3.1 MATERIALS

3.1.1 *SOLUTES*

Ketocyanine dyes (KCD A and KCD B in figure 3.1) and the dye *2, 6 – diphenyl-4-(2, 4, 6-triphenylpyridinium-1-yl) phenolate* [1] commonly known as $E_T(30)$ dye (figure 3.1) have been used in the present study. The E_T (30) dye was obtained as a generous gift from Professor Ch. Reichardt, Marburg, Germany. The ketocyanine dyes [2, 3, 4] have been synthesised in the laboratory. Ketocyanine dyes have a amino N-atom which acts as a donor (D) centre and a carbonyl group which acts as an acceptor (A). Dye A has been prepared by scheme I.
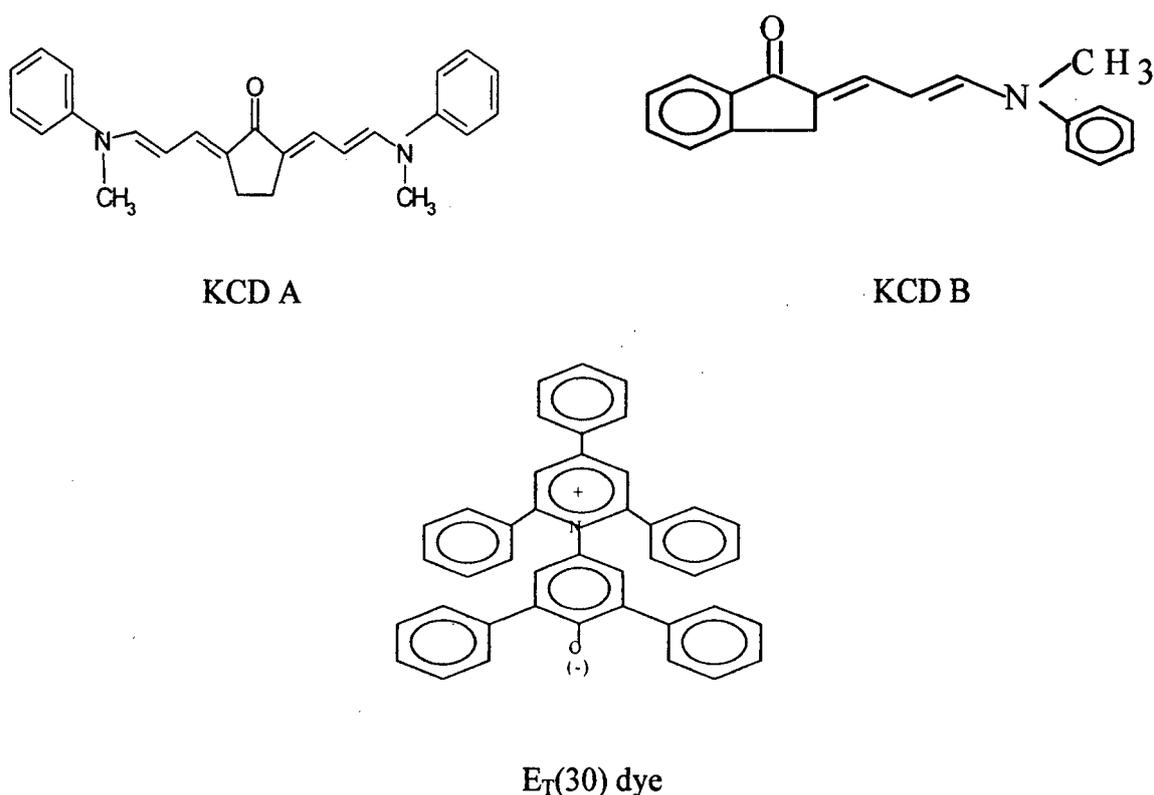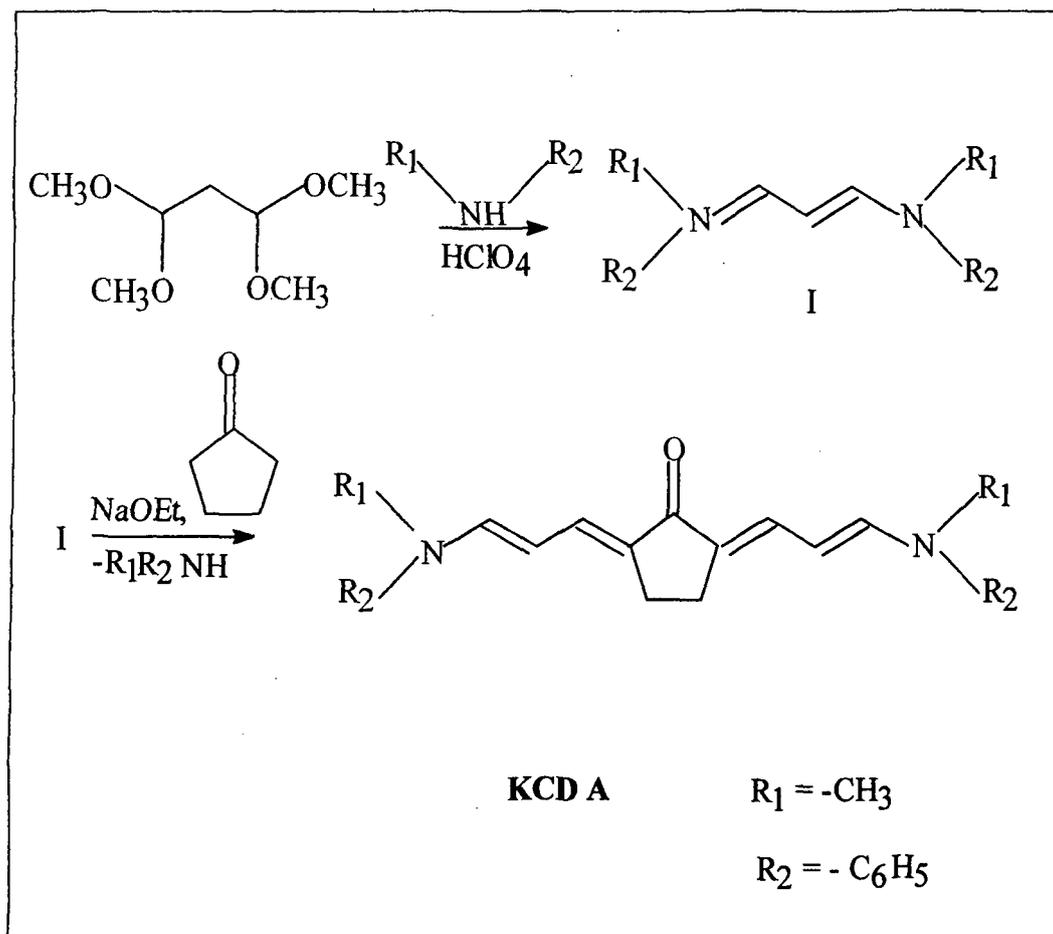

