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[60]Fullerene in Water: Microemulsion and Nanophase Formation[†]

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[60]Fullerene has zero solubility in water and very low solubility in many organic solvents. It was found that it forms reverse micelles in organic solvents in the presence of nonionic surfactants. Reverse micellization studies of fullerene solutions in the presence of a nonionic surfactant (Span60) were carried out, and the thermodynamic quantities of the reverse micellization process derived from experimental results indicate that the process is spontaneous. The solution behavior of the [60]fullerene was understood from its ability to form microemulsions from its toluene solution and water using different nonionic surfactants. Light scattering studies showed that the dimensions of these microemulsions reach a maximum of 170 nm. Phase behavior at different temperatures indicates the very high surface active nature of [60]fullerene.

Introduction

There is a growing importance of the solubilization phenomena especially in the area of nanomaterials synthesis. Solubilization of hydrophobic molecules like [60]fullerene with low aqueous solubility has been a major area of interest in recent years. Various solubilization techniques involve use of cosolvents and surfactants. Microemulsions have also drawn attention in the area of solubilization[1] as microemulsions can reduce the need for solvents. Microemulsion (μE) or swollen micellar systems represent an intermediate state between micellar solutions and true emulsions. The formation of a microemulsion requires the addition of a surface active agent so that water in oil or oil in water microemulsion may be obtained according to the components' nature and their concentration ratio, and in fact many systems require the presence of alcohol and/or salt for their formation and stability.[2] Thus, these microemulsions are different from ordinary emulsions due to their ability for spontaneous formation, transparency, thermodynamic stability, smaller particle size, and the limited range of concentrations over which they exist. It has been reported that by carefully changing the nature of the surfactant microemulsions can also display storage stability over a temperatures range of −10 °C to +55 °C and also exhibit excellent long-term dilution properties in water of varying degrees of hardness.[3]

Reverse micelles are unique systems that have immense application potential. Unlike in the case of normal micelles that are known to form in polar solvents, in a nonpolar solvent like toluene it is the exposure of the surfactant's hydrophilic headgroup to the surrounding bulk solvent that is energetically unfavorable. Thus, the hydrophilic group is sequestered in the micelle core, and the hydrophobic group remains solvent-exposed on the surface of the micelle. These reverse micelles were thought to be extremely difficult to form from surfactants with charged head groups since hydrophilic sequestration would create highly unfavorable electrostatic interactions. It is now well-known that apart from the nonionic surfactants even ionic surfactants can be used for the formation of reverse micelles.[4−6]

[60]Fullerene is an extremely hydrophobic molecule with very low solubility in many organic solvents. Various studies have been reported to understand this low solubility.[6−8] There are reports of the existence of [60]fullerene in organic solvents in the form of clusters containing a number of fullerene molecules,[9] and there is a dynamic equilibrium between the single molecule and the cluster. Thus, getting fullerene to dissolve in water and other polar solvents is challenging because of its hydrophobicity. The interest in water solubility increased after the bioactivity of C_{60} was reported,[10] and water solubility is critical to retain the bioactivity. Not only pristine fullerene but also functionalized fullerenes have been shown to have applications in drug delivery, radiation protection, MRI contrast agents, gene therapy, and photodynamic therapy. With nanomedicine being actively pursued, the biomedical application of both pristine and functionalized fullerenes has led to hectic research activity in this area highlighted recently in an excellent review.[11] Thus, several techniques have been devised to solubilize [60]fullerene in water.[12−18] However, there are few reports on the phase studies of fullerenes in solutions, more so where surfactants have been used to solubilize it. In a recent report, C_{60} has been shown to be soluble in pure nonionic surfactant (hexaethyleneglycol monododecyl ether, $C_{12}EO_6$).[19,20] It has also been reported that in stable dispersions using Triton X-100 C_{60} exists in micellar form with a mean diameter of ∼10 nm depending on the molar ratio of C_{60}/Triton X.[21] In fact, it was proposed that there could be some stabilizing effect of the C_{60} on the micelles. Among the nonionic surfactants, reverse micellization of Span60 in toluene has been well studied.[22]

Our aim was to initially study the critical reverse micelle formation of well-known surfactant, Span60 (sorbitan stearate), in the presence of [60]fullerene and then to understand the microemulsion formation of [60]fullerene in the presence of various structurally different surfactants. The thermodynamic

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quantities associated with the reverse micellization process were computed and are presented here.

