SHORT COMMUNICATION

Solubilization and stabilization of fullerene C_{60} in presence of poly(vinyl pyrrolidone) molecules in water

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Abstract Solubilizing C_{60} molecules in an aqueous medium is highly imperative in processing them in different forms of ionic or nonionic liquids, nanofluids, films and other derivatives. In this investigation, we report a facile chemical route using polymer molecules of poly (vinyl pyrrolidone) (PVP) which mediate C_{60} molecules dissolving in water in a stable solution at room temperature. Poly(vinyl pyrrolidone) molecules, soluble in water as well as many organic liquids such as *n*-butanol, ethanol, or DMF, can be useful for transferring C_{60} molecules from a non-aqueous to an aqueous system. A broad optical absorption arises over 270–520 nm when C_{60} molecules are dissolved in water, 0.001–0.065 g/L in presence of 20–120 g/L PVP molecules. It consists of a strong $\pi \rightarrow \pi^*$ absorption band (relatively sharp) lying at 294 nm in $C(sp^2)$ electrons from PVP-surface modified C_{60} molecules followed by a broad charge transfer band which extends up to 520 nm. Upon a suitable surface modification, the C_{60} molecules conquer enhanced optical absorption in both kinds of the bands. Dynamic light scattering reveals an average hydrodynamic length 181.5 nm and a polydispersity index 0.506 after a typical loading 0.065 g/L C_{60}. A zeta potential −8.3 mV with a surface conductivity 0.064 mS/cm at 6.5 pH describes a negatively charged surface structure, showing an n-electron transfer from C=O (PVP) to a nanosurface in surface modified C_{60} molecules in a weak donor–acceptor complex. Water soluble C_{60} in presence of a biocompatible compound like PVP is useful for biological, medicinal, and other applications.

Introduction

Fullerenes are important molecular systems for exploiting as a modifier to develop a variety of composite materials with functional properties. Unique physical, photochemical, and tribological properties in such systems are implemented widely in various fields such as lubrications [1, 2], biosensors [3, 4], heat-transfer [2, 5], and biomedical applications [6–8], such as photodynamic therapy, drug delivery, enzyme inhibition, antioxidant, antiviral and antibacterial activity. As C_{60} is spherical in shape, small in size, and has capability to generate reactive oxygen species, such as superoxide anion radical ($O_2^{-\bullet}$) and hydroxyl radical ($^{\bullet}OH$) under photoirradiation [7, 8], it holds high potential in biological and medical applications. Extremely low solubility of fullerenes in polar solvents and propensity towards aggregation restrict most of these applications. As a result, solubilization and stabilization of fullerenes in different media has attracted great attention in scientific community. Two strategies (i) surface functionalization by attaching hydrophilic functional groups [6–8] and (ii) surface modification by a stabilizing agent, e.g., surfactants, cyclodextrins, polymers [9–11], are widely used in solubilizing/dispersing C_{60} in water.

Poly(vinyl pyrrolidone) (PVP), a water soluble polymer, has been used extensively not only as a solubilizing agent in tailoring solubility of C_{60} molecules but also as a macroligand to form stable rheological nanofluids (NFs). It is hydrophilic with unique structure, non-toxicity, biodegradability, good complexability, and medicinal properties [9, 12]. With lone pair O and N-electrons on the lactam unit

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and ability to generate active binding site by mesomerism in presence of hydrogen donor, PVP solubilizes C_{60} molecules in water by forming a donor–acceptor complex [13–16]. Enhanced solubility in pertinent media can bring functional C_{60} properties. Aqueous C_{60} NFs have special attention nowadays in view of diverse biological and medical applications [9, 14–16].

In this article, we describe a facile route of solubilizing C_{60} molecules in water via an alcoholic solvent such as *n*-butanol. As large amount as 0.065 g/L (i.e. 90.3 μM) C_{60} could be dissolved easily when mediated through PVP molecules—a widely used medical and cosmetic dispersant and viscosity regulating agent [9, 14]. A similar sample is being prepared by using chloroform as a transferring medium but that may not be so safe for biological usages [9, 14–16]. Even small trace of residual chloroform (toxic) can bring toxicity. *n*-butanol is non-anesthetic, biodegradable, non-mutagenic, and not as toxic as chloroform. It is already in used as an artificial flavorant in butter, cheese, whiskey, ice cream, and in a wide variety of other eatables or drinks [17]. Results are discussed with optical absorption, Fourier Transform Infrared (FTIR), zeta potential (ξ), and dynamic light scattering (DLS) of selective samples.

