CHAPTER - 2

EXPERIMENTAL

2.1 Materials

2.2 Experimental Techniques

(a) CMC DETERMINATIONS :

(i) Surface Tension

(ii) Conductivity

(iii) Iodine Solubilization Method

(b) PERFORMANCE PROPERTIES

(i) Contact Angle

(ii) Viscosity

(iii) Cloud Point

(iv) Foaming

(v) Detergency

(c) SPECTROSCOPIC TECHNIQUES

(i) Fluorescence Quenching

(ii) NMR

CHAPTER - 2

EXPERIMENTAL

In this chapter, we describe, the materials and the experimental techniques used for studying the various physicochemical properties of surfactant systems.

2.1 MATERIALS

MYRJ 45 [Polyoxyethylene (8) monostearate] a nonionic surfactant [$H(OC_2H_4)_8OOC(CH_2)_{16}CH_3$] was obtained from Sigma and was used as received without any further purification. Polyoxyethylene (10) lauryl ether [$C_{12}H_{25}(OCH_2CH_2)_{10}OH$] ($C_{12}E_{10}$) and sodium dodecyl benzene sulfonate (SDBS) was also procured from Sigma and used as received. Surface tension - concentration * profiles of all these surfactants in aqueous medium did not show any minimum. at the CMC

Polyethylene glycol 400 (PEG 400) was obtained from Merck, India. Sucrose (A.R. 99%) obtained from Qualigens, India. Urea (99%) from Merck, Germany and Acetamide (98.5%) from BDH, India.

Iodine was procured from Sarabhai Chemicals, India and resublimed before use. Pyrene obtained from Fluka, Germany, was used as received. Cetyl pyridinium chloride (CpyCl) obtained from Loba Chemie, India was recrystallized twice from benzene.

2.2 EXPERIMENTAL TECHNIQUE

(a) CMC Determinations :

(i) Surface Tension :

The critical micelle concentrations of surfactants were determined by surface tension measurements using a du Nouy ring tensiometer (S.C.Dey & Co., Calcutta, India).

