PUBLICATIONS

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1. "Formation of Microemulsion : Effect of Temperature and Polyacrylamide", A.C.John and A.K.Rakshit, J. Colloid Interface Sci., **156**, 202 (1993).

2. "Physicochemical Studies of Microemulsions", Ajith S., A.C.John and A.K.Rakshit, Pure Appl. Chem. (in press).

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Formation of Microemulsion: Effect of Temperature and Polyacrylamide

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The pseudoternary phase diagram of the system involving cyclohexane, sodium dodecyl sulphate, propanol, and water was constructed for an SDS-to-propanol mass ratio 1:2. The area of the monophasic microemulsion region was computed. The effects of change of temperature and change of concentration of water-soluble polyacrylamide (PAA) on the microemulsion zone as well as the conductance, viscosity, and adiabatic compressibility of the microemulsion systems were studied. It was observed that for the water system there is a critical temperature below which the microemulsion zone increases with temperature, though at higher temperature the zone decreases within the range studied. The effects of presence of polyacrylamide above and below 0.003% (w/v) also are different from each other. © 1993 Academic Press, Inc

INTRODUCTION

Microemulsions are single-phase, thermodynamically stable, low viscosity dispersions of oil/water in a continuous medium of water/oil stabilized by a suitable surfactant or surfactant–cosurfactant mixture (1, 2). As these isotropic liquid phases occur over a specific part of the ternary phase diagram, such phase diagrams are a prerequisite for the study of microemulsions (3–5) Moreover, the properties of such fluid mixtures depend on many factors (6), such as temperature, pressure, and the nature of the components. Though the effect of pressure was found to be weak (6), the temperature has a strong impact on the phase behavior and is counted as an important experimental parameter.

As anionic surfactants are generally used in tertiary oil recovery (7), we decided to study the effect of variation of temperature over a wide range (20–70°C) of a system consisting of water (W), sodium dodecyl sulphate (SDS), and cyclohexane (O). It was observed that the above system was incapable of forming a microemulsion, and *n*-propanol was used as a cosurfactant. As it is known that the variation of the surfactant (S)/cosurfactant (CS) weight ratio changes the nature of the phase diagram, we decided to keep S/CS weight ratio as 1:2 only. Though isopropanol and higher alcohols have been used quite extensively as the cosurfactant (8–11), we did not find any study with *n*-propanol as the cosurfactant in the presence of SDS. Moreover, though polyacrylamide (PAA) (12, 13) was used quite extensively in tertiary oil recovery, there does not seem to be any study of systems containing SDS, *n*-propanol, and PAA in the present temperature range, which is of importance in an actual oil field.

MATERIALS

SDS (Trizma chemicals, Baroda, India) and PAA (BDH, England) were used as obtained. Molecular weight of PAA was over 5×10^6. *n*-Propanol and cyclohexane were purchased from Merck, India and used after purification (14). Doubly distilled water (conductance $\sim 3 \times 10^{-6}$ s cm^{-1}) was used for all sample preparations. A surface tension–concentration profile of SDS did not show any minimum.

EXPERIMENTAL

The boundaries of the single-phase microemulsion region were determined by a titration technique. A known amount of oil or water was taken with the surfactant (15) in stoppered test tubes and kept in a thermostated water bath of required temperature (±0.05°C). These mixtures were then titrated with water or oil, respectively, from a microburette. A representative triangular phase diagram is shown in Fig. 1 in which line 1 connects the end points of the titrations where turbidity disappears and line 2 connects the end points where turbidity reappears. The region bounded by these two lines (line 1 and 2) is the single-phase microemulsion zone, and its area was measured with a planimeter. By duplicate phase diagrams, it was observed that the zone areas were within 1% of each other. Studies at higher temperature were done with sealed tubes. A detailed scanning of the phase diagrams was not done, as it was time consuming and also of not much importance in present study. The temperature range studied was from 20 to 70°C in 10°C intervals and the polymer concentration range was up to 0.005% (w/v).

