FRESH CUP MAGAZINE

COFFEE, IN THE CAFÉ

How Water Works

The Water Issue

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Owing to the diversity of varieties, flavor, and craftsmanship associated with coffee, the brewed beverage is often discussed in a similar manner to wine or beer. However, coffee has a complication—coffee requires water to be added at the point of consumption. Of course, the brew method and barista's consistency also impact the final product, but a more pertinent issue lies forcefully active at a molecular level: dissolved minerals and their role in coffee extraction and flavor management.

Water is the common name for the three-atom molecule H_2O, one of the smallest chemicals, which boils at approximately 100 °C at 1 bar of pressure. H_2O is polar, meaning that within a single molecule there are regions of positive (H) and negative (O) charge. As a result, H_2O molecules interact strongly with their neighbors, forming nano-networks through alignment of positive and negative regions (shown in blue in Figure 1). A collection of H_2O molecules exists as a liquid between 0–100 °C at 1 bar, what we commonly refer to as "water."

Owing to H_2O's size and polarity, the bulk liquid is an efficient solvent, meaning it's capable of dissolving other substances. The solvation mechanism depends on the polarity of the intruding material. Permanently polar molecules (like calcium, sodium, chloride, bicarbonate) and those that are transiently polar (like ethanol, glucose) interact with H_2O in a similar fashion to the H_2O-H_2O self-interaction: they're stabilized through the alignment of positive and negative regions (depicted in red in Figure 1). Compounds that are only weakly polar (like caffeine, n-butanal) or entirely non-polar (octane, CO_2, toluene) are solvated through an encapsulation mechanism (these interactions are depicted in green).

The solvation mechanism for any particular chemical lies on the spectrum between direct interaction and encapsulation. In general, all molecules invoke some form of ordering of water around them as they're dissolved, and ordering costs energy. Molecules that require more ordering are typically less soluble in water, as water favors interactions that require the least amount of energy. For example, $CaCO_3$ (calcium carbonate) is poorly soluble in water because it takes much more energy to order water around Ca^{2+} and CO_3^{2-} than for the compound to remain in its solid state.

It is certain that your local water contains more than pure H_2O. The dissolved species, commonly referred to as minerals, are a variety of naturally occurring positively and negatively charged materials (cations and anions, respectively), and occasionally some organic molecules. While the organic compounds (those that are rich in carbon) are problematic as they can impart an undesirable smell and taste, they're easily removed with carbon filtration. Charged minerals, however, are not.

Due to the laws of physics that govern the universe (in particular the one that states that mass cannot be created or destroyed), the net charge of the solution must be zero. For every positive charge, there must be a negative counterpart. Because of the absolute requirement for a balance of charge, an understanding of how positively and negatively charged ions influence interactions between molecules helps show how variance in water composition affects extraction behavior.

