CHAPTER - 2

Materials and Methods

2.1 Preview

2.2 Materials

2.3 Experimental Techniques

2.3.1 Phase Diagram

2.3.2 Viscosity

2.3.3 Ultrasonic Velocity

2.3.4 Conductance

2.3.5 Interfacial Tension

2.3.6 Contact Angle

2.3.7 Phase Volume Measurements

2.1 PREVIEW

In this chapter various methods and materials are discussed for studying the physico-chemical properties of microemulsion systems.

2.2 MATERIALS

The cationic surfactant cetyltrimethyl ammonium bromide $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ was obtained from Trizma, chemicals India. It was recrystallised thrice from methanol : acetone (4:1) mixture and dried at 100°C for 2 h before use and kept in dry atmosphere. The surface tension - concentration profile of CTAB solution did not show any minimum at room temperature.

Cyclohexane (Sulab, India) b.p. 81°C was distilled[1] before use. n-propanol (Sulab, India) was dried over calcium sulphate and was distilled at a constant boiling temperature (96.5°C) and was stored over molecular sieves (4A°) in an Erlenmeyer flask. N,N dimethyl formamide (DMF) (Sulab, India) was freshly distilled (149-153°C) and stored over molecular sieves. Sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium chloride (KCl), potassium bromide (KBr) and potassium Iodide (KI) were AR grade obtained from Qualigens, India. Sodium nitrate ($NaNO_3$), calcium nitrate $Ca(NO_3)_2.4H_2O$ as well as magnesium chloride ($MgCl_2.6H_2O$) were of AR grade obtained from S.D.Fine Chemicals, India.

All the salts were dried in an oven at 150°C for about 2 h and cooled in a desiccator. Most of the chemicals were of AR grade and were purified whenever the purity was doubted.

Polyethylene glycol (Mol. Wt. 400) was from E.Merck, India was distilled. Polyethylene glycol (Mol. Wt. 4000) was from Sulab, India. Polyacrylamide having molecular weight $\overline{Mv} \cong 4.5 \times 10^5$ was synthesised and characterised in our laboratory[1b].

2.3 EXPERIMENTAL TECHNIQUES

2.3.1 Phase Diagram :

A simple titration technique[2-8a-c] was used to prepare the microemulsion. A known amount of cyclohexane or water (DMF) was taken with surfactant (CTAB) + cosurfactant (propanol) in a stoppered test tube and kept in a temperature controlled (accuracy ± 0.05°C) water bath.

The surfactant (CTAB) to cosurfactant (1-propanol) weight ratio was kept at 1:2. These mixtures were then titrated with water or cyclohexane respectively. After each addition the mixture was allowed to attain the temperature. The teflon tape was used to seal the test tubes to stop the evaporation. The appearance or disappearance of turbidity marks the boundary of microemulsion region or the plait point. The volume of water or oil consumed was noted. The titration was continued until the whole area of the triangular graph was noted down. The weight percentage of each component was calculated and plotted in an equilateral triangle. The points where turbidity appears were joined as well as the points where turbidity disappears were joined. The region bounded by these two lines is the single phase region (1ϕ) separated from the solid-liquid (S/L) as well as liquid - liquid (2 ϕ L/L) and liquid - liquid - liquid (triphasic -3 ϕ L/L/L) regions.

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

2.3.2 Viscosity :

Viscosity[9] of 1ϕ microemulsion was measured with a standard Ubbelohde viscometer of water flow time 75 s at 30°C. The flow time of microemulsion samples were determined at 30, 35, 40 and 45°C. The density of all samples were determined by using pyknometer of known volume. The viscosity of microemulsion samples was calculated using the following equation

$$\frac{\eta_{\mu E}}{\eta_{H_2O}} = \frac{\rho_{\mu E} \cdot t_{\mu E}}{\rho_{H_2O}\, t_{H_2O}}$$

where $\eta_{\mu E}$ = Viscosity of microemulsion

η_{H_2O} = Viscosity of water

$\rho_{\mu E}$ = Density of microemulsion

ρ_{H_2O} = Density of water

$t_{\mu E}$ = Flow time of microemulsion

t_{H_2O} = Flow time of water

For measuring the flow time the viscometer was kept vertically in a thermostatic bath for about 30 min to obtain temperature equilibrium. All flow time reading were triplicated and the error in viscosity and density were about ± 0.05%. The literature value of density of water was found to be $\rho_{H_2O} = 0.9927$ at 40°C which is almost equal to $\rho_{H_2O} = 0.9924$.

2.3.3 Ultrasonic Velocity :

The adiabatic compressibility[10-14] of microemulsion samples were measured with a multifrequency ultrasonic interferometer (MX-3, Mittal Enterprises, New Delhi, India). The adiabatic compressibility (β) of samples was given by the equation

$$\beta = \frac{1}{\rho u^2}$$

where u is the velocity of sound and ρ is the density of sample through which the sound wave was passed. The sample was kept in a cell having the movable disc from which the sound gets reflected. The movable disc was present on the top of the cell with micrometer screw attached to it. The sound waves get reflected by moving disc and distance can be measured. The sound waves are converted to electric pulse, which shows the zero deflection at every λ/2 on a scale. The disc is mounted on the micrometer screw. So that all the λ/2 can be measured in terms of millimeter. The frequency was 3 MHz for all the experiments.

2.3.4 Conductance :

Conductance of all microemulsion samples were measured with a Mullard Conductivity Bridge (U.K.). The cell constant measured was 0.6645 cm^{-1}, which was measured by using 0.1 M KCl solution as well as 0.01 M KCl solution. All the samples were made by using the conductivity water having conductance of $\cong 3.05 \times 10^{-6}$ S/cm. All samples were placed in a wide mouth sample tube and then kept in a thermostatic bath.

The conductances were measured in the temperature range of 30 to 80°C at the intervals of 10°C. At higher temperature some extra care was taken when measuring the conductance so that the evaporation was minimised. All the results were reproducible in the range of 0.1%.

2.3.5 Interfacial Tension (IFT) :

Interfacial tension[15] was measured by using the spinning drop tensiometer (University of Texas, Austin model No.500). The interfacial tension was measured between the two phases in equilibrium with either water or oil. The capillary tube was filled up with the higher density fluid and the drop was made with lower density liquid. The tube was then capped tightly and spun at different speed. The tube was spun in such way that the droplet inside the tube was elongated approximately four times to that of its diameter. The diameter (D) of droplet was measured by a travelling microscope mounted on the tube. The time for the revolution was measured. The IFT of the microemulsion samples were measured by using the following equation -

$$\mathrm{IFT} = \frac{1.23 \times 10^{3} \times \Delta\rho}{(\mathrm{Speed})^{2}} \times \frac{(D^{2})^{3}}{(n_{D})^{3}}$$

where Δρ is the density difference. D is the diameter of the droplet; n_D is the refractive index of medium for aqueous microemulsion. For, water the refractive index is 1.332. The speed and temperature were changed for different readings.

2.3.6 The Contact Angle :

The contact angle of one phase microemulsion with polytetrafluoroethylene (teflon) surface were determined by using a contact θ meter obtained as a gift from the Department of Colour Chemistry, Leeds University, U.K. The surface of teflon tape was treated with chromic acid and then with copious quantities of water, with acetone and dried before use. Atleast 10 different drops on various parts of the teflon tape, surface were made with the microemulsion and the contact angles were determined. The average of these readings are reported with error of ± 2°.

2.3.7 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 noted. Phase volumes were calculated in fractions of total volume and are reported here in following chapters.

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