There are many methods for studying the microstructure of microemulsions. Scattering or NMR methods are commonly used (16–18). The conductometric and viscometric

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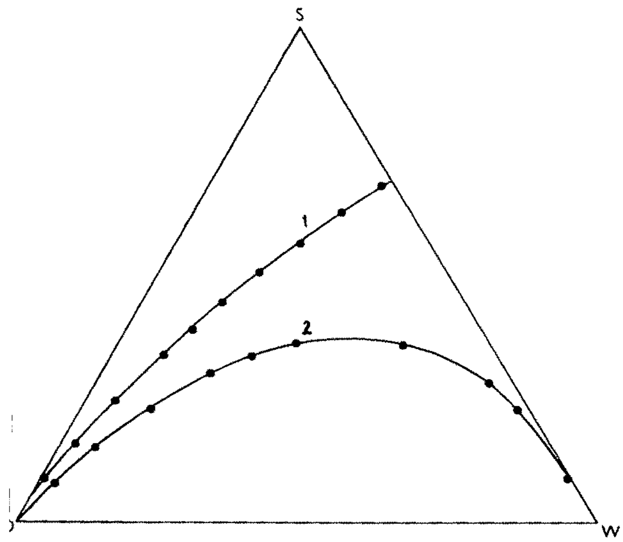

FIG. 1 Triangular phase diagram of water (W)–(SDS + n-propanol))–cyclohexane (O) system at 50°C

udies have often been used (19–21). In the present paper he latter methods are used

The conductance measurements of microemulsion samples along the entire monophasic region were performed with a Mullard Conductivity Bridge, England, and a conductivity cell of cell constant 0.1417 cm^{-1}. For the viscosity and compressibility measurements, various compositions at constant surfactant (15) weight percentage (42 5%) were prepared. As the propanol (CS) is equally soluble in both water and cyclohexane, we assume that over the whole monophasic region with 42.5% surfactant (15) percentages the composition at the interface remains constant, as SDS is insoluble in cyclohexane The viscosities of these samples were determined using an Ubbelohde viscometer, assuming Newtonian behavior of the microemulsions, and their densities were measured with a calibrated pycnometer. An ultrasonic interferometer (Mittal Enterprises, India) was used for the ultrasound velocity measurements and the adiabatic compressibilities were calculated from the relation $\beta = 1/\rho u^2$ where ρ and u are the density and ultrasound velocity, respectively

RESULTS AND DISCUSSION

Figure 1 is a representative ternary phase diagram The middle part is the isotropic one-phase microemulsion zone. The upper part constitutes a solid–liquid biphasic system and the lower part that of a liquid–liquid biphasic system. In Fig. 2a we plot percent area of the one-phase microemulsion in the triangular phase diagram as a function of temperature Clearly a maximum is observed around 40°C in absence of PAA. In Fig. 2b phase diagrams for all systems at 20, 40, and 60°C are shown The presence of a polymer in the aqueous phase alters the nature of the curve, showing minima in the case of 0.005% PAA and also around 40°C. At 0.003% PAA an invariancy is indicated of microemulsion area with temperature. Figure 3 represents the dependence of the microemulsion area on the concentration of the polymer, at various temperatures. The linearity of the plots indicates that the microemulsion area is a direct function of the polymer concentration At 20°C the microemulsion zone increased with an increase in PAA concentration. In all other systems a decrease is observed. From the variation of the slope of these lines with temperature, it was concluded that the interfacial tension increased, thereby making microemulsion formation difficult up to about 40°C before it started to decrease.

Microemulsions are formed due to very low oil–water interfacial tension (22–24), mainly because of the adsorption of surfactant and cosurfactant molecules at the interface. Moreover, as temperature increases, interfacial tension decreases (20). Thus an increase in temperature should favor the formation of microemulsion by reducing the IFT more effectively and increasing the microemulsion zone in the

