1. Introduction

1.1. **W**orking with a team of colleagues at Rice University, Houston, led by Richard E, Smalley, Harold W. Kroto, University of Sussex, Brighton, England, discovered a new form of carbon named as buckminsterfullerene[1-2] for which they awarded a Nobel Prize in 1985. The serendipitous discovery of a third natural form of carbon, stable C_{60} molecule was an unexpected result of their effort. This stable molecule consisted of exactly 60 carbon atoms. They suggested that C_{60} took the form of a closed cage resembling a soccer ball and called the molecule "buckminsterfullerene " in honor of the architect R. Buckminster Fuller. The discovery of fullerene has turned out to be one of the rare research breakthroughs that fundamentally alters conventional scientific wisdom and triggered an explosion of multidisciplinary research. It has released up new research areas in chemistry, physics, materials science, medicine, and other disciplines. Also it shows significant commercial potential for industrial applications as catalysts, lubricants, high strength fibers, pharmaceutical magic bullets, optical switches, superconductors, etc. Laboratory tests also indicate that "buckyballs" inhibit an enzyme necessary for the AIDS virus to reproduce.[3-5] Buckyballs and the new field of fullerene chemistry have attracted much attention.[6] C_{60} forms a truncated icosahedron which was confirmed by various techniques. Subsequently, Kratschmer et al developed an arc vaporization method for the mass production of fullerenes[7].Iijima opened the nano era of carbon structures with the observation of carbon nano tubes[8].

Science selected the buckyball as its Molecule of the Year in 1991[9] and the *Economist* called it the "Renaissance Molecule" in1992[10]. It was first featured in current comments in a 1988 essay on the most-cited 1985 chemistry papers[11].

1.1.1. The Discovery of fullerene

Formerly only two forms of carbon were known before the discovery of fullerene. Six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon (VI). The latter two were discovered in 1968 and 1972. Fullerenes are the third allotropic form of carbon material after graphite and diamond.

The structure of C_{60} was first predicted by Osawa[12] in 1970. The **C_{60}** molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970 [13] and discussed further in a chapter on “Superaromaticity” in a book by Yoshida and Osawa[14] in 1971; the original diagram is depicted in Figure 1.1**.** An equally imaginative article, which actually predated that work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages[15].

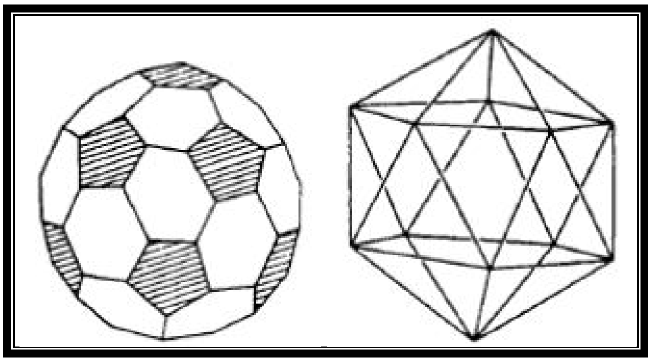


Figure 1.1: Diagram of **C_{60}**

These authors discussed (in Japanese) the “superaromaticity” which showed electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

1.2. Production

In 1990 Kratschmer reported production of fullerene by electric arc apparatus for the first time (Figure 1.2). In this technique, graphite rods were vaporized in an inert gas atmosphere. The plasma was allowed to cool by collisions with the vaporized carbon in presence of inert gas. The highest yields were observed with helium as the buffer gas and at pressures ranging between 100–200 torr. Under optimized conditions, the Kratschmer - Huffman apparatus provided 5-15% yields of the fullerene product mainly C_{60} and C_{70}.

It was found that fullerene mixture obtained from electric arc apparatus was soluble in various non-polar solvents, such as, toluene, carbon disulfide, and benzene. The soluble fullerene product also contained a complex mixture of fullerenes C_{60}, C_{70}, C_{84}, C_{92} and even higher fullerenes at that particular stage. Subsequently three main methods to synthesize buckyballs have been reported in the literature. They are:

i. Electric Arc Discharge
ii. Laser Ablation
iii. Chemical Vapor Deposition

i. Electric Arc Discharge of carbon electrodes, in presence of Ni and Y catalysts, produces several condensed species of material including amorphous carbon and single walled nanotubes[16] as shown in Figure 1.2.

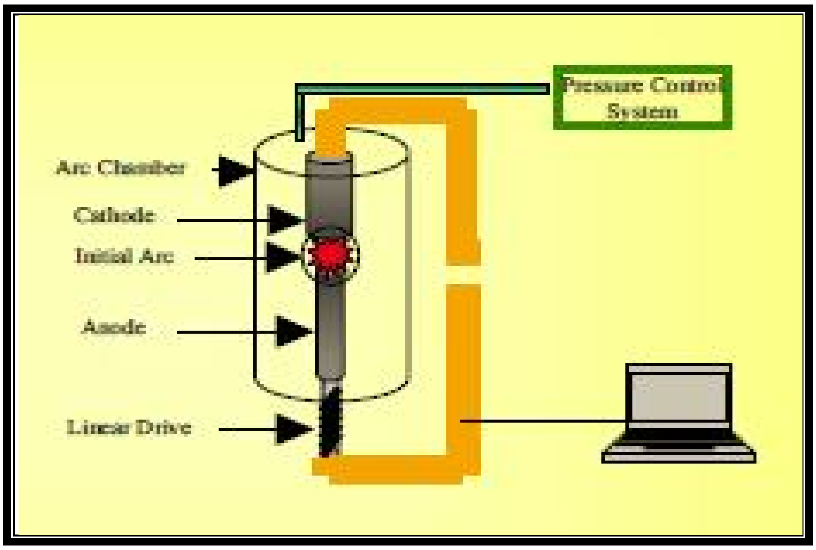


Figure1.2. Electric Arc Discharge method

ii. **Laser ablation method:**

Another very useful technique for producing fullerene clusters involves laser ablation of graphite (Figure 1.3) in a helium atmosphere[17]. Graphite is ablated at an elevated temperature. The plasma cools more slowly and growing carbon clusters have sufficient time to grow into stable fullerenes. Most efficient temperature is 1200 °C for this method.

It is possible to vary the characteristics of carbon plasma systematically through variations in the laser pulse energy and wavelength[18]. Another important feature of this process is to control systematically growth of clusters from carbon plasma.

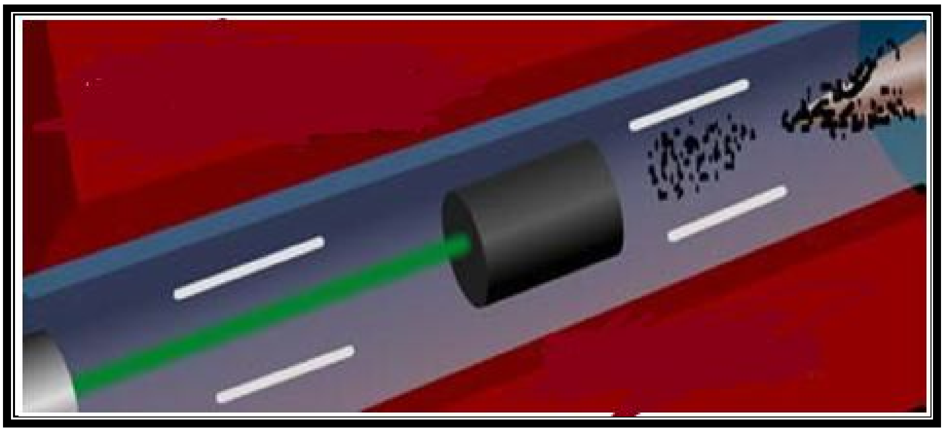


Figure1.3 Laser Ablation Method

iii. **Chemical Vapor Deposition**: This method involves the spinning process. Liquid feedstock, containing ferrocene and thiophene is mixed with hydrogen and injected into the hot zone, where an aerogel of captured and wound out of the hot zone continuously as a fiber or film (Figure 1.4 a , b). Nanotubes are being wound between spindles[19,20] .

