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VISCOMETRIC BEHAVIOUR AND MICELLAR STUDIES OF CU (II) SURFACTANT DERIVED FROM NEEM (AZADIRECTAINDICA)) OIL IN METHANOL-BENZENE MIXTURE AT 298.15 K

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ABSTRACT

Density of complexes have been measured in various concentrations and by using density data, the molar volume and apparent molar volume have been evaluated in order to determine the critical micelle concentration (CMC). Viscosity and other parameters of Cu (II) surfactant derived from karanj oil in non-aqueous solvents of varying composition has been determined at constant temperature 298.15K. The synthesize surfactants were characterized by IR NMR and Elemental analysis. In the present work, benzene and methanol have been chosen as the co-solvent as mixed solvents have tendency to interact with complex molecules and result affecting the aggregation of complex molecules. The results were used to determine the critical micelle concentration (CMC), soap-solvent interactions and the effect of chain length of the surface active molecule on various parameters. The CMC values of copper karanj soap solutions decreases with the increase in methanol the polar solvent. The conclusions with regard to solute-solute and solute- solvent interaction have been discussed in terms of well-known Masson's and Jones- Dole equations. This vital information plays an important role in various industrial and biological applications

Keywords- *Cu (II) Soap, Non-edible oils, Soap- Solvent interaction, CMC, Density and Viscosity.*

I. INTRODUCTION

Coming onto copper surfactants applicability in our day to day life, they have sufficient pharmaceutical, industrial and analytical application due to special physico -chemical behavior. Due to their ability to lower surface tension surfactants are used as emulsifiers, detergents, dispersing agents foaming agents, wetting and penetrating agents and so forth. Use of surfactants as wood preservatives, water proofing, repellency agents in various industries of rubber and paints are well known [1-2]. The present work deals with the study of density and viscosity of copper soap derived from neem oil in a ternary system. The density and viscosity measurements have been used to determine the critical micelle concentrations (CMC) of copper (II) neem soaps in non-aqueous media and apparent molar volume data have been employed to obtain information about solute-solute, solvent-solvent interactions in solutions [3-4].

II. EXPERIMENTAL

All the chemicals used were of LR/AR grade. Copper soap was prepared by refluxing the non-edible oil i.e. Neem (*Azadirectaindica*) oil (extracted from kernels and purified) with ethyl alcohol and 2N KOH solutions for 3-4 hours (Direct Metathesis). The neutralization of excess of KOH present was done by slow addition of 0.5N HCl. Saturated solution of copper sulphate was then added to it, for conversion of neutralized potassium soap into their corresponding copper soap. Copper soap so obtained was then washed with warm water and 10% alcohol at 50 ^{o}C and recrystallized using hot benzene. Molecular weights of copper soaps were determined from saponification value [5]. The copper soap is abbreviated as copper – neem (CN).

Measurement of Density

Ostwald's modification of *Sprengel's* pyknometer with a volume of about 10 ml was used for measuring the density of the soap solution in the thermo stated bath at 298.15 K. The density of the solutions was calculated by the following relationship.

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$$\rho = \frac{w}{w0} \qquad (1)$$

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

Evaluation of Molar Volume

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

$$\nabla = M_1X_1 + M_2X_2 + M_3X_3/\rho \quad (2)$$

Where 'X_1' is the mole fraction of the soap of molecular weight 'M_1' where as '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 ρ' stands for density of the solution.

Evaluation of Apparent Molar Volume

The apparent molar volume has been calculated from the density data using the following equation;

$$\phi v = \frac{M}{\rho^0} + \frac{1000(\rho^0 - \rho) \qquad (3)}{c.\rho_0}$$

Where 'ρ_0' represents the density of the solvent,'ρ' is the density of the soap solution, 'M' is the molecular weight of the soap and 'c' is the concentration of solution is mol L^{-1}.

2.4 Evaluation of Viscosity:

The viscosity of the soap solutions was calculated by the following relationship.

$$\frac{\eta^0}{\eta} = \rho_0.t_0/\rho\, t \quad (4)$$

Where η_0,η,ρ_0 ρ, t_0 and t are the viscosity, density and time of flow for the known and unknown solutions respectively.

