1. INTRODUCTION
Oil and water do not mix as water is extensively bonded and the free energy that might be gained from mixing with apolar molecules is small as compared to the free energy that would be lost from disrupting these hydrogen bonds. For some practical purposes, we want oil and water to mix. It is possible only by emulsification i.e. with the addition of suitable surfactant, leading to single phase thermodynamically stable dispersions. An explanation to this phenomenon was reported earlier in 1943 by Hoar and Schulman.\textsuperscript{1} The surfactant is required for significant lowering of the oil–water interfacial tension by the way of their adsorption, thus to help in minimizing the related free energy changes of the dispersion associated with surface formation. In 1959 Schulman and coworkers\textsuperscript{2} proposed the term "Microemulsion" for such systems. They postulated that the driving force for the spontaneous formation of such dispersed systems is the existence of a transiently negative interfacial tension between the oil and water phases, resulting in a rapid transfer of one of the two phases through the interface, producing the optimum droplet size for the given composition. It must be emphasized that the negative interfacial tension is a transient phenomenon and at equilibrium must be zero or slightly positive. The resultant water–oil–surfactant mixtures, the so called microemulsions are isotropic, normally low viscous and thermodynamically stable solutions (dispersions) having prolonged shelf life. Their average particle size fall in the range 5 – 100 nm. They are polydisperse in nature and polydispersity decreases with decreasing particle size. These systems differ from ordinary emulsions in two main respects namely thermodynamic stability and lack of turbidity. For small particles, light scattering is proportional to the square of the volume of particles\textsuperscript{3} and hence these systems with small droplet size scatter little light and are not turbid.

Ruckenstein and Chi\textsuperscript{4} have attempted to quantify the thermodynamics of microemulsion formation, stability, and the optimal droplet size. Their treatment decomposes the free energy of microemulsion formation $\Delta G_M$, into changes in the interfacial free energy, $\Delta G_i$, droplet-droplet interaction energies, $\Delta \Gamma_d$, and entropy changes resulting from the dispersion process, $\Delta S_e$. The overall sum of the three energetic components will determine whether microemulsion formation will occur or not. If $\Delta G_M$
is negative, spontaneous dispersion will lead to droplet formation and the droplet radius, $r_n$, is determined by the minimum value of $\Delta G_m$ attainable.  

The spontaneous dispersion of one liquid phase into another can occur only if the interfacial tension between the two phases is so low that the entropy effects due to the dispersion process, $\Delta S_m$, can dominate the total energy of the system. Although many surfactants can lower the interfacial tension between oil and water phases subsequently, factors such as micelle formation, solubility limits and interfacial saturation prevent the attainment of the required low values for microemulsion formation.

According to the Gibb's equation, the surface or interfacial tension of a system, $\gamma$, is related (approximately) to the amount of surface active materials preferentially adsorbed at the interface by

$$\delta \gamma = -\Gamma_i \delta \ln(C_i)$$  

where $\Gamma_i$ is the surface excess of component $i$ at the interface and $C_i$ is its concentration in the bulk solution. It is clear from equation 1 that the positive adsorption of any material at the interface will result in a lowering of the interfacial tension. The maximum value of $\Gamma_i$ attainable for a single-component surfactant system is usually limited due to solubility limits or geometric restrictions, so that very few such systems can produce the low values of $\gamma$ required for spontaneous dispersion. Two notable exceptions to that rule are sodium bis(2-ethylhexylsulfosuccinate) (Aerosol OT) and some POE nonionic surfactants at temperatures near their cloud point. In many cases this may be achieved with the addition of a cosurfactant, usually a short or medium chain length alcohol or amine. The presence of a cosurfactant helps to reduce the rigidity of the interfacial film and increases adsorption at the interface. Because of the relatively large differences in size between the surfactant and cosurfactant, the alcohol molecules, having a cross-sectional area of only a few square angstroms, can efficiently pack themselves between the larger surfactant chains at the interface. The net result is a densely packed interfacial layer (a much larger value of $\Gamma_i$) which makes possible very low and transiently negative interfacial tensions.