Materials and methods

The starting reagents of fullerene C_{60} and PVP (K-25, 28 kDa) used to develop aqueous C_{60} samples were purchased from Alfa Aesar and Aldrich respectively. In a typical experiment, two arbitrary solutions were used (1) 5.0 mg C_{60} in 5 mL toluene (i.e., 1.39 mM solution) and (2) 120 g/L PVP (i.e., 1.1 M) in *n*-butanol. Our solution-1 is bit concentrated when comparing to 1.11 mM C_{60} used earlier along with PVP (K-30) in chloroform instead of *n*-butanol [9]. Solution-1 was added to solution-2 slowly drop-wise by magnetic stirring in cold condition at room temperature followed by sonication at 50 °C. A light-brown clear solution appeared in 20 min sonication (at 20 kHz frequency and 250 W power), having 0.35 mL C_{60} solution-1 in 5 mL PVP in *n*-butanol. Then, solvents were evaporated at 100 ± 10 °C in a vacuum oven (1–3 kPa pressure) over a period of 10 h in order to dry a solid sample. A PVP-surface modified solid sample C_{60} so obtained was dissolved in ultrapure water by sonicating at 50 °C in ambient atmosphere. Then, we filtered the C_{60} complex solution by passing through a 0.45 μm Teflon filter to separate it out from any undissolved impurities which settle down in the mother solution. As large C_{60} as 90.3 μM could be dissolved through PVP (0.2–1.0 M) in water in this route. We confirmed the final C_{60} concentration in an aqueous PVP solution spectrophotometrically as follows. At first, 1% KCl in water followed by toluene

was added to the aqueous C_{60} sample for back extracting C_{60} effectively into the toluene phase [9]. After sonicating in a sonic bath for 30 min, a mixture so obtained was kept in dark so that the aqueous and toluene phases get separated each other. The upper part in the toluene phase was collected carefully with the help of a micropipette, and its characteristic 335 nm C_{60} absorption band was studied. A standard molar extinction coefficient (ε) in this band, log $\varepsilon = 4.71$ in *n*-hexane, was used as a reference for calculating the C_{60} contents in these complex solutions. According to it, a maximum solubility of C_{60} in water is found to be 90.3 μM. This is compatible to a maximum C_{60} or C_{70} solubility of 400 or 200 μM reported in water with K-30 PVP molecules but through chloroform which is highly toxic. As described by Scharff et al. [18], in a separate experiment, a 6.8 μM C_{60} in water (without PVP) was transferred through toluene in comparing the results. Aqueous C_{60} solutions with PVP molecules prepared through nontoxic solvents find specific values for cosmetics, medicinal, and other environmentally safe products.

Absorption spectra of aqueous C_{60} were measured under identical conditions on a Perkin Elmer double beam spectrophotometer (LAMBDA 1050). The sample was filled in a transparent cell of quartz (10 mm optical length) and the spectrum was recorded against a reference (water with 40 g/L PVP, or *n*-butanol) in an identical cell. Particle size distribution, ξ-value, and surface conductivity (σ_{sc}) were measured by using a Malvern Nano ZS instrument. Infrared spectra have been studied of the solutions with a Thermo Nicolet Corporation FTIR Spectrometer (Model NEXUS-870). The spectra have been recorded in an attenuated total reflectance mode using a ZnSe crystal as a sample holder.

Results and discussion

Absorption spectra

We studied optical absorption spectrum from a stock C_{60} solution prepared by dissolving 90.3 μM C_{60} in water in presence of 20-120 g/L PVP via *n*-butanol. Figure 1 shows two typical spectra measured after diluting a sample containing 90.3 μM C_{60} and 120 g/L PVP to (A) 30.1 μM C_{60} and (B) a rather dilute sample 2.0 μM C_{60} which contains 40 g/L PVP, i.e., the same amount as contained in sample-A. Such dilute samples brought down the initial absorbance that could be measured using a spectrophotometer. In sample-A, a sharp intense band arises at 294 nm, with maximum absorbance $\alpha_{max} = 2.3$ cm^{-1}, along with a broad band extending over longer wavelengths 270–520 nm with absorption maximum wavelength λ_{max} of 353 nm ($\alpha_{max} = 0.97$ cm^{-1}). In well-known transitions in C_{60} and derivatives [6, 10, 19], the 294 nm band arises in the $^1A_{1g} \rightarrow {}^1T_{1u}$

