



An acoustic levitator for single droplet evaporation kinetics

Beni B. Dangi*, Jordan M. Dixon, Shazzia Alexander and Emmanuala Noel

Department of Chemistry, Florida Agricultural and Mechanical University, Tallahassee, FL 32307, USA
beni.dangi@famou.edu

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Abstract

Evaporation kinetics of methanol, hexafluoroisopropanol, and polyethylene oxide solutions under microgravity condition were investigated utilizing an acoustic levitator and a fast-frame CCD camera. Two different regimes of evaporation kinetics were measured experimentally for both solvents. Two distinct rate constants were determined in the range of 10^{-3} s^{-1} , with overall slower decay for methanol. Total evaporation times for microliter volumes of methanol were measured under container-less acoustic levitation and compared with the evaporation times under container processed normal laboratory conditions. Significant differences in the evaporation time and trend were observed. A typical 4 μL sample of methanol evaporation time increased from 5 minutes to 45 minutes, from normal laboratory conditions to levitation. While a linear trend was observed under normal conditions, a logarithmic trend was observed under levitation. These experiments demonstrate difference in air-liquid interface dynamics due to difference in gravity and contact surface. The extended evaporation time under levitation condition can be utilized to perform and monitor reactions in a droplet which may otherwise be limited due to short droplet lifetime. Such extended lifetimes and microgravity conditions can be used in distinct environments, such as crystallization and aggregation of proteins and polymers from solutions. The set up described here can be used as a ground-based microgravity simulation device, which can quickly screen the chemical reactions to limit the payload for more expensive experiments at the international space station.

Keywords: Acoustic levitation, microgravity, solvent-air interface, crystallization, evaporation kinetics.

Introduction

In recent years, acoustic levitation¹⁻³ has been utilized in a range of scientific disciplines including but not limited to analytical chemistry, astrochemistry, material science, and pharmaceuticals^{2,4-7}. In acoustic levitation, a liquid droplet, a solid particle or a suspension is levitated slightly below the pressure nodes of the ultrasonic standing wave. Major advantages of such levitation technique lie in the removal of often complicating effects of a contacting surface on the sample. Spectroscopic and analytical detection techniques such as Fourier transform infrared spectroscopy, Raman spectroscopy, Mass spectrometry and X-ray diffraction have higher sensitivity coupled with the levitator due to absence of wall effects on sample. Hence, the levitation set up can be utilized to monitor the chemical and/or physical changes of the levitated droplet or a small solid sample. Furthermore, a levitator can be used to probe the differences due to the bulk sample size compared to small sample size^{4,8}. Such micrometer-sized particles floating in the given gas medium provide ideal laboratory conditions simulating the interplanetary dust particles or droplets in the atmospheres of planets and exoplanets⁴. Moreover, the levitated sample can be heated or cooled rapidly over very short time scales due to their small total heat capacity. Hence, a levitation device provides a versatile platform to study physical and chemical processes in free of undesired support structures as well as creating less contingent sample trapping requirements, such as electric charge and refractive index.

Evaporation kinetics of single droplet of either a pure solvent, a solution or a suspension has been of interest in understanding spray drying behavior and crystallization of inorganic and organic materials^{3,9,10}. The microgravity conditions created by acoustic levitation have just been starting to gain attention from the space science community to exploit the levitation set up as low gravity simulation platform. A number of experiments and theoretical studies show that the evaporation under acoustic levitation takes place under substantial forced convection¹¹⁻¹². Detailed models attempting to explore the physics of evaporation have been published elsewhere¹¹⁻¹³, and the readers can refer to these sources for a detailed description. Briefly, the evaporation of spherical pure liquid droplets is described by the name D²-law, which states that the evaporated mass is linearly proportional in time to the exposed area and assumes the absence of natural or forced convection forces¹¹. Here, we experimentally measure the rate constants of evaporation of pure solvents - methanol, hexafluoroisopropanol (HFIP), and polymer solutions made in HFIP - in an effort to contribute to the experimental data and test the validity of the D²-law. Furthermore, the liquid droplets can be used as a reaction medium for varieties of physical and chemical reaction processes, such as nucleation and crystallization. However, the timescales of such reactions may be longer than the evaporation time of the liquid medium. Hence, it is of prime interest to prolong the evaporation lifetime of liquid droplets. Here, we report on the evaporation times of microliter volumes of

common solvent methanol under normal container processing and under the acoustic levitation conditions showing the extended lifetime of the droplet in the later conditions.

