Effect of Fullerene Nano-spheres on Evaporation Kinetics of Fluids

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Effect of Fullerene Nano-spheres on Evaporation Kinetics of Fluids

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering

By

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B.ENG., Sichuan University, 2009

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Abstract


As the interest in fluid evaporation kinetics keeps increasing, it’s inevitably noticed that fullerene nanospheres play an important role on it. In this study, we investigate the C₆₀ nanospheres' effect on the evaporation kinetics and thermal transitions of different solvents (water, chlorobenzene) over the entire range of solubility. According to distinct polarity of different solvent, fullerene solution would behave differently, the trend of increasing in evaporation rate as the concentration increased was observed in aromatic solvents while the rate kept decreasing in water. The result of differential scanning calorimetry (DSC) and Raman spectroscopy provided an evidence about structuring in water explaining the above phenomena. Our results are in agreement with molecular dynamic simulations and strongly support the notion of molecule structure inside the solution resulting in the observed changes in evaporation rates and thermal transitions.

Key words: fullerene nanosphere, evaporation kinetic, gravimetric method, chlorobenzene, water, differential-scanning calorimetry(DSC), Raman spectroscopy.
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1. **Introduction**

Evaporation kinetics of liquids and liquid mixtures are crucial for a number of scientific, technological, industrial, and environmental issues. These include 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 \(^7,8\) and Langmuir Blodgett monolayers \(^9\).

Water evaporation kinetics are, perhaps, the most pressing in recent years. Water supply plays an essential role in urban life, to this point, evaporation kinetics of liquids and liquid mixtures are crucial for groundwater management \(^10\). A number of scientific, technological, industrial, and environmental issues rely on it. Take East Africa as an example, annual water losses through evaporation generally amount to six feet and in some cases are reported to be as great as ten feet, which poses a big issue to country’s economy and people’s life \(^11\). As the urbanization develops rapidly since 1950s, population growth places a huge pressure on water provision. With increasing water demand (at a rate of roughly 10% annually), climatic change will exasperate groundwater utility. The problem of water evaporation induced drought not only affects the metropolitan but also suburban area where the population density is high, in order to fulfill the water demand, government spends more money on water reservoir and sanitation system. One survey shows that 59% of urban people in Africa are dependent on basic sanitation and about 8% have no sanitation system \(^12,13\).

Moreover, drought has caused disastrous damage to Africa too, up to 2011, more than 400,000 refugees are in Dadaab, Kenya, where the world's largest refugee camps are located, up to 1,500 people arriving at the camps every day \(^14\). Since last century, the
study of water evaporation suppression had been initiated. The early research was devoted to find some water evaporation suppressant with smaller density than that of water, which means the substance would float on water surface. This kind of suppressant agent needs some standard properties, for example, it has to be non-toxic and flavorless, moreover, easily handled and insoluble in water. Suppressant agent will form a film upon the surface of water, which can prevent the heat from going inside the water, and it must allow the oxygen to go into water, however, the suppressant’s toxicity to aquatic life and effect are still in debate. Recent studies on liquid mixtures have provided deep understanding of the effect of molecular interaction on the thermodynamic behavior of these systems. However, the expanded interest in fullerene nanoparticles necessitates investigating fullerene effect on solvent thermodynamic behavior. This subject has been less investigated, and is still far less understood. In this study, we investigate the influence of fullerene nano-spheres on solvent evaporation kinetics of distinct fullerene solutions.

1.1 Water, toluene and chloro-benzene as model solvents

Before we detail the reason we choose water toluene and chloro-benzene as our solvent for solution, we start with a definition first: chemical association, the aggregation of atoms or molecules into larger units held together by forces weaker than chemical bond, that bind atoms in molecules. The term is usually restricted to the formation of aggregates of similar molecules or atoms. Commonly the force in solvent would be dipole, which mostly appeared between polar molecules, e.g.
hydrogen bonds between water molecules. So we separate liquid into two catalogs: associative liquid and unassociative liquid.

The solvents we selected are water, toluene and chloro-benzene. First we go into water structure in molecule scale, see in Figure 1.1\textsuperscript{[37]}. Large number of intermolecular hydrogen bonds can be formed in water, which leads to a strong interaction between \( \text{H}_2\text{O} \) molecules, as a result, water is a polar molecule. The structure of chloro-benzene is showed in Figure 1.2 \textsuperscript{[38]}.

