2. REVIEW
An extensive survey of literature reveals that a large amount of work has been carried out in the field of microemulsions. In the present presentation, only those references are discussed which have direct relevance with the selected microemulsion systems. The review has been divided into two main categories viz; (i) systems containing AOT as surfactant and (ii) systems containing Triton as surfactant.

2.1 AOT based systems

Eicke and Zulauf\textsuperscript{55} have investigated the inverted micellar aggregates and microemulsion domain of the system AOT–isooctane–water at various temperatures; AOT and water concentrations and molar ratios ($\omega = [H_2O]/[AOT]$) in the range of 0-60°C using photon correlation spectroscopy. Degree of hydration is taken as criteria for the distinction between micellar solution and microemulsions. “Free Water” concept is also discussed.

In another study Eicke \textit{et al}.\textsuperscript{56} have measured current – voltage characteristics of AOT-isooctane-water w/o microemulsions. The measured current consists of two components: an instantaneously responding part, which indicates the degree of connectivity of the dispersed aqueous nanodroplets at any given temperature and concentration and a slowly rising part, which is due to structural changes of the microemulsion induced by the electrical field.

A model for electrical conductivity of w/o microemulsion was also presented\textsuperscript{54} in which conductivity has been explained by the migration of charged aqueous droplets in the electric field. These charge droplets are formed by spontaneous number fluctuations of ions residing on the droplets and the magnitude of these fluctuations is directly related to the coulomb energy that is required to charge up a droplet. The present model for the conductivity contains no adjustable parameters and is entirely consistent with experimental results on AOT–isooctane–water microemulsions. Eicke and Struis\textsuperscript{57} have studied the diffusional behaviour as a function of copolymer concentration of the complexes formed by hydrophilic A blocks (poly(oxyethylene)) and hydrophobic B block (polysoprene), ABA block copolymers dissolved in AOT–isooctane–water microemulsion by using ($^1H$) pulsed field gradient spin-echo (PFGSE) NMR technique. A self-consistent picture of the
size and geometrical shape of these structures has been established. At very high copolymer concentrations, interlinking of nanodroplets results in larger side-branched structures, which can be considered as the onset of the three-dimensional transient network (gel). NMR results are comparable with the viscosity and conductivity patterns in these systems.

The conductivities of AOT/C_{12}E_5–hexane–water systems have also been reported and compared. AOT allows preparation of oil continuous microemulsions with more than 50% of water but show low conductivity. In comparison nonionic surfactant C_{12}E_5 with comparable amounts of water and oil displays conductivity several orders of magnitude larger. Upon addition of salt, the conductivity pattern of AOT system resembles that of C_{12}E_5 with opposite temperature dependence. A thermodynamic model has also been suggested by Eicke and others to describe the conductometrically measured variation of the percolation temperature (ΔT_c) of AOT–isooctane–water as a function of initial concentration ratio of ABA triblock copolymers and nanodroplets.

The structures and diffusion properties of AOT based w/o microemulsion containing polymer (end sulphonated polyisoprene) by static and quasielastic light scattering measurements have been determined by Eicke and Steiber. The hydrophilic head groups of the polymer stick to the surfactant covered oil/water interface, bridging the water droplets. The structure formation decreases the mobility of aqueous droplets and polymer molecules. When interdroplet distances are larger than end to end distance of the ionomer chain, osmotic modulus decreases because of the depletion force of free ionomer chain acting on the droplets i.e. with increasing polymer concentration, the ionomer chains just fit the average separation of two nanodroplets. The effect of addition of second surfactant to an otherwise thermodynamically stable microemulsion of AOT have also been investigated by the same group. The combination of AOT and C_{12}E_5 supports the formation of planar interfaces, which induces a sphere to oblate ellipsoid transition ensuring a lamellar liquid crystalline phase. Heat of adsorption of C_{12}E_5 (adsorbed on AOT–isooctane–water interface), corroborate the existence of two different interfacial state. The phase transition was inferred from combining conductometric and electro-optic Kerr effect studies.
Eicke and Meier\textsuperscript{62} have studied interfacial charge transport and mobility of nanodroplet clusters formed in these w/o microemulsions. Large reduction in the counterion mobility has been derived from a two-step adsorption process, which described the Langmuir–plot like conductivity isotherm remarkably well. It also confirmed very satisfactorily to mobility data of AOT counterion, derived from frequency-dependent dielectric dispersion measurements with singly dispersed nanodroplets of the same system as used with cluster studies. The activation energy attributed to counterion mobility allowed the calculation of minimum distance (approximately) between the positive counterion in the bulk and surfactant anion in the interface.

Bonel and coworkers\textsuperscript{20,28,63,64} have reported many significant contribution on AOT based microemulsions. Initially the measurement of dielectric complex permittivity and dynamic viscosity of AOT–dodecane–water system at low molar ratio (\( \omega \leq 10 \)) have been carried out.\textsuperscript{27} The effect of salt content and oil type have also been investigated. The experiments have been interpreted through a model based on dielectric blending law applied to ellipsoids of revolution, which assumes the electric charges to be on the surface of the dispersed objects. The model gives a good agreement between experimental and theoretical values.

The group has also investigated the various thermal transitions occurring for AOT–dodecane/isooctane–water systems\textsuperscript{63} by using differential scanning calorimetry. On analyzing experimental heats of crystallization, samples possessing free water are differentiated from samples without free water. For AOT–dodecane–water and AOT–isooctane–water systems, critical value of the molar ratio \( \omega \) is found to be 6.5 and 4.5 respectively.

The conductivity of AOT–undecane–water microemulsion has also been measured\textsuperscript{20} with respect to molar ratio \( \omega \), temperature and salinity The positions of the percolation threshold for three temperatures (\( T=15, 25 \) and 35°C) have been determined in the phase diagrams. The results are discussed with reference to the theory of percolation and are found to be in close agreement with the theoretical predictions. The effect of salinity shows the important role of the interactions between particles.
Dielectric relaxation of AOT–oil (isooctane, undecane, dodecane, cyclohexane)–water microemulsions has been measured by means of time domain spectroscopy at different volume fraction of dispersed phase (water + AOT) $\phi$ and molar ratio $\omega$. The presence of a maximum of static permittivity $\varepsilon_\infty$ associated with minimum of the relaxation frequency $\nu_R$ and a maximum of the frequency-spread parameter $\alpha$ is shown. The influence of salt content and temperature on conductivity has also been discussed. The use of percolation model shows an excellent agreement between experimental and calculated values. The viscosity of these microemulsions has been studied as a function of molar ratio $\omega$ and volume fraction $\phi$ at $T=25^\circ C$. The results have been discussed in connection with percolation model. A good agreement between experimental and theoretical results is obtained. The results are compatible with those obtained previously on conductivity and complex permittivity of these microemulsions. The results show the importance of the idea of "percolation threshold lines".

In another report, the group has studied AOT–isooctane–glycerol microemulsion at fixed $\omega=3.2$ and $T=25^\circ C$. The measured properties are electrical conductivity, viscosity and dielectric relaxation. The results have been analyzed within the framework of theory of percolation. The analogies with microemulsions of AOT–oil–water type have also been discussed.

The results obtained for conductivity, dielectric relaxation and viscosity of ternary AOT–oil (undecane, dodecane, isooctane)–water/glycerol microemulsions have been presented and discussed in context of percolation theory by Peyrelasse and Boned. The variation parameters are: volume fraction $\phi$ (water+AOT), molar ratio $\omega$, temperature, salt content of aqueous phase, nature of oil, $P_w$ (water content by weight), $P_o$ (oil content by weight) and $P_s$ (surfactant content by weight). Eight different experimental paths are followed. At constant temperature and salt content, the paths are $\omega$ = constant, $\phi$ = constant, $P_w$ = constant, $P_o$ = constant, $P_s$ = constant. The variation of temperature and salt content keeping all other factors constant is also considered. Depending on the path, different curves are obtained for the three properties. Finally, a good agreement between experimental and theoretical curves is seen by applying percolation theory.
It has also been shown\textsuperscript{28} that there is a quantitative agreement between experimental and calculated values due to percolation theory for viscosities of waterless AOT–isooctane–glycerol microemulsions. The values of the scaling exponents $\mu = 2.00 \pm 0.25$ and $s' = 1.20 \pm 0.20$ for viscosity are very close to values obtained from conductivity showing dynamical percolation. With regards to dynamic percolation, AOT–oil–water and AOT–oil–glycerol microemulsion systems behave broadly in similar way.

Dynamic viscosity, electrical conductivity and dielectric relaxation properties of waterless microemulsion AOT–isooctane–glycerol have also been studied\textsuperscript{24} as a function of temperature ($T$), volume fraction ($\phi$), molar ratio of glycerol to AOT ($\omega$) and salt content ($p_\text{s}$). The results have been discussed in terms of percolation theory. By determining $n(\phi)$ curves for various conditions, the variations of $\phi_c(T)$, $\phi_c(\phi)$, $\phi_c(p_\text{s})$ have been determined. Percolation threshold $\phi_c$ value decreases with increase in $T$ and $\omega$ but with decrease in $p_\text{s}$. This corresponds to increase in the interactions between droplets within the system.

In the recent work, phase behaviour and electrical conductivity of aqueous ternary AOT–undecane–water microemulsion system as a function of pressure (upto $\leq$ 200 bar) and volume fraction ($\phi$) of dispersed matter at constant temperature ($T$) have been reported.\textsuperscript{25} The results are presented in terms of plots of $\sigma(\phi)$ at constant $P$ and $T$ and of $\sigma(P)$ at constant $\phi$ and $T$. These are analyzed in the frame work of percolation theory. The threshold $\phi_c$ decreases as $P$ increases (at constant $T$), which corresponds to an increase in interactions. When $\phi$ and $T$ are kept constant, a threshold pressure $P_c$ (which increases as $\phi$ decreases) is introduced. The scaling exponents are almost the same as those determined at atmospheric pressure.

In a separate study\textsuperscript{26} the phase diagram of AOT–undecane–water system has been mapped in Pressure–volume fraction ($P$–$\phi$ plane) of dispersed phase. The microemulsions have been observed at $T=20^\circ$C with the molar ratio $\omega = 30$, in the pressure interval 1–40 MPa. From electrical conductivity data, percolation threshold has been estimated in the single phase zone of $P$–$\phi$ plane. It has been possible to evaluate quantitatively the
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variations of interactions with pressure and to adjust very satisfactorily both the percolation threshold line and the cloud points curve in the $P-$ curve.

