Structural Characterization of Microemulsions of Triton X-100 + 1-Pentanol/ n-Hexane/ Brine System

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Abstract

Structural characterization of microemulsions in a pseudo-ternary system, Triton X -100+1-penanol (1:5 molar ratio)/ n-hexane/ brine system has been done by using different techniques such as quasi-elastic light scattering (QELS), conductivity, viscosity and crossed polaroid microscope. Different distinct regions such as 1ϕ micellar region, a two-phase region and a very narrow three-phase region were observed in the pseudo-ternary phase diagram. Electrical conductivities and viscosities of the system with different weight fraction of water (ϕ_w) were determined and results were used to locate sub-regions of the single-phase microemulsion. The results showed that a transition from water-in-oil microstructure via bicontinuous structure to an oil-in-water microemulsion region occurred with increase in weight fraction of water ϕ_w in the system. The size of the microemulsion droplets was determined by quasi–elastic light scattering. It was found that the sizes of the droplets depended markedly on weight fraction of water (ϕ_w) and were in the range of 16-38 nm. In the upper portion (at $\phi_s > 70$) of the isotropic region of the phase diagram, the structure of microemulsion droplets is unclear.

Key words: Surfactant, co-surfactant, microemulsion, microstructure, micelles, phase behavior, phase diagram, Triton X-100, n-hexane, 1–pentanol, QELS, conductivity, viscosity.

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Introduction

Microemulsions are thermodynamic stable mixture of two immiscible solvents (polar and nonpolar) stabilized by surfactants[1]. While being microscopically homogeneous, they are structured on a microscopic length scale (10-100 Å) into aqueous and oleic microdomain separated by surfactant rich film[2]. They have wide applications in separation science[3], reaction engineering[4], environmental science[5], material science[6,7] with some unique advantages. These applications have been entirely governed by the microstructure of microemulsion droplets. Therefore, the structural characterization of the micellar aggregates is necessary before using it in any industrial fields.[25-26]

Microstructures of microemulsion have been investigated by different techniques, such as SANS[27-29], SAXS[30-32], NMR[33], QELS[34-35], fluorescence spectroscopy[35,36], conductivity[35,37-39] and viscosity[35,40] measurements. These studies reveal that the structure of microemulsion depends upon the relative amount of oil and water present, of course, on the particular choice of surfactant or surfactant plus co-surfactant. It has been observed that the structure of microemulsion crucially depends upon water–to–oil ratio.[35,37] The usual situation is that when the weight fraction of oil is small, the micro-emulsion is water continuous solution of micelles, swollen with oil and when weight fraction of dispersed water is small; the microemulsion is an oleic solution of inverted micelles swollen with water. However, the structure of micro-emulsion containing comparable amount of water and oil or with high surfactant content are not well established.[35,41] Several structures

have been proposed for such microemulsions including bicontinuous or lamellar ones, and some systems may be simply co-solubilized solutions without microstructure.[35,41]

Nonionic surfactant, Triton X – 100 (Poly-oxy tetra methyl butyl phenyl ether; molecular weight ~ 624) has been known for several years and is capable of making reverse micelles and microemulsions with broad spectrum of solubilities and has been employed in various chemical reaction[42-43] including synthesis of nanoparticles. In this context, the phase behavior and microstructures of microemulsions of Triton X-100 +1-pentanol (1:5 molar ratio) / n-hexane/ 0.1 M NaCl system has been reported which is based on investigations carried out by crossed polaroid microscope, conductivity, viscosity, and QELS measurements.

Experimental Section

2.1 Materials:

Triton X–100 and n-hexane were procured from Loba Chemical Company, India. 1-pentanol was obtained from S. D Fine Chemical Ltd., Mumbai. Sodium chloride was purchased from Merck Ltd., India. Double distilled water was used throughout the studies.

Methods

2.2 Construction of Phase Diagram: Phase diagram of Triton X–100 + 1–pentanol (1:5 molar) / n-hexane/ 0.1 M NaCl system was constructed by titration method. A known amount of surfactant and co-surfactant was taken in oil or water and subsequently the mixture was titrated with oil or water respectively till clear

to turbid or turbid to clear transition was observed. The salt solution or oil was added in a small step (typically 10 µl) to each composition and the solution was stirred gently. The resulting phases were viewed visually and through crossed polariod microscope to confirm isotropism after allowing sufficient time (typically 4-6 hours) for attainment of equilibrium at constant temperature. The entire phase diagram was mapped in the aforesaid manner.