Chloro-benzene (\( \text{C}_6\text{H}_6\text{Cl} \)) is a polar molecule, result from the strong dipole-dipole interaction. This is because of the chlorine molecule has high electro-negativity. The dipole moment of Chlorobenzene is 1.59 debyes at room temperature atmosphere, while in pure water it is 1.87 debyes \textsuperscript{[39]}.

Figure 1.3 illustrates the structure of toluene. Toluene is an aromatic compound which is non-polar, and the inter-molecular force between toluene molecules is very weak.

Compare the structure of water, chlorobenzene and toluene and intermolecular interaction, we can arrive at a conclusion. Water molecule is surely hydrophilic molecule, and toluene molecule is totally lipophilic, in another word, hydrophobic, meanwhile, chlorobenzene molecule shows amphiphilic characteristics, it exhibits lipophilic properties because of its benzene circle, and in possession of polar function group chlorine, which leads to hydrophilic \textsuperscript{[40-44]}. These crucial solvent properties will be compared with the interactions of fullerene to solvent discussed below.
Figure 1.1 Hydrogen-bonds between H\textsubscript{2}O molecules
Figure 1.2 Structure of chloro-benzene
Figure 1.3 Structure of Toluene
1.2 Fullerenes

The most famous form of fullerene molecule is [60]fullerene or C$_{60}$, made of 60 carbon atoms in a spherical shape that resembles a soccer ball, commonly known as buckyball. The existence of C$_{60}$ was predicted by Eiji Osawa of Toyohashi University of Technology in 1970 [45-47]. The fullerene (C$_{60}$) has a unique cage-like structure, which composed of 12 pentagons and 20 hexagons (Figure 1.4). It’s easy to observe C$_{60}$ is a totally non-polar molecule, result from the well-defined highly symmetric structure.

Because of C$_{60}$’s unique structure, it’s important to realize the solubility of fullerene is different from other carbon allotrope, in fact, it’s the widely known allotrope of carbon can be dissolved in common solvents at room temperature atmosphere, till now, C$_{60}$ solubility is known in over 150 solvents [48]. In Figure 1.5 [49-50], fullerene dissolved in aromatic solvents will show a purple color (deep purple for saturated) while the color of C$_{60}$/H$_2$O is brown.
Figure 1.4 Structure of C\textsubscript{60} fullerene molecule
Figure 1.5 (a) $\text{C}_{60}$ in chlorobenzene \cite{49}

Figure 1.5 (b) $\text{C}_{60}$ in water \cite{50}
1.3 Fullerene liquid interaction

The solute-solvent interaction will vary result from different factors, such as structure, polarity, etc [51-56]. From Figure 1.4, fullerene has 12 pentagons and 20 hexagons. The carbon atoms in a \( \text{C}_{60} \) molecule have their valences satisfied by two single bonds and one double bond leading to an electron configuration where the outer surface is covered with p electrons and appears to be aromatic. Thus, the high solubility implies that the solvent has a high chemical affinity to the fullerene presumably because of the strong interactions between their aromatic rings. On the other hand, \( \text{C}_{60} \) exhibits highly spherical symmetry, the entire molecule is non-polar, because the solute will show a higher solubility in solvent which has similar structure or polarity, \( \text{C}_{60} \) is an obvious hydrophobic molecule, but has solubility in aromatic solvents. In fact, \( \text{C}_{60} \) will have solubility in Chloro-benzene of 7.0 mg/ml, compared with 1.6 mg/ml in water [57-58].