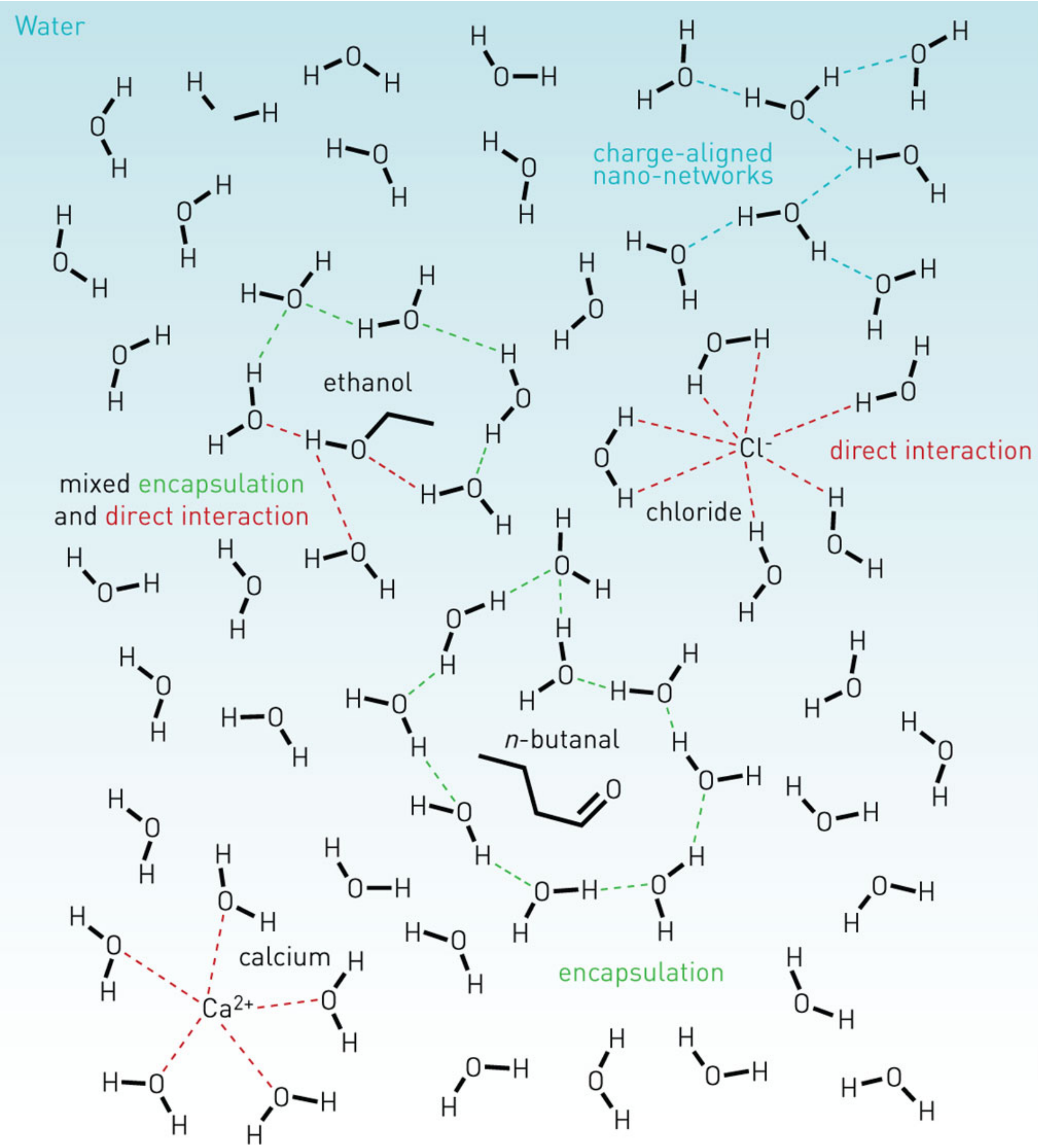
All cations and anions are relevant in the discussion of water chemistry and extraction, but several compounds heavily influence the final product in your cup. Two are magnesium and calcium, both positively charged species. These molecules use their regions of positive charge to pull flavor into coffee during the brewing process by attracting areas of negative charge on organic compounds like citric acid, for example. Another is bicarbonate, a negatively charged species that heavily influences the chemical makeup of your coffee. Bicarbonate acts chemically by neutralizing acids in coffee as it's brewed. Bicarbonate also plays an important role because of its buffering ability; in addition to donating protons, bicarbonate can also accept protons to control pH levels. Each of these ions is discussed in further detail later.

We know that dissolved cations interact with water's regions of negative charge (Figure 1 shows calcium, Ca^{2+}, installing local order by attracting the negatively charged regions of H_2O). Solvated metals, like calcium, interact with other organic molecules through the same mechanism as their interactions with water: the cations bind to atoms with negative charge. Many organic molecules are decorated with these chemical regions of negative charge. In other words, dissolved metals will stick to organic molecules that are commonly found in coffee, thus pulling them into the water. Dissolution of polar compounds is aided by increased metal content, increasing interactions that pull the compounds into water during the brewing process.

