PUBLICATIONS

LIST OF PUBLICATIONS

1. "Studies of Microemulsion : Mixed Alkane/Nonionic surfactant/water systems", Ajith S. and A.K.Rakshit, Proceedings of National Conference on Chemical & Physical Aspects of Organised Biological Assemblies, Jadavpur University, Calcutta, Feb 1991, p. 124 - 128.

2. "Properties of mixed alkane microemulsions", Ajith S. and A.K.Rakshit, J. Surf. Sci. Tech., (in press)

3. "Physicochemical studies of microemulsions", Ajith S., A.C.John and A.K.Rakshit, Pure Appl. Chem. (in press).

Studies of Microemulsion : Mixed Alkane/Non-ionic Surfactant/Water Systems

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Abstract—The effect of the variation the composition of the oil and temperature has been studied on the microemulsion area of the system oil/Brij 35 + n-propanol/water, where oil is heptane, nonane and various mixtures of these. It has been observed that the area in general increases with increase in temperature. The microemulsion area decreases in going from heptane to nonane but no linear dependence was observed.

Key words: *Microemulsion, Brij 35, Heptane, Nonane*

INTRODUCTION

Microemulsion is a single phase, optically isotropic, thermodynamically stable system [1]. This is generally composed of water, oil and surfactant. A cosurfactant, though, seems to be of necessity [2]. It has been suggested that in case of nonionic surfactants, the presence of a cosurfactant is not imperative. The microemulsions have tremendous technological implications and have been studied by various techniques [3-5]. The triangular phase diagram of the three/four component system is a must as only in some part/parts of the diagram the microemulsion is formed and therefore one needs to know the composition [6-8] of the micromulsion.

In the present study we chose nonionic surfactant, Brij 35 as one of the components. Its cloud point in water is over 100°C and hence the study of the effect of temperature on mcroemulsion will be reasonable in this case as the probability of precipitation will be minimal. We have taken pure heptane and nonane as oil and also different mixtures of the two. This way the effect of the variation of the composition of the oil on the microemulsion area can be studied. To our knowledge such type of study has not been reported earlier. As we mentioned, the nonionic surfactant was not expected to need a cosurfactant but unfortunately it was observed that Brij 35 does not form microemulsion and hence we used n-propanol as cosurfactant. The mixed alkane system was used as oil phase because of the fact that in the practical cases, e.g., in the tertiary oil recovery, the pure alkane microemulsion behaviour will not be very useful. The anionic surfactants are generally used in the tertiary oil recovery [9] but importance of using nonionic surfactants cannot be over emphasised. This is because in case of anionic surfactants the electrical properties become important whereas in case of nonionic surfacants only the chemical proparties will be important. As higher temperature effect is important in tertiary oil recovery, we sudied the microemulsion area at various temperatures.

EXPERIMENTAL

Brij 35 $[C_{12}H_{25}(OCH_2CH\ )_{23}OH]$ was from Merck, Germany and was used as received. n-Propanol (Merck, India), Heptane (S.D.'s, India) and nonane (S.D.'s, India) were used after purification by standard procedure [10]. Doubly distilled water (approx. 10^{-6}s) was used. The weight ratio between surfactant and cosurfactant was always kept at 1 : 2.

Titration technique was used to determine the one phase microemulsion region. Known amount of oil or water was taken with surfactant in a stoppered test tube and was kept in a thermostat of required temperature (±0.05°C) and titrated with water or oil respectively from a microburette. A triangular phase diagram was then plotted (Fig. 1). The area on the upper part of the line is the single phase microemulsion area and the lower part is the nonmicroemulsion part. With the help of a planimeter, the area under the curve was determined. A few systems were duplicates and the microemulsion area was found to be within 1% of each other. Higher temperature studies were done with sealed tubes. Detailed scanning of the phase diagram was avoided as it is in general time consuming and was not of much importance for the present study. The temperature range used was from 20 to 70°C. Three mixed alkane systems with mole ratios 1 : 3, 1 : 1 and 3 : 1 were used.

RESULTS AND DISCUSSION

From Table 1, it is quite clear that the microemulsion area is rather small. This is probably because the nonionic surfactant is very hydrophilic in nature due to the presence of 23 $-(OCH_2CH_2)-$ groups Moreover the cosurfactant, n-propanol, is also not hydrophobic. Probably higher alcohols, which are more hydrophobic in nature, could have given a greater microemulsion area. This part will be looked into in future. It is also seen that with increase in temperature the microemulsion area generally increases. As the temperature rises the interfacial tension generally decreases; the surfactant may bring the interfacial tension to a very low positive [11] (or probably negative [12]) value leading to higher microemulsion area. Moreover, as the temperature increases the oxyethylene groups become less solvated with water, its lipophilic character increases and hence more solubilization of oil with concommitant increase in microemulsion area takes place [13]. At a temperature around 60°C there seems to be a tendency for a decrease in the microemulsion area. It is a bit difficult to reason this out. Again, as the variation is not large a detailed discussion is precluded.

TABLE 1

The percent area of one phase microemulsion region in the phase diagrame of the system Alkane*/Surfactant/water at various temperatures.

Percentage Heptane in the mixture	Percent microemulsion area					
	20°C	30°C	40°C	50°C	60°C	70°C
100	14.2	15.01	16.34	17.15	18.24	17.80
75	10.74	11.20	12.18	13.52	14.49	14 66
50	9.64	10.10	11.03	12.53	13.05	12.99
25	8.95	9.53	10.10	11.08	11.03	10.56
0	6.99	8.31	9.53	10.62	11.89	11.26

*Alkane means mixture of heptane and nonane.

In Fig. 1, a representative triangular phase diagram is given. Only at 20°C, the phase diagram is somewhat different as can be seen from Fig. 1 (inset). This is simply because of the low Brij 35 solubility in alkane at 20°C. From Table 1, it can also be seen that the percent microemulsion area is higher in case of heptane but much lower in case of nonane. This is probably because of the lower solubility of the surfactant in nonane than in heptane.

