# SUMMARY AND CONCLUSION

Microemulsion systems which belong to the category of short range organized fluids, are a centre of attraction to scientists as well as technologists. These are transparent or translucent, macroscopically homogeneous, thermodynamically stable mixtures of water and oil stabilized by a suitable surfactant. In many cases microemulsions are considered as rather monodispersed droplets of water in oil (w/o) or oil in water (o/w). In these cases microdroplets of water or oil are enclosed in a sheath of surface active materials which stabilizes these droplets in a continuous medium of oil or water respectively. There also exists bicontinuous microemulsion whose structure is still far from clear. However the most plausible model of these bicontinuous microemulsions assume water or oil forming interconnected randomly oriented tube (conduits) like structure in an oil or water continuous medium respectively. Since the diameter of the dispersed phase domains in these unique systems are in the range of 10-100 nm, they do not scatter white light and hence are transparent in its appearance. Though numerous work have been published and various theories have been suggested to explain microemulsion structure and properties, we find that a cohesive and comprehensive theory is still lacking.

The work described in this thesis mainly deals with the phase behaviour and physicochemical properties at different temperatures of an anionic microemulsion system consisting of cyclohexane (oil), sodium dodecyl sulphate (surfactant), n-propanol (cosurfactant) and water. Surfactant to cosurfactant weight ratio was always kept constant at 1:2. Phase behaviour study included ternary phase diagrams and the phase volume measurements. The conductance, viscosity and adiabatic compressibility, were also determined. Apart from the additive NaCl, the effect of water soluble polymer polyacrylamide, often used in the oil exploration processes, was determined on the phase diagram and other properties. The effect of mixed alkanol as cosurfactant (hexanol + propanol mixtures) on all the above mentioned properties were carefully examined. Almost all the studies were performed over a wide range of temperature from 30°C to 70°C or 80°C. Finally the free energy change $\Delta G_{sol}$, enthalpy change $\Delta H_{sol}$ and entropy change $\Delta S_{sol}$ of the dissolution of oil into water (i.e. oil in water microemulsion) were also calculated and presented.

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 any additives proved that the area of monophasic microemulsion zone increases with increasing temperature upto a critical temperature and thereafter it decreases. 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 polymer polyacrylamide (PAA) was found to have generally a destabilizing effect on microemulsion and hence decreased the monophasic microemulsion region. But above a critical temperature these polymer molecules at the oil-water interface undergo some change in their configuration due to the breaking of intramolecular H-bonding. They become surface active and thereby enhance the microemulsion formation. Thus the influence of increase of temperature and the increase of PAA concentration are almost antagonistic to each other and at a certain concentration of polymer, the one phase zone remains invariant to temperature. The presence of all the three microemulsion structures, namely water in oil (w/o), bicontinuous and oil in water (o/w) in the one phase region of present ternary system was confirmed by the conductance and viscosity studies. The w/o system was distinguished by low conductance values while o/w microemulsions are characterized by their high conductance. In between these two structural regimes, the bicontinuous one, where the conductance increase is almost linear with water fraction, exists. The plots of specific conductance against water volume fraction showed rapid increase in conductance above a threshold value of water fraction which reveals the presence of percolation phenomenon in the system. Above this threshold water fraction, the water droplets undergo sticky collisions and thereby form a channel for ion migration. The temperature induced percolation, though, was found to be absent in the present case. On the contrary an overall decrease in conductance was observed with increasing temperature. This suggests a hopping mechanism for conductance in this region. Hence it was concluded that the very low conductivity shown by water in oil microemulsion samples is due to the hopping of ions from globule to globule during collision whereas the percolation obtained as a result of increasing water fraction is due to the sticky collision and channel formation. The adiabatic compressibility studies in microemulsions showed that the compressibility of microemulsions is a bulk property and is independent of its internal microstructure. Compressibility decreased linearly with increasing water fraction which was mainly due to the less compressibility of water compared to that of cyclohexane. But the temperature increase make the overall structure less rigid and thereby increased the compressibility.

