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► **To cite this version:**

Ruel Cedeno, Romain Grossier, Victoria Tishkova, Nadine Candoni, Adrian Flood, et al.. Evaporation Dynamics of Sessile Saline Microdroplets in Oil. 2022. hal-03440976v2

HAL Id: hal-03440976

<https://hal.science/hal-03440976v2>

Preprint submitted on 11 May 2022 (v2), last revised 20 Jul 2022 (v4)

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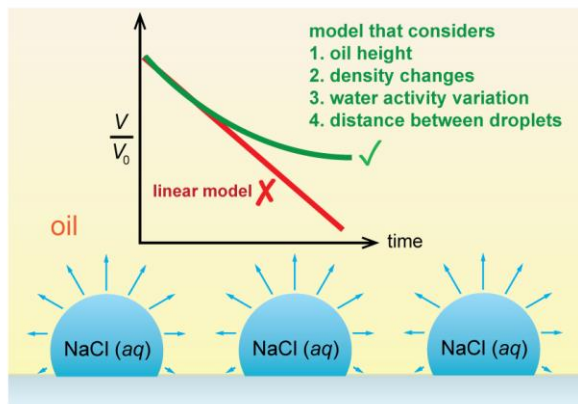
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Abstract

The occurrence of concentration and temperature gradients in saline microdroplets evaporating directly in air makes them unsuitable for nucleation studies where homogeneous composition is required. This can be addressed by immersing the droplet in oil under regulated humidity and reducing the volume to the picoliter range. However, the evaporation dynamics of such a system is not well understood. In this work, we present evaporation models applicable for arrays of sessile microdroplets with dissolved solute submerged in a thin layer of oil. Our model



accounts for the variable diffusion distance due to the presence of the oil film separating the droplet and air, the variation of the solution density and water activity due to the evolving solute concentration, as well as the diffusive interaction between neighboring droplets. Our model shows excellent agreement with experimental data for both pure water and NaCl solution. With this model, we demonstrate that assuming a constant evaporation rate and neglecting the diffusive interactions can lead to severe inaccuracies in the measurement of droplet concentration particularly during nucleation experiments. Given the significance of droplet evaporation in a wide array of scientific and industrial applications, the models and insights presented herein would be of great value to many fields of interest.

INTRODUCTION

Droplet evaporation on surfaces is ubiquitous in nature and plays a key role in a wide range of industrial and scientific applications¹ such as inkjet printing², nanostructure fabrication³, DNA chip manufacturing⁴, crystallization studies⁵, biomedical diagnostics⁶, as well as virus spreading⁷ and testing⁸. However, this seemingly “simple” process is governed by the complex interplay of many physical phenomena such as evaporative mass transfer⁹, heat conduction and convection, thermal-hydrodynamic instabilities, viscous and inertial flows, surface-tension-driven flows, contact-line pinning and depinning, buoyancy effects, and other effects.¹⁰

Given its complexity and practical significance, numerous experimental and theoretical investigations have been devoted to better understand the underlying physics of sessile droplet evaporation¹⁰. Many of these studies dealt with the evaporation of either pure liquid droplets¹¹⁻¹² or those with suspended colloidal particles which can lead to the so-called “coffee-ring effect”¹³⁻¹⁴. However, the evaporation of droplets containing dissolved salts has been rarely investigated. For instance, Takistov et al.¹⁵, Shin et. al.¹⁶, Zhang et. al.¹⁷, and Zhong et. al.¹⁸ showed that the resulting patterns and morphologies of the dried salt droplets depend on the wettability of the

surface, i.e. crystal rings would form on hydrophilic surfaces while single crystals at the center of the droplet are likely to form on hydrophobic surfaces. This suggests that surrounding salt droplets with hydrophobic liquid is a promising approach for studying nucleation inside the droplet without interaction with the hydrophobic liquid, i.e. homogeneous primary nucleation.

