The Role of Dissolved Cations in Coffee Extraction

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ABSTRACT: The flavorsome compounds in coffee beans exist in the form of aprotic charge neutral species, as well as a collection of acids and conjugate salts. The dissolution and extraction of these organic molecules is a process dependent on the dissolved mineral content of the water. It is known that different rates and compositions of coffee extraction are achieved through the control of the water "impurities", Na^+, Mg^{2+}, and Ca^{2+}, which coordinate to nucleophilic motifs in coffee. Using density functional theory, we quantify the thermodynamic binding energies of five familiar coffee-contained acids, caffeine, and a representative flavor component, eugenol. From this, we provide insight into the mechanism and ideal mineral composition of water for extraction of flavorsome compounds in coffee.

KEYWORDS: *coffee extraction, water impurities, density functional theory*

INTRODUCTION

Over the past century, the molecular constituents of roasted coffee have been characterized through distillation and chromatography.[1−5] These constituents form a complex spectrum of post-roast organic molecules, varying in flavor and intensity.[6] This work provoked a concerted effort in both universities and private institutions to harness these flavors into a balanced, delicious cup of coffee. There are, however, many variables that influence the extraction of coffee-contained compounds in water.[7] Roast, grind size, temperature, pressure, and brew time define the cupped product, but it is the water's composition that facilitates the extraction of sugars, starches, bases, and acids.[8]

The role of water and its impurities has been experimentally explored in great detail, in two separate studies conducted originally by Lockhart and co-workers[9] and later by Pangborn and co-workers.[10] Along with the interesting effects on coffee extraction, both studies also describe the role that water impurities play in both the flavor and hue of water, pre-extraction. However, these works were not exclusive of the usual variables that plague the coffee industry: other dissolved ions such as transition metals, halides, nitrate, sulfate, phosphate, and, importantly, carbonate. The role of the dissolved ions in extraction of coffee constituents is challenging to quantify experimentally, because there are many competing interactions that are both entropically and thermodynamically significant (e.g., the displacement of water from coordination spheres to form ion pairs).[11] In an attempt to simplify the problem for the end user, the Specialty Coffee Association of Europe (SCAE) devised guidelines of "ideal" water for coffee extraction.[12] These guidelines are verisimilitude in the coffee industry; the quantification of *all* dissolved ions intrinsically sums both the cationic and anionic concentrations through an ionic conductivity measurement of the total dissolved solids (TDS).[13] As a result, the SCAE suggests a range with a vague dissolved solids upper limit of dissolved solids (ca. 300 ppm TDS) for favorable extraction of coffee.

In most geographical locations the concentration of bicarbonate is higher than that of the dissolved alkaline earth metals resulting in water with high buffering ability.[14] Considering the guideline of an upper limit of 300 ppm TDS, the major water filtration and ion exchange manufacturers focus on the removal or exchange of dissolved $CO_3^{2−}$, which inherently reduces Ca^{2+} through recombination, forming scale, collectively lowering the TDS.[15,16] Conventional filtration units either have an osmotic system or filter particulates over a carbon block, while exchange units generally feature a carboxylate buffered Mg^{2+} or Na^+ channel that simultaneously decreases the Ca^{2+} concentration through ion-exchange and some carbonate (as CO_2) through the rapid column−solute proton transfer and subsequent decarboxylation. Considering the current industrial approach, it would appear dissolved ions are a commodity that must be managed and reduced, rather than harnessed.

The interaction between dissolved ion and water is species dependent. For instance, the hydration of Ca^{2+} is more exothermic than that of Mg^{2+}.[17] The dissolution of larger molecules is more complex, because the solute often has a complex array of polar motifs. In flavor chemistry, the organic components feature competing hydrophilic and hydrophobic regions, that interact with the water through hydrogen bonding, Coulombic interactions and through the formation of ordered hydrate cages.[18] Regardless, when the solutes are below water's saturation point, they do not significantly alter the electrostatics or hydrogen bonding of the bulk system.[19−21] In agreement with the work performed by Lockhart, the upper limit of dissolved ions in coffee extraction is *not* limited by saturation but rather by overextraction. In this context, we are interested in the role that dissolved cations play in the extraction of coffee constituents.

