STUDIES OF CHEMICAL REACTIONS IN MICROEMULSION

Summary of the Thesis
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SUMMARY AND CONCLUSIONS

In the first part of the thesis, the experimental investigation on physicochemical properties of Triton X 100 microemulsion is reported. Since microemulsion is a multicomponent system of different substances like oil, water and an amphiphile, its properties are different from the individual component. The concentration of oil and water decides the nature of the microstructure of the microemulsion. The studies of phase diagram, conductance, viscosity, adiabatic compressibility, effect of salt and temperature and contact angle are reported.

Study of phase diagram is important to know the solubility of different components, various phases formed, microemulsion, microstructure like water-in-oil, oil-in-water or biocontinuous. Phase diagrams of cyclohexane/TX100+n-propanol water (40°C), cyclohexane / TX100+n-propanol / DMF (40°C) and cyclohexane / TX100 + ethylpropionate/water (30°C) were constructed. Surfactant to cosurfactant ratio was kept (1:2) by weight for aqueous and nonaqueous system. For ester system (1:1) & (1:2) surfactant to cosurfactant ratio were selected. For aqueous system, the phase diagram shows only two regions; an upper surfactant rich microemulsion phase and a lower liquid-liquid biphasic phase. For the nonaqueous DMF system, a large monophasic region was obtained at the upper portion of the phase diagram. One phase microemulsion was obtained due to the low interfacial tension between oil and water by adding the surfactant. There was a higher reduction of IFT between oil and DMF in presence of TX100 than that between oil and water. Hence solubility of cyclohexane in DMF was more and that resulted in the large monophasic region for DMF system. The structure of nonaqueous microemulsion is not well established. The conductance study of DMF system shows percotation due to some microstructural changes and we assume that the DMF system is structured.

Nonionic microemulsion, induces Winsor transition with temperature as the ionic microemulsions do with electrolytes. This is because of the decrease in solubility of nonionic surfactant in water with increase in temperature and aqueous TX100 system showed such Winsor transitions with temperature. At ambient temperatures, it is completely miscible with water and hence WI type microemulsion was formed. With increase in temperature, oil becomes increasingly a better solvent due to the dehydration of polyoxyethylene group of TX100 and water expels out forming a W II microemulsion. At the intermediate temperature water-oil-amphiphile mixtures separate into three coexisting liquid (W III) within a well defined temperature interval $\Delta T=Tu-T_l$. At the mean temperature of ΔT, the surfactant is having a maximum efficiency in solubilizing water and oil rich phase. At very high surfactant concentration, a Winsor IV microemulsion was formed. The temperature versus concentration of TX100 showed a 'fish' type structure.

The separation of different phases arises from the interaction between the tail part as well as the head part of the TX100 with the solvent at different temperatures when the packing ratio (A_t/A_h) is less than unity, the system prefers oil in water structure and exists as WI. If the ratio is more than unity, water-in-oil structure is more probable and the system is WII. At an intermediate range i.e., $A_h \approx A_t$, microemulsion microstructure is bicontinuous. For polyoxyethylene surfactant like TX100, A_h is mainly determined by the extent of hydration of polyoxyethylene group and the hydration is sensitive to temperature.

When propanol was replaced by ethylpropionate in the above system the percent of the monophasic region was a bit less. The monophasic region obtained is microemulsion and not molecularly dispersed solution because TX100 forms reverse micelles in cyclohexane, ethylpropionate and also in their mixtures 1:1 (v/v). This system was showing a viscous region which was found to be liquid crystalline with crossed polaroids in a polarizing microscope. This occurs due to the strong chain - chain and head-head interaction between surfactant molecules due to long straight chains and close packed heads and less space available for solubilization. Area of monophasic region remained almost the same when the

S:CS ratio changed from 1:1 to 1:2: but viscous region is higher in 1:2 S to CS weight ratio.

Specific conductance of cyclohexane/TX100+n-propanol/water was showing a gradual increase without any percolation, an abrupt change in conductance which has been analysed by using the Scaling equation, indicating no microstructural change. Specific conductance increases with temperature due to the greater increase in the movement of the ions of higher kinetic energy gained by increasing the temperature Percolation due to temperature was absent.

Viscosity of 1ϕ microemulsion of aqueous system gradually increased with increasing water content and at higher water fraction reaching a maximum. This indicates a bicontinuous system. The viscosity activation parameters $\Delta H^{\#}_{vis}$ & $\Delta S^{\#}_{vis}$ of the viscous flow were calculated by using the Frenkel-Eyring equation. All the $\Delta H^{\#}_{vis}$ & $\Delta S^{\#}_{vis}$ values are positive and show a gradual increase with increase in weight fraction of water. This is probably due to the little microstructural changes in the system studied and bigger conduits with addition of water and hence more difficulty of flow.

