# CHAPTER-4

# Influence of water soluble polyacrylamide on cyclohexane / CTAB / 1-propanol / water system

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## 4.1 PREVIEW

Aqueous systems containing surfactants and water soluble polymers are important because of their various industrial and agricultural applications[1,2]. It is well known that water and organic liquids mix only in presence of a surfactant and a short chain alcohol wherein interfacial tension (IFT) between the two becomes very low. Such a mixed system is called microemulsion, and the presence of a polymer is expected to change the properties of the system. Various researchers have worked with such systems[3-5]. The changes in physicochemical properties are important and hence we decided to study these properties of microemulsions containing cationic cetyltrimethylammonium bromide (CTAB), cyclohexane, water and 1-propanol. Water soluble polyacrylamide (PAA) was added to the above system. We have earlier studied this system with polyethylene glycol 400 (PEG-400) in place of PAA[6], sodium dodecyl sulphate (SDS) or Brij 35 in place of CTAB[7-11]. Therefore, a comparison of various properties with earlier studies will help us to understand the effect of the cationic surfactant on such systems.

In this chapter we present the phase diagrams, conductances, viscosities and adiabatic compressibilities of the title four component system under various conditions and also in presence and absence of PAA at various temperatures.

## 4.2 EXPERIMENTAL

The cationic surfactant cetyltrimethylammonium bromide (CTAB) (Trizma Chemicals, Baroda, India) was used after crystallizing three times from a mixture of acetone and methanol (4:1, v/v) and dried at 100°C for two hours before use. The surface tension- concentration profile of aqueous CTAB solution did not show any minimum. Polyacrylamide was synthesized and characterized in our laboratory[12]. Viscosity molecular weight of PAA was found to be 4.5 x $10^5$. 1-propanol and cyclohexane were used after purification following the well known procedures[13].

Doubly distilled water (conductance ≈ 3 x $10^{-6}$S $cm^{-1}$) was used for all sample preparations. The electrolytes NaCl, NaBr, NaI, KCl, KBr, KI (AR Qualigens, India) were dried before use.

The various boundaries in the phase diagrams were determined by a simple titration technique as described earlier[7,8]. The triangular phase diagrams at various temperatures is shown in Fig.4.1. The line 'x' connects the end points of the titrations, where turbidity disappears and line 'y' connects the end points of the titrations where turbidity reappears. The region bounded by these two lines is the one phase microemulsion region (Winsor IV) containing oil, water, surfactant and cosurfactant. The temperature range studied was 30° to 60°C at 10° intervals. The triangular phase diagrams of the same system in presence of 0.005% PAA in water (w/v) are carried out. The phase diagrams of the system at 30°C in presence of 0.05 and 0.1% of PAA in water (w/v) are also done. An ultrasonic interferometer (Mittal Enterprises, New Delhi, India) was used for the measurement of ultrasound velocity and the adiabatic compressibility was calculated from $\beta=1/\rho u^2$ where ρ and u are density of the medium and velocity of sound in the medium respectively.

A Mullard conductivity bridge was used for conductance measurements. The cell constant of conductivity cell was 0.6645 $cm^{-1}$. A standard Ubbelohde viscometer and a calibrated pyknometer were used for viscosity and density measurements respectively. The interfacial tension (IFT) was determined with a spinning drop tensiometer (University of Texas at Austin, USA, Model 500). The surfactant to cosurfactant ratio was arbitrarily kept at 1:2 (w/w) throughout the work. Areas of various regions of the phase diagrams were computed with a planimeter.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Phase behaviour study :

Fig.4 (1-4) represents ternary phase diagrams at 30-60°C of the system in absence of PAA as well as in the presence of 0.005% (w/v) aqueous PAA solution. In Table 4.1 are shown the various phase regions at different temperatures. The presence of PAA changes various phase regions though the area change is not large at any given temperature. The 1ϕ area increases at the cost of the 2ϕ L/L and S/L regions.

In presence of 0.05% PAA (Fig. 4.3) as well as 0.1% PAA (Fig. 4.4) the 2ϕ S/L as well as 2ϕ L/L are the major regions of the pseudoternary phase diagrams at 30°C (Table 4.1). At low PAA (0.005%) concentration we get isotropic one phase microemulsion zone in the middle part. Fig.4.2 shows that even in presence of PAA, 1ϕ area decreases with increase in the temperature. The rates of decrease in both cases are similar.

These diagrams show that only in presence of very small amount of PAA the 1ϕ microemulsion formation is favoured. However, increase in temperature decreases the 1ϕ area. At the oil / water interface there will be PAA - surfactant array. With increase in temperature less number of surfactant molecules will be present at the interface and hence IFT will increase as shown in Fig. 4.5.

The presence of PAA at the interface decreases IFT. The PAA is hydrogen-bonded through the amide groups[14]. This gets disturbed with change in temperature. The position of alcohol and PAA in the array at the oil / water interface; the breaking and forming of hydrogen bonds among PAA molecules; the lowering of IFT at oil / water interface with increase in temperature all together determine the final 1ϕ μE area in the triangular phase diagram.

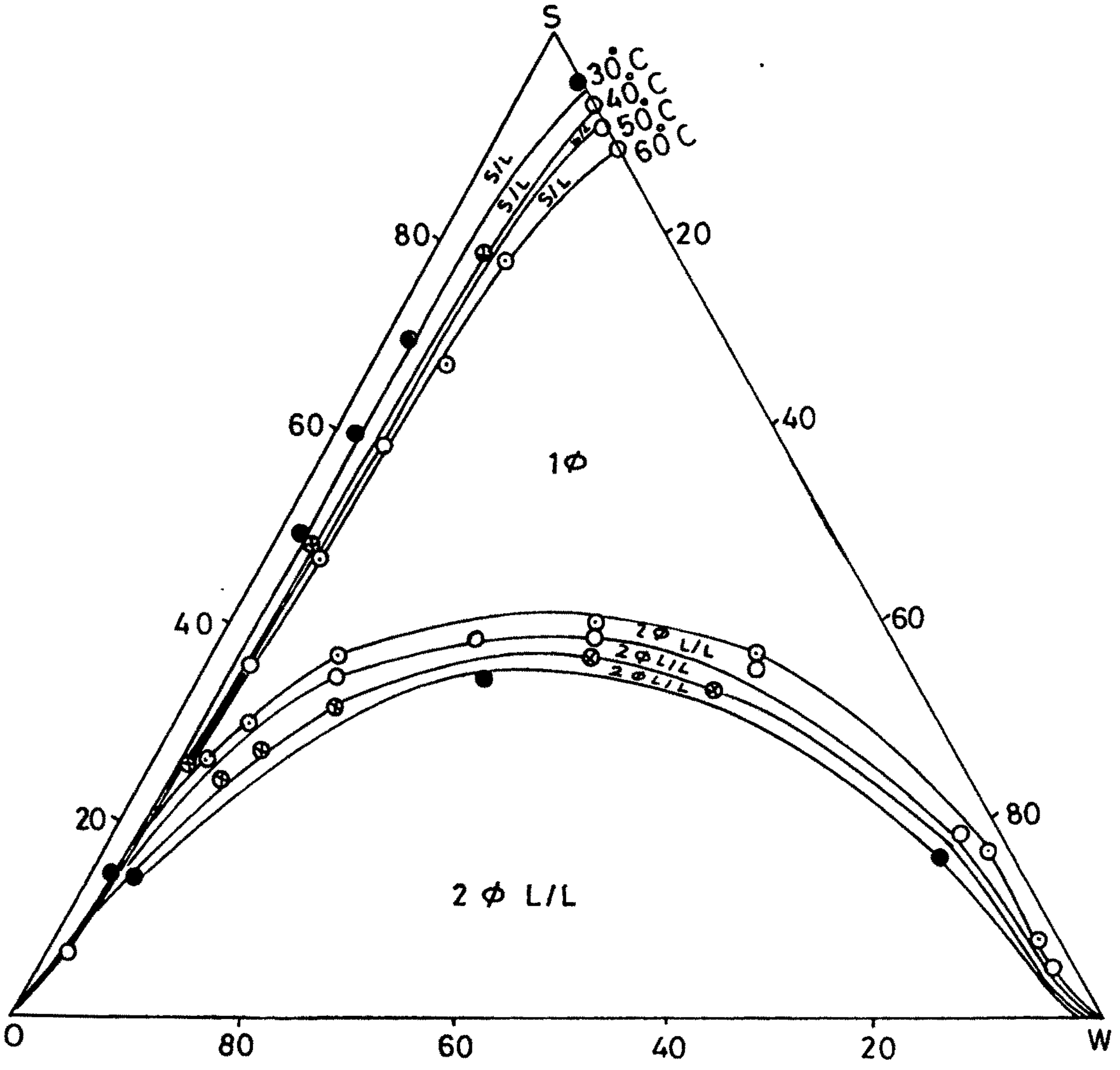


Fig. 4.1 : Pseudoternary phase diagram of the system cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / water (W) (0.005% PAA) at 30, 40, 50 and 60°C.

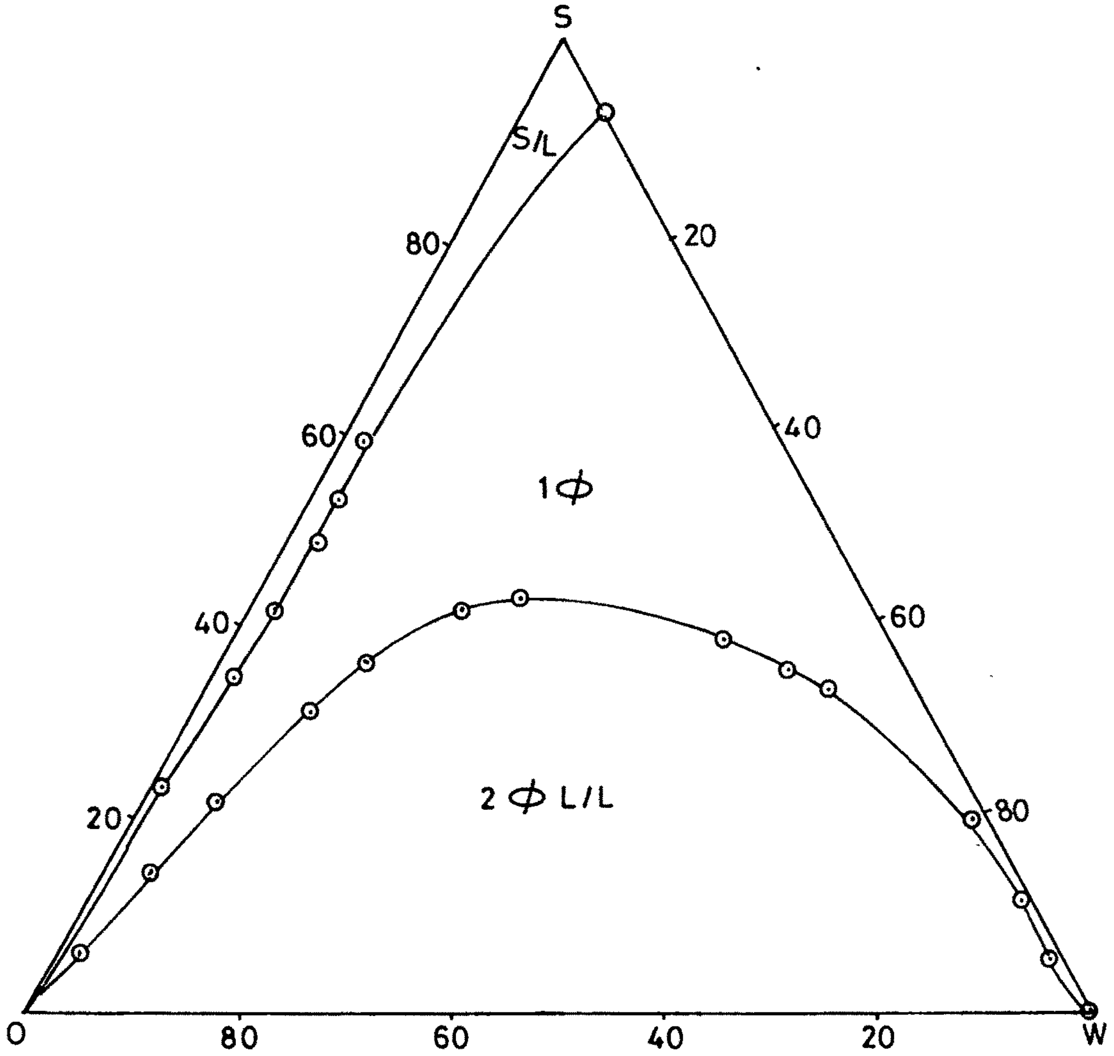


Fig. 4.2 : Pseudoternary phase diagram of the system cyclohexane (O) / CTAB + 1-propanol / water (W) (aq. 0.005% PAA) at 30°C.

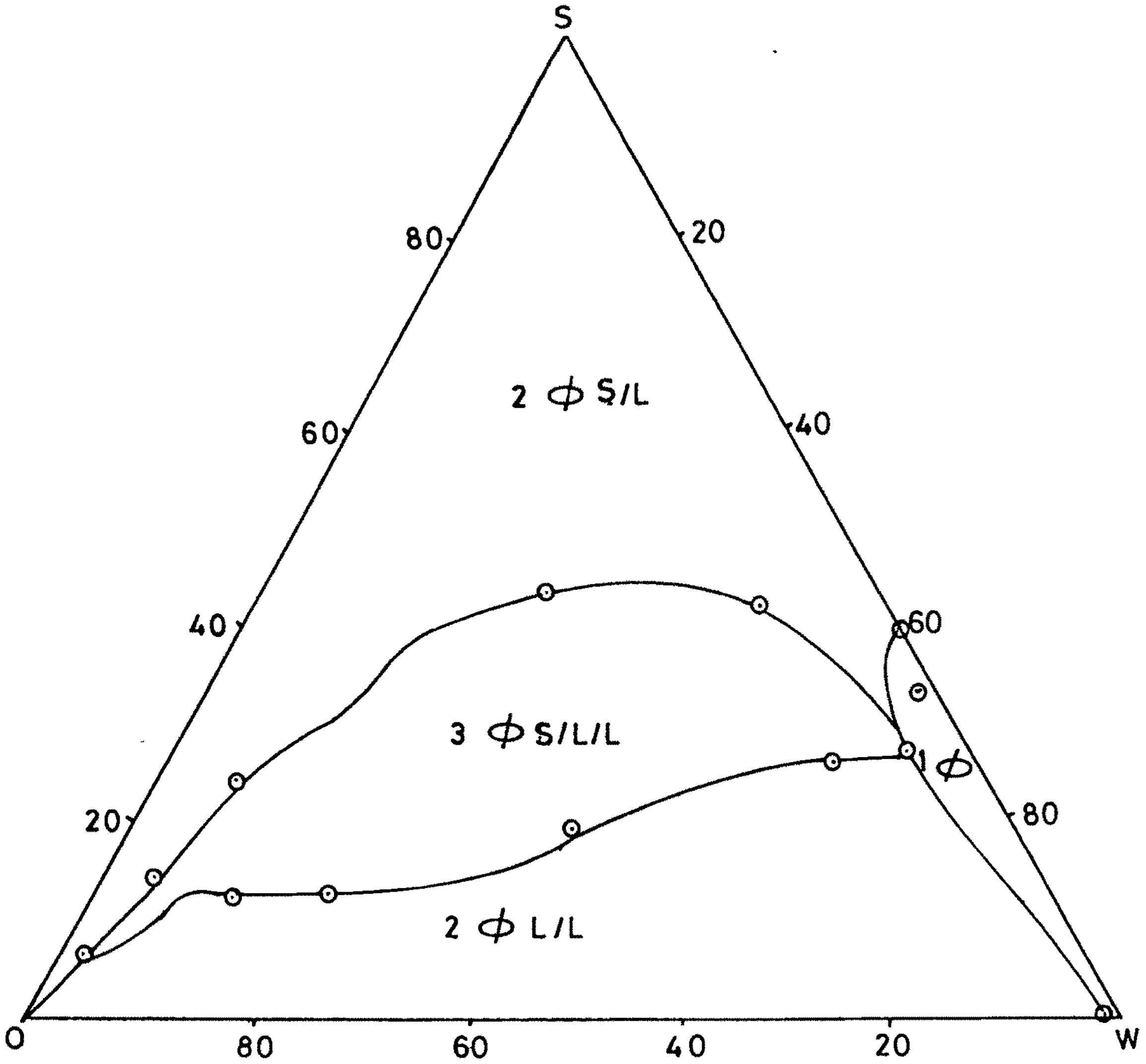


Fig. 4.3 : Pseudoternary phase diagram of the system cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / water (W) (aq. PAA = 0.1%) at 30°C.