The microemulsion regions for a typical surfactant (or more likely a combination of surfactants) is represented in the ternary diagram (figure 1) which shows schematically the phase behaviour of these systems as well as some basic structures that might occur depending on the concentration of the different components. In oil-rich domain of the
single phase region, formation of a water in oil dispersion (w/o microemulsion) is preferred and towards the water rich corner, an oil in water (o/w) microemulsion is generally preferred. For single phase mixtures of oil, water and surfactant, which fall outside these two well defined regions, it is possible that a bicontinuous microemulsion may form, in which both the oil and water have extensively connected domains so they behave as if both are the continuous phase. In case of a two-phase system, a surfactant-rich aqueous phase might be in equilibrium with an excess oil phase, denoted by 2 (also called a Winsor I system), or a surfactant-rich oil phase might be in equilibrium with an excess water phase, represented by 2 (also called a Winsor II system)\(^6\).

Due to their thermodynamic stability and high solubilization capacity, the microemulsions have found many uses in consumer products, in industrial processes\(^5,7\) and in certain specific areas of science and technology. The main application of microemulsion is that it can enhance the oil recovery from oil wells by tertiary recovery method\(^8\) up to 20%. These systems are used for extraction of metal from ores with low metal content, for soil washing,\(^9\) solar energy conservation, as lubricants and cutting oil. The microemulsions are also widely used in cosmetics and pharmaceutical products. Other microemulsions are important to the water based floor polish, paint industry, all
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Purpose cleaners, dry cleaning, cleaning fluid industry, textile industry as textile finishers and so on. Due to the variety in phase equilibria and microstructures these systems are of interest to chemists. Chemists in all fields of activity have studied chemical reactions in these solutions. A number of publications are available describing organic, inorganic and biochemical reactions in microemulsions. Together with the classical applications in detergency and lubrication, the field remains important to continue to attract a number of scientists to discover more applications of microemulsions in our daily life.

For last many years, different groups of researchers have been characterizing microemulsions with different physical properties. Among the physical measurements that are useful for identifying microemulsions are optical birefringence, sedimentation, rheology and many advanced techniques such as low angle X-ray diffraction, light scattering, ultracentrifugation, electron microscopy, conductivity, viscosity and ultrasonic velocity. Each measurement reveals some aspects of the system. It has been observed that slight variation of system constitution could induce significant changes in the physical properties of the system.

Contrary to aqueous based microemulsions there are fewer reports in the field of non-aqueous microemulsions, in which the water is replaced with some polar component. The importance of preparing non-aqueous microemulsions is that many reactions that one might want to scale down to microreactor scale occur only in non-aqueous polar solvents. Peyrelasse et al. have investigated the system AOT–isoctane–glycerol at 25°C and discussed the properties of this non-aqueous microemulsion in terms of percolation phenomenon, which is typical of aqueous microemulsions. Non-aqueous dispersions of AOT–n-heptane–glycerol have been studied using dynamic light scattering and viscosity method by Robinson et al. The properties of non-aqueous AOT based microemulsions containing polar components have also been reported by Ray and coworkers. More recently reverse microemulsions of AOT, isoctane/decane and polar solvent have been characterized by Riter et al. Dörfler et al. have mapped the phase diagrams of non-aqueous microemulsions formed by four component system of the type, Triton X-114 – pentanol–dodecane–non-aqueous liquid.
The study of effect of additives on the structure of water droplets and on the attractive interactions between the droplets of the microemulsions, is of great interest now a days in view of important number of industrial applications of such systems. There are reports on the influence of the low molecular weight additives as instance electrolytes solubilized in the water pool.\textsuperscript{35-37} The temperature of percolation can be modified\textsuperscript{38} by small quantities of additives that hinder the appearance of electrical percolation or favours it. The influence of several additives frequently used in reactions carried out in microemulsions upon the properties of system AOT–isooctane–water has been utilized by Garcia-Rio et al.\textsuperscript{39} In series of reports Alvarez et al.\textsuperscript{40-43} have measured the conductivity of these ternary systems with different additives at various temperatures and determined the temperature of percolation. The effect of high molecular additives such as polymers on surfactant aggregation and on attractive interactions between the droplets\textsuperscript{44-51} has also been investigated by several scientists. Due to a selective solubility, water soluble polymers like poly(ethyleneglycol)(PEG) are confined to the water core of w/o nanodroplets (figure 2) This restricted spatial environment of the polymer chain together with the presence of the surfactant at the surface of the droplets can be expected to lead to an interplay between steric repulsion and surfactant polymer interaction.\textsuperscript{52} The character