1.4 Effect of fullerene on evaporation kinetics of fluid

During evaporation, the stronger the forces keeping the molecules together in the liquid state, the evaporation will be more difficult. Due to the chemical and structural characteristic of \( \text{C}_{60} \) (e.g. hydrophobic and aromatic), when added in different types of solvents, the evaporation kinetics of fluids will change correspondingly. A hydrophobic solute placed in water can behave very differently depending on the size of the solute [59-67]. Considering distinct characteristics of solute-solvent relationships and solvent-solvent interaction, which are dominating during evaporation process. In solute-solvent interaction, we define the solvent “fullerophobic” and “fullerophilic”, considering the aromatic feature of \( \text{C}_{60} \) structure, interactions between \( \text{C}_{60} \) and solvent
will totally different, which represents different solubility of C$_{60}$ in different solvents. In solvent-solvent interaction, which equals to the intermolecular force in solvent, as we illustrated above, we have associative liquid and unassociative liquid, the Chart 1. below showed the solvent belongs to different types:

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<th>Associative</th>
<th>Unassociative</th>
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<td>Fullerophobic</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>Fullerophilic</td>
<td>Chlorobenzene</td>
<td>Toluene</td>
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**Chart 1. Different types of solvent according to solvent-solvent & solvent-solute interaction**

It’s easily noticed that there is one cell empty in the chart above, the unassociative and fullerophobic solvent. In fact this kind of solvent almost does not exist, if a solvent is fullerophobic, mostly, the solvent structure will be polar, since the fullerene has nonpolar structure, which agrees with the “like dissolves alike”. However, if the solvent is polar, it will have strong intermolecular dipole-dipole interaction, then the solvent is associative, which contradict the first hypothesis the solvent is unassociative. As a result, we choose three types of solvent not four.

In this study, we investigate the evaporation rate and thermal transition temperature of three solutions. First, we will investigate the effect of C$_{60}$ concentration on solvent evaporation kinetics (water and chlorobenzene in C$_{60}$/H$_2$O and C$_{60}$/chlorobenzene solutions, respectively), the data will compared with the work done before by Dr. Maher S. Amer, the evaporation kinetics of C$_{60}$/Toluene solution. Then we test the first order thermal transition temperature (melt point) of C$_{60}$/H$_2$O solutions.
2. Experimental details

The following section describes the experimental details of the investigation conducted in this study.

2.1 Materials

Water: commercially available distilled water.

Chloro-benzene: used in this study was CHROMASOLV® for HPLC, 99.9% (Sigma-Aldrich). The solvent was used as is without any further processes.

C\textsubscript{60}: the [60] fullerene used in this study was obtained from Aldrich C\textsubscript{60} fullerene (99.5%). The fullerene was used as is without any further treatment.

2.2 Solution preparation

Saturated solution is prepared by “extracting” fullerene and dissolving it from C\textsubscript{60}/toluene solution into distilled water. Because of volatile property of C\textsubscript{60}/toluene solution, C\textsubscript{60}/toluene and distilled water was mixed in a test-tube, kept sonicating the mixture until no C\textsubscript{60}/toluene phase could be observed. C\textsubscript{60}/H\textsubscript{2}O solution was centrifuged for 1 hour at a speed of 12000 rpm in order to precipitate undissolved fullerene solute, then fully saturated C\textsubscript{60}/H\textsubscript{2}O was made. (see in Fig 2.1)
Figure 2.1 C$_{60}$/H$_2$O solution centrifuge experiment
2.3 Instrumentation and experimental procedures.

2.3.1 Evaporation kinetics measurements


A gravimetric method was employed to determine the weight loss as a function of time for 10 C\textsubscript{60}/water and 10 C\textsubscript{60}/Chloro-benzene samples, respectively. The solutions are prepared by dissolving C\textsubscript{60} into solvents with different concentrations ranging from pure solvent to fully-concentrated solutions (see in Fig 2.2).

For C\textsubscript{60}/water solution, the concentration range from pure water to saturated solution (1.6 mg/ml), we can see from Fig 2.2, with different concentrations, the color of solution will vary; for C\textsubscript{60}/chloro-benzene solution, same as C\textsubscript{60}/water sample, the concentration range from pure chloro-benzene up to saturation limit (7.0 mg/ml), 10 samples are tested. Equal-section method is adopted to divide the solution into 10 different concentrations. Each sample prepared was sonicated for 30 minutes before starting the experiment (see in Fig 2.3), to ensure all solute is dissolved and the solution is homogeneous and stable. One hundred micro liter of each solutions were added into a balance (weight measuring resolution of 0.1mN), which was attached to a sensitive pressure sensor. (Illustrated in Fig 2.4 a) and b))
Figure 2.2 Samples of C$_{60}$/water solutions of different concentration
Figure 2.3 C₆₀/water sample sonicated in sonicator
Figure 2.4 (a) Connected balance and pressure sensor
Figure 2.4 (b) Close-up photograph of water in balance
As the solution sample evaporates, changes in sample weight were recorded. We link the sensor with a computer to collect data, setting is constrained to 1 data per 5 secs. The sample weight was automatically recorded as a function of time on the computer, as solvent evaporates (water or chloro-benzene) from solution at room temperature and atmosphere.

