CHAPTER 5

EFFECT OF ALKANOL MIXING ON MICROEMULSION PHASE BEHAVIOUR AND PROPERTIES

5.a. Preview

The alcohols, as cosurfactants, play crucial role in the formation, phase behaviour and properties of microemulsions. Though the necessity of alcohols in the formation of microemulsions is an established fact and is known from the days of Schulman and Winsor, the real function of these molecules remained unknown for a long time. As a result of various studies related to the role of alcohols in microemulsion formation in the last two decades, our idea in this matter is somewhat clear today.

The role of alcohols in microemulsion formation is many fold. The surfactants, available commercially, are not balanced with respect to their affinity towards aqueous and oleic phases, but can be made changed by the addition of suitable alcohols [185]. The alcohols assist the surfactant molecules to decrease the oil-water interfacial tension to very low values so that stabilization of microdroplets occur and hence the formation of microemulsion. By partitioning between aqueous and oleic phases, alcohol molecules can modify the solvent properties of these phases [185,186] i.e. making an oil phase relatively more hydrophilic or an aqueous phase comparatively more hydrophobic. The most basic function of alcohols is perhaps the exclusion of the rigid structures such as gels, liquid crystals, precipitates etc. in the oil-water-surfactant systems and thus to lower the viscosity of the system [51,186,187].

The studies performed by changing the alcohol carbon chain length in microemulsions are many [128,188,189]. The inversion of oil in water microemulsion to water in oil microemulsion as the function of increasing alcohol chain length is an established phenomenon [53]. This happens because of the increasing hydrophobicity of the interfacial layer with increasing alcohol chain length. The conductance values in microemulsions are also strongly influenced by the nature of the alcohols. Clausse et al. [55] demonstrated that the systems containing shorter alcohols upto butanol show excellent percolative behaviour of conductance with increasing water content whereas higher alcohols give either gradual increase or constant conductivity with water content. Lang et al. [56] studied alcohol chain length variation in microemulsions and found that the interdroplet interaction is more attractive in short chain alcohol containing systems and is less attractive in long chain alcohol containing systems.

For specific technological purposes such as enhanced oil recovery, mixed surfactant systems have shown more acceptable performance than a single surfactant [124,190]. Microemulsions have been formulated and studied using mixtures of two different surfactants [176,191]. But the properties of microemulsion when mixture of two different alcohols is present as cosurfactant, have been rarely evaluated [192]. Whether the microemulsion will show some intermediate averaged properties of the two constituent cosurfactants or somewhat independent properties is a fundamental question which needs answering. In this chapter we present the results of our study of microemulsion systems when the cosurfactant was various mixtures of two alkanols, hexanol and propanol, with respect to their phase behaviour and properties.

5.b. Experimental

The alkanols, propanol and hexanol were mixed together in different molar proportions and these mixtures were used as the cosurfactant in formulating microemulsions. Surfactant to cosurfactant ratio was always kept constant at 1:2 by weight. Propanol : hexanol molar ratios used were (a) 4:1, (b) 1:1 and (c) 1:4. The ternary phase diagrams were determined only at 40°C while the property studies were performed at various temperatures in the range 30°C to 70°C. As the mixed systems (b) and (c) (i.e. 1:1 and 1:4 of propanol-hexanol ratio) did not produce a three phase microemulsion formulation (Winsor III) at the particular composition studied, their optimal salinities were not determined.

Ternary phase diagram with pure hexanol as cosurfactant was also constructed.

5.c. Results and Discussion

(i) Phase Diagram

The Figs. 5.1 to 5.3 depicts the phase diagrams of the pseudoternary systems obtained upon substituting propanol with mixtures of propanol and hexanol of different molar ratios 4:1, 1:1 and 1:4 respectively. In Fig.5.4 the ternary phase diagram of the system with pure hexanol as cosurfactant is also provided. In this chapter our attention will be mainly focussed towards the Winsor IV phase and hence the other regions of highly viscous, turbid or translucent one phase and two phases were not subjected to detailed investigation. From the diagrams it can be readily seen that the features of Winsor IV domain, 'B' is strikingly influenced by the alkanol mixing ratio. In Fig.5.1 with propanol-hexanol ratio 4:1, the realm of existence of isotropic Winsor IV region assumes the shape of a curvilinear triangle [55] leaning towards a large portion of the surfactant-water base line of the phase diagram. Though similar to the pure propanol containing system in its general pattern (Fig.3.1), the area of this zone increased drastically by the presence of small amount of hexanol. The regions marked 'A' and 'C' are the usual

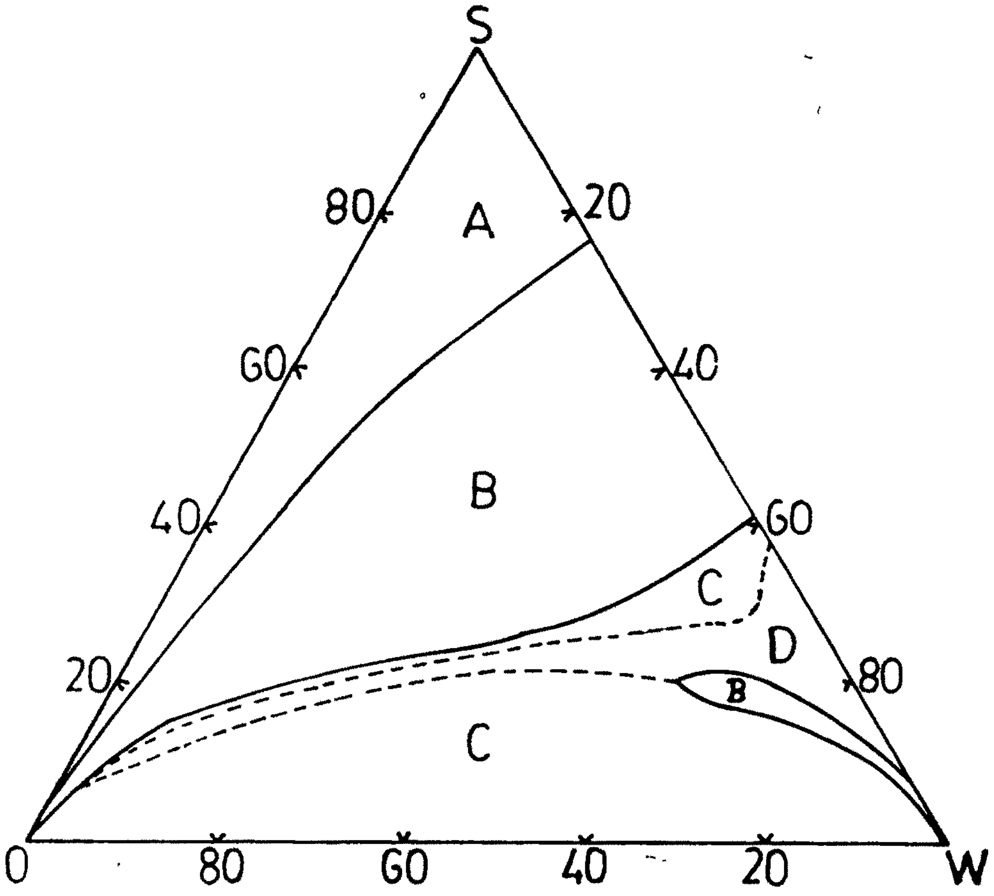

Fig.5.2
The pseudoternary phase diagram of the system at 40°C when cosurfactant is 1:1 molar mixture of propanol and hexanol (for A,B,C, etc. see text).

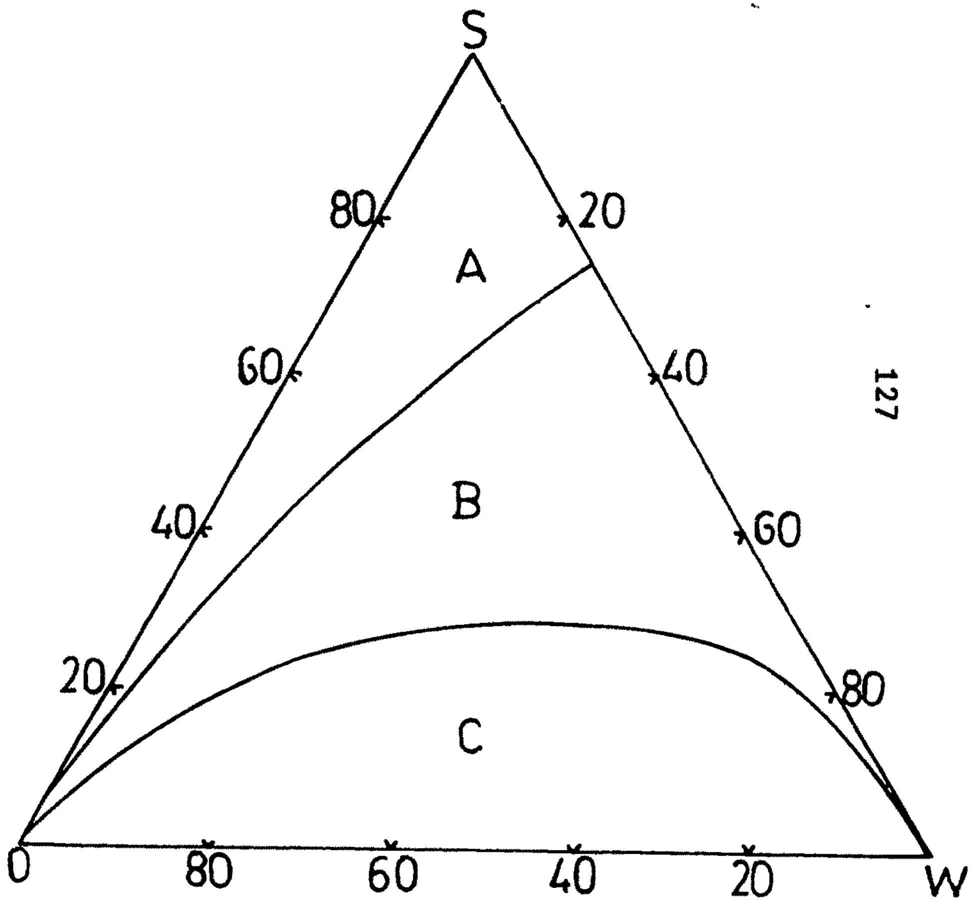

Fig.5.1
The pseudoternary phase diagram of the system Cyclohexane-SDS+cosurfactant-water at 40°C when surfactant is 4:1 molar mixture of propanol and hexanol (For A,B,C etc. see text.)

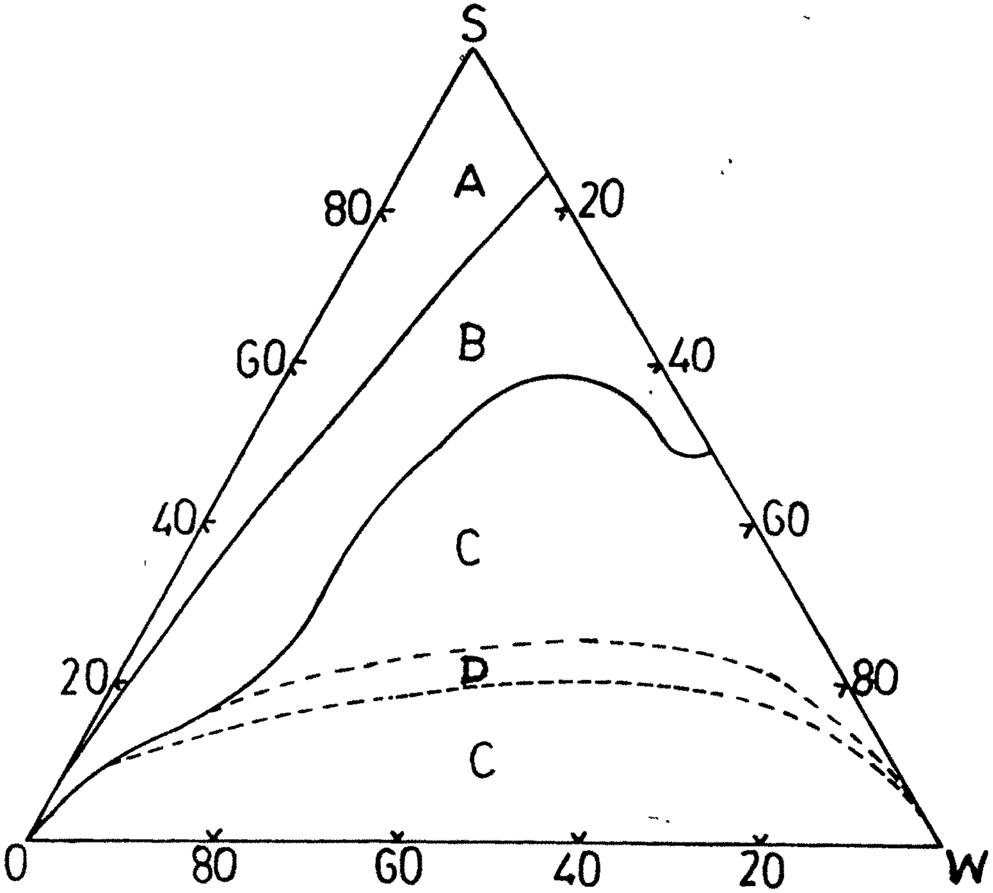

Fig.5.4
The pseudoternary phase diagram of the system cyclohexane-SDS+hexanol-water at 40°C (for A, B, C etc. see text).

