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Solubilization of Disperse orange 25 by CPC micellar solution: A Kinetic approach

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Abstract: The unique property of surfactants in aqueous solution is significantly important to solubilize water insoluble compounds. The present study is the solubilization of water-insoluble, Disperse orange 25 **(3-[N-ethyl-4-(4-nitrophenylazo) phenylamino] propionitrile)** in micellar solution of cationic surfactant, Cetylpyridinium chloride (CPC) via kinetic approach. The effective parameters such as concentration of surfactant, temperature and presence of salts (NaCl, Na_2SO_4 and Na_2CO_3) were investigated by UV–Visible spectrophotometry. The results revealed that the solubility of dye is considerably increased with increase of surfactant concentration, temperature and presence of salts. Salts effectively reduce the critical micellar concentration (CMC) of CPC and increase micelles growth hence the solubilization of dye increase in salt solution of CPC. The order of extent of solubilization in salt solution is Na_2SO_4< NaCl< Na_2CO_3. The solubilization of Disperse orange 25 by CPC micellar solution follows pseudo-first-order kinetics. In the case of NaCl, the pseudo first order rate constant value is higher than that of Na_2SO_4 due to the presence of same counter ion in CPC. Among the salts studied, Na_2CO_3 is most favorable for solubilization of Disperse orange 25 in micellar solution of CPC. Kinetic approach was also made to understand the rate of dissolution of the dye in all the cases studied. It was also observed that the rate of dissolution decreases with time.

Key words: Cetylpyridinium chloride, Disperse orange 25, micellar solubilization, kinetics.

Introduction

Solubilization by surfactants is a spontaneous phenomenon that can be widely used in detergency, emulsion polymerization, enhanced oil recovery, textile dyeing, drug delivery etc.[1,2,3]. Surfactants are amphiphilic molecules and they associate with their hydrophobic tails and hydrophilic head groups in the outer regions of the aggregate. The hydrophobic region in the interior of the micelle provides a favorable environment for solubilization of hydrophobic substrates[4]. Micellization results because of competition of two forces: the hydrophobic interaction between the tails and the electrostatic or steric repulsion between the head groups[5]. The threshold surfactant concentration which quantifies the ability of a surfactant to form micelles for the self-aggregation process is called the critical micellar concentration.[6]

Surfactants have attracted growing attention for their use in different processes of the textile industry, where the role of surfactants is very important. They are mainly used as cleaning, wetting, emulsifying, leveling and dispersing agents in order to improve finishing, printing and dyeing processes by increasing solubility and promoting uniform distribution of dyes in water[7]. The important uses of surfactants are the preparation of dye dispersions and increase the dispersions stability to achieve a uniform dyeing during the dyeing process of synthetic fibres such as polyester, nylon, etc. with disperses dyes[8].

Many studies are available on the applications of surfactants in the dyeing of hydrophobic fibers with disperse dyes. S. Padasala *et. al.* studied the solubilisation of Orange OT (hydrophobic) in aqueous solution of cationic surfactants[9]. Choi and co-workers investigated the solubilization of Disperse dyes in Gemini cationic surfactants and compared them with two conventional surfactants[10]. A.R.Tehrani-Bagha and K. Holmberg presented a review on the use of surfactants for solubilization of hydrophobic organic dyes[11] (mainly solvent and disperse dyes). K. Gharanjig and M. Sadeghi-Kiakhani have conducted 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[12]. K.Gharanjig also investigated the solubilization of a monoazo disperse dye (naphthalimide containing an ester group) in the presence of DTAB and two Gemini cationic surfactants and the results showed that the solubilization power of micelles of Gemini surfactants was greater than that of conventional surfactant micelles (DTAB) for this dye[13]. A kinetic study on the dissolution of two azo naphthalimide based synthesized Disperse dyes in the presence of dispersing agents, namely Irgasol DAM and Lyoprint EV were investigated by A. Khosravi *et. al.* at different temperatures[14].

