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A Kinetic study on solubilization of Sudan I dye by Sodium dodecylsulphate

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ABSTRACT

The solubilization of water insoluble monoazo Sudan I dye (1-Phenylazo-2-naphthol) in the micellar solution of Sodium dodecylsulphate (SDS, anionic surfactant) was investigated. The effects of surfactant concentration, temperature, amount of dye as well as the impact of salts (NaCl, Na_2SO_4 and Na_2CO_3) on solubilization were studied using UV-Vis. spectroscopy. The results showed that the micellar characteristic of SDS enhances the solubilization of water insoluble dye in aqueous solution. The kinetic study shows that the pseudo first order rate constant values increase with increase of surfactant concentration. On increasing the temperature, the rate of solubilization also increases and it was found that the temperature above 40°C is more favourable for the solubilization of selected dye. On the other hand the solubilization of dye increase with increase in the amount of dye but the rate constant values remained almost constant for different initial amounts of dye. The critical micellar concentration of SDS in salt solution is found less than that in the aqueous solution of SDS, hence the solubilization of dye increase in salt solution of SDS. Among the salts (NaCl, Na_2SO_4 and Na_2CO_3) the values of pseudo first order rate constant is higher in the case of Na_2CO_3. The present study reveals the great role of SDS micelles for the solubilization of Sudan I dye (water insoluble) in aqueous medium.

Key words: Micellar solubilization, surfactant, Sudan I dye and kinetics

INTRODUCTION

Solubilization of water-insoluble materials in the surfactant aqueous solution is important in many industrial applications such as detergency, emulsion polymerization, enhanced oil recovery, drug delivery, textile dyeing, etc.[1-3] A micelle performs quite differently than its respective monomer in an aqueous environment. The interior hydrophobic core of the micelle provides a small oil-like reservoir to solubilize substances such as dirt, dyes, hydrocarbons, drugs, etc.

Solubilization in surfactant solutions above the critical micelle concentration (CMC) offers one approach to the solubilization of water insoluble dyes in micellar solution and depends not only on the nature of the micelles but also on the structure of the solubilized dye molecules. This has been reported to be greatly influenced by external factors such as concentration, temperature, pH, ionic strength, etc.[4-7] Dye is a colored organic compound that is used to color a substrate, eg. fabric, paper, plastic etc. in a permanent way. Sudan I dye is a synthetic organic azo dye mainly used in the colouration of solvents, gasoline, ink, fats, oils, waxes, polishes etc.[8]

Kinetic study is a powerful method of investigating the rate of solubilization which can be helpful in various operations for synthetic and analytical works. The kinetic study of solubility of naphthalimide-based monoazo dyes containing N-ethyl and N-ethanoic acid groups was investigated by **K. Gharanjig *et. al.*** in the presence of a conventional monomeric DTAB and two cationic gemini surfactants (12-4-12 or 14-4-14) by UV-Vis. Spectrophotometry.[9]

K. Gharanjig and M. Sadeghi-Kiakhani has been investigated the kinetic study on dissolution of a monoazo disperse dye based on naphthalimide containing carboxylic acid in the presence of anionic and nonionic dispersing agents and studied the effect of various parameters such as temperature, time, and concentration of dispersing agents on dissolution of the disperse dye.[10] **S. Ikeda and Y. Maruyama** studied the solubilization of a water-insoluble (Sudan Red B) dye in aqueous micellar solutions of

Dodecylpyridinium chloride (DPC) in the presence of NaCl and of Dodecylpyridinium bromide (DPB) in the presence of NaBr to investigate the effects of added salt on micelle size, shape, and structure.[11] Kinetic studies on the dissolution of disperse dyes in the presence of intensifying additives, polyethylene glycol and caprolactum and addition of both were studied by **S. Veleva *et. al.*** An exponential rate equation was applied to describe the dissolution process and established that the additives increase the rate of dissolution.[12] **Choi** and co-workers also investigated the solubilization of Disperse dyes in Gemini cationic surfactants and compared them with two conventional surfactants.[13]

The present work aims to examine the solubilization of Sudan I dye in SDS concerning surfactant concentration, temperature, amount of dye and presence of salts to select optimum condition for solubilization of dye in given aqueous surfactant solution.

