CHAPTER 3

FORMATION AND PROPERTIES OF MICROEMULSION : EFFECT OF TEMPERATURE AND POLYACRYLAMIDE

3.a. Preview

Microemulsions are essentially three component systems of oil, water and emulsifiers. In the cases where mixtures of amphiphilic materials are indispensable for the microemulsion formulation, all such surface active agents, including cosurfactants,can be considered together as a single component. Such three component systems are generally rich with a variety of phases which can exist in equilibrium with each other and these phases have diverse microstructure [133,134]. It is therefore both convenient and instructive to employ a ternary representation of the system for their study. The ternary phase diagrams are a prerequisite for the study of microemulsions as these isotropic fluid phases occur over a specific part of such diagrams [36, 93]. The properties and the composition limits, within which microemulsion forms,are affected by many factors such as temperature, pressure and the nature of the components [135]. Though the effect of pressure was found to be comparatively weak [135], the temperature seems to have strong effect on the phase behaviour and may be counted as an important experimental parameter. In this chapter, studies of the effects of temperature on the monophasic microemulsion zone of the ternary phase diagram and also on the physicochemical properties viz. conductance, viscosity and adiabatic compressibility of the systems are presented.

In many applications of importance to chemical, petroleum and pharmaceutical industries, the surfactant molecules are present along with other macromolecular substances [136]. Polymers can interact with surfactants in many ways including the usual forces of interaction between any two different molecules : ion-ion, ion-dipole, dipole-diploe and vander Waals forces [137]. The study of interaction between water soluble polymers and surfactants is equally important from both fundamental as well as technological point of view. The presence of polymeric materials in the micellar solutions of surfactants can modify the self aggregation and interfacial characteristics of the surfactants [138,139]. Moreover the polymer-surfactant interaction may bring about changes in the conformation of polymeric chains [140,141]. Looking from the user view point,a better grasp of polymer surfactant interaction may help to choose a polymer - surfactant system which will meet most of the requirements in the enhanced oil recovery (EOR), formulation of agricultural products, detergents, food manufacture etc. Polymer-surfactant interaction play a very important role in detergency. Here the antiredeposition agents, used to better the detergency by avoiding the soil redeposition during the rinsing cycle, are water soluble polymers [142].

Though a number of experimental studies have been carried out to determine the changes induced by polymer molecules in the solution behaviour of surfactants, there are not many studies involving these macromolecules in microemulsion systems. The interaction of water soluble polymers with microemulsions may result in the phase separation or change in the phase boundaries of these mixtures. Polyacrylamide (PAA) is a water soluble polymer very often used in the oil field processes [143,144]. Hence its effect on the phase boundaries and properties of present microemulsion system was thought to be of much significance from the industrial point of view and hence was studied.

3.b. Experimental

To study the effect of PAA on the phase diagram and properties, water was replaced by aqueous solutions of PAA of different concentrations. Since the polymer showed the tendency to precipitate in certain compositions of the system at higher concentrations, concentrations above 0.005% (w/v) were not studied. 0.01% (w/v) PAA solution was prepared by dissolving the PAA in water by warming and the required lower concentration solutions (0.005% and 0.003% (w/v)) were prepared by diluting the 0.01% solution with the required amount of water.

3.c. Results and Discussion

(i) Phase diagram

Fig.3.1 is a representative ternary phase diagram of the system cyclohexane - SDS + propanol - water at 40°C. The region bounded by line-1 and line-2 is the isotropic one phase microemulsion zone. This microemulsion zone is attached to a portion of the zero-oil line of the phase diagram and hence this area may be a direct continuation of the region of micelles existing in water/surfactant/ cosurfactant phase diagram, similar to that reported by Boned et al.[145]. In contrast to this fact, this region does not coincide with the zero water line of the diagram which is because of the non-solubility of the ionic surfactant in the hydrophobic phase unless some amount of water is present. The portions above and below this microemulsion zone constitutes a solid-liquid biphasic region and a liquid-liquid biphasic region respectively. In the present chapter we report the results of our studies on single phase microemulsions. The two phasic systems, the solid-liquid or liquid-liquid, were not studied

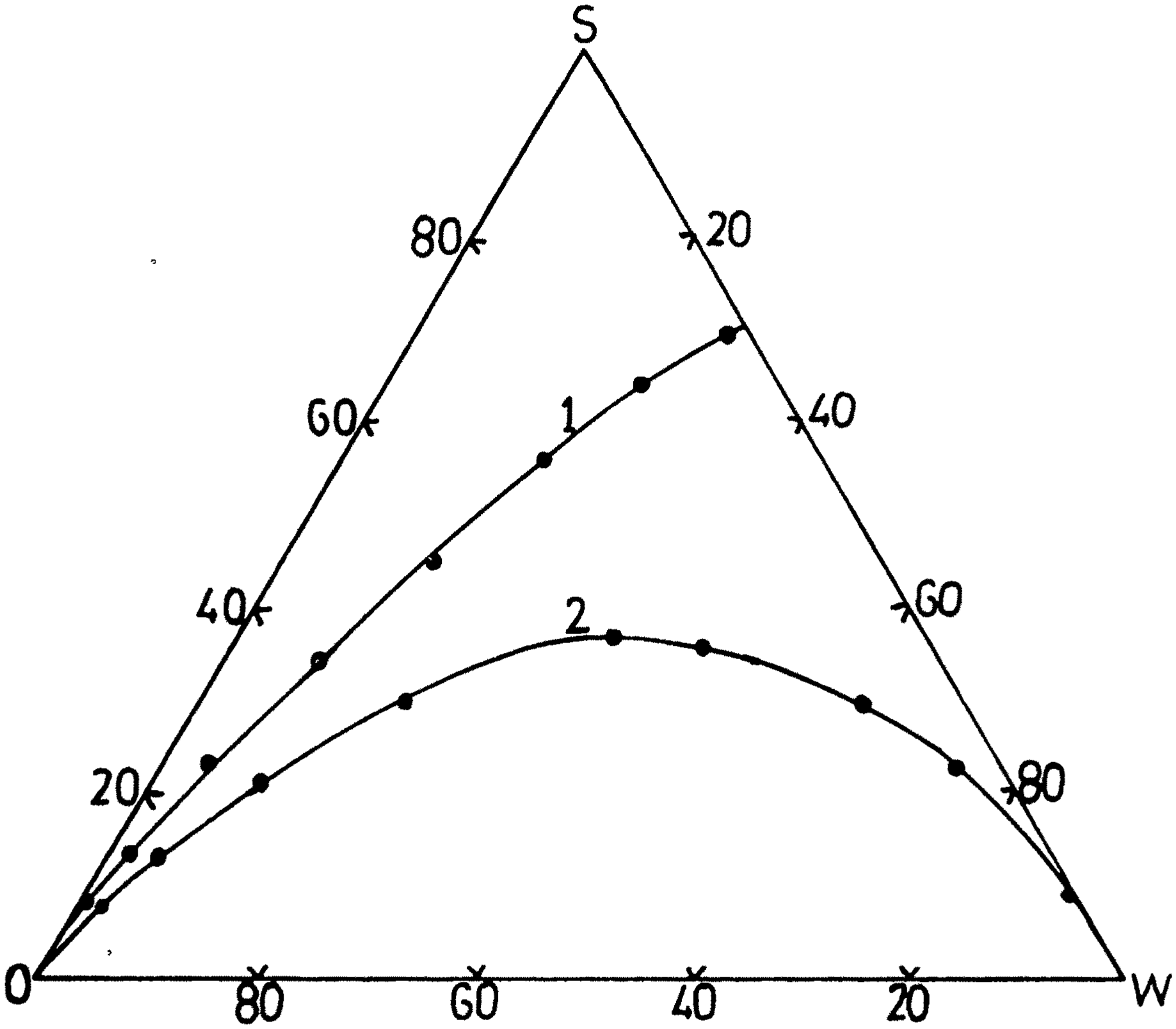

Fig.3.1 Ternary phase diagram of the system cyclohexane-SDS + propanol - water at 40°C.

at all. Fig.3.2 depicts the variation in the areas of the isotropic single phase microemulsion zones with temperature in presence and absence of polyacrylamide in the aqueous phase. The concentrations of polyacrylamide in aqueous solutions were 0.003 and 0.005%. Here the percentage area of the one phase zone in the triangular phase diagram is plotted against temperature. The monophasic percent microemulsion area vs temperature curve (Fig.3.2) shows a maximum around 40°C. In this case no polyacrylamide was used. But the presence of polymer in the aqueous phase alters the nature of the curve, showing a minimum when 0.005% (w/v) PAA is present. This minimum was also found around 40°C. At 0.003% (w/v) PAA the microemulsion area remains invariant with temperaure. In Fig.3.3 the stacked phase diagrams of the system at 20, 40 and 60°C are shown for better comparison. This indicates the boundary lines 1 and 2 in presence and absence of PAA at various temperatures. Here the phase boundaries for pure water and 0.005% PAA are shown by solid lines and dashed lines respectively. It is quite obvious from this diagram that temperature has tremendous effect on these boundary lines. Fig.3.4 represents the dependence of the microemulsion area on the concentration of the polymer at various temperatures. The linearity of the plots indicate that the microemulsion area is a direct function of the polymer concentration. At all temperatures the