Disperse dyes are nonionic, have very limited solubility in water and have substantivity for hydrophobic fibers; e.g., polyesters, nylons etc. Due to their extremely low solubility in water, dispersing agents (surfactants) are needed to maintain a fine, stable dispersion of the dye and improve its absorption and diffusion into the textile fibre during the dyeing process. The purpose of the present study was to study the effect of various parameters on solubilization and dissolution kinetics of Disperse orange 25.

Material and Method

Cationic surfactant, Cetylpyridinium chloride (CPC) and electrolytes (NaCl, Na_2SO_4 and Na_2CO_3) are purchased from Sigma-Aldrich and used as received for solubilization study. Disperse orange 25 is an azo dye (water-insoluble) was obtained from Spectrum Pvt. Ltd. Surat (India) (Figure 1).

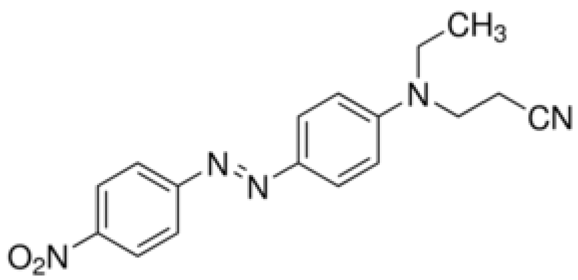


Figure 1: Chemical structure of Disperse orange 25

In order to investigate the solubilization kinetics, the specific amount of dye was added to 50 mL of surfactant solution at the required temperature with constant shaking. The samples were withdrawn from the solution at certain time intervals and centrifuged. The supernatant liquid was taken in a cuvette and diluted with acetone (1:1) and observed the absorbance at the wavelength of maximum absorbance (λ_{max}) using UV–Visible spectrophotometer.

Result and Discussion

The kinetic study of the solubilization of dye was investigated in aqueous solution of CPC. The calibration curve (absorbance vs. dye concentration) was plotted and the concentrations of dissolved dye were determined at different time intervals by the spectrophotometric method using Beer-Lambert equation:

$$A = \varepsilon\, cl \quad .... \qquad (1)$$

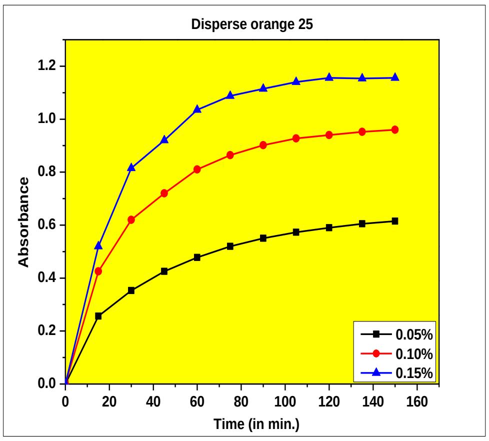
Where A is the absorbance, ε is the molar extinction coefficient, *C* is the concentration and *l* is the length of the cell. The obtained results were best fitted in pseudo first order expression,

$$\log\left(\frac{C_S}{(C_S - C)}\right) = \frac{k.t}{2.303} .... (2)$$

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[12].

Effect of surfactant concentration on dye solubilization

The effect of surfactant concentration on the solubilization of dye was evaluated at 30ºC. The results illustrate that increasing the surfactant concentration, the dye solubilization increase in water (Figure 2). The linearity of the plots between log (C_S/C_S-C) values against time shows the pseudo first order kinetics of solubilization (Figure 3). The increasing values of rate constant indicate the effectiveness of surfactant concentration on solubilization of the dye (Table 2). On increasing of surfactant concentration, more micelles are formed and available for the accommodation of dye molecules and hence enhancing the rate of solubilization.[15]



