CHAPTER 5

MIXED SURFACTANT MICROEMULSION SYSTEMS

5.1 PREVIEW

Behaviour of the surfactant systems are generally dependent on the type of the amphiphile which is,in turn, purely based on its molecular structure. Hence one does not have much control over its properties. This difficult situation is often faced by the technologists while optimising the conditions of surfactant systems. However, surfactant mixtures were found to be useful in adjusting the properties and hence commercial surfactants are usually a mixture of two or more surfactants. These surfactants might be of the same variety or of different kinds.

The technological importance of mixed surfactant systems encouraged fundamental scientists to take up these systems for further investigation.A good number of studies were devoted to mixed surfactants in the literature [223-226].

Mixing of similar species often resulted in some intermediate properties due to their collective behaviour in the system [227]. Hence linear or approximately linear mixing rules have generally been accepted for both anionic [228,229] and nonionic surfactant mixture [230,231].

But behaviour of the mixture of two dissimilar surfactants are generally more complex [232,233]. In fact this complexity developes because of their different phase behaviours even in same environment. It is known for long time that increase of temperature makes nonionic surfactants more hydrophobic while ionic surfactants more hydrophilic [134,212]. Consequently phase behaviour with respect to temperature will be expected to be opposite. Thus researchers could think of a temperature insensitive system by properly mixing these two types of surfactants. It was reported that anionic-nonionic surfactant mixtures at some optimum mixing ratio show insensitivity towards temperature in a limited range [232]. Hence anionic-nonionic surfactant mixing was proposed for enhanced oil recovery where a steady optimum formulation with respect to temperature is required [234]. Also the surfactant mixtures are known to improve the stability of emulsified systems [235].

Properties of surfactant mixtures with opposite charges are quite interesting [236,237]. It is believed that mixing of a cationic and an anionic surfactant together resulted in the formation of some sort of salt having both hydrocarbon chains together. As this mixed surfactant system has longer hydrocarbon chain and is less hydrophilic, the cmc will be obviously lower. These type of mixtures are known to exhibit strong synergy in different surface and interfacial phenomena [223,238]. Cationic-anionic mixtures at high concentrations are proposed for detergent formulations [239].

Kunieda et al. studied the mixed surfactant/water/oil ternary systems for evaluating the hydrophil-lipophil balance (HLB) of mixed surfactants experimentally [231, 240]. Determination of the HLB number for mixed surfactants is not an easy task [241-243]. Same is the case with commercial surfactants which are in general mixtures of homologues or isomers. Kunieda et al. in their article described an efficient but simple experimental method to calculate HLB number of mixed surfactants by determining phase inversion temperature (PIT) of surfactant/water/oil ternary systems.

Recently Anton et al.reported the phase behaviour of mixed surfactant-water-oil ternaries as a function of temperature and salinity [165,227]. They observed a strong decrease of optimal salinity of the ternary system when SDS-TTAB (tetradecyl trimethyl ammonium bromide) mixture was used [227]. The reason highlighted for this drastic reduction of optimal salinity was the formation of an equimolar compound of reduced charge. This was formed by the mutual interaction of oppositely charged hydrophilic groups of the surfactant molecules. They also extended the idea of temperature invarient system by mixing anionic and nonionic surfactants together in the ternary systems. This resulted in a novel surfactant-water-oil system which was insensitive to both temperature and composition [165].

Apart from these interesting studies, mixed surfactants have not been widely used in microemulsion systems. Hence properties of such systems are not well known. In the present chapter, phase behaviour and some other physical properties of two mixed surfactants (anionic-nonionic and nonionic-nonionic) are presented.

5.2 SYSTEMS STUDIED

Two mixed surfactant pseudoternary systems were selected for the investigations. The results of such investigations are presented in this chapter. These systems are heptane/Brij 35 + SDS - propanol / water (I) and heptane/ Brij 35 + Tween 20 - propanol / water (II). For both ternaries, surfactants were mixed at three different molar ratios (1:2, 1:1, and 2:1) and their properties were then compared with those of corresponding single surfactant systems.

Triangular phase diagram of all the 5 systems of I and 3 systems (pure Brij 35, Tween 20 and their 1:1

mixture) of II were constructed at 40°C. For understanding the role of temperature on the phase behaviour of system I, phase diagram of heptane/SDS+Brij 35 - propanol/ 1M NaCl were also plotted at 40°, 60° and 80°C.

Winsor transitions at all the 5 systems of I and II were studied by measuring the phase volumes at temperatures between 40°C and 80°C. NaCl concentration was varied between 0 M and 2.5 M for I and 0 M to 1.5 M for II.

Viscosity and compressibility were calculated for all the systems of I and II, at various temperatures. Only one composition of I was taken for these physical property studies. Three compositions, representing o/w, bicontinuous and w/o structure were selected from II for these studies.

5.3 RESULTS AND DISCUSSION

(a) Phase diagram

Fig.5.1 is the isothermal phase prism of the pseudoternary system heptane/Brij 35 + SDS - propanol / water at various Brij 35 : SDS mixing ratios. The temperature of the system was kept at 40°C. Top and bottom

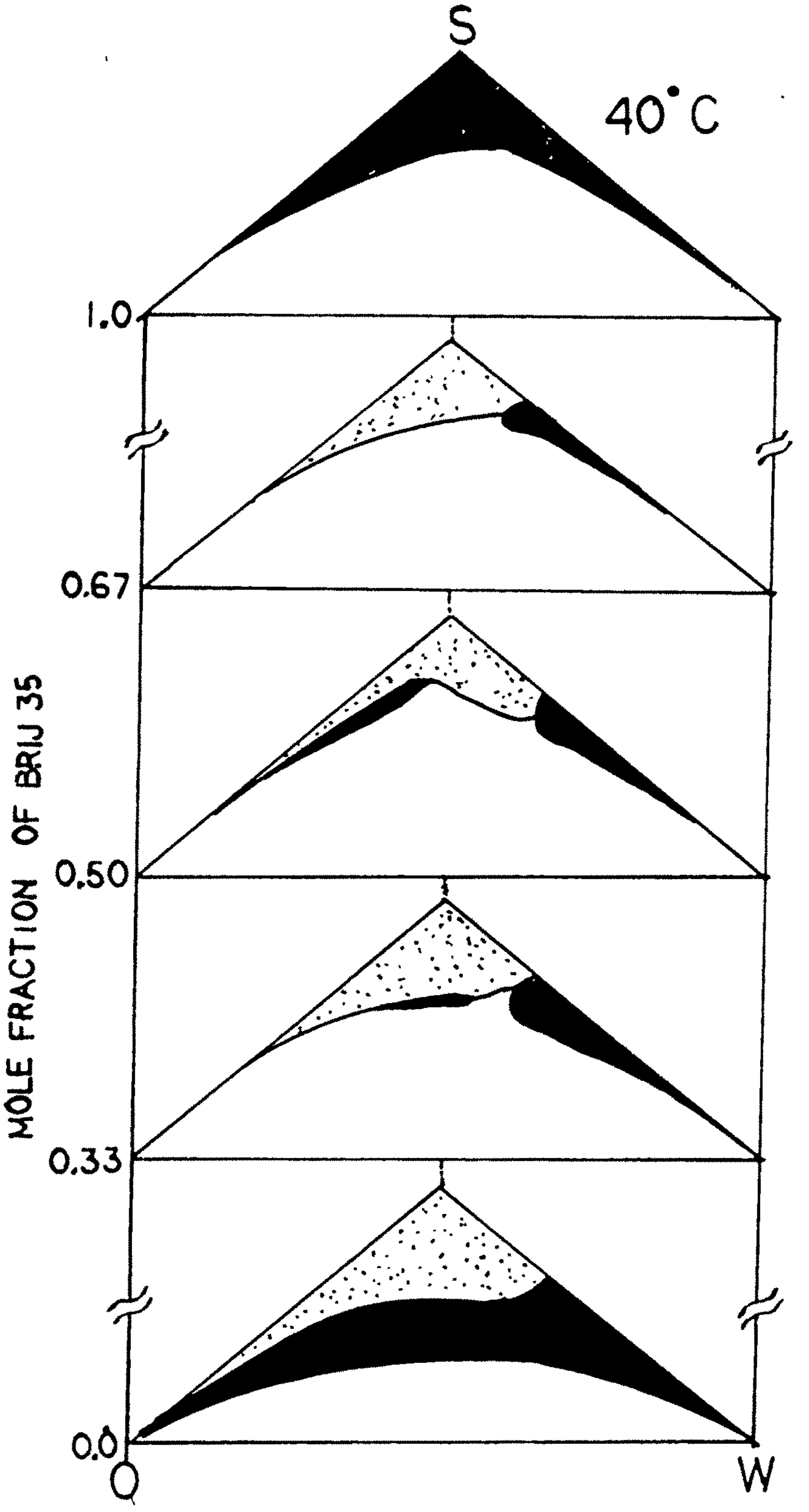

Fig.5.1 Isothermal phase prism representation of the system heptane/Brij 35 + propanol/water at various Brij 35 + SDS mixing molar ratios.
■ 1Φ (L); □ 2Φ (L/L); ▨ 2Φ (S/L)

plane of the prism represents the phase diagrams of pure Brij 35 and SDS ternary systems respectively. The patterns of these two phase diagrams are different. This is due to the solubility differences of SDS - propanol and Brij 35 - propanol combination in water and heptane. It is well known that surfactant-water and surfactant-oil miscibility gaps determine the pattern of the phase diagram [131,133]. Brij 35 - propanol combination at 1:2 weight ratio is soluble with water and oil at all proportion above 30°C.So one phase microemulsion region started from surfactant apex and extended towards the middle portion of the triangle. This region separates from the 2Ø (liquid /liquid) system which is Winsor I type with an arc type boundary. But due to the limitation of SDS solubility in water and heptane even in presence of propanol, a solid/liquid biphasic region exists at the higher surfactant part of the phase diagram. In this zone, microemulsion phase is in equilibrium with undissolved SDS particles. Towards the lower surfactant portion, SDS particles completely dissolves in microemulsion phase and 1Ø microemulsion is resulted. This region, as usual, has a lower boundary at the bottom part of the phase triangle with 2 Ø (L/L) system.

But when these two surfactants are mixed, the 1Ø zone shrunk to very small regions. Change in SDS : Brij 35 mixing ratio did not have much effect on the phase diagram. The solid/liquid biphasic region of SDS system and large liquid/liquid biphasic region characteristic of Brij 35 system are present in all the three mixed surfactant ternary phase diagrams. When 10 areas were plotted against the mole fraction of SDS in the mixture, a 'cup' type plot was obtained (Fig.5.2). This graph indicates the nonideal nature of the surfactant mixing as well as the similar properties of mixed surfactant systems inspite of its different mixing ratios.

As stated earlier when two surfactants are mixed, depending on their chemical nature, they may form an equimolar compound. If such compound is possible then that will be in equilibrium with the surfactant molecules which are in excess [227]. If the overall behaviour of the newly formed surfactant as well as the other components are similar then the system should show properties somewhat in between the properties that were shown by pure components [232,233]. In our system Brij 35 and SDS were not chemically expected to interact and hence such behaviour is not expected. The percent microemulsion areas were found to be more or less independent of mixed surfactant composition.

