2.1. Miscibility study of [60] fullerene using a non ionic surfactant Tween 80, Triton X 100 and ionic surfactants SDS, CTAB

2.1.1 Introduction

Surfactants like Triton X-100, a non-ionic neutral surfactant, is known to form micelles at a critical micellar concentration. The spherical micelles of TX-100 in water mimic artificial membranes and are most appropriate for forming stable homogeneous C_{60} dispersions. Fullerene dissolves in the hydrophobic part of the micelle core while the polar groups of TX-100 located at the micelle-water interface are in direct contact with the water molecules.

In the present investigation, a systematic and detailed account of the encapsulation and solubilization of fullerene C_{60} in aqueous micellar solutions of the non-ionic Tween- 80 Triton X-100, ionic SDS and CTAB surfactants was carried out. Both UV–VIS absorption and fluorescence emission measurements were used to get evidence on the location of C_{60} and the nature of the dispersion.

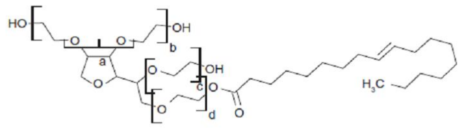
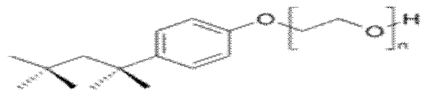
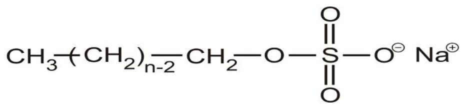
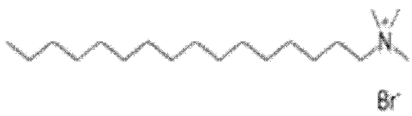
2.1.2. Materials

Surfactants like Tween 80 (Merck India), Triton X 100 (Fischer Scientific), SDS (Merck India), CTAB (Fischer Scientific) were used without any further purification. These are shown in Table 1. Toluene (Merck India) was used after further distillation and dried under 4A° molecular sieves. 1-propanol (Merck India),1-butanol (Merck India), 1-pentanol (Merck India),1-hexanol (Sigma Aldrich),1-octanol (Sigma Aldrich) used without further purification. A solution of [60]fullerene (Alfa Acer) in toluene, 1.39×10^{-4} M, was prepared and used as oil considered as single component.

2.1.3. [60]Fullerene and its microemulsion studies with non ionic surfactants Tween 80 & Triton X-100, anionic SDS and cationic CTAB surfactants

The development of microemulsion was studied by the standard cloud point method in which toluene and [60]fullerene-toluene stock solution. [60]fullerene-toluene solution was used as oil phase, Tween 80,Triton X 100, SDS and CTAB were used as surfactants along with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-octanol added as cosurfactants and double distilled water as aqueous phase. Table 2.1. Summarizes the surfactants used for miscibility study of [60]fullerene in water

Table 2.1. Surfactants used for miscibility study of [60]fullerene in water

Surfactants studied	Type	Structure
Tween 80 Polyoxyethylene (20) sorbitan mono oleate	Nonionic	
Triton X 100 $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10)	Nonionic	
SDS n=12 ⇒ sodium dodecyl sulfate	Anionic	
CTAB Cetyl trimethyl ammonium bromide	Cationic	

2.1.3.1. Phase transition to emulsion

5.0 ml of the [60]fullerene (1.39×10^{-4} M) solution was taken in the sample bottle with lid and 0.05 ml of Tween 80 was added into it and dissolved into it. To this solution 1.0 ml of cosurfactant like 1-propanol was added when homogeneous transparent mixture was obtained. To this homogeneous mixture sequential addition of 0.01 ml double distilled water was done using a Hamilton micro pipette. When water was added a white turbid layer was formed at the interface of oil phase and aqueous phase which disappeared when the contents were slightly shaken. This process of addition of water was continued till permanent turbidity remained even after the contents were shaken vigorously. This point at which transparent solution transformed into a white turbid solution is known as the point of transition from microemulsion to emulsion. Figure 2.1 explains the schematic representation of emulsion study. This process was repeated by taking different quantities of different cosurfactants like 1-butanol, 1-pentanol, 1-hexanol and 1-octanol noting the amount of water required for the transition of the phase.

