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On the Evaporation Kinetics of [60] Fullerene in Aromatic Organic Solvents

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ABSTRACT:

We investigate the effect of C₆₀ fullerene nanospheres on the evaporation kinetics of a number of aromatic solvents with different levels of molecular association, namely, benzene, toluene, and chlorobenzene. The dependence of the evaporation rate on the fullerene concentration is not monotonic but rather exhibits maxima and minima. The results strongly support the notion of molecular structuring within the liquid solvent controlled by the nature of fullerene/solvent interaction and the level of molecular association within the solvent itself.

KEYWORDS: evaporation kinetics; structuring in aromatic solvents; fullerene; Raman spectroscopy, Molecular mechanics; simulation, Colligative properties.

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1. INTRODUCTION

A number of scientific, technological, industrial, and environmental issues such as industrial drying processes, crude oil recovery and distillation processes [1], occupational health and environmental assessment of hazardous spills [2-6], and the formation of self-assembled structures [7-9] and Langmuir Blodgett monolayer films [10-14] critically depend on the evaporation kinetics of solvents and solvent mixtures. While the original thermodynamic work of Raoult and Henry on solutions as well as the molecular theory of liquids has established a strong foundation for understanding the thermodynamic behavior of liquid mixtures, and other studies [2, 15-29] on liquid mixtures have provided deep understanding of the effect of molecular interaction on the thermodynamic behavior of these systems, the expanded interest in fullerene nano-particles necessitates more elaborate investigations addressing the effect of the fullerene on the solvent thermodynamic behavior. Such effect has been addressed before [30-36] but is still not fully understood. In the present paper, we investigate the effect of C_{60} molecules on the evaporation kinetics of a number of aromatic solvents with different levels of molecular association in order to address the effect of C_{60} concentration and the effect of inter-molecular association within the aromatic solvent of the evaporation kinetics of the solution.

2. EXPERIMENTAL DETAILS

In this study, we investigate three different aromatic solvents, namely, benzene, toluene, and chlorobenzene, as models of aromatic solvents representing weak, moderate, and strong inter-molecular interactions or solvent association.

2.1. Evaporation Kinetic Experiments

A gravimetric method was used to determine the weight loss as a function of time for different C₆₀/solvent solutions. The solutions were prepared using chromatography grade solvents and Sigma Aldrich C₆₀ (99.5%) with different concentrations covering the concentration range from pure solvent up to saturation limit (for benzene, 1.6 g/l equivalent to C₆₀ mole fraction of 1.98×10^{-4} , for toluene, 2.8 g/l, equivalent to C₆₀ mole fraction of 4.12×10^{-4} , and for chlorobenzene, 7 g/l equivalent to C₆₀ mole fraction of 9.85×10^{-4}). Each sample was prepared and then sonicated in a 60 MHz ultrasonic bath (Fisher Scientific, Model FS20) for 30 minutes before the start of the experiment. 100 μ l of each solution were added to the cylindrical crucible (12 mm in diameter) of a sensitive balance (Nima Technology UK, 1222D2, with weight measuring resolution of 0.1 mN). The sample weight was automatically recorded as a function of time by a personal computer as the solvent evaporated from the solution at room temperature (298 K) and atmospheric pressure. Each test was repeated three times to ensure reproducibility. Evaporation rates reported in this study are the solvent percentage weight loss per unit time (second). Note that the surface area of the crucible was constant in all experiments. It is also important to mention that the experiments were conducted in the typically controlled laboratory environment (temperature 294 ± 1 K, pressure of 100 ± 1 KPa., and humidity of $50 \pm 5\%$). No special precautions were employed to control local temperature, pressure, and level of humidity around the crucible during the experiment (such as the use of controlled environment chamber or a ventilating hood). Results reproducibility and the clear trend of the measured experimental behavior, however, leaves no room for addressing or arguing any significant or measurable effect of such local fluctuations if, indeed, they took place.