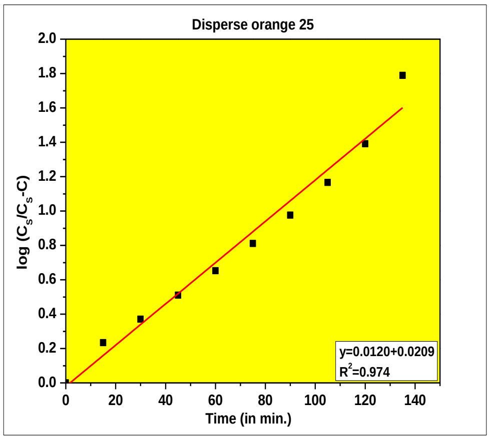


Figure 2 **Figure 3**

Figure 2: Absorbance of Disperse orange 25 Vs time for different concentrations of CPC

Figure 3: Plots of log (C_S/C_S-C) Vs time for Disperse orange 25 in 0.05% CPC (Amount of dye 20.0×10^{-3} gm, temperature 30°C)

Effect of temperature on dye solubilization

The effect of temperature on dye solubilization has shown in Figure 4 and the results indicated that the solubilization of dye increase with increase of temperature. The pseudo first order rate constant values obtained from the kinetics of solubilization at different temperatures for Disperse orange 25 also increase with increase of temperature (Table 2).

The solubilization improve with temperature basically because of an increased thermal agitation which increases the available space for more comfortable accommodation of dye molecules in surfactant micelles. The temperature above 40°C is more favorable for solubilization of Disperse orange 25.

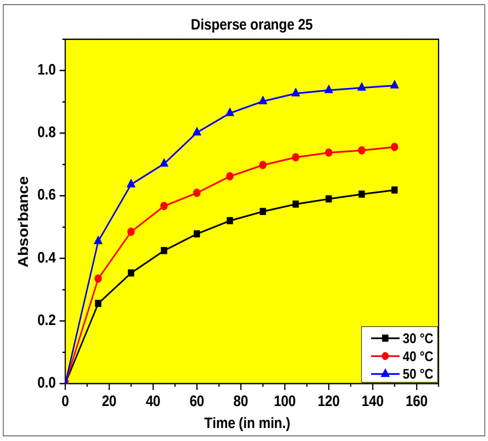


Figure 4: Absorbance of Disperse orange 25 Vs time for CPC at different temperatures (30, 40and 50°C), CPC (0.05%), amount of dye 20.0×10^{-3} gm

Effect of salts on dye solubilization

To study the effect of salts on dye solubilization, 0.01M concentration of salts (NaCl, Na_2SO_4 and Na_2CO_3) were used to prepare 0.05% CPC solution. The CMC of CPC in salt solution was determined at 30°C from surface tension method (Figure 5, Table 1). The presence of salts decreases the CMC of CPC in aqueous solution. This may be due to decrease of repulsive forces between the head groups of ionic surfactants by the ions of salt in aqueous solution[16,17]. As a result, the appearance of more micelles at a lower concentration of surfactant, increases the aggregation no. and volume of the micelle. Hence solubilization of Disperse orange 25 increases in salt (NaCl, $Na_2SO_4$and Na_2CO_3) solution of CPC (Figure 6). The order of extent of solubilization of dye in salt solution of CPC is Na_2SO_4<NaCl<Na_2CO_3 and also the rate constant values increase in the same order, which indicates that the solubilization of dye is highest in Na_2CO_3 solution (Figure 6, Table 2). This can be explained on the basis of decrease in the CMC of CPC which is in the order of: Na_2SO_4>NaCl>Na_2CO_3 (Table 2). Generally, the ions with a higher charge are more effective than ions with lower valence in the micellization process but in the case of CPC, an additional specific effect on CMC of CPC has been observed in the presence of NaCl, which is lower than Na_2SO_4 and this may be due to the presence of same counter ion (Cl^-) in NaCl that favors the micellization.

