CHAPTER 3

NONIONIC SURFACTANT MICROEMULSIONS

3.1 PREVIEW

Microemulsions are generally comprised of four components of oil, water, surfactant and cosurfactant. The amount and properties of all these components have profound influence on overall microemulsion characteristics. This dependency of the system on so many variables makes the elucidation of the structure and properties of microemulsion very complicated and difficult one.

Properties of microemulsions are very much affected by the nature of oil phase [124,125,170]. Schulman et al. studied the interaction of oil molecules with interfacial surfactant film and stressed the need of oil penetration into the surfactant film for microemulsion formation [1]. Shah and others studied this topic with various hydrocarbons and concluded that shorter chain aliphatic hydrocarbons and aromatic hydrocarbons, in preference to aliphatics, will penetrate more into interfacial film [123,176]. Finer microstructural transitions were also observed as the alkane chain length was varied [126,175]. Aveyard and coworkers reported that for lower alkanes, surfactants prefer to reside at oil phase which gave rise to w/o structure. Similarly with higher alkanes surfactant stay at the aqueous phase and o/w microemulsion was formed. But for medium chain alkanes ($N \sim 9$), surfactant molecules prefer to form a separate layer leading to so called bicontinuous structure [175].

These studies helped in modelling microemulsion systems suited to various applications [177]. Alkane mixtures are often used industrially and hence for successful modelling data for mixed alkane systems are generally needed. But very few studies are available in literature on mixed alkane microemulsions [178,179]. An earlier study regarding interfacial behaviour of three homologue organic liquid series in presence of surfactant, indicated additive character in hydrocarbon behaviour [180]. Further it was proposed that crude oil properties can be predicted from the behaviour of its components. But this principle does not seem to be true in microemulsion systems. Though there are some studies of mixed alkane microemulsions with various alkane mixtures, we note that the properties of microemulsions for such systems have not yet been systematically studied. In this chapter we present the results of our work with mixed alkane (S+CS) water microemulsions, where S and CS represent surfactant and cosurfactant respectively.

Analysis of different parameters which determine the structure transitions in microemulsion, have attracted the attention of various workers [58,63,181,182]. These studies attributed the structural transitions in microemulsion mainly to two parameters of interfacial surfactant film, viz rigidity (K) and spontaneous curvature (C_o). Oil penetration, sterric strain associated with arrangement of surfactant molecules, salinity, temperature etc. affect the values of C_o and K and hence structural transitions [58,62,181-183]. Influenced by these parameters, the oriented surfactant molecules at the interface envelope a finite volume of water or oil or become continuous in two or three dimensions [184]. This property of surfactant films enable the system to have different structures.

The microstructural changes associated with these ternary systems cause definite macroscopic phase changes. These phase changes are well exhibited in the phase diagrams. Phase diagrams are, therefore, a prerequisite for the study of all surfactant containing multicomponent systems. These clearly provide the conditions at which a particular phase can form and exist [185]. Moreover carefully carried out phase diagram study gives an insight into the system [132,134]. Hence we studied the phase diagrams in detail and we present our results here.

Microstructural properties are generally studied by scattering techniques [186,187]. These methods are very important in understanding such properties [184]. Self diffusion experiment have also been used in the microemulsions studies [48,188]. Other than these techniques, classical methods such as viscosity and conductance were also quite often employed for the structural investigations in microemulsions [189,190]. In this thesis we have used these simple techniques to study the properties of various microemulsion systems.

3.2 SYSTEMS STUDIED

Properties of five different alkane/ Brij 35 + propanol /water systems by varying alkanes were investigated. The results are presented in this chapter. Alkanes used were heptane, nonane and mixtures of these two in three different molar ratios (1:3, 1:1, and 3:1). Pseudoternary phase diagrams of all the five systems were constructed at 6 temperatures (20°, 30°, 40°, 50°, 60° and 70°C), (Fig.3.1 - 3.5). Compositions having various oil/water ratios at one surfactant concentration were selected from the microemulsion region and physical properties were studied. The properties were viscocity, conductance and adiabatic compressibility. Surfactant concentration was kept at 80% (w/w) for all studies. (Surfactant means the combination of surfactant and cosurfactant in 1:2 weight ratio unless otherwise

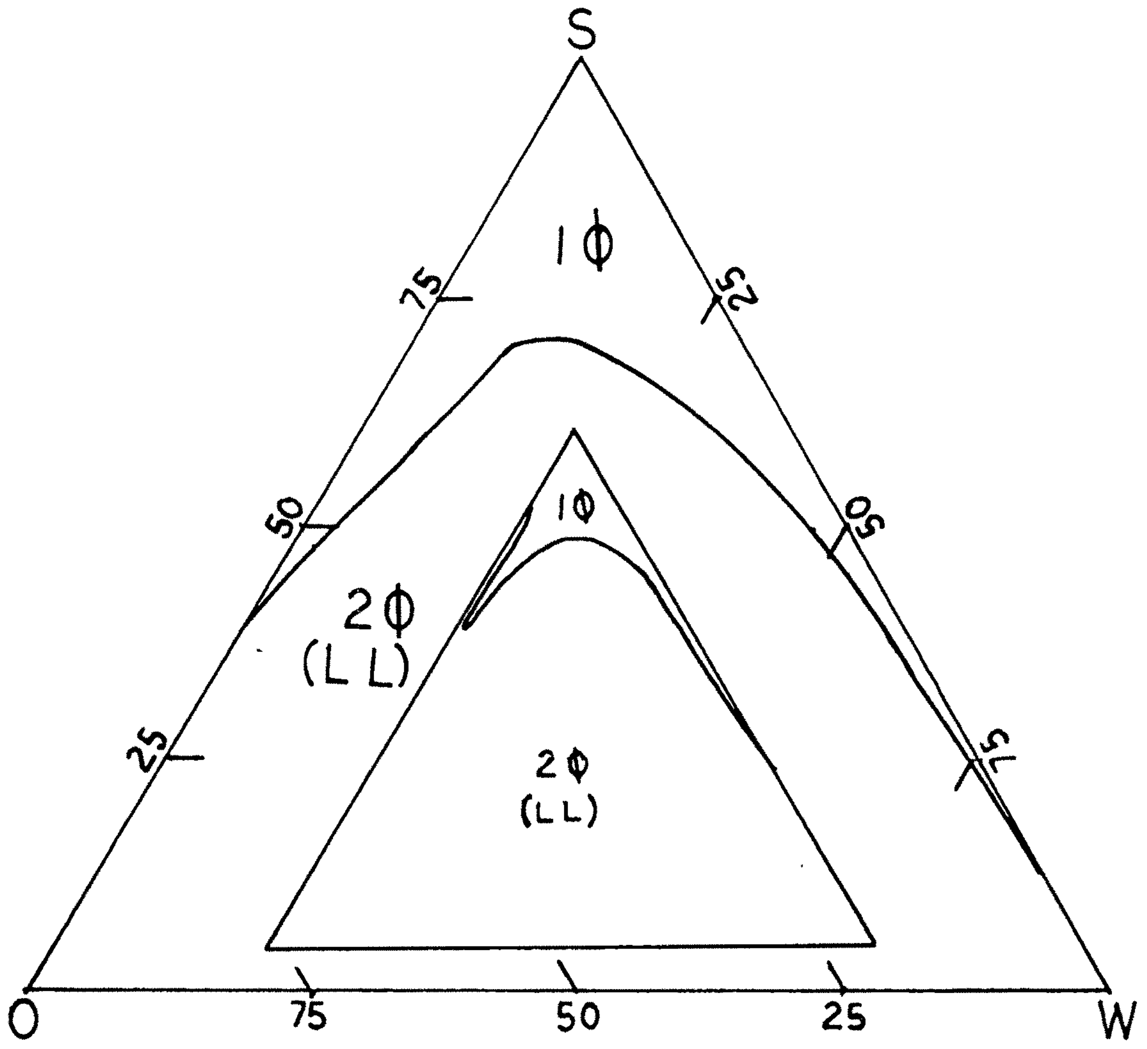

Fig.3.1 A pseudo ternary phase diagram of the system Heptane(O) Brij 35 + propanol (S)/Water (W) at temperatures between 30°C and 70°C.
Inset: Phase diagram of the above system at 20°C.

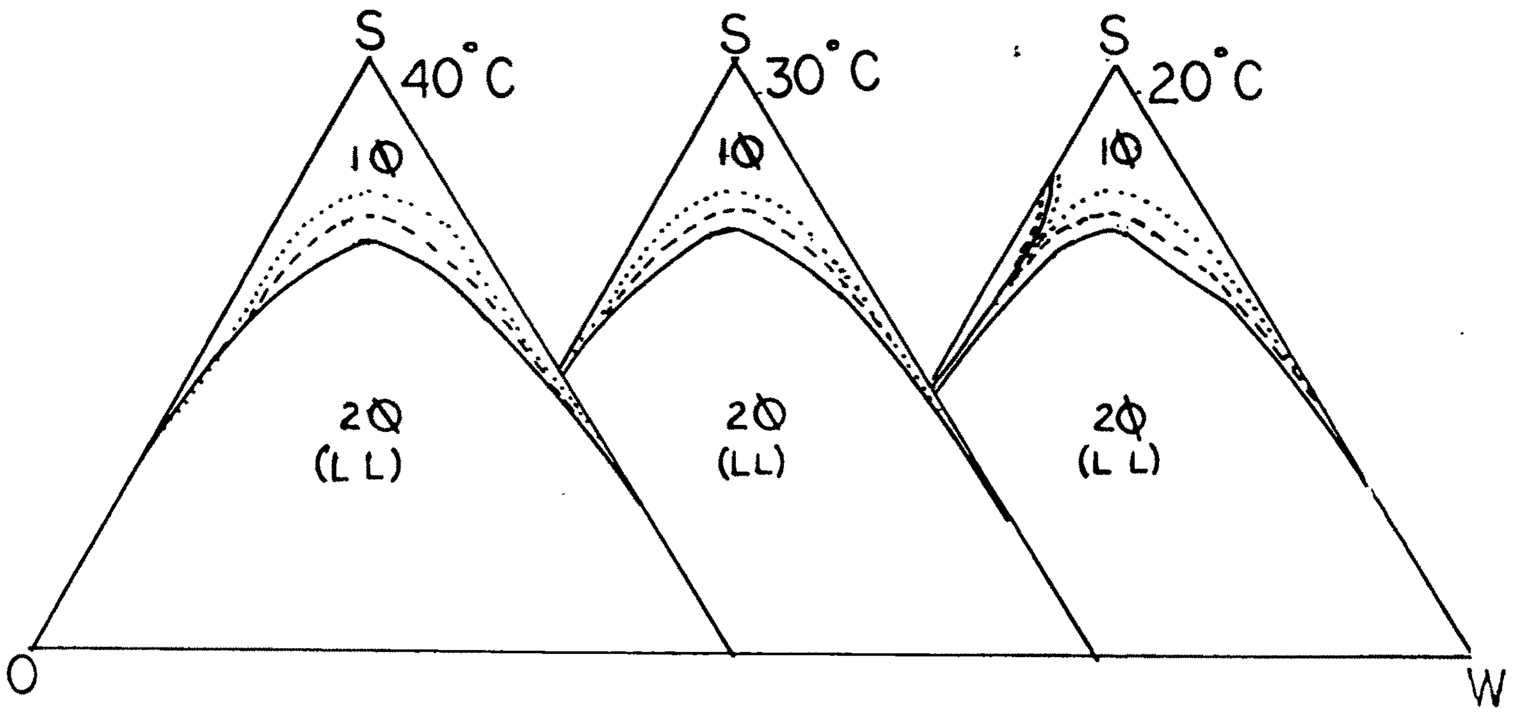

Fig.3.2 Pseudo ternary phase diagrams of the system Alakne (O)/Brij 35 + propanol (S)/ Water (W). Alkanes are ——Heptane, ... Nonane, ---- Heptane + Nonane in 1:1 molar ratio.

