INFRARED SPECTROSCOPIC STUDIES OF C_{60} AND C_{70} NANOPARTICLE INTERACTIONS WITH δ–VALEROLACTAM

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ABSTRACT.   Fourier transform infrared spectroscopy was used to investigate the interactions between C_{60} and C_{70} nanoparticles and δ-valerolactam (δ-lactam or D-lactam, the six-member heterocyclic lactam) in a toluene solvent environment. Changes in the carbonyl absorption in the lactam ring (both shape and position) were used to identify interactions between the δ-valerolactam and these nanoparticles. In a previous study, shifts in the carbonyl absorption were observed for 2-pyrrolidone (γ-lactam, the five-member heterocyclic lactam) treated with C_{60}, but only very small broadenings of the carbonyl absorption were observed when 2-pyrrolidone was treated with C_{70}. In this study, significant changes in the carbonyl absorption were observed when δ-valerolactam was treated with both C_{60} and C_{70} in a toluene solvent environment.

Keywords: Infrared spectroscopy, nanoparticles, C_{60} and C_{70}, fullerenes, δ-valerolactam (δ-lactam or D-lactam)

INTRODUCTION

The interactions of C_{60} and C_{70} nanoparticles with a number of molecular systems have been studied using a variety of analysis methods such as UV-visible, infrared, and Raman spectroscopy along with X-ray, neutron scattering, and theoretical analysis methods (Holleman et al. 1999; Kyzyma et al. 2008; Jurow et al. 2012; King et al. 2012; Kyrey et al. 2012; Tropin et al. 2013; Bowles et al. 2014; Kirsch et al. 2015, 2017; Behera & Ram 2015; Li et al. 2016). This paper describes the results of an infrared spectroscopic investigation of the interactions between both C_{60} and C_{70} nanoparticles and δ-valerolactam using toluene as a solvent environment (Aksenova et al. 2013).

The compound δ-valerolactam is a six-member, heterocyclic amide sometimes referred to as delta-lactam (δ-lactam) or D-lactam. The cyclic lactam structures have important pharmaceutical and biological applications (Midgley et al. 1992; Harreus et al. 2011). C_{60} and C_{70} nanoparticles dissolve in toluene forming a blue solution with C_{60} and a red solution with C_{70} (Ruoff et al. 1993). In this study infrared spectroscopy was used to investigate changes (both shape and position) in the carbonyl absorption of the δ-valerolactam as an indication of its interactions with the C_{60} and C_{70} nanoparticles in a toluene solvent environment. In a previous study (Kirsch et al. 2017),

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infrared spectra showed significant changes in the carbonyl absorption of 2-pyrrolidone (γ-lactam, the five-member heterocyclic lactam) treated with C_{60} indicating interactions between the 2-pyrrolidone and C_{60} nanoparticles; however, only minimal changes in the carbonyl absorption were observed when 2-pyrrolidone was treated with C_{70} nanoparticles. In this study, significant changes in the carbonyl absorption of δ-valerolactam were observed on treatment with both C_{60} and C_{70} nanoparticles indicating molecular interactions of δ-valerolactam with both C_{60} and C_{70} nanoparticles.

EXPERIMENTAL METHODS

A Digilab FTS 7000 infrared spectrometer and a circle cell fitted with a ZnSe ATR rod were used to collect spectra for the investigation by averaging 500 scans at a spectral resolution of 2 cm^{-1}. The empty circle cell was used as the single-beam spectral background for the study. The spectrometer was purged with dry air for at least an hour prior to spectral collection to minimize potentially interfering atmospheric water vapor absorptions. Solution spectra were collected over a concentration range of $\sim$ 4 to $\sim$ 20 mg of δ-valerolactam per mL toluene or toluene saturated with the nanoparticles (C_{60} and C_{70}) to identify a suitable concentration range to observe spectral changes.