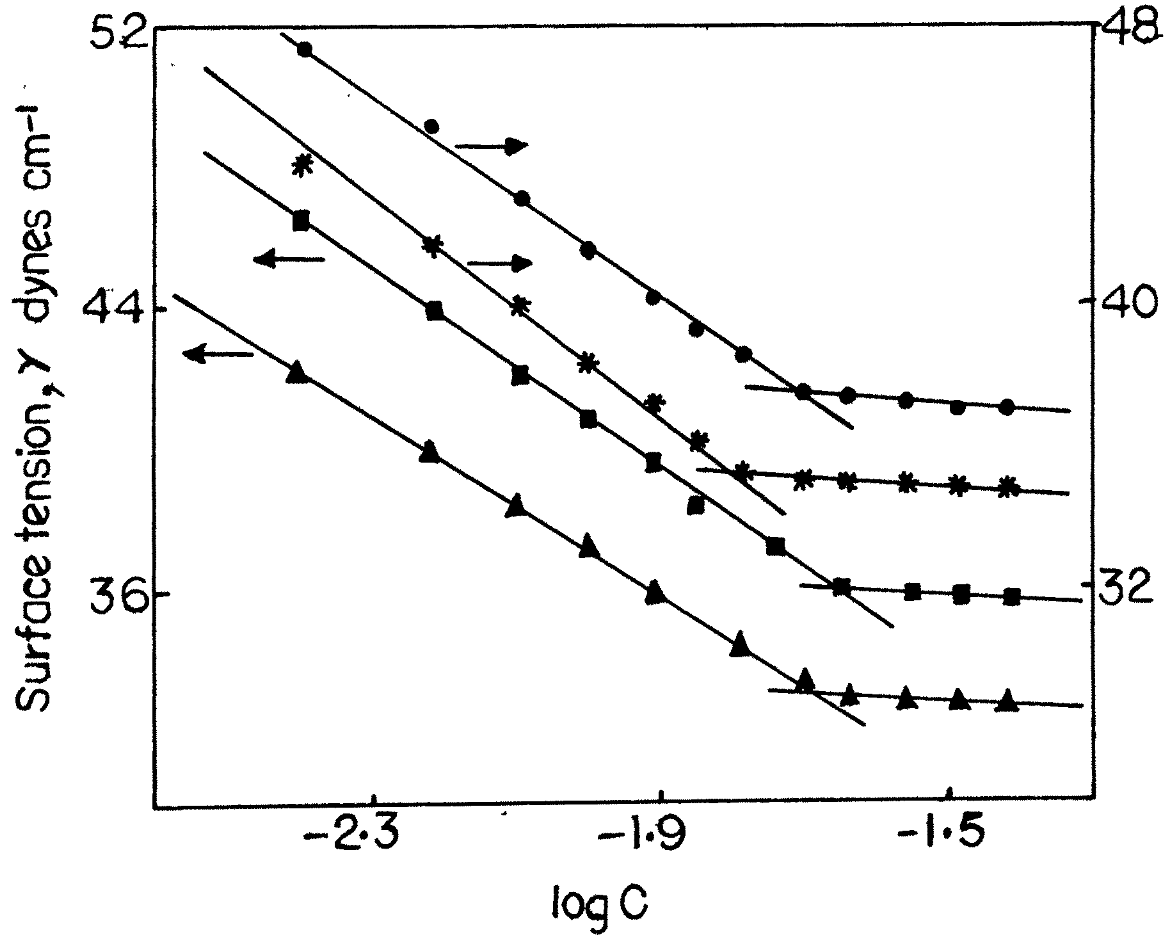

Fig. 8: Representative plots of surface tension Vs log C. ▲ 5:5 SDBS / $C_{12}E_{10}$ at 35°C; ■ 5:5 SDBS / $C_{12}E_{10}$ - 0.5% PEG 400 at 40°C; ✶ 1:9 SDBS / $C_{12}E_{10}$ at 45°C; ● 1:9 SDBS / $C_{12}E_{10}$ - 0.5% urea at 50°C.

Measurements were made at 35, 40, 45 and 50°C. The temperature was maintained constant by circulating thermostated water through jacketed vessel containing the solution. Surface tension (γ) decreases quite rapidly with increasing surfactant concentration before reaching a near plateau region. The concentration of solution was varied by adding aliquots of concentrated stock solution to a known volume of solution in the jacketed vessel by means of a 5 μl Hamilton micro syringe. The ring was thoroughly cleaned between each measurement of surface tension. The standard deviation of the mean γ was 0.5%.

how ?

The measured surface tension values were plotted as a function of the logarithm of surfactant concentration and the CMC was estimated from the break point in the resulting curve[16]. The experiments were repeated in which aqueous solution of the additives were used as solvent instead of pure water. Representative plots of surface tension (γ) - log concentration (M) are shown in Fig. 8.

The reproducibility of the surface tension concentration curves were checked by duplicate runs. The reproducibility (standard deviation of mean) in CMC was found to be ± 0.9%, calculated from the experimental CMC data from at least two runs.

(ii) Conductivity :

The critical micelle concentration (CMC) for ionic surfactant and ionic - nonionic mixed surfactants was determined by conductivity method[281-282] using a Mullard conductivity bridge (England). A dip type cell of cell constant 0.6645 cm^{-1} was used. The conductance was measured by gradual addition of known concentrated stock solution of surfactant to a given volume of the solvent placed in thermostated water bath maintained at constant temperature. The break point in the specific conductance (k)- concentration plots was taken as the CMC. Representative plots are shown in Fig. 9.

Greek letter κ (kappa?)

