CHAPTER 2

MATERIALS AND METHODS

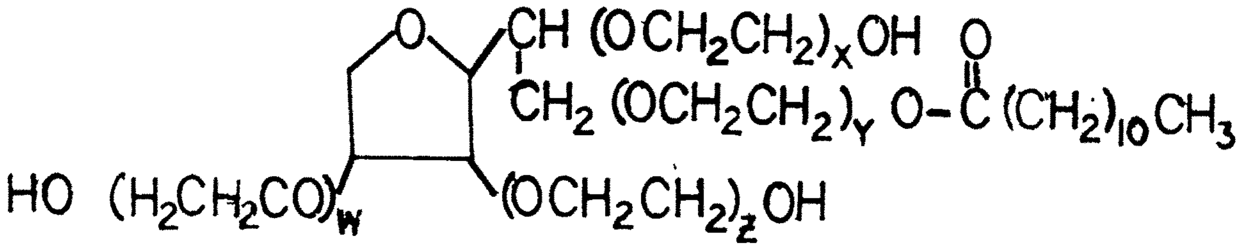
2.1 PREVIEW

In this chapter we describe the materials used and the experimental techniques employed to study the various microemulsion systems.

2.2 MATERIALS

Brij 35 [$CH_3(CH_2)_{11}\ O(CH_2CH_2O)_{23}H$] was the nonionic surfactant mainly used in the study presented in this thesis. High purity grade Brij 35 was obtained from Merck Schuchardt, Germany and was used without any further purification. Tween 20 (polyoxyethylene (20) surbitan mono laurate,(Fig.2.1)) was received from Sigma Chemicals Co., USA and also was used without further purification. Sodium dodecyl sulphate (SDS,$CH_3(CH_2)_{11}SO_4Na$) was obtained from Qualigens, India. Its purity was checked by measuring the surface tension of aqueous solution of various concentration both below and above the cmc and plotting these against concentration. No minimum was observed in the graph signifying its purity. Analar grade NaCl was obtained from Merck, India and was dried at about 150°C for more than two hours and then cooled in a desiccator before use. Alkanes (heptane and nonane) were received either from Merck (India) or SD's (India) and were used after distillation. Doubly distilled conductivity water

TWEEN 20



$W+X+Y+Z = 20$

POLY OXYETHYLENE (20) SORBITAN MONO LAURATE

Fig. 2.1 Structure of Tween 20.

(first distillation from KM_nO_4 and KOH and the distilled water so obtained was further redistilled before use)of conductance $\sim 3.0\times10^{-6}$ S cm^{-1} was used for all sample preparations. n-Propanol obtained from Merck (India) was first dried with anhydrous $CaSo_4$ and distilled at a constant temperature 96.5°C [166].

Surfactant - cosurfactant ratio influences microemulsion properties. Hence it was kept constant at 1:2 by weight throughout the studies presented in this thesis.

2.3 EXPERIMENTAL METHODS

(a) Phase diagram

Pseudo-ternary phase diagrams were constructed by titration method [167,168,43].Alkanes (heptane, nonane and their mixtures), water or Nacl solution and Brij 35 in propanol solution were the three components taken at the three corners of a triangle in the ternary phase diagram. Brij 35 is soluble in propanol and these solutions were prepared in 1:2 weight proportions. Different amounts of this solution were taken in standard joint test tubes and were mixed with known amounts of oil or water (the mixing proportion of this mixture was so adjusted that it covers the whole triangular area on titration). This mixture was then titrated against water or oil respectively. After each known addition of titrant, the test tubes were stoppered tightly with standard joint stoppers and then sealed with teflon tapes (amount of each addition of the titrant was varied from 0.02 ml to 0.1 ml depending on the requirement of the system). Then the samples were kept in a thermostatic waterbath for attaining the required temperature (± 0.1°C). Phase separation was determined visually. Appearance of slight turbidity in the system was taken to be the monophasic to biphasic transition point. Similarly clearing of the turbid system was noted on the biphasic to monophasic transition point. Formation of small water droplets underneath or separation of oil droplets above, of a biphasic (liquid/liquid) system was considered as the biphasic to triphasic conversion point. These points were observed visually during the titration process. Each sample was cooled to room temperature before opening for the addition of next aliquot. Similar scanning was done from different locations of the triangular area till the whole triangular phase diagram was covered. Volume of water or oil consumed at each phase transition was noted and the ternary compositions of the phase boundaries were calculated in weight percentage. These were then plotted in ternary diagram. Area of each phase zone was quantitatively determined using a planimeter.