A close observation on the mixed surfactant system's phase diagram indicates that both surfactants are not

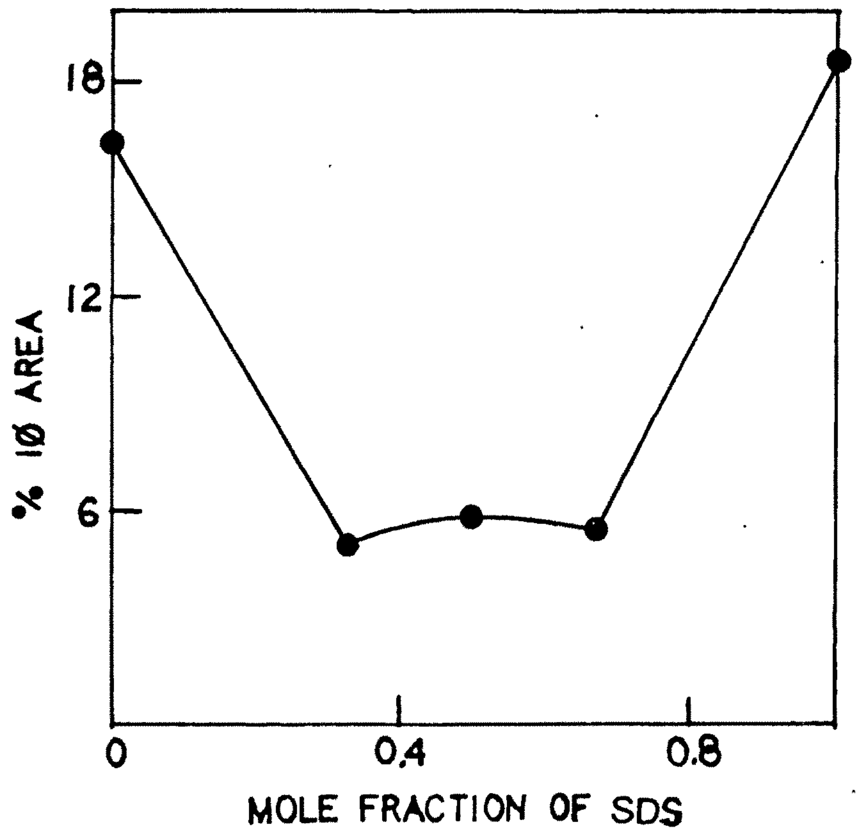

Fig.5.2 Plot of the 1Ø microemulsion area against mole fraction of SDS in the surfactant mixture for the system heptane/Brij 35 + SDS - propanol/water at 40°C.

affecting each others property. It appears, therefore, that both surfactant molecules keep individual identity in tact. This is possible only when there is practically no interaction between the two molecules. Hence we assume that there is no interaction between SDS and Brij 35 molecules here.

Fig 5.3 is the phase diagram for heptane/Brij 35 Tween 20 - propanol/water systems at 40°C. It can be seen that phase diagram pattern remains same for both single and mixed surfactant systems. Since the nature of both surfactants are similar, same pattern was expected for their mixture also. When 1ϕ areas were plotted against mole fraction of Tween 20 in the mixture, a straight line was obtained (Fig.5.4). Because of this linearity we thought that other mixed ratios will be falling on the line and hence other ratios' phasediagrams were not studied. This plot and the similar phase diagram patterns indicate the ideal mixing nature of Brij 35 and Tween 20. Both have the same HLB number, 16.9 [244]. Inspite of having the same HLB number, Tween 20 system has somewhat higher 1ϕ microemulsion area than Brij 35 system. This indicates that Tween 20 + propanol combination is relatively better microemulsion forming surfactant than Brij 35 + propanol combination in the present condition. Ability to form microemulsion is often related to the

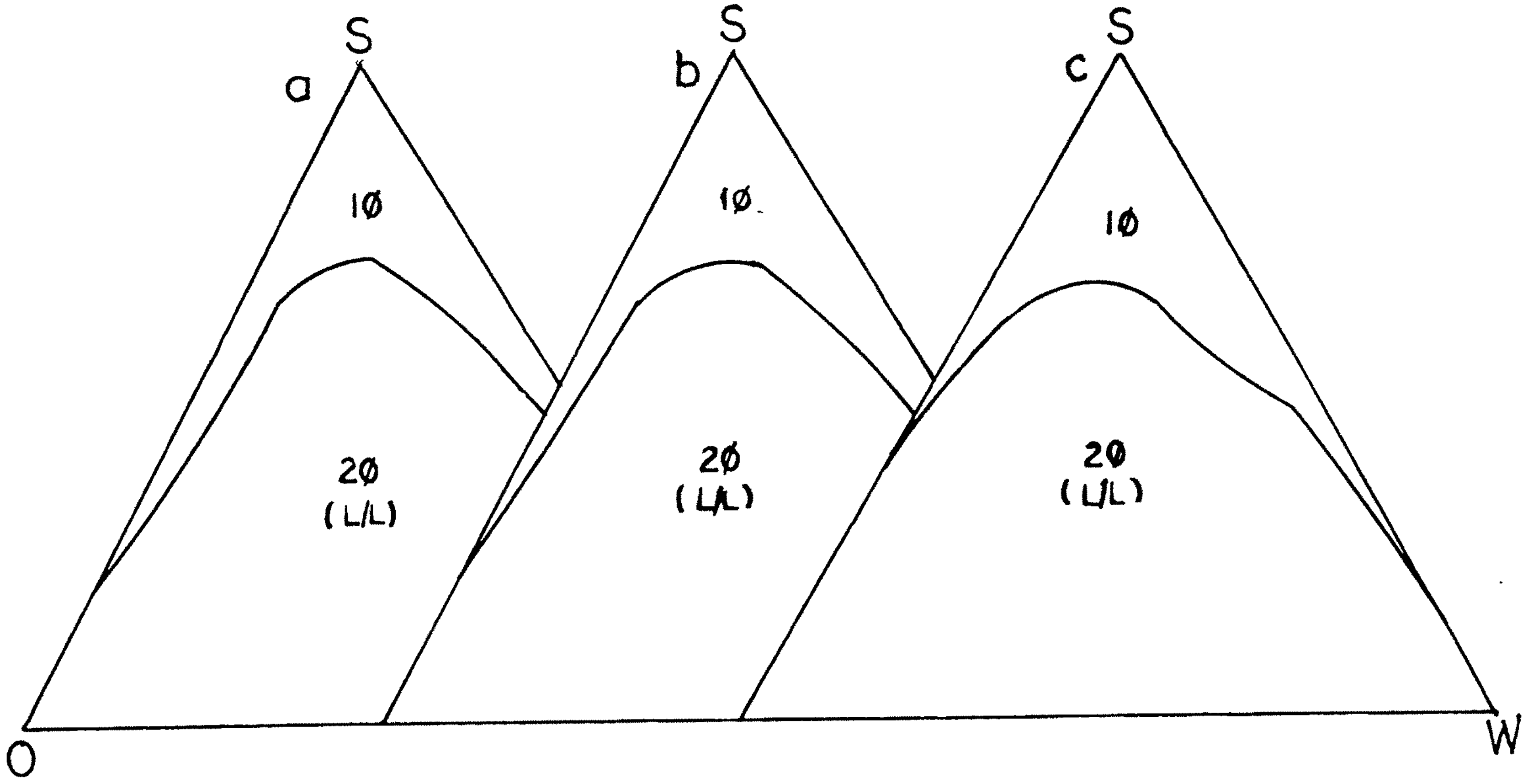

Fig.5.3 Pseudo ternary phase diagrams of the systems heptane/surfactant/water at 40°C. Surfactants are (a) Brij 35 + propanol (b) Brij 35 + Tween 20 + propanol (c) Tween 20 + propanol (1:1 mole ratio) CS/S Ratio is 2:1 by weight.

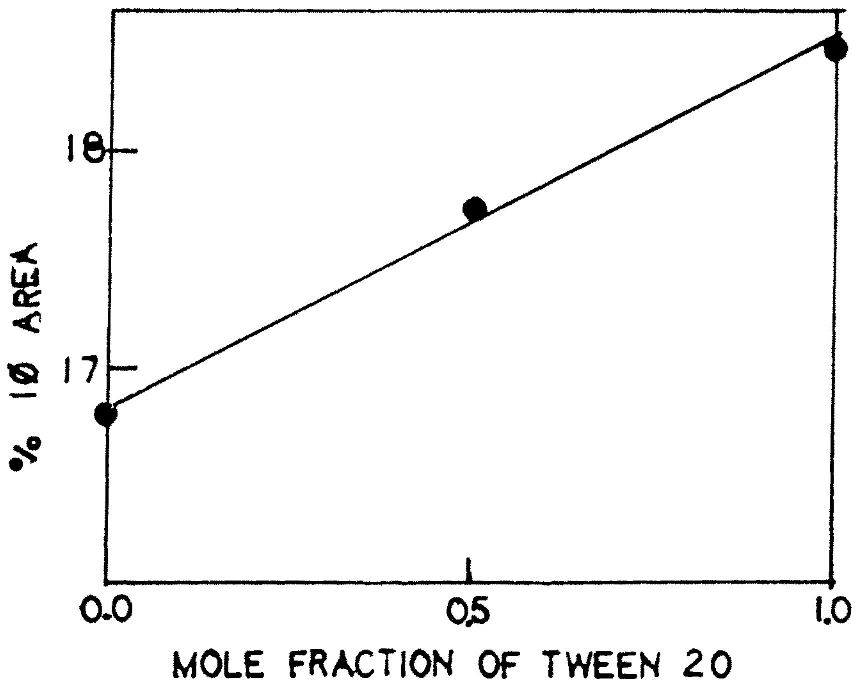

Fig.5.4 Plot of 10 microemulsion area vs mole fraction of Tween 20 in heptane/Brij 35 + Tween 20 + propanol/water at 40°C

hydrophilic or lipophilic character of the surfactant. It was reported that the HLB number of a surfactant does not always reflect its true hydrophilicity or lipophilicity in a particular system [245]. This suggests that surfactants of same HLB number need not behave similarly in all conditions. Actually HLB number is a function of the surfactant's molecular structure. But HLB is dependent on the system and the condition under which the system is present [212]. Hence we presume that though Brij 35 and Tween 20 have same HLB number, their hydrophobicity in the system may not be same. This difference is reflected in the 10 microemulsion region. The 1:1 mixed system hence should have an intermediate value and it does (Fig.5.4).