Experimental Section

Materials. Span60 (sorbitan monostearate) (Koch light laboratories Ltd., England) and Span20 (sorbitan monolaurate) were used without any further purification, and Toluene (Merck India) was dried under 4 Å molecular sieves and freshly distilled before use. A solution of [60]fullerene in toluene ($1.39 \cdot 10^{-4}$ M) was made and was used as a solvent in this study. Micellar sizes were determined on a Wyatt static light scattering instrument.

Method. Critical Reverse Micelle Formation. The transmittance of the [60]fullerene solution was determined (Elico-SL171 spectrophotometer) at room temperature and was found to be 85 %. Initially, 0.68 g of Span60 was weighed into a volumetric flask and made up to mark with [60]fullerene solution ($1.39 \cdot 10^{-4}$ M) to make a $3.3 \cdot 10^{-3}$ M solution of Span60. This was the stock solution. Different quantities of this stock solution were taken in separate volumetric flasks and diluted using the $1.39 \cdot 10^{-4}$ M [60]fullerene solution. Thus, the solutions in all the volumetric flasks had the same concentration of [60]fullerene but different concentrations of Span60. These solutions were kept in a temperature-controlled bath, and the absorbance was measured at (30 and 40) °C at 455 nm. From the plot of the absorbance and concentration, the critical reverse micelle concentration was calculated from the break point of the slope of the graph.[23]

Microemulsion Studies. The formation of the microemulsions was studied by the standard cloud point method where the solution of [60]fullerene/surfactant in toluene is the oil phase with propanol, butanol, or pentanol added as cosurfactant and water is the aqueous phase. Thus, 1.0 mL of the [60]fullerene solution ($1.39 \cdot 10^{-4}$ M) was taken in a test tube, and 0.085 g of Span60 was added when the Span60 completely dissolved. To this solution, 1.0 mL of either of the alcohols mentioned above was added as a cosurfactant. This gave a clear, homogeneous solution. It is pertinent to mention here that the major phase is the oil phase (toluene), and water is a minor phase thus giving a W/O system with the formation of reverse micelles due the presence of surfactant. This solution was then titrated by sequential addition of 0.1 mL of water using a micropipet. Initially, when water was added, a white turbid layer was formed at the interface of the oil and the aqueous phase, which disappeared immediately when the test tube was gently shaken indicating the formation of a microemulsion that is transparent. This process of adding water was continued, gently shaking the test tube after each addition until the turbidity was retained even after the contents in the test tube were shaken. The amount of water added was noted as the amount required for the transition from microemulsion to emulsion. The procedure was repeated by changing the surfactant, cosurfactant, and also the ratio of the surfactant/cosurfactant, noting the amount of water required for this transition from clear transparent solution to turbid solution in each case. On the basis of these results, triangular phase diagrams were plotted.

Results and Discussion

Critical Reverse Micelle Formation. Iodine has low aqueous solubility ($0.33 \text{ g} \cdot \text{lt}^{-1}$ at 25 °C) and is readily soluble in nonpolar solvents, giving violet solutions. The technique of determination of reverse micelle concentration (c_{rmc}) by the iodine solubilization method is well-known.[24] It has been shown that this technique can be applied to both aqueous and nonaqueous solutions.[25] Therefore, it was thought to replace the iodine molecule with the [60]fullerene molecule. Though [60]fullerene is a hydrophobic and nonpolar molecule, it seems to form a reverse micelle complex with Span60 in toluene. The $\lambda_{\max}$ of pure [60]fullerene ($1.39 \cdot 10^{-4}$ M) solution was found to be 440 nm. However, $\lambda_{\max}$ of [60]fullerene−Span60 solution was at 455 nm. This shifting of the absorbance maxima