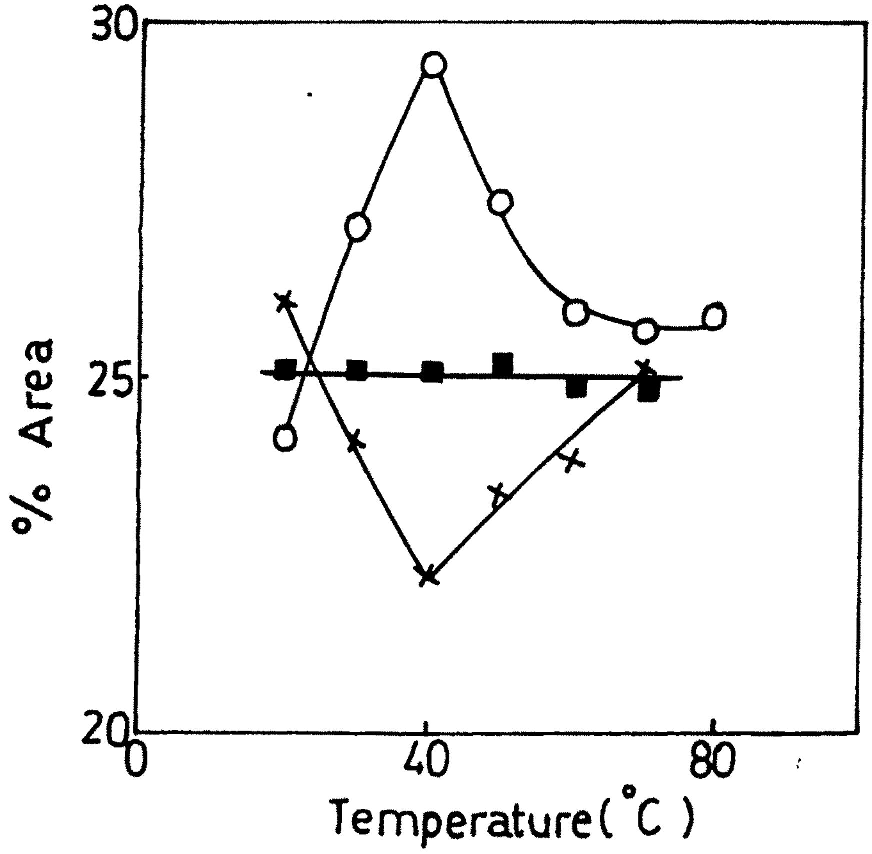

Fig. 3.2 Plot of percentage microemulsion area against temperature for the systems without PAA ○; 0.003% PAA ■; 0.005% PAA X.

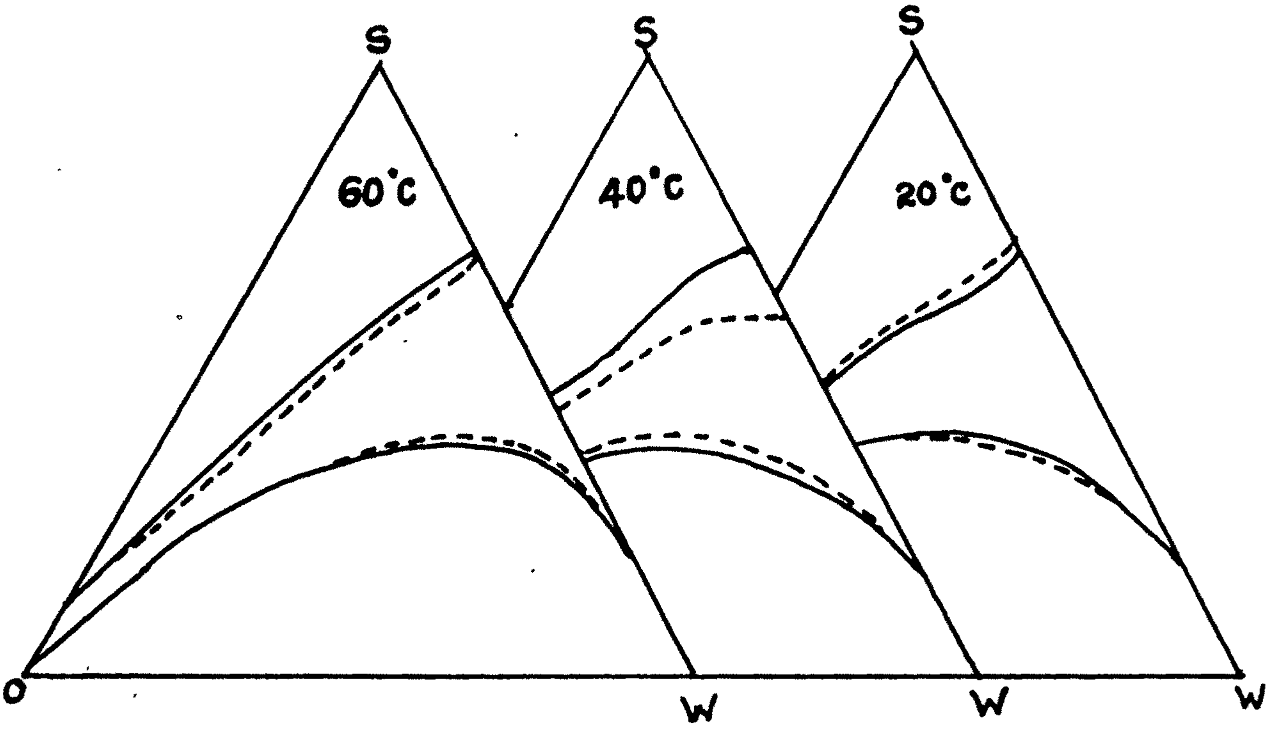

Fig.3.3 Stacked triangular phase diagrams at 60°C, 40°C and 20°C without PAA (——)and 0.005% PAA (------).