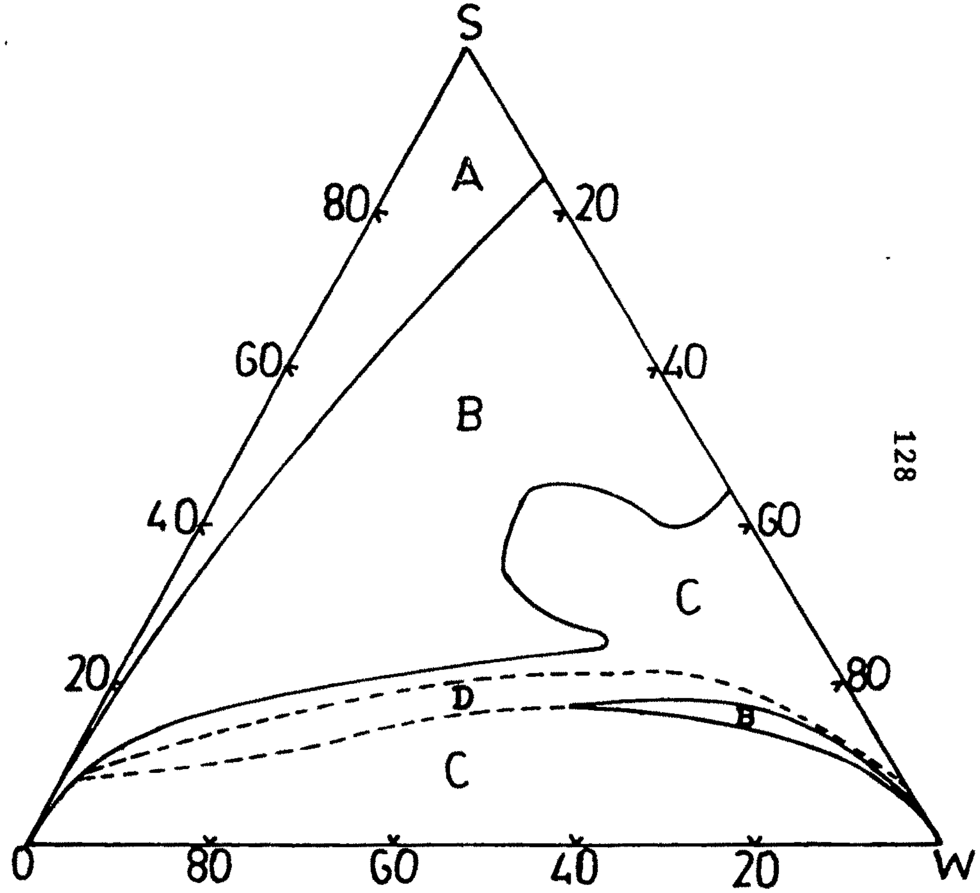

Fig.5.3
The pseudoternary phase diagram of the system cyclohexane-SDS+cosurfactant-water at 40°C when cosurfactant is 1:4 molar mixture of propanol and hexanol (for A,B,C etc. see text).

solid (surfactant)-liquid biphase region and liquid-liquid biphase region respectively. The phase diagram of 1:1 mixed alkanol system (Fig.5.2) shows drastic alterations in the configuration of Winsor IV region (B) as well as in the region below this. Unlike the previous cases of pure propanol and 4:1 mixture the Winsor IV domain splits into two disjoined zones that are separated by two narrow composition zones, a liquid-liquid two phase zone marked 'C' and a transparent or translucent viscous media marked 'D'. The bigger Winsor IV area located at the middle region of the phase diagram, lying extended from the oil apex to the surfactant-water base line, spans over a fairly broad range of compositions and coincides with this line at the middle portion. It may be noted here that this area does not originate from the water apex of the phase diagram. The small isotropic region (B) protruding into the centre of the diagram from the water apex probably implies the existence of water external microemulsion. The phase diagram with 1:4 mixing ratio (Fig.5.3) resembles more with the pure hexanol containing system (Fig.5.4). Here also the Winsor IV domain remains as two disjoined areas, the largest of which has a lower boundary with a crest and two troughs. The smaller Winsor IV region in this diagram at the water corner is still very narrow. It is seen from the Figs 5.3 and 5.4 that the lower boundary of the Winsor IV region has a large protrusion inside the one phase zone. This seems to be the characteristic of the system with hexanol or high hexanol content. One can see that at low surfactant concentration (Figs.5.1 - 5.4) a two phase system is present (C). But at a little higher concentration of the surfactant, in propanol-hexanol or hexanol system (Figs.5.2-5.4), a viscous single phase with narrow region is osberved (D). This medium looks to be a structured liquid with oil, water, surfactant and cosurfactant together. This breaks up once again at higher surfactant concentration (C). The region 'D' is available almost over the whole water-oil region. At further high surfactant concentration, a one phase low viscous microemulsion system (B) forms. The surfactant reaches its solubility limit at the upper boundary of this region and precipitates out (A).

The Winsor IV composition zone in all these mixed system phase diagrams were compared with that of pure propanol and hexanol. Fig.5.5 facilitates this comparison in which the percentage area of total Winsor IV regions in each of the phase diagrams is recorded as a function of the mole fraction of hexanol in the cosurfactant mixture. It is quite encouraging that a fairly large increase in the area of isotropic monophasic zone has been obtained when the two alcohols were mixed together. Furthermore this area remains almost invariant with the mole fraction of the hexanol in the alkanol mixture. In the case of

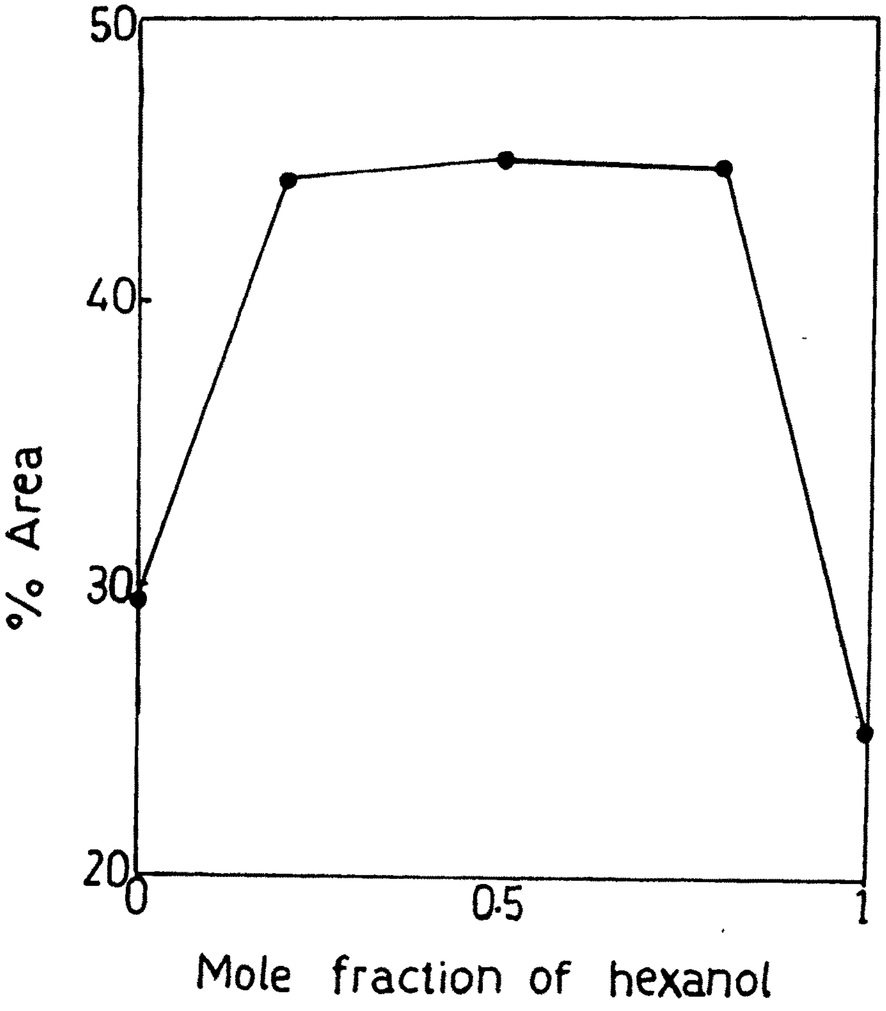

Fig.5.5 The plot of percentage area of the micro-emulsion region in the ternary phase diagram against mole fraction of hexanol.

mixing of two amphiphiles, an effective synergism or a negative synergism is generally observed [193]. In the present case we believe that an effective synergism which ends up in some intermediate averaged property of the surfactant phase,is the reason behind the large expansion of the monophasic Winsor IV region in the mixed systems. The hexanol being more hydrophobic, may combine with the less hydrophobic propanol and anionic surfactant SDS to form some type of an amphiphilic complex which has almost equal affinity towards the polar and apolar phases. This will assure an increased readiness of water and oil miscibility and result in an increased monophasic region. The mixed systems show no variation in microemulsion area. We feel that propanol-hexanol mixture forms a structured cosurfactant which is independent of the composition of the mixture. The microemulsion area is a function of that property and hence independent of the composition. The interface of water and oil carries more hexanol than propanol as the former is very less soluble in water. Therefore addition of propanol probably saturates the interface where more hexanol is present. Changes in the propanol amount does not change in the interfacial composition and excess propanol dissolves in the liquids. Hence the interface remains independent of propanol-hexanol ratio. Therefore the microemulsion area becomes independent of the ratio.

(ii) Phase Volume

In Figs. 5.6 - 5.10 results of detailed studies of Winsor transitions carried out in 4:1 propanol-hexanol mixed system, with the composition S+CS : 17.5%, O : 42.5%, W : 40%, are presented. Comparing with the results obtained for systems with pure propanol as cosurfactant (Chapter 4) the observed Winsor transitions in the present case are of similar type (i.e. Winsor I → Winsor III → Winsor II) as the NaCl concentration increases. But the effect of temperature on these transitions was found to be in opposite direction from the one seen in presence of propanol as cosurfactant. Fig.5.6 represents the inversion of water exterior lower phase microemulsion to oil external upper phase microemulsion through middle phase formation, as the function of NaCl concentration, at various temperatures of 40, 50, 60, 70 and 80°C. At these temperatures upto around 0.47, 0.47, 0.49, 0.49 and 0.51 mol dm^{-3} of NaCl respectively the composition is biphasic with microemulsion at the bottom. The respective concentrations for the above temperatures upto which the three phase Winsor III formation exists are 0.51, 0.53, 0.57, 0.59 and 0.59 mol dm^{-3}. Throughout the Winsor III phase, as the concentration of NaCl increases, the o/w microemulsion continued to change to w/o microemulsion and at the NaCl concentration limit mentioned above, the whole system changes over to upper phase microemulsion in

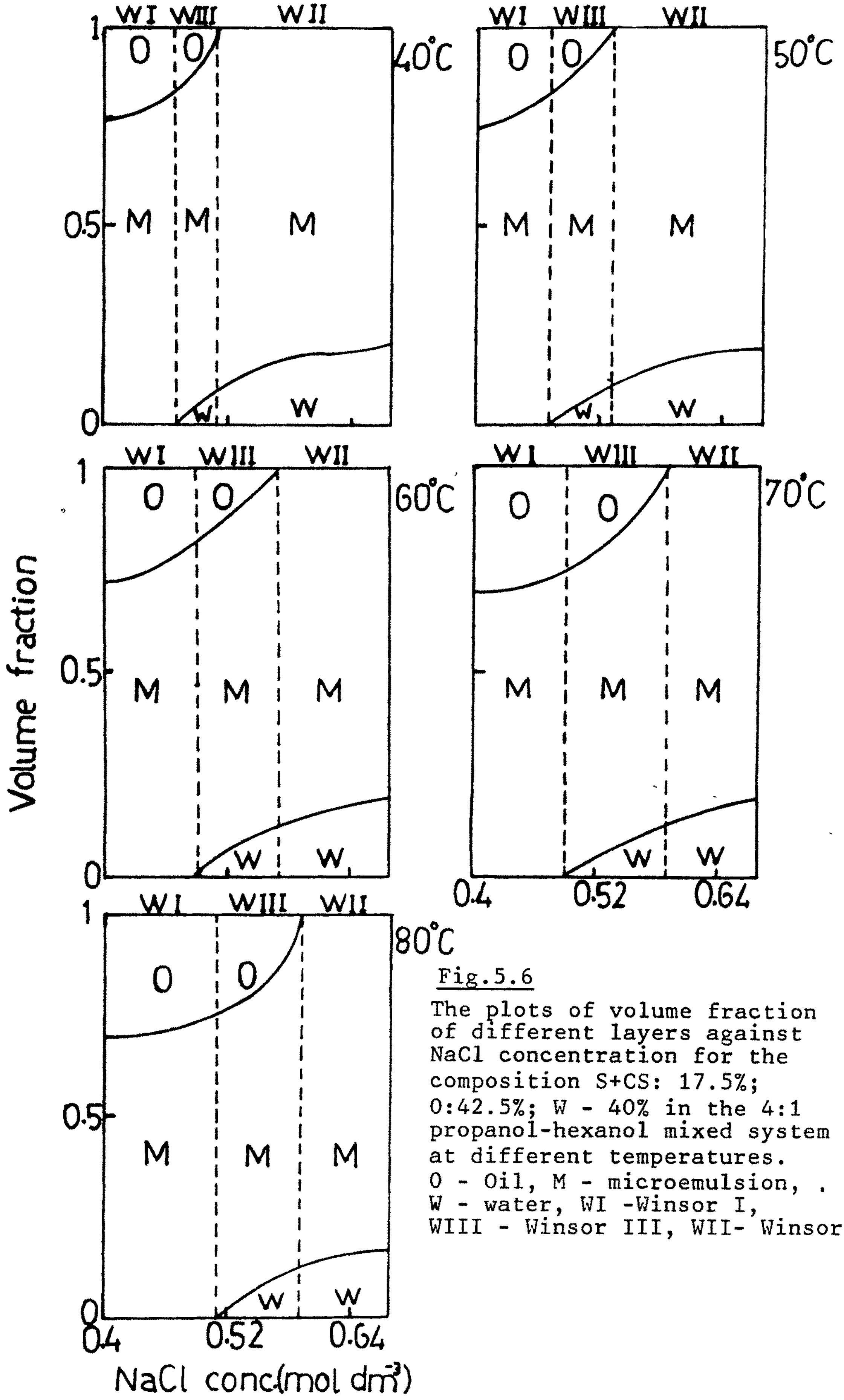

Fig.5.6

The plots of volume fraction of different layers against NaCl concentration for the composition S+CS: 17.5%; O:42.5%; W - 40% in the 4:1 propanol-hexanol mixed system at different temperatures.
O - Oil, M - microemulsion, .
W - water, WI -Winsor I,
WIII - Winsor III, WII- Winsor II.

equilibrium with excess water layer. Though the plots are similar to the ones obtained for propanol cosurfactant system, it is important to note that the NaCl concentration of Winsor III formation has been lowered considerably in this mixed system. Another difference observed in this system is in the temperature effect. The width of the three phase band increases with increasing temperature except at 80°C and also the position of these bands tend to shift towards higher salinity. The Fig. 5.7 illustrates this effect of temperature on the phase transition more explicitely. Here the variation in volume fraction of different layers are shown against increasing temperature for four different constant salinities (0.48, 0.50, 0.54 and 0.58 mol dm^{-3}). At 0.48 and 0.50 mol dm^{-3} (Fig 5.7 a & b) NaCl concentrations, as the temperature increases the volume fraction of lower most layer decreases with the simultaneous increase in the uppermost oil layer and approximately at 55°C and 75°C respectively, excess water layer disappears completely which signifies a transition from Winsor III to Winsor I. For the higher concentrations 0.54 and 0.58 mol dm^{-3} (Fig.5.7 c & d), the temperature increase regenerates an excess oil layer at the top at around 53°C and 62°C respectively which grows in its volume on moving further towards higher temperatures. The bottom most excess water layer shrinks gradually during this process. Therefore the transition has occured from a Winsor II to Winsor III formation. Thus