2.2. Raman Spectroscopy Measurements

Raman spectroscopy measurements were conducted using a Renshaw®, inVia™ Raman Microscope, equipped with an Ar⁺ laser at 514.5 nm wavelength as excitation light source in the back-scatter arrangement with a laser power of 2 mW at the sample surface to avoid sample overheating. Solution samples were tested while in a specialized liquid cell (Starna Cells- CA-USA 28B-G-5). A glass spectrophotometer cell designed to maximize internal scattering and enhance the Raman signal of the liquid samples under investigation.

2.3. Molecular Mechanics Simulations

Classical molecular mechanics simulations were performed using Dassault Biovia Materials Studio, Forcite® Module. Hexagonal ensembles, with periodic boundaries, containing a C₆₀ molecule and 6,12,24,36, and 48 molecules of the different solvents, randomly distributed around the fullerene molecule, were simulated. The ensembles were first optimized using a universal force field with energy, forces, and displacement tolerances of 1×10^{-4} kcal/mole, 0.005 kcal/mole/Å, and 5×10^{-5} Å, respectively. In Forcite® Module, the optimization process includes the optimization of the cell parameters and the position of the contents within the cell to achieve system minimum energy. While initial cell dimensions were selected to accommodate the increasing number of constituents, the equilibrated (final) cell dimensions were determined by the calculations as equilibrium achieved. The ensemble equivalent isotropic bulk modulus was calculated and compared for the three solvents investigated in this study. Molecular simulation is mainly based on inter and intra-molecular force interactions, it is not capable of including the entropic effects of the system. Hence, while we understand that the simulation can only shed light on the enthalpic aspects and effects in the system, it is still important, since it will enable

the separation between the enthalpic and entropic roles in the experimentally observed behavior of the system.

3. RESULTS

3.1. Evaporation Kinetics

The solvent weight loss (ΔW) is calculated as a percentage of the initial solvent content of each sample (W_0). Figure 1 shows typical $\Delta W/W_0$ %ages plotted as a function of time. The experimental data are found to accurately fit to a second-degree parabola of the form

$$\frac{\Delta W}{W_0} \%age = Y = at - bt^2 \quad (1)$$

where t is the time in seconds, and a and b are constants. The initial evaporation rate (IEV) corresponding to dY/dt at $t = 0$ is the parameter a in eqn. (1). The consistency in the measured IEVs for each of the tested solutions is in the range of 0.0001. The IEVs plotted as a function of initial fullerene mole fraction for chlorobenzene, toluene, and benzene are shown in Figure. 2a, 2b, and 2c, respectively. In Fig. 3, we plot the IEV (normalized according to the IEV of the pure solvent) as a function of fullerene concentration (normalized according to the saturation concentration in that particular solvent) in order to compare the evaporation kinetics and behavior for each of the three systems investigated.

For chlorobenzene, Fig. 2a, the IEV increases nonlinearly with increasing C_{60} concentration in the solution. A maximum in the IEV is observed at 70% of the saturation limit (equivalent to a C_{60} mole fraction of 7×10^{-4}). The IEV at the maximum level is 2.5 times that of the pure chlorobenzene solvent. The IEV of the solution, however, decreases at higher C_{60} concentrations. The IEV of the fully saturated solution is still 20% higher than that of the pure chlorobenzene solvent.

For toluene, Fig. 2b, the measured IEV is found to increase with increasing C_{60} concentration in the solution as well. A maximum in the IEV is observed around 35% of the saturation concentration (equivalent to a C_{60} mole fraction of 1.48×10^{-4}). A sharp drop in the IEV is observed followed by another nonlinear increase as the C_{60} concentration is increased. At its maximum, the IEV of the C_{60} /toluene solution is measured to be only 10% higher than that of the pure toluene. Also, the IEV of the fully saturated solution is about 10% higher than that of the pure toluene.