III. RESULTS AND DISCUSSION

Dilute solutions of varying concentration of Cu (II) - neem oil soap were prepared using 100% benzene, 80% benzene-methanol and 60% benzene-methanol as the solvent and they are abbreviated as CN_{100}, CN_{80} and CN_{60} respectively. It has been observed that the density of CN soap solutions is of the order of the density of the solvents. Table-1. The value of density of Cu (II) soaps in benzene is higher than that of 80% benzene–methanol which is higher than 60% benzene–methanol system.

Table 1. Density (ρ) Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene-Methanol system at 298.15 K

Concentration (mol L^{-1})	CN_{100}	CN_{80}	CN_{60}
0.0002	0.8750	0.8576	0.8443
0.0003	0.8751	0.8582	0.8445
0.0004	0.8761	0.8586	0.8450
0.0005	0.8747	0.8583	0.8442
0.0006	0.8727	0.8573	0.8428

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0.0007	0.8735	0.8581	0.8439
0.0008	0.8742	0.8588	0.8443
0.0009	0.8752	0.8590	0.8447
0.0010	0.8759	0.8596	0.8452
0.0012	0.8766	0.8598	0.8454
0.0014	0.8764	0.8600	0.8451
0.0016	0.8762	0.8596	0.8450

The values of molar volume and apparent molar volume (ϕ_v) of in pure benzene, 80% and 60% benzene-methanol system were recorded in Table-2-3.To explore the observations of various scientists in our referred system the data has also been analyzed in terms of Masson equation [6].

$$\phi v = \phi v^0 + S\sqrt{C} \quad (5)$$

Table 2: Molar Volume (V) Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene- Methanol system at 298.15 K

Concentration (mol L^{-1})	**CN_{100}**	**CN_{80}**	**CN_{60}**
0.0002	89.2839	71.9866	60.0896
0.0003	89.2762	71.9427	60.0459
0.0004	89.1820	71.9114	60.0351
0.0005	89.3293	71.9430	60.0058
0.0006	89.5345	72.0275	60.0661
0.0007	89.4623	71.9726	60.1693
0.0008	89.3922	71.9421	60.0978
0.0009	89.2967	71.9008	60.0678
0.0010	89.2350	71.8529	60.0434
0.0012	89.1759	71.8490	60.0149
0.0014	89.2075	71.8426	60.0110
0.0016	89.2381	71.8863	60.0363

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Table 3: Apparent Molar Volume (ϕ_v)Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene- Methanol system at 298.15 K

Concentration (mol L^{-1})	CN_{100}	CN_{80}	CN_{60}
0.0002	3634.5	2715.8	5071.6
0.0003	3158.0	4310.1	4459.1
0.0004	5349.8	4669.7	4923.4
0.0005	1244.4	3135.8	2214.6
0.0006	-2559.9	888.3	-776.7
0.0007	-850.0	2049.2	1235.8
0.0008	403.9	2497.1	1885.7
0.0009	1696.7	3013.9	2285.7
0.0010	2353.7	3520.7	2676.9
0.0012	2738.7	3211.6	2522.8
0.0014	2286.7	3015.8	2065.6
0.0016	1954.8	2431.5	1811.6

Here, ϕ_v represents apparent molar volume,$\phi_V^0$and S_v represents limiting apparent molar volume and limiting apparent slope respectively. $\phi_v^0$and S_v have been regarded as the measure of solute–solvent interactions and solute – solute interactions respectively (Table 4). The value of CMC as shown below (Table-5) CN_{100}>CN_{80}>CN_{60}

Table 4: Computed parameters of Masson's equation for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene- Methanol system at 298.15 K

Soap Solutions	□$_{v1}$□	□$_{v2}$□	S_{v1}	S_{v2}
CN_{100}	40552.06	-21230.78	-1759342.82	765437.07
CN_{80}	21570.47	-5552.83	-837889.89	286102.76
CN_{60}	30333.49	-4818.56	-1266000.15	236955.52

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Table 5: Value of CMC for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene-Methanol system at 298.15 K

