3.1 Materials:

3.1.1 Dye-stuffs:

In the present work three structurally different commercial disperse and cationic dyes were selected and purified by repeated recrystallization. The details are shown in Fig.5. & Fig.6.

1) C.I. Disperse Red 118
   \( \text{r.m.m.} = 473 \)

2) C.I. Disperse Violet 26
   \( \text{r.m.m.} = 446 \)

3) C.I. Disperse Yellow 42
   \( \text{r.m.m.} = 387 \)
3.1.2. Fabrics:
Well washed and scoured 100% normal polyester and cationic dyeable polyester fabrics were used.

3.1.3. Chemicals:
The anionic dispersing agent (Setamol WS, ICI) & nonionic dispersing agent (Nonyl phenol ethylene oxide 11 condensate) for dispersion of disperse dyes, carrier (Delatin TCI,S) for swelling of polyester fibres at elevated temperatures were commercial reagents. Acetic add & sodium acetate buffer solution for maintaining pH = 5.5, citric acid and disodium hydrogen phosphate (anhydrous) for maintaining pH =3.5, 4.5 & 6.5 of the dyebath during dyeing were used. For normal polyester caustic soda & sodium hydrosulfite were used for reduction clearing of dyed fabrics while nonionic surfactant,
soda ash and hydrose were used for reduction clearing of dyed cationic dyeable polyester fabrics. All the chemicals used were of laboratory reagent grade.

3.2 Methods:

3.2.1. Purification of Dyes:

Purification of disperse dyes was achieved by carrying out the extraction in acetone. The purified dyes were dried in an oven & kept in the desiccator. Finally they were kept in polyethylene container for experimental use. The purification of cationic dyes was achieved by carrying out the extraction with approximately ten times volume of ethanol. The solution was made highly concentrated, then filtered, the filtrate was collected & kept in the desiccator and allowed to remain in desiccator for overnight. Finally fine crystals were obtained. The process is repeated for two times. The purified dyes were stored in clean, air tight containers.

3.2.2. Polarographic Measurement of Dye Aggregation:

Doubly distilled water was used for all the measurements. A systronics model 1632 polarograph and recorder 1501 were used for taking measurements. A saturated calomel reference electrode (SCE) was used and different sets of mixtures were prepared by using varying amounts of surfactants (1.0-4.5 ml of 0.001 mol/l) and dye solutions (0.2-1.0 ml of 0.001 mol/l), making the total volume to 40 ml by adding doubly distilled water. The dropping mercury electrode (DME) had the following characteristics: m=1.224 mg/s (in pure water at zero applied potential Vs. SCE) and t=2 s (in doubly distilled water at 0.75 v. Vs. SCE). The height of the mercury head was 78 cm. The diffusion current $i_d$ was measured from the polarogram of the above solutions after ensuring dummy operation keeping pH = 5.5 at 30° C, 50° C & 80° C temperatures. An inert atmosphere was created by passing nitrogen through the system. A period of about 30 min. was allowed to attain equilibrium in each case. The value of D was determined using Sivaraja Iyer's method.
in combination with Ilkovic’s equation.\(^{(85)}\) The apparent molecular mass of an aggregate was determined from the empirical relationship suggested by Hilson & Mc kay\(^{(86)}\) as \(\log M' = -11.64 - 2.65 \log D\) where \(M'\) is the apparent molecular mass of an aggregate and \(D\) is the diffusion coefficient. The dye aggregation number was calculated by dividing \(M'\) by the actual r.m.m. of the dye (\(M\)).

### 3.2.3. Determination of Thermodynamic Parameters:

The thermodynamics of micellization in water has been discussed extensively in the literature.\(^{(87)}\) One treatment supposes the presence of two distinct phases i.e. an aqueous and a micellar phase at the C.M.C. and constant concentration monomers in solution, once micelles are formed. The standard free energy of micellization \(\Delta G_{mic}\) is given by

\[
\Delta G_{mic} = RT \ln C.M.C.
\]

Assuming that the aggregation number & degree of ionization are temperature dependent, the enthalpy & entropy of micellization can be determined from the temperature dependency of the C.M.C. by means of equations as follows -

1. \(\Delta H_{mic} = -RT^2 \frac{d \ln \text{CMC}}{dT}\)

2. \(\frac{(\Delta H_{mic} - \Delta G_{mic})}{T} = \Delta S_{mic}\)

Using above equations derived from solutions of surfactants in pure water, different thermodynamic parameters have been calculated for micellization in presence of different dyes, being well aware that in addition to water surfactant interaction they also include interactions of the type water dyes and surfactant-dyes. The values of \(\Delta G_{mic}\) calculated are very reliable, since they depend on accurate determination of C.M.C. This is however not the case for \(\Delta H_{mic}\) that depend on variation of C.M.C. with temperature. The method of direct measurement of thermodynamic properties of surfactant...
in aqueous solution developed by Desnoyer's & his associates (88-90) is more precise & more widely applicable since it does not depend on micelle size, shape and well defined C.M.C. However, it requires more sophisticated techniques & instrumentation not readily available.