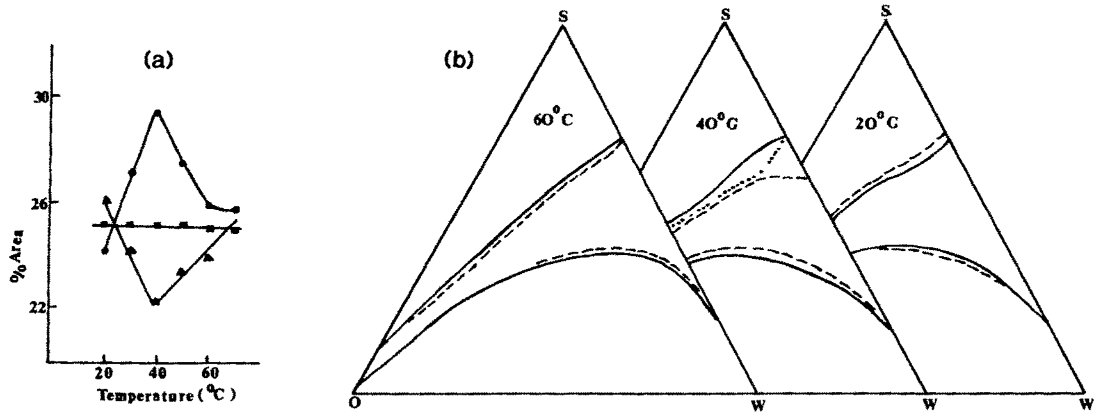

FIG 2. (a) Plots of % microemulsion area vs temperature without PAA, ●, 0 003% PAA, ■, 0 005% PAA, ▲ (b) Triangular phase diagrams at different temperatures without PAA (——) 0 003% PAA (· · · · · ·), 0 005% PAA (– – –)

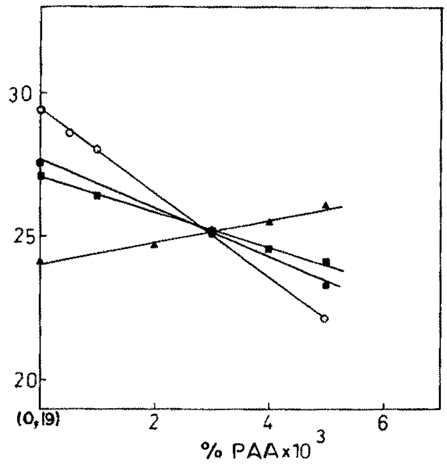

FIG. 3 Plots of % microemulsion area vs polymer concentration 20°C, ▲, 30°C, ■, 40°C, O, 50°C, ●

phase diagram (Fig 2a and 2b). An increase of temperature also causes increased thermal motion (25) of the adsorbed surfactant molecules at the interface. Above 40°C, the thermal motion of the surfactant molecules become dominant, and hence the regular array of these molecules at the interface gets distorted and moves out of the interfacial layer surrounding the droplets Hence there will be a decreased number of surface active molecules at the interface. The solubilization capacity hence decreases (25), thus decreasing the microemulsion zone above 40°C. Polyacrylamide molecules have a large number of polar amide groups with the possibility of intramolecular H-bonding between these groups. Adsorption of these molecules at the droplet surface has a destabilizing effect (26) on the microemulsion formation. A decrease in the solubilization capacity of the microemulsion in the presence of PAA has also been reported (27) earlier Above a critical temperature (40°C) the H-bonding among the amide groups of PAA molecules breaks up, rendering these polar heads free. Hence they can behave as surface-active agents and enhance microemulsion formation. Moreover, polyacrylamide was expected to be at the interface of the droplet with the medium. It has been found that (28) below 40°C, water/cyclohexane IFT decreases in presence of PAA but increases over 40°C We feel the presence of PAA in the system crowds the interfacial area and some surfactants are replaced by the PAA The effect on IFT due to PAA is much smaller than that due to the surfactants, and hence the microemulsion zone decreases However over 40°C, microemulsion zone begins to increase as due to thermal motion PAA gets desorbed from the droplet surface and is replaced by the surfactant (15) on the surface of the droplet It may be stated that the effects of temperature and PAA are somewhat antagonistic and cancel out each other in the 0.003% PAA system (Fig. 2) The effect of the adsorption of polymer molecules at the droplets and their hindering effect on the formation of the microemulsion below 40°C is more obvious from Fig. 3 It was observed that the slope the line is greater at 40°C than that of 30°C. This indica an increased effect of the polymer at this temperature c to increased adsorption on the droplets.