Parameter	**CN_{100}**	**CN_{80}**	**CN_{60}**
ρv/s c	0.00060	0.00057	0 .00055
V v/s c	0.00060	0.00057	0 .00055
ϕ_v v/s c	0.00060	0.00057	0 .00055
□ v/s c	0.00063	0.00054	0 .00051
□$_{sp}$ v/s c	0.00063	0.00054	0 .00051
□ □ v/s c	0.00063	0.00054	0 .00051
(□$_{sp}$ /c) v/s c	0.00063	0.00054	0 .00051
(□ /√c) v/s √c	0.00063	0.00054	0 .00051
□ □ □ □) ^{2} v/s c ^{2}	0.00063	0.00054	0 .00051
(1/c) v/s {1/log□ □ □ □)}	0.00063	0.00054	0 .00051
(C□ □$_{sp}$) v/s c	0.00063	0.00054	0 .00051

The viscosity data have also been interpreted in the light of Moulik's Equation and Jones – Dole Equation [7]. The viscosity and specific viscosity (η_{sp}) of CN soap solution is given in Table – 6-7. The results show that specific of CN_{100}, CN_{80}& CN_{60} also initially increases then decrease with the increase in the concentration, and after a definite concentration corresponding to the CMC of the soap solution shows increases again. The fluidity 'ϕ' which is defined as reciprocal of viscosity 'η' i.e. ϕ =1/η, of CN_{100} CN_{80} & CN_{60} soap solutions initially decrease than increases and then decrease again after a definite concentration [8-9].

The fluidity ϕ of CN soap recorded in Table-8

$$(\eta/\eta_0) - 1/\sqrt{c} = A + B\sqrt{c} \quad (6)$$

For convenience, the equation may be expressed as:

$$\frac{\varphi}{\sqrt{c}} = A + B\sqrt{c} \quad (7)$$

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Table 6 : Viscosity (η) Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene-Methanol system at 298.15 K

Concentration (mol L^{-1})	CN_{100}	CN_{80}	CN_{60}
0.0002	6.2581	6.1345	5.8740
0.0003	6.3167	6.1938	5.9304
0.0004	6.5460	6.4213	5.8777
0.0005	6.3686	6.3041	5.7635
0.0006	6.2469	6.0199	5.7033
0.0007	6.5375	6.1340	5.7592
0.0008	6.7121	6.2489	5.8159
0.0009	6.8867	6.3645	5.8741
0.0010	7.1184	6.4798	5.9317
0.0012	7.4690	6.6521	6.0481
0.0014	7.7524	6.8756	6.3297
0.0016	7.6911	6.8189	6.4367

Table 7 : Specific Viscosity (η_{sp}) Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene- Methanol system at 298.15 K

Concentration (mol L^{-1})	CN_{100}	CN_{80}	CN_{60}
0.0002	0.0098	0.0286	0.0397
0.0003	0.0192	0.0385	0.0497
0.0004	0.0562	0.0766	0.0404
0.0005	0.0276	0.0570	0.0202
0.0006	0.0080	0.0093	0.0095
0.0007	0.0548	0.0285	0.0194
0.0008	0.0830	0.0477	0.0295
0.0009	0.1112	0.0671	0.0398
0.0010	0.1486	0.0864	0.0500
0.0012	0.2052	0.1153	0.0705
0.0014	0.2509	0.1528	0.1204
0.0016	0.2410	0.1433	0.1393

Table 8: Fluidity (ϕ) Data for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene-Methanol system at 298.15 K

Concentration (mol L^{-1})	CN100	CN_{80}	CN_{60}
0.0002	0.1598	0.1630	0.1702
0.0003	0.1583	0.1615	0.1686
0.0004	0.1528	0.1557	0.1701
0.0005	0.1570	0.1586	0.1735
0.0006	0.1601	0.1661	0.1753
0.0007	0.1530	0.1630	0.1736

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0.0008	0.1490	0.1600	0.1719
0.0009	0.1452	0.1571	0.1702
0.0010	0.1405	0.1543	0.1686
0.0012	0.1339	0.1503	0.1653
0.0014	0.1290	0.1454	0.1580
0.0016	0.1300	0.1467	0.1554

Where the coefficient A and B refer to the solute–solute and solute–solvent interaction respectively.The values of A and B are evaluated from the plot of ($\psi/\sqrt{c}$) v/s $\sqrt{c}$, which is characterized by an intersection of a two straight lines for Cu (II) neem soap solution in 60 % benzene –methanol (Figure-1). Thus Jones–Dole equations [10] fit well both below and above CMC. The values of A and B so evaluated are recorded in Table -9.