Liveri and coworkers$^{65}$ have measured the ultrasonic absorption and ultrasonic velocity in AOT–$n$-heptane–water system as a function of molar concentration ratio $\omega$ at 15, 25 and 35°C. A single time relaxation equation has been used to describe the studied ultrasonic relaxation spectra in the frequency range between 15 and 250 MHz. The analysis of the fitting parameters indicates the different processes probed by the acoustic waves like the exchange of the surfactant molecules between bulk hydrocarbon and micelles, the shape fluctuation of the reversed AOT micelles and the exchange of water molecules between the polar sheath of the micelles and the water pool. The results show that water filled micelles are more floppy than bulk water. The ultrasonic spectra at 25°C have been found$^{66}$ to be dependent on $\phi$ but nearly independent on $\omega$. As $\phi$ increases, ultrasonic dynamics shifts from a single to distribution of relaxation times with occurrence of viscoelastic effects. These results have been correlated to the increased connectivity of micellar network.

In the similar study,$^{30}$ volumetric ($\rho, \beta$) and transport ($\eta, \sigma$) properties of AOT–$n$-heptane–water microemulsions have been measured over a large range of volume fraction of the dispersed phase $\phi (=0-70\%)$ and $\omega (=0-40)$ at 25°C. The density and isentropic compressibility of the micellar phase have been derived from experimental data. The volumetric properties, at high $\omega$, exhibit a trend towards enhanced water like character of the dispersed phase. At low $\omega$, there is evidence for a structural change in the hydrogen bonding network of water filling the droplets. Electrical conductivity data show the existence of percolation threshold depending on $\omega$. Below the percolation threshold, the specific conductance qualitatively and quantitatively agrees the prediction of droplet charge fluctuation model. Comparison of the viscosity and electrical conductance behaviour with $\phi$ indicates that the processes for momentum and charge transfer, even if related to the droplets cluster formation, are different.

The heat capacity and enthalpy of dilution of AOT–$n$-heptane–water microemulsions have been measured as a function of $\omega$ and volume fraction of dispersed phase $\phi$ by the same group.$^{67}$ The apparent specific heat capacity and enthalpy of dilution
of dispersed phase vary monotonically with \( \phi \), without any change in rate during the
crossover of percolation threshold. This trend indicates that even at highest \( \phi \) values, the
microemulsions are made up of water containing reversed micelles dispersed in the
hydrocarbon and intermicellar interactions decrease as \( \omega \) increases, vanishes when \( \omega \geq 20 \). The analysis of the heat capacities and dilution enthalpies are consistent and agree with
the results obtained from the volumetric and transport properties.\(^{30}\)

They have also reported\(^{68}\) electrical conductivity and complex permittivity of
AOT–heptane–water microemulsions. The experimental results have been rationalised in
terms of hopping mechanism of AOT anions with in clusters of reversed micelles. Effect of
molar ratio \( \omega \) and temperature on hopping rate and cluster dimensions has been discussed.

Calorimetric technique has been used to measure the formation enthalpy of gold
nanoparticles in AOT–\( n \)-heptane–water microemulsions\(^{69}\) as a function of molar ratio \( \omega \) at
various AOT concentrations. The size of the Au nanoparticles has been determined by
transmission electron microscopy. Radius and concentration of AOT reversed micelles
effect the energetic state and dimensions of Au nanoparticle. Some features of growth of
nanoparticles in microemulsions have been observed by analyzing the decay of calorimetric
signal.

Several experimental techniques (densitometry, refractometry, conductometry,
rheology, dielectric measurements, ultrasonics, hypersonics) have been utilized to
investigate the role played by the gelatin molecules\(^{70}\) in the observed sol gel transition
above a critical gelatin content in AOT–heptane–gelatin/water system at fixed molar ratio
(\( \omega=3.1 \)) as a function of gelatin content. The results appear consistent with the hypothesis
of a rigid network of gelatin water rods coated by surfactant molecules coexisting with
gelatin free AOT reversed micelles at the gelatin point.

In another study\(^{71}\) they have also investigated the physico-chemical properties
(density, viscosity, conductance, IR spectra and permittivity) of AOT–heptane–
formamide/\( N \)-methyl formamide microemulsions. The experimental data are consistent
with the hypothesis that these hydrophilic substances are encapsulated with AOT reversed
micelles and their structure is maintained for both systems up to percolation transition.
The observed properties of these microemulsions reveal the pivotal role of intermicellar
attractive interactions in driving percolative transition. Modification of structural and
dynamical properties of formamide and N-methylformamide, accompanying their
solubilization with in AOT reversed micelles has also been investigated.

The group\textsuperscript{72} has recently used calorimetric technique to study the precipitation of
ZnS nanoparticles with water containing reverse micelles of AOT, L-\(\alpha\)-
phosphatidylcholine, tetraethylene glycol–mono–n–dodecylether and didodecyl dimethyl
ammonium bromide as a function of \(\omega\). The results indicate that the energetic state of ZnS
nanoparticles confined in aqueous core of reverse micelles is different from that in bulk
water. Effects due to nanoparticle size, absorption of Hs–ions on the nanoparticle surface
and interactions between the nanoparticles and water/surfactant interface have been
discussed.

Moulik and coworkers,\textsuperscript{32,37,73-78} in a series of papers have investigated several
microemulsion systems. In a study,\textsuperscript{73} structural parameters i.e. radius of water pool (\(R_w\)),
effective radius of droplets (\(R_e\)), their number per unit volume, effective surface area of
water pool, aggregation number of surfactant and cosurfactant molecules per droplet at
oil/water interphase have been estimated in w/o microemulsions containing surfactant
(CTAB, SDS and AOT), oil (\(n\)-heptane, \(n\)-decane and xylene) and cosurfactant (1-butanol
and \(n\)-hexylamine) at two different temperatures 20 and 30°C and at two weight ratios of
surfactant/cosurfactant 0.33 and 0.50, conductometrically. The droplet radius has been
found to be oil dependent and follows the order \(n\)-heptane < \(n\)-decane < xylene whereas
dependence of radius on the surfactant is in order SDS>AOT>CTAB. 1-Butanol yields
greater radius than \(n\)-hexylamine with SDS and AOT. The order is reversed with CTAB.
The aggregation number of surfactant and cosurfactant per droplet increases and
decreases respectively with increase in temperature. The ratio \(R_e/R_w\) of the droplet remains
almost constant under all situations.

They have also investigated\textsuperscript{74} the effect of additives in percolation of conductance
and energetics of clustering in AOT–heptane–water. The effect of temperature has also
been investigated keeping the composition constant. Non-conjugated hydroxy bile salts,
enhance percolation whereas cationic surfactants, salts and cholesterol suppress the
process. Viscosity measurement implies association of microdroplets during percolation.
The energetic clustering has been evaluated by the determination of the dispersion concentration dependent, percolation threshold at different temperatures. The enthalpy and entropy of clustering compensate.

In another study, Moulik group have investigated the phase behaviour, conductance and viscous behaviour of non-aqueous microemulsions formed by AOT, non-aqueous solvent and oil, where different non-aqueous solvents used are formamide(FA), ethyleneglycol(EG), propyleneglycol(PG), dimethylformamide(DMF), dimethylacetamide (DMA) and oils are heptane(Hp), octane(Oc), iso-octane(i-Oc), xylene(Xy) and toluene(Tl). The ternary phase diagrams with i-Oc are more or less similar; the single phase areas have large viscous zones towards the amphiphile end. Both viscosity and conductance show percolation and internal structure formation. The intrinsic viscosity and Huggin's constant at constant© have supported spherical (or minorily ellipsoidal) nonsolvated dispersions. Viscosity equations of Vand, Moulik and Elier have been obeyed by all the systems except FA system. Calorimetrically studied, AOT - i-Oc - FA system showed exothermicity and where as system of AOT - i-Oc -EG/DMF/PG/DMA exhibited endothermicity. The enthalpies of the solutions are significantly low and the specific heats of the resultant mixtures are very close to one another.

Ray and Moulik75 have also studied the phase behaviour, transport properties and thermodynamics of AOT–alcohol–water (n= 5-8,10) system. Appreciable single-phase zones with viscous regions at higher proportions of AOT have been found for all alcohols. Electrical conductivity shows percolation phenomenon and viscosity increases with increasing shear rate. Calorimetrically determined, enthalpy of water solubilization in alcohol/AOT medium has been found to be positive. The free energy and entropy of water solubilization (derived from Gibb’s equation) are positive and negative respectively and follow a regular trend with [alcohol]/[AOT] molar ratio (R) as well as with alcohol carbon number. The enthalpies increase with increase in alcohol chain length to a maximum for heptanol and then decrease for octanol and decanol. The heptanol acts as an efficient cosurfactant with AOT and helps to produce microdroplets with increased endothermicity.

The mixing behaviour of plant oils (ricebran, saffola and clove) with water in the presence of amphiphiles (Triton X-100, Tween 60, AOT, Igepal, Na-oleate, ethanol...
cinnamic alcohol) in various ternary and quaternary combinations has also been reported by Moulik et al. The phase behaviour at different mass proportions and temperature has been studied in the absence and presence of additives such as NaCl, glucose, urea and cholesterol. The systems with ethanol and sodium oleate as amphiphile have shown maximum extent of single phase microemulsion formation. The effect of additives on the formation of biphasic and triphasic formulations, has been found to be dependent on $\omega$ and temperature. Spectral measurements of I$_3^-$ in the aqueous micropool in microemulsion of cloveoil/(ethanol+Na-oleate)/water have shown the microenvironment to be physicochemically different from bulk water.

In another report both water induced and temperature induced percolation in AOT–heptane–water microemulsion system in the presence of additives have been discussed. The hydroxy bile salts have assisting effect while Et$_4$I, C$_6$H$_5$, PhMe, naphthalene, xylene, cholesterol have resisting effects on the process. By the addition of 0.5M Na cholate, nonpercolating AOT–xylene–water system is made percolating. The scaling laws for both kind of percolation are obeyed but the equation parameters differ in magnitude. The activation energy required for percolation process has been determined but the value for different additives does not follow a general trend.

Recently, the group has studied the formation of reverse micelles of AOT in n-heptane, n-octane, isoctane, n-decane and eucalyptol, microcalorimetrically. Critical micellar concentration (CMC) and the energetic parameters of standard enthalpy, free energy and entropy of micellization ($\Delta H_m$, $\Delta G_m$ and $\Delta S_m$) have been estimated from thermograms. Entropy of water dispersions ($\Delta H_w$) has been estimated from solubility limit of water in AOT/oil mixtures and the entropy of dispersion ($\Delta S_d$) has been obtained from the Gibb's equation. The concentration of the dispersed microdroplets required in the above calculations has been estimated by measuring droplet size by dynamic light scattering method. It has been concluded that the entropy of water dissolution is $\omega$ dependent. The dissolved water may exist in three states i.e. the first transition occurs virtually at average of $\omega = 1$. For AOT/ Eucalyptol system, the initial maxima in $\Delta H_w$ is
not observed. The dispersions of water forming microemulsion and reverse micelle formation are entropy controlled processes.