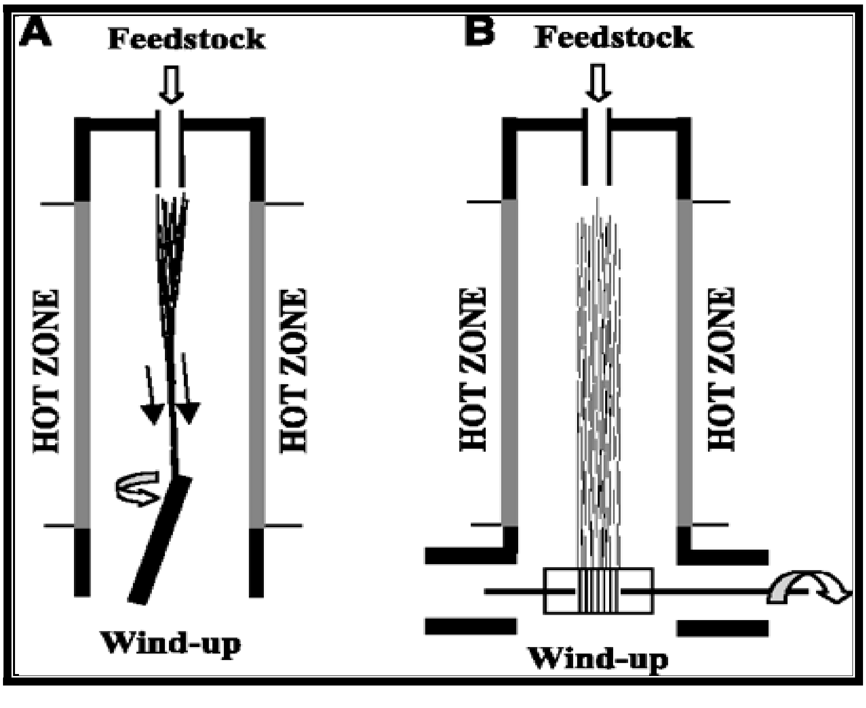


Figure 1.4.a. Chemical Vapor Deposition Method

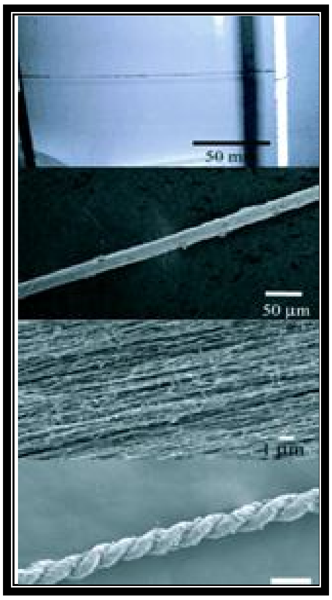
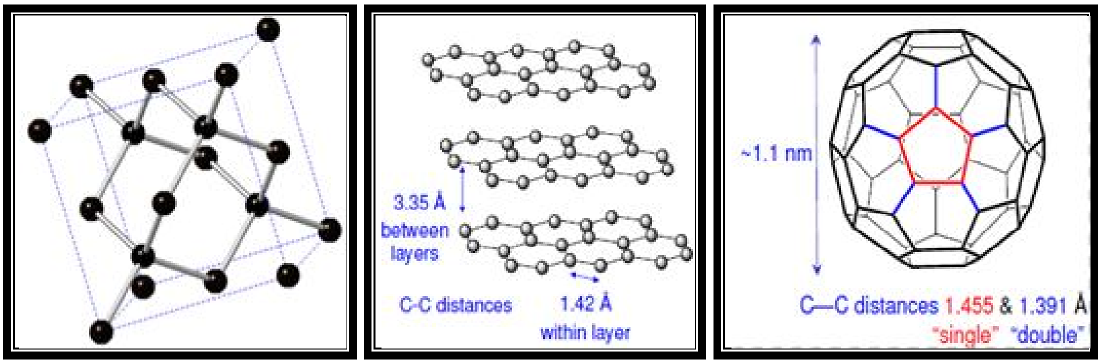


Figure 1.4.b. Chemical Vapor Deposition Method

Separation of fullerenes from each other is usually carried out by high performance liquid chromatography (HPLC). Purified fullerenes are black crystalline powders, but in solution (e.g. toluene) each of the fullerenes exhibits unique colors, for example a purple color for C_{60} and a red-wine color for C_{70}.

1.3. Structure



Diamond Graphene Fullerene

Figure 1.5 Structures of Diamond, Graphene and Fullerene

C_{60} is arranged as 12 pentagons and 20 hexagons. Fullerenes are all-carbon molecules which have the form of hollow, closed network composed of 12 pentagons and *n* hexagons and the composition C20+2*n* (*Euler's Theorem*)[21].

A second empirical rule that governs fullerene-type structures is the isolated pentagon rule (IPR). This rule, based on both steric and electronic considerations, states that two pentagons may never share a common edge. Among the 1812 distinct fullerene isomers of buckminsterfullerene, only *Ih*-C_{60} containing 12 pentagons isolated by 20 hexagons is formed in accordance with the IPR. The precise geometric structure of this isomer was determined by X-ray analysis of pristine C_{60} at low temperature [22-24], C_{60} derivatives[25], C_{60} solvate[26,27] and by solid state 13C NMR measurements[28]. These experimental conclusions confirmed the postulated *Ih*-symmetry with a mean diameter of 7.1 A^o for the sphere.

As a result of the presence of both five- and six membered rings within the structure of C_{60}, there are two types of bonds namely bonds at the junction between two six membered rings ([6,6-bonds], mean distance = 1.391 A^o), and bonds at the junction between a five and a six-membered ring ([6,5-bonds], mean distance = 1.449 A^o) [22,29] . The electronic structure of the fullerenes is such that bonds at [6,6]-ring junctions have much double bond character, while bonds at [6,5]-ring junctions are essentially single bonds[30-32]. This arrangement results in C_{60} having a strongly bond-alternated structure which can be best described as a spherical tessellation of [5] radialene and 1,3,5-cyclohexatriene subunits (Figure 1.6).

Figure 1.6: Illustration of (a) [6,6]-bond; (b) [6,5]-bond; and (c) the [5]radialene and 1,3,5-cyclohexatriene substructures of C_{60}

The chemical behavior of C_{60} mainly depends on these structural properties: The 30 bonds at the junctions of two hexagons ([6,6]-bonds) are shorter than the 60 bonds at the junctions of a hexagon and a pentagon ([5,6]-bonds).

The most striking property of the C_{60} molecule is its high symmetry. There are 120 symmetry operations, like rotations around an axis or reflections in a plane, which map the molecule onto itself. This makes C_{60} the molecule with the largest number of symmetry operations, the most symmetric molecule[33].

Fullerenes composed of less than 300 carbon atoms, or endohedral fullerenes, are commonly known as “buckyballs”, and include the most common fullerene, buckminsterfullerene, C_{60}. Giant fullerenes, or fullerenes with more than 300 carbon atoms, include single-shelled or multi-shelled carbon structures, onions, and nanotubes.

1. 4.1.Physical Properties

C_{60} is not "superaromatic" as there are no double bonds in the pentagonal rings, resulting in poor electron delocalization. As a result, C_{60} behaves like an electron deficient alkene and reacts readily with electron rich species. Some physical properties are listed below in Table 1.1

Table 1.1 Physical properties of [60[fullerene

Property	Value
Density	1.65 g cm^{-3}
Standard Heat of formation	9.08 k cal mol-^{1}
Index of refraction	2.2 (600nm)
Temperature of Sublimation	800K
Resistivity	1014 ohmsm^{-1}
Vapour Pressure	$5x10^{-6}$ torr at R.T. $8x10^{-4}$ torr at 800K

1.4.2. Thermodynamic and Kinetic Stability of C_{60}

The heat of formation of pristine C_{60} has been determined theoretically and experimentally by calorimetry to be 10.16 kcal mol^{-1} per C-atom (relative to graphite with 0.0 kcal mol^{-1} per C-atom). [34] Also in comparison to diamond (0.4 kcal mol^{-1} per carbon atom), C_{60} is a energy-rich carbon allotrope. Due to this C_{60} is one of the most strained molecules, which is stable under standard conditions.