It is known for long time that temperature influences anionic and nonionic surfactants in different ways [134, 165,212]. Hence we decided to investigate the effect of temperature on heptane/SDS+Brij 35-propanol/water system. However Brij 35 system is not very sensitive to temperature like other nonionic surfactant systems [134]. But this system becomes sensitive to temperature in presence of NaCl which could be observed in chapter 4. Hence we replaced water with 1 M NaCl solution in order to study the temperature effect. SDS and Brij 35 were mixed at 1:1 molar proportion and the phase diagram of heptane/

Brij 35 + SDS- propanol/ 1 M NaCl system were studied at temperatures 40°, 60° and 80°C. The results are shown in a phase prism (Fig.5.5). All Winsor phases (microemulsion in equilibrium with water $(\bar{2})$, microemulsion in equilibrium with oil $(\underline{2})$, microemulsion is in equilibrium with water and oil (3) and a one phase microemulsion) are present in the pahse diagram. Temperature variation seems to change the system from one form to other. The overall sequences of these transformations are similar to that observed for nonionic surfactant systems. One of the reason for this type of behaviour is rather low influence of temperature on the properties of anionic surfactants. On the other hand temperature has strong influence on the properties of nonionic surfactants. Hence 1:1 molar mixture of the two is expected to behave like nonionic surfactant as far as temperature is concerned. It was observed that SDS+propanol system has similar Winsor transitions like nonionic surfactant system with respect to temperaure [246]. Temperature induces Winsor I → III → II transition in both the systems. Generally Winsor transition observed for all ionic surfactant systems, with respect to temeprature, are in the order of Winsor II→II → I. It was observed by others that SDS system shows Winsor II → III →I transition when it is used in combination with higher alkanols [209]. When a series of propanol + hexanol mixtures at various compositions were used as the cosurfactant, Winsor transition sequence changes from one

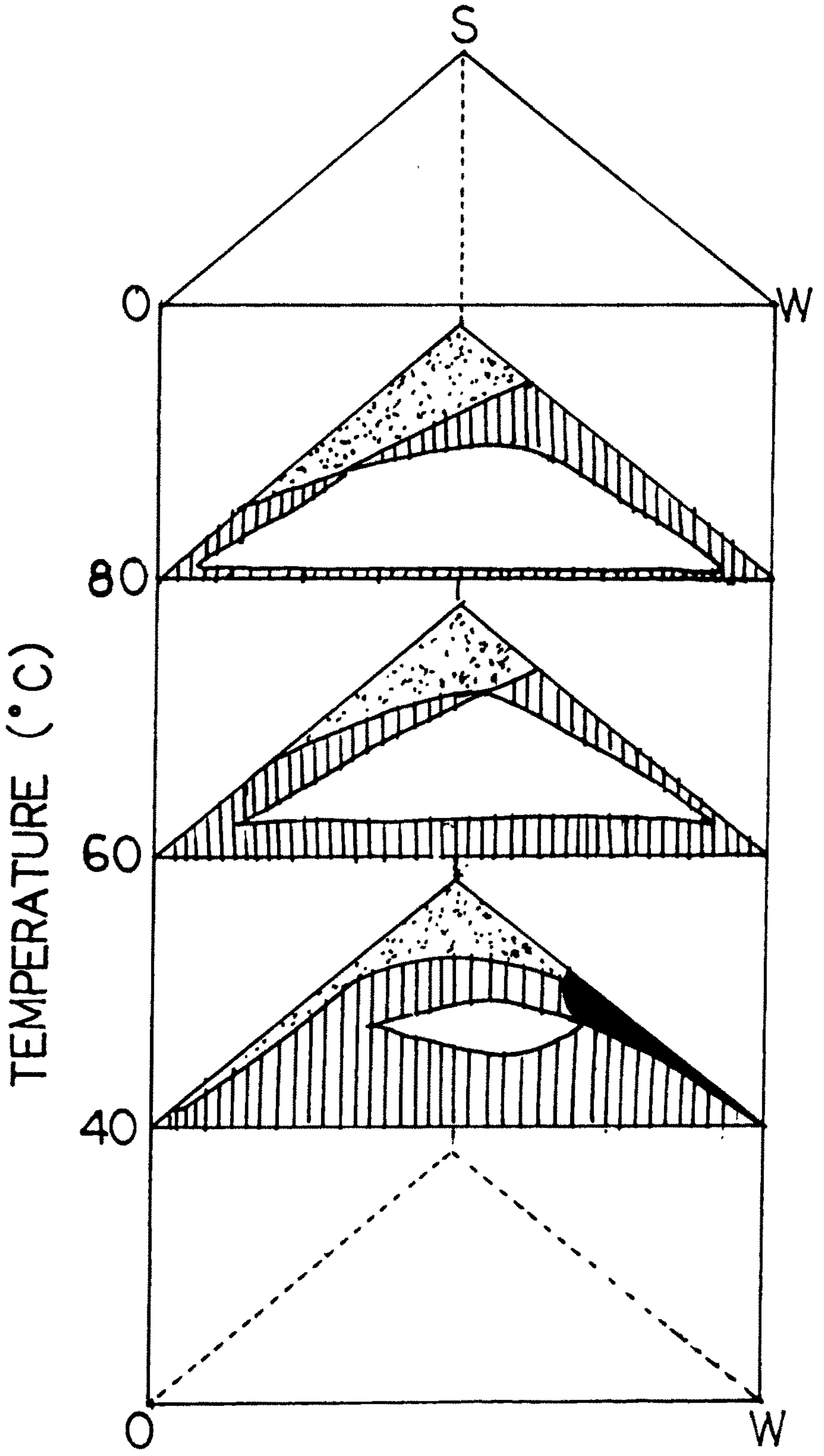

Fig.5.5 Phase prism representation of the system Heptane/ Brij 35 + SDS-propanol/1 M NaCl at various temperatures Brij 35 + SDS is mixed at 1:1 mole ratio.
■ 10 ; ▥ 20 (L/L); □ 30 (L/L/L); ⊡ 20 (S/L)

form to other at a certain mixing composition [246]. It seems that when propanol is used as the cosurfactant, even ionic surfactants behave some what similar to nonionic surfactants as far as Winsor transition is concerned.

For the mixed surfactant systems (Fig.5.5), the 1Ø microemulsion region was found to exist only at 40°C. The three regions (1Ø, 2Ø and 3Ø) are found to coexist at a particular point. We like to stress on the fact that it is quite possible to miss this point of coexistance in the phase diagram determination and one needs to be conscious about this so called 'triple point'. At higher temperature The one phase domain is conspicuous by its absence. 3Ø zone present in the diagram expands with rise of temperature at the expense of 1Ø and 2Ø regions. These phase changes are due to the microstructural changes taking place in the system with rise of temperature. Microstructural transitions in microemulsion are based on the property of the interfacial surfactant film. The tendency of the surfactant film to bend towards either water or oil side is described by the value of the spontaneous curvature (C_o) [247]. Microemulsion assumes an o/w structure for positive values of C_o and w/o structure for negative values. When C_o is close to zero, a bicontinuous structure forms [80,247]. These parameters are seemed to have a close relation with the surfactant geometrical terms, A_t and A_h proposed by Aveyard et al.[71]. Comparing with the suggestions of Aveyard et al. one can say that when $C_o > 0$, $A_h > A_t$ and when $C_o < 0$, $A_h < A_t$ and $C_o \sim 0$ indicates $A_h \sim A_t$ (see chapter IV, p. 96).

The spontaneous curvature can be varied in different ways [80,248]. For ionic surfactants, due to the high electrostatic repulsion of head group in water, the groups are apart and C_o is positive. But addition of salt shields the charges , electrostatic repulsion decreases and there by C_o decreases to zero or even negative. Similarly for nonionic surfactant, at lower temperatures, due to larger hydration of polar head, the head groups are far apart and C_o is positive. However due to rise of temperature, the oxyethylene head groups become less solvated and hence the groups come nearer to each other. That is the positive C_o value decreases and tends to zero or even negative [80]. The structural transitions occurs in microemulsion phase with change of temperature and salinity as these affect the nature and stability of the droplet.

The one phase microemulsion present at 40°C is on the water rich side. Hence it is expected to have water external structure (o/w microemulsion). As the concentration of the surfactant is reasonably high (S+CS is around 60% or less) the surfactant continuous or a bicontinuous form may not be totally rejected. But if we have o/w microemulsion which is much more probable, C_o may be taken as positive. But it is already known that increase of temperature brings down C_o to zero or negative. That is o/w structure changes over to bicontinuous or w/o [80]. When the system composition is fixed, this change can take place only by expelling the excess water and oil as two separate phases. Thus system changed to 2ϕ or 3ϕ depending on the composition. This causes the disappearance of 1ϕ microemulsion region above 40°C and the expansion of other regions. Winsor I → III, i.e. $\underline{2} \rightarrow 3$, transition with increase of temperature is generally observed. The 2ϕ region present at lower temprature is Winsor I ($\underline{2}$). With increase of temperature these Winsor I ($\underline{2}$) system starts to transform to Winsor III (3). The 3ϕ area expands with increase of temperature. This can be clearly seen from Fig.5.5.

The solid-liquid biphasic zone, which was observed when SDS was present, remained almost invariable with temperature. Infact it decreased a bit due to the solubility of SDS at higher temperature.

Phase changes observed at certain composition of the pseudo ternary system by changing one of the experimental variable and surfactant mixing ratio can be represented by a bidimensional,mixing composition versus experimental variable map. Experimental variable (temperature or NaCl concnetration) was plotted in Y axis and molefraction of one of the surfactant was plotted at X axis. Fig.5.6 and 5.7 are such phase diagrams for heptane/Brij 35 + SDS - propanol/water system. The composition was fixed at 30/30/40 by weight respectively. The phase diagram may be divided into three parts - SDS rich, Brij 35 rich and mid part. In Fig.5.6 NaCl concentration was the experimental variable. Winsor I system ($\underline{2}$), which exists along all the three portion of the phase diagram at 40°C narrowed down to a small strip along Brij 35 rich and mid part range at higher temperature. This happened due to the widening of the 3ϕ region around lower NaCl concentration. Winsor II system ($\overline{2}$) which was present only at SDS rich region at 40°C, slowly did extend to middle portion with rise of temperature. These phase changes are due to different nature of the surfactant mixture. At lower temperature and at low NaCl concentration, Brij 35 rich, SDS rich and equivalent surfactant mixtures are all highly hydrophilic and consequently form Winsor I ($\underline{2}$) system. However with increase of NaCl concentration all surfactant mixtures became relatively more devoid of water to behave as lipophilic and form Winsor III (3). However with further increase of NaCl concentration, 3ϕ system transforms to $\overline{2}$ at very high SDS rich region. This is probably due to the fact that the concentration of nonionic surfactant is low and NaCl effect on it did reach its limiting value. The

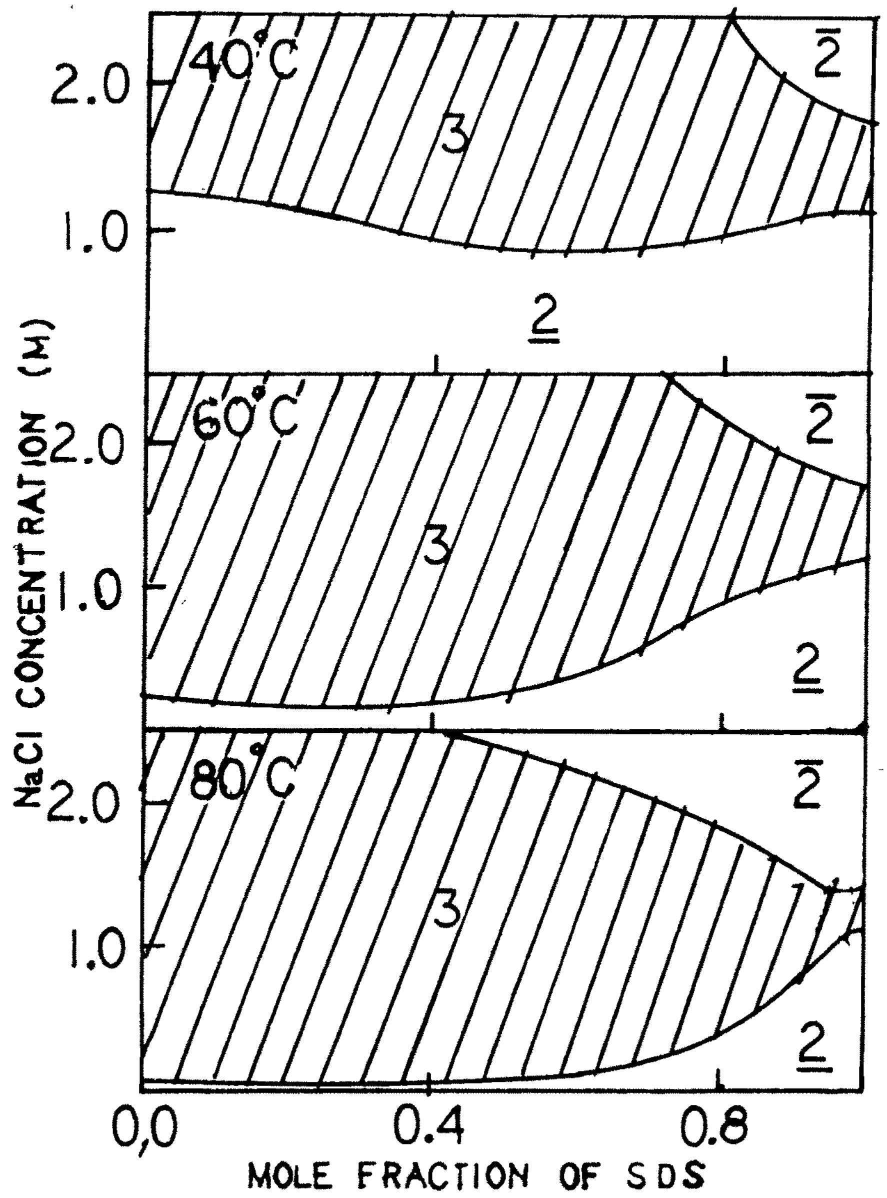

Fig. 5.6 NaCl concentration vs SDS mole fraction phase map for the system Heptane/Brij 35 + SDS -propanol /water at various temperatures. $\underline{2}$ - Winsor I, $\bar{2}$ Winsor II, 3 Winsor III.