For benzene, Fig. 2c, the dependence of the IEV of the solution on the C_{60} concentration is more interesting than for the previous two cases. In fact, it shows a number of maxima and minima as the C_{60} concentration is increased. It is interesting to note that the highest evaporation rate recorded is 2.3 times that of pure benzene. While the first evaporation rate maximum is observed at 0.2×10^{-4} mole fraction, three other maxima are observed as the C_{60} mole fraction is increased, roughly around 0.6×10^{-4} , 1.0×10^{-4} , and 1.6×10^{-4} mole fractions. The evaporation rate at these maxima decreases linearly as the fullerene concentration is increased. The IEV of the fully saturated solution is measured to be 20% higher than that of the pure benzene solvent.

3.2. Molecular Mechanics Simulations

Figure 4 depicts an example of a geometrically optimized molecular ensemble used in the current molecular mechanics simulations with a fullerene molecule interacting with 24 molecules of chlorobenzene within periodic boundary conditions. A 3×3 supercell is also shown in the figure. It is clear from the figure that the equilibrated (energy minimized) structure exhibits an open structure nature due to the complex multi-body enthalpic interaction in the investigated

ensemble. Figure 5 a, b, and c depicts the calculated equivalent isotropic bulk modulus of the ensemble plotted as a function of the number of solvent molecules interacting with a single fullerene molecule for the solvents benzene, toluene, and chlorobenzene, respectively. It is important to note that the x-axis in all plots is reversed to resemble the experimental results in which the fullerene concentration in the system increases from left to right as shown by the added arrows in Figure 6, a, b, and c. While the simulation results do not resemble the experimental data quantitatively, as discussed in the experimental section, the results clearly show that qualitatively the three systems behave exactly as observed in the experimental results; the simulation results show for benzene that the bulk modulus decreases linearly with increasing fullerene concentration, for toluene a sinusoidal inflection with the bulk modulus decreasing and then increasing as the fullerene concentration increases in the system, and for chlorobenzene that the bulk modulus decreases to reach a minimum and then increases as the fullerene concentration increases in the system. Noting that the solvent evaporation rate does indirectly depend on the bulk modulus, it is clear that the current simulation results agree with the experimental evaporation kinetic results and show that the complex solute/solvent and solvent/solvent enthalpic interactions are crucial for the behavior of the investigated systems.

3.3. Raman Spectroscopy

In the analysis of the Raman spectroscopy data we focus on three important aspects of a Raman investigation: the shifts in peak position of the solvent molecules shedding light on the solvent/solvent interaction, the integrated intensity of solvent Raman bands (area under the fundamental bands of the solvents) providing insight in the quantitative presence of the solvent species within the laser/solvent interaction volume (typically in the range of $1 \mu\text{m}^3$), and the

shifts in the fundamental Raman bands of the fullerene molecules that give insight in the fullerene/solvent interactions.

Figure 7 a, b, and c depicts the integrated intensity of solvent Raman bands as a function of the normalized fullerene concentration (i.e., 0 refers to pure solvent and 1 refers to saturation) in the cases of benzene, toluene, and chlorobenzene, respectively. In all figures, it is clear that the integrated intensity of the solvent is reduced linearly as the concentration increases, a result that is very well expected as the solvent concentration in the system is reduced. The interesting and important part of the results is the further reduction (minima) in the integrated intensity observed superimposed on the linear reduction. For benzene (Figure 7a), four minima can be observed around 0.1, 0.3, 0.5, and 0.8 fullerene normalized concentration. These minima are well aligned with the four maxima observed in the benzene evaporation rate (Figure 3). For toluene (Figure 7b) two minima can be observed around 0.3 and 0.7 concentration in close agreement with the maximum near 0.3 concentration and the full recovery of the minimum in the toluene evaporation rate (Figure 3). For chlorobenzene two minima are observed (between 0.2 and 0.3 and between 0.6 and 0.7 concentration). These minima are, again, very close to the maxima observed in the chlorobenzene evaporation rate (Figure 3).