But for every positive charge that facilitates extraction by grabbing onto oxygen- and nitrogen-rich compounds in coffee and pulling them into the water, there is a negative charge that can act on solvated acids. In water, the most active acid-buffering anion is bicarbonate. In coffee, most of the acidic molecules interact strongly with bicarbonate, effectively negating their acidic character. This comes as a mixed blessing as certain acids have undesirable flavor (quinic acid is one) while others are pleasant and desirable (our friend citric acid).

The ideal water should facilitate an extraction of organic molecules with cations, but mediate the intense acidity and unpleasant flavors through chemical reaction with bicarbonate.

It is immensely challenging to design water with high levels of flavor-extraction ability (cations), without the inclusion of detrimental anions to either flavor or machine. There is a fine balance and the window for success is narrow. Here, we will explore the physical challenges associated with obtaining designer water.



Water (H_2O) forms charge-aligned nano-networks, depicted through blue dotted lines. Other molecules can interact with these charged regions of water. The calcium ion (Ca^{2+}) is positively charged, and therefore mandates the negatively charged O to align towards it. Similarly, chloride (Cl^-) attracts the positively charged regions of water (H), and there is a direct interaction between water and the species dissolved in it. Some molecules do not feature significantly polarized regions, like ethanol and n-butanal. In the case of ethanol, some nanonetworks may be formed (shown in red), while other encapsulating water networks form around the less-polar regions. Oil separates from water because the water network is stronger than the encapsulation network. (Image: Christopher Hendon. Photo at top: Jamie Street.)

The chemistry of solvated ions

Singly-charged cations:
Sodium (Na^+) and Potassium (K^+)

All metal ions can be considered as a point of positive charge in three-dimensional space. The magnitude and density of this charge is determined by parentage of the metal. Sodium and potassium ions carry a single positive charge that is relatively diffuse (they have low density). Water itself is highly polar, so naturally the metal ion and the OH^2 will orient towards each other. However, given the charge density of the metal and the high dipole of water, the strongest cation-anion interaction is achieved with water itself. In other words, there are very few other compounds with partially negative charge (like water) that will stick more strongly to Na^+ and K^+ than water itself. Hence, these cations serve little purpose in aiding extraction of coffee-contained molecules because they bind to water so efficiently.

But sodium and potassium ions should still be considered as indicators of chemistry far more sinister. Given that charge neutrality is required by physics, the presence of these positive charges mandates the presence of counter-charges (anions such as bicarbonate and chloride). Therefore, water rich in sodium (more than 50 ppm) is usually an indicator that either your coffee will taste bad (due to associated bicarbonate stifling the perceived acidity in the cup) or the machine is in danger of corrosion (due to solvated chloride).

Doubly-charged cations:
Magnesium (Mg^{2+}) and Calcium (Ca^{2+})

Earth's crust contains a variety of calcium and magnesium salts, which frequently come in contact with and dissolve in water. Mg^{2+} and Ca^{2+} have a tendency to stick to regions of negative charge, but unlike Na^+ and K^+, the doubly charged cations bind to both water and to other organic molecules. This is due to both their increased charge density and their increased size, which mandates an increase in ordered water to solvate the ion itself. This interaction can act in favor of extraction by pulling flavor from ground coffee (citric acid extracts rapidly in metal-rich water), but calcium can also be detrimental if you want to hide less flavorsome but highly polarized molecules (like ethyl acetate) that may be present in the roasted coffee. However, Ca^{2+} can also be problematic when in high concentrations as it forms an insoluble salt with carbonate, limescale. This can impair or even ruin a machine. Mg^{2+} is generally safe to consume, with no discernible negative impact on flavor, and no risks for machine health, because magnesium carbonate, $MgCO_3$, is not readily formed in appreciable quantities.