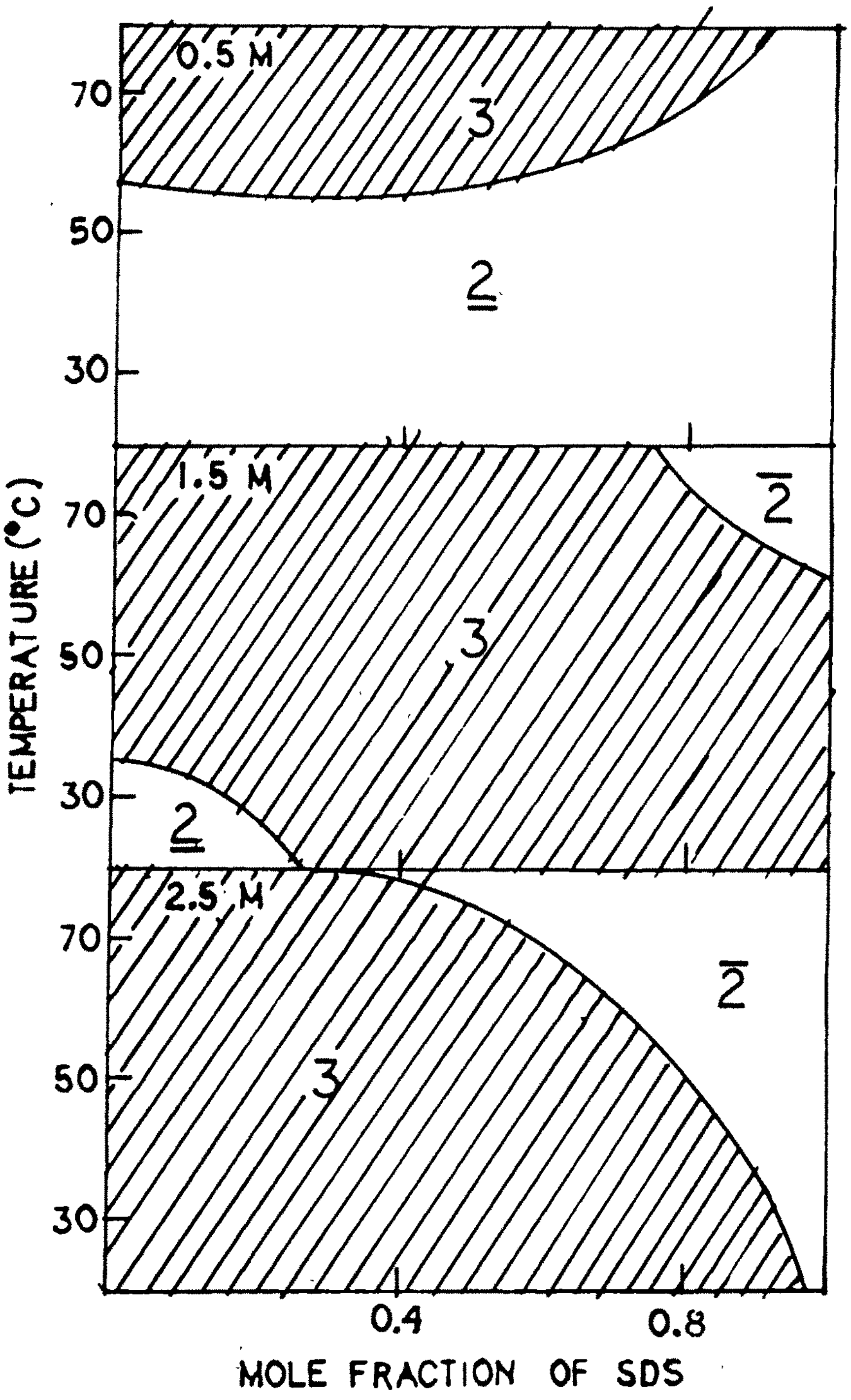

Fig.5.7 Temperature v s SDS mole fraction phase map for the system Heptane/Brij 35 + SDS - propanol/water at various NaCl concentrations.

formation of different types of Winsor forms is due to some balance of hydrophilicity and lipophilicity. At high SDS concentration that balance favour condition to form $\overline{2}$ region. Increase of temperature also tilts the balance of hydrophilicity and lipophilicity in the surfactant mixture to form a 3ϕ or a $\overline{2}$ system. Thus at 60° and 80°C, the surfactant mixtures acheive the required balance in HLB for the transition to Winsor III even at lower NaCl concentration. Thus 3 region widened. It can be seen that phase behaviour at SDS rich portion is decided by NaCl concentration alone. Temperature has only mild influence on it.

Similar phase map with temperature as the experimental variable is given in Fig.5.7. It is clear that the 3 phase region is maximum when NaCl concentration is about 1.5 M. At lower or higher concentrations, this region decreases. The hydrophil-lipophil balance (not the number) that was discussed earlier (Chapter 4, P.82) is very sensitive to temperature and this balance tilts towards relatively more hydrophobicity with increase of temperature. If it tilts towards more hydrophilicity, then $\underline{2}$ is formed and if it tilts towards more hydrophobicity then $\overline{2}$ will form. In between 3ϕ is obtained. These diagrams (Fig.5.6 & 5.7) stresses that this tilt is affected by both temperature and NaCl concentration.

Fig.5.8 represents similar diagram for heptane/Brij 35 +Tween 20 - propanol / water system.As both surfactants are nonionic in nature phase behaviour is highly dependent on temperature. The HLB number of both the surfactants is 16.9. Hence phase behaviour of both the surfactants should be somewhat similar. HLB of the surfactant mixture is not tilted to such an extent towards hydrophobicity on addition of NaCl or rise of temperature so as to form $\bar{2}$ system. The microemulsion phase in the $\underline{2}$ phase system has o/w structure. (i.e. spontaneous curvature is positive). The temperature or NaCl effect is not sufficiently large to make the curvature negative. Hence the transition to $\bar{2}$ is absent. In presence of SDS, as discussed earlier, this change was possible.

(b) Winsor transitions

A more quantitative picture about the phase changes in these mixed systems can be observed from Figs. 5.9 - 5.14.

Figs.5.9 and 5.10 represent the Winsor transitions in heptane/Brij 35 + propanol/water system at composition of 30/30/40 by weight. The results at 40°C and 80°C are shown in the figures. At 40°C, only pure SDS system experience the complete Winsor transitions (Winsor I → III → II). All

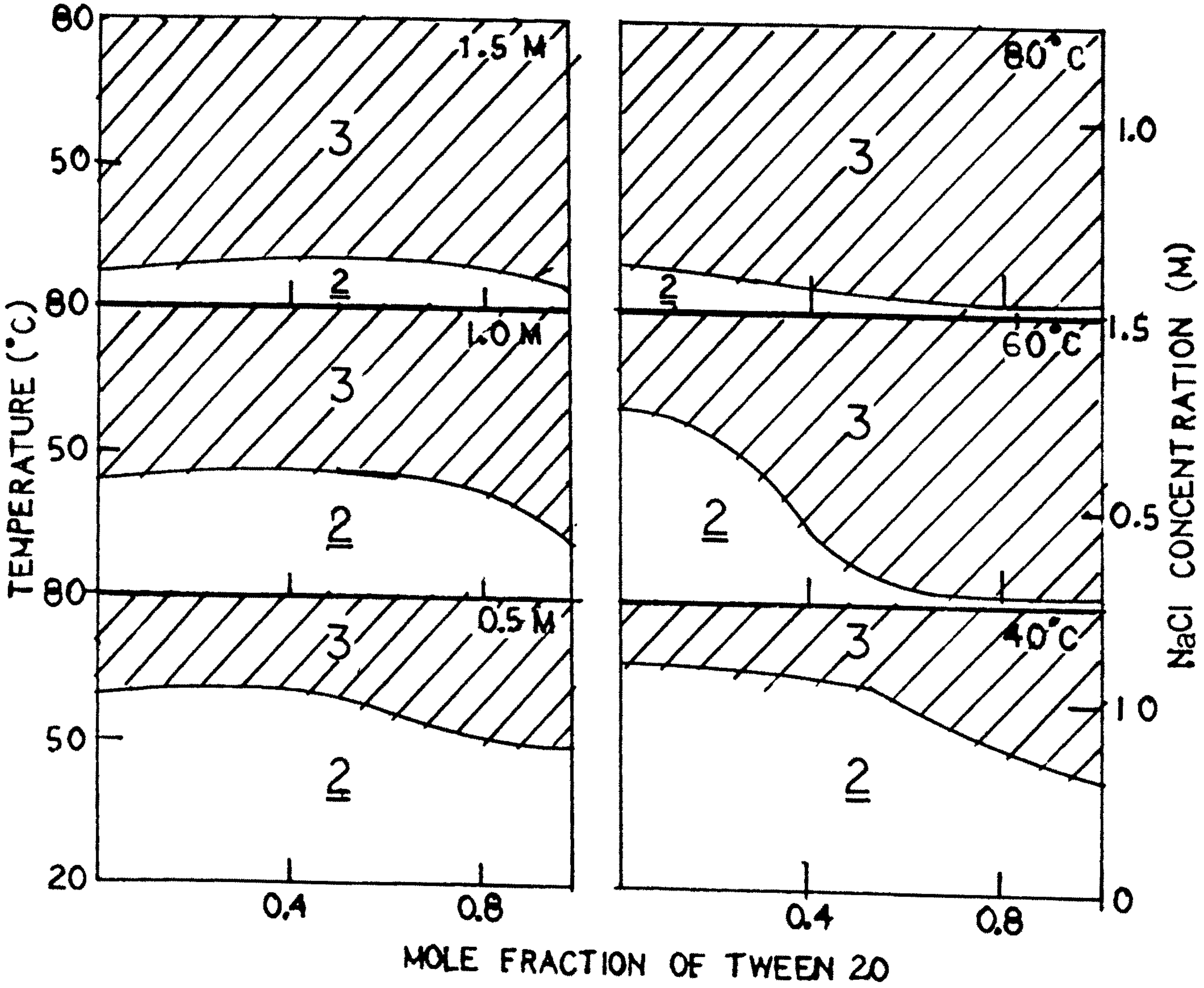

Fig.5.8 Phase map for the variation of Tween 20 with (a) Temperature and (b) NaCl concentration for Heptane/Brij 35 + Tween 20 -propanol/water.