(3) ($\pi \rightarrow \pi^*$) transition in $C(sp^2)$ from PVP-surface modified C_{60} molecules whereas the broad band arises in a charge transfer (CT) band out of a C_{60}–PVP complex consisting of C_{60} molecules dispersed through PVP molecules. In sample-B, an increased PVP-content relative to C_{60} molecules causes a marked red-shift in the $^1A_{1g} \rightarrow {}^1T_{1u}$ (3) band up to 302 nm ($\alpha_{max} = 0.74$ cm^{-1}) in a modified profile with CT band at 363 nm ($\alpha_{max} = 0.41$ cm^{-1}) which is also shifted significantly over longer wavelengths.

The C_{60} spectra shown in Fig. 1 are different from those reported earlier by Ungurenasu and Airinei [14] on a similar aqueous 44 μM C_{60} solution containing PVP molecules but prepared by using chloroform instead of n-butanol. In this case, a bit broader band appears at 325 nm and that does not change much in average position as well as intensity when the PVP (K-25) content has varied from 7.0 to 14 g/L. A weak band (an order of lower $\alpha_{max} = 0.51$ cm^{-1} value) follows over longer region, with average λ_{max}-value 415 nm. Also this band, which was assigned to a CT band, does not vary much with PVP-content. A comparison of these results reveals that n-butanol doles out to be a better medium than chloroform in surface-grafting C_{60} molecules with a promptly rigid and stable polymer PVP layer. The surface layer leads to converge $C(sp^2)$ electrons on the C_{60} molecular surface so that the $\pi \rightarrow \pi^*$ transitions do not encounter significant red shift in weak microscopic interactions with the surrounding. On poor solubility (under 9.4 mg/L) in a weakly polar solvent such as n-butanol [20], C_{60} disperse easily in as small size as single molecule, suitable to bond PVP molecules (a macroligand) in a surface layer in form of a donor–acceptor complex. Such complex molecules disperse easily via PVP molecules in n-butanol. In contrast, comparatively high solubility (and large solute–solvent interactions), i.e., as large as 160 mg/L [21] in a nonpolar solvent such as chloroform hardly allows dispersing C_{60} of single molecule.

Broad band features observed in the $\pi \rightarrow \pi^*$ transition as well as the CT band in PVP-surface modified C_{60} molecules indicate that PVP molecules are cross-linking the C_{60} molecules in a specific structure. During a pulsed sonication used in hot condition, dispersed C_{60} molecules (modified with a thin surface PVP layer) in water in a solution possibly reorder via PVP molecules in part from the solution. To resolve this observation, we studied absorption spectrum in C_{60} molecules dissolved in water without involving any surface modifier. As shown in the inset of Fig. 1, the $^1A_{1g} \rightarrow {}^1T_{1u}$ (3) characteristic band is red-shifted to 344 nm and it exhibits a relatively smaller $\alpha_{max} = 0.42$ cm^{-1} value. Expectedly, water is not sharing a polymer bridging with the C_{60} molecules. Instead it forms merely a clathrate-like network on a C_{60} molecule [18]. Another broad band centered at 455 nm is assigned to orbitally forbidden singlet–singlet transition in the $C(sp^2)$ electrons of C_{60} [19]. Presence of a surface modifier of PVP molecules causes accumulation of $C(sp^2)$ electrons on the C_{60} nanosurface that results in a blue-shifted band at 295 nm in the quantum confinement effect. Absence of 455 nm band indicates that PVP molecules encapsulate the C_{60} molecules. A quantum mechanical calculation yields three distinct excited π^* states in C_{60} molecule designated as $^1T_{1u}$ (1), $^1T_{1u}$ (2), and $^1T_{1u}$ (3) lying at 408, 376 and 328 nm above the ground level $^1A_{1g}$ [19]. Among them, the $^1A_{1g} \rightarrow {}^1T_{1u}$ (3) band is the most intense, with oscillator strength $f_{osc} = 0.37$.