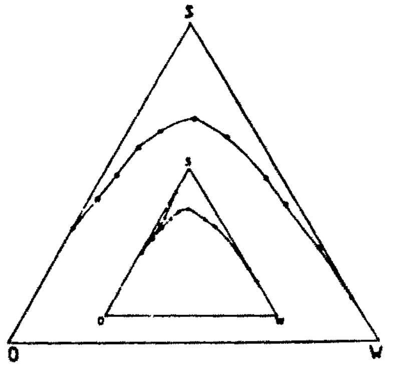

Fig. 1. Triangular phase diagram of water/surfactant/heptane at 40°C. Inset : at 20°C. W represents water, S represents surfactant and cosurfactant together, O represents either oils (nonane or heptane) or their mixtures.

In Fig. 2 the percent of micromulsion area is plotted against the mole fraction of nonane in mixed alkane. It is obvious that the variations in the microemulsion area of the mixed systems are not that large and also it is clear that there is no linear relationship. At higher temperatures of 60 and 70°C, the concave nature of the curve is quite obvious with the minima around nonane mole fraction of 0.75.

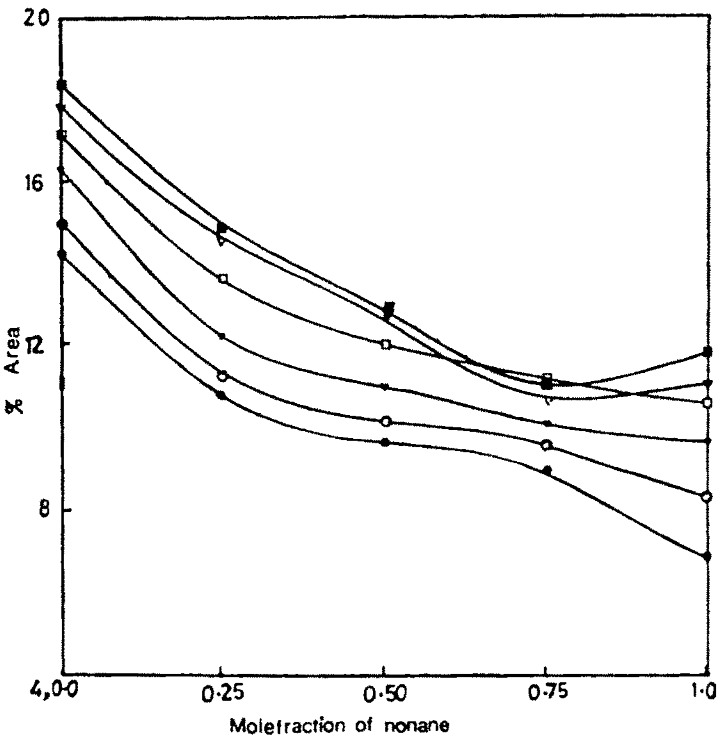

Fig. 2. Plot of microemulsion area vs mole fraction of nonane in the mixture.

20°C● ; 30°C O , 40°C ▿ ; 50°C □ ; 60°C □ ; 70°C ▿ .

Hence we conclude that the study of microemulsion area at higher temperature and with mixed alkane systems are important as it helps in the modelling of the crude oil in the oil fields. It has generally been suggested earlier [14] that the interfacial tension between water and mixed systems vary linearly with one of the components of the mixed system. We find that even if that is so, the amount of microemulsion formed does not necessarily follow the same relation.

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[IN PRESS]

Properties of Mixed Alkane Microemulsions

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Abstract

Different alkane mixtures were used as oil phase to determine the effect of such mixing on the physical properties of the alkane/ Brij 35 + propanol/ water microemulsions. The alkanes were various mixtures of heptane and nonane. Viscosity of microemulsions was nonlinear in nature as a function of heptane mole fraction in alkane mixtures. Viscosity of mixed alkane microemulsions were almost same. Conductance and viscosity studies indicate that the systems retain their bicontinuous nature through out though surfactants, because of reasonably high concentration , can also form a continuous structure. The activation enthalpies and entropies of viscous flow were computed for all systems. Adiabatic compressibility of the systems were also determined. All studies were made in between 30 and 70°C.

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Introduction

Explosive increment of research activities in microemulsion during last decade is because of its potential use in tertiary oil recovery. Microemulsions are formed due to very low water/ oil interfacial tension. The microemulsion flooding can , theoretically , extract crude oil even from the pores of the underground rocks.

Current literature [1-2] has considerable amount of work on modeling of microemulsions. Shah et.al. [3] have investigated extensively the effect of various parameters viz. salinity, alkane chain length and the nature of cosurfactant on the phase behaviour and solubilizing power of microemulsions. Many other researchers have also done similar studies [4-8] . The majority of these studies though, were done with pure components and hence do not provide enough information for systems where hydrocarbon mixtures were involved. We failed to locate systematic studies of the alkane mixture microemulsions, their formation and their properties. Hence in this paper we present some properties e.g. conductance, ultrasonic velocity, viscosity etc. of a few nonionic surfactant microemulsion systems ~~with~~ at mixed alkanes at different temperatures.

Methods and Materials

Brij 35 ($C_{12}H_{25}(OCH_2CH_2)_{23}OH$) from Merck (Germany) was used as received. Propanol, heptane, nonane (S.D.'s,India), purified by standard methods [9] , and doubly distilled water (conductance $\sim 3 \times 10^{-6}$ S cm^{-1}) were used.

Propanol was the cosurfactant and the cosurfactant/ surfactant ratio was 2 : 1 by weight. Three different mixtures of heptane and nonane (1: 3, 1:1 and 3:1 mole ratios) were used as the oil phase. 0.1 M NaCl was used as the aqueous phase for conductivity measurements with a Mullard conductivity bridge. Viscosity was obtained with a standard Ubbelohde viscometer and ultrasound velocity was with the help of an ultrasonic interferometer (M3, Mittal Enterprises, New Delhi). Standard pyknometer was used for density determination. The standard deviation in density and viscosity measurements were $\pm$0.005 % and $\pm$0.4 % respectively.

