CHAPTER 3

PHYSICOCHEMICAL PROPERTIES OF TRITON X 100 MICROEMULSIONS

3.1 Preview

Microemulsion is a multicomponent mixture of two immiscible liquids, oil and water stabilized by a surfactant or a mixture of a surfactant and a cosurfactant. Prerequisite for studying the properties of such fluid mixtures is a knowledge of their phase diagram as it is a function of temperature, pressure and the nature of components. Preliminary study of microemulsion involves the determination of the phase diagram[232-236]. This also indicates the total number of phases, the nature of phases at any composition as well as the transition point between the phases. The phase diagram is generally plotted as an equilateral triangle where each corner represents one of the pur components. The surfactant-cosurfactant mixture (S) is considered as one component only for this purpose and occupies one corner of the triangle . The water (W) and oil (O) are the other two components and pure water and oil occupy other two corners of the triangle. In this chapter, we have discussed the pseudoternary phase diagram formed by cyclohexane/TX100+n-propanol (1:2)/water; cyclohexane/TX100+n-propanol (1:2)/DMF and cyclohexane/ TX100+ethyl propionate/water. Physical properties like, conductance, viscosity, adiabatic compressibility, contact angle, cloud point, fish phase diagram studies were carried out and the discussed. Experimental procedures were discussed in detail in chapter 2.

3.2 Results and Discussion

a. Phase Diagram

Fig 3.1 shows the pseudoternary phase diagram of an aqueous system composed of cyclohexane/TX100+n-propanol/water with 1:2 surfactant to cosurfactant weight ratio at 40°C. TX100 was used as the surfactant because of its

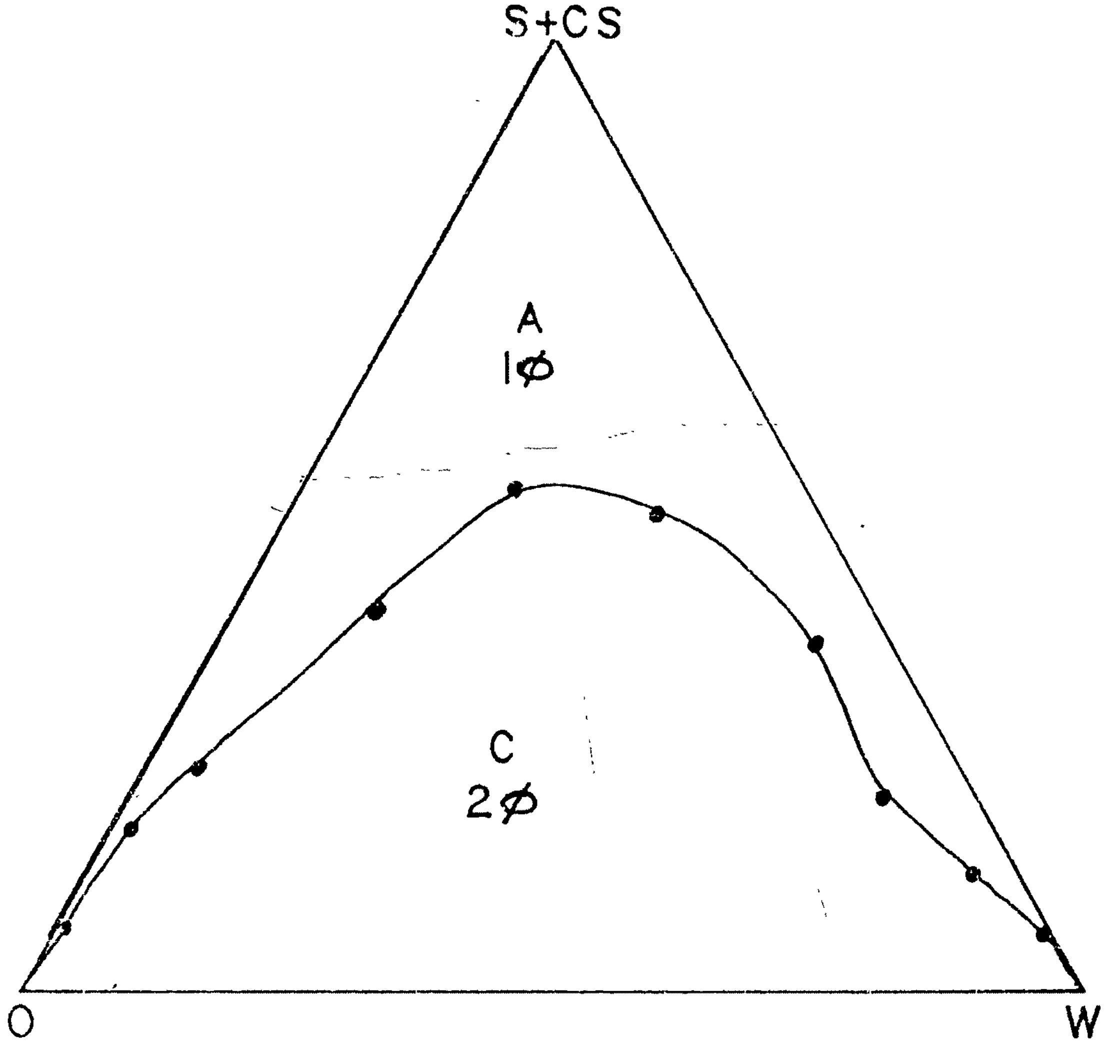
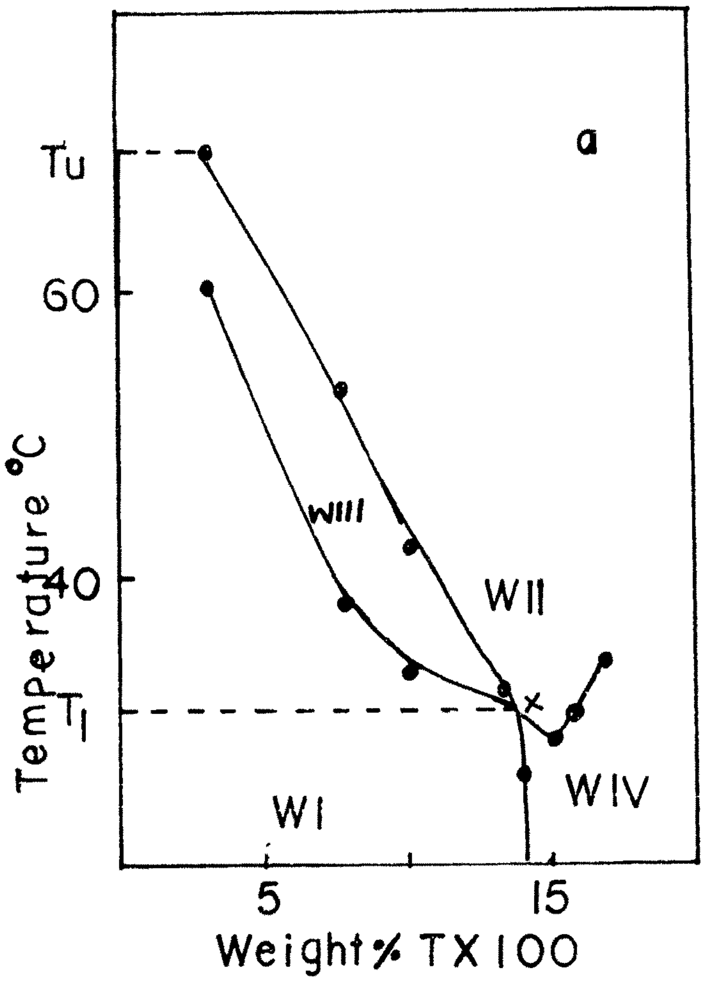


Fig. 3.1 Pseudoternary phase diagram of cyclohexane/TX100+n-propanol (1:2)/water at 40°C.



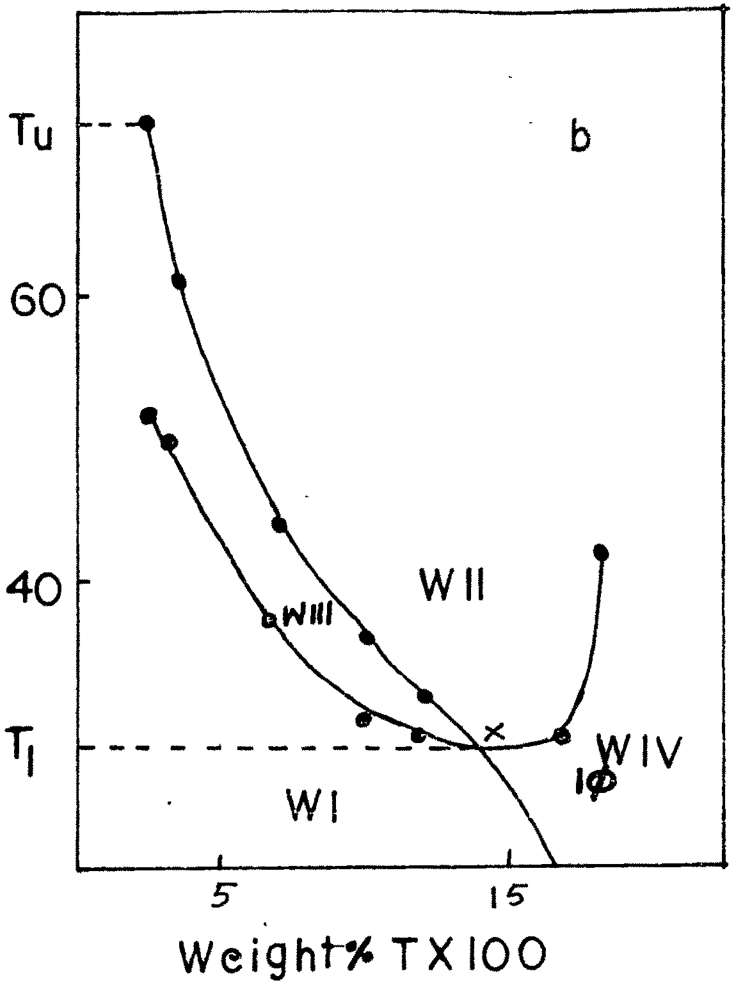


Fig.3.2a Fish phase diagram of cyclohexane / TX100 + n - propanol (1:2)/water; 20% water

Fig.3.2b 20% cyclohexane

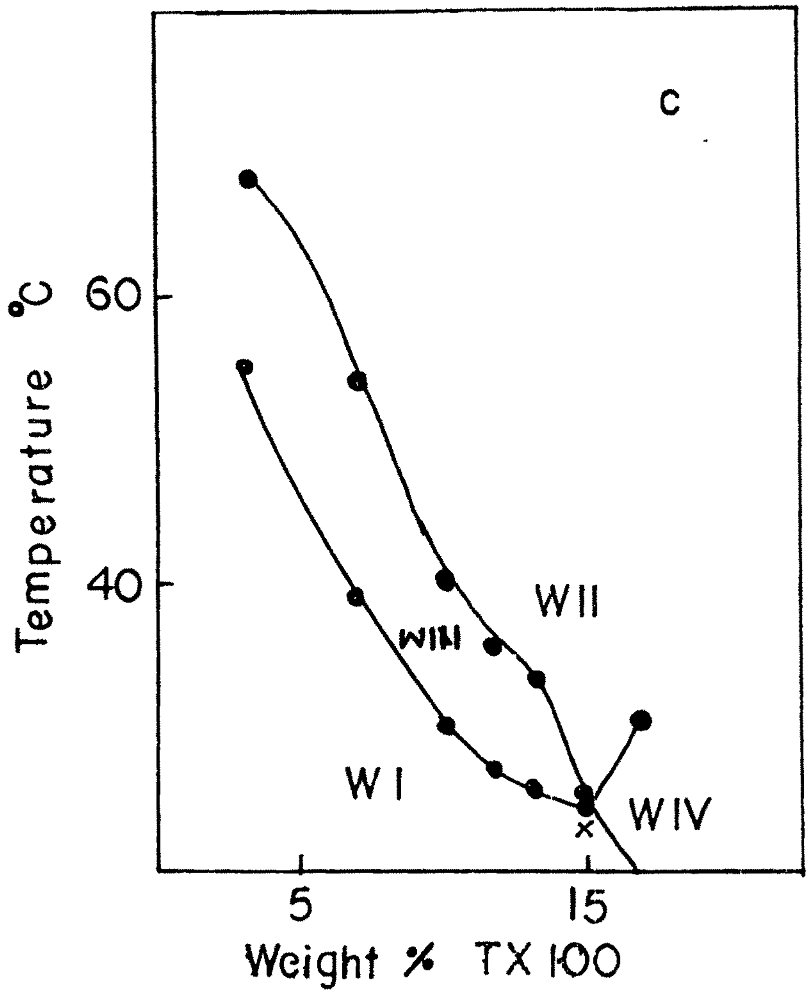


Fig.3.2c 1:1 (w/w) O/W.

industrial applications.[237-239] n-propanol was the cosurfactant. Water and cyclohexane ~~was~~ were used as the polar and nonpolar solvents, respectively. The phase diagram shows two distinct regions. The boundary line shows the region of phase separation. Generally, the surfactant - water and the surfactant - oil miscibility gaps determine the phase diagram pattern. Above 55% surfactant (S+CS)), it shows a single phase microemulsion [Winsor IV, (WIV)] at any oil/water ratio and WIV extends to both oil and water corners. Below this surfactant composition, it shows a liquid-liquid biphasic region. With high amount of surfactant, the interfacial tension gets reduced, due to the presence of S+CS monolayer at oil/water interface.

Fish Phase Diagram

At ambient temperatures nonionic amphiphiles are in general completely miscible with water and hence a WI type microemulsion exists. With further increase in temperature, oil becomes increasingly a better solvent due to the dehydration of TX100 and water expels out forming a WII microemulsion. At the intermediate temperature, H_2O-oil-amphiphile mixtures separate into three coexisting liquid phases (WIII) within a well defined temperature interval $\Delta T = T_u - T_l$. Where T_u and T_l are the temperature corresponds to the maximum of the upper boundary of the three phase body and minimum of the lower boundary of the three phase body respectively. At the mean temperature T of ΔT, one finds a maximum of the efficiency of the amphiphile in homogenizing water and oil and a minimum of the interfacial tension between the water rich and the oil phase.