The application of contemporary computational chemistry is a useful tool for studying such interactions. Here we propose an accessible quantum chemical approach for quantifying the

binding of coffee organics to familiar dissolved metal ions, Na^+, Mg^{2+}, and Ca^{2+}. We have selected five archetypal acids (**1**–**5**), caffeine (**6**), and eugenol (**7**) as representatives of the larger class of organic derivatives found in varying concentrations in roasted beans (Figure 1).[22] Of the five acids, lactic (**1**) and
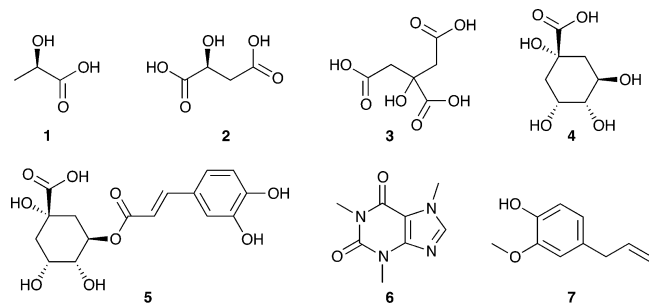

Figure 1. Seven compounds contained in roasted coffee, displaying a range of functionality. There are five carboxylic acids in increasing molecular weight: lactic acid (**1**), malic acid (**2**), citric acid (**3**), quinic acid (**4**), chlorogenic acid (**5**), an alkaloid, caffeine (**6**), and a flavor note, eugenol (**7**).

malic (**2**) acids embody sour notes, while citric acid (**3**) has an appealing sweet flavor. Quinic acid (**4**) and its larger derivative chlorogenic acid (**5**) are considered to taste pungent and unpalatable.[23,24] Caffeine (**6**) was included as an archetypal aromatic alkaloid (and is weakly basic, $pK_a = 14$),[25] while eugenol (**7**) is a delightful woody note found in coffee, wine, and whisky.[26,27] It should be noted that some acids exist as the potassium salt in the bean. As we will discuss later in this paper, K^+ displays significantly weaker binding to coffee constituents because it is both diffuse and singly charged. Here, we consider the acids in their free acid form, because the relative binding energies of the charge neutral molecules coordinating to ions represent the weakest possible interactions, highlighting the significance of the ionic species.

■ MATERIALS AND METHODS

All quantum-chemical calculations were performed using the FHI-aims quantum chemical package.[28] FHI-aims is an all-electron code that uses atomic-like orbitals numerically truncated for the inclusion of diffuse and polarization functions. The electronic wave functions are constructed using the combination of these numeric atom-centered basis functions. A converged "tight" basis was employed, which installs d, f and g functions on the O atoms, and scalar relativistic effects were included. Convergence criteria were set to 1×10^{-6} eV per system, corresponding to approximately 5×10^{-5} eV per atom. This criteria is comparatively high to other recent publications featuring similar methods.[29,30]

The thermodynamic relative binding energy of two compounds is defined by

$$E_T = E_{ab} - (E_a + E_b) \qquad (1)$$

where the relative binding energy, E_T, is equal to the difference between the bound product, E_{ab}, and the individual components, E_a and E_b. These energies are relative to the molecular states, and thus the magnitude of these energies is only directly comparable within our experiment. Local structure optimizations were performed using the forces from the density functional, PBE (Perdew−Burke−Ernzerhof) exchange-correlation potential (V_{xc}^{KS}).[31] The PBE functional was selected for its desirable trade off between speed and qualitative energies. We tested other familiar hybrid exchange-correlation functionals such as PBE0 (Perdew−Burke−Ernzerhof with the inclusion of 25% Hartree−Fock exchange, 75% correlation) and B3LYP (Becke and Lee−Yang−Parr functional, common in organic

chemistry modeling), and PBE produced the same trends in less than half the time.[32]

The consideration of the water interactions is important. There is a long-standing problem in computational modeling of water because it is unclear how many water molecules must be included before one is considering *liquid* water and not a collection of gaseous water molecules. Explicit water molecules severely increase computation time; to circumvent this problem, a familiar approximation is the inclusion of a polarizable continuum model (PCM) that mimics solvents through the application of a dielectric continuum, which acts to screen charges. The PCM (dielectric constant of H_2O, ϵ, = ca. 80) was tested for the calcium series and produced a consistent 30% decrease in relative binding energies. Given the linear nature of the adjustments using a PCM, we elected to exclude it to increase the speed and accessibility of these computations. We consider this acceptable, because values computed using PCM and explicit water are at the limitations of computational power today and still do not produce absolute energies but rather relative binding energies. As a result, our method is accessible and accurate, within the error of the methods and within the limitations of computational chemistry at the time of writing.