We determined f_{osc}-values in the individual bands observed in the absorption spectra in C_{60} molecules in aqueous solutions by using the standard relation [22],

$$f_{osc} = 4.31 \times 10^{-9} \int_{-\infty}^{\infty} \varepsilon \, dv, \tag{1}$$

where ε, i.e., α_{max}-value per unit concentration of C_{60} molecules in mole/L and $v = \lambda^{-1}$ expresses the band in an energy scale. As given in Table 1, a maximum f_{osc}-value

Fig. 1 Absorption spectra in a 30.1 μM and b 2.0 μM C_{60} dissolved in water in presence of 40 g/L PVP via n-butanol, with a spectrum of C_{60} (6.8 μM) in water in the inset
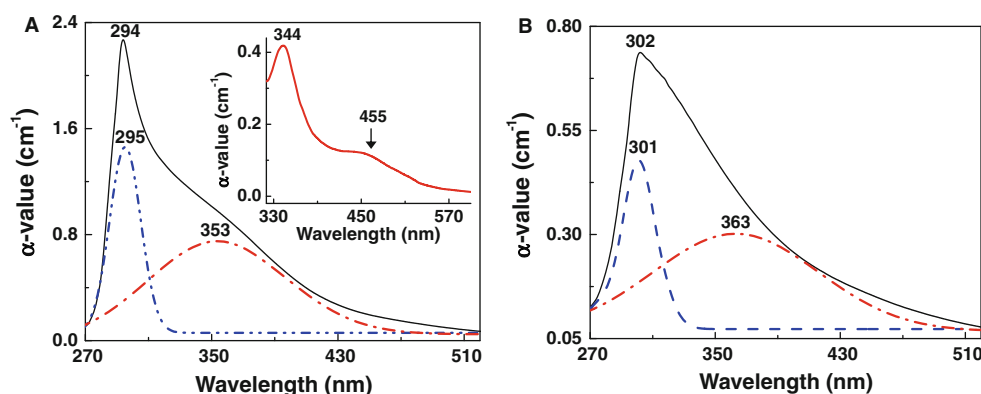
Table 1 The values for λ_{max}, α_{max}, ε_{max}, and f_{osc} determined from absorption spectra in C_{60} molecules in aqueous solutions

Properties	Aqueous-A		Aqueous-B		Aqueous-C
	Band-1	Band-2	Band-1	Band-2	Band-1
λ_{max}-value (nm)	295	353	301	363	344
A_{max}-value (cm^{-1})	1.46	0.75	0.48	0.30	0.42
ε_{max}-value (M^{-1} cm^{-1})	45,200	23,160	2,08,330	1,30,700	61,764
f_{osc}-value	0.26	0.43	1.49	3.37	0.41

Values refer to deconvoluted bands. Aqueous-A: 30.1 μM C_{60} with 40 g/L PVP in water, Aqueous-B: 2.0 μM C_{60} with 40 g/L PVP in water, and Aqueous-C: 6.8 μM C_{60} in water

3.37 is found for the CT band (after the deconvolution in Fig. 1) in sample-B which contains PVP monomers in as large number as 0.18×10^6 per C_{60} molecule. This f_{osc}-value is decreased markedly by almost an order of magnitude in sample-A upon a pretty smaller number density of PVP monomers by a factor ∼ 15. Poly(vinyl pyrrolidone) molecules are also helpful in promoting f_{osc}-value in the $^1A_{1g} \rightarrow {}^1T_{1u}$ transition in C(sp^2) electrons in C_{60} molecules but by a smaller factor ∼ 6. Such a high f_{osc}-value results in only when C(sp^2) electrons congregate on a nanosurface of single C_{60} molecules in a chemical association with an adhesive molecular PVP-surface-layer in a hybrid structure.

Zeta potential and DLS bands

In understanding mechanisms of solubilizing and immobilizing C_{60} molecules when dispersed in water in presence of PVP molecules, we studied ξ-bands and DLS bands from a stock solution. Here, PVP molecules serve as both a solubilizer and an immobilizer for C_{60} molecules at molecular scale. Experimental data could be collected only from dilute samples by 10–15 times in water (average 6.5 pH). As shown in Fig. 2, a sample-A of 30.1 μM C_{60} with 40 g/L PVP used to study optical spectrum in Fig. 1 displays two well-separated bands apart at −2.21 and −21.3 mV. The first band is prominent and it shares about 67% integrated intensity in the two bands. Primarily C_{60} molecules which are encapsulated in PVP molecules in a stable surface layer exhibit this band. The other band ascribes to PVP molecules which are merely dispersed via solvent H_2O molecules. According to it, an average ξ-value −8.3 mV is estimated from the observed band profile, with $\sigma_{sc} = 0.064$ mS/cm. When relative fraction is increased in PVP molecules in sample-B, the two bands merge into a single sharp band, with fwhm ∼ 11 mV (full-width at half peak intensity), showing an average −18.2 mV ξ-value and

