The impact of solvent relative permittivity on the dimerisation of organic molecules well below their solubility limits: examples from brewed coffee and beyond

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The formation of aqueous intermolecular dimers is governed by both the nature and strength of the intermolecular interactions and the entropy of dissolution. The former interaction energies are determined by the polarity of the solvent and the functionality of the solute. Using quantum chemical methods, we probe the energetics of dimer formation of representative compounds found in coffee well below their solubility limits. We find that with the exclusion of entropy, the dimer formation is thermodynamically unfavorable with negligible dependence on the dielectric medium.

Introduction

Water plays an important role in a wide variety of chemical reactions because of both its redox ability and its efficiency as a solvent. A single H_2O molecule is small, and a collection of H_2O molecules interact strongly with their neighbors through H-bonding. The large dipole moment and amphiprotic nature of water results in bulk H_2O remaining a liquid to relatively high temperatures (and low pressures) compared to other similarly sized molecules.

One physical property that arises from a combination of the bulk polarisation, polarisability and packing (*i.e.* intermolecular distance between neighbouring H_2O) is the relative permittivity (ε, formally termed the 'dielectric constant'). By definition, ε is the temperature-dependent ratio of the electric field strength in a material compared to the same field in a vacuum ($\varepsilon_{vac} = 1$). Chemically this can be thought of as how efficiently the material screens charge. While some materials feature very high dielectric constants (for example $\varepsilon_{BaTiO_3} = 1230$ (ref. 1)), water features one of the highest of any solvent, $\varepsilon_{H_2O}^{20°} = 80.1$.[2]

Though water's dielectric constant is relatively high, this property is affected by the advent of dissolution of other species. Take for example the addition of salt (NaCl) to water. Though pure H_2O is an electrical insulator, the dissolution of NaCl results in a bulk electrical conductor (where NaCl is the electrolyte). The mode of conductivity in water is through ionic

capacitance rather than band-transported electrons (where metallic materials have infinite relative permittivity). Yet the dissolution of salt in water results in a decreased relative permittivity, Fig. 1a, due to an increased net order in the water.[3,4] An example of the first coordination sphere of a solvated Na^+ is shown in Fig. 1b. This order decreases the ability of H_2O to geometrically orient to screen electric fields produced by solvated molecular multipoles. This effect is also observed, albeit to a lesser extent, upon the addition of sugar to water, Fig. 1a.

In most cases the dissolution of materials in water is governed by an increase in net entropy, and the solubility limit of any material is reached when $\Delta G = 0$. However, when well below the solubility limit of a given compound, an entropy-
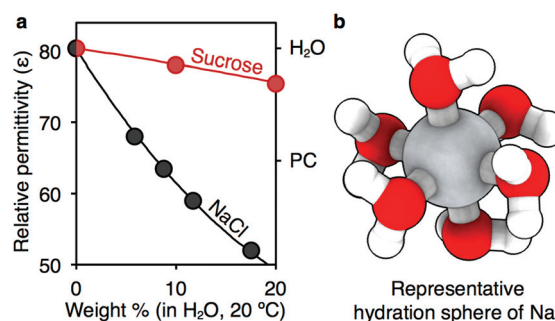

Fig. 1 The temperature-dependent relative permittivity (ε) of water is modified through the incorporation of salt (NaCl)[31,32] or sugar (sucrose)[33] (a). The dielectric constant of propylene carbonate (PC) is presented for reference. The decrease in ε is attributed to the formation of extended solvation spheres around guest molecules and ions, an example of the six-coordinate first solvation sphere of Na^+ is shown in (b).[34]

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independent model (*i.e.* a quantum mechanical thermo-dynamic model) provides insight into the nature of the solvated species.

Thus, as water solvates organic compounds with an array of polarisations, the net dielectric constant of bulk water decreases. As a result, one might conclude that water with solvated organics would become a less-effective solvent. Furthermore, this change in polarity could be substantial enough to result in stronger intermolecular interactions between solvated species than with the solvent itself, facilitating the formation of dimers and higher order oligomers. Indeed, this observation is validated for the classic example of oil separating from water, where oil phase separation occurs above the solubility limit.