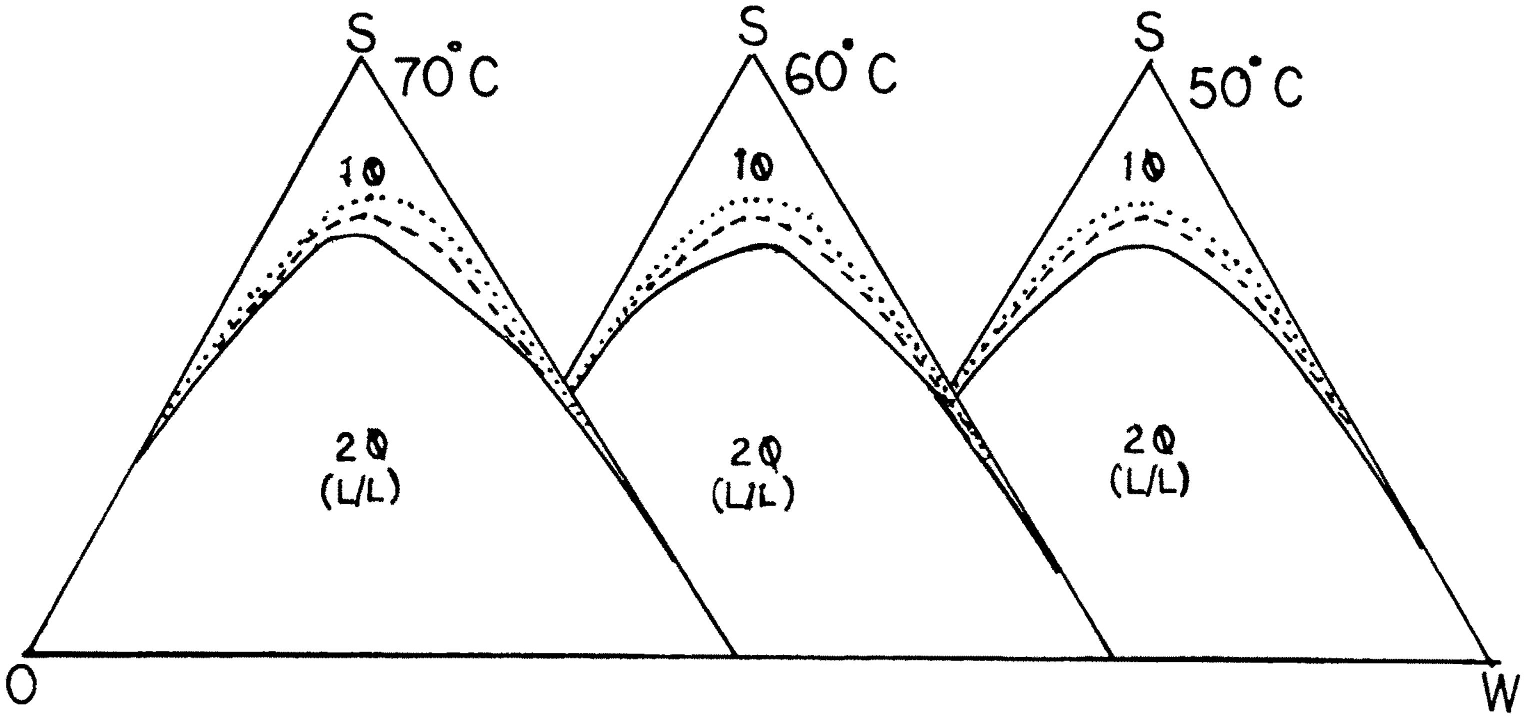

Fig.3.3 Pseudo ternary phase diagram sof the system Alkane (O)/Brij 35 + propanol (S) /Water (W). Alkanes are Heptane, ...Nonane, ------ Heptane + Nonane in 1:1 molar ratio.

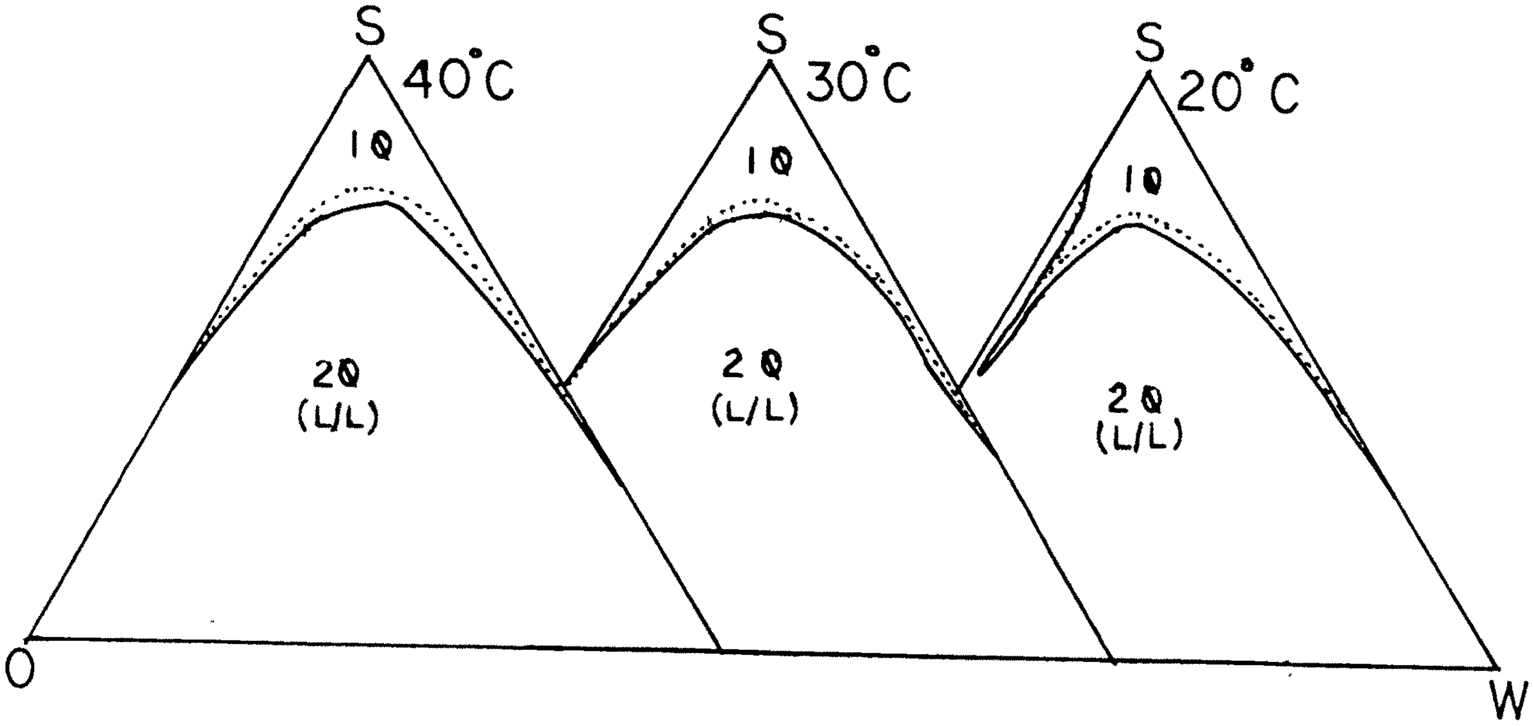

Fig. 3.4 Pseudo ternary phase diagrams of the system Alkane (O)/Brij 35 + propanol (S) /Water (W) where alkane are the mixture of heptane and nonane —— Heptane + Nonane in 3:1 molar ratio. ...... Heptane + Nonane in 1:3 molar ratio.

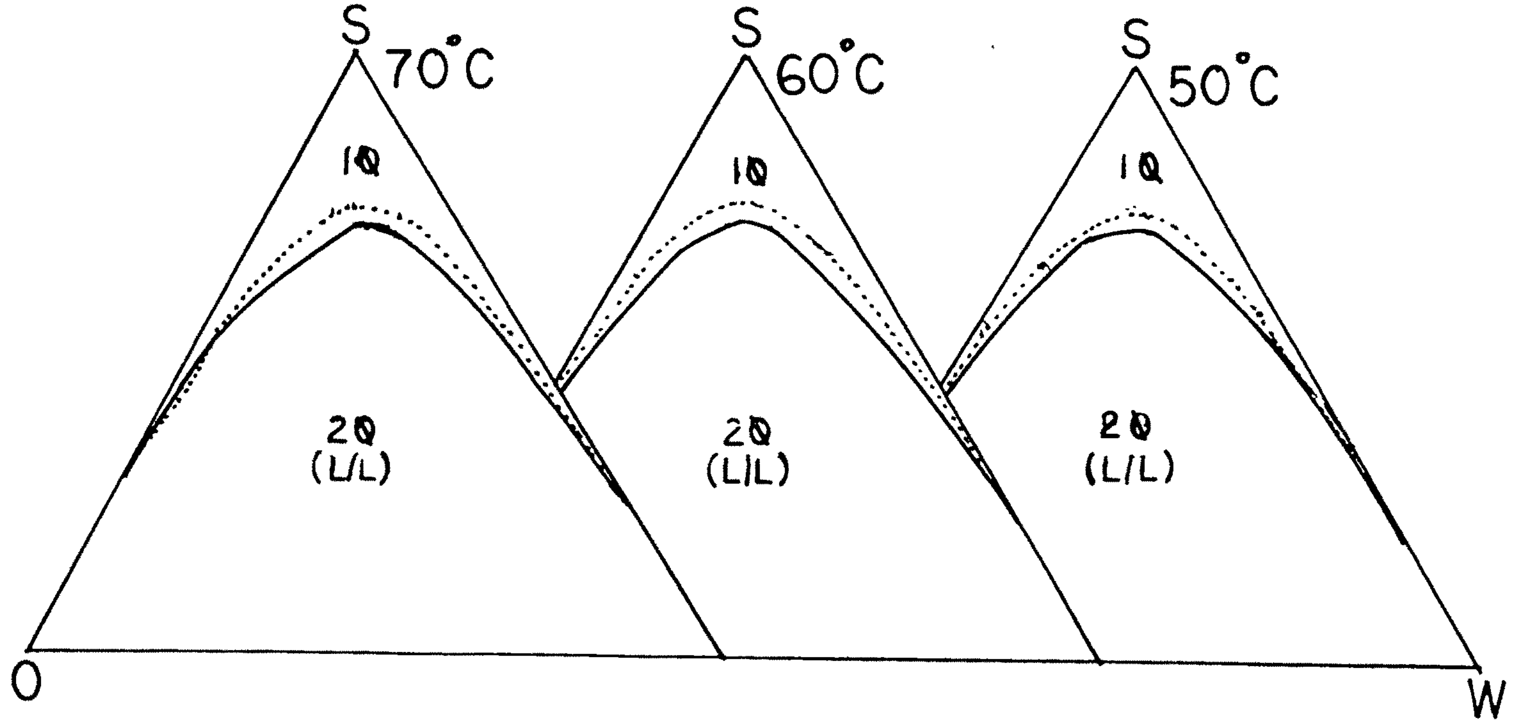

Fig.3.5 Pseudo ternary phase diagrams of the system Alkane (O)/Brij 35 + propanol (S) /Water (W where alkane is the mixture of heptane and nonane ——— Heptane + Nonane in 3:1 molar ratio. .... Heptane + Nonane in 1:3 molar ratio.

mentioned). Temperature was varied from 30° to 70°C with 10°C interval for viscosity and conductivity measurements. Adiabatic compressibility was determined only upto 60°C. Eight aliquotes of 1 Ø microemulsion system at oil/water weight ratios of 0.0526, ratios of 0.111, 0.333, 0.667, 1.50, 3.0, 9.0 and 19.0 were used for conductance measurements. Out of these, six systems were selected for compressibility study. Viscosity measurements were carried out for 4 systems with various OWR (0.11, 0.667, 1.50, 9.0) (OWR indicates oil water ratio).