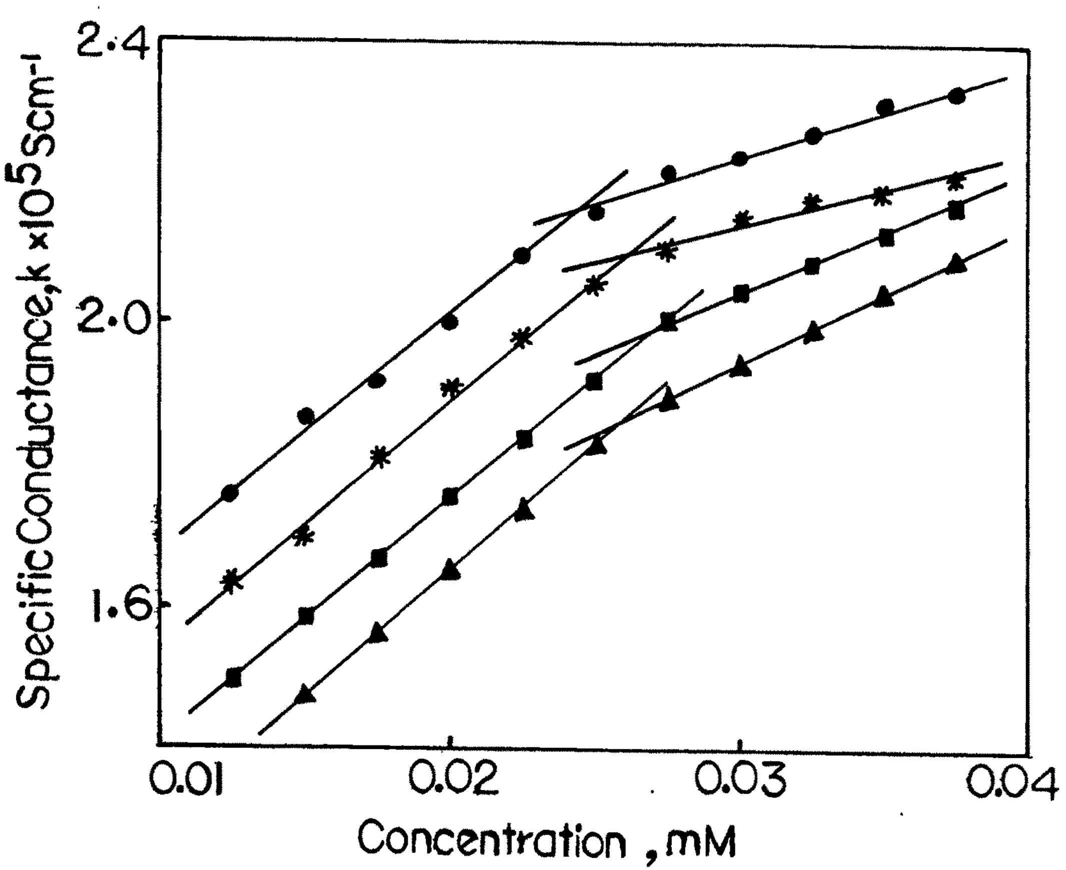

Fig. 9 : Representative plots of specific conductance (k) Vs C. ▲ 5:5 SDBS / $C_{12}E_{10}$ - 0.7% urea at 50°C; ■ 5:5 SDBS / $C_{12}E_{10}$ - 0.3% PEG 400 at 45°C; ✱ 9:1 SDBS / $C_{12}E_{10}$ - 0.5% at 35°C; ● 7:3 SDBS / $C_{12}E_{10}$ at 50°C.

(iii) Iodine Solubilization Method :

The CMC's of nonionic surfactant was also determined by iodine solubilization method[283]. This method is based on the colour change of I_2 when nonionic surfactant (i.e. micelles) are added to iodine solution. This method has an advantage of small molecular size of I_2 compared to that of the surfactant molecule. Hence, the micelle formation is least affected in comparison to other large dye molecules that are customarily used for the CMC determination by spectral shift. However, this method is applicable only to nonionic surface active agents, and systems devoid of any interaction between surfactant and added solute molecules.

A stock solution of iodine was selected to transmit 80% of the light transmitted by pure water. The λ_{max} of iodine in water was found to be 380 nm which shifts down to 360 nm in presence of surfactant. A series of surfactant solutions of various concentrations were prepared by dilution using the iodine mixture (i.e. of 80% T) as solvent. These solutions were kept in thermostated bath for sufficient time, and percentage transmittance (% T) was measured at 360 nm. Log % T was plotted against log C (surfactant concentration) and the break point in the plot was taken as the CMC. Representative plots are shown in Fig. 10. The transmittance measured at least twice for each solution to check the reproducibility. Moreover, experiments were repeated with fresh samples. The error in the CMC was found to be less than 1%. The probability of iodine reacting with the additives was checked previously as well as at this time, no change in the transmittance of additive iodine systems was observed for atleast 2 hrs. Moreover, the surface tension and this method gave the same CMC value.