3.2.4. Determination of Binding Ratio By Spectrophotometric Method:

The absorption of light by the dye solutions was determined with a systronics spectrophotometer model 106 at 30° C, 50° C & 80° C temp. The molar extinction coefficients were calculated from equation 3 as follows.

\[ \varepsilon = \frac{1}{C_d} \log \frac{I_o}{I} \]

Where \( I_o \) & \( I \) are the intensities of light passing through the solvent & solution, \( C \) is the molar concentration of solute and \( d \) is the thickness of the absorption cell in cm. To determine the binding of dye the absorption of the following sets of mixtures (Total volume made to 10 ml. by adding doubly distilled water) was measured at pH = 5.5 and at 30° C, 50° C & 80° C temperatures respectively.

(a) 5 ml of 0.001 mol/l surfactant solution (Setamole.WS / Nonyl phenol E 011 & Delatin TCI) + 0.1 ml of 0.01 mol/l dyebath.

(b) 1 ml of 0.01 mol/l dyebath + varying amounts (1-4.5 ml) of 0.001 mol/l surfactant solution.

(c) Dyebath samples containing varying concentration ratio of dyes only (0.2-1.0l of 0.01 mol/l) A period of about 30 min. was allowed in each case to attain equilibrium. Sets (a), (b), & (c) were used to determine \( \varepsilon_b \) (Molar extraction coefficient of bound dye), \( \varepsilon_a \) (Apparent molar extinction coefficient).
and $\varepsilon_t$ (Molar extinction coefficient of free dye) respectively in Klotz's equation (72):

$$\alpha = (\varepsilon_a - \varepsilon_b) / (\varepsilon_t - \varepsilon_b).$$

Where $\alpha$ is the fraction of the bound dye knowing $\alpha$ and total concentration of dye the concentrations of bound & unbound dye and binding ratio were calculated.

The results of spectrophotometry have been correlated with other obtained by a polarographic method.

Thus in the present work disperse & cationic dyes were added to aqueous dyebath in presence of surfactants & dye aggregation was determined by polarography and spectrophotometry.

### 3.2.5 Low Temperature Dyeing Method:

100% Polyester & Cationic dyeable polyester fabric samples were pretreated in the pots with & without solvents viz. Benzyl alcohol & per chloro ethylene in a room at about $27^\circ C$ temperature & then well squeezed. Then the fabric samples were taken for dyeing in the dyebath containing 0.5% dispersing agent at constant temperature of $81^\circ C$ keeping $m:1; r = 1:100$ and the $pH$ of the dyebaths were varied from 3.5 to 6.5 in steps of 1.0 using acetic acid: sodium acetate & other buffer mixtures with the help of $pH$ meter with various hardness of process waters (50 ppm & 100 ppm). The dyeings were carried out in dye pots made of stainless steel in a thermostatically controlled machine & the heating was done electrically in a waterbath with & without different solvents. Pretreated fabrics were immersed in different dye baths in cold & dyeings were carried out by raising the temperature from $27^\circ C$ to $80^\circ C$ at a rate of $2^\circ C/min$. Then the dyebaths were maintained at $80^\circ C$ for 40 minutes. During dyeing string was continued throughout & then after dyeing the dyebaths were allowed to cool. The fabric samples were then rinsed, reduction cleared & dried. The exhausted dyebaths were brought back to
the original volume for the measurement of optical density with systronics spectrophotometer type 106 after stand calibration. Then the results were tabulated in Table No. 43 & 44.

3.2.6 Method of Measurement of Melting Points of Dye Aggregates:

Melting points of dye aggregates which were centrifuged at 2000 r.p.m. & 6000 r.p.m. with 2:5 dispersing agent : dye 1: 2.5 carrier : dispersing agent:dye in a Remi make C24 centrifuge machine were measured with the help of melting point apparatus and the results were tabulated in Table No. 45.