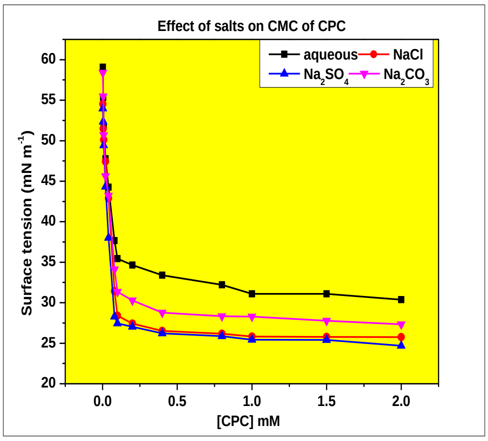


Figure 5: Effect of salts (NaCl, Na_2SO_4 and Na_2CO_3 (0.01M)) on CMC of CPC in aqueous solution at 30°C

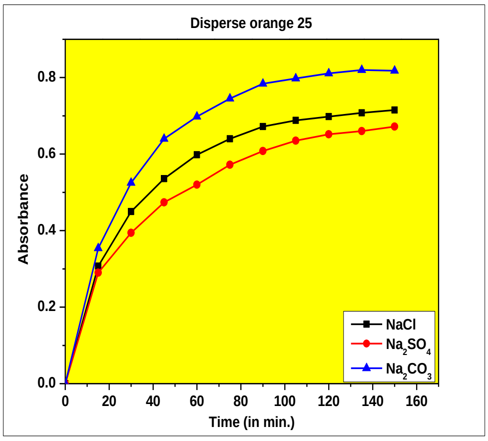


Figure 6: Absorbance of Disperse orange 25 Vs time for different salts (CPC (0.05%), temperature 30°C, amount of dye 20.0×10^{-3} gm, salt (0.01M)

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

Salt→	H_2O	NaCl	Na_2SO_4	Na_2CO_3
CMC (mM)	1.07	0.484	0.574	0.401

Dissolution Rate of Dye in CPC Solution

The kinetics of solubilization of Disperse orange 25 has also been concerned through dissolution approach. The concentrations of dissolved dye are plotted against log t for different concentrations, amount of dye, temperature and salts (Figure 7,8, 9, 10). The slopes of linear plots are constant rate of dye dissolution (K) and are reported in Table 2. The results revealed that in all cases dissolution of dye increase with time.

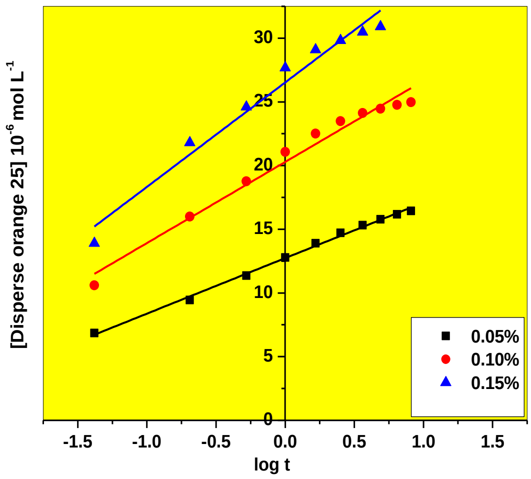


Figure 7: Plots of concentration of dissolved dye Vs logarithm of time (Effect of [CPC] on dissolution of Disperse orange 25)

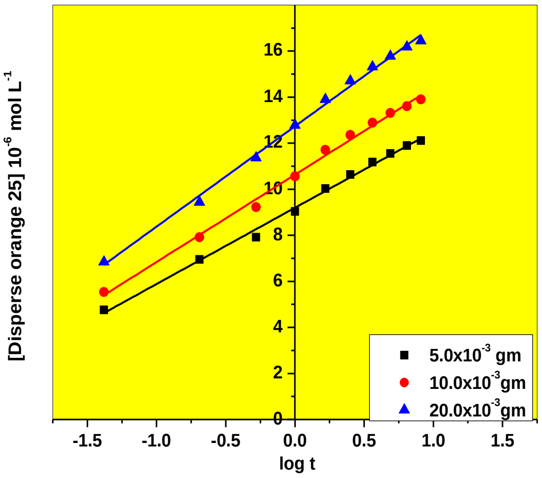


Figure 8: Plots of concentration of dissolved dye Vs logarithm of time (Effect of initial amount of Disperse orange 25 on dissolution)