![Polymer (PEG) within the water droplets of w/o microemulsions.](image)

Fig. 2. Polymer (PEG) within the water droplets of w/o microemulsions.
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of the interactions between the polymer and the surfactant has a major influence on the microemulsion systems.53

With these developments in view, it was decided to pursue further the non-aqueous based microemulsion systems for the present study. The spectrum of non-aqueous polar components or so called water replacement components for the microemulsification was broadened. In the present work mainly the non-aqueous microemulsions using anionic surfactant (AOT) have been prepared because being double chained surfactant it provides a high degree of solubilization of oil and water without further addition of cosurfactant. This leads to the formation of thermodynamically stable ternary systems, which are less complex and are easy to study than the systems having four or five components. Molecules of AOT dissociate into negatively charged head groups $\text{SO}_4^-$ and positive counterions $\text{Na}^+$. Under the influence of an electric field, these charges can accumulate on the inner surface of the micelles, giving rise to polarization and affecting the properties of the systems. A set of non-aqueous microemulsion systems, to study the behaviour of nonionic surfactant Triton X-114, has also been prepared. In addition, the effect of additives covering a wide range of molecular weights [mono $\rightarrow$ poly(ethyleneglycol)] on the aqueous microemulsions, has also been analyzed.

The prepared microemulsions have been characterized by using a number of techniques viz. Phase behaviour, conductivity, viscosity, density and ultrasonic velocity. The knowledge of the microemulsion phase behaviour is an important prerequisite to the consideration of the possible practical applications of particular microemulsion system. Such knowledge allows the choice of the single phase region in which different physical properties can be measured.

Electrical conductivity measurement provide information on attractive interactions, charge generation, distribution, transport and mobility of charge carriers. In number of w/o microemulsions, the conductivity of the systems increases sharply to several orders of magnitude with increase in volume fraction ($\phi$) which is due to percolation phenomenon. The overall process is assumed to consist of several steps; firstly a diffusional approach of two droplets, secondly the exchange of ionic species and thirdly a diffusional separation of the droplets. The exchange of ionic species can occur
via a fusion-fusion mechanism or by surfactant molecules jumping from one droplet to
another. By varying temperature or composition of w/o microemulsions, the formation of
droplet clusters up to an infinite droplet cluster can frequently be observed when the
volume fraction of dispersed phase reaches a critical value ($\phi_c$) at constant T.

The results of conductivity are analyzed by using theoretical model by Grest et
al.\textsuperscript{19} based on dynamic picture of percolation. The existence and position of threshold
depends on interaction between the droplets, which control the duration of the collision
and the degrees of interface overlapping and hence the probability of hoping or merging.
Building up of conductivity needs attractive interactions and $\phi_c$ decreases when the
strength of these interactions increases. Percolation threshold ($\phi_c$) allows the calculation
of $\Delta G^a$, free energy for droplet clustering. Negative free energy is the driving force for
the clustering of the droplets. The conductivity of the microemulsion can also be
explained with the help of droplet charge fluctuation model of Eicke et al.\textsuperscript{54} According to
this model, the dispersed phase is in the form of droplets in the dispersion medium. These
charged droplets are formed by spontaneous number fluctuations of the ions residing on
the droplets. The magnitude of these fluctuations is directly related to the coulomb’s
energy that is required to charge up a droplet.

Similarly viscosity of the system has been be interpreted with reference to the
phenomenon of percolation\textsuperscript{22-24,28} Different equations \textit{i.e.} Einstein, Brinkman, Saito,
Mooney and Krieger have also been utilized to check the validity of experimental relative
viscosity ($\eta_r$). Ultrasonic has proved to be a useful tool for gaining information on the
dynamics of liquid systems. Ultrasonic velocity data is used to characterize the
compressional elasticity of the microemulsions. The ultrasonic velocity and density data
enables the calculation of isentropic compressibility\textsuperscript{30} ($k_s$), which is more sensitive to
structural changes occurring in the solutions and to the interactions between solute and
solvent. The interfacial region of a droplet should show different compressibility
characteristics relative to that of the remaining portion of the micro phase droplets
because of the chemical and electrical gradients that can occur across the interfacial
region, particularly when surfactant species are located at the surface. An attempt has
been made to compute density ($\rho_m$) and isentropic compressibility ($k_{s,m}$) of the micellar
phase from the experimental $\rho$ and $u$ data.