They have also investigated\(^{37}\) the phase behaviour as well as the volume- and temperature- induced percolation in AOT–heptane–water system in the absence and presence of additives, sodium cholate (NaC) and sodium salicylate (NaS). The scaling parameters have been observed to be not in agreement with the predicted values. The energetics of droplets clustering leading to percolation have also been estimated. The amphiphile coated size of water nanodroplets, their diffusion coefficient and polydispersity have been estimated in pre- and post percolative stages.

Robinson et al.\(^{19}\) have used viscosity and dynamic light scattering methods to calculate size and aggregation number of reversed micelles formed by AOT–cyclohexane/toluene/chlorobenzene–water system. For the viscosity method, procedure for deriving values of aggregation number from particles of variable density has been described. The dynamic light scattering method yields single exponential correlation functions from which the values of translation diffusion coefficient and micelle radius can be derived. Satisfactory agreement has been found among methods and according to both the methods droplet size is found to depend on molar concentration ratio of surfactant to water (\(\omega\)) but is independent of solvent and concentration at a fixed \(\omega\). In a separate study small angle neutron scattering (SANS) measurements\(^{31}\) have been made for a series of AOT–stabilized w/o microemulsions containing AOT, D\(_2\)O and hydrocarbon. The intensity pattern has been used to extract a value for the radius of water core \(r_w\). In heptane, the radii (\(r_w\)) are found to follow linear relationship with (D\(_2\)O)/(AOT) concentration ratio \(\omega\). At 20°C and \(\omega=20\), the structure of water droplet system is dependent on the hydrocarbon chain length of the oil medium but with increasing length of alkane chain (i.e. from \(n\)-heptane to dodecane) showed increasing discrepancies with a fitted function based on monodisperse sphere in SANS patterns. This effect has been attributed to polydispersity and indicates that the droplet size distribution within these microemulsion systems is much larger.

They have also studied AOT stabilized dispersions of glycerol in \(n\)-heptane using dynamic light scattering and viscometry.\(^{80}\) One mole of AOT in heptane can disperse five
moles of glycerol. The resulting solutions consist of discrete spherical droplets of glycerol stabilized by surfactant. Droplet size is independent of temperature but depends on molar ratio \( \alpha \). The apparent interfacial area occupied per AOT molecule is 20% less in glycerol dispersions than in corresponding water dispersions.

Koper et al.\(^81\) have measured the viscosity of AOT–isooctane–water microemulsion system as a function of the droplet volume fraction at different temperature for two values of mole ratio; 35 and 25. It has been concluded that microemulsion droplets behave as solid sphere because of (i) the low volume fraction dependence of the relative viscosity follows Einstein's relation (ii) at sufficiently low temperatures the coefficients of second and third order terms in the volume fraction expansion of the relative viscosity equal to those found for latex and silica spheres. It has also been observed that at higher temperatures, the droplets aggregate reversibly.

Another report by Koper et al.\(^82\) deals with the aggregation behaviour of microemulsion droplets, especially water droplets covered with a mono molecular surfactant layer in oil. A model has been proposed that describes the aggregation of microemulsion droplets into chain like aggregates from a thermodynamic point of view. The model has been shown to be capable of explaining experimental data measured in AOT-isooctane-water microemulsion. Recently, the results of dielectric permittivity, low shear viscosity and electrical birefringence measurements\(^83\) have also been discussed to obtain quantitative information on aggregation in droplet phase microemulsions. The data consistently yield a rather large binding free energy between two aggregated microemulsion droplets.

Chen and coworkers\(^84\) have performed extensive measurements of shear viscosity, ultrasonic absorption and ultrasonic velocity in AOT–decane–water microemulsion system. A rapid increase in static shear viscosity has been observed whereas corresponding ultrasonic absorption shows unambiguous evidence of viscoelastic behaviour only for the volume fraction of the droplets greater than 0.30. The absorption data for various volume fractions and temperature can be reduced to a universal curve by scaling both the absorption and frequency by the measured static shear viscosity. The ultrasonic absorption
can be interpreted as coming from the high frequency tail of viscoelastic relaxation, describable by the Cole-Cole relaxation formula with unusually small elastic module.

They have also reported precise measurements of the time correlation function in a pseudocomponent w/o microemulsion system made of AOT-decane-water close to its consolute critical point and percolation threshold. Systematic studies of the intensity correlation functions using a correlator with a logarithmic sampling time, show sizable deviation from a single exponential decay. It has been shown that an extension of the dynamic droplet model is able to account for the non-exponential behaviour at intermediate and long times. The line width is in satisfactory agreement with the model, which also takes into account the finite size of the microemulsion droplets.

In another report, an extended phase diagram for an ionic microemulsion system made of AOT-n-decane-water has also been deduced from a very extensive electrical conductivity and neutron scattering measurements. The diagram shows high temperature phase transitions, which explain some original features. The electrical conductivity data obtained in the lamellar phase, has been explained by a phenomenological model.

They have also performed a series of spinodal decomposition measurements of AOT-decane-water system. The measurement were made by a temperature jump from one phase droplet microemulsion to two-phase droplet microemulsions using the time resolved light scattering intensity technique. The typical scattering intensity distribution is in good agreement with recent dynamic scaling theories.

Chen and group have also performed extensive study of AOT-decane-water microemulsion system using small angle light scattering (SALS) at fixed ω=40.8 and changing temperature (T) and volume fraction of dispersed phase (φ). They were able to observe all the phase boundaries of complex phase diagram with a percolation line and many structural organizations within it. A structural transition from a droplet microemulsion to a bicontinuous one is described in detail. The loci of this transition are located several degrees above the percolation temperatures and are coincident with the maxima observed in shear viscosity. It has been analyzed from the data that both the percolation phenomenon and this novel structural transition are derived from a large scale aggregation between microemulsion droplets.
Majolino et al.\textsuperscript{89} have reported the results of measurement of the shear viscosity as a function of temperature and of water volume fraction for AOT–decane–water system in the concentration range $0 \leq \phi \leq 0.73$. To obtain a very dense glass-forming liquid, the packing fraction of w/o spherical droplets has been changed accordingly. In relative viscosity, a well-defined maxima has been observed at different concentrations and the corresponding temperature values decrease with increasing $\phi$. The data is discussed by considering the system as colloidal one having aggregation phenomenon. The results are compatible with those obtained by light scattering measurements that gives clear evidence of the presence of a large structural order at the glass transition.

$^1$H and $^{13}$C NMR spectra have been utilized by Antalek et al.\textsuperscript{90} to study environmental changes and surfactant packing transitions in AOT–acrylamide–toluene–water reverse microemulsions with change in concentration of cosurfactant (acrylamide). These studies were motivated by the observation of cosurfactant–triggered threshold transition in electron transfer for various reduction and oxidation reaction in these highly resistive microemulsions. The present results indicate that interfacial packing transition of AOT occurs at about same cosurfactant concentration 2-3% (w/w) as the threshold transition observed electrochemically and also provides a physical basis for the percolation threshold reported for these microemulsions. The self diffusion coefficient\textsuperscript{91} of same system have also been measured. A distinct increase has been identified in water proton diffusion above the percolation threshold in cosurfactant chemical potential. The increase has been assigned to water transport through fraction aggregates and clusters. Above threshold, increasing apparent partitioning of water and cosurfactant into continuous pseudophase yields an order parameter for estimating percolating cluster volume and shows that cosurfactant preferentially segregates into these clusters.

The same group has used electrical conductivity and NMR to study AOT–toluene–water microemulsion\textsuperscript{92} containing varying amounts of acrylamide as cosurfactant. The acrylamide increases interfacial flexibility and facilitates transient formation of water channels between particles during collision. The direct probing of the acrylamide by NMR shows that the hydrophilic amide points towards the water pool and the hydrophobic tail is
coupled to the AOT alkyl chains. These structural features enhance understanding of associated electron, proton and ion transport in these microemulsions.

In the more recent study time domain dielectric spectroscopy\(^9^3\) have been applied on the same system (AOT–toluene–water) and observed static percolation induced by increasing cosurfactant concentrations. A dynamic partitioning model has been used to estimate the volume of percolating fractal clusters and yields an order parameter for w/o to percolating cluster microstructural transitions. This order parameter has also been derived from self-diffusion data. For microstructural transitions driven by three different field variables, chemical potential, temperature and disperse phase volume fraction, this order parameter show that the onset of percolation corresponds to the onset of increasing water proton self-diffusion which corresponds to the formation of bicontinuous microstructures and further the onset of transformation to middle phase microemulsion.

Using conductivity and self-diffusion measurements at 45°C, Antalek et al.\(^9^4\) have shown that the reverse micelle to sponge phase transition proceeds in a sequence of two continuous transition and is defined quantitatively by an order parameter. This is the first study to quantify the \textit{onset} of sponge phase formation within in single phase domain, as a function of composition.

Xenakis and group\(^9^5\) have studied the effect of enzyme trypsin or chymotrypsin on AOT based w/o microemulsions using conductivity and luminescence decay measurements. With the addition of enzyme, percolation threshold is shifted and the shift is dependent on enzyme concentration. The luminescence decay profiles of Ru(bpy)\(^3^-\) in the presence of quencher is also dependent on enzyme presence and its concentration.

The group has also studied w/o microemulsion based on lecithin or AOT to solubilize lipase from Pseudomonas cepacia.\(^9^6\) The enzyme activity was tested in catalysis of esterification reaction between lauric acid and various short chain aliphatic alcohols. Out of the both microemulsion systems, lipase is found to be more specific for propanol in lecithin. From florescence energy transfer measurements which is used to detect the site of localization of the enzyme molecule, it has been concluded that in both cases, enzyme is found to be close to the surfactant interface but efficiency of transfer is more pronounced in AOT systems. Time resolved luminescence quenching has also been applied to both
systems, to probe structural modifications of microemulsion system induced by the presence of lipase.

Recently, the structural and catalytic properties of cutinase in w/o AOT–isoctane microemulsion system have also been investigated. In the esterification reaction of lauric acid with pentanol, cutinase follows a bell shaped trend at ω=9. Michaelis constant (K_m) and Maximum apparent velocity (V_max) have been determined by kinetic studies. Electron paramagnetic resonance (EPR) spectroscopy studies of active site labeled cutinase in microemulsions with varying ω values shows that in all the microemulsions, the mobility of label is higher in aqueous solution. Upto ω= 9, there is an increase in both activity and active site mobility but at higher ω, the mobility of the bound spin label further increased where as enzyme activity dropped is considerably.