3.3 RESULTS AND DISCUSSION

(a) General Pattern of the Phase Diagram

Figs 3.1-3.5 show the phase diagram of different alkane/Brij 35 + propanol/water system at various temperatures. Upper part of the boundary is the monophasic microemulsion region (1 Ø), (properties of this monophasic region were studied). Lower part of the boundary line is liquid/liquid biphasic region (2 Ø) where microemulsion is in equilibrium with excess oil (Winsor I). Phase diagram patterns are similar for all systems at all temperatures studied. The diagram at 20°C is a little different though (Fig.3.1 (inset)).

Generally nonionic surfactants are found to be sensitive to temperature (191,192), as its solubility in what? decreases with increase of temperature. Hence various phase changes with changes in temperature was expected in this case. However in this particular system, the phase diagram remained reasonably unchanged with temperature. Phase diagram remained simple with only monophasic and biphasic regions atleast upto 70°C. This was not very abnormal, though, as the nonionic surfactant used is very hydrophilic [120].

Shape as well as the presence of different zones in the phase diagram are decided by water-surfactant and oil-surfactant miscibility gaps [131,132,134]. By the term miscibility gap, which was originally used by Kahlweit et al. [120,131,132,134], we mean the temperature range within which the binary mixtures (or certain mixing composition of the mixture) exhibits mutual immiscibility. Nonionic surfactant is miscible with water at ambient temperatures. But with increase of temperature, its hydrophobic nature increases and at certain temperatures surfactant rich phase separates from aqueous phase. This temperature is commonly known as cloud point of the surfactant. This is the lower critical temperature for surfactant-water miscibility gap and is denoted here as T_β

Nonionic surfactant - oil miscibility gap exists at comparatively lower temperature. Nonionic surfactants are generally hydrophilic at lower temperature. Hence oil-surfactant mixture is immiscible at low temperature. But this incompatibility fades away with rise of temperature and at certain point, it becomes miscible. This point is the upper critical point (T_{α}) for oil-surfactant miscibility gap. Interplay between these two miscibility gaps determines the phase diagram pattern and makes it more complex [120]. For the present surfactant (Brij 35 + propanol), we observed that T_{β} was above 100°C and T_{α} was below 30°C. Thus for the temperature range between these two (i.e. $T_{\beta} > T > T_{\alpha}$), the phase diagram pattern remained simple and invarient.

Thus all the phase diagrams of the system alkane/Brij 35 + propanol/water at temperature between 30°C and 70°C were of the same pattern with only monophasic and biphasic regions. But as the oil-surfactant miscibility gap exists in the system at 20°C, phase diagram was slightly different from those at other temperatures (Fig 3.1inset).

One phase microemulsion region was more concentrated on the higher surfactant region of the phase diagram. Also area of this particular zone was not appreciable. Brij 35 is a highly hydrophilic surfactant and propanol is also not hydrophobic. Hence efficiency of this combination to bring down the IFT of water with the alkanes is poor. Therefore large amount of surfactant is required to lower the interfacial tension between water and oil for the microemulsion formation. Area of this region changes with the variation of alkane phase and temperature.

(b) Microstructure of the system

As mentioned above, the present study mainly concentrated on higher surfactant concentration region. Very few studies have been reported on microemulsions having high percentage of surfactant [193]. Hence not much information about the microstructure of microemulsion at the high surfactant concentration regions are available in the literature. Thus our interest was to try to understand the microstructural changes in this region.

Fig.3.6 shows the variation of specific conductance with water volume fraction of heptane and nonane microemulsion systems at 80% surfactant concentration. Conductivity of the system increases with increase of water volume fraction. Percolation phenomenon, which is an interesting property of microemulsion, was not observed here. This type of conductance variation is not very common in microemulsion system. This indicated that the

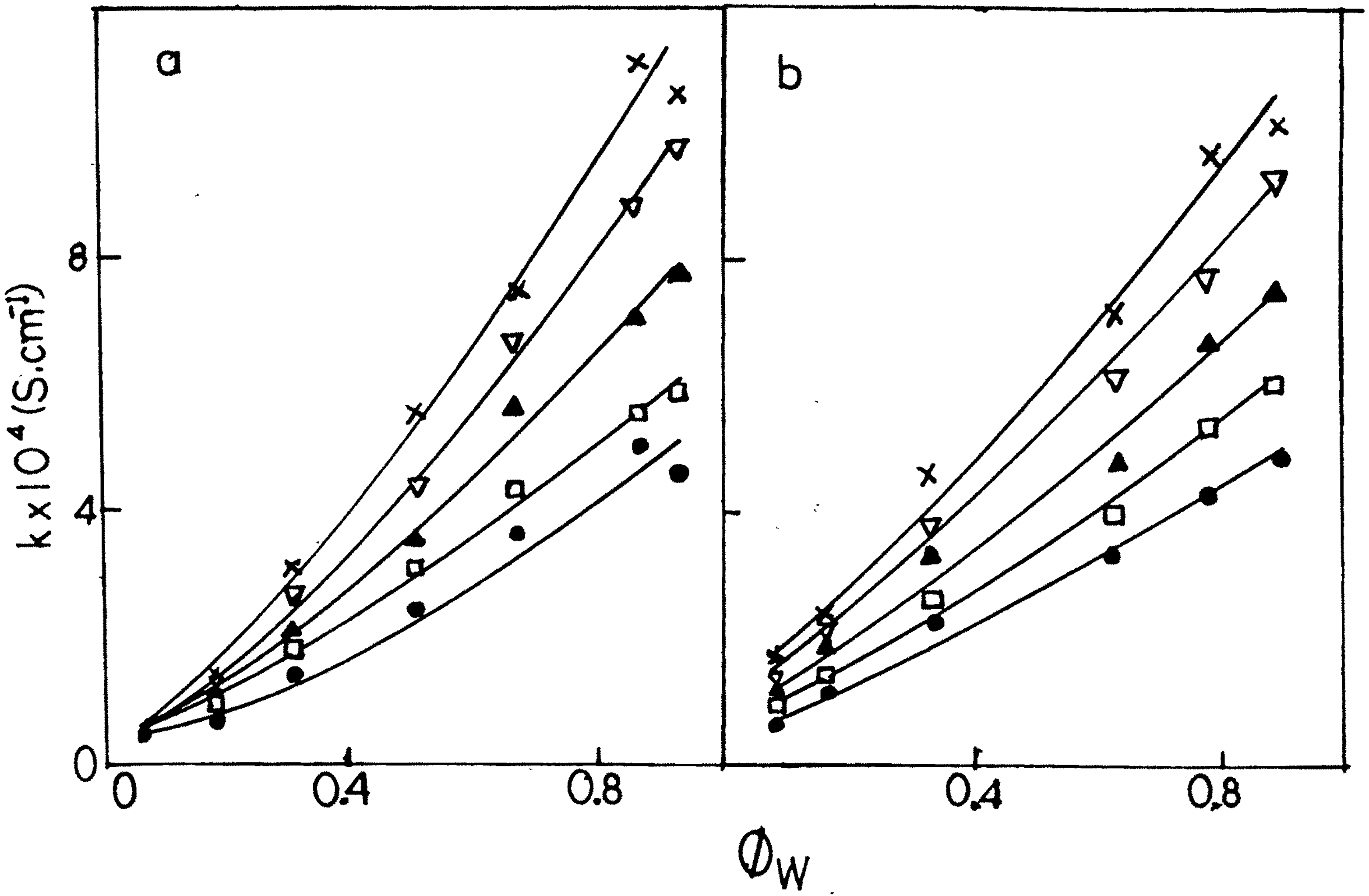

Fig.3.6 Variation of the specific conductance (k) of the Alkane/Brij 35 + propanol/ Water microemulsion with water volume fraction ($\emptyset_W$) at various temperatures Alkanes are (a) Heptane and (b) Nonane. Surfactant concentration is 80% (w/w) ● 30°C, □ 40°C, ▲ 50°C, ▽ 60°C, × 70°C.

system in these compositions was either a molecularly dispersed solution or exist in a single structured form through out. Ninham et al. reported same type of conductance plot for tetradecane - DDAB (didodecyl dimethyl ammonium bromide) - water system [61,62,119]. This anomalous behaviour was explained by assuming the existance of bicontinuous structure throughout. But considering the amount of propanol present in the system (53%), the former proposal (of a molecularly dispersed system) cannot be readily overruled. Propanol, due to its facile solubility in water and alkane, can destroy the microstructure of the system. We examined this possibility by determining the particle distribution curve of some selected compositions.The particle distribution curves were recorded on a particle analyser (B-90, Brookhaven Co., USA) at Bhabha Atomic Research Centre, Trombay, Bombay, India. Particle distribution curves for two systems of same composition, but one contains only propanol as the solubilizing agent and other containing the mixture of Brij 35 and propanol are shown in (Fig.3.7). For propanol only system (Fig.3.7b) all particles are in the range of 1 nm. Hence a molecular dispersion can be assumed for water/propanol/alkane system. But when propanol was used in combination with Brij 35 (Fig.3.7a),the particle size obtained was much higher which indicated the presence of aggregated