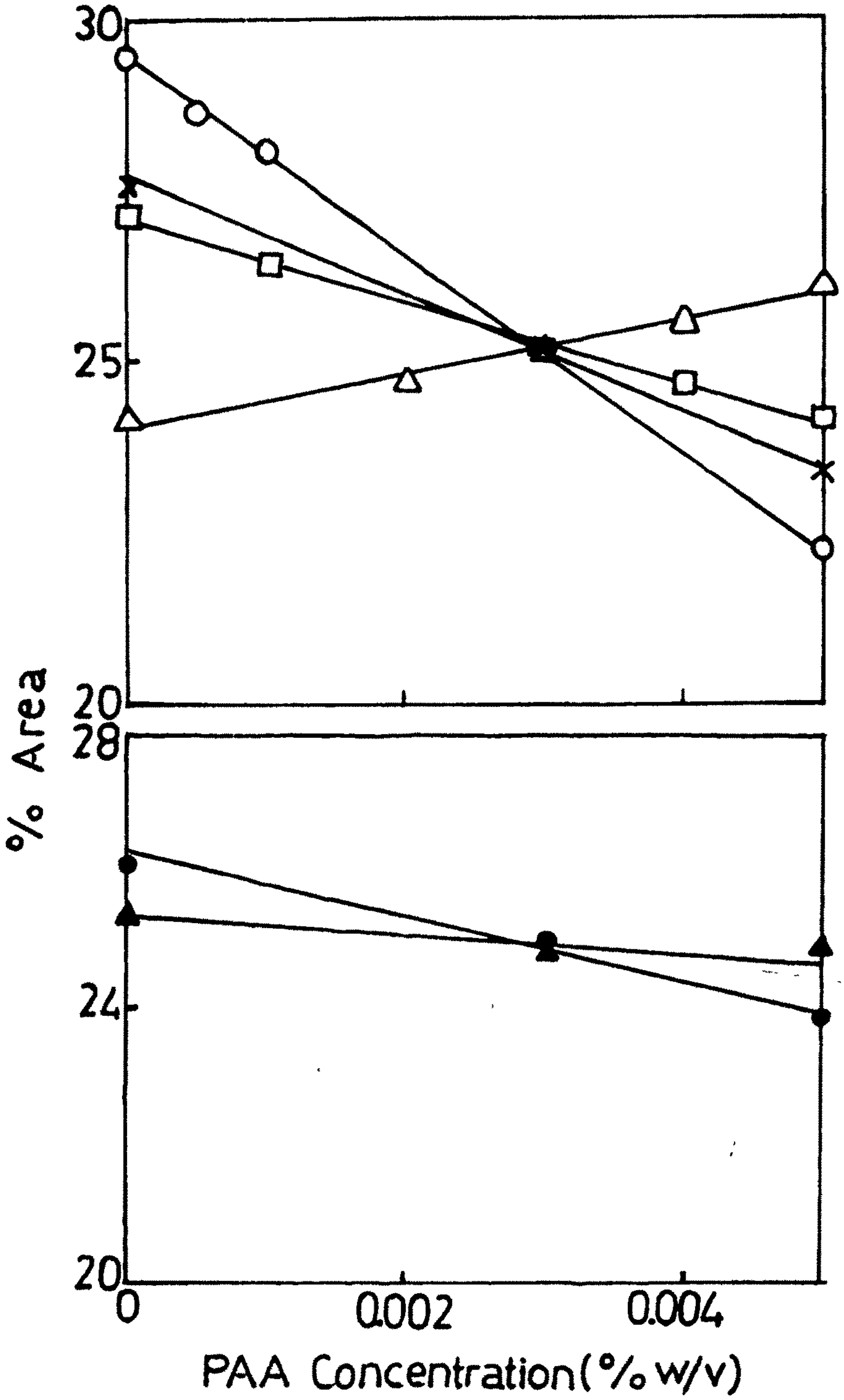

Fig. 3.4 Plots of percentage microemulsion area vs PAA concentration at temperatures 20°C △; 30°C □; 40°C ○; 50°C X; 60°C ●; 70°C ▲.

microemulsion zone decreased with increase in PAA concentration showing a negative slope except at 20°C where a positive slope was present. The slopes of the various lines present in Fig.3.4 were computed. These slopes were then plotted against temperature (Fig 3.5). A sharp minimum was observed at around 40°C. From the presence of this minimum it was concluded that the nature of the system changes drastically around 40°C. Polyacrylamides are expected to be intramolecularly hydrogen bonded. Its presence at the oil/water interface increases the interfacial tension (IFT). At around 40°C, this hydrogen bond breaks up and we have long chain non hydrogen bonded polyacrylamide at oil/water interface. This brings down the IFT and thereby favouring the microemulsion formation at higher temperature.

Microemulsions are formed due to the lowering of oil-water interfacial tension to an ultralow value mainly because of the adsorption of surfactant and cosurfactant molecules at the interface [7,94,111]. Generally increase in temperature decreases the oil-water interfacial tension [146]. This is because of higher kinetic energy and hence a diffused interface i.e. relatively more miscibility. Hence an increase in temperature is expected to favour relatively more formation of microemulsion by reducing the IFT. This should result in increasing the microemulsion

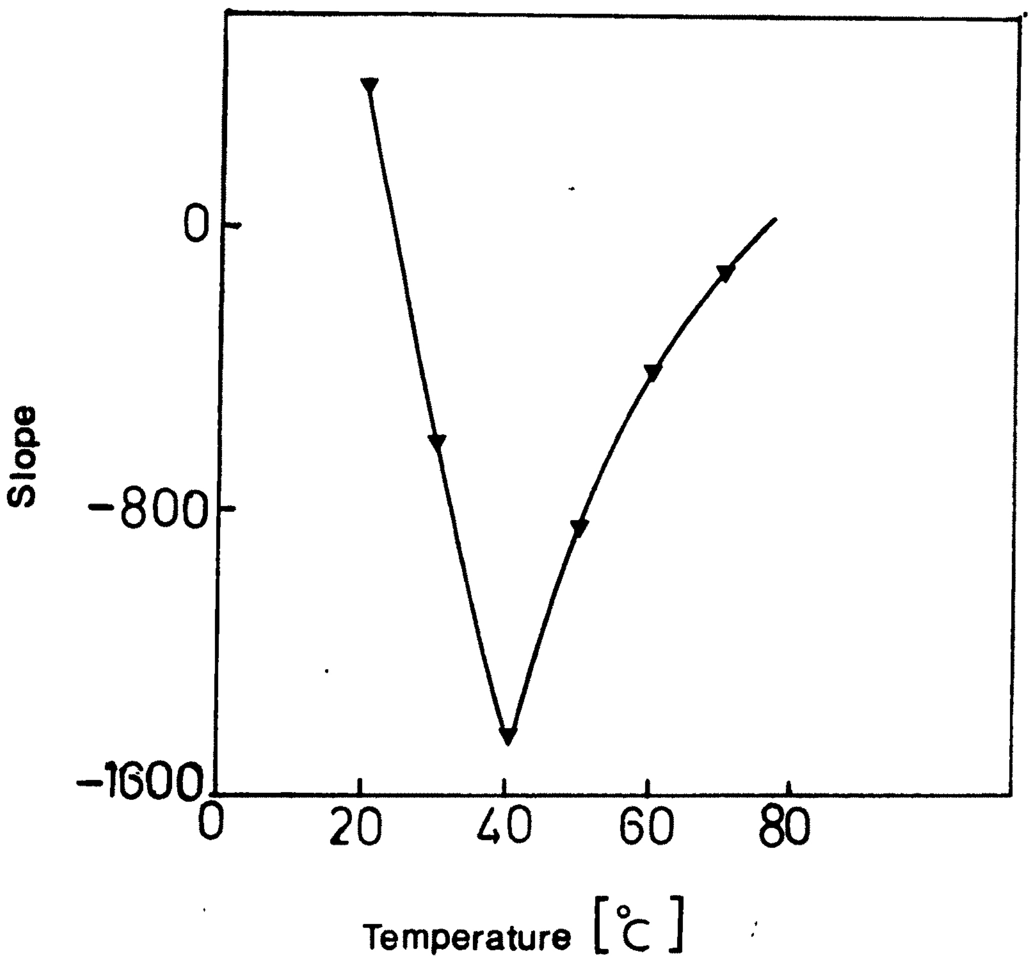

Fig.3.5 Plot of slopes of the straight line graphs in Fig.3.4, against temperature.

zone in the phase diagram [147]. The increase of temperature also causes increased thermal motion [64] of the adsorbed surfactant molecules at the interface. Probably above 40°C, the thermal motion of the surfactant molecules becomes predominant and the regular array of these molecules at the interface gets disturbed and molecules are likely to move out of the interfacial layer surrounding the droplets. Hence there will be a decreased number of surface active molecules at the interface which will concomitantly result in the decreased solubilization of oil into water or vice versa [64], thus decreasing the microemulsion zone above 40°C. Polyacrylamide molecules have large number of polar amide groups with the possibility of intramolecular hydrogen bonding between these groups as mentioned earlier. The presence of such polymeric materials generally has a destabilizing effect on microemulsions [148]. A decrease in the solubilization of aqueous phase into the surfactant containing oil phase in the presence of PAA has been reported by Moulik et al. [82]. But above a critical temperature (40°C) the H-bonding among the amide groups of PAA molecules breaks up rendering the polar heads free. This probably enables them to behave as surface active agent and thereby enhance the microemulsion formation.

Moreover, polyacrylamide is expected to be at the droplet-medium interface. From the interfacial tension measurements it was observed that at 35°C (i.e. below 40°C) in presence of 0.005% PAA the water/cyclohexane interfacial tension decreased from the value of 34.54 mNm^{-1} (without PAA) to 33.21 mNm^{-1} while at 48°C (i.e above 40°C) it increased from 32.71 mNm^{-1} (without PAA) to 33.92 mNm^{-1}. These values were determined in our laboratory. We feel that the presence of PAA in the microemulsion system overcrowds the interfacial area and some surfactants are replaced by the PAA. The effect on interfacial tension due to PAA is much smaller than that due to the surfactants and hence the microemulsion zone decreased. However, above 40°C, microemulsion zone increased as due to thermal motion larger PAA molecules get desorbed from the droplet surface and is replaced by the surfactant on the surface of the droplet. It may be stated here that the effects of temperature and PAA are somewhat antagonistic and cancel out each other in the 0.003% PAA system (Fig.3.2). The effect of the adsorption of polymer molecules on the droplets and their hindering effect on the formation of microemulsion is more obvious from the area versus PAA concentration profiles (Fig 3.4). It may be noted that the slope of the 40°C line is greater (i.e. more negative) than the 30°C line which indicates an increased effect of the polymer at this temperature.

