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C₆₀ FULLERENE AGGREGATION IN HEXANE/TOLUENE SOLUTIONS

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Abstract: The refractive indices of the hexane/toluene binary were measured and the excess refractive index n^E was calculated. The n^E values showed negative values over the entire concentration range (0-1.0) and were most negative at ~ 0.55 mole fraction of toluene. This maximum concentration was chosen as the working medium for dissolving fullerene C₆₀ and obtained as a result. The fullerene solution was investigated using UV-Vis light spectroscopy and dynamic light scattering (DLS) techniques. DLS showed a dominant peak at $\approx 65-70$ nm and weaker peak at $\approx 100, 160$ and 250 nm. The observed changes in absorption intensity, along with the broadening of the spectral bands, indicate the formation of fullerene clusters driven by intermolecular interactions and aggregation. The results obtained will serve as a useful resource for the synthesizing nanocomposite materials.

Keywords: hexane, toluene, fullerene C₆₀, excess refractive index, DLS, UV-Vis absorption spectroscopy.

GEKSAN/TOLOL ERITMALARIDA C_{60} FULLERENINING AGREGATSIYASI

Annotatsiya: Geksan/tolol binar eritmasining nur sindirish ko'rsatkichlari o' lchandi va ortiqcha nur sindirish ko' rsatkichi n^E ni hisoblandi. n^E qiymatlari butun erish konsentratsiya diapazonida (0-1.0) manfiy qiymatlarni ko' rsatib va tololning ~ 0.55 mol ulushida eng manfiy qiymatga ega bo' ldi. Ushbu maksimal konsentratsiya fulleren C_{60} ni eritish uchun ishchi muhit sifatida tanlandi va natijada olinadi. Fullerenli eritma UV-Vis spektroskopiyasi va yorug' lik dinamik sochilishi (DLS) metodlari yordamida tadqiq qilindi. DLS spektriga ko' ra $\approx 65-70$ nm da dominant va $\approx 100, 160$ va 250 nm da kuchsizroq piklarga ega. UV-Vis yutilish spektri intensioligida kuzatilgan o' zgarishlar, spektral polosalarning kengayishi molekulalararo o' zaro ta'sirlar va natijada agregatsiya tufayli fulleren klasterlari paydo bo' lganini ko' rsatdi. Olingan natijalar nanokompozit materiallar sintez qilishda foydali manba bo' lib xizmat qiladi.

Kalit so' zlar: Geksan, tolol, fulleren C_{60} , ortiqcha nur sindirish ko' rsatkichi, DLS, UV-Vis yutilish spektroskopiyasi.

АГРЕГАЦИЯ ФУЛЛЕРЕНА C_{60} В РАСТВОРАХ ГЕКСАН/ТОЛУОЛ

Аннотация: Были измерены показатели преломления бинарной смеси гексан/толуол, и рассчитан избыточный показатель преломления n^E . Значения n^E оказались отрицательными на всём диапазоне концентраций (0-1.0) и были максимально отрицательными примерно при мольной доле толуола ~ 0.55 . Эта концентрация была выбрана в качестве рабочего раствора для растворения фуллерена C_{60} , и раствор был получен в итоге. Раствор фуллерена исследовали с помощью спектроскопии УФ-видимого света и динамического рассеяния света (DLS). DLS показало доминирующий пик при $\approx 65-70$ нм и слабые пики при ≈ 100 , 160 и 250 нм. Наблюдаемые изменения интенсивности поглощения, вместе с расширением спектральных полос, указывают на образование кластеров фуллерена под воздействием межмолекулярных взаимодействий и агрегации. Полученные результаты будут полезны для синтеза нанокomпозитных материалов.

Ключевые слова: гексан, толуол, фуллерен C_{60} , избыточный показатель преломления, динамическое рассеяние света, УФ-видимая абсорбционная спектроскопия.

