/s* c	0.0010	0.0011	0.0012	0.0013	0.0011	0.0012	0.0013	0.0014
ϕ *v/s* c	0.0010	0.0011	0.0012	0.0013	0.0011	0.0012	0.0013	0.0014
$\psi/\sqrt{c}$ *v/s* $\sqrt{c}$	0.0010	0.0011	0.0012	0.0013	0.0011	0.0011	0.0011	0.0014

This is an agreement with the fact that there is a decrease in the CMC values with the increase in the number of carbon atom in the hydrophobic chain. Viscosity of copper soap derived from various edible oils in 40% methanol-benzene follows the order:

$$CSo > CSe > CG > CM$$

The above trend clearly demonstrates that the viscosity of the soap solutions increases with an increase in the average molecular weight of the soap.

3.2.3. Important Equations

It has been found that Einstein and Vand's equations are equally applicable to copper soap solution in 40% methanol-benzene mixture. But Thomas equation gives no plausible inference due to irregular data. The change in the values of molar volume below and above CMC may due to the fact that entrapping of solvent molecules below CMC is dissimilar to the entrapping of solvent molecules above CMC. From comparison of the result of copper soap in both the solvents, it maybe suggested that the values of molar volume was higher in 20% methanol-benzene mixture than that of 40% methanol-benzene mixture.

Furthermore, the viscometric data below and above CMC have also been interpreted in terms of Moulik's equation and pertaining parameters M and K. The order of M and K below and above CMC follows the order:

$$M_2 > M_1 \text{ and } K_1 > k_2$$

Jones-Dole equation is also applicable to copper soap in 40% methanol-benzene mixture. The values of A_1, A_2 and B_1, B_2 was calculated and the trend observed similar to that of copper soap in 20% methanol-benzene mixture.

A review of the results shows that below the CMC, the value of coefficient B_1 is larger than the value of coefficient A_1. This trend indicates that below the CMC, the solute-solvent interaction is more pronounced than solute-solute interaction. The trend of these coefficient is shown below-

$$A_1 < A_2 \& \quad B_2 < B_1$$

The order $A_2 > A_1$ is inconsonance with the expectations that solute-solute interaction becomes stronger after CMC as the micellar aggregation takes place. For all the copper soap, the positive values indicate a strong alignment of solvent molecules which reveals the structure forming the behavior of solvent.

Literature survey [39, 40] reveals that the positive value of A suggests a strong solute-solute interaction. In our referred system, the values of A_1 and A_2 are positive and they follow the order$A_1<A_2$. Thus, it is suggested that solute-solute interaction becomes stronger after CMC as the micellar aggregation takes place as compared to before CMC.

Further A_1 and A_2 (solute-solute) interaction in 20% methanol-benzene mixture was found higher than in 40% methanol-benzene mixture. This may be accounted in terms of change in the mobility of the solute with a change in the dielectric constant of the medium. The positive value of B indicated a strong alignment of solvent molecules with solute, which reveals the structure forming behavior of the solvent.

The decrease in B values B_1(40%) < B_1 (20%) showed that solute-solvent interactions are influenced by the increase in the non-polar solvent content in the system below and above CMC.

CONCLUSION

The viscosity parameters are important to understand the colloidal behavior, CMC characteristics and nature of the complexes. These studies indirectly help in identifying the structural insight, physical and biochemical properties of above metallic soaps. The present research work makes an attempt to prepare surface active compounds from metal and natural oils. It has been found that the beneficial effects of the synthesized biologically active molecules, agrochemicals and pharmaceuticals are still open for further research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

The authors pay their sincere gratitude to UGC for Financial support, Principal, S. D. Govt. College, Beawar, S.P.C. Govt. College Ajmer Rajasthan (India) for providing necessary research facilities to accomplish this study.

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