(ii) Conductance

The specific conductance of various samples taken along the monophasic microemulsion region of the ternary phase diagram was plotted against water volume fraction in Fig.3.6 at various temperatures. These samples range from low water content ones to very high water containing ones. A fairly good percolative mode of conductance with two percolation thresholds [149], a 'water percolation threshold' and an 'oil percolation threshold',was obtained. We believe that this is not a peculiarity of the system, but rather a general pattern showing the continuous inversion of water in oil microemulsion (w/o) to oil in water microemulsion (o/w). Below a critical water volume fraction, termed as 'water percolation threshold' the conductance is very low, though higher than that in pure oil. This portion of the plot signifies the water in oil structure of microemulsion and the measured conductance in this region is due to electro- phoretic movements [150] of the monodispersed water globules in the oil continuum. Above the water percolation threshold the conductance rises sharply with the increase of water volume fraction, because of an efficient transfer of ions through the oil phase by way of a special transport mechanism. Two different mechanisms, "hopping" [151] and "sticky collision" [152], have been suggested for this

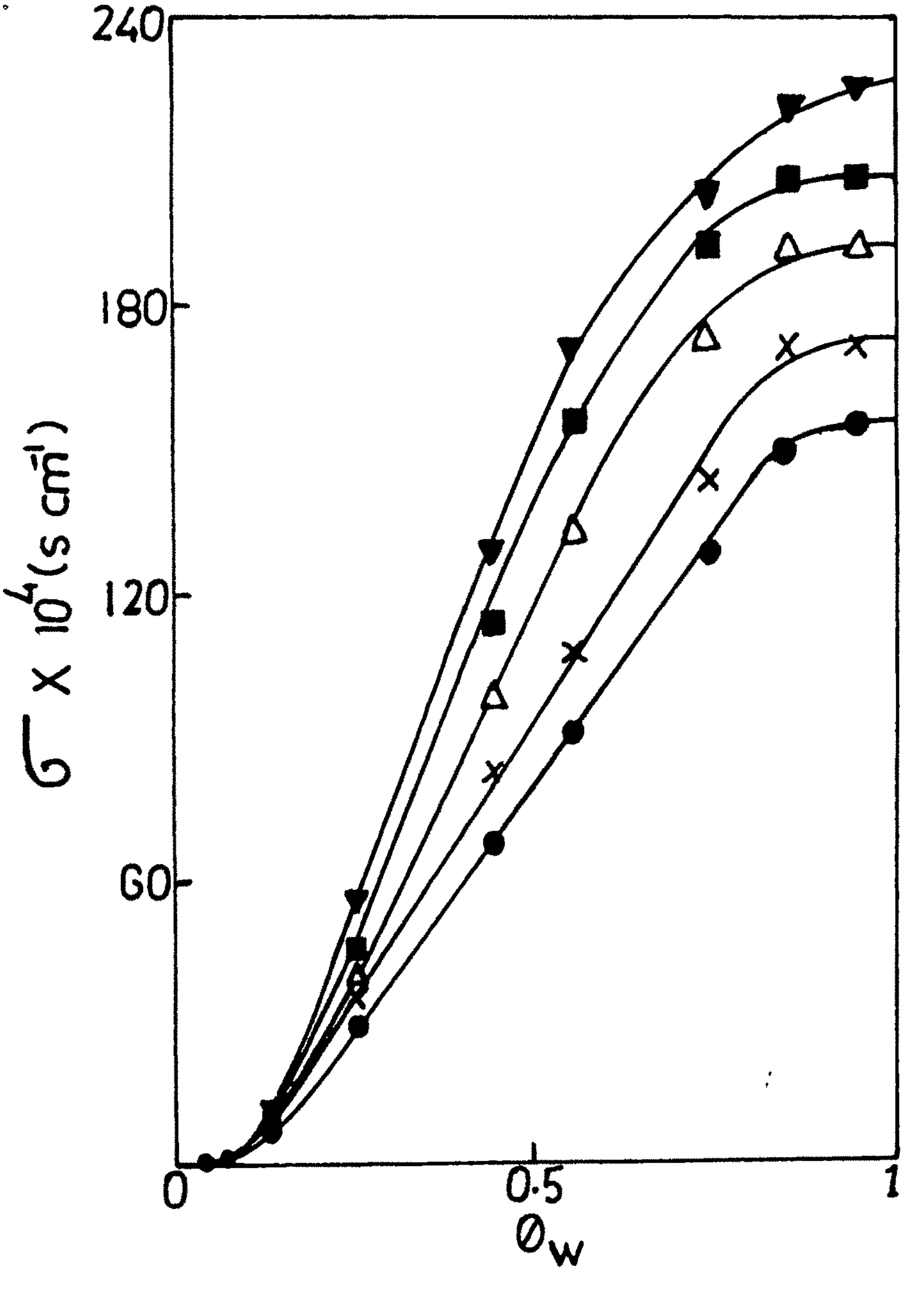

Fig.3.6 Specific conductance of microemulsions (σ) as a function of water volume fraction (ϕ_w) at various temperatures. 30°C ●; 40°C X ; 50°C △; 60°C ■; 70°C ▼ .

behaviour. "Hopping" mechanism suggests that the water globules are always in random Brownian motion and when the two globules come in close contact with each other, the ions from the surface of the droplets move on to the next one in a continuous process of movement resulting in enhanced conductance. According to the "Sticky collision" mechanism, when water microdroplets come close together they undergo sticky collisions to form continuous channels or conduits through which the ions can migrate easily [153]. This will also result in the increase in conductance. Hence in this range of water fraction a bicontinuous picture for the microemulsion seems to be appropriate. With further increase in the water volume fraction, the conductance profile levels off, showing a transition to a water continuous microemulsion at the oil percolation threshold [149]. Hereafter there is no further effect of addition of water on the conductance, since the water forms the continuous medium and oil is the droplet. Thus from the nature of the specific conductance - water fraction profiles, the existence of w/o (low conductance), o/w (high conductance) droplet structures as well as bicontinuous structure is evident. It may also be noted from the figure that at higher temperatures the percolative behaviour of conductance is higher. The temperature increase should favour the collisions of the dispersed water domains and effective merging of them to form water channels above the percolation threshold. This effect can be seen more clearly in temperature induced percolation studies of w/o microemulsions reported earlier [154]. In this "temperature percolation" phenomenon, if a water in oil microemulsion of constant composition is subjected to increasing temperature, a rapid increase in the conductance can be observed at a particular temperature.

In Fig.3.7 the variation of specific conductance with temperature for four different microemulsion samples, of varying water to oil volume ratios, is presented. At very low water-oil ratio (0.04 and 0.08) where the microemulsion is of water in oil type, we obtained neither a temperature percolation nor a gradual increase of conductance with temperature. Instead a generally overall decline in conductance was observed. However in the case of higher water-oil ratios, the conductance increased more orderly with temperature and this was due to the increasing mobility of charge through the medium. The unexpected decrease in conductance with increasing temperature for low water-oil ratio microemulsions can be understood from the dynamic "hopping" mechanism for conductance, as explained earlier, in which the charge transport takes place by hopping of ions from globule to globule. The increase of temperature causes an increased Brownian movement of the water droplets in the oil medium. As a result the time span of each water droplet being

