CHAPTER 4

EFFECT OF AN ELECTROLYTE ON NONIONIC SURFACTANT MICROEMULSIONS

4.1 PREVIEW

Water-oil-nonionic surfactant - electrolyte systems have attracted increasing attention from the researchers for both practical and theoretical reasons. The former includes the possible use of these systems in tertiary oil recovery. Theoretically, study of these systems developed much interest especially due to their extra ordinary rich phase diagrams. The diversity of the phase diagrams results from the critical phenomena that generally nonionic surfactant systems show.

Considerable amount of studies have been reported on such systems and marked changes in their properties with varying electrolyte concentration were observed [150,201]. Sensitivity of the ionic surfactant systems towards electrolyte is obvious [202,203]. But the role of electrolyte on the properties of nonionic surfactant systems is not so obvious. Moreover the properties of these nonionic surfactant systems are highly dependent on the temperature. Hence it would be very intriguing to study these kind of systems at different tempratures. The present chapter deals with studies of Alkane/Brij 35 + propanol/water systems in presence of various amounts of NaCl and also at different temperatures.

A necessary basis for the discussion of the properties of such systems is the understanding of their phase behaviour. This could be achieved by studying the changes in the phase diagram with temperature, electrolyte concentration, nature of the oil phase etc. Phase diagram studies conducted by Kahlweit et al.are highly informative [132-133]. With the empirical relations developed to explain the phase diagrams, one should be able to predict the phase changes observed. It was suggested that the appearance of 3ϕ region is due to the interplay between water-surfactant and oil-surfactant miscibility gaps [134]. Infact these miscibility gaps are highly sensitive to the concentration of the electrolyte.

Presence of Winsor transitions with changing NaCl concentration is an established phenomenon [147,149,204]. With increase of electrolyte concentration, systems change from Winsor I (microemulsion phase is in equilibrium with excess oil) to Winsor II (microemulsion is in equilibrium with excess water) through a narrow Winsor III (microemulsion is in equilibrium with both excess oil and water). These changes are due to the microstructural changes in the microemulsion phase. It was understood that, in Winsor I system microemulsion phase has oil in water (o/w) structure while in Winsor II, its structure is water in oil (w/o). A bicontinuous structure was proposed for the middle phase microemulsion (Winsor III type). Aveyard et al. described these various Winsor forms through a simple diagram (Fig.4.1) [71]. Single phase microemulsion is termed as Winsor IV type.

In nonionic surfactant system similar phase changes were also observed with change of temperature [205]. Ionic surfactant systems generally show a transition of the form (W.II → III → I) with respect to temperature [206].

The structural changes in microemulsion, which in turn induces Winsor transitions, were generally explained by the nature of interfacial surfactant film. This interfacial surfactant monolayer was characterized by either surfactant molecular geometry [61,207,208] or by two important parameters of the monolayer called rigidity (K) and spontaneous curvature (C_o) [76,78]. It was observed that these parameters were functions of NaCl concentration [61,76,78,81,207,208].

The phase volume measurements could be used to determine the optimum salinity of the system through the so called 'salinity scan'. Healy and Read defined optimum salinity as the salinity at which there is an equal uptake of oil and water in the middle phase microemulsion [209]. This is very important for tertiary oil recovery purposes.

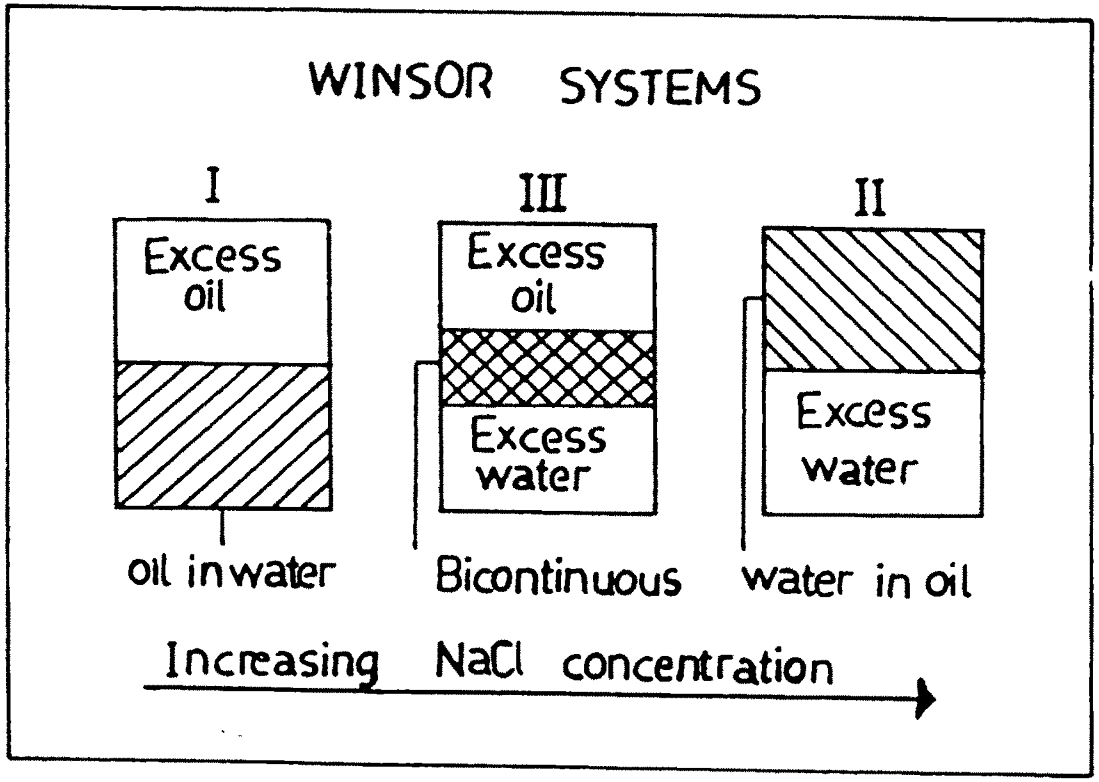

Fig.4.1 Pictorial representation of Winsor transitions I → III → II as the function of increasing NaCl concentration.

Kahlweit et al.in their detailed phase diagram studies of nonionic surfactant system, noted that cloud point of the surfactant (they termed it as the lower critical temperature of water-surfactant miscibility gap (T_β), see chapter III, p 44) is critical in deciding the phase diagram pattern [133]. Also, cloud point is a measure of the nonionic surfactant's hydrophilic or hydrophobic character. Higher the number of polyoxyehtylene (POE) groups in the surfactant, higher is the hydrophilicity of the surfactant and hence higher will be its cloud point [200]. Mechanism of clouding of nonionic surfactant in aqueous solution was well studied [210,211]. The microemulsion cloud point is sensitive to the nature as well as the amount of components which form the microemulsion. This complexity makes the cloud point study of microemulsions highly interesting and important. Recently Siano et al.described a method to determine the molecular weight of water soluble polymers by measuring microemulsion cloud point at various concentrations of the polymer [193].

Physical properties like viscosity of microemulsion are important for various technological applications. But not much studies are available which relate the viscosity values with amount of electrolyte in the system. In one of the earlier studies, peaks observed in viscosity versus NaCl concentration plot was interpreted as the evidence of structural transition [201].

It has been reported that systems with highly hydrophilic nonionic surfactants like Brij 35 system become temperature sensitive only in presence of an electrolyte [120]. Hence in this chapter we report the study of phase behaviour and some other physical properties like viscosity, compressibility, cloud point, Winsor transitions etc. at various temperatures and NaCl concentrations.

4.2 SYSTEMS STUDIED

In the present chapter, effect of NaCl at various concentration on the alkane/Brij 35 + propanol/water microemulsions were studied at different temperatures (30°-80°C). Alkanes used were heptane, nonane and their mixtures. The effect was studied on phase diagrams at various temperatures (40°-80°C). Viscosity and adibatic compressibility of different oil-water ratios of the microemulsion systems were studied at various NaCl concentration and temperature. Presence of NaCl induces Winsor transitions in the system. The volume fraction of each phase was measured at various temperature as a function of NaCl concentration. The cloud point, an important characteristic of nonionic surfactant systems, was studied in detail over a range of NaCl concentration, surfactant concentration and oil/water ratio. Some measurements of interfacial tension were also done and are reported here.

4.3 RESULTS AND DISCUSSION

(a) Phase diagram

Fig.4.2 (a &b) is the phase prism representation of the system alkane/Brij 35 + propanol / water showing the phase changes observed with changing NaCl concentrations at 80°C (earlier in chapter III, we presneted the phase diagrams at 0 M NaCl from 20 to 70°C). In absence of NaCl, only Winsor I and Winsor IV types are present in the ternary phase diagrams. Addition of NaCl induces marked changes in the phase diagram. When water was replaced by 1 M NaCl, a large area was covered with Winsor III type formation. When 1 M NaCl solution was used instead of water in microemulsion formation all the four Winsor types were found present in phase diagram. This type of changes were observed earlier also [120].

Winsor III system, which exhibits maximum miscibility between oil and water to the microemulsion phase, forms

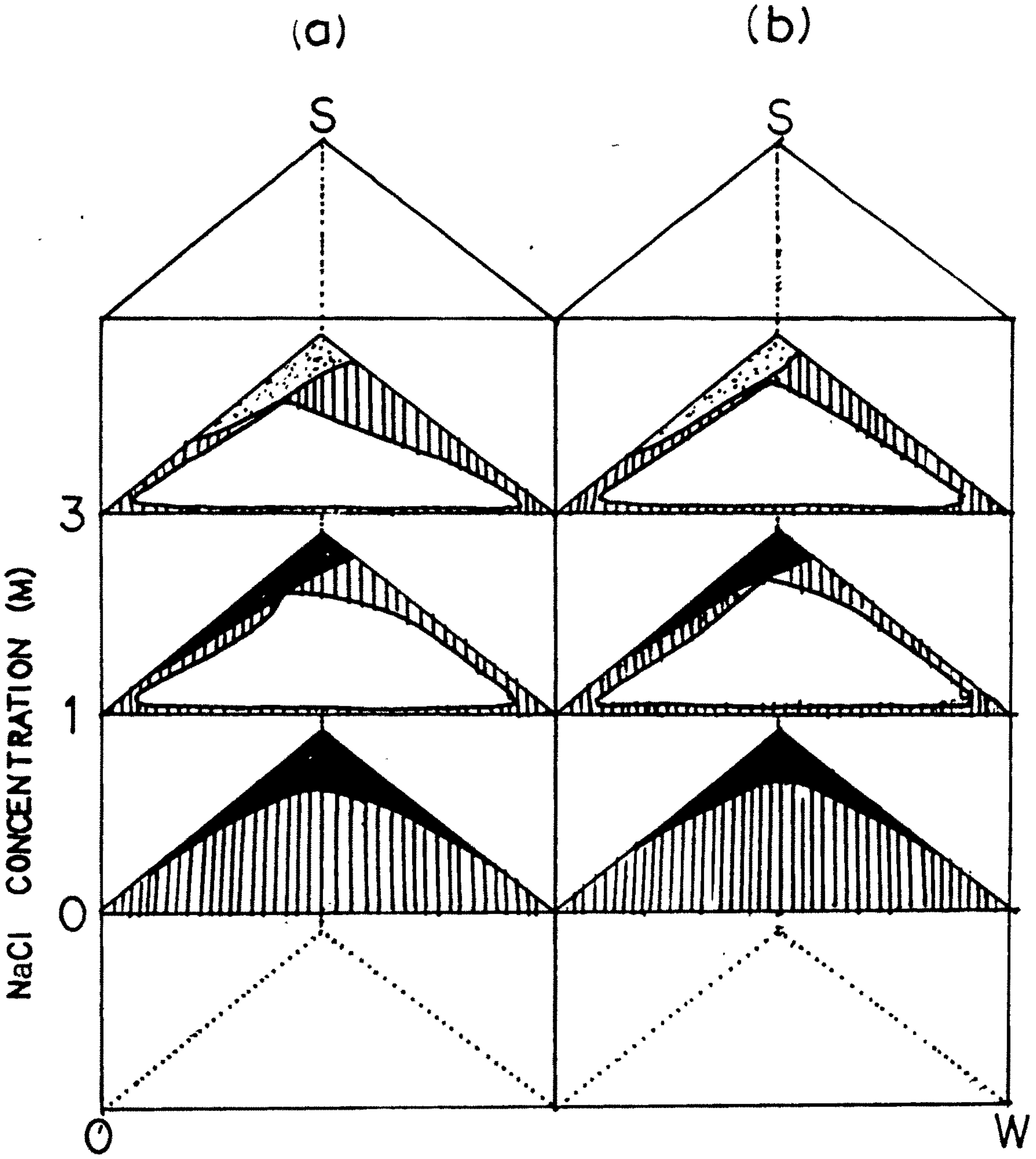

Fig. 4.2 Isothermal phase prism representation (at 80°C) of the system alkane (O)/Brij 35 + propanol (S)/water (W) at various NaCl concentration. (a) heptane (b) nonane.
■ 10, ▥ 20 (L/L), □ 30 (L/L/L), ⊡ 20 (S/L) regions.

only when the surfactant achieves an optimum hydrophil-lipophil balance i.e. HLB [212]. HLB of the surfactant is sensitive towards electrolyte concentration (especially for ionic surfactants) and/or temperature (for nonionic surfactants) [81,213]. The above mentioned HLB is different from the HLB number that is associated with each surfactant . HLB is the hydrophilic-lipophilic balance that the surfactant experiences in a particular system [214]. According to Griffin's concept, HLB number is a number which characterizes a particular surfactant molecule and is not a function of variables like temperature, pressure, salt concentration etc. [215]. This number is used by formulation chemists to choose surfactants for emulsion formulations. But HLB indicates the lyophilic or lyophobic character that the surfactant shows in a particular environment and it changes with temperaure, pressure, salt concentration, composition of surfactant and the type of oil etc. [21,216,218].