The Walden product remains almost the same at lower weight fraction of water, at all temperatures. It gradually increases with increasing weight fraction of water and at higher weight fraction of water, it does not remain a constant. At lower water level, it behaves as a normal solution and the rate of change of λ and η with temperature are not the same at higher percentage of water.

Contact angle values showed a gradual increase; it can be either oil continuous or water continuous structure as supported by conductance and viscosity data. Specific conductance of cyclohexane/TX100+n-propanol/DMF sharply increased indicating a percolation,though the percolation was not observed when the propanol was absent. Specific conductance study showed a microstructural change from oil to DMF through a bicontinuous structure when the DMF content increases.

Viscosity of DMF system in presence of propanol was lower than that without propanol as cosurfactant. Viscosity remains almost a constant for the system which contains no cosurfactant and there is a decrease in the viscosity with the addition of cyclohexane. Adiabatic compressibilty decreased with an increase in the DMF concentration. Contact angle θ of 1ϕ microemulsion without n-propanol values are almost as high as that of pure DMF with Teflon. In presence of n-propanol, the values are similar to the system which does not have propanol upto 25% cyclohexane showing a similar structure upto this concentration. It can be concluded that microemulsion formed by cyclohexane/TX100+n-propanol/DMF is structured.

Specific cnductance values of 1ϕ region of cyclohexane/TX100+ ethylpropionate/water were very low indicating a water-in-oil microstructure. Higher conductance at lower temperature also indicates a water-in-oil structure. Adiabatic compressibility showed a linear dependency on water content; it decreased with increasing amount of water due to the more structured nature of water than cyclohexane. Adiabatic compressibility was higher at higher temperature. Viscosity decreases with increasing weight fraction of oil with 1:1 S to CS ratio and with 1:2 S to CS, it increases with increase in oil fraction. Surfactant - cosurfactant ratio becomes a major factor in viscosity of the systems studied. Viscosity of S to CS (1:2) is less than that with 1:1 due to the dilution of the system. The dependency of viscosity on temperature is systematic; it decreases with increasing temperature. Viscosity activation quantities $\Delta H^{\#}_{vis}$ (activation enthalpy) and $\Delta S^{\#}_{vis}$ (activation entropy) were calculated. A diabatic compressibility decreases with addition of water as water is more structured than cyclohexane. Adiabatic compressibility is higher at higher temperature. Contact angle values of the 1ϕ liquid with teflon indicate oil continuous system with water probably dispersed as droplets.

Effect of electrolyte on TX100 microemulsion was studied. It did not induce a 3ϕ (WIII) microemulsion system; a Winsor IV to Winsor II transition occured. This probably was due to the less number of hydrophilic group compared with Brij 35 wherein 3ϕ (WIII) system with electrolytes was obtained. The cloud point was determined for aqueous microemulsion systems. At lower water content, there was no clouding till 100°C.

The second part of the thesis presents the kinetic studies of some model reactions in ionic and nonionic microemulsions formed by Sodium dodecyl sulphate, Cetyl trimethyl ammonium bromide and Triton X 100. The reaction studied were oxidation of potassium iodide by potassium persulphate, acidic hydrolysis of methyl acetate and alkaline iodination of acetone. Microemulsions were prepared and characterized before carrying out the reactions. The reactants were added to the microemulsion in trace amounts to avoid the changes of physical properties of microemulsion.

The change in oil-water ratio affects the structure of microemulsion and hence it affects the rate of reaction also. The tiny microdroplets provides higher internal interphase and the reaction occur at higher rate than the bulk phase. Both polar and nonpolar substrates can be soluble in microemulsion and hence the local concentrataion of substrate also may be different.

The oxidation of iodide by persulphate in microemulsion was followed spectrophotometrically. The concentration of surfactant is kept constant at 42.5% by weight and the oil-water composition was changed in SDS and CTAB microemulsion. The concentration of TX100 was kept 55% by weight. The reactants are mixed up in the reaction cuvette. The increase in absorbance due to liberation of I_2 was recorded at λmax. Both pseudo first order and second order rate constants were calculated in all the microemulsion systems. The reactions in SDS microemulsion was faster than in the pure aqueous system. The oxidation of iodide by persulphate in CTAB and TX100 microemulsion is inhibited with respect to pure aqueous system. Both the pseudo first order and second order rate constants were obtained from the required linear plots.