Conductivity measurements: Conductivity measurements were taken with a Delica Impendence Bridge Model 12 K of Mita Muses Kenkyusho Ltd., Tokyo, Japan. All measurements were performed in a thermostated water bath at 30°C with a precision of 0.01°C.

Viscosity measurements: The viscosity of micellar solutions were measured by using an Ostwald viscometer placed in a thermostated bath. Following formula was used to compute the viscosity of unknown solution

$$\eta = (t / t_0) (\rho / \rho_0) \eta_0$$

where, η = viscosity of micellar solution

t = time for flow of a known volume of micellar solution

t_0 = time for flow of the same volume of water

ρ = density of micellar solution at 30°C,

ρ_0 = density of water at 30°C and

η_0 = viscosity of water at 30°C

QELS measurements: QELS measurements were carried out to determine hydrodynamic diameter of microemulsion droplets by using Brokhaven 9000 model 200 SM. All samples were filtered through millipore filter size 0.2mm to remove dust particles. Photo–count functions

were analyzed with 136 channel multibit correlator. Micellar diffusion co-efficient were computed for various samples. The hydrodynamic diameter, D_h of the micellar aggregates were obtained from diffusion co-efficient by using Stocks-Einstein equation.

$$D_h = kT/3\pi\eta Do$$

Where,

k = Boltzmann constant, T = absolute temperature,

Do=diffusion co-efficient, η=viscosity of the bulk medium.

Results and Discussion

Phase diagram of pseudo-ternary system, Triton X-100 + 1-pentanol (1:5 molar ratio)/ n–hexane/ 0.1M NaCl system was dermined at 30°C and shown in figure 1. Different distinct regions *viz* isotropic single phase, a two-phase and a point like three-phase region are shown in the phase diagram. There are two distinct isotopic regions, the first one is in the water corner and the second isotropic region has been found in the upper portion of the phase diagram which touches the vertex of oil and surfactant and has been extended up to 40% of water in the middle of the phase diagram. There is no any mesophase present in the phase diagram.

Conductivity :

Electrical conductivity of microemulsions were measured at 30°C along different dilution lines (dotted lines in figure 1) as a function of weight fraction of water, ϕ_ω and shown in figure 2. It can be seen that at $\phi_\omega < 10$, conductivity is very low and at $\phi_\omega > 10$, it starts to increase.

At $\phi_\omega \sim 22$, conductivity is more than three orders of magnitude than it was at $\phi_\omega \sim 10$. These curves exhibit well-known percolation behavior.[35,37] The existence of all the three microstructured regions namely water-in-oil, bicontinuous and oil-in-water microemulsion can be predicated from the nature of the plot. The water-in-oil microemulsions are distinguished from very low conductivity. As the amount of water increases, conductivity though increases monotonically, remains very low until a critical water fraction $\phi_\omega \sim 10$. This critical water fraction is termed as percolation threshold[35] at which inverted micellar droplets undergoes sticky collision to form continuous channel-like structures conduits through which hoping of charges takes place. As a result, conductivity increases. The absolute value of ϕ_ω at which percolation is observed decreased slightly from path I to IV. This may be due to decrease in the droplets size so that hoping of the charge becomes a little bit difficult through the droplets. At $\phi_\omega > 22$, structural inversion from bicontinuous to a water continuous microemulsion takes place with high conductance value ($>1 \times 10^{-2}$ mho). Thus, the conductivity profiles clearly shows that the upper sub-region of the isotropic region is inverted micellar region, at $\phi_\omega H \approx 10\text{-}22$, the region is bicontinuous structure and $\phi_\omega > 22$, oil-in-water microemulsion exist in the one-phase isotropic region of Triton X-100 + 1- pentanol/ 1-hexane/ 0.1M NaCl system. Further, in the upper region of the isotropic phase, surfactant is present more than 70% and only 15-20 % hexane is present. In such case a huge amount of surfactant (70%) can not be solubilized in 15-20% of hexane. On the basis of conductivity behavior, it is assumed that 1-pentanol which is used as a co-surfactant act as a co- solvent along with hexane and Triton X-100 forms water-in-oil microemulsion.

