

Freeze/Thaw-Induced Carbon Dioxide Trapping Promotes Emulsification of Oil in Water

Oil and water are not miscible and quickly phase separate when stirring is stopped. Adsorption of molecular surfactants or polymeric dispersants at hydrophobic interfaces is commonly used to generate oil-in-water emulsions, although substantial, constant shearing efforts are usually necessary in the process.¹ It has been shown by Pashley's group^{2,3} first and later on by others⁴ that freezing/(pumping)/thawing oil/water mixtures spontaneously generate metastable oil dispersions. This observation has been made reproducibly, many times, and in many conditions (for reviews, see ref 5). This discovery, which applies to other solutes than oil (e.g., hydrophobic polymers,² graphene⁶) could have practical implications in various fields such as cleaning,^{3b} drug delivery,⁷ surfactant-free emulsion polymerization,⁸ or water desalination,⁹ to cite only a few.

The chemistry and physics behind this emulsification phenomenon are not understood yet.^{3d,10} Some have suggested that the air dissolved in water would preferentially sit at the oil interface in a state of (nano)bubbles,¹¹ leading to colloidal instability. By removing gas after freezing and prior to thawing, one would favor the generation of (meta)stable droplets through a cavitation process. However, the fact (among others¹²) that pumping gas in between freezing and thawing steps is not necessary to observe emulsification (vide infra) contradicts the proposed mechanism, leaving space for speculation. More recently, other authors have studied the effect of degassing water on the surface tension, the density, and the electrical conductivity of water, without noting significant variations.¹³

It was also shown in freeze/thaw experiments that oil/water interfaces become measurably negatively charged, which is believed to contribute to their relative stability, from a colloidal standpoint. The adsorption of hydroxide anions at water/hydrophobic interfaces has often been invoked to explain the phenomenon, although some groups refuted this justification.¹⁴ Indeed, hydroxide adsorption on hydrophobic surfaces is inconsistent with the large pH range over which negative zeta potentials are usually observed. On the contrary, the adsorption of bicarbonates on such hydrophobic surfaces is a more likely explanation that we have recently presented¹⁵ by carefully considering the complex equilibrium in water between the different carbonated species.¹⁶ For that matter, even if the importance of CO₂ in water has long been recognized in certain fields of physical chemistry (for instance, by playing on the efficiency of ion-exchange membranes¹⁷), its role in the formation of emulsions has indeed hardly ever been considered until our recent work.

In this Viewpoint, we interpret past literature anew and present complementary experimental evidence of how bicarbonate adsorption allows surfactant-free oil in water emulsions to form. The reason why freeze/thaw cycling allows generation of stable oil-in-water emulsions is proposed to arise from enhanced HCO₃⁻ production and adsorption at oil/water interfaces. We also argue that saturating water with CO₂ gas is

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an additional way to increase bicarbonate content in water (particularly when in conjunction with freeze/thaw cycling), without significantly raising the ionic strength, a key point to generate metastable droplets.

Since Pashley showed in 2003 that freezing and thawing mixtures of oil and water improves the stability of the generated droplets,² many different trials and characterizations have been made to explain this simple observation. Varying the nature of the solutes (oil,^{3a,c,7,18} pH,^{3a,c,19} salts^{3a,19}) or the method of preparation (e.g., separate freeze/thaw of oil and water,^{4a} addition of solvent,²⁰ etc.) have been looked into. To summarize the findings, the nature of the oil hardly affects the process of emulsification but plays a crucial role in the stability of the oil droplets formed. Also, literature suggests that pH must be maintained above 3 to observe emulsification, and salts were found to decrease the colloidal stability of the emulsions formed, whether they had been added prior to freeze/thaw or after. Degassing between each freezing and thawing step has no effect on emulsification,^{4a} nor does the postaddition of air^{4a} or nitrogen.^{2,3a} On the other hand, bubbling nitrogen (without freeze/thaw cycles)² or removing gases under vacuum do not promote emulsification.