INVESTIGATION RESULTS

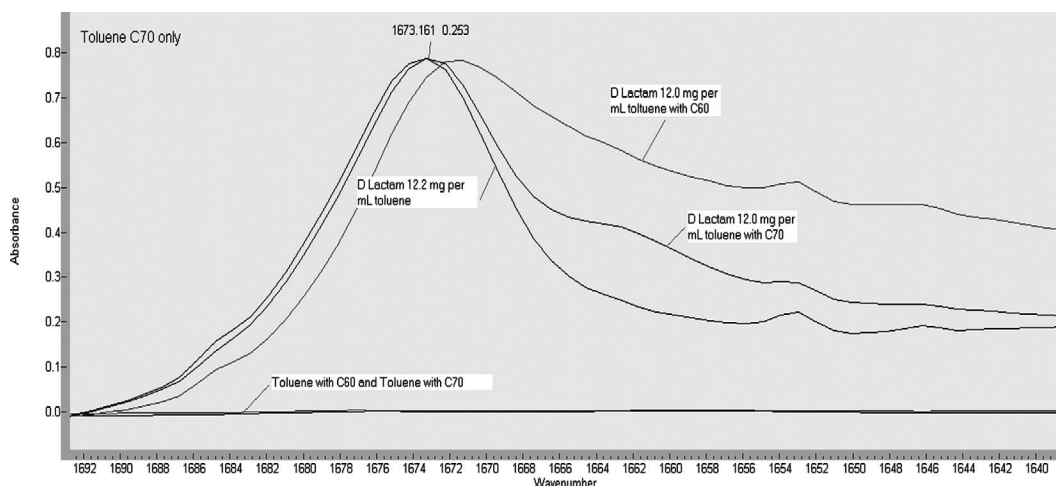Figure 1 contains the spectrum of δ-valerolactam (D-lactam) in toluene, the spectrum of δ-

Figure 1.—The spectra of 12.2 mg of δ–valerolactam (D-lactam) per mL toluene, the spectra of 12.0 mg of δ–valerolactam per mL toluene saturated with C_{60}, and the spectra of 12.0 mg of δ–valerolactam per mL toluene saturated with C_{70} are shown. The spectra of toluene saturated with C_{60} and C_{70} also are included.

valerolactam in toluene saturated with C_{60}, and the spectrum of δ-valerolactam in toluene saturated with C_{70} at concentrations of 12 mg of δ-valerolactam per mL toluene or toluene saturated with the nanoparticles. The spectra of toluene saturated with the nanoparticles also are included in Fig. 1, and they do not show any spectral absorption in the region of the δ-valerolactam carbonyl absorption, between 1640–1690 cm^{-1}.

Examination of the spectra in Fig. 1 shows both a small shift ($\sim$ 2 cm^{-1}) to lower wavenumbers and significant broadening on the low wavenumber side of the carbonyl absorption of the δ-valerolactam (D-lactam) resulting from its treatment with C_{60}. The spectra in Fig. 1 also show the appearance of a new spectral absorption (at $\sim$1662 cm^{-1}) when δ-valerolactam was treated with C_{70} at this concentration level. These changes in the shapes and positions of the carbonyl absorptions indicate interactions between δ-valerolactam and both C_{60} and C_{70} nanoparticles.

The interactions between the nanoparticles (C_{60} and C_{70}) and δ-valerolactam are very likely governed by an equilibrium process. Of course, shifting the equilibrium toward a complex formed between δ-valerolactam and the nanoparticles could result from increasing the concentration of either the nanoparticles or the δ-valerolactam. Changing the concentrations of the nanoparticles is limited by their low solubility in the toluene solvent and the use of saturated solutions of the nanoparticles in this study. The solubility of C_{60} is

2.8 mg of C_{60} per mL toluene (Ruoff et al. 1993). Increasing the concentration of δ-valerolactam would certainly shift the equilibrium toward any complex formed between the δ-valerolactam and the nanoparticles; however, it would also increase the amount of the δ-valerolactam not interacting with the nanoparticles that contains the infrared probe, the lactam carbonyl bond. The carbonyl absorption of the non-interacting δ-valerolactam at higher concentrations could cover up the carbonyl absorption of any complex formed between the δ-valerolactam and nanoparticles and interfere with its observation. So, the experimental challenge is to add enough δ-valerolactam to form a complex, but not enough δ-valerolactam to cover up the absorption of the complex formed with the absorption of non-interacting δ-valerolactam.