Catalytic activity of microemulsion is due to the charges on substrate, steric effect and electrostatic interaction between the hydrophilic head of surfactant molecule and the substrate. In SDS microemulsion, there is a repulsive interaction between the anionic micelles and the anionic reactants. This leads to the increased local concentration of the reactant and an easy approach of the two reactants to each other and hence the reaction may occur faster.

In the case of CTAB microemulsion, the rate of reaction is decreased due to the attractive interaction between the cationic micelles and the reactants and this will provide an approachability barrier to the reactants and hence the reaction occurs at slower rate.

In the case of TX100 microemulsion, the reaction is inhibited due to the steric fatcor. TX100 does not carry a charge; it is a neutral molecule but the hydrophilic long chain of hydrated polyoxyethylene has large volume and may hence offer some steric hindrance to the movement of anionic substrates and hence their approach may be inhibited and the reaction becomes slower.

The effect of temperature on rate constant was studied. The rate increased with increasing temperature. As the temperature increases, it induces higher thermal instability to the associated complex and the product is formed at a faster rate. When the temperature increases, the interfacial tension between oil and water decreases and more number of tiny microdroplets are formed and it provides more interfacial area and hence the reaction rate is higher.

Effect of changing water-oil ratio on rate constant was also studied. With decreasing water content, the rate constant increases. Increasing reaction rate with decreasing water content is due to many factors. The reactants are hydrophilic in nature and they get hydrated in the aqueous phase and the reaction also mainly occurs at the aqueous phase. So the solubilization site affects the reaction rate. Increase in water content results in the dilution of the reactants in the aqueous phase. When the water content increases, the dilution of the reactants in the aqueous phase occur i.e., the local concentration of the reactants are lower and hence the rate is lower.

The rate of reaction increases with decrease in molar ratio $[H_2O]/[S]$. The reaction rate increases with decrease in the water activity by the following mechanism :

$$I^-_{solv} + (S_2O_8^{2-})_{solv} \rightleftarrows (IS_2O_8^{2-})^{\#}_{solv} + nH_2O$$

$$\text{So } k_{obs} = \frac{k_o(\gamma_{I^-} \cdot \gamma_{S_2O_8^{2-}})}{\gamma^{\#}} \cdot \frac{1}{a^n H_2O}$$

The water activity in microemulsion decreases with decreasing water content due to the interaction between water molecules and the surfactant molecules; Some water molecules pass through from the bulk as shown by the above mechanism.

The positive kinetic salt effect for reactions between ions of the same sign was interpreted as a consequence of the greater destabilization of the initial state compared with that of the transition state, caused by the electrolytes present in the reaction media. Or in other words, it is due to the increase of the effective concentration of the reactants because a part of the water present in the media of reaction is involved in the hydration of the background electrolyte. It also happens due to the increase in the ionic strength in the system.

Methyl acetate hydrolysis was studied with aqueous HCl kinetically in SDS, CTAB and TX100 microemulsions. The catalytic effects of SDS and CTAB were compared by studying the reaction with constant surfactant composition of 42.5% by weight and by changing oil-water ratio. The reaction was studied in CTAB and TX100 containng systems with constant water fraction (5%) and changing surfactant to oil ratio.

Pseudofirst order rate constant of acidic hydrolysis of methyl acetate indicates that the reaction is faster in SDS, CTAB and TX100 microemulsions. The catalytic order of the reaction rate can be written as SDS > CTAB > TX100. This order is due to the difference in the local concentration of the catalyst H^+ at the reaction site.

In SDS microemulsion, the local concentration of H^+ which is the catalyst, is higher at the Stern layer due to the presence of anionic micelles and it has higher catalytic activity and hence the higher reaction rate. In the case of CTAB, though there is a repulsive interaction between the cationic micelles and H^+, H^+ may bind to the Br^- counter ions and it is not really away from the reaction site. In TX100 microemulsion system the surfactant molecule is neutral and therefore the presence of H^+ as catalyst is less available because of the absence of the ionic Stern layer. This therefore resulted in lower reaction rate; but the microheterogeneity of the system with large internal interphase increases the reaction rate with increasing temperature and decreasing water content.

Iodination of acetone in alkaline SDS microemulsion was studied in alkaline medium. Even though both iodine and acetone is partitioned between polar and nonpolar phase, the reaction is assumed to take place in the aqueous phase as NaOH is insoluble in the oil phase. The rate constant increases with temperature and with decreasing water content.