SUMMARY AND CONCLUSION

The results of the physico chemical investigation of the quarternary Alkane/Brij 35 + Propanol/Water system are presented in this thesis. Alkanes used were heptane, nonane and their mixtures. The ratio of the surfactant (Brij 35) and cosurfactant (n-propanol) was kept 1:2 by weight for all studies. These systems were investigated mainly with the techniques like phase diagram, viscosity, conductance, adiabatic compressibility etc. These were done at various temperatures ranging between 20° - 80°C.

Phase diagrams of multicomponent systems are generally a prerequisite for the study of their physico chemical properties. Also oil-surfactant-water phase diagrams are extra ordinary rich and hence quite intriguing to study. A detailed phase diagram study was carried out on the above mentioned psuedoternary system and presented in the initial part of the thesis. It was observed that phase diagrams of the system alkane/Brij 35 + propanol/ water remain simple with only monophasic and biphasic zones at all temperatures between 30° and 70°C. Nonionic surfactant systems generally show different phase changes with temperature and their phase diagrams are extremely complex. However the phase diagrams of the present system is simple at all temperatures. Phase diagram at 20°C is slightly different from those at higher temperatures. The phase diagram pattern and its temperature invariancy was explained by the absence of water-surfactant or oil-surfactant miscibility gaps in the studied temperature range.

Monophasic microemulsion zone exists mainly on the higher surfactant part of the ternary phase diagram. Most of the studies were performed on the single phase microemulsion, that is the system generally contains high percentage of surfactant (Brij 35 + propanol). The concentration is 80% of the mixture i.e. Brij 35 itself is about 27% by weight.

The conductance and viscosity are the main properties that we studied for the monophasic microemulsion. The nonpercolative nature of the conductance variation with water fraction indicates that the system is either a molecularly dispersed solution or exist in a single structured form through out. A particle distribution curve, obtained by light scattering measurements, rules out the possibility of molecularly dispersed solution. Further analysis of conductance data using Scaling law and viscosity studies strongly suggest the presence of bicontinuous structure at all oil-water ratios in this range. We presume that this happened due to the poor penetration of alkane molecules to the interfacial film.

The results obtained from the phase diagram as well as the viscosity studies of mixed alkane (heptane+nonane) microemulsion systems are pointing towards the nonlinear nature of alkane mixing. The variation of percentage microemulsion areas as well as the viscosity values against mole fraction of one of the mixing alkane exposes its nonlinearity in microemulsion media. Moreover the values of all mixed alkane systems are alike irrespective of their different mixing ratios. Conductance and compressibility values are not much sensitive to the oil phase and hence effect of mixed alkanes is not obvious. The trends in the variation of these physical properties with water or oil fraction in the system tells that microstructure of the system remained unaffected by alkane mixing.

Influence of temperature on the phase behaviour of this nonionic surfactant system is found to be very weak. The microstructure at higher surfactant concentration, variation of viscosity, conductance and compressibility with various parameters were not changed within the temperature range studied. This anomalous behaviour is due to the high hydrophilicity of the surfactant-cosurfactant combination. It was observed that the absolute values of these physical properties, though, changed with change of temperature.

Presence of electrolyte totally changed the nature of the phase diagram. The system became temperature sensitive in presence of NaCl. A detailed study, representing the changes observed on both the phase behaviour and physical properties of the system under the influence of NaCl, are presented.

The ternary phase diagrams were enriched with all Winsor type phases when water was replaced with 1 M NaCl. The 30 zone, which developed in presence of NaCl, widened with the rise of temperature. The shift in the HLB of the surfactant, because of the influence of different parameters, is the reason for the phase changes observed. Presence of an electrolyte in the aqueous phase and also the rise of temperature promote the hydrophobicity of the nonionic surfactant. This 'lipophilic shift' of the surfactant's nature is the reason for this marked changes.

Phase volume measurements arising out of Winsor transition in multi component systems are more quantitative in approach. These were studied as a function of temperature, NaCl concentration, oil-water ratio (OWR) etc. Increase of temperature and NaCl concentration, effect the phase volumes in similar fashion and hence induce same type of Winsor transitions (Winsor I → III). Both the above mentioned variations make the surfactant more hydrophobic by reducing the water-surfactant interaction. Hence similarity in their influence on this system is not unexpected. But it was very surprising that even the extreme conditions like using 2.5 M NaCl concentration and raising the temperature upto 80°C failed to induce Winsor III → II transition on the studied compositions. Generally Winsor III formation exists in a narrow range of NaCl concentration or temperature. The Winsor III changes over to Winsor II with further increment of NaCl concentration or temperature. This expected change over was not observed. This unexpected result was explained by evoking the surfactant geometrical term called 'packing factor'. As per the simplified version introduced by Aveyard et al., packing factor is somewhat related to the ratio of A_t and A_h where they are the effective cross sectional areas of tail region and head group of the surfactant respectively.

