CHAPTER 2

MATERIALS AND METHODS

2.a. Preview

In this chapter the details of chemicals used and the various experimental methods employed for the study are presented.

2.b. Materials

The surfactant sodium dodecyl sulphate (SDS) (Qualigens, high purity) was obtained from Glaxo Labs, India. It was used without further purification. Aqueous solutions of SDS of various concentrations were made and surface tensions were determined by Wilhelmy plate method. The surface tension-concentration profile of SDS did not show a minimum signifying its purity. Cyclohexane was purchased from Merck, India and n-propanol from either Merck, India or SD's, India and were used after purification as described below. Cyclohexane was passed through a chromatographic column of silica gel in the lower section and basic alumina in the upper section to remove aromatic impurities and then subjected to distillation prior to use [126]. Propanol was dried with anhydrous calcium sulphate and distilled at a constant temperature 96.5°C [126]. This was then stored in the presence of molecular sieves [126]. n-Hexanol from BDH, England was distilled before use. Doubly distilled water

(conductance $\sim 3\times10^{-6}$ S cm^{-1}) was used throughout the study for all sample preparations. Molecular weight of polyacrylamide (PAA) was over 5×10^{6} (supplier's data) and it was obtained from BDH, England. NaCl (analar) was from Merck, India.

The surfactant-cosurfactant ratio is one of the influential parameters on the microemulsion phase behaviour, structure and their properties. In this study this ratio was always kept constant at 1:2 by weight and these two components together constitutes the surfactant phase throughout this thesis unless specific mention is made to the contrary.

2.c. Methods

(i) Ternary phase diagrams

An usual titration technique [127,128] was adopted for the determination of pseudoternary phase diagrams of the system at various conditions. Known amounts of oil or water was taken with surfactant (S+CS) in stoppered test tubes and kept in thermostatically controlled water bath of required temperature ($\pm$0.05°C). On attaining the temperature these mixtures were titrated with water or oil respectively from a microburette of 0.02 ml accuracy.

After each addition the mixtures were allowed to attain the temperature. The appearance or disappearance of turbidity marks the boundary of microemulsion region and the amount of water or oil consumed at this juncture was noted down. The end point was determined visually. The weight percentage of each component (water,oil and surfactant) was then calculated and plotted in the triangular graph. The set of points at which turbidity disappears and the set of points at which the turbidity reappears were joined together separately. The region bounded by these two lines is the single phase microemulsion zone and its area was measured with a planimeter for the sake of comparison. A complete scanning of the phase diagram was done by starting from various points along the oil-surfactant line or water-surfactant line and titrating with the third component. After each addition the development of different phases (monophase, biphase or triphase) were checked and the composition was marked in the diagram. This procedure was continued until the whole area of the triangular graph was covered. For higher temperature studies the test tubes with standard joints were sealed with teflon tape. Phase diagram of a few systems were duplicated. It was observed that the zone areas were within 1-2% of each other. All phase diagrams were, ofcourse, not duplicated. A few microemulsion samples were selected randomly and checked for the

stability for prolonged time. They were found to be stable within the temperature range studied.

(ii) Phase Volume Measurements

The phase volume measurements were carried out using narrow graduated, standard joint stoppered test tubes. These test tubes were calibrated before their use. A particular composition was selected from the ternary phase diagram and the components were mixed together, to note the layer separation, every time replacing water with various increasing concentrations of aqueous NaCl solution . These were then kept in a constant temperature water bath. On attainment of temperature they were shaken and reequilibrated. The volume of each layer was noted down. The average of two such runs was taken as the final volume.

(iii) Conductance

For the electrical conductivity measurements, various compositions of microemulsions along the one phase region were prepared carefully. Keeping these samples in a thermostated water bath their conductances were measured, with a Mullard conductivity bridge (England) and a conductivity cell of cell constant 0.1417 cm^{-1}, at various

temperatures. The cell constant was determined using a standard KCl solution. For higher temperature measurements extra care was taken to minimise the evaporation of solvents. The conductance values were multiplied with cell constant to get specific conductance and was plotted against various parameters. It is generally assumed that the surfactant ions are completely adsorbed at the oil-water interface and there by does not act as charge carriers, which the counter ions do.

(iv) Viscosity Measurements

Viscosity of the samples were determined with a standardised Ubbelohde viscometer of flow time 91.6 secs for water at 30°C. The samples were selected along a constant surfactant weight percentage line in the ternary phase diagram and their densities were determined with a calibrated pyknometer at various temperatures. These samples were then loaded into the viscometer. The viscometer was placed in perfectly perpendicular position and kept at required temperature in a controlled temperature bath for atleast one half hour before the flow time was noted. The flow time was always duplicated. The average of these two flow times (the difference was never more than 0.3 secs) was taken for the calculation of absolute viscosity using the relation

$$\eta_1 = \eta_2 \rho_1 t_1 / \rho_2 t_2$$

where η_1 and η_2 were the viscosities, ρ_1 and ρ_2 were the densities and t_1 and t_2 were the flow times in seconds for the microemulsion sample and water respectively. The water viscosity at various temperatures were taken from the literature [129]. The water density at 40°C was determined and was found to be 0.9927 g/ml which compares favourably with literature value of 0.99224 [129]. Hence at other temperatures literature values were used. The errors in viscosity and density were ± 0.5% and ± 0.05% respectively.

(v) Adiabatic Compressibility

Adiabatic compressibility of a solution can be calculated using the relation $\beta = 1/\rho U^2$ where U is the velocity of sound through the medium and ρ is the density of the medium [130-132].

Ultrasound velocity through microemulsion samples was measured using a multifrequency ultrasonic interferometer,(Model MX-3, Mittal Enterprises, New Delhi, India). Samples were prepared and taken in the jacketted cell of the instrument. Water was circulated through the jacket from a constant temperature water bath

to keep the samples at the required temperature. Turning the vernier screw and noting the deflection in the micro ammeter of the instrument, wave length of the sound wave passing through the sample was determined. Average of ten such readings was taken as the actual wave length. The experiments were carried out at a constant frequency 1 MHz and it was multiplied with the wavelength to obtain the velocity of the sound passing through the medium. From the velocity and density of the medium adiabatic compressibility of the sample was computed using the relation mentioned earlier.

(vi) Interfacial Tension Measurements

Interfacial tension measurements between two different phases were done by a spinning drop tensiometer (model 300, assembled at the University of Texas) at the Institute of Reservoir Studies, ONGC, Ahmedabad, India. The capillary tube of this instrument was filled with the high density liquid and a drop of the low density liquid was introduced into this capillary tube with the help of a syringe. After capping the capillary tightly, it was fixed to a rotator and the temperature was set by a heating device attached to the rotator. The speed of the rotator was gradually increased and adjusted in such a way that the length of the elongated droplet is approximately four

times that of its diameter. The speed of the rotator was noted from the digital counter and the diameter of the elongated droplet was determined with a travelling microscope. The densities of the liquid phases were determined with the help of a digital densitymeter. The experiment was repeated by changing the speed of the motor and the IFT was calculated using the equation

$$IFT = \frac{1.234 \times \Delta\rho \times \left(\frac{D}{1.332}\right)^3}{P^2}$$

where 1.234 is an instrument constant and was supplied by the manufacturer. $\Delta\rho$ the density difference between the two liquids, D minor axis of the elongated droplet, 1.332 a correction factor for the refractive index of the glass of the capillary tube (supplied by the manufacturer) and P- the time in milliseconds per revolution.

The average of four IFTs was taken as the final interfacial tension between the two liquid phases.