(b) Performance Properties :

(i) Contact Angle 'θ' :

The contact angles of the surfactant solutions with teflon tape were measured with the help of contact 'θ' meter[284-285] obtained as a gift from Department of Colour Chemistry, Leeds University, Leeds, U.K. For this purpose, a strip of

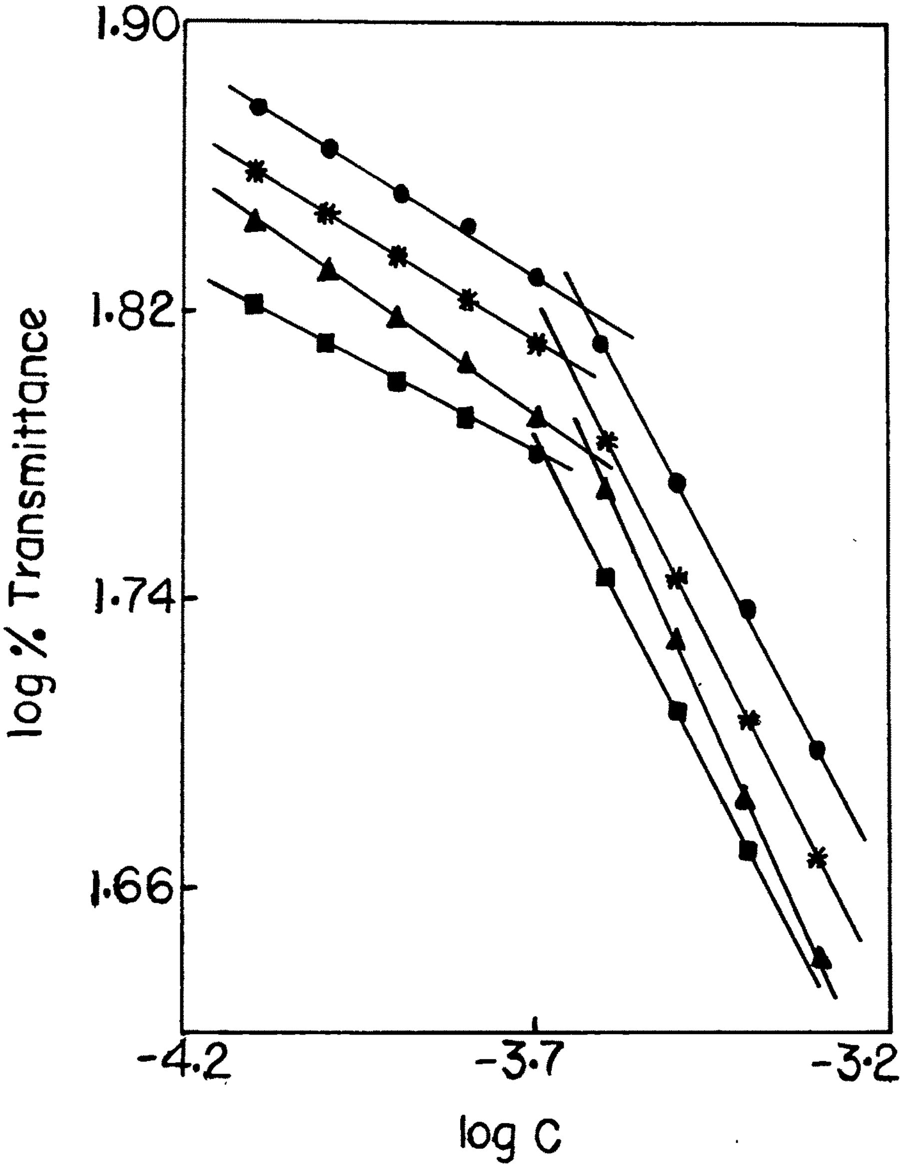

Fig.10: Representative plots of % transmittance Vs log C. ■ 0.0% additive at 45°C; ▲ 1.0% PEG 400 at 50°C; ✱ 1.0% PEG 400 at 45°C; ● 0.05% sucrose at 35°C.