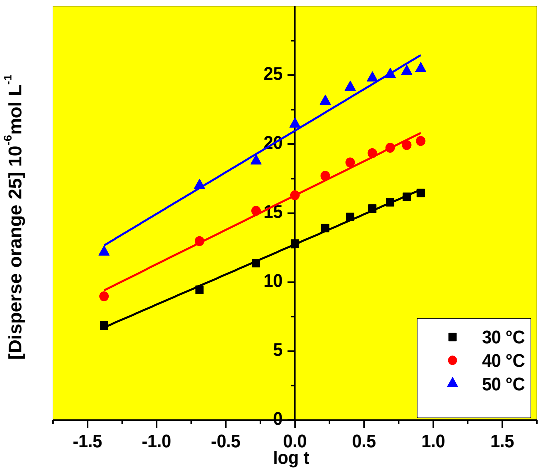


Figure 9: Plots of concentrations of dissolved dye Vs logarithm of time (Effect of temperature on dissolution of Disperse orange 25 by CPC)

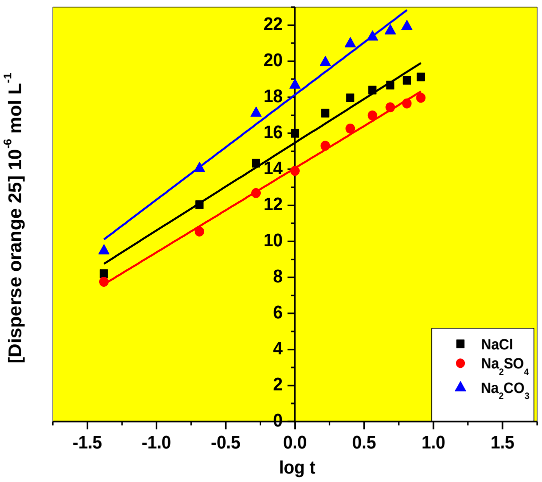
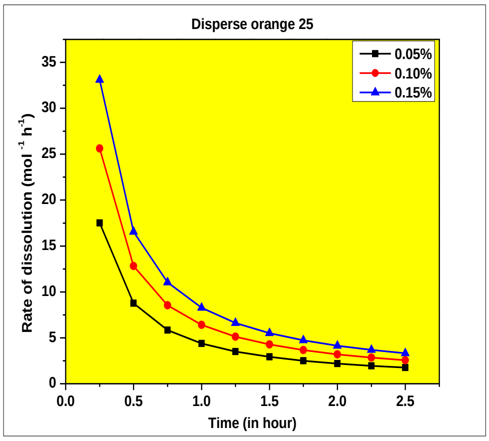


Figure 10: Plots of concentration of dissolved dye Vs logarithm of time (Effect of salt on dissolution of Disperse orange 25)

The rate of dye dissolution in micellar solution was calculated using the following equation.

$$\text{Rate of dissolution} = \frac{K}{t} \quad \text{.... (3)}$$

It is found that the rate of dissolution decreases with increase of time for all the cases studied (Figure 11,12,13,14).



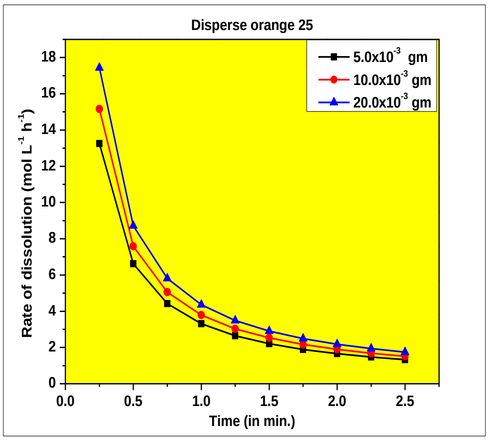
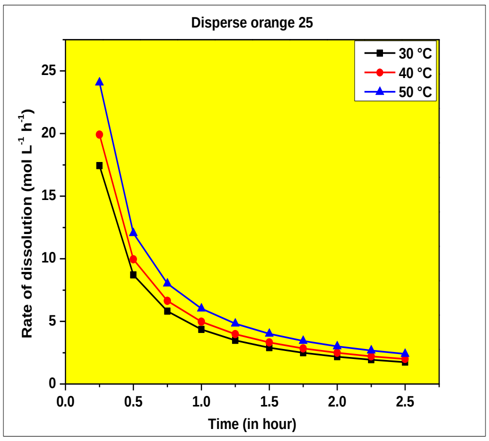