Finally, container-less drying of suspensions or solutions of various solutes is of prime interest in various industries; such as pharmaceuticals, biomedical and ceramics. The container less processing removes the unwanted and often unknown container wall effects in the solidification of solute molecules. Evolution and agglomeration of protein structure with time in solution have been studied utilizing the acoustic levitation with analytical probes^{6,14}, since amorphous forms of drugs usually have a higher solubility than their crystalline form, use of amorphous formulation increases solubility and intake of active pharmaceutical ingredients. The acoustic levitation can produce phase-pure forms of amorphous drugs which is difficult to produce otherwise¹⁵. The acoustic levitation or a suspended droplet has also been used to examine the drying behavior of microdroplets of polymer dispersions to understand the film formation process¹⁶⁻¹⁷. Here, we study drying behavior of polyethylene oxide (PEO) in methanol of various concentrations. The PEO was selected as a model compound due to commercial availability, solubility, and its potential in drug delivery system¹⁸⁻¹⁹.

Materials and methods

The experimental setup depicted in the schematic diagram (Figure-1) permitted recording of the size and time of evaporation of droplets in an acoustic levitator [Tec5USA, T-121378] which suspended droplets of pure solvent or solution in

the air using acoustic radiation pressure from intense sound waves in order to balance the force of gravity. The levitation node, which changes according to gas pressure, density, and levitation power was optimized by adjusting the distance between the transducer and reflector with the micrometer attached at the top of the reflector¹. The levitator transducer was operated at a fixed frequency of 56 kHz and amplitude between 4 to 6 Watts and while a sound wave reflector operated at typically 10 mm from the transducer to create nodes for sample suspension. An oscilloscope [Tektronix, TDS2012CC041875] was used to monitor the sound waves and resonance conditions throughout the experiment. A small amount (typically 1-2 μ L) of the sample was placed at the levitation nodes using a 100 μ L needle syringe [Hamilton, 81020, 7750-13] for further monitoring. After placement of the droplet, a timer was started, and any changes observed were monitor using Thorcam software [Thorlabs Inc.]. An initial snapshot was taken at the placement of the droplet and at desired time intervals thereafter. The evaporation of the droplets was captured at regular time intervals by the CCD camera [Thorlabs, 340M-USB, 200 frames per second] and a zoom lens [Thorlabs, MVL6X12Z, MVL6X05L] placed at a distance of 7.94cm from the levitator. The solvents examined were methanol [Sigma Aldrich, 34860], hexafluoroisopropanol (HFIP), as well as a solution of polyethylene oxide (PEO) [Sigma Aldrich, 1546853] dissolved in methanol. The distance between the transducer and reflector was optimized to keep the droplet at the central node for greater stability of the droplet. After experimentation, analysis of the data and images was performed by the Thorcam software which also controlled the imaging equipment.

