# CHAPTER-5

# Phase behaviour of aqueous / non-aqueous microemulsion : effect of PEG-4000

## 5.1 PREVIEW

In the recent past the microemulsion system has been extended to include the non-aqueous systems. The studies on micellization in non-aqueous systems by Evans[1-3] and collaborators and on the liquid crystals by Friberg et al.[4-5] have generated interest among the technologist as well as theoreticians. In non-aqueous microemulsion the polar solvent of aqueous microemulsion, water is replaced by non-aqueous polar solvent like glycerol, formamide, dimethyl sulfoxide, $\gamma$-butyro lactone and acetonitrile etc. But little is known about the microstructure of these mixtures. Several studies, where water was polar component, discuss about the structure of aqueous microemulsion by different techniques like conductance, viscosity, SANS, NMR etc. But very few reports are available regarding non-aqueous microemulsion. Like aqueous microemulsion, non-aqueous microemulsion also show the structure like oil in water or water in oil or bicontinuous where water was replaced by non-aqueous polar solvent.

Percolation phenomenon[6] was also observed in this kind of system. Critical micelle concentration in the polar organic solvent is higher, as there is a reduction of aggregation. But the amphiphilicity of a surfactant in polar organic solvent allows for exploration of a variety of microemulsion with different properties.

So, it is necessary to study the physicochemical properties of non-aqueous microemulsion. Recently, the effect of PEG on non-aqueous polar solvent with anionic surfactant AOT in presence of isooctane and n-heptane has been reported[6]. As there is no report on the effect of polyethylene glycol on cationic non-aqueous microemulsion, we decided to study the physicochemical properties of aqueous, non-aqueous and mixed aquo-nonaqueo microemulsions. Also there are reports by Lattes et al[7]. who investigated the Diels-Alder addition of methylacrylate to cyclopentadiene in various formamide microemulsions by using CTAB, cationic surfactant. Thus, it is known that the endo/exo selectivity of the reaction increases with increasing polarity of the solvent. The non-aqueous medium in the form of formamide, improves the yield of the reaction. Also, they got the good stereo selectivities at high concentrations. So, we studied all the physicochemical properties of aquo-nonaquo[8-10] microemulsion at higher surfactant plus cosurfactant concentrations. Agreement between the changes in conductivity and endo/exo[11-12] selectivity were found. It was also observed that the reaction was taking place in oil continuous phase of the microemulsion. Also it shows that in formamide rich zone the endo/exo ratios obtained were virtually the same as found in alcohol rich microemulsion. Hence, it seems likely that the reactions take place at the interface between droplet and continuous phase. Recent study shows that there is solvation of the metal ion by ethylene glycol[6] molecules. There are certain microemulsion systems which are very interesting as they can be directly applied in the field of micro colloids whose sizes can be controlled by that of the droplets used in their formation, biological[13-15] systems etc. So it was thought important to study the following systems.

## 5.2 EXPERIMENTAL

N, N, dimethyl formamide was the polar liquid. The systems studied were cyclohexane / CTAB + 1-propanol / DMF and cyclohexane / CTAB + 1-propanol / DMF (1% PEG-4000). For both the systems surfactant and cosurfactant were mixed at 1:2 weight ratios and their properties were compared with those of the corresponding aqueous systems.

Triangular phase diagram of all the systems were constructed in between 30 to 60°C. The phase diagrams at 40°C were constructed with 1%, 10% as well as 20% PEG-4000 in DMF polar liquids. Conductance of above systems were measured at constant surfactant and cosurfactant at 45%. Temperature effect was determined at 40 to 80°C. The effect of constant DMF at 17.5% and the effect of constant cyclohexane at 17.5% were studied at 40°C.

Viscosity and compressibility were determined at different temperatures in absence and presence of 1% as well as 10% PEG-4000 and 1% PEG-4000 respectively.

Interfacial tension of the system were measured by varying the concentrations of surfactant CTAB. Effects of salts were also noted. The contact angle of microemulsion samples with polytetrafluoroethylene (Teflon) (Samson, India) were measured.

Also the phase diagram of a pseudoternary system cyclohexane / CTAB + 1-propanol / DMF + water were studied to compare with above system. Viscosity, conductance, adiabatic compressibility and contact angle were measured at 45% surfactant and cosurfactant. The contact angle of system was measured as a function of oil, polar liquid and surfactant (CTAB), cosurfactant (1-propanol) as well as mixture of both DMF plus water.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Phase behaviour of non-aqueous microemulsion :

The pseudoternary phase diagrams of the system cyclohexane / CTAB + 1-propanol / DMF in the temperature range of 20 to 60°C at 10°C interval are graphically presented (Fig. 5.1 to 5.4). Surfactant to cosurfactant ratio was kept 1:2 (w/w). The upper part of phase diagram from the corner of surfactant and cosurfactant show solid / liquid binary system in equilibrium with one phase liquid system and one phase (1$\phi$ L) liquid system (2$\phi$ S/L) is in equilibrium with two phase liquid / liquid system (2$\phi$ L/L).

From the pseudoternary phase diagram it can be seen that by increasing the temperature from 20 to 40°C the one phase region Winsor (IV) starts increasing and after 40°C the one phase region (1$\phi$) once again decreases. The one phase (1$\phi$) liquid area and 2$\phi$ (L/L) area increase at the cost of the 2$\phi$ (S/L) area. After 40°C two phase regions (liquid/liquid) is increasing at the cost of both one phase Winsor (IV) and 2$\phi$ (S/L) regions. All areas were measured and computed by the planimeter and are presented in Table 5.1. When compared with the regions of the pseudoternary phase diagram of the aqueous microemulsion systems, it was observed that the one phase

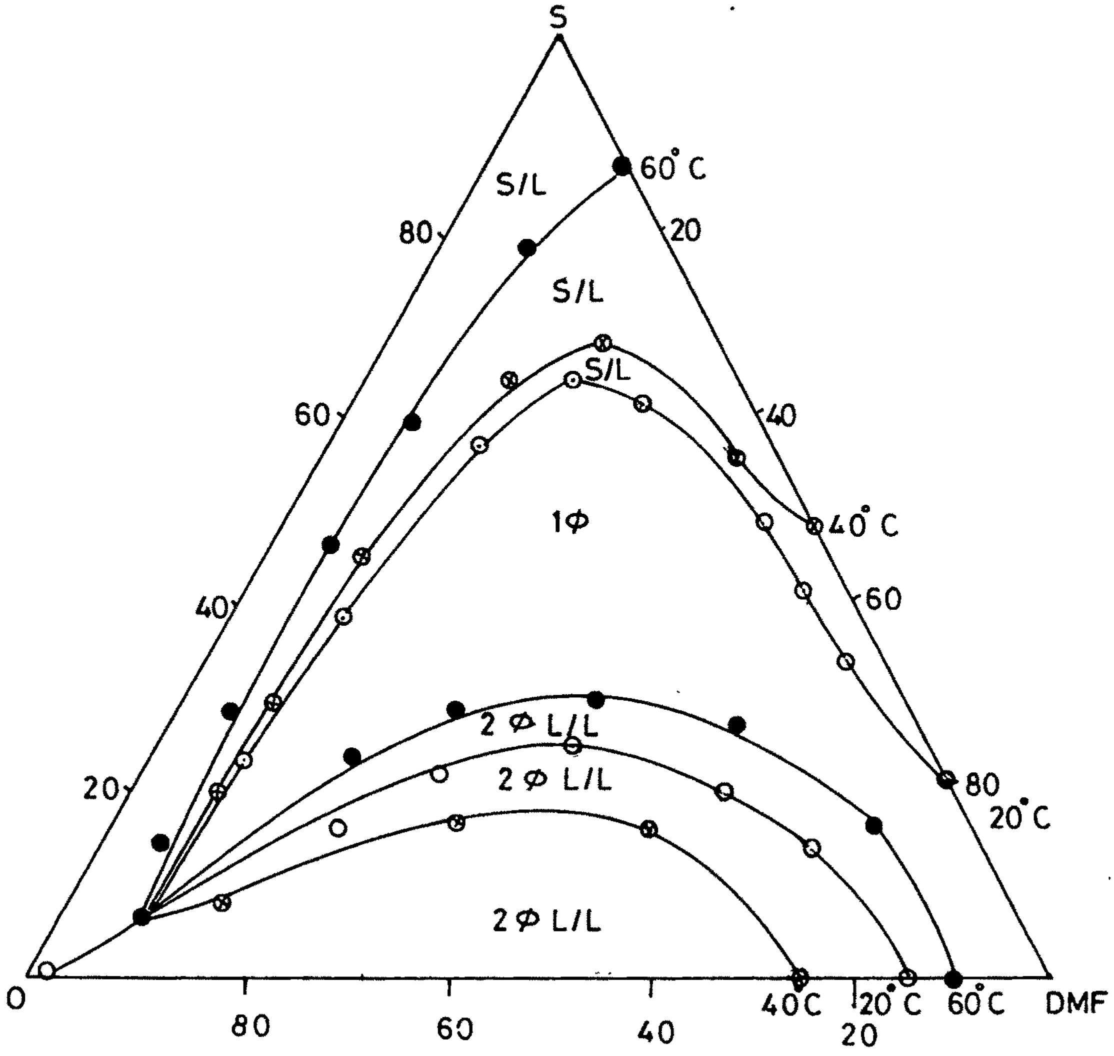

Fig. 5.1 : Pseudoternary phase diagram of system cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF (D) at (O) 20°C, (⊗) 40°C, (●) 60°C.

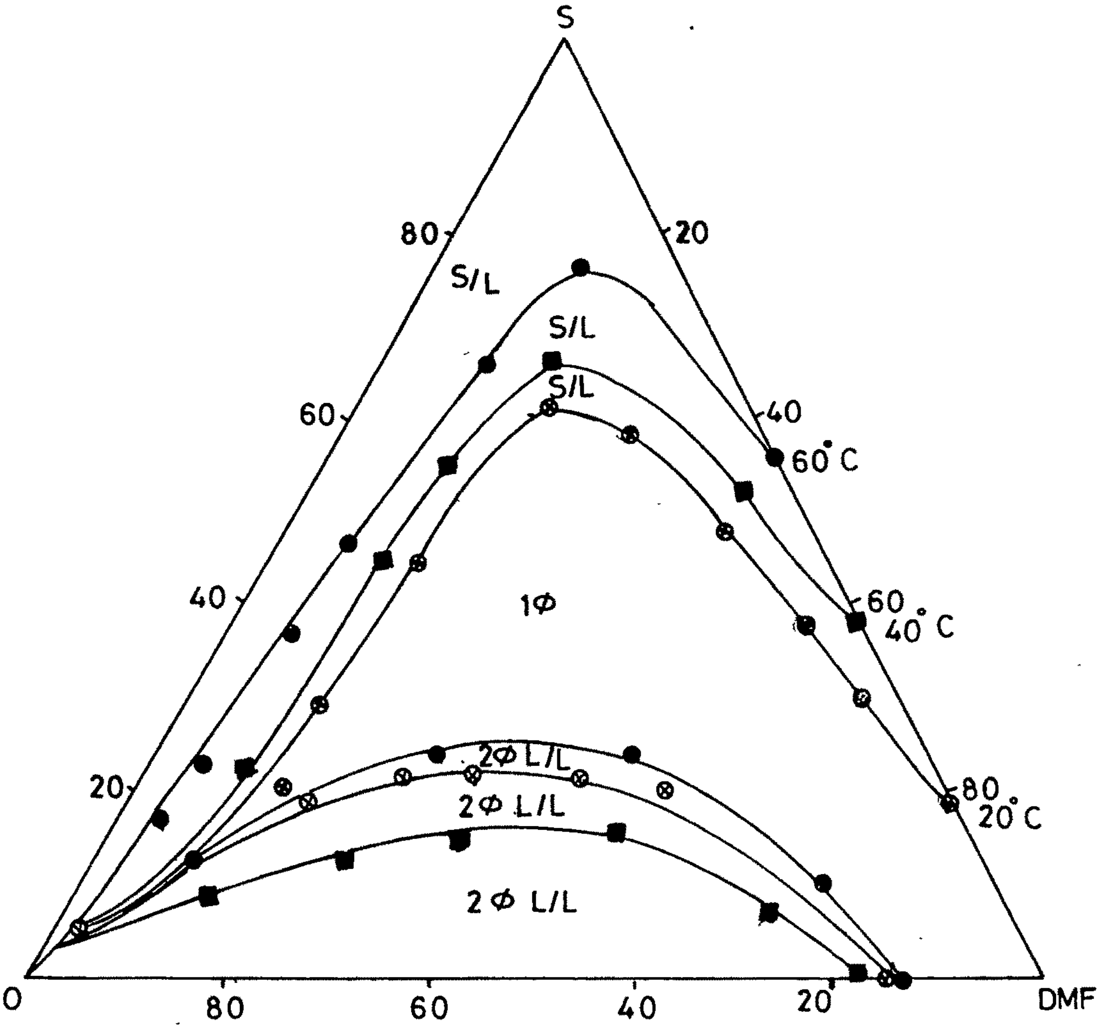

Fig. 5.2 : Pseudoternary phase diagram of cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF at (⊗) 20°C, (■) 40°C, (●) 60°C with 1% PEG-4000 (w/v).