The specific conductance of the microemulsion samp is plotted against water volume fraction in Fig. 4 at vario temperatures A fairly good percolative mode of condu tance, with two percolation thresholds (29), was obtain We believe that this is not a peculiarity of the system, b rather a general pattern showing the continuous inversi of a water-in-oil microemulsion to an oil-in-water micr emulsion Below the critical water volume fraction, call the water percolation threshold, the conductance is very lo though higher than that of pure oil. This is because of t electrophoretic movements (30) of the monodispersed wat globules in a continuous oil medium Above the water pe colation threshold the conductance rises sharply with t increase of water volume fraction, as there is an efficie transfer of ions through the oil phase by way of a speci transport mechanism Two different mechanisms, "hopping (31) and "sticky" collision (32), have been suggested f this behavior "Hopping" suggests that when the microdro lets are in close contact, the surfactant ions from the surfac of the droplets "hop" along resulting in enhanced conduc tance But according to the "sticky collision" mechanism when water microdroplets come in close contact they undergo sticky collisions to form continuous channels (conduits) through which the ions are transferred (33) Wit 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 Hence there is no further effect of addition of water on conductance. It may also be noted from Fig. 4 that at highe temperatures the percolative behavior of the conductance was higher. The temperature increase favored the collisions of the dispersed water droplets and effectively forming water conduits This effect is seen easily in temperature-induced

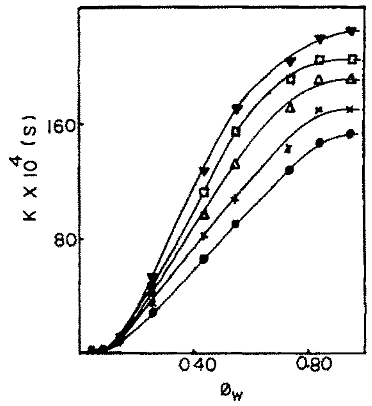

FIG 4 Specific conductance of microemulsions as a function of water volume fraction for various temperatures· 30°C, ●, 40°C, ×, 50°C, △, 60°C, □, 70°C, ▼

ercolation studies (34) of W/O microemulsions The study f the effect of PAA on the conductive behavior of the system as shown that neither percolation nor conductance was significantly affected by the presence of PAA. This indicates at PAA is not providing any barrier for surfactant ions to nove. This supports the "sticky collision" rather than "hoping," as in the latter case some barrier was expected to be resent.

The variation in viscosity of the microemulsions with the ater volume fraction at constant surfactant (15) weight ercentage 42.5 is shown in Fig. 5 At this condition the aximum range of variation in the oil/water ratio could be tudied A maximum is observed at nearly 0 75 volume fraction of water at the lowest temperature studied. The height f the maximum diminishes with increase in temperature It may also be noted that the increase in temperature shifts the position of the maxima toward the lesser water volume. The observed maxima in the viscosity also indicates the structural transitions from a bicontinuous microemulsion regime to an oil-in-water regime The addition of water to a bicontinuous structured microemulsion results in an increased diameter (35) of the water-filled conduits, resulting in the continuous increment in the viscosity with water-volume fraction A change in the viscosity was no longer expected after the transition to an oil-in-water microemulsion, as the water forms the continuous phase. However, the observed decrease in viscosity is due to dilution effect. From the diminished heights of the maxima in Fig. 5 it is obvious that the structural changes are not prominent at higher temperatures. The observed shift in the maxima toward less water fraction indicates an earlier transition to the water continuous regime The plots of ln η against T^{-1} give fairly good straight lines from which $\Delta H^{\ddagger}_{vis}$, the activation energy for the viscous flow, were calculated (Table 1). The presence of PAA in the aqueous phase increases the viscosity of the microemulsion samples, though the nature of the viscosity–ϕ_w plots remains unaltered The adiabatic compressibility study (Fig 6) shows that the compressibility of these isotropic mixtures is linearly and inversely related to their water content for a constant surfactant weight ratio. Hence the compressibility of the microemulsion is a bulk property and is independent of the internal structure of these fluids The linear decrease of β with water fraction is expected, as water is less compressible than oil (cyclohexane) But the slopes of these plots indicate that the change in compressibility of the oil-rich microemulsion with respect to temperature is larger than the change in compressibility of the water-rich microemulsion with respect to temperature. The compressibility–temperature profiles shown in Fig. 7 also reveal a linear relationship. The constant increment in compressibility is due to the less rigid structure of the microemulsion at higher temperature With increased oil content, the importance of water conduits

TABLE 1

Activation Energy for the Viscous Flow of Different Microemulsion Compositions in Presence and Absence of PAA