In another paper, two w/o microemulsions have also been formulated with lecithin and AOT to solubilize lipase from Pseudomonas cepacia. The site of localization of the enzyme with in different microdomains of the dispersed phase is investigated by applying the fluorescence energy transfer techniques. The non-radiative energy transfer from the Trp residues of lipase to adequate acceptor molecules such as cis-parinaric acid, is examined. The results show that in both the microemulsion systems, lipase is localized near the surfactant membrane but interface is less penetrable in lecithin than with AOT.

Peck et al. have developed a unified classical and molecular thermodynamic model and applied on AOT–oil (propane to decane)–water systems to predict the phase behaviour and interfacial properties of microemulsions. A modified Flory–Krigbaum theory has been used to describe the interactions between surfactant tail and solvents, while the ionic head group interactions have been treated with Poisson–Boltzman equation. The calculated values of interfacial tension and bending moment of the interface are incorporated into classical thermodynamic framework to satisfy Gibb's absorption equation on the interface. It has been concluded that the enthalpic contribution dominates that of the configurative entropy, while the opposite is true for the larger alkanes.

Peck and Johnston have used the same model to study the pressure effects on both the curvature and phase behaviour of AOT-propane-brine microemulsion and to identify quantitatively the role of intermicellar interactions and micelle-micelle interactions.
A supplementary model is used to calculate the strength of attractive interactions over a wide range of conditions and an important distinction is made between systems with small water to oil ratio and those where the water to oil ratio is much larger, on the order of unity. In the latter case, micellar radius is controlled primarily by intermicellar interfacial interactions, specifically the enthalpic propane-surfactant tail interactions whereas for the system with small water to oil ratio, micellar radius is dependent on attractive micelle–micelle interactions. The radius increases with increase in pressure and reaches maximum controlled by intermicellar interfacial interactions. A good agreement between experimental and predicted values is observed over a wide range of water to oil ratios.

Bellocq\textsuperscript{50,51} have studied the effect of Poly(ethylene glycol) (PEG) (M.wt.=20,000) on the phase behaviour of AOT–isooctane–water system. By replacing water with aqueous solution of PEG, stability of microemulsion and lamellar phases is affected and upto 17% by weight of water can be replaced by polymer. The solubility of PEG in w/o droplet depends on the relative sizes of water core (R\textsubscript{w}) and the polymer (R\textsubscript{p}) and on temperature. At high R\textsubscript{w}/R\textsubscript{p} ratios, polymer induces inversion of microemulsion from o/w to w/o, which is similar to effect of addition of NaCl. In this phase diagram, there exists a PEG concentration range, where hydrophilic property of AOT is balanced at 25°C. Electric conductance and light scattering data indicate that the presence of PEG in the water core of inverse micelle lead to decrease of attraction between the micelles.

Cavasino \textit{et al.}\textsuperscript{101} have dealt into the kinetics of water replacement in cationic palladium (II) aquo complex [Pd(Et\textsubscript{4}dien)(H\textsubscript{2}O)]\textsuperscript{2+} by thiourea, methylthiourea and ethylthiourea at 25°C in AOT-heptane-water microemulsion over a wide range of molar ration ω at constant surfactant concentration of 0.13 mol dm\textsuperscript{-3}. By applying pseudophase model, the kinetic data indicate that there is a weak partitioning of the nucleophiles between water core and AOT interface, while the palladium complex is strongly associated with negatively charged surfactant interface. All the substitution reactions occur only in AOT interfacial region with rates close to bulk water. The partition coefficients of nucleophiles increase with increasing their hydrophobic characters where as reaction rates decrease as ω increases. In continuation to this investigation, they have studied\textsuperscript{102} at 25°C the kinetics of the substitution reaction.
\[ \text{[Pd(en)X]}^{2+} + Y \rightarrow \text{[Pd(en)YT]}^{2+} + X \]

at square-planar palladium(II) complexes in AOT–heptane–water microemulsion as a function of the AOT concentration at the constant values \( \omega \) values of 3,8 and 20,30. In the reaction en = ethylenediamine and \( X = 2,2' \)-bipyridine(bipy) or 4,4'-dimethyl - 2,2'-bipyridine and \( Y = \text{en or N,N dimethylethylenediamine(dmen)} \). The conditions used in this work are such that, at a given \( \omega \) value, the amount of water in the microemulsion varies in the proportion to the AOT concentration, but the water droplets donot change their size. The kinetic results are quantitatively analyzed by a rate expression derived by applying the pseudophase model. It has been concluded that the "effective" pseudophase volume (per mole of AOT) in which reaction occurs is not a constant parameter for AOT-stabilized microemulsions when \( \omega \) is changed and increases as the interfacial AOT layer curvature becomes larger. This result is of particular interest in kinetic studies of chemical reactions performed in these micro heterogeneous media.

Kawai Hirai and coworkers\(^{103} \) have utilized dynamic light scattering (DLS) and viscosity in w/o AOT–isooctane–water microemulsion. Two coefficients have been measured relating to hydrodynamic interparticle interaction. The \( \omega \) dependence of these coefficients in the range of 5-15 shows a critically different tendency compared to that of \( \omega = 15-50 \). The existence of oligomeric phase in \( \omega \) range 5-15 using SAXS experiments is in good agreement with their previous results.

In a separate report, SANS experiments have been carried out on AOT–hexane/heptane–water system\(^{104} \) to clarify the relation between the appearance of superconductivity and internal structure of AOT microemulsions. The system has been treated by using solvent-contrast variation method and a change of the excluded volume of AOT molecule at low \( \omega \) value has been observed and discussed.

Mays and Ilgenfritz\(^{105} \) have employed time resolved luminescence quenching technique to investigate cluster dynamics in ionic w/o AOT microemulsions. At constant surfactant concentration and water to surfactant molar ratio, the exchange of material between clusters in AOT microemulsions with different alkane oils has been analyzed. Under these conditions the percolation temperatures are shifted to lower values with longer chain alkane oils. The activation energies required to break surfactant monolayer in
pre-percolative regime is 126–188 kJmol\(^{-1}\) and longer the alkane-oil chain of the solvent, the higher is the activation energy. The rate constant for exchange between clusters at the percolation threshold is \(3.8 \times 10^8\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) for all microemulsions studied. From the observed dynamics it has been concluded that in the percolated state, the droplet structure is maintained, although the shape-restoring interfacial forces are weak. The decay kinetics are not stretched exponential, implying that the averaged droplet arrangement in a cluster on a millisecond time scale is not fractal.

Ilgenfritz and coworkers\(^{106}\) have also reported investigations on the percolation of aqueous phase and compared the systems stabilized by ionic AOT and nonionic Igepal surfactants. Effect of temperature, high electric field and solute (especially small molecules) has been observed on the percolation curves. The conductivity data has been compared with viscosity data. The electric field measurements allow to study the dynamics of the clustering of water droplets to form network of percolation channels. By monitoring electrical conductivity and electrical birefringence, slow build up and fast decay of percolating structures have been examined. A simple estimation of the intrinsic Kerr constant is given for the microemulsion droplets deformed in the electric field.

The dielectric properties of AOT reverse micelles in carbon tetrachloride and \(n\)-heptane have been measured in the frequency range 0.02-20 GHz as a function of \(\omega\) by Santucci and coworkers\(^{107}\). The dielectric relaxation is affected markedly by interparticle interactions. These interactions in turn depend upon oil chain length, \(\sigma\) and on addition of small amounts of electrolyte. The IR absorptions in C-O stretching region of AOT molecules have been recorded to give information on the relative population of different AOT rotational isomers in the various examined systems. A correlation has been observed between the presence of attractive interactions and composition of AOT rotamers, supporting the hypothesis that the intermicellar interactions are favoured by a particular orientation and packing of non polar AOT molecules in the micellar aggregates.

They have also reported the effect of changing nature of counter ion (replacing Na\(^+\) ion of AOT by Mg\(^{2+}\)) on the hydration mechanism and dynamic properties of AOT micro-aggregates\(^{108}\) by measuring the dielectric permittivity by a frequency domain coaxial technique in the range of 0.02–3 GHz as a function of surfactant concentration and water
content. A relaxation phenomenon has been observed whose behaviour depend on surfactant hydration and particle interactions. These obtained results have been compared with NaAOT system, showing significant differences in dynamical properties and particle interactions.

The effect of replacing Na⁺ counterion of AOT by Cu²⁺ on the hydration mechanism of AOT reverse micelles have also been studied by IR spectroscopy. The results of ternary systems Na (AOT)–carbon tetrachloride–water and Cu (AOT)₂–carbon tetrachloride–water show significant differences in the interactions of Na⁺ and Cu²⁺ counterions with water molecules and the SO₃⁻ head group of AOT.

Recently the group has measured the high frequency dielectric response in the range 0.01-20 GHz as a function of φ at fixed $\omega=11$ of AOT reverse micelles in n-heptane. A relaxation phenomenon, connected to AOT ion pair diffusion at water-surfactant interface has been observed. This relaxation is affected by interparticle interaction modulated by adding different amount of NaCl. IR study has been performed on the carbonyl stretching band of AOT molecule in the micellar aggregates to reveal the connection between intensity of attractive interactions among the droplets and the stereochemical configuration of AOT molecules. The results support the hypothesis that attractive inter-micellar interactions are favoured by a particular orientation and packing of non-polar tails of AOT molecules in the micellar aggregates.

Li et al. have studied the microstructure of AOT–n-heptane–water microemulsion system using FTIR spectroscopy. With increasing water content $\omega$ (1 to 60), intensity of O-H stretching vibration varies from 3050 to 3750 cm⁻¹ where as frequency changes from 3493 to 3417 cm⁻¹. Four types of circumstances of water exist in the microemulsion system located around 3590±20 cm⁻¹, 3520±10 cm⁻¹, 3465±10 cm⁻¹ and 3270±20 cm⁻¹ have been estimated after O-H stretching bonds and are resolved by curve fitting. The stretching band of carboxide split into two peaks located at 1739±2 cm⁻¹ and 1722±2 cm⁻¹ and intensity ratio $I_r = [I_{1739}/I_{1722}]$ decreases with $\omega$. The variations are due to both the hydration of head group and the different conformation in AOT molecule.

In another study, they have investigated the interaction of water with polar head groups in reversed micelles of AOT and NaDEHP [Sodium bis(2-ethylhexyl)phosphate] by
Fourier Transform infrared spectroscopy (FT-IR). O–H stretching bands of water in both systems varied with water content $\omega$. With increasing $\omega$ (1 to 20), O–H stretching frequency shifts to higher frequency, approaching the frequency of bulk water, whereas frequency of sulfonate and phosphate decrease indicating the hydration of surfactants in both systems. Results show that water molecules encapsulated in reverse micelles are similar to that in bulk form when $\omega > 16$ in AOT system and $\omega > 12$ in NaDEHP system.