Cloud point, which is characteristic of all nonionic surfactant, was determined in microemulsion media over a wide range of NaCl concentration and oil-water ratios. This temperature was found to be inversely related to the NaCl concentration. Even a decrease of 80°C was achieved on the cloud point by using 2.1 M NaCl concentration. Cloud point passed through a minimum when it was plotted against alkane percentage in the system. After this minimum, cloud point continuously increased with further increase of oil percentage and above 12% (w/w) of oil, clouding was practically absent. Changes in the surfactant concentration and alkane phase also affect the cloud point. It was understood that the associated efforts of the electrolyte and the cosurfactant was the reason behind the large reduction of cloud point experienced in the system. These results stress that microemulsion cloud point is a multivariable dependent phenomenon. Each component of the microemulsion formulation has profound influence on the cloud point.

Introduction of salinity in the system increased microemulsion viscosity. But further addition of NaCl, in the studied range, did not have much influence on its viscosity value. However, adiabatic compressibility passed through a minimum when plotted against NaCl concentration. This might suggest that there was some optimum NaCl concentration at which a comparatively more ordered and less compressible structure would exist. From these studies we also noted that higher alkanes suppress the influence of NaCl.

Results obtained from mixed surfactant systems were discussed in the last part of the thesis. Two types of surfactant combination were used. These were (i) two nonionics, i.e. Brij 35 and Tween 20 and (ii) anionic -

nonionics, i.e. SDS and Brij 35. When the combination of SDS and Brij 35 was used as the surfactant, the available 10 microemulsion area was very low. Moreover this small area was found to be constant irrespective of different surfactant mixing ratios. The phase diagram pattern was similar at various temperatures in presence of 1 M NaCl. The phase changes observed with rise of temperature were similar to those of nonionic surfactant systems. Nonionic surfactants are generally more sensitive to temperature than ionic surfactants. Hence their combination might behave like nonionic surfactant as far as temperature is concerned.

Phase behaviour of nonionic and ionic surfactant systems are quite opposite with respect to temperature. Hence some mixing ratio of the two could produce a temperature invarient system. We investigated this possibility by phase volume measurements at various NaCl concentration and as a function of temperature. Three different SDS + Brij 35 mixtures (1:2, 1:1 and 2:1 molar ratios) were investigated for this purpose. But phase behaviour of all mixing ratios of SDS and Brij 35 were found to be temperature sensitive. This was explained by the rather different HLB (not number) of SDS + propanol combination from other SDS + cosurfactant mixtures.

The physical properties like viscosity and compressibility also changed nonlinearly with the change of SDS and Brij 35 mixing ratio.

But when Brij 35 was mixed with Tween 20 (two similar type of surfactants), the microemulsion properties exhibitted ideal mixing trend. The one phase microemulsion area of the mixed surfactant system was the average of the areas (taking number of moles into consideration) of the two single surfactant systems. This linearity was observed in the other physical properties also.

These studies with surfactant mixtures prove that the surfactant mixing can result either into a totally different property from their single surfactant counterparts (e.g.SDS + Brij 35 system) or just an average property of their components (like Tween 20 + Brij 35 system).

Lastly we have calculated the thermodynamic parameters ΔG, ΔH and ΔS for oil solubilization in aqueous solution of the surfactant-cosurfactant combination.

When the amount of solute is very small, Gibbs free energy change for the solubilization process,

$$\Delta G = RT \ln X$$

where X is the mole fraction of the solute. Using this relation, free energy change associated with oil solubilization in aqueous solution of surfactant and cosurfactant was calculated for all studied systems. ΔG vs temperature (T) plot was found to be linear and ΔS was calculated from the slope . These two values were used to calculate ΔH. It was observed that ΔG values become less negative with increase of surfactant concentration. ΔH values are generally not very high but the negative values show the exothermic nature of the process. ΔS values are positive indicating the randomness associated with the solubilizing process. For alkane/Brij 35 + propanol /water system ΔH and ΔS values compensate fairly well with compensation temperature at 331°k.