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Roles of Reversible and Irreversible Aggregation in Sugar Processing

Minori Uchimiya[*]

USDA-ARS Southern Regional Research Center, 1100 Robert E. Lee Boulevard, New Orleans, Louisiana 70124, USA

*fax: (504) 286-4367, phone: (504) 286-4356, email: sophie.uchimiya@ars.usda.gov

Abstract

Colloids (1-1000 nm particles) in sugar cane/beet juice originate from non-sucrose impurities (polyphenolic colorants, residual soil, polysaccharides) of the plant materials; additional colloids form during the high temperature processing. Colloids are reactive towards aggregation, sorption, desorption, and redox/hydrolysis/thermal transformation reactions. Both DLVO (van der Waals and electrostatic) and non-DLVO (involving hydrophilic colloids) interactions control the stability of colloids in juice. Heteroaggregation causes a range of feedstock and end-product problems including turbidity, viscosity, color, gelling, crystallization, starch ghost, and heat transfer problems. Even after intensive clarification and refining, trace colloidal impurities on white (refined) sugar remain to cause a problem known as acid beverage floc. Acid beverage floc is an example of DLVO-type aggregation of oppositely charged particles at decreased pH. Examples of irreversible aggregates include starch ghost and recalcitrant organomineral composites formed at elevated temperature that resist heat transfer. Fundamental knowledge in

aggregation kinetics is necessary to predict the occurrence of undesirable aggregates as pH, ionic strength, temperature, and sucrose concentration changes during the processing of sugar cane/beet juice.

Keywords

Polyphenol; Bioenergy; Aquasol; Macromolecule; Fermentable sugar

Introduction

Colloids (1-1000 nm particles) in sugar cane/beet juice are heterogeneous and originate from non-sucrose impurities of the plant materials: starch and other polysaccharides, protein, tannin, and residual soil (silica, clay and Fe/Mn (hydr)oxides) (Figure 1). During the storage and high temperature processing, deterioration products and precipitates add to the colloidal pool. The size range of colloids fall under the category of "soft matter" that is easily deformable/compressible and has low shear modulus (G) (Ikeda and Zhong, 2012). Hydrophilic colloids include gelatin, starch, gum, protein, and biocolloids (microorganisms) (Mathews et al., 2000). Mineral particles have variable charge because of pH- and ionic strength-dependent dissociation of surface functional groups (Petosa et al., 2010). Clays in trace soil on sugar crop have: (i) fixed charge balanced by interlayer alkaline earth cations and (ii) amphoteric charge of the edge sites, broken –OH edges and other heterogeneous surface sites (pits, corners). Aggregation of different colloidal particles (heteroaggregation) causes a range of feedstock and end-product problems, including gelling, crystallization, turbidity, viscosity, color, heat transfer problems, and acid beverage floc. This critical review will explore the identify and fundamental chemistry of problematic colloidal impurities in sugar (sugarcane and beet) feedstock that will similarly impact the sugar processing/refining (for food products) and renewable energy/product industry. Behaviors of mineral and polymeric colloids (that are present in cane juice) in dilute sucrose solution will be described first. Then, the influence of elevated temperature and viscosity (in concentrated sucrose solution) will be examined on the colloidal stability.

Dissolved and particulate constituents of cane and beet juice

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Much like other food products, sugar cane/beet juice is a highly heterodisperse system involving different sugar structures of varying reactivities. In addition to sugar molecules (mono- and disaccharides), there are polysaccharides, high molecular weight (MW) polyphenolic colorants, minerals, and additional colloidal impurities (Godshall et al., 2002). Monosaccharides are <1 nm, polysaccharides are ≈100-1000 nm, and starch granules are ≈10-100 μm (Ikeda and Zhong, 2012) (Figure 1). Carbohydrate is a polyhydroxy aldehyde (aldose) and ketone (ketose) that exists primarily in the closed-ring structure (Bruice, 1998) (Figure 2). Because sucrose does not contain a hemiacetal group, it does not mutarotate to form the reactive open-ring aldehyde and ketone (Bruice, 1998). However, sucrose undergoes acid-catalyzed hydrolysis to form invert (reducing) sugar: glucose and fructose (Andrews et al., 2002). As shown in Figure 2, protonation at the bridging oxygen of glycosidic bond draws electrons away from C1 of glucose and C2 of fructose to induce C-O bond fission and produce glucose and fructose (Yamabe et al., 2013). Figure 2 shows the bond fission by fructose that is slightly more thermodynamically favorable than on the glucose side (Yamabe et al., 2013).

Reducing sugars such as glucose and fructose are reactive because of hemiacetal and hemiketal groups that are in equilibrium with a small amount (0.02% for glucose) of redox-active open-ring aldehyde and ketone (Figure 2). Reduction of carbonyl carbon (by H_2+Pd/C, $NaBH_4$) forms alcohol, while oxidation forms carboxylic acid (Bruice, 1998). Consumption of the open-ring structure shifts equilibrium to form more open-chain aldehyde and ketone. In addition, carboxylic acid oxidation product catalyzes acid hydrolysis of sucrose (Figure 2). Mild oxidant Br_2 oxidizes aldose but not ketose. Tollens' reagent (diamminesilver(I)) oxidizes both, because basic pH first converts ketose to aldose by keto-enol tautomerization that is catalyzed by acid and base (Figure