The phase equilibria is shown (Fig 3.2a, 2b, 2c) by the temperature versus weight fraction of surfactant. At higher surfactant concentration the extension[56,240] of one phase and multiphase region occurs. It shows a fish type structure. This type of nature was also observed by Strey et al.[240] and Kahlweit et al.[56] The extension of the three phase region decreases with increasing TX100. At very high surfactant concentration, we get a WIV microemulsion only. The minimum of the lower boundary of the three phase body gives T_l, the maximum of the upper measure for the efficiency of the amphiphile, namely the minimum amount of amphiphile required for completely solubilizing water and oil. Smaller the value of α, the more efficient the amphiphile is or larger the solubilization capacity. The point X is defined by α and its temperature T(which lies close to the mean temperature $\bar{T}$) of the three phase body. Below and above T, the efficiency of the amphiphile is much lower and differs. Because the three phase body does not lie parallel to the base, the mean temperature $\bar{T}$ of the three phase body loses its meaning[11].

Phase rule can be applied to the triple point at which all the Winsor regions coexist. If 'f' is the number of degrees of freedom, 'n' the number of components, and 'p' is the number of phases of the system, the phase rule can be written as [241].

$$f = n - p + 2 \qquad \text{..........(2)}$$

2 refers to the independent variables, temperature and pressure. In a microemulsion, concentration of microheterogeneous particles is to be considered as it affects the thermodynamic properties of the system. For a 1ϕ system, obeying above equation, there are (n-1) independently variable concentrations assuming n=4 and (n-2) and (n-3) for 2ϕ and 3ϕ systems respectively. So the independently variable concentrations are 3, 2, 1 for 1ϕ, 2ϕ, 3ϕ systems respectively. So the number of degrees of freedom at the triple point is 4-6 + 2=0. So when either temperature or concentration changes, the number of degrees of freedom also changes.

The separation of three phases arises from the interactions between the tail part as well as the head part of the TX100 with the solvent at different temperatures[56]. This phenomenon is explained by Aveyard et al[242] by the effective cross sectional areas A_h of the hydrophilic head group and A_t of the hydrophobic chain under condition where $A_h > A_t$, two phase systems consisting of an oil-in-water (O/W) microemulsion in equilibrium with an excess oil phase (WI) can be formed. W/O microemulsion in equilibrium with an excess aqueous phase are formed when $A_h<A_t$. If $A_h \approx A_t$, a bicontinuous structure is promoted.

Therefore, a mutual solubility is achieved and hence the formation of a Winsor IV system. With lesser amount of surfactant and a larger amount of either of the liquids, a narrow region of 1ϕ microemulsion towards the oil and water corners are obtained. The role of surfactant-cosurfactant mixture at the interfacial film is to reduce the interfacial tension between the oil and water and thereby achieve the solubility. With less amount of surfactant and the high amount of oil and water, the interfacial tension between cyclohexane and water is not reduced to form a 1ϕ microemulsion and it remains a liquid-liquid biphasic region. Only, a very small amount of oil or water gets solubilized in water or oil respectively. With less amount of either water or oil, the interfacial tension is reduced so that they solubilize each other to form a 1ϕ microemulsion. In presence of n-propanol, the system does not show any liquid crystalline region as it inhibits the liquid crystal formation. In otherwords, the alcohols tend to reduce the chain-chain interaction energy of the primary amphiphiles stabilizing the microemulsion [109]. The percent areas of 1ϕ and 2ϕ regions are given in Table 1.

Fig 3.3a shows the nonaqueous pseudoternary phase diagram composed of cyclohexane/TX100/DMF. N, N-Dimethyl formamide (DMF) was used as the polar liquid instead of water. Many organic chemical reactions are possible in this medium because of the high solubility of the reactants in the polar and nonpolar medium. This system shows two distinct regions in the phase diagram like that of aqueous system. Above the boundary line, the system exists as a monophasic microemulsion and below it, there is a biphasic region. The surfactant apex shows a single phase region and this gradually extends to the DMF corner. At higher concentrations of cyclohexane, the solubility decreases and a liquid-liquid biphasic region exists where the microemulsion is in equilibrium with excess cyclohexane (oil). Formation of a one phase micellar system in a cyclohexane - DMF mixed solvent is possible at high cyclohexane and low DMF concentration.

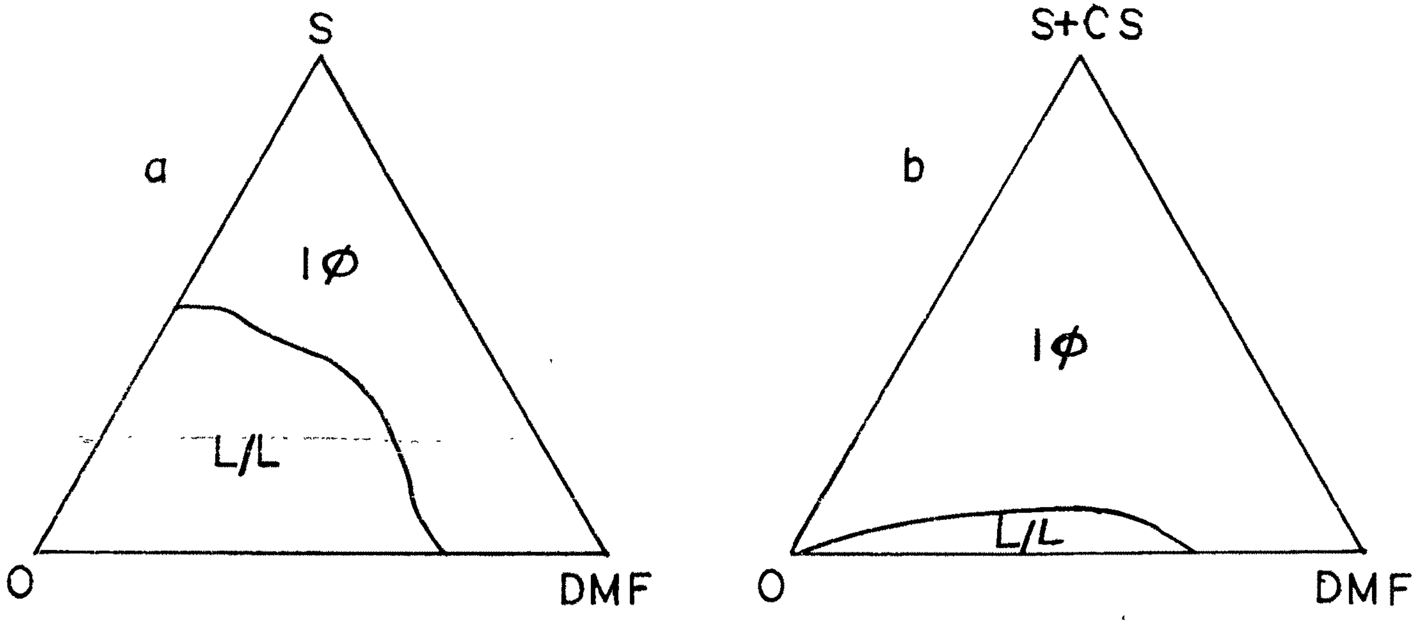


Fig.3.3 Pseudoternary phase diagram of

a. Cyclohexane/TX100 /DMF at 40°C
b. Cyclohexane / TX100 + n-propanol (1:2)/DMF at 40°C.

However, as the concentration is low, it is difficult to show the region in the phase diagram, at this scale.

Fig 3.3b shows the effect of n-propanol as the cosurfactant on the phase diagram. It shows a drastic effect in increasing the one phase region. The one phase microemulsion area covers almost 90% of phase diagram. Below 10%S concentration, there exists a liquid - liquid biphasic region around the 50% cyclohexane concentration range. As the cyclohexane concentration increases and that of DMF decreases, more monophasic microemulsion area becomes available by the addition of n-propanol. When medium chain alcohol is chosen, both the oil and the alcohol are only partially miscible with water, it enters the amphiphilic monolayer and reduces the interfacial tension between cyclohexane and DMF further and hence increases the efficiency of the amphiphile and this results in a larger one phase area[109,244]. Generally, nonionic surfactants show liquid crystalline phase in presence of water but TX100 with DMF did not show such phase[59,232,233]. Glycerol, formamide with alkyl polyglycol ether and hydrocarbon[59] also does not show any liquid crystalline region. We have also observed the same.

A pseudoternary phase diagram was constructed at 30°C with ethyl propionate as cosurfactant by replacing n-propanol (Fig 3.4(a-c)]. The surfactant to cosurfactant weight ratio is 1:0, 1:1 & 1:2 respectively. Esters are an important group of compounds used in cosmetics and also in pharmacy,[243,244] and an evaluation of the conditions to prepare microemulsions from this class of compounds would therefore fill an important need.

At surfactant apex we get a one phase microemulsion extending towards the oil corner for 1:1 system. The centre of the phase map shows a large viscous region and the base of the phase diagram shows a liquid-liquid biphasic region. A small one phase microemulsion region at the water corner was also observed. The viscous fluid was found to be liquid crystalline with crossed polaroids in a polarizing microscope[243]. The liquid crystal formation occurs due to the strong

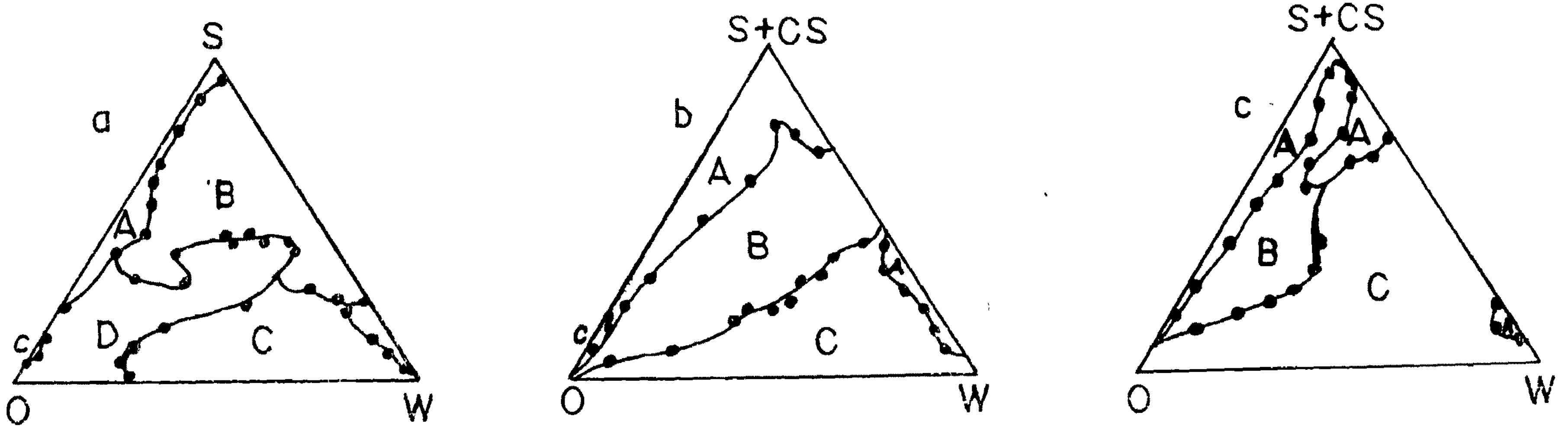


Fig.3.4 Pseudoternary phase diagram of

a. Cyclohexane/TX100 / Water at 30°C
b. Cyclohexane/TX100 + ethyl propionate (1:1)/Water at 30°C.
c. Cyclohexane/TX100 + ethylpropionate (1:2)/Water at 30°C.

Table 1 : **% area of various regions of pseudoternary phase diagrams.**

Region	O/TX100+P(1:2)/ W	O/TX100/DMF	O/TX100+TP(1:2) /DMF	O/TX100/W	O/TX100+EP(1:1)/W	O/TX100+EP (1:2)/W
A 1ϕ	35.2	57.0	90.7	8.8	22.4	22.2
B Visc	-	-	-	35.3	40.3	32.0
C 2ϕ (L/L)	64.8	43	9.3	30.7	37.3	45.8
D 2ϕ L/Vis	-	-	-	25.2	-	-

chain-chain and head-head interaction between surfactant molecules due to long, straight chains and close packed heads. Since, there is much less space available for solubilization in rigid liquid crystal structures than in the more flexible types of micelles, the liquid crystal formation limits the solubilization capacity of the solution.

Ethyl propionate is highly hydrophobic and seems not to have much effect in reducing the oil-water interfacial tension. Hence one phase microemulsion is difficult to get with small percentage of surfactants. With higher surfactant concentration, interfacial tension gets reduced to a low value and it solubilizes both oil and water, forms a monophasic region around the surfactant apex. With very small amount, i.e. very low percentage of cyclohexane, interfacial tension is sufficiently reduced to solubilize both the water and ethyl propionate in presence of TX100 at the interfacial film. However, with 1:2, TX100-ethyl propionate weight ratio, the phase map becomes complicated (Fig. 3.4b). One phase microemulsion region is a narrow strip along the oil-surfactant axis. However, the overall 1ϕ area remains essentially same in both cases. A large liquid-liquid biphasic area was obtained. This seems to arise at the cost of viscous region of Fig 3.4b.

Higher percentage of ethyl propionate decreases the solubility of TX100 due to its higher hydrophobicity. In Table 1, the percent area of various regions of phase diagram under both conditions are presented. We believe that the one phase liquids obtained area A of the Figs 3.4 (a-c) are microemulsions and are not molecularly dispersed simple solution. This is because, by definition, a homogeneous mixture of oil and water in presence of surfactant is a microemulsion.