Concentration studies were carried out to determine the optimum concentration level of δ-valerolactam to generate a δ-valerolactam - nanoparticle complex and still allow the observation of its carbonyl absorption. Figure 2 shows spectra collected at approximately 19, 12, and 7 mg of δ-valerolactam per mL toluene and toluene saturated with C_{60}. The spectra in Fig. 2 show a small shift ($\sim$2 cm^{-1}) to lower wavenumbers and significant broadening of the carbonyl absorption by δ-valerolactam treated with C_{60} at 19 and 12 mg of δ-valerolactam per mL toluene saturated with C_{60}. At a concentration near 7 mg only a minimal change of the carbonyl absorption is
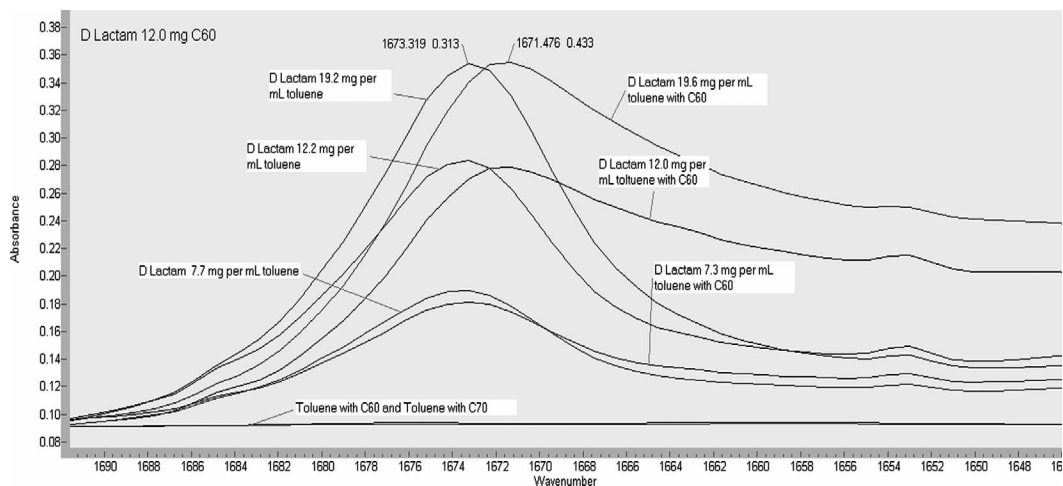
Figure 2.—The spectra of 19.2, 12.2, and 7.7 mg of δ–valerolactam (D-lactam) per mL toluene, and the spectra of 19.6, 12.0, and 7.3 mg of δ–valerolactam per mL toluene saturated with C_{60} are shown. In addition, the spectrum of toluene saturated with C_{60} is included. The spectral peak heights have been adjusted to help clarify spectral changes along the wavenumber axis; therefore, peak intensities do not quantitatively represent concentrations of δ–valerolactam.

observed on treatment of the δ-valerolactam with C_{60}.

