

**EFFECT OF SURFACTANT HEAD GROUPS ON THE EXTENT OF SOLUBILIZATION OF SUDAN I DYE****Madhu Khandelwal^{1*}, Ampily J.S.², Bijendra Rai¹, Geetha Sarasan¹**¹Department of Chemistry, Holkar Science College, Indore, Madhya Pradesh, India²Department of Chemistry, R. Sankar Memorial SNDP Yogam Arts and Science College, Koyilandy, Calicut, Kerala, India*Corresponding author: madhu.khandelwal15@gmail.com**ABSTRACT**

An important property of micelles in aqueous solution is their ability to increase the solubility of water insoluble compounds. In this work, the solubilization of Sudan I dye was studied in micellar solutions of three surfactants, possessing the same hydrocarbon tail but different hydrophilic head groups, namely sodium dodecylsulphate (SDS), dodecyltrimethylammonium bromide (DTAB), and dodecyl pentaethyleneoxide ($C_{12}EO_5$). From the result of CMC, the CMC of $C_{12}EO_5$ is much lower than DTAB and SDS. The results showed that, irrespective of the surfactant type, the solubility of Sudan I dye increased linearly with increasing surfactant concentration, as a consequence of the association between the dye and the micelles. The solubilization power and values of micelle-water partition coefficient calculated and found that these values are higher for $C_{12}EO_5$ than DTAB and SDS. Solubilization at micellar surface as well as in hydrophobic core of micelles that increase the solubilization of dye in $C_{12}EO_5$ micellar solution and much lower value of CMC are responsible for high solubilization power of it. The enhanced solubility of dye in DTAB micellar solutions than SDS is a resultant of electrostatic interaction between the positively charged surfactant head group and the polar groups present in the dye structure. The anionic surfactant SDS presented the least solubilization power as a result of electrostatic repulsions between the dye and the anionic surfactant head groups. The free energy of solubilization is energetically favorable for $C_{12}EO_5$ than DTAB and SDS.

Keywords: Micellar solubilization, Sudan I dye, Surfactant. Solubilization Power, Partition Coefficient**1. INTRODUCTION**

Surfactants are amphiphilic molecules with distinct hydrophobic and hydrophilic regions in their chemical structures. Depending on their chemical structures they can be nonionic, cationic, anionic, zwitter ionic etc. [1-3]. They are known to play important role in many processes of interest in both fundamental and applied sciences. Surfactant molecules arrange themselves into organized molecular assemblies known as micelles and the concentration above which micelles form is called the critical micelle concentration [4]. Characteristic feature of the surfactants are micelle formation and solubilization of water-insoluble substances by micelles. Therefore, the critical micelle concentration (CMC) is the single most useful quantity and important parameter for characterizing the surfactants. The CMC results from a delicate balance between attractive forces of hydrophobic interaction among the nonpolar surfactant tails and the repulsive force results from steric and electrostatic interactions (in the case of ionic and zwitterionic surfactants) between the surfactant polar head groups [5].

Micelles have remarkable ability to solubilize wide variety of water insoluble compounds such as hydrocarbons, dyes, drugs, etc. in their hydrophobic domain, so most of the industrial applications are based on micellar solubilization. The architecture of the surfactant molecule is a significant factor that affects the solubilization of dye in micellar solution and it quantifies by molar solubilization capacity or solubilization power and micelle-water partition coefficient [6].

S.W.H. Shah *et. al.* determined the partition coefficient (Kc) of various aromatic acids between the bulk and micelles of Sodium dodecylsulfate (SDS) at 25°C by differential spectroscopic method [7]. Solubilization power of ionic and non ionic surfactants for the hydrophobic dyes was evaluated by Rajdeep singh [8]. Carlota O. Rangel-Yagui investigated the molar solubilization capacity of three surfactants possessing the same hydrocarbon tail but different hydrophilic head groups for ibuprofen drug (IBU) [9].

In this work, the influence of the hydrophilic portion of surfactant's head group on micellar solubilization of the

Sudan I dye was investigated. Three different surfactants, a nonionic (dodecyl pentaethyleneoxide), a cationic (dodecyltrimethylammonium bromide), and an anionic (sodium dodecylsulphate), all presenting the same tail length, were studied.