Shift in the HLB of nonionic surfactant with changing temperature was noted by many researchers [212,219]. At ambient temperatures nonionic surfactants were highly hydrophilic and hence completely miscible with water. But with rise of temperature, the attractive interactions of the polar head group of the surfactant and water decreases (dehydration of head group occurs) and the repulsive force between tail region and water starts dominating. Thus its hydrophobicity increases [134]. Hence HLB is a function of the system itself and not only of the molecular structure of the component.

Generally nonionic surfactants achieve the required HLB for 3Ø formation due to the required increase of temperature [78,134]. But it was also reported that nonionic surfactants, having large number of polyoxyethylene group, remain unaffected by the change of temperature to an extent [174]. Brij 35 has 23 oxyethylene groups and the cosurfactant used (propanol) was also not hydrophobic. Hence relative temperature independency of this surfactant was expected. They might be affected by temperature at very high value which was difficult to achieve at atmospheric pressure (we were not in a position to work at high pressure). But addition of salt like NaCl tends to 'salt out' the amphiphile head group which resulted in the decreased hydrophilicity of the amphiphile [149]. This effect combined with the shift to higher hydrophobicity due to the rise of temperature helped the system to acquire the HLB to form the 3Ø system. Hence the ternary phase diagram for alkane / Brij 35 + propanol/ 1 M NaCl at 80°C contains a large 3Ø region.

When the NaCl concentration was increased to 3 M, the one phase microemulsion region was completely replaced by a solid/liquid biphasic (microemulsion is in equilibrium with excess solid NaCl) region. That is the system is too saline to form a Winsor IV type.

We discussed earlier that addition of an electrolyte helps to decrease the water-nonionic surfactant interaction [149] and this increases surfactant's hydrophobicity. At this decreased hydrophilic state, the surfactant system became sensitive to temperature. Fig 4.3 (a & b) exhibits these results. When the acqueous phase was 1 M NaCl solution, 3ϕ region developed in the phase diagram even at 40°C for heptane system. This zone expanded at the expense of 2ϕ region with the rise of temperature. This is because of the increased hydrophobicity of the surfactant at higher temperature. Due to the higher lipophilic character of the surfactant, 3ϕ system can form even at lower surfactant concnetration. The larger oil-water ratio could also be accomodated in the middle phase microemulsion. These factors helped in widening the 3ϕ region. Areas of both heptane and nonane 3ϕ regions were plotted against temperature in Fig 4.4. It shows a linear increase with temperature for both the systems.

It could also be seen in Figs 4.3 (a & b) that at 40°C, 3ϕ region exists only in heptane system.

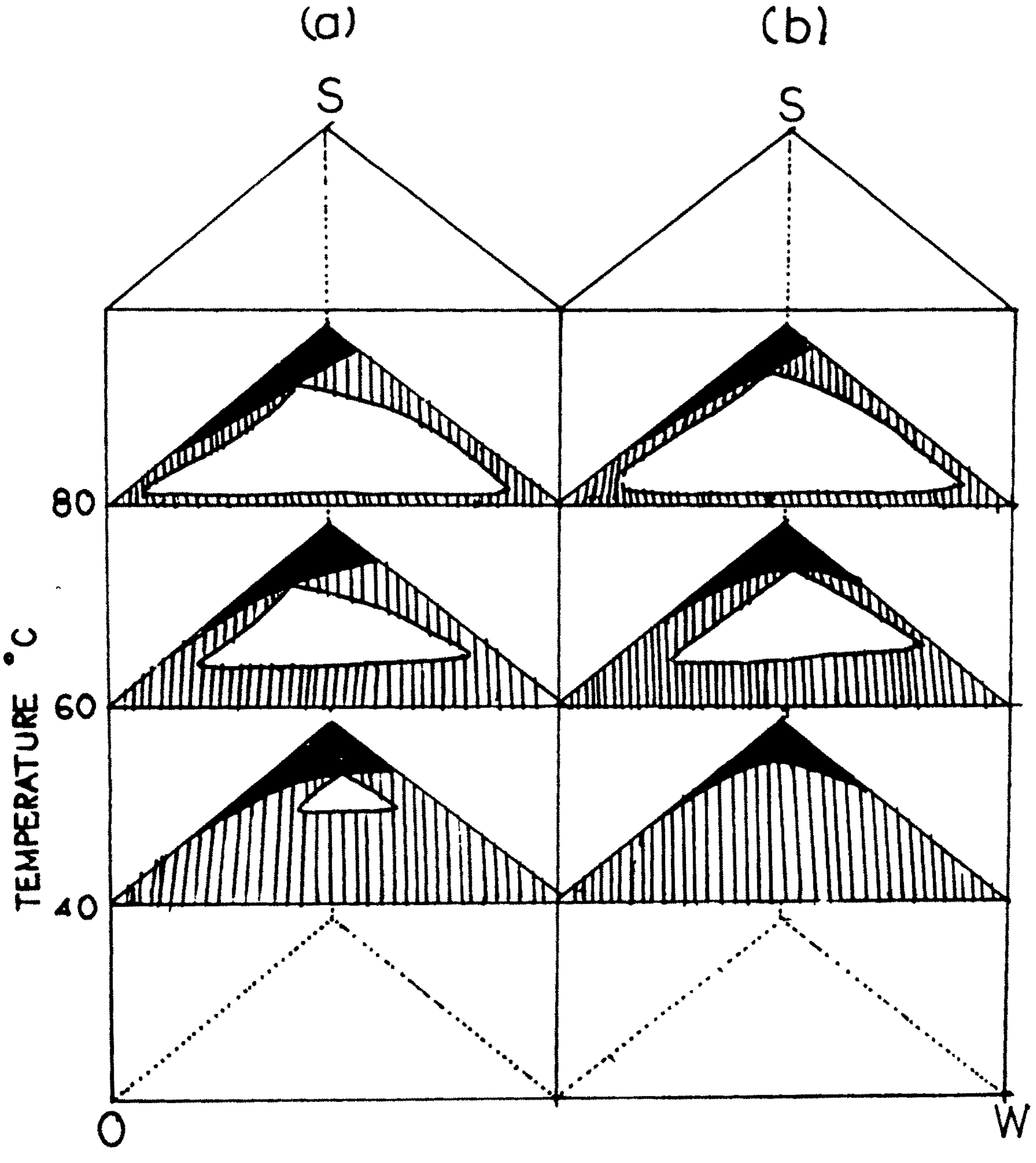

Fig-4.3 Phase prism representation of the system Alkane(O)/ Brij 35 + propanol (S)/ 1M NaCl (W) at various temperature ■ 1φ, ▥ 2φ (L/L), □ 3φ (L/L/L) regions. Alkanes are (a) Heptane (b) Nonane.

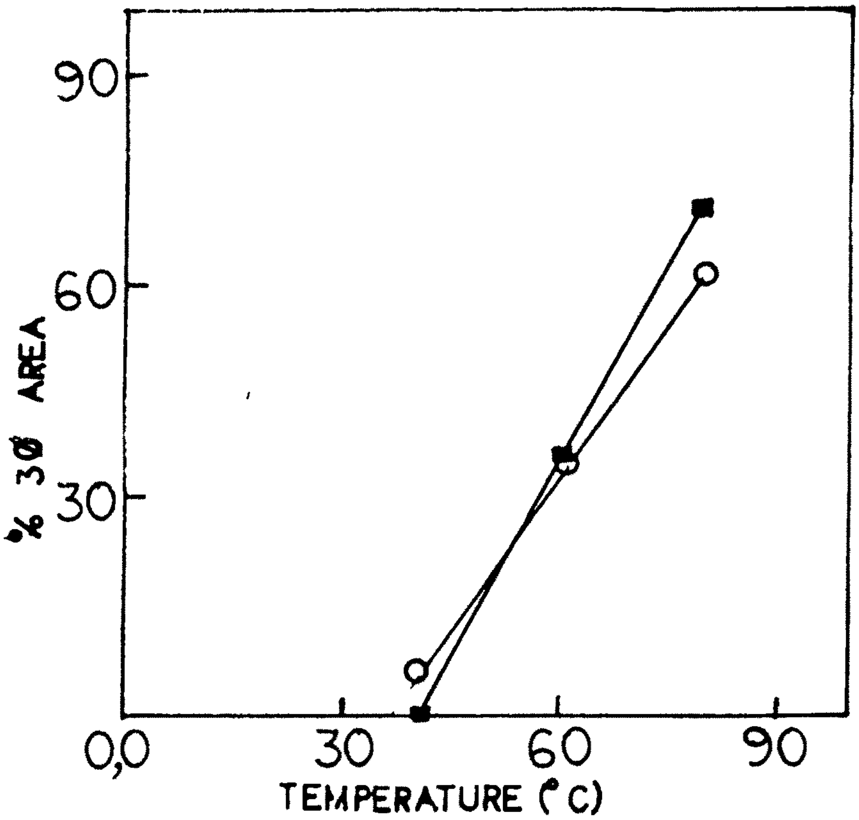

Fig.4.4 A plot of percentage 30 area in Alkane/ Brij 35 + propanol/1M NaCl phase diagrams vs temperature. ○ Heptane, ■ Nonane.

Nonane/Brij 35 + propanol/1 M NaCl system's ternary diagram at 40°C is very much similar to Nonane/Brij 35 + propanol/water system at the same temperature. This implies that concentration of NaCl used (1 M NaCl) was not sufficient to affect the phase behaviour of nonane system at 40°C. It suggests that higher the alkanes, higher will be the amount of electrolyte required to introduce certain changes in the phase diagram. This is because higher alkanes are relatively more hydrophobic and hence more NaCl is rquired to affect the water structure to get the needed HLB.

It is obvious that any variation in the area of a particular zone will certainly be opposite to the variation of another zone. Hence the possibility of the existence of any compensation effect among the 1ϕ , 2ϕ and 3ϕ regions were examined by plotting these areas together three dimensionally (Fig.4.5). It seems that in heptane system an approximate 1ϕ - 2ϕ compensation effect exists while in nonane system similar compensation was not observed. Also it is clear from the figure that no linear compensation between 3ϕ - 1ϕ or 3ϕ - 2ϕ system exists.

Phase behaviour of these multicomponent system at equal o/w weight ratio with changing temperaure and

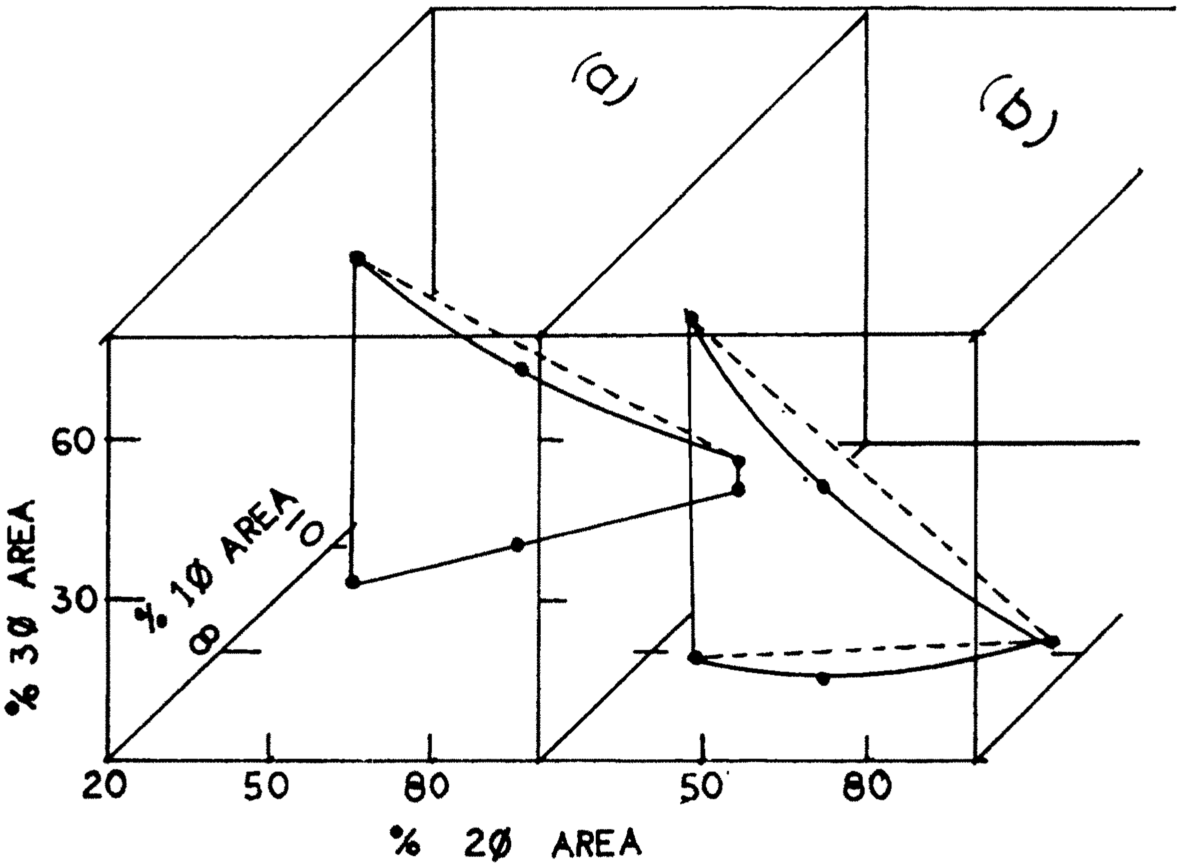

Fig.4.5 Three dimensional representation of 10, 20 and 30 areas of the system Alkane/Brij 35 + propanol /1M NaCl . (a) Heptane and (b) Nonane

surfactant concentraiton could be confortably followed by the two dimensional phase diagram. Such phase diagram for heptane system was shown in Fig.4.6. Decrease in area of 2ϕ region with increase of temperature could be seen in the Fig.4.6. This 2ϕ region was made up of two different types of liquid grouping. The left hand side of the broken line is a nonequilibrium state, though kinetically stable and reproducible. With increase of temperature, this part becomes narrower. Rise of temperature lowers the viscosity of the liquid component and it also enhances the microemulsion formation . These effects helps in phase seperation and this nonequilibrium state, formed due to slow phase seperation, narrows down. However within the temperature range studied (upto 80°C), this so called nonequilibrium state remains present. It did not break up atleast in 48 hours. It seems to break up slowly after that but still it was not quite yet measurable. Nonane system also behave similarly.