Figures 8 a, b, and c, shows the shift in Raman fundamental bands as a function of the normalized fullerene concentration of the solution for benzene, toluene, and chlorobenzene, respectively. In the case of benzene (Figure 8a), four maxima (indicating blue shifts) can be observed around 0.1, 0.3, 0.5, and 0.8 concentration. It is also important to note that the observed peak position shifts are within 1.5 to 2 wavenumbers. While such shift is not huge, it is still 10 times the resolution of our Raman spectrometer. In the case of toluene (Figure 8b) a blue shift maximum is followed by a red shift minimum (around 0.3 and 0.7 concentration). The results

indicate that both the molecular in-plane and out-of-plane modes show the same behavior as observed for the system's evaporation. It is also interesting to note that the shifts observed for the in-plane mode (around 520 cm^{-1}) are in the range of 5 wavenumbers. This is much larger than in benzene, but much smaller than the shifts (in the range of 20 wavenumbers) recorded for the out-of-plane mode (around 890 cm^{-1}). In the case of chlorobenzene (Figure 8c) the fundamental chlorobenzene band around 300 cm^{-1} assigned to in-plane hydrogen rocking and out-of-plane chlorine asymmetric bending (see insert) shows two blue shift maxima around 0.2 and 0.6 concentration. The fundamental band around 1000 cm^{-1} assigned to in-plane stretching of hydrogen atoms combined with pinching of carbon atoms (see insert) shows, in turn, a single blue shift maximum centered around 0.5 concentration. Such blue shifts are indicative of more restricted thermal fluctuations experienced by the solvent molecules or, in other words, a structures solvent environment.

Figure 8 depicts the peak position of the fundamental fullerene molecule band around 1580 cm^{-1} as a function of the normalized concentration of the three solvents used in our study. The figure shows the response of the fullerene molecule to the solvent environment around it: two blue shift maxima centered around 0.3 and 0.7 concentration with a very clear decrease in the Raman peak position shift in the direction from chlorobenzene to benzene. This experimentally measured behavior is in excellent agreement with the fact that the strength of interaction between the solvent and fullerene decreases from chlorobenzene to benzene, and, hence, the lower fullerene fundamental shifts.

4. DISCUSSIONS:

Our current investigation shows that evaporation rates as a function of fullerene mole fraction, in the investigated aromatic solvents shown in Figs. 2-4 are very unique indeed. The results showed that, in all cases, the saturated fullerene solutions had a higher evaporation rate than pure solvents. These results are in excellent agreement with what Ginsburg et al. have reported [37-41]. The unique finding of our current results is the very clear maxima and minima behavior measured. Such behavior was different than that reported for fullerene molecules interacting with water which showed a linear decrease in the water evaporation rate as the fullerene concentration is increase up to saturation level [36]. For aromatic solvents of this type, in general, it has been shown that as the C_{60} fullerene molecules are dissolved in aromatic solvents, a highly bonded layer of the aromatic solvent is formed around the fullerene molecule. Such a solvent shell is reported to be so strongly bound to the limit that it survives thermal evaporation up to the point where C_{60} starts to sublime [42]. The formation of such tightly bonded C_{60} /solvent clathrates is accompanied by the formation of a thicker region of open structured solvent molecules (a solvophilic shell) that extends away from the C_{60} /solvent clathrates. It is important to emphasize here that, as we refer to structuring in liquid solvents, we typically mean a state of depressed thermal fluctuations. The formation of such open structured solvent is what is believed to result in the higher solvent evaporation rate observed in this study and similar other studies, as has been reported in the literature [30, 31, 33, 35, 37-41, 43]. Current Raman spectroscopy measurements and molecular mechanics calculations point clearly to the interpretation of the evaporation rates results along the notion of restricted thermal fluctuation in the solvent (blue shifts in the Raman band positions leading to a more open i.e. less dense and less bulk modulus) as confirmed by molecular mechanics results. The amazing agreement among

the evaporation kinetics, spectroscopic shifts, and bulk modulus trends do, indeed, leave no room for doubt regarding our current interpretation.

To this end, it is expected that, as the fullerene mole fraction is increased in the fullerene/aromatic solvent system, the volume fraction of the solvophilic open structure regions also increases and, hence, the measured evaporation rate increases. Such a notion is also in agreement with the measured increase in solution compressibility, using Brillouin spectroscopy [44], since an open structure with higher compressibility would, unsurprisingly, have lower cohesive energy density and, hence, would exhibit a higher evaporation rate.