2). Stronger oxidants like nitric acid can oxidize -OH (primary alcohol, C6 of glucose in Figure 2, is most easily oxidized), in addition to the carbonyl C of aldehyde and ketone. Reducing sugars also react with amino acids (Maillard reaction) followed by polymerization to form colored macromolecules that are less water soluble (Friedman, 1996) (Figure 2). Maillard reaction can produce acrylamide, a suspected carcinogen (Mottram et al., 2002; Stadler et al., 2004). Reducing sugars detrimentally lower the sucrose recovery during crystallization by increasing the solubility of sucrose (Andrews et al., 2002). On the other hand, redox transformation and hydrolysis can be utilized to convert mono- and polysaccharide into bioproducts and biofuels, especially when the sugar price is low (Godshall, 2001). These reactions also provide a measure for the feedstock quality, e.g., total fermentable sugar (sucrose+glucose+fructose). For example, monosaccharides can be identified by the formation of yellow crystalline solid (osazone) by the reaction of phenylhydrazine with aldose and ketose (Bruice, 1998).

Post-harvest formation of macromolecular impurities in cane juice occurs via (i) Maillard reaction, (ii) caramelization (thermal degradation of reducing sugars), and (iii) oxidative coupling of phenols to form melanin (Jansen, 2010) (Figure 2). Catechol colorants in cane juice (Nguyen and Doherty, 2012) having low reduction potential rapidly and irreversibly react with O_2 (autoxidation) near neutral pH (Borraccino, 2001; Lee et al., 2007a). Figure 3 shows one- and two-electron oxidation products of hydroquinone and catechol colorants. Aromatic rings (i) decrease the two-electron standard reduction potential of dihydroxybenzenes by resonance stabilization and (ii) protect the fully oxidized quinone from irreversible nuclephilic addition reactions (Uchimiya and Stone, 2009). As shown in Figure 3 for hydroxide ion as the nucleophile, the attack at carbonyl carbon is fast and reversible (Bishop and Tong, 1964).

Michael addition reaction is a slower and irreversible covalent addition at the α–β conjugated system (Figure 3). The highly reducing hydroxyhydroquinone product rapidly oxidize to hydroxy-p-benzoquinone (Brunmark and Cadenas, 1989). Because the addition at carbonyl carbon is reversible, products of Michael addition accumulate over time and become the main product of the nucleophilic attack (Bruice, 1998). Quinones are reactive towards various nucleophiles (Nikolantonaki and Waterhouse, 2012): hydrogen sulfide (Perlinger et al., 2002), sulfite (Youngblood, 1986), thiol (Doong and Chiang, 2005), and amine (Weber et al., 1996). Because higher pH enhances the reaction with OH^- as well as O_2, darker color develops at higher pH. In addition, (poly)phenols are more soluble at high pH because of high pK_a (Martell et al., 2004). Figure 4 presents transmission electron microscopy (TEM) image of a model reaction in juice between phenolic impurities and iron. Initial conditions were 50 μM p-benzoquinone, 250 μM Fe^{II}, 50 mM MES buffer (pH 5.9), and 0.10 M NaCl (Uchimiya, 2005). Although Fe^{III} hydroxide particles were washed repeatedly with water before TEM analysis, biofilm-like polymeric coating (dark shade) is visible on amorphous Fe^{III} hydroxide (Figure 4). Hydrophilic, macromolecular coating (dark shade) can stabilize the hydrophobic, variable charge amorphous ferric hydroxide particles (needle-like structures in Figure 4) in dilute sucrose solutions.

Polysaccharide impurities (starch, dextran) in sugar crops contain ten to several thousand monosaccharide units connected by the glycosidic bonds (Bruice, 1998). Cellulose (β-1,4'-glycosidic linkages) and starch are two of the most common polysaccharides in nature. Starch in sugarcane is a semicrystalline granule having 1-10 μm diameter that gelatinize at 65-80 °C (Lemos et al., 2013). Starch is composed of ≈20% amylose and ≈80% amylopectin (Figure 1). Starch granules store hydrophilic glucose polymers amylose and amylopectin for a controlled

enzymatic release of glucose (Debet and Gidley, 2007). Amylose is composed of several thousand D-glucose units with α-1,4'-glycosidic linkages. Amylopectin is a branched polysaccharide containing α-1,6'-glycosidic linkage, in addition to α-1,4'-glycosidic linkage, and is one of the largest molecules found in nature. The α-1,4'-linkage of amylose in starch cause it to form a left-handed helix that is extensively H-bonded with water (Bruice, 1998), making starch water-soluble. Because of a branch point at every 10-20 glucose units, amylopectin is more stable than amylose, and less prone to from a helix (Mathews et al., 2000). Dextran is formed microbially from sucrose in sugar cane especially during rainy season (Lemos et al., 2013). Dextran is a α-1,6'-linked polymer of glucose with α-1,2'-, α-1,3', or α-1,4'branch points (Mathews et al., 2000) and also composes the dental plaque (Bruice, 1998).

Calcium phosphate and polyacrylamide (PAM) are used to promote aggregation and sedimentation during juice clarification while minimizing sucrose hydrolysis by raising pH (Figure 2) at elevated temperature (Doherty, 2011). Calcium phosphate (as well as Ca oxide and carbonate) phases can strongly sorb organic and inorganic impurities. Amorphous phases and defect sites are likely to be the reactive sites for sorption as well as aggregation (Stumm and Morgan, 1996). Fenton reaction, when used to remove color during sugar refining (Nguyen and Doherty, 2012), forms Fe(III) hydroxides (Figure 4) that will participate in heteroaggregation, much like Ca phosphate. Stability of the agglomerated suspension depends on the sedimentation rate and volume (Bennett, 1958). When particles aggregate and settle rapidly, sedimentation volume is large and the suspension is unstable. Figure 14.4 of Stumm and Morgan (1996) modeled the changes in particle size distribution by coagulation and sedimentation. Small (<100 nm) particles are expected to aggregate rapidly to form ≈100 nm sized stable aggregates

(Mathews et al., 2000). Intermediate particles slowly aggregate with a lesser size change. Large (>10 µm) particles are stabilized mainly by sedimentation (Figure 6).