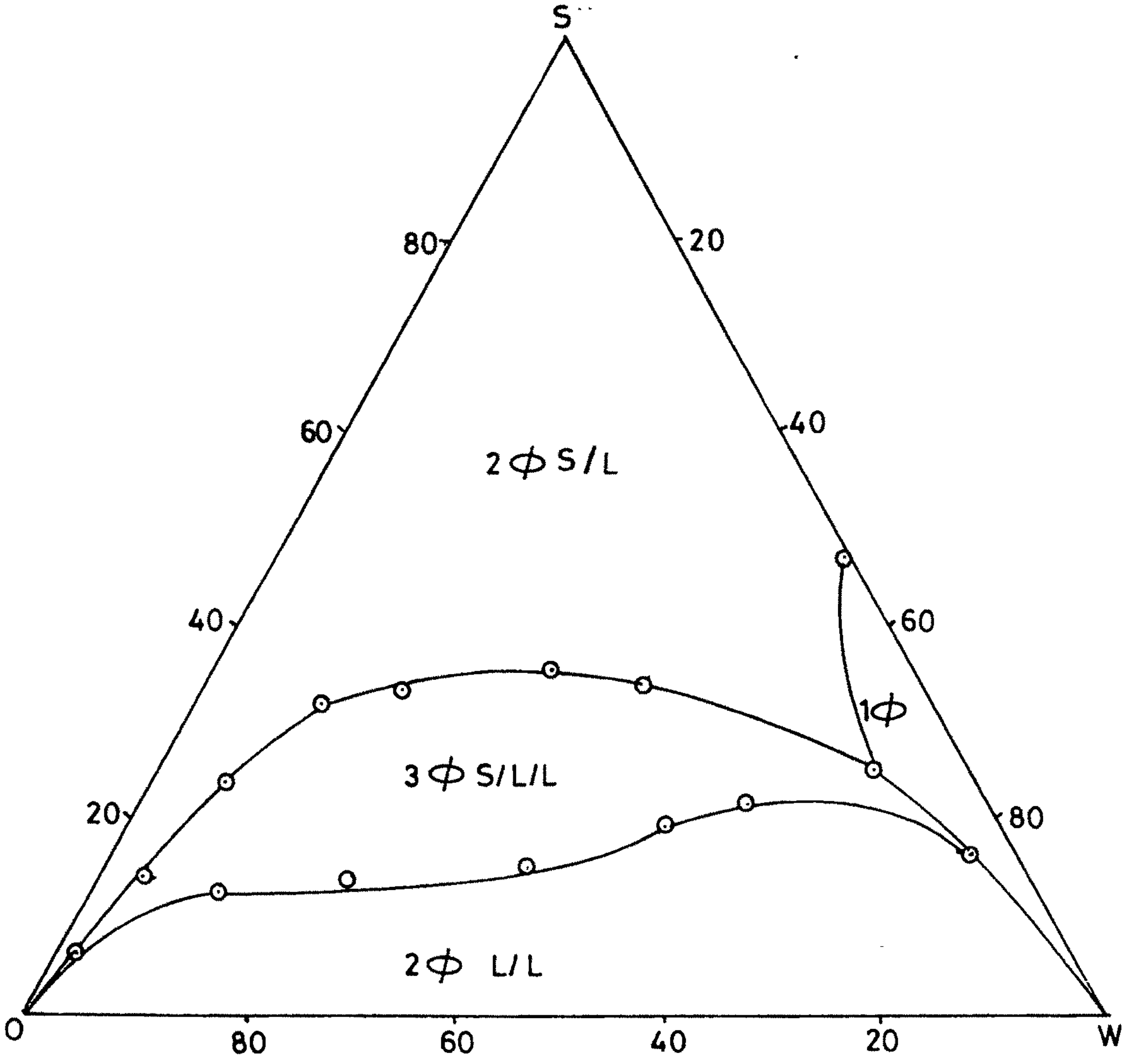


Fig. 4.4 : Pseudoternary phase diagram of the system cyclohexane (O) / CTAB + 1-propanol (S) (1:2) / water (W) (aq. PAA 0.05%) at 30°C.

Table 4.1 - Percentage phase regions in the pseudoternary phase diagram of cyclohexane / CTAB / 1-propanol / X

| X | Temp., °C | 1ϕ (L) | 2ϕ (L/L) | 2ϕ (S/L) | 3ϕ (L/S/L) |
|---|---|---|---|---|---|
| Water | 30 | 45.20 | 49.30 | 5.40 | -- |
| 0.005% Aq.PAA | 30 | 47.1 | 49.0 | 3.80 | -- |
| Water | 40 | 41.1 | 53.80 | 5.0 | -- |
| 0.005% Aq.PAA | 40 | 43.20 | 51.9 | 4.8 | -- |
| Water | 50 | 36.1 | 59.2 | 4.60 | -- |
| 0.005% Aq.PAA | 50 | 39.8 | 55.8 | 4.3 | -- |
| Water | 60 | 35.7 | 60.2 | 4.0 | -- |
| 0.005% Aq.PAA | 60 | 36.3 | 59.8 | 3.8 | -- |
| 0.05% Aq.PAA | 30 | 5.2 | 35.7 | 30.1 | 29 |
| 0.1% Aq.PAA | 30 | 4.5 | 31.9 | 35.6 | 28 |

### 4.3.2 IFT study :

We have also determined the IFT (Fig. 4.5) between the upper oil (O) and middle microemulsion (M) as well as between middle (M) and lower water (W) levels of a 3$\phi$ WIII system which was obtained in presence of 1M NaCl. However, (Fig. 4-5) in presence of PAA the IFT of W/M interface actually decreases, as $V_w/V_o$ increases which favours the miscibility of various phases. The O/M IFT values remain constant. It should also be noted that 0.008% PAA decrease the IFT to very very low value, lower than the 0.005% PAA does. Therefore, our suggestion[7] that the PAA might be working as cosurfactant at about 40°C is substantiated.

### 4.3.3 Conductivity study :

Fig. 4.6-11 are representative plots showing the variation of the specific conductance ($\sigma$) of the microemulsion with water volume fraction, $\phi_w$, at different temperatures. The variation of conductance was smooth and no sudden change of conductance was observed at any temperature even when (S + CS) concentration was changed from 45% to 65%. The similarity of conductance changes proves the absence of percolation in these systems. It can be noted that the conductance is lower in 65% (S + CS) system in comparison to that in 45% (S + CS) system. This is because in the second case at the same $\phi_w$, there are more water molecules and hence greater ionization of CTAB and therefore higher conductance. It is also to be noted that the conductance at any temperature increases with the increase in the water-soluble PAA concentration (Fig. 4.7). We have mentioned that no conductance percolation was observed in this system presented in 4.13 was also seen earlier in presence of PEG-400[6], but this is in contrast to some other systems reported in literature[15]. Further, it was suggested[16] that specific conductance $\sigma$ (mechanism is presented in Fig.4.12 is of sticky collision) of microemulsion obeys the relation $\sigma \propto (\phi_w - \phi^p_w)^t$ where $\phi_w$ is the volume fraction of water [i.e. volume of water / (volume of water + volume of oil)] and $\phi^p_w$ is the percolation threshold. For a bicontinuous system the value of 't' was suggested to be equal to 8/5. The plots of $\sigma^{5/8}$ vs $\phi_w$ gave very good straight lines indicating bicontinuous nature of the system. Moreover, the magnitude

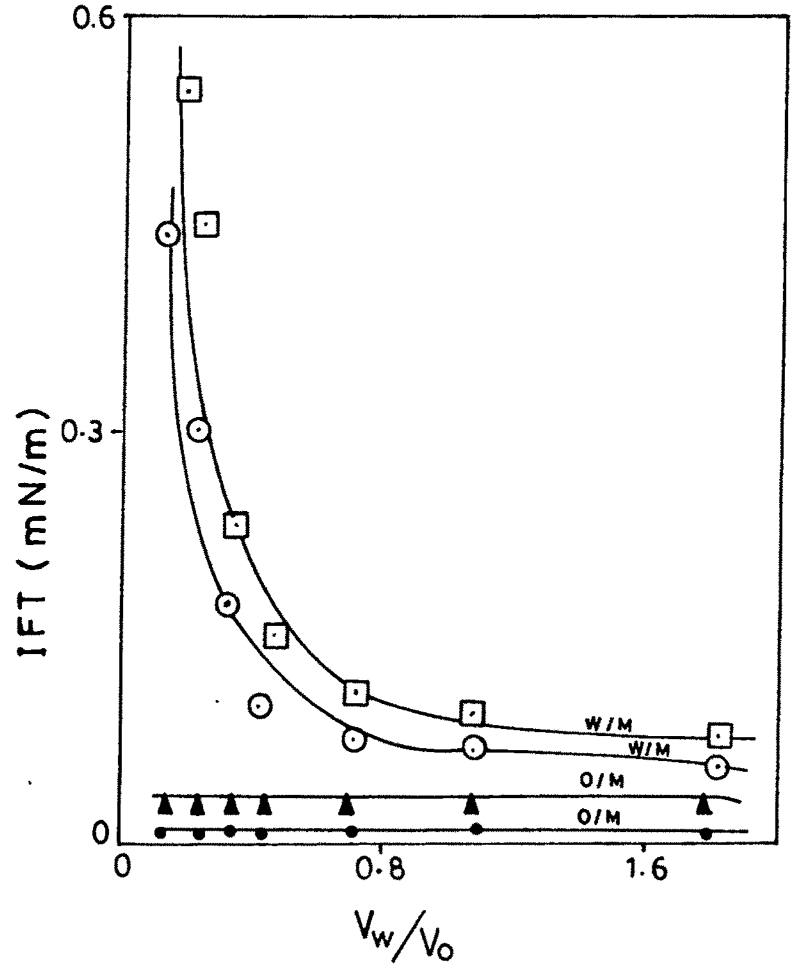


Fig. 4.5 : The variation of interfacial tension (IFT) as a function of water / oil volume ratio at 40°C with (W/M) (□) 0.005% PAA, (O) 0.008% PAA with O/M, (▲) 0.005% PAA, (●) 0.008% PAA.

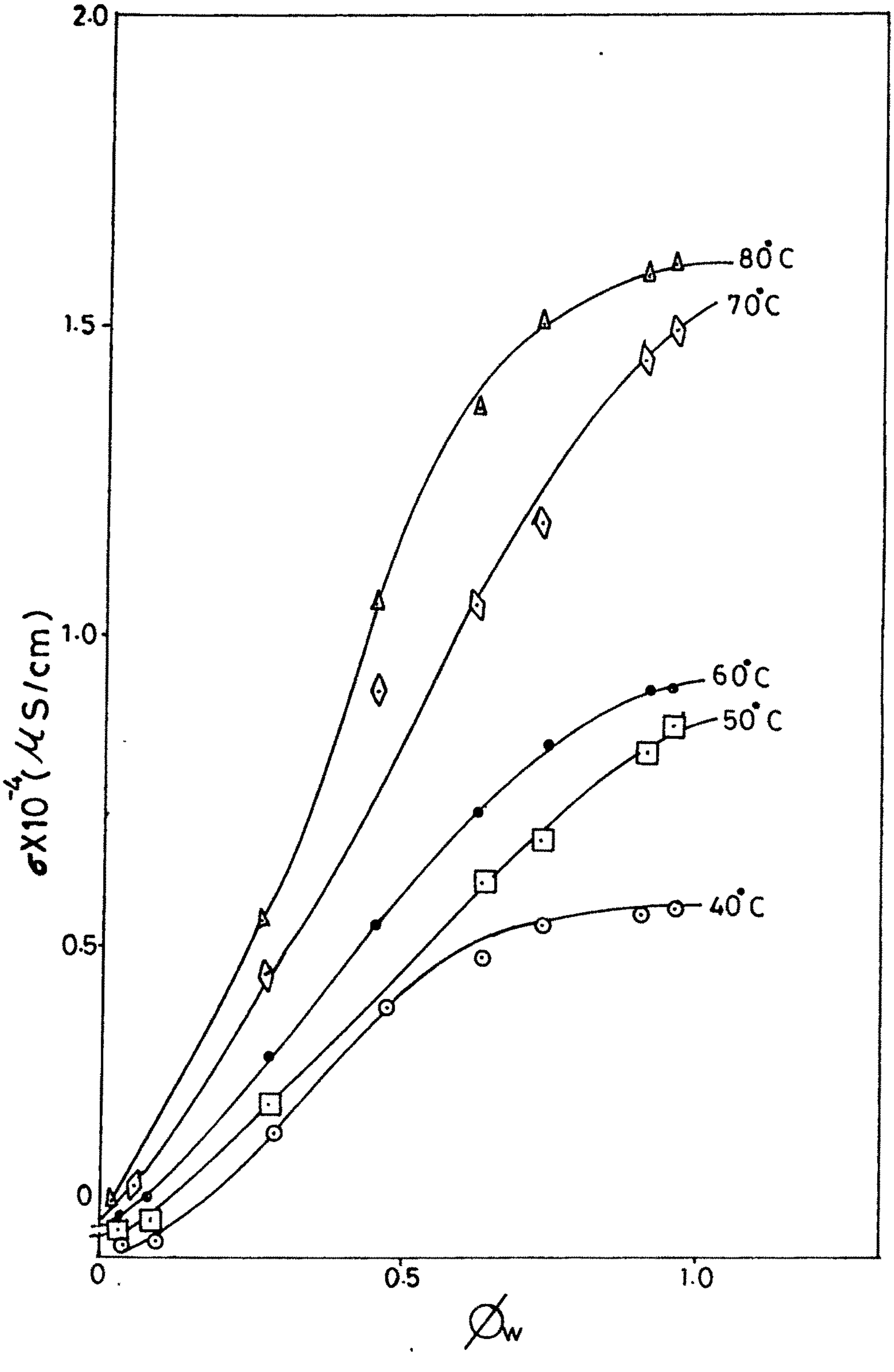


Fig. 4.6 : Plot of specific conductance (σ) (μs/cm) against volume fraction of water at 40, 50, 60, 70 and 80°C with S+CS 45%; 0.1% PAA.

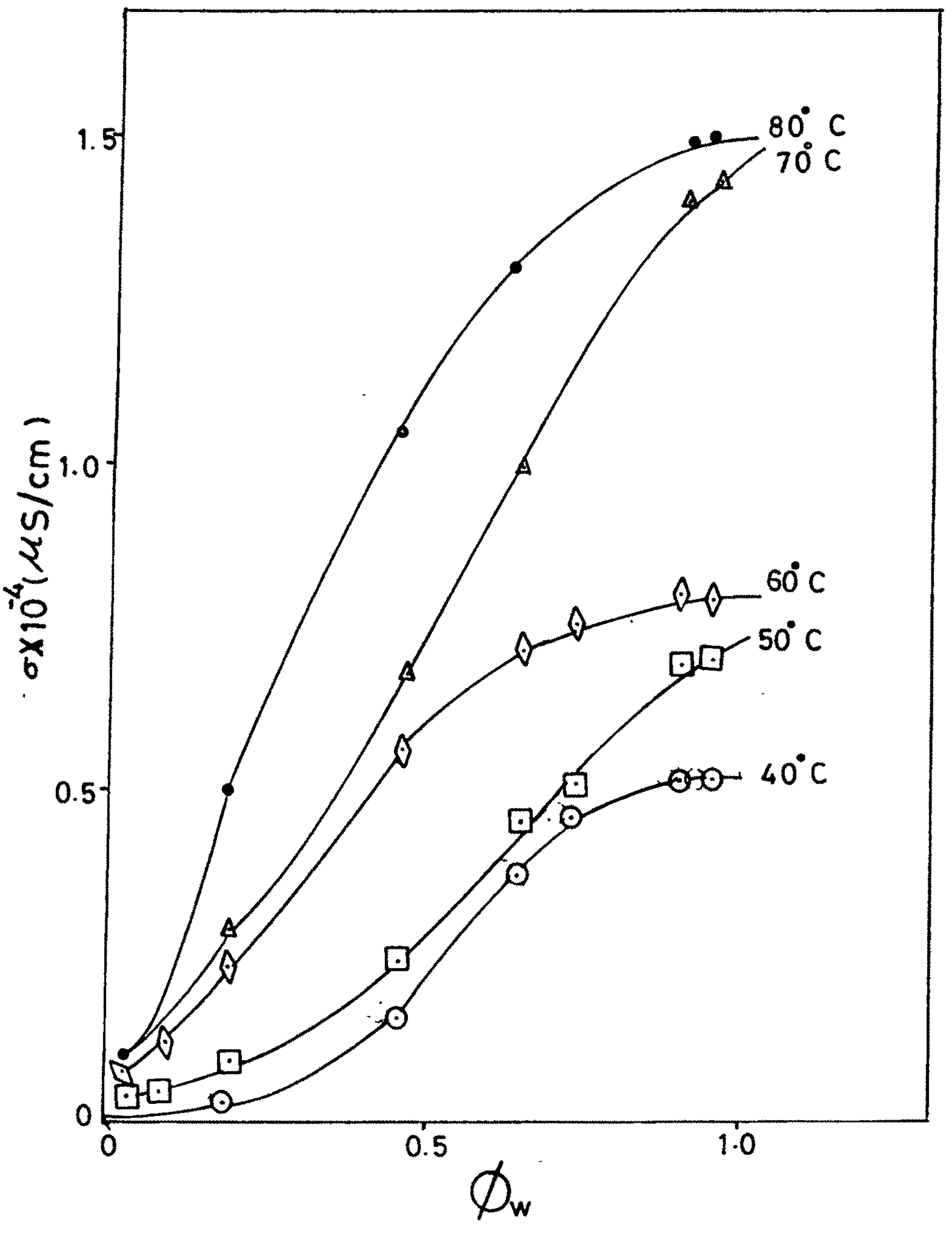


Fig. 4.7 : Plot of specific conductance (σ) (μs/cm) against volume fraction of water at 40, 50, 60, 70 and 80°C with S+CS 45%; 0.05% PAA.