	$\Delta H^{\ddagger}_{vis}$ (kJ/mol)			
Composition surfactant (15)/ oil/water	Water (without PAA)	0 001% (w/v) PAA	0 003% (w/v) PAA	0 005% (w/v) PAA
42 5/2 5/55	21 41	22 18	22 49	23 14
42 5/7 5/50	22 41	21 96	22 07	23 07
42 5/12 5/45	21 81	22 40	21 24	22 40
42 5/22 5/35	19 94	20 03	19 94	20 53
42 5/32 5/25	18 42	19 14	18 49	19 97
42 5/40/17 5	18 77	19 21	19 23	18 39

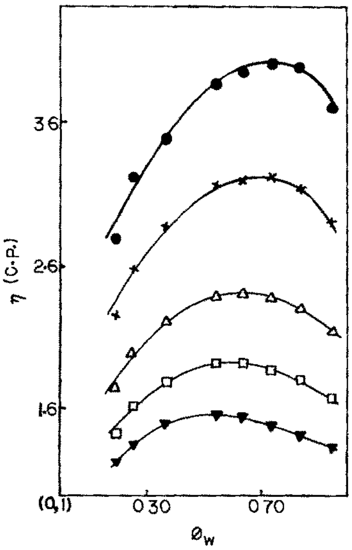

FIG 5. Viscosity of microemulsion as a function of water volume fraction, 42 5 wt% S at various temperatures 30°C, ●, 40°C, ×, 50°C, △, 60°C, □, 70°C, ▼

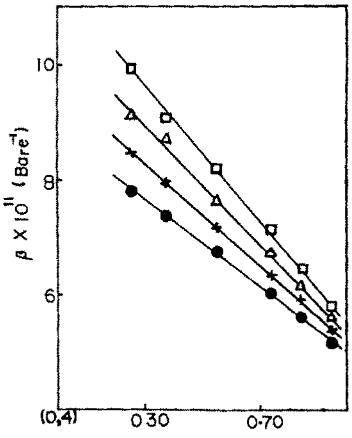

FIG 6. Adiabatic compressibility as a function of water volume fraction 42 5 wt% S at various temperatures 30°C, ●, 40°C, ×, 50°C, △, 60°C, □

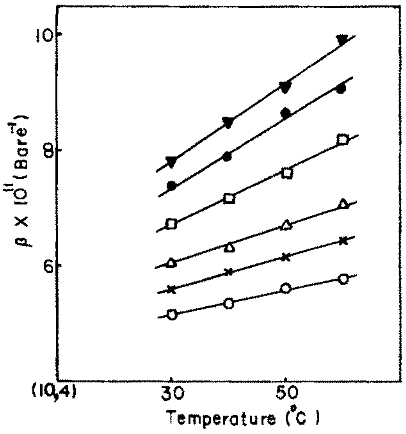

FIG 7 Adiabatic compressibility of microemulsions at different o/w ratio as a function of temperature at 42 5 wt% S 0 045, ○, 0 15, ×, 0 28, △, 0 64, □, 1 3, ●, 2 29, ▼

which give rigidity to the structure decreases, and hence the compressibility increases. The presence of PAA up to 0.005% (w/v) has no effect on the compressibility values

CONCLUSIONS

The temperature and additives are two parameters which affect the one-phase microemulsion region in a ternary phase diagram. With increasing temperature the microemulsion zone increases up to a critical temperature and thereafter it decreases The presence of polymer PAA generally has a destabilizing effect on microemulsions, and hence decreases the one-phase microemulsion region. But above a critical temperature these polymer molecules behave as surface-active agents and thereby enhance the microemulsion formation Thus the effects of temperature and PAA are almost antagonistic to each other.

Our studies reveal the existence of two percolation thresholds, in the inversion of a w/o microemulsion to an o/w microemulsion. The increase of temperature has a tendency to shift the bicontinuous o/w boundary toward a lesser water fraction. The adiabatic compressibility of the microemulsion is a bulk property and is independent of its internal structure

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Physicochemical Studies of Microemulsions

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Viscosity and conductance of various microemulsion systems were studied over a range of temperature (30-80°C). The phase diagram of two systems studied were (I) alkane/Brij 35 (s)/water and (II) cyclohexane/NaDS(s)/ water. n-Propanol was used as cosurfactant (cs) for both systems. The cs/s weight ratio was kept at 2. The nonane and heptane were used as alkanes in system I. The effect of NaCl on phase diagrams was found to be drastic at higher concentrations. For the nonionic Brij 35 systems, the effect of increase in temperature and increase in NaCl concentration were in the same direction. The conductance surprisingly decreases with increase in temperature for system II at very low w/o ratio. The Winsor transitons were also studied. The thermodynamic quantities for the solubilization of oil in water or water in oil for both systems at various surfactant concentrations were computed. All these are discussed here.