TX100 forms reverse micelles in cyclohexane, ethyl propionate and also in there mixtures 1:1 (v/v). We used the iodine solubilization[246] method to find the reverse cmc (rcmc) values and these were 1.6, 2.0 & 2.51 mM at 30°C respectively.

This shows that the system is microemulsion with the possibility of droplet formation. These are much higher than those in water and this was reported earlier by E.W. Kaler and coworkers[59] who suggested that the surfactants in various nonaqueous media aggregate into micelles. The higher cmc suggests that the aggregation and the structure formation are more inhibited in nonaqueous medium. In Table 1, the percent area of various regions of phase diagrams are presented.

b. Conductance

Specific conductance versus weight fraction of water in fig 3.5a shows steady increase in conductance indicating the same structure for the monophasic region studied. It does not show any percolation,[247,248] a sudden change in conductance indicating a microstructural change when the amount of water and the temperature change.

Variation of specific conductance with temperature shows the normal trend. It increases with increasing temperature due to the greater increase in the movement of the ions of higher kinetic energy gained by increasing the temperature. However, it does not show percolation due to temperature also. The phenomenon of percolation is studied by applying the scaling equation [249,250].

$$\sigma \quad = k\,(\phi_w - \phi_w^P)^t$$

where ϕ_w & ϕ_w^P are the water volume fraction and percolation threshold respectively. The exponent 't' depends upon the value of ϕ_w. For low values of ϕ_w, 't' assumes the value of 8/5, but changes to unity at higher values of ϕ_w. The conductance at low ϕ_w obeys the relation $\sigma \alpha\, (\phi_w - \phi_w^P)^{8/5}$.

On plotting $\sigma^{5/8}$ against water fraction ϕ_w, at low ϕ_w, the intersection of the X-axis (i.e. ϕ_w) with σ is ϕ_w^P, termed the percolation threshold. $\sigma^{5/8}$ vs ϕ_w plot (Fig 3,5b) at low ϕ_w passes through the origin. This means the absence of percolation threshold. This also indicates no drastic structural change in the

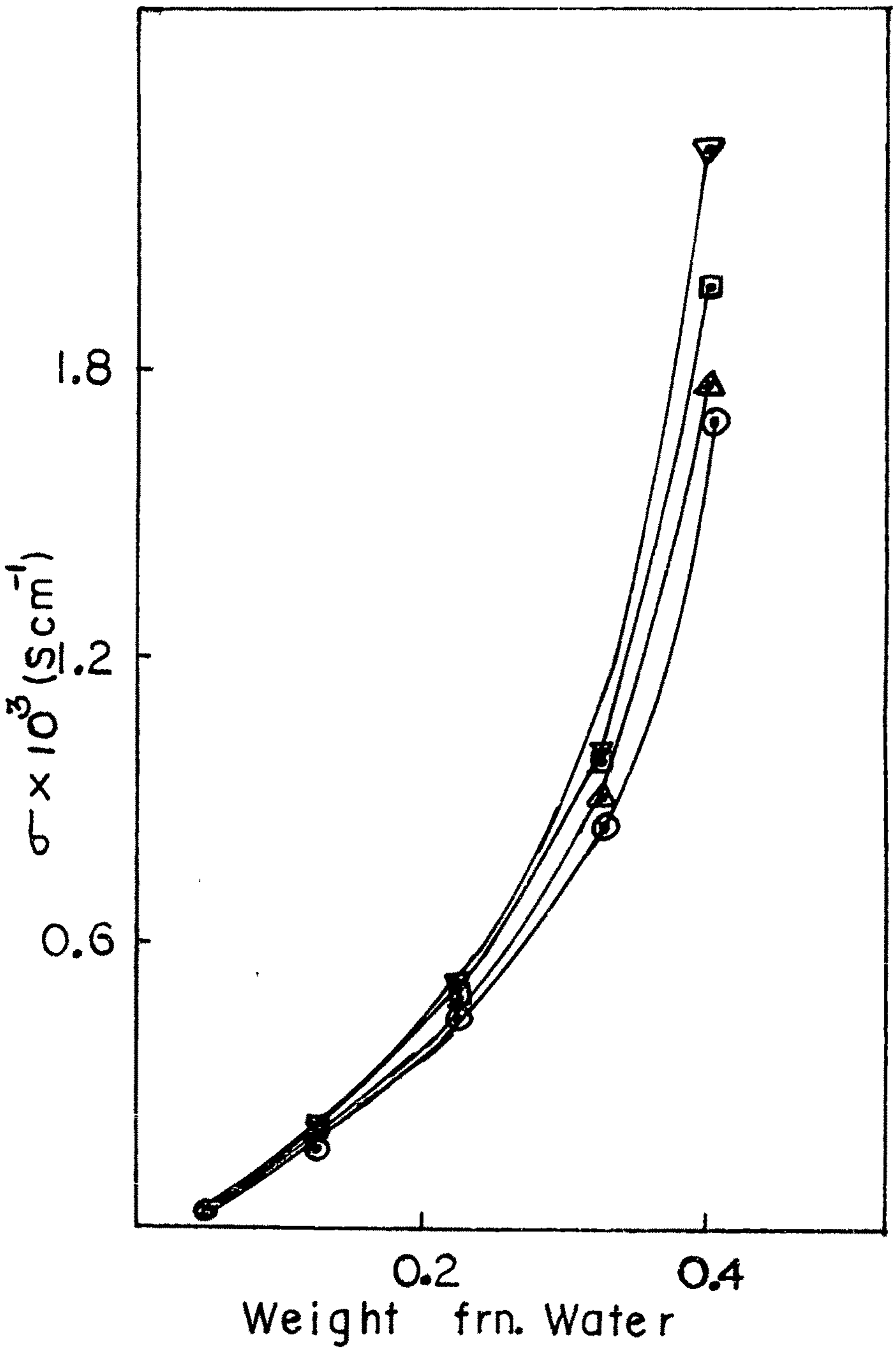


Fig 3.5a Plot of specific conductance (σ) vs weight fraction of water for cyclohexane/TX100 + n-propanol (1:2)/Water.
⊙ 30°C; ◬ 35°C; ⊡ 40°C; ▽ 45°C

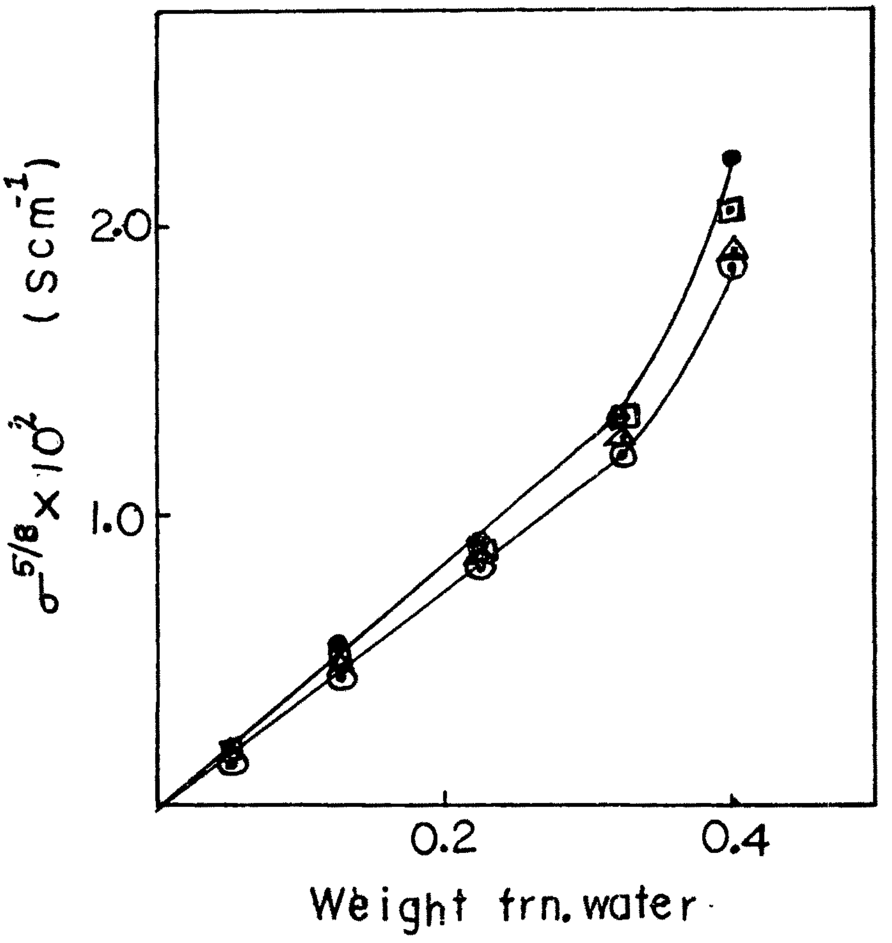


Fig. 3.5b Plot of $\sigma^{5/8}$ vs weight fraction of water for cyclohexane/TX100 +n-propanol/water.

⊙ 30°C; △ 35°C; ⊡ 40°C; ● 45°C

system. The structure is probably bicontinuous where interconnected conduits of water in oil medium or vice versa are present. In this case water forms interconnected conduits giving the pathway for the movement of ions (Fig 1b).[251,252] The water channels are assumed to be rapidly fluctuating, disconnecting and reforming and thus allows the ions to move through the conduits.

For nonaqueous system, the specific conductance increases from a low DMF content to a high DMF content at 15% S concentration (Fig 3.6a). Sodium iodide (0.01M) used as the electrolyte to induce the conductance. The system does not show any percolation behavior which suggests a single structured form at different compositions studied. The specific conductance increases gradually as the DMF concentration is raised. This suggests the absence of percolation and also the absence of any microstructural change. The increase is much sharper in the system where a cosurfactant n-propanol was present. This indicates that percolation cannot be totally neglected when n-propanol was also present. However, no percolation was observed in an alkane/Brij 35+n-propanol/water nonionic aqueous microemulsion.[253] The steady increase in specific conductance with the addition of DMF suggests a similar type of structure over the entire cyclohexane/DMF range studied. In the aqueous microemulsion of Brij 35,[253], percolation was observed at high W/S ratios. We have not studied a system with a higher DMF/surfactant weight ratio. However, in the presence of n-propanol, the DMF/TX100 ratio becomes much higher. When NaI is the electrolyte, it resides in the DMF pool of the microemulsion. The structure is bicontinuous and a DMF continuum. At a high cyclohexane concentration, a change to a cyclohexane continuum also seems to occur as O/D ratio becomes very high.

It was suggested by Ninham et al[254,255] that the specific conductance of a microemulsion, is proportional to the volume fraction of the polar solvent DMF, ϕ_D. i.e. $\sigma\alpha(\phi_D-\phi_D{}^P)^t$ where $\phi_D{}^P$ is the percolation threshold, i.e. the concentration above which percolation can be seen. It was also suggested that for a bicontinuous

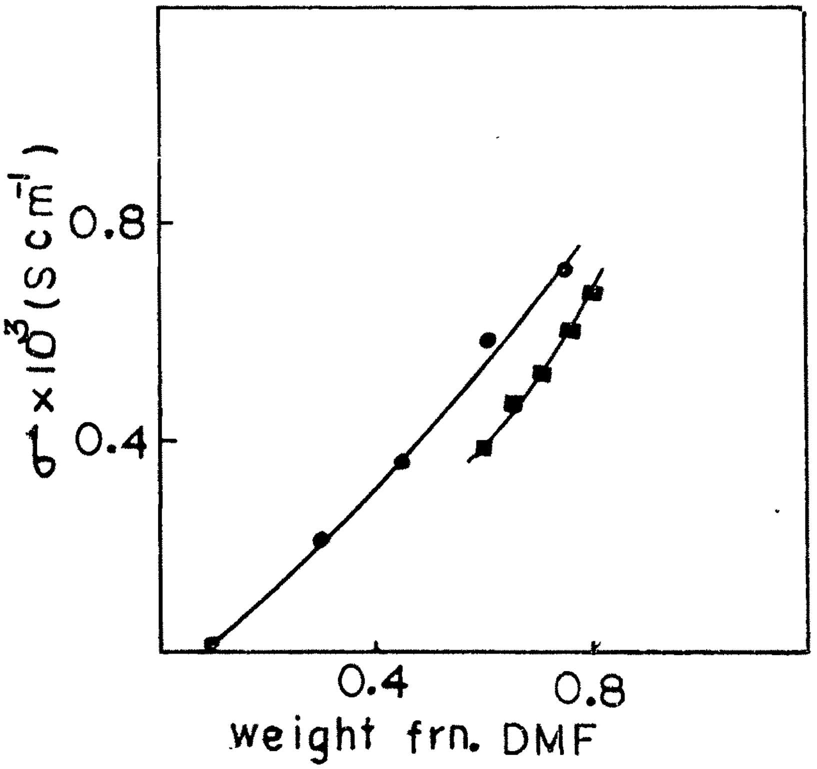


Fig. 3.6a Plot of specific conductance (σ) vs weight fraction of DMF for

● Cyclohexane/TX100+n-propanol (1:2) /DMF.

■ Cyclohexane/TX100/DMF.

