

Chapter - 6

SUMMARY AND CONCLUSIONS

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Microemulsion is a multicomponent system of different substances like oil, water and an amphiphile. Its properties are different from the individual components. The concentration of oil and water decides the nature of microstructure of the microemulsion. Microemulsions are considered as rather monodispersed droplets of water in oil (w/o) or oil in water (o/w) or bicontinuous. It is essential to find its microstructure. In the bicontinuous microemulsions water or oil are almost in equal amount. Determining the phase boundaries is a way to characterize e.g. shape of phase boundaries gives hints on the number of coexisting phases in the specific phase regions. The pseudoternary phase diagram contains information about the system and therefore the changes in any variable like temperature, oil, etc. effect the diagram.

The different chapters in the thesis deal with properties of microemulsion. In the different chapters, different cationic microemulsion system consisting of cyclohexane (oil), CTAB (surfactant), n-propanol (cosurfactant) and water have been studied with different additives like salts and water soluble polymers.

Surfactant to cosurfactant weight ratio were always kept constant at 1:2. Phase behaviour study included pseudoternary phase diagrams and the phase volume measurements. The conductance, viscosity and adiabatic compressibility were also determined in presence of salts like NaCl, NaBr, NaI, KCl, KBr and KI both in presence and absence of PEG-400 were determined. Water was also replaced by polar solvent dimethyl formamide and also with 1:1 (DMF + Water) and the phase diagram and other properties were determined. The effect of polyacrylamide and the effect of PEG-400 were seen on all the properties such as viscosity, conductance, adiabatic compressibility, volume measurements etc. at constant 45% S + CS.

All properties were carefully examined. All studies were performed over a wide range of temperature from 30 to 70 or 80°C. Finally the effects of mixed systems were seen and the viscosity, conductance and adiabatic compressibility were measured.

The temperature and additives are two parameters which affect the one phase microemulsion region in a ternary phase diagram. Though the ionic surfactants are comparatively less sensitive towards temperature than nonionic surfactants, the phase diagram determination at various temperatures without additive proved that monophasic region decreases since the biphasic region increases. This is because of the disturbance caused by the thermal motion of amphiphile molecules, on the regular array of molecules at the interface above the critical temperature.

The presence of polyethylene glycol (PEG-400) was found to have generally destabilizing effect on microemulsion. But decrease in the monophasic region is overall compensated and hence the presence of PEG has not much effect on the phase diagram. In the presence of PEG, the interface becomes relatively different and hence the IFT between water and microemulsion (w/m) as well as between oil and microemulsion (o/m) is different by about 0.1 mN/m. The specific conductance measurement (σ) versus volume fraction of water (ϕ_w) for one phase system shows that the conductance is due to the sticky collision. Since conductance increases slowly and no percolation threshold was seen the structure of μE is assumed bicontinuous throughout. In the case of 45% S + CS the conductance is higher than 65% S + CS respectively since at higher S + CS, the water content is lower. The viscosity versus ϕ_w plots in the presence and absence of PEG show that there is a maximum observed which indicates that the structure changes, from bicontinuous to o/w regime. In the presence of PEG the viscosity is higher because PEG-400 is more viscous than water and hence the overall increase in viscosity is observed. Using the Frenkel-Eyring equation

$$\ln \frac{\eta V}{N_h} = \frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R}$$

the ΔH^\ddagger and ΔS^\ddagger could be computed. The ΔH^\ddagger values are higher in relatively high viscous, more water containing systems than in more oil containing low viscous systems. Also, the values show that the ΔH^\ddagger values for systems with PEG becomes lower than those without PEG. This is because the rate of variation of ηV with temperature at low oil concentration is in the presence of PEG, which is less than in the absence of PEG.

In the case of salt effect study, the effect of added electrolyte NaCl in the ternary system was highlighted with the formation of the three phases, a middle microemulsion phase in equilibrium with excess lower water and excess upper oil layers. The phase diagram determination at various NaCl concentrations with PEG showed that the nature of diagram changes drastically depending upon the electrolyte concentration. Where three phases are in equilibrium with two phase liquid / liquid. Since it is a contribution from 2 phase liquid / liquid increasing which by increasing PEG-400 the three phases are also increased. Various Winsor transitions (type I to type III to type II) were observed as a volume measurement study. All the transitions were observed from 30 to 80°C. Using different salts i.e. NaCl, NaBr, NaI, KCl, KBr and KI it is seen that from Cl⁻ to Br⁻ to I⁻, the Winsor transition concentrations are lowered. However changing the cation does not make much difference. This shows that the anions control the appearance of the 3 ϕ region. PEG-400 has no much effect on it.

The volume fractions of various layers as a concentration of the halides determined in the absence and also in the presence of 10% PEG-400. The initiation concentration of 3 ϕ area did not change. We also studied the volume fraction of different layers as a function of the electrolytes in the temperature range of 30-80°C. If volumes of the oil and water in microemulsion phase and also the volume of microemulsion represented

by V_o , V_w and V_m respectively in WIII formation then the solubilization parameter of oil, V_o/V_m and water, V_w/V_m can be plotted as a function of halide concentrations. The concentration of the halides at which the parameters are equal is called optimal salinity (OS). We observed that the OS did not change with temperature.

In presence of PAA (0.005% w/v) also, the effect of the temperature was absent. We found that PAA change the magnitude of the optimal salinity to much lower concentration of electrolyte. In the presence of halides, 3 ϕ system appeared because of favourable hydrophilicity and hydrophobicity induced in the surfactant system by the halides. The salinity of the solution effects the ionic surfactant μE system in the same way as the temperature effects the nonionic systems. The effect of PEG-400 is negligible on optimal salinity values. Thus, we observed that PAA was relatively more hydrophobic than PEG-400 and the OS in presence of PAA was less than in presence of PEG-400. Adiabatic compressibility (β) at various temperatures with a constant S + CS concentration was determined. As the concentration of water increases, β decreases. This is expected since water is less compressible than the solvent. When water is replaced by non-aqueous solvent like DMF in presence of CTAB and 1-propanol plus cyclohexane it also gives the microemulsion which is termed non-aqueous microemulsion. The interfacial tension of this system was found to be $\sim 10^{-2}$ mN/m. The later part of thesis present physicochemical properties of microemulsion, formed by DMF, cyclohexane, CTAB and 1-propanol as well as DMF + Water.

Conductance study shows that the structure of microemulsion is bicontinuous. Phase diagram showed that one phase (1 ϕ) area increases upto 40°C by increasing the temperature. PEG-4000 stabilizes the μE formation, with water one phase area in presence of water is lesser than the one phase area obtain in the DMF, when salt is added to the system, the system does not result into three phase system.

The conductance increases with temperature. The viscosity in non-aqueous system was lower than the aqueous system and did not show any maximum. Viscosity show that the structure of microemulsion remains same throughout the entire range of study. The mix system presented shows that one phase area remains in between aqueous and non-aqueous as water is more polar so comparatively it shows almost all the physicochemical properties like viscosity, conductance, adiabatic compressibility etc. are in between those in water and DMF systems though an additive characteristic was not observed.