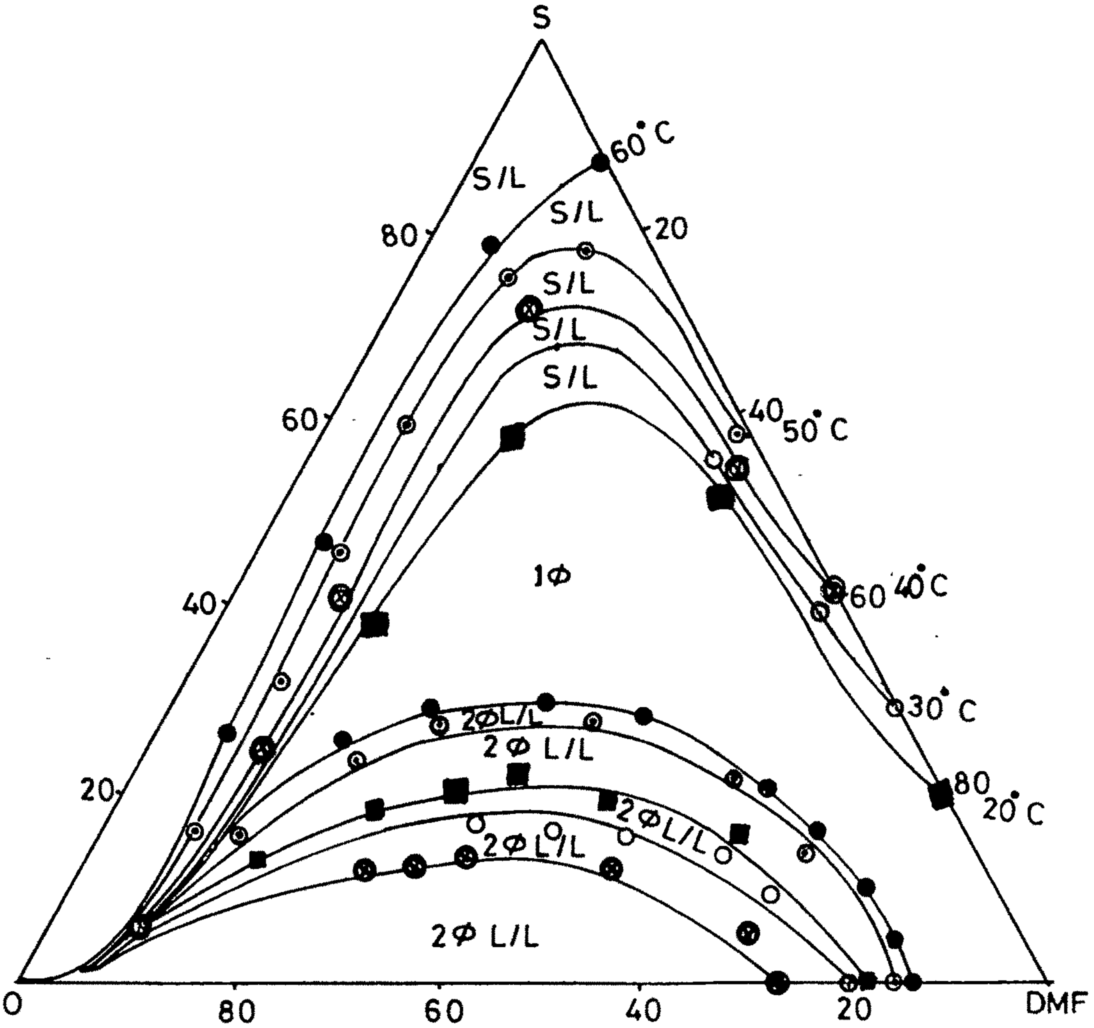

Fig. 5.3 : Pseudoternary phase diagram of cyclohexnae (O) / CTAB + 1-propanol (S) (1:2) / DMF at (■) 20°C, ( O ) 30°C, (⊗) 40°C, (⊙ ) 50°C, ( ●) 60°C with 1% PEG-4000 (w/v).

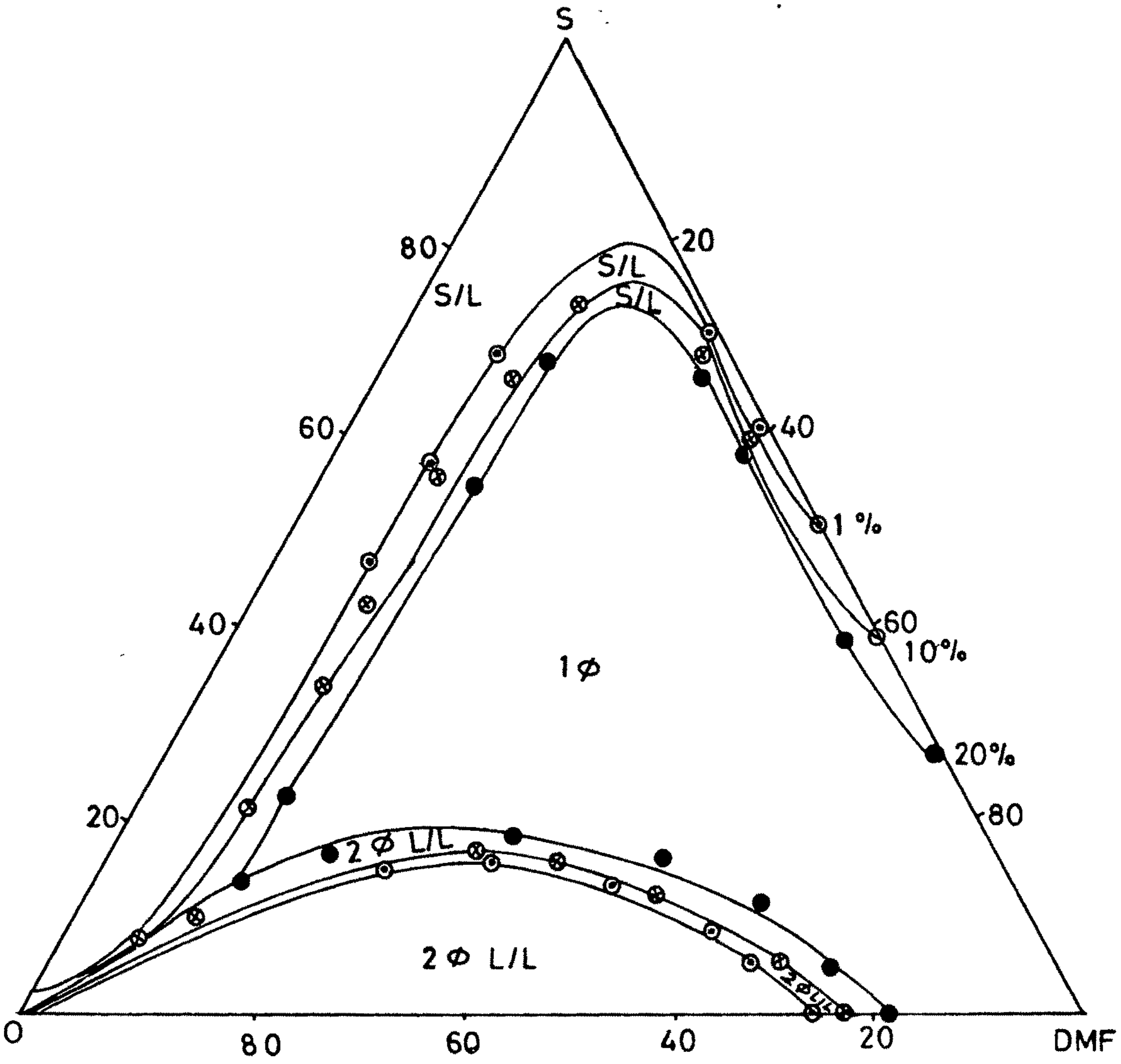

Fig. 5.4 : Pseudoternary phase diagram of cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF with (1%), (10%) and (20%) w/v PEG-4000.

Table 5.1 : Percentage Phase Regions in the Pseudoternary Phase Diagram of Cyclohexane / CTAB : 1-propanol is 1:2 (w/w) / 'X'

| 'X' | Temperature (°C) | 1ϕ (L) | 2ϕ (L/L) | 2ϕ (S/L) |
|---|---|---|---|---|
| DMF | 20 | 51.10 | 29.10 | 19.80 |
| DMF | 30 | 52.30 | 31.30 | 16.40 |
| DMF | 40 | 54.60 | 30.20 | 15.20 |
| DMF | 50 | 52.0 | 33.70 | 14.30 |
| DMF | 60 | 50.10 | 36.10 | 13.80 |
| DMF (PEG-4000 1%) | 20 | 52.10 | 21.20 | 26.70 |
| DMF (PEG-4000 1%) | 40 | 53.20 | 21.90 | 24.90 |
| DMF (PEG-4000 1%) | 60 | 52.80 | 24.40 | 22.70 |
| DMF (10% PEG-4000) | 40 | 51.70 | 22.40 | 25.30 |
| DMF (20% PEG-4000) | 40 | 50.19 | 22.11 | 27.70 |
| (30:70) DMF + Water | 40 | 49.80 | 44.10 | 6.09 |
| (70:30) DMF + Water | 40 | 50.20 | 42.57 | 7.22 |
| (50:50) DMF + Water | 40 | 49.50 | 44.29 | 6.20 |

(WIV) area is larger in non-aqueous pseudoternary phase diagram in comparison to that in an aqueous system at the corresponding temperature.

The effect of different percentage of polyethylene glycol shows that the nature of phase diagram remains the same i.e. upper corner of the phase diagram shows solid / liquid binary system in equilibrium with one phase and one phase (1ϕ) liquid remains in equilibrium with two phase (2ϕ) (liquid/liquid) region. The addition of 1% (w/v) polyethylene glycol 4000 shows that with addition of 1% (w/v) of PEG-4000, the one phase (1ϕ) microemulsion region does not change much with temperature, indicating that a temperature independent microemulsion is formed. The addition of more PEG-4000 i.e. 10%, 20% (w/v) shown in Fig. 5.4 that there is no further change in the one phase (1ϕ) region though some changes occurred in the aqueous system. Thus the monophasic region is not dependent on the concentration of PEG-4000 in this non-aqueous μE. Thus, the overall stability of the monophasic region is increased by PEG-4000 though it seems that the stability and the percentage region are independent of PEG-4000 concentration.

Fig.5.5a and 5.5b show the interfacial tension as a concentration of CTAB in this system where the interfacial tension measured with cyclohexane was kept 57% (v/v) constant, 1-propanol 3% (v/v) and other components were varied. But the concentration of cosurfactant was kept constant which shows that IFT is decreasing upto $10^{-2}$ $mNm^{-1}$ so there is a probability of formation of microemulsion.