As suggested earlier, the broadening of the carbonyl absorption of the δ-valerolactam on treatment with C_{60} results from an equilibrium process generating an overlap of the carbonyl absorptions from both non-interacting and inter-acting δ-valerolactam. Spectral subtraction has been shown to be a valuable tool in separating overlapping spectral absorptions resulting from a mixture of absorbing species (Gillette & Koenig 1984; Honigs et al. 1985; Yang 1994; Siyuan et al. 2010). Figure 3 shows the result of the subtraction of the spectrum of δ-valerolactam times a 0.73
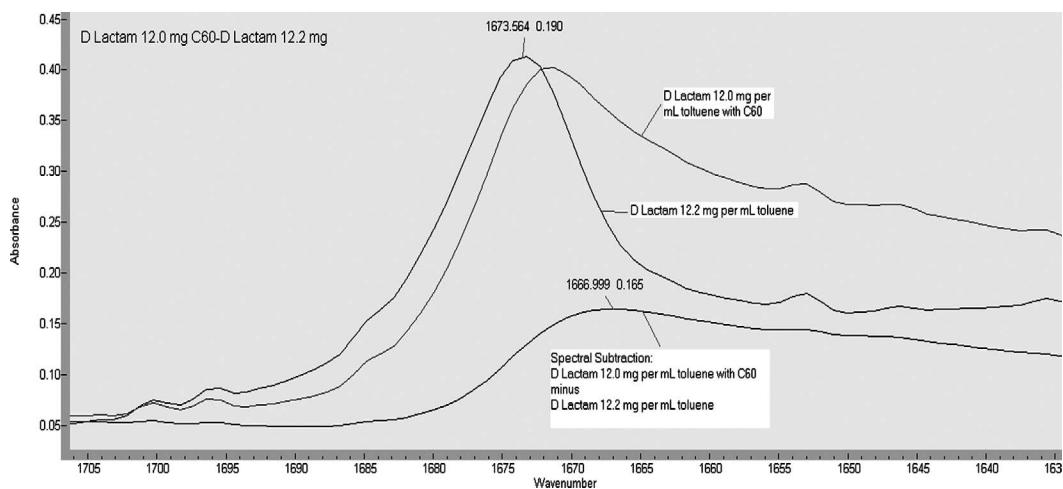

Figure 3.—The spectra of δ–valerolactam (D–lactam) in toluene and toluene saturated with C_{60} are shown at a 12 mg per mL concentration level. In addition, the spectra resulting from the subtraction of the spectra of δ–valerolactam in toluene from the spectra of δ–valerolactam treated with C_{60} are shown. The spectral subtraction factor was 0.73. Subtracted Spectra = (12.0 mg of δ–valerolactam (D-lactam) per mL toluene saturated with C_{60}) minus (12.0 mg of δ–valerolactam (D-lactam) per mL toluene) × 0.73. Spectral peak heights have been adjusted to clarify positioning along the wavelength axis.
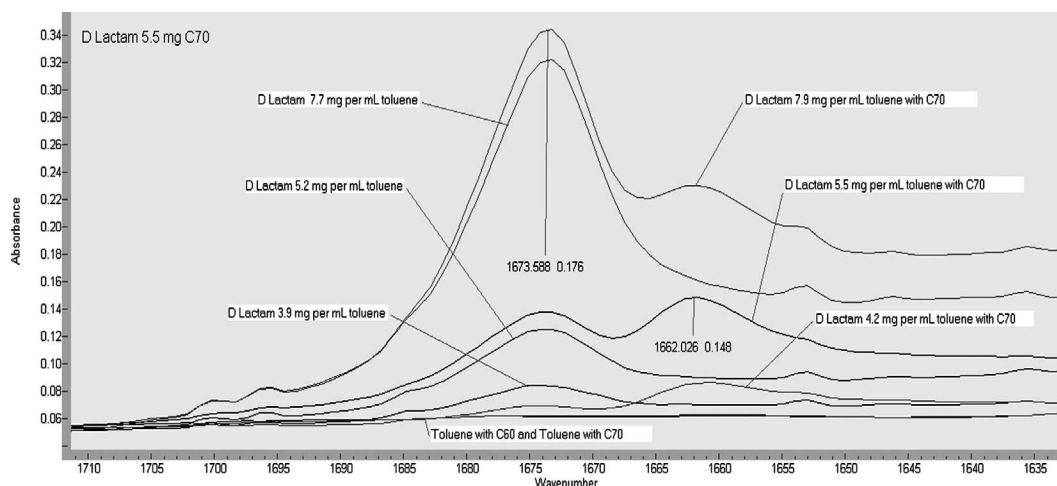
Figure 4.—The spectra of 7.7, 5.2, and 3.9 mg of δ–valerolactam (D-lactam) per mL toluene, and the spectra of 7.9, 5.5, and 4.2 mg of δ–valerolactam per mL toluene saturated with C_{70} are shown. In addition, the spectrum of toluene saturated with C_{70} is included. Spectral peak heights have been adjusted to clarify positioning along the wavelength axis and do not indicate absolute concentrations of δ–valerolactam.