polytetrafluoroethylene (PTFE) obtained from Samson, India was washed with chromic acid and water, rinsed in acetone and dried before use. The surfactant solution was placed as a drop on PTFE surface using a microsyringe. Contact angles 'θ' were determined and the averages of at least four determinations are reported. The error in contact angle is ± 1°. All measurements were carried out at room temperature (~ 27°C). The contact angles of surfactant solutions were also determined in presence of different concentrations of additives.

(ii) Viscosity :

The viscosity measurements for the surfactant solutions were done using an Ubbelohde viscometer at different temperatures of 35, 40, 45 and 50°C. The viscometer was placed in a thermostated water bath maintained at constant temperature. The flow times were determined with the help of a hand held stop watch. The densities of the surfactant solutions were determined using a pyknometer.

(iii) Cloud Point :

The cloud points of surfactant solutions was determined by visually noting the temperature at which the turbidity was observed[118]. The temperature at which the turbidity disappeared on cooling was also noted. Hence, the cloud point were the averages of the appearance and disappearance temperatures, this difference being no greater than 0.6°C, of the cloudiness under constant stirring.

(iv) Foaming :

The foaming efficiency of the surfactant solution was determined by measuring the initial foam height. The Ross-Miles[286] method was used. About 200 ml of surfactant solution of known concentration is allowed to fall into 50 ml of the same solution through a column of 90 cm and 1.5 cm internal diameter. The flask is kept in a thermostated water bath maintained at constant temperature. The initial foam height was observed after all the solution ran out in the column. The reproducibility of initial foam height values were within ± 2%.

(v) Detergency :

The detergency effect of the surfactant solutions were determined by dye solubilization / dye removal efficiency method[256]. Known concentration of water insoluble dye, Blue 2089 [9,10 anthracene dione 1,4 bis (methyl amine)] of 5% (w/v) in benzene was used. About a drop i.e. 0.05 ml of this dye solution is placed on a cotton fabric (3.5" x 3.5") and dried thoroughly. The fabric is now placed in 100 ml of known concentration of surfactant solution and kept under constant stirring. 3 ml of this solution was withdrawn at regular time intervals. The absorbance of these solutions were determined at λ_{max} of 645 nm using a UV-visible (Shimadzu-240) spectrophotometer.

(c) Spectroscopic Techniques :

(i) Fluorescence Quenching :

The micellar aggregation number of the surfactants used were determined by steady state fluorescence quenching method[287-289]. The spectra was recorded on a Shimadzu RF5000 spectrofluorophotometer. Pyrene was used as the luminiscence probe and cetyl pyridinium chloride was used as quencher. The excitation spectra was collected at 385 nm. The pair pyrene / cetyl pyridinium chloride (CpyCl) assure that the residence time of the quencher into the micelle is much longer than the fluorescence lifetime of the probe. Solutions were prepared according to the following procedure :

An aliquot of a stock solution of pyrene in acetone was transferred into a flask and the solvent was evaporated slowly by passing a stream of nitrogen. The surfactant solution was added, the probe being solubilized in the micelles after thorough shaking of the solution in the flask. Pyrene and surfactant concentration were kept constant at 10^{-6} M and 5 mM respectively and the quencher concentration was varied from 0 to 12 x 10^{-5} M. These values give [pyrene] / [micelle] and [quencher] / [micelle] ratios about 0.01 and less than 0.8, respectively, assuring Poisson distribution.