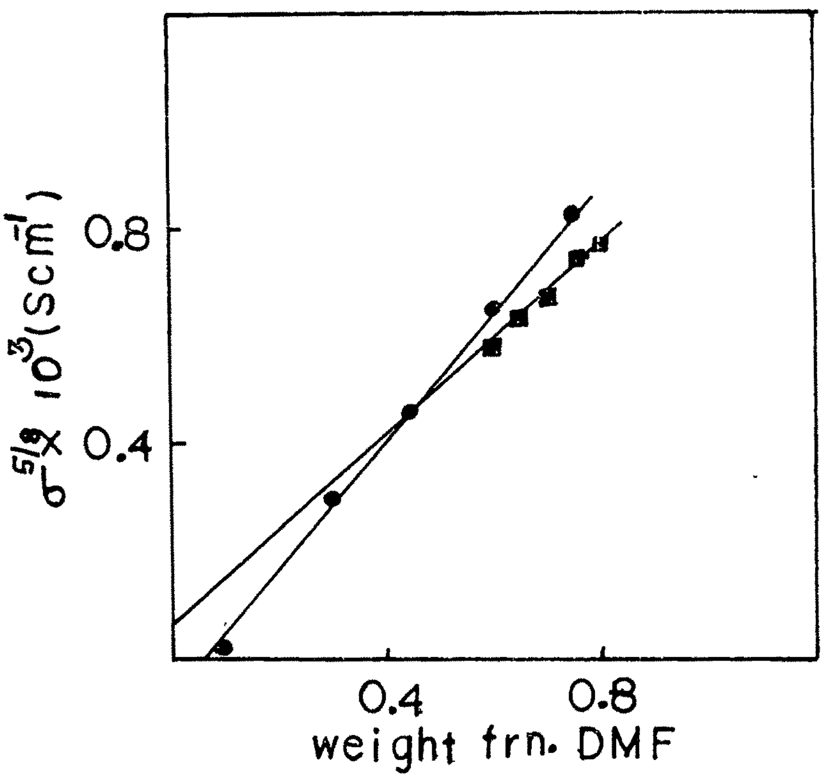


Fig.3.6b Plot of $\sigma^{5/8}$ vs weight fraction of DMF for

● Cyclohexane/TX100 + n-propanol (1:2) /DMF.

■ Cyclohexane/TX100/DMF.

system t=8/5 i.e. $\sigma \alpha (\phi_D - \phi_D^P)^{8/5}$ or $\sigma^{5/8} = k(\phi_D - \phi_D^P)^t$ where k is the proportionality constant. Thus a plot of $\sigma^{5/8}$ versus ϕ_D should meet the X axis at ϕ_D^P. Fig 3.6b represents such a plot; such a plot was also seen in aqueous microemulsion. For a system, without n-propanol, a negative ϕ_D^P is obtained indicating no percolation in the system at all. However, for a DMF/TX100 + n-propanol/cyclohexane system, a low ϕ_D^P is observed at 0.15 weight fraction of DMF. This indicates that the percolation threshold does exist in this case though percolation is not very high. This also indicates some type of change in the structure from a DMF continuum to a cyclohexane continuum through a bicontinuous form. Peyrelasse et al[256] also observed percolation in a nonaqueous microemulsion.

For equal volumes of formamide and oil, small angle neutron scattering spectra indicates the existence of bicontinuous structure for nonionic systems.[59,257] Light scattering study of formamide/ 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol / SDS/ p-xylene and glycerol / SDS / hexano shows no structure[63,64] though AOT+glycerol[65] is structured. In formamide/CTAB/ hydrocarbon[59] systems, a sudden increase in electrical conductivity as composition is varied along the monophasic phase boundary has been interpreted as a percolation transition consistent with the presence of a structured solution, and small angle X-ray scattering measurements, suggest a 'filament' microstructure.

Specific conductance versus water volume fraction for the system cyclohexane/TX100+ethylpropionate/water with 1:1 S to CS weight ratio is plotted in Fig 3.7 along the monophasic region with 80% S composition. Electrical conductivity increases steadily even though the magnitude is very low, with increase of water fraction and it does not show any percolative behavior[254-256,258,259]. Initially the specific conductance increases and at higher water fraction, the conductance decreases. This is probably because as the water conduits increases in diameter on addition of water, the concentration of salt decreases and hence the conductivity decreases at higher water fraction. The nonpercolative conductance variation in these systems and also the very low conductance indicate

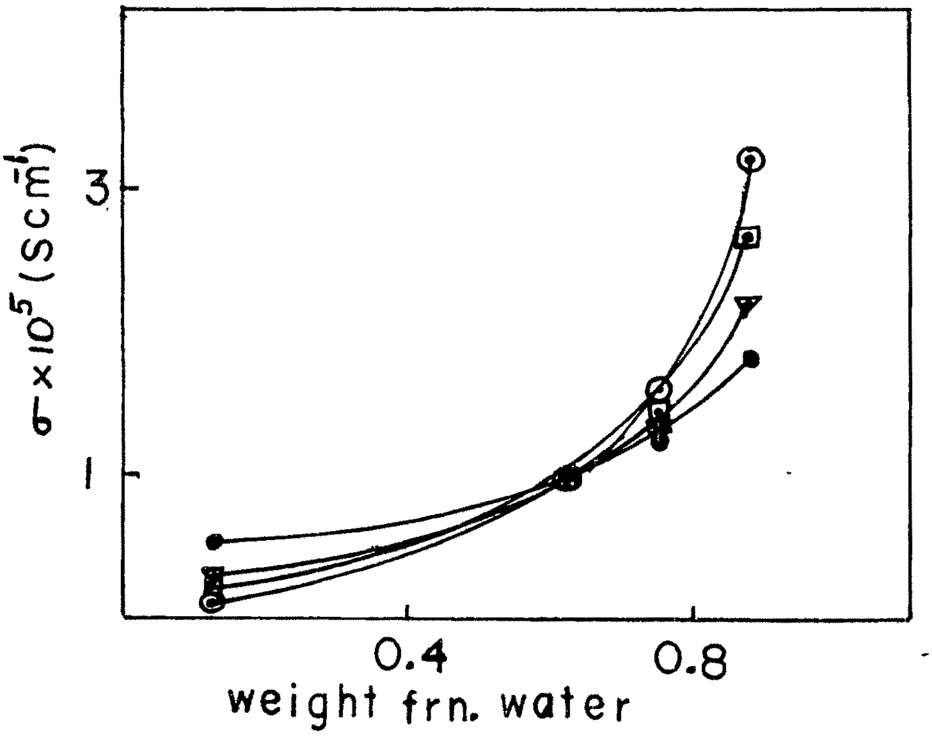


Fig. 3.7 Plot of specific conductance (σ) vs weight fraction of water for cyclohexane/TX100 + ethylpropionate (1:1)/ water

⊙ 30°C; ⊡ 35°C; ▽ 40°C; ● 45°C

water in oil structure. An interesting feature of the graph is the higher conductance at lower temperature, at high weight fraction of water. This also indicates a W/O microemulsion. All the additional water molecules go into the inner parts of the almost electroneutral inverse microdroplets, which grow both in size and number[260,261] and hence the conductivity may be decreased at higher temperature due to the less freedom of mobility.

Specific conductance of one phase microemulsion for 1:2 S to CS ratio was studied with constant water fraction of 2.5% by weight. It was not possible to look at the variation of conductance over the whole oil-water region at a fixed surfactant composition. At this low weight percent of water, no measurable conductance was observed with 0.1M and 1M NaCl. The NaCl concentrations are with respect to water only. Specific conductance of one phase microemulsion with 1:1 S to CS ratio for constant water weight percentage of 2.5 also does not show conductance. This may be due to the nature of the system which is W/O microemulsion. The percentage amount of water is too little and is dispersed over the whole oil region. Therefore, the ions of electrolytes have not much freedom of transport and hence cannot induce any observable conductance.

c. Viscosity

Viscosity of 1ϕ microemulsion of cyclohexane/TX100+n-propanol/water system against weight fraction of water is shown in Fig 3.8. It increases gradually with increasing water content and later reaches a maximum at about 35% water. This type of maximum was reported earlier for TX100 system with butanol as cosurfactant by Moulik et al[16]. Viscosity increase with increasing water fraction is the characteristic of a bicontinuous system[254]. Bicontinuous structure in microemulsion indicates waterfilled interconnected conduits in oil medium. Increase of water fraction swell the conduits and hence increase the viscosity[16, 262]. The observed decrease in viscosity beyond the maximum is believed to be due to a dilution effect.

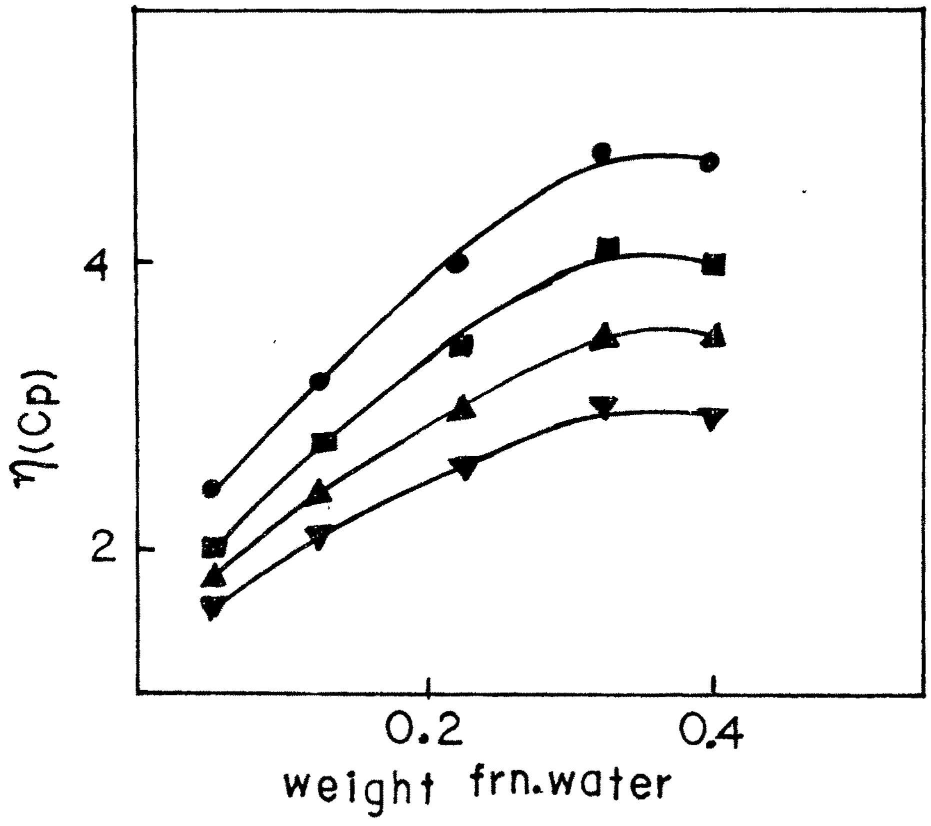


Fig.3.8 Plot of viscosity vs weight fraction of water for cyclohexane / TX100 + n-propanol (1:2)/water.
● 30°C; ■ 35°C; ▲ 40°C; ▼ 45°C

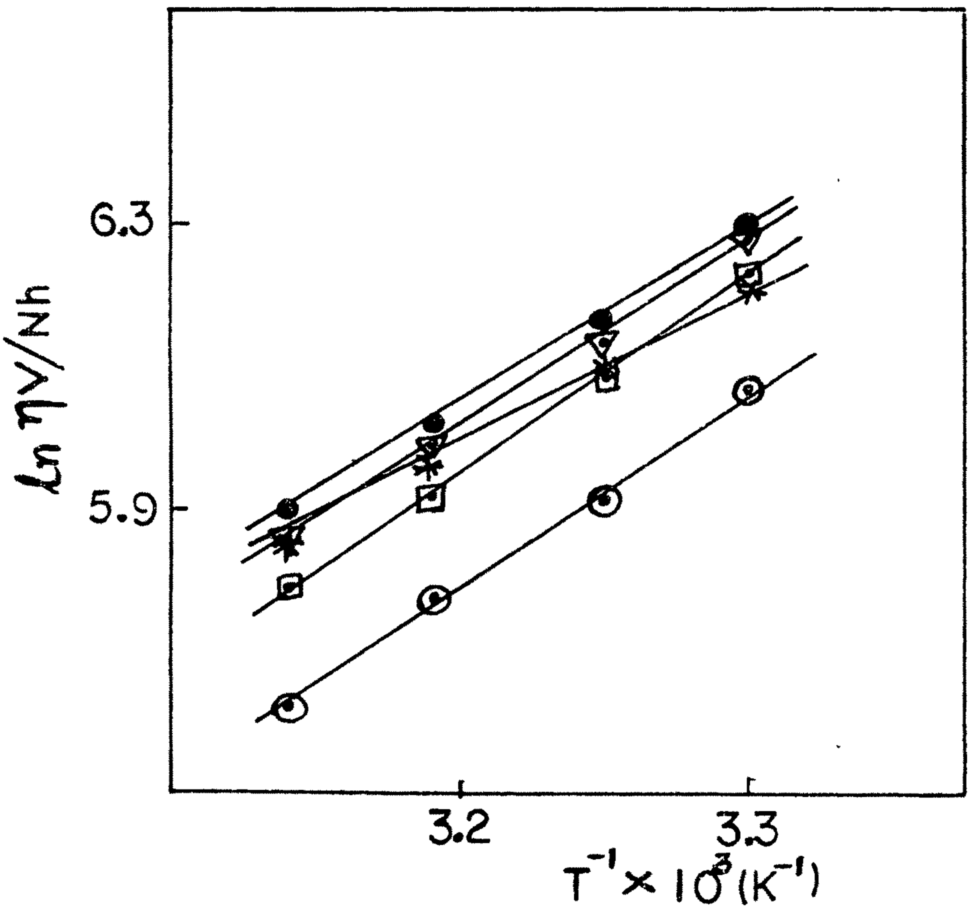


Fig. 3.9 Plot of $\ln \frac{\eta V}{Nh}$ vs T^{-1} for

cyclohexane/TX100 + n-propanol (1:2)/water

⊙ o/w = 5/40; ⊡ o/w=12.5/32.5; ▽ o/w=22.5/22.5;

● o/w=32.5/12.5; ✱ o/w=40/5

Table 2 : **Viscosity activation parameters of viscous flow.**

a			b			c		
O/TX100+P (1:2)/W			O/TX100 + EP (1:1)/W			O/TX100+EP (1:2)/W		
Wt% Water	$\Delta H_{VIS}^{\#}$ k Jmol^{-1}	$\Delta S_{VIS}^{\#}$ Jmol^{-1}K^{-1}	Wt% Water	$\Delta H_{VIS}^{\#}$ k Jmol^{-1}	$\Delta S^{\#}_{VIS}$ Jmol^{-1}K^{-1}	Wt% Water	$\Delta H_{VIS}^{\#}$ k Jmol^{-1}	$\Delta S_{VIS}^{\#}$ Jmol^{-1}K^{-1}
40.0	23.2	26.1	65	13.4	-6.4	60	20.5	17.5
32.5	22.8	23.5	55	10.0	-18.1	55	16.8	6.0
22.5	21.4	18.6	45	15.9	-0.6	50	15.3	1.1
12.5	20.1	13.9	35	16.3	-0.9	45	14.8	-0.6
5.0	20.1	14.3	-	-	-	-	-	-

Table 2a shows the viscosity activation parameter $\Delta H^{\#}_{VIS}$ & $\Delta S^{\#}_{VIS}$ of the viscous flow calculated by using the Frenkel-Eyring equation.[263]

$$\ln \frac{\eta V}{Nh} = \frac{\Delta H^{\#}_{VIS}}{RT} - \frac{\Delta S^{\#}_{VIS}}{R} \qquad \text{.............(1)}$$

where N, h & V are Avogadro number, Planck's constant, molar volume of solution respectively. $\Delta H^{\#}_{VIS}$ & $\Delta S^{\#}_{VIS}$ are the viscosity activation enthalpy and entropy respectively. From the slope and intercept of the straight line graphs obtained by plotting

$$\ln \frac{\eta V}{Nh} \quad \text{against } 1/T \text{(Fig 3.9)}$$

$\Delta H^{\#}_{VIS}$ and $\Delta S^{\#}_{VIS}$ were calculated. All the $\Delta H^{\#}_{VIS}$ & $\Delta S^{\#}_{VIS}$ values are positive and show a gradual increase with weight percent of water (Table 2). This, probably is due to the little microstructural change in the system studied and bigger water conduits with addition of water and hence more difficulty of flow.