In the context of crystallization studies, we need to ensure spatial homogeneity of droplet temperature and composition. However, in microliter droplets, it has been shown that various internal and Marangoni flows can lead to temperature and concentration gradients¹⁹⁻²⁰. To address this, we reduce the droplet size down to picoliter range²¹ and we reduce the evaporation rate by immersing the droplet in oil under regulated humidity.²² The oil bath also serves as a thermal buffer which minimizes temperature gradients due to evaporation. To extract nucleation parameters from such experiments²³, it is crucial to determine how the volume, and so supersaturation of microdroplets, evolve with time. In modeling the evaporation rate, Soulié et. al.²⁴ reported that the droplet volume varies linearly with time within the early stages of evaporation. Given that the later stages of evaporation are crucial for the analysis of nucleation, we need a model that works even for the later stages. Since we are dealing with arrays of concentrated salt microdroplets immersed in a film of oil, there are additional phenomena that need to be accounted for. First, the variable diffusion distance due to the presence of oil film separating the microdroplet and air must be taken as an additional parameter. Second, the density of the microdroplet changes as water evaporates. Third, the equilibrium concentration at the interface varies with time because water activity decreases as solute concentration increases (Raoult's law).²⁵ Fourth, the diffusive interactions due to the presence of neighboring microdroplets must be accounted for.²⁶ In this work, we derive expressions describing the evaporation dynamics that account for these four additional phenomena based on well-established mass transfer equations. We then validate our model with experimental data²⁷. Moreover, we highlight that (1) surprisingly, different contact-line behavior such as constant contact angle (CCA), constant contact radius (CCR), and stick-slide (SS) leads to comparable evolution of microdroplet volume within the time of nucleation, and (2) failure to account for diffusive interactions between microdroplets nor the changes in colligative properties can lead to significant overestimation of their concentration. The objective of the model presented here, is to extract the supersaturation ratio at nucleation from the simultaneous observation of hundreds of microdroplets.

ACKNOWLEDGEMENTS

R. Cedeno acknowledges the financial support of Vidyasirimedhi Institute of Science and Technology (VISTEC) and the Eiffel Excellence Scholarship (N°P744524E) granted by the French Government.