Adiabatic compressibility (β) of the microemulsion was calculated by $\beta = (\rho u^2)^{-1}$ where ρ and u are the density and ultrasonic velocity in microemulsion. The operating frequency was 1 MHz. 3 and 5 MHz were used for a few systems and no appreciable difference in β values were observed when compared with 1 MHz data. Hence 3 and 5 MHz were not used in general. The standard deviation in u was $\pm$0.4 %.

Eight different aliquots of one phase microemulsions (having 80 % surfactant) with various oil/ water weight ratios (0.0526, 0.111, 0.333, 0.667, 1.5, 3.0, 9.0 and 19.0) were used for conductance measurements. The term surfactant here means both surfactant and cosurfactant . Four different composition microemulsions were chosen for the viscosity (Table I) and six for adiabatic compressibility measurements at regular intervals (Table II) . Viscosity and conductance were studied at five different temperatures (± 0.1°C) ranging from 30 to 70°C at 10°C interval. Sound velocity could not be determined at 70°C and hence compressibility was calculated only at other four temperatures.

Results and Discussion

Fig.1 is a representative ternary phase diagram of mixed alkane- surfactant-water system. This diagram was determined by the well known titration method. Phase diagram of all systems show similar pattern with difference in the area of monophasic region. Selected compositions for the physical property study are marked in the diagram. A detailed scanning of the phase diagrams was not done, as it was time consuming and of little importance in the present study. However the preliminary studies indicated that there was no three phase zone. Below surfactant concentration of 10 % or so, very viscous liquid was obtained over the entire range of oil/water ratios. No semisolid was at all obtained.

Fig.2 shows variation of specific conductance as a function of water volume fraction at various temperatures. Percolation,(an abrupt increase in electrical conductivity at certain water volume fraction) which represents the microstructural changes in microemulsion [10] , is absent . The steady increment of electrical conductivity with increase of water fraction indicates that the present system has same structure over the entire o/w range at this surfactant concentration. However, percolation was observed at high water/surfactant ratios. Nonpercolative conductance variation in mixed alkane systems indicates a bicontinuous structure. High surfactant concentration (Brij 35 ~ 27 %) may also introduce a continuous surfactant structure. Therefore we feel that both continuous Brij 35 and bicontinuous water conduits are probably present. The percolation behaviour does not change with the change in the alkane composition indicating that the microstructure of the microemulsions is independent of the alkane mixture composition. A gradual change to discrete particle structure may be observed when surfactant concentration decreases [11] .

Fig. 3 shows the variation of absolute viscosity of these systems with weight percentage of water. Viscosity steadily increases with increase of water fraction for all mixed systems. This type of variation characterises a bicontinuous structure [12,13] . Bicontinuous structure in microemulsion indicates water filled interconnected conduits in oil medium [12] . Increase of water fraction swells the conduits and hence increase in viscosity [13] . As can be seen from Fig. 3 the lines at any one temperature for various systems are almost parallel (but not exactly parallel) indicating that the nature of oil phase does not have much influence on the mode of viscosity variation.

Temperature plays an important role on the physical properties of microemulsions. In Fig. 3, it is observed that the slopes of the lines decrease with rise of temperature. This variation of the slope with temperature is reasonably linear ($r = 0.986$) and on extrapolation one can obtain a temperature where the slope is zero (T_p). Over this temperature no change in viscosity is expected on furthur addition of water. It is evident that this temperature is a function of alkane composition. A plot of T_p against alkane mixture composition shows a maximum at 0.5 mole fraction nonane (Fig. 4) indicating that this system is irregular - somewhat different from the rest.

From Fig. 5, it is obvious that the viscosity of most of the mixed alkane microemulsions are almost similar inspite of different mixing compositions. No linear variation is observed when viscosity is plotted against the mole fraction of nonane. This is true at all temperatures. This property was quite unexpected as the ideal nature of the heptane - nonane mixing is ~~expected~~ granted. But phase diagrams of these systems also indicate the same behaviour. Hence it is clear that though heptane and nonane are ideally miscible, such behaviour is not observed in the properties of microemulsions as the alkane mixture composition is changed. Here properties of all mixed alkane microemulsions are similar inspite of different alkane composition and deviate much from those of pure alkanes.

Efforts have been made to calculate various activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) from the viscosity measurements for polymeric [14] as well as micellar solutions and interpret the results in terms of structural changes [15] . We have extended those relations to microemulsion systems. It is known that [14]

$\ln(\eta V/Nh) = \Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R$ where N, h and V are Avogadro number, Plank constant and molar volume respectively. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are activation enthalpy and entropy of the viscous flow respectively. The plot of $\ln(\eta V/Nh)$ vs T^{-1} is linear ($r = 0.99$) and the slope gives $\Delta H^{\ddagger}$ and the intercept $\Delta S^{\ddagger}$. These are given in Table I. It is observed that both the enthalpy and entropy values of different systems are very near to each other. The maximum deviation being about 7 % . This supports our earlier statement that the mixed alkane microemulsions are all similar and independent of alkane composition.

In Fig. 6A the linear variation of adiabatic compressibility with water volume fraction of different systems are shown. This linearity indicates that the increase of water fraction decreases adiabatic compressibility. Fig. 6B shows that

β linearly increases with temperature. Increase of temperature increases the hydrophobicity of the interfacial surfactant film due to dehydration of the polyethylene oxide chain [16] . Moreover rise in temperature should provide enough kinetic energy to loosen the interfacial film. These two effects are expected to enhance the penetration of the alkane molecules into the interfacial film, swelling the dispersed phase. Hence compressibility is higher at higher temperature.