Each test was repeated to ensure reproducibility. Evaporation rates reported in this study are the solvent (water or chloro-benzene) percentage weight loss per unit time (secs). On the other hand, 50 micro liters of $C_{60}$/chloro-benzene solution were used for every run.

Here, we can illustrate the procedure of $C_{60}$ solution evaporation kinetics by the following chart.
2.3.2 Determination of the melting point of C$_{60}$/H$_2$O solutions

The melt point as a function of concentration is tested for 5 C$_{60}$/H$_2$O solution samples.

For C$_{60}$/H$_2$O solution, the concentration range from pure distilled water to fully-concentrated (1.6 mg/ml), the solution was divided into 5 concentrations equidistantly.

In this experiment, two methods are used to examine the melt point of solution. Former one was using cubed ice to cool a vial of solution, whose temperature was measured by thermometer (accuracy 0.1°C), combined with the time elapsing recorded by stopwatch, the data was recorded every 5 seconds. At first, we considered using liquid nitrogen to cool down the C$_{60}$/H$_2$O solution, however, the liquid nitrogen posed two problems: First, if we use glass vial to prepare the solution, the glass vial would be shattered immediately as liquid nitrogen was added in, even very little amount. Second, if we change glass vial to PTFE material, we will have a new problem, it’s difficult to observe whether the thermal-couple is only in touch with the solution, not the bottom or wall of vial.

Eventually, we came across another method, the latter way was froze a vial of solution with a thermal-couple together then measured the temperature change of thermal-couple by thermometer (accuracy 0.1°C) as time elapse recorded by stopwatch.(see in Fig 2.5).
Figure 2.5 $C_{60}$ solution melt from frozen
The latter way was more applicable for it was easy to observe the condition in the vial. There is one importance need to mention that the thermometer can only measure the temperature of thermocouple’s tip. In both methods, a temperature plateau would occur which was the melt point of solution with different concentrations. Melt point reported in this paper are plateau temperatures (°C) versus different concentrations. All experiments were accomplished at room temperature and atmospheric pressure.

2.3.3. Differential Scanning Calorimetry (DSC) Measurements.

Evaporation temperature and enthalpy of evaporation were determined for water/C$_{60}$ solutions of different concentrations using a TA Instruments Differential Scanning Calorimeter Q200. Samples were heated at 5 degrees/minute rate between room temperature and 130 ºC. Figure 2.6 shows a picture of the instrument.

2.3.4. Raman Spectroscopy Measurements.

Raman measurements of water/C$_{60}$ solutions of different concentration were performed using a Renishaw® 2000 Raman microscope equipped with a 532 nm laser for sample excitation and 1800 groove/mm grating for spectral analysis. Figure 2.7 shows a picture illustration a model of the spectrometer used in this study.
Figure 2.6 TA instrument
Figure 2.7 Renishaw® 2000 Raman spectrometer.
3. Results

Figure 3.1 showed the weight loss as a function of time in two saturated C$_{60}$/water samples. The weight loss was calculated through the reading from the pressure sensor of LB, where $W_0$, and $W_f$, respectively, represented the initial weight and final weight, so $Y = \frac{W_0 - W_f}{W_0}$. In this plot $Y$ represented the weight loss and $X$ was the time in seconds, the weight loss to time was fitted to a second degree polynomial $Y = M_0 + M_1 \cdot X + M_2 \cdot X^2$, where $M_0$, $M_1$, $M_2$ are parameters. The initial evaporation rate (IEV) in this case is the parameter $M_1$ in the polynomial equation used to fit the experimental results.