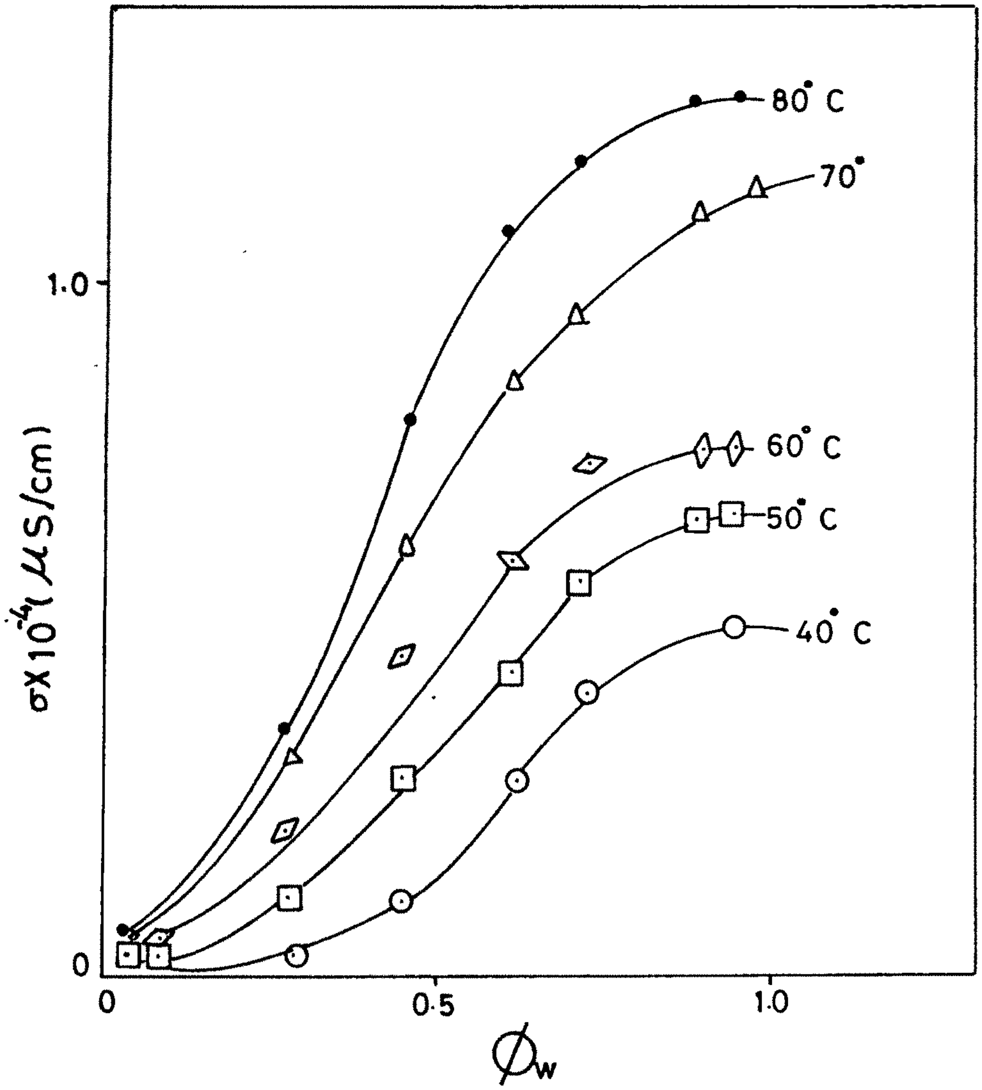


Fig. 4.8 : Plot specific conductance (σ) (μs/cm) against volume fraction of water at 40, 50, 60, 70 and 80°C with S+CS 45%; 0.005% PAA.

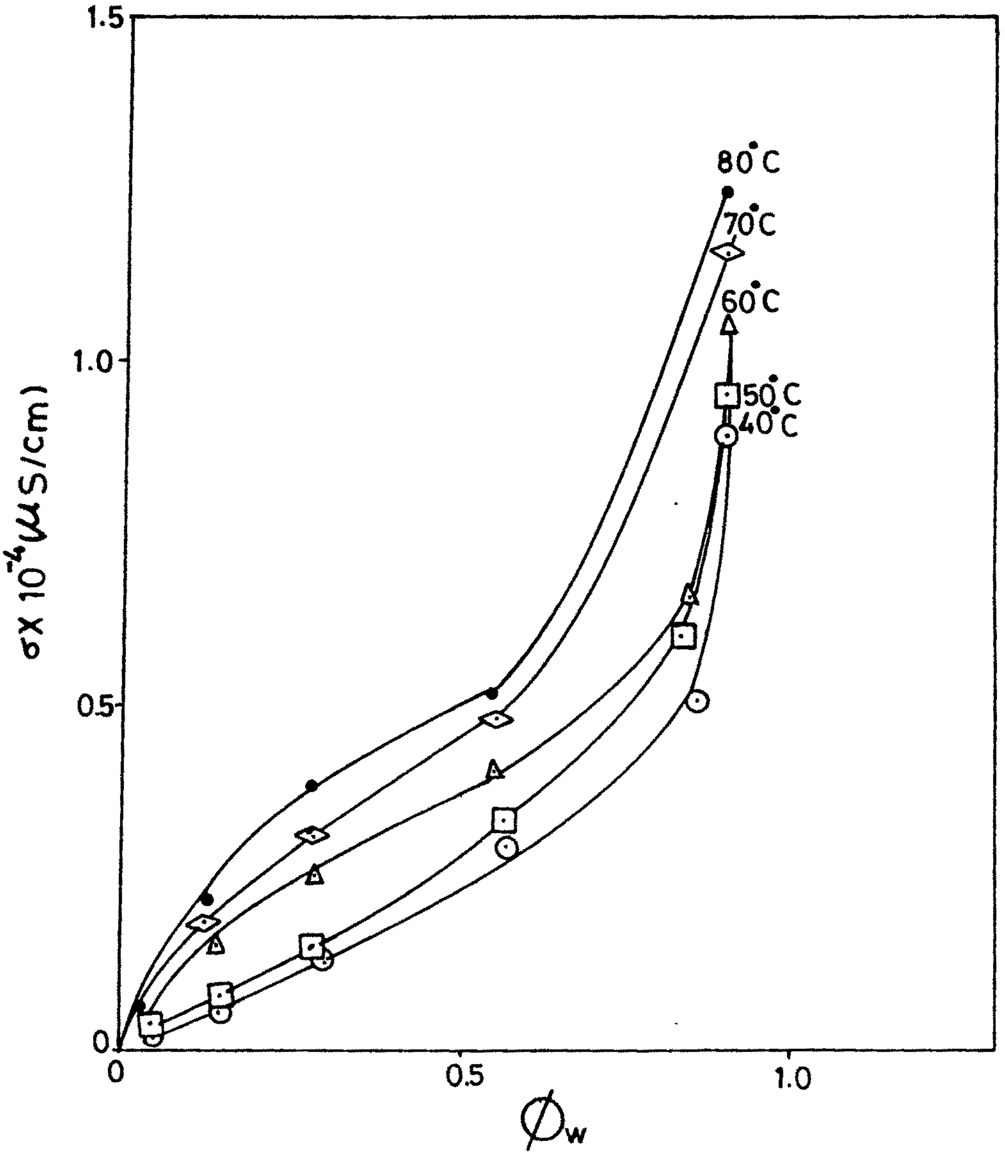


Fig. 4.9 : Plot of specific conductance (σ) (μs/cm) against volume fraction of water at 40, 50, 60, 70 and 80°C with S+CS 65%; 0.1% PAA.

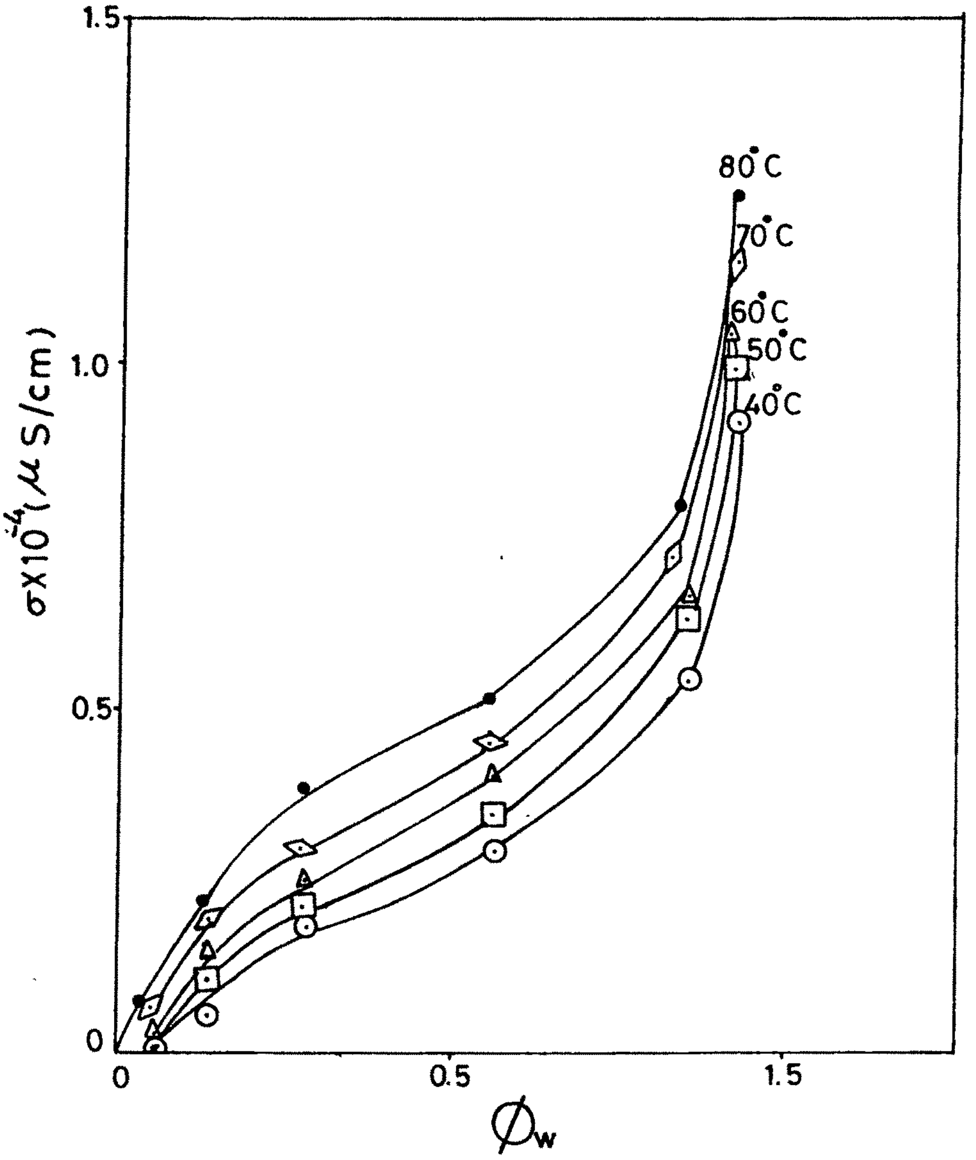


Fig.4.10 : Plot of specific conductance (σ) (μs/cm) against volume fraction of water ($\phi_w$) at 40, 50, 60, 70 and 80°C with S+CS 65%; 0.05% PAA.

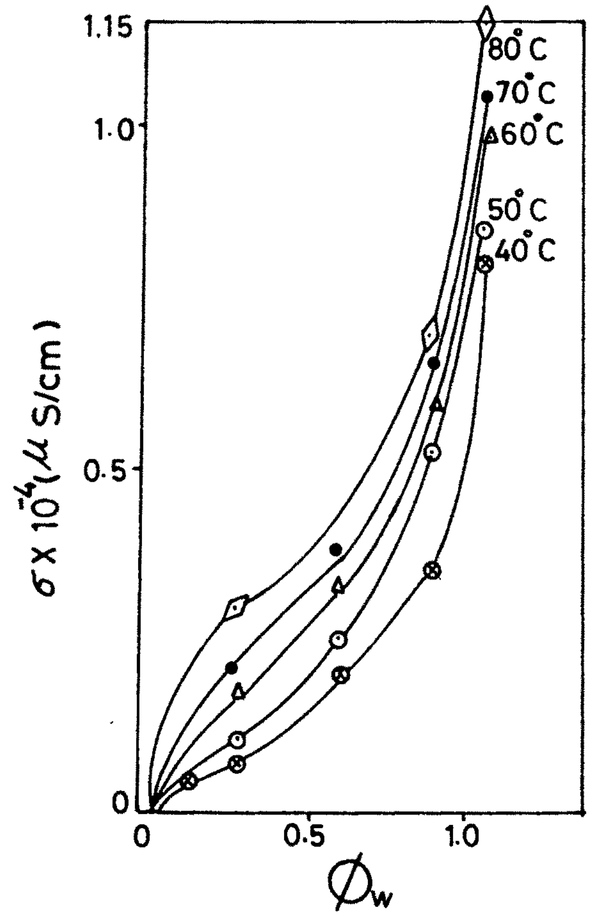


Fig. 4.11 : Plot of specific conductance (σ) (μs/cm) against volume fraction of water ($\phi_w$) at 40, 50, 60, 70 and 80°C; 0.005% PAA.

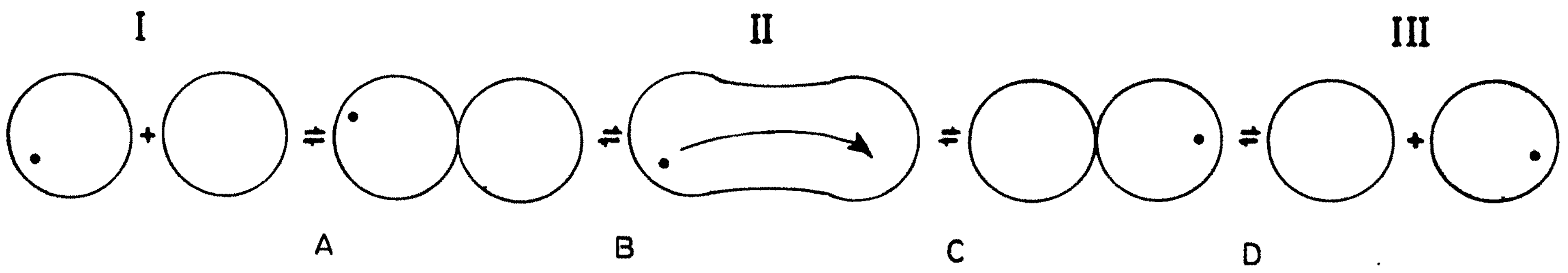


Fig. 4.12 : Schematic representation of ion transport through the droplets according to the sticky collision or transient droplet merging mechanism (●) presents the ion.