In highly dimer-directing conditions (*i.e.* approaching the solvent saturation limit) it has been shown that a variety of molecules form *in situ* dimers based on changes in dielectric constant;[5–9] however, in more moderate conditions (*i.e.* at realistic beverage concentrations) the dimerisation effect was not clear. Motivated by a recent publication[10] that explored the entropic motivation for caffeine to dimerise or aggregate as a function of the dissolution of sugar, salt and other water-soluble species, we sought to isolate the quantum mechanical energetics of free-molecule and dimer stabilities in a range of dielectric media. Notably, we are probing the local intermolecular interaction energetics. This is particularly important in the context of the addition of sugar to brewed coffee, as it has been proposed that the addition of organic compounds may provoke caffeine to dimerise (speculatively impacting the perceived flavour of the beverage).[11] It should be noted that an experimental report of caffeine dimerisation was reported, but in this study there was no appreciable difference between 500 and 1000 mg L^{-1} (concentrations we observe in an average cup of coffee).[12]

By virtue of the model, the solvent continuum is in infinite excess;[13] the molecular energies are representative of a solvated molecule well below its solubility limit. We elected to probe the propensity for dimerisation in caffeine and two other representative compounds that frequently occur in brewed coffee well below their solubility limits: linalool (delight-fully fruity and floral) and *n*-octane (a representative hydrocarbon that might be formed in the roasting process),[14–16] Fig. 2. These are particularly compelling selections as linalool and octane both share C_8 backbones. Similarly, linalool and caffeine both contain H-bonding motifs and regions of aliphatic unsaturation. Hence, these three molecules span a range of intermolecular interaction strengths, from weak octapole (van der Waal's forces) to strong intermolecular H-bonds. They also demonstrate a range of solubility and chemical functionality, and provide a simple but accurate description of some of the flavorsome compounds in coffee.

Computational method

All quantum chemical calculations were performed in GAMESS-US,[17] a free all-electron software package. Monomeric and dimeric structures of octane, linalool, caffeine and H_2O were constructed in Avogadro[18] (a free visualisation software package) and initially optimised with the UFF force field[19] (the so-called Universal Force Field, that recovers reasonable starting geometries for organic molecules). From previous theoretical and experimental studies, it was found that the absolute geometry of the dimer structures of H_2O and caffeine were relatively geometry-insensitive, as long as the H-bond and π-interactions were maintained, respectively.[20–22] As a result, our structures reflect one of many minimum energy geometries in a relatively shallow potential energy well. For both linalool and octane, two chemically sensible geometries were constructed and the lowest energy structure was chosen in each case.

The monomeric and dimeric UFF-optimised structures were then imported to GAMESS-US and were further geometrically optimised using the B3LYP hybrid-GGA functional (a functional that yields accurate geometries and electronic structure for organic molecules) with a 6-311+G(d) basis set (a sufficiently large set of mathematical functions to describe the electron density). This functional and basis has been repeatedly validated to provide a favorable balance between computational expense and reliable structure/energetics for most organic molecules.[23–26] The convergence criteria was set to 0.25 kcal per molecule (equating to 0.01 eV per atom, and sufficient for systems containing H-bonding).

A pseudo-solvent polarisable continuum model (PCM, a dielectric screening parameter that simulates the stabilisation effects of a solvent without the inclusion of explicit atoms) was used to simulate solvation of the monomeric and dimeric species in various dielectric media. Among other parameters, the PCM has preset values for ε and a geometric packing term dependent on the solvent identity. This geometric packing term is related to the size and shape of the solvent molecules, but is only included such that the PCM has some inhomogeneity (to better represent the bulk). GAMESS-US offers several parameterised 'common' solvents; we elected to use the preset dielectrics of water $\left(\varepsilon_{H_2O}^{20°} = 80.1\right)$, DMSO $\left(\varepsilon_{DMSO}^{20°} = 46.7\right)$, methanol $\left(\varepsilon_{CH_3OH}^{20°} = 32.7\right)$, ethanol $\left(\varepsilon_{C_2H_5OH}^{20°} = 24.5\right)$ and
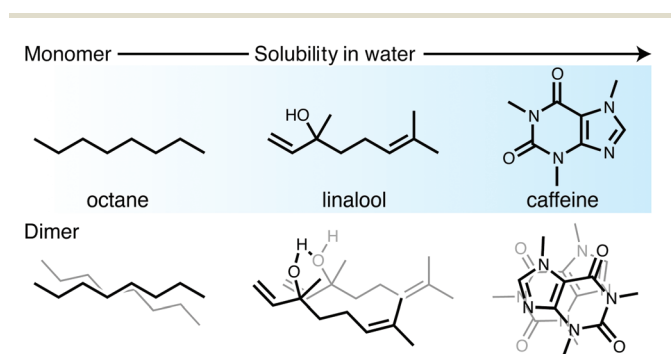