Figure 3.2 illustrated the normalized IEV as a function of normalized C$_{60}$ concentration in toluene. This plot was reproduced from Prof. Amer’s work with his permission $^{[36]}$. Normalized IEV of pure solvent was fixed to 1, the following IEV were ratios between solutions and pure solvent. Normalized concentration set the saturated solution to concentration 1, while unsaturated solutions had a concentration below 1. This plot showed an increasing trend of IEV while the concentration was increasing, then IEV arrived at a peak when concentration reached around 0.35. IEV would not change until the concentration increased to 0.5, after this point, IEV restarted to grow but almost linearly.
Figure 3.1 Typical evaporation kinetic curves obtained in this study showing weight loss percentage as a function of time for a two samples of saturated C$_{60}$ in water solution.
Figure 3.2 Initial evaporation rate as a function of Buckyball concentration in toluene. [reproduced from Ref. Amer, Maher S. and Abdu, Mahmoud T. (2009), Philosophical Magazine Letters, 89:10, 615 by permission of Prof. Amer].
Figure 3.3 exhibited the initial evaporation rate (IEV) as a function of concentration of C$_{60}$/Chlorobenzene solution. From the curved showed, the IEV increased as the concentration increased before the concentration arrived at around 5 mg/ml. As the concentration increased to around 5 mg/ml, the IEV hit the peak, it stabilized as the concentration kept increasing, which was observed a drop in IEV as the concentration ascended. Unit for IEV is sec$^{-1}$.

Figure 3.4 was the normalized IEV versus the normalized concentration of C$_{60}$/Chlorobenzene solution. The pure chlorobenzene initial evaporation rate was fixed to 1, and the following IEV was recorded as the ratio to the pure sample instead of the true speed. From the x-axis, normalized concentration begun from 0 to 1, “0” represented the pure solvent, “1” represented the saturated C$_{60}$/Chlorobenzene solution. The realation between IEV and concentration was the same as Figure 3.3.
Figure 3.3 Initial evaporation rate as a function of Buckyball concentration in chlorobenzene.
Figure 3.4 Normalized initial evaporation rate as a function of normalized Buckyball concentration in chlorobenzene.
Figure 3.5 showed the average IEV as a function of C$_{60}$/H$_2$O concentration. A generally decreasing trend was observed in IEV average as the concentration increased. Actually, the IEV kept fluctuating as the concentration increased, however, the average evaporation rate gradually decreased. It started from the pure distilled water and ended up with fully-concentrated C$_{60}$/water sample, unit for IEV was denoted second$^{-1}$.

Figure 3.6 was the normalized IEV versus the normalized concentration of C$_{60}$/water solution. The pure water initial evaporation rate was set to 1, other evaporation rates were replaced by ratio of different concentration to pure solvent. Because of the decreasing trend of IEV to increasing concentration, so the following normalized rate was smaller than 1. The x-axis, normalized concentration ranged from 0 to 1, “0” represented the pure water, “1” represented the saturated C$_{60}$/water solution. The same as Figure 3.5, IEV would decrease as the concentration increased, almost linearly.

Figure 3.7 is the comparison of normalized evaporation as a function of fullerene normalized concentrations in different solvents. The figure showed BB/Chlorobenzene exhibited the highest evaporation rate but C$_{60}$/H$_2$O was the slowest, toluene was in between. Another fact observed was the IEV would increase as the solution concentration increased when solvent was toluene or chlorobenzene, and the IEV decreased as the concentration kept increasing when solvent was water.
Figure 3.5 Initial evaporation rate as a function of Buckyball concentration in water.
Figure 3.6 Normalized initial evaporation rate as a function of normalized Buckyball concentration in water.
Figure 3.7 Comparison of the normalized evaporation as a function of fullerene normalized concentrations in different solvents.
Figure 3.8 was the Differential Scanning Calorimetry (DSC) thermograms from room temperature (25°C) to 130 °C showing the heat flow of representative C$_{60}$/ water solutions as a function of temperature. Seen from the figure, different concentration would result in different first-order thermal transition temperature, as the concentration increased, the first-order thermal transition temperature (boiling point) increased. According to the Gaussian fit result. (see in Figure 3.9). Figure 3.10 showed the evaporation enthalpy of [60]fullerene solution in water at different concentrations. It is important to note that the measured evaporation enthalpy increases linearly with the Buckyball concentration in water.