1.4.3. Solubility of C_{60}

Fullerenes signify the only soluble allotrope form of carbon with a marked solubility in a wide range of organic solvents. The solubility of C_{60} in organic solvents is significant to enable purification and chemical modification. In general, the solubility in the majority of solvents is very little, because C_{60} exhibit a high tendency for aggregation. Moreover the interaction between the solvent molecules and C_{60} is very weak, since the fullerene is a nonpolar molecule. The solubility of C_{60} in polar solvents such as methanol and water is nearly zero. This low solubility can also be seen in the case of alkanes as solvents, whereas the solubility in chloro alkanes is slightly enhanced. The best solubilities are obtained in aromatic solvents and carbon disulfide. Good solvents for fullerenes are CS_2, toluene, xylene, and chlorobenzene. Fullerene solutions are colored, because of electron transitions[35-37]. The colour of fullerene solutions is attributed to the π-π^* electron transition. The color of different fullerenes in toluene is summarized in Table 1.2 and shown in Figure 1.7.

Table 1.2. Colour of different Fullerenes in toluene

Fullerenes	Color of the Solution	Molar mass (g/mol)
C_{60}	purple/violet	720.6
C_{70}	brick-red	840.7
C_{76}	light yellow-green	912.76
C2v-C_{78}, D3-C_{78}	maroon, golden	936.8
C_{84}	brown	1008.84
C_{86}	olive-green	1032.86

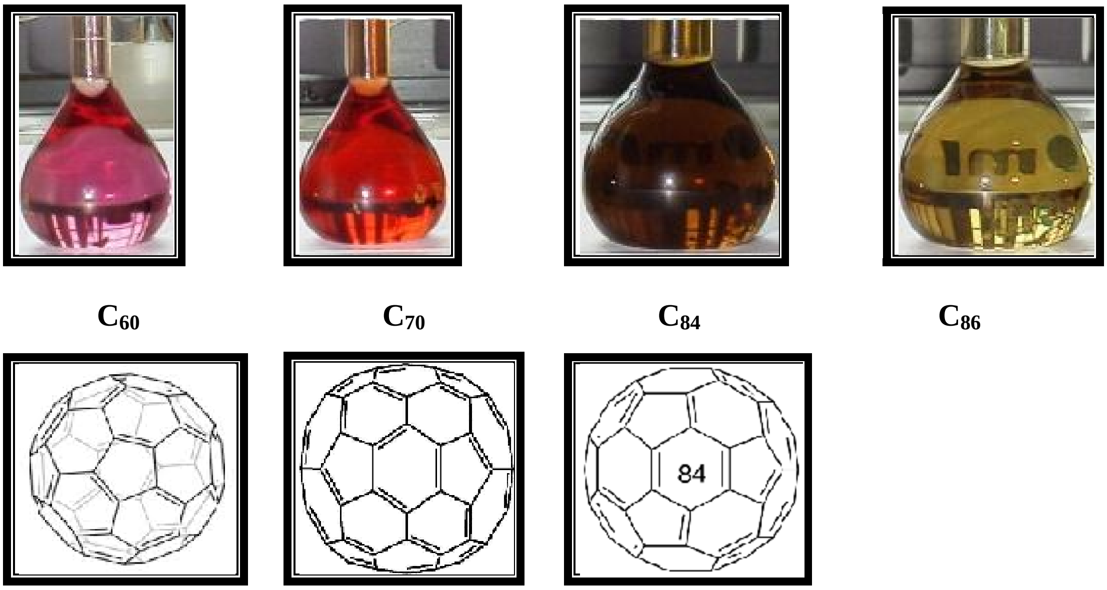


Figure 1.7 Fullerene solution in Toluene

The solubility of C_{60} has been studied in about 150 solvents[38]. The relationship of solubility with the polarizability, polarity, molecular size and cohesive energy density of the solvent was explained by Ruoff et al. The main conclusion was that no specific parameter could explain C_{60} solubility, but parameters like molecular size showed some correlations[39]. Same type of positive correlations with solvent size (expressed as molar volume) with solvents having minimal polarity or charge were observed in other studies[38]. Solubility of C_{60} showed an unusual temperature dependence in a number of solvents[40], decreasing with increased temperature. Heymann estimated the water solubility of $C_{60} < 10^{-9}$ mg/L [41]. Table 1.3 summarizes the solubilities of C_{60} in the most common solvents[38, 40,42-43].

Solubility correlations of [60]fullerene, the solubility parameters and variation of solubility parameters with the molar volume ratio in different solvents like alkanols (n=1,2,3,4,5,6,8), alkanes, halogenated hydrocarbons and other solvents were extensively studied by Murthy et al[44]. According to the data observed [60] fullerene showed more solubility in high boiling solvents except CS_2.

Table 1.3. Solubility of C_{60} in most common solvents.

Type	**Solvents**	**Solubility (mg/mL) at 25 °C**
Alkanes		
	n-pentane	**0.004** ^{a}**, 0.005**^{b}
	cyclopentane	**0.005** ^{b}
	n-hexane	**0.040**^{a}**, 0.043**^{b}
	cyclohexane	**0.051** ^{a} **,0.036** ^{b}
	octane	**0.025** ^{a}
	isooctane	**0.026**^{a}
	decane	**0.070** ^{a}**, 0.071** ^{b}
	dodecane	**0.091** ^{a}
	tetradecane	**0.126** ^{a}
	Decalines	**4.6** ^{b}
	cis- decalin	**2.2** ^{b}
	Trans-decalin	**1.3** ^{b}
Haloalkanes	di-chloromethane	**0.254** ^{a}**,0.26** ^{b}
	Chloroform	**0.16** ^{b}
	carbon tetrachloride	**0.447** ^{a} **, 0.32** ^{b}
	1,2-dibromomethane	**0.50** ^{b}
	trichloriethylene	**1.4** ^{b}
	Tetrachloroethylene	**1.2** ^{b}
	Freon TF (dichlorotrifluoroethane)	**0.020** ^{b}
	1,1,2-trichlorotrifluoroethane	**0.014** ^{b}
	1,1,2,2-tetrachloroethane	**5.3** ^{b}
Polars	methanol	**0.000** ^{b}
	ethanol	**0.001** ^{b}
	nitromethane	**0.000** ^{b}
	nitroehane	**0.002** ^{b}
	acetone	**0.001** ^{b}
	acetonitrile	**0.000** ^{b}
	N-methyl-2-pyrrolidone	**0.89** ^{b}

Type	**solvents**	**Solubility (mg/mL) at 25 °C**
benzenes	toluene	**2.150** [a] **,2.8** [b]
	benzene	**1.440** [a] **, 1.7** [b]
	mesitylene	**0.997** [a] **,1.5** [b]
	xylenes	**5.2** [b]
	tetralin	**16** [b]
	benzonitrile	**0.410**[b]
	fluorobenzene	**0.59** [b]
	nitrobenzene	**0.80** [b]
	bromobenzene	**3.3** [b]
	anisole	**5.6** [b]
	chlorobenzene	**7.0** [b]
	1,2-dichlorobenzene	**27** [b]
	1,2,4-trichlorobenzene	**8.5** [b]
naphthalenes	1-methylnaphthalene	**33** [b]
	dimethylnaphthalene	**36** [b]
	1-phenylnaphthalene	**50** [b]
	1-chloronaphthalene	**51** [b]
miscellaneous	tertrahydrofuran	**0.000** [b]
	carbon disulfide	**5.160** [a] **, 7.9** [b]
	tetrahydrothiophene	**0.030** [b]
	2-methylthiophene	**6.8** [b]
	Dioxane	**0.041** [a]
	pyridine	**0.89** [b]

a. Ref 40, b. Ref. 38

In different experimental studies fullerene solutions showed unusual properties [45-50]. Such as non-monotonous temperature dependence of solubility[46-49] and concentration dependence of C_{60} heat of solution have been found. Also, the ability to form crystallosolvates has been observed for both C_{60} and C_{70} fullerenes in some organic media [51-56]. From the fundamental point of view the investigation of fullerene solubility and thermodynamics of fullerene solvation in various solvents can be helpful for better understanding of the solvation processes of a huge hydrophobic non-electrolyte particle. Such studies are also important for technological applications, especially for efficient separation of different fullerenes. Therefore, investigation of fullerene solubility in non-aqueous solvents is of a great importance because it can help us to find appropriate solvents for separation of C_{60}, C_{70} and higher fullerenes from fullerene containing soot.

It is a great theoretical challenge to establish correlations between the solubility of fullerene and the different characteristics of the solutes and the solvents. In the case of fullerenes, the main challenge was to find suitable solvents for their extraction purpose of the first studies from soots and for their chromatographic separation. The solubility of C_{60} fullerene in tetrachloromethane, toluene and tetrachloromethane–1,2-dichlorobenzene mixtures has been investigated in a wide range of solvent compositions within 298.15–338.15 K temperature interval [56]. The solubility of C_{60} was determined at room temperature in seven normal alcohols, four isoalcohols, four diols, one triol, and seven alkanes by Heymann etal[57]. Low solubility of C_{60} in octane was confirmed.