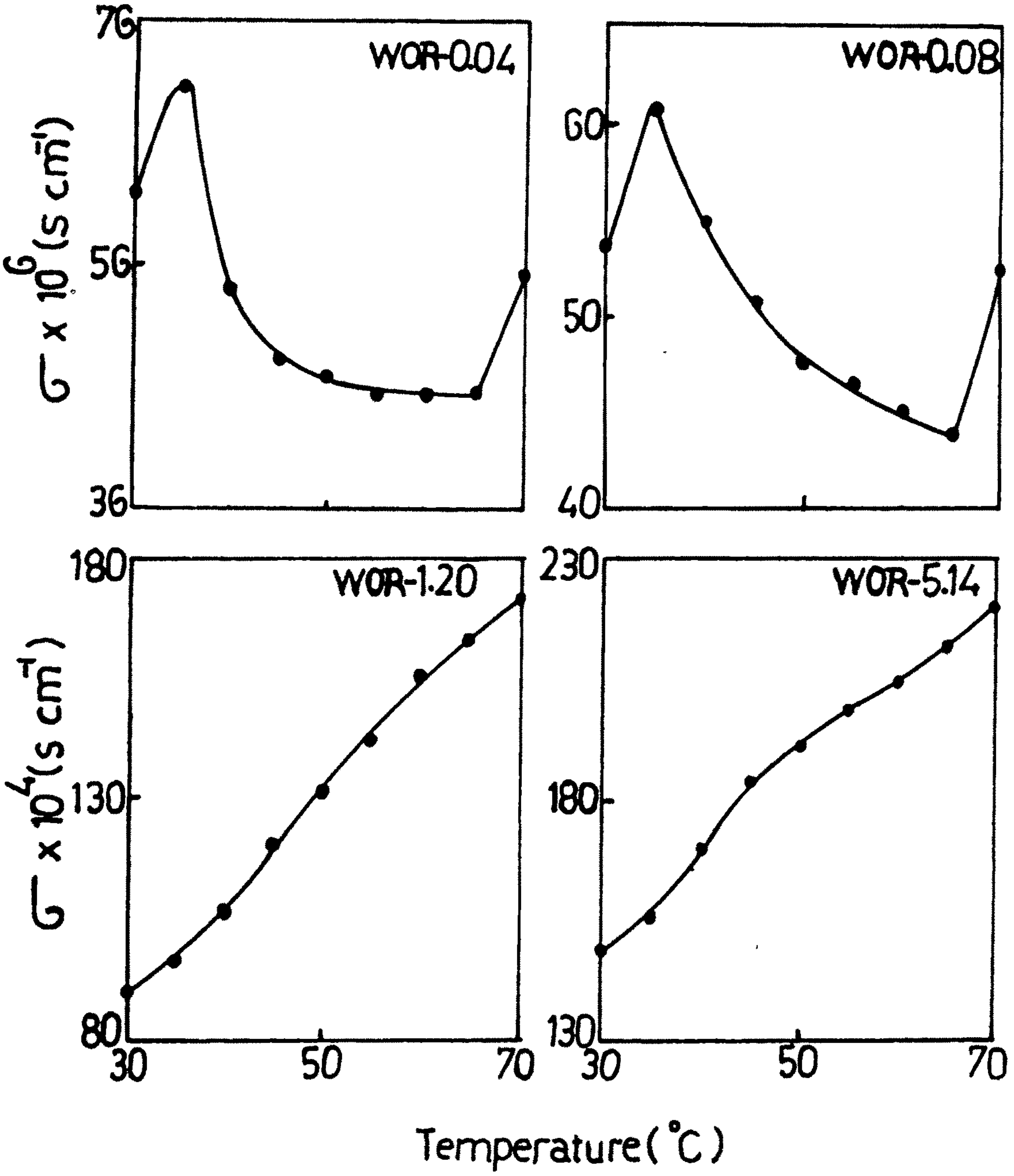

Fig.3.7 Plots of specific conductance (σ) of four different water in oil microemulsion samples of various water-oil ratios (WOR), against temperature.

found near a second globule diminishes there by minimizing the probability of ion hopping along the globules. That is, we suggest that the residing time of the two droplets is lower than the time required for hopping. This lowers the conductance values regularly with temperature increase. At higher water concentration, that is higher water-oil ratio, the residing time of the water droplets increases and becomes higher than the hopping time. Hence it is possible for the ions to move resulting in the higher conductance. At still higher water-oil ratio, channel formation may be the reason for higher conductance.

The study of the conductive behaviour of microemulsion in presence of PAA has shown that neither the percolative pattern nor the conductance was affected significantly by the presence of this polymer. This is illustrated in Fig.3.8 where the specific conductance-water fraction plots obtained on the 42.5 percentage constant surfactant line of the phase diagram (Fig 3.8(a)) was compared with the corresponding conductance curves obtained in the presence of 0.005% (w/v) PAA (Fig.3.8(b)). This indicates a non contribution of PAA towards the conductance as expected of a nonionic polymer. This also signifies that PAA was not providing any barrier for charge carrying ions to move. This indicates a channel

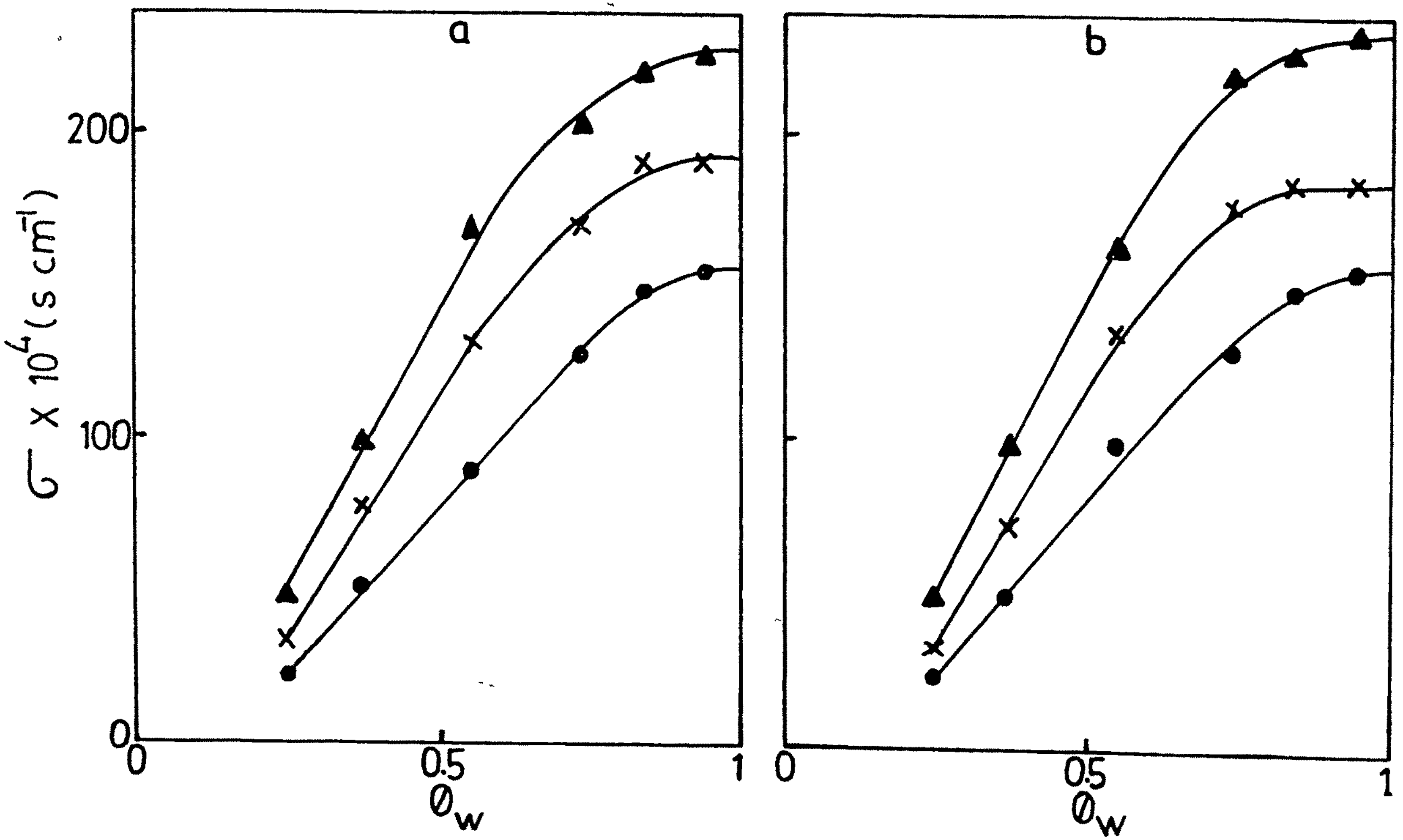

Fig. 3.8 The specific conductance (σ) vs water fraction ($\emptyset_w$) plots (a) without PAA and (b) 0.005% aqueous PAA at three representative temperatures 30°C ●; 50°C X ; 70°C ▲.

formation, that is supports the "sticky collisions" (Fig.3.9). The "hopping" mechanism seems to be absent. In the case of "hopping" the adsorbed PAA molecules at the interface could have provided some type of a barrier to the ion jumping from droplet to droplet. The presence of PAA at the interface indicates a high energy requirement for hopping mechanism.