The variations of viscosity and adiabatic compressibility are opposite to each other. This is clear from a comparison of Fig. 3 and Fig. 6A. Similar results were noticed earlier [17,18] . From Table II it is seen that the variation of the composition of the oil phase has no effect on compressibility when the oil/ water ratio is kept same.

Conclusion

It can be concluded from the present work that the properties of the mixed alkane microemulsions cannot be predicted from the properties of pure alkane microemulsions. However like pure alkane systems , these mixed alkane systems have bicontinuous structure throughout at 80 % surfactant concentration. A continuous structure due to high surfactant concentration can not be ruled out though. Adiabatic compressibility study indicates that the dispersed phase is swelled because of alkane penetration with rise of temperature.

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Table I

Viscosity Activation Enthalpies and Entropies of Oil-Surfactant-Water System. Surfactant is 80 % w/w (see text).

Oil Heptane/Nonane (mole ratio)	Weight percent water	$\Delta H^{\ddagger}$(kJ mol^{-1})	$\Delta S^{\ddagger}$(J mol^{-1}K^{-1})
1 : 1	2.0	17.4	1.1
	8.0	20.2	9.8
	12.0	21.2	13.0
	18.0	22.3	16.6
1 : 3	2.0	17.8	2.4
	8.0	20.1	9.0
	12.0	21.0	13.9
	18.0	23.0	18.7
3 : 1	2.0	16.6	-1.0
	8.0	20.1	9.4
	12.0	21.3	12.9
	18.0	22.1	16.0

The standard deviation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are ± 3.0 % and ± 1.0 % respectively.

Table II

Adiabatic Compressibility (β) at 1 MHz of Oil-Surfactant-Water System at Various Temperatures. Surfactant is 80 % (w/w) (See text)

Oil Heptane/Nonane (mole ratio)	Weight percent water	$\beta \times 10^{11}$ $cm^2 dyne^{-1}$ Temperature °C			
		30	40	50	60
1 : 1	18	6.0	6.2	6.5	7.0
	15	6.3	6.8	7.3	7.6
	12	6.7	7.2(7.5)†	7.6	8.3
	8	7.2	7.6	8.1	8.8
	5	7.6	8.2	8.7	9.5
	2	7.8	8.7	9.1	9.7
1 : 3	18	5.9(5.9)†	6.2	6.6	6.9
	12	5.9	6.9	7.3(7.6)*	7.7
	8	7.1	7.6	8.0	8.8
	2	7.8	8.5(8.4)†	8.9	9.6
3 : 1	18	5.9	6.2(5.9)†	6.6	7.1
	15	6.3	6.7	7.0	7.6
	12	6.7	7.1	7.5	8.1(7.7)*
	8	7.3	7.8	8.2	9.0
	5	7.9	8.2	8.7	9.4
	2	8.2	8.5	9.0	9.5(9.7)*

† at 5 MHz   * at 3 MHz

Legends

Fig. 1 Pseudo ternary phase diagram of mixed alkane/ Brij 35 + propanol/ water system at 40°C. Mixed alkane is heptane + nonane 1:1.

Fig. 2 Plot of specific conductance vs volume percent of water of the system Mixed alkane/ Brij 35 + propanol/ 0.1 M NaCl aqueous solution at 80 % w/w surfactant. Mixed alkane is heptane (1) + nonane (1).
✖ 30°C ; ● 40°C ; ▲ 50°C ; ■ 60°C ; ○ 70°C.

Fig. 3 Variation of absolute viscosity with weight percent water at various temperatures : ✖ 30°C ; ○ 40°C ; ■ 50°C ; ▲ 60°C ; ● 70°C.

(A) Heptane + Nonane 1 : 1. (B) Heptane + Nonane 3 : 1.
Surfactant 80 % w/w.

Fig. 4 Variation of $T_{p\phi}$ against the mole fraction of nonane in the alkane mixtures in the microemulsions.

Fig. 5 Plot of absolute viscosity vs nonane mole fraction in alkane mixtures at 80 % w/w surfactant at various temperatures : ✖ 40°C ; ▲ 50°C ; ■ 60°C ; ● 70°C.

Fig. 6 Variation of adiabatic compressibility with (A) volume percent of water at 80 % w/w surfactant. alkane mixture is 1 : 1. ● 30°C ; ▲ 40°C ; ■ 50°C ; ✖ 60°C.

(B) with temperature at various weight percent of Water. ✖ 2 ; ○ 5 ; ▼ 8; ■ 12 ; ▲ 15 ; ● 18.