### 5.3.2 Viscosity Study :

Viscosity of 1ϕ microemulsion of cyclohexane / CTAB + 1-propanol / DMF against weight fraction of DMF is shown in Fig. 5.6 and 5.7. The viscosity was measured for the different system by varying weight fraction of DMF as well as cyclohexane by keeping S+CS at constant weight fraction of 45%. In Fig. 5.6, it is shown without PEG-4000 and in Fig.5.7 also with PEG-4000. It increases gradually with increasing DMF content. The rate of change of viscosity is almost constant. It shows that a

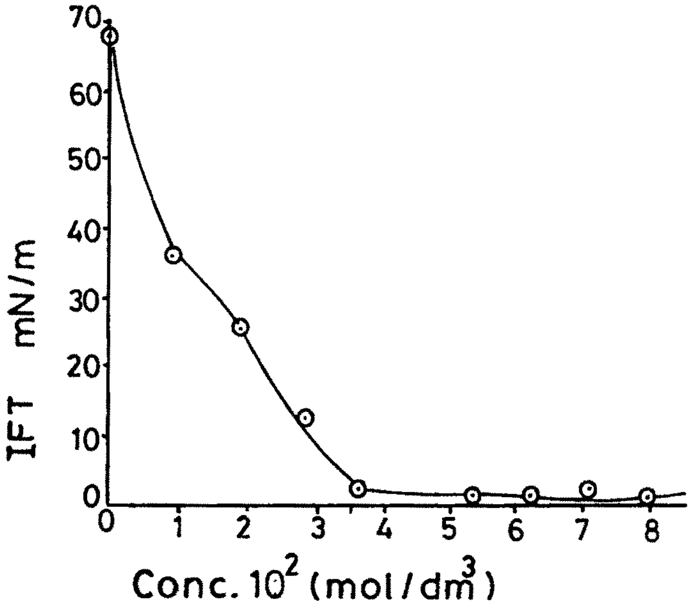

Fig. 5.5a : Plot of interfacial tension IFT (mN/m) as a function of concentration of CTAB (mol/dm$^3$).

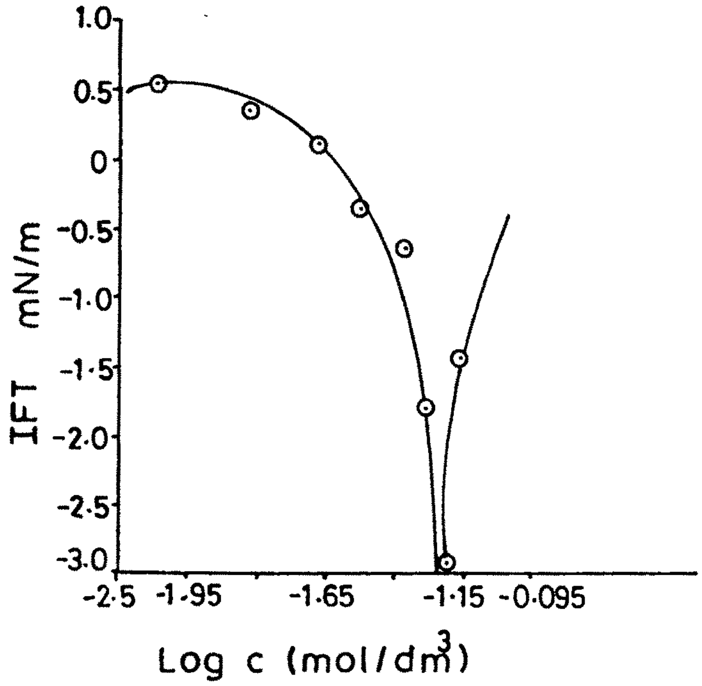

Fig. 5.5b : Plot of log interfacial tension IFT (mN/m) as a function of log concentration of CTAB (mol/dm$^3$).

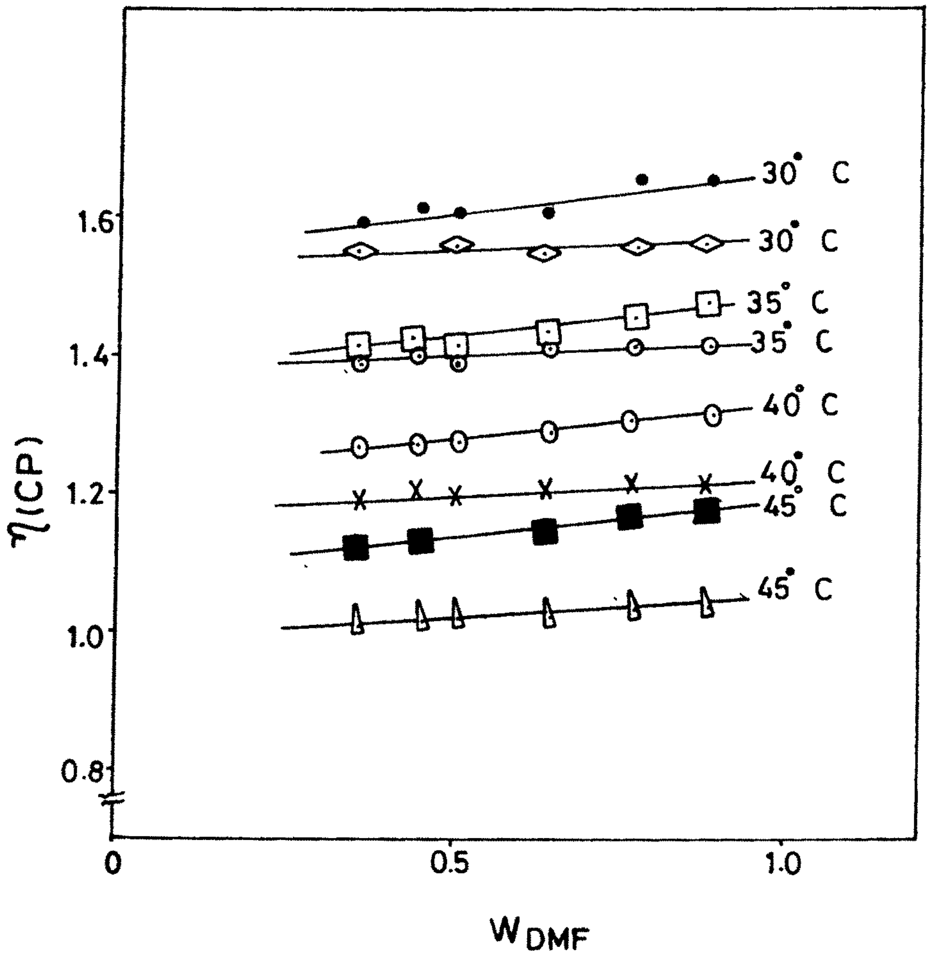

Fig. 5.6 : Plot of viscosity η(cp) Vs weight fraction of DMF $W_{DMF}$ with 45% S+CS

| | With 1% PEG-4000 | | Without PEG-4000 |
|---|---|---|---|
| at | 30°C (●) | at | 30°C (◈) |
| | 35°C (⊡) | | 35°C (⊙) |
| | 40°C (⊙) | | 40°C (×) |
| | 45°C (■) | | 45°C (△) |

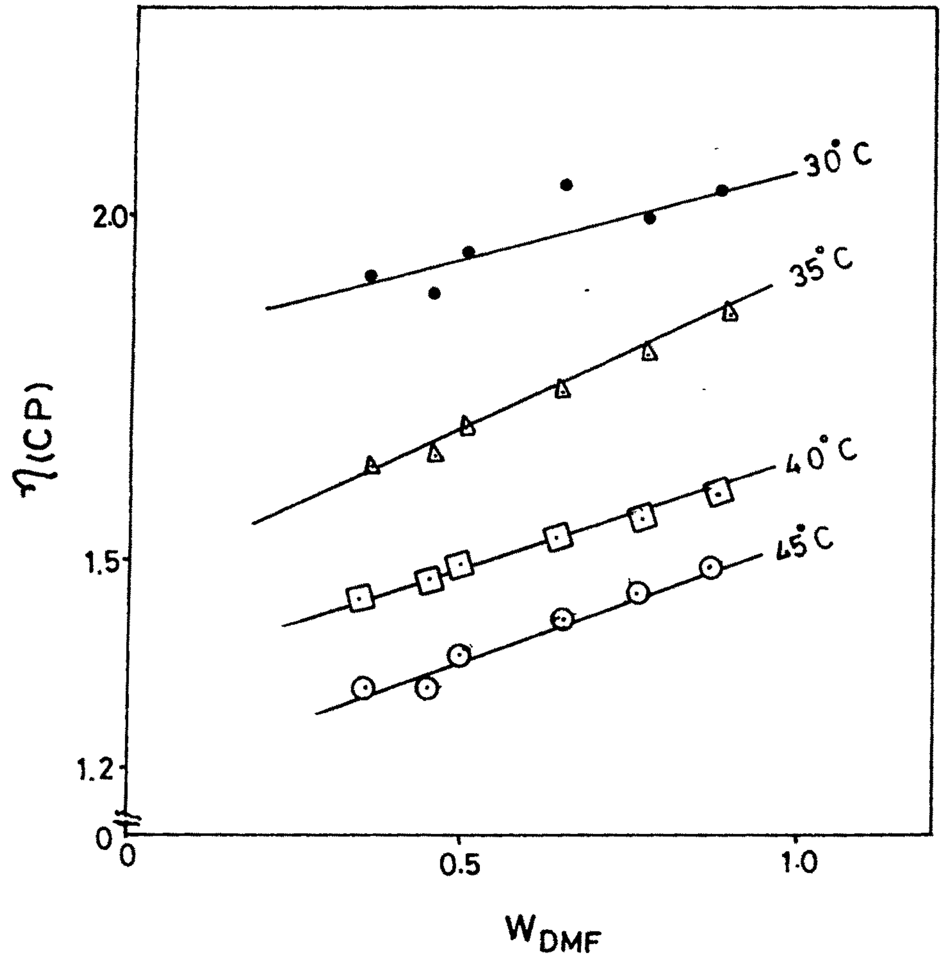

Fig. 5.7 : Plot of viscosity η(CP) Vs weight fraction of DMF ($W_{DMF}$) with 10% PEG-4000 at 30, 35, 40 and 45°C.

decrease in viscosity was generally due to a decrease in the size of DMF conduit. However, in this case the decrease in viscosity may be due to the structural changes of the microemulsion as the O/D ratio decreases (here D presents DMF). It was observed in the aqueous system that because of dilution, a decrease in viscosity was observed when the concentration of water became high. However, when DMF was used no such maximum was observed.

### 5.3.3 Conductance Study :

For non-aqueous system, the specific conductance increases from a low DMF content to a high DMF content at 45% surfactant concentration (Figs. 5.8 to 5.12). The system does not show percolation behaviour at 40°C, which suggests a single structured form of different compositions studied. The specific conductance increases gradually as the DMF concentration is raised. This suggests the absence of percolation and also absence of any microstructural change. However, at 70°C and 80°C the extrapolated line bisects little to the 'x' axis which is negligible. Since it is from very high weight fraction of DMF ($W_{DMF}$) to zero weight fraction of DMF ($W_{DMF}$). Thus, we can neglect the percolation phenomena in this system.