(b) Phase volume measurements

Winsor transitions at 30% surfactant concentration at different oil/water ratio were studied. NaCl concnetration, temperature and the nature of the oil phase were the parameters varied.

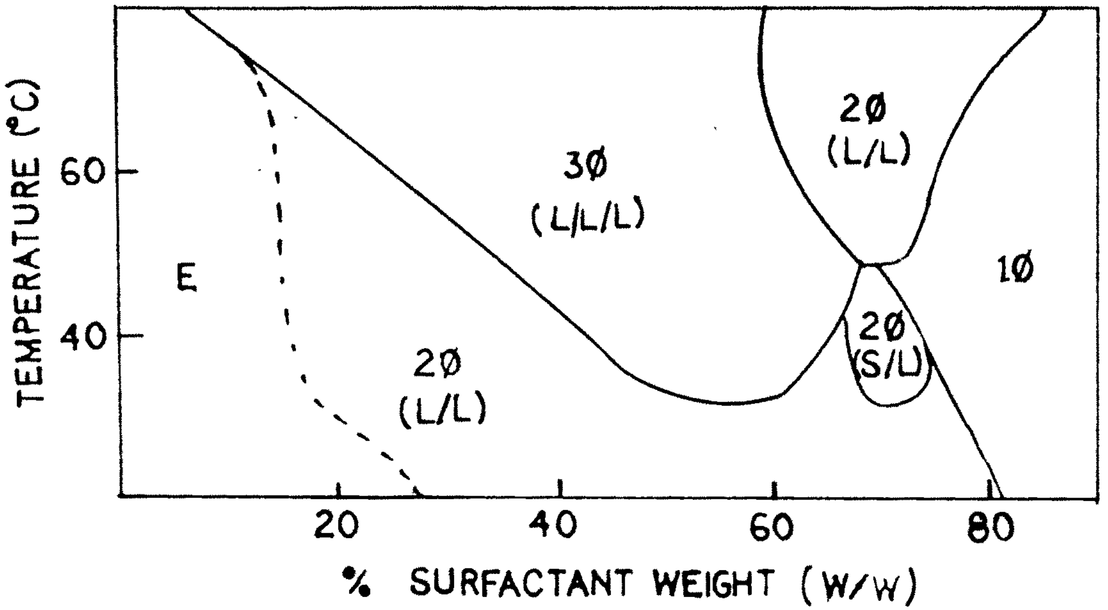

Fig-4.6 Surfactant concentration–Temperature two dimensional phase diagram of the system heptane/Brij 35 + propanol/1 M NaCl at equal heptane/1M NaCl weight ratio. E - Nonequilibrium emulsion phase.

Figs 4.7 (a & b) show the phae volume fractions of the alkane/Brij 35 + propanol/water system with increasing NaCl concentration at different temperatures. The alkanes were heptane and nonane. At low salinity the system exist as Winsor I. At comparatively higher salinity, Winsor I → III transition takes place. But this transition salinity was found to be sensitive to temperature. Transition salinity shifts to lower concentrations with increasing temperature. Generally the Winsor III system exists only over a narrow range. At higher salinity the system changes over to Wisnor II type where microemulsion phase was in equilibrium with excess water [209]. However in the present system, such transition was not observed. Even at extreme conditions like 80°C temperature and using 2.5 M NaCl solution, Winsor III type persists. This indicates that the surfactant composition was not sufficiently hydrophobic to dissolve the excess oil phase completely and thus change over to Winsor II. This was evident from the interfacial tension (IFT) measurements carried out on this systems (Fig.4.8). The procedure for this measurements has been discussed in p. 31 of this thesis. IFT between middle phase (microemulsion phase) and upper phase (oil phase) was fairly high (of the order of 1 mNm^{-1}). It did not decrease appreciably even with increase of temperature. Generally for nonionic surfactant system, IFT between microemulsion phase and oil phase

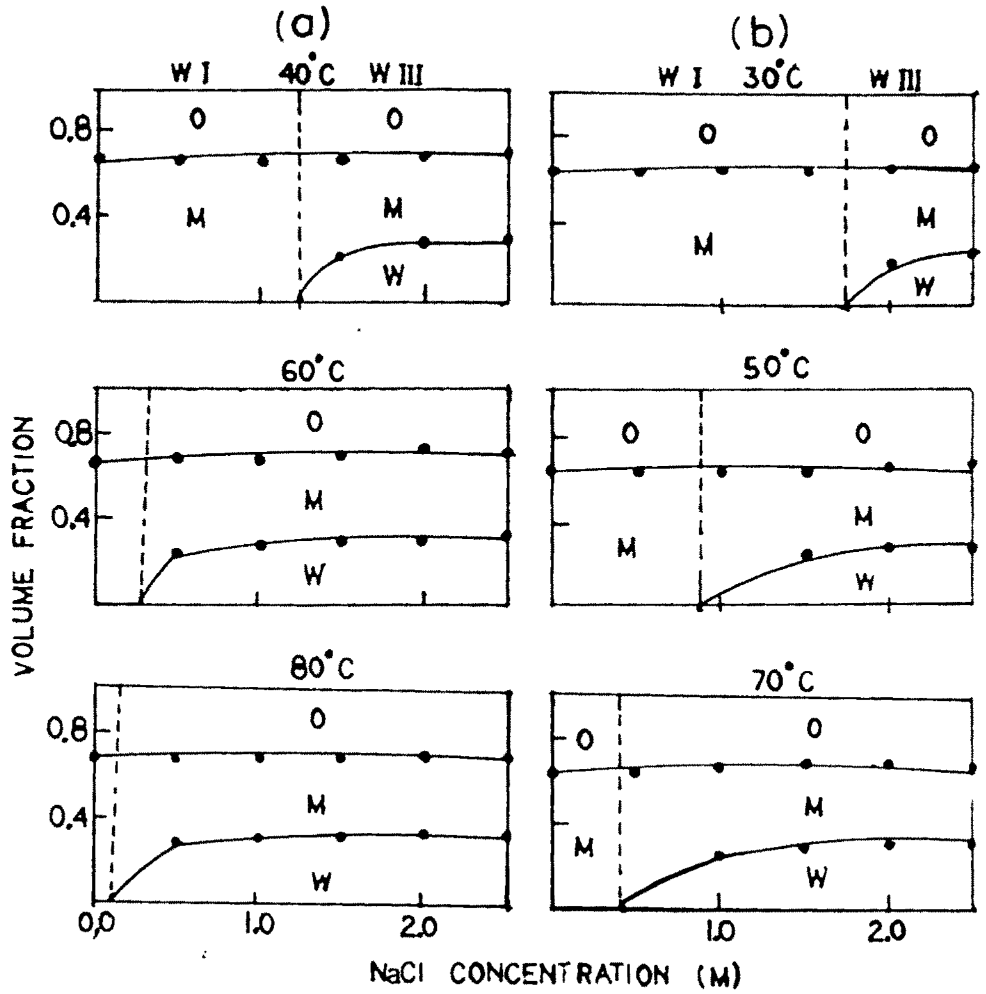

Fig.4.7 The plot showing the volume changes of different phases with changing NaCl concentration of Alkane/Brij35 + propanol/water system
W - Aqueous phase , M - microemulsion phase, O - Oil phase.
For details see text. (a) Heptane (b) Nonane
W I & III represent Winsor I & III systems

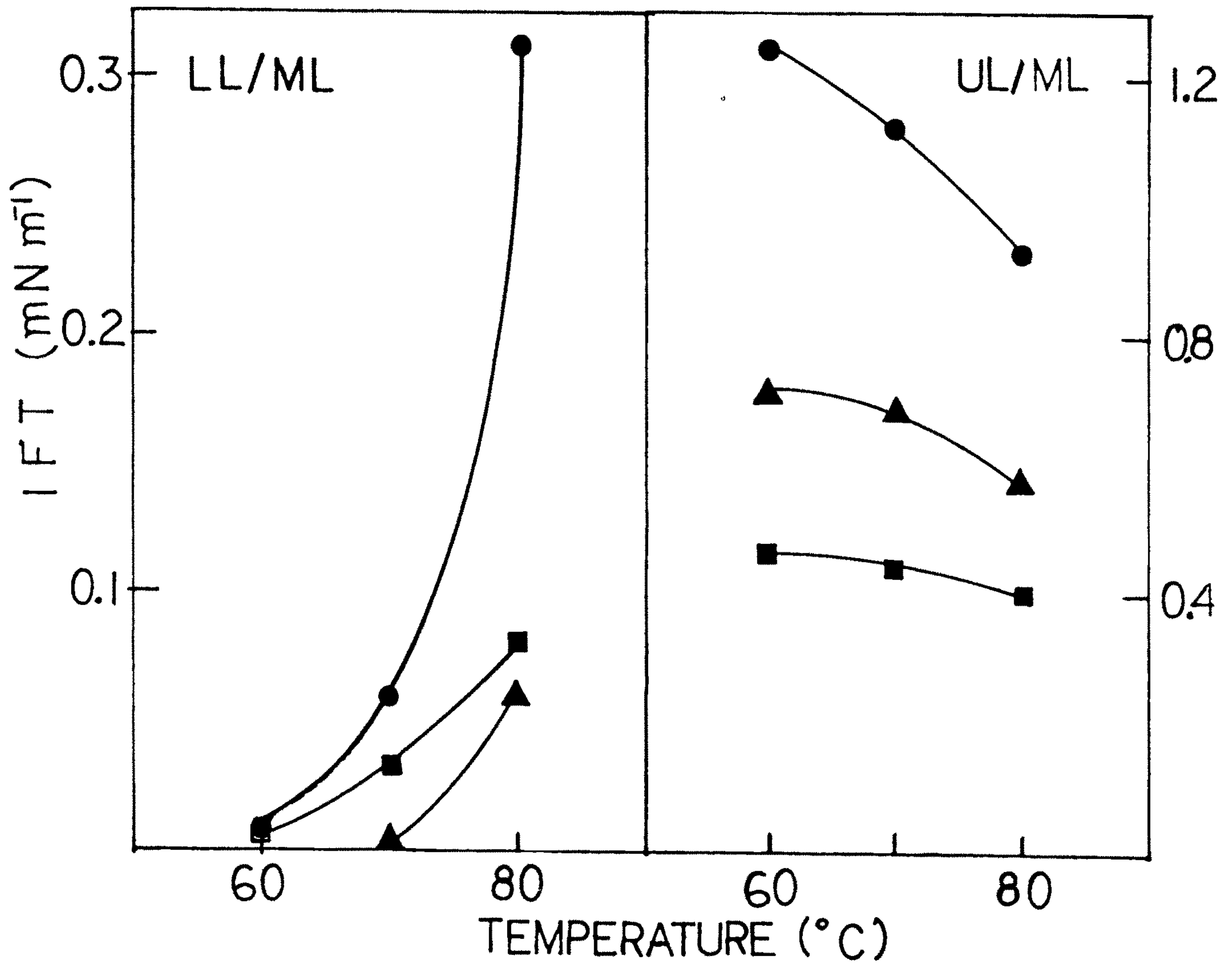

Fig. 4.8 Interfacial tension between different phases of Alkane (30%)/Brij 35 + propanol (30%)/water (40%) Winsor III system as a function of temperature. LL - Lower aqueous phase, ML - Middle micoremulsion phase, UL - Upper oil phase. ■ Heptane, ▲ Heptane+Nonane (1:1), ● Nonane.

decreases drastically with increase of temperature. Here the IFT between microemulsion phase and aqueous phase is highly sensitive to temperature. It increased to a fairly high value with increase of temperature. Thus the water forms a separate lower layer and thus the system remains a three phase one. Figs 4.9 (a & b) give the variation of volume fraction of different phases with change of temperature. The nature of the diagram is similar to the volume fraction versus concentration of NaCl curve. As a corollary to the earlier observation, here Winsor I → III transition temperature was lowered as NaCl concentration was increased. At 2.5 M NaCl only Winsor III system is present at all temperatures. In absence of NaCl the system exists only as Winsor I at all temperatures.

It could be seen from these figures that both NaCl and temperature influence only the Winsor I→ III transition point. Once Winsor III type is formed, the middle phase volume remained more or less invarient to both parameters.

Fig 4.7 also shows the effect of alkane nature on the Winsor transition. For lower alkane (heptane) transition occurs at a lower salinity.