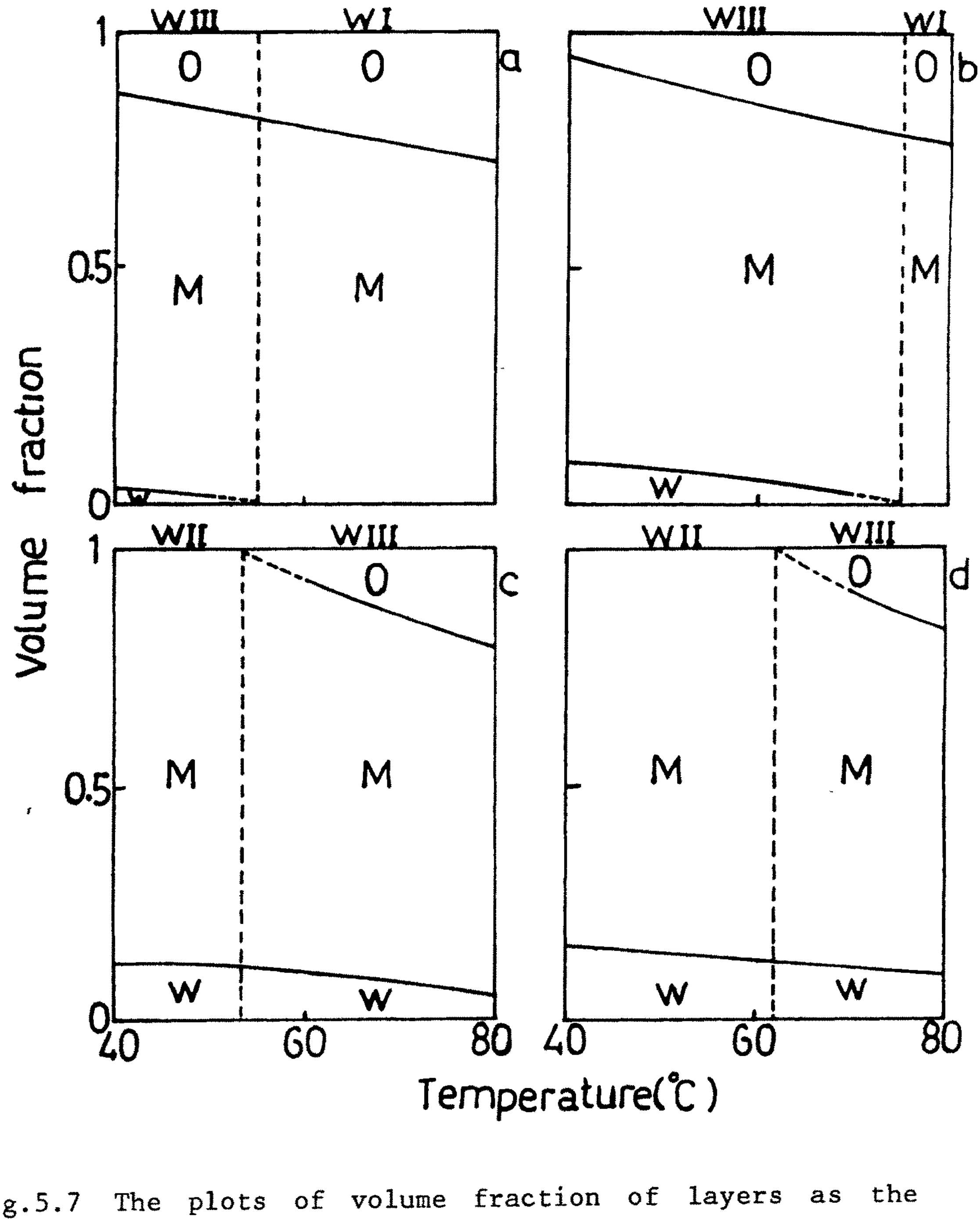

Fig.5.7 The plots of volume fraction of layers as the function of temperature at different NaCl concentrations (a) 0.48 M (b) 0.50 M (c) 0.54 M, d) 0.58 M (Symbols as in Fig. 5.6).

from the observed results in Fig.5.7, it is evident that the temperature induces a phase transition which is in the opposite direction (i.e. Winsor II ⟶ III ⟶ I) contrary to the observed trend in the propanol system (Chapter 4). Here the attention may be directed to the fact that as ionic surfactants are not very sensitive to temperature change as the nonionic surfactants are, the complete transition,Winsor II ⟶ III ⟶ I was not obtained, but only some part of it depending upon NaCl concentration. The optimal salinity of the composition was determined, as discussed earlier in chapter 4, at various temperatures from the plots of solubilization parameters of oil and water against salinity (Fig.5.8 a & b). Fig.5.9 correlates these optimum salinity values with rising temperature. A nonlinear increase in the optimum salinity values with increasing temperature is again an observation contrary to those observed in the propanol system where it actually decreases. The Winsor III formation and hence the optimal salinity at lower NaCl concentration may be attributed to the increased hydrophobicity of the interfacial film separating the oil and water domains. As described in the previous chapter a middle phase microemulsion in equilibrium with oil at the top and water at the bottom is a characteristic feature of hydrophilic - lipophilic balance of the amphiphile system. Incorporation of a small amount of hexanol in the surfactant system can increase

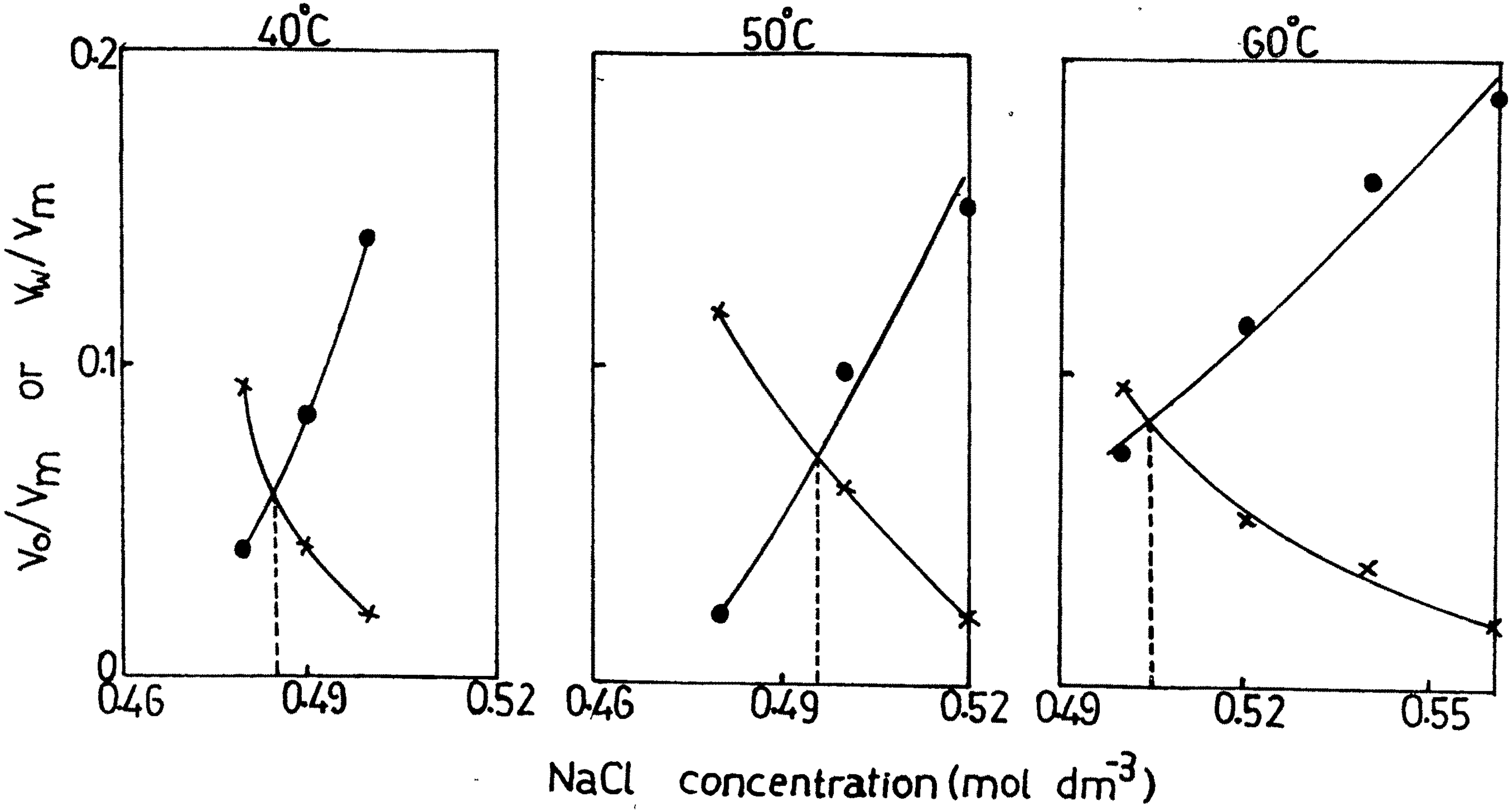

Fig.5.8a Plots of V_o/V_m ● and V_w/V_m × against NaCl concentration for the composition S+CS : 17.5%, O : 42.5 %, W : 40% of the 4:1 mixed system at 40, 50 and 60°C.

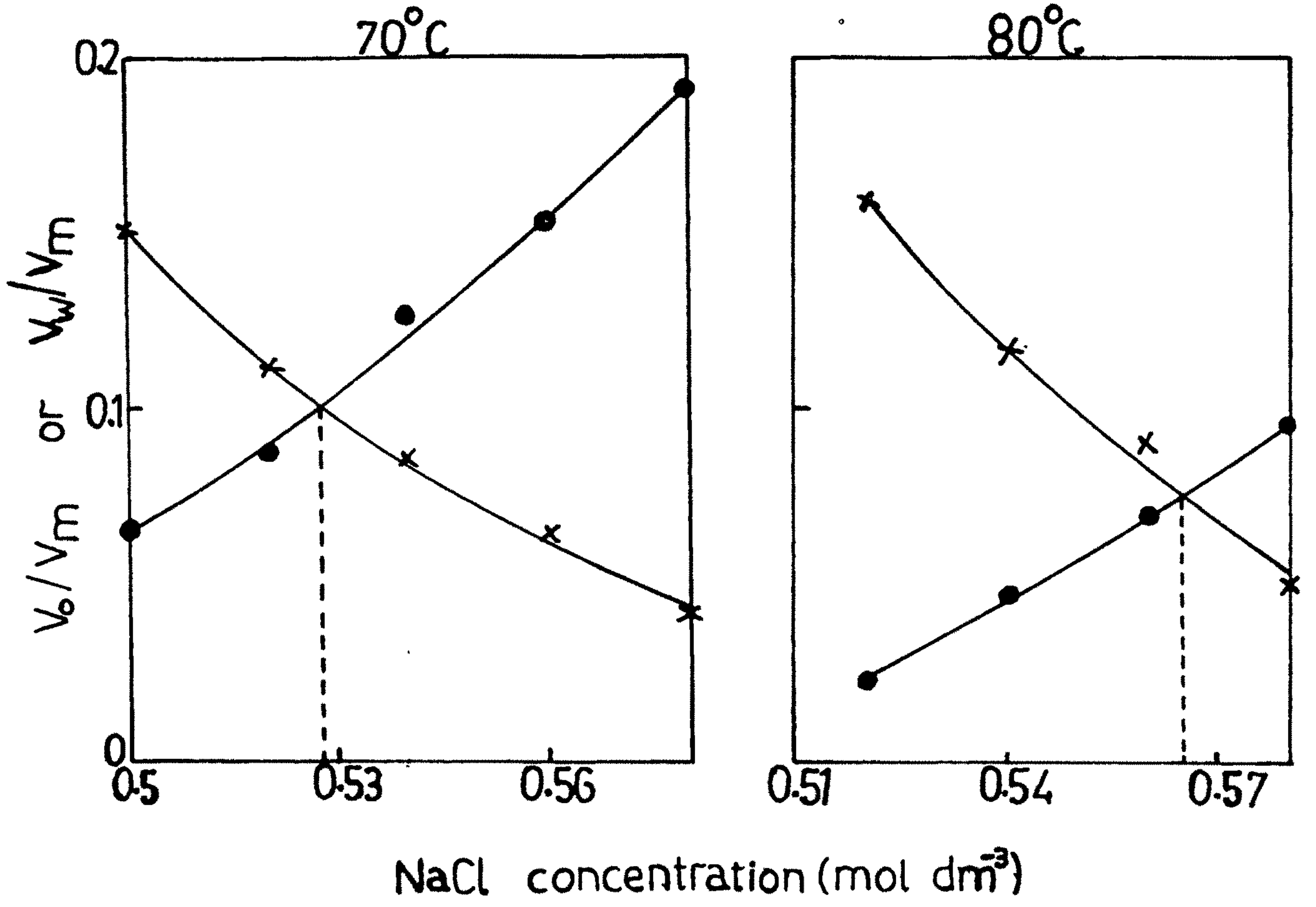

Fig.5.8b The plots of V_o/V_m ● and V_w/V_m × against NaCl concentration at 70 and 80°C.