Thus, the structure is bicontinuous. Also by applying Lagourette's equation $\sigma^{13,16}\ \alpha\ (\phi_D-\phi^P_D)^t$ where $\phi^P_D$ is the percolation threshold i.e. the concentration above which percolation can be seen. It was also suggested that for bicontinuous system $t = 8/5$ i.e.

$$\sigma\ \alpha\ (\phi_D-\phi^P_D)^{8/5} \text{ or } \sigma = k\ (\phi_D-\phi^P_D)^{8/5} \text{ or } \sigma^{5/8} = k'\ (\phi_D-\phi_D^P) \text{ where } k' = k^{5/8}$$

where $k'$ is constant. Thus, a plot of $\sigma^{5/8}$ versus $\phi_D$ should meet 'X' axis at $k'\phi^P_D$. Fig.5.10 represents such plot and similar plots have been observed in many aqueous system. Peyrelasse et al.[17] observed percolation in a non-aqueous microemulsion. Fig.5.11 and 5.12 show that at constant DMF ($W_{DMF}$) = 17.5% as well as cyclohexane there is no change in structure. There is an absence of the percolation which is seen from the plot of $\sigma^{5/8}$ vs DMF weight fraction ($W_{DMF}$) which is because of extrapolation at high DMF ($W_{DMF}$) weight fraction to low DMF ($W_{DMF}$) weight

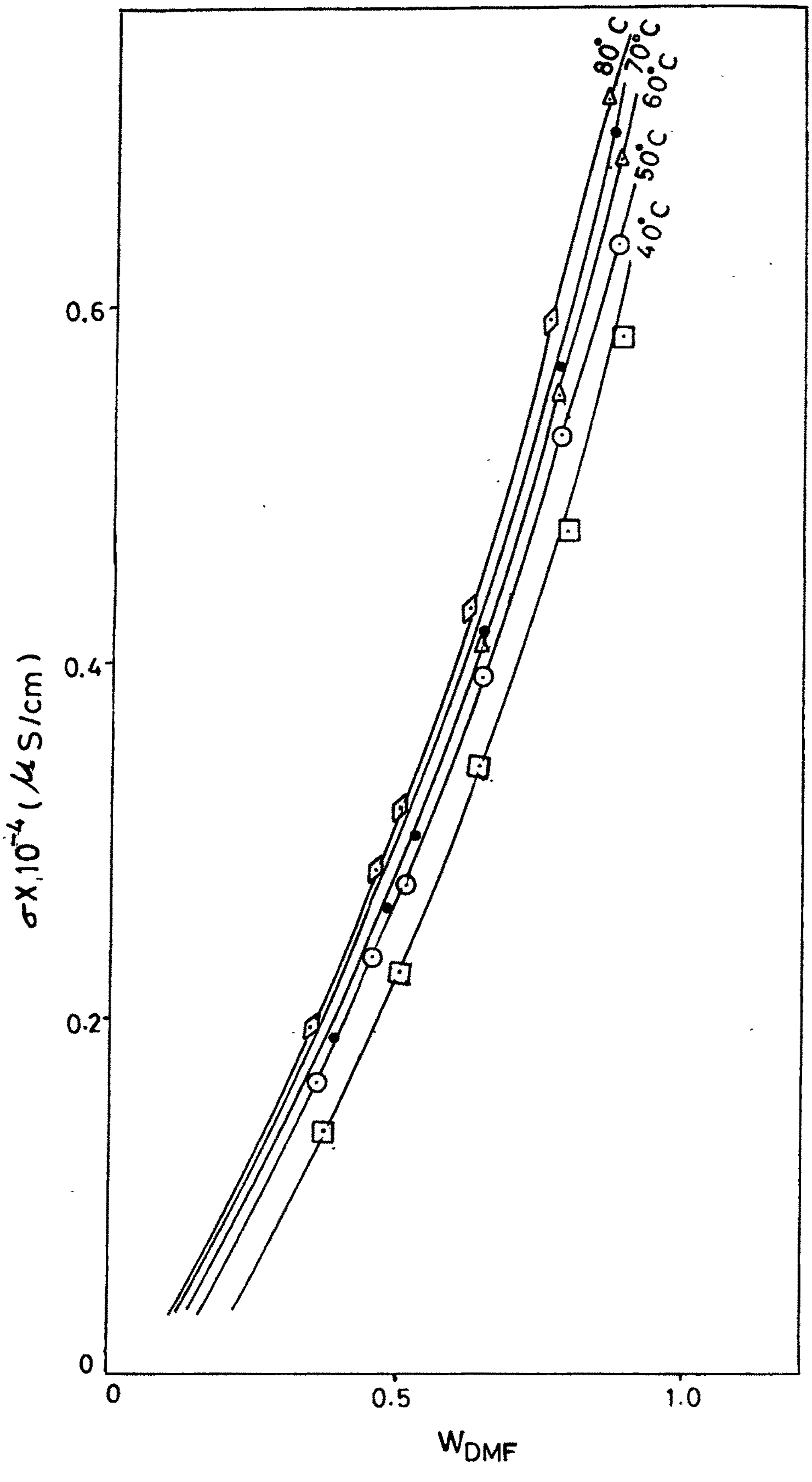

Fig. 5.8 : Plot of conductance σ (μs/cm) Vs weight fraction of DMF ($W_{DMF}$) at 40, 50, 60, 70 and 80°C.

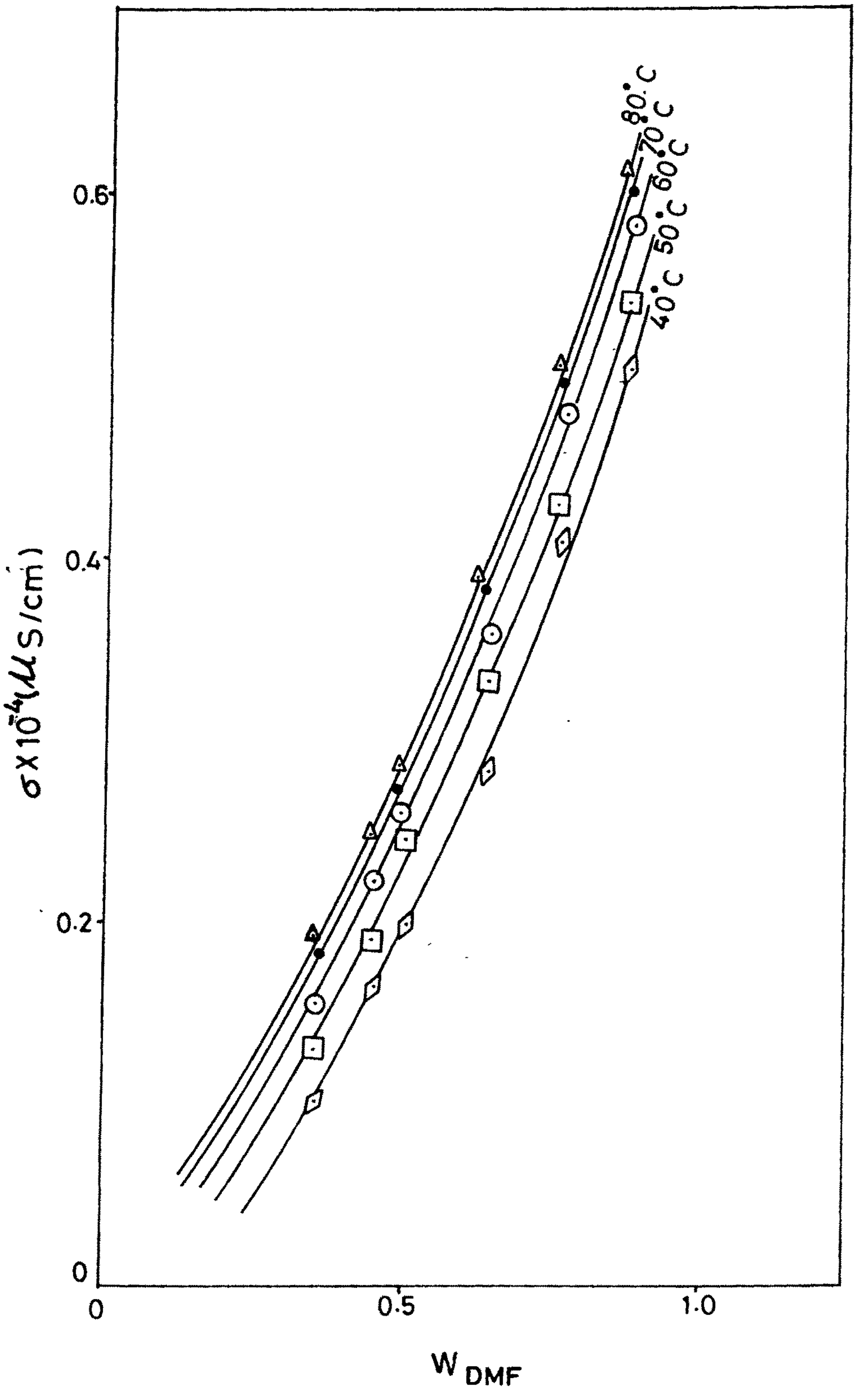

Fig. 5.9 : Plot of conductance σ (μs/cm) Vs weight fraction of DMF ($W_{DMF}$) at 40, 50, 60, 70 and 80°C with 1% PEG-4000.

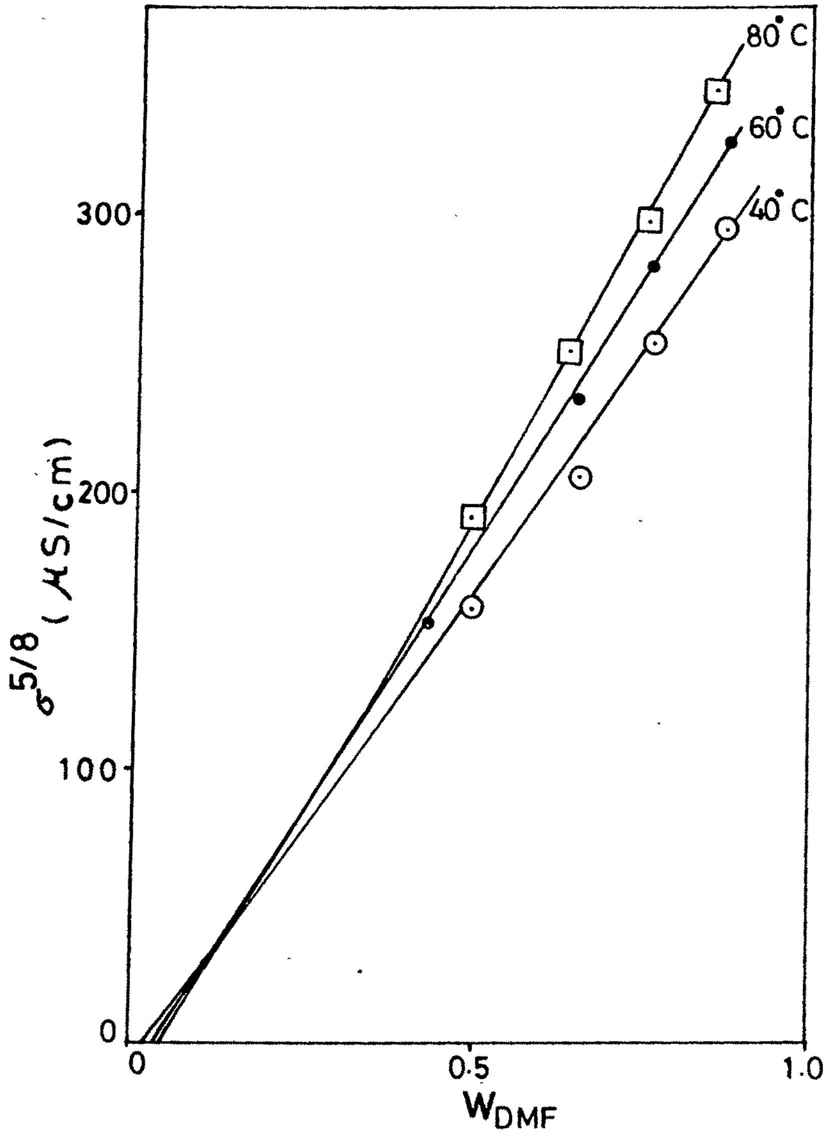

Fig. 5.10 : Plot of $\sigma^{5/8}$ (μs/cm) Vs weight fraction of DMF ($W_{DMF}$) at 40, 50, 60, 70 and 80°C.