The Fig.3.10 illustrates the variation of conductance measured along a line, directed towards the surfactant apex of the phase diagram on which the water-oil weight ratio is 4, against surfactant mass fraction. The initial conductance declined gradually with increasing surfactant mass fraction and at around 0.52 mass fraction of surfactant the conductance became constant and did not change any further as surfactant concentration was further increased. It is interesting to note that this constancy was observed at 0.52 mass fraction at all temperatures. Along this line of water-oil ratio as we move upwards, though the water to oil ratio remains constant, the combined volume of water and oil and hence the effective amount of water in the mixture decreases simultaneously with increasing surfactant. This will decrease the dissociation of SDS molecules in the mixture and cause a decrease in the initial conductance. A structural diversity can be postulated from these observed

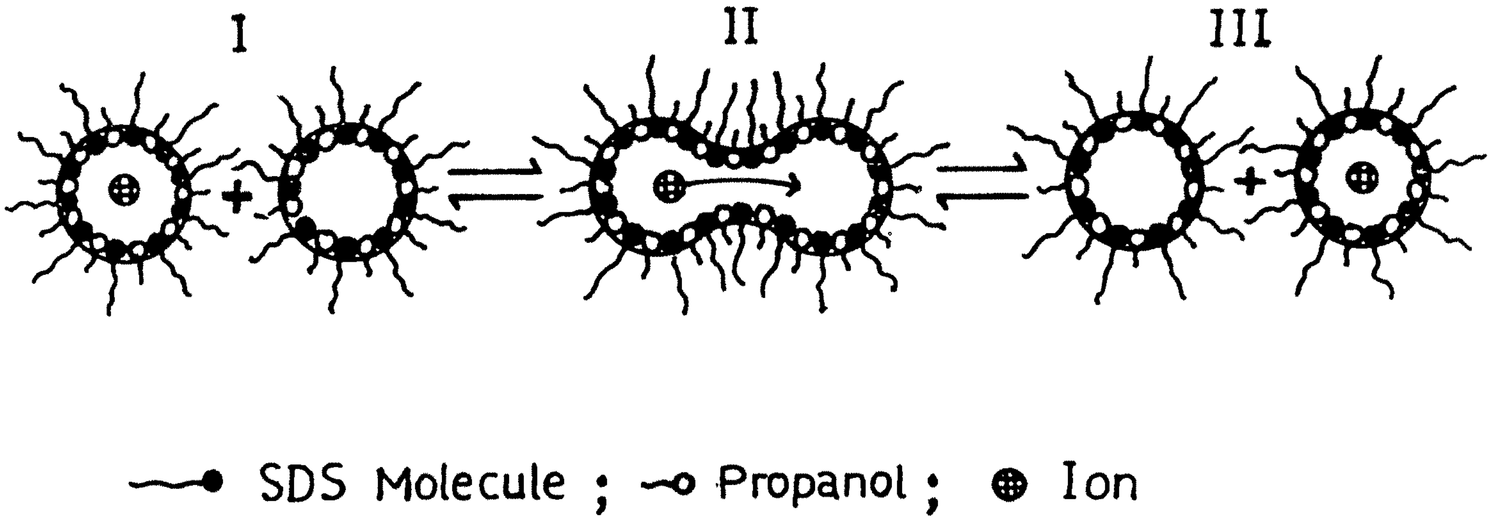

Fig. 3.9 A schematic representation of ion transport through the droplets according to the sticky collision or transient droplet merging mechanism.

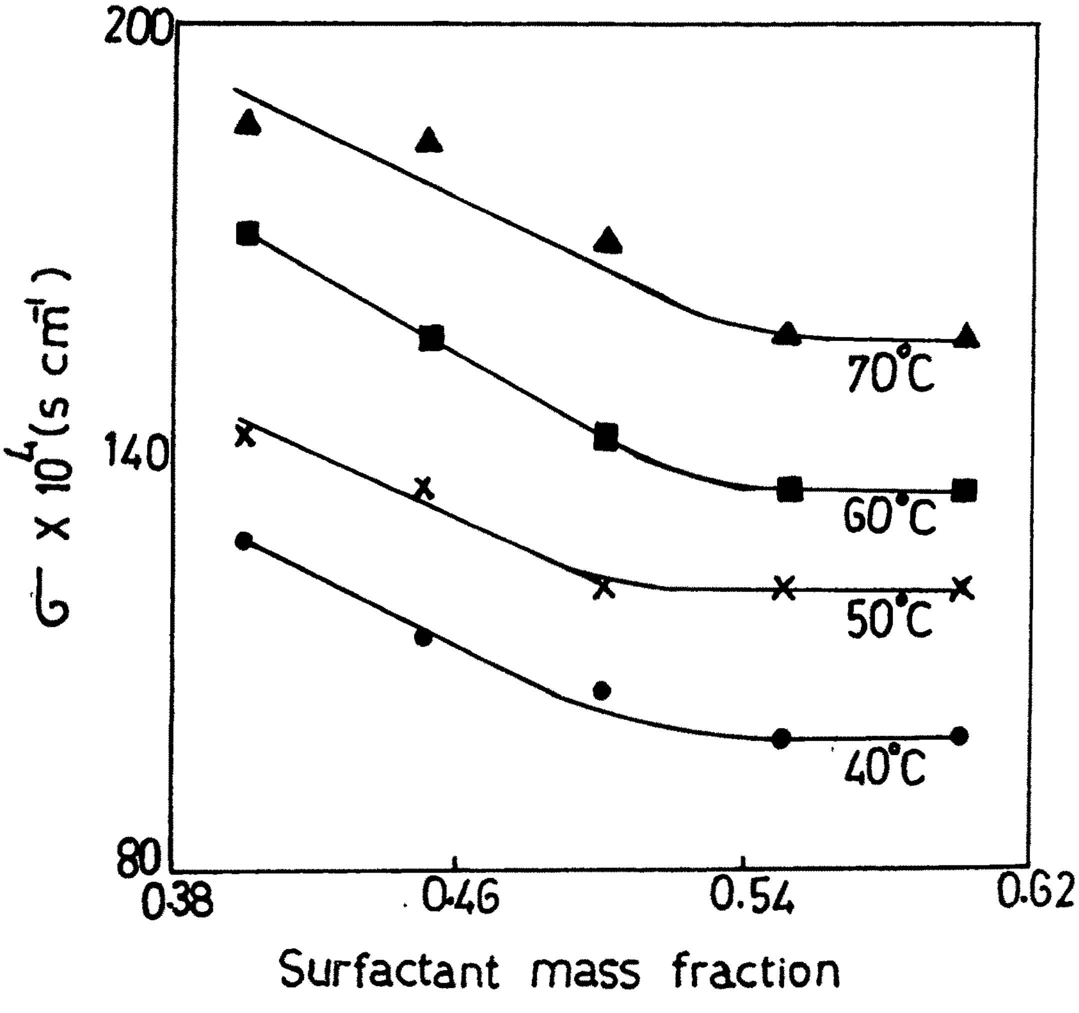

Fig.3.10 Variation of specific conductance (σ) against surfactant mass fraction, along a line of constant water-oil weight ratio 4 at various temperatures.

conductance profiles. When the water-oil ratio was high (i.e. oil concentration was low) and the surfactant concentration was low, the microemulsion could be water continuous and exhibit higher conductance. At this constant water-oil ratio, on adding more and more surfactant, the system transforms itself from water continuous to a probable surfactant continuous or a bicontinuous state and at very high surfactant fraction it assumes a surfactant rich state independent of the water-oil ratio. This was found true in a previous study carried out in our laboratory on a nonionic microemulsion system of alkane, Brij 35, propanol and water [68]. In this system, the properties studied along the 80% surfactant line of the phase diagram showed the existence of a bicontinuous structure throughout the water-oil weight ratio.

(iii) Viscosity

The variation in viscosity of the microemulsions, with constant surfactant weight percentage 42.5, against water volume fraction is shown in Fig 3.11a. Along this surfactant line in the phase diagram it was possible to study a fairly good range of variations in the water-oil ratio. The viscosity increased gradually with increase of water fraction, attained a maximum and decreased