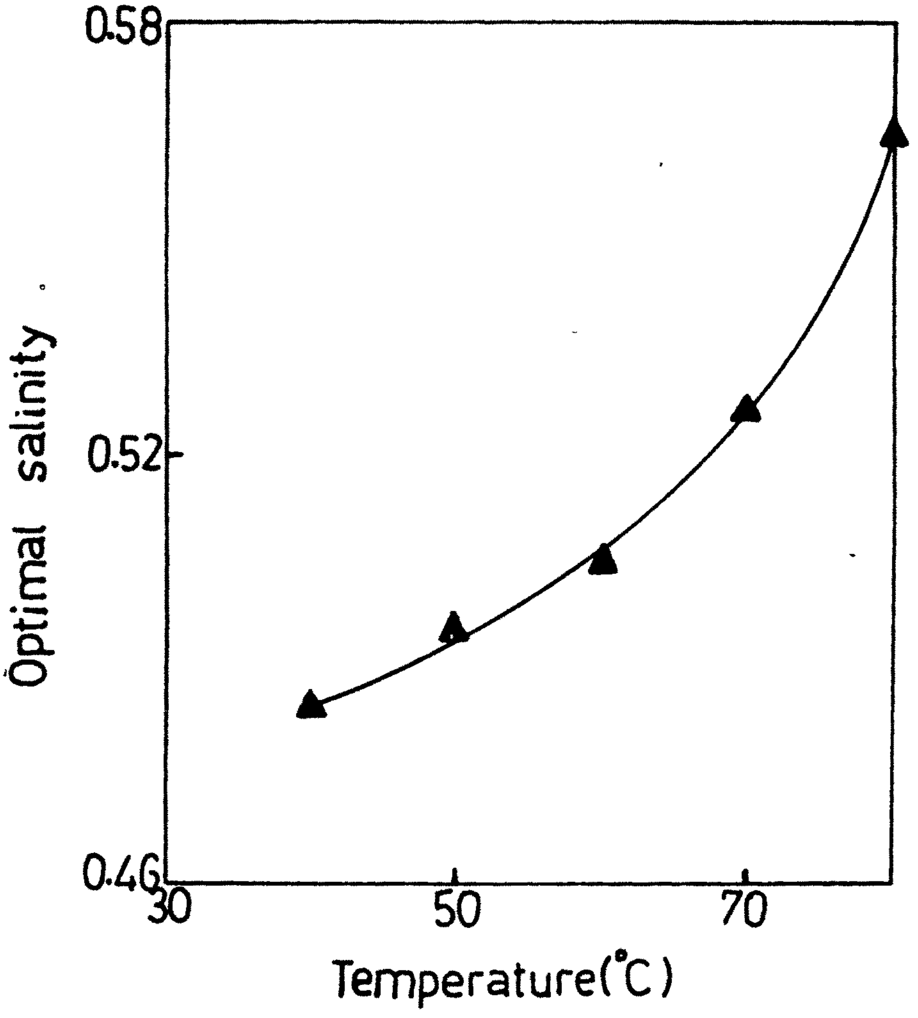

Fig.5.9 The variation of optimal salinity against temperature for the 4:1 propanol-hexanol mixed system.

the hydrophobic nature of the interfacial surfactant film. When the interfacial amphiphilic layer becomes more near to the hydrophilic- lipophilic balanced state, it requires lesser amount of electrolyte (NaCl) to form Winsor III. This is the reason behind the Winsor I → Winsor III transition taking place at much lower NaCl concentration and the optimal salinity values lowered to almost half the values obtained in propanol case.

It is commonly known that the ionic surfactants and the nonionic surfactants behave dissimilarly towards temperature [88,137]. With increasing temperature oil becomes an increasingly better solvent for the nonionic surfactants. On the other hand, the ionic surfactants turn increasingly hydrophilic with rising temperature because of the dissociation of more number of head groups [88]. In the present case of propanol-hexanol mixture, due to the hydrophobic nature of hexanol molecules, the surfactant molecules at the interfacial layer are not fully dissociated. But the temperature increase can facilitate their dissociation and thus the surfactant phase can become increasingly hydrophilic. This increased hydrophilicity demands more NaCl for the formation of three phase and hence this three phase formation occurs towards higher NaCl concentration and So is the optimal salinity.

However when the surfactant system contained only propanol as cosurfactant (Chapter 4), one can expect two different types of effects in the system. In the less hydrophobic environment of the interfacial region, more surfactant molecules may be considered to be in the dissociated form. This will minimize the role of temperature in the dissociation process and the surfactant may be considered to be comparitively more insensitive to temperature. Another effect of propanol is because of the partitioning of these molecules between oil, water and the interface. In the aqueous phase these molecules may reside with weak hydrogen bonding with water molecules. Temperature increase breaks up these hydrogen bondings and these alcohol molecules can migrate to the interfacial region making these interface more hydrophobic. When this increasing hydrophobic effect of the interface overcompensate the hydrophilicity increase, due to lesser number of surfactant dissociation, the net effect will be a more hydrophobic interfacial film at higher temperatures. This should naturally decrease the demand for the electrolyte to attain a hydrophilic-lipophilic balance. That is why the optimum salinity decreases with temperature in that case (chapter 4). Thus it may be concluded that the continuous increase in optimal salinity of propanol-hexanol (4:1) mixed system with temperature is caused by the increasing hydrophilicity of surfactant phase due to dissociation of surfactant molecules where as the decrease observed in propanol system is resulted by increasing hydrophobic nature of interfacial region due to the migration of more alcohol molecules towards this region.

Fig. 5.10 represents the variation of microemulsion layer recorded against the salinity during the transition from Winsor I to Winsor II. These profiles also differ from the previously recorded ones in the fact that the minimum corresponding to the optimum salinity is either absent or not very prominent. Instead the constant increment in the volume fraction shows a deviation some where near the optimum salinity at 40, 50 and 60°C and a little more prominent minimum at 70 and 80°C. The positions of optimal salinity are marked by the dotted lines. The absence of minimum at optimum salinity positions are because of the noncompensative effect of water expulsion towards the oil intake effect. In the Winsor I region at very low salinity, the volume increase is driven by the dissolution of excess oil into the microemulsion medium and the sharper increase than in the propanol system signifies more sensitiveness of the oil intake towards salinity. At the Winsor I – Winsor III boundary, the decrease in volume due to water expulsion does not overcompensate the increase due to oil intake and

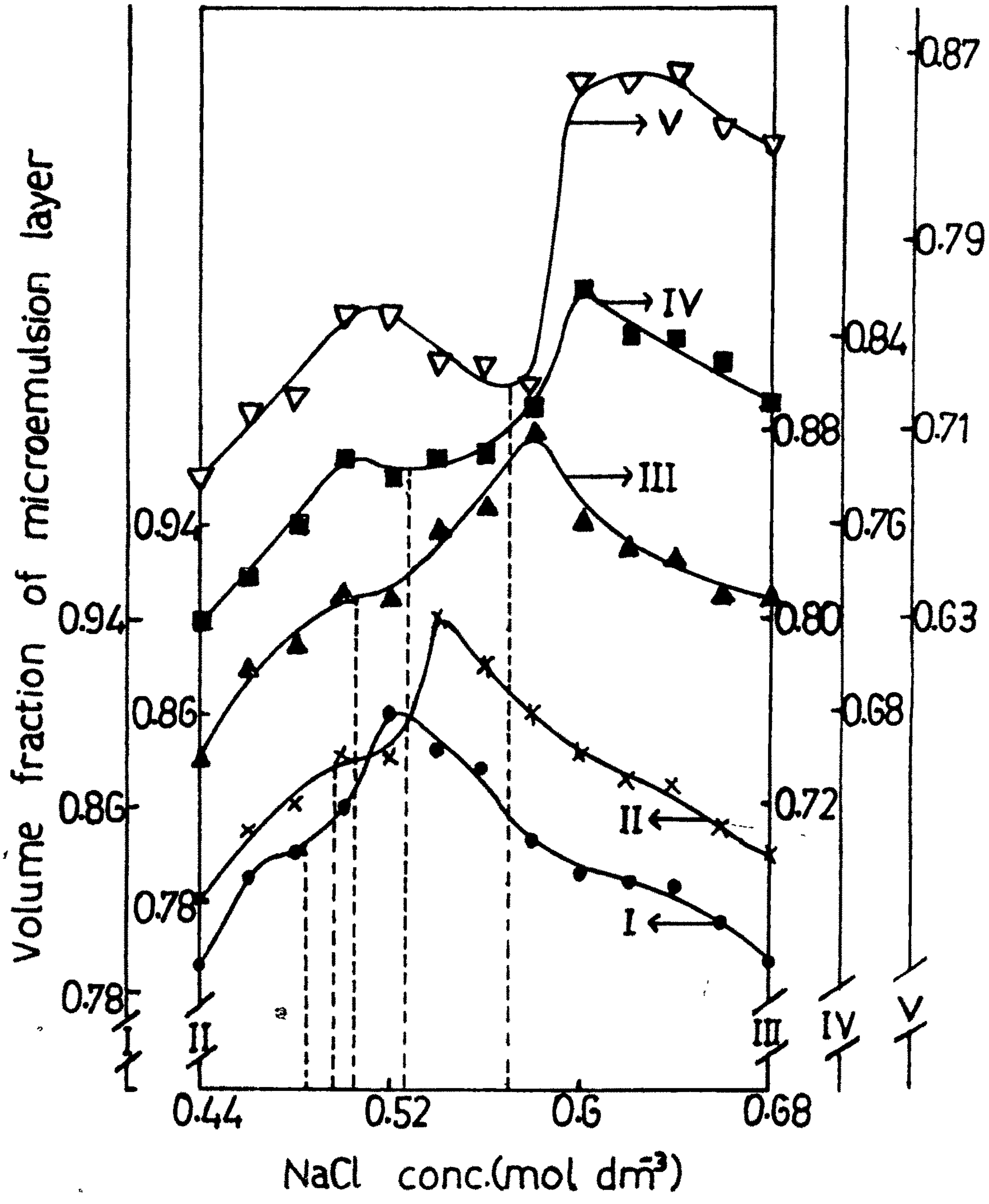

Fig. 5.10 The change in volume fraction of the microemulsion layer as the function of salinity in the 4:1 mixed system at temperatures 40°C ● ; 50°C X ; 60°C ▲ ; 70°C ■ ; 80°C ▽ .

the plots show only a slight deviation in their path at 40, 50 and 60°C. Above the optimal salinity, sharp increase followed by the decline signifies the transition from Winsor III to Winsor II. Thus from the overall variation in the graph, it is clear that the effect of oil dissolution into the microemulsion is much more pronounced than the water expulsion during Winsor transitions.

The phase volume measurements and the Winsor transition studies performed in the other two propanol-hexanol mixed systems, namely 1:1 and 1:4, have shown that a three phase microemulsion formation (Winsor III) is completely absent in these systems. Hence optimum salinity could not be determined. Instead of Winsor III, a monophasic microemulsion (Winsor IV) band was found to be present at the position where Winsor III was seen in earlier cases. Figs. 5.11 and 5.12 demonstrate the sequence of these different formations with increasing salinity for the two mixed sytems 1:1 and 1:4 respectively at various temperatures. In Fig. 5.11, as the salinity increases, the system remains biphasic upto a certain NaCl concentration. The system is microemulsion in equilibrium with oil. The addition of small amount of NaCl changes the equilibrium towards a system where more oil is dissolved in the microemulsion phase and further increase of NaCl completely transforms the formulation to a Winsor IV one. Addition of NaCl affects the availability

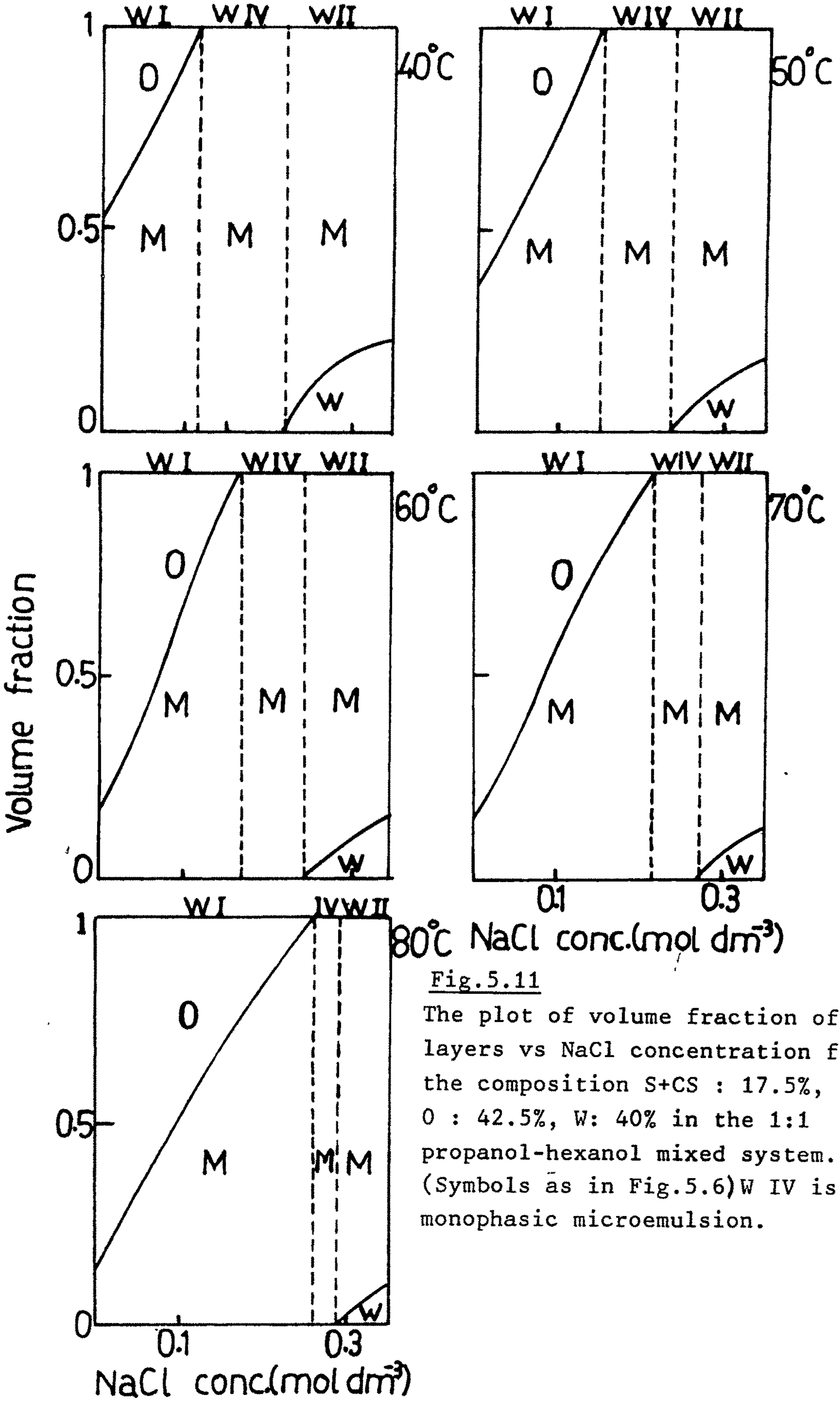

Fig.5.11

The plot of volume fraction of layers vs NaCl concentration for the composition S+CS : 17.5%, O : 42.5%, W: 40% in the 1:1 propanol-hexanol mixed system. (Symbols as in Fig.5.6) W IV is monophasic microemulsion.