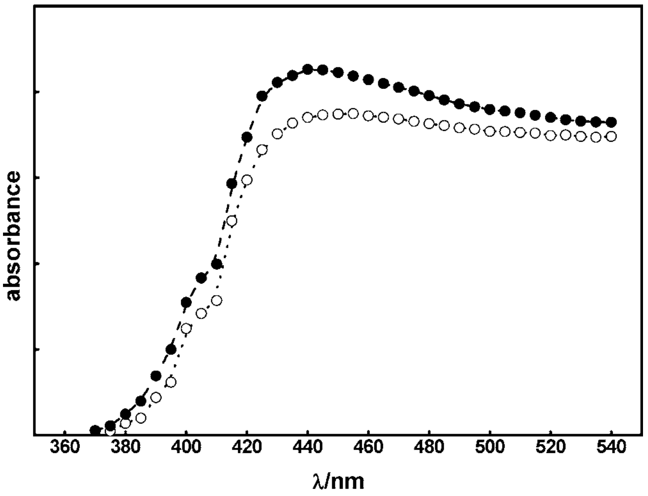

Figure 1. Plot of absorbance vs wavelength to determine $\lambda_{\max}$ of [60]fullerene−Span60 solution.

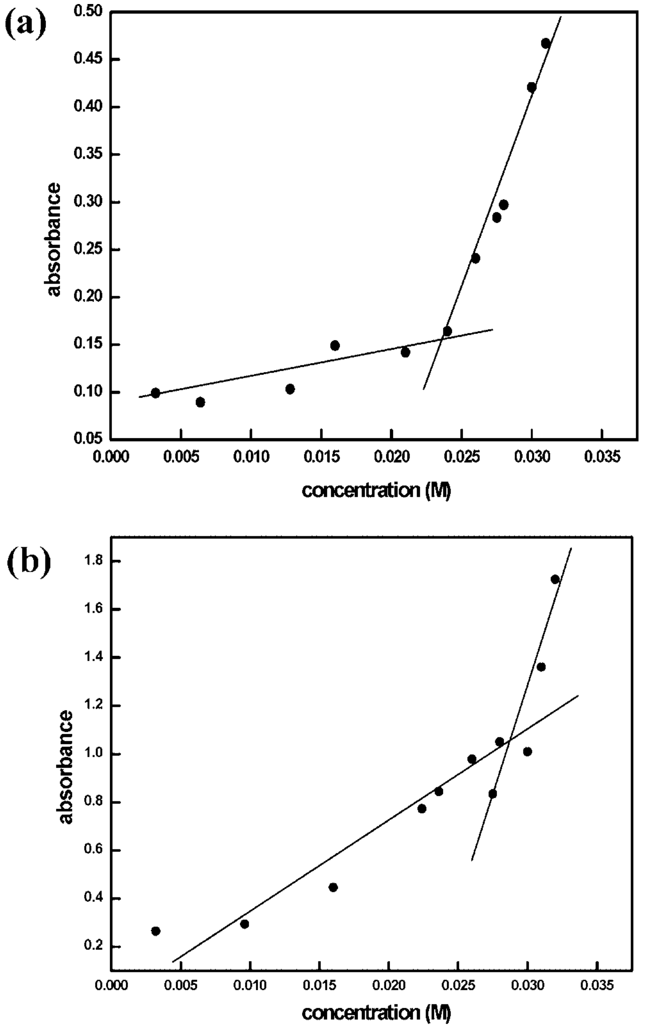

Figure 2. Plot of absorbance vs concentration of Span60 in the presence of [60]fullerene to determine c_{rmc} at (a) 30 °C and (b) 40 °C.

Table 1. Critical Reverse Micelle Concentration, Free Energy, Enthalpy, and Entropy of Reverse Micellization of Span60 in Toluene−[60]Fullerene Solution at 30 °C and 40 °C

temperature (°C)	C_{rmc}	$-\Delta G^{\mathrm{o}}_{\mathrm{rm}}$	$-\Delta H^{\mathrm{o}}_{\mathrm{rm}}$	$-\Delta S^{\mathrm{o}}_{\mathrm{rm}}$
>30	0.0240	99.66	112.92	13.26
40	0.0284	100.12	126.37	26.25

to a longer wavelength is similar to that observed in the iodine−surfactant solutions. Thus, there seems to be some interaction between the [60]fullerene and the surfactant leading to the shift in the λ_{max}. The location of the fullerene molecule in the solution is of interest, and the fullerene−reverse micelle complex gives rise to this new λ_{max} that shows a shift of 15 nm. The plot is shown in Figure 1. It can be observed that the transmittance of the reverse micelle complex solution is lower than that of the pure fullerene solution.