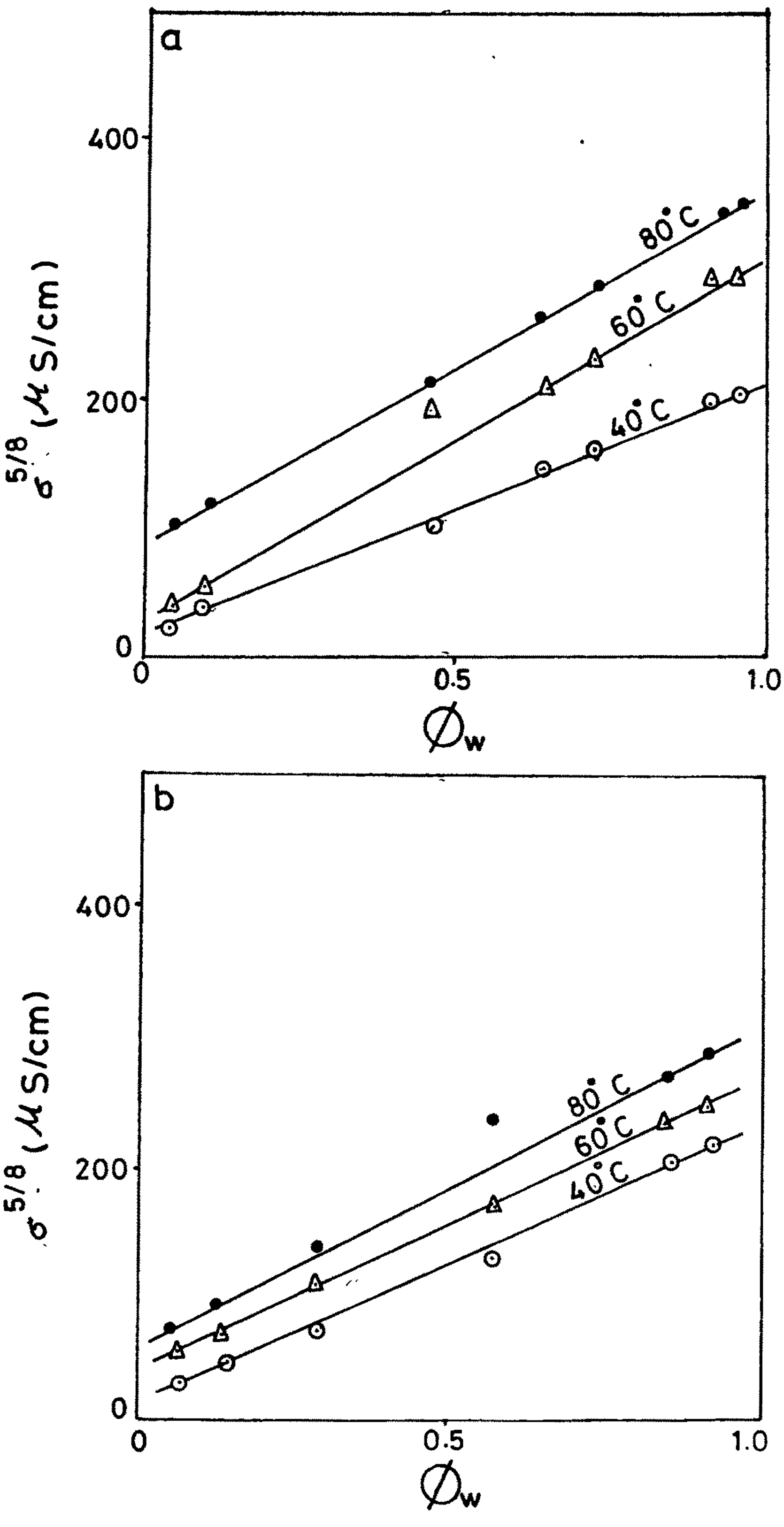


Fig. 4.13 : Plot of $\sigma^{5/8}$ against volume fraction of water ($\phi_w$), $\sigma$ is the specific conductance (μs/cm) a = 45% S+CS, b = 65% S+CS with 0.005% PAA at 40, 60 and 80°C.

of $\phi^{P}_{w}$ was found to be negative, which is an impossibility and therefore we suggest that the microemulsion is bicontinuous at all compositions.

### 4.3.4 Viscosity study :

In Fig. 4.14-19 are the representative plots of viscosity $\eta$ vs $\phi_w$ in presence of PAA at various temperatures are shown. The concentration of S + CS mixture was kept constant at either 45% or 65%. It may be noted that the viscosity shows a constant increase with increase in $\phi_w$. This indicates that the water channel present in the bicontinuous structure grows in size with increase in water concentration thereby increasing the viscosity of the system[17]. The $\eta$-$\phi_w$ plots show a maximum. The height of the maximum decreases with increase in temperature. The maximum was observed at lower $\phi_w$ with increase in temperature. For the system with SDS[7] the behaviour was similar though the shift in the position of the maximum was much more prominent. The presence of maximum also indicates a change from a bicontinuous structure to an oil in water regime. However, the viscosity should have been constant which is seen in 65% S + CS system. In case of 45% S + CS system, the decrease is probably because of the dilution. In contrast to SDS system[7] the maximum is much sharper here indicating that the structural changes are reasonably prominent.

The Frenkel-Eyring equation, i.e., $\ln \eta V/Nh = \Delta H^{\neq}_{vis}/RT - \Delta S^{\neq}_{vis}/R$ was used[18] to compute the activation quantities of viscous flow. The plot is linear and the computed $\Delta H^{\neq}_{vis}$ values are given in Table 4.2. The values increase with increase in water content both in presence of PAA and in absence of it. The presence of PAA increases the viscosity of the system as was seen earlier[7]. This probably indicates polymer surfactant interaction in these cases.

### 4.3.5 Volume measurement study :

The ionic surfactants do not form a $3\phi$ microemulsion system [Winsor (W) III] because of high hydrophilicity. However, the presence of an electrolyte decreases the hydrophilicity and increases the possibility of the $3\phi$ formation. The force of ion-ion

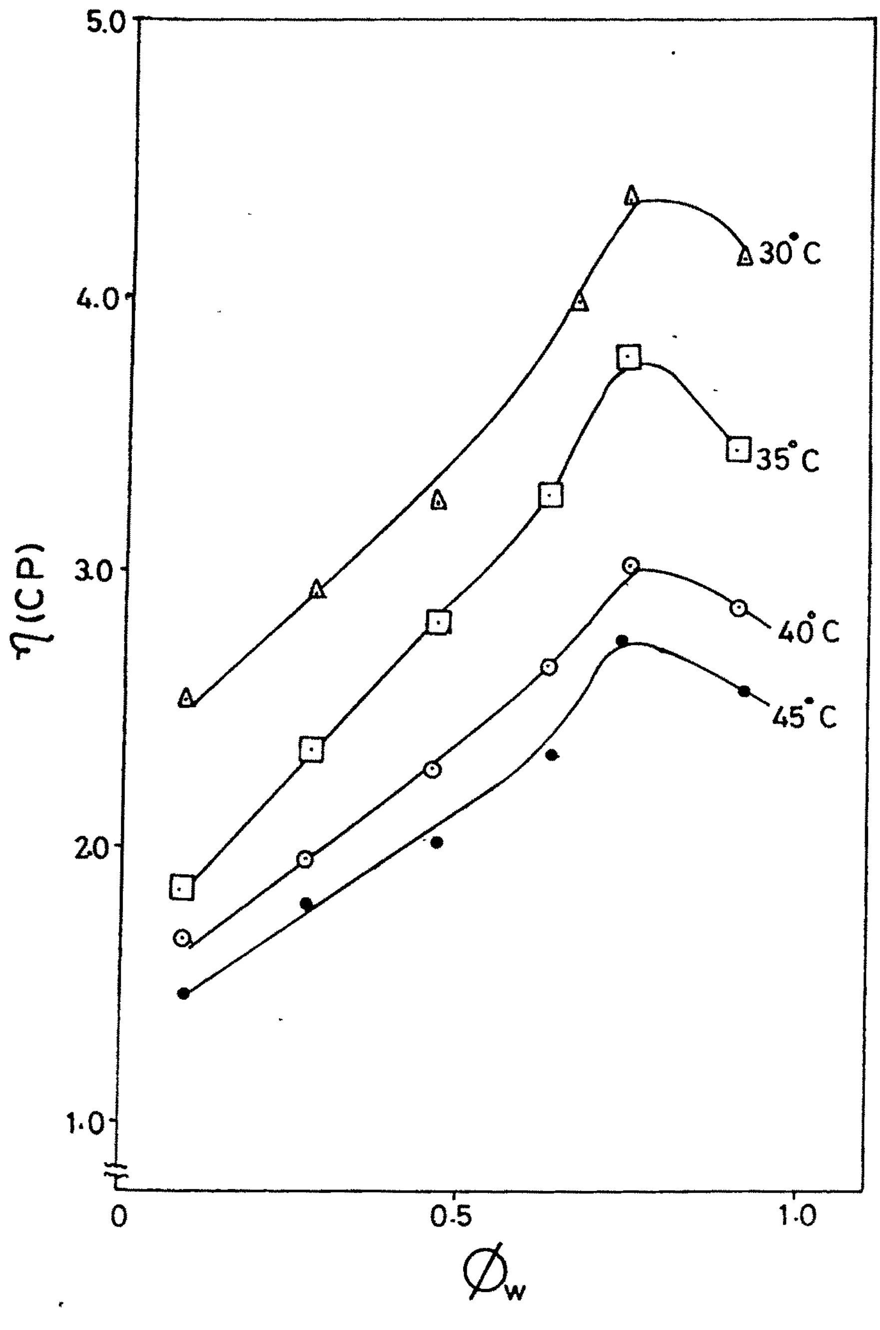


Fig. 4.14 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C; S+CS 45%; with 0.1% PAA.

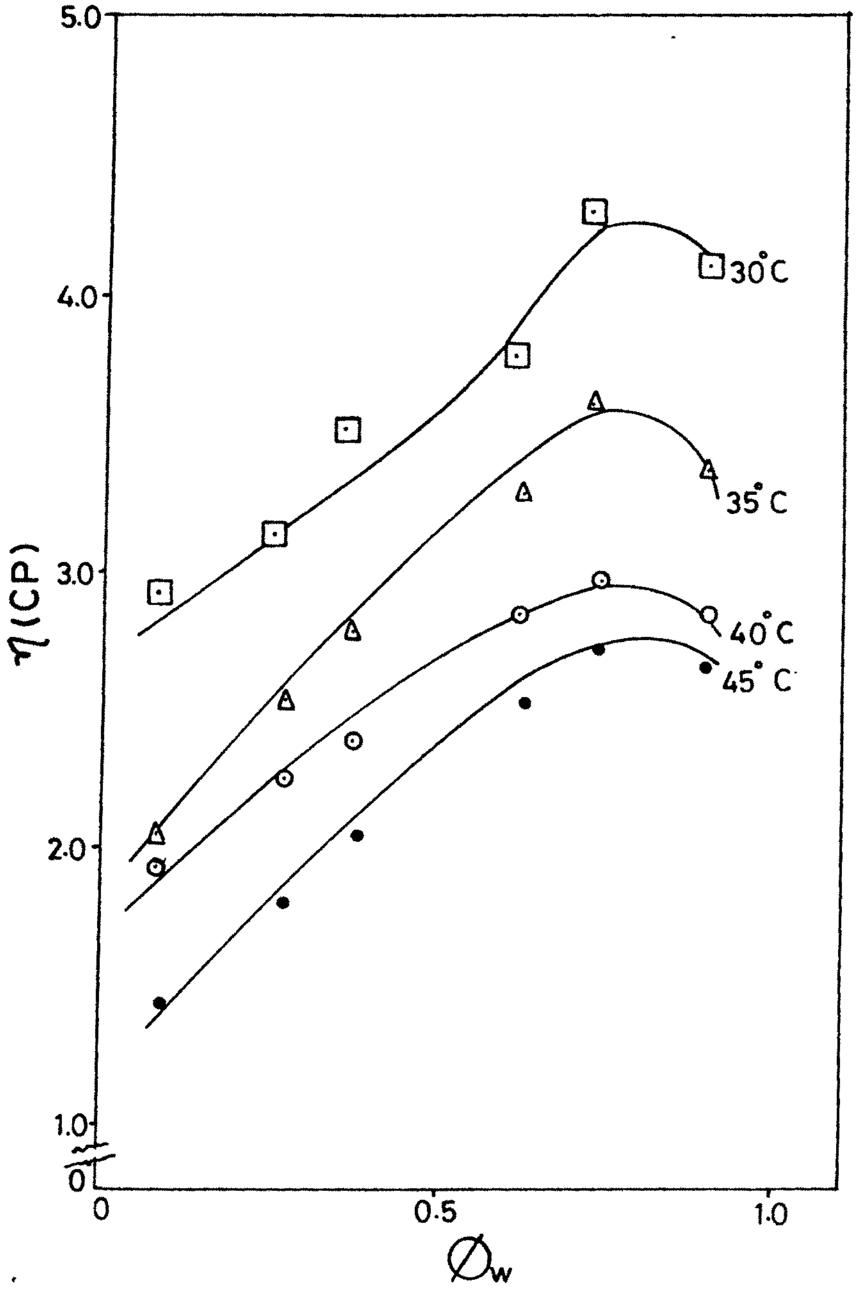


Fig. 4.15 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C; with 0.05% PAA.

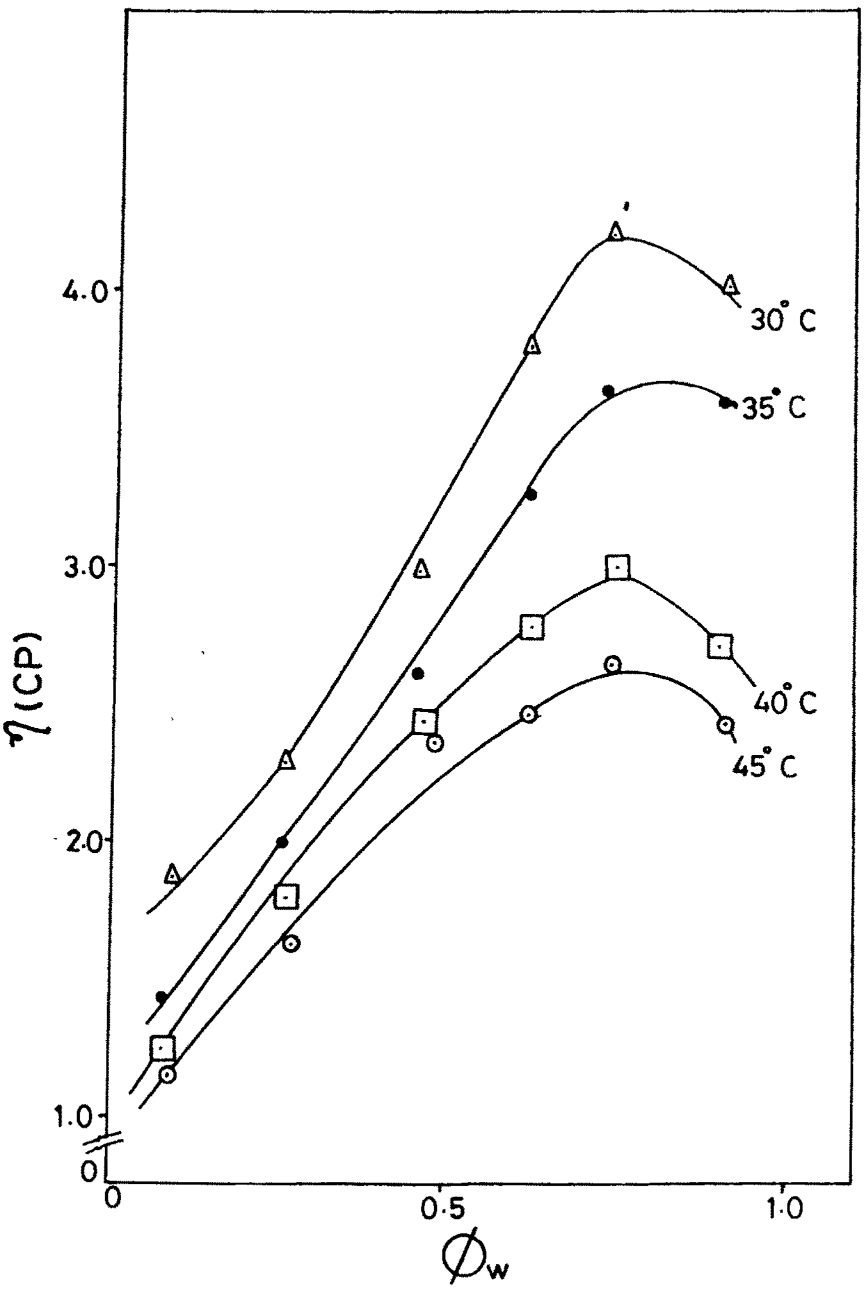


Fig. 4.16 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C; S+CS 45%; with 0.005% PAA.