Fig. 2 Three representative molecules found in brewed coffee presented in increasing solubility in pure H_2O:[35] octane, linalool and caffeine. These compounds possess a range of chemical functionality including extended π-systems, H-bonding sites and, in the case of octane, exclusively weak van der Waals (vdW, or octapole) interactions.

acetone $\left(\varepsilon_{C_3H_6O}^{20°} = 20.7\right)$. The packing differences did not contribute significantly to the total energies (exemplified by the relatively flat dimer energy in H_2O, Fig. 3). In all cases, solvent–solute intermolecular interactions are not accounted for explicitly as here the 'solvent' is merely a polarisable continuum. We calibrated the error in our PCM model by comparing $E\left(_{H_2O}^{monomer}\right)$ and $1/2 E\left(_{H_2O}^{dimer}\right)$ in 'bulk water' (*i.e.* $\varepsilon_{H_2O}^{20°} = 80.1$). The error in the PCM was found to be systematically 0.05 kcal; this value is used as the error bar in Fig. 3 and shown schematically in the top panel of Fig. 4. Furthermore, the PCM model was found to reproduce the bond energy of bulk H_2O, with the aqueous –O–H–O– bond energy computed to be −6.3 kcal mol^{-1}, which is comparable to experimental measurements for water H-bond energies (*ca.* 5 kcal).[27–29] The absolute energetic difference is to be expected, as the B3LYP functional has been shown to systematically over-bind in certain intermolecular systems. For the purposes of this paper we are interested in the relative energetics, rather than their absolute values.

Dimer formation energies were computed using the simple equation:

$$E_{solvent}^{formation} = E_{solvent}^{dimer} - 2E_{solvent}^{monomer} \quad (1)$$

and monomer and dimer solvation energetic costs were defined as:

$$E_{solvation}^{cost} = E_{vac}^{monomer} - E_{solvent}^{monomer} \quad (2)$$

Fig. 4 A comparison between the solvation energies of two non-interacting monomers and the dimer. (a) Water exhibits similar salvation energies in both the monomeric and dimeric configurations (due to the entire molecule contributing to these intermolecular interactions). (b) Octane also has little cost associated with forming the dimer (but in this case this is due to the octane molecules only weakly interacting). (c) Linalool has both hydrophilic and hydrophobic regions and hence the formation of the dimer significantly reduces the net polarization of the material (therefore greatly decreasing the interaction between the dimer and solvent continuum). (d) Similarly, caffeine shows the largest deficit in solvation energy from forming the dimer. (e) The dimer solvation cost can be computed as the difference between two free monomers and one dimer. Squares are used to show equivalent data points.

where a similar construction can be applied to the dimeric species.

Dimerisation energetics

The explicit water dimer was included in the dimerisation study as a metric for computational error. In Fig. 3, the H_2O dimerisation energy (from eqn (1)) was found to be consistently *ca.* 6.3 kcal mol^{-1}, independent of the solvent continuum. Furthermore, the packing differences between solvents were found to be unsubstantial, as observed by the planarity of the water dimer energy. This solvent-independent dimer energy is to be expected as the H-bond is the strongest bond considered in this paper, and should not be significantly destabilised in lower ε PCMs.

Similarly, both octane and linalool demonstrated solvent-independent dimer formation energetics. However, the magnitude of the dimer formation energy is markedly different between H_2O, octane and linalool. Both linalool and water feature highly polarised O–H bonding, and are expected to have similar dimer formation enthalpies (*ca.* −6.0 and −6.3 kcal mol^{-1}, respectively).
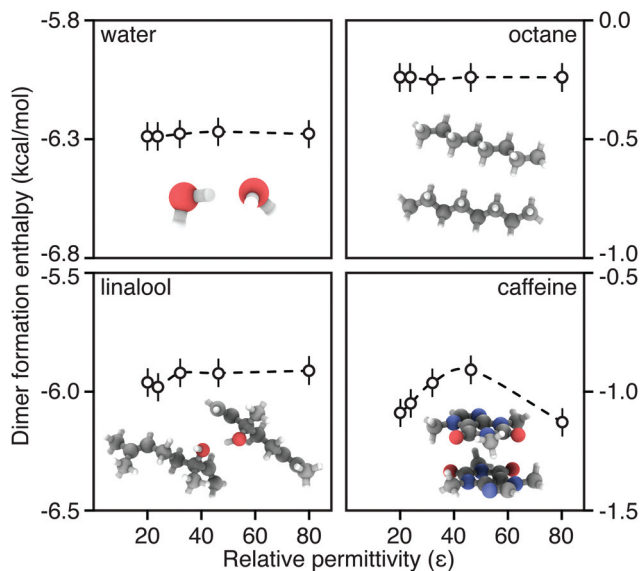