The effect of dilution of the surfactant concentration on absorption was done at this new λ_{max} of 455 nm. The absorbance values were plotted against the Span60 concentration, and clear break points were observed in the plots. The concentration at the break point was taken as c_{rmc} of reverse micellization. The same procedure was adopted to plot the absorbance versus the concentration of the surfactant at two different temperatures. These were found to be 0.024 and 0.0284 at (30 and 40) °C, respectively. The plots are shown in Figure 2. The variation of the absorbance with concentration shows a clear break at a particular concentration after which the increase in the absorbance was steep. The slope was sharper at lower temperature than at 40 °C indicating the effect of temperature on the stability of the micelle.

From the values of c_{rmc}, the thermodynamic quantities can be calculated using the well-known equations at different temperatures. The standard free energy, enthalpy, and entropy of reverse micellization were calculated (valid for nonionic surfactant) using the following equations and are shown in Table 1.[22]

$$\Delta G^{\mathrm{o}}_{\mathrm{rm}} = RT \ln(c_{\mathrm{rmc}})$$

$$\Delta H^{\mathrm{o}}_{\mathrm{rm}} = -RT^2 d \ln(c_{\mathrm{rmc}})/dT$$

$$\Delta S^{\mathrm{o}}_{\mathrm{rm}} = (\Delta H^{\mathrm{o}}_{\mathrm{rm}} - \Delta G^{\mathrm{o}}_{\mathrm{rm}})/T$$

Figure 3 shows the variation of the micellar size with the concentration of the surfactant, i.e., Span60, as measured by the static light scattering technique. Though less information is available on the aggregation numbers in nonaqueous media, it is known that the aggregation number increases with dipole−dipole attraction between the polar headgroups and also the steric requirements at the polar headgroup.[25,26] Thus, it seems that the presence of the large fullerene molecule at the core of the micelle results in this typical behavior. The miceller size increases with concentration of the surfactant and then decreases. A large increase in micellar size is observed as the critical point is approached. The micellar growth and subsequent decrease in micellar size is due to the dissociation of surfactant molecules as its concentration increases. This kind of behavior, to our knowledge, has not been observed before for other nonaqueous systems and seems to arise primarily due to the presence of the [60]fullerene. However, the addition of water that is solubilized in the interior of the micelle in nonqueous media has been shown to increase the aggregation number.[27]

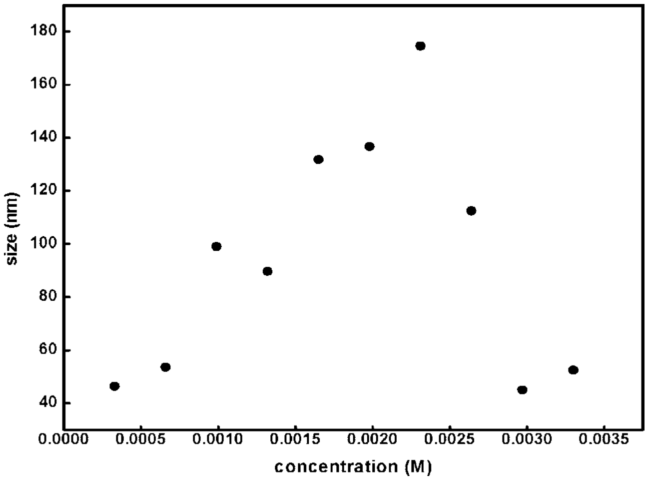

Figure 3. Plot of micellar size variation with concentration as measured by light scattering.

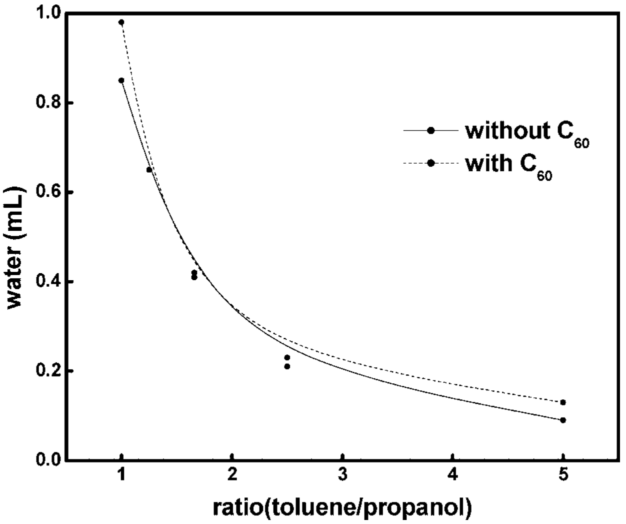

Figure 4. Water consumed vs ratio of toluene/propanol in the [60]fullerene−Span60 system.