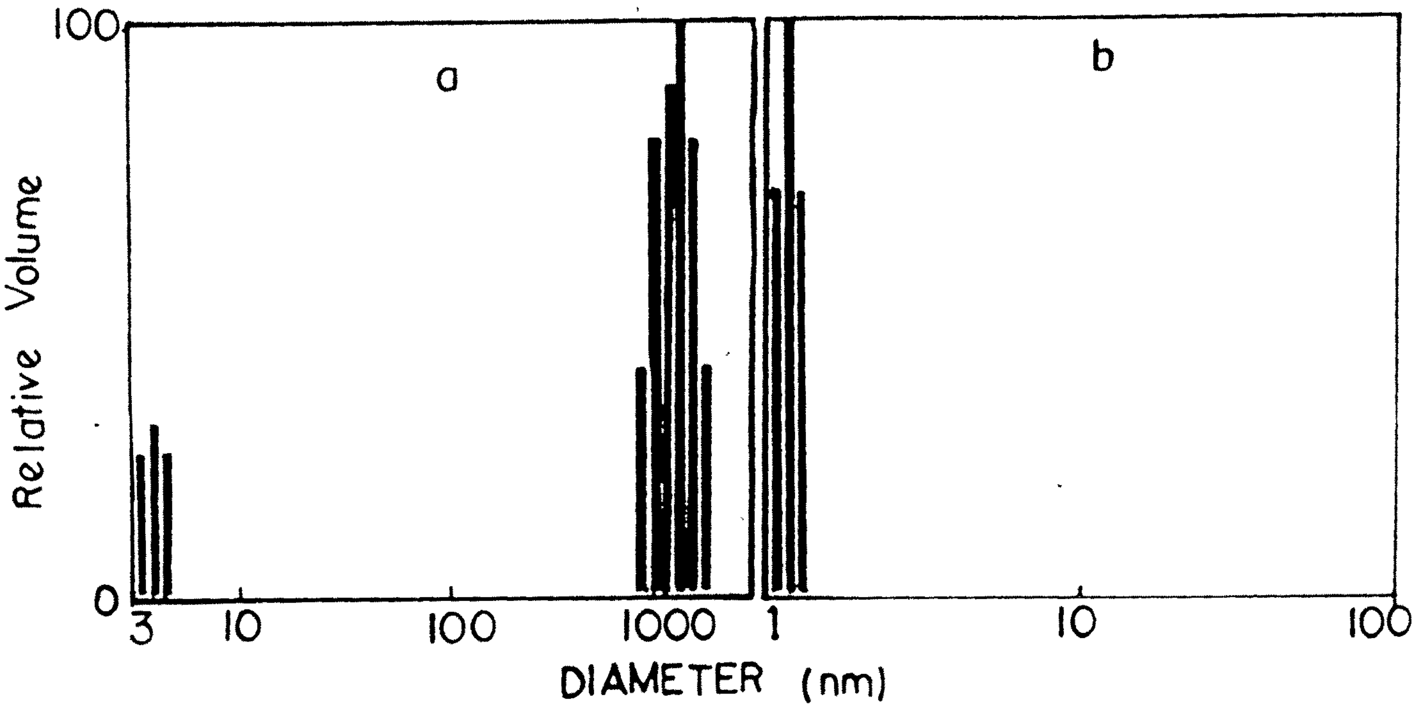

Fig.3.7 Particle distribution curve obtained by Light scattering measurements for the system heptane/amphiphile/water where the amphiphile is (a) Brij 35 + propanol and (b) propanol.

structure. Hence we presume that our system, in the range, studied, is a bicontinuous one.

Moreover, according to scaling law [194], specific conductance of microemulsion, $k \propto (\emptyset - \emptyset_p)^t$ where $\emptyset$ is the volume fraction of water in the microemulsion and $\emptyset_p$ is the percolation threshold. When the system is bicontinuous, t = 8/5 i.e.,

$$k \propto (\emptyset - \emptyset_p)^{8/5}$$

Then the plot of $k^{5/8}$ versus $\emptyset$ should meet X axis at $\emptyset_p$ which is threshold volume fraction of water [195]. In Fig.3.8 such plot for the given system is presented. It can be seen that the graph almost passes through the origin (infact it has a small positive intercept), indicating the presence of bicontinuous structure from beginning and extended to entire range of o/w ratio.

In Fig.3.9 we present the variation of absolute viscosity of both heptane and nonane microemulsion with water weight percentage in the total system. Here too the nature of the curves deviate from the general trend where they change with microstructural transitions [196,47]. For the given system absolute viscosity of microemulsion steadily increased with increase of water weight percentage. This type of viscosity variation is a

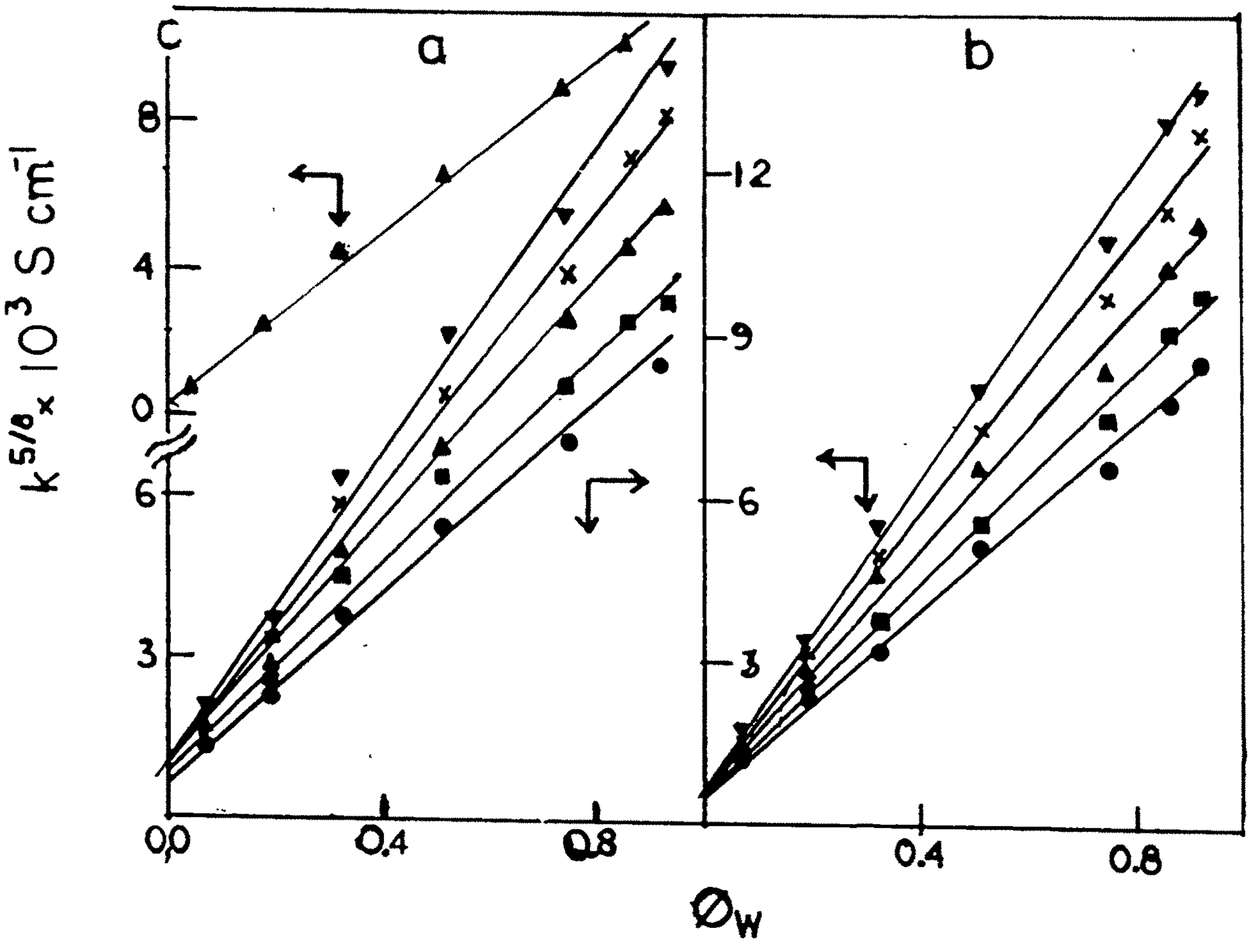

Fig. 3.8 Plot of (specific conductance, k)$^{5/8}$ vs volume fraction of water ($\emptyset_w$) in alkane-water combination of the system Alkane/Brij 35+ propanol/water at various temperatures. Alkanes are (a) heptane (b) nonane and (c) heptane + nonane (1:1). ● 30°C; ■ 40°C; ▲ 50°C; ✕ 60°C; ▼ 70°C.

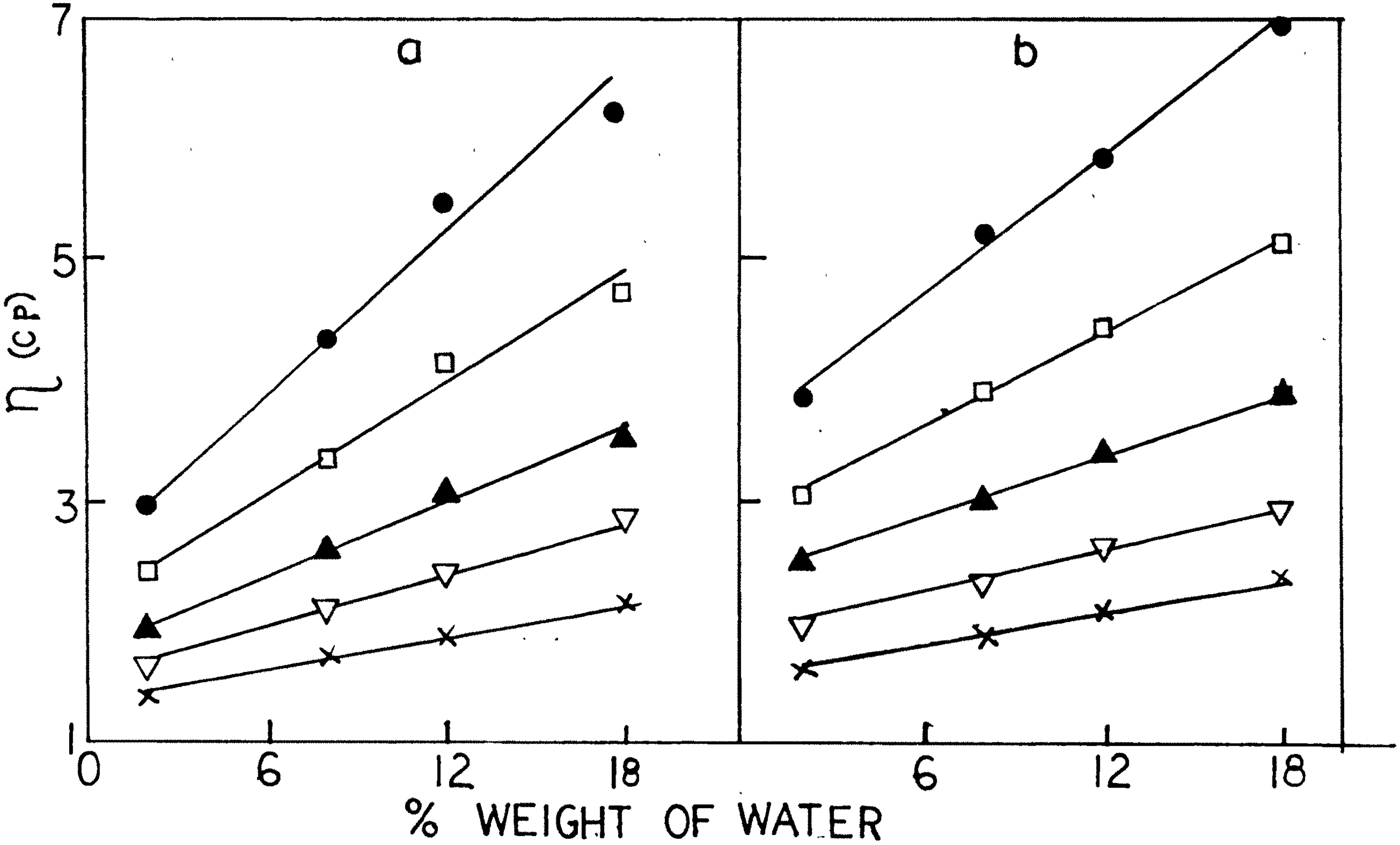

Fig. 3.9 Change of absolute viscosity (η) of the Alkane/Brij 35 + propanol/water microemulsion vs water percentage int he system at various temperatures. Alkanes are (a) Heptane and (b) Nonane. Surfactant concentration is 80% (w/w)
● 30°C, □ 40°C, ▲ 50°C, ▽ 60°C, × 70°C.

characteristic of bicontinuous structure [61,62]. Increase of water fraction increases the diameter of the water conduits to oppose discontinuity in the structure [61]. Larger the diameter of the conduits, the greater will be the viscosity of the system. As long as the system exists in a bicontinuous structure, its viscosity steadily increases with increase of water fraction.