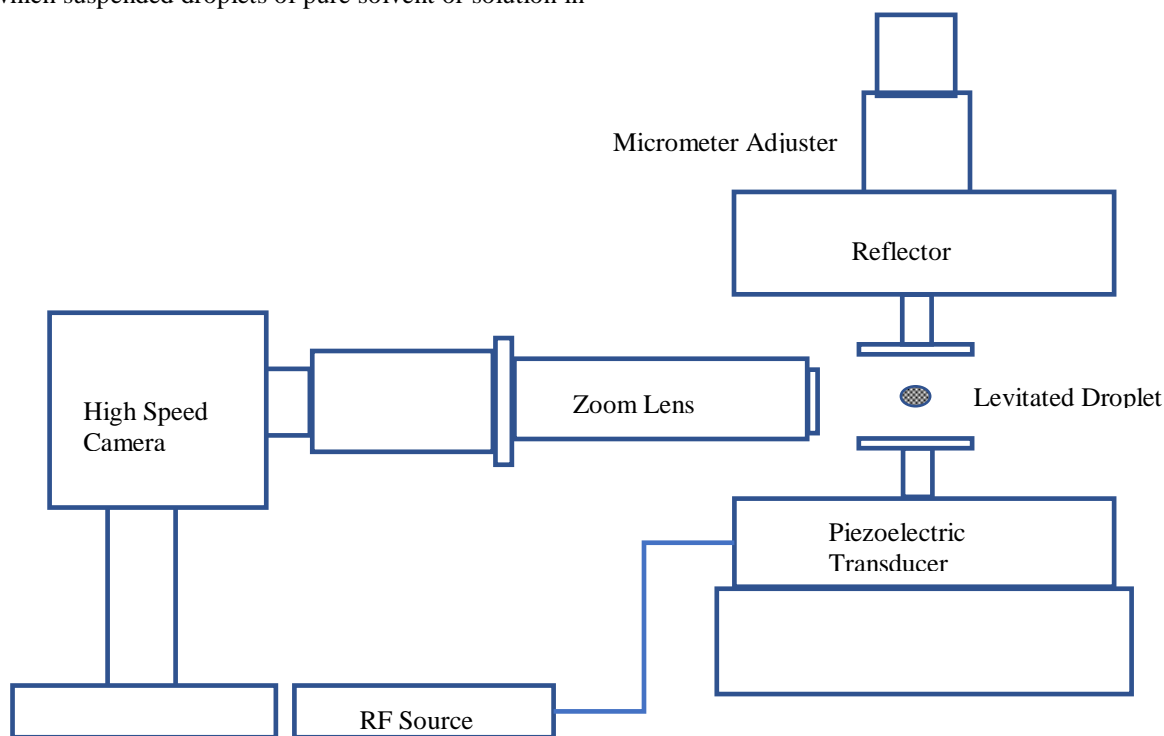


Figure-1: Schematics of the experimental set up for evaporation studies under acoustic levitation. Sketches are not drawn in scale.

Size measurements using Thorcam required pixel to distance conversion. Conversions were calibrated using a ruler, which corresponded at 74 pixels to 800 μ m vertically and 68 pixels to 800 μ m horizontally. The surface areas of droplets were calculated either by measuring the diameter for spherical shapes or by measuring the length and width for rectangular shapes. Once surface areas and volumes were evaluated and confirmed, the numbers were recorded on a spreadsheet for comparison and analysis of each trial. These data were plotted and analyzed with built-in functions using Origin Pro software [Originlab Corp]. Similarly, solutions of PEO in methanol at various concentrations were monitored. In experiments comparing the size profiles of droplets of PEO/methanol solution of different concentrations, the surface areas were normalized to 2 mm² and the standard deviation was calculated from multiple trials. Trials for PEO/methanol solution formed solid precipitates which were later captured, crushed and analyzed using Fourier Transform Infrared (FTIR) Spectroscopy [Agilent Technologies, Cary 630 FTIR] for the presence of solvent in the processed samples. The PEO/methanol solutions were also electro spun using a custom system²⁰ and analyzed using the FTIR. Both of these were then compared with the FTIR spectrum of pure PEO sample. Additional experiment to observe evaporation of solvents under typical laboratory conditions were conducted. For the contained environment, a volume of methanol is measured using a micropipette and transferred to an empty porcelain basin or small beaker. An electronic balance with an accuracy of ± 0.1 mg was used to monitor the mass and hence evaporation times of the methanol.

Results and discussion

Figure-2 compares the evaporation times of methanol under levitating microgravity conditions and those of normal laboratory conditions for various sample volumes; respective data points exhibited by the circles and squares. Each point represents the evaporation time corresponding to the initial volume of samples. An about 10-times increase in droplet lifetime in levitation were observed compared to normal laboratory conditions for sample volumes ranging from 0.2 to 4 μ L volumes. To extract the kinetics of evaporation, complete evaporation of methanol and HFIP were recorded.

The evaporation trends of two solvents, hexafluoroisopropanol (HFIP) and methanol, exhibit a sharp decline in the surface area of the levitated droplet followed by a steady decline as shown in Figure-3. Overall, HFIP evaporates faster than methanol. The experimental data were best fit with two rate constants for each solvent. The first order kinetic fits of the data, the natural log of surface area versus time, reveal two regimes of decay in the amount of solvent as shown in Figure-4. The corresponding rates for fast and slow decay, respectively were determined as follows: $6.60 \pm 0.63 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$ and $1.45 \pm 0.02 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$ for methanol; and $6.52 \pm 1.07 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$ and $5.75 \pm 0.50 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$ for HFIP, respectively. A comparison of the methanol evaporation rate constant from the literature¹⁰ shows the value