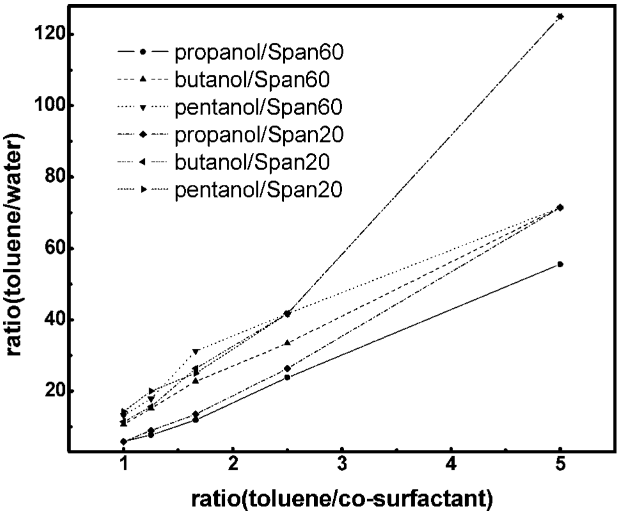

Figure 5. Plot of change in the ratio of the toluene/cosurfactant on the formation of the microemulsion.

Microemulsion Studies. The results of the experiments indicate that [60]fullerene is stable in the microemulsions. As compared to a microemulsion system where there is no [60]fullerene, the presence of [60]fullerene seems to increase the amount of water required for the transition from micro-

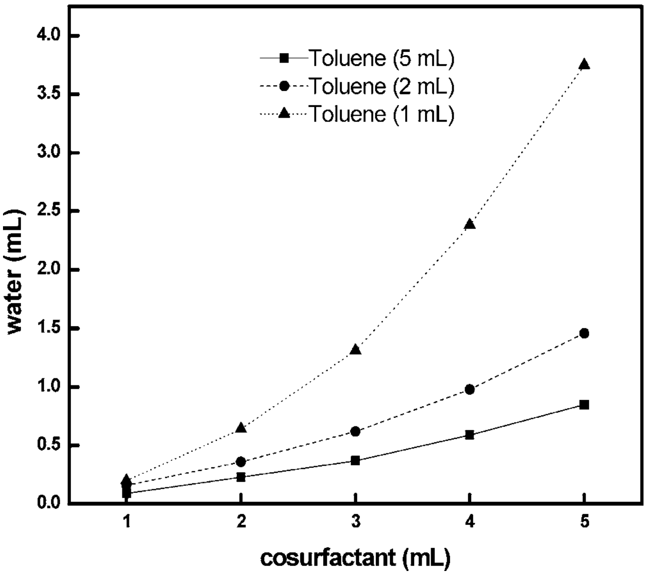

Figure 6. Plot of effect of change in toluene quantity on the quantity of water required for emulsion formation at different concentrations of cosurfactant (propanol).

emulsion to emulsion. This is shown in Figure 4. Thus, the higher the cosurfactant content, the more water is required for the transition from microemulsion to emulsion.