It has been reported that tetradecane/DDAB/water microemulsion retains its bicontinuity due to the poor penetration of oil molecules into the interfacial surfactant film [61,62,119]. Highly penetrating oils need more curved surface which induces spherical structure to the aggregate [62]. If the penetration is less, system prefers bicontinuous structure. In the present system, though heptane and nonane are not highly hydrophobic like tetradecane, the interfacial film is too hydrophilic because of the presence of large amount of Brij 35 and n-propanol molecules. Hence here also penetration of oil molecules must be poor. This results in the formation of a bicontinuous system.

Steric factors present in the interfacial surfactant film also control the microstructure [58]. The steric strain associated with the spherical arrangement of large number of surfactant molecules around small water or oil domains prevents the formation of discrete structures (w/o and /or o/w). Hence the system exists as bicontinuous.

A study of adiabatic compressibility (β) was also performed on the microemulsion systems at various temperatures (30°, 40°, 50°, and 60°C). Fig.3.10 is the β versus water percentage plot. Linear decrease of β with increase of water percentage is expected because water has lower β than alkanes. Water is less compressible than alkanes because of its highly structured nature which is absent in the alkanes. As the system is bicontinuous the overall compressibility observed is the sum of the effect on the water conduits and also the alkane externals. The effect of propanol, which is present in large percentage and also somewhat structured, cannot be neglected.

(c) Nature of alkane mixing

Three different mixtures of heptane and nonane (1:3, 1:1, 3:1 molar ratios) were used as the alkane phase to prepare microemulsion systems. Properties of these mixed alkane systems were then compared with those of pure alkane microemulsions.

Variations of conductivity of the microemulsion with water fraction is given in Fig.3.11. Fig.3.12 carries the

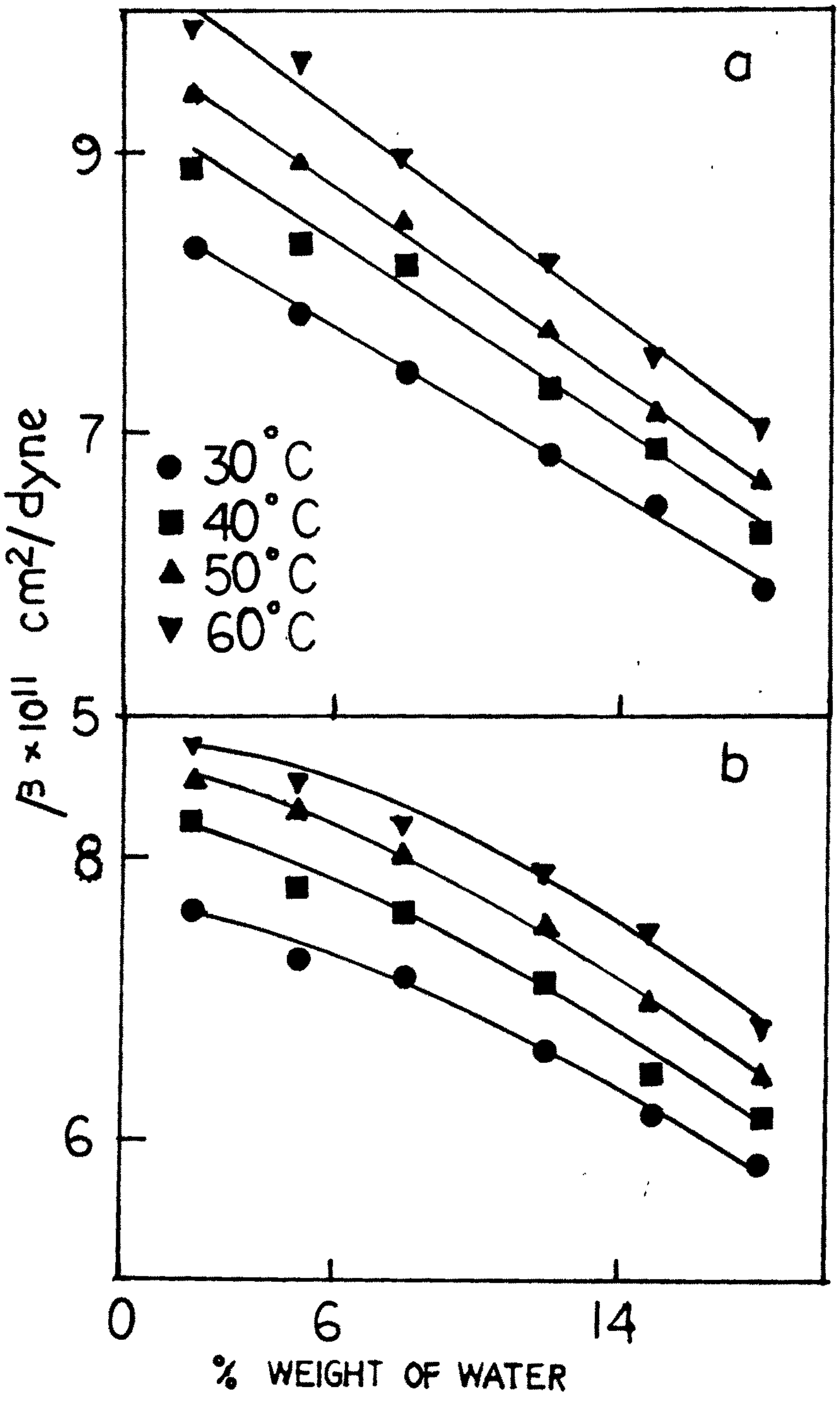

Fig.3.10 Plot of adiabatic compressibility vs water weight percent in the microemulsion system for (a) Heptane and (b) Nonane. Surfactant concentration is 80% (w/w).

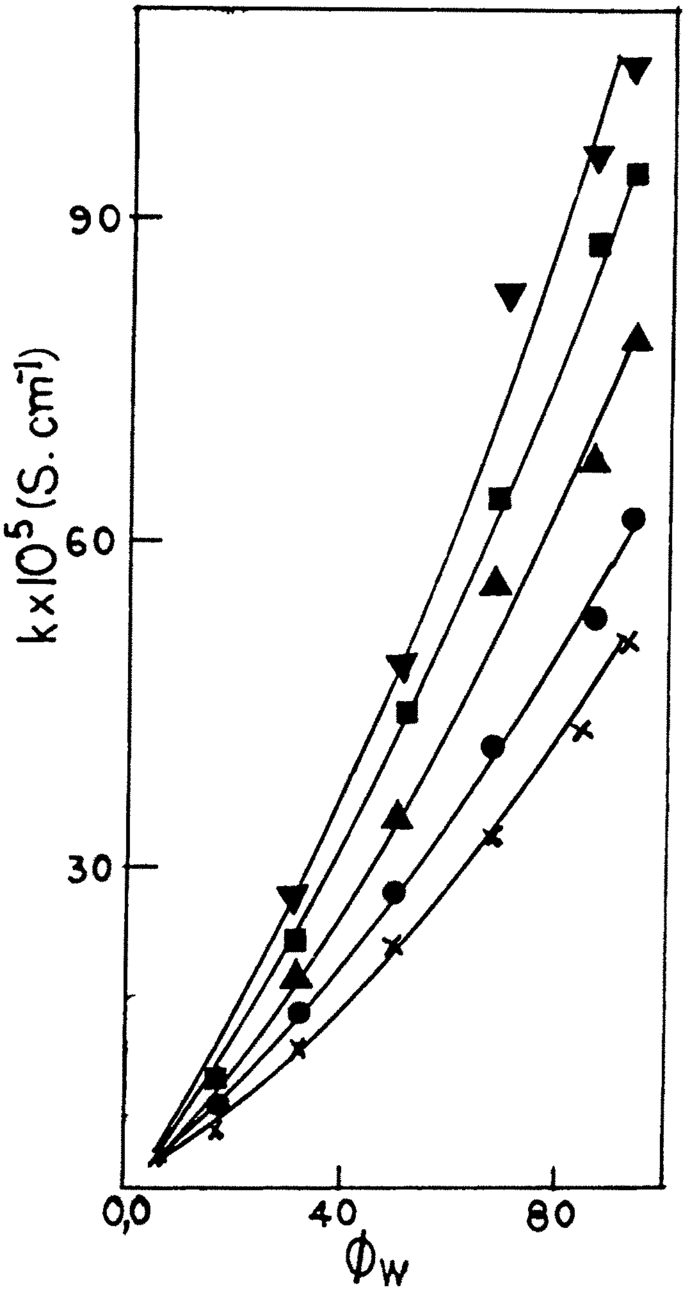

Fig. 3.11 Variation of specific conductance (k) of mixed heptane + nonane (1:1) microemulsion with water volume fraction (ϕ_w) at 80% surfactant concentration. × 30°C, ● 40°C, ▲ 50°C, ■ 60°C, ▼ 70°C.