$\sigma_{sc} = 0.150$ mS/cm. Such a large ξ-value arises due to effectively small C_{60} molecules in this sample as evident from hydrodynamic lengths (L_{hd}) determined from the DLS spectrum described below. An increased surface area in a small C_{60} molecule adsorbs concomitantly large number of PVP molecules over it to give rise an enhanced C=O non-bonding (n) electron transfer to the C_{60} molecule. In view of increased numerical values, the two parameters extend a correlation to concomitantly enhanced optical absorption in this specific sample (Table 1). A negative ξ-value is result of an effectively negative charge confined on a nanosurface of C_{60} molecules designed in support with a rigid surface PVP layer. A transfer of C=O n-electrons from a nucleophilic PVP molecule to an electrophilic C_{60} molecule share the localized surface charge density. Virgin C_{60} molecules dispersed in water in a nanocolloid (7 pH) include adsorbed H_2O molecules, showing a different band at −45 mV [23]. Hydroxylation of C_{60} surface causes more effective n-electron transfer from H_2O molecules.

In Fig. 3, the DLS spectrum exhibits three well-separated bands in three different effective L_{hd}-values 459.1, 23.87 and 7.51 nm in sample-A, with an average L_{hd}-value 181.5 nm and a polydispersity index (PDI) 0.506. The first band, which is prominent, attributes to PVP encapsulated C_{60} molecules that reveal an intense ξ-band. The second and third bands, having 51 and 22% peak intensity of the first band respectively, arise in PVP molecules dispersed in solution and those which bridges a surface-interface on a C_{60} molecule, respectively. As a matter of fact, an increased number of PVP molecules relative to C_{60} molecules in sample-B thus results in a manifested intensity of the corresponding band near 16 nm and it masks the third band as a shoulder at more or less the same L_{hd}-value as in the above sample. As given in Table 2, an average L_{hd}-value 24 nm is estimated from the total band profile, with a PDI 0.544. Such a small L_{hd}-value signifies that an increased relative PVP-content helps in an efficient encapsulation of C_{60} molecules in water.

Vibraional spectra

We studied interactions between C_{60} and PVP molecules in water in terms of the vibrational bands. Figure 4 compares the FTIR bands in PVP molecules (a) before and (b) after adding C_{60} molecules in a typical amount 2.0 μM used in making the samples for other studies. There is a marked enhancement in band intensity in C=O (1640 cm^{-1}) and C–N (1497, 1466, 1447, 1321, and 1294 cm^{-1}) stretching vibrations in the pyrrolidone ring of PVP molecules when C_{60} molecules interact with the surface PVP molecules via an n-electron rich C=O moiety. Also Borodko et al. [24, 25] observed similarly enhanced intensities in these modes but in PVP encapsulated Pt and Rh nanocrystals.