Some phase diagrams were duplicated and areas were found to be within 1% of each other.

b) Viscosity

Viscosity of microemulsion samples was measured with a standard Ubbelohde viscometer of flow time 91.6 secs for water at 40°C. Flow time of each sample was measured and absolute viscosity was calculated by comparing the values with that of water.

$$\eta_m = \eta_w \times \frac{\rho_m \cdot t_m}{\rho_w \cdot t_w}$$; $\eta_m, \eta_w, t_m, t_w, \rho_m, \rho_w$

were the viscosities, flow times, and densities of single phase microemulsion (m) and water (w) respectively. Density of each sample was measured using standard pyknometer. Viscosity and density of water at different temperatures were taken from literature [169]. Viscometer was placed in a thermostatic bath for sufficient time (atleast 30 minutes) so that the solutions reached the required temperature. Then flow time of the solutions was determined. All flow time readings were duplicated and average value was taken for the viscosity calculation. Standard deviations in density and viscosity measurements were ± 0.05% and ± 0.5% respectively. The water density value determined at one temperature, tally well with the literature value (ρ_w=0.9927 g/ml at 40°C, cf ρ_w=0.9922 g/ml at 40°C) [169].

c) Conductance

Conductance of all microemulsion samples was measured with a Mullard conductivity Bridge (U.K.). The cell constant of the conductivity cell used was 0.1416 cm^{-1} which was determined by using 0.1 and 0.01 M KCl solutions. Aqueous phase of the microemulsion samples for conductance measurements was 0.1M NaCl unless otherwise mentioned. Readings were taken by keeping the samples at constant temperature bath. Extra care was taken in terms of keeping the cell tightly packed in the sample tube while taking readings particularly at higher temperature. This was done to minimise the escape of solvent vapours from the sample. Results were found to be reproducible (variations were found to be within ± 1%).

d) Ultrasonic Velocity

Adiabatic compressibility of a given solution can be calculated using the relation, $\beta = 1/\rho . u^2$ where u is the sound velocity in the fluid medium and ρ is the density of the medium [170-172].

Ultrasonic velocity was measured with a multifrequency ultrasonic interferometer (M-3, Mittal Enterprises, New Delhi, India). Samples were taken in a jacketted cell below which a quartz crystal was present. This cell was mounted on a platform through which the electric connections were made with the measuring device of the instrument. Sound waves produced were allowed to pass through the solutions before they get reflected from the disc which was present on the top of the cell. Disc can be moved up and down with the help of the screw gauge attached to the micrometer. The disc was moved in any one direction and at the length span of $\lambda/2$, ammeter of the measuring device showed maximum deflection. On an average ten readings were noted and mean wavelength was taken for the velocity calculations. All the experiments were carreid out at 1 MHz. A few measurements were taken at 3 MHz and 5 MHz too. As there was not any perceptible deviation in 'u',the β values calculated from 1 MHz data are presented in this thesis unless mentioned otherwise. Water was circulated from a temperature controlled water bath through the cell to keep the solution at required temperature. The experiments were randomly repeated and the maximum standard deviation of the mean was found to be ± 0.3%.

e) Interfacial tension (IFT)

IFT between different phases was measured by a spinning drop tensiometer (model 300, assembled in the

University of T~~a~~exas) at the Institute of Reservoir Studies, ONGC, Ahmedabad, India. The capillary tube was filled with higher density liquid and a small drop of lower density liquid was introduced with the help of a syringe. After caping it tightly, the capillary was fixed on the rotator. The temperature was set at required value by a heating device attached to the rotator. The speed of the rotator was adjusted in such a way that the length of the elongated droplet was approximately four times to that of its diameter. Time for one revolution (P) was noted from the digital counter and the diameter (D) was determined using a travelling microscope. Density of the liquid phases were determined with a digital density meter IFT between the phases are related with the diameter (D), time for one revolution (P), and the density gradient between the phases (**$\Delta\rho$**) by a relation

$$\text{IFT} = 1.234 \times \Delta\rho \times (D/1.332)^3/P^2$$

where 1.234 is an instrumental constant and 1.332 is correction factor for refractive index of the glass of the capillary tube. Both these values were provided by the instrument supplier. The experiment was repeated by changing the speed of revolution and readings were reproducible (standard deviation was less than 1%).

f) Cloud Point

Cloud point of the microemulsion samples was taken as the temperature at which clouding appears in the system

[173,174]. Each composition was taken in a standard joint test tube and was sealed with teflon tapes. These test tubes were then kept in a thermostatic water bath. The temperature of the bath was increased in regular intervals till the clouding appears in the samples. Then a second series of experiment were done where the temperature interval was further narrowed in that particular range and cloud point was determined accurately. Declouding temperature was also noted while cooling. Average of these two readings was taken as the cloud point of the system. Randomly cloud point measurements of various samples were repeated and values were found to be consistant within ± 0.5°C.

g) Phase Volume Measurements

Different ternary compositions were taken in graduated test tubes which were sealed with teflon tapes. The components were mixed thoroughly by shaking and kept in a water bath. The temperature of the water bath was controlled at a particular value (±0.1°C). After the samples attained the required temperature, it was shaken well and kept for phase separation. Volume of each phase was then noted. Phase volumes were calculated in fractions of total volume and reported here.