Fig. 3 The formation enthalpies of dimers of water, octane, linalool, and caffeine in various pseudosolvents. Intermolecular stabilisation is greater for more polarised interactions (*e.g.* H-bonding in water or linalool), and account for *ca.* 6 kcal mol^{-1} increase in stability. Weaker intermolecular interactions (*e.g.* vdW and π-interactions) account for 0.2–1 kcal mol^{-1} stabilisation. These weaker interactions are not significant at room temperature, where thermal/kinetic energy is large enough to break these transient bonds.
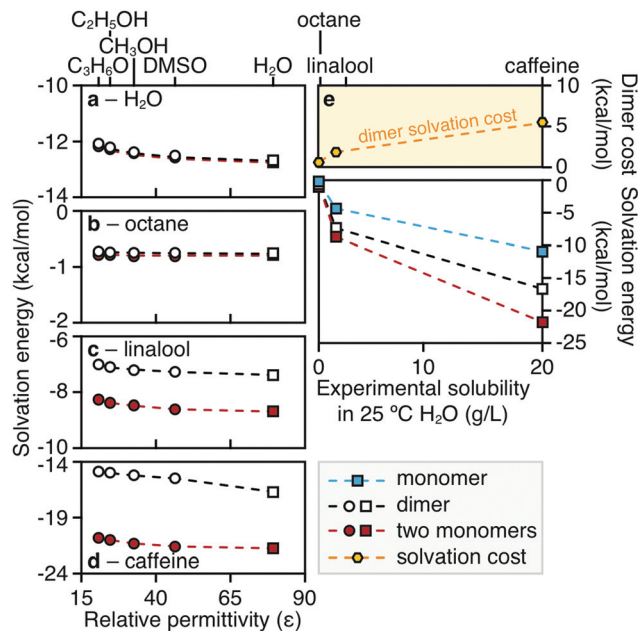
Their differences are attributed to the lower polarisation of the C–O–H bond in linalool. Conversely, intermolecular octane interactions are dominated by weak octapole interactions (van der Waals' forces). This is reflected in the weak intermolecular bond formation energy (*ca.* 0.2 kcal mol^{-1}).

The strongest intermolecular interaction of the caffeine dimer is through-space non-covalent π-stacking (*i.e.* a quadrupole interaction). Quadropole interactions are typically much weaker than an arbitrary H-bond in bulk H$_2$O. As a result, we would not expect the caffeine dimer energy to be greater than that of water. Furthermore, there is evident solvent packing dependence in the caffeine model: the disfavored formation enthalpy hump in DMSO is a computational artifact. This arises because the π-stacking caffeine interaction is so weak that numerical noise is a contributing factor. In summary, Fig. 3 shows that compared to the intermolecular interactions of H$_2$O and linalool, the intermolecular interactions of caffeine and octane are much weaker than the self-interaction of water.

Solvation energetics

Another contributing factor to the thermodynamic formation of dimers is the solvation cost associated with forming larger organic dimers. We might anticipate that the solubility of an organic compound (where the dimer can be though of as one compound for this purpose) decreases with molecular size (a combination of entropic and enthalpic effects). We can estimate the latter from DFT. From eqn (2), the solvation energies of $2E_{\text{monomer}}$ (shown in purple, Fig. 4a) and E_{dimer} (shown in blue, Fig. 4a) are presented. Intermolecular interactions are analogous to including explicit solvent, where the polarisability of the neighboring molecule can act to screen some of the charge, rather than relying entirely on the PCM. As a result, all explicit intermolecular interactions should reduce the polarisation of the dimer, and hence interact less strongly with the solvent. We used this self-interaction as our estimation of error in the calculation: a perfect PCM model should show no energetic difference between the solvation energy of a single H$_2$O-dimer intermolecular interaction and a free monomer in a continuum that accurately represents the bulk (in this case a free H$_2$O in PCM = water). Indeed, the calculations were found to be precise, with an error of 0.05 kcal mol^{-1}. Furthermore, the solvation energy is expected to decrease proportionally to the dielectric constant of the solvent. The magnitude of this effect is seen in the minor destabilisation in all molecules in Fig. 4a–d. This effect is certainly real, but negligible in this context.