3.3 Some Model Calculations:

3.3.1 Aggregation Number:

For disperse Red 118, the value of $i_d$ calculated for dye concentration of $0.2 \times 10^{-3}$M was found to be $1.32 \mu A$. By applying this value, $D$ was calculated as under:

$$i_d = K \times n \times D^{1/2} \times C \times (M)^{2/3} \times (t)^{1/6}$$

$$1.32 = 607 \times 4 \times D^{1/2} \times 0.3(1.224)^{2/3} \times (2)^{1/6}$$

$$D = 4.7 \times 10^{-6} \text{ cm}^2/\text{sec.}$$

Now, Log $M'$

$$= -11.64 - 2.65 \text{ Log } D$$

$$= -11.64 - 2.65 \text{ Log } (4.47 \times 10^{-6})$$

$$M' = 345$$

$$\frac{M'}{M'} = 345 / 473 = 0.73$$

and Aggregation Number $= \frac{\text{Mol Wt. of Disperse Red 118}}{M'}$

$$= 345 / 473 = 0.73$$
3.3.2 Thermodynamic Parameters:

Different thermo-dynamic parameters i.e. $\Delta G_{mic}$, $\Delta H_{mic}$ & $\Delta S_{mic}$ were determined. Graph of aggregation number Vs. $\log_{10}$ Molarity of surfactant was plotted (Figure No. 16). From this graph value of CMC was calculated by drawing tangent to the curve. For Disperse Red 118 having concentration of $0.2 \times 10^{-3}$ M, the value of CMC of surfactant was found to be $3.6 \times 10^{-3}$ at 30 °C and $5.50 \times 10^{-3}$ M at 50 °C respectively. The values of $\Delta G_{mic}$, $\Delta H_{mic}$ and $\Delta S_{mic}$ were calculated as follows:

$$\Delta G_{mic} = RT \ln \text{CMC}$$

$$= 8.34 \times 303 \times \ln (3.6 \times 10^{-3}) \times 10^{-3} \text{ KJ/mole}$$

$$= -14219.09 \text{ KJ/mole}$$

$$= -14219.09 / 4.2$$

$$= -3.38 \text{ Kcal/mole at 30 °C}$$

Similarly, $\Delta G_{mic}$ at 50 °C = $RT \ln \text{CMC}$

$$= 8.34 \times 323 \times (5.5 \times 10^{-3})$$

$$= -3.34 \text{ Kcal / mole}$$

$$\Delta H_{mic} = RT^2 \frac{d \ln \text{CMC}}{dT}$$

$$= -R \frac{T_1T_2}{T_1 - T_2} \ln \frac{\text{CMC}'}{\text{CMC}}$$

$$= -8.34 \times \frac{303 \times 323}{323 - 303} \ln \left(\frac{5.5 \times 10^{-3}}{3.6 \times 10^{-3}}\right)$$

$$\Delta H_{mic} = -4.18 \text{ Kcal/mole}$$
Now,
\[ \Delta \text{Smic} = \frac{\Delta H_{\text{mic}} - \Delta G_{\text{mic}}}{T} \]
\[ = \frac{-4.18 - (-3.38)}{303} \]
\[ = 0.003 \text{ e.u. at } 30^\circ C \]

And similarly,
\[ \Delta \text{Smic at } 50^\circ C = \frac{-4.18 - (-3.34)}{323} \]
\[ = 0.0026 \text{ e.u.} \]

3.3.3 Calculation of Binding Ratio

\[ \varepsilon_{\text{app}} = \frac{\log (\frac{K}{I})}{(C_1 + C_2) d} \]

Optical density with surfactant \((0.2 \times 10^{-3} M)\)
\[ = \frac{0.112}{(0.0002 + 0.00002) \times 1} \]
\[ = 509.09 \]

\[ \varepsilon_s = \frac{\text{Optical density without surfactant}}{c \times d} \]
Optical density of 10 ml solution containing 0.1 ml dye plus 5 ml surfactant each 0.2 x 10^3 M

\[ \varepsilon_b = \frac{0.05}{0.0002 \times 1} = 250 \]

\[ \varepsilon_b = \frac{1.367}{(0.00002 + 0.00001) \times 1} = 45567 \]

\[ \alpha = \frac{\varepsilon_{\text{app}} - \varepsilon_b}{\varepsilon_f - \varepsilon_b} = \frac{509 - 45567}{250 - 45567} = 0.9943 \]

Concentration free dye = \( \alpha \times \) Concentration of dye in solution

\( = 0.9943 \times (0.2 \times 10^3) \)

\( = 1.989 \times 10^4 \)

Concentration bound dye = 0.2 x 10^3 - 1.989 x 10^4
\[ \text{Binding Ratio} = \frac{\text{Moles of Bound dye}}{\text{Total mole of surfactant}} \]

\[ = \frac{1.10 \times 10^{-6}}{0.2 \times 10^{-4}} \]

\[ = 0.06 \]