2. EXPERIMENTAL

2.1. Material and Methods

The cationic surfactant dodecyltrimethylammonium bromide, DTAB was purchased from Spectrochem pvt. Ltd and anionic surfactant SDS (sodium dodecylsulphate) procured from Sigma-Aldrich. Non ionic surfactant dodecyl pentaethyleneoxide (C₁₂EO₅) received from Agarwal industries, emulsifiers manufacturing company located at Indore (M.P.). Sudan I dye (water-insoluble) is an azo dye and also known as solvent yellow 14 (Fig. 1), purchased from HIMEDIA.

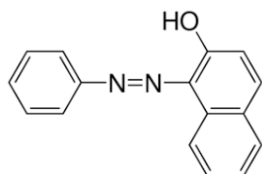


Fig. 1: Chemical Structure of Sudan I dye

2.2. Critical micelle concentration (CMC) determination

The CMC of the surfactants at 30°C was determined in aqueous solution by conductivity/surface tension method. The determination of CMC for SDS and DTAB were based on the change in conductance with surfactant concentration. The conductivity measurements were performed with digital Systronics conductivity meter (306). The CMC determination for C₁₂EO₅ was based on the change in surface tension with surfactant concentration.

2.3. Solubility determination

Calibration curve of the dye in alcohol is constructed as a function of the dye concentration for measuring the solubility of dye in aqueous micellar solution (Fig. 2). The absorbance values were observed at the wavelength of maximum absorption (λ_{\max} 478 nm) using UV-Visible spectrophotometer. The plot between absorbance Vs dye concentration is linear and used for determination of the molar extinction coefficient (ϵ) by the Beer-Lambert equation:

$$A = \epsilon c l \quad (1)$$

Where A is the absorbance, c is the concentration and l is the optical path length.

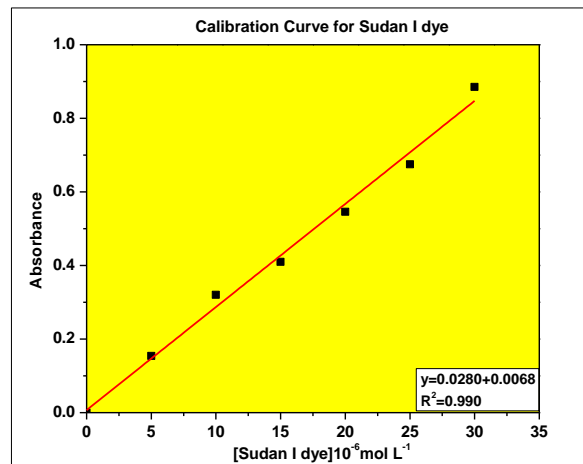


Fig. 2: Calibration curve of Sudan I dye

The solubility of Sudan I dye in SDS, DTAB and C₁₂EO₅ solutions were measured at different surfactant concentrations at 30°C. Specific amount of dye was added to vials containing 50 mL of surfactant solution (DTAB, SDS and C₁₂EO₅). The sample vials were then rotated up to specific time or until equilibrium achieved and after this period, the samples were centrifuged. The centrifugate was diluted with alcohol (1:1) and observed the absorbance at the wavelength of maximum absorbance of dye spectrophotometrically. Solubility curves were plotted between S_{total} and C_{surf} for Sudan I dye in the case of all surfactants studied.

Solubilization power of surfactants is the efficiency of surfactants to solubilize the compounds and defined as the number of moles of the solute (dye) that can be solubilized per mole of micellized surfactant.

$$SP = \frac{S_{\text{total}} - S_w}{C_{\text{surf}} - \text{CMC}} \quad (2)$$

S_{total} is the total dye solubility, S_w is the molar solubility of dye in water, C_{surf} is the molar concentration of surfactant in aqueous and CMC is the critical micelle concentration of the surfactant [4,10]. The solubilization power of a specific surfactant can thus be determined from the slope of its solubility curve after the CMC of surfactants.

The molar micelle-water partition coefficient, K_M , can be calculated using the equation [9].

$$K_M = \frac{SP(1 - \text{CMC})}{s_w} \quad (3)$$

The SP and K_M are useful for quantitative determination of the solubilization efficiency of a surfactant and can be used for comparing different surfactants.