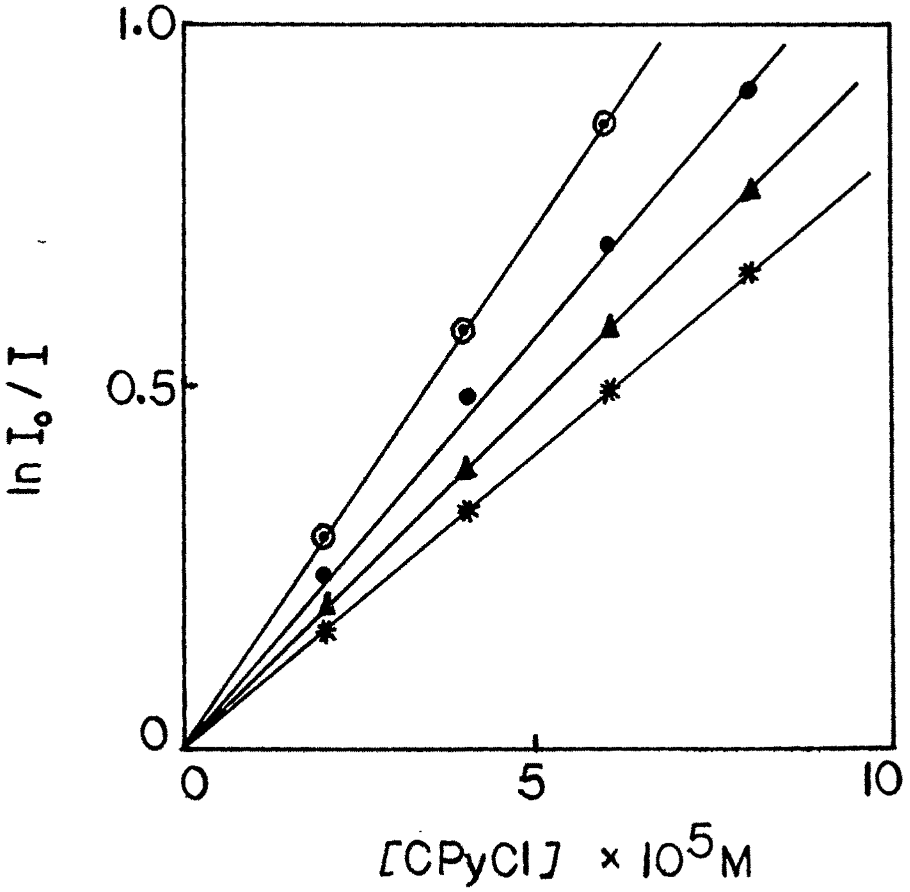

Fig. 11 : Representative plots of ln I_o/I Vs [CPyCl]. ⊙ 7:3 SDBS / $C_{12}E_{10}$ - 0.3% Urea; ● 7:3 SDBS / $C_{12}E_{10}$ - 0.7% Urea; ▲ $C_{12}E_{10}$ - 0.1% PEG 400; ✖ 7:3 SDBS / $C_{12}E_{10}$ sucrose.

As the Poisson distribution is assumed to be valid for the equilibrium of solubilizates between aqueous and micellar phases, the equation to be applied is -

$$\ln I = \ln I_o - [Q] / [M]$$

$$= \ln I_o - N_{agg} \frac{[Q]}{[S] - [CMC]}$$

hence,

$$\ln I_o / I = N_{agg} \frac{[Q]}{[S] - [CMC]}$$

where [Q], [M] and [S] are the concentrations of quencher, micelles and total surfactant respectively. I_o and I are the intensities in the absence and presence of quencher. From the slope of the plot ln I_o/I against [Q] and the CMC, the aggregation number was computed (Fig. 11). All determinations were carried out at room temperature (~27°C).

NMR :

The ^1H NMR measurements were carried out in deuterium oxide (D_2O, 99.9 atom% D Aldrich) solvent at about 25°C. The mixed solutions of SDBS and $C_{12}E_{10}$ with total concentrations of 0.3 M were prepared for SDBS mole fractions 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0, respectively. ^1H NMR spectra were recorded with JEOL JNM FX-100 FTNMR spectrometer operating at 100 MHz and using deuterium field frequency lock on solvent D_2O. ^1H NMR chemical shifts were referred to internal TMS (tetramethyl silane, Aldrich). The proton longitudinal relaxation times (T_1) were measured using a (180°-τ-90°, FID) pulse sequence by the inversion recovery method. The relaxation times were calculated by the nonlinear least square fit using the instrument inbuilt software (provided by JEOL, Japan).