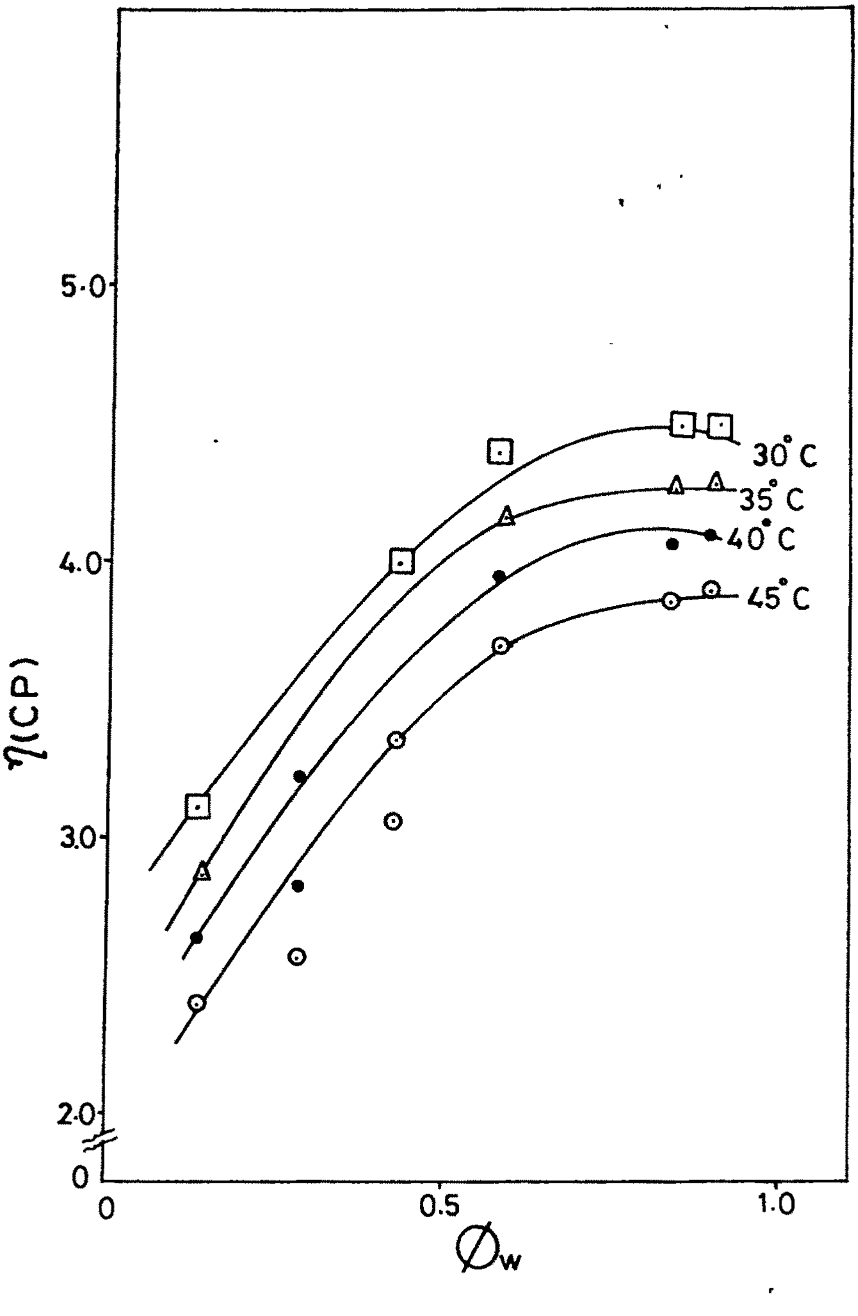


Fig.4.17 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C; S+CS 65%; with 0.1% PAA.

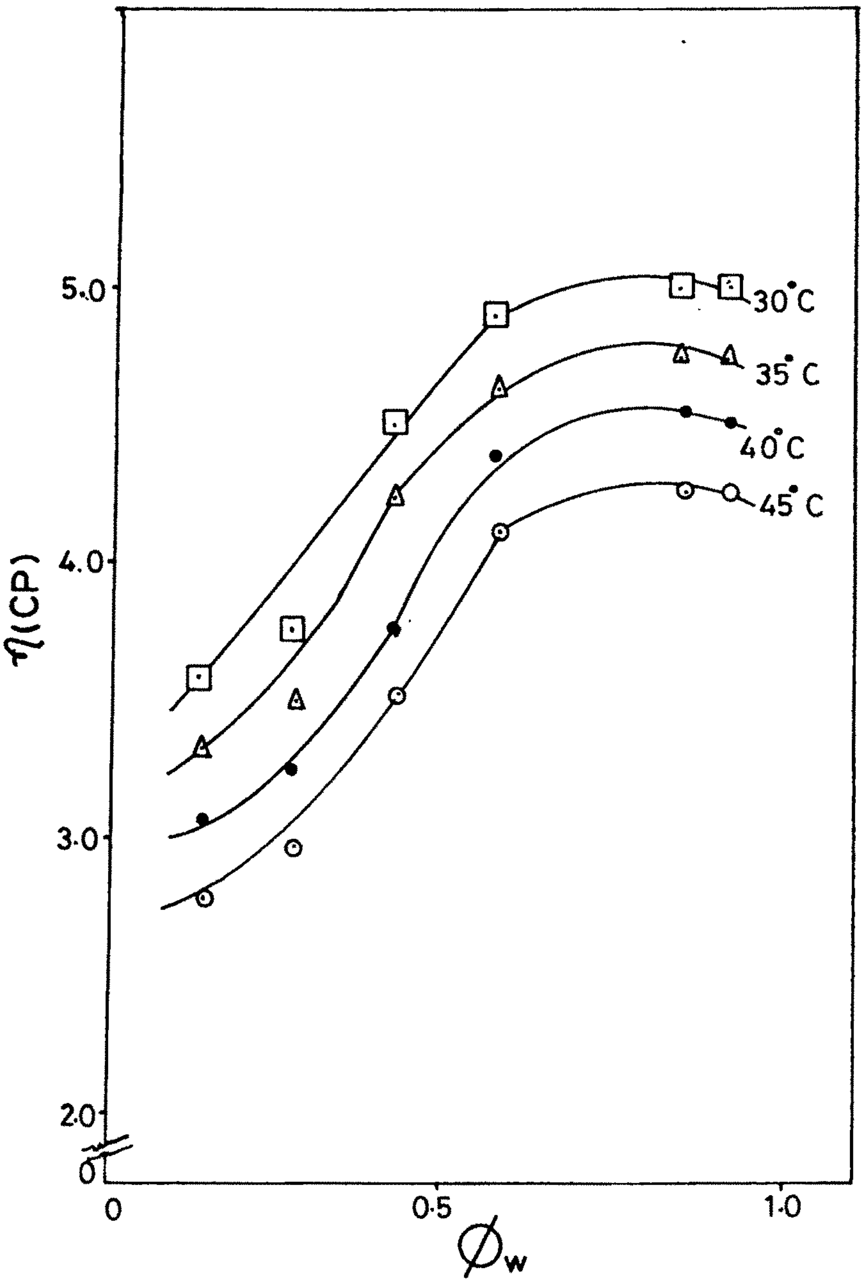


Fig. 4.18 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C. S+CS 65%; with 0.05% PAA.

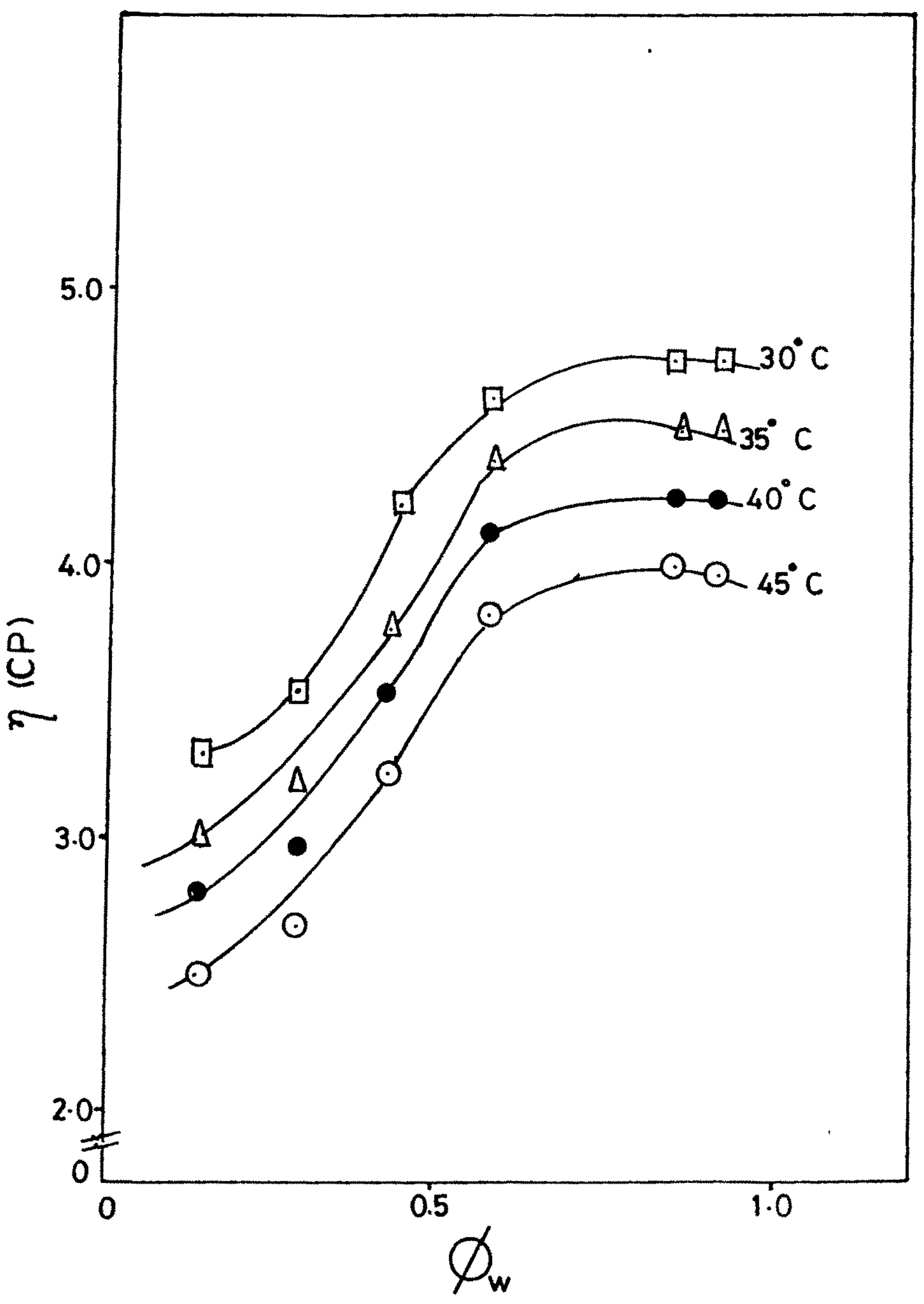


Fig. 4.19 : Plot of viscosity η(CP) Vs volume fraction of water ($\phi_w$) at 30, 35, 40 and 45°C, S+CS 65%; with 0.005% PAA.

Table 4.2 - The activation enthalpy $\Delta H^{\neq}_{vis}$ (kJ/mol) for viscous flow at various oil/water ratios.

| **System O/W** | **in the absence of PAA** | **in the presence of 0.005% PAA** |
|---|---|---|
| 45% S + CS | | |
| 50/5 | 17.1 | 18.0 |
| 45/10 | 19.3 | 18.2 |
| 27.5/27.5 | 22.5 | 22.1 |
| 12.5/42.5 | 23.3 | 24.0 |
| 2.5/52.5 | 25.0 | 30.6 |
| 65% S + CS | | |
| 30/5 | 14.8 | 2.5 |
| 25/10 | 15.4 | 2.8 |
| 15/20 | 20.0 | 3.0 |
| 10/25 | 21.4 | 7.5 |
| 2.5/32.5 | 25.4 | 8.3 |

repulsion is reduced in presence of the electrolyte[18]. The addition of electrolyte eventually causes a lower phase microemulsion (WI) to an upper phase microemulsion (WII) through a middle phase microemulsion (WIII). In Fig. 4.20 and 4.23, representative plots of such transitions are shown. In Table 4.3 the concentrations of various electrolytes required for such Winsor transitions at different temperatures are presented. It can be noted that temperature does not have any effect on the electrolyte concentrations required for the WI → WIII as well as WIII → WII transitions. In presence of 0.005% PAA, the electrolyte concentrations for both transitions are different from those in absence of PAA which is contrary to the effect of PEG-400 where no difference was observed[6] even at high concentration of 10% PEG-400. Various alkali halides were used both in presence and absence of PAA. As the halide ions were changed from $Cl^-$ to $Br^-$ to $I^-$, the required concentrations for WI → WIII as well as WIII → WII seem to decrease as was also observed in presence of PEG-400. The required concentration of KI for both transitions is the smallest among the six sodium and potassium halides used. Probably the large size of the ions in this salt induces the transformations early. In presence of PAA the concentrations of electrolytes required for Winsor transitions are much lower than those observed in absence of PAA. However, the relative efficiency of the electrolytes to show Winsor transitions remain similar. PEG-400[6] is soluble in both cyclohexane and water whereas PAA is not and hence is present at the interface and helps in the Winsor transitions, which PEG-400 does not do.

We also studied the volume fraction of different layers as a function of electrolyte concentration in the WIII region in the temperature range 40-80°C. If $V_o$, $V_w$ and $V_m$ are the volumes of oil, water and microemulsion respectively then the solubilization parameters[19] $V_o/V_m$ and $V_w/V_m$ can be plotted against the electrolyte concentrations. Some representative plots are shown in Figs. 4.22 and 4.23. The concentration at which both the solubilization parameters are same is known as optimal salinity (OS). In Table 4.4, the optimal salinity values so determined are presented. In our earlier studies for this system in presence of PEG-400[6], no effect of temperature was