Introduction

Investigating fullerene in different polar solutions is important in many ways. These processes mainly depend on the formation, stability, and changes of large clusters of polar C_{60} in various solvents [1–4]. Understanding and identifying these processes is crucial for several promising practical applications. In particular, controlling the size of clusters in highly polar colloidal C_{60} solutions is important for fullerene's pharmaceutical and biomedical uses. Dissolved in one solution and in a mixture of two solutions, the solubility of fullerenes varies, and this solubility affects the formation of fullerene aggregates and their size. This also makes it necessary to assess the interaction between the two solvents in advance. This means that the interaction between the two solvents should be determined in advance. In this case, studying the interactions between molecules could be easily and quickly done using refractometry [5–9]. Studying fullerene aggregates, DLS and UV-Vis spectroscopy are widely used [10–14].

In this case, the method of UV-Vis spectroscopy appears to be the most convenient as a basis for studying the kinetics of the processes. The application of this method can result in detailed information about the kinetics of the aggregate formation in solutions under different conditions, which will offer both verification of various theoretical models and specification of the numerical values of parameters for equations of the theory. For this purpose, it is necessary to allocate a section in the UV-Vis spectrum, corresponding to the absorption of the fullerene bonded in complexes; that is, to subtract the contribution from light absorption caused by unbound C_{60} molecules entering the solution from the solid phase during the dissolution process and to consider aggregation of the fullerene. DLS beyond UV-Vis spectrum was applied to fullerene solutions in toluene/hexane mixtures, one of the best methods to understand what kind of interactions occur related to aggregation processes and their sizes. Using them in combination is very important for a better understanding of the phenomenon.

In the present work, the excess refractive index of the hexane/toluene binary system are investigated over the full composition range, and the DLS and UV-Vis characterization of C_{60} dissolved in a solution close to the composition at which the excess refractive index attains its minimum. This report shows that these two, data sets are physically connected: the same molecular-packing anomaly that produces the excess refractive index minimum in the pure solvent mixture also marks a regime of reduced, spatially heterogeneous solvent quality that promotes the aggregation of C_{60} . The aim of the present article is to examine and discuss observed aggregate sizes to the known mechanisms of fullerene nanoparticle formation.

Experimental section

Materials

Fullerene C_{60} powder (purity $\geq 99.8\%$) was purchased from SES Research (USA) and used without any further purification. Toluene and hexane (reagent grade, $\geq 99.8\%$ purity), obtained from Sigma-Aldrich (USA), were used without additional treatment.

Preparation and refractometry of hexane/toluene solutions

Binary solutions of hexane/toluene were prepared by mass across the whole composition range (0–1.0 mole fraction) and converted to mole fractions using the pure-component densities. The refractive indices of each mixture, as well as those of the pure liquids, were measured five times at $T=298.15$ K and atmospheric pressure, using a thermostated Abbe-type refractometer at the sodium D-line (or the corresponding equivalent working wavelength), and the average values were obtained. The excess refractive index was calculated as

$$n^E = n_{mix} - (x_1 n_1 + x_2 n_2)$$

where n_{mix} is the experimentally measured refractive index of the mixture and n_1 , n_2 are the refractive indices of pure hexane and pure toluene, respectively [8].

Preparation of the C_{60} solution and characterization

For the optical measurements presented here, 0.5 mg of C_{60} fullerene 2 was prepared in 5 ml of toluene/hexane solution and allowed to fully dissolve at the molecular level under gentle magnetic stirring in the dark for several hours. The resulting solution was measured while freshly prepared. UV-Vis absorption spectra of the C_{60} solutions were acquired on a Shimadzu UV-2700 double-beam spectrophotometer (Japan) across the 300–800 nm range. The size of C_{60} aggregates formed in the binary solvent systems was determined by DLS, performed on a Malvern Zetasizer Nano ZEN 3600 (Malvern Instruments Ltd., Worcestershire, UK).