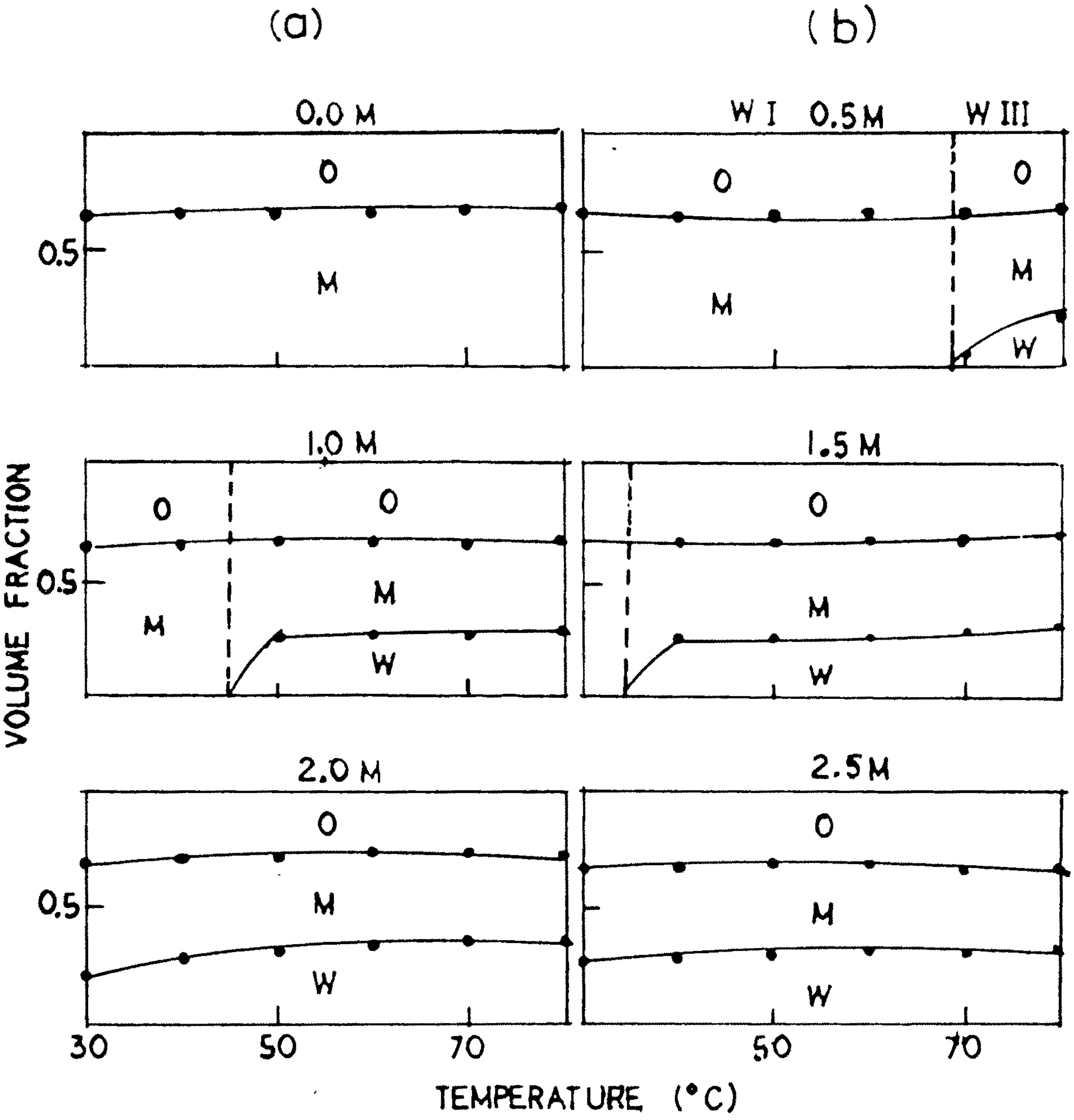

Fig.4.9 Volume Fraction - Temperature plots of various Winsor formations. System is Alkane/Brij 35 + propanol/water in presence of NaCl (0.0 - 2.5 M) (a) Heptane, (b) Nonane.

Winsor transitions with changing NaCl concentration and temperature together for heptane system are shown in a 3 dimensional representation (Fig 4.10).

These results could be very well explained by considering the surfactant geoemtrical packing ratio, which was introduced by Mitchell, Ninham and others [207,208] and further simplified by Aveyard et al. [71,82]

Ninham and others suggested that, if 'V' is the effective volume of surfactant molecule and a_o and l_c are the effective head group area and surfactant tail group extended length respectively, then the term packing factor = $V/a_o l_c$. This term dictates the structure of surfactant aggregates. Recently Aveyard and coworkers suggested a simplified version of this idea (71,82). 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 4.11(a)). The 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. Instead it is the effective value 'insitu' in the surfactant monolayer that counts. Hence

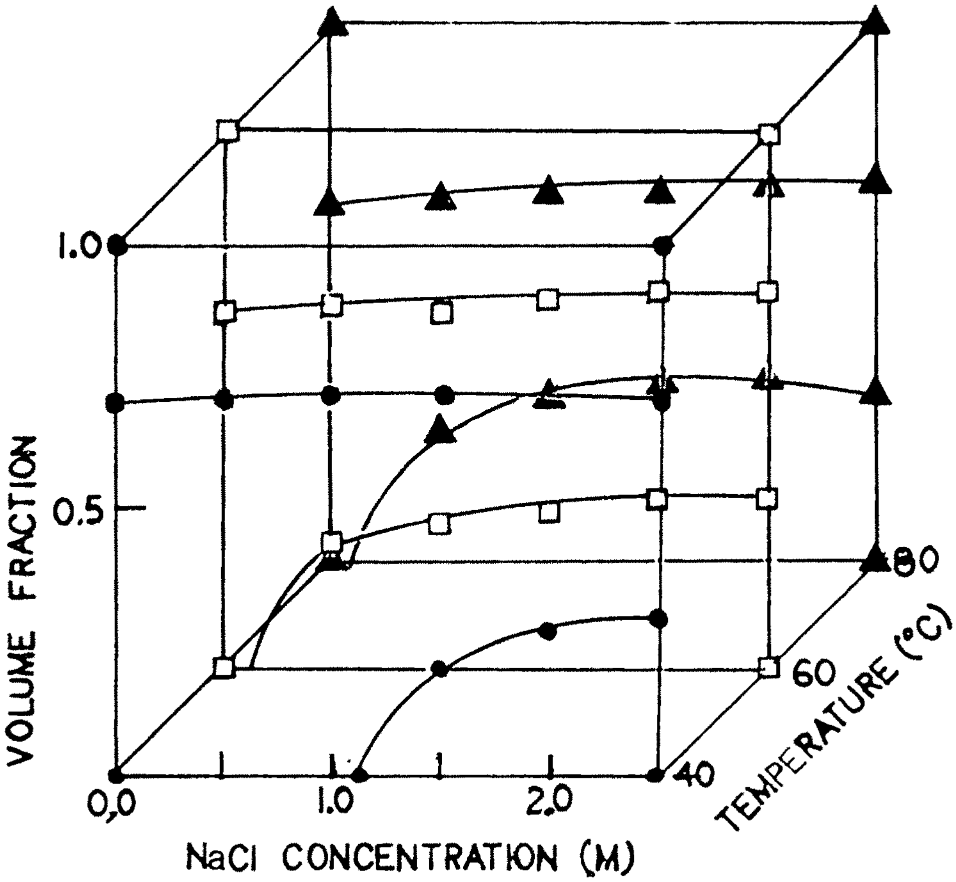

Fig.4.10 A three dimensional representation of the variations of phase volume fraction with changing temperature and NaCl concentration for the system heptane/Brij 35 + propanol/water.

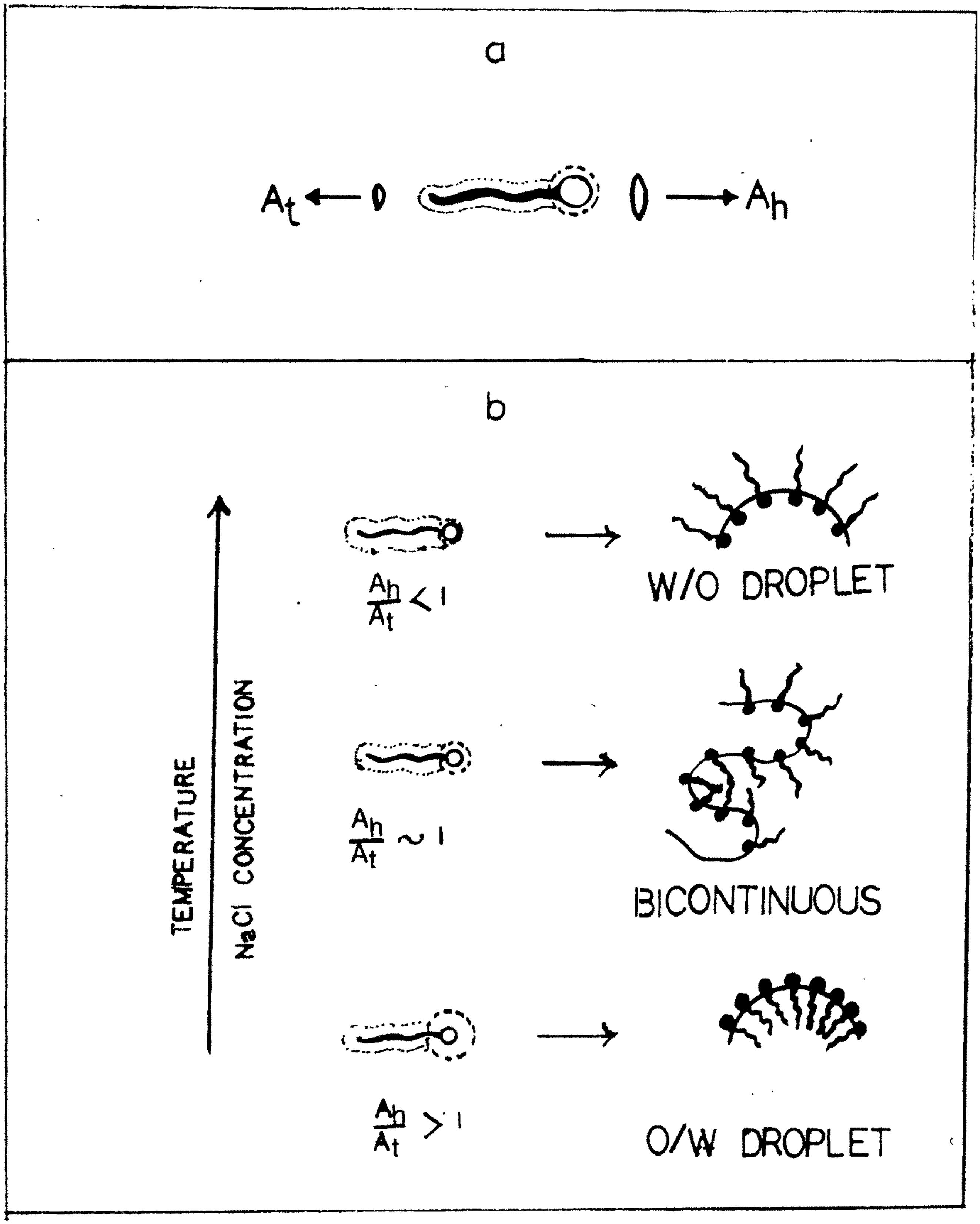

Fig.4.11 Changes on the effective surface areas of head group (A_h) and tail region (A_t) of the surfactant at the influence of electrolyte concentration and temperature

the packing ratio is affected by many factors including hydrophilicity of head group, ionic strength of the solution, pH, temperature and nature and amount of cosurfactant (Fig.4.11 (b)) [71]. 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 1 ($A_h < A_t$) water in oil structure is more probable and the system changes to Winsor II. At an intermediate range (i.e. $A_h \sim A_t$) microemulsion appears as bicontinuous and thus develops the 3ϕ system (Winsor III).

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. 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 etc. [71]. 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 and electrolyte concentration [71]. Increase of temperature dehydrate the polyoxyethylene group [220]. Similarly an electrolyte, when present in the formulation, tends to dehydrate the oxyethylene group by getting hydrated itself. This results is the 'salt 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. Aveyard et al.determined A_h value for $C_{12}E_5$ type surfactant in water-heptane system. The values are found to be around 0.40 nm^2 [71]. But for the present surfactant ($C_{12}E_{23}$), due to its large number of POE group, solvated water molecules around the head group will be more than in the $C_{12}E_5$ surfactant. This is due to the zig-zag nature of the single bonded oxyethylene chain. This will increase the value of A_h in $C_{12}E_{23}$ to some extent. If the single bond did not have free rotation character, the A_h value of both 'E_5' and 'E_{23}' would have been same. But A_h for E_{23} would be higher than E_5 as the various 'E' groups are joined together by free rotational single bond.

Moreover Ninhan et al. pointed out that higher the hydrophilicity of the head group, higher will be the value of A_h [208]. Hence A_h for the present surfactant is believed to be higher than 0.40 nm^2 suggested by Aveyard et al.for $C_{12}E_5$.

The value of A_t calculated for the system heptane /$C_{12}E_5$/ water was about 0.37 nm^2. But we presume that the value for $C_{12}E_{23}$ system would be slightly less than this. Due to the higher hydrophilicity of the surfactant, a portion of the hydrocarbon part of the surfactant may likely to be pulled into the water phase. This opposes the swelling of the tail region by the nonpolar solvent. 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_c)[221]. That is it increases A_t. As the cosurfactant (i.e. propanol) is not hydrophobic , we think that this effect would not have much prominence here. Propanol is not hydrophobic enough to affect the value of A_t appreciably. Though the presence of propanol might slightly increase the A_t value, due to the poor penetration of alkane to the surfactant tail region, the value of A_t for $C_{12}E_{23}$ system must be less. Thus at low NaCl concentration and temperature, $A_t < A_h$ and packing ratio value is less than one. Therefore the system exists as Winsor I. As discussed earlier, the increase of NaCl concentration and temperaure dehdyrate polyoxyethylene group and thus A_h value decreases. At the same time, in view of the increased hydrophobicity of the surfactant molecule, alkane starts penetrating the tail region, though feebly. This might swell the surfactant tail slightly . Thus there is slight increase in A_t. Hence by increasing the NaCl concentration to a particular level or by increasing the temperature to a reasonably high value, keeping all other experimental variables constant, the A_h value can be brought down to the level of A_t. Thus system changes from Winsor I to III by increasing the temperature and/or NaCl concentration (Figs 4.7 & 4.9).

In Fig.4.7 , one sees that Winsor I-III transition takes place at an earlier stage for heptane system. It was reported by many authors that lesser the alkane chain number, higher is the penetration of the alkane in the surfactant film [123]. We have already seen that more penetration of alkanes mean large value for A_t. Though the penetration of both the alkanes are comparatively weak here, penetration of heptane will be more than by nonane. Hence A_t value will be higher for heptane system at any particular stage. Considering that the other factors are similar, A_h need to be lowered to a lesser extent in heptane to make it equal to A_t. This, in turn, lowers the concentration of NaCl needed for the Winsor I→III transition.