KCD A   KCD B

$E_T(30)$ dye

Figure 3.1: Indicator solutes used in the present study e.g. ketocyanine dyes (KCD A and KCD B) and $E_T(30)$ betaine dye.
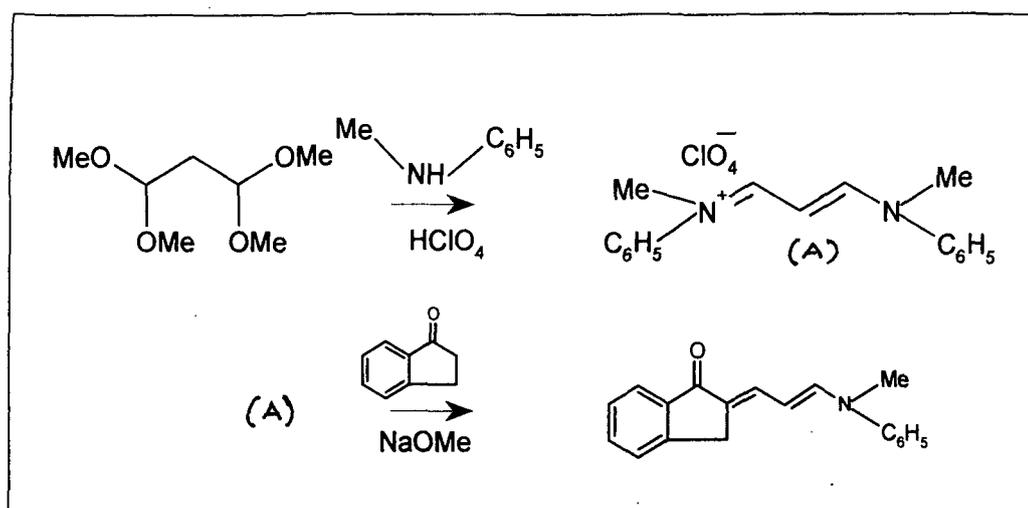
scheme I

Dye A: *1,1,3,3-tetramethoxypropane* and *N-methylaniline* [SIGMA] were mixed in 1:2 mole ratio in ethanol and *perchloric acid* (60 %) was added to it. The mixture was kept in water bath at 50^0 C for half an hour, allowed to cool to room temperature and then stored overnight in a refrigerator. The immediate compound precipitated as yellow needles, which was then filtered, and vacuum dried. Metallic *sodium* (3.7 g) was added to anhydrous *methanol* (80 ml) very slowly and the solution was allowed to cool. To this cold solution the intermediate compound (28.5 m mol) and *cyclopentanone* (14.0 m mol) were added. The mixture was then refluxed for two hours. The crude orange precipitate was filtered, washed several times with water and then with methanol and dry ether. The orange crystals were then dried in vacuum. Purity of the compound was checked by noting the melting point and spectral characteristics; thus, melting point: (found 245^0 C with decomposition, lit. 230-255^0

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C with decomposition), IR spectral data (found peaks at 1608, 1570,1490 cm^{-1}, lit. 1610, 1570, 1490 cm^{-1}), absorption and fluorescence spectral data (UV-Visible absorption maximum found at 503 nm in ethanol, lit. 505 nm; fluorescence maximum found at 589 nm in ethanol, lit. 590 nm in ethanol).

Dye B: This is structurally very similar to dye A. The dye has been synthesized according to the scheme II.

scheme II

Perchloric acid was added to a solution of *1, 1, 3, 3-tetramethoxy propane* (25 m mol) and *N-methylaniline* (50 m mol) in ethanol. The mixture was kept at 50°C for 30 minutes and stored overnight in a refrigerator to give yellow needle-like intermediate compound (A). The product, A, (14.25 m mol) was added to a solution of *sodium methoxide* and *indanone* (14 m mol). The mixture was refluxed for 2 hours and the golden yellow precipitate was filtered off, washed with water, methanol and diethyl ether. Finally the solute was purified by repeated crystallization and dried in vacuum. Purity of the prepared compound was checked by C, H, N analysis (*calculated*: C=82.88%, H=6.22%, N=5.09% *observed* : C=82.54%, H=5.96%,N=5.08%) and IR data (peaks at 1613 cm^{-1}, 1565 cm^{-1}, 1506 cm^{-1}, 1466 cm^{-1} in KBr disc).

3.2 SOLVENTS

Solvents used are methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, *t*-butanol, octan-1-ol, acetone, acetonitrile, dichloromethane, ethylacetate, benzene, tetrahydrofuran, cyclohexane, n-hexane and water.