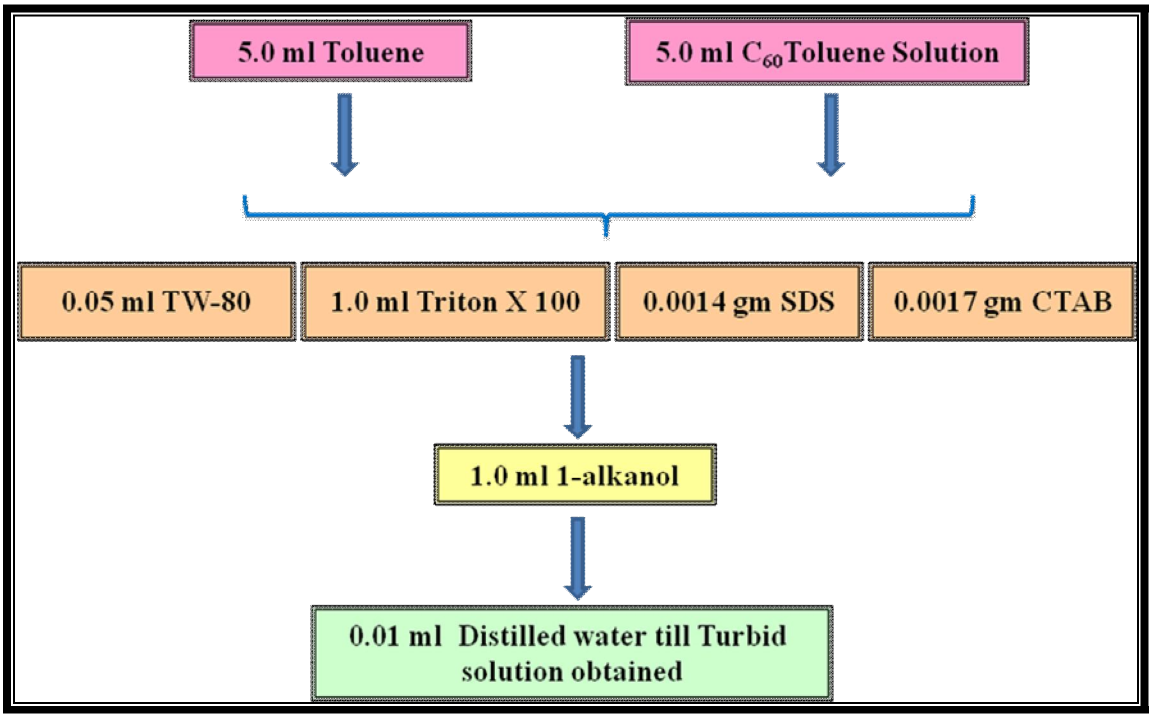


Figure 2.1. Schematic representation of emulsion study

Similarly, phase transitions from clear to turbid were studied using Triton X 100, SDS and CTAB surfactants using the above mentioned compositions for all the other components such as water, oil and cosurfactants from 1-propanol to 1-octanol. In this study, 0.1 ml of surfactant was used in all the solutions. Composition used for SDS surfactant was 0.0014gm and for CTAB was 0.0017gm in all the titration studies.

Effect of variation of amount of co-surfactants on the nature of solution with and without [60] fullerene

Effect of variation of amount of co-surfactants on the nature of solution with and without [60] fullerene was studied by the phase transition in the solution. Amount of water required for the phase transition with the variation in the ratio of Toluene/1-alkanol in the various systems was noted. Based upon the amount of water required for the transition, this was plotted to know the effect of addition of different co surfactant and the presence of [60] fullerene in the microemulsion system.

2.1.3.2. Transition from emulsion to micro emulsion

Similarly, fixed quantity of surfactant Tween 80 and Triton X 100 were dissolved into predetermined amount of water in a sample bottle for the respective studies. Into this preset amount of the [60] fullerene solution in toluene was added to get a white turbid solution. This turbid solution was titrated against sequentially 0.01ml co-surfactant like 1-propanol to get transparent clear solution, which was the transition point of emulsion to microemulsion phase. Figure 2.2 explains the schematic representation of microemulsion study. This process was repeated by increasing the amount of [60] fullerene solution in toluene and using different co-surfactants like 1-butanol, 1-pentanol, 1-hexanol and 1-octanol.