1.4.4. Fullerenes in Water

Main methods of preparation of fullerene dispersions in water are listed below:

- Physical Condensation
- The Solvent Exchange Method
- Physical Condensation-Extraction
- Dispergation of the Solid in Water
- Chemical Condensation

The nature of C_{60} and other neutral fullerenes in the aqueous medium is very different as they are non-wettable (approximate solubility of $C_{60}<10^{-9}$ mg/L)[55-56]. C_{60} tends to adsorb onto itself or on other matrices due to the unfavorable free-energy in aqueous media. C_{60} solubility in water is similar to the non-polar hydrophobic molecules such as polyaromatic hydrocarbons, which strongly combine with organic carbon in biological systems. C_{60} solubility in aqueous media is possible by using following techniques.

a. Chemical modification of C_{60} by using hydrophilic functional groups like hydroxyl groups[58-60]. Plenty of water soluble fullerene derivatives like fullerols have been explored and include organic acids[61-62] and electrophilic additions[63].

b. C_{60} also can be solubilized in water by using various surfactants, polymers such as. polyvinyl pyrrolidone (PVP)) and natural macromolecules like 'γ-cyclodextrin, sucrose, and dextran (40 kDa) [64-66].

c. Stable aggregate suspensions of C_{60} can be formed at the micro- to nano-scales in aquoues media and other polar solvents [67-70].

Extraordinary one-pot method to directly generate fullerenols was proposed for highly water soluble C_{60} derivatives consisting of reduction with Na-K alloy and successive stirring in presence of O_2, giving polyhydroxylated fullerenols which are highly water soluble, from strongly basic to medium acidic conditions[71.]

The affinity of pure C_{60} fullerenes with water was studied[72]. Although C_{60} has always been known as hydrophobic, this hydrophobicity does not remain when contact between C_{60} and water is forced by mechanical stirring. Light scattering measurements and transmission electron microscopy observations revealed the presence of C_{60} aggregates remaining stable in water after stirring, with a large nanometric size range. C_{60} was dissolved in toluene-water mixture under sonochemical activation, and after toluene evaporation a stable aqueous solution remained[73].

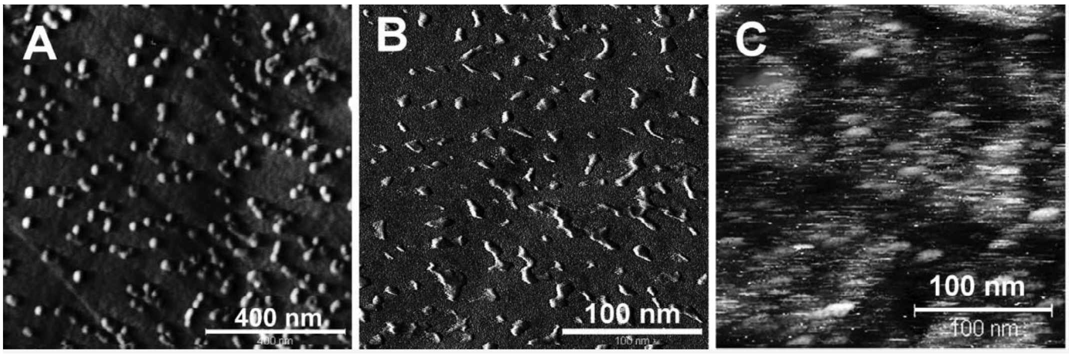


Figure 1.8 AFM images of C_{60} clusters deposited from A) water-toluene dispersion; B) water-methyl benzoate dispersions; C) STM image of C_{60} from toluene solution.

To prevail over the difficulty of the solubilization of C_{60} in aqueous phase, various methods have been adopted:

(i) synthesize water-soluble C_{60} derivatives by chemically attaching hydrophilic functional groups to the pristine C_{60},

(ii) solubilize C_{60} by suitable carriers which have hydrophobic cores or bilayers.

To fulfill this intention macromolecules including γ-cyclodextrin[74], calixarene[75], several aqueous micellar media[76-80], block co-polymers[81-83] and vesicular solutions formed by surfactants[84] have been used.

As functionalizing C_{60} for enhancing its solubility has directed to disruption of its symmetry and pseudo-aromaticity, restricting its potential applications, main concentration is focused to minimize the toxicity of water-soluble fullerenes for their use in drug delivery applications. Surfactant solutions promote a versatile solubilization method, since their micellar environment is chemically inert towards fullerenes.

Micelle forming surfactants increase the solubility of sparingly water-soluble substances for use in biological applications.

Affinity of pure C_{60} fullerenes with water was studied. According to light scattering measurements and transmission electron microscopy observations, the C_{60} aggregates remain stable in water after mechanical stirring, with a large nanometric size range. Affinity of C_{60} was explored for non toxic applications by forcing dispersion of C_{60} particles in water without any external restriction but mechanical stirring[72].

The influence of humic acid and sunlight on the dispergation of C_{60} was studied by Issakon etal[85]. In particular study of an aqueous suspension of nanoscale C_{60} aggregates (aqu/C_{60}) were produced by stirring in water with Suwanee River Humic Acid (humic acid) and water from Call's Creek, a small stream near Athens, GA. The study demonstrated that sunlight and humic acid have significant effects on the concentration, size, and zeta potential of aqu/C_{60}[85].

Supramolecular method for the synthesis of well-defined pristineC_{60}/polymer colloid nano composites in water was developed by Wang et al in which colloids consisting block copolymer micelles and emulsion particles. The nano composites found comprising core-shell structure with C_{60} aggregated on the surface of emulsion particles or micellar cores. These water-soluble, structurally defined C_{60}/polymer suprastructures were achieved through the self-assembly of pristine C_{60} with polymer colloids including block copolymer micelles and emulsion particles with opportunities in the future for the synthesis of "colloidal molecules" using supramolecular chemistry[86].

Characterization of solubilized and encapsulated fullerene C_{60} in non ionic TX -100 micelles were done by Patnaik etal. 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 are suitable for forming stable homogeneous C_{60} dispersions. A systematic and detailed encapsulation and solubilization of fullerene C_{60} in aqueous micellar solutions of the non-ionic TX-100 surfactant was investigated. The location of C_{60} in the hydrophobic core of the micelles was confirmed by UV–vis absorption and fluorescence emission measurements. The solubility of entrapped C_{60} in the aqueous TX-100 micellar solution was estimated to be 0.015 mM. The stability of aqueous dispersion of C_{60} in the TX 100 micellar medium, the redox behavior of the encapsulated micellar phases and localization of C_{60} in the inner hydropobic part of the micelles were confirmed[87].

The solubility of fullerene C_{60} and its antioxidant activity was investigated using nine different surfactants such as Tween 20, Tween 60, Tween 80, Triton X-100, PVP, polyoxyethylene(10)lauryl ether, n-dodecyl trimethylammonium chloride, myristyl trimethylammonium bromide and sodium dodecyl sulphate in bio relevant medium by Torres et al. UV visible studies confirmed the presence of fullerene C_{60} in the surfactant micelles. High radical scavenging activity, comparable to that of aqueous suspension of fullerene and butylated hydroxytoluene (BHT) obtained from micellar solutions of fullerene with Triton and polyoxyethylene lauryl ether were showed by lipid peroxidation tests . The highest efficacy on fullerene solubilization (>85%) was achieved by non ionic surfactants. As per results obtained from UV/VIS and DLS study, it was shown that ionic surfactants had lower solubilization power and non-ionic surfactants like the Tween group (T20, T60, T80) and $C_{12}E_{10}$ had better solubility. The micellar solutions of fullerene with ionic surfactants (SDS, MTAB, DTAC) and surfactants from the Tween group (T20, T60, T80) hindered antioxidative properties of C_{60}. Micellar solutions of fullerene with $C_{12}E_{10}$, Triton X-100 found more potential for using C_{60} in aqueous media[88].