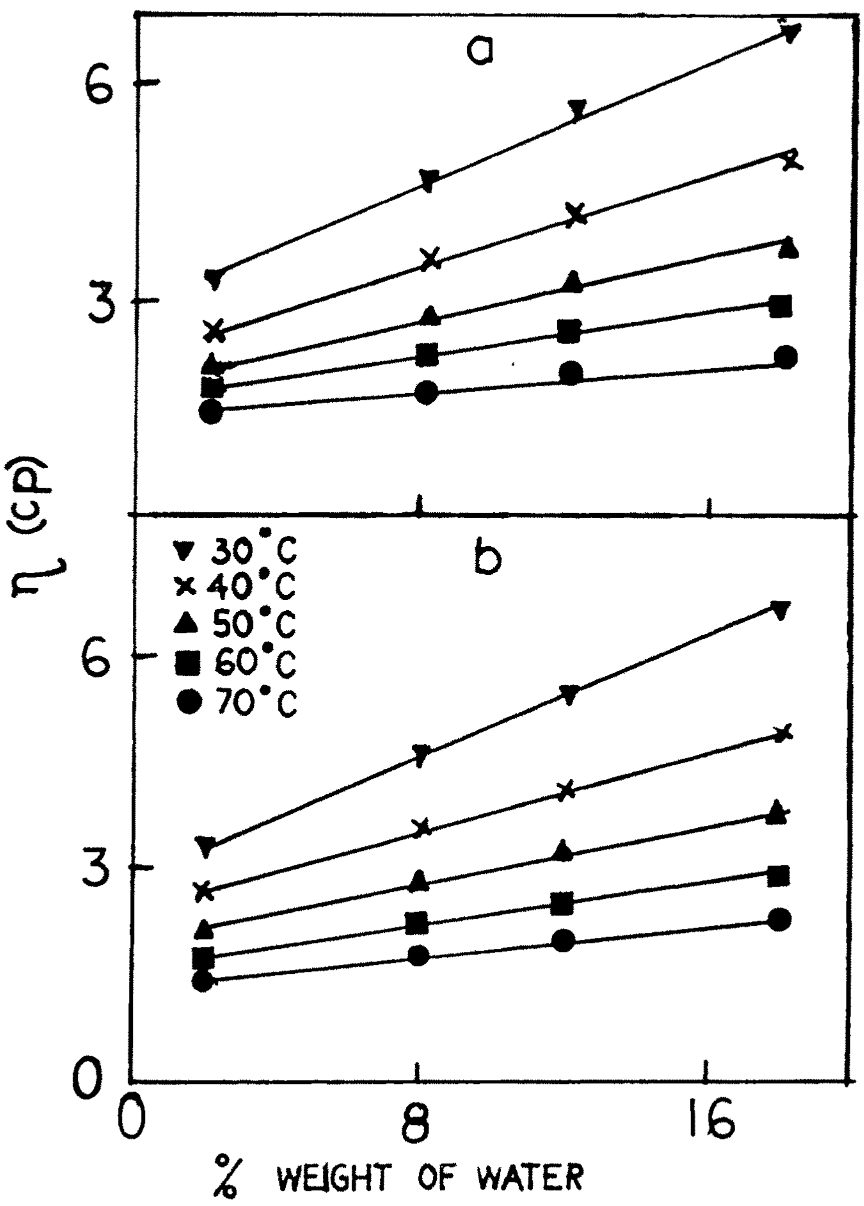

Fig. 3.12 Plot of absolute viscosity (η) vs weight percentage of water in the Alkane/Brij 35 + propanol/ water system at 80% (w/w) surfactant concentration. Alkanes are
(a) heptane + nonane (3:1)
(b) heptane + nonane (1:1)

plot of viscosity values against weight percentage of water in the system. Similar type of variations were obtained as those with heptane and nonane microemulsions. Therefore it was assumed that microstructure of mixed alkane microemulsion was exactly similar to the microemulsions formed with pure alkanes. A plot of k5/8 with ϕ (Fig. 3.8c) show straight line with positive intercept indicating bicontinuous structure as discussed earlier.

In Fig. 3.13, areas of one phase microemulsion region of all the systems are plotted against mole fraction of nonane in the alkane mixture. Microemulsion area decreased as heptane was replaced by nonane in the oil phase at all temperatures. Considering the nature of the surfactant system used, this decrease was anticipated. However, variation of mixed alkane microemulsion areas was rather unexpected. Changes in microemulsion area did not follow linear relation of mixing. At 60°C and 70°C, concave nature of the curves are quite obvious with minimum around 0.75 molefraction of nonane. The variations among monophasic areas of mixed alkane microemulsions are not large. However there are some differences as can be noted from Table 1.

The nonlinear nature of alkane mixing in microemulsion is reflected in the viscosity values also

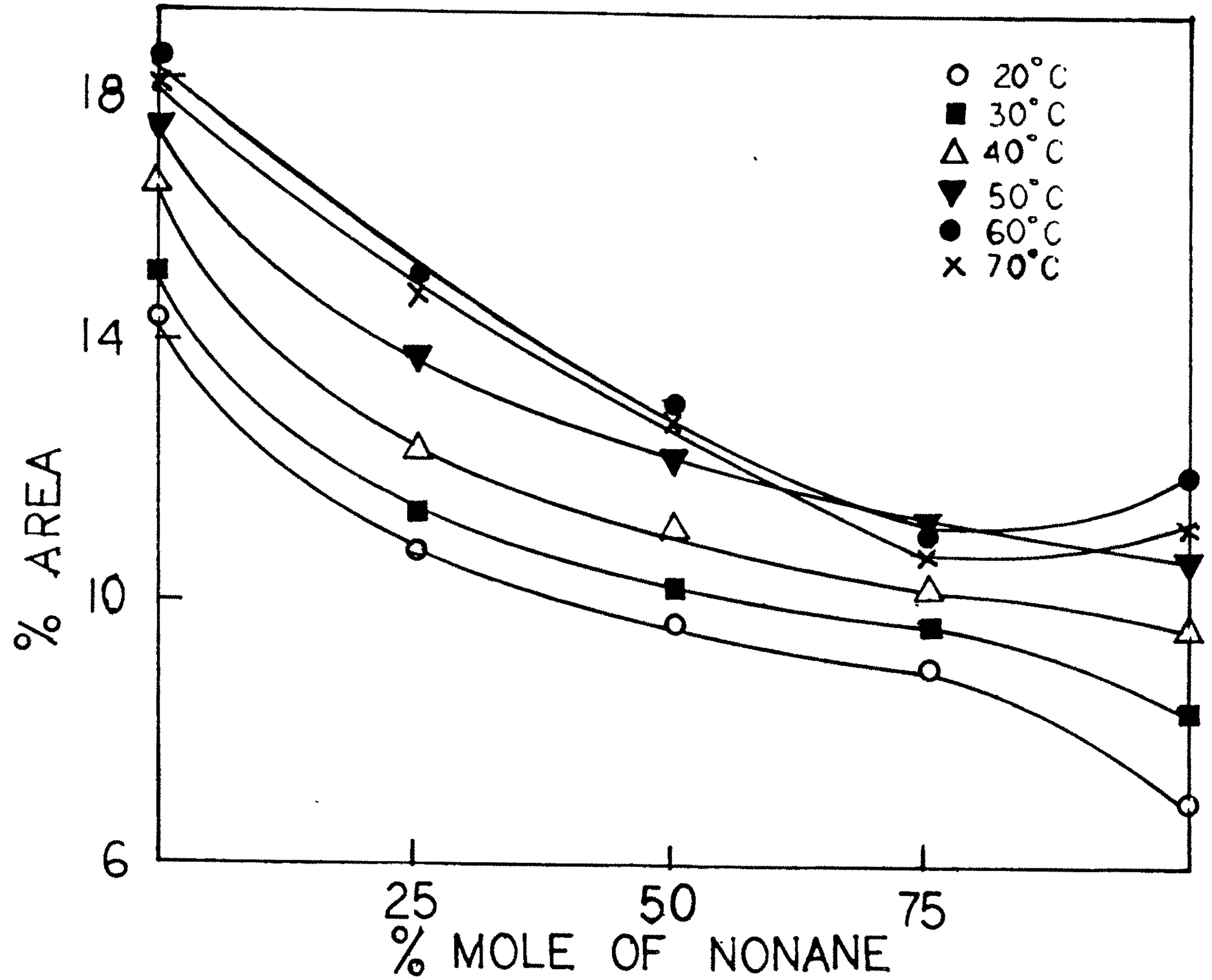

Fig.3.13 Variation of 10 microemulsion area of the pseudo ternary Alkane/Brij 35 + propanol/water system with nonane percentage in the heptane+nonane mixture.

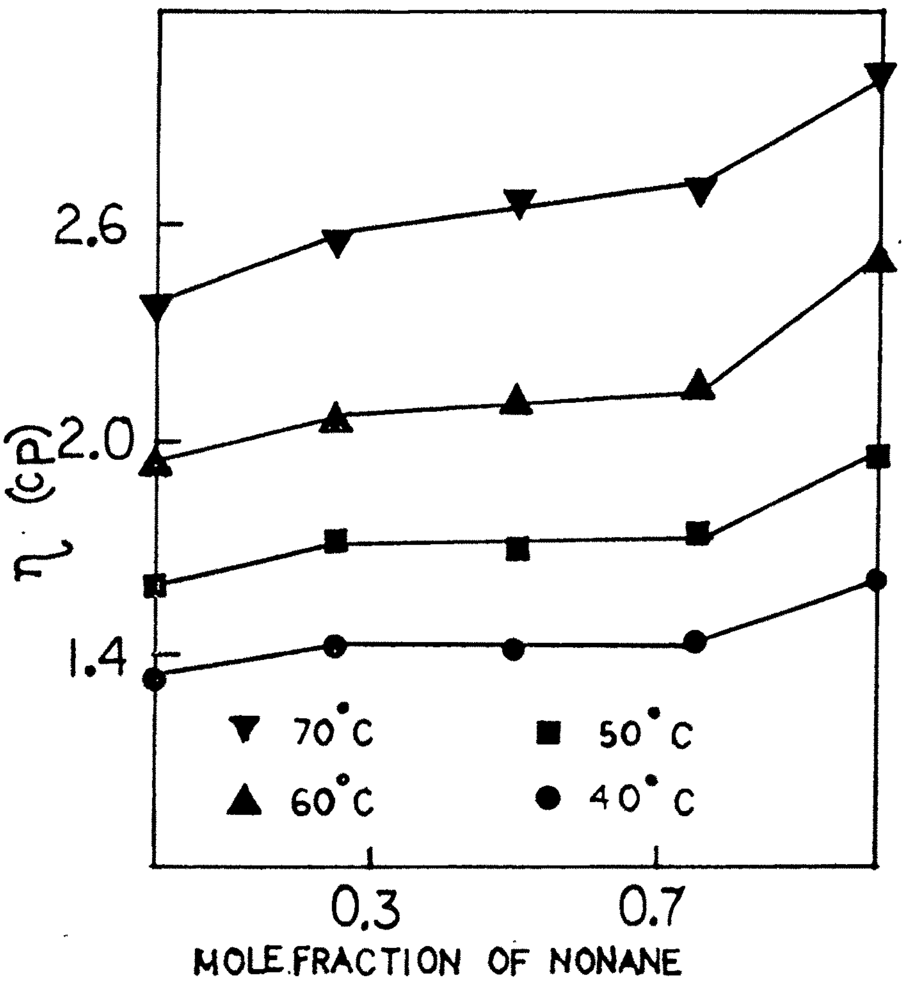

Fig.3.14 Plot of microemulsion viscosity vs mole fraction of nonane in the mixture of heptane and nonane for the system Alkane/Brij 35 + propanol/water.

TABLE 3.I

The percent area of one phase microemulsion region of the system Alkane*/Brij 35 + propanol/Water.

Percentage Heptane in the mixture	Percentage microemulsion area 20°C	30°C	40°C	50°C	60°C	70°C
100	14.2	15.01	16.34	17.15	18.24	17.80
75	10.74	11.20	12.18	13.52	14.49	14.66
50	9.64	10.00	11.03	12.53	13.05	10.56
25	8.95	9.53	10.10	11.08	11.03	10.56
0	6.99	8.31	9.53	10.62	11.89	11.26

* Alkane means heptane, nonane and their mixtures.

(Fig.3.14). For a given microemulsion composition and at a particular temperature, viscosity of mixed alkane microemulsions are similar inspite of its different alkane mixing ratio. This behaviour was found to be present at all temperatures.

These results indicate that the properties of mixed alkane systems are not highly sensitive to the mixing ratio. They behave more or less in similar fashion inspite of different mixing ratio.

Efforts have been made to calculate various viscosity activation parameters ($\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$) from the viscosity measurements of polymeric [197] as well as micellar solutions [198] and interpret the results in terms of structural changes. We have extended those ideas to microemulsion systems.