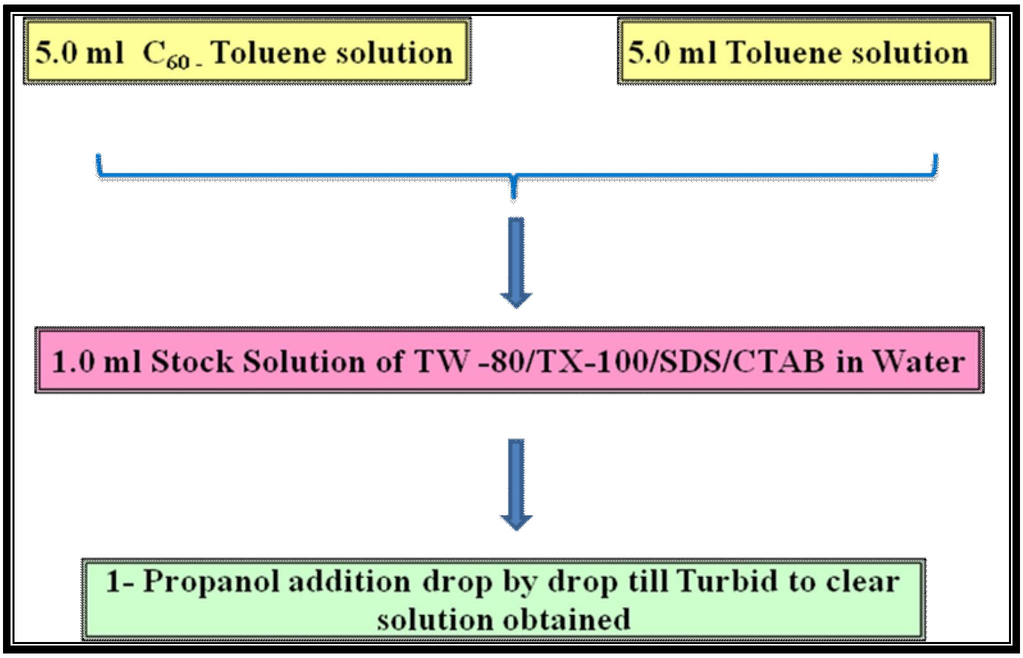


Figure 2.2. Schematic representation of microemulsion study

2.1.3.3. Phase Behavior Study

Ternary phase diagrams are very helpful to understand the role of surfactant in the microemulsion systems. In the ternary phase diagram each vertices corresponds to a pure component like surfactant, oil and water. The composition of specific mixture of all the components is represented as a point inside the triangle. In the pseudo ternary phase diagrams, surfactant and cosurfactant are considered as a single component. Noting down the amount of co surfactant required for the transition of emulsion to microemulsion phase, pseudo ternary phase diagrams were plotted to observe the effect of presence of [60]fullerene in the microemulsion system. Pseudo ternary phase diagrams were plotted to observe the effect of presence [60]fullerene in the microemulsion system.

As microemulsion region is a useful parameter to detect the solubilising capacity of a microemulsion system, our study was directed to the determination of microemulsion stability and the resulting thermodynamic parameters by the formation of pseudo ternary phase diagrams containing [60]fullerene using an non ionic, anionic and cationic with a wide range of cosurfactants. Area under the curve as well as upper area of the curve was calculated using digital planimeter (Koizumi, PLA COM, KP-90) with accuracy of $\pm 0.2\%$.

2.1.3.4. Critical Reverse Micelle Formation

The total transmittance of [60]fullerene was determined by SHIMADZU UV-2450 spectrophotometer. The transmittance was 85% at room temperature. By adding predetermined amount of Tween 80, Triton X 100, SDS and CTAB into 100 ml volumetric flask and diluting with [60]fullerene solution (1.39×10^{-4} M) a 3.3×10^{-3} M solution of each surfactant was obtained. Thus a stock solution of SDS (3.3×10^{-3} M) was prepared by dissolving it into Ethanol**:**[60]fullerene solution (1.39×10^{-4} M) solution (1**:**4).