Incorporation of C_{60} into an artificial lipid membranes studied by Hungerbhler and Guldi etal .C_{60} incorporated into the three types of vesicles such as DODAB(di octa decyl dimethyl ammonium bromide - positively charged head group), Lecithin(dipalmitoylphosphatidylcholine Zwitter ionic and DHP(dihexadecyl hydrogen phosphate-negatively charged) can be reduced to C_{60}*- radical anions by propan-2-ol radicals for homogeneous solutions [18]. The yields of C_{60} reduction in the vesicles, from the measured changes in absorption and the respective extinction coefficients of C_{60} were found highest for the positively charged vesicle DODAB and lowest for the negatively charged DHP[89-90]. It was found that electron transfer from $(CH_3)_2C^*(OH)$ radicals to C_{60} was considerably slowed down upon embedding the C_{60} into γ-cyclodextrine (a water-soluble complex) as compared to homogeneously dissolved C_{60} by Guldi etal[89].

Solubilization of fullerenes into water with polyvinyl pyrrolidone, applicable to biological tests was studied by Nakajima Yamakoshi et al. Where C_{60} and C_{70} were solubilized in water with poly(viny1pyrrolidone) (PVP) a widely used medical and cosmetic dispersant and viscosity regulating agent. The results suggested that C_{60} itself is present in a PVP micellar system and that the red-shift of UV-VIS spectra was found due to an intermolecular interaction between C_{60} and PVP. The aqueous solutions of C_{60} and C_{70} remain stable and clear for more than a month at room temperature[91].

Electron transfer studies in C_{78} ,C_{76} , C_{70} and C_{60} surfactant(Triton X- 100) aqueous solutions were done by Guldi. Surfactant capped fullerene solutions were prepared by stirring a mixture of Triton X-100 (reduced form) and C_{60}, C_{70}, C_{76}, and C_{78} at 50^0C.
C_{60} (*Ih*) and several higher fullerenes, namely, C_{70} (*D*5*h*), C_{76} (*D*2), and C_{78} (*C*2V), have been solubilized via capping with suitable surfactant Triton X 100(reduced form). Excited states and reduced states of these surfactant systems were probed by photolytic and radiolytic techniques. Direct reduction of surfactant capped fullerene monomers have been studied by means of time-resolved pulse radiolysis with measurements being conducted in the near-IR region which ensured solubilization of higher fullerenes by surfactants in the state of monomeric dissolution[92.]
Bemmason et al studied the solubilization of C_{60} in solvents like 1-octanol, 2-octanol, & in aqueous micellar solutions of two types of Triton **X** , and phospholipid (phosphatidylcholine) liposomes with the help of UV spectroscopy. Drawing the results from spectroscopic criteria of solute-solvent and solute-solute interactions, micellar incorporation of C_{60} molecules and state of colloidal liposome solutions was examined. The information obtained from the spectra in alkane and octanol as well as from the C_{60} thin films were used for the specific study. From the spectroscopic studies it was concluded that C_{60} could be dispersed in micellar solutions of Triton X-100 and Triton X-100, showing that the fullerene molecules were being confined in the interior hydrophobic part of the micelles. The fullerene dissolved in the hydrophobic portion of the micelle core while the polar OH groups were located at the micelle-water interface showing direct contact with the water molecules. As per results obtained C_{60} was incorporated into phosphatidylcholine liposome colloidal solutions as aggregates. Their

findings concluded that micellar and liposome solutions could be used to move individual C_{60} molecules, or groups of molecules, to biological cells[93].

Solubilization of C_{60} in aqueous micellar solution of Triton X 100 was carried out by Beeby et al. The results proved possibility of preparing micellar solutions of C_{60} using Triton-X100 surfactant under controlled conditions, which signified the presence of C_{60} was either as monomer or colloidal aggregates depending on the molar ratio $X = [C_{60}]/[TX]$[77]. Remarkable stability of C_{60} in micelles also was confirmed by Beeby et al and well defined C_{60} dispersions formed using non-ionic surfactant (TX-100) micelles and stability of dispersion studied[94].

Stabilization of water-soluble fullerene monomers was studied by Guldi et al using flash photolysis and pulse radiolysis technique, applied to the generated excited and reduced states of fullerene monomers and fullerene clusters[95]. Capping the surface of water-soluble fullerene derivatives with surfactants (cetyl trimethyl ammonium chloride or Triton X-100) was found to exclude formation of fullerene clusters and, so to stabilize fullerene monomers. Incorporation of C_{60} into the assemblies like vesicular and micellar membranes in aqueous environment showed that a solution of C_{60} in an aqueous Triton X-100 micellar system (prepared by stirring) showed a brownish color, signified that the C_{60} was not located in the inner hydrophobic part of the micelle. Surfactants, in particular Triton X-100 and BRIJ 35, have been effectively employed to solubilize pristine C_{60} in aqueous media in reasonable yields[96-98].

A salt-free catanionic surfactant system, tetradecyltrimethyl ammonium laurate (TTAL), was constructed by mixing tetradecyltrimethyl ammonium hydroxide (TTAOH) and lauric acid (LA)[99]. The ability to solubilize a fullerene mixture of C_{60} and C_{70} of different phases in different regions was tested. The colloidal stability and phase behavior of fullerene/TTAL/H_2O hybrids were investigated under controlled parameter.

Vesicular structures was seen for the zero-charged vesicle phase after fullerene solubilization by TEM, but rheological measurements showed that the samples became more fluid after fullerenes were incorporated into the hydrophobic micro domains of the aggregates.

Electrochemical behavior of cast vesicle films C_{60}/TTAL on glassy carbon electrode was studied in different aqueous solutions in which TTABr, SDS, C_{14}DMAO, KCl, $CaCl_2$, NH_4Cl, tetraethyl ammonium chloride and tetra butyl ammonium chloride aqueous solutions were used as electrolytes[100]. Comparing the various surfactant aqueous solutions, the cationic TTABr(tetradecyltrimethylammonium bromide) is better than zwitter ionic C_{14}DMAO(tetradecyldimethylamine Oxide) and anionic SDS (sodium dodecyl sulfate)in mediating the electron-transfer of C_{60}. It was found the cationic TTABr is better than zwitter ionic C_{14}DMAO and anionic SDS in mediating the electron transfer of C_{60} on the basis of the cyclic voltammograms of surfactant aqueous solutions.

Redox behavior of a water soluble malonic acid derivative of C_{60} was studied in which water-soluble malonic acid derivative of C_{60} was dissolved and reduced in aqueous solution. These studies were supported by photochemical excitation studies[101]. Well-defined, water-soluble C_{60}/micelle with varied amounts of C_{60} sitting on the surface of micellar cores were prepared via the self-assembly of PS-*b*-PDMA block copolymer micelles and C_{60}[102].

Effect of encapsulating agents on dispersion status[103] and photochemical reactivity of C_{60} in the aqueous phase and photochemical production of reactive oxygen species by C_{60} in the aqueous phase during UV irradiation[104] was studied by Hongkim et al using TX 100, Brij 78, Brij 35, SDBS, TX 405, TX 100-R, TX 405, Brij 78 .

A mechanism of photochemistry and reactive oxygen production by fullerene suspensions in water was also studied by Wiesner et al. In this study, production of both singlet oxygen and superoxide by UV photosensitization of colloidal aggregates of C_{60} in water was measured by two distinct methods: electron paramagnetic resonance (EPR) with a spin trapping compound, and spectrophotometric detection of the reduced form of the tetrazolium compound XTT [105].

A polydispersed colloidal system was formed when solution of C_{60} in toluene was mixed with surfactant Triton X 100 in water after the evaporation of toluene. System showed particle size mainly from 10 to 100 nm. The study revealed that in particular system fullerene may exist in the form of solubilized molecules within surfactant micelles upto some extent and partly as solid species stabilized by the surfactant[106].

The silica coated fullerene C_{60} clusters have been produced by microemulsion technique by Meghea et al. The ternary phase diagrams in water-TX-114-tetraethylorthosilicate (TEOS) system at different temperatures were constructed, followed by establishing the influence of clusterization and solubilization agents in choosing the pseudoternary system[107]. The study of the phase equilibrium in ternary systems consisting in water, oil and a nonionic surfactant is important for the synthesis of microemulsion processes and also for enhancing the mutual solubility of water and oil under the action of a surfactant. The application of microemulsifying in ternary and pseudo ternary systems was studied, with the aim of preparing clusters of fullerene C_{60} and their coating with silica. Observations interpret the fact that microemulsions represent a suitable medium for the formation of reproducible and stable fullerene clusters, due to the tailored shape and size of the colloidal aggregates.