Furthermore, we would like to comment on the transferability of our methods to foreign systems. Following the aforementioned procedure, relative binding energies can be consistently calculated. In this case, we have neglected macroscopic variables, such as explicit water. This assumption is certainly not always applicable: this approximation yields poor results in, for instance, protein folding computations. However, there are many applications in which gas-phase computations may be informative, and we encourage the application of quantum mechanics to other chemical problems.[30]

■ RESULTS AND DISCUSSION

Dissolved cations interact with the nucleophilic motifs of solvated coffee constituents. This interaction may be understood with classical electrostatics:

$$U_r = \frac{(\mathbf{q}_i \cdot \mathbf{q}_s)}{r^2} \qquad (2)$$

where the interaction energy U_r is proportional to the charge of both the ion and solute ($\mathbf{q}_i$ and $\mathbf{q}_s$) divided by the interatomic separation, r^2. With this considered, we would anticipate that the more localized charged species should interact more strongly with molecular multipoles. Upon geometry optimization, we recover an equilibrium local minimum energy structure, where the metal ions interact strongly with electron rich motifs. A representation of the equilibrium geometries of each ion−solute cluster is shown in Figure 2, with the notable bond lengths between metal ion and nucleophilic motif listed in Table 1.

The summary of the binding energies is shown in Figure 3, with H_2O-M^{n+} interaction included as a reference. The dissociation of metal-coordinated water is a process driven by entropy, however there is a thermodynamic competitive displacement of metal-coordinated water molecules by compounds **1**-**7**.[17] For coordination and interaction, the coffee compounds are thought to require a higher E_T than the H_2O-M^{n+}. This poses an interesting problem for Na^+ rich water: the binding of **6** and **7** are less favorable than water itself, suggesting that Na^+ does not facilitate extraction of caffeine or eugenol. The **1**-**5**-Na^+ interaction is of comparable energy to the H_2O−Na^+; the extraction of the five acids are not dramatically influenced by the presence of Na^+. First generation exchange filtration units featured a Ca^{2+}/Na^+ ion-exchange column: from our results, this only serves to decrease scale build up, at the deficit of extraction ability of some compounds.
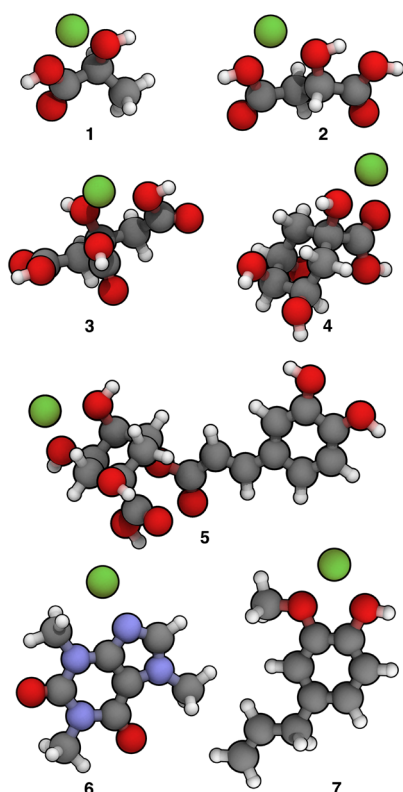
Figure 2. Equilibrium coordination environments of lactic (**1**), malic (**2**), citric (**3**), quinic (**4**), and chlorogenic acid (**5**), caffeine (**6**), and eugenol (**7**). Hydrogen, carbon, nitrogen, oxygen, and magnesium are shown in white, gunmetal, periwinkle, red and green, respectively.

Table 1. Interaction Lengths of Each Metal Ion to the Nearest/Most Nucleophilic Site, as Shown in Figure 2[a]

	1	2	3	4	5	6	7	H_2O
Ca^{2+}	2.21	2.19	2.23	2.15	2.22	2.22	2.21	2.20
Mg^{2+}	1.93	1.92	1.96	1.93	2.00	1.97	1.96	1.92
Na^+	2.25	2.26	2.25	2.24	2.24	2.28	2.24	2.23

[a]Distances are stated in Å.
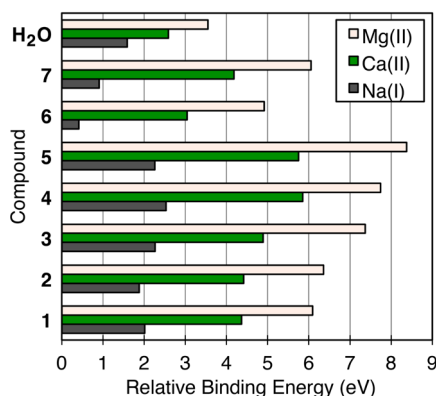
Figure 3. Gas phase binding energies of compounds **1**−**7** and H_2O to Na^+, Mg^{2+}, and Ca^{2+}, in gray, beige, and dark green, respectively.