The decreased frequency of sulfonate stretching band upon hydration is due to the weakening of sodium-sulfonate interaction and an associated increase in their spatial separation. Addition of more water does not appear to change the electronic environment and there is no further frequency shift after the reverse micelles are fully hydrated.

Caboi et al.\textsuperscript{115} have studied the microstructural features of ternary microemulsion system CaAOT–n-decane–water by viscosity, conductivity, dynamic light scattering and NMR self diffusion measurements. As observed from phase diagram, the microemulsion region is shrinked as compared to corresponding NaAOT system. Viscosity data show the occurrence of non-spherical particles at high volume fraction $\phi_s$ where as percolation in conductivity measurement is observed at $\phi_s^c = 0.142$ along an oil dilution line at constant $\omega = 26.4$. The percolation threshold is not temperature dependent in the range 15-30°C, thus static percolation is suggested. By comparing diffusion coefficients calculated from composition and those obtained by DLS and NMR measurements, spherical droplets with hard sphere behaviour occur at low $\phi_s$. The microstructure of the system has been discussed in view of different approaches based on percolation theory, attractive interactions among discrete particles and multiconnected water network. Microstructural evolutions can be justified in terms of transient fission–fission processes among the droplets occurring over timescales that are comparable with the experimental observation times.

SANS studies have been performed by Capuzzi et al.\textsuperscript{114} on Ca(AOT)\textsubscript{2}–decane–water system and a consistent reduction of one phase region has been observed in this system as compared to parent sodium system. Microemulsions of Ca(AOT)\textsubscript{2}–decane–D\textsubscript{2}O and Ca(AOT)\textsubscript{2}–decane-D\textsubscript{22}–H\textsubscript{2}O have been studied at 25°C for an oil dilution line at constant $\omega = 25.1$, as a function of decane concentration and of surfactant volume
fraction, \( \phi_n \), in the range \( 0.0186 \leq \phi_n \leq 0.0937 \) for D\(_2\)O system or \( 0.0249 \leq \phi_n \leq 0.0886 \) for corresponding decane-d\(_{22}\) system. SANS spectra show the presence of polydisperse droplets in the diluted region while at high concentration, percolation occurs. The droplets have a 21.3Å average radius with polydispersity around 22%. The mean area per polar head group and principal geometrical parameters has also been estimated.

Han et al.\(^{115} \) have reported the transporting behaviour of metal ions such as Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cr\(^{3+}\) and Cr(VI) from water phases into w/o microemulsions AOT–heptane–water. The experimental results show that all of these metal ions studied except Cr (VI) have high transport ratios. In continuation they have studied the effect of addition of mobile carrier (2-pyridylazo)-2-naphthol on transport of ion Cu\(^{2+}\) in the same microemulsion system of AOT and heptane.\(^{116} \) The addition of mobile carrier increases the Cu\(^{2+}\) transport ratio from 70% to 100%. Moreover, Cu\(^{2+}\) has high enrich times (6 times) and recovery ratio (100%) under given conditions of de-emulsion.

An et al.\(^{117} \) have presented precise coexistence curve measurements of a ternary microemulsion, consisting of AOT, decane and water, at constant pressure and a constant ratio \( \omega (40.8) \) within about 10K temperature range above the critical temperature. The experimental results have been analyzed to determine the critical exponent \( \beta \) and the critical amplitude \( B \) and to examine the size of asymptotical range and the anomalies of the diameters for different choices of order parameters. The present results confirm that the pseudo binary mixture of the microemulsion belongs to 3D Ising universality class. In a region sufficiently close to the critical temperature, the shapes of coexistence curves may be characterized by simple scaling with the 3D Ising value of critical exponent. Same type of work has been done by the group on AOT–octane–water system\(^{118} \) and similar results have been obtained irrespective of the nature of the system.

Nagao et al.\(^{119} \) have investigated the pressure effect (\( P \approx 0.1–83.5 \) MPa) on the structure of a three component AOT–n-decane–water microemulsion system at \( \omega = 40.8 \) and \( \phi = 0.6 \). At \(-50 \) MPa, phase transition from disorder microemulsion to order lamellar structure through a coexisting region has been observed. The pressure dependence of the repeat distance and the correlation length in both high and low pressure phases have been calculated from the scattering profiles.
In a recent study, the group\textsuperscript{120} has used small angle neutron scattering technique to investigate pressure induced phase transitions in AOT–n-decane–water system. The samples, 20.9\%, 22.4\% and 23.0\% of AOT, dissolved in equal proportions of water and oil, are known to be a dense w/o droplet structure at ambient temperature and pressure. At higher pressure, the system turned into two phases; a lamellar phase at the lower part of the cell and a bicontinuous phase in the upper part. Mean repeat distance of each structure is pressure dependent. The disorder parameter both in w/o droplet structure at lower pressure and in bicontinuous structure at higher pressure followed a unique function.

Suarez \textit{et al.}\textsuperscript{46} have studied the effect of addition of polymers to AOT–alcohol–decane–water microemulsions on the interdroplet attractive interactions by electrical conductivity and time resolved fluorescence quenching (TRFQ) method. Three types of polymers have been used: (i) water soluble polymer; polyoxyethylene glycol (POEG), polyacrylamide (PAM) and polyvinyl alcohol (PVA) (ii) oil soluble polymer; polybutadiene (PBD) and (iii) a polymer which is partitioned between water and oil phases; polypropyleneglycol (PPG). Addition of POEG, PAM, PVA and PPG decreases the attractive interactions between the droplets whereas addition of PBD increases it. The mean droplet size has been investigated by TRFQ, in the case of POEG. In another paper,\textsuperscript{48} the group has observed that conclusion found for AOT based microemulsions, is also true for w/o microemulsions formed by the anionic surfactant (SDS) and two cationic surfactants (HTAB and DBDAC).

Gonzalez-Blanco \textit{et al.}\textsuperscript{121} have used steady state and time resolved fluorescence quenching techniques to obtain the photophysical parameters of acridone in w/o microemulsions of AOT–isooctane–water. The results point to the existence of two species of acridone in equilibrium, localized at micellar interface and in the water pool respectively. In the presence of two different molecular weight polyvinyl pyrrolidinone polymers, the two species of acridone are also detected. The pseudo equilibrium constant and number of water molecules needed to displace acridone from organic interface to water pool have been determined in the presence and absence of polymer and have been compared with those obtained in non-perturbed microemulsions. Their differences are
related to the average droplet occupancy and with charges of water pool polarity induced by water soluble polymers.

IR spectroscopy and UV-Vis absorption spectra have been recently used by the same group to investigate the properties of water pool of w/o microemulsions formed by AOT–cyclohexane/isooctane/toluene–water. From IR water spectra, four different water species have been detected, the relative amounts of which are dependent. The position of maximum of the probe (methyl orange) in the absorption spectra, determines the water pool dielectric constants. The polarity of the system depends on the nature of solvent and the amount of water content solubilized in the system.

Garcia-Rio et al.9 have investigated the influence of several additives (electrolytes, D2O, ureas, thioureas, amines, formamides and ethylene glycol) frequently present in reactions carried out in microemulsions, upon the properties of AOT–isooctane–water system. Electrolytes (salts, HCl, NaOH, guanidium chloride) hinders percolation phenomenon and decreases both the microemulsion viscosity and its capacity to water solubilization whereas ureas, thioureas, formamides and ethyleneglycol have opposite effect. But the behaviour of amines are confusing. Comparison of the 1H NMR chemical shifts corresponding to the microemulsion water under different conditions, in the presence and absence of these additives, indicates that the additive used do not significantly alter the state of w/o microemulsions.

They have also interpreted the kinetics of solvolysis of diphenyl methyl chloride, 4– nitrophenyl chloroformate, benzoyl chloride, p–anisoyl chloride and bis(4– nitrophenyl) carbonate in AOT–isooctane–water microemulsions with various φ(=4–50) by using pseudophase model. According to this model, the substrates have been assumed to be distributed between isooctane and interface phases. The work provides kinetic evidence of changes in the structuredness of the interface of AOT microemulsions as φ is decreased. The precise effect of these changes on the solvolysis of the guest molecules depends on the solvolysis mechanism (SN1 or SN2). It has been suggested that kinetic studies of this type may be useful for differentiating between mechanisms.

In another report the group has determined the kinetics of nitroso group transfer from 2–ethoxy ethyl (EEN) and 2–bromo ethyl (BEN) nitrite to the secondary amines
piperazine (PIP), N-methyl benzyl amine (NMBA) and morpholine (MOR) in AOT–isoctane–water microemulsions. It has been considered that the alkyl nitrites would initially be distributed in all the three pseudo phases and the amine determines the place of reaction. The results have been explained quantitatively in terms of a model in which the reagents are distributed among the aqueous, organic and AOT film surfactant, with the aqueous pseudo phase and the surfactant film as loci of the reaction.

The influence of several additives i.e. Crown ether (18-crown-6) and Kryptand complexes (Kryptand-222, Kryptand-221, Kryptand 211) on the properties of AOT–isoctane–water has been investigated by the group. The additives have important effect on electrical percolation phenomenon, may be due to their ability to macrocycle the complex ions and transfer them to interface. Medium and high macrocyclic concentration favour electrical percolation. The effect has been related to interfacial association of AOT head groups and has been explained in terms of critical packing parameter. The results have been compared with the influence of small additives as electrolytes or small organic molecules.

Alvarez et al. have measured the electrical conductivity of ternary AOT–isoctane–water systems with various additives at different temperatures. The various additives are urea, methyl urea, 1,3–dimethyl urea, 1,1–dimethyl urea, tetramethyl urea, thiourea, methyl thiourea, 1,3–dimethyl thiourea and tetramethyl thiourea. From the data, the percolation temperature (T_p) has been determined. It has been concluded that thioureas are more effective in advancing the process of percolation than their oxygenated analogue. The degree of methylation of urea or thiourea provokes a greater effect on the percolation.

In another report, the effect of secondary amines (morpholine, piperidine, piperazine, pyrrolidinone, dimethyl amine and N–methyl amine) on the same ternary system has been studied. Most of the amines hinders the percolation, may be due to increase of partial dissociation of amine into ammonium and hydroxide ion. Among the studied amines, morpholine is the exceptional case i.e. it lowers T_p. The effect exercised by the presence of sodium salts e.g. NaCl, NaBr, NaI, NaSCN and Na_2SO_4 on the conductivity of the same system has also been analyzed. The temperature of percolation
is practically independent of the sodium salt taken. A delay in the process of percolation has been observed as compared to that without additive in each case.