A particularly interesting feature,^{3b} later studied in detail by Francis,²¹ resides in how the values of pH and conductivity of degassed solutions depend on the sample preparation process: solutions that have been subjected to freeze/thaw do not show the same values as those degassed with nitrogen bubbling (Figure 1). In nitrogen bubbling, the pH increases from 5.7 (typical of distilled water) to 7.0, while conductivity drops down to an exceptionally low value of 0.07 μS/m. Both results are expected given that the removal of acidic CO₂ (which allows one to reach pH neutrality) is accompanied by a progressive withdrawal of bicarbonate anions, therefore severely decreasing conductivity to almost nil. In a freeze/thaw process, the conductivity more than doubles (from 0.75 up to 1.9 μS/m) while the pH increases up to 7.0 after several cycles have been applied; authors could not explain either observation at the time (see Figure 1).

As far as the conductivity change is concerned, a recent study showed that freezing water down to -20 °C in the presence of excess CO₂ (dry ice) increases the conductivity of protein stock solutions.²² The authors proposed that when

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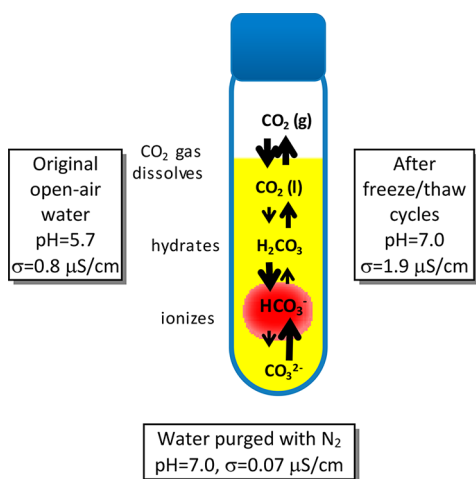


Figure 1. Evolution of the physical–chemical properties of water upon freeze/thaw steps or bubbled with nitrogen gas (from ref 21). In the center is the proposed schematic pathway followed by CO_2 molecules when the water freezes (increased concentration in water) and melts (transformation into hydrates and then bicarbonate anions) (from ref 22).

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samples are frozen, excess CO_2 resides in water in an H_2CO_3 state and is further transformed into bicarbonate anions upon returning to room temperature. The phenomenon is accompanied by an irreversible decrease in pH, as the authors evidenced by using pH-sensitive colorimetric dyes. We infer that such an explanation must also apply to normal atmospheric conditions. Indeed, the solubility of CO_2 in water goes from 39 to about 77 mmol/L when decreasing the temperature from 20 to 0 °C.²³ The change in conductivity observed by Francis²¹ as an outcome of the freeze/thaw cycling may be ascribed to enhanced production of bicarbonate anions. We propose that by carrying out several freeze/thaw cycles all acidic CO_2 molecules present in the form of H_2CO_3 in the medium,²³ gradually transform into bicarbonate anions.

As far as pH change is concerned, however, the observed rise of pH to 7.0, as described by Francis and confirmed here (vide infra), remains unclear: a transformation from H_2CO_3 to bicarbonate should be accompanied by the detectable generation of H^+ ions, which we found no evidence of here. Many parameters change when decreasing the temperature (ionization equilibrium, CO_2 solubility and hydration, pK_a 's, etc.), but none of these allows an explanation of this pH trend.²⁵ As reported by Loerting and Bernard in their article devoted to H_2CO_3 ,^{24a} it is indeed “of interest to study the rates of protonation/deprotonation in glassy water or ice matrices at low temperatures rather than in aqueous solution” and, shall we add, its implication in the transformation of CO_2 into bicarbonates.²⁶

Given that freeze/thaw generates extra bicarbonate ions, the latter can adsorb to oil/water interfaces in greater quantities and promote stability of the droplets, as proposed previously.¹⁵ The phenomenon must occur after coming back to room temperature and for a given amount of time, even after staying in open air. With this explanation in mind, the different observations made in numerous freeze/thaw studies now make sense. The removal of all gases from an oil/water mixture is not key to stabilizing droplets. Freezing leads to a significant increase in solubilized CO_2 , and whether or not the sample is pumped before thawing it has in fact little effect on the process; the same can be said about reintroducing gases after freeze/thaw steps. On the other hand, bubbling nitrogen removes CO_2 before it has a chance to transform into bicarbonates, which the very low conductivity observed in this latter case would support. All other necessary features (i.e., pH above 3.0, low salt concentration) comply with the low content of bicarbonate ions available in the bulk of water for colloidal stability (typically on the order of 10^{-5} M).¹⁵