Fig. 2 Distribution of ξ-values in **a** 30.1 μM and **b** 2.0 μM C_{60} dissolved in water in presence of 40 g/L PVP. Samples were diluted five times in water in measuring the data
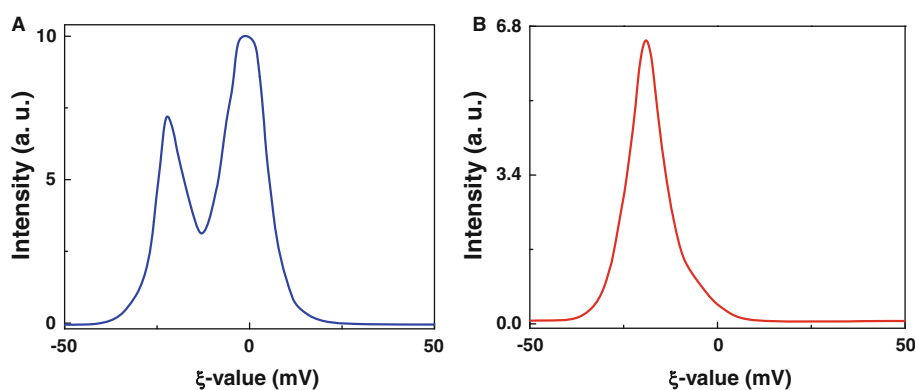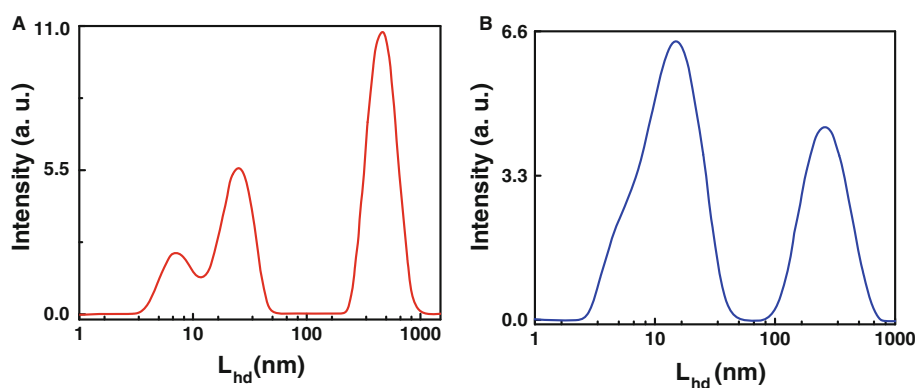
Fig. 3 Distribution of L_{hd}-values in **a** 30.1 μM and **b** 2.0 μM C_{60} dissolved in water in presence of 40 g/L PVP. Samples were diluted five times in water in measuring the data

Table 2 The values for ξ, σ_{sc}, L_{hd}, and PDI determined from zeta potential and DLS in aqueous C_{60} solutions

Properties	Aqueous-A	Aqueous-B
Average ξ-value (mV)	−8.3	−18.2
σ_{sc}-value (mS/cm)	0.064	0.150
Average L_{hd}-value (nm)	181.5	24.0
PDI	0.506	0.544

Aqueous-A: 30.1 μM C_{60} with 40 g/L PVP in water and Aqueous-B: 2.0 μM C_{60} with 40 g/L PVP in water. Samples were diluted five times in water in measuring the data

These results confer that PVP bonds to C_{60} surface with a CT interaction between the pyrrolidone ring and C_{60} nanosurface. No significant change in positions in these vibrations briefs a weak CT interaction of PVP molecules with C_{60} surface steered by a steric effect [24, 25].

Now, let us comment how a PVP polymer molecule (dispersed in *n*-butanol) can form an adhesive surface layer on a C_{60} molecule when added to a dilute liquid C_{60} solution in toluene before transferring to an aqueous medium of our interest in this work. As demonstrated in Fig. 5, a dispersed PVP molecule (a) in a weakly polar protic solvent such as *n*-butanol undergoes mesomerism with its lactam ring (b) so that it becomes active in reacting locally on a nascent C_{60} surface. A rather reactive PVP
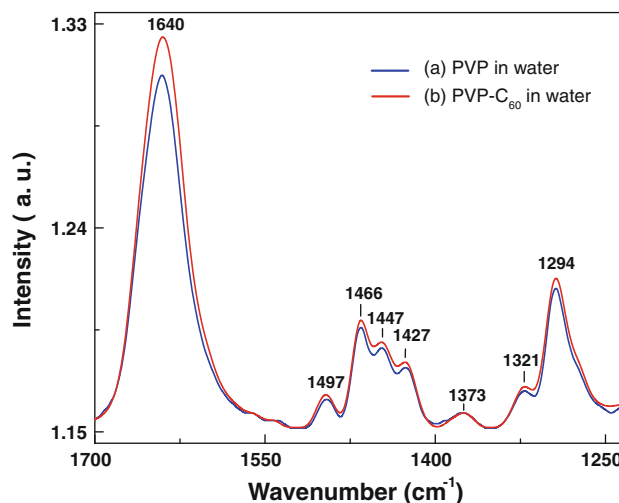
Fig. 4 FTIR spectra in PVP molecules (*a*) before and (*b*) after adding 2.0 μM C_{60} in 40 g/L PVP in water.