Introduction

Microemulsions have attracted curiosity of scientists due to their structural complexity as also the potential for obtaining the miscibility of oil and water. Significant amount of work dealing with the effect of salinity on the formation of microemulsions are already available. Oil chain length, nature of surfactants and cosurfactants, temperature etc. are the factors which control the optimal salinity of these systems (1,2). In this article we present the effect of temperature and high salinity on a couple of oil - water - surfactant systems.

Materials and Methods

Brij 35 (Merck, Germany) and SDS (Qualigens, India) were used as received. n-Propanol, cyclohexane, heptane and nonane from SD's India were used after purification. NaCl (A.R.) was obtained from Merck,India.

Surfactant to cosurfactant ratio was kept at 1:2 by weight through out the study. Phase diagrams, conductance and viscosity were determined as described earlier (3). The systems selected for the investigation are alkane/Brij 35 + propanol/water (I) and cyclohexane/SDS + propanol/water (II).

Results and Discussion

The Figs.1 and 2 are the comparative phase prism representation of the systems I and II respectively at various NaCl concentrations. The presence of NaCl in high concentration totally changes the nature of the phase diagram of both the systems. High salinity introduces three phase region in the phase diagram. Formation of the three phase zone which exhibits maximum miscibility of oil and water occurs only when the surfactant strikes an optimum balance between its hydrophilicity and lipophilicity. The high hydrophilicity of the surfactant here prevents it from forming a three phase region with pure water. But the presence of the electrolyte diminishes the water-surfactant interaction. Thus it achieves the required hydrophilic - lipophilic balance for the formation of three phase region. Similar effect can be achieved for the nonionic surfactant system (I) by increasing the temperature also. At low temperature the phase diagram remains similar to that of non brine systems, but at higher temperature variations are observed. Thus the effects of NaCl and temperature are in the same direction for the systems where nonionic surfactants, which show cloud points, are present. For the system II the phase diagram pattern is invariant with temperature. This is because the ionic surfactants do

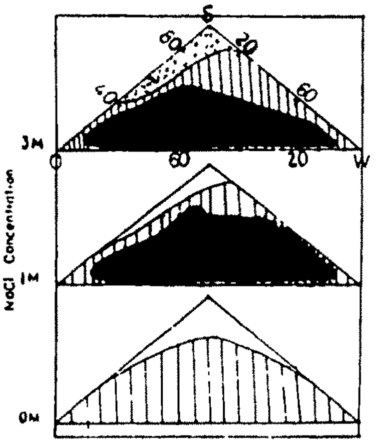

Fig.1 Phase prism representation of system I (see text)
■-L/L/L; ▥-L/L, ☐-L,
☐-So/L (L=liquid, So=solid)

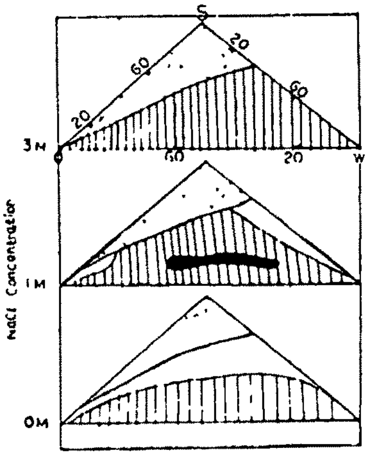

Fig 2 Phase prism representation of system II (see text.) Symbols as in Fig.1

not show any cloud point. As the salinity increases to 3M, monophasic region disappears in both the cases. It is also clear from fig.2 that only solid/liquid or liquid/liquid biphasic regions are obtainable in SDS-cyclohexane system.