The thermodynamic possibility for dimer formation can be thought of as a competition between the formation enthalpies presented in Fig. 3 and the cost to solvate the newly-formed, less-polar dimer (presented in grey, Fig. 4e). We can state that if the solvation cost is greater than the dimer formation enthalpy—and we discount entropy in these models—the dimer would not be expected to be thermodynamically stable.

The solvation energy of octane is low in all solvents (Fig. 4b) as the C–H and C–C bonding is intrinsically non-

polar. As a result, the formation of a dimer compared to two free monomers yields essentially no difference in solvation cost (Fig. 4e). In this case, entropy contributions would dominate the solubility limit of octane. This is a rational outcome; octane is experimentally highly volatile, due to its lack of strong intermolecular interactions, and clearly does not interact strongly with H$_2$O as it phase separates.

Owing to the inclusion of the secondary alcohol, linalool is marginally more soluble in water than its saturated and dehydrated analogue, octane. Thus, dimerisation of linalool is expected to result in the solvation cost increasing as the polar regions have been self-passivated (Fig. 4c). Given the solvation cost is approximately 1 kcal mol^{-1}, and the dimer formation energy is −6 kcal mol^{-1}, a thermodynamic driving force for the formation of the dimer could be expected.

The same cannot be said for caffeine. Caffeine is reasonably soluble in water (20 g L^{-1} at 25 °C), but the dimerisation is only favorable by *ca.* 1 kcal mol^{-1} (Fig. 3). The solvation cost of the dimer (5 kcal mol^{-1}, Fig. 4d) is greater than the dimer formation enthalpy (−1 kcal mol^{-1}), suggesting that the dimer formation is highly unfavorable. Experimentally, this would suggest caffeine exists as a free monomer well below its solubility limit. In all cases, the solvation energy for the free monomer is greater than the dimerisation energies presented in Fig. 3. Indeed, a DOSY NMR experiment would shed valuable light on these problems and is certainly an avenue we intend to explore in the near future.

Implications

From our quantum mechanical models we were able to isolate the mode and associated energetics of dimerisation of a small set of compounds frequently found in coffee and other beverages. By mass, espresso contains *ca.* 10% coffee compounds while filter coffee is more dilute at *ca.* 1.5%. Considering the decrease in relative permittivity of water containing solvated organics, we might expect that a cup of coffee has a dielectric constant lower than native bulk water. But from our work, this effect should not thermodynamically provoke dimerisation if the guest molecules are more polarisable than the solvent.

From relatively simple computations and chemical arguments, we elucidated that the strongest intermolecular dimer interaction was H-bonding in water itself (also found, to a lesser extent, in linalool). More broadly, the energetics of the intermolecular interaction were determined by the extent of polarisation of the solute. As a result, it was found that both caffeine and octane were weakly interacting (less than 1 kcal mol^{-1}). The dimer formation in all cases is relatively unperturbed by the dielectric medium. Instead, the solvation energy is substantially higher for the free monomer in all cases. This suggests that when well below the solubility limit of the compounds examined here, and when entropy is excluded (which is implicitly accounted for in compounds 'well below their solubility limits'), it was found that these compounds will likely exist as free monomeric species.

Applying these findings to the real world, we must consider that coffee is served above 0 K. From the Boltzmann equation 90 °C water (a typical coffee temperature) provides 0.72 kcal mol^{-1} of kinetic energy. Given our systematic over-estimation of dimer bond energy, it is possible that this influx of kinetic energy is likely greater than the dimer formation enthalpy of both octane and caffeine. However, the most compelling result is gleaned from comparison to experimental results that implicitly include entropy: caffeine is highly soluble in water. At the marginal caffeine concentrations observed in brewed coffee,[30] it is likely that caffeine (and octane) exists as a free monomer.

Acknowledgements

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