3. RESULTS AND DISCUSSION

The CMC of DTAB and SDS were observed from the break point in the conductance (κ) versus concentration plots for DTAB (Fig. 3) and SDS (Fig. 4) at 30 °C. Fig. 5 shows the surface tension (γ) versus surfactant concentration plots for $C_{12}EO_5$, at 30 °C. Again, the CMC is obtained from the intersection point between the straight lines for low and high surfactant concentrations. The results of CMC for the three surfactants studied are summarized in Table 1. The values of CMC obtained for DTAB, SDS and $C_{12}EO_5$ in water are in agreement with previous values reported in literature [11-13].

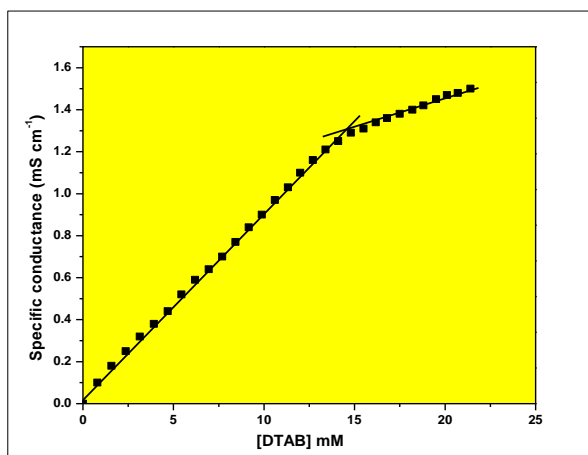


Fig. 3: Specific conductance as a function of DTAB concentration at 30°C

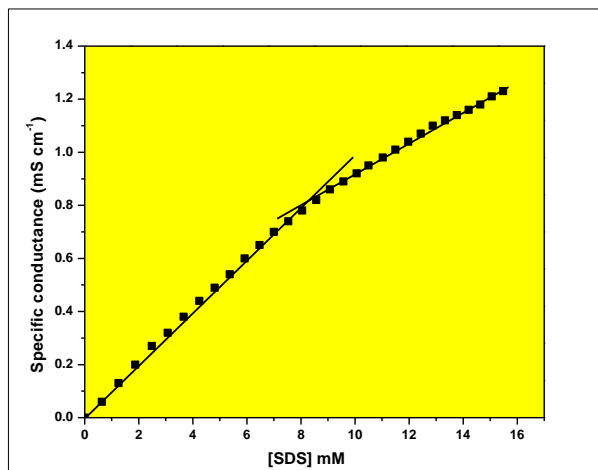


Fig. 4: Specific conductance as a function of SDS concentration at 30°C

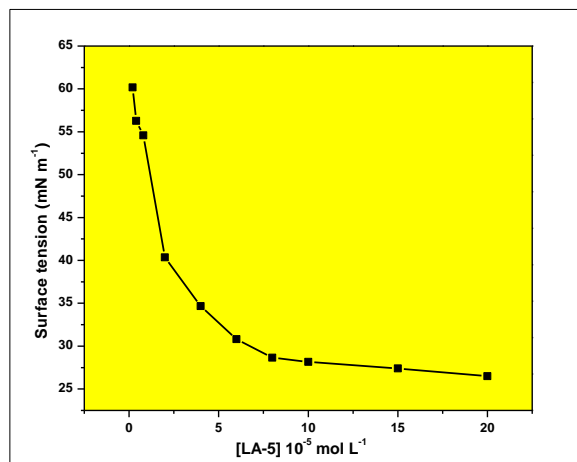


Fig. 5: Surface tension as a function of $C_{12}EO_5$ concentration at 30°C

Table 1: Critical Micelle Concentrations of DTAB, SDS and $C_{12}EO_5$

Surfactant	Critical Micelle Concentration (mM)
DTAB	14.34
SDS	8.26
$C_{12}EO_5$	0.067

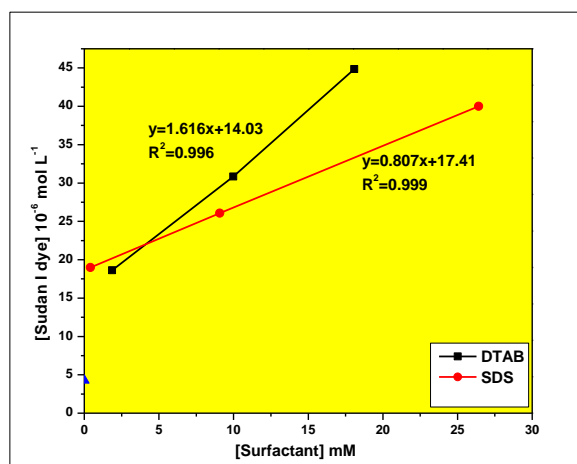


Fig. 6: Solubility curve of Sudan I dye as a function of DTAB and SDS concentration at 30°C in aqueous medium