Fig.3 shows the Winsor transitions in the systems as a function of NaCl concentration at different temperatures (40°C & 60°C). Synergistic effect of temperature and NaCl in I is more obvious here (Fig.3a). At low temperature transition from Winsor I (O/W + oil) to Winsor III occurs at high salinity. The higher the temperature lower the salt concentration, tending to zero at very high temperature (> 70°C). In system II the transition occurs from lower level (LL) to middle level (ML) and then to upper level (UL) microemulsion with increasing salinity. The higher temperature influence these transitions nominally by inducing somewhat early transition (Fig.3b). In the salinity range studied, system II shows three Winsor formations whereas in system I only Winsor I and III are observed. The optimal salinity of a system was described as the salinity at which there is an equal solubilization of oil and brine ($\gamma o/m = \gamma m/w$) (4). This is true in Winsor III formations. Hence it is concluded that the temperature lowers the optimal salinity in both I and II. Similar type of behaviour was observed earlier also (5).

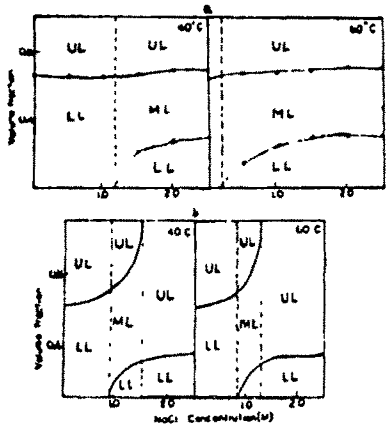

Fig.3 Various volume fractions of (a) System I (b) System II as a function of NaCl concentration.(Upper, middle and lower layers are UL, ML & LL)

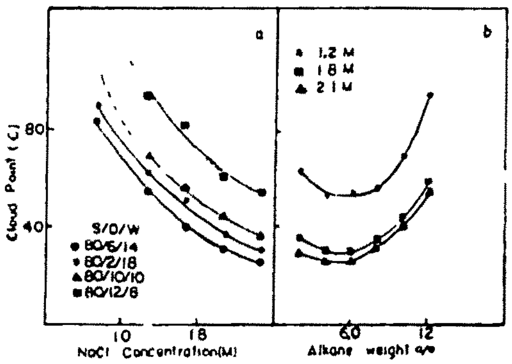

Fig.4 Variation of cloud point of system I with (a) NaCl concentration at various compositions and (b) alkane weight percent.

Fig. 4 represents the variation of cloud point of system I with NaCl concentration and alkane weight percentage. High salinity brings down the cloud point sharply from above 100°C to 25°C (Fig.4a). The variation of cloud point versus alkane weight percentage (Fig.4b) passes through a minima, which depends on the oil. The initial decrease of the cloud point here can be attributed to the increased hydrophobicity of the system by the addition of the alkane. But further growing of oil phase facilitates the solubility of surfactant molecules in oil. Hence, the cloud point at higher temperature. It was shown earlier that more soluble the surfactant in oil phase higher was the cloud point (6). Hence the rise in cloud point with increase of alkane weight fraction. The microemulsion samples with higher alkane fraction do not show the clouding below 100°C.

In Fig.5 specific conductance of four oil continuous microemulsion samples of system II at various w/o ratios (0.05, 0.08, 0.12, 0.16) and containing 0.5M NaCl is plotted against temperature. At the lower w/o ratios, there are decrease in conductance. These are contradictory to what has been termed as 'temperature percolation', but this rather surprising trend was observed earlier also (7). Moreover at w/o = 0.16 the conductance increases at higher temperature with a similar trend at w/o = 0.12. Besides the viscosity of these samples shows a continuous decrease with temperature which is non-complementary to the conductance variation though the complementary was expected from the Walden's rule. Among the two approaches proposed for the conductance behaviour of microemulsions, a dynamic model developed recently assures the charge transport by 'hopping' of ions through the globules during their random collisions (8). As temperature increases, there is increased kinetic energy of the water droplets in the oil continuum. Hence each droplet spends lesser time in the vicinity of another droplet at low w/o ratios while they collide. This decreases the probability of the conducting ions to hop along from globule to globule and hence decreased

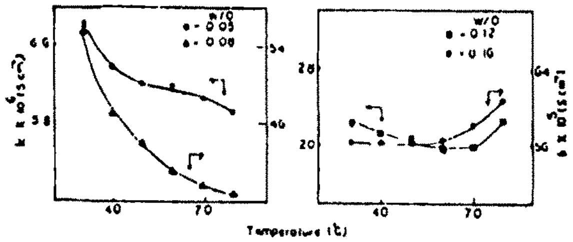

Fig 5 Variation Sp. conductance of system II with temperature at different w/o ratio