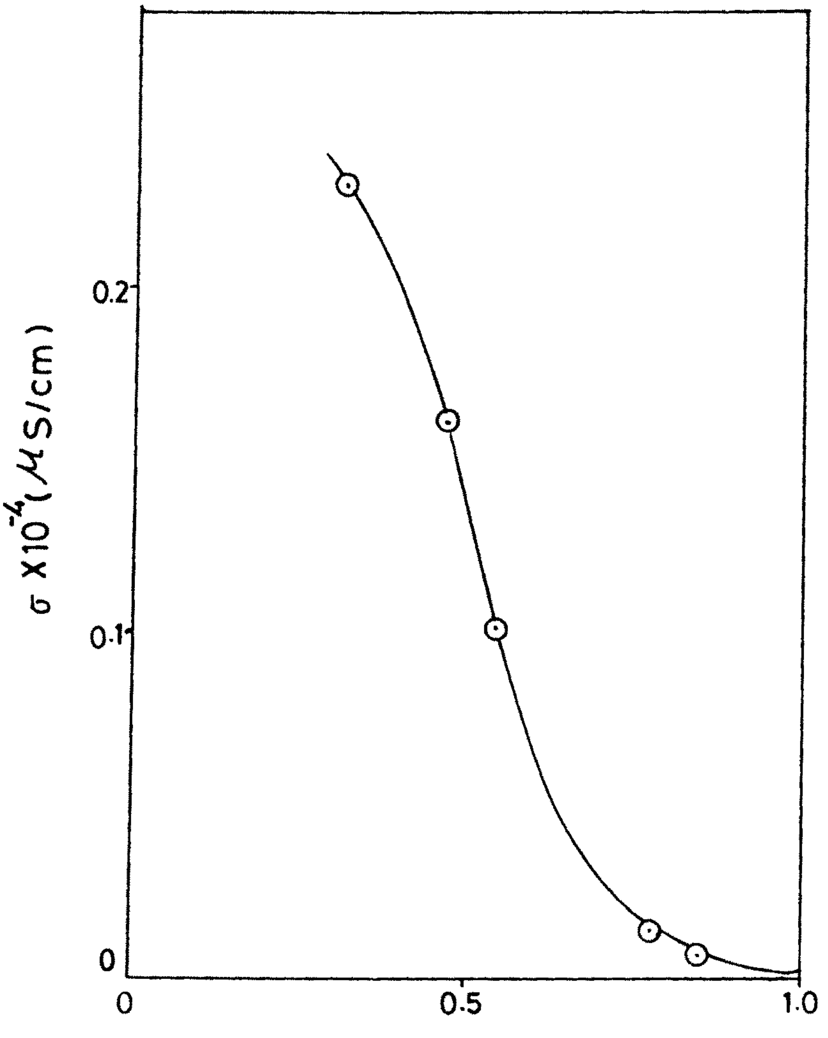

Fig. 5.11 : Plot of specific conductance σ (μs/cm) against weight fraction of cyclohexane (W cyclohexane) at constant DMF = 17.5% at 40°C.

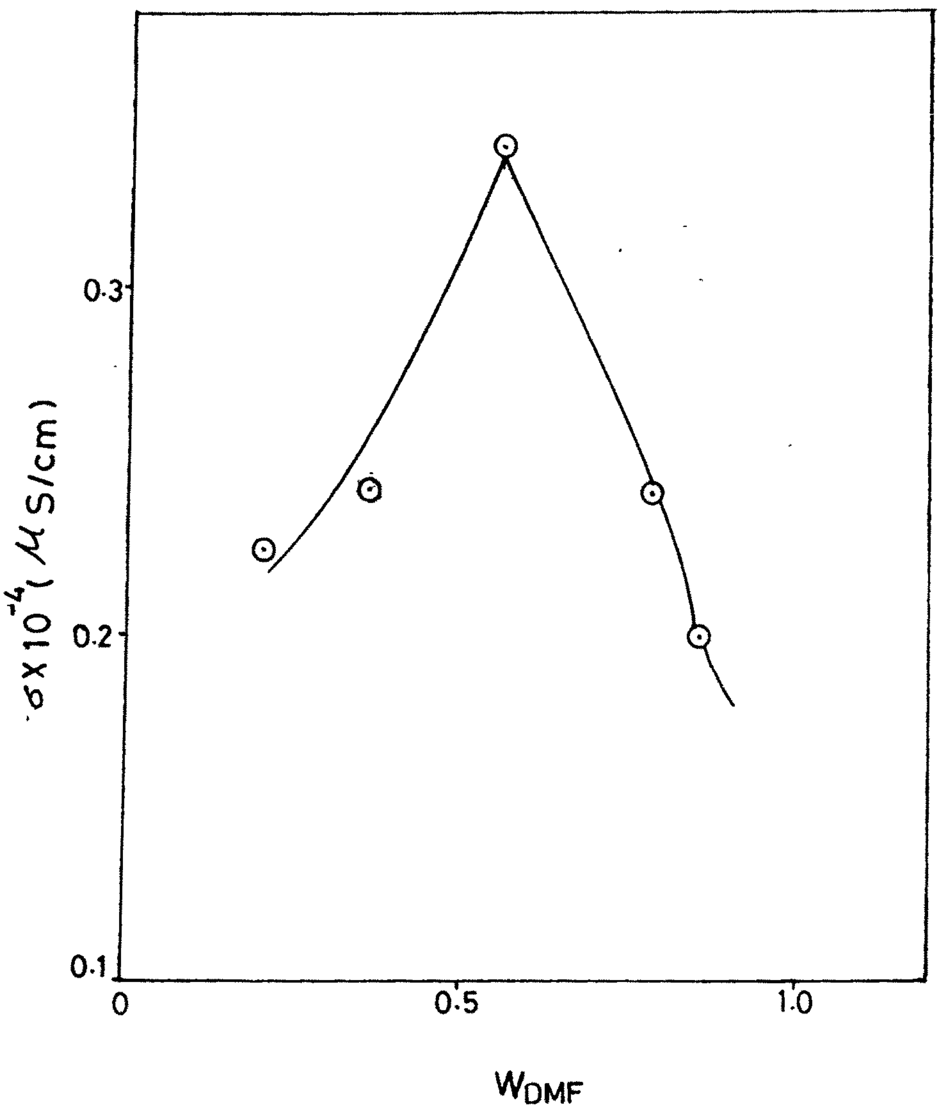

Fig. 5.12 : Plot of specific conductance σ (μs/cm) Vs weight fraction of DMF ($W_{DMF}$) cyclohexane at constant cyclohexane = 17.5% at 40 °C.

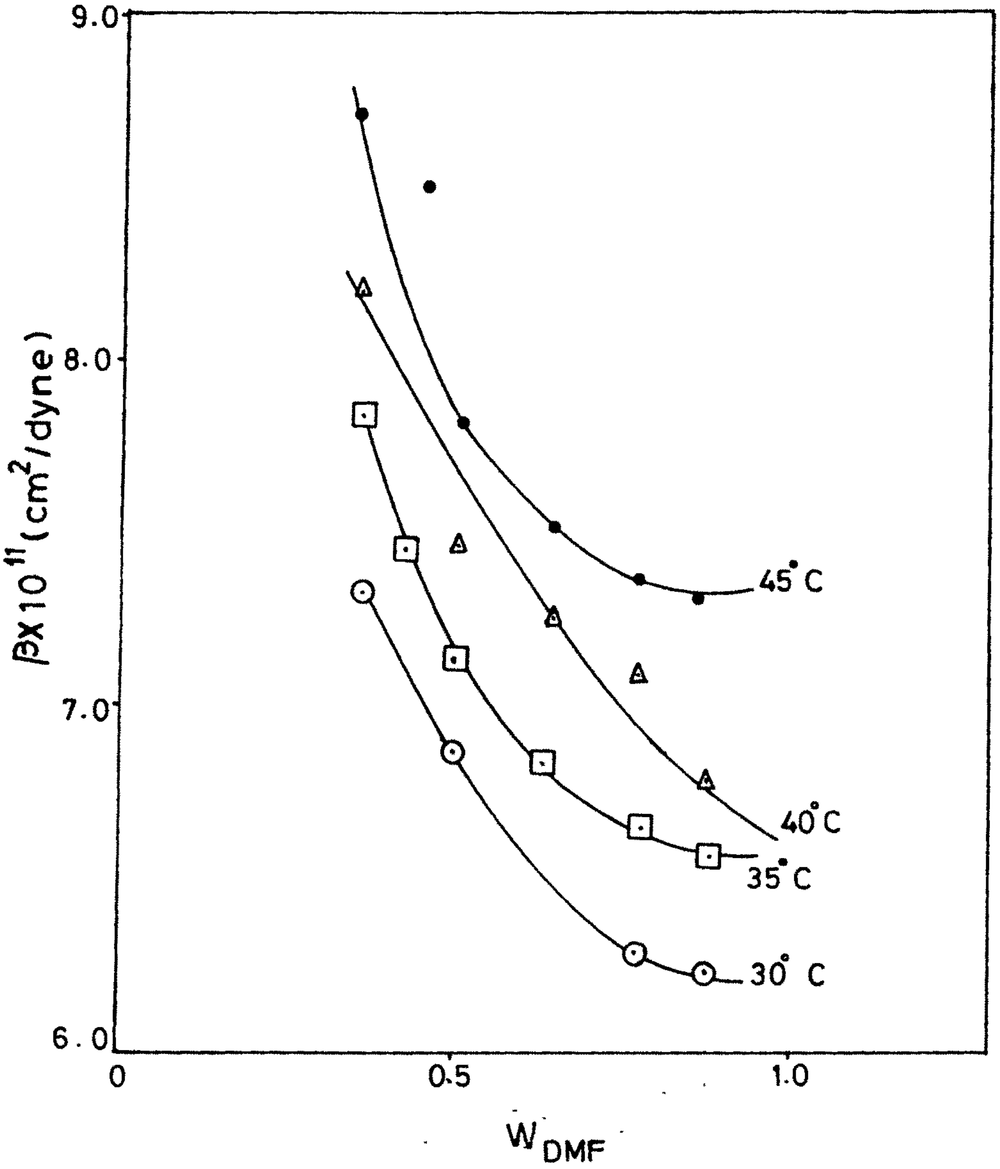

Fig. 5.13 : Plot of adiabatic compressibility (β) against weight fraction $W_{DMF}$ at (⊙) 30°C, (⊡) 35°C, (△) 40°C, (●) 45°C.

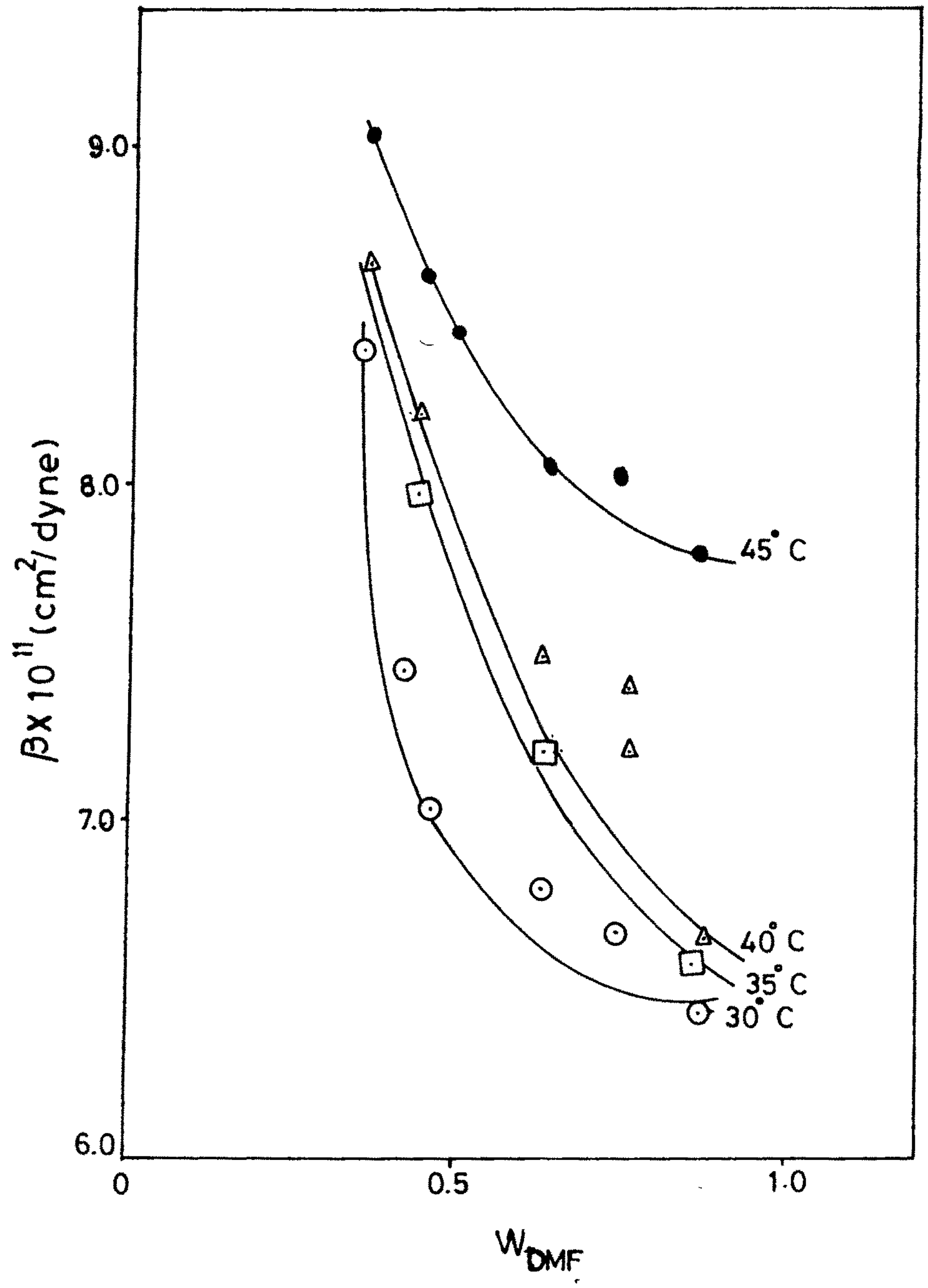

Fig. 5.14 : Plot of adiabatic compressibility (β) Vs weight fraction W$_{DMF}$ with 45% S+CS, 1% PEG-4000. (⊙) 30°C, (⊡) 35°C, (◬) 40°C, (●) 45°C.