As can be seen, the CMC of ionic surfactants (SDS and DTAB) are considerably higher than the CMC of the nonionic surfactant $C_{12}EO_5$, since repulsive interactions of the ionic head groups limit the micelle formation and thus increase the CMC of ionic surfactants. Critical micelle concentration (CMC) of the surfactant is greatly affected by the molecular architecture of the surfactant (nature of the head group and alkyl chain). The solubility

plots of Sudan I dye as a function of the surfactant concentration (mM) are represented for DTAB, SDS, (Fig. 6) and for C₁₂EO₅ (Fig. 7). Irrespective of the surfactant type, the solubility of dye increased linearly with increasing surfactant concentration, as a consequence of the association between the dye and the micelles.

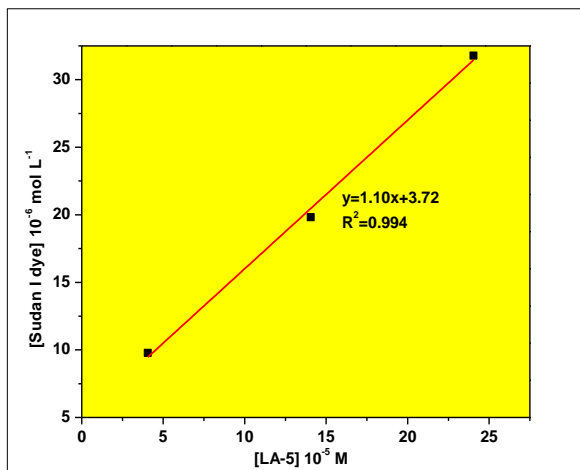


Fig. 7: Solubility curve of Sudan I dye as a function of C₁₂EO₅ concentration at 30°C in aqueous medium

Table 2: Solubilization power (SP) and molar micelle-water partition coefficient (K_M) of surfactants

Surfactant	Sudan I dye (5.0×10 ⁻³) gm		
	SP (10 ⁻³)	R ²	K _M (10 ²)
DTAB	1.61	0.996	3.72
SDS	0.81	0.999	1.86
C12EO5	110.00	0.994	256.64

The values of solubilization power (SP) and molar micelle-water partition coefficient (K_M) calculated from the 2 and 3 equations and presented in Table 2. It is found that the solubilization power increase in the order of C₁₂EO₅> DTAB>SDS. The extent of solubilization is higher for non ionic surfactant than cationic and anionic surfactants. It can also be seen from the Table 2, that C₁₂EO₅ have high value of partition coefficient than ionic surfactants (DTAB and SDS).

In the case of C₁₂EO₅, presence of the oxyethylene groups as hydrophilic group in the structure of the C₁₂EO₅ had a positive effect on the solubilization capacity. Unlike ionic surfactants (small polar head groups), micelles formed by nonionic surfactants (PEO) have an alternative sites for solubilization. A larger space

that is polyoxyethylene, may work as a site of solubilization of semipolar compounds, such as dyes, drugs, etc. In this case, for C₁₂EO₅, hydrogen bond formed between polar groups of Sudan I dye (-OH group) and the polyoxyethylene head groups drive the dye to the outer portion of the micellar core [14, 15]. Solubilization at micellar surface as well as in hydrophobic core of micelles increases the solubilization of dye in C₁₂EO₅ micellar solution. Solubilization at micellar surface decreases the CMC, which further increase the volume of hydrophobic core of micelles and enhances the solubilization of dye in C₁₂EO₅ micellar solution.

The enhanced solubility of dye in DTAB micellar solutions is a resultant of electrostatic interaction between the positively charged surfactant head group and the polar groups present in the dye structure. Thus there are two types of interactions involved in solubilization of dyes in micellar solution of cationic surfactants (i) hydrophobic interaction between dye molecules (hydrocarbon part of dye molecule) and hydrophobic part of surfactant, which solubilize the dye in inner core of the micelle and (ii) electrostatic interaction between -OH polar group of Sudan I dye with cationic head groups of surfactant which solubilize the dye in the palisade layer of the micelle.