From the DSC results, the boiling temperature of the BB/water solutions was also measured. Figure 3.11 showed the solution boiling point as a function of C$_{60}$ concentration in the solution. It is important to note that the boiling point also increased with increasing the [60] fullerene concentration in the solution.

According to Gibbs Free Energy definition, $\Delta G=\Delta H-T\Delta S$, during evaporation, $\Delta G=0$.

The DSC results were used to calculate the change in the evaporation entropy of water ($\Delta S_{ev}$) as shown in equation 3.1

$$\Delta S_{ev.} = \frac{\Delta H_{ev.}}{T_{ev.}}$$

(3.1)

Figure 3.12 showed the change in evaporation entropy of water as a function of fullerene saturation as normalized to the values of pure water.
Figure 3.8 Differential Scanning Calorimetry (DSC) thermograms between RT (25°C) to 130 °C showing the heat flow of representative BB in water solutions as a function of temperature.
Fig 3.9 Pure water Gaussian fit curve

\[ y = m_1 + m_2 \exp\left(-\left(x - m_3\right)^2/m_4^2\right) \]

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<th>Value</th>
<th>Error</th>
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<td>0.095185</td>
</tr>
<tr>
<td>m2</td>
<td>-67.236</td>
<td>0.27223</td>
</tr>
<tr>
<td>m3</td>
<td>99.007</td>
<td>0.018998</td>
</tr>
<tr>
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<td>4.3368</td>
<td>0.025951</td>
</tr>
<tr>
<td>Chisq</td>
<td>13757</td>
<td>NA</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9797</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure 3.10 Evaporation enthalpy of [60]fullerene solute in water at different concentrations.
Figure 3.11  Evaporation temperature of fullerene solutions in water as a function of fullerene concentration as measured by DSC.
Figure 3.12 Change in evaporation entropy (relative to that of water) as calculated according to equation $\Delta S = \Delta H/T_{ev}$, based on data acquired from DSC experiment.
In Figure 3.13, temperature was measured as a function of time for frozen C$_{60}$/water solution. Two important facts were observed from the plot. First, each solution would hit a plateau after put in room temperature, which was the first-order thermal transition temperature, it was the melting point of solution. And the melting point would increase as the concentration increased, which exhibited the same tendency as boiling point. Second, before the curve arrived at the plateau, the temperature would overshoot beyond the melting point, arrived at a peak then dropped down to stabilize during melting, this observation would not be discussed in this paper, but the phenomena were noticed in every sample.

Figure 3.14 illustrated Temperature as a function of time for frozen C$_{60}$/H$_2$O solution samples. It was observed the melting point almost increase linearly as the C$_{60}$/H$_2$O solution concentration increased. $R=0.98984$, which was rather close to 1, the curve was almost linear. The range of solution concentration was ranged from pure solvent to saturated sample.

Raman spectroscopy of the water/fullerene solutions was also measured at different fullerene concentrations. Compared the Raman spectrum of pure water, shown in Figure 3.15, Figure 3.16 showed the Raman peak positions for the three main water peaks at different fullerene concentrations. The results showed that while a red shift in the v3 mode can be observed as the fullerene concentration increased, a blue shift was observed in the v2 mode while the v1 mode did not show much disturbance. Such results indicate some sort of structuring in the water molecules as we would discuss in the discussion part.
Figure 3.13 Temperature as a function of time for frozen solution samples of fullerene buckyballs in water.
Figure 3.1 Melting points of fullerene solutions in water as a function of fullerene concentration as measured from the plateau in Figure 3.13

\[ y = -0.0061225 + 0.2415x \quad R = 0.98984 \]
3.15 Raman spectrum of pure water
Figure 3.16 Raman peak position as a function of fullerene concentration in water indicating a structuring and mostly clustering of water molecules.
4. Discussions

Based upon the experimental results obtained in this study, it is clear that Fullerene Nanospheres do affect the evaporation kinetics of different liquids. Such effect does depend on the exact nature of fullerene/solvent interaction and the specific nature of the solvent itself.