A maximum in the evaporation rate can be understood along the notion that at certain C_{60} mole fraction within the system the open structured solvent around the fullerene molecules is maximized, and so is the evaporation rate. It is important to note that the extent of the open structured solvent around a fullerene structure will depend on the fullerene/solvent interaction. More importantly, the stability of the open structured solvent will depend on the solvent/solvent interaction. Associative solvents are expected to be able to sustain such structuring more than non-associative solvents.

Once a maximum in the evaporation rate is reached, indicative of a maximum in the volume of the open structured solvent within the system, any increase in the fullerene mole fraction is expected to reduce the volume of the open structured solvent by tightly binding some of the solvent molecules to the newly introduced fullerene molecules in the system. This would result in a reduction in the measured evaporation rate, as observed in Fig. 2. Following the same notion, as the increased evaporation rate can be understood on the basis of solvent restructuring (the formation of more open structured solvent), the measured loop-like behavior with sudden

drop in the evaporation rate in the case of toluene (Fig. 3) can be understood as a phase transition in the solvent that takes place around a fullerene mole fraction of 1.6×10^{-4} and leads to a more ordered and tightly bound structure (at least as ordered as the original, undisturbed pure toluene) with low evaporation rate. To this end, the measured loop-like behavior can be explained as follows: The formation of a toluene shell that is tightly bound to a fullerene molecule causes the creation of a solvophilic shell that has a higher rate of evaporation than pure toluene. As the fullerene mole fraction is increased more such solvophilic shells are created and, hence, the measured evaporation rate increases. As the fullerene mole fraction reaches 1.48×10^{-4} , apparently, the solvophilic shells have connected to each other, rendering a medium with maximum evaporation rate (the maximum in Fig. 3). Further increase in the fullerene mole fraction beyond the maximum would lead to the creation of more clathrates and would force the formation of tightly bound toluene molecules at the expense of the solvophilic network already maximized in the system. This should lead to a gradual reduction in the evaporation rate as observed in the C_{60} /chlorobenzene system (Fig. 2). The fact that the observed reduction in the evaporation rate in the toluene case, however, is rather a drop than a gradual decrease, most plausibly indicates a collapse in the open structured toluene formed around the fullerene molecules. Further increase in the fullerene mole fraction (beyond 2.1×10^{-4}) apparently disturbs such tight structure, causing the observed relative increase in the evaporation rate (Fig. 3). Such explanation is along the same notion as the interpretation of super-molecular structures observed, using small angle X-ray spectroscopy SAXS, in both toluene and p-xylene interacting with C_{60} [30]. The interpretation is also in agreement with recent thermodynamic investigations of enthalpic interactions between C_{60} and aromatic solvents which concluded that the interactions are mainly entropically controlled [34, 45].

The collapse of the open structured solvent in the case of toluene and not chlorobenzene mentioned above indicates that chlorobenzene is more capable of supporting an open structure around the fullerene molecules than toluene. This is basically supported by the fact that chlorobenzene is a more associative solvent than toluene with higher values of dipole, surface tension, and boiling point. At the point of maximum evaporation rate it is possible to calculate the radius of the solvophilic sphere formed around the fullerene molecules to get a rough estimate for the long-range structuring effect of C_{60} in the solvent [30, 35]. If we model the system at this fullerene mole fraction as a number of fullerene/solvent clathrates surrounded by spherical shells of open structured solvent, the volume of the spherical shells can be estimated, which gives the radius of the solvophilic sphere formed around the fullerene molecules or the range of the fullerene-affected zone within the solvent.