We just described the changes that probably occurs for the Winsor I-III transition. Here after A_t is expected to increase sharply with further increase of temperature and electrolyte concentration. At some point A_t becomes higher than A_h and second transition (W III → W II) takes place. As the Figs (4.7 & 4.9) show, this did not happen in the present system. (It was observed though, that such transitions are possible in these systems also when the cosurfactant/surfactant ratio is high. This increase certainly makes the surfactant combination more hydrophobic and can solubilize the excess oil phase to form the Winsor II system. In the present system Winsor III to II transition was observed when CS/S weight ratio was 9.0 (fig.4.12). But in this thesis, we have presented results of the studies where CS/S weight ratio is only 2).

Aveyard measured the variation of A_t and A_h values with changing NaCl concentration [71]. It was observed that A_h changes only when the system is oil in water microemulsion (Winsor I). Hence once the system is changed over to Winsor III, the variation in the values of A_t/A_h ratio will be purely dependent on the changes of the magnitude of A_t. But as explained above,the penetration of alkanes to the hydrocarbon tail of the surfactant is reasonably low in the present system (i.e. when CS/S ratio is 2) and hence A_t does not change appreciably. This prevents the ratio to achieve the desired magnitude of more than 1 and consequently the Winsor III→II transition remains unavailable within the temperature and salinity range studied.

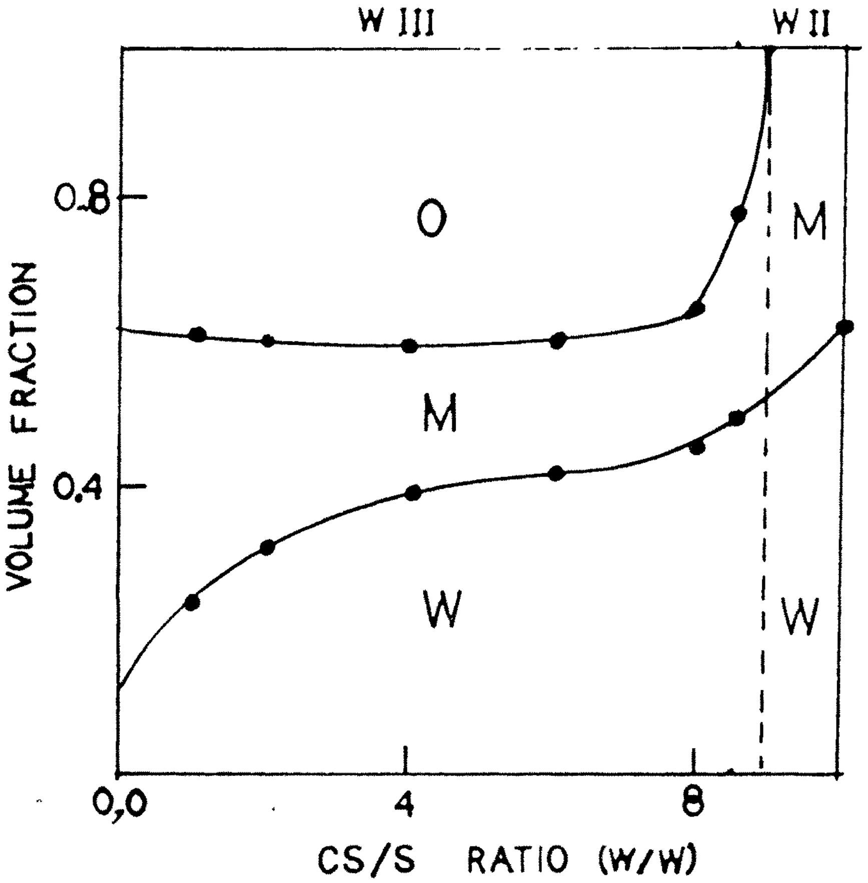

Fig.4.12 Plot of volume fraction vs cosurfactant-surfactant ratio . Winsor III → II tractions. O - Oil phase, M - microemulsion phase and W - aqueous phase.

We measured the phase volume changes at different oil/water ratios also (Figs 4.13, 4.14). It could be noted that changing oil/water ratio did not influence the middle phase volume appreciably. It thus seems that the values of A_h and A_t are independent of the amount of water or oil. Also generally no Winsor transition was observed in the studied oil/water ratio. Except in one case (for heptane system at 60°C), the system remains similar through out. i.e if Winsor I system exists at low water fraction, change of the oil-water ratio does not have any effect on Winsor I system. Only there is a change in the volume of lower phase at the expense of oil phase.

(c) Cloud Point

Fig.4.15 (a & b) shows the change of cloud point of both heptane and nonane with change of NaCl concentration. A regular decrease of cloud point is observed with increase of salt concentration. Similar results were obtained with water soluble polymers also [193]. When the NaCl solution used was 2.1 M, for a particular composition of heptane system, the cloud point was down to 20°C. That is a decrease of more than 80°C. This dramatically shows the influence of NaCl to modify the nature of a nonionic surfactant containing formulation . The clouding in the present system is not only due to the presence of NaCl but

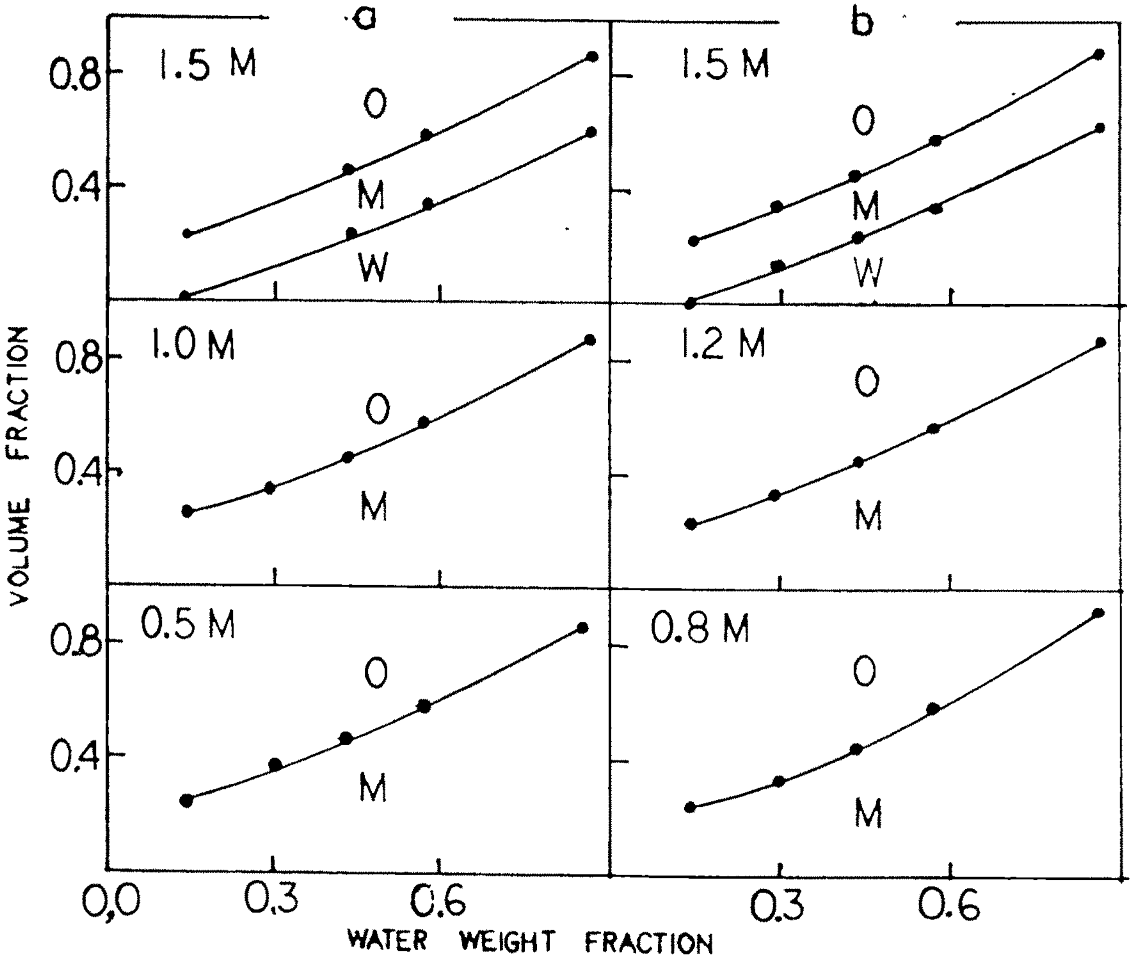

Fig.4.13 Representative plots of volume fraction vs water weight fraction at various NaCl concentration at 60°C (a) Heptane/Brij 35 + propanol/water (b) Nonane /Brij 35 + propanol/water.

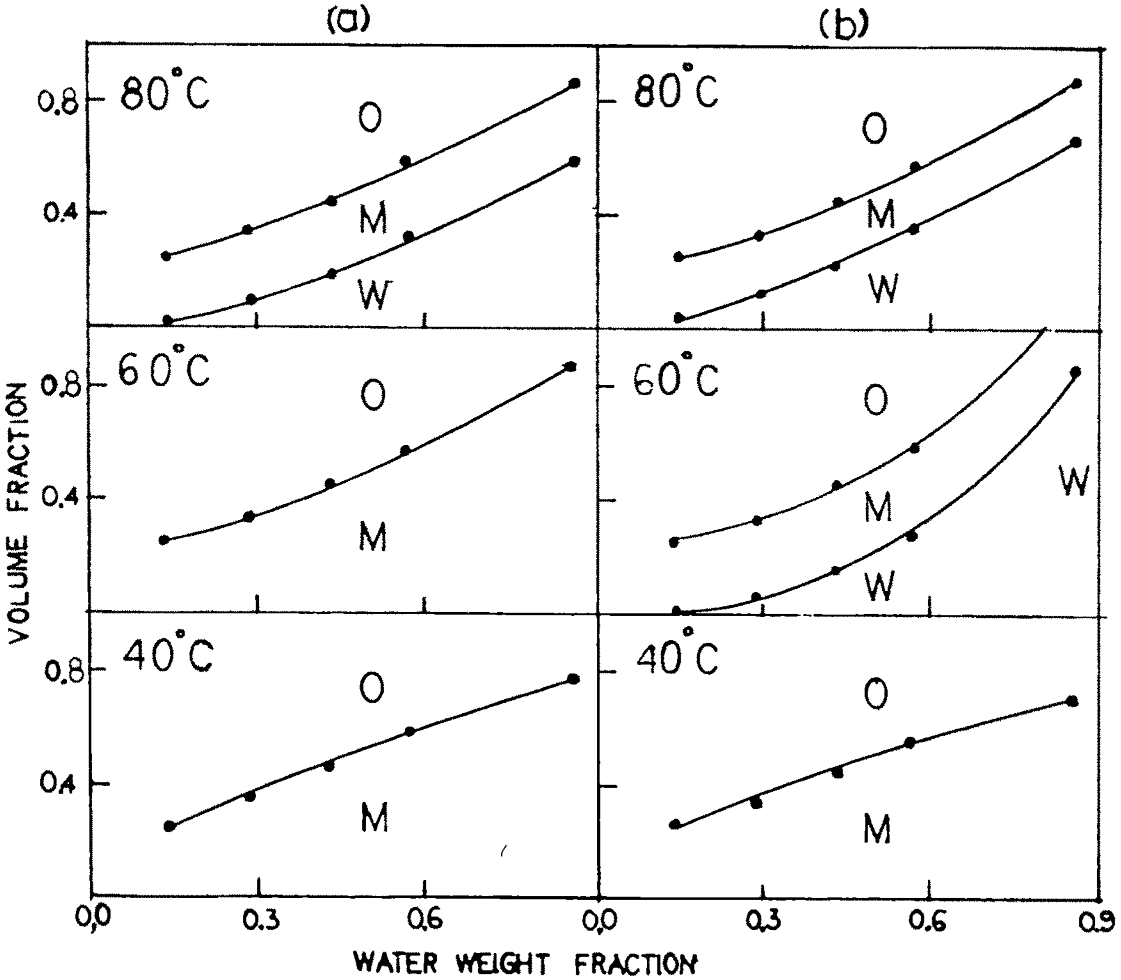

Fig. 4.14 Representative plot of volume fractions vs water fraction in alkane-water combination at various temperatures (0.8 M NaCl concentration) (a) Heptane/Brij 35 + propanol/water (b) Nonane/Brij 35 +propanol/water.