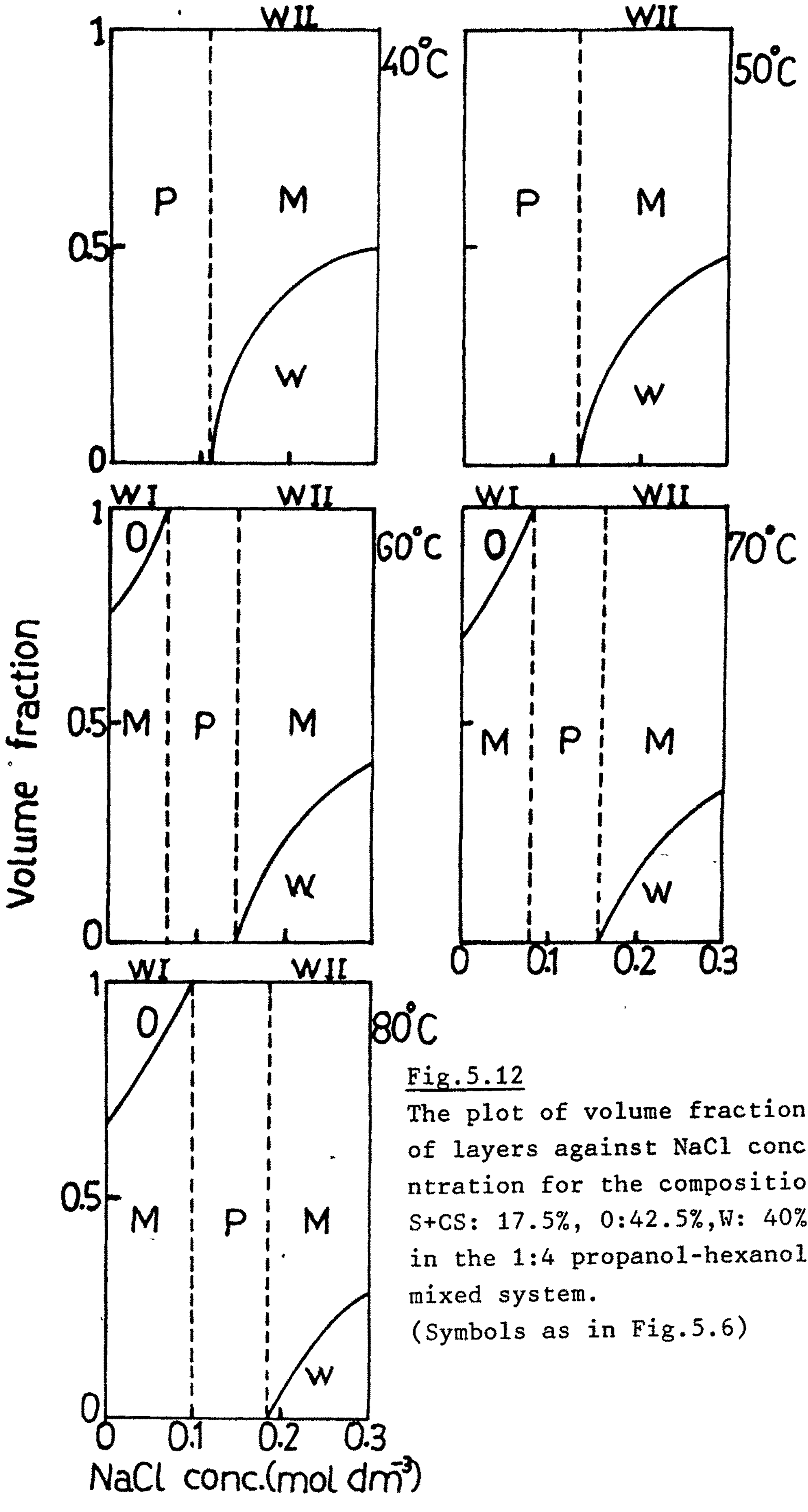

Fig.5.12
The plot of volume fraction of layers against NaCl concentration for the composition S+CS: 17.5%, O:42.5%,W: 40% in the 1:4 propanol-hexanol mixed system.
(Symbols as in Fig.5.6)

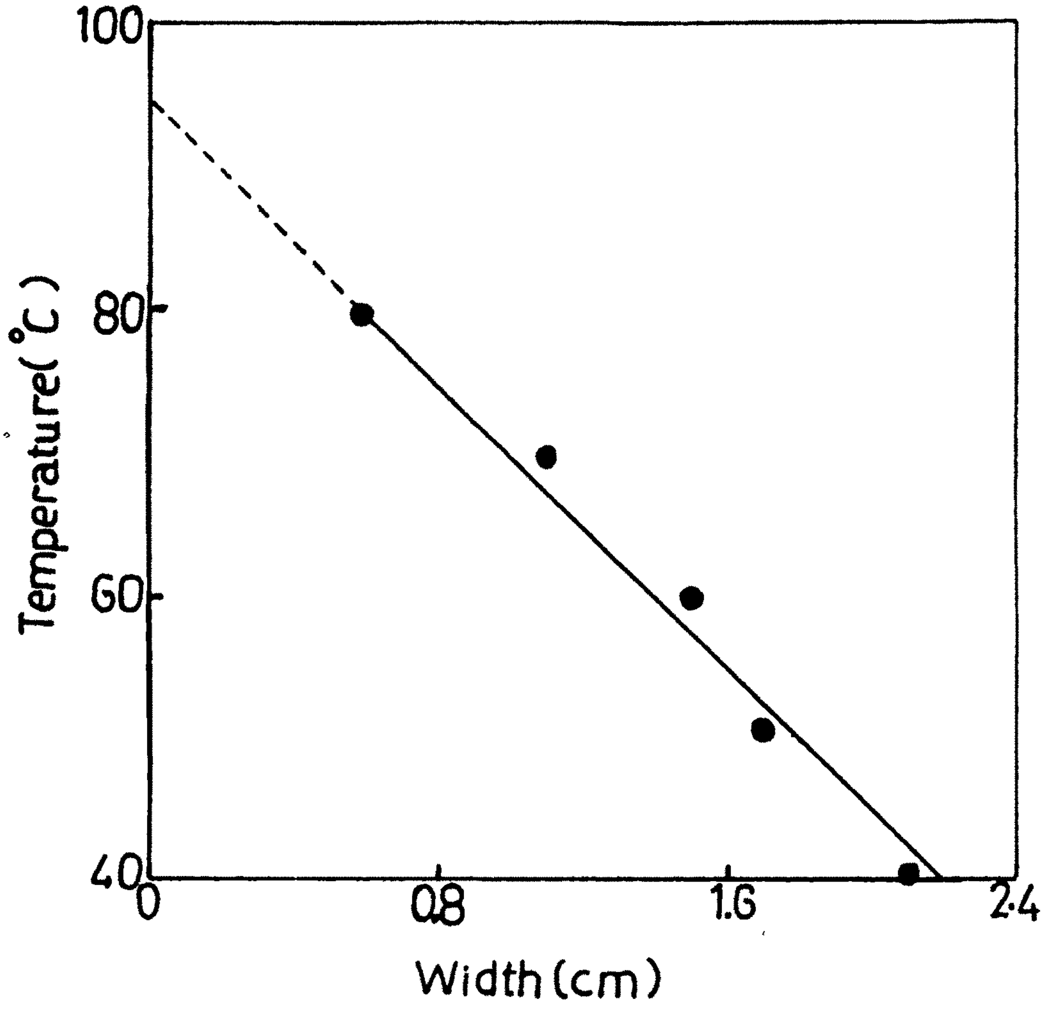

Fig.5.13 : The plot of width of Winsor IV band in the Fig 5.11 against temperature.

of water to form microemulsion. As NaCl is hygroscopic,the microemulsion loses water and the formulation changes gradually over to the oil external with water and NaCl remaining present in the microemulsion system. Further increase of NaCl slowly brings the solubility limit of NaCl to the fore and it precipitates out. The precipitate takes water with itself and hence separates out as Winsor II system. Since the oil uptake and the water expulsion processes are nonsimultaneous, a Winsor III formation does not make its appearance. But since the width of the Winsor IV regime decreases upon increasing the temperature, a Winsor III type may be expected at a temperature higher than 80°C. The plot of the width of Winsor IV band against temperature is almost a straight line (Fig.5.13) which may be extrapolated to obtain a temperature above which a Winsor III replaces the Winsor IV formation. This temperature was found to be approximately 94°C. Unfortunately it was not possible to confirm this temperature experimentally.

For the mixed system 1:4 the phase changes against increasing salinity are much more complicated than the other mixing ratios (Fig.5.12). At 40 and 50°C, two different formations (Winsor II and form 'P') and at higher temperatures 60, 70 and 80°C three different forms (Winsor I, II and form 'P') were observed. The portion bounded by the dashed lines, marked 'P' constitutes a translucent highly viscous medium whose viscosity gradually decreases with increasing salinity and ultimately changes into a Winsor IV medium close to the boundary of Winsor II. It was difficult to exactly determine this transition boundary. The shifts in the transition boundaries in Figs 5.11 and 5.12 towards higher NaCl concentrations with temperature increase implies that the effect of temperature on the phase transitions of these systems is also in the same direction as that of 4:1 mixed system.

Fig.5.14 is an alternate semi-quantitative representation of various types of formations evolved as a result of alkanol mixing, in correlation with their salinity. The formations Winsor I, Winsor III, Winsor II, Winsor IV and the translucent viscous medium are represented as $\underline{2}$, 3, $\overline{2}$, the dotted region and the shaded region respectively. The gradual replacement of Winsor III by Winsor IV formation in between Winsor I and Winsor II as a result of increasing hexanol mole fraction is more obvious from these diagrams. At the common point where the Winsor III and Winsor IV formations coincide each other (i.e. at approximately 0.33 mole fraction of hexanol) a direct transition from Winsor I to Winsor II may be expected with increasing salinity. The so called viscous

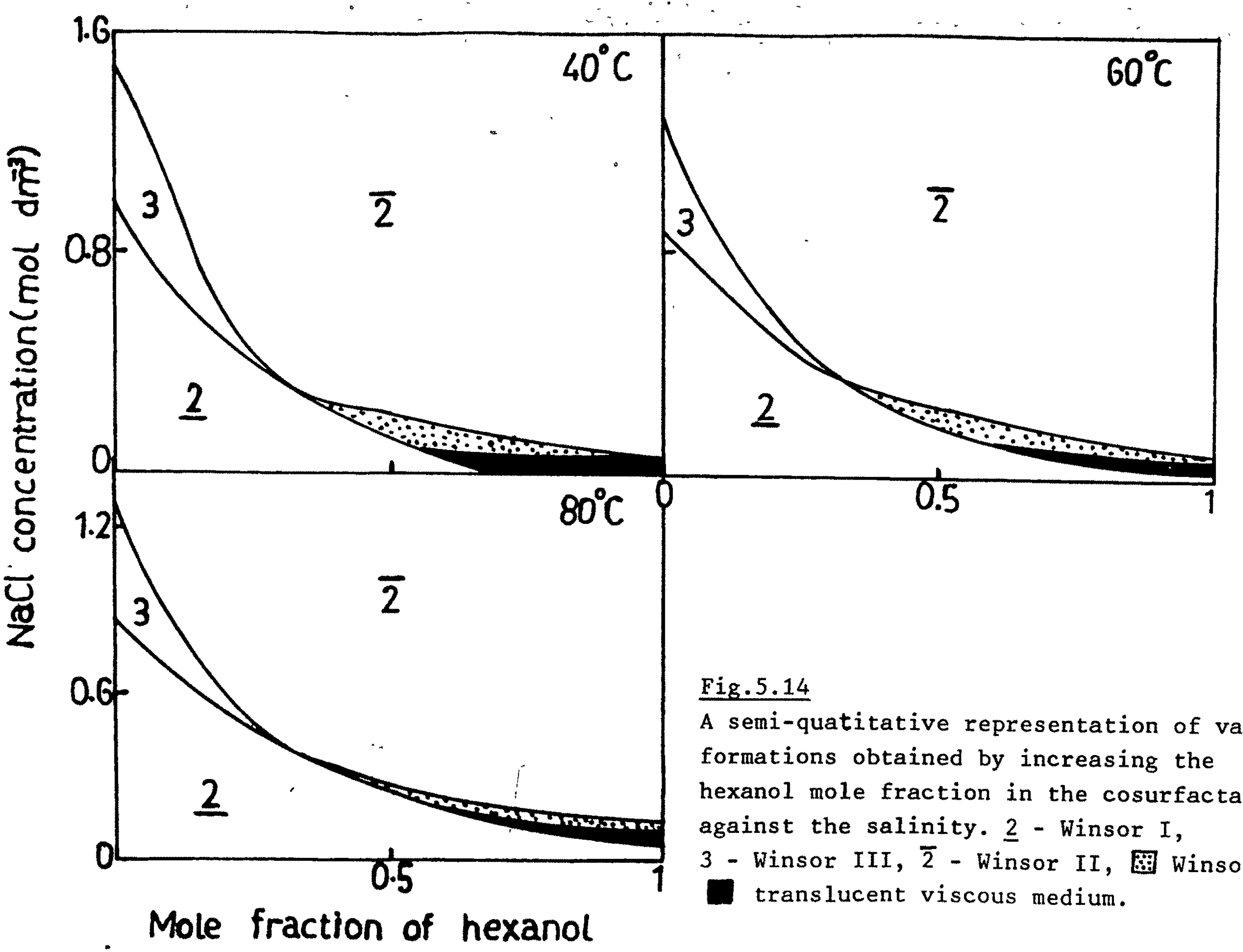

Fig.5.14

A semi-quatitative representation of various formations obtained by increasing the hexanol mole fraction in the cosurfactant, against the salinity. $\underline{2}$ - Winsor I, 3 - Winsor III, $\overline{2}$ - Winsor II, ▨ Winsor IV ■ translucent viscous medium.

region decreases with higher temperature which is expected.