The critical reverse micelle formation of non ionic surfactant Span60 (sorbitan stearate), in the presence of [60]fullerene was studied by Murthy et al[108]. Based upon the study microemulsion formation of [60]fullerene in the presence of various structurally different surfactants like span 60 and Brij 35 were carried out. The thermodynamic quantities of the reverse micellization process obtained from experimental results indicated that the process was 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. The dimensions of these microemulsions reached a maximum of 170 nm were observed by Light scattering studies. Phase behavior at different temperatures specified the very high surface active nature of [60] fullerene. The results also pointed out the fact that with the increase in the cosurfactant amount, a larger amount of water was essential for the formation of the emulsion and the microemulsion system required the cosurfactants for the formation and stability.

Molecular solutions of C_{60} may possess a dual nature and be a kind of “missing link” between true nonelectrolyte solution and a lyophobic colloidal system were concluded by Nikolay O. Mchedlov-Petrossyan in the recent review[109].

1.5. Chemistry

Two important features are observed from the structure of [60]fullerene

i) the delocalization of electrons is very poor in [60]fullerene so it shows more reactivity than alkenes and gives more stability to the fullerene derivatives

ii) [60]fullerene has no hydrogen atom or any other group attached to it .
So it can not undergo substitution reactions but substitution can take place on its derivatives.

Since the discovery of fullerenes, a broad variety of chemical modifications with C_{60} were performed. In general these modifications can be classified in five different topics. These are summarized in Figure1.9 [110-116].

Exohedral addition reactions, including nucleophilic- and radical additions, cycloadditions, hydrogenations, oxygenation and halogenation

a) Substitution of carbon atoms in the fullerene framework with different atoms, e.g. boron or nitrogen, leading to heterofullerenes
b) Encapsulation of one or more atoms inside the fullerene cage, yielding endohedral fullerenes
c) Ring-opening and fragmentation reactions, which could be used for subsequent endohedral functionalization
d) Reduction reactions with electropositive metals, e.g. alkali- and alkaline earth metals, yielding alkali metal fullerides

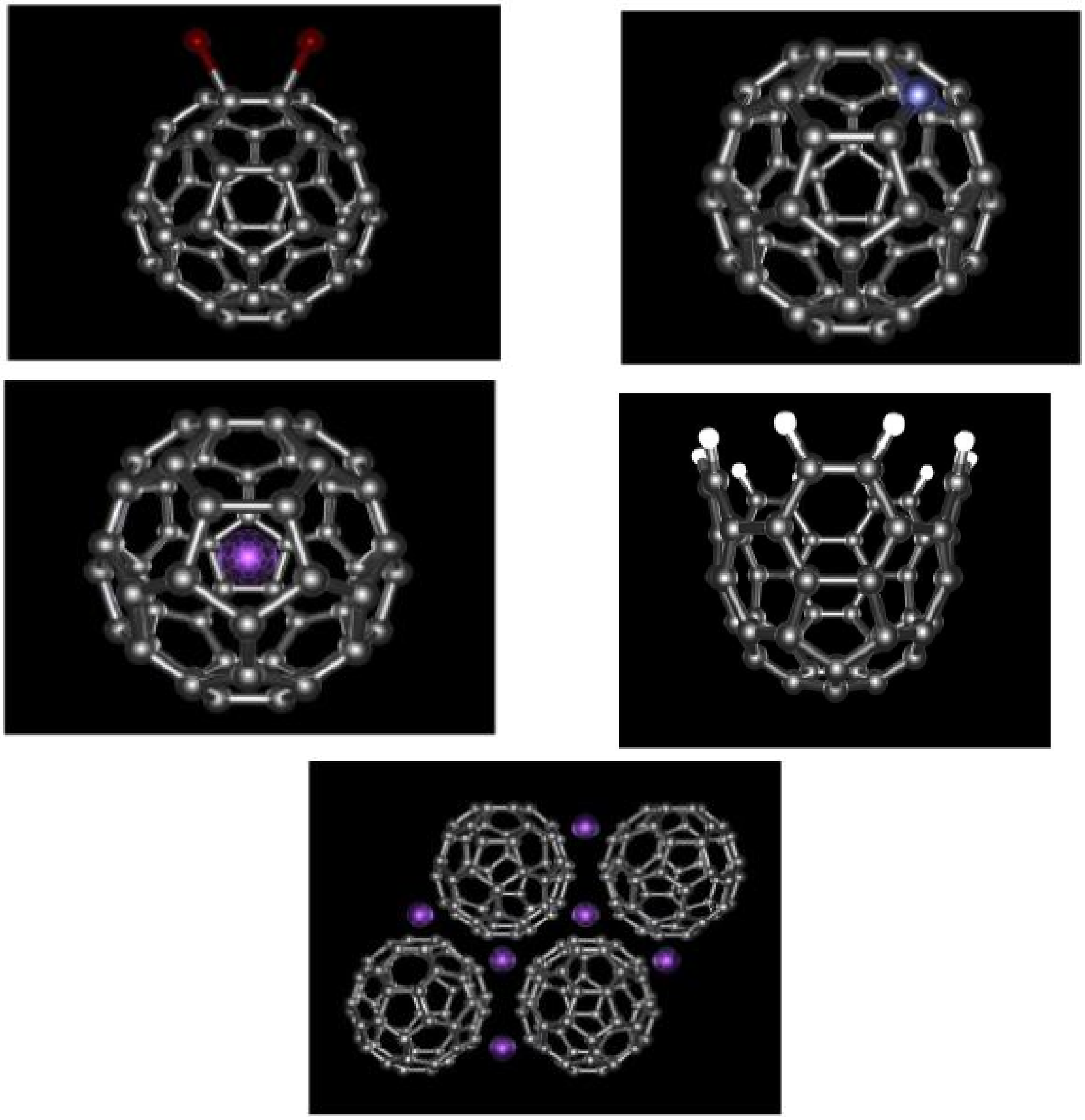


Figure 1.9. Overview of the possible modifications of C_{60}. (a) Exohedral functionalization; (b) Heterofullerenes; (c) Endohedral functionalization; (d) Cage-opening modifications and (e) Alkali metal fullerides.

The following classification lists the mainly used reactions for the chemical exohedral functionalization of C_{60}:

- Cyclopropanation with carbon nucleophiles[117,118]
- DIELS-ALDER-type [4+2]-cycloadditions [119,120]
- Photochemical [2+2]-cycloaddition of α, β-unsaturated ketones [121,122]
- [3+2]-cycloaddition using diazo compounds, azomethine ylides and azides [123-130]
- Nucleophilic addition of Grignard or organolithium compounds[131]
- Complexation of transition metal complexes[132]
- Oxygenation, osmylation, halogenation and hydrogenation[133]

1.6. Reactions of [60] fullerene:

C_{60} properties furthermore can be modified via chemical functionalization of its surface, via complexation, and by endohedral compounds formation[113,116,131,133-135] as shown in Figure 1.10.