of $4.5 \times 10^{-2} \text{ mm}^2 \text{ s}^{-1}$, fairly in good agreement with our measurement. These data show that typically 10 minutes of droplet lifetimes can be used for processes where these solvents can be used as a reaction medium or reactants, such as crystallization²¹⁻²². While the HFIP evaporated faster overall, two regimes of evaporation were observed for both solvents. Such observations of two distinct rates indicate deviation from the standard D² law, which is often used to describe the evaporation kinetics^{5,14,23}. Indication of deviation from the standard D²-law as it describes evaporation lies in the multiplicity of decay kinetics. Previous studies that have explored similar experiments only identified one regime of evaporation kinetics whereas our first order kinetic fits for the evaporation for pure methanol and HFIP solvents display two; a regime for initial, fast decay and one for sequential, slow decay. Even though the physics model required to describe the two regimes are not clear, it is important to note that we distinctly measured the two evaporation regimes. While the two rates for HFIP differ by less than 20%, it is over 400% difference for methanol. Perhaps the most important result is the overall faster decay of HFIP compared to methanol which can be attributed to the stronger intermolecular forces in the later solvent. Readers who are interested in detailed theory are referred to physical and mathematical models that attempt to describe the evaporation process under acoustic levitation^{7,11-13}.

A single droplet solution of polyethylene oxide (PEO) in methanol is levitated and monitored using the high-speed camera to follow the solidification of dissolved PEO. As shown in Figure-5, the droplet not only decreases in size but becomes more spherical in shape with time lapse, as shown by the inserted pictures in Figure-5 at 0, 10, 20 and 35 minutes from the initial levitation time. Note that after 35 minutes, the droplet size remains fairly constant indicating completion of evaporation of solvent from the solution and forming an aggregate of the PEO. Different concentrations, ranging from 2 mg/mL to 20mg/mL, of PEO in HFIP were monitored for determination of the evaporation times. These data are plotted in Figure-6, normalized to a typical initial droplet surface area of 2 mm². Initial decay times for solutions were observed similar to that of the solvent. However, due to concentration difference, differences in surface area were observed at later times. At 2 mg/mL and 5mg/mL, no significant differences were observed while the 20mg/mL is distinct in evaporation rates and total time required for evaporation. These solidified samples were then collected for solvent content analysis using Fourier transform infrared FTIR spectroscopy. Dried samples analyzed with FTIR for composition show incomplete evaporation of the solvent (broad peak around 3300cm⁻¹ due to -OH group of HFIP) despite solid and dry appearance. Upon electro spinning the PEO/HFIP solution in laboratory conditions, a better match to the FTIR data of pure PEO structure is revealed as shown in Figure-7, permitting the conclusion that any remaining solvent is trapped in the inner surface during evaporation under levitation conditions. Hence, levitation drying of solution may be actually more useful when uniform mixing of solvent, to a

small percentage, to a solute material is required. When remnants of the solvent are undesirable, electro spinning the sample or heating for a short period of time at controlled temperature can be utilized.

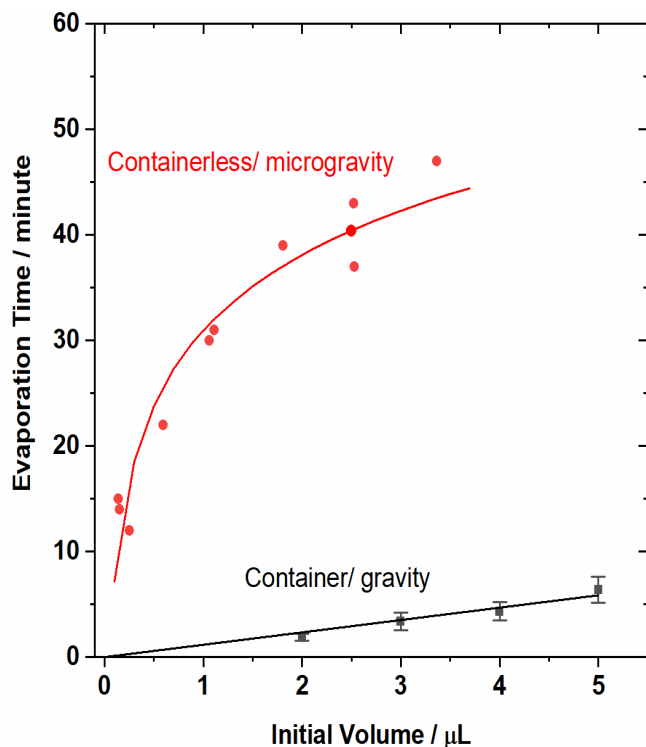


Figure-2: Evaporation times of methanol under levitation conditions (circles) and normal laboratory conditions (squares) for various sample volumes.

