Study on the Absorption Properties of C_{60} in Micellar Aqueous Solutions and Mechanisms for Solubilization

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Abstract: C_{60} is successfully solubilized in micelle of six kinds of surfactants and UV/Vis spectra of C_{60} in micellar system are studied. It is found that Brij-35 is the most efficient surfactant for solubilization of C_{60} and the possible states of C_{60} existed in surfactants are also studied. Experiments of surface tension show that the sites for solubilization of C_{60} not only depend on the sorts of surfactants but also on their structures.

Keywords: C_{60}; absorption; micelle; solubilization.

Since the successful preparation and mass synthesis of $C_{60,}$ tremendous interests have been evoked in its unusual full-carbon structure like football and physical and chemical properties, which have been studied carefully and systematically. However, such works are mainly carried out in organic solvents, especially in arene solvents (benzene or toluene), due to the water-insoluble nature of C_{60}. In 1992, Anderson *et al.*[1] first obtained the water-soluble C_{60} successfully *via* cyclodextrin (CD) enclosing, so as to open a new way for studying of C_{60} in aqueous solutions. After that, Priyadarsini *et al.*[2] improved the method and concentration as high as 1.0×10^{-4} mol/L of C_{60} can be obtained. Hungerbuler[3], Beey[4] and Eastoe[5] *et al.* reported that C_{60} could be solubilized in TritonX-100, of which Eastoe [5]*et al*. suggest that ionic surfactants like SDS, CTAB and AOT are ineffective for dispersing $C_{60.}$ But more detailed studies on the solubilization of C_{60} with various surfactants, for example, the sorts, stability properties, mechanisms for solubilization and a fluorescence or a phosphorescence prob study *et al.* have not been reported and these are very interesting to us. In this paper, C_{60} is solubilized in the micelle of six kinds of surfactants (sodium dodecyl sulfate (SDS), sodium lauryl sulfonate (AS), cetyltrimethylammonium bromide (CTAB), Brij-35, Triton X-100 and Triton X-200 and effectiveness for solubilization are studied systematically and characterized by UV/Vis spectra at the same time. In addition, the interaction mechanisms of C_{60} with different surfactants *via* surface tension experiments are also studied.

Experimental

C_{60} (+99.9%, was purchased from Yin-Han Hi-Tech Co. Limited of Wuhan and stock solution were prepared with toluene. SDS and AS were twice recrystallized from 95% EtOH. CTAB, Brij-35, Triton X-100 and Triton X-200 were all used as received. UV/Vis absorption spectra were recorded with a HITACHI 220 UV/Vis spectrophotometer.

An amount of stock solution of SDS, AS, CTAB, Brij-35, Triton X-100 and Triton X-200 was separately piped into 10ml comparison tube, then diluted to final volume with water to get various concentrations of surfactants (from<CMC to >CMC). Transferred the above solutions into 20 ml beaker, then piped a volume of C_{60}/toluene stock solution into it and shaked for homogeneity of the solution. After evaporated the toluene gently with continuously shaking at controlled temperature of 60℃~70℃, cooled down to room temperature to obtain a yellow-brown transparent stable micellar dispersion.

Results and Discussion

As shown in **Figure 1.** solubilization of C_{60} are more efficient in non-ionic surfactants than in ionic surfactants, the effectiveness of solubilization is Brij-35>Triton X-100>CTAB>SDS≈AS≈Triton X-200, of which Brij-35 is the most efficient. It is noted here that the concentration of solubilization for C_{60} is Triton X-100 > Brij-35, but in fact,Brij-35 is more efficient than Triton X-100 for dispersing C_{60} although they are both non-ionic surfactants. **Table 1.** shows more details.

Figure 1 Solubilization concentrations for C_{60} in various surfactants (1 CTAB 2 AS 3 SDS 4 Triton X-200 5 Brij-35 6 Triton X-100)

Table 1. The physical properties of C_{60} in various surfactants

surfactants	type	effectiveness for solubilizion of C_{60}	the maximum concentrations of C_{60} solubilized (mol/L)	color
SDS	anionic	general	1.6×10^{-5}	Pale-yellow
AS	anionic	general	2.0×10^{-5}	Pale-yellow
CTAB	cationic	better	1.7×10^{-5}	Pale-yellow
Brij-35	non-ionic	best	2.58×10^{-5}	transparent-yellow
Triton X-100	non-ionic	good	4.1×10^{-5}	yellow-brown
Triton X-200	anionic	general	1.7×10^{-5}	pale-yellow

•Here,the effectiveness for solubilization of C_{60} in various surfactants is according to (a)the time for solubilizaton (b) the transparent degree of solution (3) the stability of solution