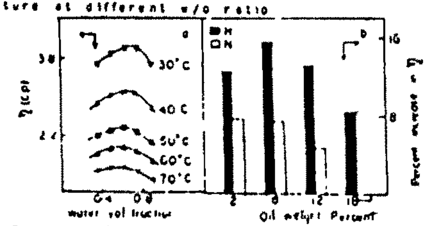

Fig 6 (a) Viscosity of system II as function water volume fraction at various temperature
(b) Percentage increment of viscosity for system I (80% S+CS) microemulsion when water was replaced by 1M NaCl, H=Heptane, N=nonane microemulsions.

conductance. Thus the decrease in conductance with increase in temperature supports the hopping mechanism rather than the sticky collision. But for higher w/o ratio, the water droplet density becomes high enough for the formation of a sort of water clusters with temperature elevation. This enhances the possibilty of ion transport and there by conduction.

Fig. 6a represents the results of viscosity measurement carried out in presence of 0.5M NaCl along the one phase region of system II at a constant surfactant weight percentage. The increase in the diameter of water filled conduits in a bicontinuous structure with water addition (9) accounts for the rise in the viscosity profiles. The position of the peak observed marks the transition to o/w structural regime. Viscosity of the microemulsion I increased when salinity was introduced to the system. Fig. 6b compares the percentage increase in heptane and nonane microemulsions when water was replaced by 1M NaCl. It can be seen that heptane microemulsion has larger increment than nonane microemulsion at all compositions. Thus hydrophobicity of the system controls the influence of NaCl. Similar effect was observed in the cloud point studies. Same concentration of NaCl lowers the cloud point of nonane microemulsion to a much lesser extent than heptane system (data not shown). Hence there exists some antagonistic effect of salinity and alkane chain length of the hydrocarbon in system I. Similar conclusions were reported earlier also (10).

For very small solubility Free energy of solubilization can be calculated by the well known relation ΔG_{sol} = RTln X where X is the molefraction of the solute. For the formation of microemulsion, i.e. o/w or w/o at specific surfactant and cosurfactant concentration, ΔG_{sol} can be calculated using the same relation (11). In Figs. 7 and 8 plots

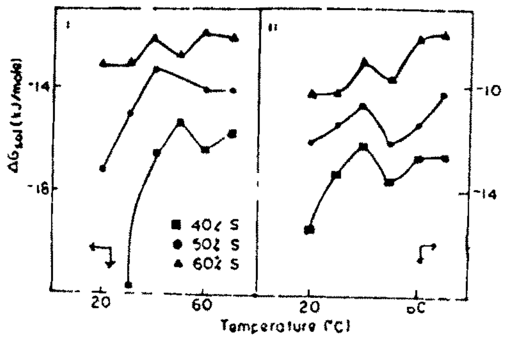

Fig.7 Variation of ΔG_{sol} for o/w micro-emulsion in system I. (i) nonane (ii) heptane containing systems

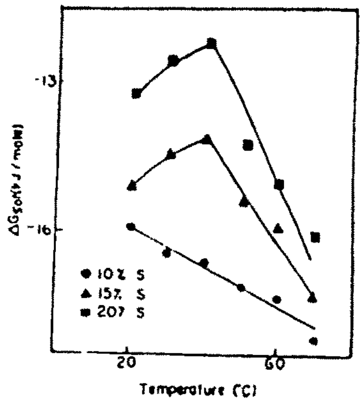

Fig 8 ΔG_{sol} of o/w in system II as a function of temperature.

of so calculated ΔG values against temperature are shown for some of the systems. The nonlinear nature of the plots indicates that ΔG_{sol} is not a function of temperature only. ΔG_{sol} - T plot for o/w microemulsion passes through a maxima for both the systems. At this temperature of maxima, ΔG_{sol} becomes equal to the enthalpy change for the process. The negative value of ΔH_{sol} indicates that solubilization in microemulsion media is an exothermic process. Further it can also be seen that though the system I and II are totally different, the ΔG_{sol} and ΔH_{sol} data do not differ much. Free energy change was also calculated for w/o microemulsions in system I. It is interesting to see that for w/o system ΔG_{sol} - T curve shows a minima rather than a maxima. We believe that the maxima (for o/w system) and minima (for w/o system) are characteristics of the two different microemulsion systems.

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