Viscosity :

The bulk viscosity measurements were carried out at 30°C along different dilution lines II-IV (figure 1) and results are shown in figure 3. All the samples of microemulsions show Newtonian behavior. It can be seen that viscosity increases with increase in weight fraction of water ϕ_w. attains a maximum value and decreases with further increase in ϕ_w. It is known[35] that the macroscopic transport properties such as viscosity in micellar solutions is controlled by their microstructures. The bulk viscosity responds to changes in both the structure of the aggregates and their mutual interactions. Transition from small to large micelles is accompanied by a significant increase in viscosity. The initial rise in viscosity reflects an increase in the inter-droplet interaction and corresponds to oil continuous microemulsion, which is also confirmed by conductivity measurements. It is expected that the hydrophilic chains of Triton X-100 are strongly hydrogen bonded allowing the interaction between the droplets. The inter-droplet interaction increases with increase in droplet size. At $\phi_w > 22$, water continuous microemulsion exists which is also confirmed by conductivity measurements. The hump between $\phi_w \approx 15\text{-}22$, confirms phase inversion from oil continuous to water continuous microemulsion through bicontinuous structure.

Quasi-Elastic Light Scattering (QELS):

Droplet size measurements were performed by QELS along different dilution lines IV (dotted lines in figure 1) and the

corresponding sizes (hydrodynamic diameter in mn) are shown in figure 4. It was found that the upper region of the phase diagram containing higher concentration of Triton X-100 and co-surfactant ($\phi_s > 80$) does not show droplet like structure. In this region, it is presumed that the droplets are too small to be measured by QELS or droplets do not exist in this region.[22-23, 35] As the weight fraction of water ϕ_w was increased more than $\phi_w > 20$, a good correlation was obtained and corresponding size was computed and plotted in the Figure 4. It can be seen that apparent hydrodynamic diameter D_h of the droplets increases with increase in weight fraction of water along all dilution lines. As the weight fraction of water increases, more and more ?Triton X-100 gets solubilized in water leaving more and more 1-pentanol to be solubilized in 1-hexane from the interface.[48] Thus, with increasing weight fraction of water ϕ_w, droplet size increases and this is what reflected in our QELS measurements.

Demarcation of Different Microstructured Sub-regions in a single-phase Isotropic Region:

The variables such as weight fraction of oil or water, concentration of surfactant, temperature and presence of electrolytes can lead to changes in the structures of micrio-emulsion.[27,31,34] Macroscopic properties of microemulsion like conductivity, viscosity and phase behavior can be correlated to the fluid microstructure. The techniques like those used above *i.e.* conductivity and viscosity provide valuable information about the structural behavior of the microemulsion by determining the nature of continuous phase and detecting phase inversion and percolation phenomenon,

where as the QELS measures droplet size of microemulsion in the entire one-phase isotropic region of the phase diagram. Based on these investigations, different microstructured sub-regions are demarcated and shown in figure 5.

Region 1: The absence of significant QELS signals in the upper portion of the phase diagram (hatched region Figure 5) shows that there is a large area of isotropic region where various components coexist in one transparent fluid phase without forming micelles like aggregates. Similar results were reported by Bellocq and Fourehe[41] for surfactant-alcohol-oil-water system. Our results are consistent with the microemulsion model of Bothorel *et. al,*[49] in which a certain region of the ternary system can not be described either by water-in-oil or oil-in-water microemulsion or micelles since the filling co-efficient of both type of micelles would be higher than the random close sphere packing. In this excluded region, the droplets of the systems probably consist of small hydrated surfactant aggregates solvated by alcohol dispersed in oleic (1-pentanol+n-hexane) medium.

Region 2 : In this region, ratio of water to oil is greater than one, microemulsions are highly conducting so they must be water continuous. This result suggests that oil-in-water microemulsion is restricted to a small domain. However, independent characteristic sizes from QELS are consistent with the presence of micelles structures. Thus, the microemulsions in region 2 are aqueous solutions of oil-swollen micelles.

Region 3: In this region, ratio of water to oil is less than one and conductivity is four orders of magnitude smaller than region 2.
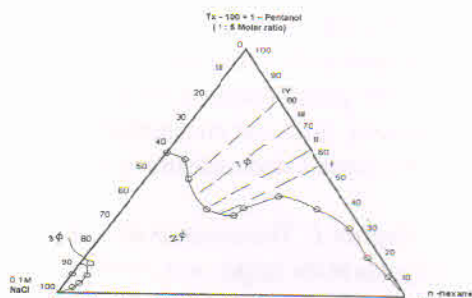
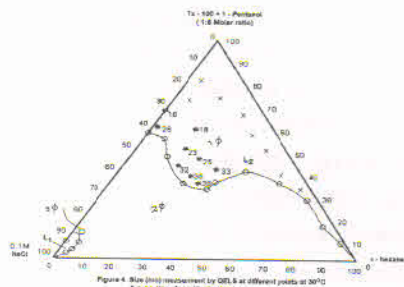Figure 1. Phase diagram of Tx - 100 + 1 - Pentanol / n- hexane / 0.1 M NaCl at 30°C

