CHAPTER 2

EXPERIMENTAL

materials & methods

In this chapter, we describe, the materials and the experimental techniques used for studying the physical properties of microemulsion systems and the kinetics of chemical reactions.

2.1 Materials

Triton X 100 (TX100), a nonionic surfactant [$CH_3C(CH_3)_2\ CH_2C(CH_3)_2\text{-}\phi\text{-}O\text{-}(CH_2CH_2O)_{9.5}H$], was obtained from Sigma and was used as received without further purification. Sodium dodecyl sulfate (SDS) was procured from Qualigens, India and used as received. Surface tension-concentration profile of aqueous SDS solution did not show any minimum. Cetyl trimethyl ammonium bromide (CTAB) was purchased from S.d. Fine. It was recrystallized thrice from a 3:1 acetone-methanol[135,208,209] mixture and dried at 60°C for 48h before use. The surface tension-concentration profile of CTAB solution did not show any minimum at room temperature.

Cyclohexane (Merck, India) b.pt. 81°C (Lit. 80.74°C) [218] was distilled before use. n-Propanol was dried over calcium sulphate and was distilled at a constant boiling temperature[210] and was stored with molecular sieves (4Å) in an Erlenmeyer flask. N-N Dimethyl formamide (DMF), (Merck India) was freshly distilled and stored over molecular sieves. Ethyl propionate and Methyl acetate were obtained from National Chemicals, Baroda and distilled before use (b.pt. 99°C & 56.8°C respectively). Lit. values are 99.1°C & 57.5°C[218]

Sodium chloride, Potassium chloride, Potassium dichromate, Iodine, Oxalic acid and Sodium hydroxide were AR grade and obtained from Qualigens, India. Iodine was purified by sublimation process. The salts were dried in oven and cooled in a desiccator. Potassium persulfate was from s.d. Fine, India. Sodium iodide was from Loba chemicals, Bombay, India and Sodium thiosulphate was from BDH, India. Hydrochloric acid was obtained from Merck, India. Most of these were AR grade and used without further purification. Whereever purity was doubted, the proper purification was done.

2.2 Experimental technique

a) Physicochemical properties

Phase diagram

A simple titration technique[211-214] was used for the preparation of microemulsion. A known amount of cyclohexane or water/DMF was taken with surfactant (S+CS) in stoppered test tubes and kept in a temperature controlled (± 0.05°C) water bath. These mixtures were then titrated with water or cyclohexane respectively from a microburette. After each addition, the mixtures were 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 and the amount of water or oil consumed at this juncture was noted down. The titration was continued until the whole area of the triangular graph was covered. The weight percentage of each component was then calculated and plotted in a triangular graph.[215-217] Both surfactant and cosurfactant constitutes the surfactant phase throughout the study. The surfactant to cosurfactant ratio was kept either 1:2 or 1:1 by weight. 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.

Physical properties were studied with constant surfactant (S+CS) composition with changing oil/water ratios at different temperatures from 30 to 45°C.

For the electrical conductivity measurements, various compositions of microemulsion along the one phase region were prepared carefully. Keeping these samples in a thermostated waterbath, 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. The measured conductance values were multiplied with cell constant to get the specific conductance and was plotted against the weight fraction of the polar liquid ie either with water or DMF. Microemulsion was formed with 0.1M solution of sodium chloride or sodium iodide by replacing the pure polar solvent to induce the conductance as TX100 is nonconducting.

Viscosity

Viscosity of the microemulsion was determined with a specially fabricated four limb Ubbelohde viscometer kept at the thermostated bath. The densities of these systems were measured with a pyknometer at various temperatures. The perpendicularly placed Ubbelohde viscometer in the water bath was filled with microemulsions kept for half an hour before determining the flow time with a hand held stop watch. The process was repeated till a reproducible result was obtained. The absolute viscosity was calculated using the relation,

$$\eta_1 = \eta_2 \frac{\rho_1 t_1}{\rho_2 t_2} \quad \text{where } \eta_1 \text{ and } \eta_2$$

were the viscosities, ρ_1 & ρ_2 were the densities and t_1 & t_2 were the flow times in seconds for the sample and water respectively. The water viscosity and density at various temperatures were taken from the literature.[218]

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.[219-223]

Ultrasound velocity through the microemulsion samples was measured by the method of interference using a multifrequency ultrasonic interferometer (Mittal Enterprises, New Delhi, India). Samples were prepared and taken in the jacketed cell of the instrument; below the cell, a quartz crystal is fixed and the instrument generated ultrasound waves by this pulsating quartz crystal. The jacketed cell containing the solution was mounted on a disc through which electrical connections were done to an ammeter. On moving vernier screw attached to the top of the jacketted cell, the microammeter shows the deflection due to the passage of sound waves through the sample. The point at which it shows the maximum deflection is noted. The difference between two such successive readings gives $\lambda/2$. Average of such readings was taken and λ was calculated. The experiments were carried out at a constant frequency of 1MHZ 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 samples was computed using the relation mentioned earlier.

Contact angle

The contact angles of one phase microemulsion with a polytetrafluoro ethylene[224,225] (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. At least 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 $\pm 2^\circ$.

Cloud Point

The cloud point[48,49] of the microemulsion was determined by finding the temperature at which the cloudiness appears for the particular compositions. The particular composition of the microemulsion samples along the monophasic region is prepared in standard joint test tubes. The tubes were sealed with teflon tape and kept in a temperature controlled water bath initially at lower temperature. After attaining the temperature, the temperature of the bath was raised gradually and the temperature at which it started clouding was noted. The process was repeated in the reverse order by cooling and the temperature is noted at which it becomes a clear solution. The average of these two temperature is reported as the cloud point with an error of ± 0.5°C.