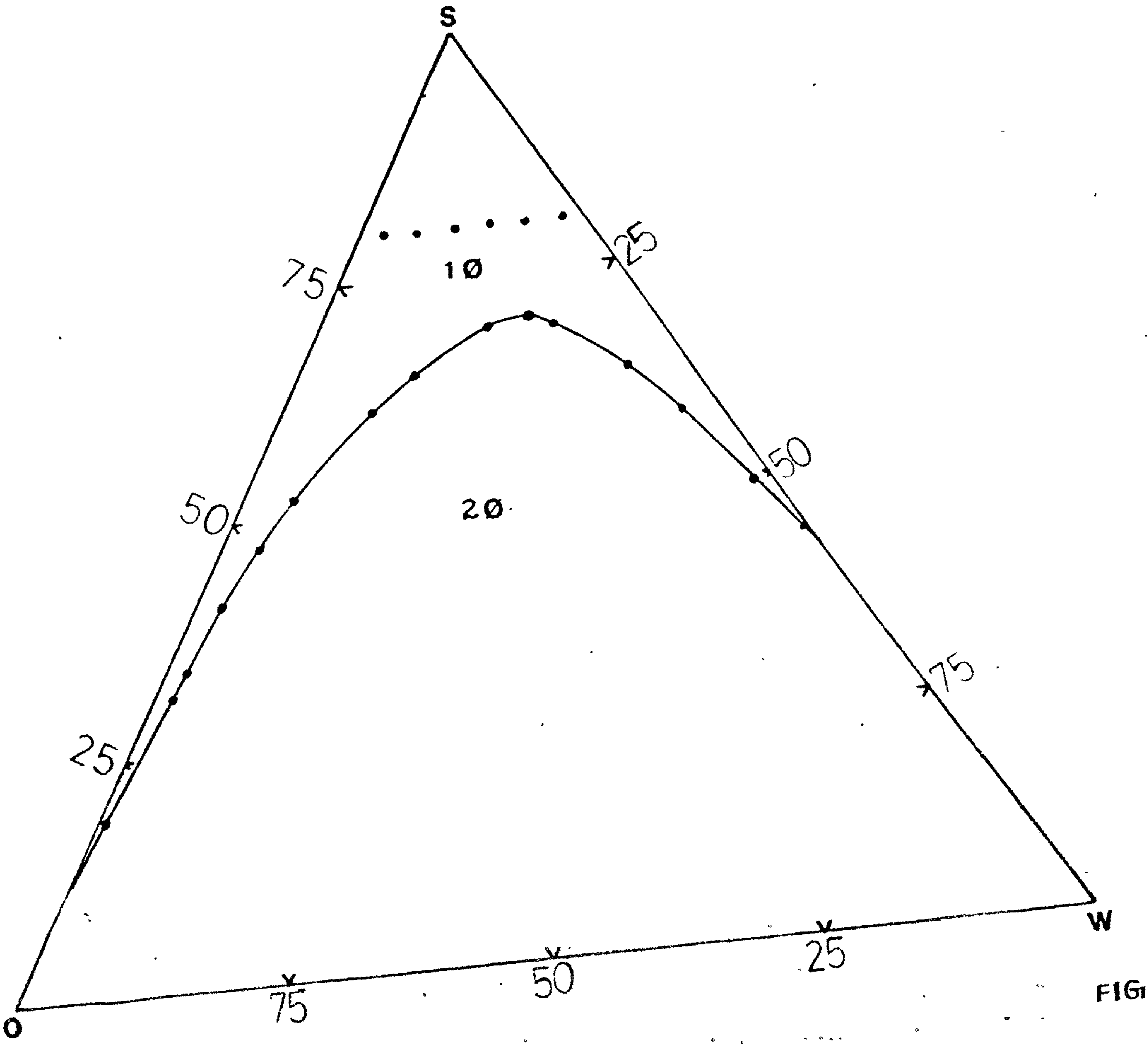

FIG -1

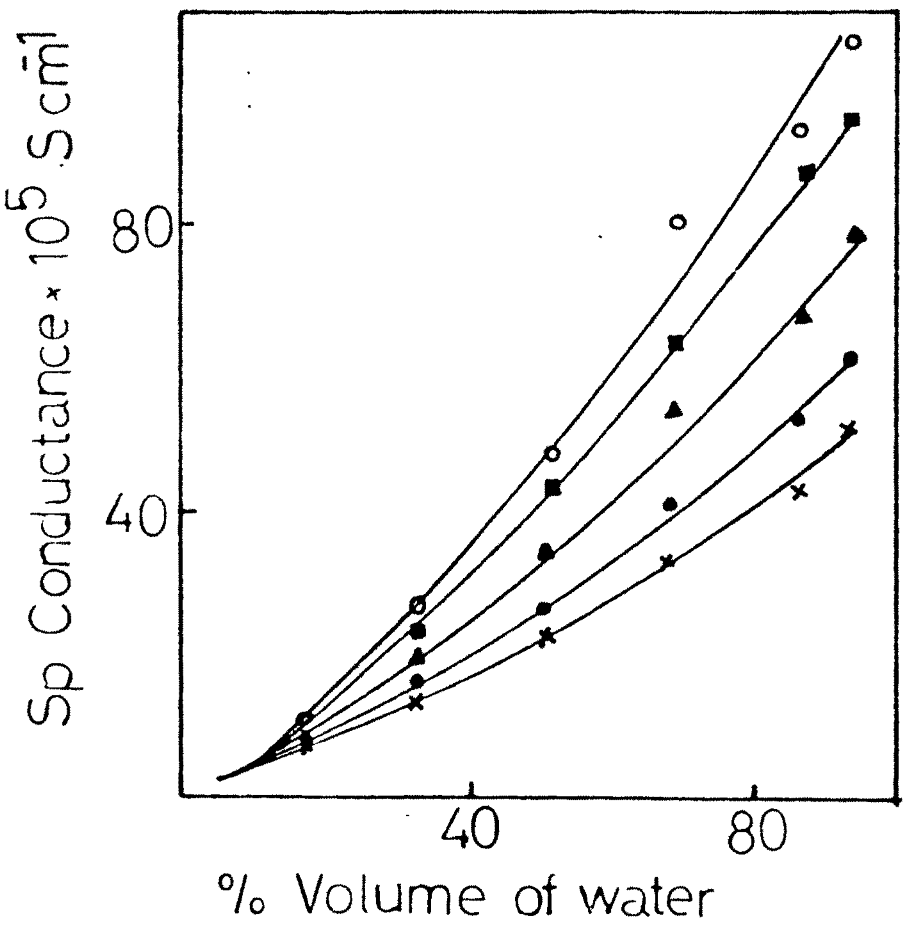

FIG 2

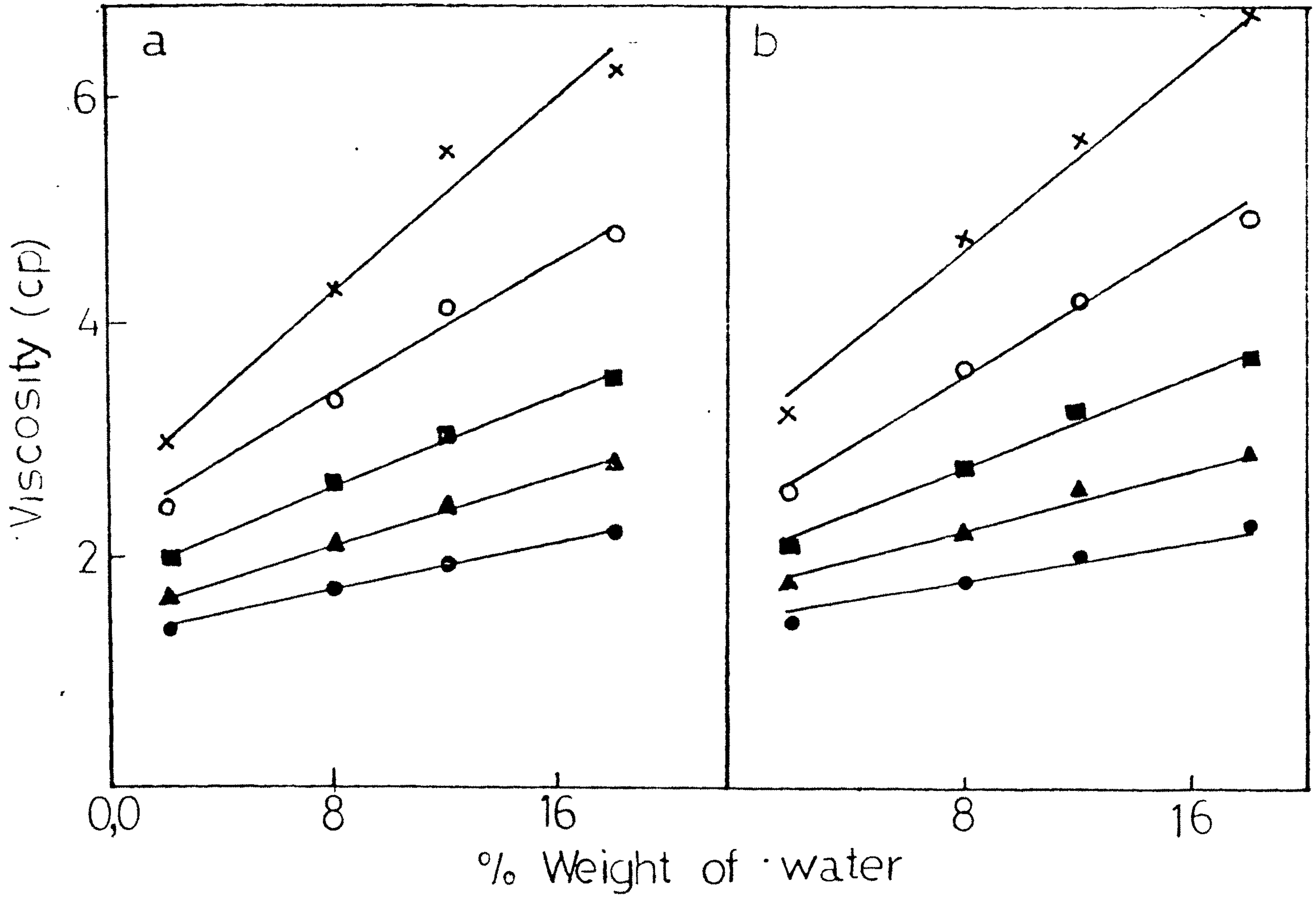