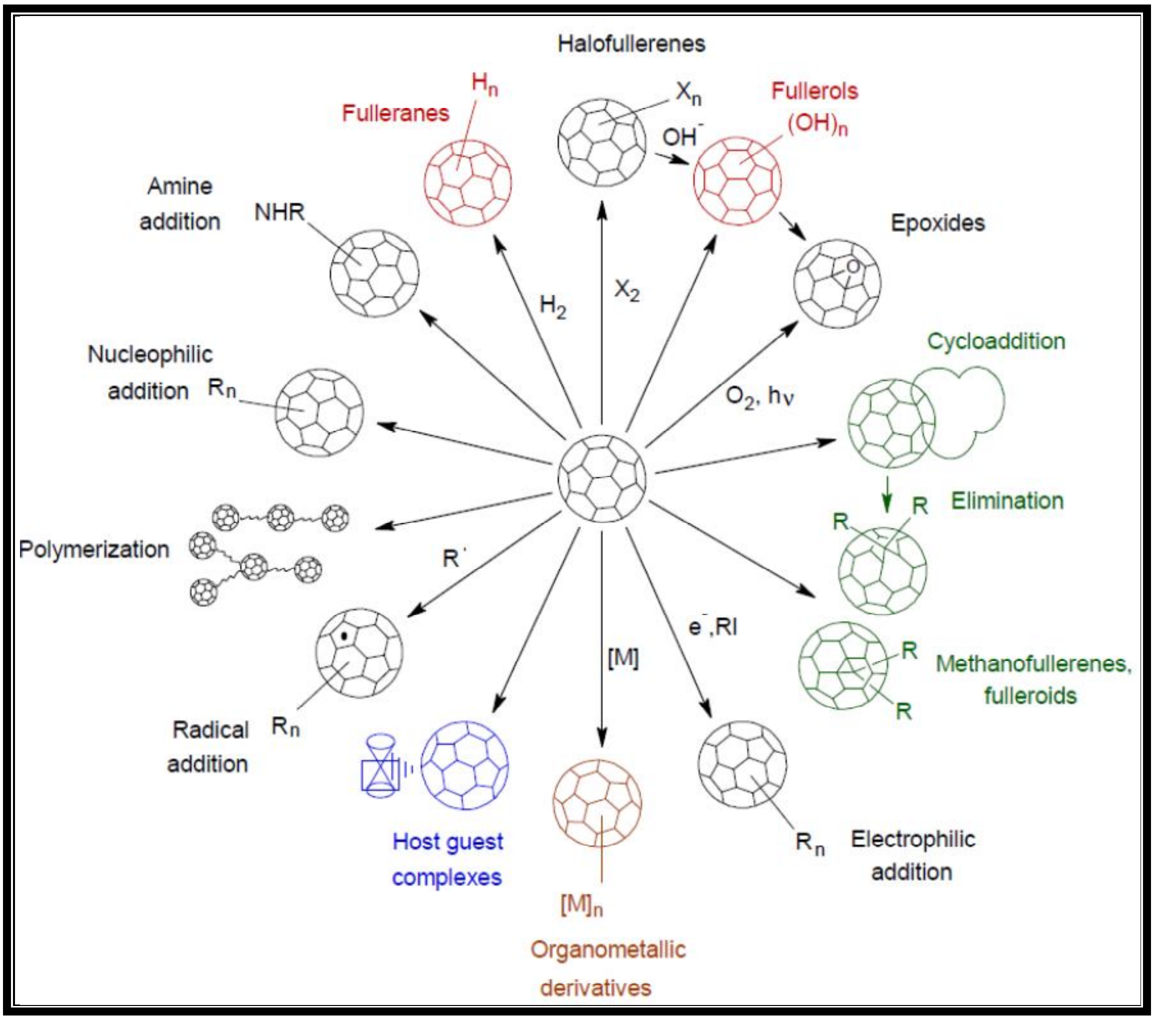


Figure 1.10. Examples of reactions involving C_{60}

1.7. Applications

Lubricants **anti friction/ anti wear coating**

(tungsten disulfide fullerene-like nanoparticle)

Figure:1.11. Industrial applications of fullerene

1.7.1. Polymers

The incorporation of fullerenes in polymers would potentially provide most of the fullerene properties to the polymer[136]. Electroactive polymers can be obtained, or polymers with optical limiting properties can be obtained[137].Fullerenes embedded in polymers become more easily processible. These polymers can be used for surface coating, photoconducting devices, and to build novel molecular networks. Different type of fullerene polymers (all-carbon polymers) has been obtained by irradiation of oxygen-free films or solutions of C_{60}[138,139] as well as by heating AC_{60} crystals (A= K, Rb, Cs)[140]. A quasi-linear structure, derived from [2+2] cycloadditions of C_{60} double bonds leading to four-membered rings, has been proposed for these polymers[141, 142].

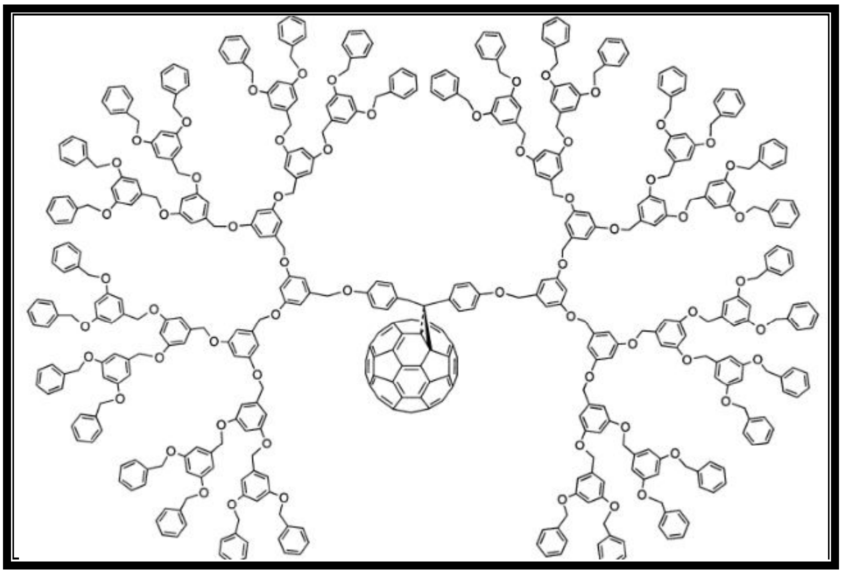


Figure 1.12 A dendrimer built on a fullerene nucleus

1.7.2.Thin films

Thin films with fullerenes are of high attention for transferring the remarkable fullerene properties to bulk materials by simple surface coating. Self-assembled monolayers (SAM) [143-145] and Langmuir films are being increasingly used, as controlled organized structures can be achieved.

1.7.3. Electro optical devices

Chemically modified fullerenes play a significant role in the design of novel molecular electronic devices[146, 155] and in particular for applications in artificial photosynthesis. Number of electron-rich groups has been covalently attached to C_{60}, which acts as an electron acceptor.

1.7.4. Liquid crystals : The first thermotropic liquid crystal containing two cholesterol units attached to a methanofullerene has been synthesized and its mesomorphic behavior was examined[147,156]. Different mesogenic groups were covalently linked to Phase transitions were detected at relatively low temperatures, but the detailed thermotropic properties were not reported.

1.7.5 Bio medicine:

Fullerenes have been found applications as neuroprotective agents[148], HIV-1 protease inhibitors[149, 150], antioxidants[151], X-ray contrast enhancers[152], and drug delivery transporters[153] in biological systems. Fullerenes readily accumulate and their aggregates can facilitate electron transfer across cell membranes due to van der Waals interaction, a phenomenon which could be effective on photosynthesis and biomedicine[154,155]. C_{60} molecule has approximately the same radius as the cylinder that describes the active site of the HIVP and since the derivatives of C_{60} is primarily hydrophobic, which shows a strong hydrophobic interaction between the C_{60} derivative and active site surfaces. This interaction could make C_{60} derivatives inhibitors of the HIVP.

A water-soluble C_{60} derivative intended to covalently attach to proteins such as ZME-018 as an initial step in the direction of targeted fullerene immunotherapy has been reported[153]. A single-drug chemotherapeutic agent such as a recently reported C_{60}–paclitaxel conjugate could be employed for fullerene immunotherapy.

Fullerenes are used in nanomedicine technologies due to their size and ability for various surface modifications as nanostructured materials, for tools and diagnostics as fullerene-based sensors and as nanotherapeutics[156]. Fundamental properties of fullerenes such as extremely high hydrophobicity, high cohesive force between fullerene molecules, photo activity[157], ability to accept and release electrons[158], and relatively high reactivity[159], allow their structural modifications. Using combinations of Nucleophilic and electrophilic additions, cycloadditions and radical additions, it is favoured to covalently bond any class of organic compounds to a fullerene core. These structural and electronic characteristics of fullerene C_{60} offer possibility for performing various types of chemical transformations [160-163] due to which a wide variety of biologically active water-soluble fullerenes could be obtained. Several fullerene compounds have shown potential as anticancer drugs and diagnostic agents[164, 165]. The biological behavior of fullerenes is associated to their chemical modifications and light treatment[166-170]. Fullerenes show high antioxidative activity in lower concentrations but they are also capable to initiate lipid peroxidation process and to increase ionic permeability of biomembranes, especially after treatment with light[166,167, 171,172] .