(iii) Conductance

Figs. 5.15 - 5.17 illustrate the water induced percolative conductance at various constant temperatures for the mixed systems 4:1, 1:1 and 1:4 respectively. One can readily notice significant changes in the nature of percolative conductance as the mole fraction of hexanol in the alkanol mixture increases. A steep increase in conductance over a threshold water volume fraction is seen for all systems. The conductance remains very low initially and rapidly attains high values whose onset occurs at higher values of water fraction ($\emptyset_w$) as the alkanol mixture becomes increasingly hexanol rich. The order of increase in conductance values computed with respect to the initial low values are shown in Table 5.1. The order decreases when the alkanol mixture contains more and more hexanol. The observed specific conductance-water fraction profiles of the mixed systems may be compared with the previous observations made by Clausse et al.[55] for benzene or Lang et al.[56] for chlorobenzene containing formulations. In these studies, the electrical conductivity - water fraction plots for various pure alkanols of increasing carbon chain length demonstrates that shorter alkanols from ethanol to butanol show fairly

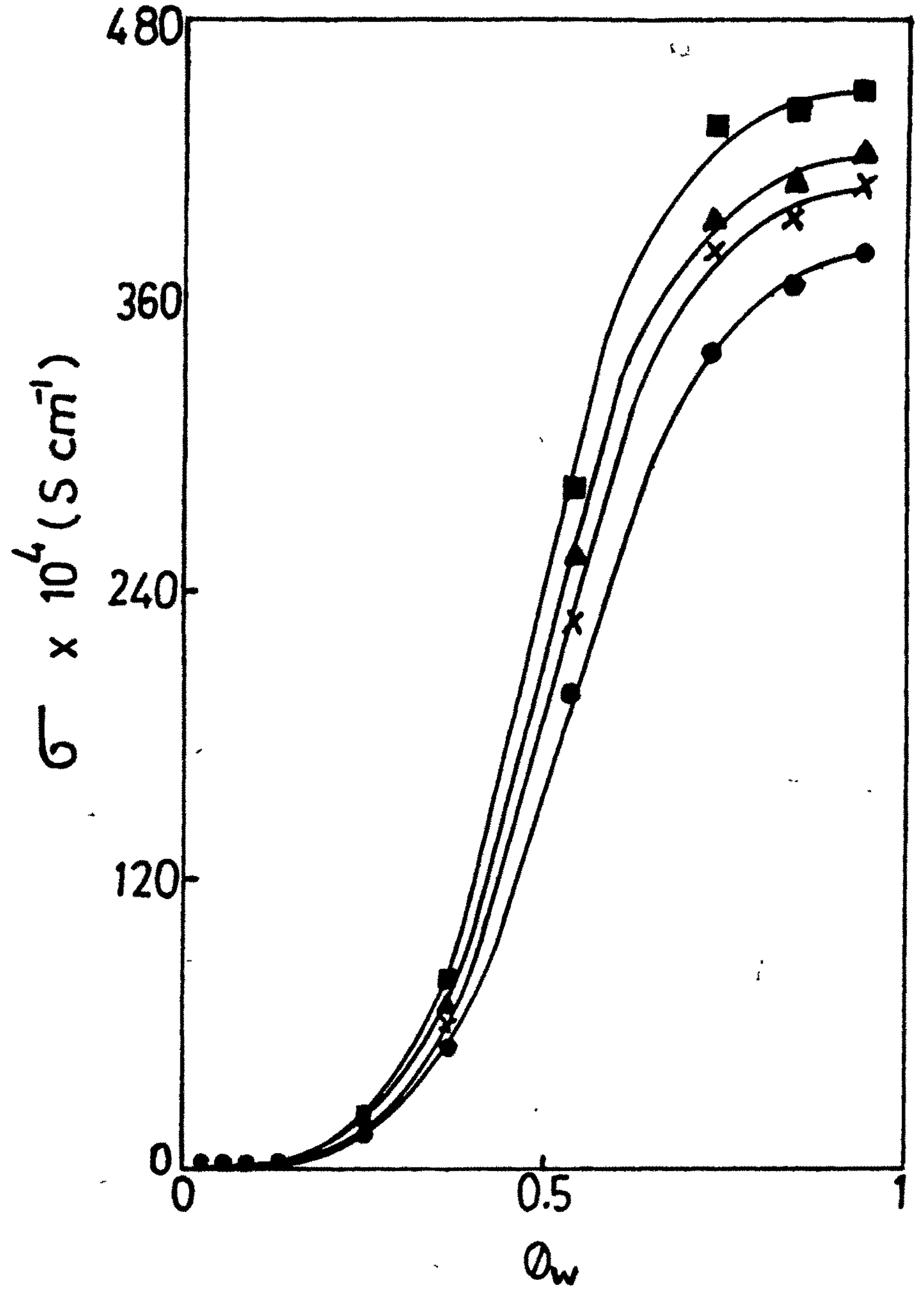

Fig.5.15 The plot of specific conductance (σ) against water volume fraction ($\emptyset_w$) for the 4:1 propanol-hexanol mixed system at temperatures 40°C ● ; 50°C X ; 60°C ▲ ; 70°C ■ .

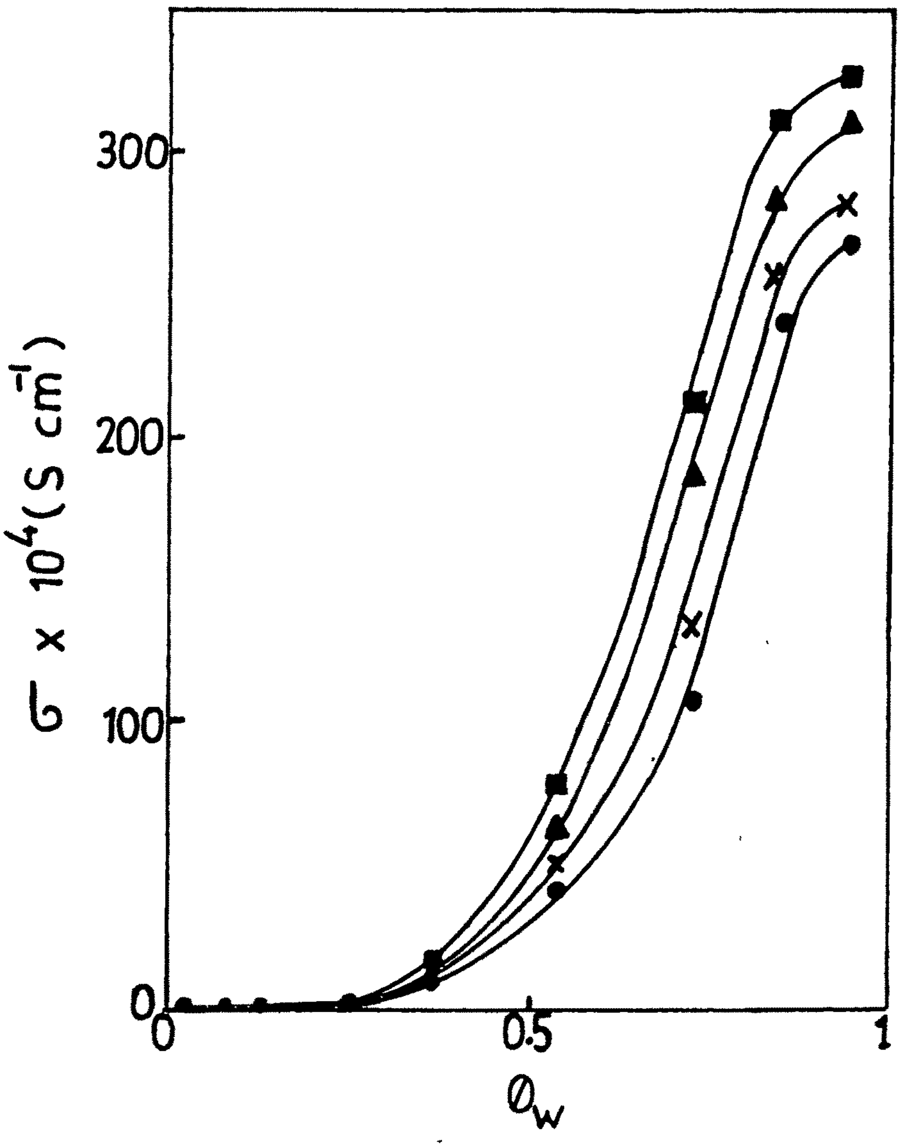

Fig.5.16 The plot of specific conductance (σ) against water volume fraction (ϕ_W) for the 1:1 propanol-hexanol mixed system at temperatures 40°C ● ; 50°C X ; 60°C ▲ ; 70°C ■ .

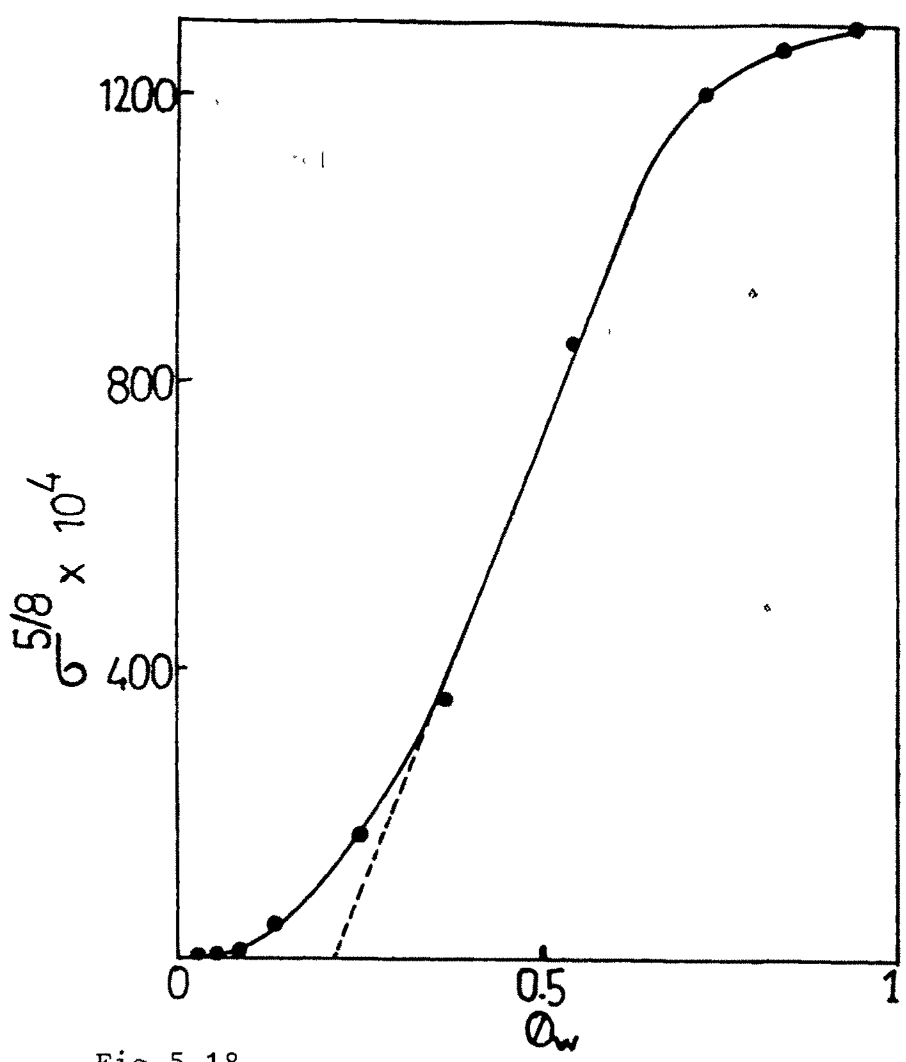

Fig.5.18
The plot of $\sigma^{5/8}$ against water volume fraction ($\emptyset_w$) for the 4:1 propanol-hexanol mixed system at 40°C.

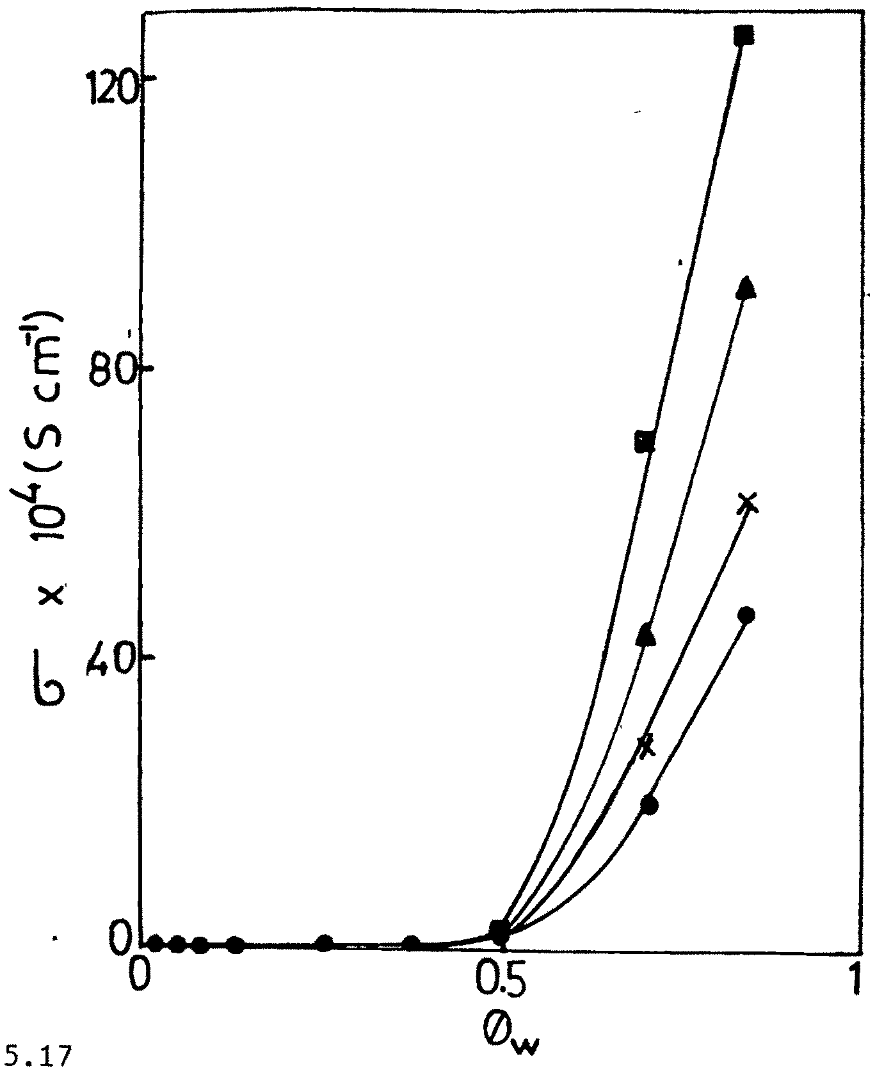

Fig.5.17
The plot of specific conductance (σ) against water volume fraction ($\emptyset_w$) for the 1:4 propanol-hexanol mixed system at temperatures 40°C ● ; 50°C × ; 60°C ▲ ; 70°C ■ .