Aggregation in dilute sucrose solution

We shall first discuss hydrophobic colloids in dilute aqueous solution. Influence of viscosity (Brix; wt% sucrose determined by refractometry) and water activity in concentrated sucrose solution will be discussed in the subsequent section. Colloids (1-1000 nm particles) are ubiquitous in nature, and can exceed the proportion (wt%) of micrometer-sized particles (Mathews et al., 2000). Colloids are continuously generated, change size, and are removed by aggregation (particle-particle interaction) and deposition/sedimentation (particle-surface interaction in Figure 5-6). The term "flocculation" sometimes refers to the presence of bridging polymers, but is often used interchangeably with "coagulation". Aggregation results from collision and sticking (Mathews et al., 2000). The frequency of collision (to bring particles within the distance for attachment) depends on convection, diffusion, and gravity (Hahn and O'Melia, 2004). Agitation by mixing, centrifugation, and by changes in temperature, pH, and ionic strength trigger the aggregation of colloids to a thermodynamically more stable agglomerated state (Ikeda and Zhong, 2012; Song et al., 2012). As shown in Figure 5, the energy barrier (kT) controls the kinetics of aggregation and deposition (Hahn and O'Melia, 2004). Reduction of ionic strength or increase in hydrodynamic shear will re-suspend aggregates in the secondary minimum (Petosa et al., 2010). Because of lower energy barrier (kT), nanoparticles (≈1-100 nm) tend to aggregate and deposit in the primary minimum irreversibly, and do not as easily re-suspend. "Stable" colloids refer to a slow change in the state of dispersion lasting seconds to years.

Aggregation mechanism can be explained by van der Waals attraction and electrical (diffuse) double layer (Coulombic) repulsion terms embedded within Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Verwey and Overbeek, 1948; Petosa et al., 2010). van der Waals force is inversely proportional to the square of the intercolloid distance, and is independent of ionic strength. Electrostatic repulsion (attraction for oppositely charged particles) energy is strongly dependent on pH and ionic strength. Two negatively charged surfaces aggregate via slow, reaction-limited aggregation at low electrolyte concentration due to repulsive electrostatic forces. When electrolyte concentration exceeds the critical coagulation concentration, charge screening results in a fast, diffusion-limited aggregation driven by attractive van der Waals forces (Chen and Elimelech, 2009; Petosa et al., 2010). Divalent cations screen charge more effectively than monovalent cations. Calcium may enhance colloid deposition by forming cation bridges (Chen and Elimelech, 2008). An important assumption of DLVO theory is that colloids are monodisperse particles of near-spherical shape.

Steric hindrance, hydrophobic and magnetic (for Fe oxides) interactions, solvation, hydration, capillary effects, and hydrogen bonding also play a role in colloid aggregation and deposition (Petosa et al., 2010). These non-DLVO forces are prevalent in food colloids (Ikeda and Zhong, 2012). Sorption of proton, hydroxide, metal ions, ligands, macromolecules, and other solutes change the surface charge, potential, and the stability of colloids. Colloid stabilization by steric repulsion is especially important for particles with adsorbed layers of polymers and surfactants (Petosa et al., 2010) (Figure 6). When hydrophilic materials, e.g., proteins, polysaccharides, are adsorbed on the particle, denser hydration shell (Ebbinghaus et al., 2007) can stabilize the colloid especially at high ionic strength (Petosa et al., 2010). Alkaline pH induces precipitation of

hydroxide, phosphate, and carbonate minerals in cane juice, which may serve as cementing agents for aggregates (Czimczik and Masiello, 2007). Melanin (Turick et al., 2002) and related polymerization products of catechols are known adhesives (Lee et al., 2007a; Lee et al., 2007b) that can further enhance aggregation and deposition (Figure 6).

Sugar crops contain macromolecules such as tannin with MW range of 500-20,000 Daltons. The size of macromolecular aggregates can exceed 0.45 μm, crossing the line from dissolved to particulate phase (Davis and Edwards, 2014). Macromolecules having ionizable functional groups (carboxyl, hydroxyl, sulfuric, amino) are elongated in basic and low ionic strength solutions (Davis and Edwards, 2014). Acidic or high ionic strength solutions cause macromolecules to become coiled and precipitate (Davis and Edwards, 2014). Low MW compounds can form aggregates stabilized by hydrophobic and H-bonding interactions (Sutton and Sposito, 2005; Schmidt et al., 2011). These aggregates can organize into micelles in water and behave similarly to polyphenolic macromolecules that are soluble in base and precipitate in acid (Sutton and Sposito, 2005; Schmidt et al., 2011).