3.2.1 *Solvent purification and drying*

All the solvents were purified and dried by standard procedures [5, 6, 7] as follows

Methanol (E. MERCK, INDIA) was first dried over lime and then distilled. The distillate was dried by means of magnesium activated with iodine as follows. To a flask, provided with a reflux condenser, were added 0.5 g of iodine, 5 g of magnesium and 50 - 75 ml of the methanol. The flask was then warmed until the iodine disappeared. If vigorous evolution of hydrogen did not occur, 0.5 g of iodine was added and the mixture heated until all magnesium was converted to methylate. An additional 900 ml of methanol was then added and the mixture boiled for half an hour under reflux. The product was distilled with exclusion of moisture in an all glass apparatus. Finally it was kept over molecular sieve (3Å) and distilled.

Ethanol was obtained from commercial "dehydrated alcohol" (BENGAL CHEMICAL, INDIA). "Dehydrated alcohol" was dried over lime and then distilled. It was purified by a procedure similar to that described for methanol.

Propan-1-ol (E MERCK, INDIA) was purified by treatment with anhydrous potassium carbonate and distilled. The distillate was purified by treatment with magnesium activated with iodine.

Propan-2-ol (E MERCK, INDIA) was dried by refluxing with calcium oxide, and distillation. This was followed by treatment with magnesium activated with iodine.

Butan-1-ol (E MERCK, INDIA) was dried over anhydrous potassium carbonate and distilled. The fraction boiling at 118^0 C / 760 mm Hg was collected.

t-butanol (E MERCK, INDIA) was distilled after treatment with lime. The distillate was again treated with anhydrous potassium carbonate and distilled. The fraction boiling at 82^0 C / 760mm Hg was collected.

Octan-1-ol (SRL, INDIA) was distilled and dried over molecular sieve 4Å.

Acetone (E. MERCK, INDIA) was purified by boiling the commercial product with potassium permanganate, and the distilled product was treated with anhydrous potassium carbonate, and again distilled. Finally, the solvent was distilled with molecular sieve 3Å.

Acetonitrile (E. MERCK, INDIA) was dried over calcium chloride, refluxed repeatedly with phosphorous pentoxide until no colour appeared on the oxide. It was distilled and kept over anhydrous potassium carbonate. The decanted liquid was again distilled and stored over molecular sieve (3Å).

Dichloromethane (E. MERCK, INDIA) was washed with saturated sodium bicarbonate solution and with ether, dried over calcium chloride and distilled. The distillate was then refluxed with phosphorous pentoxide and fractionated. It was finally distilled with molecular sieve 4 A^0.

Ethylacetate (E. MERCK, INDIA) was dried over potassium carbonate for two weeks, filtered, distilled and the first and the last portions of the distillate was discarded. The middle fraction was redistilled over phosphorous pentoxide in an all glass apparatus and finally it was dried over molecular sieve 4 A^0 and redistilled.

Benzene (E. MERCK, INDIA) was kept over calcium chloride for few days, the decanted liquid was distilled and the distillate was refluxed with sodium. Benzophenone is added to the system and refluxed again till the dark blue colour persisted. Pure benzene was distilled out of the mixture.

Tetrahydrofuran (E. MERCK, INDIA) was passed through a column of alumina, then refluxed with sodium for several hours and distilled.

Cyclohexane (E. MERCK, INDIA) was passed through a column of silica gel and then distilled.

n-Hexane (E.MERCK, INDIA) was passed through a column of silica gel and then distilled.

Water Triply distilled water was used. Distillation was done in an all-glass apparatus. All the solvents were distilled just before use.

3.2.2 Solvent Properties for pure solvents

Some important and relevant parameters for pure solvents have been listed in table 3.1. The parameters include: (i) the dielectric constant (ε) and refractive index (n) [8, 9], (ii) the $E_T(30)$ scale of solvent polarity [10, 11].