The effect of two different surfactants, i.e., Span60 (sorbitan mono stearate) and Span20 (sorbitan mono laurate), and different cosurfactants on the microemulsion formation is shown in Figure 5 which shows the correlation between the ratio of toluene/cosurfactant and the ratio of toluene/water. The idea of taking the ratios was that this is a better indicator of the effect of [60]fullerene since its concentration in the microemulsion remained the same in all the experiments. Initially, the effect of the change in the ratio of the toluene/cosurfactant on the water required for the formation of the emulsion was studied. As the cosurfactant was changed from propanol to butanol to pentanol, a decrease in water required was observed resulting in the decrease in the toluene/water ratio. Thus, as expected, when the polar nature of the cosurfactant decreases, i.e., as the carbon chain increases, the water required for the formation of the emulsion is decreased. In other words, the window for the stable microemulsion formation was reduced. However, no significant change was observed when the surfactant Span60 was replaced with Span20, even though the tail or the hydrophobic part of Span20 is smaller as compared to that of Span60. This indicates that the micelle formed was independent of the chain length and depended only on the polar head which is the sorbitan group in these two surfactants. The sorbitan headgroup is essentially a five-membered substituted furan ring that is in close proximity to the [60]fullerene and the water molecules that go into the reverse micelle. It was also observed that when the surfactant was changed to Brij 35 the water required for the emulsion formation was higher (not shown here) and could be due to the structural difference between the Span type of surfactant and the Brij type of surfactant. The polar headgroups of Span60 and Span20 are the same, i.e., a cyclic five-membered ring, whereas the Brij 35 is a linear nonionic surfactant. The interaction between the [60]fullerene and the cyclic ring structure of the surfactant at the core of the micelle leads to this kind of behavior. Thus, the structure of the surfactant does have a major role to play in the formation of the emulsion in these systems.

A similar study on the effect of the concentration of the nonpolar solvent (toluene) on the microemulsion formation was also done. At a fixed concentration of [60]fullerene, it was observed that with the reduction in the amount of the nonpolar solvent (toluene) in the system more water is required for the emulsion formation. In other words, the transition from the microemulsion to the emulsion requires more water to be added with the increase in the cosurfactant quantity. Thus, at a fixed concentration of [60]fullerene and Span60, the higher quantities

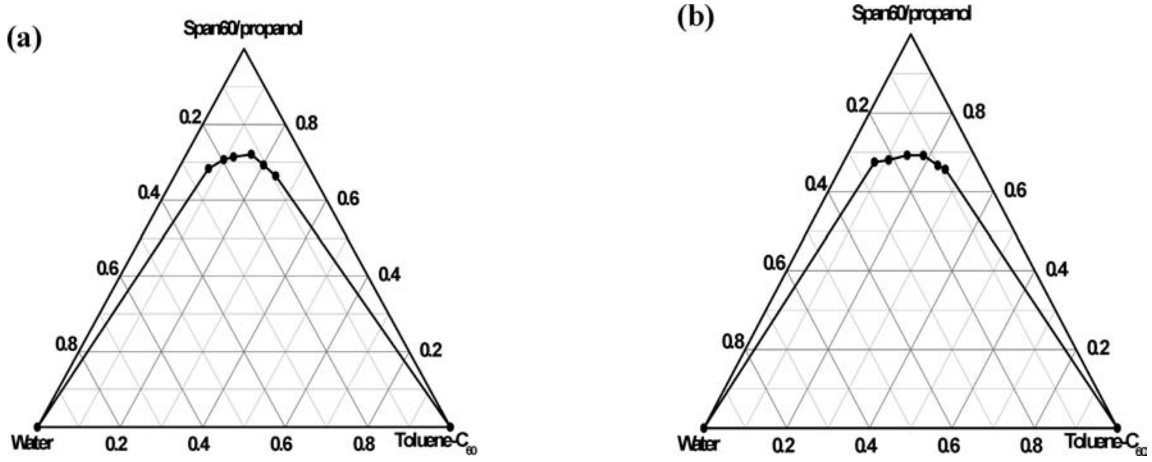

Figure 7. Triangular phase diagram for the [60]fullerene/Span60/water system in the presence of cosurfactant at (a) 30 °C and (b) 40 °C.

Table 2. Monophasic and Biphasic Regions Formed by the System of C_{60}−Toluene−Water and Surfactants at Different Temperatures

		without C_{60}			with C_{60}		
surfactant	temperature (°C)	total area (cm^2)	biphasic (cm^2)	monophasic (cm^2)	total area (cm^2)	biphasic (cm^2)	monophasic (cm^2)
Span 60	30 °C	13.2	10.8	2.4 (18.2 %)	13.4	10.3	3.1 (23.1 %)
	40 °C				14.8	11.5	3.3 (22.3 %)
Brij 35	30 °C	12.5	9.1	3.4 (27.2 %)	12.7	8.5	4.2 (33.1 %)
	40 °C				12.6	8.2	4.4 (34.9 %)