Given that carbonic acid is about 10 times more soluble in oils than in water,²⁷ some experimental results reported by different teams led us to hypothesize that CO_2 content in the oil phase, and its transfer to water in certain conditions, must have a role in the occurrence of oil emulsification, or lack thereof. For instance, mixing oil and water phases that have been either (i) submitted separately to freeze/thaw cycles^{4a,28} or (ii) separately ultrafiltrated against a third water solution^{9b} does not generate emulsions. On the contrary, mixing oil and water phases that have been ultrafiltrated against one another does promote oil emulsification. These three situations suggest that emulsification can only occur when transfer of CO_2 from oil to water is possible or prevented otherwise, whether freeze/thaw cycles are applied or not.

Next, we present a selection of freeze/thaw experiments carried out using highly purified hexadecane (following a procedure described before^{15,29}) and either (i) plain distilled water (so as to reproduce the experiments of Pashley et al.²) or (ii) CO_2 -saturated distilled water (at a pressure of about 2.7 atm, implying an H_2CO_3 content of about 1.5 mol %). The emulsification process was tracked by examining the evolution of pH, conductivity, oil droplet size (by optical microscopy), and zeta potential as a function of the number of freeze/thaw cycles. Most importantly, using ^1H NMR, we measured the fraction (usually small) of spontaneously emulsified oil. All data are summarized in Table 1 (experimental conditions are given in the Supporting Information, section S1).

Table 1. Evolution of pH, Conductivity, and Emulsified Oil of HD/Water Systems^a

| freeze/thaw cycles | pH | conductivity σ ($\mu\text{S}/\text{m}$) | HD emulsified Content ($\times 10^2$ wt %) |
|---------------------------|-----|--|---|
| plain water | 6.1 | 0.4 | 3.5 |
| 1 | 6.3 | 1.9 | 4.2 |
| 2 | 6.5 | 2.0 | 3.8 |
| 3 | 6.9 | 1.8 | 4.7 |
| CO_2 -sat. water | 4.6 | 20.4 | 4.0 |
| 1 | 4.8 | 20.3 | 7.4 |
| 2 | 5.0 | 18.2 | 8.6 |
| 3 | 5.2 | 15.8 | 6.7 |

^aFor the record, the theoretical pH and conductivity of deionized water are 5.3 and 0.8 $\mu\text{S}/\text{m}$, respectively.