Influence of sucrose concentration and viscosity

As the sucrose becomes concentrated by evaporating water at elevated temperature, sucrose-sucrose (vs. sucrose-water) interactions become increasingly important (Benítez et al., 2009). In addition, dispersed particles increase the effective viscosity of the entire system. Different equations are used to predict the colloidal behaviors in viscous solutions (Ikeda and Zhong, 2012). Aggregation of colloids must be investigated at a known brix. Water activity and sucrose hydration depend on the concentration of sucrose (Starzak et al., 2000). In dilution sucrose

solution ($\approx$55.5 M water), -OH group of sucrose ($pK_{a,1}$=12.57, $pK_{a,2}$=13.45; 25 °C, I=1.0) (Martell et al., 2004) is extensively hydrogen bonded with water having a similar pK_a of 13.997 (Figure 6). Dense hydration shells are expected to form around –OH groups of sucrose (Starzak et al., 2000). As the sucrose concentration increases by evaporation of water, water-water and water-sucrose hydrogen bonds become replaced by inter- and intramolecular hydrogen bonding of sucrose molecules (Figure 6). Because sucrose is denser than water, aggregates (that sink in water) float in a concentrated sucrose solution.

Near supersaturation (elevated temperature and sucrose concentration), sucrose molecules collide more frequently, and dimmers and trimers arrange themselves into aggregates (swarm, cluster) of $\approx$6 sucrose as the onset of crystallization (Starzak et al., 2000). In a concentrated sucrose solution, apparent concentration of Ca^{2+} and oxalate ions exceed the activity under ideal conditions (Doherty, 2006). Consequently, the solubility product constant (K_{SO}) of calcium oxalate and other important precipitates in sugar juice processing changes at elevated temperature and sucrose concentration (Doherty, 2006).

Techniques to study the behaviors of colloids

Dynamic light scattering (DLS) (Palmer and Von Wandruszka, 2001, 2009), transition electron (TEM) (Baalousha et al., 2006), scanning electron (SEM), and atomic force (AFM) microscopy (Pan et al., 2008), size-exclusion chromatography, and sedimentation velocity measurements (Gimbert et al., 2005; Kawahigashi et al., 2005) are often used to monitor the changes in size and charge of colloids as a function of pH and ionic strength. Experimental artifacts can result from sample preparation, especially drying (for TEM) that triggers aggregation. Advanced

spectro/microscopic techniques such as near-edge x-ray fine structure spectroscopy, nuclear magnetic resonance, and scanning transmission x-ray microscopy have emerged to reveal nano-scale colloidal interactions historically considered to result from polymers and macromolecules (Sutton and Sposito, 2005; Lehmann et al., 2008; Schmidt et al., 2011).

DLS provides polydispersity index and count rate (an estimate of particle concentration) for in situ observation of aggregation kinetics. DLS noninvasively measures the fluctuations of scattered light intensity as a result of Brownian motion (Petosa et al., 2010). Stroke-Einstein equation is used to convert diffusion coefficients of particles/molecules undergoing Brownian motion into hydrodynamic sizes. Brownian diffusion and collision frequency increase with decreasing particle size (Petosa et al., 2010). Because larger particles scatter more light, fractionation by centrifugation and filtering is necessary to observe smaller particles. Viscosity of sucrose solution can be determined from the diffusion speed of a known sized polystyrene latex standard (Zetasizer, 2009). Other light scattering techniques for the size measurement include small-angle light scattering and fluorescence correlation spectroscopy (Petosa et al., 2010). Electrophoretic mobility (U_E) is determined using laser doppler velocimetry (Zetasizer, 2009), and is converted to zeta potential (z) using the Henry equation:

$$U_E = \frac{2\varepsilon z f(K_a)}{3\eta}$$

where ε is the dielectric constant of dispersant, η is viscosity of solution, and $f(K_a)$ is Henry's function. Smoluchowski approximation uses 1.5 for large (>200 nm) particles in aqueous media at high ionic strength (mM range) (Zetasizer, 2009).

There are limited reports on the fundamental colloidal property of cane/beet juice, although its importance has been recognized for decades (Bennett, 1958). Aluminosilicate, silica, and iron

oxide are considered to compose colloids in cane juice (Thai and Doherty, 2012). Hydrophilic coatings (protein, polysaccharides, and organic acids) on these particles resulted in slightly negative zeta potential of -2 to -5 mV at pH 7.8 and 4 mM KCl (Thai and Doherty, 2012). To protect electrodes on the capillary cell, cane juice samples needed to be diluted to 15 Brix; zeta potential in undiluted solution was extrapolated using different dilutions. Trash in sugarcane (leaves and other non-stalk components) caused more negative zeta potential of juice and inhibited clarification by Ca phosphate and polyacrylamide (Thai and Doherty, 2012). Particle size in juice (before clarification) distributed in micrometer range (40±5 μm) (Thai and Doherty, 2012); however the sample was not filtered. Similarly, no particles below 1 μm were observed in sweet sorghum juice before and after clarification (Andrzejewski et al., 2013). Because larger (micrometer-sized) particles scatter more light and dominate the size distribution obtained by DLS, filtration, in addition to centrifugation/dilution, is necessary to observe smaller (<1 μm) particles in juice.