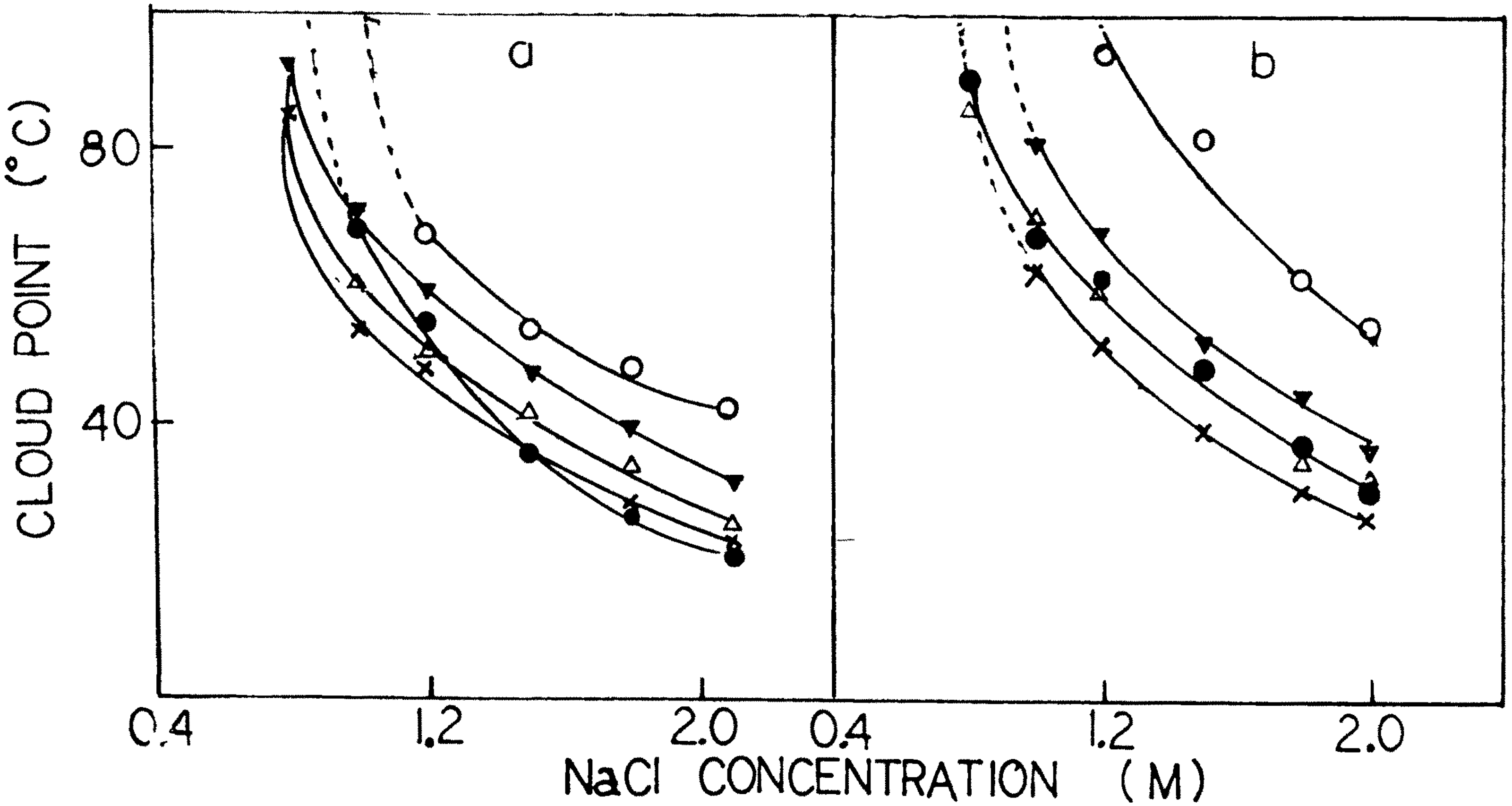

Fig.4.15 Cloud point vs NaCl concentration plot of Alkane/Brij 35 + propanol (80% w/w)/water system (Percentage alkane in the system in ● 2% ; × 6%; △ 8%; ▼ 10%; ○ 12%.)
(a) Heptane (b) Nonane.

cosurfactant also plays a very important role. It is known that incorporation of cosurfactant molecules in surfactant aggregates enhances the oil penetration to it. The clouding effect is due to the influence of NaCl in producing enough lipophilic shift in the surfactant's nature at comparatively lower temperature. The propanol also makes the system relatively more hydrophobic and there by decreases the cloud point. The role of propanol was verified by doing separate experiment. Aqueous solution of the surfactant in presence of NaCl at lower concentration did not show the cloud point below 100°C. But it became cloudy with addition of propanol. Similarly water-surfactant-propanol system also did not show this phenomenon in the absence of NaCl. Thus it could be concluded that the associated effects of NaCl and propanol were responsible for this clouding phenomenon. The presence of alkane in the system should also affect the cloud point of the microemulsion. But this point could not be proved directly as in case of propanol, because of the very low solubility of alkane in aqueous solution of Brij 35 when propanol is absent.

When cloud point was plotted against oil weight percentage, the plot passes through a minimum in both the alkane systems (Fig.4.16). A lipophilic shift in the system causes the decrease in microemulsion cloud point

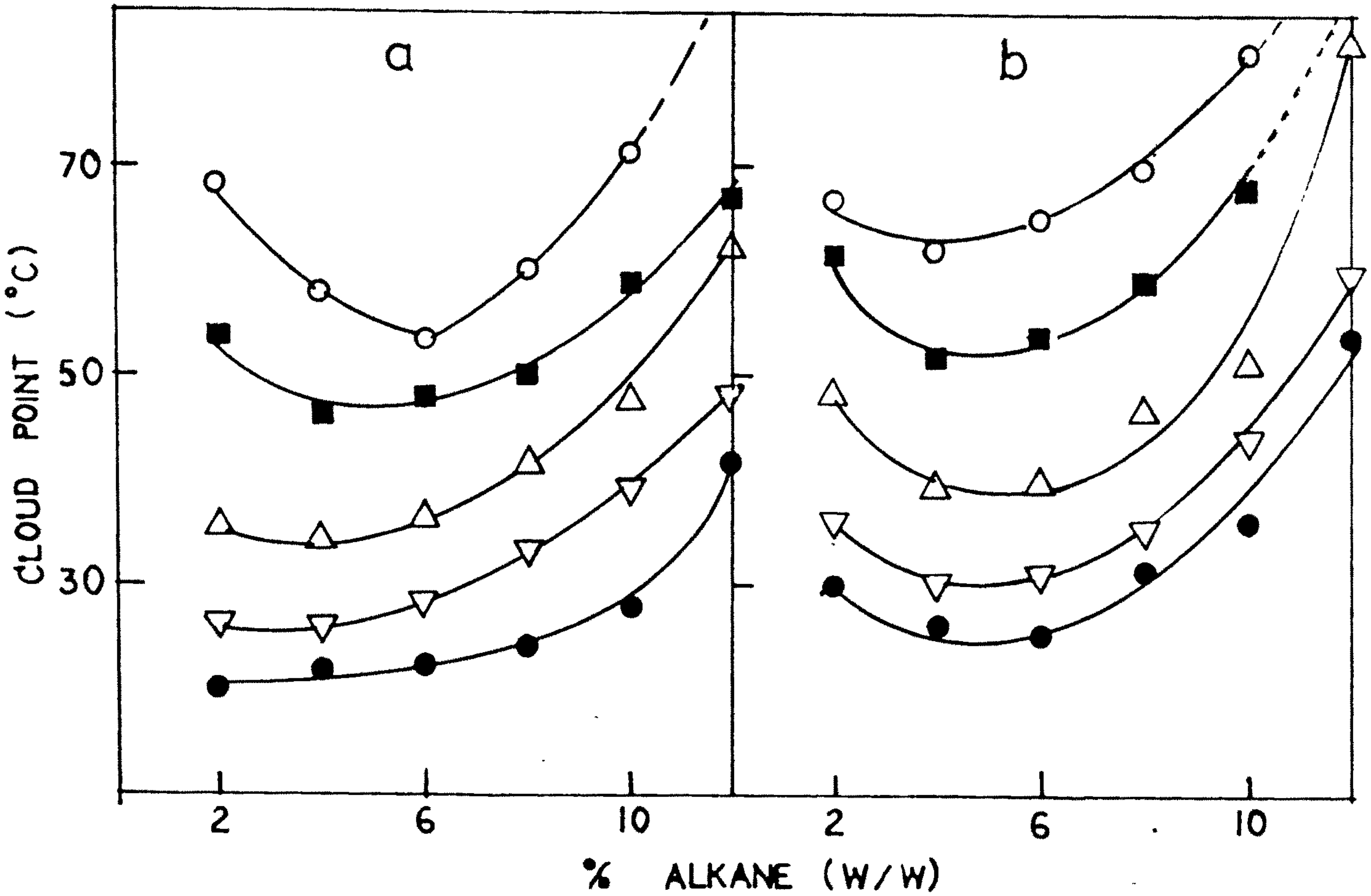

Fig.4.16 the cloud point vas percentage alkane plot at various NaCl concentrations of Alkane/Brij 35 + propanol (80% w/w)/water system.
○ 1.0 M; ■ 1.2 M; △ 1.5 M; ▽ 1.8 M; ● 2.1 M. NaCl concentration.
(a) Heptane (b) Nonane.

[193]. This shift can happen with increase of electrolyte concentration or by increase of alkane fraction. Obviously longer alkanes produce higher effect. Here an initial increase of oil fraction causes a lipophilic shift in the system and that caused the minimum in the plot. But further increase of alkane fraction resulted only in continuous rise of this temperature. From Fig.4.15 it was understood that lowering of cloud point is directly proportional (though not linearly) to the amount of NaCl in the system. This NaCl content is directly related to the amount of water in the system. Increase of alkane fraction means decrease of water in the present study as surfactant concentration was kept constant. This in turn, indicates the decrease of NaCl content in the system with increase of alkane fraction. Hence cloud point increases after having an initial 'dip'. With increase of oil phase, more and more surfactant molecules migrate to oil phase. This also prevents early precipitation of the surfactant. With further addition of oil phase, cloud point rises to higher values and crosses 100°C which cannot be determined at atmospheric pressure. Thus clouding practically disappears above 12% (w/w) of alkane in the system.

A three dimensional representation of cloud point variation with NaCl concentration and oil weight percentage in the system is given in figs 4.17 and 4.18.

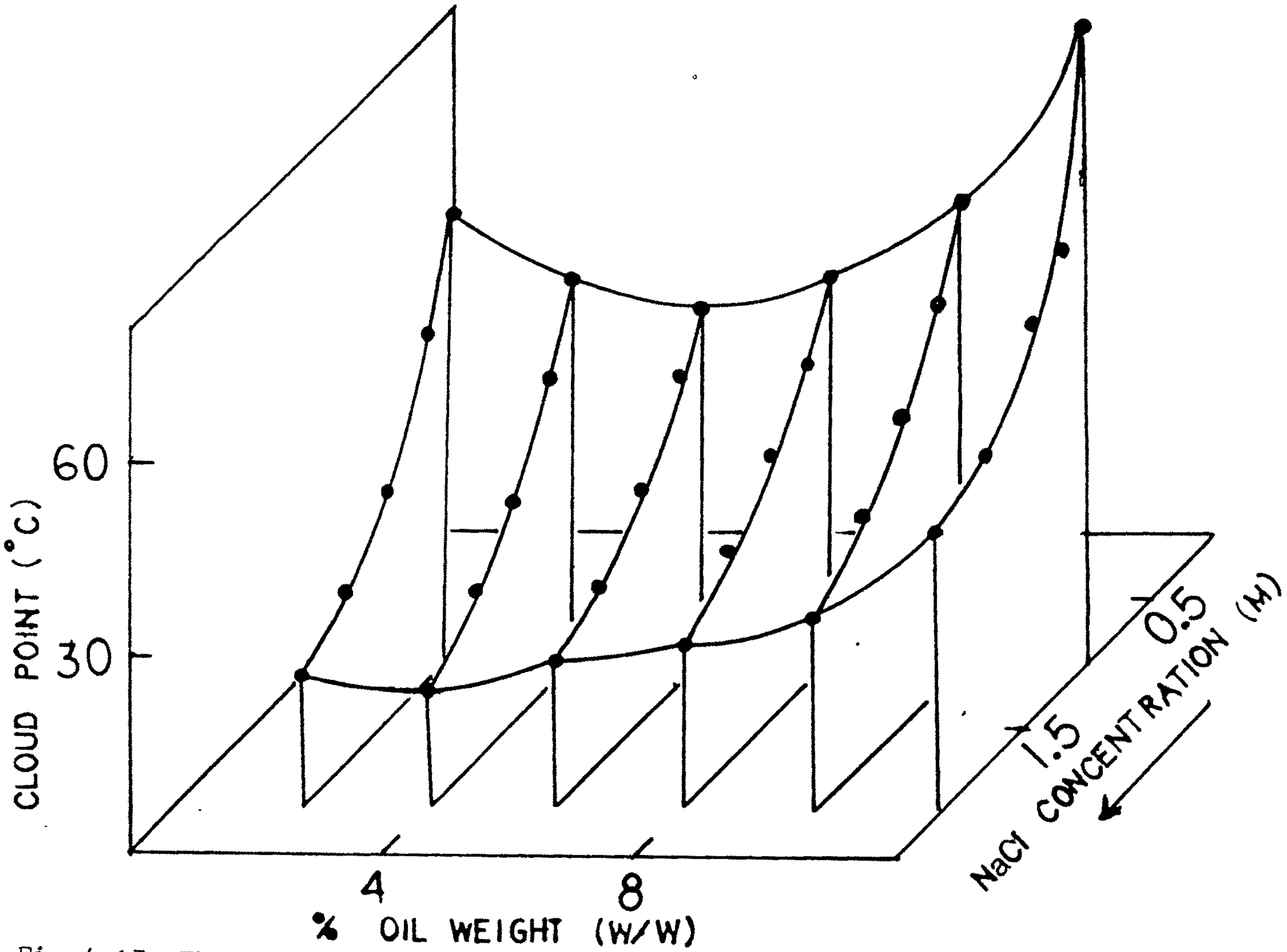

Fig.4.17 Three dimensional representation of the variation of cloud point for the system heptane/Brij 35 + propanol/water simultaneously with heptane and NaCl concentrations.