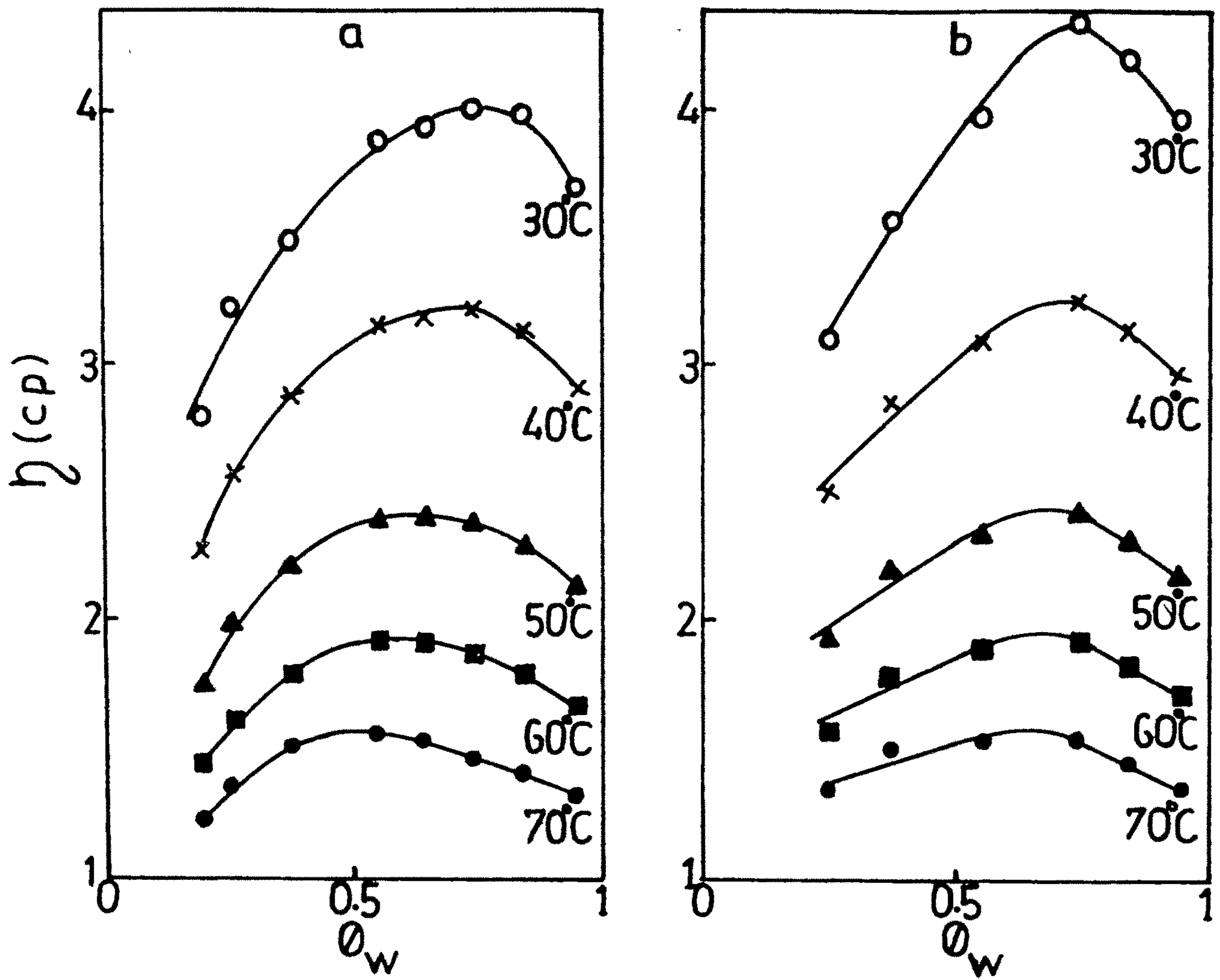

Fig.3.11 Plots of viscosity (η) vs water volume fraction ($Ø_w$) at various temperatures, for the systems (a) without PAA and (b) 0.005% PAA.

thereafter. A maximum was observed at nearly 0.75 volume fraction of water at the lowest temperature studied (30°C). With increasing temperature the height of the maximum was found to diminish. It may also be noted that the increase in temperature shifts the position of the maximum towards the lesser water volume fraction. The observed maximum in the viscosity also indicated a probable structural transition from bicontinuous to oil in water microemulsion regime. The addition of water to a bicontinuous type of microstructure results in the increase in diameter of the water filled conduits in the oil medium [155]. This would eventually cause a continuous increment in the viscosity of the fluid medium with water addition. But a change in the viscosity was no longer expected after the transition to a water external microemulsion structure. However the observed decrease in viscosity beyond the maximum is believed to be due to a dilution effect. From the diminished heights of the maxima it is obvious that the structural changes are not so prominent at higher temperatures. The observed shift in the maxima towards lesser water fraction indicate an earlier transition to the water continuous structure. The presence of PAA in the aqueous phase resulted in the slight increase in the viscosity of the microemulsion compositions with water fractions lying towards the right side of the maxima while it diminished the viscosity of compositions towards the left side of the peak. In other words the PAA increased the viscosity of water external microemulsions where as it decreased the viscosity of the bicontinuous systems. This may be noted from the corresponding points in Fig.3.11a and Fig.3.11.b.

The decrease in the viscosity of three different microemulsion compositions, with the same surfactant weight percentage but differing water-oil ratios, with increasing temperature is shown in the Fig.3.12. It can be noted that the decrease is nonlinear in nature and hence viscosity is not a direct function of temperature.

The Eyring-Frenkel equation for viscous flow can be written as [156].

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

where V, N,h,R and T are molar volume of the solution, the Avogadro number, Planck's constant, universal gas constant and Kelvin temperature respectively. From the slope and intercept of the straight line graphs obtained by plotting ln ηV/Nh against T^{-1}, the viscosity activation quantities $\Delta H^{\#}$ (Activation enthalpy) and $\Delta S^{\#}$ (Activation entropy) were calculated (Table 3.1). The correlation coefficients were 0.99 or more. With increasing oil component (decreasing water component) among various compositions, both $\Delta H^{\#}$ and $\Delta S^{\#}$ values were found to have a decreasing

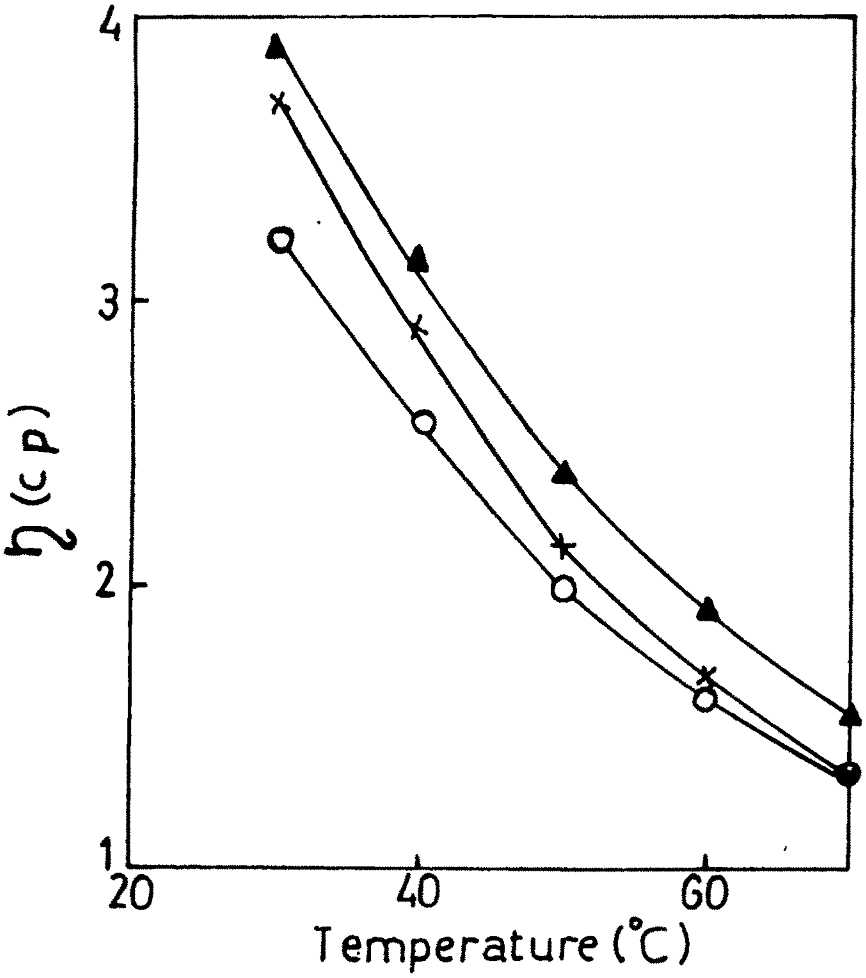

Fig.3.12 Representative plots showing the variation of viscosity (η) against temperature for the microemulsion samples of water-oil ratios 22 X ; 1.55 ▲ ; 0.44 O .

TABLE 3.1

Activation enthalpy $\Delta H^{\#}$ and activation entropy $\Delta S^{\#}$ for the viscous flow of microemulsions containing Water (without PAA) and various aqueous PAA solutions.

Percentage composition surfactant/oil/water	$\Delta H^{\#}$ kJ/mol			
	Water (without PAA)	0.001% (w/v) PAA	0.003 % (w/v) PAA	0.005 % (w/v) PAA
42.5/2.5/55	21.83	21.70	21.98	22.67
42.5/7.5/50	21.90	21.59	21.61	22.65
42.5/12.5/45	21.31	21.02	20.77	22.67
42.5/22.5/35	19.44	19.50	19.41	19.92
42.5/32.5/25	18.04	18.47	17.88	18.25
42.5/40/17.5	18.02	18.59	18.48	17.66
	$\Delta S^{\#}$ Joules			
42.5/2.5/55	25.32	24.90	25.74	27.72
42.5/7.5/50	24.31	23.28	23.42	26.47
42.5/12.5/45	21.51	20.59	19.75	25.40
42.5/22.5/35	14.17	14.47	14.13	15.75
42.5/32.5/25	8.90	10.29	8.36	9.44
42.5/40/17.5	8.07	10.35	9.87	7.23

trend both in presence and absence of PAA. In high water containing compositions, increasing addition of polymer to the system decreases the $\Delta H^{\#}$ values slightly at the beginning before it increases to a maximum value at 0.005% (w/v) PAA concentration. But in the higher oil containing samples the $\Delta H^{\#}$ values show a reverse trend. The similar type of variations were observed in the $\Delta S^{\#}$ values also with increasing PAA concentration.