MATERIAL AND METHOD

Surfactant, Sodium dodecylsulphate (SDS) and salts (NaCl, Na_2SO_4 and Na_2CO_3) were purchased from Sigma-Aldrich for experiment and used as received for the solubilization study. Sudan I dye (water-insoluble dye) was selected and procured from HIMEDIA. It is an azo dye (Figure 1) and also known as solvent yellow 14.

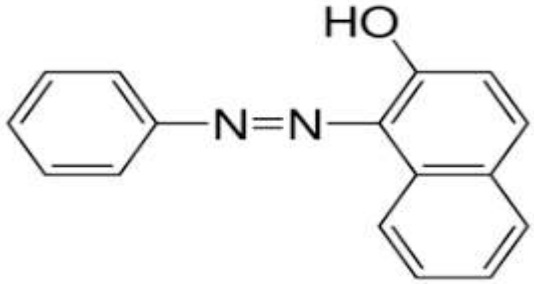


Figure 1: Chemical Structure of Sudan I dye

ABSORPTION MEASUREMENT:

The solubility of Sudan I dye in the presence of SDS surfactant was measured spectroscopically as follows: Different concentrations of anionic surfactant (0.25%, 0.50%, and 1.00%) were prepared using distilled water. Finely powdered Sudan I dye (3.00×10^{-3}gm) and 50 mL of surfactant solution was mixed together in an Erlenmeyer flask. These solutions were shaken vigorously at 30°C. The effect of temperature on the kinetic study has been studied by experimenting with 0.25% SDS solution and 3.00×10^{-3}gm of Sudan I dye at different temperatures (30, 40 and 50°C).

To investigate the effect of amount of dye on solubilization, the study was carried out at various initial concentrations of dye for a definite surfactant concentration and at a specific temperature (30°C).To study the effect of salts on solubilisation, 0.01M concentration of salts (NaCl, Na_2SO_4, Na_2CO_3) were used to prepare 0.25% SDS solution. The samples were withdrawn from the solution at particular time intervals and then centrifuged. The centrifugate was diluted with alcohol (1:1) and observed the absorbance at the wavelength of maximum absorbance (λ_{max}) using UV–Vis. spectrophotometer.

RESULTS AND DISCUSSION

Kinetic study of solubilization of dye in the presence of SDS

The kinetic study of solubilization of Sudan I dye was investigated in a micellar medium of SDS.

The concentration of dissolved dye at different time intervals were calculated from the slope of the calibration curve (Figure 2) using Beer-Lambert equation:

$$A = \varepsilon\, cl \quad \text{.....} (1)$$

$$c = \frac{A}{\varepsilon l} \text{.....} \quad (2)$$

Where A is the absorbance, ε is the molar extinction coefficient, *C* is the concentration and *l* is the length of the cell.

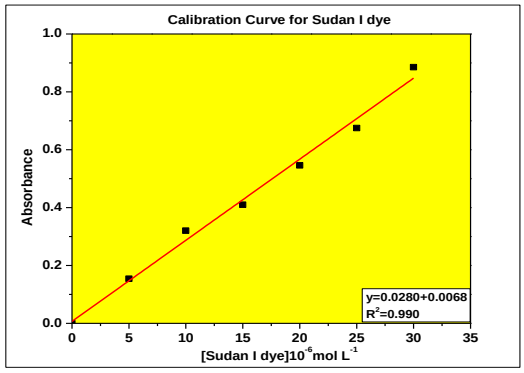


Figure 2: Calibration curve of Sudan I dye

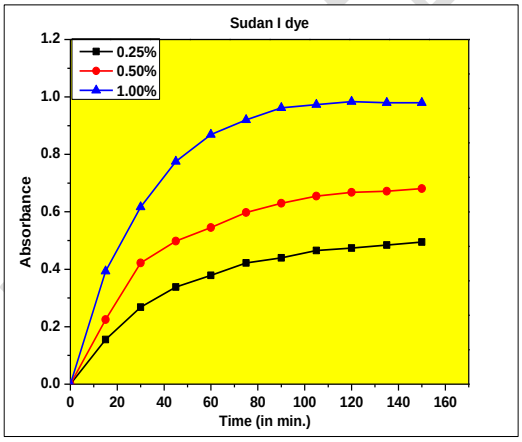
The obtained results were best fitted in pseudo first order equation,

$$\log\left(\frac{C_S}{(C_S-C)}\right) = \frac{k.t}{2.303} \text{.....(3)}$$

Where C_S (mol L^{-1}) and C (mol L^{-1}) are dye concentrations at equilibrium time and at different time intervals respectively and k is the rate constant, t is the time in minutes.[9]