Results and discussion

Excess refractive index

Binary solutions of toluene with n-alkanes have been shown to exhibit increasingly negative excess molar volumes with increasing molecular weight difference between the two components, with toluene + hexane and toluene + n-pentane giving the most negative V^E values among the homologous alkane series [15]. This observation is in direct agreement with the present n^E data. Hexane is a flexible, nonpolar molecule with non-aromatic character [16]. Similarly reported that among

six binary mixtures containing n-alkanes and aromatic or cycloaliphatic components, the toluene/hexane system showed the largest negative excess molar volume, which is associated with the structural difference between the two components. The fact that the extremum of n^E is not located at the equimolar composition, but is shifted toward at ~ 0.55 mole fraction of toluene is consistent with the size and shape asymmetry of the two components. The concentration at which the interactions between the two components are maximal was chosen to observe fullerene aggregation.

Table 1. Experimental mole fraction, refractive index, excess refractive index and excess refractive index for hexane/toluene.

X , toluene	n	n^E
1.0	1.4910	0.0000
0.917661779	1.4721	-0.0087
0.832027226	1.4623	-0.0080
0.742894351	1.4524	-0.0069
0.650044315	1.4404	-0.0074
0.553239637	1.4270	-0.0089
0.452222167	1.4174	-0.0060
0.346710787	1.4058	-0.0046
0.236398798	1.3923	-0.0045
0.120950942	1.3797	-0.0028
0.0	1.3676	0.0000

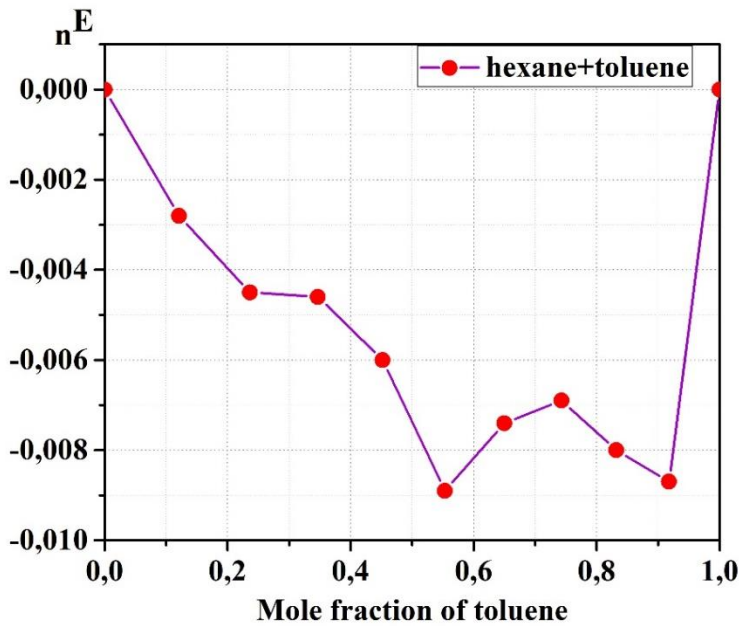


Figure 1. Excess refractive index for binary solutions of hexane/toluene components.

DLS analysis

DLS analysis of the freshly prepared C₆₀ fullerene solution in the mixed hexane/toluene solvent system revealed a distinctly multimodal particle size distribution (Figure 2), indicating the spontaneous formation of C₆₀ nanoclusters upon solvent exposure. The DLS spectrum displays a dominant, well-resolved peak centered at approximately 65 nm, with a particle concentration intensity of $\sim 2.0 \times 10^7$, which accounts for the majority of the scattering signal and represents the predominant nanocluster population in solution. In addition to this primary peak, two secondary populations are clearly resolved: a moderate peak centered around 100 nm and a smaller peak near 155–160 nm. A minor, broad shoulder is also observed in the 230–270 nm range, with a much lower relative intensity, suggesting the presence of a small fraction of larger aggregates even in the freshly prepared sample. Overall, the particle size distribution spans from 30 nm to 300 nm, with the bulk of the population confined to the sub-100 nm range.