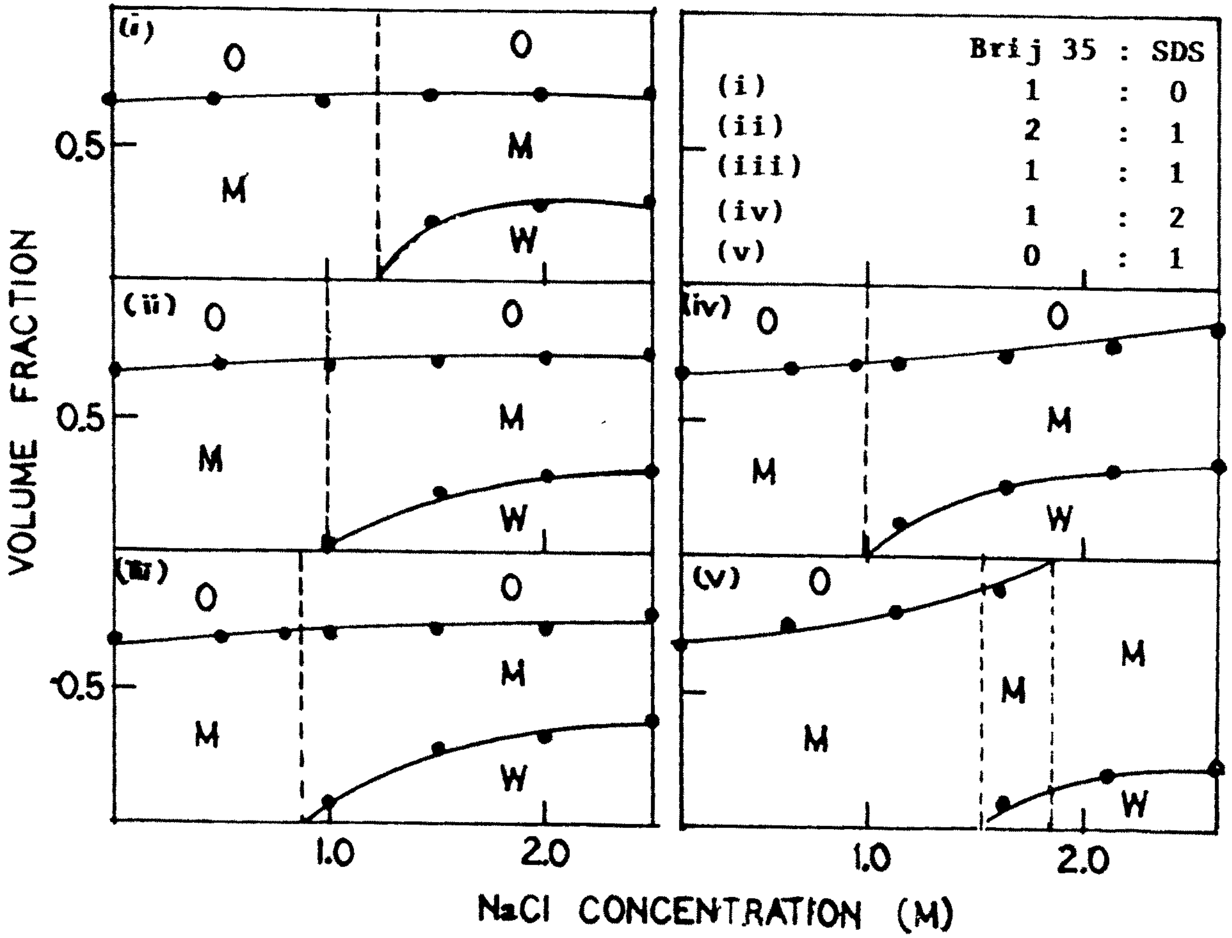

Fig.5.9 Plot of volume fraction vs NaCl concentration of the Heptane (O)/ Brij 35 +SDS-propanol (S)/Water (W) system at various Brij 35 +SDS mixing ratios. The composition of O/S/W in 30/30/40 by weight. Temperature is 40°C.

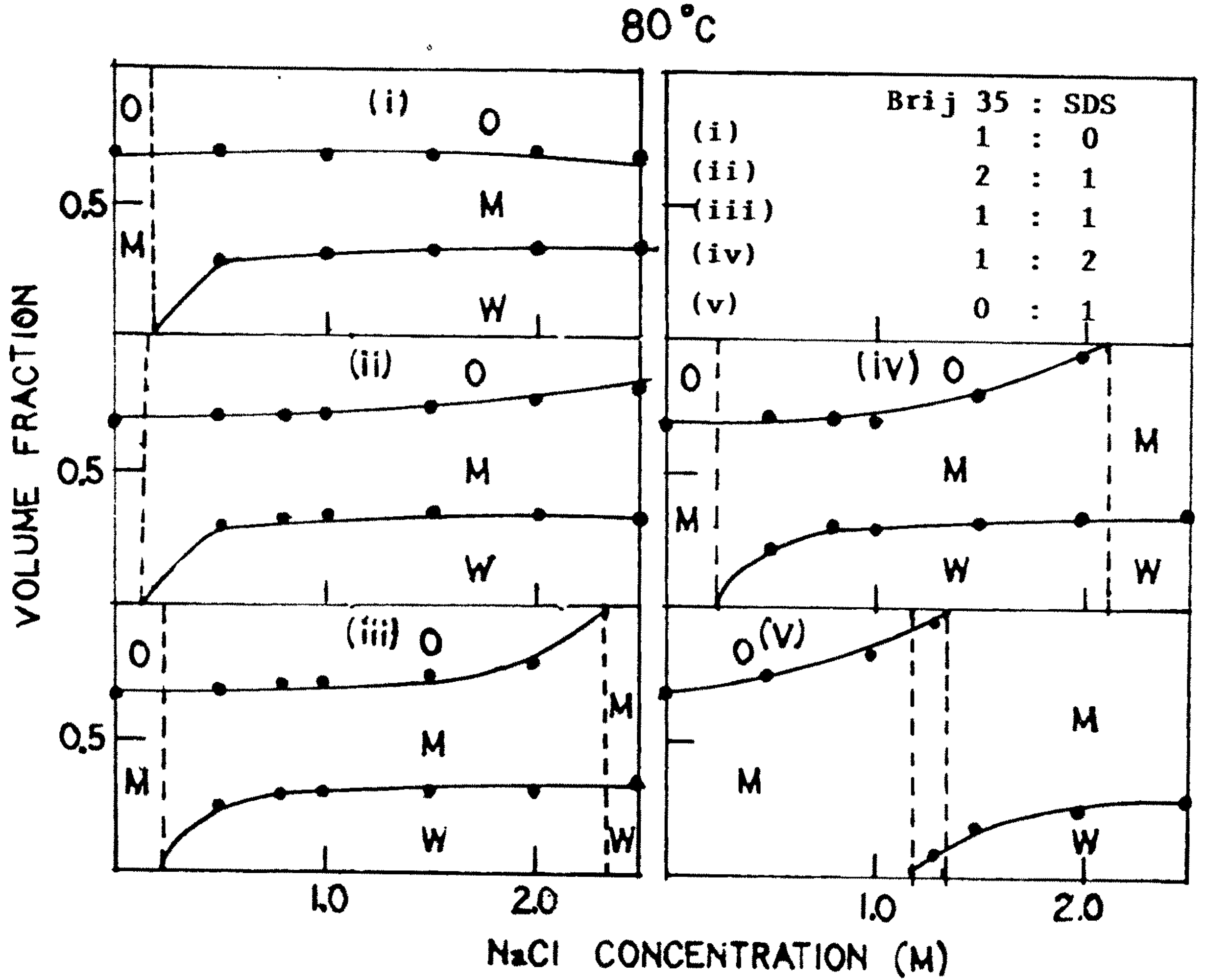

Fig.5.10 Variation of volume fraction of different Winsor phases for the system Heptane (30%)/Brij 35 + SDS-propanol (40%)/Water (30%) with NaCl concentration at various Brij 35 +SDS mixing molar ratios.

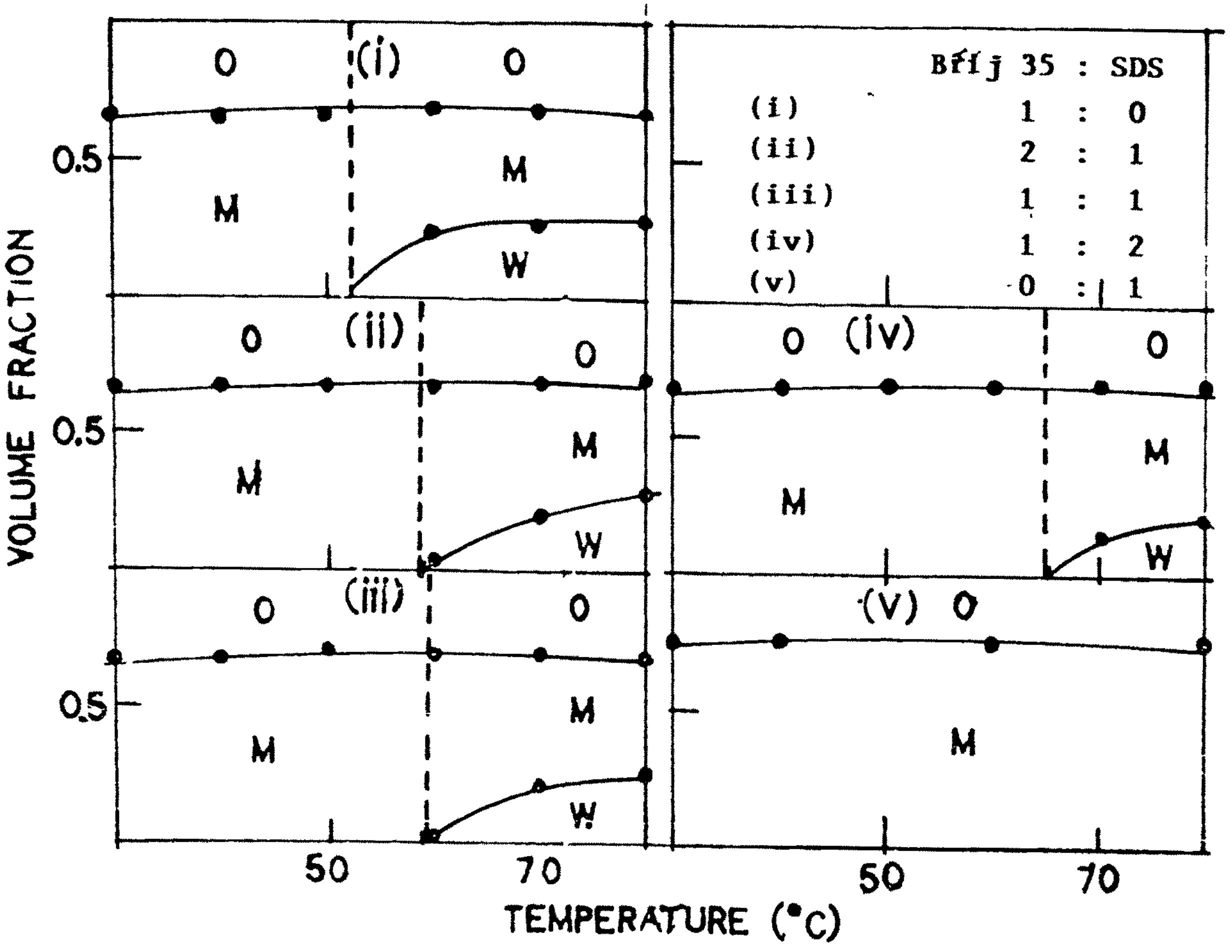

Fig.5.11 Plots of volume fraction vs temperature for the system Heptane/Brij 35 + SDS - propanol/0.5 M NaCl at various Brij 35 + SDS mixing ratios.