Figure 2. gives the UV/Vis spectra of C_{60} solubilized in Brij-35. It can be shown that the absorption peaks in visible domain are at 340 nm and 430 nm, separately, which evidently distinct from the absorption of monomeric C_{60}, but displays the probable characteristic

absorption of colloidal C_{60}[3] or can be attributed to the special interaction of C_{60} with poly (ethylene oxide) groups. While in the ionic surfactants like SDS, AS and CTAB, there have only weak absorptions at 340 nm and 430 nm. Again, we found in our experiments that the absorbance of C_{60} solubilized in surfactants decreases with the setting time. A few days later, some of aggregates of C_{60} can be seen in the bottom of comparison tube when surfactants are SDS, AS and CTAB. But this aggregation behavior of C_{60} is invertible. When Brij-35 are used, the absorption peaks at 340 nm and 430 nm are still good. The solution is still transparent and there have not any aggregates produced after standing for half a year and even more.

Figure 2 (a) Absorption spectrum of C_{60} in toluene; (b) Absorption spectrum of Brij-35/C_{60} aqueous solution; (c) Absorption spectrum of (b) with five times amplification

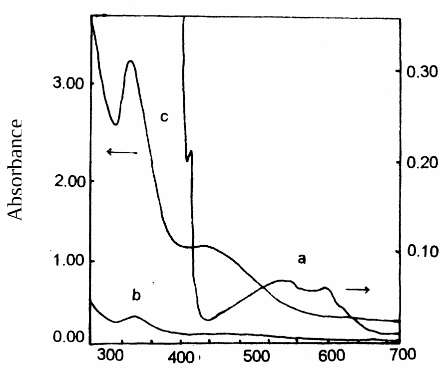
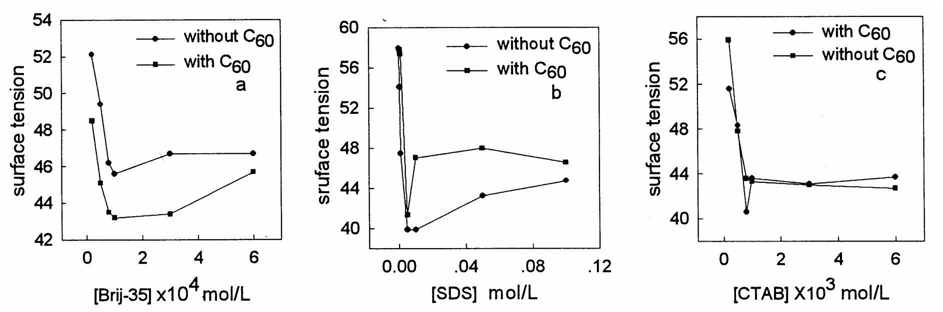


Figure 3 Plot of surface tension of micellar solutions versus surfactant concentrations (a, in Brij-35 b, in SDS c, in CTAB)



As shown in **Figure 3**, when non-ionic surfactants like Brij-35 and Triton X-100 being used for solubilization of C_{60}, the surface tension with C_{60} are evidently less than that of surfactants without C_{60}, while for anionic-surfactants, such as SDS, it is justly as apposed to above circumstance and for cationic-surfactants like CTAB, there have little changes. It is shown by this that C_{60} is likely to change the microenvironment of micelles when it being solubilized in, about which the change is different with surfactants.

Recently, Andrew Beeby[6] and we found that Tween-20 is also much better for dispersing C_{60} and in our investigation, when concentration of Tween-20 being 5×10^{-3} mol/L, the concentration of C_{60} that could be solubilized has been as much as 1×10^{-4} mol/L and even higher. This C_{60}/Tween-20 micellar solution is also transparent orange-yellow and much stable. We think it much better to understand the mechanisms for solubilization in supramolecular chemistry interactions of Tween 20 a moderate long poly (ethylene oxide) units with π -system $C_{60.}$

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References

1. T. Andersson, K. Nilsson, M. Sundagl, G. Westman, and O. Wennerstrom, *J. Chem. Soc., Chem. Commun*., **1992**, 604.
2. K. I. Priyadarsini, H. M. han, A. K. Tyagi, J. P. Mittal, *J. Chem. Soc*., **1994**, *98*, 4756.
3. H. Hungerbuhler, D. M. Guldi, K. D. Asmus, *J. Chem. Soc*., **1993**, *115*, 3386.
4. A. Beeby, J. Easteo, R. K. Heenan, *Chem. Soc., Chem. Commun*., **1994**, 173.
5. J. Eastoe, E. R. Crooks, A. Beeby, R. K. Heenan, *Chem. Phys. Letters*., **1995**, *245*, 571.
6. A private letter from Andrew Beeby, (Department of Chemistry, University of Durham, U. K.), 1998, 5, 15.

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