The Frenkel Eyring equation [197,199] can be written as

$$\ln (\eta V/Nh) = \Delta H^{\#}/RT - \Delta S^{\#}/R$$

where N, h and V are Avogadro number, Plank constant and molar volume of solution respectively. $\Delta H^{\#}$ and $\Delta S^{\#}$ are the viscosity activation enthalpy and entropy respectively. The plot of ln (ηV/Nh) vs T^{-1} was linear (correlation coeff > 0.99), η was the experimental value. Molar volume 'V' was calculated by the summation of molecular weights of all components, i.e. $M = \sum N_i M_i$ where N_i is the molefraction of the component 'i' and M_i is the corresponding molecular weight. The experimentally determined microemulsion density was then used to calculate the molar volume.

$\Delta H^{\#}$ was calculated from the slope and $\Delta S^{\#}$ was obtained from the intercept of the plot. The magnitudes of these quantities for all systems are given in Table II. $\Delta H^{\#}$ and $\Delta S^{\#}$ values of all mixed alkane microemulsions at a particular OWR, in general, show a similarity,where as the values of pure heptane and pure nonane systems vary from each other.

(d) Effect of temperature on microemulsion properties.

Generally the nonionic surfactant microemulsions are sensitive towards temperature [131,132,134,191]. We investigated the effect of temperature on these microemulsion systems over a wide range (20°-70°C) to determine the change in properties due to temperature.

From the earlier description, Fig (3.1-3.14), it was obvious that the properties like nature of phase diagram,

TABLE 3.II

Activation enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) values of *Alkane/Brij 35 + propanol/ water system at 80% Brij 35 + propanol concentration.

Percentage heptane in the mixture	$\Delta H^{\#}$ kJ/mol				$\Delta S^{\#}$ J/mol /K			
	water weight percent							
	2	8	12	18	2	8	12	18
100	16.5	18.7	21.6	20.9	-0.7	5.6	14.2	12.6
75	16.6	20.1	21.3	22.1	-1.0	9.4	12.9	16.0
50	17.4	20.2	21.2	22.3	1.1	9.8	13.0	16.6
25	17.8	20.1	21.6	23.0	2.4	9.0	13.9	18.7
0	17.8	21.2	20.5	23.0	1.3	12.1	10.8	18.6

* Alkane means heptane, nonane and their mixtures

microstructure, behaviour of mixed alkanes in microemulsion media ramained invarient to temperature. Effect of temperature on the nonionic surfactant system was significant only around cloud point. Any temperature lower than the cloud point has only feeble influence [120].

Fig.3.15 shows the change of microemulsion area with temperature. Area of all systems steadily increases with rise of temperature upto about 60°C. At 70°C the magnitude of the areas somewhat decreases at all compositions. Increase of microemulsion area of the present system with temperature was in the expected line. At low temperature Brij 35 is highly hydrophilic. But as the temperature increases, as for any nonionic surfactant [200], lipophilic character of Brij 35 increases. Hence interaction with alkane molecules increases. This, in turn, favours microemulsion formation. Also decrease in IFT between oil and water with increase of temperature helps to widen this region.

A close look on Fig.3.9 indicates that with increase of temperature, the slopes of the lines in the viscosity - concentration of water plot gradually decreases. This probably means that influence of water fraction on viscosity values of microemulsion decreases with increase

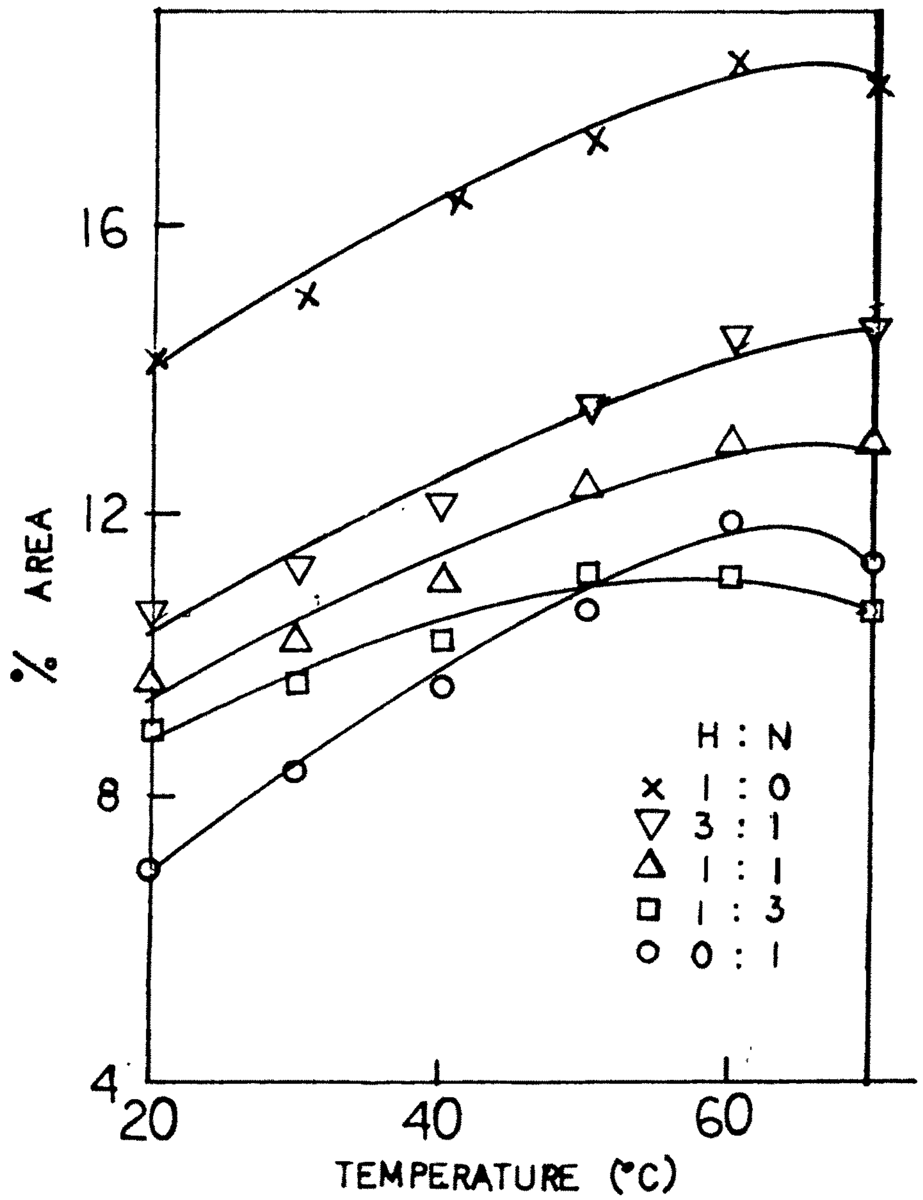

Fig. 3.15 Variation of 10 microemulsion areas with temperature for the system Alkane/Brij 35+ propanol/water. Alkanes are Heptane (H), Nonane (N) and their different mixtures.

of temperature. We presume that this might be due to the breaking of microstructure of the system with increase of temperature. Also we found that the variation of the slope with temperature is a reasonably good straight line (correlation coefficient = 0.986). Hence on extrapolation of this plot of slope versus temperature, one can obtain a hypothetical temperature (T_p) above which viscosity of the microemulsion remains invariant to water fraction in the system. In Fig.(3.16) this temperature (T_p) is plotted against alkane mixing ratio. The graph passes through a maximum at equal molar ratio of heptane and nonane. Mixing of equal moles might be giving some sort of stability to the microstructure.

It has generally been found that absolute viscosity and equivalent conductance are inversely proportional to each other and their product is a constant quantity (Walden product). But this was not found to be true for some microemulsion system [172]. The product of our viscosity and conductance data do not show any constancy. In Fig.3.17, this so called Walden product of certain systems are plotted against temperature. It decreased steadily with increase of temperature. (For calculating Walden product, viscosity values were of water system without NaCl and conductance values were of the corresponding systems with 0.1 M NaCl. It was observed

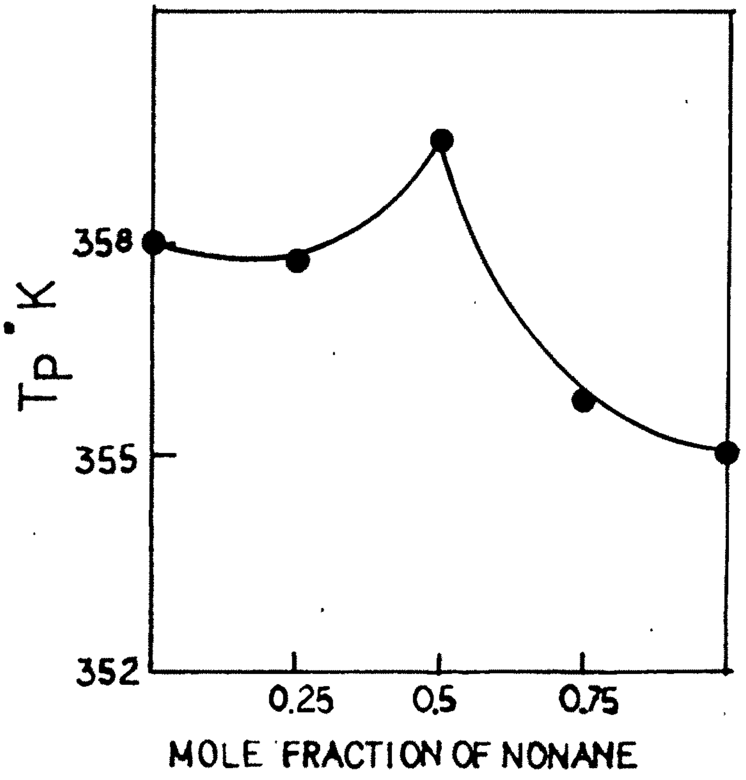

Fig.3.16 Change of T_p with mole fraction of nonane in the mixture of Heptane and Nonane.