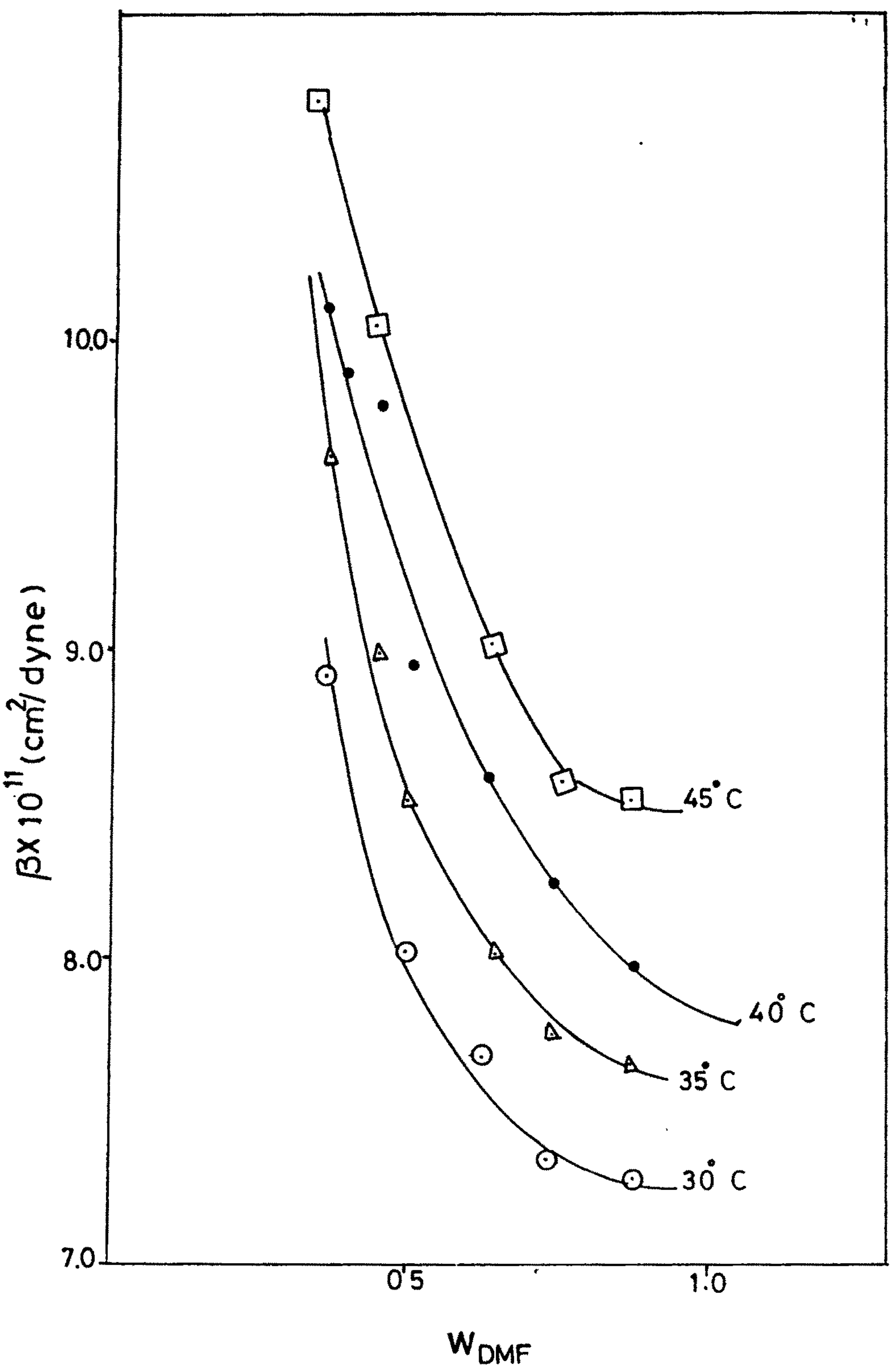

Fig. 5.15 : Plot of adiabatic compressibiloty (β) against weight fraction $W_{DMF}$ with 45% S+CS with 10% PEG-4000. (⊙) 30°C, (△) 35°C, (●) 40°C, (⊡) 45°C.

fraction. Thus temperature percolation is also absent. Addition of 1% PEG-4000 showed decrease in the conductance because it is soluble in DMF and probably remains at the interface between an oil and DMF. So there is an increase in conductance with increase in temperature. There is no percolation threshold present. Hence, with increase in temperature the structure remains bicontinuous.

### 5.3.4 Adiabatic compressibility :

The Fig.5.13-5.15 show the variation of adiabatic compressibility (β) as a function of the weight fraction of DMF. Compressibility (β) decreases with increase in the weight fraction of DMF. The change in the temperature show that compressibility (β) decreases which shows the expected behaviour[16,18,19] but compared to pure aqueous the compressibility is more because of DMF and hence the structure is less rigid compared to pure aqueous. The polymer PEG-4000 had no significant effect on the compressibility.

### 5.3.5 Phase behaviour of mixed aquo-nonaquo microemulsion :

It is necessary to study the phase behaviour of aqueous and non-aqueous microemulsion. Large number of studies show the behaviour of mixed surfactant, cosurfactant or oil. So it is necessary to study the effect of polar mixed liquid on microemulsion.

Figs. 5.16 to 5.18 show the phase behaviour of the system cyclohexane / CTAB + 1-propanol / DMF + water. DMF + water were kept at 50:50 weight[20,21,22,23] by weight. Earlier study show that CTAB is able to form the micelle in the DMF + water[23]. Phase diagrams of all systems show similar pattern with differences in the area of monophasic regions. The studies indicate the different ratio of DMF + water at 30°C. The different zones studied show that solid / liquid (2ϕ), are in equilibrium with liquid / liquid (2ϕ) and one phase (1ϕ) liquid. Addition of salt added to the system did not result in the three phase formation as was observed earlier in the aqueous system. All the measured phase areas are presented in the Table 5.1.

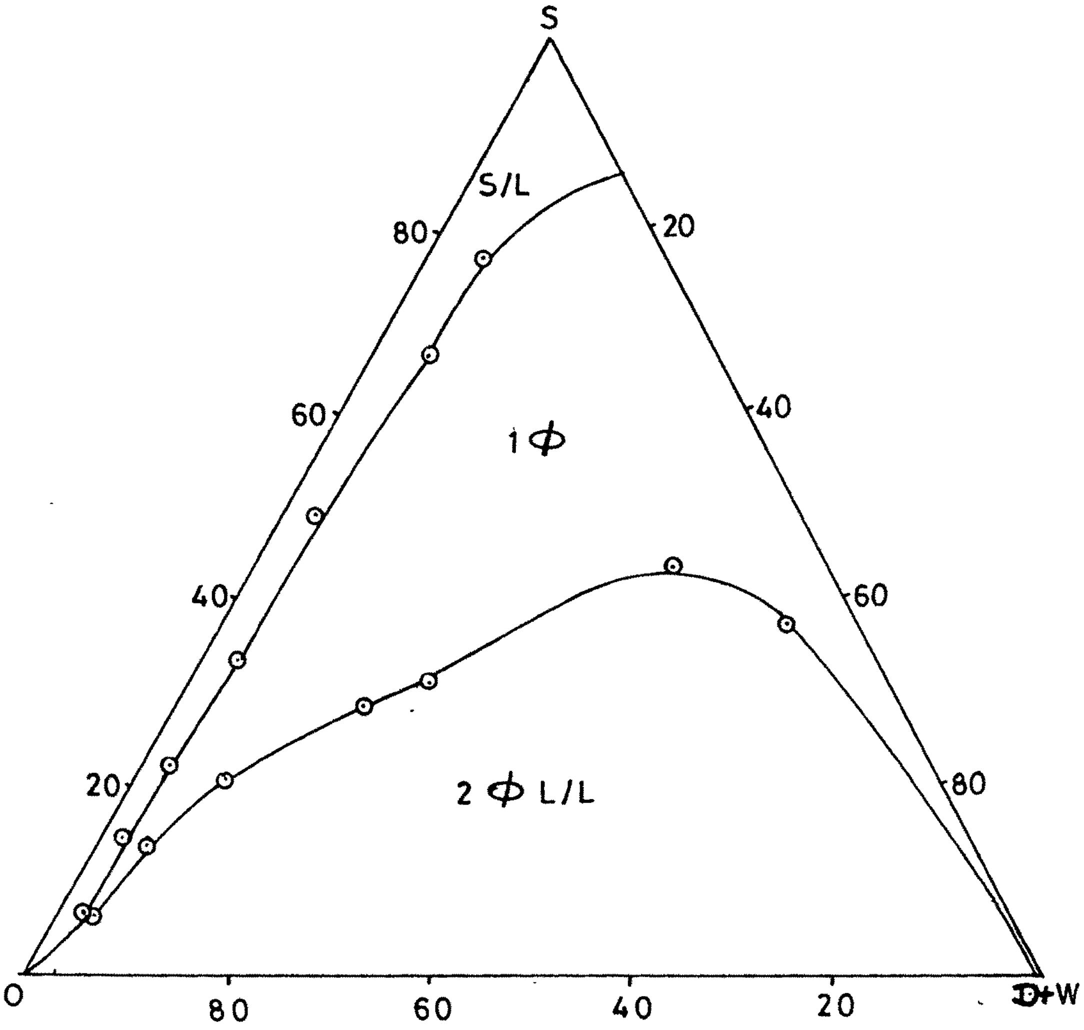

Fig. 5.16 : Pseudoternary phase diagram of cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF + Water (D+W) (50:50) (w/w) at 30°C.