REFERENCES

1. Zang, D.; Tarafdar, S.; Tarasevich, Y. Y.; Dutta Choudhury, M.; Dutta, T., Evaporation of a Droplet: From physics to applications. *Phys. Rep.* **2019**, *804*, 1-56.
2. Yoo, H.; Kim, C., Experimental studies on formation, spreading and drying of inkjet drop of colloidal suspensions. *Colloids Surf., A* **2015**, *468*, 234.
3. Chen, J.; Liao, W.-S.; Chen, X.; Yang, T.; Wark, S. E.; Son, D. H.; Batteas, J. D.; Cremer, P. S., Evaporation-Induced Assembly of Quantum Dots into Nanorings. *ACS Nano* **2009**, *3* (1), 173-180.
4. Dugas, V.; Broutin, J.; Souteyrand, E., Droplet evaporation study applied to DNA chip manufacturing. *Langmuir* **2005**, *21*, 9130.
5. Hammadi, Z.; Candoni, N.; Grossier, R.; Ildefonso, M.; Morin, R.; Veessler, S., Small-volume nucleation. *C. R. Phys.* **2013**, *14*, 192.
6. Sefiane, K., On the Formation of Regular Patterns from Drying Droplets and Their Potential Use for Bio-Medical Applications. *Journal of Bionic Engineering* **2010**, *7*, S82-S93.
7. Bhardwaj, R.; Agrawal, A., Likelihood of survival of coronavirus in a respiratory droplet deposited on a solid surface. *Physics of Fluids* **2020**, *32* (6), 061704.
8. Zhang, J.; Mahalanabis, M.; Liu, L.; Chang, J.; Pollock, N.; Klapperich, C., A disposable microfluidic virus concentration device based on evaporation and interfacial tension. *Diagnostics* **2013**, *3*, 155.
9. Semenov, S.; Starov, V. M.; Velarde, M. G.; Rubio, R. G., Droplets evaporation: Problems and solutions. *The European Physical Journal Special Topics* **2011**, *197* (1), 265.
10. Larson, R. G., Transport and deposition patterns in drying sessile droplets. *AIChE J.* **2014**, *60* (5), 1538-1571.
11. Picknett, R. G.; Bexon, R., The evaporation of sessile or pendant drops in still air. *J. Colloid Interface Sci.* **1977**, *61*, 336.
12. Stauber, J. M.; Wilson, S. K.; Duffy, B. R.; Sefiane, K., Evaporation of droplets on strongly hydrophobic substrates. *Langmuir* **2015**, *31*, 3653.
13. Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A., Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **1997**, *389*, 827.
14. Li, Y.; Diddens, C.; Segers, T.; Wijshoff, H.; Versluis, M.; Lohse, D., Evaporating droplets on oil-wetted surfaces: Suppression of the coffee-stain effect. *Proceedings of the National Academy of Sciences* **2020**, *117* (29), 16756-16763.
15. Takhistov, P.; Chang, H., Complex Stain Morphologies. *Ind. Eng. Chem. Res.* **2002**, *41*, 6256.
16. Shin, B.; Moon, M. W.; Kim, H. Y., Rings, Igloos, and Pebbles of Salt Formed by Drying Saline Drops. *Langmuir* **2014**, *30*, 12837.
17. Zhang, J.; Borg, M. K.; Sefiane, K.; Reese, J. M., Wetting and evaporation of salt-water nanodroplets: A molecular dynamics investigation. *Physical Review E* **2015**, *92* (5), 052403.
18. Zhong, X.; Ren, J.; Duan, F., Wettability Effect on Evaporation Dynamics and Crystalline Patterns of Sessile Saline Droplets. *The Journal of Physical Chemistry B* **2017**, *121* (33), 7924-7933.
19. Hu, H.; Larson, R. G., Analysis of the Effects of Marangoni Stresses on the Microflow in an Evaporating Sessile Droplet. *Langmuir* **2005**, *21* (9), 3972-3980.
20. Efstratiou, M.; Christy, J.; Sefiane, K., Crystallization-Driven Flows within Evaporating Aqueous Saline Droplets. *Langmuir* **2020**, *36* (18), 4995-5002.
21. Grossier, R.; Hammadi, Z.; Morin, R.; Magnaldo, A.; Veessler, S., Generating nanoliter to femtoliter microdroplets with ease. *Appl. Phys. Lett.* **2011**, *98* (9), 091916.
22. Cedeno, R.; Grossier, R.; Lagaize, M.; Nerini, D.; Candoni, N.; Flood, A. E.; Veessler, S., Nucleation in Sessile Saline Microdroplets: Induction Time Measurement via Deliquescence-Recrystallization Cycling *Faraday Discuss.* **2022**, *accepted*.

23. Grossier, R.; Tishkova, V.; Morin, R.; Veessler, S., A parameter to probe microdroplet dynamics and crystal nucleation. *AIP Advances* **2018**, *8* (7), 075324.
24. Soulié, V.; Karpitschka, S.; Lequien, F.; Prené, P.; Zemb, T.; Moehwald, H.; Riegler, H., The evaporation behavior of sessile droplets from aqueous saline solutions. *PCCP* **2015**, *17* (34), 22296-22303.
25. Popov, Y. O., Evaporative deposition patterns: Spatial dimensions of the deposit. *Physical Review E* **2005**, *71* (3), 036313.
26. Hatte, S.; Pandey, K.; Pandey, K.; Chakraborty, S.; Basu, S., Universal evaporation dynamics of ordered arrays of sessile droplets. *J. Fluid Mech.* **2019**, *866*, 61-81.
27. Rodríguez-Ruiz, I.; Hammadi, Z.; Grossier, R.; Gómez-Morales, J.; Veessler, S., Monitoring Picoliter Sessile Microdroplet Dynamics Shows That Size Does Not Matter. *Langmuir* **2013**, *29* (41), 12628-12632.