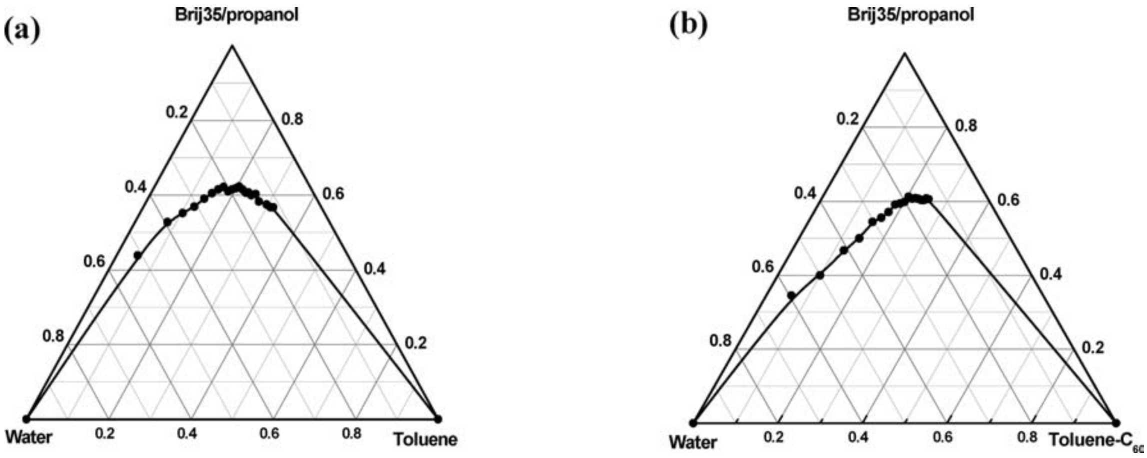

Figure 8. Triangular phase diagram for the Brij35 surfactant in (a) the absence of [60]fullerene and (b) in the presence of [60]fullerene.

of cosurfactant helped in forming stable microemulsions. These results are shown in Figure 6.

On the basis of the results obtained from different experiments, triangular phase diagrams were drawn for the microemulsion systems to study the effect of structure and temperature on the stability of the microemulsions. The representative phase diagrams for Span60 are shown in Figure 7, where the weight fractions of components were plotted. In both the figures, the upper part is the monophasic microemulsion region (1ø´). The lower part is the liquid/liquid (L/L) biphasic region (2ø´). In the biphasic region, the microemulsion is in equilibrium with excess oil (toluene). Figure 7(a) is for the system at 30 °C, whereas Figure 7(b) is for the same system at 40 °C. In both cases, propanol was the cosurfactant. The phase diagrams remained reasonably unchanged for the system at room as well as at high temperature thus indicating that the microemulsions formed were stable even at 40 °C. The areas under the curve (biphasic) as well as the upper area of the curve (monophasic) were calculated using a digital planimeter (Koizumi, PLA COM, KP-90) with accuracy of ± 0.2 %. The results are summarized in Table 2 for different surfactants and at different temperatures. In the case of the Span60−[60]fullerene microemulsion system, the area of monophasic microemulsion region (1ø´) was found to be 3.1 cm^2 at 30 °C and 3.3 cm^2 at 40 °C. Clearly, at higher temperature the area of the monophasic microemulsion region increases. In the case of Brij35 in the absence of [60]fullerene, the area calculated was found to be 3.4 cm^2 and in the presence of [60]fullerene 4.2 cm^2 (Figure 8). Thus, in the case of Brij35, the area under the curve is more in the presence of fullerene. The same trend as for Span60 was observed in the case of structurally different nonionic surfactant Brij35, and the area increased from 4.2 cm^2 at 30 °C to 4.4 cm^2 at 40 °C.

Conclusions

All the thermodynamic quantities for the formation of reverse micelle are negative. This shows that the process of reverse micellization is spontaneous and exothermic, and the c_{rmc} increases as the temperature increases. Phase diagrams drawn to understand the behavior of the [60]fullerene in the microemulsion system show that in the presence of fullerene the monophasic microemulsion region is more than in the absence of fullerene. With the increase in the cosurfactant amount, a larger amount of water is required for the formation of the emulsion. A two-phase system means that the microemulsion system requires the presence of cosurfactants for the formation and stability. These results can be extended to increase the solubility of [60]fullerene in polar medium either by using a single surfactant or by use of mixed surfactants.

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