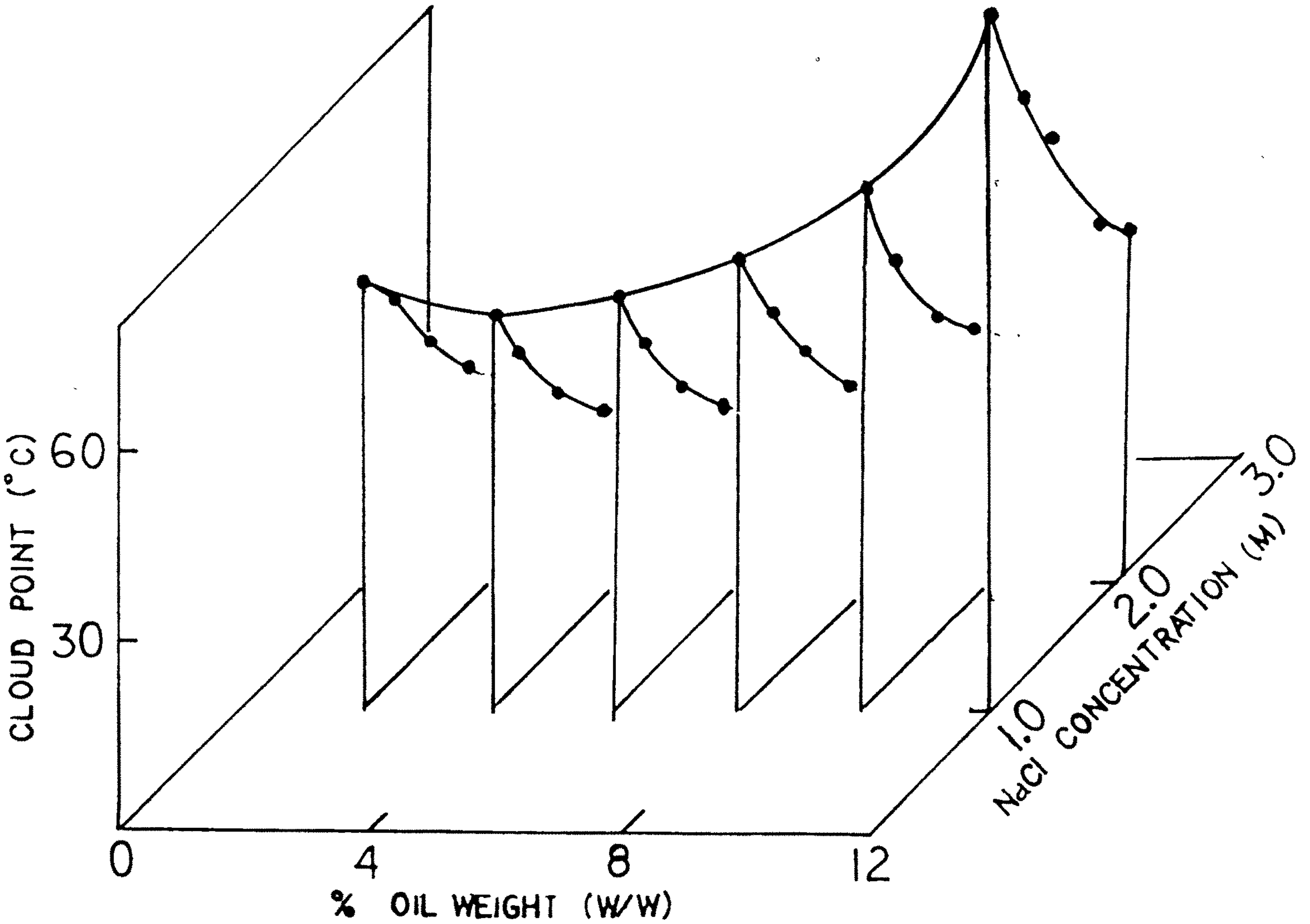

Fig.4.18 Three dimensional representation of the simultaneous variation of cloud point with alkane and NaCl concentrations for the system Nonane/Brij 35 + propanol/water.

NaCl concentration was plotted in opposite directions for heptane and nonane systems to get a clear view of the variation at lower and higher NaCl concentration. Cloud point of nonane system are found to be comparitively higher than heptane microemulsion systems. It was reported by Shinoda et al. that lower the solubility of the surfactant in the oil phase, higher will be the cloud point [217]. The solubility of Brij 35 ($C_{12}E_{23}$) would naturally be lower in nonane compared to heptane.

Generally cloud point of nonionic surfactant system is meausred at lower surfactant concentrations and it was suggested that cloud point is not much sensitive to the surfactant concentration in that range [210,211]. However we measured the cloud point of some selected systems at different surfactant concentrations (reasonably high) ranging from 50% (w/w) to 80% (w/w). We kept oil-water weight ratio constant (1:9) during this study. It was found that it changes drastically with change of surfactant concentration (Fig.4.19). For heptane microemulsion system, cloud point increases regularly after an initial decrease. For nonane and mixed alkane systems, one phase microemulsion of the above mentioned o/w ratio was not formed below 70% and 60% (w/w) surfactant concentration respectively and hence cloud point could not be determined. But above these

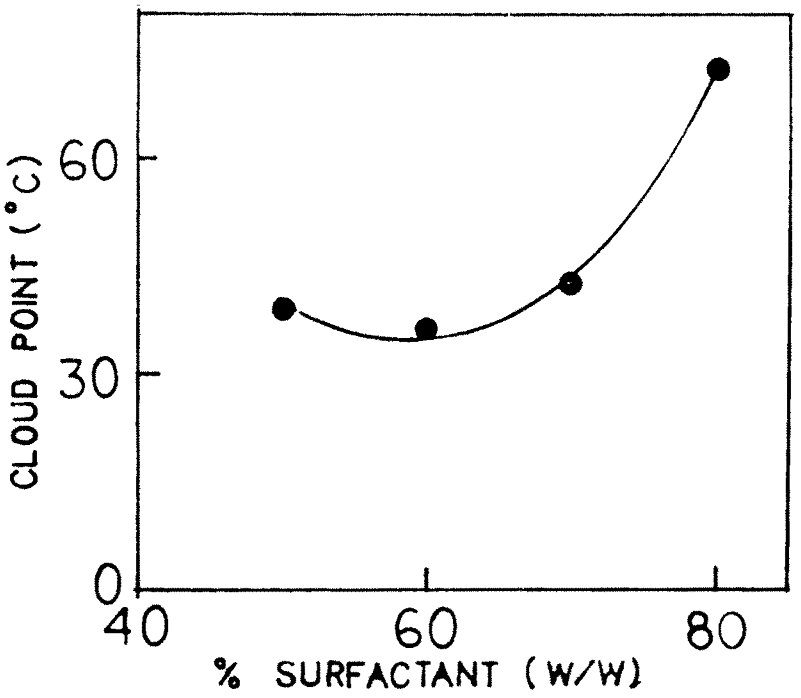

Fig.4.19 Plot of cloud point vs surfactant (Brij 35+propanol) concentration of the system heptane/Brij 35 + propanol/ 1 M NaCl. OWR = 1:9

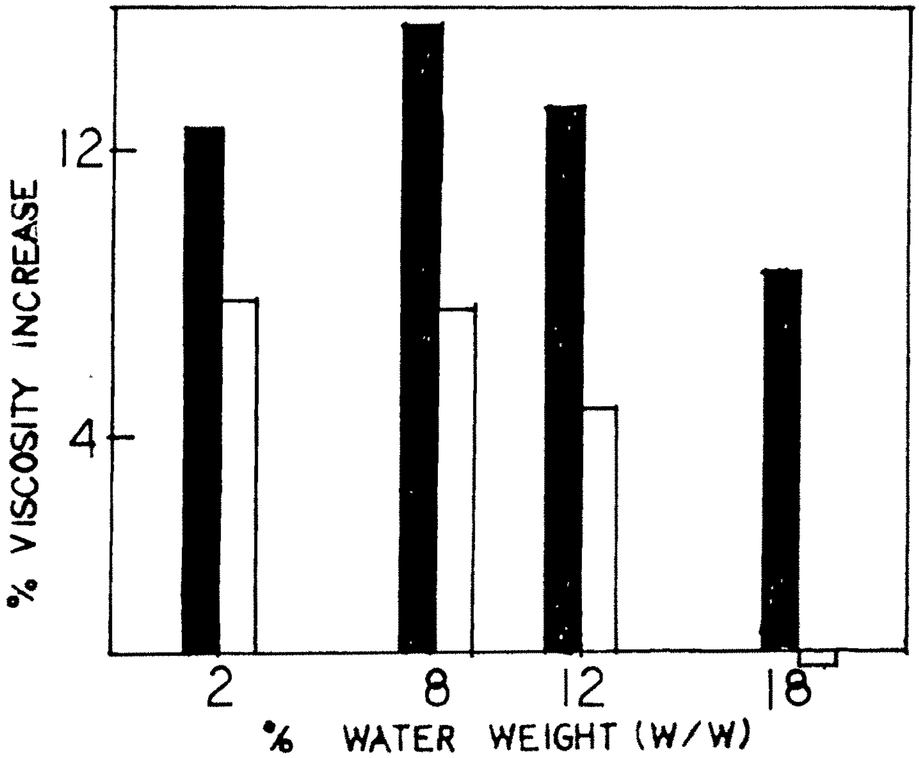

Fig.4.20 Plot showing the percentage increase of viscosity when water was replaced by 1 M NaCl in the system alkane/Brij 35 + propanol (80 % w/w)/water.
■ Heptane ☐ Nonane

concentrations an increase of cloud points similar to those in heptane system were observed.

Cloud points of heptane + nonane (1:1) mixed microemulsion systems were also determined at various NaCl concentrations and for different compositions. The variations of cloud point with both increasing NaCl concentrations and oil weight percentage is exactly similar to that in both heptane and nonane systems. Cloud points of all studied systems are given in Table I.

From these results it could be concluded that cloud point of the present alkane/Brij 35 + propanol/water system is an inverse function of NaCl concentration. These cloud point is also a function of oil/water ratio. Nature of oil phase also affects the value. Altogether one would say that any lipophilic shift producing change in the surfactants nature lowers the cloud point.

(d) Viscosity

Presence of NaCl modifies the microstructure of microemulsions. Hence obviously it affects its viscosity values also. Viscosity of all the systems increased when 1 M NaCl solution was used as aqueous phase instead of pure water. The percentage increment of different

TABLE 4.I

Cloud points of the system Alkane (O)/Brij 35 + propanol (S)/Water (W) at 80% (w/w) surfactant (Brij 35 + propanol) concentration.

Alkane	System S/O/W	Cloud point (°C) at different NaCl concentrations 0.8	1.0	1.2	1.5	1.8	2.1
Heptane	80/2/18	-	68	54	35	26	20
	80/4/16	82	58	46	34	26	22
	80/6/14	85	53	48	36	28	22
	80/8/12	92	60	50	41	33	24
	80/10/10	84	71	59	47	39	28
	80/12/8	-	-	67	62	48	42
Nonane	80/2/18	90	67	62	48	36	30
	80/4/16	-	62	52	39	30	26
	80/6/14	84	65	54	40	31	26
	80/8/12	86	70	59	47	34	32
	80/10/10	-	81	68	51	44	36
	80/12/8	-	-	94	82	60	54
Heptane + Nonane (1:1)	80/2/18	-	73	54	42	32	26
	80/4/16	-	66	51	40	31	33
	80/6/14	-	68	58	42	32	28
	80/8/12	-	72	61	45	36	33
	80/10/10	-	-	56	56	46	42
	80/12/8	-	-	-	75	67	48

compositions of heptane and nonane systems are shown in Fig.4.20. Increment in the viscosity of nonane microemulsion is much less compared to heptane microemulsion at all compositions. Even a slight decrease was observed in nonane system at very low water content. These results indicate that the efficiency of NaCl to modify the microstructure of nonane microemulsion is comparatively weak. It is similar to the earlier observations in phase diagram, phase volume measurements and cloud point studies. In all the studied phenomena, higher NaCl concentration was required to get appreciable changes in nonane systems.

Fig.4.21 shows the variation of viscosity values of a particular microemulsion composition (alkane (8%)/Brij 35 + propanol (80%)/ water (12%) by weight) with increasing NaCl concentration. Introduction of salinity in the system increases the viscosity. But further addition of NaCl in the studied range did not have much effect. This type of viscosity variation of microemulsion with salinity was reported earlier also [222].

In fig.4.22 viscosity values of alkane/Brij 35 + propanol/ 1M NaCl was plotted against water weight percentage. The nature of the graph is almost similar to the system without NaCl. Though a slight deviation from

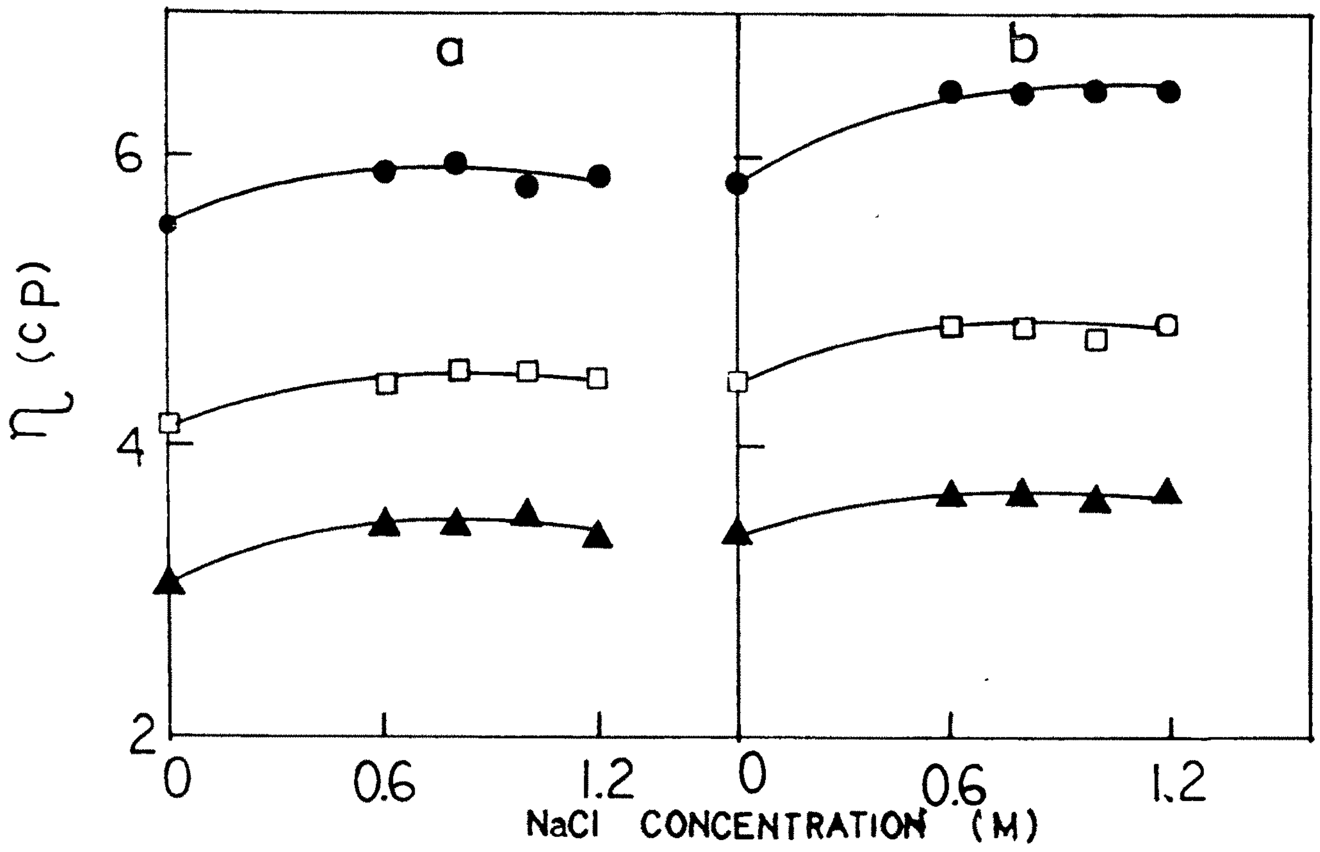

Fig.4.21 Plots of viscosity vs NaCl concentration of Alkane (8%)/Brij 35 + propanol (80%)/water (12%). ● 30°C; □ 40°C; ▲ 50°C . (a) Heptane (b) Nonane.