FIG. 3

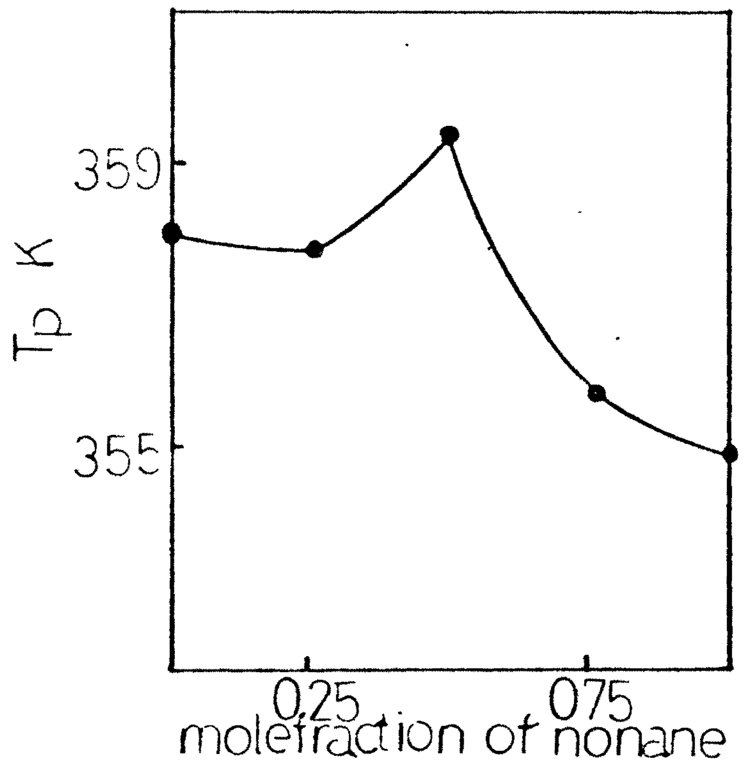

FIG. 4

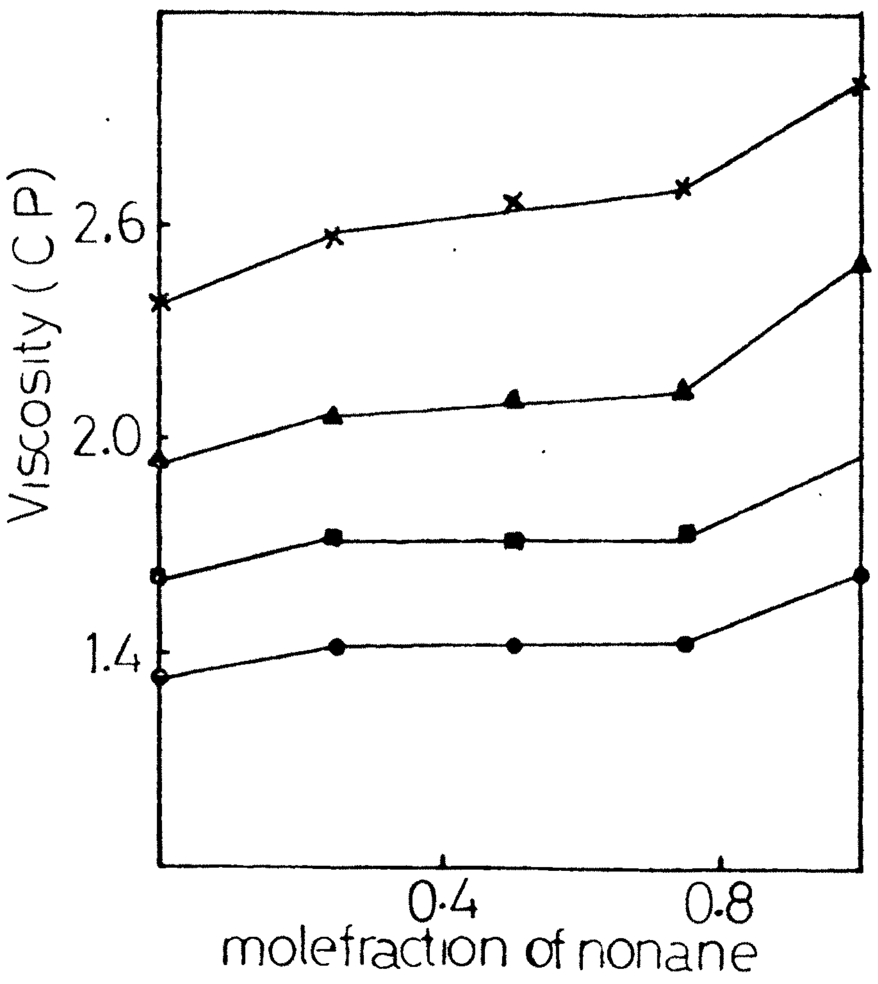

FIG. 5