Effect of surfactant concentration on dye solubilization

The effect of surfactant concentration (0.25%, 0.50% and 1.00%) on the solubilization of Sudan I dye was evaluated at 30°C. The result shows (Figure 3) that the solubility of the dye increases with the increase of surfactant concentration. Kinetic study of solubilization of Sudan I dye for different concentrations of SDS were carried out and plotted log (C_S/C_S-C) values against time (Figure 4). The linearity of the plots shows the pseudo first order kinetics of solubilization and the values of rate constant calculated from the slope values are reported in Table 2. This is because of micelles, which are spontaneously formed with the addition of more surfactant leads to increase the micellar concentration or the micellar growth in the bulk of the surfactant solution and thereby enhancing the rate of solubilization (Figure 5) by accommodating more dye molecules.[4]



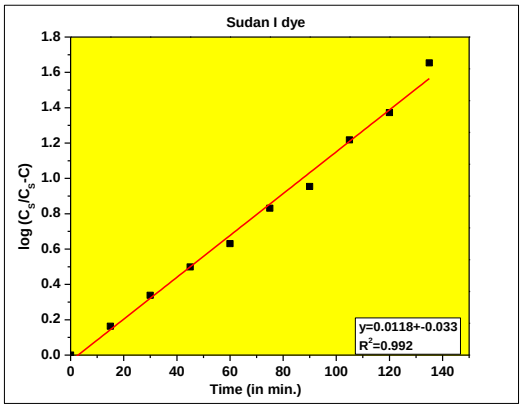


Figure 3 **Figure 4**

Figure 3: Absorbance of Sudan I dye Vs time for different concentrations of SDS

Figure 4: Plots of log(C_S/C_S-C)Vs time for Sudan I dye in 0.25% concentration of SDS (Conditions: amount of dye 3.0×10^{-3}gm, temperature 30°C)

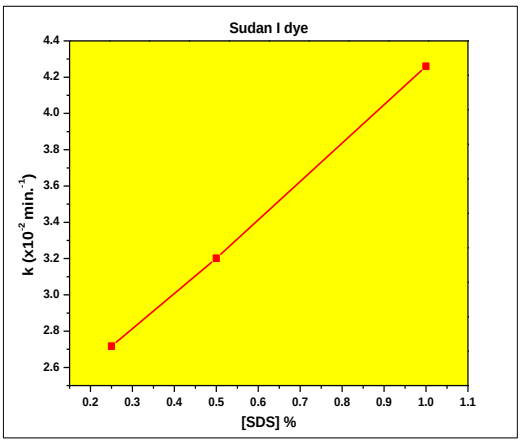


Figure 5: Effect of [SDS] on pseudo first order rate constant for Sudan I dye

Effect of temperature on dye solubilization

The effect of temperature on solubilization of dye has shown in Figure 6 and the pseudo first order rate constant values obtained from the kinetics of solubilization at different temperatures for Sudan I dye (Table 2). The results indicated that the solubilization of dye increase with increase of temperature and the rate of solubilization also increase with increase of temperature (Figure 7). Due to thermal agitation, mobility of molecules increases and available space for easy accommodation of dye molecules increase in surfactant micelles.[1]