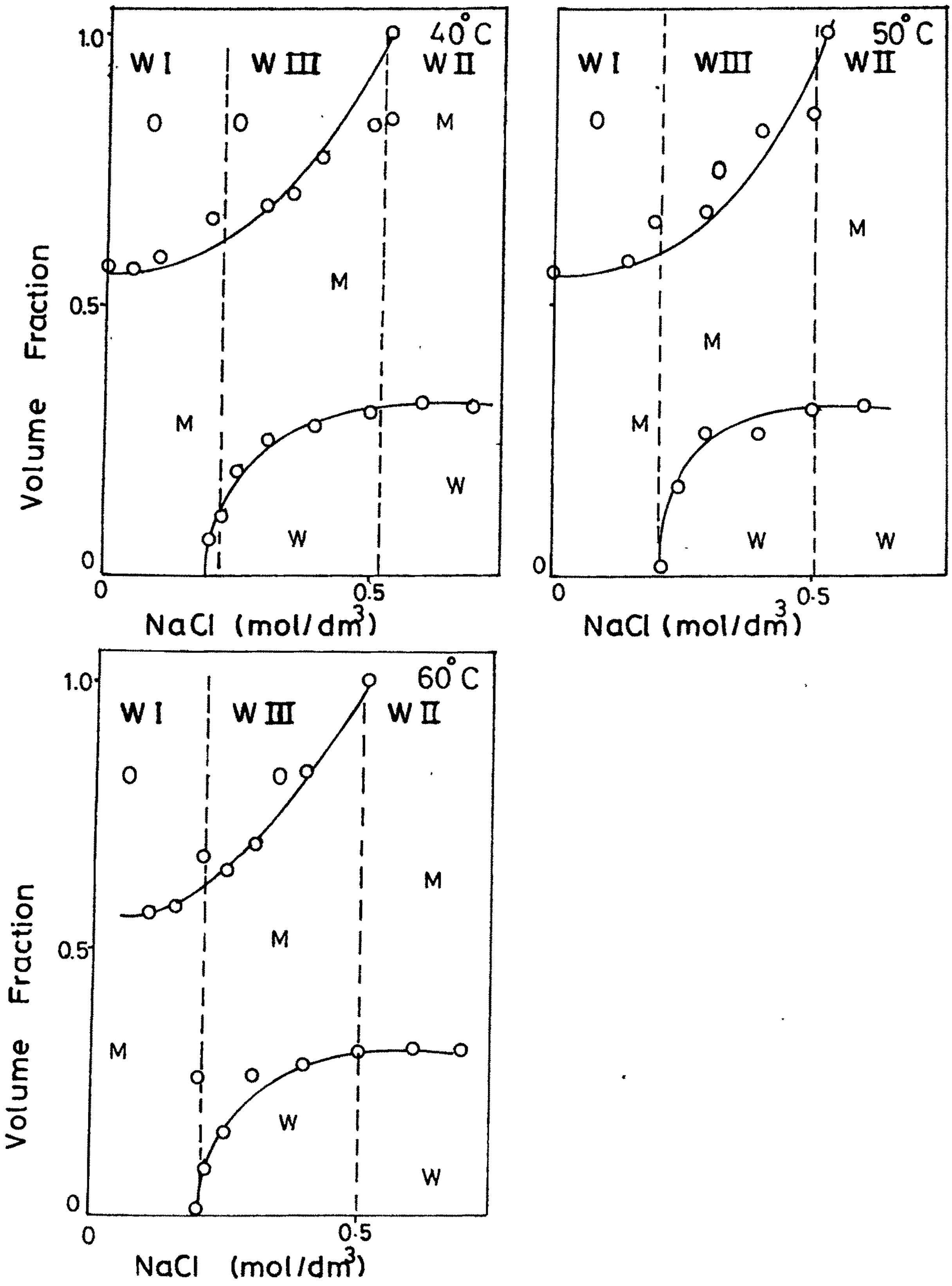
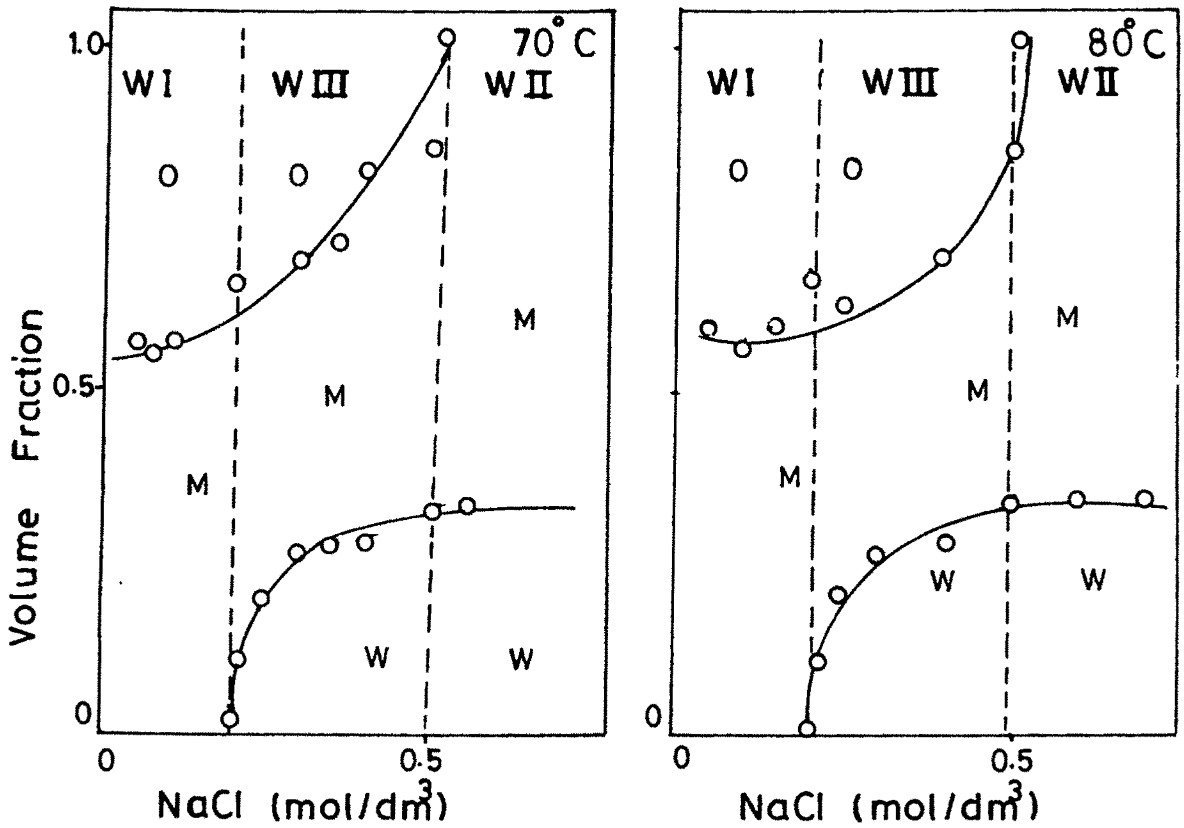


Fig. 4.20 : Representative plots of volume fractions as a function of NaCl (mol/dm$^3$) at in presence of 0.005% PAA at 40, 50, 60, 70 and 80°C.


Volume Fraction
1.0
0.5
0
0
0.5
NaCl (mol/dm$^3$)
70°C
WI
WIII
WII
O
M
W
80°C
WI
WIII
WII
O
M
W
0
0
0.5
NaCl (mol/dm$^3$)

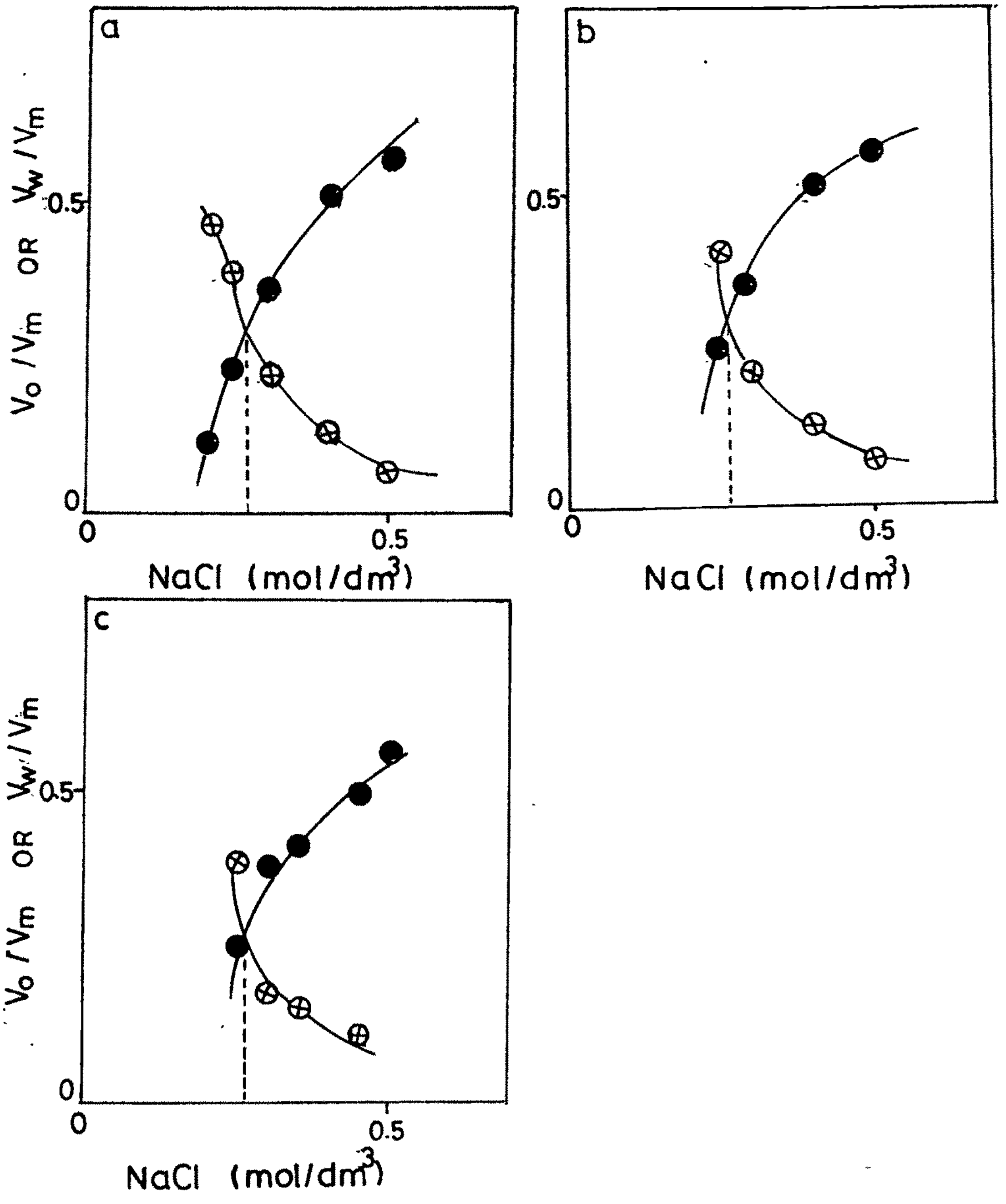
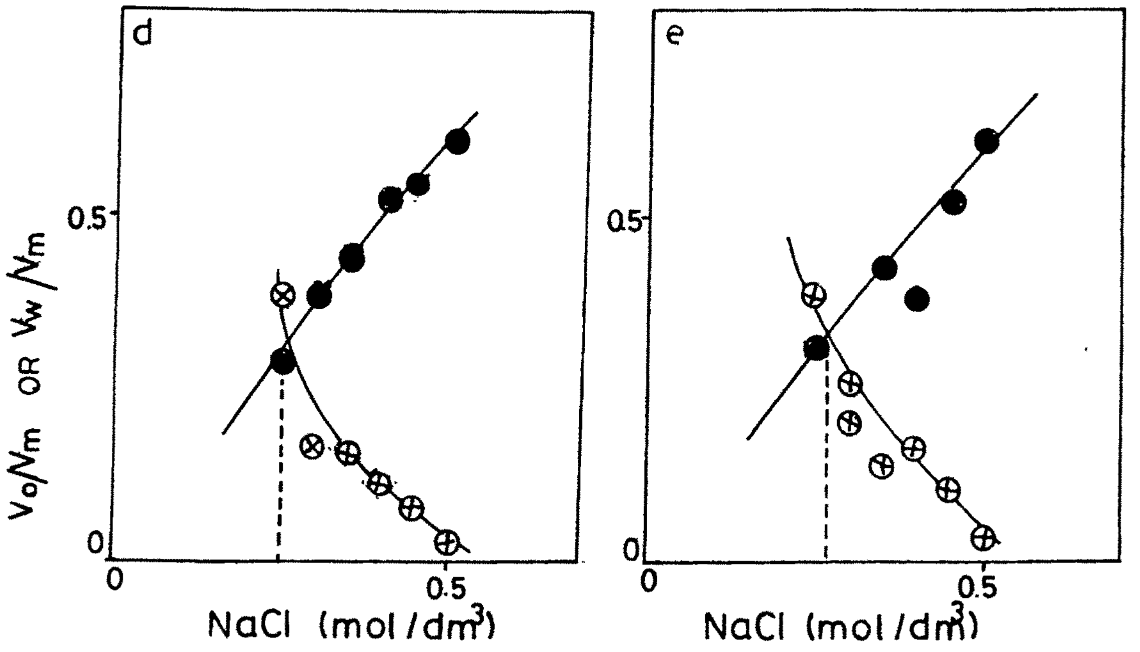


Fig. 4.21 : Plot of Vo/Vm (●) and Vw/Vm (⊗) as a function of NaCl (mol/dm$^3$) concentration Vo and Vw are the volumes of oil and water in microemulsion. Vm is the volume of microemulsion a, b, c, d, e at 40, 50, 60, 70 and 80°C with 0.005% PAA.


d
e
0.5
0
0
0.5
0.5
0
0
0.5
$V_o/V_m$ OR $V_w/V_m$
NaCl (mol/dm$^3$)
NaCl (mol/dm$^3$)

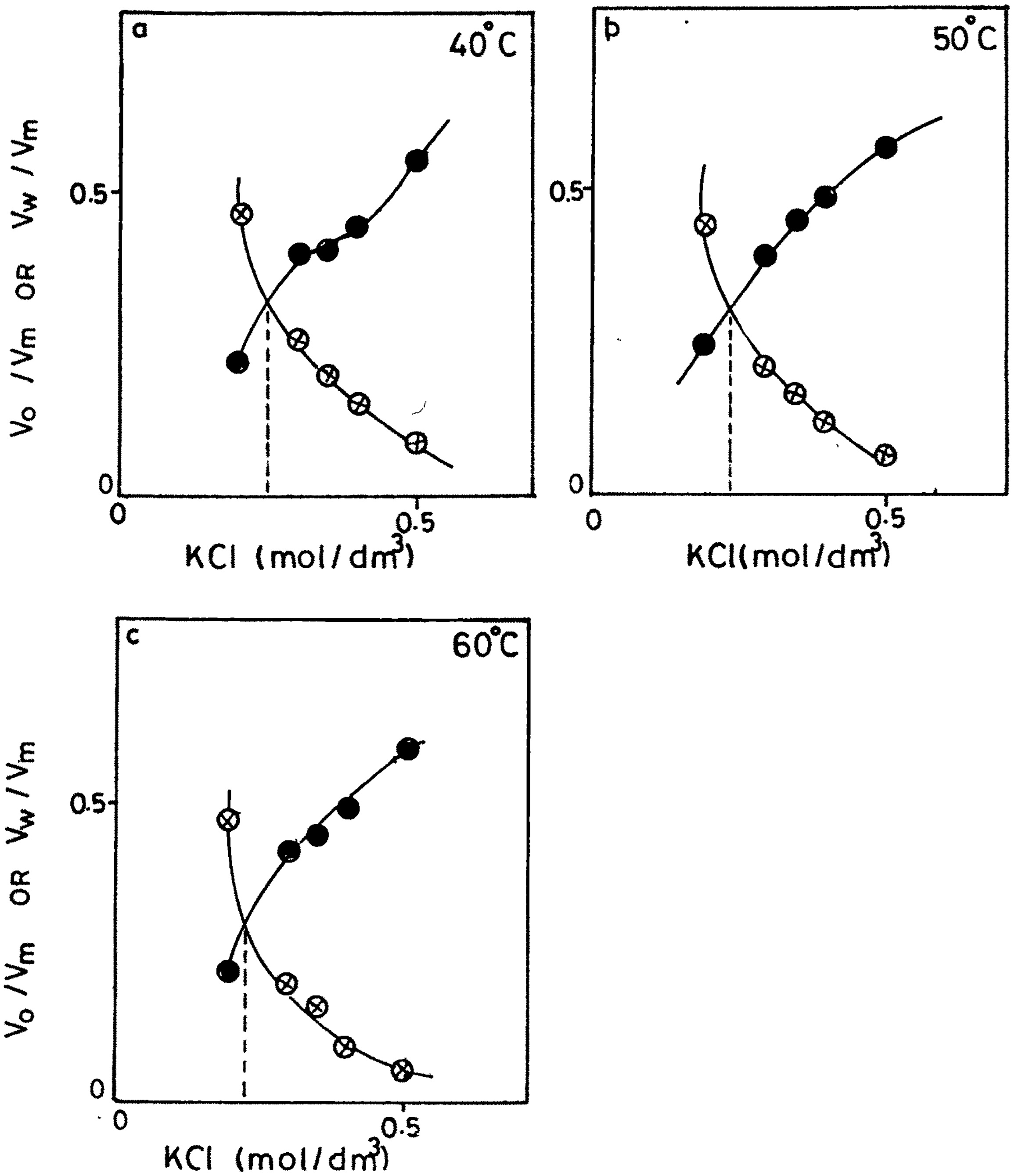


Fig. 4.22 : Plot Vo/Vm (●) and Vw/Vm (⊗) as a function of concentration of KCl (mol/dm$^3$) with 0.005% PAA Vo and Vw are the volumes of oil and water in microemulsion a, b, c, d, e and 40, 50, 60, 70 and 80°C.