molecule so obtained contains a head-group of a lactam ring of a reactive site (Fig. 5c) on the carbon backbone. As a result, when adding to an electron deficient C_{60} molecule, an electron rich PVP molecule thus gets adsorbed readily onto a nascent carbon surface via O-atoms of the head-groups (Fig. 6a), forming a polymer surface layer. A model in Fig. 6b describes that a hybrid composite structure incurs of a surface modified C_{60} molecule with a stable adhesive surface PVP layer. In this model PVP adsorption
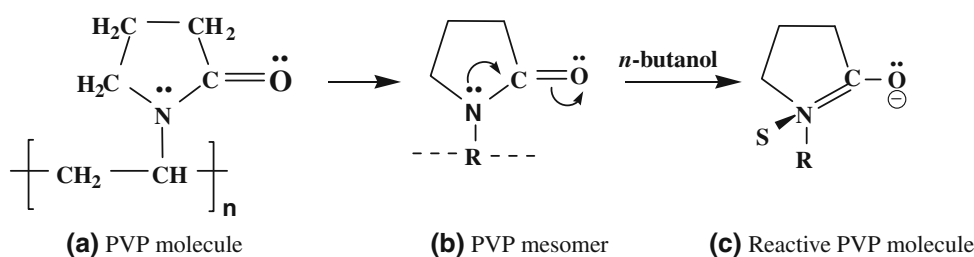
Fig. 5 Generation of a reactive site in (*a*) a PVP molecule in *n*-butanol as a result of mesomerism in (*b*) the lactam ring such that it serves (*c*) an efficient electron donor. R: part of carbon chain of a PVP molecule and S: *n*-butanol
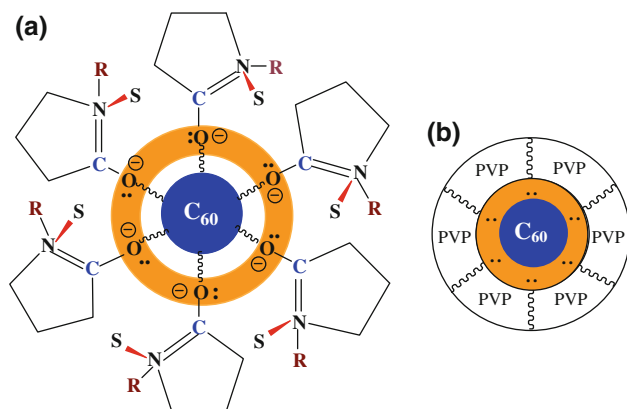

Fig. 6 A model adsorption of **a** electron donors of PVP molecules on nascent surface of a C_{60} molecule in forming **b** a hybrid composite structure with an enhanced density of n-electrons in support with an adhesive PVP-surface-layer. *n*-butanol (S) evaporates out when drying a solution to a solid sample. Actual number of PVP molecules present on the C_{60} surface stands much larger than a qualitative figure put over here

on a molecular C_{60} surface, the number of PVP molecules taken on a model C_{60} molecule is merely qualitative. The actual number would be much larger according to effective surface of the C_{60} molecule. An electron rich surface, i.e., a negative charge surface, turns up by confining C=O n-electrons on a molecular C_{60} surface as observed in the ξ-bands.

Conclusions

A facile route using a biocompatible material such as PVP molecules as a mediator is explored to develop an aqueous C_{60} fluid at moderate temperature. It is shown that dispersed PVP molecules of a dilute sample in a weakly polar solvent of *n*-butanol serve as both a solubilizer and an immobilizer for C_{60} molecules. Using such a precursor, as much C_{60} molecules as 0.065 g/L (90.3 μM) could be dissolved easily on 120 g/L PVP in water. A strong $\pi \rightarrow \pi^*$ absorption band occurs at 294 nm along with a broad CT band extending over longer wavelengths up to 520 nm. A markedly enhanced ε_{max}-value, i.e., as large as

$2,08,330 \ M^{-1} \ cm^{-1}$, incurs in this band when PVP molecules cobridge an adhesive surface layer on C_{60} molecules. Accumulation of C=O (PVP) n-electrons on a nanosurface of C_{60} molecules in such configuration favors the $\pi \rightarrow \pi^*$ transition. FTIR bands brief markedly enhanced intensity in the C=O and C–N stretching vibrations of chromophoric groups of PVP molecules in presence of C_{60} molecule as a result of a CT interaction of PVP functional groups with the C_{60} surface. Model structures are proposed corroborating the results that PVP molecules (hydrophilic steric stabilizer) help C_{60} molecules in solubility as well as stability in water. Using a biocompatible and medicinal PVP compound inflates possible applications of aqueous C_{60} fluids and derivatives in biological, medicinal, and other devices.

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