Problems caused by aggregation in cane/beet juice

Colloids are the suspected cause of diverse problems in the industrial processing and use of sugar: turbidity, viscosity (Ferreira et al., 2008), color (Andrews et al., 2002), acid beverage floc (Clarke et al., 1997), starch ghost (Zhang et al., 2014), and heat transfer problems (Doherty, 2006; Eggleston et al., 2011). Acid beverage floc is a flocculated turbid/haze "cotton ball" formed in acidified carbonated soft drinks (5-10% refined sugar) after several days standing (Clarke et al., 1997). The formation of acid beverage floc is tested at 50 brix by setting pH to 2 using phosphoric acid (ICUMSA, 2007). Aggregation (to form floc) results from the pH

decrease, and aggregates can be re-dispersed by hand shaking. These behaviors indicate DLVO-type interaction involving charged colloids trapped at secondary minimum (Figure 5). For beet sugar, Clarke et al. (1997) proposed heteroaggregation of oleanolic acid and other ionizable derivatives of saponin with oppositely charged protein and peptide upon acidificaiton. This is a distinctively different interaction from non-DLVO interactions involving hydrophilic food colloids that are relatively insensitive to pH and ionic strength, e.g., pectin colloids in cloudy apple juice (Benítez et al., 2009).

Different compounds are suspected to cause the acid beverage floc from refined (white) beet and cane sugar: residual polysaccharides (dextran and starch) in cane, and surfactants in beet sugar (Lemos et al., 2013). These macromolecular impurities sorb on white sugar during crystallization. For both beet and cane white sugar, additional floc-forming particles are: lipids, activated carbon, protein, biofilm, and silica (Iciek et al., 2012). While it is important to identify the individual particles contributing to the floc formation, aggregation kinetics must be evaluated on the basis of particle size and charge distribution, in order to predict the solution chemistry that will lead to floc formation.

Heat-induced formation of stable macromolecules

Preceding section described heteroaggregation induced by the changes in pH and ionic strength. These interactions are often reversible, and involve trapping in the secondary minimum (Figure 5). At elevated temperature, however, covalent bond formation and other irreversible changes in the particle structure can produce stable, recalcitrant particulate matter. These recalcitrant particulate matters have low heat conductivity and high heat resistivity and impair the

heat transfer during concentration of sugarcane juice (Eggleston et al., 2011). For example, hard-to-boil massecuites (mixture of sugar crystals and mother liquor resulting from the crystallization process) are considered to originate from macromolecules in deteriorated sugarcane (Eggleston et al., 2011). Boiling rate could be improved by adding HCl and H_2O_2 to the vacuum pan (Eggleston et al., 2011), suggesting the importance of polyaromatic impurities. In addition to organic (macromolecular) impurities, calcium oxalate monohydrate and silica (SiO_2) deposit on the surface of evaporator units to cause a similar heat transfer problem (Yu et al., 2002). The inorganic deposit is compact and hard, and is difficult to remove by chemical cleaning (Doherty, 2006). The scale slows down the entire operation, and causes sucrose decomposition by extending the residence time in the evaporator unit (Doherty, 2006). Slagging and fouling are common problems during high-temperature industrial processing (Abdullah et al., 2010). Lower Si/K and Ca/K ratios of incoming stream is desirable, because of higher melting point of Si oxides and Ca silicates than K carbonate/chloride (Abdullah et al., 2010).

Biopolymers such as protein and polysaccharides exist in ordered/crystalline form to minimize hydration-driven swelling (Zhang et al., 2014). Above the melting temperature, however, biopolymers dissolve in water in a process called gelatinization. During gelatinization, semicrystalline starch granules swell and burst to release hydrophilic amylose and amylopectin that bind water and increase the viscosity of solution. Amylopectin double-helix swell by replacing H-bond between amylopectin chains (intramolecular) to that with water in a process called crystallite melting (Zhang et al., 2014). This is when "starch ghost", a swollen, hydrated form of starch granules, forms. The formation of starch ghost depends on shear (mixing), water content, and temperature (Waigh et al., 2000; Zhang et al., 2014). Amylase digestion study indicated that

starch ghost was non-ordered, entangled amylopectin (Zhang et al., 2014). Highly branched, high MW amylopectin entangled to form a stable solid structure (Figure 5). Lipid and protein did not impact the structural integrity of ghost. Like amylopectin, dextran is highly branched and may behave similarly at elevated temperature. Covalent cross-linking of polysaccharide chains is another proposed mechanism of irreversible ghost formation (Debet and Gidley, 2007). Amylose, on the other hand, is dilutant/inhibitor of starch swelling. Similarly, agar and gelatin are held together by non-covalent bonding, and do not form ghost upon heating in water to gelatinize (Debet and Gidley, 2007).

Knowledge gap and prospects

Fermentable sugar (sucrose+glucose+fructose) feedstock has a viable marketplace in first-generation biofuels, renewable bioproducts, as well as a variety of food products. Regardless of end-uses, colloidal non-sugar impurities will impose challenges and opportunities during feedstock processing and optimization. Fundamental understanding in colloid chemistry of juice is a necessary step to evaluate the feedstock quality for different end-uses. Sugar cane/beet juice is a dynamic system containing heterogeneous impurities that engage in hydrolysis, redox, and thermal transformation, sorption, desorption, and aggregation concurrently. The rate of each reaction depends on the temperature, solute/water activity, pH, ionic strength, viscosity, and shear. Even after intensive clarification and refining, trace colloidal impurities on refined sugar remain to cause a problem known as acid beverage floc. DLS and related colloid characterization techniques are currently underutilized for sugar feedstocks. Kinetics of heteroaggregation (changes in colloid size and charge distribution over time) in juice matrix must be systematically studied as a function

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of solution chemistry. Fundamental knowledge in heteroaggregation kinetics is necessary to predict the changes in juice quality caused by the deterioration during the heat treatment, storage, and transport and by changes in the quality of harvested sugar crops.