In the case of chlorobenzene, the maximum evaporation rate is observed at a C_{60} mole fraction of 7×10^{-4} (see Fig. 2), hence, using the established mole volume of $101.405 \text{ cm}^3/\text{mole}$ for chlorobenzene, the volume of chlorobenzene surrounding each fullerene molecule (after dividing by Avogadro's number) can be estimated as $2.4 \times 10^{-19} \text{ cm}^3$ or 240 nm^3 . Such a volume represents a spherical shell with an inner radius equal to that of the fullerene/solvent clathrate. Based on density functional theory, we determine the effective radius of the fullerene/solvent clathrate to be 1.05 nm, 0.85 nm, and 0.80 nm for chlorobenzene, toluene, and benzene, respectively (taken as the inner radius of the spherical shell). This renders a value of 8.3 nm for the outer radius or, in other words, the long-range interaction distance around the fullerene molecule. In the case of toluene, the maximum evaporation rate is observed at a C_{60} mole fraction of 1.48×10^{-4} (see Fig. 3), hence, using the established mole volume of $92.14 \text{ cm}^3/\text{mole}$ for toluene, the volume of toluene surrounding each fullerene molecule can be estimated as $1.19 \times 10^{-18} \text{ cm}^3$. This renders a

value of 6.6 nm for the outer radius. Hence, while chlorobenzene can support an open structured shell with a radius of 8.3 nm, toluene can only support a shell with a radius of 6.6 nm. This result is in agreement with the fact that chlorobenzene is a more associative solvent than toluene. It should be noted that the calculated radii of interaction within the investigated solvents represent the minimum interaction distance due to the fact that we use the density of undisturbed solvents in our calculations. Disturbed solvents (more open structure) are expected to have a lower density; hence, the interaction range is expected to be longer than the distances calculated here.

Based on the above discussion, the evaporation rate of fullerene solution in a non-associative solvent (i.e., a solvent not capable of sustaining solvophilic shells), such as benzene, should show a series of maxima followed by collapse behavior as observed in Figs. 4 and 5. In this case, as fullerene molecules are added to benzene, the formation of a tightly bound shell followed by a very unstable open structured shell would result in an increase of the evaporation rate. The collapse of such unstable open structured shells then would reduce the observed evaporation rate and subsequent cycles would be observed. It is important to note that the observed steady decrease in the evaporation rate at the consecutive maxima further supports the current interpretation of the results. A total of four evaporation rate maxima is observed around 0.2×10^{-4} , 0.6×10^{-4} , 1.0×10^{-4} , and 1.6×10^{-4} fullerene mole fractions, as shown in Fig. 4. Following the above method and using the established mole volume of benzene of $89.12 \text{ cm}^3/\text{mole}$, the long-range interaction distances around a fullerene molecule corresponding to each maximum would be 12.0 nm, 8.4 nm, 7.1 nm, and 6.0 nm, respectively.

In this context, it is important to address the fact that the observed oscillations in the evaporation rates of the investigated solutions as a function of fullerene concentration are not quite in agreement with the established colligative properties [46-49]. The essence of colligative

properties is that as a solute is added to a solvent the solvent molecules are diluted and, hence, its molar entropy increases solely based on the mole fraction of the solute and independently of the nature of the interaction between solute and solvent. Assuming a Raoultian behavior for the solvent, the value of its molar entropy in solution can be determined as

$$S_m = S_m^o - R \ln x_s \quad (2)$$

where S_m and S_m^o are the molar entropies of liquid solvent in the solution and pure state, respectively, R is the gas constant, and x_s is the mole fraction of solvent in the solution. Such increase in the molar entropy of the solvent in the solution is a direct result of the increased randomness of its molecules in the system and has been associated, for several decades, with the phenomena of melting point depression, boiling point elevation, and vapor pressure depression in solutions where the solute has molecular size comparable to that of the solvent molecules, such as rock salt in water [50]. However, it is scientifically valid to argue that when the presence of a solute molecule results in a structuring phenomenon in the solvent (it is important to emphasize again that, as we refer to structuring in liquid solvents, we mean a state of depressed thermal fluctuations) then the essence of the colligative properties theory is violated and the molar entropy of the liquid solvent should not increase steadily with the solute mole fraction, according to eqn. (2), but rather should depend on the exact nature of the formed structure in the solvent. The question would boil down to: At what solute size is deviation from colligative properties behavior observed? In a recent study, Amer and Wang [36] have measured a 14 °C elevation in the boiling point of C₆₀/water saturated solutions, which is almost 4 orders of magnitude higher than the evaporation point elevation predicted by the colligative theory. The evaporation point elevation, according to the colligative properties theory, can be calculated as