Table 3.1. Solvent parameters for pure solvents at 298 K

Sl. No.	solvents	ε^a	n^a	$E_T(30)^b$ (kcal mol^{-1})
1	water	78.4	1.33	63.1
2	methanol	32.6	1.33	56.3
3	ethanol	24.3	1.36	51.9
4	propan-1-ol	20.1	1.38	50.7
5	propan-2-ol	19.9	1.37	48.6
6	butan-1-ol	17.2	1.40	50.2
7	t-butanol	10.4	1.39	43.9
8	octanol-1-ol	10.3	1.43	48.5
9	acetone	20.7	1.36	42.2
10	acetonitrile	37.5	1.34	46.0
11	dichloromethane	8.93	1.42	41.1
12	ethylacetate	6.02	1.37	38.1
13	benzene	2.27	1.50	34.5
14	tetrahydrofuran	7.60	1.41	37.4
15	cyclohexane	2.00	1.43	31.2
16	n-hexane	2.02	1.37	31.0

^{a} Ref. 8 and 9, ^{b} Ref. 10 and 11.

3.3 Surfactants used in the study

Sodium dodecyl sulphate, SDS, (SIGMA) and Cetyl trimethyl ammonium bromide, CTAB, (LANCASTER) were purified by repeated recrystallisation from ethanol. Triton-X100, TX100 (SIGMA) of purity > 99% was used as received.

3.4 METHODS

3.4.1 *Measurement of solubility*

For solubility measurements saturated solutions of the solute were prepared by agitating the closed flaks containing the solute in a solvent (or in a micellar medium) with proper sonication in a thermostat kept at 298 ± 0.5K for a long time (at least 24 hours). The concentration of a saturated solution in a particular solvent was determined spectrophotometrically after proper dilution with that solvent / micellar medium. The molar absorptivity of the dye is almost independent of solvent (~ ± 2% variation). The average value has been found to be 6.4×10^{4} M $^{-1}$ cm $^{-1}$. Concentrations were determined from the calibration curve drawn for each solvent (/ micellar medium) composition. To check the reproducibility and saturation, solubility for a particular system was determined in a number of replicate measurements (at least three) and the average was taken. The accuracy of the measured solubility is ± 10%.

3.4.2 *Absorption spectral measurements*

UV-Vis Absorption spectroscopy

Absorption spectral measurements were performed on a SHIMADZU UV 2101 PC UV-VIS spectrophotometer fitted with a temperature controlled unit (Model TB-85 Thermobath, SHIMADZU). Some measurements were also performed on a SHIMADZU UV 1601 PC UV-VIS spectrophotometer fitted with an electronic temperature controller unit (TCC – 240 A, SHIMADZU). The maximum energy of absorption, expressed by *E(A)*, is related to the longest wavelength absorption band maximum, λ_{abs}, of the probe molecule as.

$$E(A) \ / kcal \ mol^{1} = 28590 / \ \lambda_{abs} \ (nm) \qquad (3.1)$$

To check the reproducibility of the absorption maximum, replicate measurements were done. The precision of such measurement was ±1 nm. The inaccuracy of ±1 nm in the measurement of λ_{abs} leads to a ± 0.1kcal mol $^{-1}$ inaccuracy in the measurement of *E(A)*.

3.5 Preparation of solution

Solutions were prepared immediately before the experiment. Mixed solvents were prepared by carefully mixing the components by weight. Special care was taken to avoid

contamination by air/moisture during mixing of the solvent components. When two of the components in a ternary solvent mixture were immiscible, solvent compositions representing (i) completely miscible zone, i.e. above the binodal curve and (ii) on the binodal curve were studied. Binodal curves for the ternary solvent mixtures were determined as follows. Known amount of the two components are mixed and third component is added until the system previously consisting of two layers become homogeneous, or vice versa. Quantities of three components for which this occurred gave one point in the binodal curve. For the absorption spectral studies the concentrations of solutes were varied in the range $10^{-4} - 10^{-5}$ M. For preparing solutions of surfactant mixtures the required amount of surfactant was added to triply distilled water, and the contents were sonicated in an ultrasound sonicator (JENCOS, UK, Model T80) for a considerable period.

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