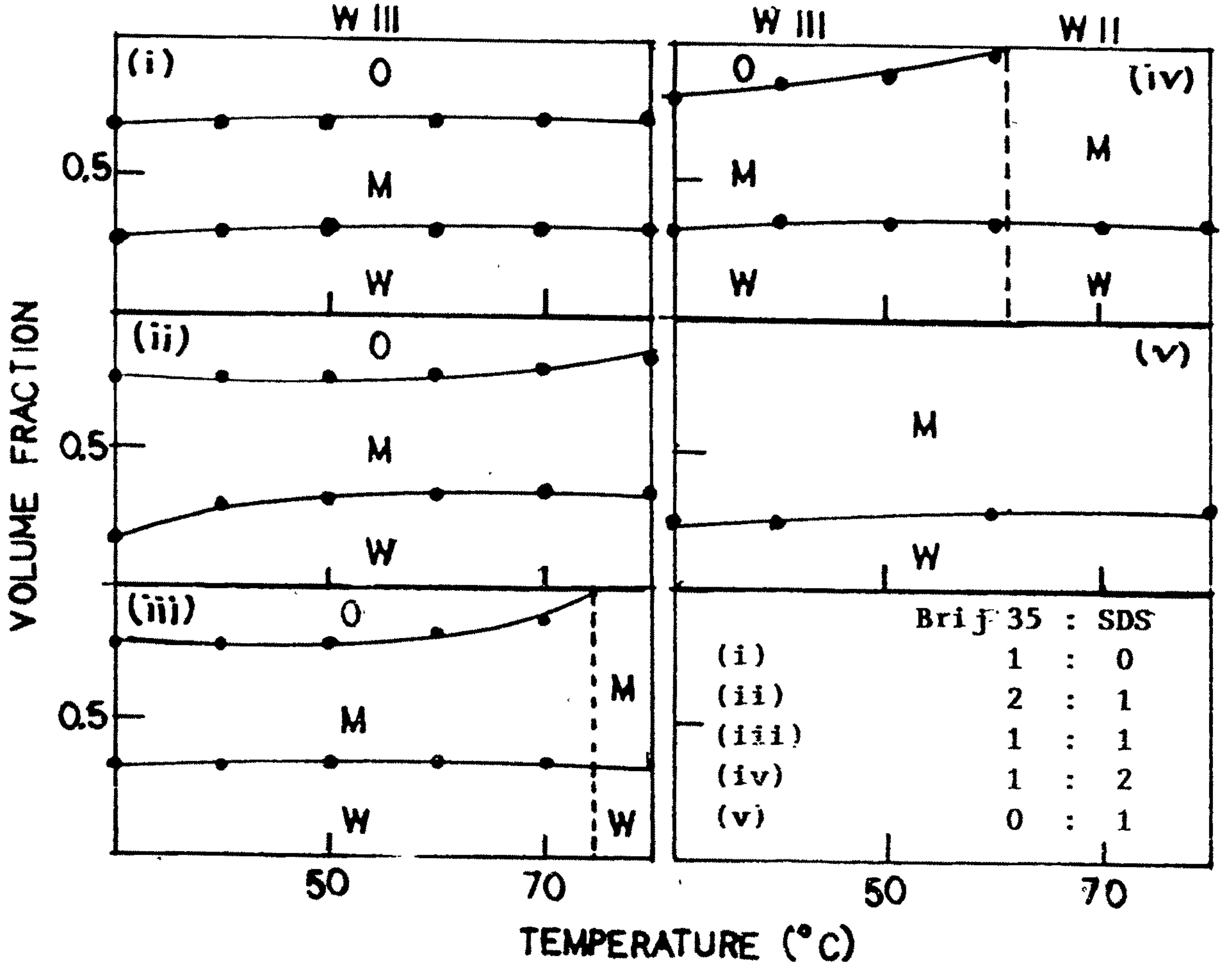

Fig.5.12 Plots of volume fractions of different Winsor phases of the system Heptane (O)/Brij 35 + propanol/2.5 M NaCl (W) vs temperature. The composition is 30/30/40 respectively.

the mixed surfactant systems exist either as Winsor I or Winsor III in the salinity range studied. No Winsor II was observed. This shows the predominant effect of Brij 35 in the mixture at lower temperature. But at 80°C (Fig.5.10) two of the mixed systems (1:1 and 1:2 of Brij 35 : SDS) experienced all Winsor transitions. Brij 35 rich mixed system (2:1) also shows a tendency to transit from Winsor III to Winsor II. But the maximum salinity used was not just enough to have it. It is well known that at elevated temperature, nonionic surfactants are increasingly hydrophobic in nature [205,212]. Same is the case with ionic surfactants at higher salinity [201,212]. Hence it would be expected that the combination of these two effects will make the surfactant mixture enough lipophilic to form Winsor II system at higher temperature and salinity.

Winsor transitions were studied as a function of temperature also. The results at lower (0.5 M) and higher (2.5M) NaCl concentrations were shown in Figs 5.11 and 5.12. It can be noted that all the mixed surfactant systems are sensitive to temperature.

The optimum formulation of a surfactant mixture regarding a specific property with various experimental variables can be represented by an equation proposed by Anton et al.[227].

$$Y_{mix} = X_1Y_1 - X_2\ Y_2 \qquad (1)$$

Where 'Y' represents any of the experimental variable (like temperature, salinity etc.) and 'X' is the molefraction of the surfactant component. If the experimental variable is temperature and the surfactant mixture is an anionic-nonionic one, then Y_1, Y_2 terms have opposite signs [227]. This is because the temperature effect on any property for the ionic and nonionic surfactants,in general,is in opposite direction.

Temperature induces a Winsor I → III → II transition in microemulsion where nonionic surfactants are present [153,205] while a reverse transition (Winsor II → III → I) is observed for microemulsions with ionic surfactants [134,201]. Hence at some mixing ratio, Y can be zero, i.e. the equation becomes,

$$0 = X_1Y_1 + X_2Y_2 \quad \cdots\cdots\cdot \quad (2)$$

From Figs 5.11 and 5.12 some interesting observations can be made with respect to equation (2). At 0.5 M NaCl concentration temperature induces Wisnor I→III transition in Brij 35 containing system. For SDS containing one no such transition was observed. Only one type of system (Winsor I) exists within the temperature. studied. Hence equation (2) immediately indicates no temperature independent system by mixing the two surfactants and that is obvious from Fig.5.11. As discussed earlier for getting a temperature independent system the two components independently should have mutually opposite Winsor transitions. In 2.5 M NaCl solution (Fig.5.12) Brij 35 one show only Winsor III formation, where as SDS one, Winsor II ($\bar{2}$) form. Hence again a temperature independent system is unexpected within the temperature range studied. Figs. 5.12 (b,c,d) attest to that observation. As has been pointed out earlier (P.141) both Brij 35 and SDS phase behaviour follow the same nature in presence of n-propanol as cosurfactant. Hence in these mixed systems of SDS-Brij 35, a temperature independent behaviour for any property was unexpected from equation (2) and that is what was observed.

Figs 5.13 and 5.14 exhibit the Winsor transition observed in heptane/Brij 35 + Tween 20 - propanol/water system with changing NaCl concentration and temperature. Only Winsor I → III transition was obtained at all mixed and pure systems within the studied experimental conditions. It is clear from the figures 5.13 and 5.14 that Winsor I → III transition takes place earlier when Tween 20 fraction in the mixed surfactant increased. As both the surfactants are similar type, a mixed surfactant system with temperature independent properties are not expected as per equation(2) (P. 158) and no such systems was found also. A somewhat linear property was expected and

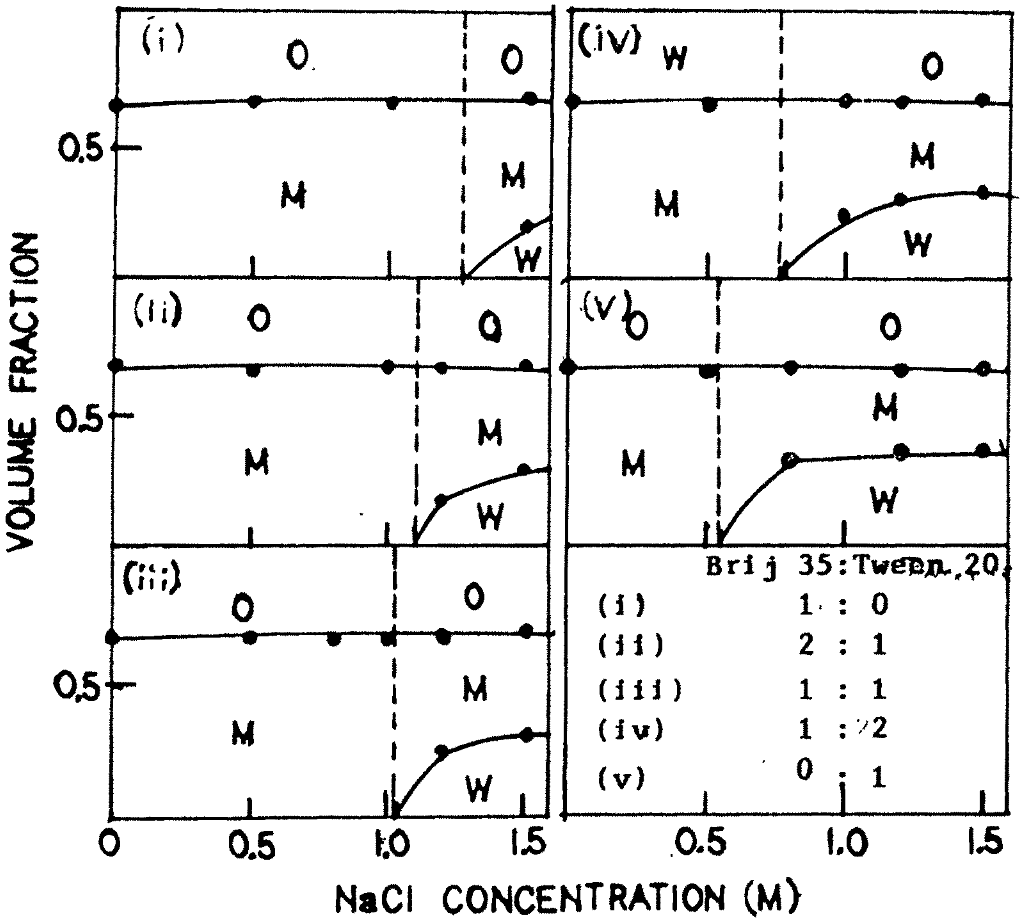

Fig. 5.13 Plot of volume fractions of different Winsor phase of the system Heptane/Brij 35 + Tween 20 - propanol/ Water (W) vs NaCl concentration of the aqueous phase at 40°C.