Singly-charged anions:
Fluoride (F^-) and Chloride (Cl^-)

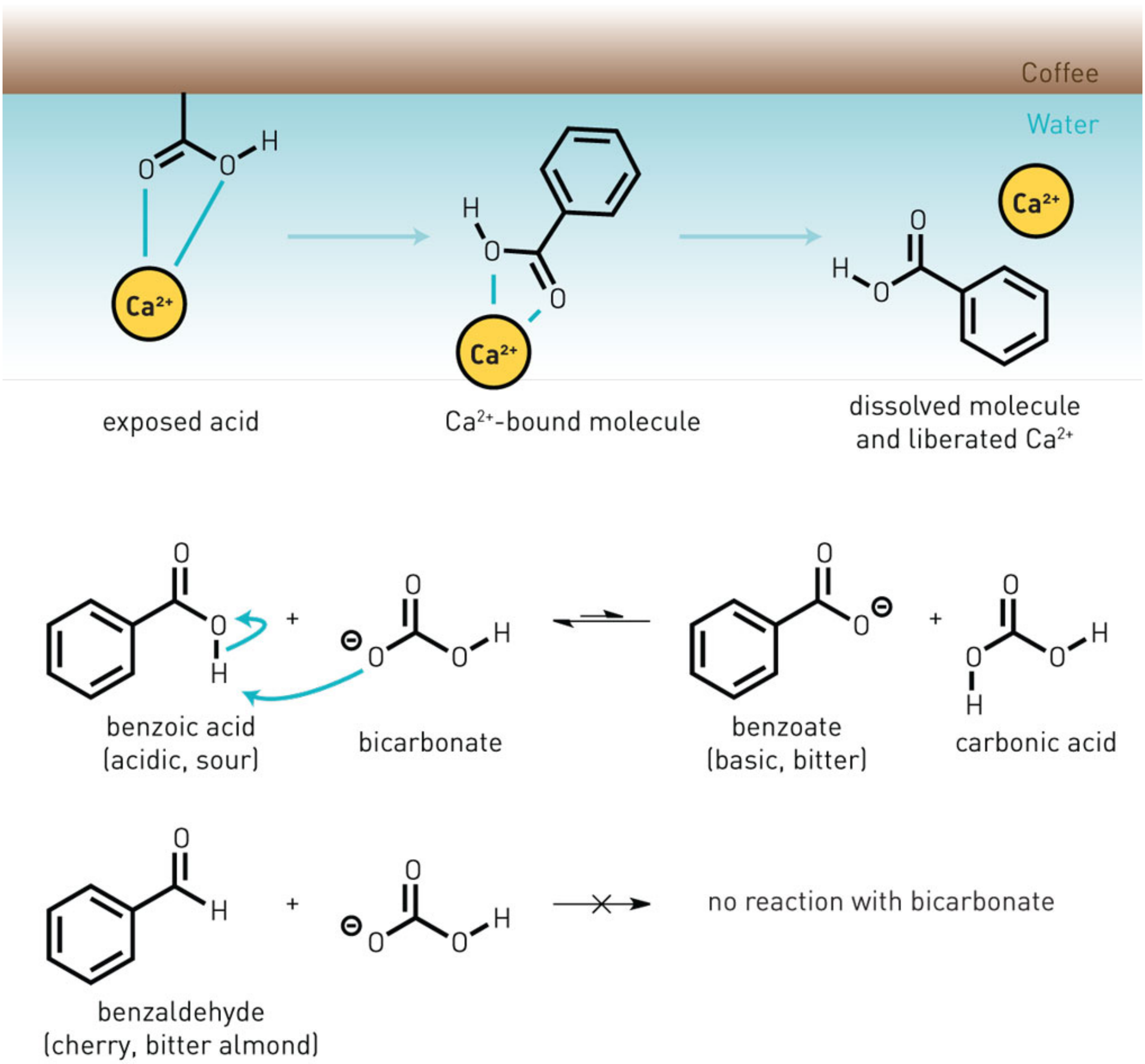
Fluoride is the smallest anionic water-soluble species and is infrequently found in levels greater than approximately 1.5 mg/L (1.5 ppm). At levels found commonly in water (ca. 1 mg/L), fluoride contributes positively to health, and has no adverse impact on coffee brewing. Chloride (Cl^-) is slightly larger than fluoride yet carries the same negative charge. Chloride is by far the most commonly solvated anion, and should not be confused with chlorine (Cl_2), which is used to mediate bacterial growth in fresh water. Chloride is a valuable counter-ion as it balances the charge of the liquid with no adverse health or flavor effects.