Recently the group has also investigated the effect of amides (formamide, N-methyl formamide, N,N-dimethyl formamide and N-methyl-N-nitroso-p-toluene sulfonamide) and ethylene glycol on the above studied system. The behaviour observed for all cases corresponds to decrease in the temperature of percolation.

The fraction of bound water in the water core, water core radius, thickness of bound water layer and effective head group area of the surfactant for AOT–isoctane–water and AOT–cyclohexane–water systems have been calculated from the aggregation parameters and chemical shift of water proton reasonance data by Maitra. It has been concluded that because of the flexibility of the surfactant molecule due to internal rotation about C-C bond of ethane skeleton of the succinic acid part, the system form stable w/o microemulsions. The detailed calculation of the packing factor of surfactant for various sizes of droplets has been made and has been found to be one of the favourable condition for the formation of w/o microemulsion.

Jada et al. have investigated electrical conductivity and rate constant $k_c$ associated with the exchange of material upon collision between droplets in AOT–oil (hexane to dodecane)–water by time resolved fluorescence method. Percolation in conductance occurs only in system where $k_c > (1-2) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. This result supports the hypothesis that above percolation threshold, the conductivity is due to motion of counter ions through water tubes or channels or fusion between droplet in droplet clusters. The length and number of these transient tubes and in turn the conductivity would increase rapidly above the percolation threshold.

Multicomponent sticky hard–sphere–droplet model has been used for the analysis of SAXS intensity curves obtained from AOT–isoctane–water microemulsions at various concentrations and temperatures by Robertus et al. The pair correlation function for microemulsion droplets has been used for interpretation of SAXS results. The results reveal the presence of strong interactions between droplets and solvent medium. Dielectric properties of these microemulsions have been described in terms of polarizability of medium. The structural parameters extracted from SAXS analysis have
been used to calculate the correction term to Clausius–Mossotti equation for the polarizability of the microemulsion system. Good agreement is found between observed and calculated polarizabilities.

Tingey et al.\textsuperscript{129} have investigated the vander Waals attractive interactions between aqueous droplets in AOT–water–alkane (from methane to isoctane) and noble gases (krypton and xenon) systems at different $\omega$. The phase behaviour of microemulsions formed in supercritical and near-critical solvents to those formed in conventional "subcritical" liquids have been compared to assess how these vander Waal forces affect the phase behaviour of such systems. The results point to a key role for such attractive interactions in cases where steric considerations, due to solvent size and shape, may be neglected. Calculated interactions are qualitatively consistent with experimental results of phase behaviour studies in such systems.

In a short communication Kallay et al.\textsuperscript{120} have interpreted the electrical conductivity of AOT–isoctane–water system on the basis of the distribution of ionic charges among the droplets. The charging energy is approximated by the Born energy. Hydrodynamic radius, has been distinguished from the water core radius. A comparison of Boltzmann statistics with the fluctuation theory, indicates that the former approach is more realistic due to its consideration of the discrete nature of charge, while the latter better fits the data.

Kotlarchyk et al.\textsuperscript{131} have studied the small angle X-ray scattering (SAXS) of AOT–decane–water microemulsions with respect to volume fraction of dispersed phase ($\phi$) ranging from 0.60 to 0.95 and between temperature 3 to 65°C, in order to delineate clearly the phase behaviour. At fixed $\omega=40.8$, the resulting phase diagram, indicates three distinct structural domains, namely, droplet phase L\textsubscript{2}, a high temperature lamellar phase L\textsubscript{alpha} and a low temperature L\textsubscript{3} phase consisting of randomly connected lamellar sheets. In order to study the structural and dynamical properties of L\textsubscript{3} phase, dielectric relaxation, shear viscosity and quasielastic light scattering measurements of the systems have been carried out. It has been found that L\textsubscript{3} phase exhibits Newtonian behaviour up to a shear rate of 790 s\textsuperscript{-1}, in contradiction to previous theoretical considerations. The phase exhibits two distinct relaxation modes. A relaxation time of $\sim$1 ms characterizes the Brownian motion.
of a single lamellar sheet, while the motion of the entire interconnected sheet assembly has a relaxation time on the order of 1s.

Structural parameters i.e. aggregation number (n) and radius of aqueous core (r_w), for AOT–decane–water system at different ω (molar ratio of water to AOT) have been calculated and compared with the values obtained experimentally by other methods like small angle neutron scattering, sedimentation and viscosity measurements by Casado et al. A good agreement has been observed between the two. Kinetics of reaction, oxidation of iodide ions by peroxide sulfate, in same microemulsion system has been studied in order to calculate the value of rate constant. The microemulsion structure, therefore, appears to have effect on reaction rate in addition to the effect mediated by its influence on the ionic strength of medium.

Vanag and Hanazaki have presented a new finding of the frequency-multiplying bifurcation of ferroin-catalyzed Belousov–Zhabotinskii oscillatory reaction in w/o microemulsions of AOT. This bifurcation occurs only at large φ_w and when the system is flowing at very low rate. Clusters of microemulsion droplets at high φ_w behave as minioscillators and their mutual coupling determines the mode of bifurcation. It has been found that bromine produced in oscillatory reactions is stored in the organic phase and governs the bifurcation by enhancing coupling between clusters.

The effect that microemulsion droplet size and concentration have on conductivity have been presented by Alexandridis et al. for AOT–oil–water system on wide composition (ω = 0–50) and temperature range (T = 10–62°C). Percolation in conductivity has been observed only for systems with ω>15. The percolation temperature (T_p) decreases with increasing ω. An increase in molecular weight of alkane solvent shifted the percolation threshold to lower temperatures and dispersed volume fraction values. The estimation of the free energy, enthalpy and entropy of clustering values from an association model of droplet clustering has been described. The influence of microemulsion droplet size and concentration and the effect of apolar solvent type on droplet clustering energetics have also been discussed. The enthalpy of cluster formation, ΔH°_cl, has been found to be positive, indicating that the transfer of microemulsion droplets from solution to the percolating cluster is an enthalpically disfavoured endothermic
process. A positive entropic contribution, $\Delta S^\circ_{\text{cl}}$, is the driving force for clustering. Both $\Delta H^\circ_{\text{cl}}$ and $\Delta S^\circ_{\text{cl}}$ increase with increasing droplet size and the molecular weight of the apolar solvent.

Ma et al.\textsuperscript{135} have studied oxidation of iodide by persulfate in w/o microemulsion formed by mixture of anionic (AOT) and nonionic (NP-6) surfactant, water and heptane. The reaction rate is appreciably higher in microemulsion formed solely by AOT than in a conventional aqueous medium. The incorporation of nonionic surfactant deteriorates the catalytic effect of the microemulsion.

Adachi et al.\textsuperscript{136} have elucidated the kinetics of solute extraction in AOT water in oil/brine two phase system. The rate process of the tryptophan extraction has been examined by measuring the time evolution of the concentration profiles of tryptophan near the liquid/liquid interface in a static diffusion cell and a flow function cell. An anomalous phenomenon has been observed for the solute transfer when water is coextracted to the microemulsion phase, whereas the anomaly disappeared while using microemulsion presaturated with water. The interfacial rate process played an essential role in extraction of solute with the presaturated microemulsion. Out of number of affecting factors, organic solvents had a great effect on the interfacial rate process indicating that the fusion process between a microemulsion droplet and the liquid-liquid interface is the rate determining step.

The self diffusion coefficients of the two polar species (dilute aqueous solution of either N–methyl formamide or tetramethyl ammonium chloride) in the three different surfactant–oil–polar solvent microemulsions system (with the surfactants AOT, DDAB and tetraethylene glycol dodecyl ether C\textsubscript{12}E\textsubscript{4} respectively) have been studied by Jonstroemer et al.\textsuperscript{137} In AOT system, a region of dominating aggregate diffusion process has been found at lower temperatures. With increasing temperatures, structural changes cause a crossover to a dominating molecular diffusion in a medium similar to a neat aqueous solution. This implies a cross over to a bicontinuous network at higher temperatures. In contrast no such region has been found in DDAB and C\textsubscript{12}E\textsubscript{4} systems. A dominating or almost dominating molecular diffusion process has been detected even when the absorption diffusion coefficients of the polar solvent species are low.
Kazakov et al.\textsuperscript{138} have determined a phase diagram of pseudobinary solvent-drop mixtures in AOT–decane–water microemulsion system for $\phi = 35.6$. Coexistence curves have unsymmetrical shapes typical of binary mixtures, due to self-organization by the components but the shapes of symmetrical co-existence curves can be described by simple scaling equations whose parameters confirm that these microemulsions belong to an Ising–like system universality class.

The Kerr constant has been determined for AOT–dodecane–water microemulsion by Acosta et al.\textsuperscript{139} to test the validity of the theoretical approach of Linden et al.\textsuperscript{140} The binding modulus of the curved surfactant monolayer along different paths of the phase diagram has been measured. A good agreement between experimental and theoretical results has been obtained only for the concentrations far from phase transition regions. The Kerr constant, viscosity and relaxation times have been measured in microemulsion based gels, as a function of gelatin concentration. At low bipolymer concentrations, Kerr constants do not vary too much but in certain concentration range (about 3–4%), a sharp increase, similar to those of electrical conductivity and viscosity has been observed. Characteristic size of anisotropic microstructures has been estimated.

Hamdan et al.\textsuperscript{141} have reported the phase equilibria of AOT/Tween 20–hydrocarbon–water to prepare alcohol free microemulsions for potential use as carriers in pharmaceutical applications. The alcohol free microemulsions have been readily prepared at various weight ratio of surfactant to hydrocarbon (decane and $p$-xylene) and water. The microemulsion region is dependent not only on the surfactant ratios but also on the nature of hydrocarbon. It has been concluded that aromatic hydrocarbon show more defined area as compared to aliphatic hydrocarbon. Dielectric constants for AOT reversed micelles in cyclohexane at a frequency of 1 MHz and at temperature 25°C for molalities of AOT from 0 to 0.04 mol kg$^{-1}$ have been determined by Tanaka and Okazaki.\textsuperscript{142} The apparent dipole moments for the mixed solutes have been calculated. The process of formation of w/o microemulsions and the molecular interactions in the micellar core have been discussed in terms of hydration of AOT.

Kurumada et al.\textsuperscript{143} have qualitatively estimated the dynamical structures by dynamic light scattering and the rheological measurements for AOT–heptane–water–NaCl
system in the concentrated region up to 50-60% of volume fraction of molecular aggregates. A very slow mode of relaxation stands out, by introducing clusters of the aggregates owing to attractive interactions between the aggregates, with increase in volume fraction. Even at high volume fraction of aggregate, the effect of the attractive interactions is not negligible, but for higher salinity conditions, the retardation effect on the decay of the concentration fluctuations due to the attractive interaction is stronger.

