Physicochemical studies of microemulsions

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Abstract

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
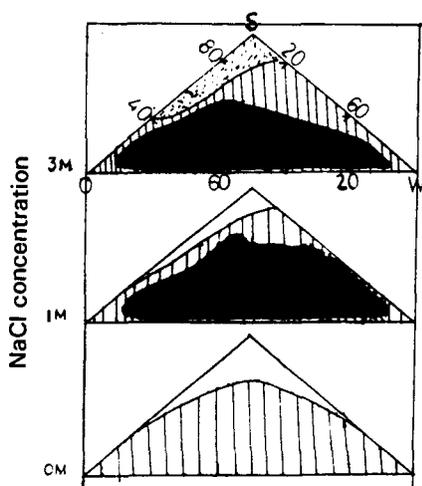

Fig.1 Phase prism representation of system I (see text)
■-L/L/L; ▦-L/L; ☐-L;
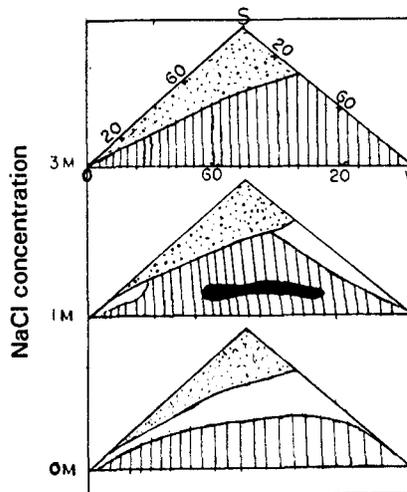▦ - So/L (L=liquid, So=solid)

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

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

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 ($Y_{o/m} = Y_{m/w}$) (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).
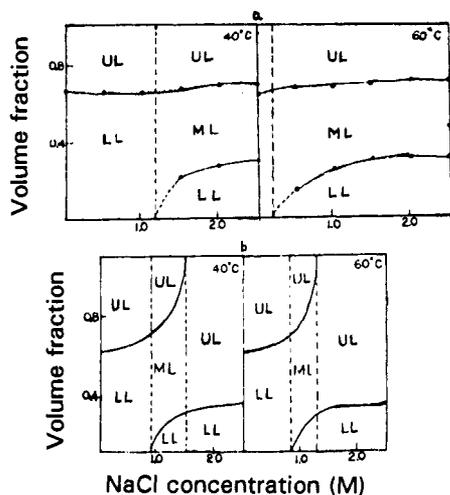

Fig.3 Various volume fractions of (a) System I (b) System II as a function of NaCl concentration.(Upper, middle and lower layers are UL, ML & LL)
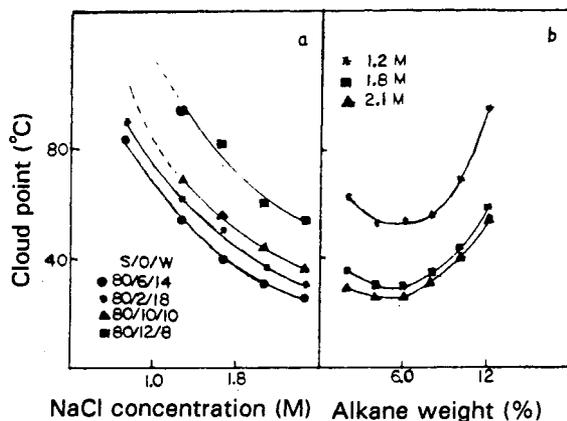

Fig.4 Variation of cloud point of system I with (a) NaCl concentration at various compositions and (b) alkane weight percent.

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 conductance. Thus the decrease in conductance with increase in temperature supports the hopping mechanism rather than the sticky
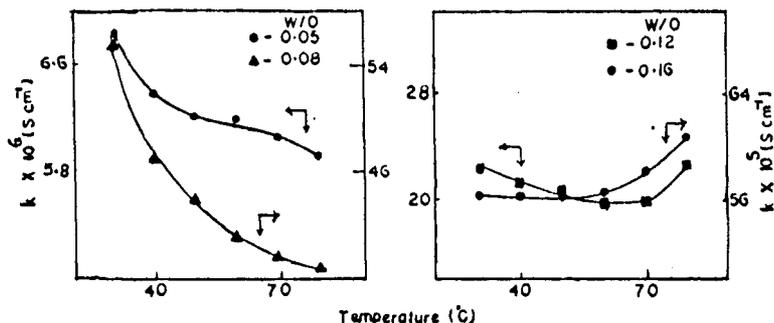

Fig.5 Variation SP. conductance of system II with temperature at different w/o ratio.
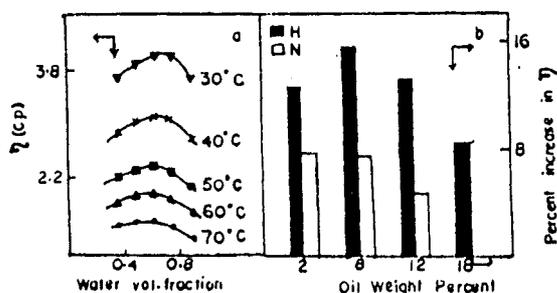
Fig.6 (a) Viscosity of system II as function water volume fraction at various temperature.
(b) Percentage increment of viscosity for system I (80% S+CS) microemulsion when water was replaced by 1M NaCl. H=Heptane, N=nonane microemulsions.

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 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
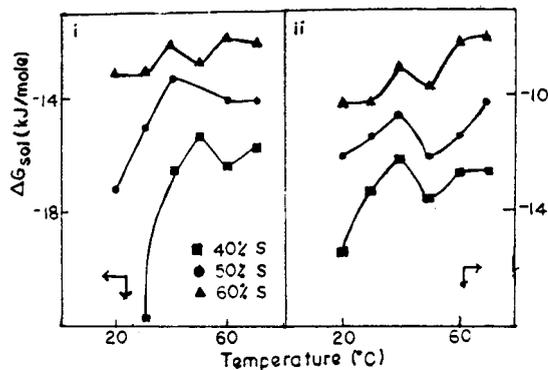
Fig.7 Variation of ΔG_{sol} for o/w microemulsion in system I. (i) nonane (ii) heptane containing systems.
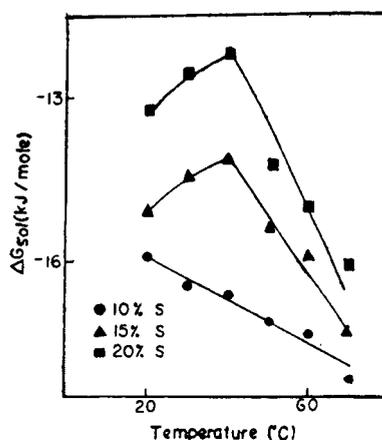
Fig.8 ΔG_{sol} of o/w in system II as a function of temperature.

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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