4.1 Effect of fullerene on chlorobenzene evaporation kinetics

As shown in figure 3.3, the evaporation rate (IEV) of fullerene chlorobenzene solution depends sharply on the fullerene[60] concentration in the solution. As shown in Fig 3.3 and 3.4, the IEV of the solution peaks up around the concentration of 5 mg/ml, corresponding to a high evaporation rate that is over twice of the evaporation rate of pure chlorobenzene. It is also interesting to note that the evaporation rate of the fully concentrated solution is lower, than the peak of the maximum evaporation rate, however, still higher than the pure chlorobenzene. Such behavior has been observed before [36,47] and has been interpreted along the notion of solvent structuring due to the presence of fullerene nanospheres in the solution. It has been argued that once fullerene nanospheres are dissolved in aromatic solvent, a highly bonded layer of the aromatic solvent (the chlorobenzene in this case) is formed around the fullerene molecule. The formation of such tightly bonded layer of solvent molecules around the fullerene molecule is accompanied by the formation of a thicker region of open structured solvent molecules. The formation of such open structured solvent is what believed to results in the higher solvent evaporation rate observed in this study and similar other studies as has been reported in the literature for other types of aromatic solvent. (benzene, toluene, and xylene) [31-36]. The peak behavior observed in the case of chlorobenzene (Fig 3.2, 3.3) ,
however, is different from the ( rise and collapse ) behavior observed earlier by Amer et al.[36] while investigating the evaporation kinetics of fullerene solutions in toluene (Shown in Fig 3.2). such difference in behaviors can be expected due to the nature of solvent-solvent molecule interactions. Toluene is known to be unassociative kind of solvent, where interaction (association) of solvent-solvent molecules is minimum. On the contrary, clorobenzene is known to be a highly associative solvent, where interaction of solvent-solvent is strong due to the polar nature of clorobenzene molecule, characterized by dipole moment of 1.59 debyes. Hence, it can be postulated that the strong interaction among the clorobenzene molecules is what enables the support of the highly open structure and does not allow it to collapse once formed as observed in the toluene-fullerene system. This result brings attention to the important role played by the solvent itself in the solution evaporation kinetics. In addition, it opens the door for a rich uncharted filed of structuring in aromatic solvent upon interaction with fullerene nanospheres.

4.2 Fullerene water solution evaporation kinetics

Investigating the evaporation kinetics of fullerene-water solutions, reveals the fact that the interaction between fullerene molecules in fullerene-water solutions are completely different than their interaction with aromatic solvents such as clorobenzene. In this case, as shown in figure 3.5, the IEV of buckyball fullerene solutions in water, decreases as the fullerene concentration increases. As shown in figure 3.6, IEV rate of fully saturated fullerene-water solution was almost 80% of the IEV rate of pure water. In addition, as observed in figure 3.5 & 3.6, the decrease of water evaporation rate did not peak at any concentrations, however, it kept decreasing linearly as the fullerene concentration
increased in the solution. This linear decrease in the evaporation rate of water molecules out of fullerene-water solution, indicates that the nature of fullerene-water interaction and mechanism by which it affects the evaporation rate are different from those in the previous case of fullerene-aromatic solutions. The observed behavior for this case can be understood along the notion that once fullerene molecules are interacting with water molecules, they push the water molecule together due to the well-known hydrophobic nature of the fullerene molecules. Computer simulation studies investigated water–fullerene interaction using molecular dynamic simulation supports such type of interaction [68-69]. According to such theoretical studies, once a fullerene nanosphere is dissolved in water, the water molecules form a highly immovable layer around the fullerene molecule and the water structure was found to be compressed together away from such “jammed” layer of water molecules. In fact, Amer et. al.[70] have shown using molecular dynamic simulation that in fullerene-water solutions with 1:96 molecular ratio, the present of fullerene in the solution causes a rise in the internal pressure of water equivalent to applied external hydrostatic pressure on the water in the range around 2 GPa. Such pressure rise in the system of water molecules is naturally expected to be more closely structured and less movable than pure liquid water, hence the observed decrease in the evaporation rate can be understood.

The differential scanning calorimetry (DSC) measurement of the fullerene-water solution shown in figure 3.8 clearly indicated a linear increase in the evaporation enthalpy($\Delta H_{ev}$), shown in figure 3.10, accompanied by a linear increase in the evaporation temperature (shown in figure 3.11). such increase in both evaporation enthalpy and temperature can
also explain the observed decrease of the room temperature evaporation rate of the solution measured and shown in figures 3.5 and 3.6.