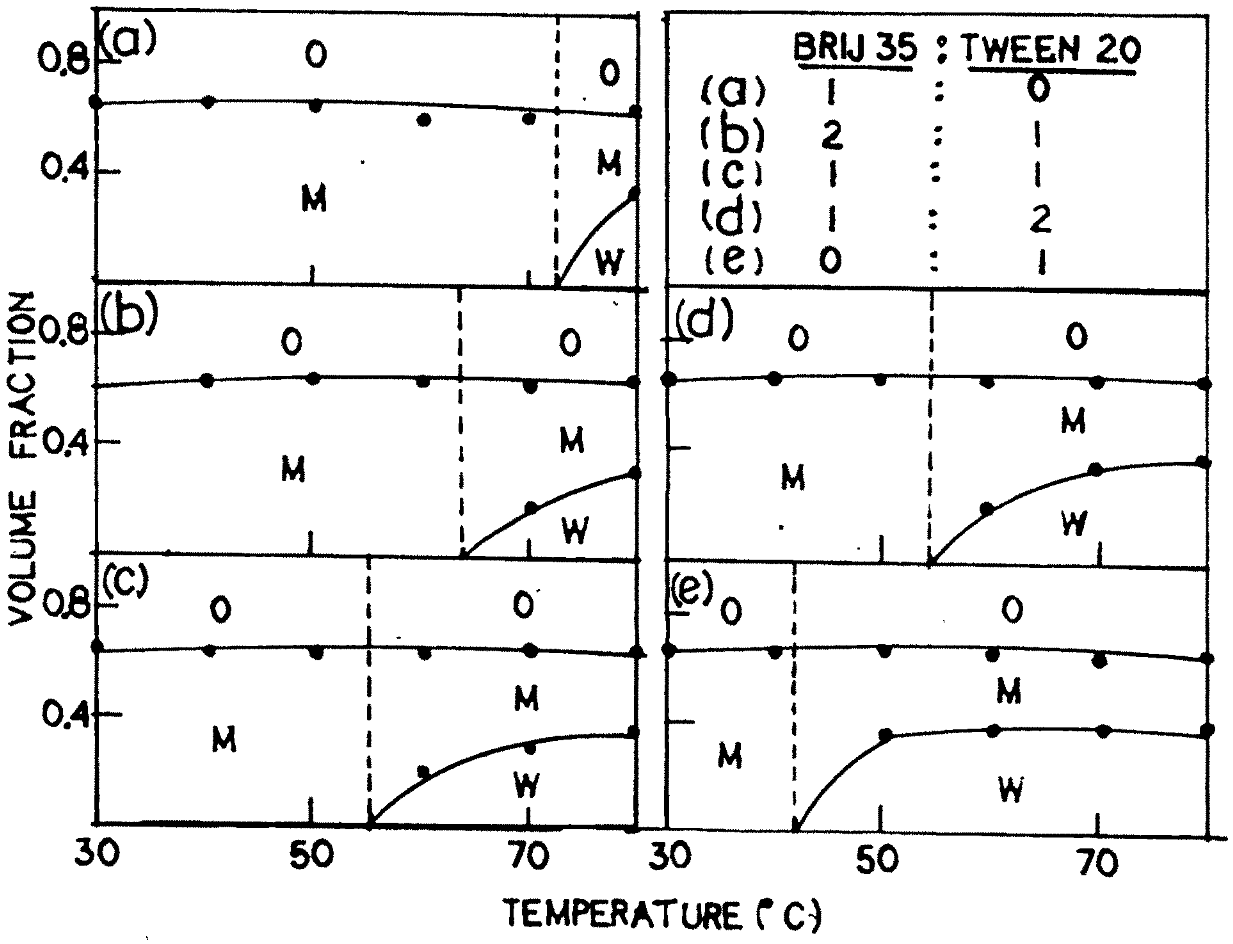

Fig.5.14 Plots of the volume fractions of different Winsor phases vs temperature at different Brij 35 + Tween 20 mixing molar ratios for the system Heptane/Brij 35 + Tween 20 + propanol/0.5 M NaCl.

seems to be present.

Salinity scan is important only when both the Winsor transitions (Winsor I → III and III → II) are present as in that case optimum salinity could be determined. We observe that such Winsor transitions are present only in two mixed surfactant systems (1:1 and 1:2 molar ratios of Brij 35 : SDS system at 80°C). Hence optimum salinity of these systems were determined from the salinity scan (Fig.5.15). Optimum salinity was found to be 0.92 and 0.88 moles.dm^{-3} for 1:1 and 1:2 system respectively. Higher the SDS content, lower is the optimum salinity. This is also along the expected line as SDS will dissociate to some extent and hence would provide Na^+ to the system and thereby bring down the overall NaCl concentration.

(c) Viscosity and Compressibility

Physical properties like viscosity and compressibility were also studied on these mixed surfactant systems. Heptane/SDS + Brij 35 - propanol / water forms 1Ø microemulsion only at a very narrow region of the phase diagram. Hence only one composition was selected for studying these physical properties. The composition taken was 2.5/50/47.5 by weight for heptane/ Brij 35 + SDS - propanol/water respectively. In Fig.5.16

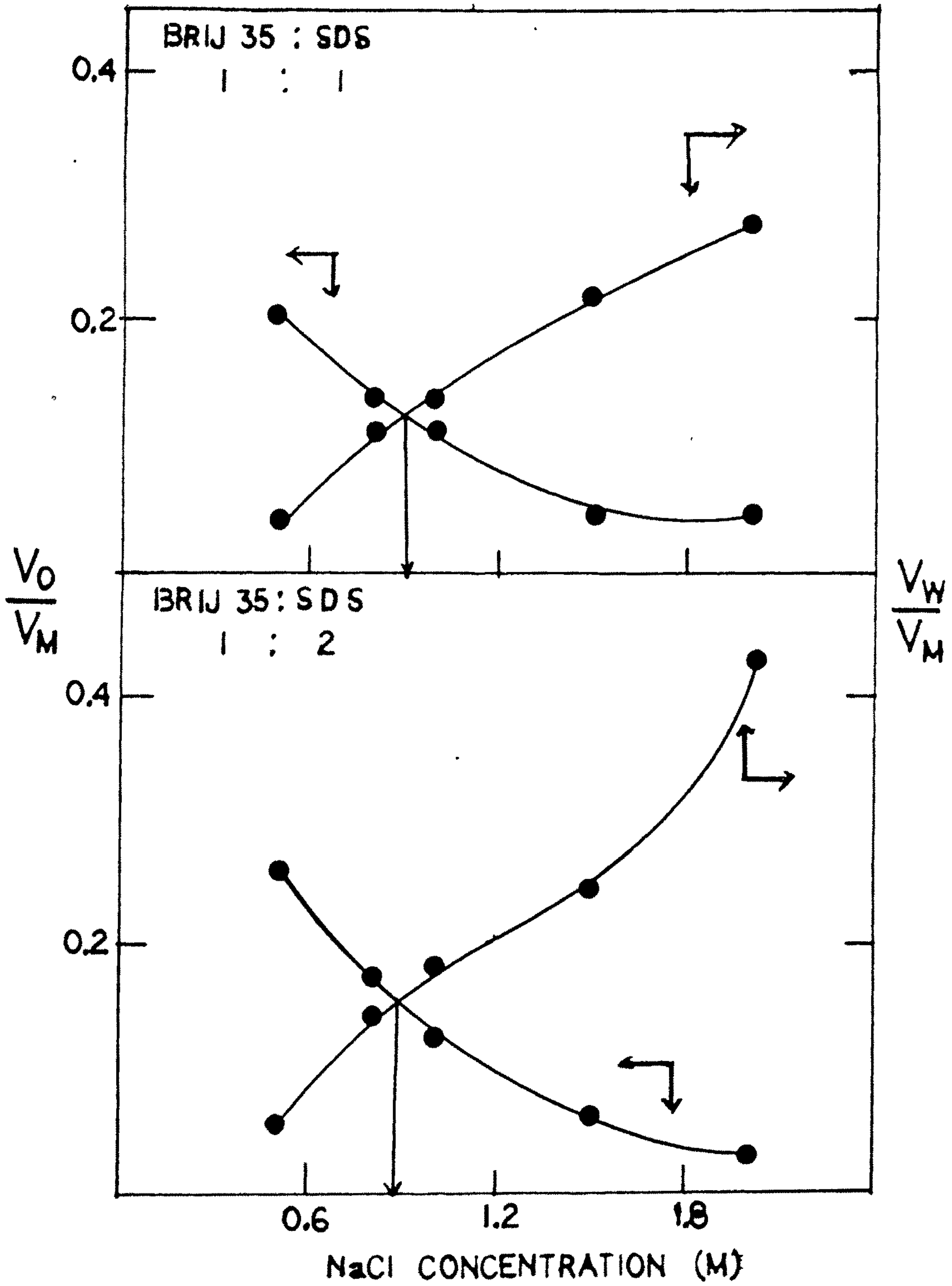

Fig.5.15 The plot showing the salinity Scan for the system Heptane/Brij 35+SDS-propanol/Water at 80°C V_o, V_m and V_w represents the volume of oil phase, microemulsion phase and water phase respectively.