The effect of added electrolyte NaCl in the ternary system was highlighted with the formation of the three phase, a middle microemulsion phase in equilibrium with excess lower water and excess upper oil layers. The phase diagram determination at various NaCl concentrations showed that the nature of the diagram changes drastically depending upon the electrolyte concentration. At low concentration (0.5 mol $dm^{-3}$) the diagram resembled the water system without NaCl, but at higher concentration (1 mol $dm^{-3}$), the one phase region splitted into two with the appearance of a three phase region at the middle and at very high concentration (3 mol $dm^{-3}$) all one phase and three phase regions disappeared completely. That is above a certain concentration, the ternary phase diagram contains only a solid-liquid biphasic region and a liquid-liquid biphasic region. Various Winsor transitions (type I to type II) were observed as the NaCl concentration was increased. All transitions were observed at all temperatures upto 80°C. The temperature increase brought down the Winsor transition boundaries (i.e. Winsor I - Winsor III boundary and Winsor III - Winsor II boundary) towards lower NaCl concentrations and thus helped in earlier transitions. The optimum salinity, determined by plotting oil uptake - microemulsion layer as well as water uptake -microemulsion layer volume ratios against salinity, showed a gradual decline followed by a constancy with increasing temperature. This suggests that the temperature and salinity effect are similar (in the case of various Winsor transitions). That the rise in temperature makes the interfacial surfactant film more hydrophobic is believed to be due to some speciality of propanol or propanol-SDS combination, as generally the temperature increase makes an anionic surfactant system more hydrophilic. The conductance study performed in presence of NaCl (0.5 mol $dm^{-3}$) also showed the percolation behaviour with the increasing water fraction. The presence of electrolyte increased the percolation threshold value ( $\emptyset_w^p$ ). The ratio between maximum and minimum conductance in this case was lower than where no NaCl was present. The viscosity and adiabatic compressibility values of microemulsions decreased slightly by the presence of NaCl in the system. A decreased interaction between the droplets or interfacial layer and the breakage of H-bonds between different molecules within the fluid are the causal factors in the decrease of viscosity. Increased oil penetration into the interfacial region made a more rigid interface and hence decreased the compressibility.

The mixing of two different amphiphiles often result in synergism and exhibit properties far in excess than what are shown by individual components. Two cosurfactants propanol and hexanol were mixed in various proportions and a significant increase in the monophasic microemulsion zone was observed. The mixed systems behaved independent of their mixing ratios in producing the total one phase area though the overall pattern of the diagram changed. The more hydrophobic a surfactant system, the less will be the amount of electrolyte required to bring about the inversion of lower phase microemulsion (Winsor I) to the upper phase microemulsion (Winsor II). The Winsor transition studies in the mixed systems showed that less amount of electrolyte is needed to undergo Winsor transitions, as the hexanol in the mixed systems increase . Further the presence of hexanol as a cosurfactant component made the oil dissolution into the microemulsion layer more sensitive towards electrolyte. Thus a small increase in the electrolyte concentration could dissolve the excess oil layer completely into the microemulsion layer before the separation of the aqueous layer began. As a consequence the Winsor III formation disappeared completely and a Winsor IV (single phase microemulsion) appeared in between Winsor I and II. The effect of temperature was in the opposite direction compared to what we observed earlier where propanol was the cosurfactant. i.e. The temperature increase favoured Winsor transitions which were in the direction of II → III → I indicating that the interfacial film became increasingly hydrophilic with temperature rise. Thus it may be concluded that the effect of temperature on the present system depends on the mixing ratio of the two alkanols and a formulation exists on the propanol–hexanol ratio scale where the system becomes totally insensitive to the temperature. The conductance study in the mixed alkanol systems revealed that the phenomenon of percolation diminished with increasing hexanol mole fraction. The percolation threshold values increased continuously as a result of decreased interdroplet attractive interaction when more and more propanol molecules in the interfacial layer were replaced by hexanol molecules. This type of behaviour was observed in earlier studies of pure alcohols with increasing carbon chain lengths. Hence it may be stated that the various mixed systems of propanol and hexanol are imitating the other pure alcohols of intermediate chain length between these two (i.e. butanol or pentanol). The variations exhibited in the viscosity and adiabatic compressibility of the monophasic microemulsion samples formulated by the mixed alcohols,indicate that the mixing of two alkanols does not obey additivity rule. The increased viscosity and decreased compressibility with increased hexanol fraction were indicative of more rigid interfacial layer and therefore a relatively more compact system.

Considering oil as the solute and water (with surfactant and cosurfactant) as solvent, the free energy of dissolution of oil into water i.e. the free energy of formation of oil in water microemulsion was calculated, for very low oil concentrations, using the equation

$$\Delta G_{sol} = RT \ln X$$

where X is the mole fraction of oil in the mixture. From the plots of $\Delta G_{sol}$ against temperature (°K), the $\Delta H_{sol}$ and $\Delta S_{sol}$ of o/w microemulsion formation were calculated. With increasing surfactant concentration $\Delta G_{sol}$ became relatively more positive indicating impossibility of o/w microemulsion formation at very high surfactant concentration. The enthalpy changes for microemulsion formation were positive indicating that the process was endothermic. The corresponding entropy changes ( $\Delta S_{sol}$) were reasonably high and increased with increasing surfactant concentration. That is, the system became more randomized with increasing surfactant concentration. The enthalpy and entropy changes associated with oil in water microemulsion formation were found to compensate each other fairly well.