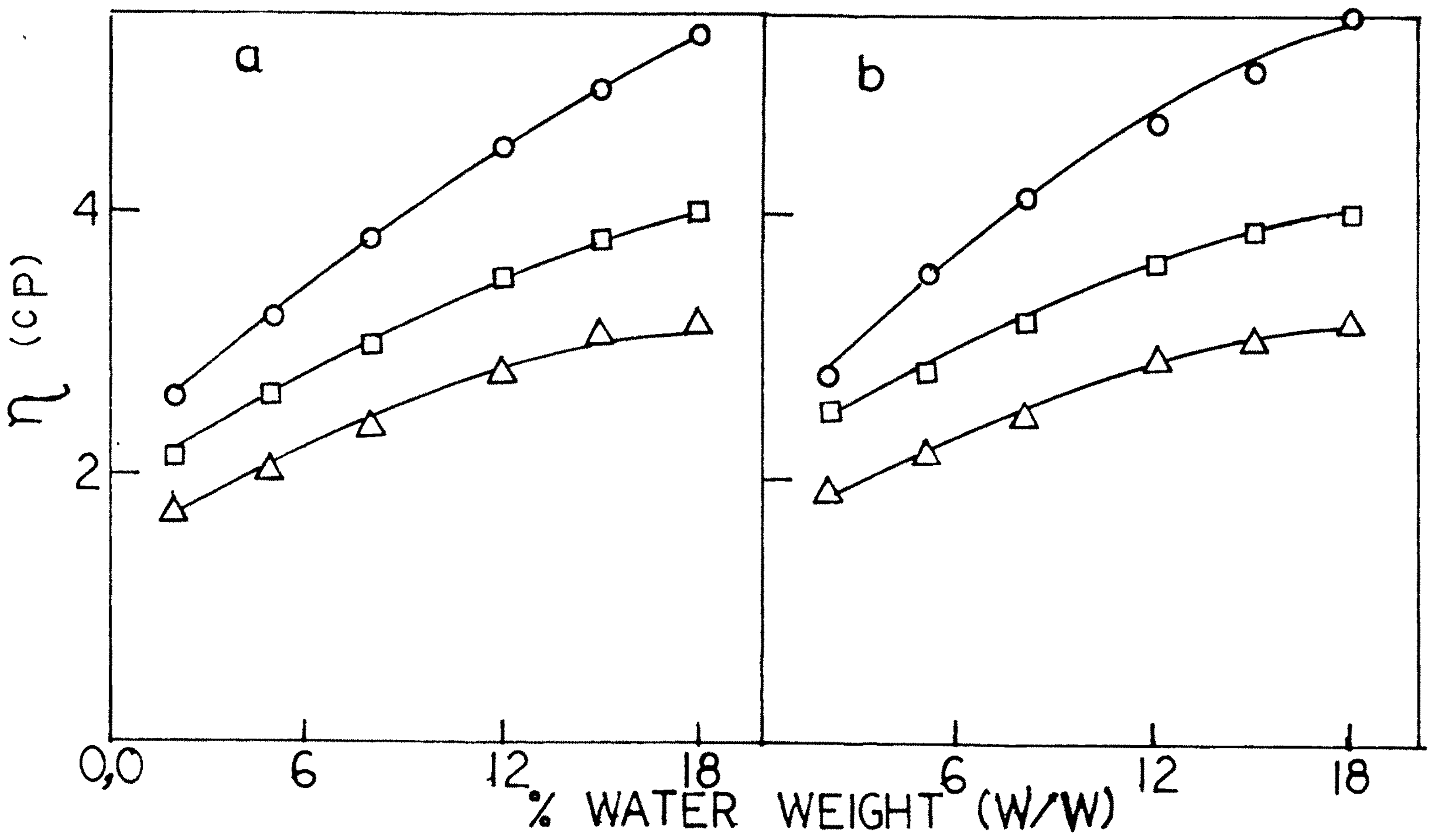

Fig.4.22 Plots of viscosity of the system Alkane/Brij 35 + propanol (80%)/1 M NaCl against water weight percentage. ○ 30°C; □ 40°C; △ 50°C. (a) Heptane and (b) Nonane.

the linearity cannot be overruled, no indication of structural transition was observed. The system remained bicontinuous even in presence of NaCl.

Winsor transitions discussed earlier showed that presence of NaCl could produce only Winsor I → III transition i.e. oil in water to bicontinuous. It reveals that once the system became bicontinuous, the microstructure remains invariant to NaCl concentration or temperature i.e. a system which is already bicontinuous is not expected to have any structural transition induced by NaCl further. Hence we could not note any microstructural change from the viscosity studies when 1 M NaCl solution was used. Viscosity values of all studied systems are compiled in Table II.

These viscosity values were used to calculate the activation enthalpy of viscous flow using the well known relation [199].

$$\eta = A\, e^{\Delta G^{\#}/RT}, \quad \text{then}$$

$$\ln \eta = \ln A - \Delta S^{\#}/R + \Delta H^{\#}/RT$$

As $\Delta S^{\#}$ is independent of temperature we can write

$$\ln \eta = B + \Delta H^{\#}/RT$$

Plot of $\ln \eta$ vs T^{-1} is a perfect straight line. $\Delta H^{\#}$

TABLE 4.II

Viscosity of the system Alkane (O)/Brij 35 + propanol (S)/1M NaCl solution (W) at 80% S concentration.

Alkane	System S/W/O	Viscosity (cp) at 1M NaCl concentration and at different temperatures (°C)		
		40	50	60
Heptane	80/18/2	5.35	4.01	3.11
	80/15/5	4.92	3.80	3.06
	80/12/8	4.49	3.52	2.78
	80/8/12	3.81	2.98	2.38
	80/5/15	3.20	2.57	2.03
	80/2/18	2.60	2.14	1.71
Nonane	80/18/2	5.50	4.15	3.18
	80/15/5	5.08	3.86	3.03
	80/12/8	4.70	3.62	2.90
	80/8/12	4.12	3.17	2.48
	80/5/15	3.54	2.79	2.22
	80/2/18	2.78	2.51	1.91

was claculated from the slope. These values are presented in Table III. It is obvious that $\Delta H^{\#}$ was not much different when OWR was changed.

(e) Adiabatic Compressibility (β)

Adiabatic compressibility of particular composition of both the heptane and nonane systems were calculated at various NaCl concentrations. The composition selected was 80/8/12 for Brij 35 + propanol/ alkane/water system. When β values of heptane microemulsion were plotted against NaCl concentration, the graph passes through a definite minimum (Fig.4.23). This minimum was found to be drifting towards lower NaCl concentration with the rise of temperature. The presence of NaCl at low concentration might help in making the water structure more compact and ordered. This caused the initial decrease of β . But at high concentrations, NaCl disrupts the structure due to very large intake of water molecules for solvation. Due to this structural disruption, compressibility of the system increases. This minimum was not prominent in nonane system. This was not surprising considering the relatively weaker influence of NaCl on nonane system.

In Table IV, of some system at 80% (w/w) surfactant concentrations are presented with the corresponding oil

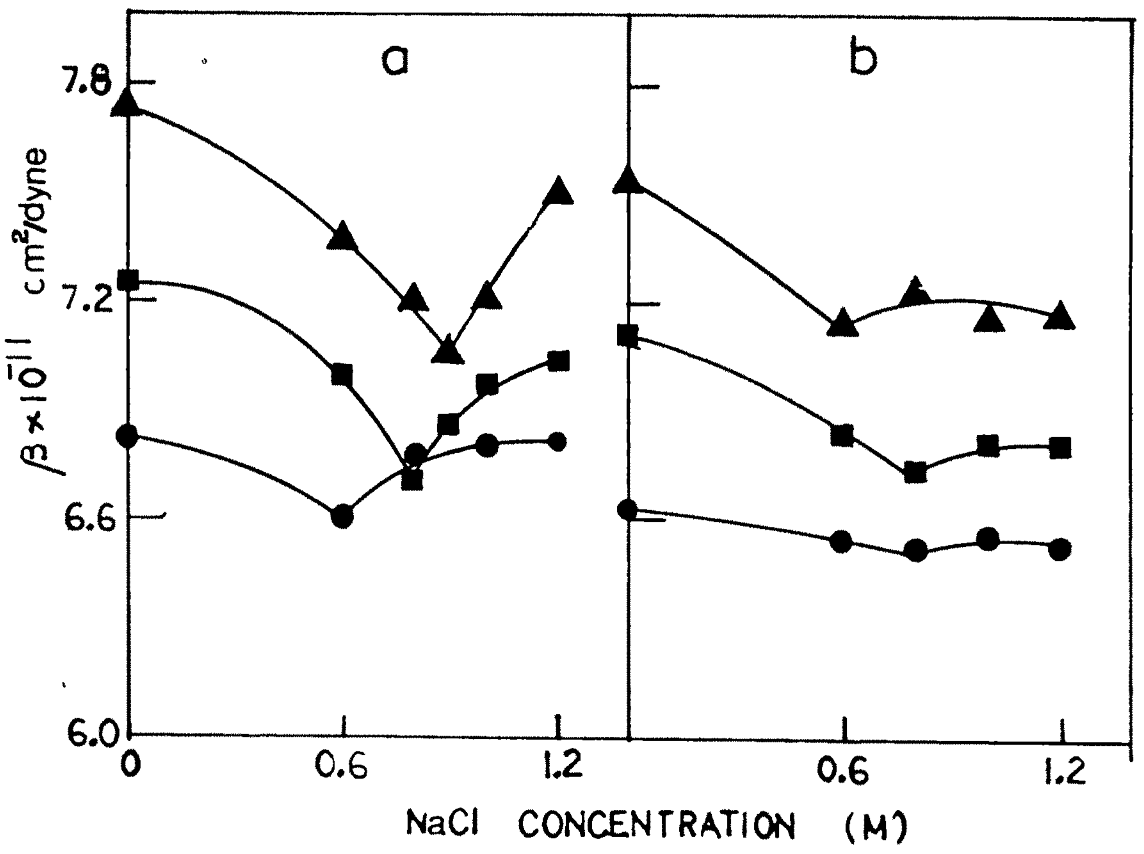

Fig.4.23 Plots of adiabatic compressibility of the system Alkane (8%)/Brij 35 + propanol (80%)/Water (12%) vs NaCl concentration. ●30°C; ■ 40°C; ▲50°C (a) Heptane (b) Nonane

TABLE 4.III

Activation enthalpy of viscous flow for the system Alkane (O)/Brij 35 + propanol (S)/Water (W) in presence of NaCl.

Alkane	Composition			$\Delta H^{\#}_{vis}$ kJ/mole at different NaCl concentrations			
	S	W	O	0.6 M	0.8 M	1.0 M	1.2 M
	80	18	2			23.50	
Heptane	80	15	5			20.59	
	80	12	8	21.57	22.35	20.77	22.22
	80	8	12			20.39	
	80	5	15			19.71	
	80	2	18			18.13	
	80	18	2			27.31	
	80	15	5			22.39	
Nonane	80	12	8	22.99	22.69	20.93	22.95
	80	8	12			21.99	
	80	5	15			20.21	
	80	2	18			16.18	

NOTE : Various oil water ratio was used with 1.0 M NaCl solution. At other NaCl concentration only one oil water ratio of 8/12 was studied.

TABLE 4.IV

Adiabatic compressibility (β) values of the system Alkane (O)/ Brij 35 + propanol (S)/1M NaCl (W), in presence of NaCl.

Alkane	Composition			$\beta \times 10^{11}$ cm^2/dyne		
	S	W	O	30°C	40°C	50°C
	80	18	2	6.11	6.27	6.67
	80	12	8	6.70	6.98	7.21
Heptane	80	8	12	7.24	7.68	8.10
	80	2	18	7.96	8.50	9.04
	80	18	2	5.77	6.14	6.37
Nonane	80	12	8	6.56	6.82	7.16
	80	8	12	6.84	7.16	7.56
	80	2	18	7.59	8.18	8.71
	80	18	2	5.96	6.16	6.41
Heptane+	80	12	8	6.36	6.92	7.36
Nonane	80	8	12	7.02	7.50	7.91
(1:1)	80	2	18	7.74	8.33	8.86

percentage. Both heptane and nonane systems show the same linearity which was observed in absence of NaCl also. It is also quite obvious that the compressibility is linear with temperature even in absence of NaCl. For mixed alkane systems also similar type of behaviour was observed.

These results indicate that, though the presence of NaCl changes the absolute values of β , the mode of variations with different parameters remained more or less same when compared with the systems without NaCl. The phase diagrams do change drastically though with high NaCl concentration.