The experimental value of η is in centipoise and molar volume is in cm^3 mol^{-1}. The unit of N & h is taken to be molecule mol^{-1} and J sec $molecule^{-1}$ respectively. After introducing the conversion factors,

$$\frac{\eta V}{Nh} \quad \text{becomes}$$

$$\frac{10^{-1} \times 10^{-4}\ Kg\ m^{-1}\ S^{-1} \times 10^{-6}\ m^3\ mol^{-1}}{molecule \times mol^{-1} \times 10^{-2}\ Kg\ m^2\ S^{-1}\ molecule^{-1}}$$

and hence $\eta V/Nh$ is a unitless quantity.

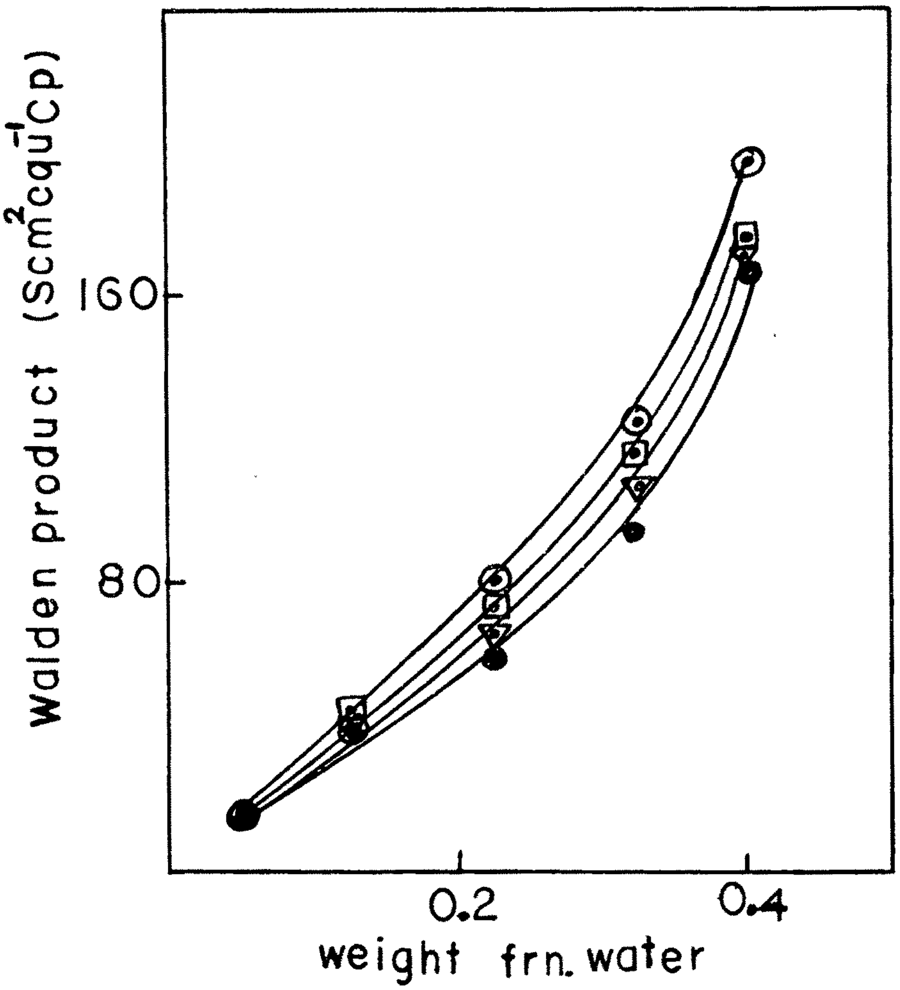


Fig. 3.10 Plot of Walden product ($\lambda\eta$) vs weight fraction of water for cyclohexane/TX100+ n-propanol (1:2) / water
⊙ 30°C; ⊡ 35°C; ▽ 40°C; ● 45°C

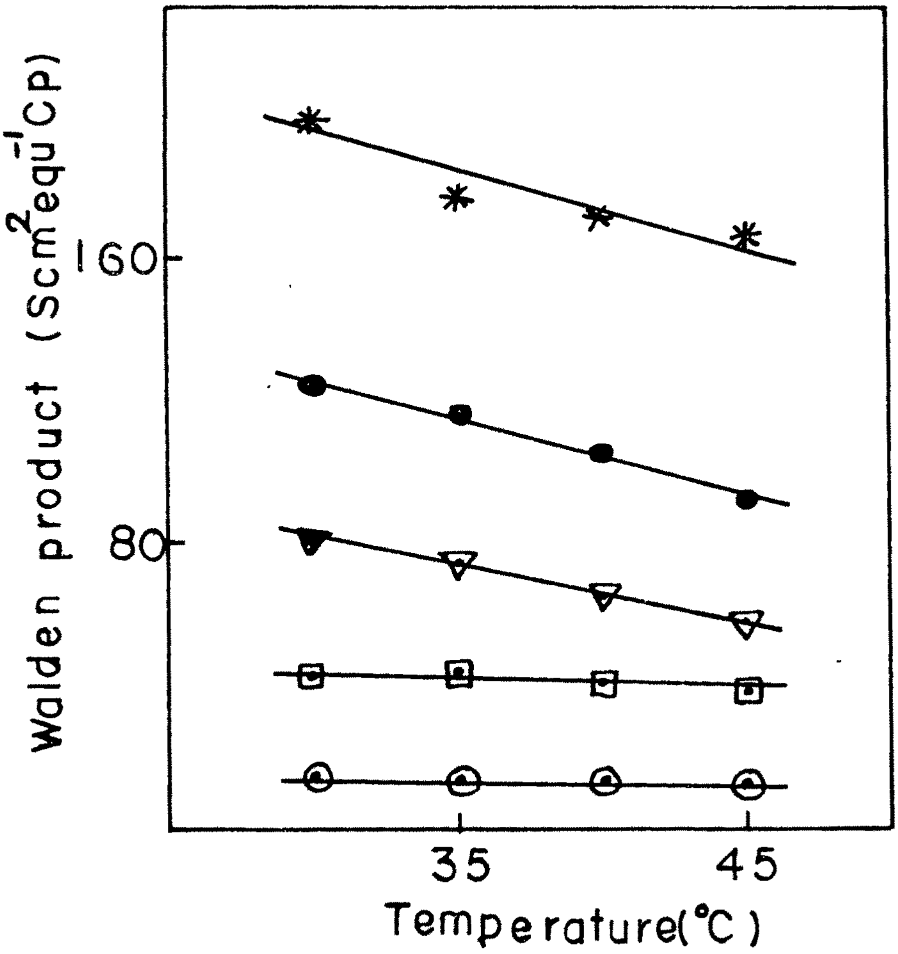


Fig. 3.11 Plot of Walden product (λη) vs temperature for cyclohexane/TX100+n-propanol (1:2)/water.
⊙ o/w = 40/5; ⊡ o/w=32.5/12.5; ▽ o/w=22.5/22.5;
● o/w=12.5/32.5; ✳ o/w=5/40

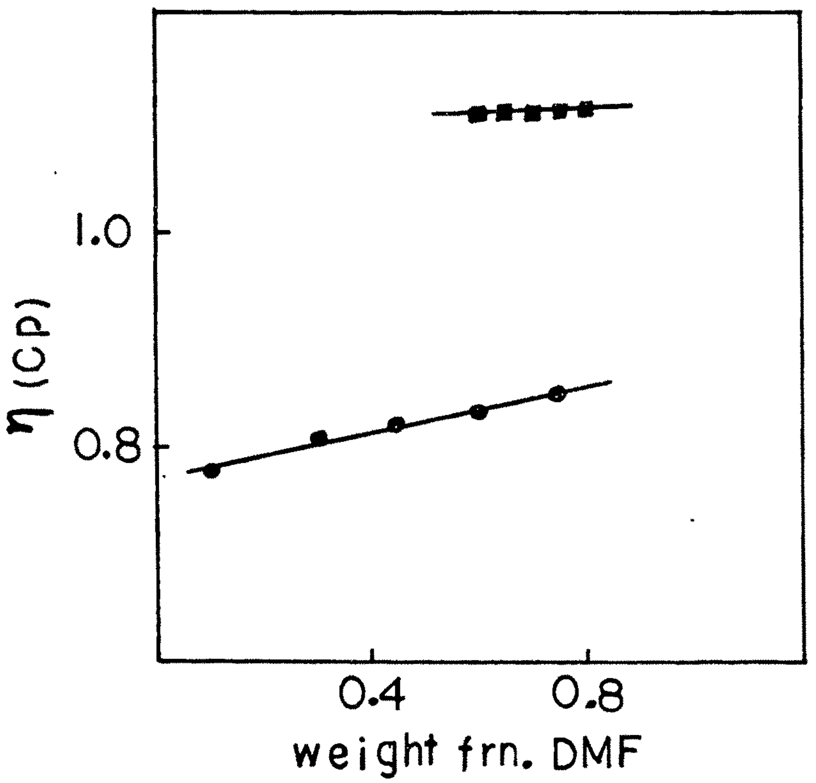


Fig. 3.12 Plot of viscosity (η) vs weight fraction of DMF for
● Cyclohexane + TX100+n-propanol (1:2)/DMF
■ Cyclohexane / TX100 / DMF.

It has generally been found that absolute viscosity and equivalent conductance are inversely proportional to each other and their product is a constant quantity (Walden product)[16]. But this was not found to be true for some microemulsion systems. The plot of Walden product versus weight fraction of water in Fig 3.10 indicates that at lower weight fraction of water, it remains almost the same at all temperatures and it gradually increases with increasing weight fraction of water. At higher weight fraction of water, it does not remain a constant. Walden product as a function of temperature is presented in Fig 3.11. At lower water level, the Walden product is almost a constant showing that at lower water level, it behaves as a normal solution, i.e. viscosity and conductance reasonably compensate each other. At higher percentage of water, there is a decrease in $\lambda\eta$ with increase in temperature. This has been observed earlier by other research workers also[16]. This is because the rate of change of λ and η with temperature are not the same.

In Fig 3.12, the variation of η with varying DMF amount is shown. The surfactant concentration was kept constant at 15% by weight. It is clear that viscosity remains almost constant indicating that the change in DMF content does not have any observable effect on the microstructure of the microemulsion. In presence of n-propanol, the viscosity is somewhat lower. This may be due to the use of less TritonX 100(5%) where n propanol was 10%. In this case, there is a continuous decrease in the viscosity with the addition of cyclohexane. It was mentioned earlier that in the case of an aqueous microemulsion[49,194], a decrease in viscosity was generally due to a decrease in the size of the water conduit. However, in this case, the decrease in viscosity may be due to the structural changes of the microemulsion as the O/D ratio increases. It is not prudent to make more specific comments as the changes in viscosity are not large. The dilution effect brings the viscosity down in the case of an aqueous system, though this was not observed here within the concentration range studied.