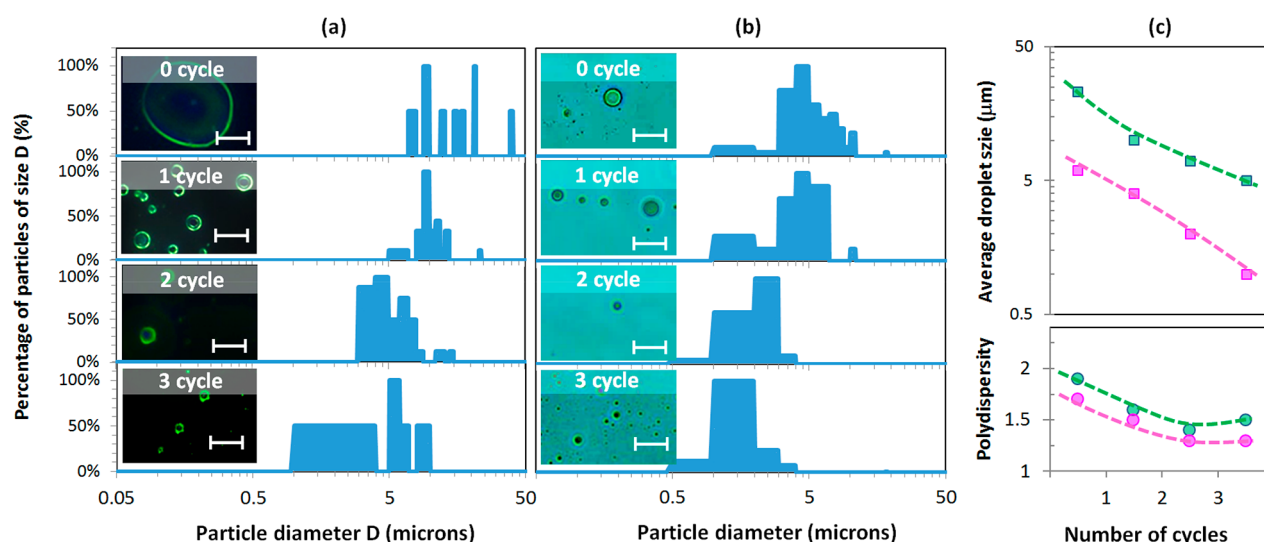


Figure 2. Freeze/thaw-induced emulsification. Evolution of the diameter distributions of particles formed in oil/water mixtures when up to three freeze/thaw cycles are applied, using either (a) plain water or (b) CO_2 -saturated water. Typical optical microscopy photographs are added as insets, the white scale representing $20\ \mu\text{m}$ in all cases. (c) Plots showing the average size of the polydispersity, extracted from (a) and (b).

Similarly to Francis et al.'s report,²¹ we first observed that the pH gradually increases with freeze/thaw steps, regardless of the type of water used for the experiment, i.e., plain or CO_2 -saturated. With plain water, however, conductivity doubles with the number of freeze/thaw cycles, while it declines for the CO_2 -saturated water—a decrease attributed to the consumption of excess protons (of high mobility) during the freeze/thaw steps. Remarkably, the fraction of emulsified oil doubled in the CO_2 -saturated water, but in both cases, it remained unaffected after three cycles. Note that the emulsified fraction is quite low (on the order of 0.08 wt % in the best case, i.e., with CO_2 -saturated water).³⁰

It is in the oil droplets size (Figure 2a,b) and zeta potential (Figure S2) measurements that the most striking differences are observed between the two types of water used. In plain water, droplets continuously decrease in size with the number of freeze/thaw cycles, reaching approximately $5\ \mu\text{m}$ in diameter after three cycles. This value corresponds to the size of oil droplets spontaneously formed in CO_2 -saturated water even without freeze/thaw. If freeze/thaw steps are applied to the CO_2 -saturated water system, the droplet size further drops down to an average of $1\ \mu\text{m}$, namely, the resolution of the optical microscopy used. The size distributions are large (from 0.2 to a few microns), which is typical of an emulsification process. The zeta potential of these droplets, measured after each cycle, remains constant except for the last cycle (Figure S2). Note that larger values were found with plain water (around $-23\ \text{mV}$) as compared to CO_2 -saturated ones (around $-15\ \text{mV}$). The discrepancy may come from differences in both size and pH between samples (Table 1). A definitive point is that, in both cases, these values are too low to envision colloidal stability for these objects in the long run or upon introducing salts. A last remark concerns the fact that water crystallization seems essential for the emulsification to occur. In a series of blank experiments where we refrigerated the samples prepared with plain water to $4\ ^\circ\text{C}$, without freezing them, we did not observe any emulsification after three refrigerating/warming cycles.

To complete these findings, we carried out interfacial tension (IFT) measurements with samples saturated with

different gases, namely, air, nitrogen, argon, and CO_2 , in the same manner as depicted in our previous study.¹⁵ At short time, typically on the order of a few or tens of seconds, adsorption onto the interface of bicarbonates in water follows the same kinetics (Figure 3). At longer time, however, IFT