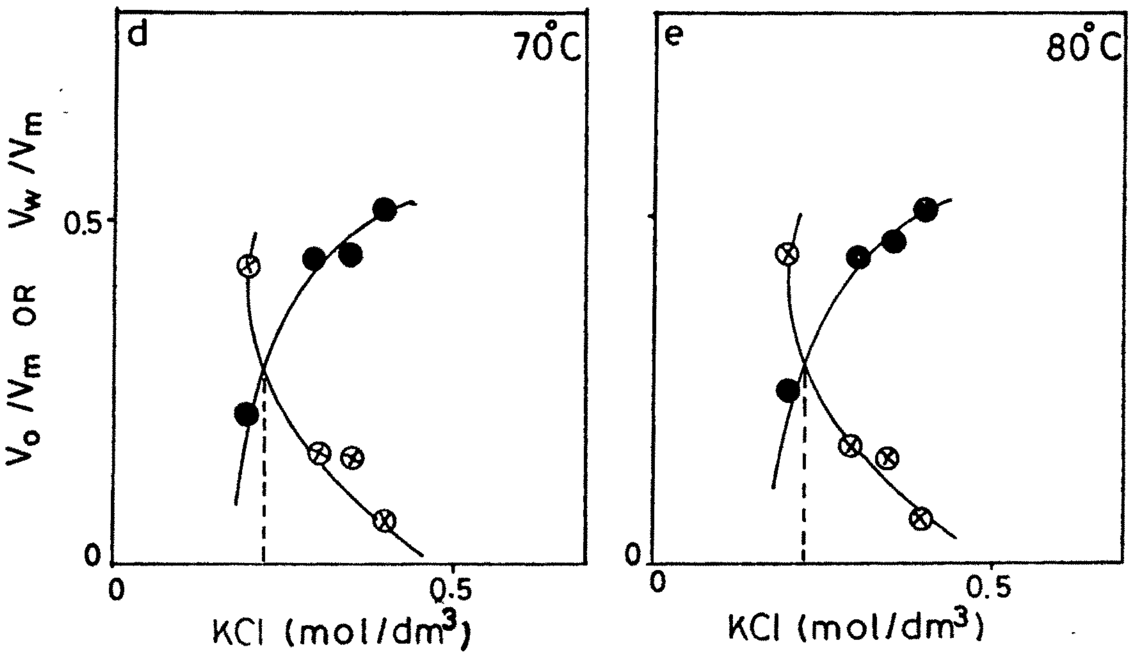

d
70°C
e
80°C
$V_o/V_m$ OR $V_w/V_m$
0.5
0
0
0.5
KCl (mol/dm$^3$)
0
0
0.5
KCl (mol/dm$^3$)

Table 4.3 - Concentrations of halides (M) in various Winsor transitions at different temperatures for the system cyclohexane / CTAB / 1-propanol/X-$H_2O$.

| WINSOR I TO WINSOR III | | | | | X | WINSOR III TO WINSOR II | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 40°C | 50°C | 60°C | 70°C | 80°C | | 40°C | 50°C | 60°C | 70°C | 80°C |
| 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | NaCl | 0.47 | 0.47 | 0.47 | 0.47 | 0.47 |
| 0.18 | 0.19 | 0.20 | 0.20 | 0.20 | NaCl with 0.005% PAA | 0.52 | 0.51 | 0.50 | 0.50 | 0.50 |
| 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | NaBr | 0.57 | 0.57 | 0.57 | 0.57 | 0.57 |
| 0.03 | 0.04 | 0.06 | 0.06 | 0.06 | NaBr with 0.005% PAA | 0.58 | 0.57 | 0.56 | 0.56 | 0.56 |
| 0.14 | 0.14 | 0.14 | 0.14 | 0.14 | NaI | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| 0.05 | 0.06 | 0.06 | 0.06 | 0.06 | NaI with 0.005% PAA | 0.51 | 0.51 | 0.50 | 0.50 | 0.50 |
| 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | KCl | 0.54 | 0.54 | 0.54 | 0.48 | 0.48 |
| 0.19 | 0.19 | 0.20 | 0.20 | 0.20 | KCl with 0.005% PAA | 0.51 | 0.51 | 0.50 | 0.50 | 0.50 |
| 0.14 | 0.14 | 0.14 | 0.14 | 0.14 | KBr | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 |
| 0.09 | 0.10 | 0.11 | 0.11 | 0.11 | KBr with 0.005% PAA | 0.42 | 0.42 | 0.42 | 0.42 | 0.42 |
| 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | KI | 0.27 | 0.27 | 0.27 | 0.26 | 0.26 |
| 0.05 | 0.06 | 0.06 | 0.06 | 0.60 | KI with 0.005% PAA | 0.35 | 0.35 | 0.35 | 0.34 | 0.34 |

Table 4.4 - The optimal salinity (molar) at various temperatures for the system cyclohexane (42.5%) / CTAB + 1-propanol (17.5%) / X in presence of various electrolytes.

| X (40%) | Electrolytes | 40°C | 50°C | 60°C | 70°C | 80°C |
|---|---|---|---|---|---|---|
| Water | NaCl | 0.39 | 0.39 | 0.39 | 0.38 | 0.38 |
| 0.005% Aq. PAA | NaCl | 0.27 | 0.26 | 0.26 | 0.26 | 0.26 |
| Water | NaBr | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| 0.005% Aq. PAA | NaBr | 0.23 | 0.24 | 0.24 | 0.22 | 0.22 |
| Water | NaI | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 |
| 0.005% Aq. PAA | NaI | 0.11 | 0.14 | 0.14 | 0.11 | 0.11 |
| Water | KCl | 0.32 | 0.32 | 0.32 | 0.30 | 0.29 |
| 0.005% Aq. PAA | KCl | 0.25 | 0.24 | 0.23 | 0.22 | 0.23 |
| Water | KBr | 0.20 | 0.20 | 0.20 | 0.15 | 0.15 |
| 0.005% Aq. PAA | KBr | 0.19 | 0.20 | 0.20 | 0.17 | 0.17 |
| Water | KI | 0.11 | 0.11 | 0.11 | 0.11 | 0.10 |
| 0.005% Aq. PAA | KI | 0.08 | 0.09 | 0.09 | 0.08 | 0.08 |

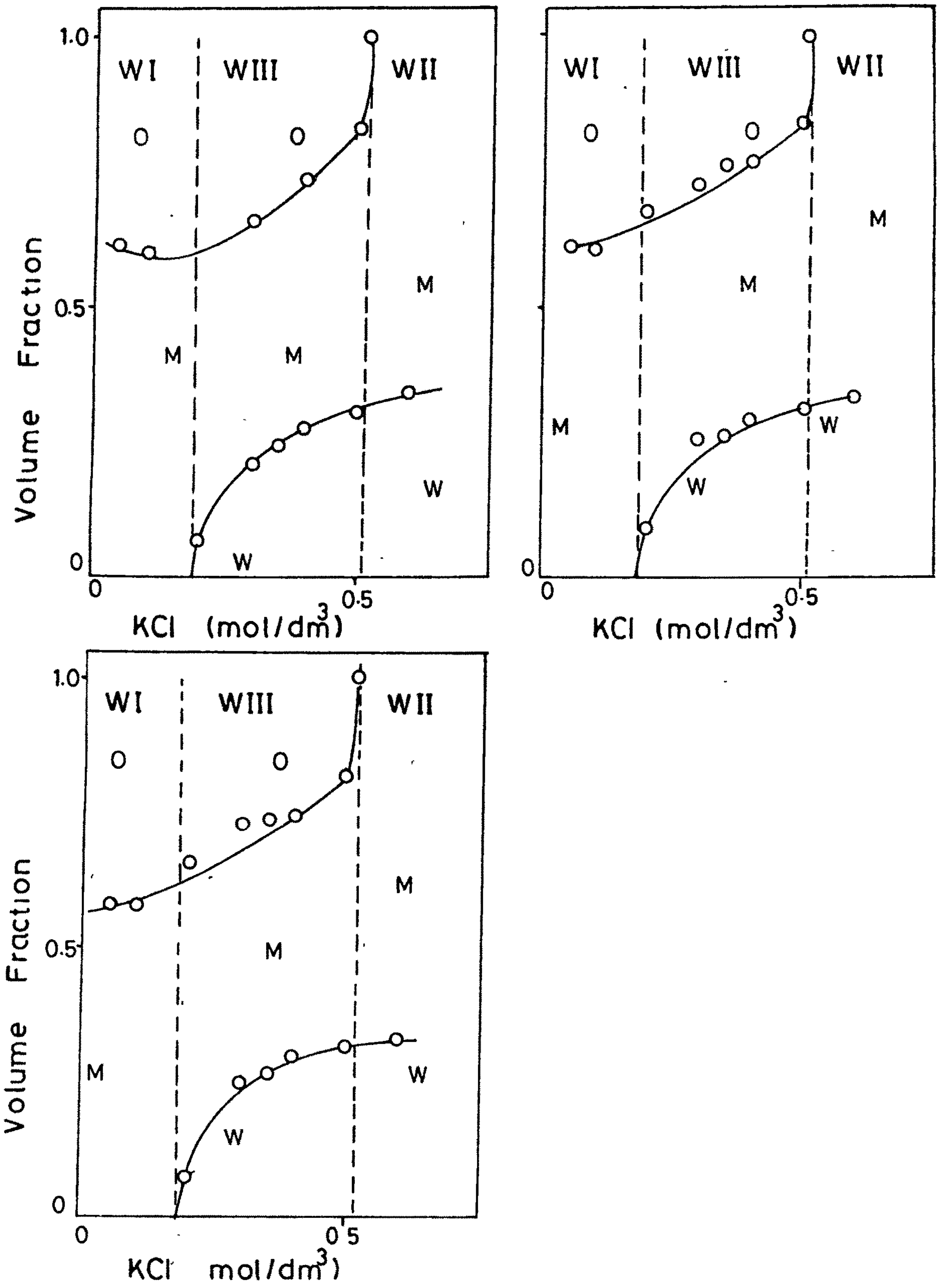
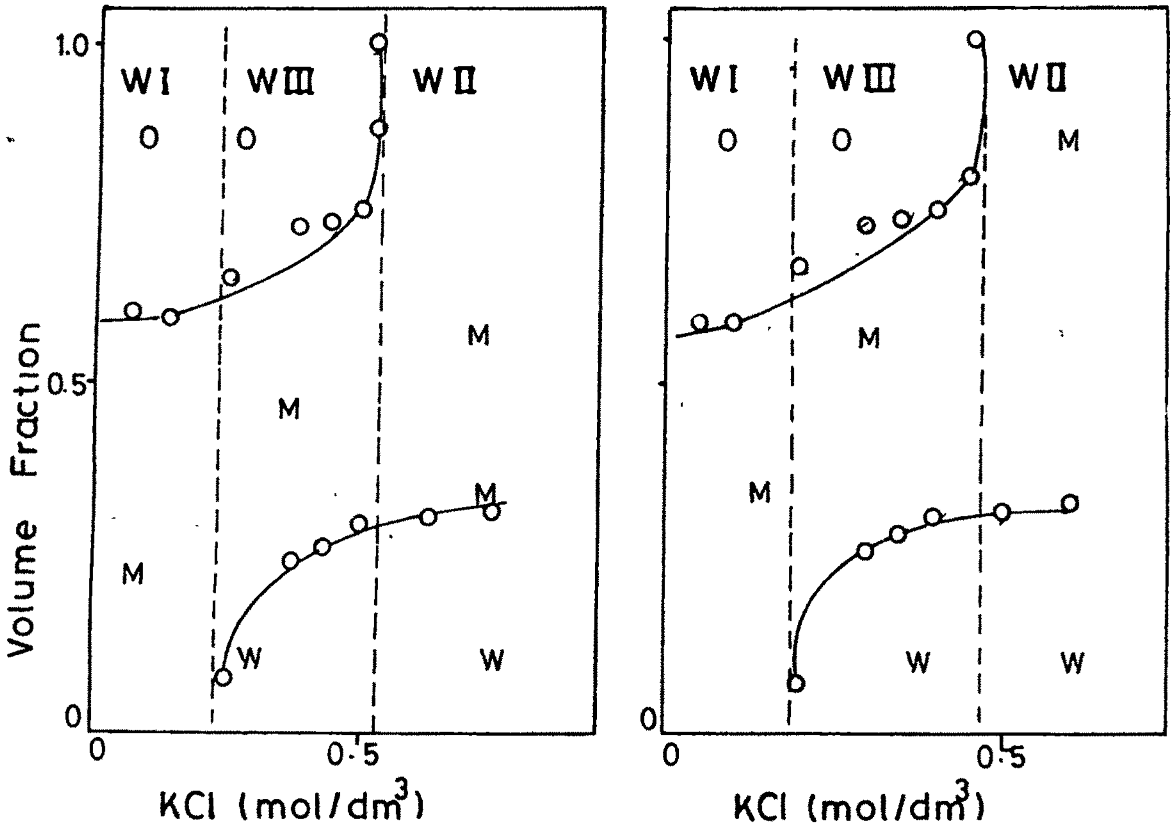


Fig. 4.23 : Plot of volume fraction as a function of concentration of KCl (mol/dm$^3$) in presence of 0.005% PAA at 40, 50, 60, 70 and 80°C.


Volume Fraction
1.0
0.5
0
KCl (mol/dm$^3$)
0
0·5
WI
WIII
WII
O
M
W

observed. In presence of PAA (0.005%) also the effect of temperature is absent. In presence of halide ions, three-phase system appears because of the favourable hydrophilic-hydrophobic balance induced in the surfactant system. The different halides affect this balance differently and it seems that the alkali metal ions do not have much effect on this balance. The interfacial amphiphile layer is affected by the halide ions and at some concentration of halide ions the hydrophil-lipophil balance, which is required for WIII formation is achieved.

As we have suggested earlier[6], the cosurfactant (1-propanol) increases the hydrophilicity of the system to such high values that increase in temperature does not have much effect on the hydrophilicity and hence the optimal salinity (OS) remains same. The cosurfactant, 1-propanol, is partitioned between oil, water and the interface. Hydrogen bond is formed between 1-propanol and water. Increase in temperature breaks the hydrogen bond and propanol moves towards the interface making it more hydrophobic. Increase in temperature makes ionic surfactants hydrophilic and probably the hydrophilic-hydrophobic balance is achieved thereby and this balance remains independent of temperature. PAA is relatively more hydrophobic than PEG-400 and, therefore, OS in presence of PAA should be less and that was observed. The OS values were further explored; the difference between OS (NaCl) and OS (NaBr) was found to be almost equal to that between OS (KCl) and OS (KBr). Similarly [OS(NaCl) - OS(KCl)] was found to be almost equal to [OS(NaBr) - OS(KBr)] or [OS(NaI) - OS(KI)]. All the possible combinations show similar behaviour whether PAA was present or not. Therefore, we suggest that the optimal salinity is a function of the ions constituting the electrolyte rather than the electrolyte itself and it is the halide ion which is relatively more important. This was observed earlier also[6].

### 4.3.6 Adiabatic compressibility study :

We have also determined adiabatic compressibility $\beta$ at various temperatures with a constant S + CS concentration. A representative plot is shown in Fig. 4.24-27. It is

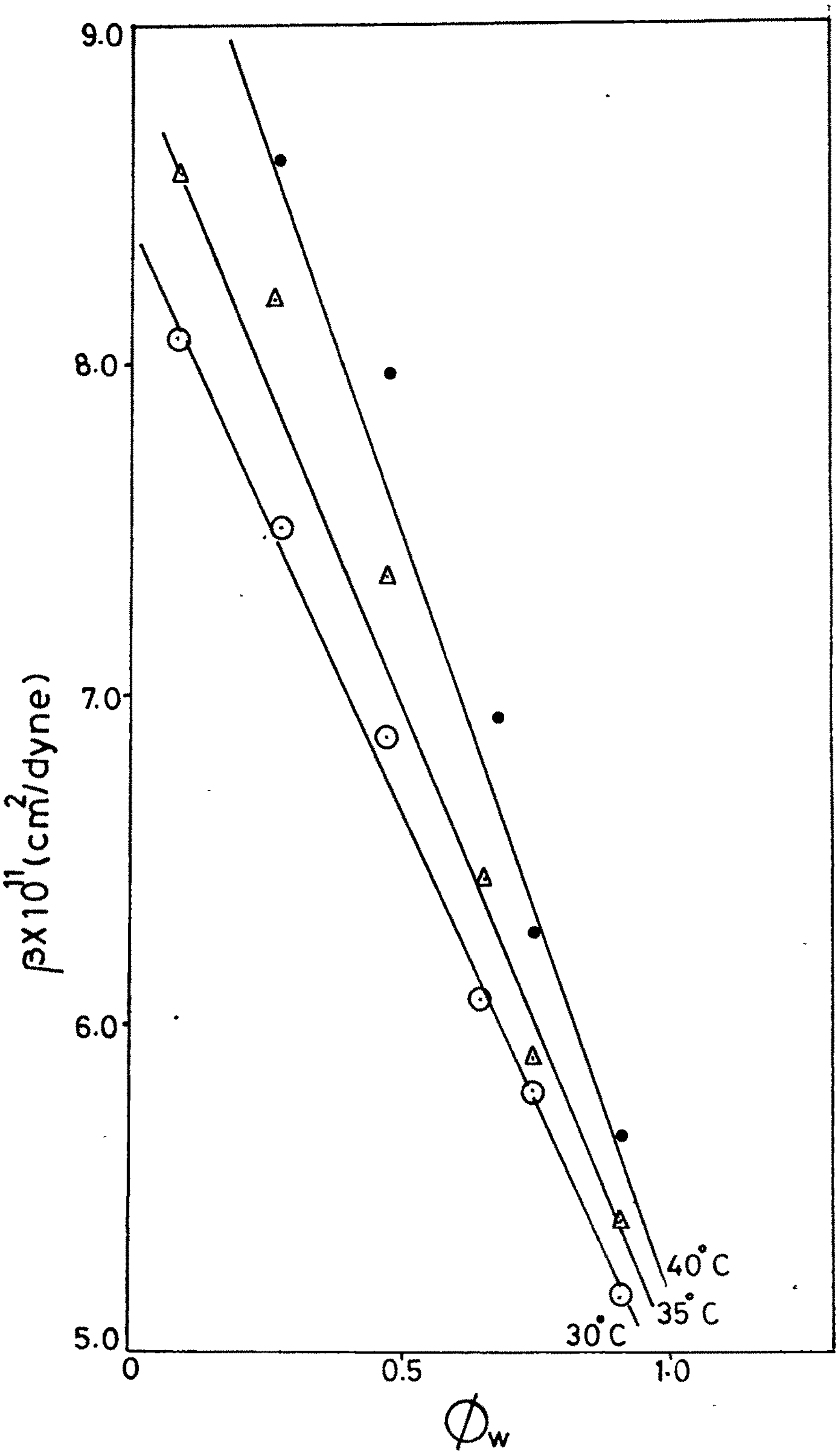


Fig. 4.24 : Plot of adiabatic compressibiloty (β) against volume fraction of water with S+CS 45%; 0.05% aq.PAA at 30, 35 and 40°C.