subtraction factor from the spectrum of δ-valerolactam treated with C_{60}. The subtraction factor adjusts for differences in concentrations, baselines, and molar absorptivity of the absorbing species.

The idea of the subtraction process is to remove the absorption of the non-interacting δ-valerolactam from the spectrum of overlapping absorptions yielding the spectral absorption of the δ-valerolactam interacting with the nanoparticles. The subtraction process yields a spectrum with absorption at 1667 cm^{-1} that corresponds to the carbonyl absorption of δ-valerolactam interacting with C_{60}.

Figure 4 shows spectra collected at approximately 8, 5, and 4 mg of δ-valerolactam per mL toluene and toluene saturated with C_{70}. The spectra in Fig. 4 show the appearance of a new carbonyl absorption near 1662 cm^{-1} resulting from the treatment of δ-valerolactam with C_{70}. As the concentration changes from about 8 to 4 mg of δ-valerolactam per mL toluene saturated with C_{70}, the relative intensity of the absorption at 1662 cm^{-1} increases significantly compared to the parent absorption at 1674 cm^{-1}. The spectra in Fig. 4 indicate the complex formed between δ-valerolactam and C_{70} is characterized by carbonyl absorption near 1662 cm^{-1}.

DISCUSSION AND CONCLUSIONS

The observed shifts of the δ-valerolactam carbonyl absorptions to lower wavenumbers on treatment with C_{60} and C_{70} suggest that its interaction with the nanoparticles occurs through the lone-pair electrons of the oxygen part of the carbonyl bond in its amide structure (Kirsch et al. 2015, 2017). A number of studies suggest that nanoparticles are good electron acceptors for molecular systems (Charvet et al. 2012; Schubert et al. 2013; Stranius et al. 2014). A recent study of the interactions of 2-pyrrolidone (γ-lactam, the five-member heterocyclic lactam) with C_{60} also showed a shift of the carbonyl absorption to lower wavenumbers suggesting an interaction through the oxygen lone-pair electrons of the carbonyl bond in the lactam structure (Kirsch et al. 2017). The amide structure has been traditionally described by two resonance structures resulting from the lone-pair electrons on the nitrogen being delocalized into the amide carbon–nitrogen chemical bond generating a minor resonance structure with a carbon–oxygen single bond (Avram & Mateescu 1970). If the lone pair electrons of the oxygen on the δ-valerolactam are donated into the antibonding molecular orbitals of the C_{60} or C_{70} (Feng et al. 2008), the resonance structure containing the single bonded CO is stabilized a bit more yielding a lower wavenumber infrared absorption of the carbonyl group in the amide structure. Figure 5 shows this oxygen lone-pair donation model, and describes its impact on the carbonyl absorption (Behera & Ram 2015).