The relative binding energy of (**1**−**7**)−Mg^{2+} is highest in all cases, with the E_T proportional to the charge density of compounds **1**−**7**. Mg^{2+}-rich water is paramount if increasing extraction yield is important. There is, however, a subtle but important increase in the relative binding energy of **1**−**3**

relative to **4** and **5** to Mg^{2+} compared with Ca^{2+} (if only by approximately 5%). This is desirable, suggesting Mg^{2+}-rich water would bind to marginally more of the desirable flavors in coffee, although the macroscopic effects of this would be better probed experimentally. The high binding energies of the undesirable acids, **4** and **5**, is less pleasing. Relative to other ions, Mg^{2+} would significantly increase the extraction of these compounds, which may have implications for both the consumer's health and his enjoyment of the cup.[33,34] In this case, the importance of the dissolved carbonate and other bases are important. Bicarbonate/carbonate interacts strongly with **5** (pK_a = 2.66), neutralizing some of this less desirable acid, versus the interaction with the smaller acids, **1**−**3** (pK_a = 3.86, 3.40, and 3.14, respectively). This interaction is outside the scope of this article but is certainly important and is a direction we intend to explore in the future.

Similar binding trends are observed for Ca^{2+}; however, the relative binding energy is lower than that of Mg^{2+} in all cases. The binding energy of **6**−Ca^{2+} is comparable to H_2O−Ca^{2+}; this is the only instance in which one of the divalent cations interacts weakly with an electron-rich motif. This is not a surprising result as the electron density of caffeine is delocalized across the conjugated aromatic motif, resulting in low binding energies to all metal ions (in the case of Na^+, almost noninteractive). Considering the results from Table 1, the binding energies are evidently proportional to charge and inversely proportional to the ionic radii. Hence we do not need to explore the binding of K^+ because it is anticipated that E_T is even lower than that of Na^+. Thus, the K^+ found in the bean in the form of salts can be considered very weakly bound, if not labile (ions concerned in this paper would be anticipated to displace the K^+). This effect is amplified if the acids exist as the conjugate bases, and thus our study represents a conservative representation of the binding of coffee constituents to dissolved ions in water.

Based on our thermodynamic experiments, a compelling argument can be made for the favorable exchange of Ca^{2+} for Mg^{2+} to increase extraction yield, with no deficit to coffee flavor, and the additional benefit of removing the source of lime scale. We also emphasize the surprising result that Na^+ binds weakly to most neutral compounds in coffee beans, suggesting that sodium rich water is of no benefit to the consumer, besides removing the source of scale build up. Thus, if the motivation is to extract the most coffee constituents (i.e., instant coffee), then Mg^{2+}-rich water is most suitable. If the motivation is to achieve the best balance of flavors for a given lighter roast coffee, then both Ca^{2+} and Mg^{2+} do a comparable job,[35] with Mg^{2+} having the added feature of preventing scale formation.

It should be noted that there is not one particular composition of water that produces consistently flavorsome extractions from *all* roasted coffee. Rather, there is water that has the most extracting ability (i.e., cation-rich), and the resultant flavor depends on the balance between both the cations in solution and the quantity of bicarbonate present (acting as a buffer). Furthermore, each bean is roasted to taste optimal when brewed with the water it was roasted to. We acknowledge this point, and emphasize that this work elucidates the important role that dissolved ions play in facilitating the extraction process.

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Notes

The authors declare no competing financial interest.

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(12) The SCAE suggest that water with ≤300 ppm total dissolved solids is well-suited for the application. This seems to be vague based on the work we have proposed herein. A summary of the SCAE guidelines is provided in this link: http://tinyurl.com/onpcsms.

(13) The measurement of TDS is intrinsically flawed because the ionic mobilities are dependent on diffusion rates, coordinations spheres, and most importantly charge. As a result, the application of TDS for quantifying water components is certainly debatable.

(14) The impact of dissolved bicarbonate is problematic because both bicarbonate and water are polyprotic buffers. Regardless, water hardness is publically accessible information, an example of which is neatly summarized for the UK here: http://tinyurl.com/nowade8.

(15) http://www.brita.net.

(16) http://www.bwt-wam.com.

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(18) Indeed, the formation of hydrated cages is an entropically driven process that pushes against the formation of local ordering of water around a hydrophic motif. However, the effect of dissolution is very small, because the electronic structure of water is not grossly affected by dissolved solids.

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