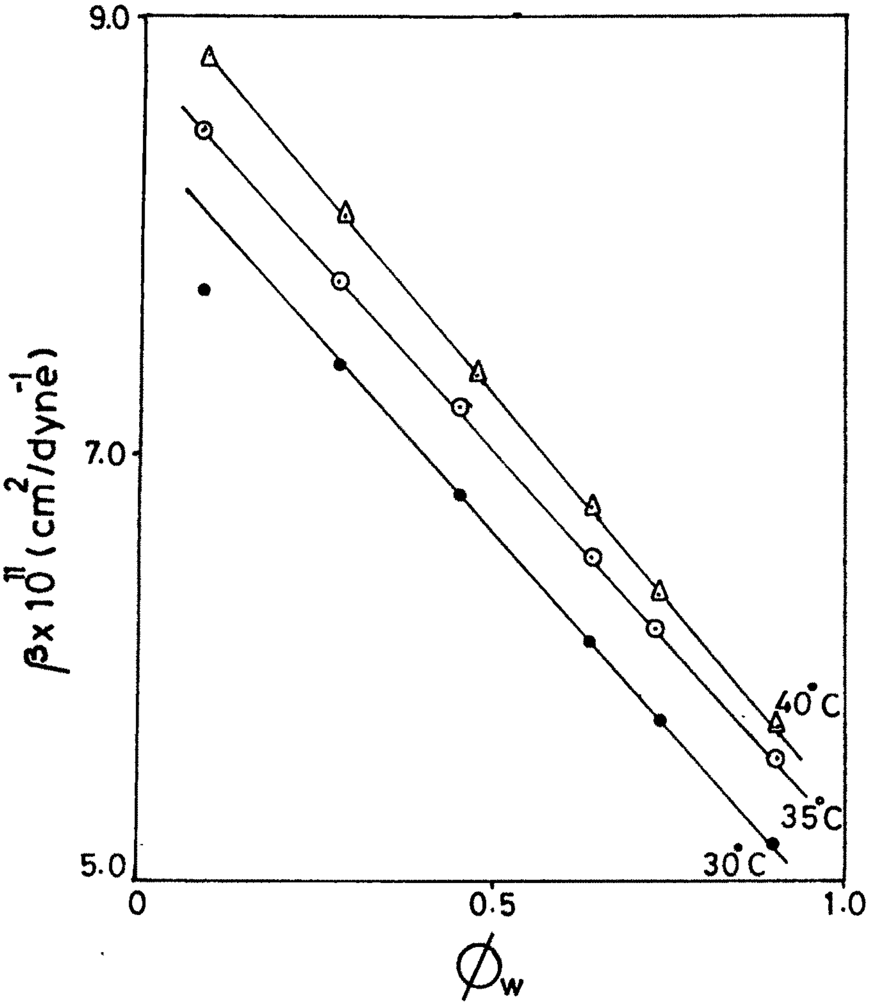


Fig. 4.25 : Plot of adiabatic compressibility (β) against volume fraction of water with S+CS 45%; 0.005% aq.PAA at 30, 35 and 40°C.

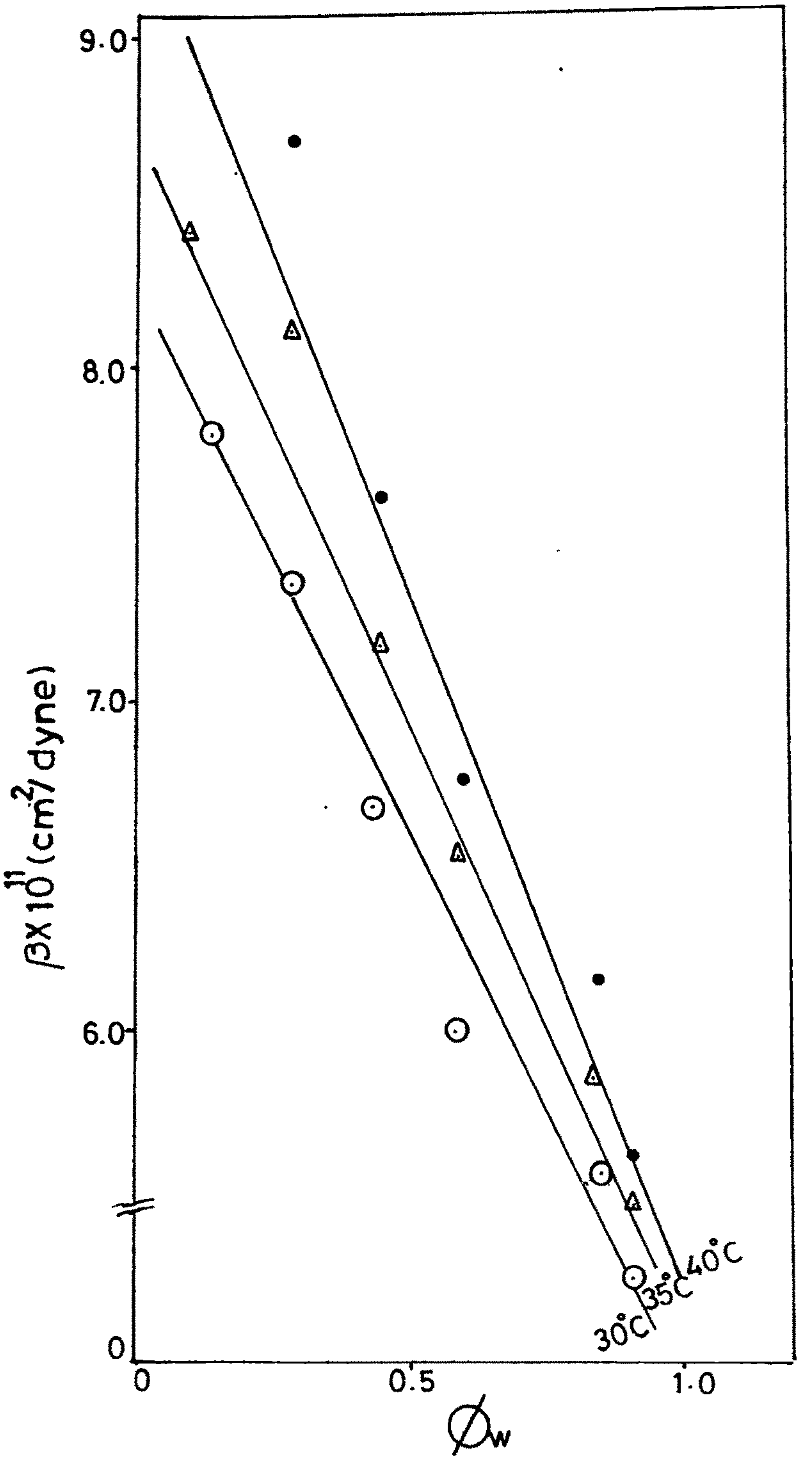


Fig. 4.26 : Plot of adiabatic compressibility (β) against volume fraction of water with S+CS 65%; 0.1 aq.PAA at 30, 35 and 40°C.

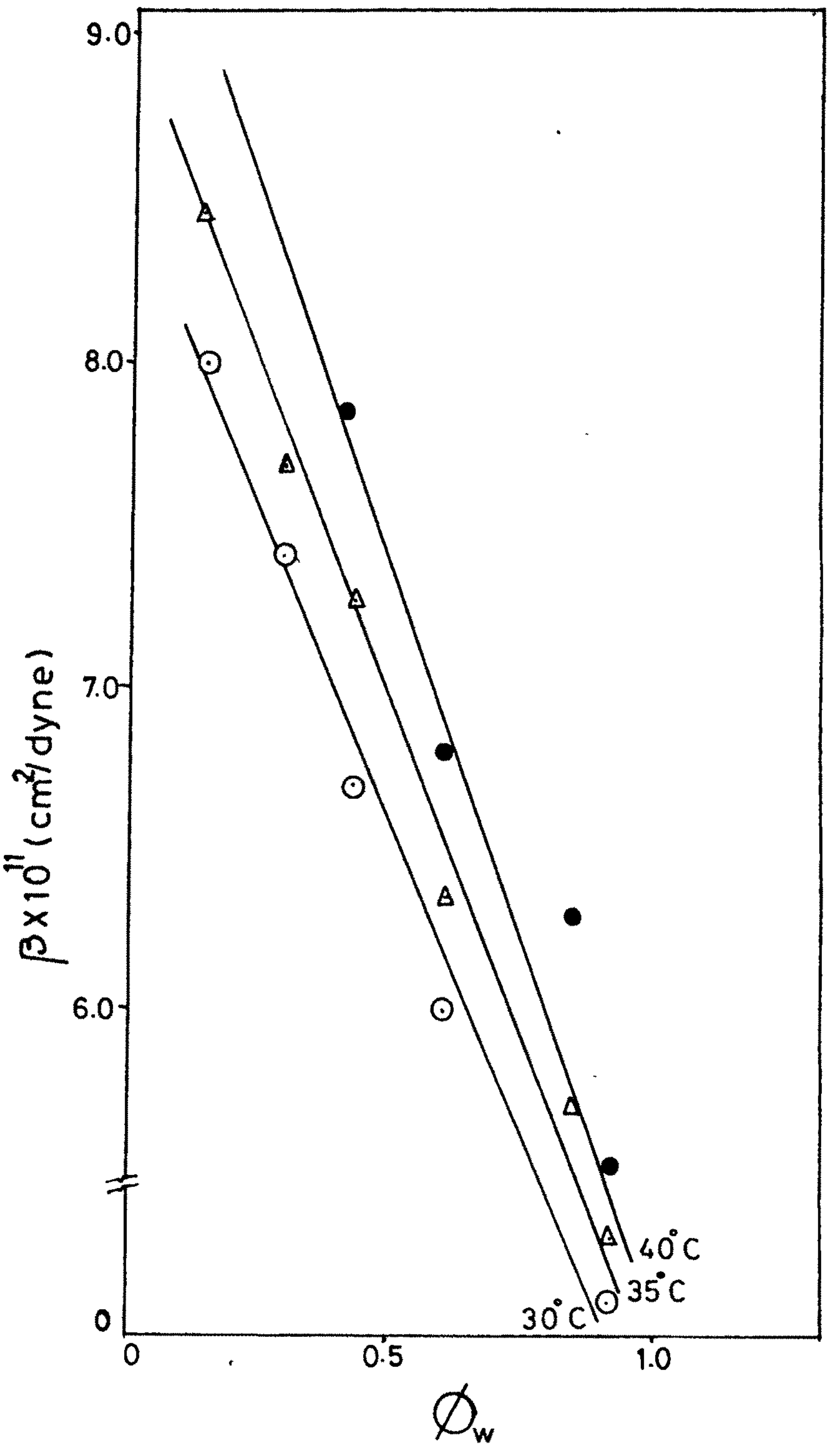


Fig. 4.27 : Plot of adiabatic compressibility against volume fraction of water with 65% S+CS; 0.05% aq.PAA at 30, 35 and 40°C.

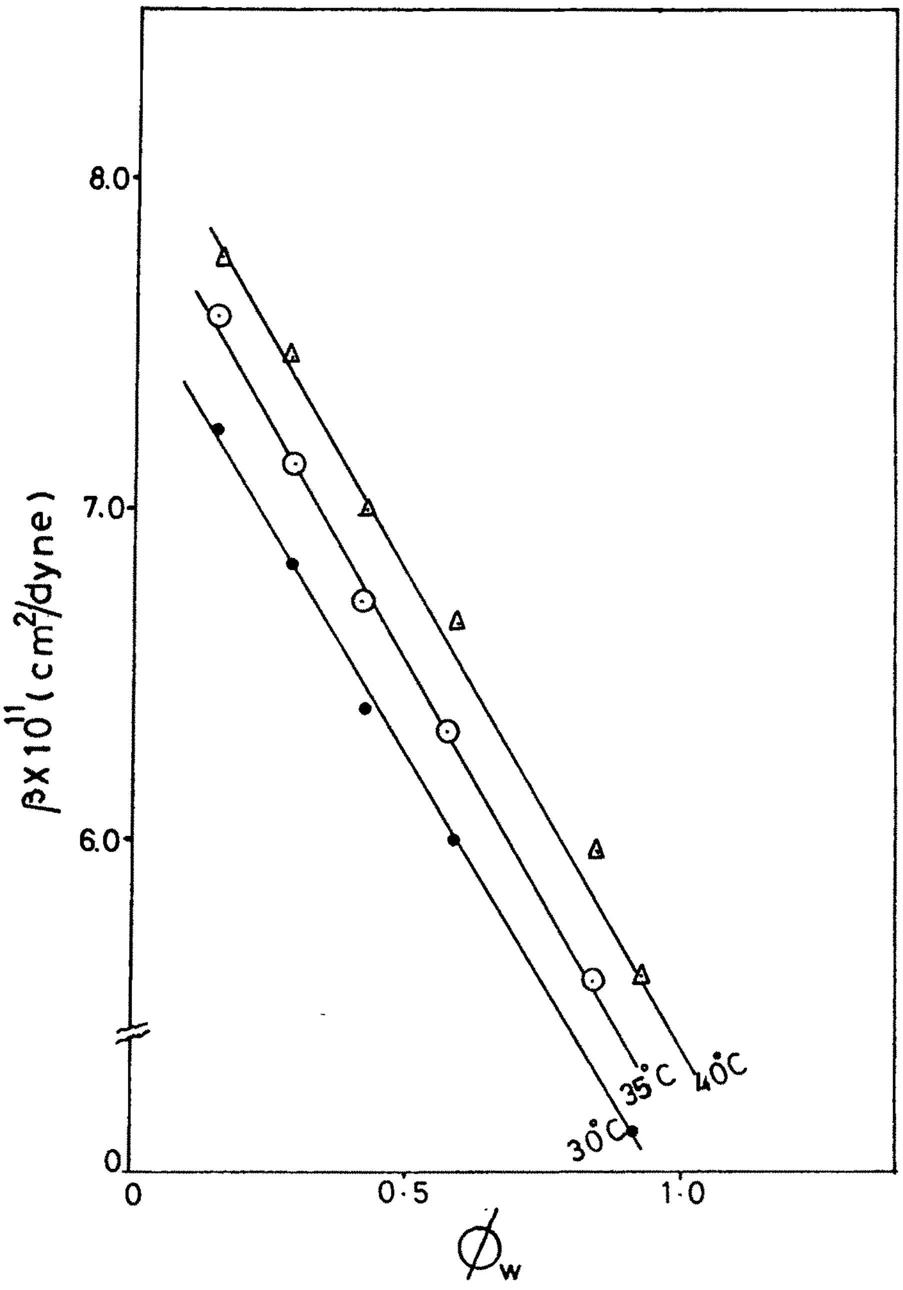


Fig. 4.28 : Plot of adiabatic compressibility against volume fraction of water with 65% S+CS; 0.005% aq.PAA at 30, 35 and 40°C.

seen that as the concentration of water increases, β decreases. This was expected as the water is less compressible than cyclohexane. The higher compressibility at higher temperature is well known. We also noted that higher the PAA concentration, the lower is β indicating that in presence of PAA the system is more rigid and less sensitive to pressure variations. The presence of PAA at the droplet surface makes the system rigid.

The effect of polyacrylamide in the title four-component system is somewhat different from that of PEG-400. The difference is particularly observed in phase diagram, IFT, optimum salinity etc. though the relative variation of viscosity, surface tension, etc., remain similar. The temperature does not seem to have any effect on most of these properties, which is quite different from the behaviour of non-ionic surfactant microemulsions.

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