(iv) Adiabatic Compressibility

The adiabatic compressibility studies of microemulsion samples taken along the 42.5% surfactant line in the phase diagram show that the compressibility of these isotropic mixtures was linearly and inversely related to their water content (Fig.3.13). Hence it can be assumed that the adiabatic compressibility of microemulsions is a bulk property and is independent of the internal structure of these fluids. The linear decrease in compressibility with water fraction was expected, since water is less compressible than oil (cyclohexane). The slopes of these plots evidenced that the change in compressibility of the oil-rich microemulsion with respect to temperature was larger than the change in compressibility of the water-rich microemulsion with respect to temperature. This is also because the compressibility of water is less viable to

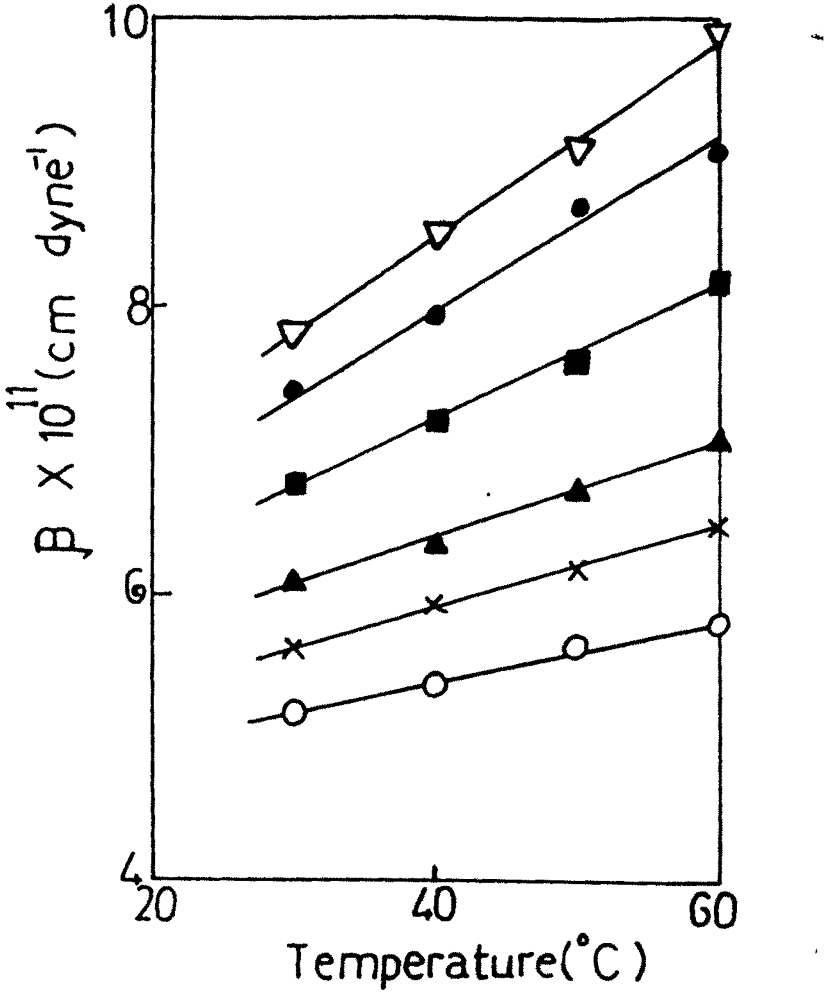

Fig. 3.14 Adiabatic compressibility (β) as a function of temperature for the microemulsion samples of different water-oil ratios 22 ○ ; 6.67 X ; 3.60 ▲ ; 1.56 ■ ; 0.77 ● ; 0.44 ▽ .

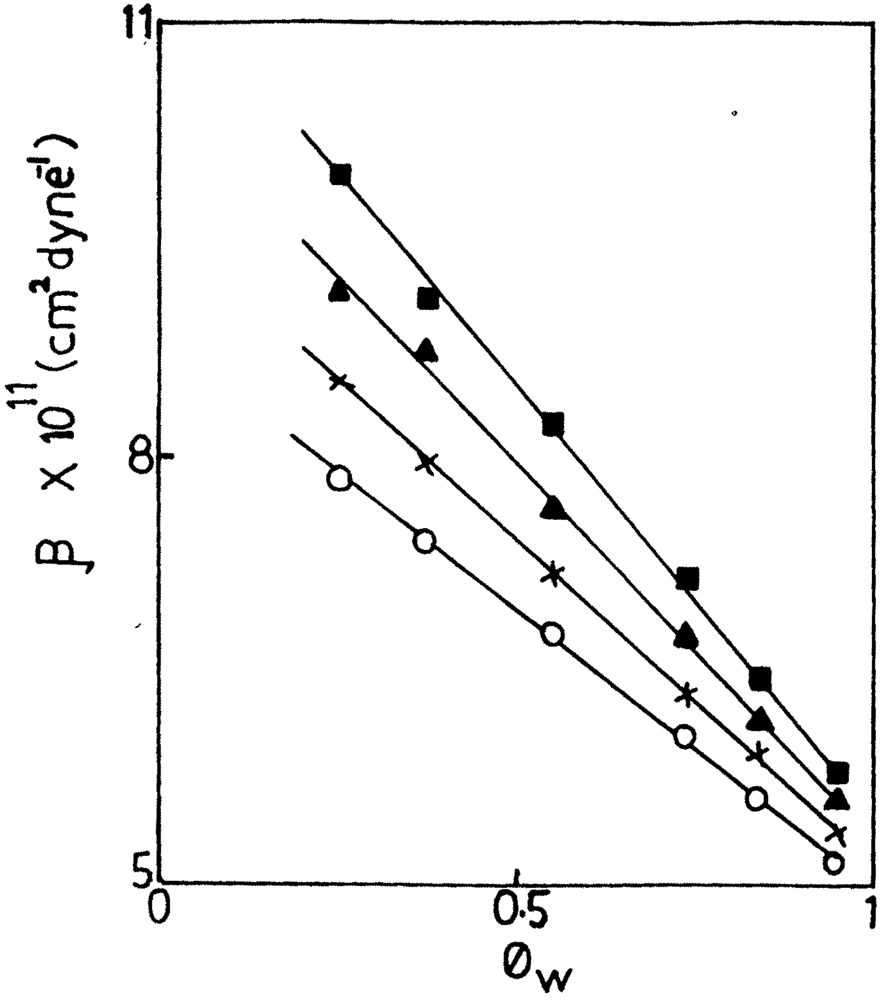

Fig.3.13 Adiabatic compressibility (β) as a function of water volume fraction ($\emptyset_w$) at various temperatures: 30°C ○; 40°C X ; 50°C ▲; 60°C ■.

TABLE 3.2

Adiabatic compressibility (β) of different microemulsion compositions containing water (without PAA) and 0.005 % (w/v) aqueous PAA solution.

Percentage composition surfactant/oil/water	water (without PAA)				0.005 % (w/v) PAA			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
42.5/2.5/55	5.16	5.36	5.61	5.76	5.11	5.32	5.57	5.79
42.5/7.5/50	5.60	5.90	6.15	6.47	5.61	5.79	6.18	6.46
42.5/12.5/45	6.05	6.33	6.73	7.13	5.99	6.35	6.83	7.01
42.5/22.5/35	6.76	7.18	7.63	8.20	6.79	7.27	7.85	8.31
42.5/32.5/25	7.40	7.95	8.72	9.05	7.41	8.08	8.57	9.17
42.5/40/17.5	7.80	8.50	9.12	9.94	8.00	8.48	9.07	10.01

variations with temperature than that of cyclohexane. The compressibility temperature profiles shown in Fig.3.14 also reveal a linear relationship between these two factors. The constant increment in compressibility was due to the less rigid structure of the microemulsion at higher temperature. With increased oil content, the importance of water conduits which bring rigidity to the structure decreased and hence the compressibility increased. The polymer effect studied on compressibility also revealed that the presence of PAA upto 0.005% (w/v) had no significant effect on the compressibility values (Table 3.2).