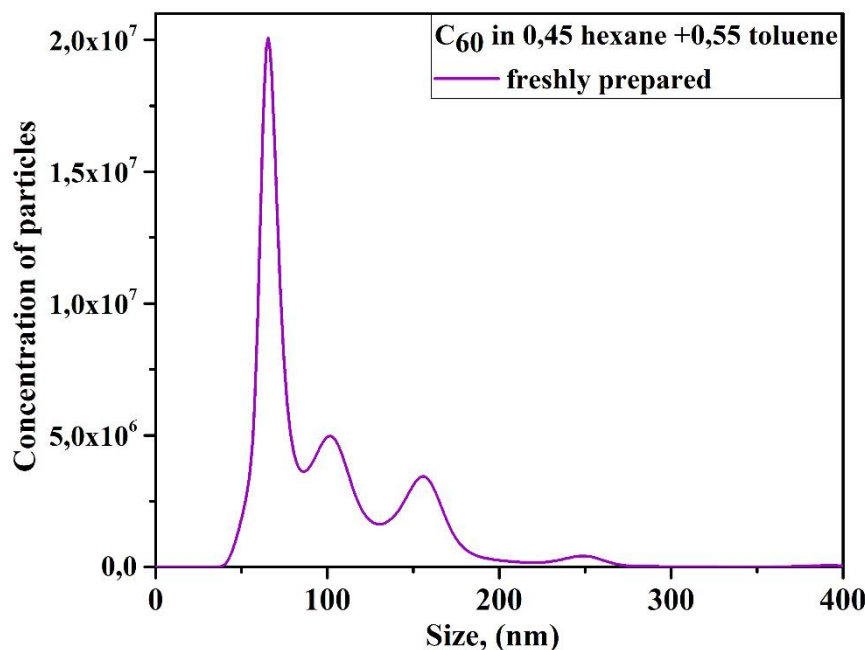


Figure 2. DLS spectrum of the C_{60} hexane/toluene sample at different storage times. The fixed concentration of C_{60} fullerene in solution was 0.1 mg/ml.

Toluene is a comparatively good solvent for C_{60} due to π - π interactions between the aromatic ring and the fullerene cage, whereas hexane is a poor solvent owing to its non-polar, aliphatic character and the absence of comparable electronic interactions. In the hexane/toluene mixture used here, the reduced overall solvation power relative to pure toluene promotes nucleation and growth of C_{60} nanoclusters through a solvent-mediated self-assembly process, in which individual C_{60} molecules first form small nuclei that subsequently aggregate into larger.

The dominant ~ 65 nm population most likely corresponds to the primary, kinetically stable nanocluster species formed shortly after mixing, representing an early stage of aggregation in which nucleation has proceeded to a well-defined, relatively narrow size regime. The appearance of additional, lower-intensity peaks at ~ 100 nm and ~ 155 nm can be attributed to secondary aggregation events, in which primary ~ 65 nm clusters collide to form larger, less abundant assemblies. This stepwise progression rather than a single continuous distribution suggests that cluster growth in this solvent system proceeds through discrete, quantized aggregation states rather than a purely random coalescence process, a behavior that has also been reported for C_{60} nanoclusters formed via solvent-exchange methods in other binary solvent systems. The minor shoulder near 250 nm, though low in relative intensity, indicates that a small subpopulation of larger aggregates is already present, even before any extended storage. This is an important observation because it implies that the nucleation and early-stage growth of C_{60} clusters begin essentially immediately upon mixing and are not solely a function of long-term storage.

UV-Vis spectra of C_{60} solution in the hexane/toluene

The UV-Vis spectrum of a freshly prepared C_{60} solution in hexane/toluene is shown in Figure 3. The observed peak in the region of 405–410 nm is attributed to C_{60} and is due to electronic transitions in the fullerene cage. Accordingly, since hexane is a poor solvent for fullerenes, a large portion of C_{60} is still dissolved as single molecules. After this peak in the region of 450–600 nm, the absorption drops sharply and forms a band of low intensity. These weakly visible spectra are characteristic of C_{60} and are usually explained by slightly visible transitions when the solvent medium breaks the symmetry of the molecule.