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References

Abdullah, H., Mediaswanti, K.A., Wu, H., 2010. Biochar as a fuel: 2. Significant differences in fuel quality and ash properties of biochars from various biomass components of mallee trees. Energy and Fuels 24, 1972-1979.

Andrews, L.S., Godshall, M.A., Moore, S., 2002. Sucrose degradation under model processing conditions. Journal of Food Science 67, 1621-1624.

Andrzejewski, B., Eggleston, G., Powell, R., 2013. Pilot plant clarification of sweet sorghum juice and evaporation of raw and clarified juices. Industrial Crops and Products 49, 648-658.

Baalousha, M., Motelica-Heino, M., Coustumer, P.L., 2006. Conformation and size of humic substances: Effects of major cation concentration and type, pH, salinity, and residence time. Colloids and Surfaces A: Physicochemical and Engineering Aspects 272, 48-55.

Benítez, E.I., Genovese, D.B., Lozano, J.E., 2009. Effect of typical sugars on the viscosity and colloidal stability of apple juice. Food Hydrocolloids 23, 519-525.

Bennett, M.C., 1958. Zeta potential and sedimentation behaviour in flocculated cane sugar juice. Nature 182, 1439-1440.

Bishop, C.A., Tong, L.K.J., 1964. The reversible addition of hydroxide ion to quinones. Tetrahedron Letters, 3043-3048.

Borraccino, R.K., M.; Giot, R.; Agathos, S. N.; Nyns, E.; Naveau, H. P.; Pauss, A., 2001. Abiotic transformation of catechol and 1-naphothol in aqueous solution: Influence of environmental factors. Wat. Res. 15, 3729-3737.

Bruice, P.Y., 1998. Organic Chemistry. Prentice Hall, New Jersey.

Brunmark, A., Cadenas, E., 1989. Redox and addition chemistry of quinoid compounds and its biological implications. Free Radical Biology and Medicine 7, 435-477.

Chen, K.L., Elimelech, M., 2008. Interaction of fullerene (C 60) nanoparticles with humic acid and alginate coated silica surfaces: Measurements, mechanisms, and environmental implications. Environ. Sci. Technol 42, 7607-7614.

Chen, K.L., Elimelech, M., 2009. Relating colloidal stability of fullerene (C60) nanoparticles to nanoparticle charge and electrokinetic properties. Environmental Science and Technology 43, 7270-7276.

Clarke, M.A., Roberts, E.J., Godshall, M.A., 1997. Acid beverage floc from beet sugars. Zuckerindustrie 122, 873-877.

Czimczik, C.I., Masiello, C.A., 2007. Controls on black carbon storage in soils. Global Biogeochemical Cycles 21.

Davis, C.C., Edwards, M., 2014. Coagulation with hydrolyzing metal salts: Mechanisms and water quality impacts. Critical Reviews in Environmental Science and Technology 44, 303-347.

Debet, M.R., Gidley, M.J., 2007. Why do gelatinized starch granules not dissolve completely? Roles for amylose, protein, and lipid in granule "ghost" integrity. Journal of Agricultural and Food Chemistry 55, 4752-4760.

Doherty, W.O.S., 2006. Effect of calcium and magnesium ions on calcium oxalate formation in sugar solutions. Industrial and Engineering Chemistry Research 45, 642-647.

Doherty, W.O.S., 2011. Improved sugar cane juice clarification by understanding calcium oxide-phosphate-sucrose systems. Journal of Agricultural and Food Chemistry 59, 1829-1836.

Doong, R.A., Chiang, H.C., 2005. Transformation of carbon tetrachloride by thiol reductants in the presence of quinone compounds. Environ. Sci. Technol. 39, 7460–7468.

Ebbinghaus, S., Seung, J.K., Heyden, M., Yu, X., Heugen, U., Gruebele, M., Leitner, D.M., Havenith, M., 2007. An extended dynamical hydration shell around proteins. Proceedings of the National Academy of Sciences of the United States of America 104, 20749-20752.

Eggleston, G., Côté, G., Santee, C., 2011. New insights on the hard-to-boil massecuite phenomenon in raw sugar manufacture. Food Chemistry 126, 21-30.

Ferreira, S.J., Kossmann, J., Lloyd, J.R., Groenewald, J.H., 2008. The reduction of starch accumulation in transgenic sugarcane cell suspension culture lines. Biotechnology Journal 3, 1398-1406.

Friedman, M., 1996. Food browning and its prevention: An overview. Journal of Agricultural and Food Chemistry 44, 631-653.

Gimbert, L.J., Haygarth, P.M., Beckett, R., Worsfold, P.J., 2005. Comparison of centrifugation and filtration techniques for the size fractionation of colloidal material in soil suspensions using sedimentation field-flow fractionation. Environmental Science and Technology 39, 1731-1735.

Godshall, M.A., 2001. Future directions for the sugar industry. International Sugar Journal 103, 378-384.

Godshall, M.A., Vercellotti, J.R., Triche, R., 2002. Comparison of cane and beet sugar macromolecules in processing. International Sugar Journal 104, 228-233.

Hahn, M.W., O'Melia, C.R., 2004. Deposition and Reentrainment of Brownian Particles in Porous Media under Unfavorable Chemical Conditions: Some Concepts and Applications. Environmental Science and Technology 38, 210-220.

Iciek, J., Błaszczyk, I., Biernasiak, J., Lisik, K., Wojtczak, M., 2012. Floc in acidified solutions of white sugar - A literature review. Zuckerindustrie 137, 449-453.