Table 9: Computed parameters derived from different equations for Cu (II) Neem Soap solutions in 100 % Benzene, 80 % Benzene - Methanol and 60 % Benzene- Methanol system at 298.15 K

Soap	Moulik's Equation				Jones – Dole Equation			
	M_1	M_2	K_1	K_2	A_1	A_2	B_1	B_2
CN_{100}	1.1934	0.7940	-0.5092	0.5904	14.2240	-20.8360	-568.7400	838.7300
CN_{80}	1.2706	1.0250	-0.6990	0.1467	19.2100	-3.2990	-760.7000	191.0500
CN_{60}	1.1315	1.0240	-0.3150	0.0714	9.0115	-0.9610	-352.2800	77.7870

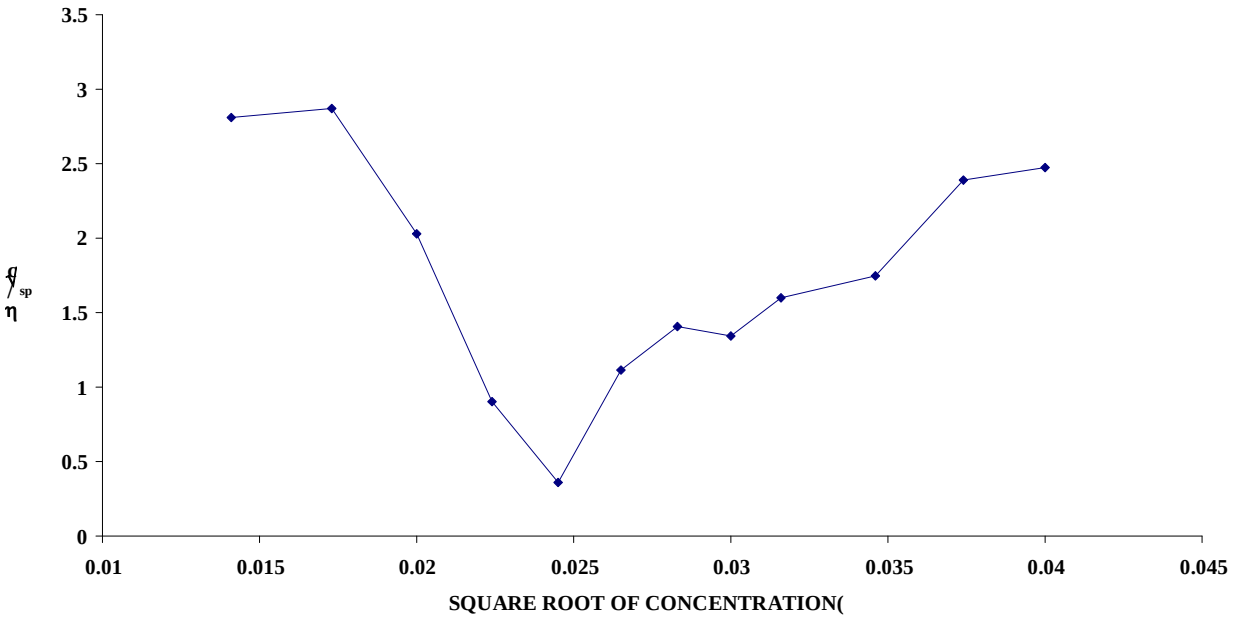

Figure- 1 : PLOT OF Hsp/√c Vs SQUARE ROOT OF CONCENTRATION FOR COPPER (II) NEEM SOAP SOLUTIONS IN 60% BENZENE (METHANOL)

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IV. CONCLUSION

The present research work makes an attempt to prepare surface active compounds from metal and natural non - edible oils. It is found that the beneficial effects of the synthesized biologically active molecules, agrochemicals and pharmaceuticals are still open for further research.

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