Major Resonance Structure with double bonded C=O and higher wavenumber absorption

Donation of oxygen lone pair electrons to the nanoparticles stabilizes the minor resonance structure resulting in a shift of the carbonyl IR absorption to lower wavenumbers

Minor Resonance Structure with single bonded C-O and lower wavenumber absorption

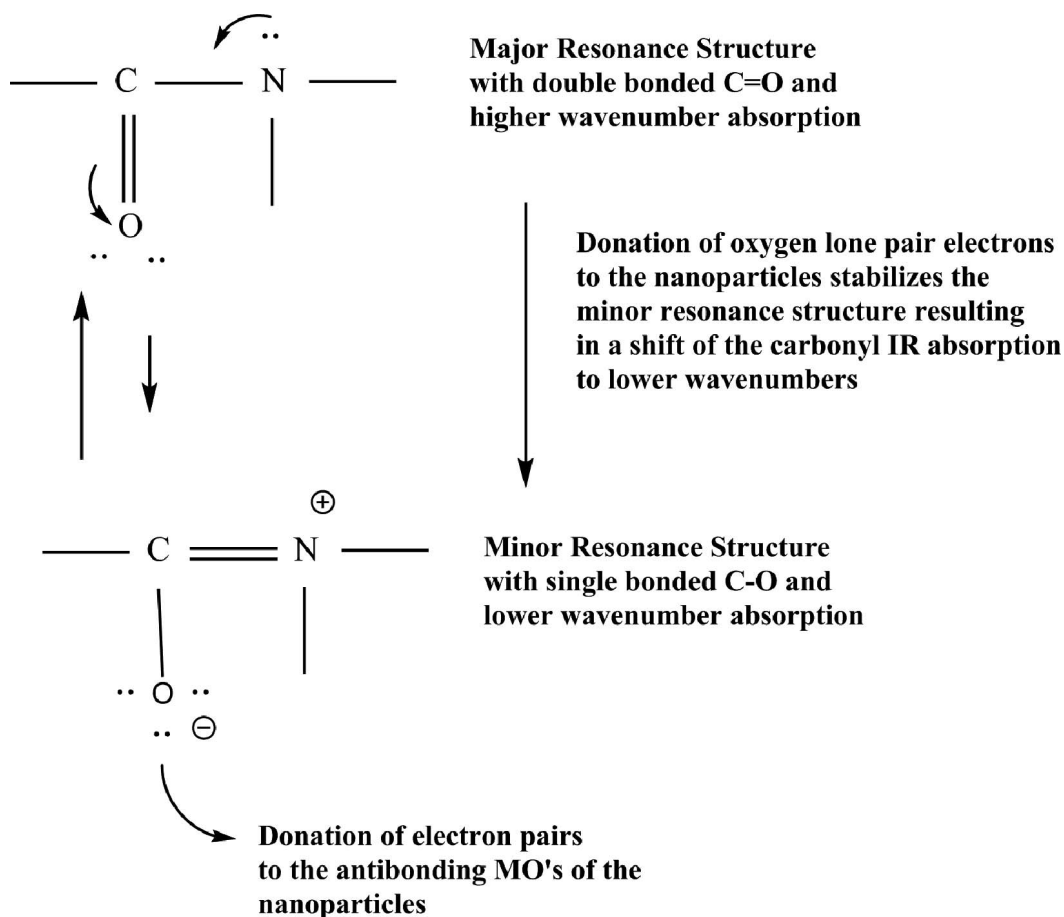**Donation of electron pairs to the antibonding MO's of the nanoparticles**

Figure 5.—Resonance structure model with oxygen, lone pair donation to the nanoparticles resulting in an increase in the stability of the resonance structure with the single bonded carbonyl supports a shift of the carbonyl absorption to lower wavenumbers.

In summary, the observed changes in the carbonyl absorption of δ-valerolactam indicate that interactions occur (a complex is formed) between δ-valerolactam and both C_{60} and C_{70}. The shifts of the carbonyl absorption to lower wavenumbers suggest an interaction resulting from donation of the electron pairs from the oxygen part of its amide functionality into the antibonding MO's of the nanoparticles (C_{60} and C_{70}). Spectral subtraction of δ-valerolactam in toluene from δ-valerolactam treated with C_{60} in toluene generates a spectrum with an absorption at $1667 \, cm^{-1}$ that is in reasonable agreement with the new carbonyl absorption observed at $1662 \, cm^{-1}$ when δ-valerolactam (D-lactam) is treated with C_{70}.

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