ICUMSA Method GS 2/3-40 *The ICUMSA 10-Day Acid Beverage Floc Test for White Sugar* International Commission for Uniform Methods of Sugar Analysis (2007).

Ikeda, S., Zhong, Q., 2012. Polymer and colloidal models describing structure-function relationships. Annual Review of Food Science and Technology 3, 405-424.

Jansen, T.M., 2010. Raw sugar quality from a refiner's perspective. International Sugar Journal 112, 250-256.

Kawahigashi, M., Sumida, H., Yamamoto, K., 2005. Size and shape of soil humic acids estimated by viscosity and molecular weight. Journal of Colloid and Interface Science 284, 463-469.

Lee, H., Dellatore, S.M., Miller, W.M., Messersmith, P.B., 2007a. Mussel-inspired surface chemistry for multifunctional coatings. Science 318, 426-430.

Lee, H., Lee, B.P., Messersmith, P.B., 2007b. A reversible wet/dry adhesive inspired by mussels and geckos. Nature 448, 338-342.

Lehmann, J., Solomon, D., Kinyangi, J., Dathe, L., Wirick, S., Jacobsen, C., 2008. Spatial complexity of soil organic matter forms at nanometre scales. Nature Geoscience 1, 238-242.

Lemos, L.R., Nogueira, A., Wosiacki, G., Lacerda, L.G., Demiate, I.M., 2013. The Influence of Different Amounts of Dextran and Starch in Crystallized Sugar in the Formation of Floc in Acidic Carbonated Solutions and Alcoholic Solutions. Sugar Tech 15, 65-70.

Martell, A.E., Smith, R.M., Motekaitis, R.J., 2004. Critically Selected Stability Constants of Metal Complexes Database. U. S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD.

Mathews, C.K., van Holde, K.E., Ahern, K.G., 2000. Biochemistry. Benjamin/Cummings, San Francisco, CA.

Mottram, D.S., Wedzicha, B.L., Dodson, A.T., 2002. Food chemistry: Acrylamide is formed in the Maillard reaction. Nature 419, 448-449.

Nguyen, D.M.T., Doherty, W.O.S., 2012. Phenolics in sugar cane juice: Potential degradation by hydrogen peroxide and Fenton's reagent. International Sugar Journal 114, 309-315.

Nikolantonaki, M., Waterhouse, A.L., 2012. A method to quantify quinone reaction rates with wine relevant nucleophiles: A key to the understanding of oxidative loss of varietal thiols. Journal of Agricultural and Food Chemistry 60, 8484-8491.

Palmer, N.E., Von Wandruszka, R., 2001. Dynamic light scattering measurements of particle size development in aqueous humic materials. Analytical and Bioanalytical Chemistry 371, 951-954.

Palmer, N.E., Von Wandruszka, R., 2009. The influence of aggregation on the redox chemistry of humic substances. Environmental Chemistry 6, 178-184.

Pan, B., Ghosh, S., Xing, B., 2008. Dissolved organic matter conformation and its interaction with pyrene as affected by water chemistry and concentration. Environmental Science and Technology 42, 1594-1599.

Perlinger, J.A., Kalluri, V.M., Venkatapathy, R., Angst, W., 2002. Addition of hydrogen sulfide to juglone. Environ. Sci. Tech. 36, 2663-2669.

Petosa, A.R., Jaisi, D.P., Quevedo, I.R., Elimelech, M., Tufenkji, N., 2010. Aggregation and deposition of engineered nanomaterials in aquatic environments: Role of physicochemical interactions. Environmental Science and Technology 44, 6532-6549.

Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S.,

Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478, 49-56.

Song, M., Yuan, S., Yin, J., Wang, X., Meng, Z., Wang, H., Jiang, G., 2012. Size-dependent toxicity of nano-C 60 aggregates: More sensitive indication by apoptosis-related bax translocation in cultured human cells. Environmental Science and Technology 46, 3457-3464.

Stadler, R.H., Robert, F., Riediker, S., Varga, N., Davidek, T., Devaud, S., Goldmann, T., Hau, J., Blank, I., 2004. In-depth mechanistic study on the formation of acrylamide and other vinylogous compounds by the maillard reaction. Journal of Agricultural and Food Chemistry 52, 5550-5558.

Starzak, M., Peacock, S.D., Mathlouthi, M., 2000. Hydration number and water activity models for the sucrose-water system: A critical review. Critical Reviews in Food Science and Nutrition 40, 327-367.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry. Wiley-Interscience, NY.

Sutton, R., Sposito, G., 2005. Molecular structure in soil humic substances: The new view. Environmental Science and Technology 39, 9009-9015.

Thai, C.C.D., Doherty, W.O.S., 2012. Characterisation of sugarcane juice particles that influence the clarification process. International Sugar Journal 114, 719-724.

Turick, D.E., Tisa, L.S., Caccavo, F., 2002. Melanin production and use as a soluble electron shuttle for Fe(III) oxide reduction and as a terminal electron acceptor by *Shewanella algae* BrY. Applied and Environmental Microbiology 68, 2436-2444.

Uchimiya, M., 2005. Thesis: Electron Transfer Reactions between Quinones and Iron in Aqueous Environments. Department of Geography and Environmental Engineering, Johns Hopkins University, Baltimore, Maryland.

Uchimiya, M., Stone, A.T., 2006. Aqueous oxidation of substituted dihydroxybenzenes by substituted benzoquinones. Environmental Science and Technology 40, 3515-3521.