The solubilization at micelle surface weakens the repulsion between the polar head groups of the surfactant, thus lowering the CMC of surfactant and micelle shape may be transforming from spherical-to-cylindrical with increase the hydrophobic core of micelles and hence increases the solubilization of dye in DTAB micellar solution.

The lack of interaction between anionic head groups and the polar groups of dye molecules at the micellar surface of anionic surfactants causes a decrease influence on solubilization. The dye should be located only in the inner core of SDS micelles with hydrophobic interactions and reduce the possible sites of solubilization of dye in SDS micelles and hence the lower values of SP and micelle-water partition coefficient.

The standard free energy of solubilization, ΔG_s° (kJ/mol), can be represented by the following expression [15].

$$\Delta G_s^\circ = -RT \ln K_M \quad (4)$$

R is the universal gas constant and T is the absolute temperature and K_M is the molar partition coefficient between the micelle and the aqueous phase. The ΔG_s°

values were calculated for all surfactants and the results are presented in Table 3.

Table 3: Free energy of solubilization (ΔG_s°) for Sudan I dye

Surfactant	Sudan I dye ΔG_s° kJ mol ⁻¹
DTAB	-14.909
SDS	-13.177
C ₁₂ EO ₅	-25.581

The ΔG_s° values for all systems studied are negative, indicating spontaneous solubilization. The lowest value was observed for C₁₂EO₅ micellar system, confirming that the solubilization process is energetically more favorable in non ionic micellar systems. On the contrary, the highest ΔG_s° value corresponded to the SDS micellar system.

4. CONCLUSION

In this work, the influence of the surfactant head group on the extent of solubilization of Sudan I dye was investigated. The anionic surfactant SDS presented the least solubilization profile for dye as a result of electrostatic repulsions between the dye and the surfactant head group, whereas the cationic surfactant DTAB provided the higher solubilization power of dye due to the electrostatic and hydrophobic interactions. The highest solubilization power of C₁₂EO₅ micellar solutions was a consequence of hydrophobic interaction with dye and also the larger site provided by PEO surfactant head groups through hydrogen bonds with polar groups of dye. Moreover the low CMC of C₁₂EO₅ is also favorable for high solubilization power. From the present study it is clear that the non ionic surfactant

(C₁₂EO₅) is the best one among the surfactants studied for the solubilization of Sudan I dye.

5. REFERENCES

- Rosen MJ. *Surfactants and Interfacial Phenomena* 3rd ed., New York: John Wiley & Sons; 2004.
- Tadros TF. *Applied Surfactants: Principles and Applications*, New York: Wiley, John Wiley & Sons; 2005.
- Holmberg K, Jönsson B, Kronberg B, Lindman B. *Surfactants and Polymers in Aqueous Solution*. 2nd ed., Chichester: John Wiley & Sons; 2003.
- Tehrani-Bagha AR, Holmberg K. *Materials*, 2013; **6(2)**:580-608.
- Rangel-Yagui CO, Pessoajr A, Blankschtein D. *Braz. J. Chem. Eng.*, 2004; **21(4)**:531-544.
- Atwood D, Florence AT. *Surfactant systems: Their chemistry, pharmacy and biology*, New York: Chapman and Hall; 1983.
- Shah SWH, Naseem B, Naeem K, Malik QM. *J. Surf. Sci. Technol.*, 2001; **17(1)**:49-56.
- Singh R. *Master Sci. Thesis*, Chalmers Univ. Gothenburg, Sweden; 2012.
- Rangel-Yagui CO, Hsu HWL, Pessoa-Jr A, Tavares L C. *Brazilian J. Pharm. Sci.*, 2005; **41(2)**: 237-246.
- Alvarez-Nunez FA, Yalkowsky SH. *Int. J. Pharm.*, 2000; **200**:217-222.
- Yadav SK. *Arch. Appl. Sci. Res.*, 2013; **5(5)**: 105-109.
- Bhattarai A., Shah SK, Limbu K. *Sci. World*, 2014; **12(12)**:41-43.
- Zhang R, Zhang L, Somasundaran P. *J. colloid interface Sci.*, 2004; **278**:453-460.
- Rosen MJ. *Surfactants and Interfacial Phenomena* 2nd ed., New York: John Wiley & Sons; 1989.
- Torchilin VP. *J. Control. Rel.*, 2001; **73(2-3)**:137-172.