Ferreira Marques and others\textsuperscript{144} have studied reverse micelles in AOT–isooctane–water mixtures as function of AOT concentration ($C_{\text{AOT}}$), $\omega$ and temperature (21 to 60°C) using positron annihilation life time spectroscopy (LS). The life time of organic phase corresponds to the value for isooctane but is lower than the value for pure water. This may be due to out-diffusion of positronium from water cores to isooctane. The diffusion equations imply two fitting parameters, radius of water aggregates and transmission factor. The sphere radius increases with $C_{\text{AOT}}$ and $\omega$ and more importantly with T. The value of sum of intensities is much lower than positronium intensity in isooctane but close to the value found for pure water. It has been thus concluded that positronium formation occurs primarily in the aqueous part of micelles, the water aggregates representing efficient traps for the positions while they are slowing down in the solutions.

Radiman\textsuperscript{145} has used freeze fracture electron microscopy in AOT–heptane–water system at $\omega$ = 65 to show the fairly monodisperse globular structure of the L$_2$ phase. It has been observed that significant polydispersion can be induced by adding water soluble polymer.

NMR and conductivity measurements have been used in AOT–decane–water system to study the mechanism of transport of components in the percolation region below and above the percolation temperature threshold by Feldman \textit{et al.}\textsuperscript{146} Transfer of charge carriers may take place by two different mechanisms \textit{i.e.} either by the transfer of counterions from one droplet to another through water channels or hopping of surfactant ions from droplets with in clusters. The results support the hypothesis that conductivity and dielectric polarization below percolation threshold is mainly due to first mechanism. Above the percolation threshold, the latter mechanism also appears but first mechanism still dominates.
Petrov et al.\textsuperscript{147} have presented results from the measurement of forces between macroscopic mica surfaces immersed in AOT-decane-brine system. Presence of lamellar like structures has been confirmed due to appearance of a force barrier at separation of 40–60 nm. The relative position of the sample with in the phase diagram has impact on the transition region. Close to excess water phase boundary, apart from the layered structure, attractive interactions due to capillary forces are observed. This attraction becomes dominant over the repulsive barrier closer to microemulsion/water phase boundary. On the border, only long range (~120 nm) attraction remains. In contrast to other samples of capillary condensation, the whole force profile has been measured. The above observed phenomenon is explained by simple thermodynamic model.

Baptista and Tran\textsuperscript{148} have studied microemulsion of negatively charged (AOT) and positively charged (dodecyl methyl butyl ammonium bromide and benzyl dimethyl hexadecyl ammonium chloride) surfactants below and above the percolation thresholds by electrical conductivity, near IR absorption and thermal lens spectrometry. AOT microemulsions undergo percolation at high concentration about 27% of water (v: v) and show no variation in the thermal lens effect (θ/ΔPo). In contrast, in microemulsions with positively charged surfactants, percolation occurs at low concentration (10% of water v: v) and it is in this region that thermal lens effect as a function of water undergoes changes. These results indicate that small reversed micelles are present in AOT microemulsions above and below percolation threshold whereas positive microemulsions form larger interconnected aggregates or bicontinuous structures in solution above percolation threshold concentrations.

Mays\textsuperscript{149} has reported the existence of clusters in w/o microemulsions of AOT by performing time resolved luminescence quenching measurements using the probe Tb (pda)\textsubscript{3}. The fast exchange has been attributed to intercluster quenching and is dependent on temperature. The slow exchange is due to intercluster exchange and is accelerated within one phase region. Below percolation threshold, rate constant obeys an Arrhenius relation but in percolation domain, it deviates from linearity due to aggregate collisions, which disturb the exchange transition state. The activation entropy has been discussed in terms of clustering entropy (ΔS\textsubscript{cl}) due to an aggregation equilibrium prior to exchange.
results reveal that, the upper phase boundary occurs due to the presence of strong interactions and micellar clustering while lower phase boundary represents the approach of spontaneous radius of curvature. FTIR spectroscopy analysis indicates a large percentage of "free" unbound solubilizate in the water pool of this system.

Nees and Wolff\textsuperscript{152} have photolyzed n-Methylhydroxy stilbazolium bromide in aqueous and non-aqueous AOT lyotropic liquid crystal systems and in isooctane based inverted AOT micelles or microemulsions. A competition between trans-cis photoisomerization and photodimerization is found. The AOT–glycerol phase diagram exhibits a lamellar phase between 35 and 75\% AOT wt/wt. and an inverted hexagonal phase at > 85\% AOT. The clearing temperatures $T_{L\text{I}}$ and $T_{\text{m}}$ were found to be sensitive to the presence of small amount of three n–alkylhydroxystilbazolium bromides and depends on its concentration and the degree of photoconservation. The phase transitions can be induced isothermally by irradiating samples at temperatures close to the transition temperatures.

A graft copolymer, with hydrophilic poly(ethylene glycol)monomethyl ether (MPEG) side chains grafted onto a hydrophobic poly(dodecylmethacrylate) (PDMA) backbone, has been synthesized and solubilized in AOT–cyclohexane–water microemulsion by Holmberg \textit{et al.}\textsuperscript{153} At low concentrations (1-3 \text{wt \%}), the copolymer increases the viscosity of system up to 100-fold whereas volume ratios of AOT, water and cyclohexane can vary viscosity only by 1 order of magnitude. The results are interpreted in terms of polymer droplet cross-linking, caused by the solubilization of the hydrophilic side chains into water droplets of the microemulsion.

Meier\textsuperscript{49} has studied the effect of polymer [poly(oxyethylene)] on L\textsubscript{2} phase of anionic and nonionic microemulsion systems. Attractive interactions between anionic surfactant and polymer lead to polymer adsorption at interface whereas in nonionic systems, due to repulsive interactions between polymer and surfactant only sterical considerations are important. Temperature induced cluster formations are shifted because of increase of surfactant monolayer's elastic bending modulus. This modulus influences directly the temperature--induced droplet cluster formation in w/o microemulsions. Polymer molecules larger than the droplet dimensions can only be dissolved in the
microemulsions with the help of these attractive polymer/surfactant interactions and cause a polymer-induced droplet cluster formation. These results indicate that microemulsions have a great potential as a model system for the study of polymer/colloid interactions.

Marchio and Douglas\textsuperscript{154} have recovered Bovin serum ablumin (BSA) from AOT–isoctane–water microemulsion as a solid precipitates that is virtually free of surfactant by the addition of isoctane or 0.01 v/v 1-butanol. The recovery has been greater when the fractional occupancy of BSA is higher and the extent of dilution is greater. Proteins, which interact with the microemulsion interface, are more likely to be recovered.

Steady state and transient techniques have been utilized by Laia and Costa\textsuperscript{155} to study the photophysics of fluorescent probe bis [4–(dimethyl amino)phenyl] squaraine (HSq) in AOT–isoctane–water microemulsions. The interaction of HSq with water occurs only in excited state and is rate controlled with bimolecular rate constant \( k_q = 3.87 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1} \) accounting for non-radiative processes. The parameters obtained enable the distinction of processes occurring in the hydrophobic and hydrophilic interfacial domains and the estimation of number of water molecules per AOT molecule in each domain, respectively three and nine.

The effect of SDS and 1-octanol on the phase behaviour of AOT–decane–water/NaCl system has been studied by Sager.\textsuperscript{156} The two additives have been chosen to mimic the effect of surface-active impurities such as hydrolysis products of AOT. The study has been carried out to clarify some contrariety of AOT phase diagrams and to explain the origin of an isolated two-phase island, which is peculiarity of AOT system.

2.2 Triton based systems

In the literature, there are fewer reports pertaining to Triton based microemulsions. Therefore binary mixtures of Triton have also been included in the present review.

Conductance measurements have been used by Moulik and group\textsuperscript{157} in the determination of extent of micellar hydration of TX-100 micellar solution in 5 mM NaCl. In addition, intrinsic viscosity has helped in evaluating asymmetry of the micellar particles and their average axial ratio. The shape of micelles has been observed to be oblate spheroids, whose sizes are variable with temperature. Micellar volume, hydrated radius,
radius of gyration, diffusional coefficients and partial molar volumes of TX-100 micelles have been determined. Comparison of partial molar volumes of TX-100 micelles with molar volume of pure TX-100 have suggested a volume contraction due to immobilization of the water phase by the hydrophilic head groups of TX-100. Both urea and tetraethyl ammonium bromide have decreased the intrinsic viscosity while Na₂SO₄ has increased it significantly at low concentrations and has finally decreased intrinsic viscosity at high concentration.

To confirm the validity of Bruggeman’s equation of hydrated dispersions, the extent of hydration of five poly(ethylene glycol) (PEG 200, 300, 400, 600, 1000) has been determined from the measurement of viscosity and conductance by Moulik and coworkers.¹⁵⁸ The Bruggeman equation has been applied to evaluate the extent of hydration of 16 o/w microemulsions derived from both aliphatic and aromatic oils (hexane, heptane, decane, xylene, toluene) and stabilized by two nonionic surfactants (TX-100 and Tween 20) and three cosurfactants (1-butanol, 1-hexanol and n-hexylamine). The hydration of microemulsions depend on the type of surfactant, surfactant/cosurfactant ratio as well as oil type. Xylene and toluene derived microemulsions have exhibited greater hydration than those derived from hexane, heptane and decane.

Rau et al.¹⁵⁹ have used Pyrene excimer fluorescence to study the structure of TX-100 aqueous micelles. Critical micellar concentration (CMC) has been found to be temperature independent. With rise in temperature, aggregation number increases while number of micelle decreases. The micellar and liquid crystal phases of aqueous TX-114 and aqueous C₁₋₋CONH(CH₂CH₂O)₆CH₂CH₂OH surfactant systems have been studied by Heusch.¹⁶⁰ Mesomorphism occurs down to CMC. Lamellar phases occur in the miscibility gaps.

Sharma et al.¹⁶¹ have measured enthalpies and heat capacities of aqueous solutions of TX-100 both in monomeric and micellar states at 25, 35 and 45°C. From the data enthalpies and heat capacities of micellization (ΔHₘ and ΔC_pₘ) at 30 and 40°C have been evaluated. With increase in temperature, ΔC_pₘ decreases in both states but decrease in micellar state is more prominent. The results have been interpreted in terms of the temperature dependence of hydrophobic hydration of the monomers and the micelles.
NMR study of 3-component (TX-100, iodine, carbon tetrachloride) system carried out by Rakshit and Dixit\textsuperscript{162} have shown that the solubilized iodine is present in the reverse micelles and that the surfactant interacts with iodine through O of –OH group present in the core. Rakshit and group\textsuperscript{163} have also determined CMC of mixed aqueous solutions of cationic (CTAB) and nonionic (TX-100) surfactants conductometrically at 35–50°C and at various composition ratios of surfactants (keeping concentration of TX-100 constant and varying concentration of CTAB). From the slope of electric conductance and concentration plots above and below CMC, degree of ionisation of mixed micelles has been calculated. The wetting properties, foaming efficiency and viscosity of mixed surfactants have been measured at 45°C.