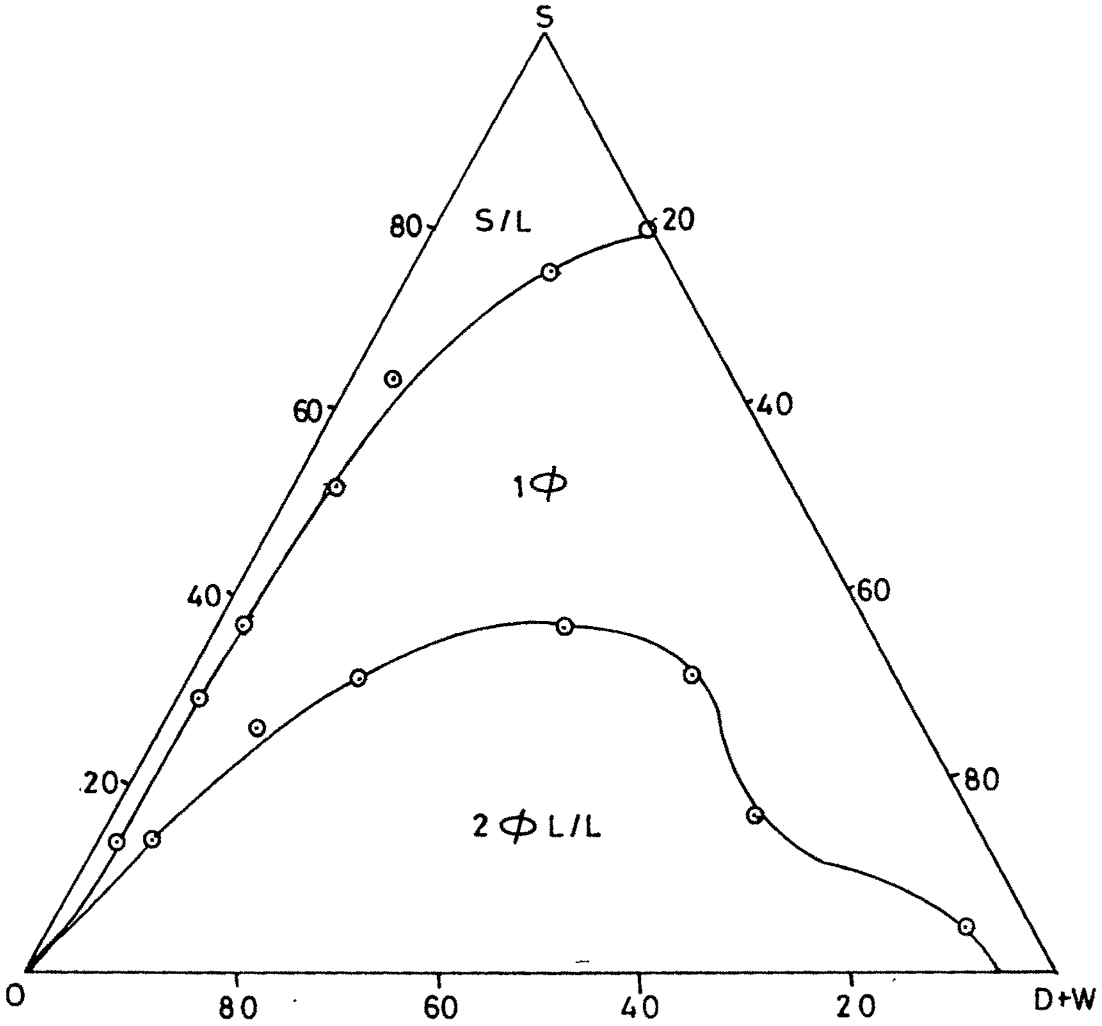

Fig. 5.17 : Pseudoternary phase diagram of cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF + Water (D+W) (70:30) w/w at 30°C.

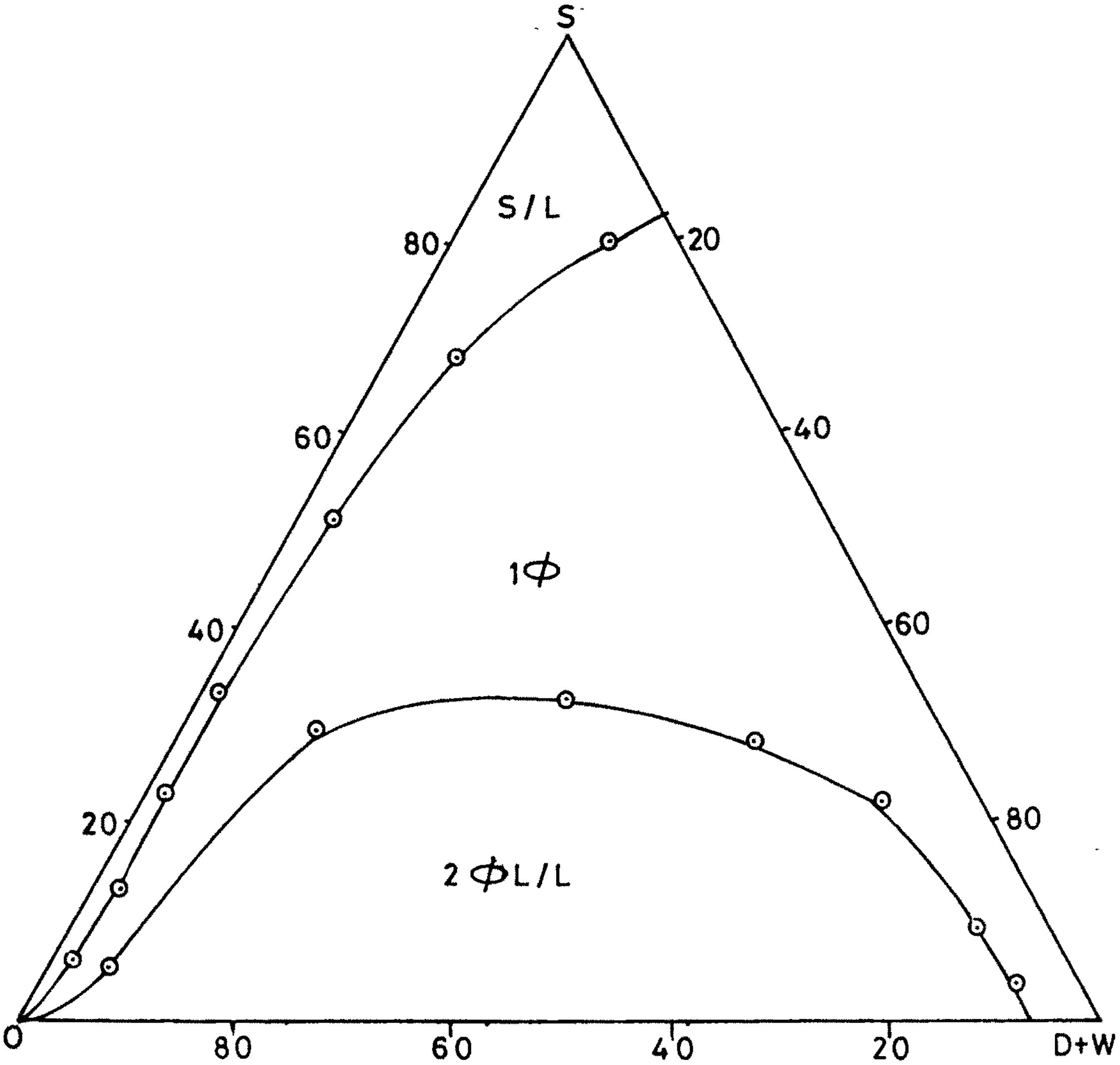

Fig. 5.18 : Pseudoternary phase diagram of cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / DMF + Water (D+W) (30 : 70) at 30°C.

In this chapter, we present the physicochemical properties of the monophasic region of the above mentioned system. The monophasic region measured is presented in the Table 5.1. Since the water is more polar than DMF the phase areas show more similarity towards water as water concentration increases. So as the percentage of water increases the solid / liquid region decreases but liquid / liquid region increases which compensate the one phase region. We studied the physicochemical behaviour with 50:50 of DMF + water. All the properties have been studied at constant 45% S + CS.

### 5.3.6 Conductance study :

Fig. 5.19 show the variation of conductance as a weight fraction of water + DMF i.e. $W_{D+W}$. Conductance measurement show that with increase in temperature it increases but around $W_{D+W} > 0.6$ there is some type of a non-continuity. Thus, the structure of microemulsion remains bicontinuous in the above region studied. By applying the Lagourette equation $\sigma^{13,16} \propto (\phi_{D+W} - \phi^{P}_{D+W})^{t}$ where $\phi_{D+W}$ is the weight fraction of DMF + water i.e.

$$\frac{\text{weight of (D+W)}}{\text{weight of (D+W) + weight of oil (O)}}$$

From this relation, we found that there is no percolation in this system (Fig.5.19b).

### 5.3.7 Viscosity Study :

Fig. 5.20 show the variation of viscosity $\eta$(cp) as a function of weight fraction of the DMF + water, a maximum is observed around 0.75 concentration of DMF + water, which indicates the change in the system from bicontinuous to O / DMF + Water regime. The decrease in viscosity is probably because of the dilution by further addition of DMF + water. The viscosity was taken at the different temperatures from 30 to 45°C which show that with DMF + water with temperature, the viscosity is increasing with increasing temperature. The surfactant + cosurfactant concentration was kept at 45%.

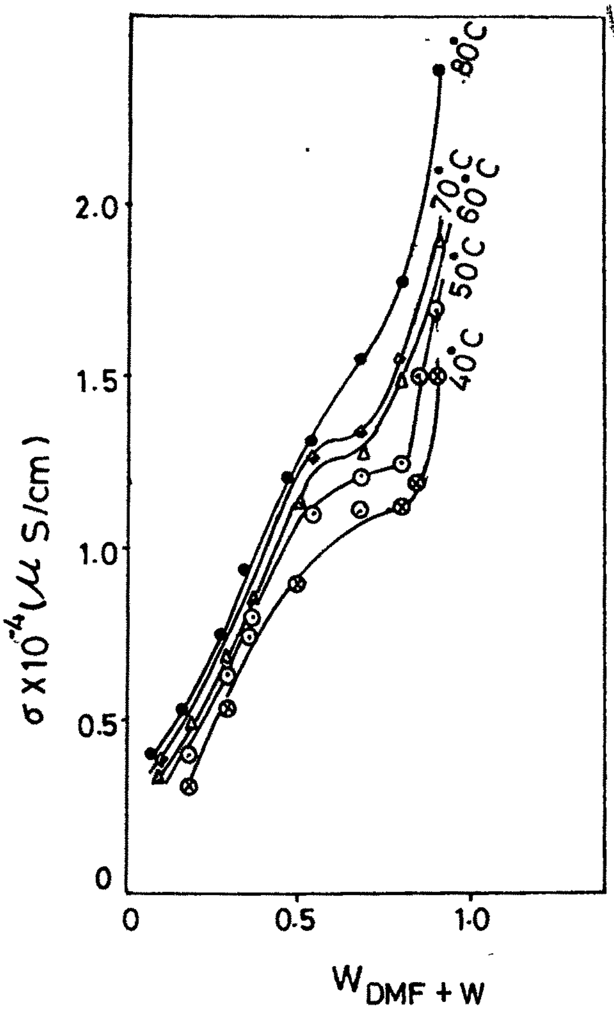

Fig. 5.19a : Plot of specific conductance (σ) against weight fraction DMF + Water ($W_{D+W}$) (50:50 w/w).