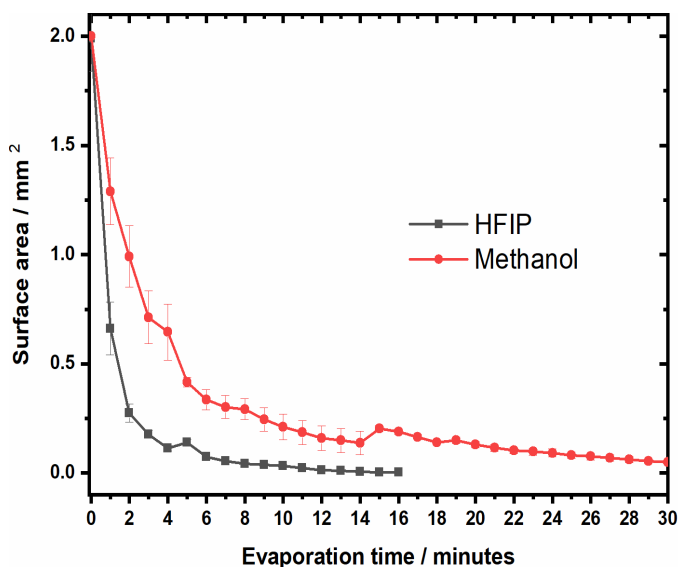


Figure-3: Surface area of levitated droplets of methanol (circle) and hexafluoroisopropanol (HFIP, square) at various times.

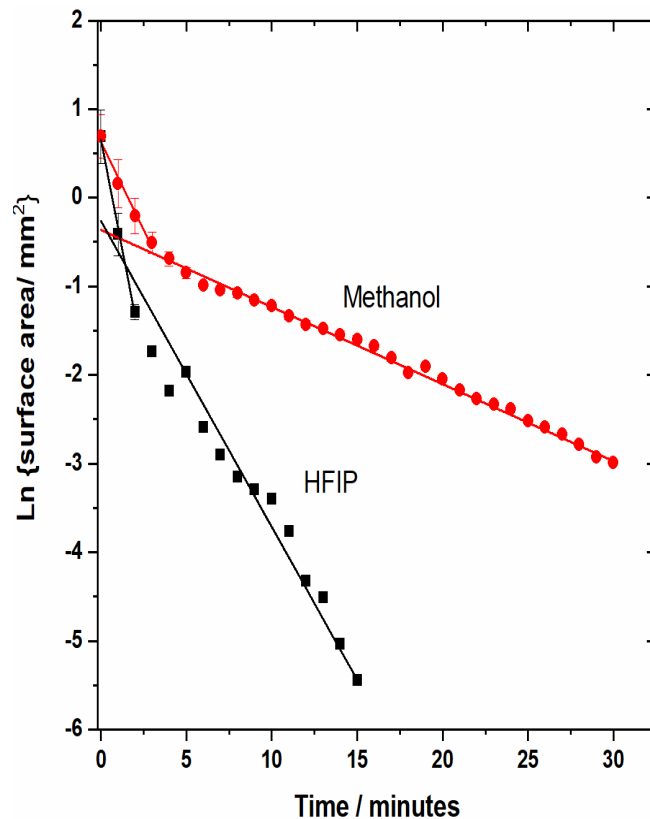


Figure-4: First order kinetic fits for the evaporation for pure methanol (circle) and HFIP (square) solvents.

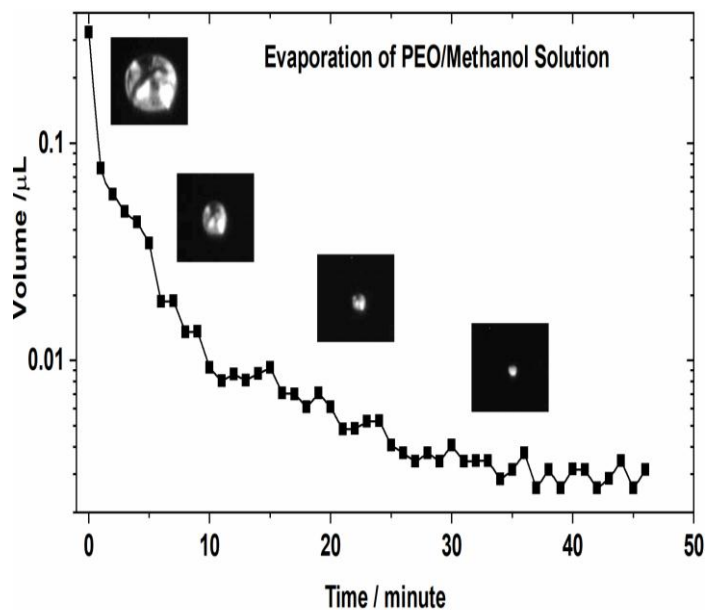


Figure-5: Size variation of the levitated droplet of the solution of polyethylene oxide (PEO) in methanol. The inserted pictures show the size at corresponding times of measurement.