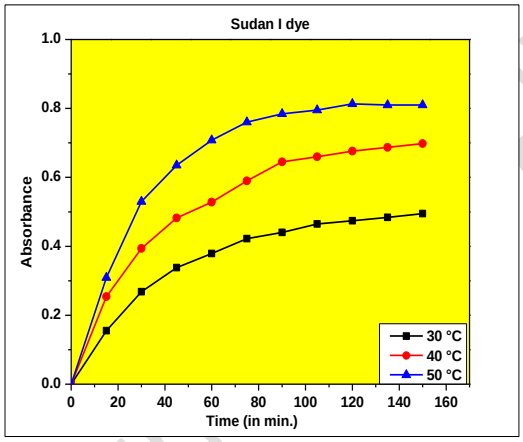


Figure 6

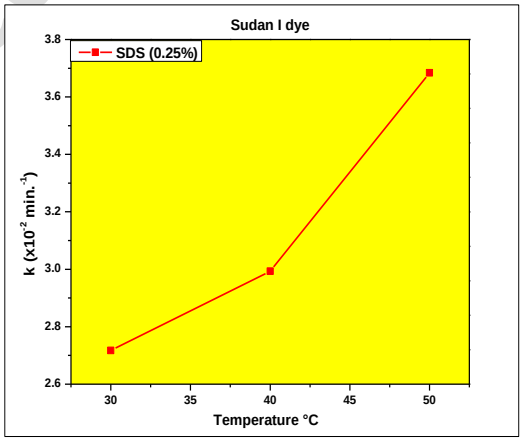


Figure 7

Figure 6: Absorbance of Sudan I dye Vs time for SDS at different temperatures (30, 40 and 50°C (Conditions: SDS concentration (0.25%, amount of dye 3.0×10^{-3}gm)

Figure 7: Effect of temperature on pseudo first order rate constant for Sudan I dye

Effect of amount of dye on solubilization

The solubilization of dye increase with increase of amount of dye (Figure 8) and the rate constant values obtained from the slope of plots (log (C_S/C_S-C) Vs time) are almost same for different amounts of dye for Sudan I dye (Table 2). The plot of pseudo first order rate constant Vs amount of dye is a straight line parallel to X axis which shows the first order dependence of solubilization rate with respect to amount of dye (Figure 9).

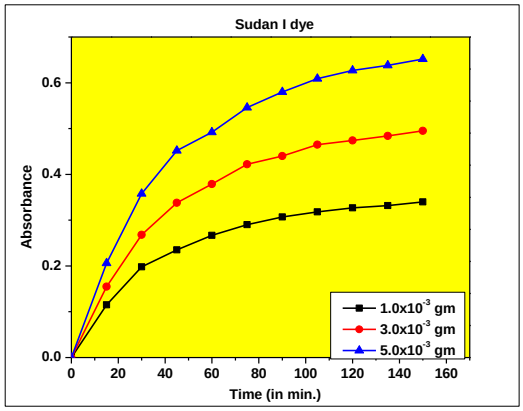


Figure 8

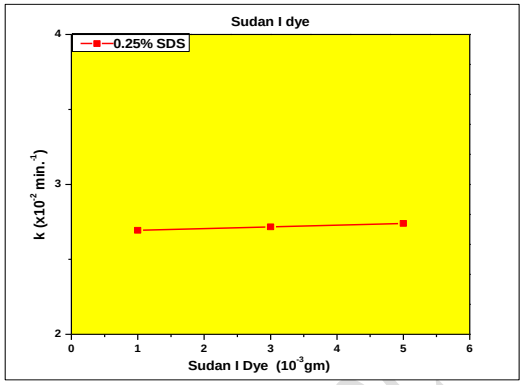


Figure 9

Figure 8: Absorbance of Sudan I dye Vs time for different initial amounts of dye
Figure 9: Effect of amount of dye on pseudo first order rate constant for Sudan I dye (Conditions: SDS concentration (0.25%), temperature 30°C)

Effect of salts on dye solubilization

The significant role of inorganic salts, when added to the surfactant solutions are reported.[4,14,15] The presence of salts decreases the CMC of surfactant in aqueous solution,[16,17,18] as a result the appearance of more micelles at a lower concentration of surfactant and increases the aggregation no. and volume of the micelle. Electrolytes in a solution of ionic surfactant decrease the repulsion between ionic head groups which again decrease the thickness of the electric double layer and consequently the CMC decreases (Figure 10, Table 1). The presence of salts (NaCl, Na_2SO_4 and Na_2CO_3) in the aqueous solution of SDS increases the solubilization of Sudan I dye (Figure 11). Hence salt solution of surfactant enhances the rate of solubilization. The results of rate constant (Table 2) shows that the solubilization of Sudan I dye in salt solution of anionic surfactant follows pseudo-first-order kinetics with relatively good correlation coefficients. Among the salts, the rate of solubilization of dye is higher for Na_2CO_3 than NaCl and Na_2SO_4 solution (Figure 12). The CMC of SDS is lower in Na_2CO_3, because of the higher charges on ions of salts have larger impact on aggregation as well as the ionic strength of Na_2CO_3 is higher than Na_2SO_4.