Upon Calculating the change in entropy upon evaporation based on the equation

\[ \Delta S_{ev.} = \frac{\Delta H_{ev.}}{T_{ev.}} \]

for fullerene water solutions of different concentrations, it was found that the change in evaporation entropy (\(\Delta S_{ev.}\)) increases linearly as the fullerene concentration increases in the solution. Realizing that, the entropy of the vapor state of water can be considered as a constant, the results shown in figure 3.12 indicates that the entropy of the liquid state of the solution decreases in comparison to the entropy of liquid state of pure water as the fullerene concentration increases in the solution. Regarding the entropy as a measure of randomness of the structure, the results in fig 3.12 indicates that the liquid structure of water molecules is less random for higher fullerene concentration compared to its state in pure water. Such results are in good agreement with the aforementioned argument of the higher internal pressure, and can also explain observed linear decrease in the evaporation rate shown in figure 3.5 and 3.6.

4.3 Thermal- transitions in fullerene- water solutions

Thermal transitions in fullerene water solutions are meant here to mainly focus upon the solid-liquid transition as well as a liquid vapor transition in the solutions. In the previous section, we have discussed the liquid-vapor transition through the evaporation kinetics, and it’s very clear the evaporation temperature of water increases as the fullerene concentration increases in the solution as shown in figure 3.11. In this part, we will
continue our discussion by considering the solid-liquid transition in fullerene-water solutions as a function of fullerene concentration. It is clear in figure 3.13 that the solid-liquid transition temperature ($T_m$) of the fullerene/water solutions increases as the fullerene concentration increases in the solution. Such increase in the melting temperature was found to be linear as fullerene concentration increases in the solution as shown in figure 3.14, the experimentally observed increase in the melting point of fullerene/water solutions as the fullerene concentration increases, comes as no surprise considering the internal pressure argument mentioned above that was observed in the molecular dynamic simulation of Amer et al.\cite{70} It is widely known that pure water melting point increases with applied external pressures, to the point that, pure water also observed to solidify at a room temperature 298 K (25ºC), at external applied pressure between 2.2 and 2.5 GPa.\cite{71,72} Hence, as indicated that the present of fullerene molecules causes an increase in the water internal pressure in the range around 2 GPa. The observed slight increase in the melting point of the solution can be understood as the result of increased internal pressure on the water molecules. It is important to note that the crystal structure of the solid ice formed from pressurized water (typically referred to as VI and is based upon tetragonal crystals) is different from the that of solid ice formed due to reducing the temperature of water at ambient pressure (known as hexagonal Ice)\cite{73}.

Finally, the argument of more structured water molecules in the liquid state at higher fullerene concentration is further supported by the Raman spectroscopy results in figure 3.16, the observed red-shift in the $v_3$ peak associated with asymmetric stretch and the no change in the $v_1$ peak associated with the symmetric stretch mode, in addition the slight blue shift in the second order $v_2$ peak associated with the fundamental bending mode \cite{74}.
can be only understood along the notion of structured water molecules or better structured water molecules in the liquid form of the solutions compared to their structure of liquid form of pure water. The exact nature of the more structured liquid form can be deduced from more involved spectroscopy investigations, however, this would be considered outside this scope of the current investigation and beyond the level of investigation provided in this master thesis. However, the results presented in figure 3.16 constitute a good start for more detailed future investigations.
5. Conclusion

Based on the current investigation, several concluding remarks can be withdrawn; First of all, it is clear that the presence of fullerene nanospheres in solution with different liquids does affect the evaporation kinetics of the liquid. Secondly, such effect may increase or decrease the evaporation kinetics depending on the exact nature of the fullerene /liquid interaction. In the systems investigated, the fullurophilic liquids were found to show an increase in the evaporation rates while follurophobic liquids were found to show a decrease in evaporation rates. The change in evaporation rates was explained based upon structural changes in the liquids. Thirdly, it was found that liquid-liquid interaction also plays a role in the exact evaporation kinetics. Finally, it was found that thermal transitions in fullerene/water solutions are mainly controlled by the effect of fullerene molecules on the structure of water in the liquid state.
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