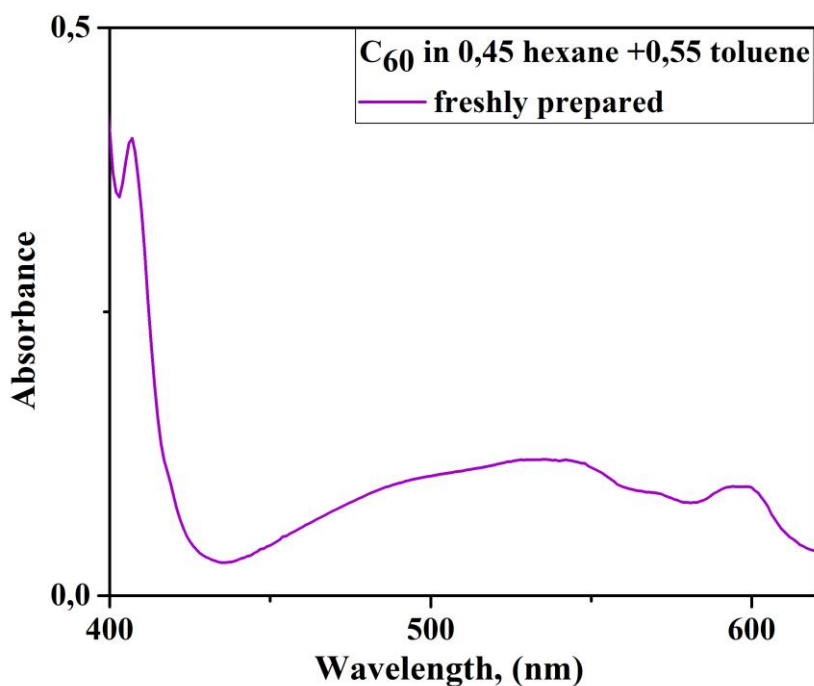


Figure 3. Changes in the UV-Vis absorption spectra of C₆₀ in a hexane/toluene. C₆₀ concentration is constant and ~0.1 mg/ml.

The slightly raised baseline across the visible range may also reflect a small contribution from light scattering, suggesting that not all C₆₀ remains as isolated molecules but that some degree of association into larger species is already present in the freshly prepared solution. This behavior can be explained by the balance of intermolecular forces in the mixed solvent. C₆₀ molecules interact with each other mainly through **van der Waals forces**, which are weak individually but become significant because of the large, polarizable surface of the fullerene cage. In good solvents like toluene, **π - π interactions** between the aromatic ring of toluene and the C₆₀ surface help keep molecules apart by surrounding them with solvent. Hexane, however, is non-polar and lacks an aromatic ring, so it cannot form these favorable interactions with C₆₀. As the hexane fraction increases, C₆₀-solvent interactions weaken relative to C₆₀-C₆₀ van der Waals attraction, an imbalance often described as a **solvophobic effect**. Because of this effect, individual C₆₀ molecules tend to associate with one another rather than remain fully solvated, favoring the onset of molecular aggregation. This process can begin quickly once hexane is introduced into the toluene solution, which may explain the small optical changes observed even in the freshly prepared sample.

Conclusion

The excess refractive index of hexane/toluene solutions was negative across the entire composition range, reaching its minimum at ~ 0.55 mole fraction of toluene, reflecting strong molecular-packing asymmetry between the components. Using this solvent composition, C₆₀ solutions displayed a multimodal DLS distribution dominated by ~65 nm nanoclusters, alongside minor populations at ~100, 160 and 250 nm. UV-Vis spectra confirmed coexisting molecularly dissolved and aggregated C₆₀. These results demonstrate that solvent packing anomalies directly promote C₆₀ self-assembly via van der Waals and π - π interactions.

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Foydalanilgan adabiyotlar

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