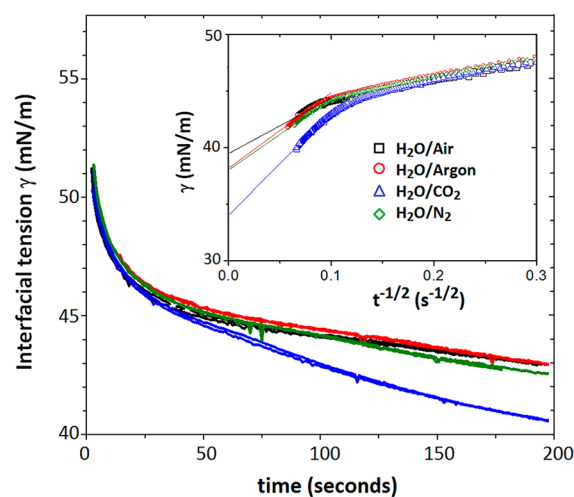


Figure 3. Interfacial tension measurements of ultrapurified HD drops in water in different atmospheric environments: (black) air, (red) argon, (green) nitrogen, (blue) CO_2 . Inset: best fit using a diffusion-limited model (see ref 15 for details).

measurements on the CO_2 -saturated one show a deeper decrease than that in the other environments, as also shown by the best fit when applying a diffusion model (inset in Figure 3). On the other hand, we did not see striking differences between air-stored samples and nitrogen- or argon-bubbled ones. IFT extrapolated at long time (γ_0) was found to be as low as $28\ \text{mN/m}$ for CO_2 -saturated samples, to be compared to the $38\ \text{mN/m}$ value for the air-exposed sample, and $36\ \text{mN/m}$ for gas-bubbled samples (Figure S3).

In conclusion, we have exposed in this Viewpoint how emulsification of oil in aqueous solutions after freeze/thaw steps is consistent with bicarbonate formation. Combining

CO₂-saturation of water with freeze/thaw cycling is simply a way to enhance the phenomenon. To help assess how universal this phenomenon is and how it applies to important real-life situations (e.g., the fate of CO₂ in icebergs), several points need to be addressed for experimentalists as well as theoreticians: (i) although different spectroscopic techniques³¹ have been used recently to detect ions at interfaces, the direct observation of bicarbonate at interfaces remains a challenge; (ii) the physics of the phenomenon (i.e., the driving force for this adsorption, as well as its (ir)reversibility) is still not understood; the existence of a “permeable” boundary condition (i.e., carbonates are soluble on each side of the oil/water interface, most probably under different forms) makes the derivation of the Henderson–Hasselbach equation, which links the pK_a, the pH, and the degree of dissociation of an acid or a base, extremely complex and unaddressed so far, to the best of our knowledge; (iii) the role of ions other than carbonates and, more generally, the importance of the ionic strength remain open.

Finally, beyond the topic of bicarbonate adsorption at oil/water interfaces, one may question some finding on slightly positively charged interfaces (typically of a few mV) in conditions different from those presented here, e.g., water drops pipetted into silicone or alkane oil³² or large CO₂ gas bubbles introduced in water.³³ Carbonation may again be a possible explanation for these new atypical observations, for instance, considering the adsorption and weak ionization of acidic H₂CO₃ on interfaces in these apolar media.

Xibo Yan[†]

Antonio Stocco^{‡,§}

Julien Bernard^{†,§}

François Ganachaud^{*,†,§}

[†]Université Lyon, INSA, CNRS, Ingénierie des Matériaux Polymères, F-69003 Lyon, France

[‡]Université Strasbourg, CNRS, Institut Charles Sadron, F-67000 Strasbourg, France

[§]University of Pennsylvania, CNRS, Solvay, Complex Assemblies Soft Matter Lab, 350 Patterson Boulevard, Bristol, Pennsylvania 19007, United States

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b02919.

Materials and methods, data on preliminary and laboratory experiments, and a discussion on ionization equilibration at low temperature (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: francois.ganachaud@insa-lyon.fr.

ORCID

Antonio Stocco: 0000-0002-5524-4323

Julien Bernard: 0000-0002-9969-1686

François Ganachaud: 0000-0003-2658-2734

Notes

The authors declare no competing financial interest.

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(29) Some preliminary experiments were carried out in one author's kitchen, using table olive oil and soda-streamed distilled water. For the sake of clarity of the present Viewpoint, these data, originally discussed in the main text, were shifted to Supporting Information (section S3).

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