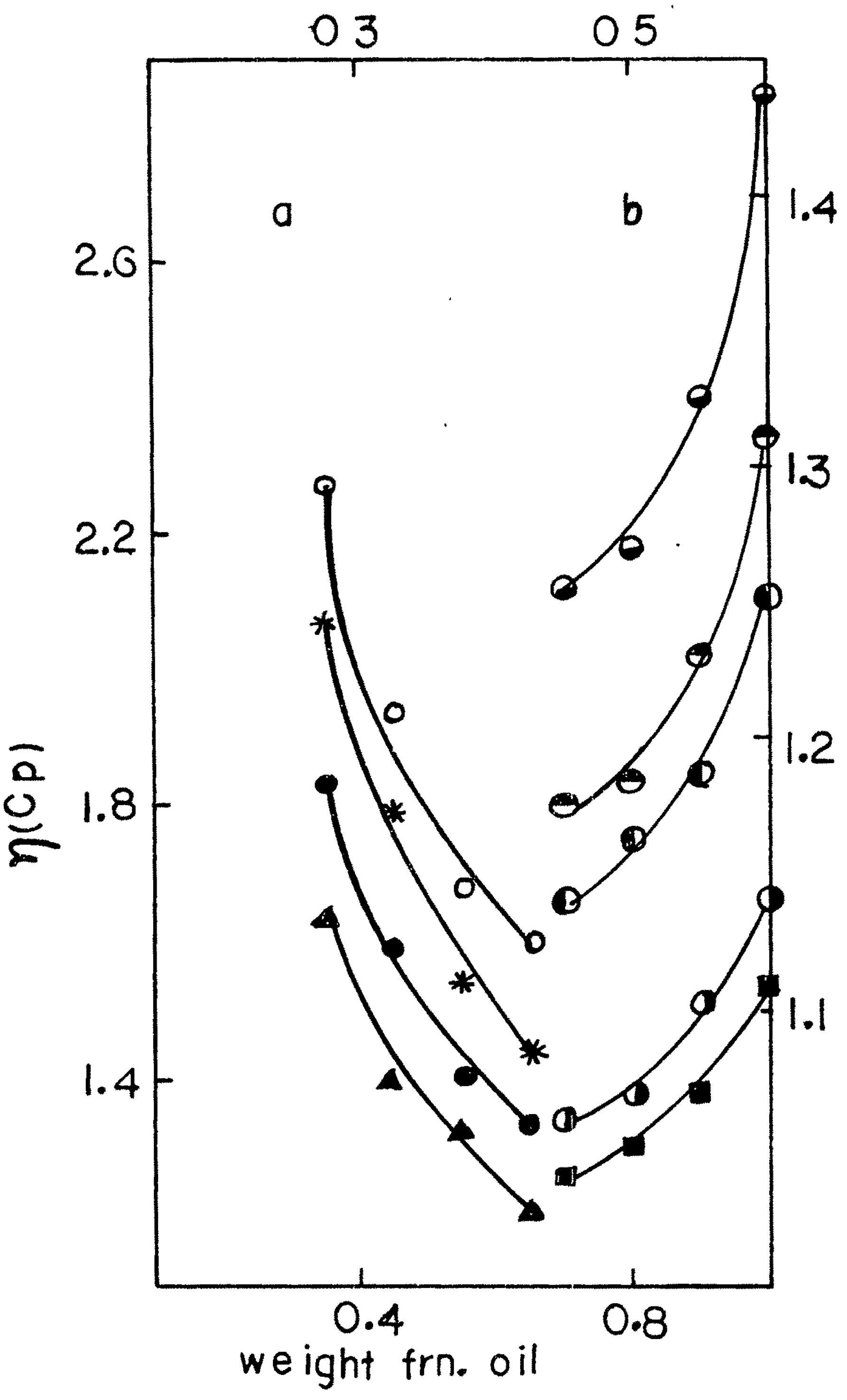


Fig.3.13 Plot of viscosity (η) vs weight fraction of
a. cyclohexane/TX100 + ethyl-propionate (1:1) / water.
○ 30°C; ✳ 35°C; ● 40°C; ▲ 45°C.

b. cyclohexane/TX100+ethylpropionate (1:2) / water.
◒ 30°C; ◓ 32.5°C; ◐ 35°C; ◑ 37.5°C; ■ 40°C

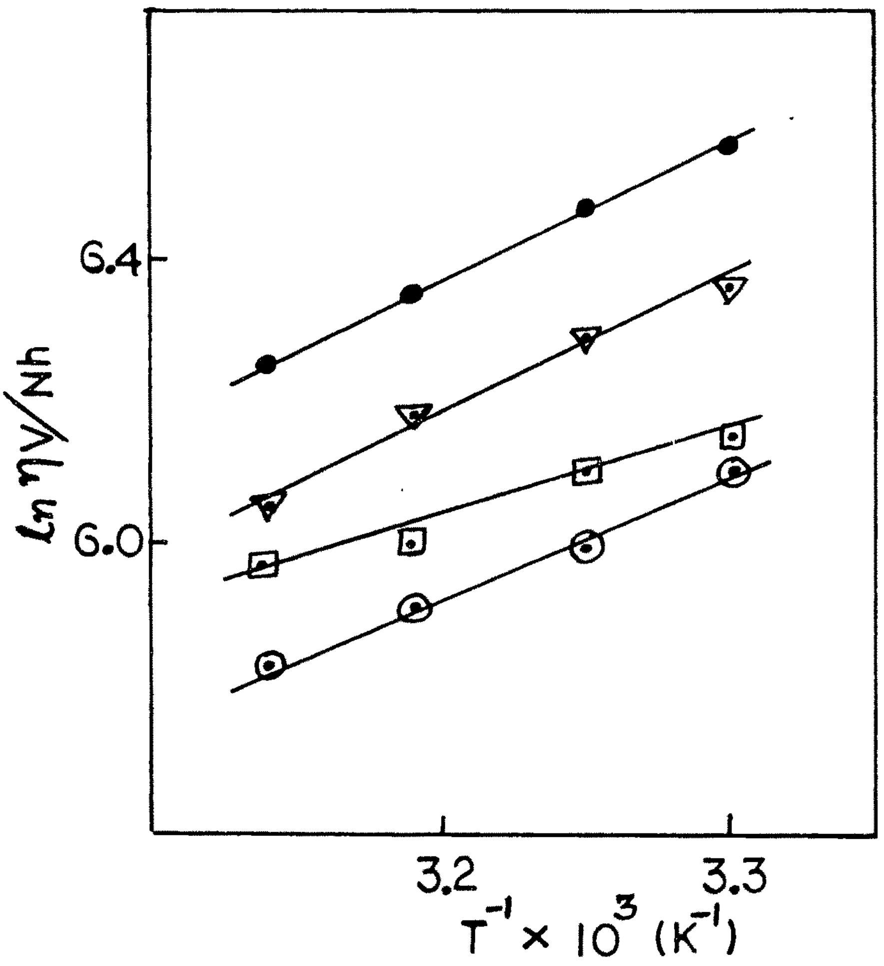


Fig. 3.14 Plot of $\ln \frac{\eta V}{Nh}$ vs T^{-1}

a. Cyclohexane/TX100 + ethylpropionate (1:1) / water
● o/w=35/2.5; ▽ o/w= 45/52.5; ⊡ o/w=55/42.5;
⊙ o/w= 65/32.5

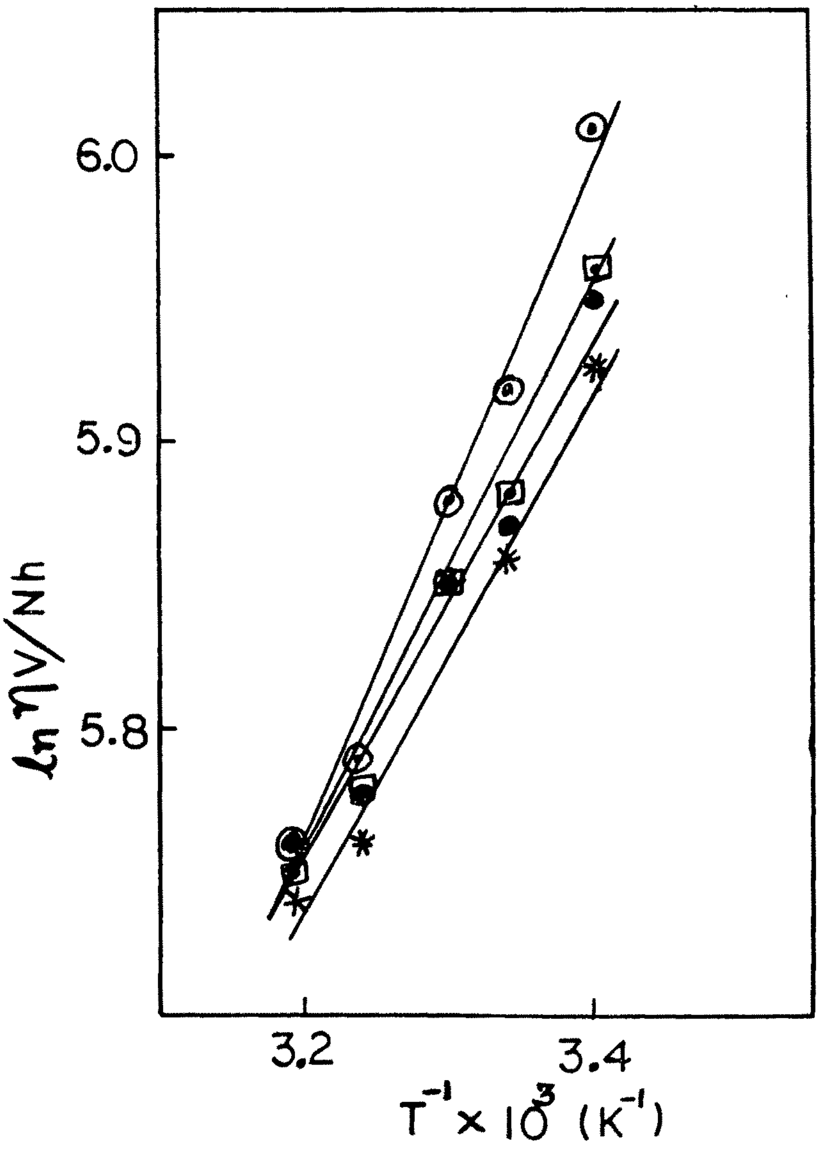


Fig.3.14 b. Cyclohexane / TX100 + ethylpropionate (1:2) / water
● o/w=45/2.5; ✱ o/w=50/47.5; ⊡ o/w=42.5/55;
⊙ o/w= 37.5/60

Viscosity of one phase microemulsion of cyclohexane/TX100+ ethylpropionate/ water with constant weight fraction of water is plotted against varying oil fraction for 1:1 and 1:2 S to CS ratio in Fig 3.13. Viscosity decreases with increasing weight fraction of oil with 1:1 S to CS ratio and with 1:2 S to CS, it increases with increase in oil fraction. In the case of 1:1 S to CS ratio, the surfactant mixture is viscous and flow time increases with respect to surfactant and decreases with respect to oil. So the surfactant - cosurfactant ratio becomes a major factor in the viscosity of the compositions studied. Viscosity of system with S to CS ratio 1:2 is less than that with S to CS ratio 1:1 may be attributed to the dilution of the system. The dependency of viscosity on temperature is systematic. In both cases, it decreases with increasing temperature. The viscosity activation quantities $\Delta H_{VIS}^{\#}$ (activation enthalpy) and $\Delta S_{VIS}^{\#}$ (activation entropy) were calculated by applying the Frenkel Eyring equation (Eq. 1). From the slope and intercept of the straight line graphs, obtained by plotting ln $\eta V/Nh$ against 1/T (Fig 3.14) $\Delta H^{\#}_{VIS}$ and $\Delta S^{\#}_{VIS}$ were calculated for 1:1 and 1:2 S to CS weight ratio (Table 2b & 2c).

d. Adiabatic Compressibility

Adiabatic compressibility of the monophasic region is plotted against water fraction for the aqueous system in Fig 3.15. It is a linear function of water content. It decreases with increasing amount of water. This is because water is more structured than cyclohexane. The adiabatic compressibility β is a macroproperty. The higher W/O ratio will induce less compressibility. Increase of temperature increases the hydrophobicity of the interfacial surfactant film due to dehydration of the polyethylene oxide chain of TX100[264,265]. Moreover rise in temperature, should provide kinetic energy to loosen the interfacial film. Also at higher temperature, the water is less structured. These effects are expected to enhance the penetration of the cyclohexane molecules into the interfacial film, swells the dispersed phase and therefore the compressibility will be higher at higher temperature.

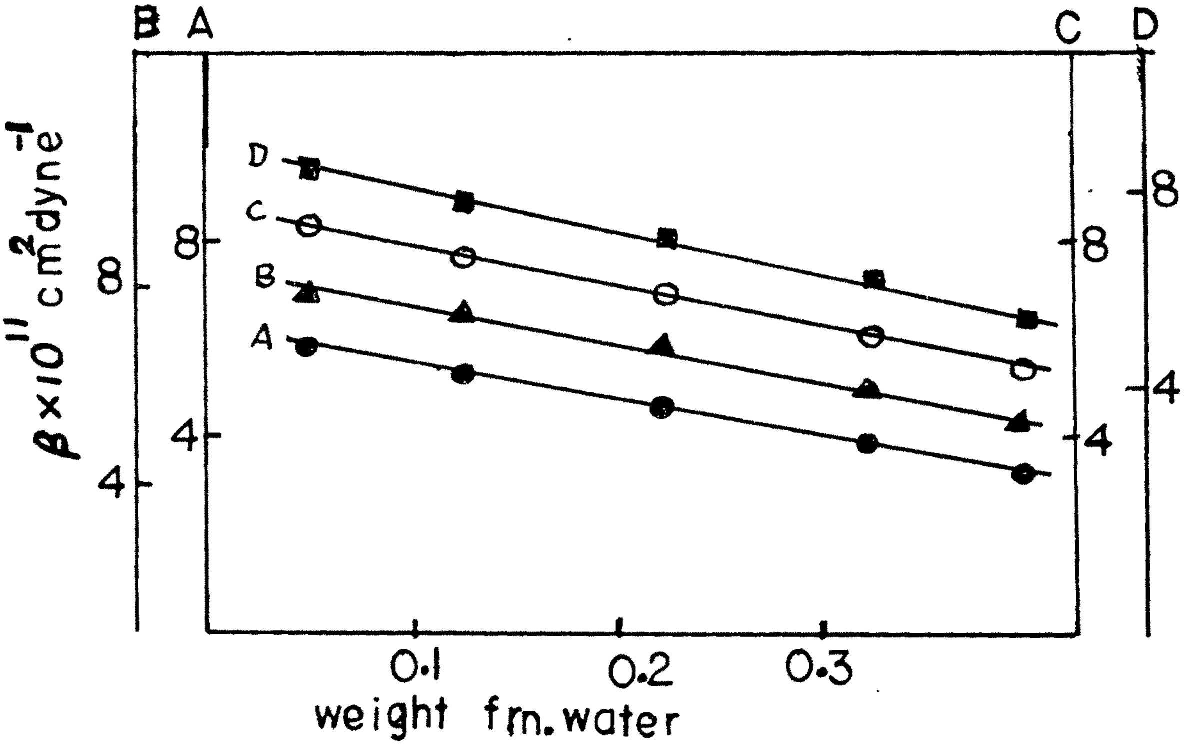


Fig. 3.15 Plot of Adiabatic compressibility (β) vs weight fraction of water for cyclohexane/TX100 + n-propanol (1:2)/ water.
● 30°C; ▲ 35°C; ○ 40°C; ■ 45°C.