Fish phase diagram

Fish phase behaviour or the partial phase behaviour was studied at different temperatures. Samples were prepared with fixed composition of water and oil with 1:1(w/w) ratio of oil and water and adding surfactant by keeping the total weight percentage100.[11,48,55,226,227] The samples were kept in a temperature controlled bath initially at a low temperature. The samples represent different phases which was noted visually in each samples. The temperature was increased gradually and the different phases were again noted. The process was repeated till it shows Winsor transitions[55,79,228] to get 'fish' type of phase diagram. The phase diagram is represented as a function of α (weight of S/ (weight of hydrocarbon + weight of water)) with temperature. The process is done with constant water and oil composition 20% w/w also.

b) Kinetic Studies

For kinetic studies, the microemulsion was prepared with trace amounts of reactants to avoid the phase separation. For the oxidation of potassium iodide by potassium persulphate, a microemulsion with aqueous potassium iodide and another one with aqueous potassium persulphate were prepared. The concentrations of potassium iodide and potassium persulphate were taken by considering the total volume of water in the microemulsion and not for the total volume of microemulsion as these are insoluble in cyclohexane.[145] The reaction was followed spectrophotometrically[143-146] by a UV-240 Shimadzu spectrophotometer. The reaction cell containing potassium iodide was thermostated in the cell compartment which was jacketed with water circulation from a thermostated bath. Potassium persulphate solution was thermostated in the water bath and after attaining the temperature the microemulsion with potassium persulphate was added to the microemulsion with potassium iodide in the quartz cell. The reaction was monitored by measuring the increase in absorbance due to the liberation of iodine at a λmax of 360 nm. The increase in absorbance was noted at regular time intervals and the k values were calculated for the first and second order reactions using the following equations.[229-231]

For second order

$$kt = \frac{1}{a_0-b_0} \ln \frac{b_0(a_0-x)}{a_0(b_0-x)}$$

where k is the rate constant. the time (t) is in sec, a_0 & b_0 , are the initial concentrations of potassium iodide and potassium persulphate respectively and x is the amount of iodine liberated at each time and for the first order,

$$k\ (t_2-t_1) = \ln \frac{(a - x_1)}{(a - x_2)};$$

k , is the rate constant. $(a-x_1)$ & $(a-x_2)$ are the concentrations of potassium persulphate unreacted at time t_1 and t_2.

The kinetics of the reaction in CTAB microemulsion was studied by a spectronic 20 colorimeter. (Bausch & Lomb). Potassium iodide microemulsion was taken in the cell and thermostated in a water bath. Potassium persulphate microemulsion was also thermostated separately in a stoppered bottle. The reaction was started by adding the required amount of $K_2S_2O_8$ solution to potassium iodide solution in the cell, stirred it and the absorbance was noted at a λmax of 360nm. The increase in absorbance was noted at regular time intervals and the solution was stirred well before taking the reading at each time. The potassium iodide and potassium persulphate solutions were mixed in the 2:1 volume ratio. The reaction was carried out for constant surfactant composition and changing oil-water compositions. The reaction was studied at various temperatures from 25°C to 45°C.

Kinetics of hydrolysis of methyl acetate was studied by a titration method. An acidic microemulsion was prepared with A.R. grade HCl. Aqueous part contained 1% HCl in the total amount of microemulsion and thermostated at the required temperature. Methyl acetate was also thermostated separately in a stoppered bottle. To 7ml of acidic microemulsion in a stoppered test tube, 2ml of methyl acetate was added and mixed well and 1ml of the reaction mixture was withdrawn at regular time intervals and was placed in ice cold water to quench the reaction. The unreacted HCl was determined by titrating against a standard NaOH solution, standardized using a standard oxalic acid and the rate of reaction was calculated for the first order using the equation.[229-231]

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

i.e., $$k = \frac{2.303}{t} \log \frac{T_\infty - T_0}{T_\infty - T_t} ;$$

Where k, is the rate constant, a is the initial concentration corresponds to $T_\infty - T_0$, T_0 is the initial titre value, T_∞ is the final titre value; (a-x) is the concentration at a time t, ie., $T_\infty - T_t$, T_t is the titre value at time t. The reaction is carried out at various temperatures from 35 to 45°C. The reaction solution remains homogeneous throughout the study. For SDS and CTAB containing systems, the reaction was studied with constant surfactant concentration and changing oil-water concentration ratio. The reaction in CTAB and TX100 microemulsion was studied with constant water fraction and changing oil-surfactant composition. It has also been studied with constant water and changing surfactant-oil concentrations.

Kinetics of iodination was studied by using a UV-240 Shimadzu Spectrophotometer. A microemulsion was prepared with particular composition and Iodine was dissolved in it and the concentration was determined by titrating against a standard thiosulphate solution which was standardized by a standard potassium dichromate solution. The microemulsion solution containing I_2 (3ml) was taken in the cuvette and thermostated in the cell compartment which was connected to a constant temperature bath with a water circulation. The reaction was started by adding 0.1 ml of acetone to it and the decrease in absorbance was noted at regular time intervals at λmax of 355 nm and the rate of reaction was calculated for the second order. For all the studies using a spectrophotometer the λmax was determined by plotting the absorbance of the iodine solutions under the experimental condition with the wavelength of light.