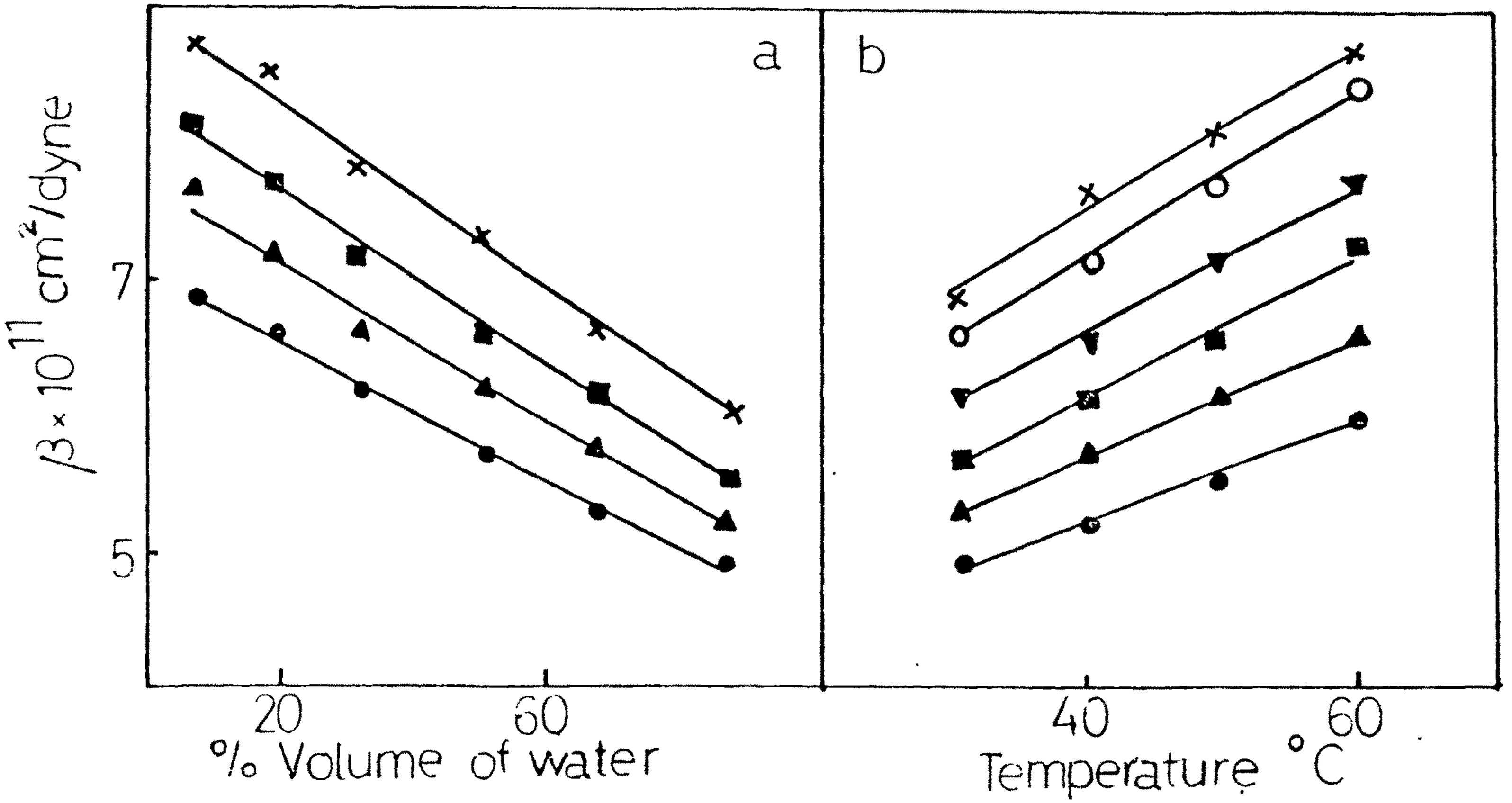
$\beta \times 10^{11}$ cm^2/dyne
7
5
a
20
60
% Volume of water
b
40
60
Temperature °C