These solutions were used as a stock solution for the spectroscopic studies. Different quantities of this stock solution were added into different volumetric flasks and diluted sequentially with the [60]fullerene (1.39×10^{-4} M) solution, used as a solvent for the determination of critical micelle formation value of the Tween 80,Triton X 100,SDS and

CTAB surfactants in presence of [60]fullerene. All these diluted solutions had same concentration of [60]fullerene and different concentrations of each surfactant. The absorbance was measured at 342 nm at30ºC and 40°C in a temperature controlled bath. The critical reverse micelle was determined from the break point of the slope the graph of absorbance verses concentration of the surfactant.

2.1.3.5. Fluorescence Study of microemulsions of [60]fullerene

Fluorescence is a property of atoms or molecules, in which a particle or molecule can absorb a photon, which leads to the release of another photon of a longer wavelength. Atoms are excited by an energy source which causes them to jump to a higher energy state. This energy state is usually unstable, and the atom will usually return to its ground state via the release of a photon of particular wavelength, usually in the ultraviolet spectrum as shown in Figure 2.3. As there is a relationship between concentration and fluorescence intensity, the data can be analyzed and represented as a graph of intensity vs. wavelength.

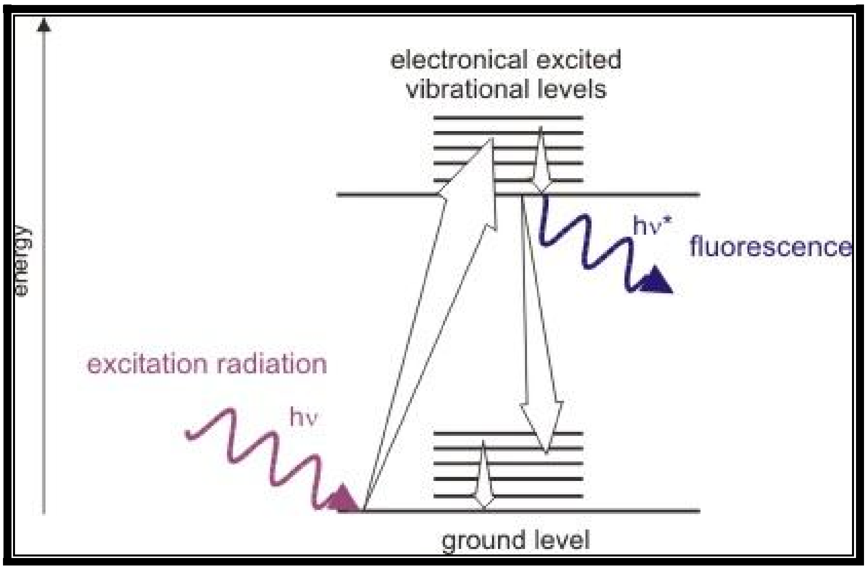


Figure 2.3. Fluorescence spectroscopy

Fullerenes C_{60} exhibit interesting physicochemical properties in solutions, especially due to their unique chemical structures and their good electron accepting abilities. Solubility of fullerenes in different organic solvents and their unusual solvatochromic behavior, the ability of the fullerenes to form aggregates in solutions, and their electron transfer and charge transfer interactions with variety of electron donors, are the subjects of extensive research activities for more than one decade. Due to the exotic structures and the remarkable electron accepting properties, fullerenes display interesting solvatochromism, aggregation behavior and the charge transfer and the electron transfer characteristics. The vibrant colors of fullerenes, C_{60} and C_{70}, in solutions, their excellent electron accepting properties, and high yields of singlet oxygen on their photoexcitation have generated tremendous interest in the study of their photophysical and photochemical properties. Fullerenes have ability to act as electron relays and to generate long lived excited states so it has made them an important class of photochemically active compounds. For fluorescence studies microemulsion samples were prepared of specific composition of [60]fullerene-Toluene(0.9 ml)/Surfactants/Co surfactants/water system. Samples were protected by keeping them in N_2 atmosphere for 18h in dark covered with aluminum foil. The fluorescence spectrum was taken on SHIMADZU RF-5301 PC spectrofluorometer at room temperature at 340 nm excitation.