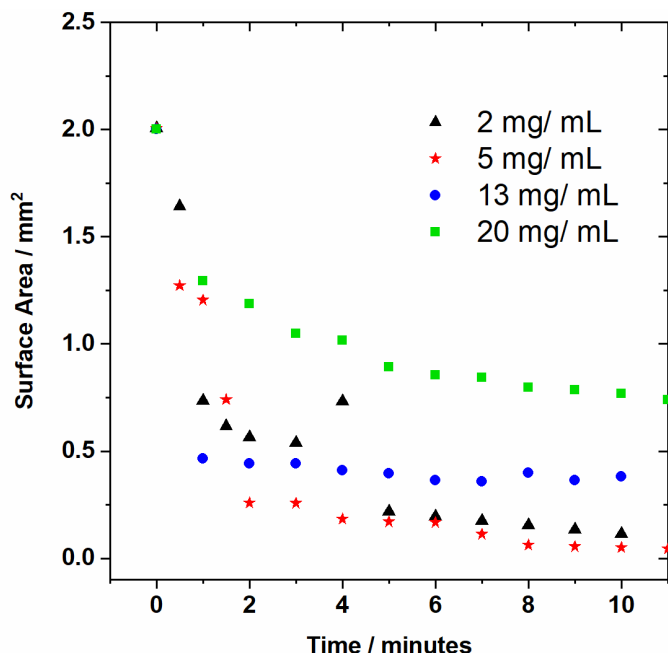


Figure-6: Size profile of PEO solutions in HFIP in the levitator. No significant differences in time profiles were observed for concentrations below 5mg/mL.

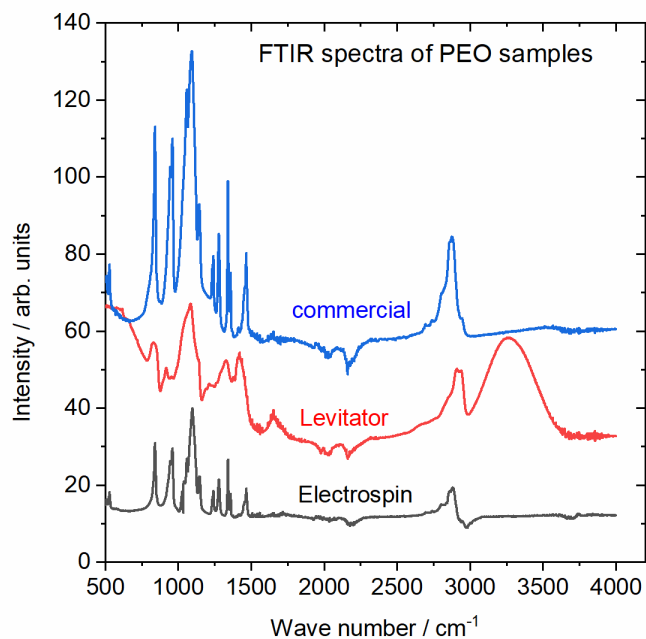


Figure-7: Fourier transform infrared spectra of commercial PEO, levitator dried and electrospin dried samples from the PEO solutions.

Conclusion

Evaporation kinetics of common solvents were measured under acoustic levitation and normal container processing conditions. Life time of micro liter volume droplets were increased by 10

times under levitation conditions compared to the container evaporation conditions. Such an extended life time can be very useful in nucleation or crystallization reactions where the droplet life time is the limiting factor. The container-less drying of suspensions or solutions of PEO solute was presented as a case study. The solution drying under container-less conditions can be expanded to model solutions applicable to pharmaceutical, biomedical and ceramics industries. The set up described here can be used as a ground-based microgravity simulation device, which can quickly screen the chemical reactions to limit the payload for more expensive experiments at the international space station. Furthermore, evaporation rates of the solvents were measured under microgravity conditions, which can be useful in the experiments in the outer space, where these solvents are used in chemical reactions. Finally, the set up presented is currently being modified to accommodate the levitator in a process chamber where reactions can be performed under controlled pressure, temperature and radiation conditions thereby experimentally simulating the varieties of environmental conditions. The process chamber is also being interfaced with the *in situ* Raman spectroscopic system for reaction monitoring.

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