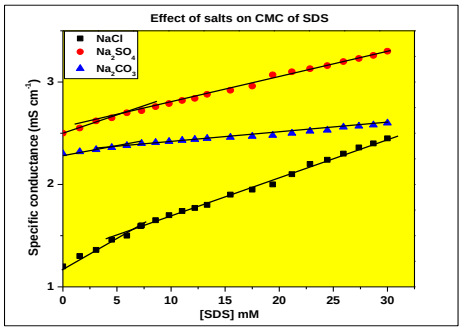


Figure 10: Effect of salts (NaCl, Na_2SO_4 and Na_2CO_3 (0.01M)) on CMC of SDS in aqueous solution at 30°C

Table 1: Effect of salts on CMC of SDS at 30°C

Salt→	-	NaCl	Na_2SO_4	Na_2CO_3
CMC (mM)	8.26	6.45	5.60	4.99

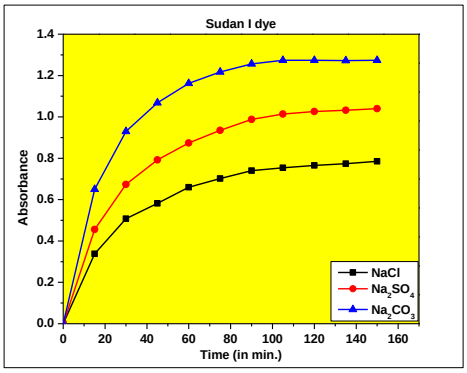


Figure 11

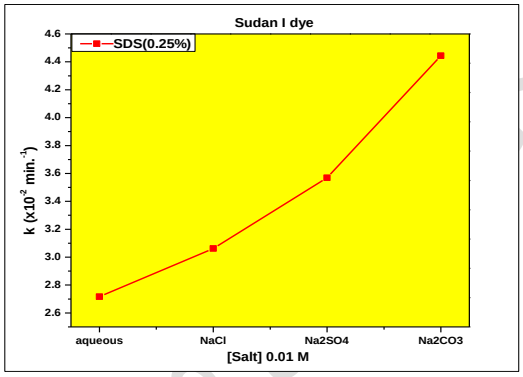


Figure 12

Figure 11: Absorbance of Sudan I dye Vs time for different salts
Figure 12: Effect of salt on pseudo first order rate constant for Sudan I dye
(Conditions: SDS (0.25%), temperature 30°C, amount of dye 3.0×10^{-3} gm, salt 0.01M)

Table 2: Effect of surfactant concentration, temperature, amount of dye and salt on rate constant for solubilization of Sudan I dye

Surfactant con. (%)	Amt. of dye (gm)	Temp. °C	Salt	Rate constant k ($\times 10^{-2}$ min^{-1})	R^2
0.25	3.0×10^{-3}	30	-	2.717	0.995
0.50	"	"	-	3.201	0.988
1.00	"	"	-	4.260	0.982
0.25	3.0×10^{-3}	30	-	2.717	0.995
"	"	40	-	2.993	0.985
"	"	50	-	3.684	0.997
0.25	1.0×10^{-3}	30	-	2.694	0.995
"	3.0×10^{-3}	"	-	2.717	0.995
"	5.0×10^{-3}	"	-	2.740	0.987
0.25	3.0×10^{-3}	30	NaCl	3.062	0.997
"	"	"	Na_2SO_4	3.569	0.989
"	"	"	Na_2CO_3	4.444	0.981

CONCLUSION

The kinetic study of solubilization of Sudan I dye in SDS micellar solutions was investigated to find out the rate of solubilization. The investigation revealed that soubilization of dye by SDS follows pseudo first order kinetics. The increasing rate constant values obtained with the increase of surfactant concentration clearly explains the role of surfactant concentration on the solubilization of the dye. Increase of thermal agitation greatly influences the rate of solubilization. The constant values of rate constant with different amounts of dye shows the first order dependence of solubilization rate with respect to amount of dye. The rate of solubilization of dye is higher in Na_2CO_3 than NaCl or Na_2SO_4 solution because of lower CMC of SDS in Na_2CO_3 solution according to strength of the salts (Hofmeister series). Solubilization of hydrophobic dyes in micellar solution is important in textile industry, chemical industry as well as in chemical research such as biochemistry, analytical chemistry, environmental chemistry etc. So the present kinetic study of solubilization of Sudan I dye, both in the presence and absence of salts is helpful to various industries where ever this dye is in use.

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