FIG. 6

[IN PRESS]

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

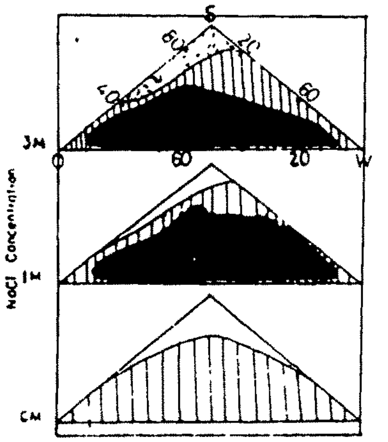

Fig.1 Phase prism representation of system I (see text)
■-L/L/L; ▥ - L/L; □-L;
▦ - So/L (L=liquid, So=solid)

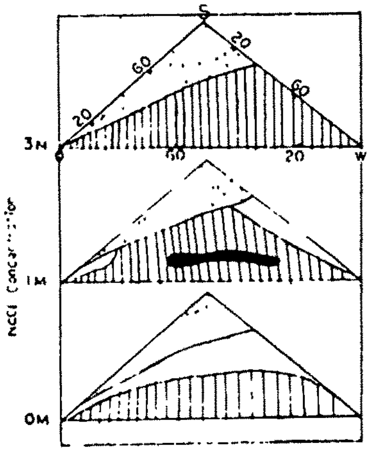

Fig.2 Phase prism representation of system II (see text.) Symbols as in Fig.1

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).

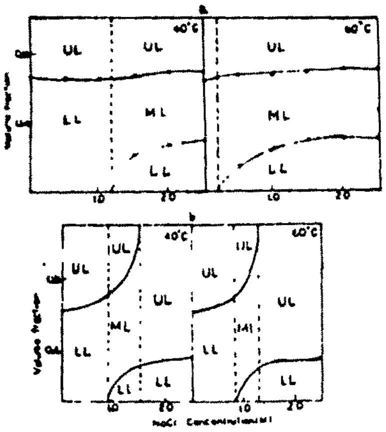

Fig.3 Various volume fractions of (a) System I (b) System II as a function of NaCl concentration. (Upper, middle and lower layers are UL, ML & LL)

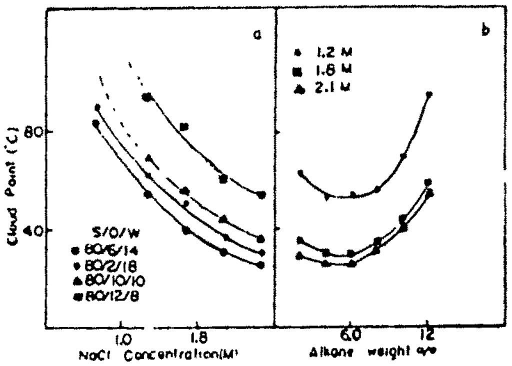

Fig.4 Variation of cloud point of system I with (a) NaCl concentration at various compositions and (b) alkane weight percent.

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

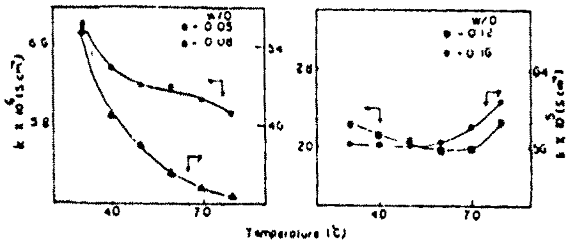

Fig.5 Variation SP. conductance of system II with temperature at different w/o ratio

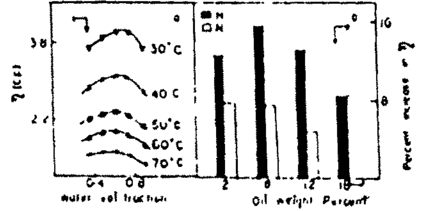

Fig 6 (a) Viscosity of system II as function water volume fraction at various temperature
(b) Percentage increment of viscosity for system I (80% S+CS) microemulsion when water was replaced by 1M NaCl, N-Heptane, N-nonane microemulsions.

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

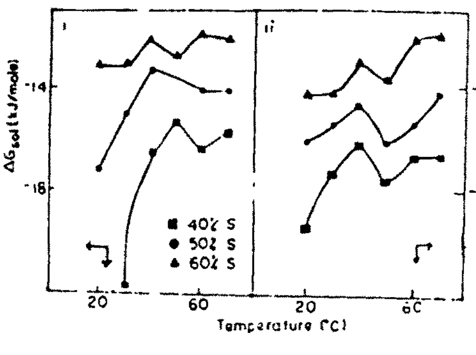

Fig.7 Variation of ΔG_{sol} for o/w micro-emulsion in system I. (i) nonane (ii) heptane containing systems.

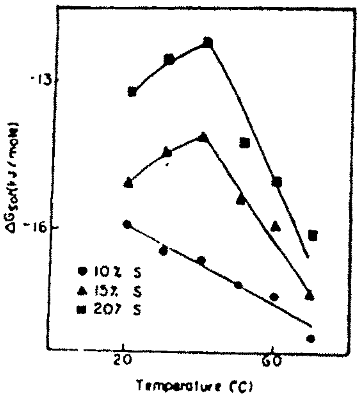

Fig.8 ΔG_{sol} of o/w in system II as a function of temperature.

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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