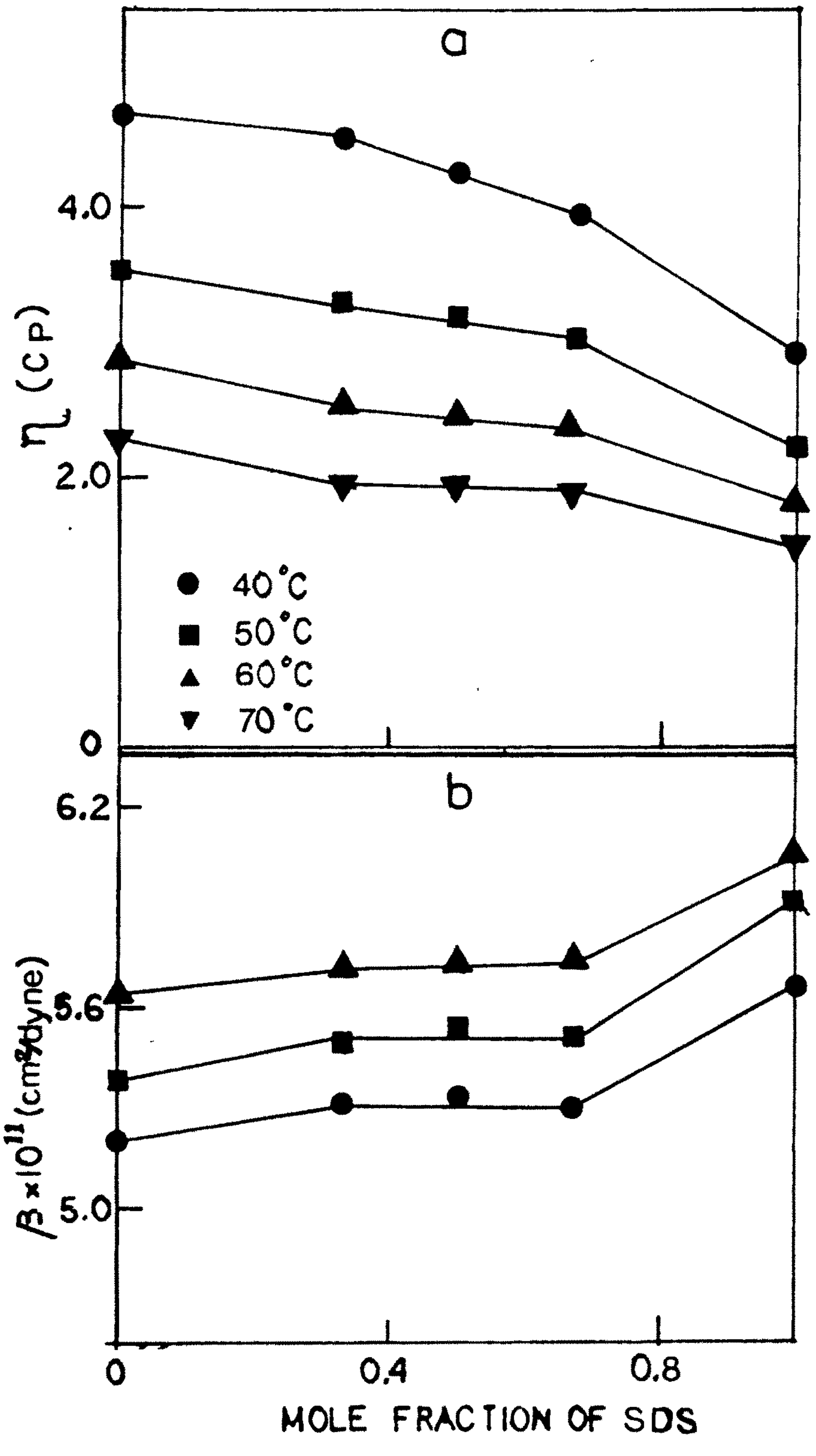

Fig.5.16 Plots of (a) viscosity and (b) adiabatic compressibility of the system Heptane/Brij 35 +SDS-propanol/water vs mole fraction of SDS in the mixture of SDS and Brij 35.

viscosity and adiabatic compressibility values are plotted against mole fraction of SDS. Viscosity of the SDS system is lower than that of Brij 35 system. But the variation of viscosity values with mole fraction of SDS was not found to be linear.

Viscosity of such dispersions are dependent mainly on the size of the dispersed droplets and viscosity values of continuous medium [64,82]. Higher the size of the dispersed droplets, higher will be the viscosity [82]. Hence the ratio of the two viscosities will be a measure of the relative droplet size. The efficiency of the Brij 35 + propanol combination to bring down the interfacial tension between water and oil is less compared to SDS + propanol combination. Hence SDS + propanol disperses oil more efficiently in water phase. Therefore the droplet size of SDS containing microemulsion is lesser than the Brij 35 containing ones. Thus SDS system has lower viscosity. The more SDS added, the droplet size decreases and hence viscosity decreases. But the differences in the viscosity values among the mixed surfactant systems are lesser than expected from ideal mixing. The droplet size is also a function of temperature. At higher temperature of 70°C, the viscosity value of mixed systems are almost same indicating almost same droplet size.

As generally observed, variation of adiabatic compressibility (β) is opposite to viscosity variation [70,249]. SDS system has higher compressibility than Brij 35 system. But interestingly all the mixed surfactant systems at constant temperature have similar β values. This stresses the nonlinear nature of the SDS + Brij 35 mixing.

The product of η and β though, were not found to be constant at different temperature. That is, though the nature of variation is opposite, the rate of variation is not same. But when the product was plotted against temperature, it did show an approximate linear variation.

Fig 5.17 gives the variation of viscosity values of heptane/ Brij 35 + Tween 20 - propanol / water system against the molefraction of Brij 35 in the surfactant mixture. As this sytem has fairly wide 1ϕ zone, three compositions representing o/w, bicontinuous and w/o structure were chosen for the study.

At all the three compositions, viscosity of Tween 20 systems have lower viscosity than Brij 35 one. That is Brij 35 system has relatively higher droplet size than Tween 20. From the phase diagram studies, it is obvious that Tween 20 + propanol is better surfactant combination

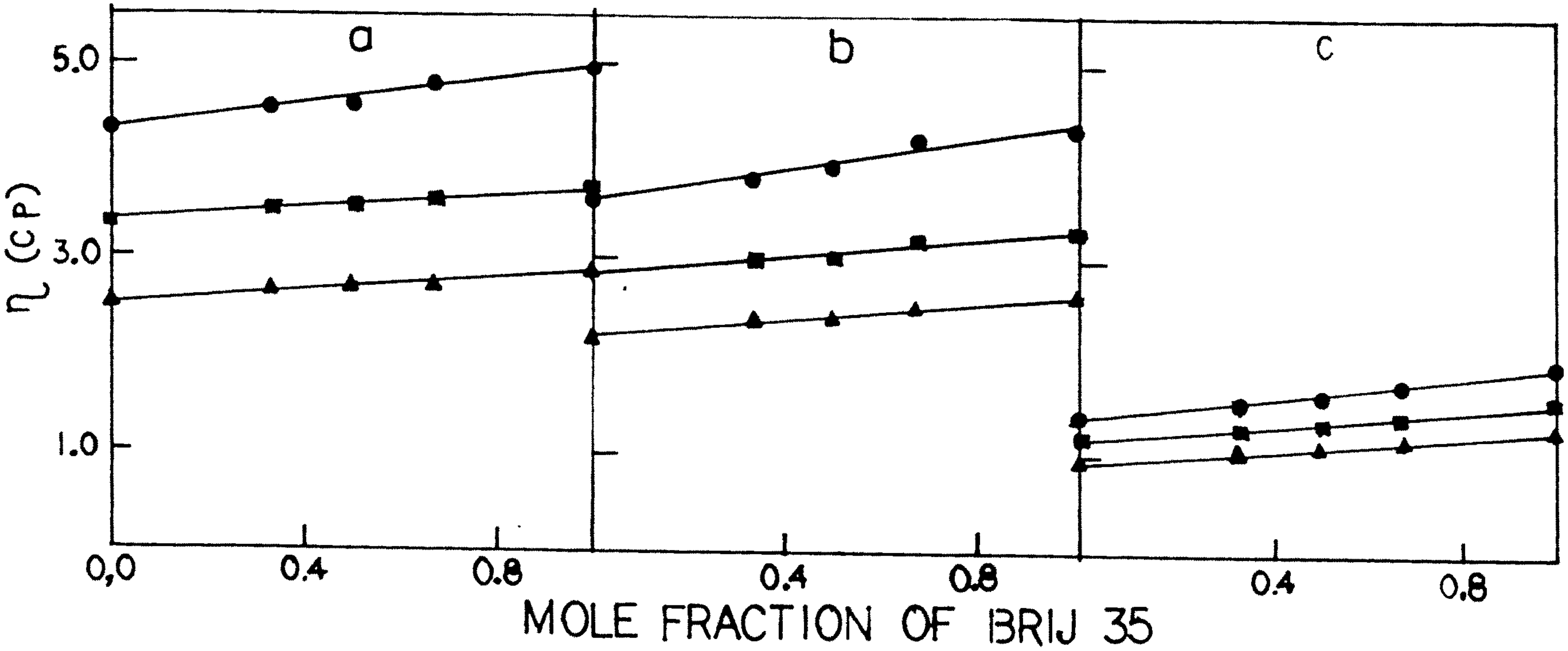

Fig.5.17 Plots of viscosity vs mole fraction of Birj 35 in the mixture of Brji 35 and Tween 20 for the system Heptane (O)/Brij 35 + Tween 20 -propanol (S)/Water(W) at different compositions. (a) 2/60/38 for O/S/W (b) 10/75/15, (c) 38/60/2 ● 40°C; ■ 50°C; ▲ 60°C.

than Brij 35 + propanol. Hence it is expected that Tween 20 lowers the interfacial tension more efficiently than Brij 35 and thereby disperses the oil or water effectively to form smaller size droplet. Linearity obtained in the viscosity versus mole fraction of Brij 35 plot indicates additive mixing property. This linearity is due to their collective behaviour at the interface. The two surfactants being similar type, this was expected from Anton's earlier idea [227].

Viscosity values decrease when the system changes from o/w (Fig.5.17(a)) to bicontinuous (Fig.5.17 (b)) and then to w/o (Fig.5.17 (c)). As stated earlier viscosity values of these systems are dependent on the viscosity of the continuous medium [64],especially when the amount and type of the surfactant is fixed. Water has higher viscosity than oil and microemulsion system become increasingly oil continuous when it changes from o/w to bicontinuous and then to w/o. Hence viscosity deceases in that order (Fig.5.17).

The viscosity values are used to calculate the activation enthalpy for viscous flow. Viscosity is related to temperature by the well known Frankel-Eyring equations [197,199]. The relation is $\eta = A\, e^{\Delta G^{\#}/RT}$. Hence,

$$\ln\eta = \ln A + \Delta G^{\#}/RT$$

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

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

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

where B is a constant and other quantities have their usual significance. In Table I these $\Delta H^{\#}$ values are tabulated. The error in the $\Delta H^{\#}$ values are of the order of 10%. Hence it is clear that at any particular composition, the $\Delta H^{\#}$ values are almost independent of the surfactant ratios. For Brij 35 + Tween 20 system, when the oil-water ratio was varied from one extreme to the other, the values differ significantly. The $\Delta H^{\#}$ values are relatively larger when water is in excess. This is because water is more viscous than heptane and hence more energy is neded for the movement. From the data of the biconitnuous (75/15/10 of S/W/O) system, it is seen that $\Delta H^{\#}$ values are close to that of high water content system (60/38/2 of S/W/O). This probably signifies that this bicontinuous system has relatively more water continuous structure.

Compressibility values for Brij 35 + Tween 20 were tabulated in Table II. Though a regularity was observed with the variation of surfactant mixing ratio, the values are very close to each other. This prevents further discussion about their variation.

TABLE 5.I

Activation enthalpy of viscous flow of mixed Heptane (O)/Surfactant + propanol(S)/Water (W) system at various mixing ratios.

Surfactant	Compositions	$\Delta H^{\#}$ kJ/mole of various molar mixing ratios of the surfactant				
	S/W/O	1:0	2:1	1:1	1:2	0:1
SDS:Brij 35	50/47.5/2.5	20.5	22.2	23.9	24.5	21.4
Brij 35:Tween 20	60/2/38	17.5	16.7	16.0	16.4	16.9
	75/15/10	22.1	22.6	21.8	20.5	22.0
	60/38/2	23.3	24.4	22.8	23.4	23.0

TABLE 5.II

Adiabatic compressibility (β) of the system Heptane (O)/ Brij 35 + Tween 20 + propanol (S)/Water (W)

Composition O /S/W	Molar mixing ratio of Brij 35 : Tween 20	$\beta \times 10^{11}$ cm^2/dyne at 40°C	 50°C	 60°C
38/60/2	1 : 0	9.4	9.9	10.6
	2 : 1	9.6	10.3	11.0
	1 : 1	9.7	10.4	11.2
	1 : 2	9.7	10.5	11.3
	0 : 1	9.9	10.6	11.4
10/75/15	1 : 0	6.9	7.5	8.0
	2 : 1	7.0	7.5	9.0
	1 : 1	7.0	7.5	8.0
	1 : 2	7.1	7.6	8.0
	0 : 1	7.1	7.6	8.1
2/60/38	1 : 0	5.4	5.5	5.7
	2 : 1	5.4	5.6	5.9
	1 : 1	5.4	5.7	5.9
	1 : 2	5.4	5.7	6.0
	0 : 1	5.6	5.7	6.0

From these studies with mixed surfactant systems, one point becomes clear that mixing of similar type of surfactants will be linear while that of different types may not be so.