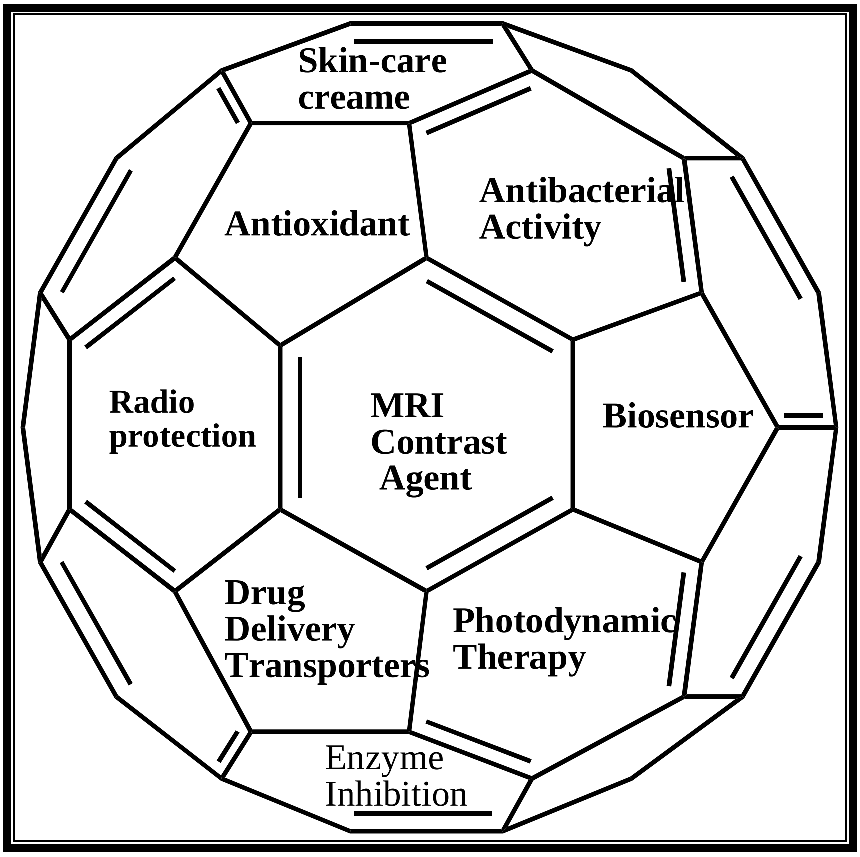


Figure 1.13. Potential biological applications of Fullerene

1.7.6. Skin Care

Active oxygen or free radicals is one of the causes of various skin problems, which lead to wrinkle formation and skin irritation. Antioxidants are effective to resolve this problem. Vitamin C and E are known as good antioxidants but fullerene shows 172 times more potential than Vitamin C[173,182]. Some of the commercial medical products containing fullerene are available in market as shown in Figure 1.16.

Figure. 1.14. Commercial cosmetic products containing fullerene

a. Fullerene Whitening Toner b. Vitamin C 25% + Fullerenes whitening serum

c. Fullerene Whitening Mask d. Fullerene C_{60} day creame

d. Under eye cream

1.7.7. Water-soluble fullerene derivatives

Irradiation of suspensions with water soluble fullerene derivatives show their pro-oxidative activity for application in bio-nanotechnology, e.g. for the photodynamic therapy of transformed cells. Prylutskyy et al. showed that UV and X-ray radiation of thymocytes suspension considerably increased the pro-oxidant properties of fullerene-containing composite, which resulted in higher DNA cleavage and accumulation of low-molecular DNA fragments[170]

1.7.8. Protective effects of carboxy fullerenes

Water-soluble carboxylic acid derivatives of a fullerene act as free radical scavengers and have been investigated as protective agents against oxidative stress[171]. Antibacterial activity of carboxyfullerenes was extensively evaluated by Tsao et al[172-174].

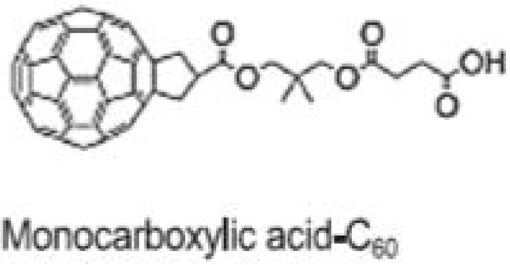


Figure 1.15 Monocarboxylic acid- C_{60}

1.7.9. Antiviral activity

Anti HIV-1 protease activity is one of the most attractive fields of research on the biological activity of fullerene derivatives[175,176]. The main idea for the synthesis of fullerene derivatives with anti HIV-1 activity was based on the formation of strong hydrophobic interactions between HIV-1 protease and C_{60} derivatives. Most effective compound was p,p'-bis-succinimide, derivative of p,p'-bis (aminoethyl)-phenyl fullerene C_{60} [177-179].

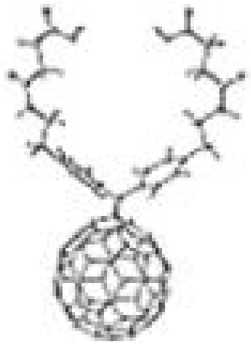


Figure 1.16 p,p'-bis (aminoethyl)phenyl fullerene[60]

1.7.10. Fullerenes as drug and gene delivery agents

Water-soluble fullerene derivatives cross the external cell membrane and localize preferentially to the mitochondria [180].The first synthesized C_{60}-based chemotherapeutic is C_{60}-paclitaxel conjugate(Figure 1.17). It was designed as a slow-release drug-delivery system for liposome aerosol delivery to the lungs. A paclitaxel fullerene derivative has been obtained by covalent linkage of the drug to the C_{60} by means of an ester, the hydrolysis of which presents a favorable kinetic profile, with consequent release of paclitaxel[181]. The *in vitro* tests show a good anticancer activity, holding out hope for enhancing the drug efficacy *in vivo*.

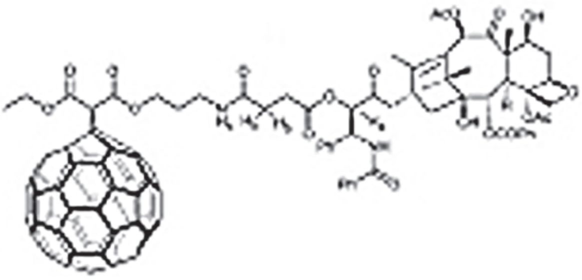


Figure 1.17. C_{60} – paclitaxel conjugate

Aim of the Thesis

Fullerenes have applications such as an antioxidant, in enzyme inhibition, for antibacterial activity, as MRI contrast agent etc. that require aqueous solubility. Therefore the dispersion of fullerene in aqueous media is very much essential. The main procedures used to transport fullerenes into water are physical and chemical condensation, extraction, and even direct dispergation in water. Solubilization by surfactant micelles and related species and covalent modification also may be used.

As [60] fullerene is hydrophobic molecule and has less solubility in water and other polar solvents, many attempts were made to incorporate [60] fullerene in aqueous media. One of the method to solublise [60] fullerene into water is via formation of microemulsion using different kinds of surfactants. To enhance the solubility of C_{60} in water and in other polar solvents micellar or vesicular solubilization was reported .The miscibility of water, oil and surfactant depends upon the overall composition of all components which can be explained by psuedoternary phase diagrams.

It is reported that in presence of water, surfactants can form reverse micelles in polar organic media. A w/o microemulsion hydration of hydrophilic droplet is also a reverse micelle in which the amount of water is less and is bounded by the capacity of hydration of the hydrophilic head group of amphiphile; therefore the pool water is rigid. In w/o microemulsion as the amount of water increases the hydration requirement of the surfactant head groups, both bound and free water prevail in the pool.

According to the previous findings, work on solubilization of [60] fullerene was done by using individual surfactants but there is no significant data regarding the microemulsion region containing [60] fullerene to prove its solubility in aqueous media. As microemulsion region is a useful parameter to detect the solubilising capacity of microemulsion system this work emphasizes on the determination of microemulsion system and study the psuedoternary phase diagrams containing [60] fullerene, using surfactants with a wide range of cosurfactants. It may also contribute to better understanding of the solution behavior and solution chemistry of fullerenes in polar medium by using different surfactant or mixed surfactant systems.

The main focus will be on:

a. Miscibility/solubility studies of [60]fullerene in water by using various surfactants.
b. Study the micellar solubilization of [60]fullerene in water using different surfactants
   i. **SDS**
   ii. **CTAB**
   iii. **Tween 80**
   iv. **Triton X 100**

The focus of the study was on the role of cosurfactants on the microemulsion formation [60] fullerene & study the nature of microemulsions with the help of ternary phase diagrams and evaluate the thermodynamic properties like ΔG°, ΔH° and ΔS° of microemulsion systems of [60] fullerene. The formation of reverse micelle at different temperatures will lead to the better understanding of the interaction between the hydrophobic surface of the fullerene and the polar water molecules.