In another study, the phase diagram, viscosity, adiabatic compressibility, specific conductance and contact angle of nonaqueous microemulsion system containing TX-100–cyclohexane–DMF has been determined\textsuperscript{164} at 40°C. By the addition of cosurfactant (1–propanol), one phase microemulsion area is increased and the system shows percolation. Contact angle measurements of TX-100–cyclohexane–DMF system at various cyclohexane /DMF ratios show a DMF continuous system but in the presence of 1–propanol, the contact angle values show a continuous change indicating an O/DMF to bicontinuous to DMF/O structure. NaI does not introduce a three phase liquid system.

They have also determined the pseudoternary phase diagram\textsuperscript{165} of TX-100–ethylpropionate–cyclohexane–water system at 30°C. The one phase microemulsion area has been obtained over a small area. Viscosity, conductance and adiabatic compressibility values at various temperatures show the expected trend. The addition of NaCl changes the one phase microemulsion to a Winsor II system, no Winsor III system has been obtained. Conductance and contact angle data show an oil continuous system at a constant surfactant weight fraction. The microstructure of the Winsor IV seems to be w/o microemulsion.

Time domain spectroscopy has been used by Sjoeblom and Gestblom\textsuperscript{166} to measure the dielectric spectra of Triton N-42–dodecane–water system between 50MHz and 11GHz. The permittivity has been discussed in relation to the models consisting of rather well-defined aggregates. Several dielectric dispersion regions have been observed and the
relaxation modes are attributed to the relaxation mechanisms of the different chemical compounds within the microemulsions.

Marszall has observed that the cloud point of mixed ionic-nonionic surfactants (SDS–TX-100) is lowered drastically by a number of electrolytes at lower concentration than the cloud points of nonionic surfactants only. The results have indicated that the factors affecting the clouding phenomenon of mixed surfactants at low concentration of ionic surfactants are electrostatic in nature. The change in the original charge distribution of mixed micelles at a fixed SDS–TX-100 ratio as a function of electrolyte concentration, depends mostly on the valency number of the cations (counterions) and the kind of the anion (co-ion) and is independent of the type of monovalent cation (counterion).

La Mesa et al. have studied the phase diagram of TX-100–decanol–water system. The phase sequence has been rationalized by introducing a model, which accounts for entropy of mixing terms, surface energy terms, packing constrains and hydration forces. The model has been used to predict the region of existence of micellar and hexagonal phases. For the latter the agreement with experiment is satisfactory. With regard to the micellar region, the agreement is less good, since the model does not account for the micelle shape and size transitions.

In another study, the group has determined the phase diagram of the system composed by water, glycerol, TX-100, an industrial aryl alkyl surfactant with polyoxyethyleneglycol chain as polar head group, in wide temperature range, to get information on the links between solvent effect and the formation of organized surfactant assemblies. The occurrence of solution and anisotropic phases is quite sensitive to the amount of glycerol as well as to the temperature. Experimental study on transport properties has been made to get information on aggregate structure, as well as on micelle size and shape on obstruction to solvent free diffusion.

Dörfler and Borrmester have mapped the phase diagram of non-aqueous microemulsions formed by four components of the type, TX-114 – pentanol–dodecane–water/DMSO/γ-butyrolactone/acetonitrile. The substitution of water by polar liquids have increased the phase region of microemulsions in ternary phase diagrams in the sequence water < acetonitrile / γ-butyrolactone < DMSO. With increasing temperatures an
extension of microemulsion region has been observed whereas presence of electrolyte NaClO₄ produces the opposite effect. The formation of microemulsion in butylmonoglycolether-decane-formamide/ethyleneglycol/1,3-butyleneglycol systems, is similar except that the regions are not dependent on temperature.

Zhu et al. have investigated the effects of water content, temperature and presence of CaCl₂ on aggregation number, surfactant monomer concentration and size of aggregates of reverse micelles of TX-100 in cyclohexane using partial pressure-vapor pressure osmometry and quasielastic light scattering techniques. Addition of water reduces monomer concentration while raising temperature increases it. At 30°C and ω=10 aggregation number reaches a maximum of n = 40.4. Apparent size parameter of dry reverse micelles i.e. hydrodynamic diameter (Dₜₐ) of dry reverse micelles at 25°C is constant in concentration range investigated and decreases in the order

Wet reverse micelles > salt-containing aggregates > dry reverse micelles.

A model is proposed for the description of the observed aggregation behaviour, which is based on the penetration of cyclohexane into the polar core of TX-100 reverse micelles.

Pal has used coaxial cylinder viscometer to study the rheological behaviour of o/w emulsions prepared from TX-100 at different concentrations. The emulsions produced at high surfactant concentrations are highly flocculated in nature whereas their rheological behaviour is of non-Newtonian, shear thinning type. The presence of a yield stress has been indicated.

Self diffusion coefficients for both aqueous solution and neat TX-100 have been calculated by Slisenko et al. by studying quasi elastic light scattering of slow neutrons at different surfactant concentrations above and below CMC. The vibrational state lifetimes and diffusion jump lengths have been calculated.

Cummings et al. have discussed the increased fluorescence intensity of pyrene due to indirect excitation by TX-100 in mixed solutions of pyrene, TX-100 and β-Cyclodextrin (β-CD). The ternary complex is formed below CMC because above CMC, pyrene is displaced from β-CD cavity, which is accompanied by a subsequent incorporation of pyrene into the interior of micelle.
The CMC and aggregation number of TX-100 in the mixture of ethyleneglycol and water have been measured by Ye et al. using surface tension and fluorescence decay methods. The discontinuity of the surface tension curves indicate that TX-100 forms micelles in ethyleneglycol, although its CMC (0.05 M at 20°C) is greater than that of water. The aggregation number of TX-100 in ethyleneglycol from fluorescence decay is 25 (30°C) in comparison with 97 in water. The aggregation number is reduced by addition of ethyleneglycol in aqueous solutions of TX-100. These results can be interpreted in terms of more favourable interactions between molecules of ethyleneglycol and TX-100 than between water and TX-100.

Subramani and Madamwar have studied the influence of glycerol and NaCl on the stability of arginase entrapped in reverse micellar system TX-100–hexanol–hexane. The entrapped enzyme shows improved stability, further enhanced by the addition of glycerol and NaCl. SANS measurements have been reported by Goyal et al. for micellar solutions of TX–100 in D₂O for a wide range of concentration at ambient temperature. The analysis of data at ambient temperature shows that the micelles are oblate ellipsoids of revolution with an axial ratio around 2 even at low TX–100 concentration (1%). In the hydrophilic region about 20 moles of D₂O per surfactant molecule has been observed. Information about intermicellar interactions is obtained by applying Baxter’s sticky hard model on experimental data. The model provides a qualitative interpretation of the temperature dependence of data.

The effect of formic acid, acetic acid, oxalic acid, methanol, ethanol, propanol, glycol, glycerol and glucose on the cloud point of nonionic surfactants TX-100 and TX-114 has been determined by Wu and Gu. The addition of aliphatic acids and alcohols increase the cloud point whereas presence of glycerol, glucose, glycol decrease it. These effects have been explained in terms of surfactant solubility.

The characteristic radius, scattering density, specific surface area, degree of hydration and aggregation number of micelles formed by aqueous (H₂O–D₂O mixture) solutions of TX-100 have been determined by Bulavin et al. Micelles formed in TX-100 solutions with concentrations below 9.6 mmol/dm³ have a constant characteristic radius of 7.6 nm. As the concentration increases, the character of interaction between micelles
changes, which is reflected by the total hydration and steric reputation prevailing over the vander Waal’s attraction.

Sharma et al.\textsuperscript{179} have measured surface tension and specific conductance for aqueous solution of DTAB and TX-100 in pyridine at 25, 35 and 45°C to evaluate surface and thermodynamic properties of micellization, absorption of liquid-air interface and transfer of surfactant from aqueous to mixed solvent (water + pyridine). Counter ion association constant ($\alpha$) and limited equivalent conductance ($\Lambda_0$) have been calculated from conductance data. Micellization is favoured both by entropy gain as well as energy effects in DTAB system but in TX-100–pyridine–water system, it is favoured by a large entropy gain alone.

The positron-annihilation technique (PAT) has been applied by Das and Ganguly\textsuperscript{180} to study the molecular association phenomenon of TX-100 and formation of reversed micelles in mixed solvents of butanol (Bu) and $n$-heptane (Hp). The Positronium (Ps) parameter is sensitive to self-aggregation phenomenon of TX-100. At a critical concentration of surfactant 1.5 mM coined as the operational CMC of TX-100 in both (1:1) and (1:2) Bu-Hp system, the intensity of long lived Ortho-Ps component, $I_3$ and its life time $\tau$3, Para-Ps intensity show a remarkable change.

Gu and Schelly\textsuperscript{181} have investigated reverse micelles and w/o microemulsions of three individual polyoxyethylene p-tert.-octylphenylether (OPE$_n$, $n = 5,7$ and 9) components in TX-100 and cyclohexane by controlled partial pressure vapour pressure osmometry (CPP–VPO), dynamic light scattering and transient electrical birefringence methods. The mean aggregation number, apparent hydrodynamic diameter and probable shape of the aggregates as a function of water content $\omega$, temperature and concentration of surfactant and cosurfactant ($n$-hexanol if added) have been calculated. The effect of length of the hydrophilic chain of surfactant and the presence of cosurfactant on equilibrium properties and dynamic behaviour of the aggregates have been described.

Mandal \textit{et al.}\textsuperscript{182} have studied solution dynamics of 4-aminophthalimide (4-AP) in w/o microemulsions of TX-100 in mixed solvents containing 30% benzene and 70% $n$-hexane by using picosecond time-resolved stokes shift. The steady state emission spectrum of 4-AP in this microemulsion is different from that in TX reverse micelles or in water.
indicating that in microemulsion 4-AP molecule stays in water pool and the micropolarity of water pool is very much different from that of bulk water. In TX microemulsions 4AP exhibits wavelength dependent fluorescence decays and a growth in nanosecond time scale at long wavelength. The solvation dynamics of 4-AP in TX microemulsion is bimodal with a short component of 0.74 ns and a very long component of 29.73 ns. This is similar to the solvation dynamics of coumarin 480 in AOT microemulsions in the large water pools of AOT-decane-water microemulsion.