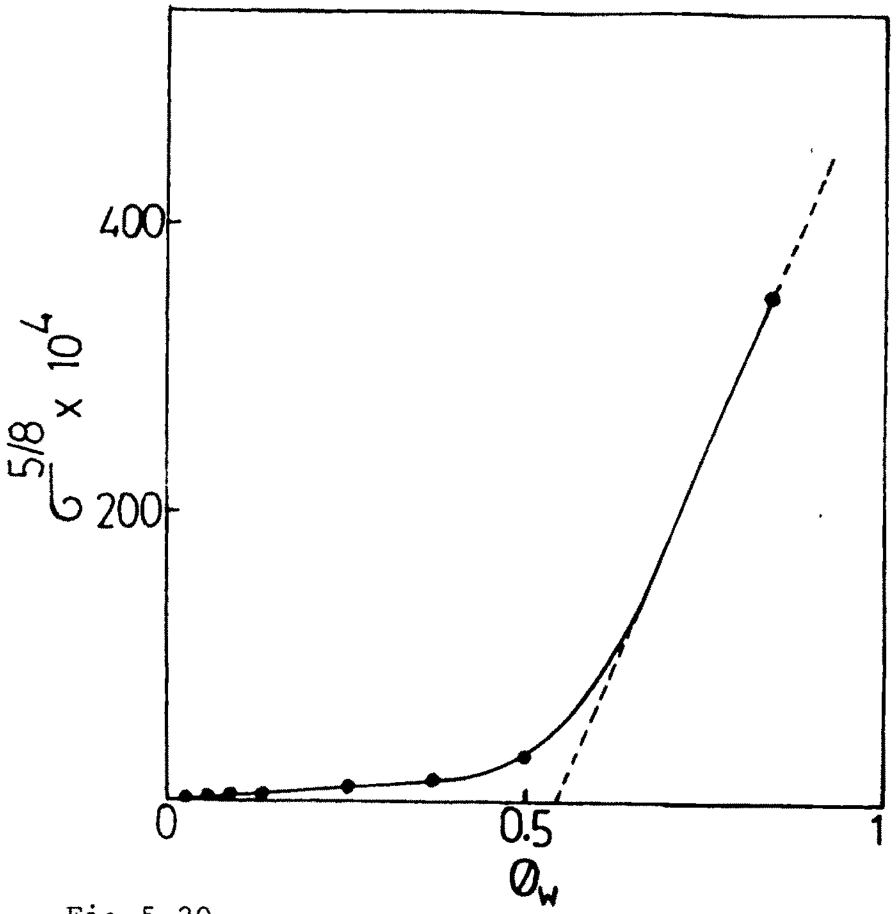

Fig.5.20
The plot of $\sigma^{5/8}$ against water volume fraction ($\emptyset_w$) for the 1:4 propanol-hexanol mixed system at 40°C .

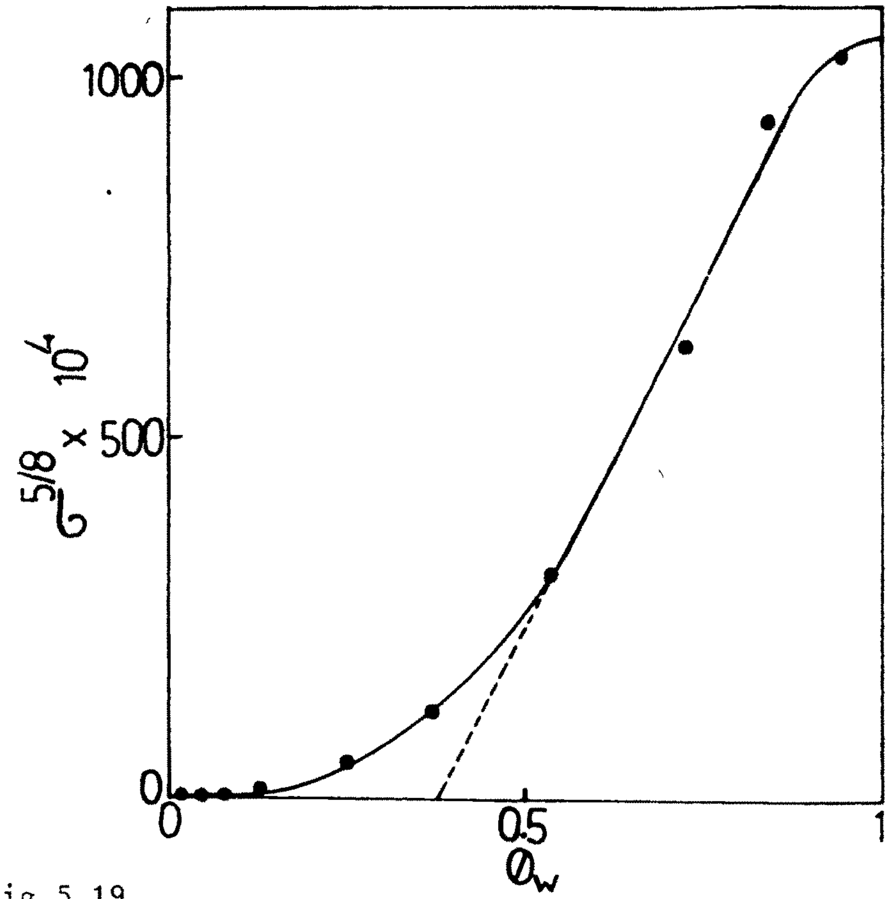

Fig.5.19
The plot of $\sigma^{5/8}$ against water volume fraction ($\emptyset_w$) for the 1:1 propanol-hexanol mixed system at 40°C.

TABLE 5.1

Approximate order of conductance increase during percolation process in pure propanol and various propanol-hexanol mixed systems.

Temperature (°C)	Propanol	Propanol - Hexanol Mixed Systems		
		4:1	1:1	1:4
40	43	36	33	31
50	48	41	38	31
60	52	45	42	37
70	56	50	47	42

good percolation behaviour and for the higher alcohols the conductivity does not increase. For pentanol the variation is more or less smooth similar to the 1:4 mixed system of the present study and the longer chain alcohols from hexanol upwards are characterised by either a monotonous decrease sometimes followed by a small increase or a very flat variation. Further when the alcohol chain length increases the percolation occurs at increasing $\emptyset_w$ [56], which is termed as percolation threshold $\emptyset_w^P$. On the basis of this comparison it is worth relating that the present mixed alkanol systems are exhibiting somewhat intermediate properties as that of butanol or pentanol in its conductivity behaviour. According to the scaling theory [179], the percolation threshold values ($\emptyset_w^P$) determined from the plots of $\sigma^{5/8}$, where σ is the specific conductance, against water fraction $\emptyset_w$ (Figs.5.18 - 5.20) are presented in Table 5.2. The drastic increase in these threshold values with increasing hexanol mole fraction reveals the increased necessity for water phase to form water channels through which the ion transport can occur. In other words,the droplets undergo less favourable sticky collision, at low water concentration in presence of hexanol, and merging to form the conduits which are the pathway for exchange of materials (ions). This conduits through which the ions can move, is a characteristic feature of the bicontinuous structure of microemulsion and

TABLE 5.2

Percolation threshold ($\emptyset_w^p$) in terms of water volume fraction for pure propanol and various propanol-hexanol mixed systems.

Temperature (°C)	Propanol system	Propanol-Hexanol mixed systems		
		4:1	1:1	1:4
40	0.05	0.21	0.37	0.54
50	0.06	0.21	0.36	0.53
60	0.06	0.21	0.34	0.53
70	0.06	0.22	0.32	0.53

as mentioned in earlier chapters the structure of the microemulsion studied within this span of water concentration is bicontinuous i.e. from $\emptyset_w^p$ to about 0.8 volume fraction of water over which the microemulsion structure changes.

From the light scattering studies it was proved that the interdroplet attractive interactions in water in oil microemulsion decreases when the alcohol chain length increases [194-196]. Calculation of the interaction potential between the water droplets is based on the assumption that the attractive interactions between globules arise from the interpenetration of the droplet interfacial layer which will bring the droplet water cores close to each other [197,198]. The interfacial layer is composed of surfactant and alcohol molecules having their polar head groups in contact with aqueous phase and their hydrocarbon chains in contact with oleic phase. If n_s is the number of carbon atoms in surfactant molecules and n_a is the same in alcohol molecule, then the extent to which the interfacial layer interpenetration can occur is determined by the difference n_s-n_a and also by the coiling of the surfactant tail since $n_s > n_a$. In the absence of alcohol this coiling of the surfactant tail is more [199]. The theory predicts that the interdroplet interaction becomes more attractive when n_a and/or n_s decreases [200].

In the present study of mixed alkanol systems, as the shorter propanol molecules are increasingly replaced by longer hexanol molecules, the difference $n_s - n_a$ decreases. Moreover when the interfaces are packed with increased number of longer alcohol chains, the surfactant tails get uncoiled and straighten up. These two effects make the interdroplet interaction less possible. As a result an effective sticky collision and merging of droplets is not easily possible and the system requires more water to form water channels. This is why increased θ_w^P value is observed at higher hexanol fraction.

In Figs. 5.21-5.23 the variation in electrical conductivity of two water in oil microemulsion samples, with water-oil volume ratios 0.05 and 0.09, are shown against temperature for each mixed alkanol system. In all these systems the conductivity increases steadily and almost linearly with temperature rise in contradiction to the previous case of propanol with water-oil ratios 0.05 and 0.08 where a declining trend was noticed (Chapter 3 and 4). Increasing number of dissociation of surfactant molecule head groups which produce more number of charged particles in the medium is the cause for the constant increment in the conductance with temperature elevation which was relatively absent in the case of pure propanol containing formulation (Chapters 3 and 4).

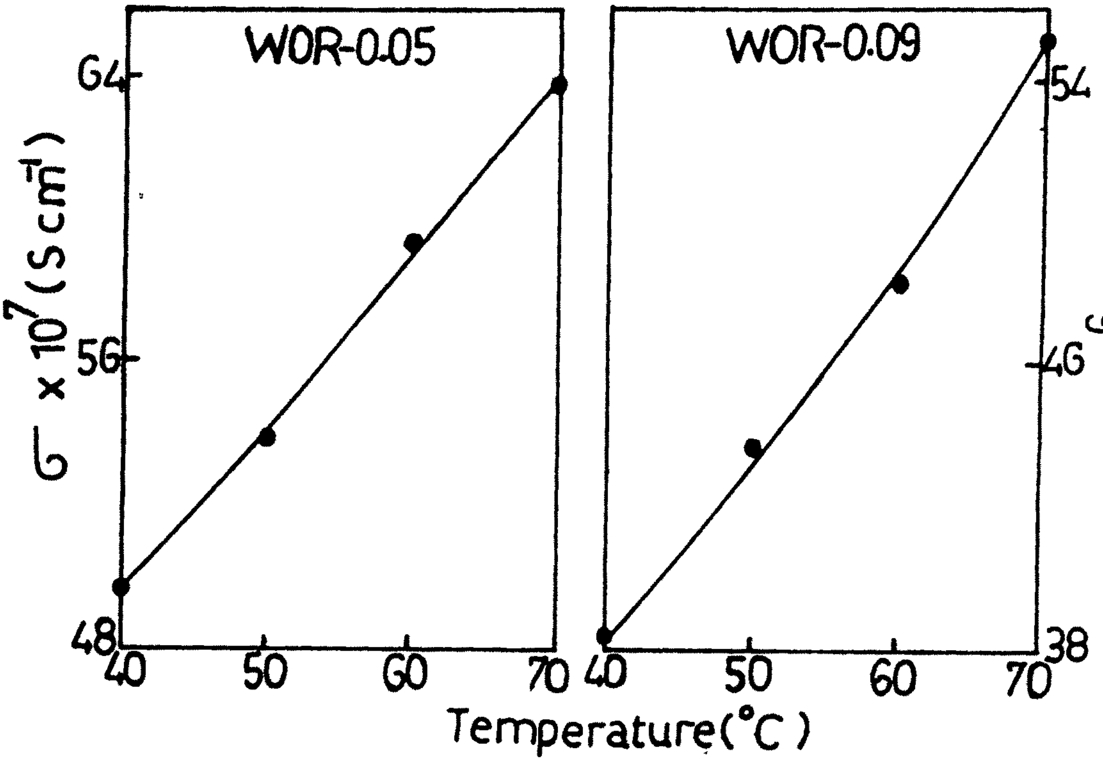

Fig.5.21 Variation of specific conductance (σ) against temperature in the 4:1 propanol-hexanol mixed system at various WOR.

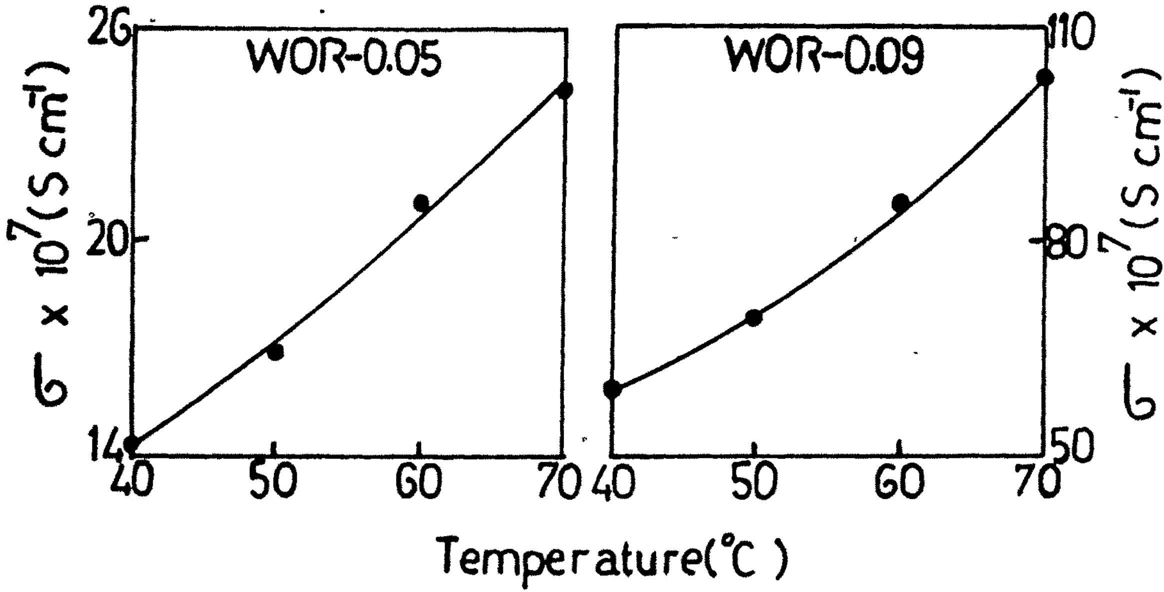

Fig.5.22 Variation of specific conductance (σ) against temperature in the 1:1 propanol-hexanol mixed system at various WOR.