However, chloride can cause catastrophic damage to equipment made of stainless steel, through the catalytic oxidation of Fe to Fe^{2+}, causing pitting corrosion. This occurs to some extent in all concentrations of chloride.

Bicarbonate (HCO_3^-)

Water and atmospheric carbon dioxide react to form low concentrations of carbonic acid through the reaction: $CO_2 + H_2O \rightarrow H_2CO_3$. Carbonic acid then further reacts with water to form bicarbonate and hydronium (as the water becomes progressively more acidic), through the reaction: $H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$. Bicarbonate can then react with both donors and acceptors of H^+ (meaning acids and bases) to counter dramatic swings in pH.

In the context of coffee, bicarbonate may act to mask excessively unpleasant acids through buffering their H^+ into the bicarbonate cycle, but even subtle concentration differences in HCO_3^- can result in massive effects on the perception of acidity in brewed coffee. As noted earlier, bicarbonate also forms an insoluble salt with calcium at high temperatures known as limescale. The more acidic molecules present in the water, the more bicarbonate is required to neutralize them. Perceived acidity is increased with diminishing HCO_3^- concentrations.



Dissolved Ca^{2+} (shown in yellow), binds to exposed molecules in coffee, binding temporarily to them and then extracting them into the water. In this case, the acidic and sour-tasting benzoic acid is extracted with the assistance of Ca^{2+} . Once in the water, benzoic acid interacts with basic solvated compounds like bicarbonate in a conventional acid-base reaction to form benzoate (a basic and bitter compound) and carbonic acid. Other molecules, like the structurally similar benzaldehyde are extracted in a similar manner, but are not affected by dissolved bases. (Image: Christopher Hendon.)

The paradox

In coffee extraction and flavor management, the goal is to obtain a balanced cup that features no offensively acidic characteristics, but also no flat and chalky notes. Thus, we are in pursuit of water which has relatively high dissolved cation concentrations, and low bicarbonate and chloride concentrations such that we can extract what we want from the coffee, and buffer away the negative acidity associated with common acids found in coffee. And do this without destroying the machine.

The issue is, however, that we cannot do better than physics allows. It is impossible to achieve water with high Ca^{2+}/Mg^{2+} concentrations and low HCO_3^- and Cl^- concentrations without the inclusion of other anions to charge balance. For every positive charge there is an associated negative charge somewhere in solution. (The sharp eye may have noted that, indeed, Figure 1 defies the laws of physics: the solution has a net positive charge!) There is a constant battle between machine corrosion (by the inclusion of Cl^-) and perceived acidity (through the presence of HCO_3^-), and other common anions (including the strongly basic ^-OH, the poo-inducing SO_4^{2-} and other negatively charged species). Short of formulating your own water, or filtering in a creative manner, modulating water chemistry remains a challenge. Identifying the makeup of your incoming water and selecting the correct filtration unit are paramount in enabling you and your café the best chance of making a consistently good espresso shot.

—Christopher Hendon is a post-doctoral researcher at Massachusetts Institute of Technology and co-author of Water for Coffee. *For more information on filtration in the café, check out our article here.*