From Figs 3.5a & 3.15, it is clear that specific conductance and adiabatic compressibility also show an inverse relationship. With increase in volume fraction of water, when specific conductance increases the β decreases. However, with increasing temperature, conductance and increase. Variation of viscosity and adiabatic compressibility is opposite to each other when they are plotted against water fraction. Similar results were repoted for TX100 system with butanol as cosurfactant[16].

The adiabatic compressibilities of one phase microemulsion system with varying DMF-Cyclohexane ratios at a constant surfactant concentration 15% w/w are shown in Fig 3.16. It is obvious that the adiabatic compressibility decreases with an increase in the DMF concentration. DMF is a relatively more structured solvent than cyclohexane and hence the compressibility decreases.[47-49, 81,253] This is basically a macro property and it does not give much information of the microstructural nature of the medium.

The linear variation of adiabatic compressibility with water weight fraction at various temperatures with 80% S concentration is shown in Fig 3.17 for the ester system. This linearity indicates that the increase of water fraction decreases adiabatic compressibility since β is a macroproperty. Water is more structured than cyclohexane and therefore higher w/o ratio will induce less compressibility. Generally, nonionic surfactants are temperature sensitive. Increase of temperature increase the hydrophobicity of the interfacial surfactant film due to dehydration of the polyethylene oxide chain of TX100[264]. The rise in temperature, provides relatively more kinetic energy to loosen the interfacial film. Also at higher temperature, the water is less structured as the hydrogen bonds get broken. These effects enhance the penetration of the cyclohexane molecules into the interfacial film. causes the swelling of the dispersed phase and therefore the compressibility will be higher at higher temperature. From the Figs. 3.7 & 3.17, it is clear that specific conductance and β show an inverse relationship at lower temperature and at lower weight fraction of water. At higher weight fraction of water, the specific

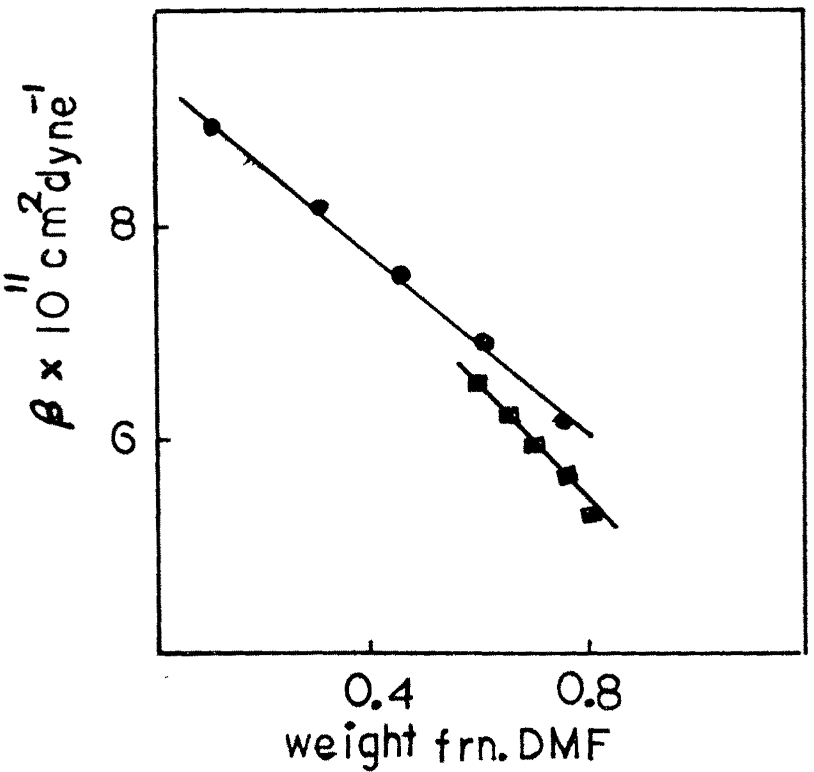


Fig. 3.16 Plot of Adiabatic compressibility (β) vs weight fraction of DMF for

- ● Cyclohexane/TX100 + n-propanol (1:2)/DMF.
- ■ Cyclohexane / TX100 / DMF.

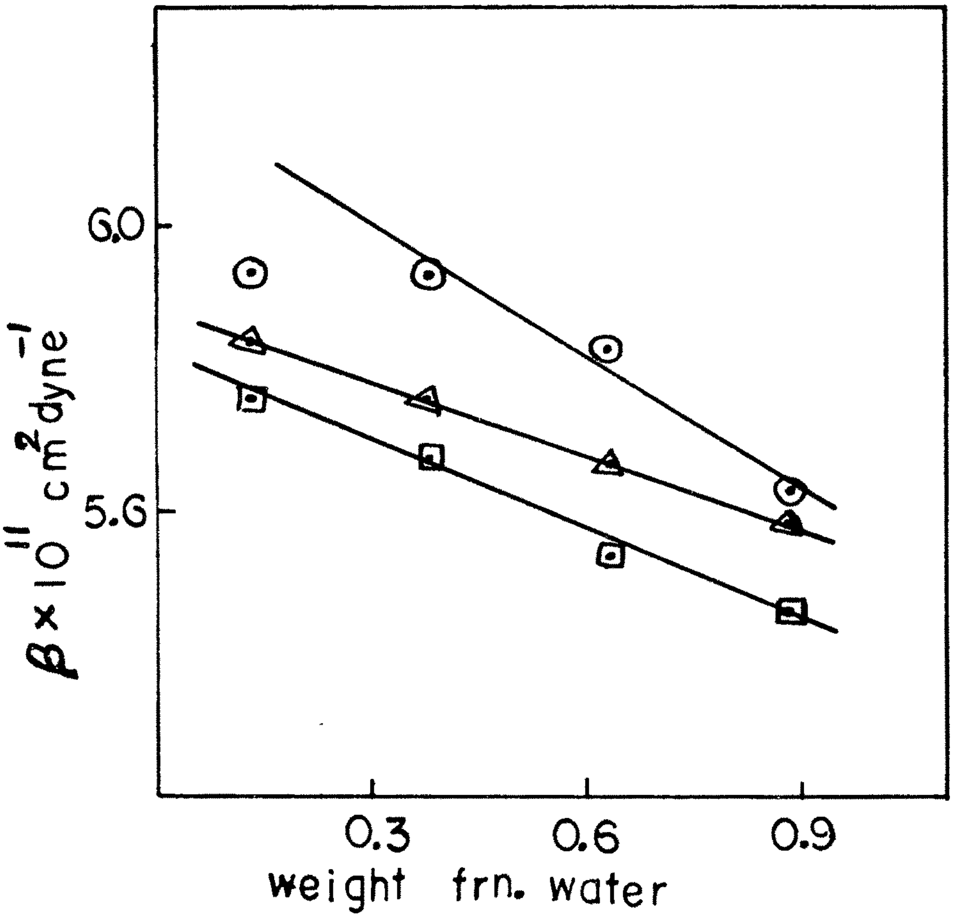


Fig.3.17 Plot of Adiabatic compressibility (β) vs weight fraction of water. Cyclohexane/TX100 + ethyl propionate (1:1)/water.

conductance decreases with increasing temperature. β always increases with increasing temperature and it decreases with increase in weight fraction of water.

e. Contact angle

The contact angle θ for the various microemulsion systems composed of TX100 is tabulated in Table 3. In Table 3a the contact angle values of the aqueous systems with teflon surface are shown. These show a gradual increase. Therefore the microemulsion can be either oil continuous or water continuous. We assume a single structured system and there is no structural change and hence it is assumed to be a bicontinuous structure as supported by conductance and viscosity data.

Table 3b shows the contact angles θ of 1ϕ microemulsion of DMF system with teflon. Microemulsions without n-propanol have values almost as high as that of pure DMF with teflon. This suggests that the DMF of the microemulsion is in contact with the teflon. The presence of n-propanol values are similar to the system which does not have propanol upto 25% cyclohexane. This indicates that both microemulsions have similar structures upto this concentration range. Further addition of cyclohexane changes the contact angle in a gradual fashion. Hence we assume that an O/D to D/O structural change occurs and in the middle composition range, a bicontinuous system may be present where the surfactant (TX100 with n-propanol) is 15% by weight.

Table 3c shows the contact angle θ values for the ester system. From Table 3c, it can be concluded that for the system, with surfactant-cosurfactant ratio 1:1, the system is oil continuous with water probably dispersed as droplets. For 1:2 S to CS system, the contact angle is studied with constant water fraction. Low, somewhat constant readings were obtained indicating that the system was too hydrophobic and there was no structural change and the system here also seems to be oil continuous.

f. Effect of salt

In the case of ionic surfactant, the electrolyte like NaCl, decreases the hydrophobicity and there is a possibility of the formation of a three phase

Table 3 a&b : Contact angle θ obtained for aqueous and nonaqueous microemulsion.

a				b							
Cyclohexanol/TX100+Propanol/(1:2) Water (O) (S) (W)				Cyclohexane / TX100/DMF (O) (S)				Cyclohexane/TX100+Propanol(1:2)/DMF (O) (S)			
O	S	W	θ^o	O	S	DMF	θ^o	O	S	DMF	θ^o
0.0	0	100	152.0	0	0	100	132	0	0	100	132
5.0	55	40	72.0	5	15	80	131	10	15	75	121
12.5	55	32.5	69.0	10	15	75	118	25	15	60	103
22.5	55	22.5	67.0	15	15	70	117	40	15	45	89
32.5	55	12.5	64.0	20	15	65	114	55	15	30	86
40.0	55	5.0	61.0	25	15	60	99	70	15	15	65
100.0	55	0	56.0	100	0	0	56	100	0	0	56

Table 3c : **Contact angle θ obtained for cyclohexane/TX100+ethylpropionate(EP)/water system.**
(O) (S) (W)

O/TX100+EP (1:1)/W				O/TX100+EP (1:2) /W			
O	S	W	θ°	O	S	W	θ°
0	0	100	152	0	0	100	152
2.5	80	17.5	72	45	52.5	2.5	50
7.5	80	12.5	69	50	47.5	2.5	50
12.5	80	7.5	67	55	42.5	2.5	49
17.5	80	2.5	65	60	37.5	2.5	50
100.0	0	0	56	100	0	0	56

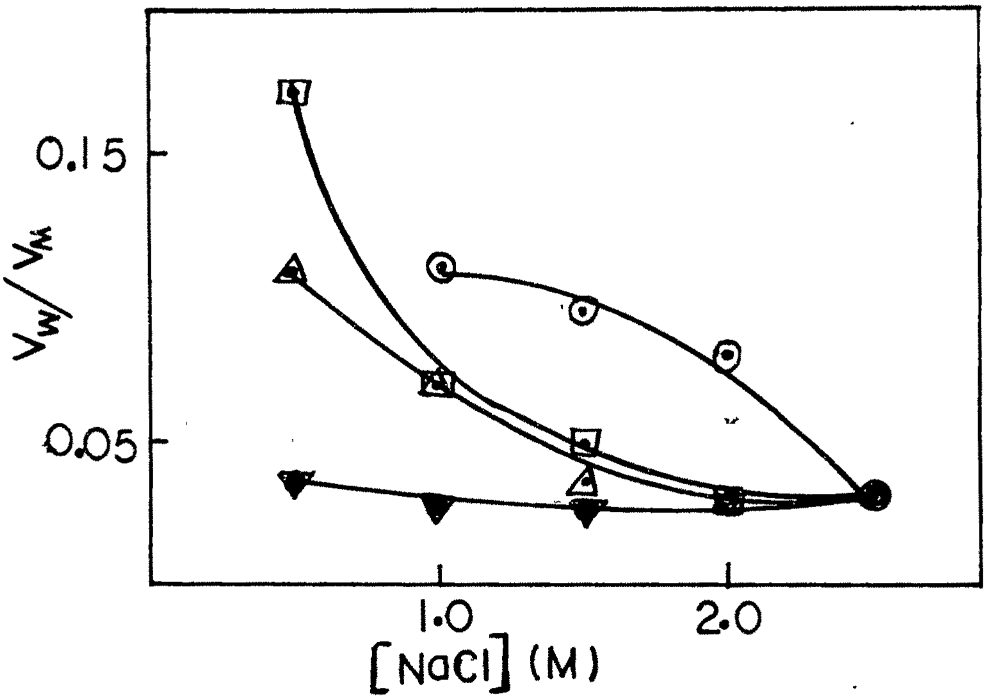


Fig.3.18 Plot of $\frac{Vw}{Vm}$ vs [NaCl] for
cyclohexane/TX100 + n-propanol(1:2) / water
⊙ 30°C; ⊡ 40°C; △ 50°C; ▽ 60°C; ● 70°C

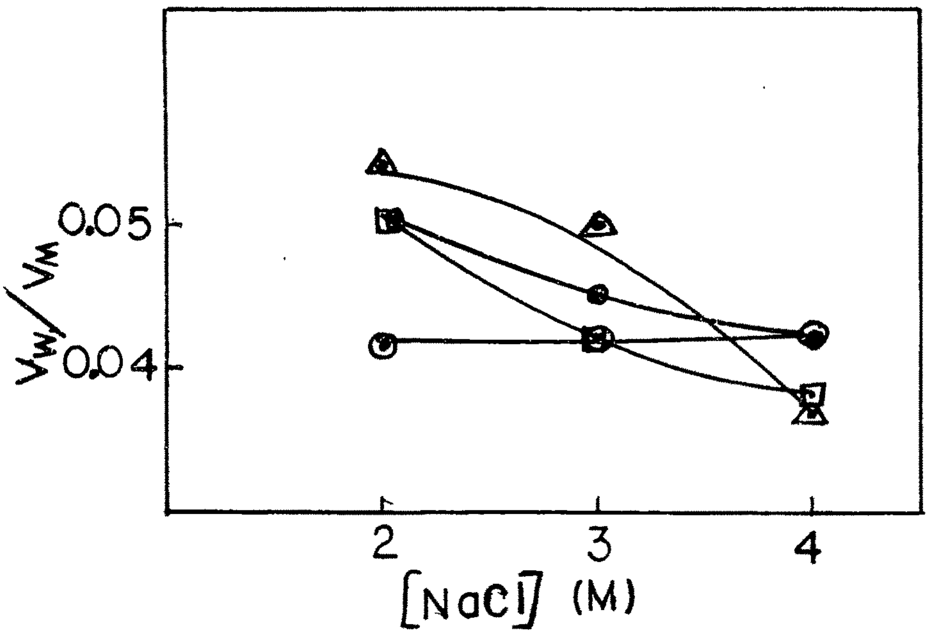


Fig. 3.19 Plot of $\frac{Vw}{Vm}$ vs [NaCl] for
cyclohexane/TX100 + ethyl propionate (1:1)/water
⊙ 40°C; ⊡ 50°C; △ 60°C; ● 70°C

microemulsion. A three phase formation is usually obtained when a surfactant system attains a favourable balance between its hydrophilicity and hydrophobicity[92]. The repulsive interaction between the charged head groups are screened by the electrolytes. Continued addition of electrolyte leads to microemulsion phase containing equal amount of oil and water. At fairly high electrolyte concentration, the interaction of the surfactant with electrolyte is diminished. Thus it forms a middle phase microemulsion by achieving a favourable hydrophilic - hydrophobic character (HLB) to solubilize equal amounts of oil and water. At large ionic strength, the interaction of the surfactant head groups with water gets reduced to a level when they are outweighed by the larger entropy available in the oil phase. This ultimately lead to the inversion of microemulsion to an oil continuous upper phase microemulsion.