$$\Delta T = i k_b m \quad (3)$$

where ΔT is the change in the evaporation temperature for the solution, i is the van 't Hoff factor (equal to 1 in the fullerene case), m is the solution molality, and k_b is the ebullioscopic constant of the solvent. Applying eqn. (3) to the case of the fully saturated C_{60} /water solution, with a concentration of 1.6 g/L, the molality is 2.22×10^{-3} mole/L. Using the documented value for the ebullioscopic constant of water, $k_b = 0.52$ °C/m [50], the elevation in evaporation point is around 1.2×10^{-3} °C. Such deviation from the well-established colligative properties behavior can be explained by water structuring, a postulate that has been confirmed by calculating the molecular entropy of the solvent (water) as a function of the solute (fullerene) concentration and showing that it decreases linearly with increasing solute concentration (solvent structuring in a more close packed form) [36]. Similar experimental results have been reported for C_{60} in benzene and *p*-xylene solutions, where three and two orders of magnitude difference have been observed in the evaporation point, respectively [39]. Hence, our current results along with previous results published in the literature raise the important question about the validity of the colligative properties theory in systems containing nanosized solutes that are well into the nanoscale regime.

5. CONCLUSIONS

We have investigated the effect of fullerene nanospheres on the kinetics of evaporation for three aromatic solvents with different levels of molecular association. In addition to the observed dependence of the evaporation rate on the fullerene concentration in the solution, the results indicate that such dependence is controlled by the level of association within the aromatic

solvent. The results of evaporation kinetics, Raman spectroscopy, and molecular mechanics simulations can be interpreted based on structuring within the solvents leading to the formation of open structures that promote higher evaporation rates. Such structuring is clearly controlled by the exact nature of the fullerene/solvent interaction as well as the level of molecular association within the aromatic solvent, which, in turn, determines the stability of the open structured solvent. Our, and other, recent results on nano-particle solutions point out the crucial role played by the solute size and shape as well as the level of interaction among the solvent molecules for a system's behavior, a phenomenon that calls for fundamental review of the colligative properties theory to account for the aforementioned factors.

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FIGURE CAPTIONS:

Figure 1. Typical weight loss as a function of time for two C_{60} /benzene solutions depicting results consistency.

Figure 2. Normalized initial evaporation rate as a function of fullerene mole fraction in a) chlorobenzene, b) toluene, and c) benzene. The curve is a cubic spline fit to guide the eye.

Figure 3. Normalized initial evaporation rate as a function of normalized C_{60} concentration for all aromatic solvents investigated in this study.

Figure 4. Ensemble of one fullerene molecule interacting with 24 chlorobenzene molecules under constant temperature and pressure as used in the molecular mechanics simulations.

Figure 5. Molecular mechanics bulk modulus results for the fullerene/ a) benzene, b) toluene, and c) chlorobenzene ensembles. Note the reversed x-axis to represent the correct direction for comparison with the experimental results.

Figure 6. Integrated intensity of Raman fundamental modes in a) benzene, b) toluene, and c) chlorobenzene as a function of normalized fullerene concentration, showing local reduction in benzene molecule concentration indicative of less solvent molecules within the laser interactive volume. Dashed lines are smooth fits to guide the eye.

Figure 7. Measured shifts in Raman fundamental modes of a) benzene, b) toluene, and c) chlorobenzene as a function of fullerene normalized concentration. Dashed lines are smooth fits to guide the eye.

Figure 8. Measured shifts in fullerene Raman fundamental modes as a function of normalized fullerene concentration for all three aromatic solvents investigated in this study. Dashed lines are smooth fits to guide the eye. Shifts in pure solvents are fixed at zero for comparison reasons.

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 3

Figure 4.

Figure 5a

Figure 5b

Figure 5c

Figure 6a

Figure 6b

Figure 6c

Figure 7a

Figure 7b

Figure 7c

Figure 8