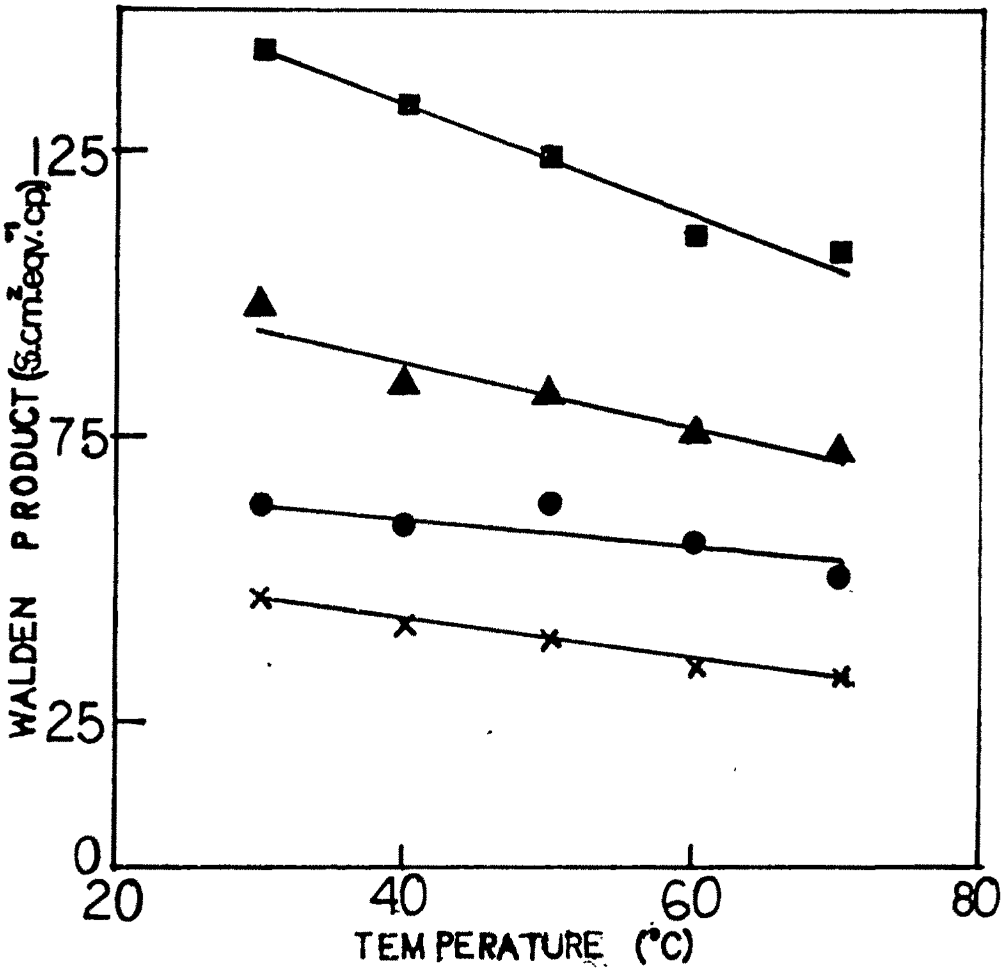

Fig.3.17 Variation of Walden product of the microemulsion system with temperature at various water percentage of the system. × 2 % ; ● 8 %; ▲ 12% ; ■ 18 % .

that the viscosity values of microemulsions, where the aqueous phase was 0.1 M NaCl, were not different in any significant way from those of the microemulsions where NaCl was absent).

Adiabatic compressibility of various systems were found to increase linearly with temperature (Fig.3.18). The rise of temperature should provide enough kinetic energy to loosen the interfacial film.This is expected to enhance the penetration of alkane molecules into the interfacial film, thereby swelling the dispersed phase. Hence compressibility was higher at higher temperature.

Variation of viscosity and adiabatic compressibility are always opposite to each other when they are plotted against temperature and water fraction of the system (Fig.3.19). Similar results were noted earlier also [70].

It can hence be concluded that though rise of temperature upto 70°C did not affect the structural transition as well as phase behaviour of the present system, other physical properties like viscosity and adiabatic compressibility were influenced by temperature. The composition of the oil (i.e. heptane - nonane ratio) also seems to have not much effect on viscosity etc. However, single phase microemulsion area is affected. This

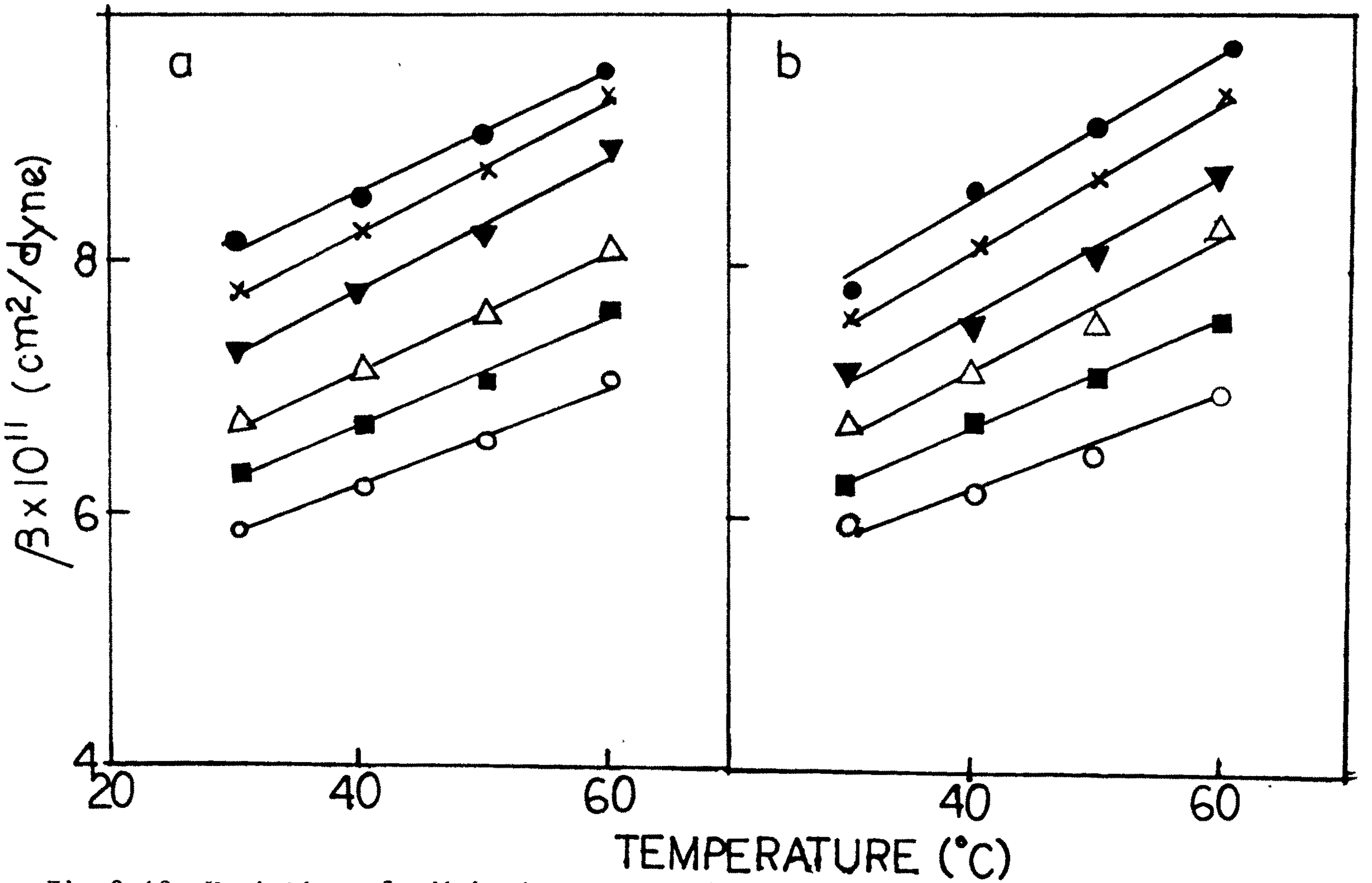

Fig.3.18 Variation of adiabatic compressibility with temperature for the system mixed alkane (O)/Brij 35 + propanol (S)/Water(W) at different compositions of O/S/W ○ 2/80/18, ■ 5/80/15, △ 8/80/12, ▼ 12/80/8, × 15/80/5, ● 18/80/2. Alkane mixture is heptane + nonane as (a) 3:1 and (b) 1:1 mole ratios.

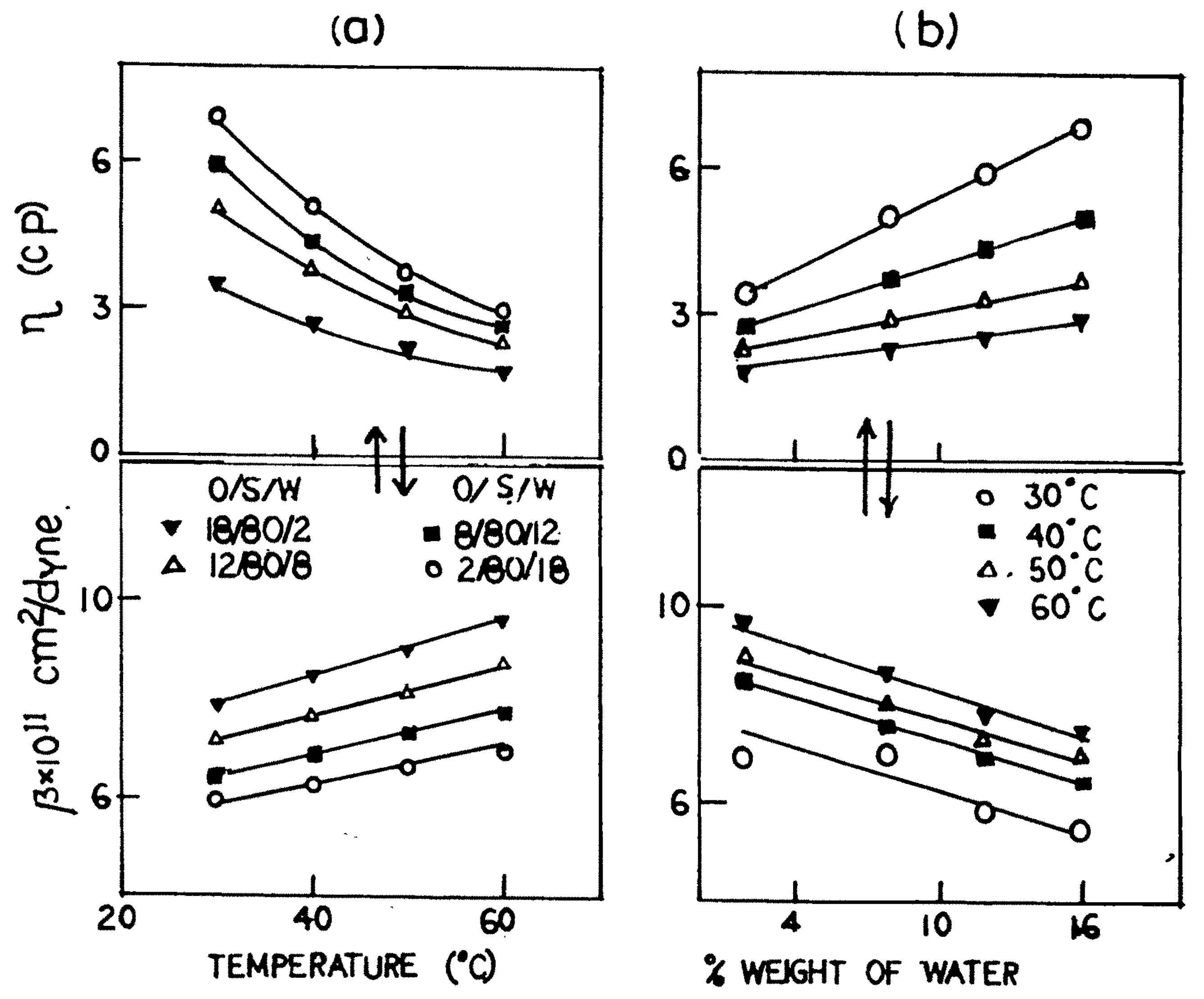

Fig.3.19 The plot showing mutually opposite variations of viscosity (η) and compressibility (β) of the system. Heptane + Nonane (1:3) [O]/Brij 35 + propanol [S]/water (W). (a) against temperaure and (b) water weight percentage.

happens because the viscosity, compressibility etc. are very much dependent on temperature. The hydrophilicity, which determines the phase behaviour, was not much changed and hence not much changes are observed in the phase diagram.