We have studied the effect of electrolyte on one phase microemulsion of different TX100 microemulsions. The concentration of NaCl ranging from 0-4M and the temperature varies from 30 to 20°C. But we did not get a 3ϕ microemulsion. We obtained a one phase (WIV) to Winsor II transition (Fig 3.18 & 3.19).

The phase transitions with changing electrolyte concentration and temperature could be very well explained by considering the surfactant geometrical packing ratio which was introduced by Mitchell, Ninham and coworkers[93,266] and further simplified by Aveyard et al[267, 268].

Ninham and others[93,266] suggested that if 'V' is the effective volume of surfactant molecule and a_o and l_o are the effective head group area and surfactant tail group extended length respectively, then the packing factor is equal to $V/a_o l_o$. This term dictates the surfactant aggregation. Aveyard and coworkers[267,268] suggested a simplified version of this idea. They proposed that the packing factor introduced by Ninham and others would be approximately equal to the ratio A_t/A_h where A_t and A_h are the effective cross sectional surface areas of tail region and head group of the surfactant molecule respectively (Fig 3.20a)[267]. The

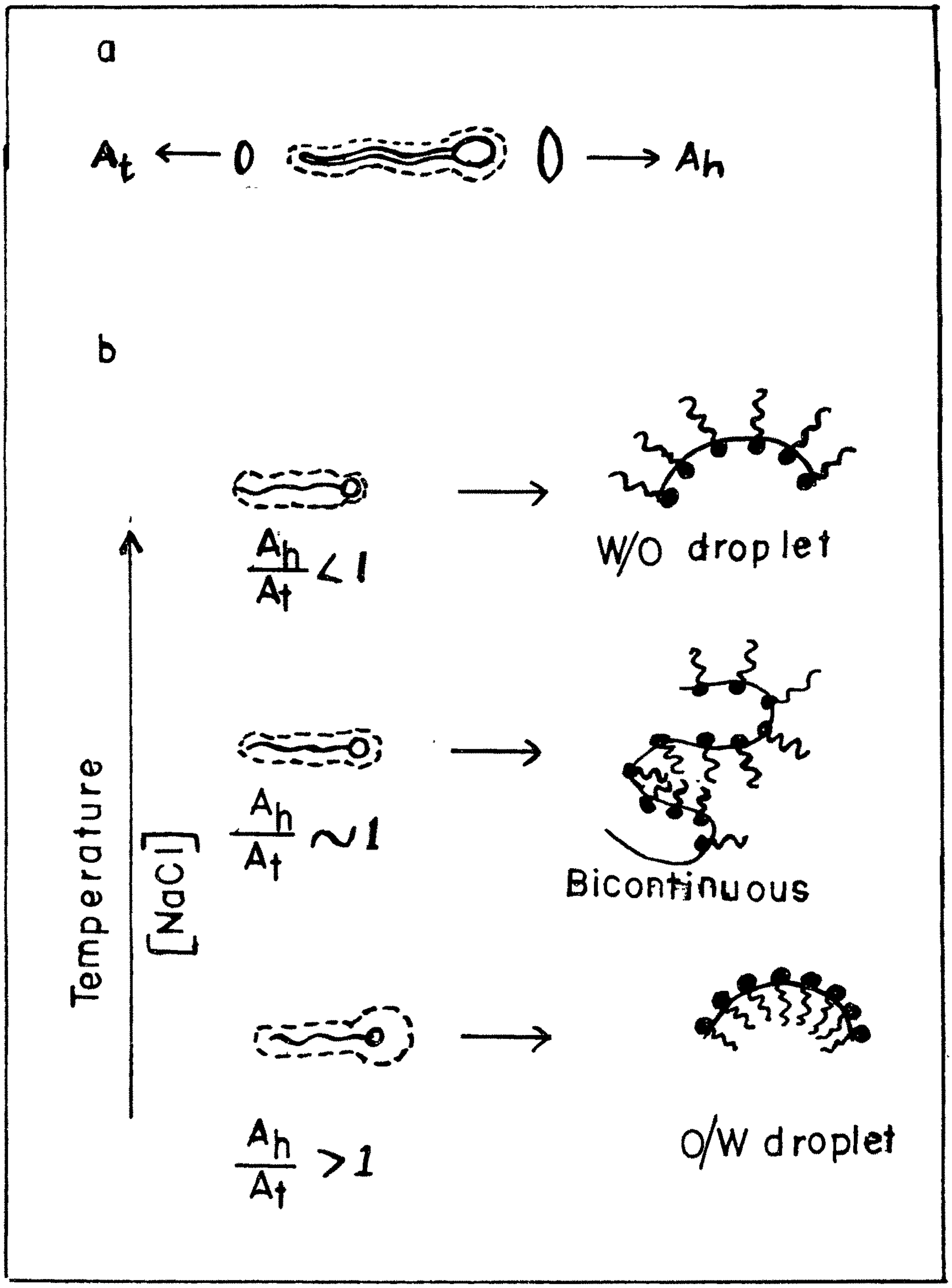


Fig. 3.20 Change of effective surface areas of head group (A_h) and tail region (A_t) of the surfactant at the influence of electrolyte concentration and temperature.

microstructural changes in microemulsion and as a consequence, Winsor transitions are controlled by this ratio. The values of A_t and A_h are not those of the bare geometrical values of an isolated surfactant molecule. It is the effective value 'insitu' in the surfactant monolayer that counts. Hence the packing ratio is affected by many factors including hydrophilicity of head group, ionic strength of the solution, pH, temperature, nature and amount of cosurfactant. When the packing ratio has the value less than unity i.e. ($A_h > A_t$), the system prefers oil in water structure and hence the system exists as Winsor I. If the ratio is more than unity ($A_h < A_t$) water in oil structure is more probable and the system is Winsor II. At an intermediate range is ($A_h \approx A_t$) microemulsion appears as bicontinuous and thus form a 3ϕ microemulsion. (Fig 3.20b)[267]

As A_h and A_t are the effective sizes and not the bare size, for the same surfactant, these values vary from system to system. This variation can be attributed to various factors. Aveyard et al[267] listed these factors as

i) electrostatic repulsion between neighbouring ionic head groups.
ii) Solvation of the surfactant tail group by the nonpolar solvent.
iii) Hydration of the surfactant head group[268].

For polyoxyethylene type surfactants, A_h is mainly determined by the extent of hydration of POE group. It has been shown that the hydration is sensitive to temperature[264,268] and electrolyte concentration. Increase of temperature dehydrate the polyoxyethylene group. Similarly an electrolyte, when present in the formulation, tends to dehydrate the oxyethylene group by getting hydrated itself. This is the 'salting out' of the oxyethylene group. Thus at low temperatures and/or absence of an electrolyte, the oxyethylene groups are largely surrounded by water molecules, i.e the oxyethylene groups are solvated by water. This increases A_h to a high value. Ninham et al[266] pointed out that higher the hydrophilicity of the head group, higher will be the value of A_h. But cyclohexane/TX100+ethylpropionate/ water system is highly hydrophobic and the alkane starts penetrating the tail region and swells the surfactnt tail region and there is increase in A_t. Aveyard measured the variation of A_t and A_h values with changing NaCl concentration[268]. It was observed that A_h changes only when the system was oil in water microemulsion.

Generally, incorporation of cosurfactant into surfactant aggregate is expected to increase the mean volume of the surfactant molecule without affecting its head group area (A_h) and extending length of the surfactant tail (l_o). As ethylpropionate is hydrophobic, we assume that this will affect the A_t appreciably and it increases. In presence of salt and higher temperature, the polyoxyethylene group gets dehydrated; that A_t increases & A_h decreases. So we assume a higher penetration of the alkane in the surfactant film and this might swell the surfactant tail slightly because of the increased hydrophobicity of the surfactant molecule. As $A_h < A_t$, the packing ratio becomes more than 1, and water-in-oil structure is more probable and the system changes to Winsor II. So we presume that cyclohexane/TX100+n-propanol/water and cyclohexane/TX100+ethylpropionate/ water system are having a water-in-oil structure for the compositions studied. Brij35[253] system, because of its large number of ethylene oxide group form a 3ϕ microemulsion whereas TX100 with its less number of ethylene oxide group cannot induce a 3ϕ system. This has also been noted for nonaqueous systems by other research workers also[269].

By the use of special surfactants[56] or by changes in temperature,[56,70,112,123] salinity[81,82,270,171] or the amount and nature of cosurfactant,[227,270] a middle phase microemulsion can be made that coexists with both water and oil. We could get such middle phase microemulsion (see fish phase diagram) for cyclohexane/ TX100 +n-propanol (1:2)/water by gradually increasing the temperature through a Winsor I Winsor III Winsor II transitions.

g. Cloud point

Cloud point is an important property of nonionic surfactants. Cloud point study of TX100 & TX114 with various additives like halides, acetamide, sucrose,

Table 4 : Cloud point of cyclohexane/TX100+propanol/Water.
(O) (S) (W)

0	S	W	CP°C
40.0	55	5	-
32.5	55	12.5	-
22.5	55	22.5	45.6
12.5	55	32.5	47.4
5	55	40.0	-

urea has been reported earlier[272]. Cloud point study of alkane/Brij35 +n-propanol/aq NaCl with different concentration of NaCl was also reported earlier[253]. The cloud point study cyclohexane/TX100 + n-propanol/water along the monophasic region at 55% S shows that at lower water (5% & 12.5%) and oil (5%) content, there is no clouding till 100°C (Table 4). However at oil-surfactant-water ratio 22.5/55/22.5 and 12.5/55/32.5, clouding was observed at 45.6 & 47.4°C respectively. The clouding appeared due to the dehydration of the polyoxyethylene groups with increase in temperature. For a microemulsion system, cosurfactant and the hydrocarbon affects the clouding. At intermediate concentration of oil and water, due to the difference in the interaction of surfactant with oil and water, the dehydration of the surfactant takes place by increasing the temperature and hence the clouding.

Conclusion

The phase diagram study of cyclohexane/TX100+n-propanol/water shows an upper monophasic region and lower L/L region. Fish phase diagram shows that with gradual increase in temperature, the system induces a W I→W III→W-II transitions. Gradual increase of specific conductance with increasing weight fraction of water shows that it is probably of bicontinuous nature. Gradual increase of viscosity with increasing water fraction is also characteristic of bicontinuous system. Viscosity reaches a maximum at higher weight fraction of water. Adiabatic compresibility decreases with increasing weight fraction of water. Contact angle data also shows a bicontinuous structure for this aqueous system. NaCl could not induce a 3ϕ system; WI→ WIII→WII transitions were obtained with increasing the temperature.

Microemulsions can be formed with a polar organic liquid like DMF and show physical properties somewhat similar to those of aqueous systems. The presence of n-propanol as a cosurfactant changed the area of a one phase microemulsion drastically; increasing it by more than 2 times that of the aqueous system. The physical properties changed, but the similarity of the changes in the properties remained the same as a function of the DMF concentration. The effect of an electrolyte which shows phase changes in an aqueous microemulsion was not observed in this nonaqueous microemulsion. The presence of n-propanol as cosurfactant induces the presence of O/D, bicontinuous and D/O structural patterns.

Pseudoternary phase diagrams of water cyclohexane / TX100 + ethylprioponate ratio as 1:0, 1:1, 1:2 were obtained. This was done to determine the effect of an ester i.e, ethylpropionate as a possible cosurfactant. The percent area of single phase Winsor IV region was very low. A large birefringent viscous region was observed for 1:1 system which gives way to a large extent to L/L biphasic region when surfactant/cosurfactant ratio was changed to 1:2. The higher percentage of ethylpropionate makes the system more hydrophobic. The magnitude of conductance value is very low. At higher water fraction and at higher temperature, the conductance decreases. It shows that it is a W/O microemulsion. Two phase system was obtained by the effect of sodium chloride on one phase Winsor IV system and no Winsor III system was obtained. The conductance, viscosity and contact angle values indicate a W/O microstructure.