Figure 11 **Figure 12**

Figure 11: Effect of [CPC] on rate of dissolution
Figure 12: Effect of initial amount of dye on rate of dissolution



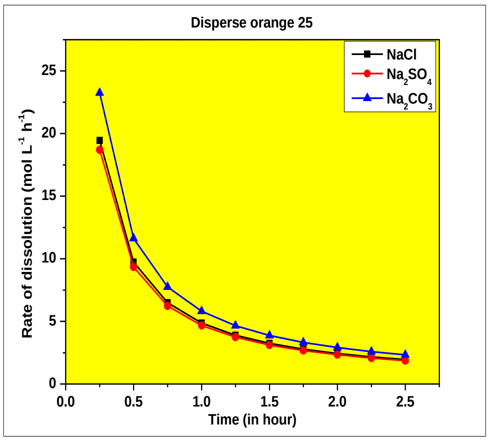


Figure 13 **Figure 14**

Figure 13: Effect of temperature on rate of dissolution
Figure 14: Effect of salt on rate of dissolution

Table 2: Effect of surfactant concentration, temperature and salt on rate constant and constant rate of dye dissolution for solubilization of Disperse orange 25

Surfactant con. (%)	Amount of dye (gm)	Temp. °C	Salt	Rate constant k ($\times 10^{-2}$ min^{-1})	R^2	Constant rate of dye dissolution K_D ($\times 10^{-6}$ mol L^{-1})	R^2
0.05	20.0×10^{-3}	30	-	2.763	0.974	4.359	0.996
0.10	20.0×10^{-3}	"	-	3.340	0.990	6.366	0.975
0.15	20.0×10^{-3}	"	-	3.892	0.991	8.198	0.967
0.05	20.0×10^{-3}	30	-	2.763	0.974	4.359	0.996
"	20.0×10^{-3}	40	-	3.016	0.989	4.977	0.989
"	20.0×10^{-3}	50	-	3.500	0.988	6.020	0.977
0.05	20.0×10^{-3}	30	NaCl	3.224	0.991	4.864	0.978
"	"	"	Na_2SO_4	2.901	0.984	4.673	0.993
"	"	"	Na_2CO_3	3.569	0.988	5.814	0.978

Conclusion

Solubilization of Disperse dyes in micellar solution of surfactant has great interest in textile dyeing industries**.** The effect of surfactant concentration, temperature and presence of salts on solubilization of Disperse orange 25 in micellar system of CPC has been investigated using UV–Visible spectrophotometric method. The result reveals that the solubility of dye increase with increasing the surfactant concentration, temperature and presence of salts. The kinetics of solubilization of dye in aqueous surfactant solution follows pseudo first-order. The increasing rate constant values obtained with the increase of surfactant concentration is due to the formation of more micelles at higher concentration and hence increasing the solubility. On increasing the temperature pseudo first order rate constant values increases due to thermal agitation which increases the available space for more comfortable accommodation of dye molecules. The presence of salts studied shows the positive effect towards the solubility of Disperse orange 25 in micellar solution of CPC. Among the salts studied, the rate of solubilization of dye is higher in case of Na_2CO_3. In the case of NaCl, the rate constant value is higher than Na_2SO_4 due to the presence of same counter ion in CPC. The rate of dissolution of dye is found to be decreasing with time. The present kinetic study of solubilization of Disperse orange 25 by the micellar solution of Cetyl pyridinium chloride (CPC) would be beneficial for textile dyeing industries.

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