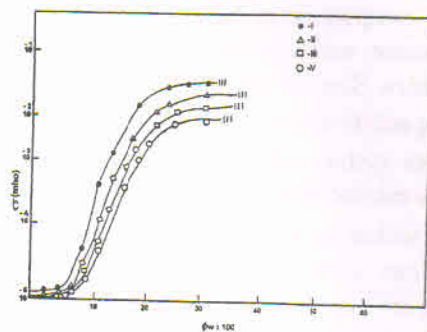Figure 3. Plot of Conductivity vs weight fraction of water φw at different dilution lines of the system Tx - 100 + 1 - pentanol / n - hexane / 0.1 M NaCl at 30°C
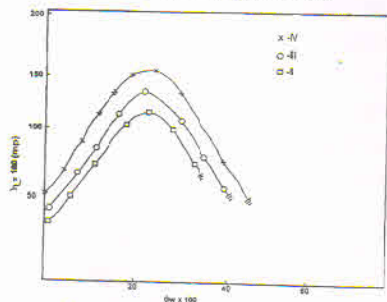

Figure 2. Plot of viscosity vs weight fraction of water φw at different dilution lines of the system Tx - 100 + 1 - pentanol / n - hexane / 0.1 M NaCl at 30°C

Figure 4. Size (nm) measurement by QELS B at different points at 30°C
L • = nm size, ● = nm size (nm)

Figure 5. Pseudoternary phase diagram displaying different sub - regions.
Please see the text.

QELS signals were very low which were unable to measure droplet size in this region. However, conductivity profiles and viscosity measurements show the presence of w/o micelles structures. Quantitative determination of micelle size depends on understanding the influence of inter-droplets interactions on the QELS signal. Cazabat and Langevin *et al.*[50] had investigated the interactions between w/o micelles and found that micelles interact primarily with hard

sphere repulsions, but also with small attractive interaction, which increases near phase boundaries. The presence of salt reduces these interactions. Therefore, in the micellar aggregates (at low ϕ_ω) interactions will be small. Thus, all these results are consistent with the picture of the w/o microemulsions as oleic solutions of invited micelles swollen with water. The conductivity profile could be explained by the presence of strong attraction between w/o micelles (*i.e.* the formation of channels of droplets) or by equilibrium between w/o micelles and highly conducting smaller aggregates dispersed in an oleic medium.

Region 4: In this region where the weight ratio of water to oil is close to one, conductivity, viscosity, and QELS measurements were taken along several dilution paths (line I to IV). At low ϕ_ω, water in the microemulsion is restricted and the oil is

continuous, conductivity is extremely low. Microemulsion is diluted with brine, the conductivity rises steeply with increase in ϕ_ω above the percolation threshold (figure 2) and this suggests a transition from a non-conducting to a conducting structure. Above the percolation threshold along lines I to IV, bicontinuous structures exist. The droplets are organizing when the amount of n-hexane increases. The conductivity minimum is probably due to the formation of a w/o microemulsion followed by a transition to a water continuous microemulsion. Thus, the region 4 is bicontinuous structure subregion. and this is confirmed by conductivity, viscosity and QELS measurements. *It is estimated that the uncertainly to locate the boundaries of region 4 should be less than ±5 %.*

Conclusions

The phase behavior and structural characterization of microemulsions of the pseudo-ternary Triton X-100 + 1–pentanol (1:5 molar ratio)/ n–hexane/ 0.1M NaCl brine system investigated by Polaroid microscope, conductivity, viscosity, and QELS measurements at 30°C. These techniques reveal the presence of various microstructured subregions in one-phase isotropic region of the phase diagram. Water and oil continuous microemulsion are inter-connected with each other through bicontinuous structure in the same isotropic region. 1–Pentanol, which was used as a co-surfactant, acts as a co-solvent along with n–hexane at higher surfactant concentration. In the upper portion (at $\phi_s > 80$) of the phase diagram, the structure of microemulsion droplets is unclear. In this region, it is presumed that the droplets are too small to be measured by QELS or droplets do not exist in this region. The size of the microemulsion droplets increases with increase in weight fraction of water and were found in the range of 16-38 mm in lower portion of the isotropic region of the phase diagram.

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