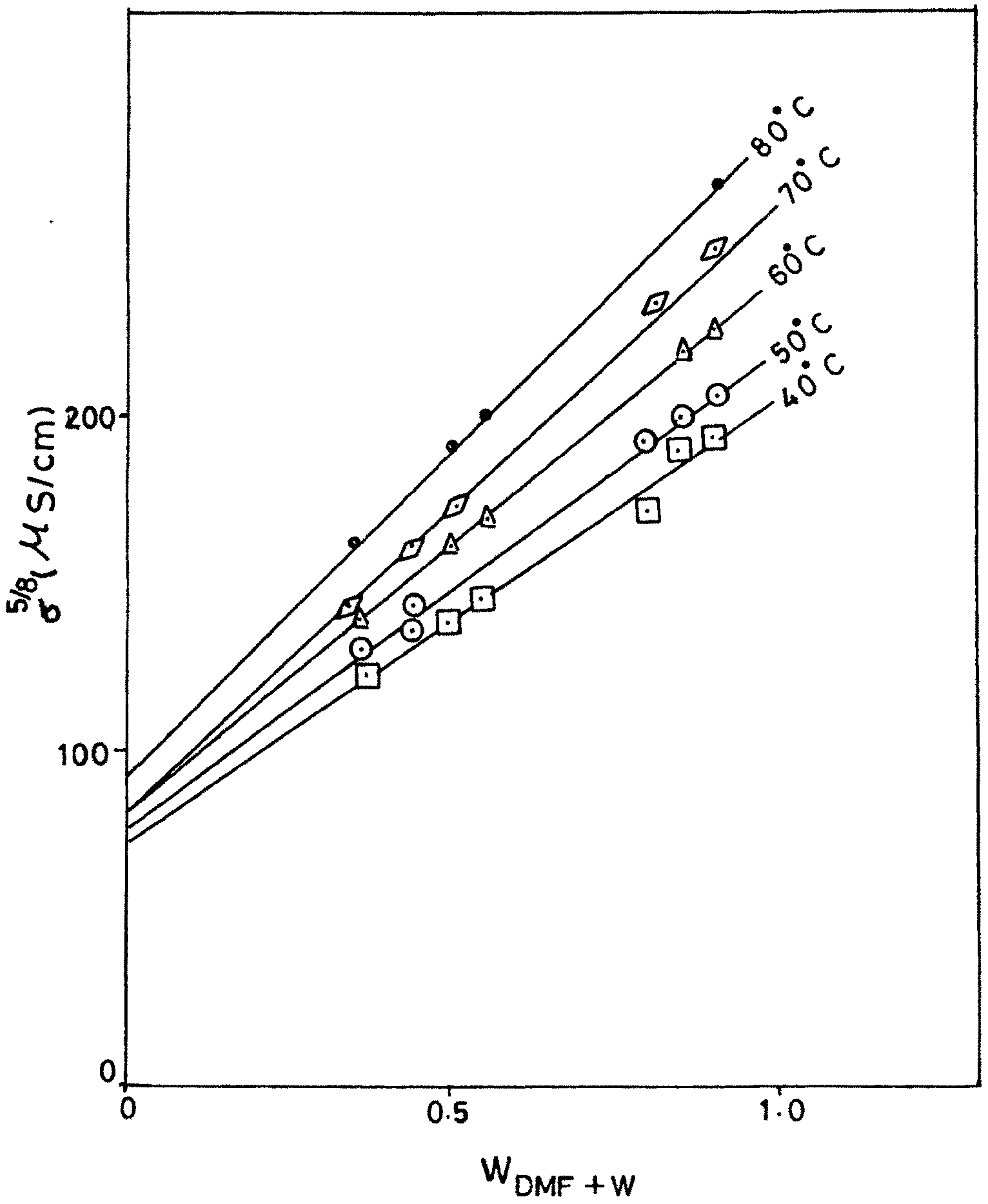

Fig. 5.19b : Plot of specific $\sigma^{5/8}$ against weight fraction DMF + Water ($W_{D+W}$) (50:50 w/w).

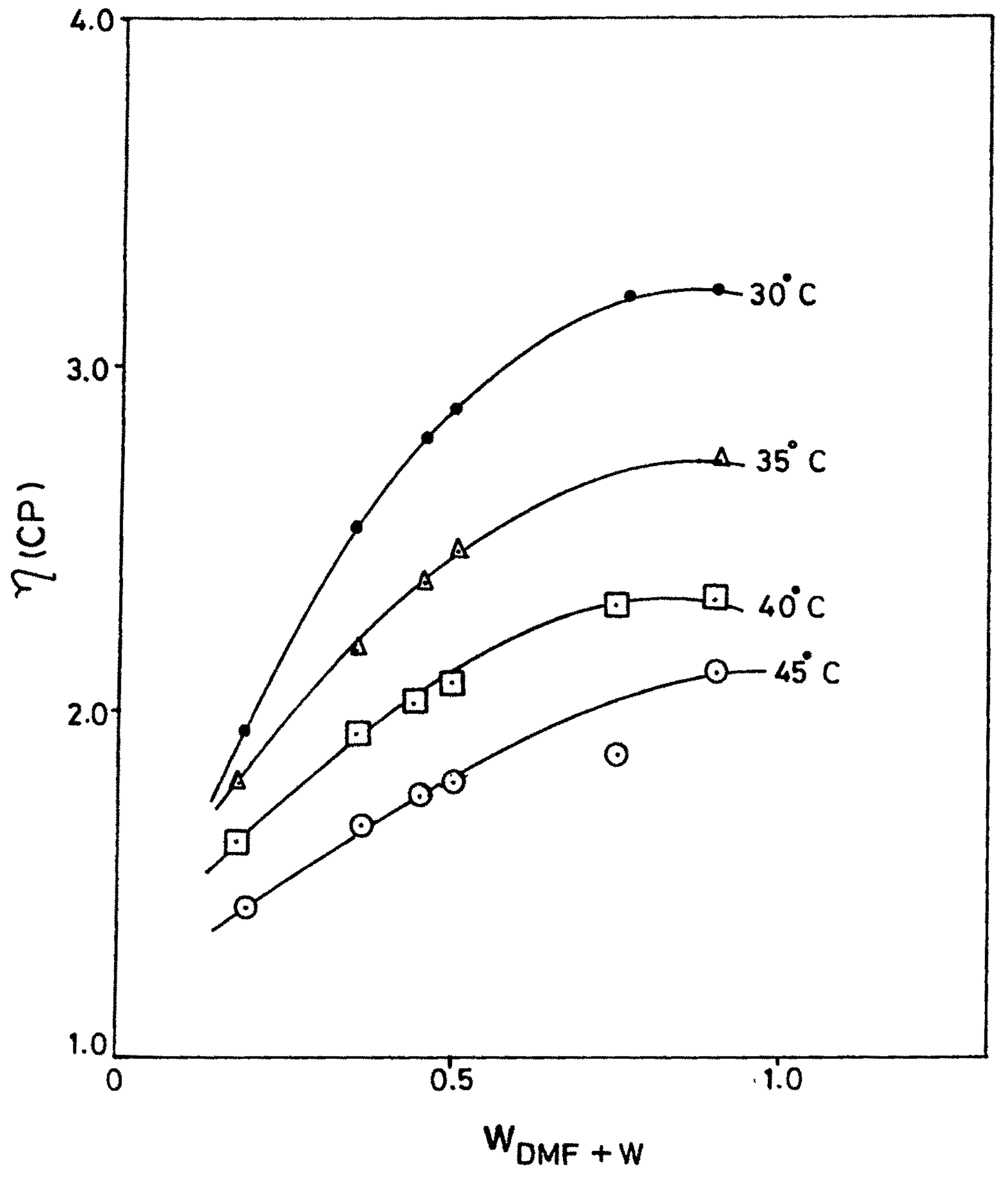

Fig. 5.20 : Plot of viscosity η(CP) Vs weight fraction DMF + Water ($W_{D+W}$) (50:50 w/w) at 30°C, 35°C, 40°C and 45°C.

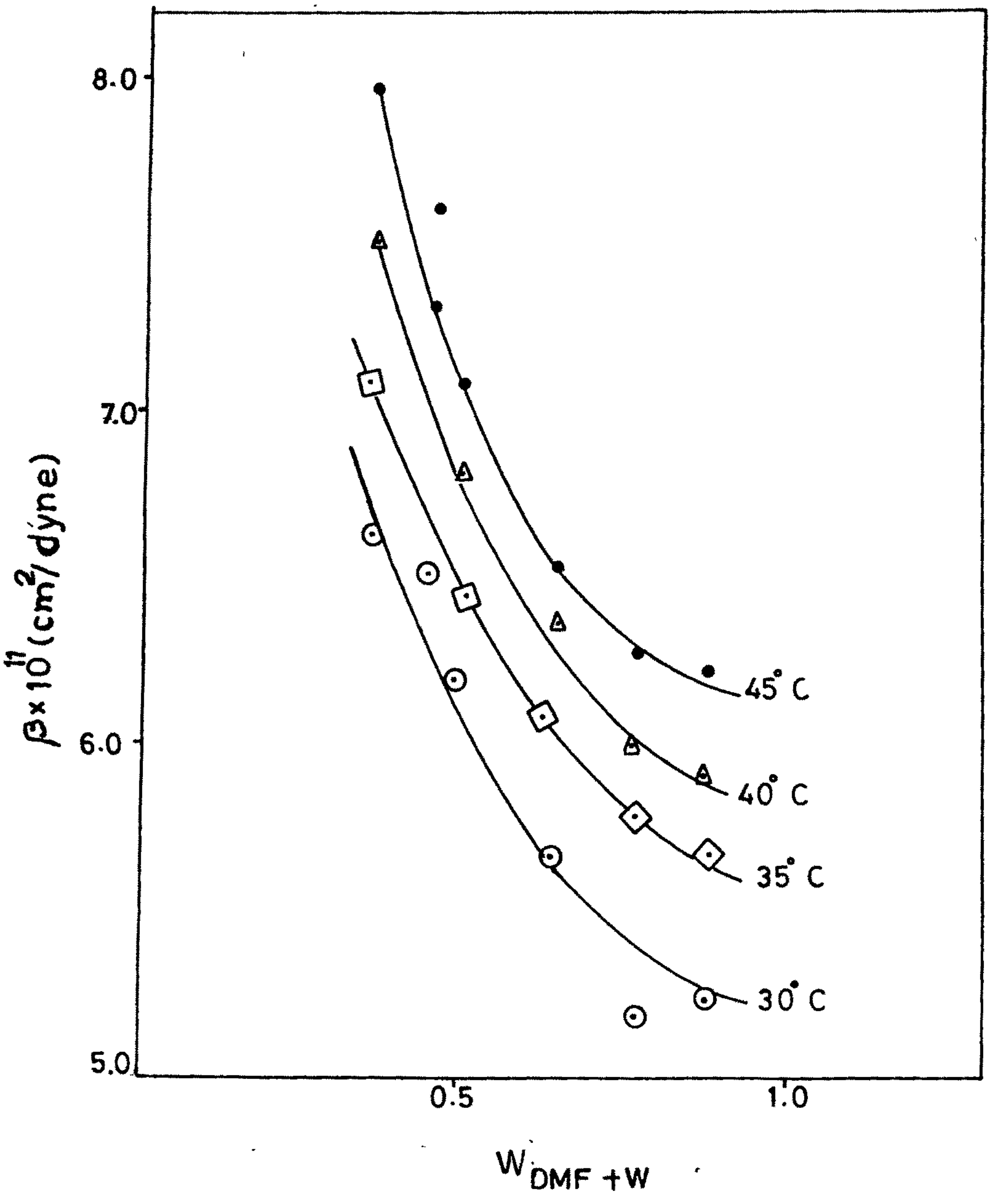

Fig. 5.21 : Plot of adiabatic compressibility (β) at weight fraction DMF + Water ($W_{D+W}$) (50:50 w/w) at 30, 35, 40 and 45°C.

Table 5.2 : Contact Angle of Microemulsion with Teflon at Room Temperature :

| Cyclohexane / CTAB + 1-propanol / DMF (1:2) | | | | Cyclohexane / CTAB + 1-propanol / DMF + water | | | |
|---|---|---|---|---|---|---|---|
| **O** | **S + CS** | **DMF** | **θ°** | **O** | **S + CS** | **DMF + Water** | **θ°** |
| 0 | 0 | 100 | 132 | 0 | 0 | 100 | 118 |
| 10 | 45 | 45 | 76.5 | 35 | 45 | 20 | 76.3 |
| 12.5 | 45 | 42.5 | 84.5 | 30 | 45 | 25 | 84.2 |
| 20 | 45 | 35 | 88.8 | 27.5 | 45 | 27.5 | 88.4 |
| 27.5 | 45 | 27.5 | 112.3 | 20 | 45 | 35 | 97.7 |
| 30 | 45 | 25 | 116.2 | 12.5 | 45 | 42.5 | 108.9 |
| 35 | 45 | 20 | 120.3 | 10 | 45 | 45 | 112.2 |
| 100 | 0 | 0 | 56 | 100 | 0 | 0 | 56 |

### 5.3.8 Adiabatic compressibility study :

Fig.5.21 shows the adiabatic compressibility as a function of water + DMF weight fraction. The compressibility was determined at various temperatures with constant S + CS concentration of 45%. It is seen that as the weight fraction of the mixed liquid decreases in the μE the compressibility (β) decreases which is an expected behaviour but compare to pure aqueous the compressibility is more because of the presence of DMF and hence the structure is less rigid compare to pure aqueous and more rigid compare to pure non-aqueous systems. In other words the compressibility lies somewhere in between.

### 5.3.9 Contact angle measurement study :

The contact angle of the μE with the teflon surface were measured for the different weight fraction of oil, surfactant + co-surfactant (CTAB + 1-propanol) and DMF. The contact angle measurement[16] shows that it decreases with increase of weight fraction of oil, surfactant and DMF. The contact angle measurement shows that there is a change in structure of microemulsion. All the measured contact angles are given in the Table 5.2 for the systems. Also, we believe that in the DMF + water system there is a structure change from bicontinuous to O / DMF + water in the middle system. The addition of salt did not give the three phase system. All the data are shown in Table 5.2.

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