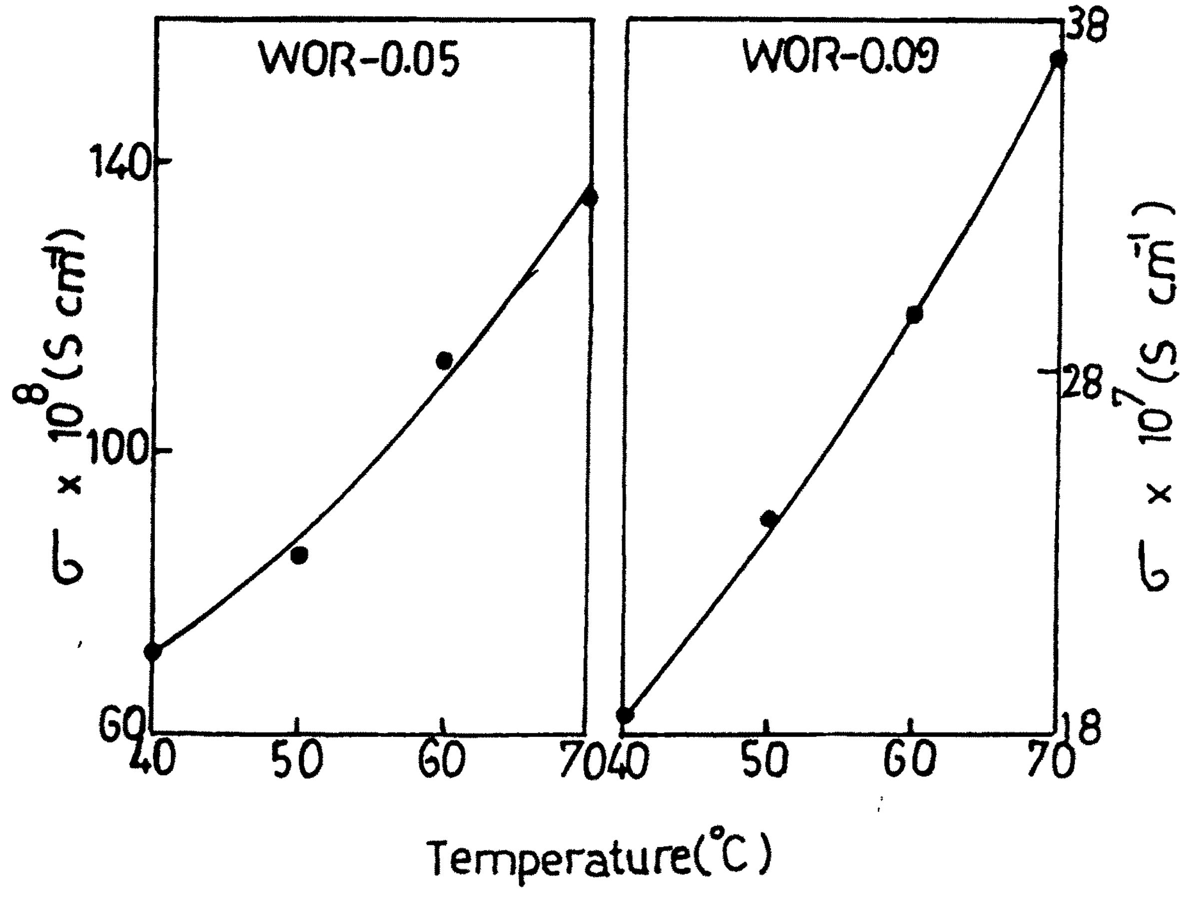

Fig.5.23 The variation of specific conductance (σ) of w/o microemulsion samples of different water oil ratio (WOR) against temperature in the 1:4 propanol-hexanol mixed system.

(iv) Viscosity

In Fig. 5.24 the variation in viscosity of three different microemulsion compositions, (I) S+CS : 42.5%, O : 40%, W : 17.5%, (II) S+CS : 42.5%, O : 22.5%, W: 35 %, (III) S+CS : 42.5%, O : 7.5 %, W : 50%, are plotted against increasing hexanol mole fraction in the alkanol mixture. For all the three compositions the viscosity increases with hexanol mole fraction. This variation is nonlinear in nature which characterises the nonideal mixing of the two alkanols in the microemulsion formulation. Nevertheless in the case of maximum oil containing composition (I), the viscosity values of the mixed formulations fall remarkably on a straight line though the values of pure alkanols deviate from this straight line path. However no such linearity was shown by the maximum water containing sample (III).

One of the basic functions of the alcohol is to eliminate the rigid structures such as gels, liquid crystals etc. by accommodating itself in between the surfactant molecules [51,186,187]. This will produce an interfacial layer of closely packed surfactant and cosurfactant molecules with increased mobility and fluidity. The lower alcohols are comparatively more efficient in imparting fluidity to the interface than the

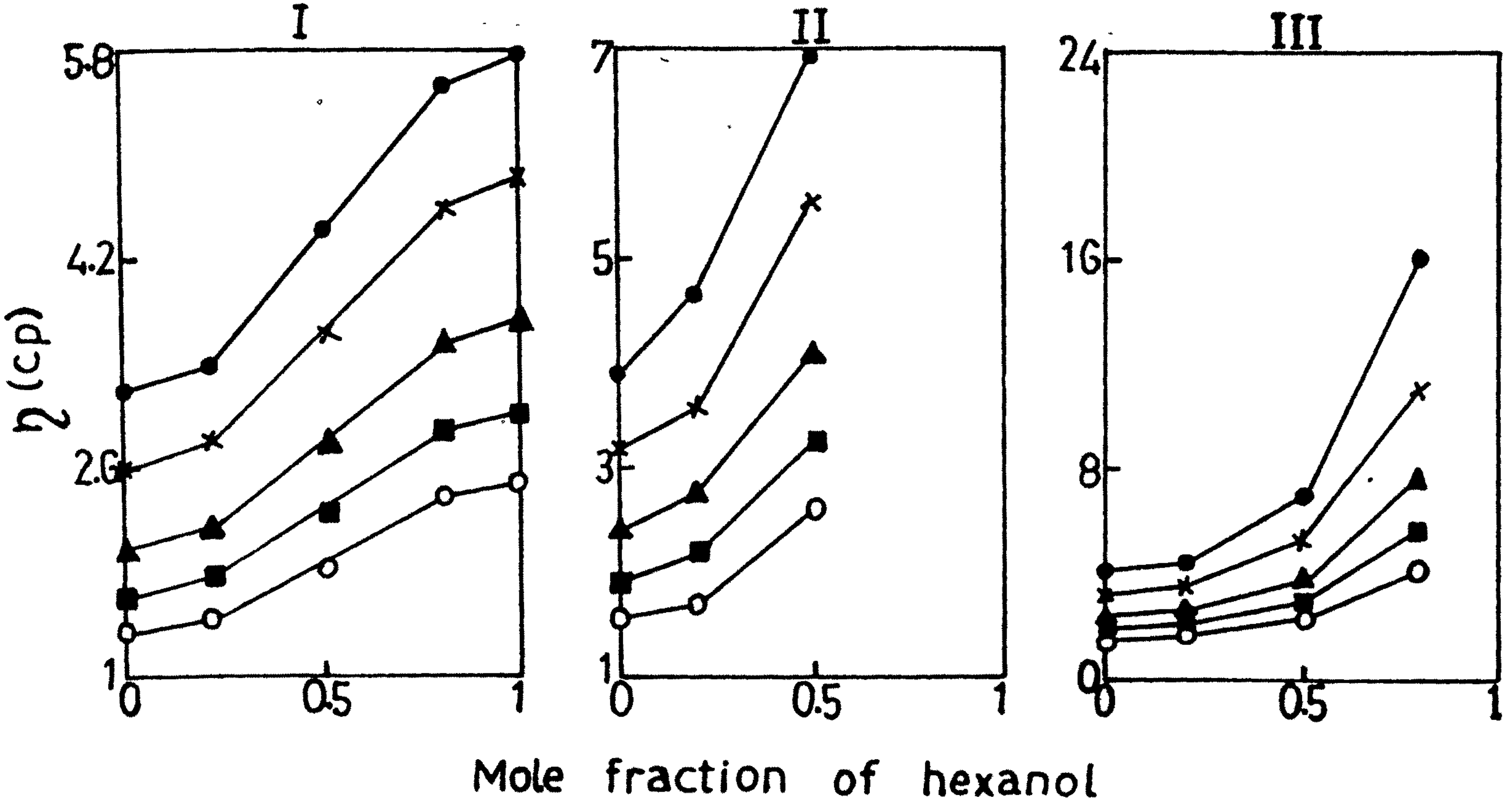

Fig. 5.24 The plots of viscosity (η) vs mole fraction of hexanol in the cosurfactant mixture for three different compositions ((I) S+CS : 42.5%, O: 40%, W:17.5% (II) S+CS: 42.5%, O: 22.5%, W : 35% (III) S+CS: 42.5%, O: 7.5%,W: 50%) at temperatures 30°C ●; 40°C ✕ ; 50°C ▲; 60°C ■ ; 70°C ○ .

higher alcohols [201]. This is because of the void formations created by the difference in n_s and n_a in the aliphatic layer of the interfacial film [201]. On the other hand increasing the alcohol chain length leads to an increase in the hard sphere radius [202] as well as the rigidity of interface [203]. As the (n_s-n_a) in the case of higher alcohols is less, they can pack themselves between the surfactant molecules more compactly with less void formations. In the present study,it is speculated that the continuous increase in the viscosity of the samples with increasing hexanol fraction is due to the increasing rigidity or decreasing fluidity of the interface. Continuous replacement of propanol with a much higher homologue, hexanol, resulted in a more rigid interface and hence the viscosity increased. The dissimilarity between the viscosity variations in compositions I and III is probably due to the difference in the affinity of hexanol towards oil and water phases. Hexanol is readily miscible with oil phase while it is only sparingly soluble in water phase. Hence in sample I containing more of oil phase than water, the viscosity variation is linear in the intermediate range and in sample III no such regularity occurs. From Fig.5.24 it can be seen that at any particular hexanol concentration the viscosity of the formulation increases as water-oil ratio increases at constant surfactant concentration of 42.5%. The increase in water and decrease in oil amount increases the chance

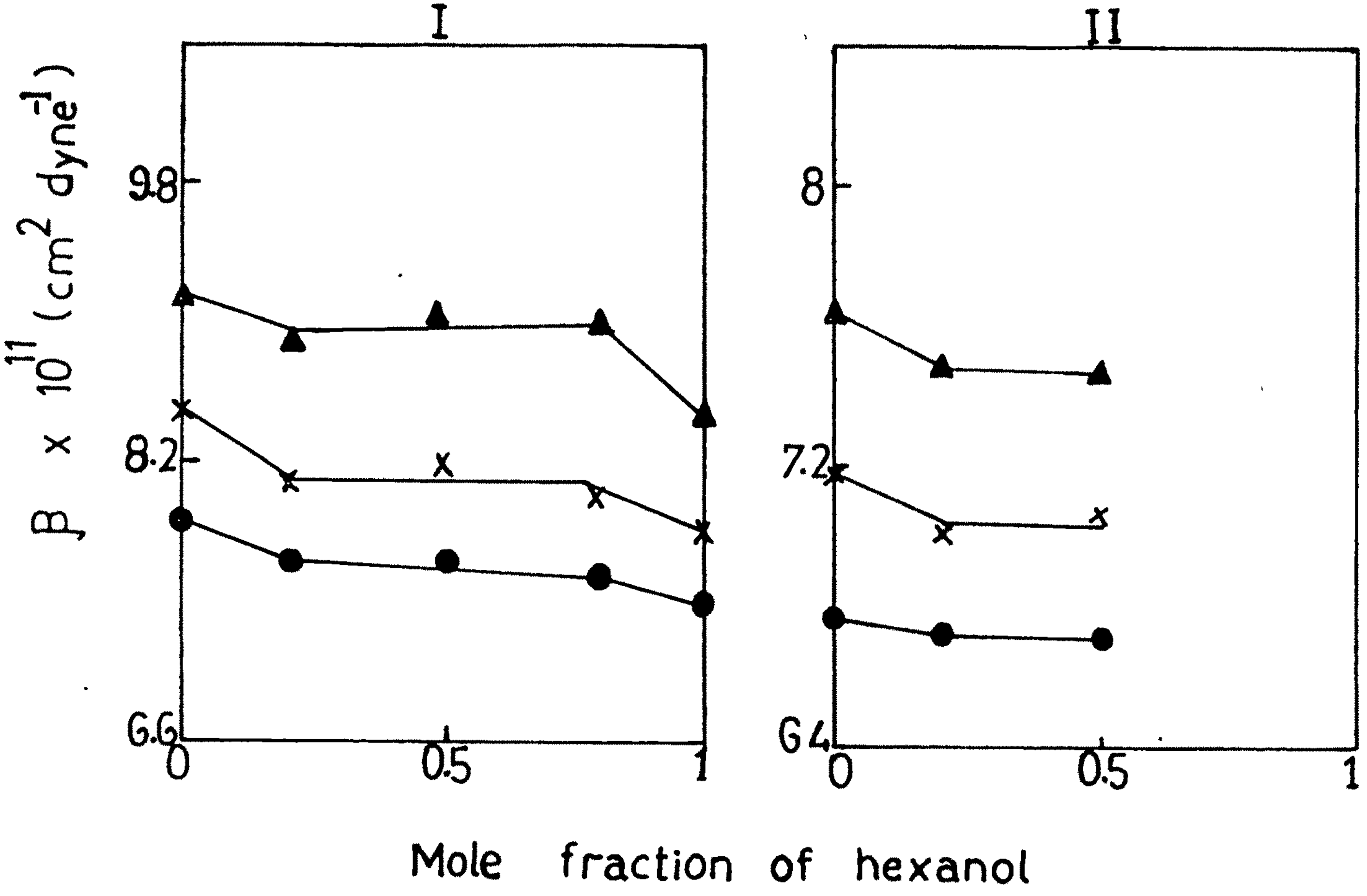

Fig.5.25 The plots of adiabatic compressibility (β) vs mole fraction of hexanol in the alkanol mixture for two compositions ((I) S+CS: 42.5%, O: 40%, W:17.5% (II) S+CS: 42.5%, O: 22.5%, W: 35%) at temperatures 30°C ● ; 40°C × ; 50°C ▲ .

of forming more water conduits. These conduits might even be broad. This will increase the viscosity of the system which is observed in these graphs. This indicates the presence of bicontinuous structure here. Increase of hexanol gives stiffness to the interfacial layer and hence both conduit formation and stiffness together increases the viscosity.

(v) Adiabatic Compressibility

The adiabatic compressibility measured for the composition I and II plotted as the function of increasing hexanol mole fraction (Fig. 5.25) also illustrates a nonlinear variation as in the case of viscosity study. Thus the nonideal nature of alkanol mixing holds true in the compressibility variations also. Here the compressibility shows a decline with hexanol mole fraction increase. For the composition I, the compressibility values of the mixed systems also may be fitted into an almost straight line. The decreasing compressibility values with increasing hexanol fraction is in agreement with the previous argument of increased interfacial film rigidity and such type of opposite compressibility variation to that of viscosity has been reported earlier [83]. The viscosity and adiabatic compressibility changes are opposite to each other. This is expected and we discussed this in earlier chapters.