Uchimiya, M., Stone, A.T., 2009. Reversible redox chemistry of quinones: Impact on biogeochemical cycles. Chemosphere 77, 451-458.

Verwey, E.J.W., Overbeek, J.T.G., 1948. Theory of the Stability of Lyophobic Colloids. Elsevier Amsterdam.

Waigh, T.A., Gidley, M.J., Komanshek, B.U., Donald, A.M., 2000. The phase transformations in starch during gelatinisation: A liquid crystalline approach. Carbohydrate Research 328, 165-176.

Weber, E.J., Spidle, D.L., Thorn, K.A., 1996. Covalent binding of aniline to humic substances. 1. Kinetic studies. Environ. Sci. Technol. 30, 2755-2763.

Yamabe, S., Guan, W., Sakaki, S., 2013. Three competitive transition states at the glycosidic bond of sucrose in its acid-catalyzed hydrolysis. Journal of Organic Chemistry 78, 2527-2533.

Youngblood, M.P., 1986. Kinetics and mechanism of the addition of sulfite to p-benzoquinone. J. Org. Chem. 51, 1981-1985.

Yu, H., Sheikholeslami, R., Doherty, W.O.S., 2002. Composite fouling characteristics of calcium oxalate monohydrate and amorphous silica by a novel approach simulating successive effects of a sugar mill evaporator. Industrial and Engineering Chemistry Research 41, 3379-3388.

*Zetasizer Nano User Manual* Malvern Instruments Ltd., Worcestershire, United Kingdom (2009).

Zhang, B., Dhital, S., Flanagan, B.M., Gidley, M.J., 2014. Mechanism for starch granule ghost formation deduced from structural and enzyme digestion properties. Journal of Agricultural and Food Chemistry 62, 760-771.
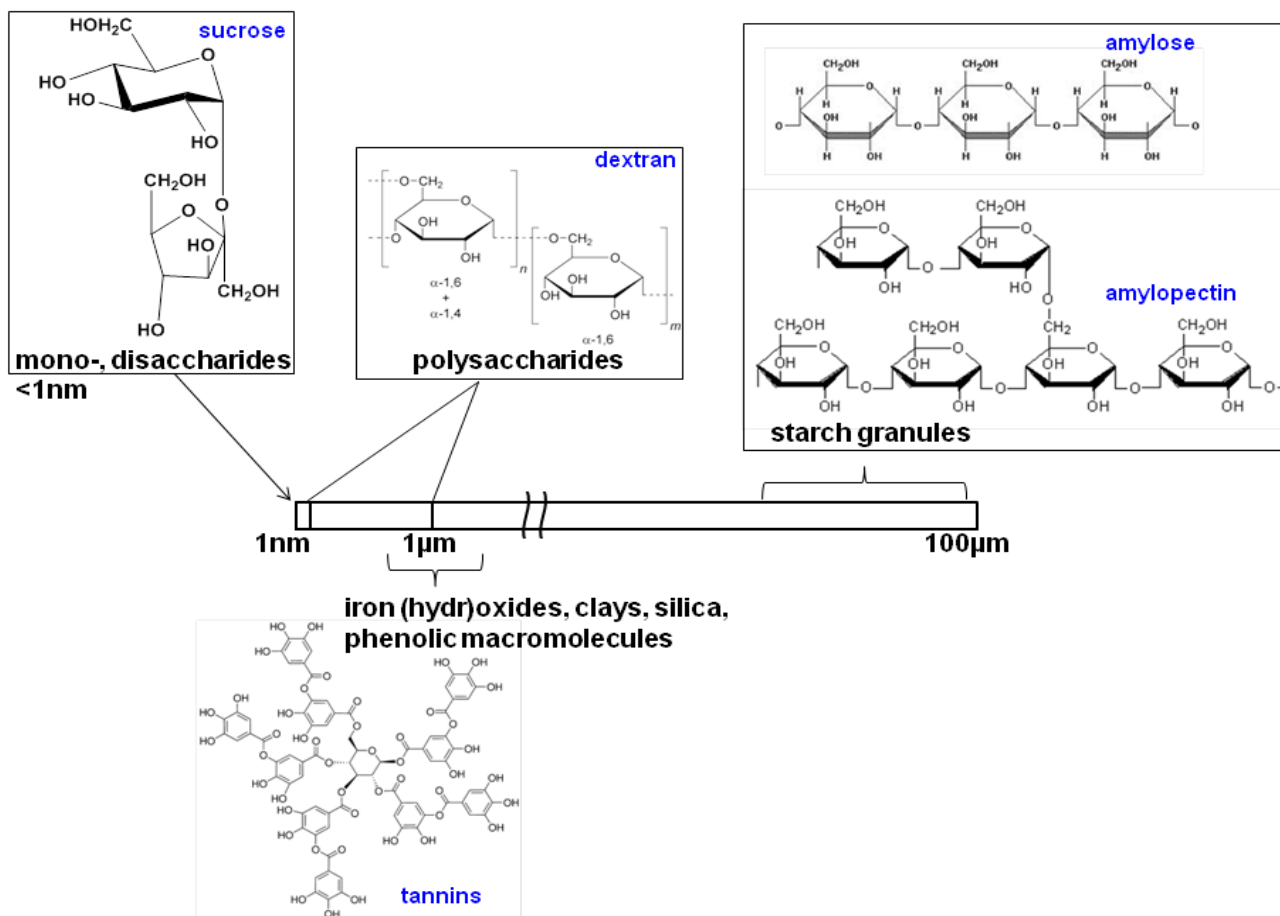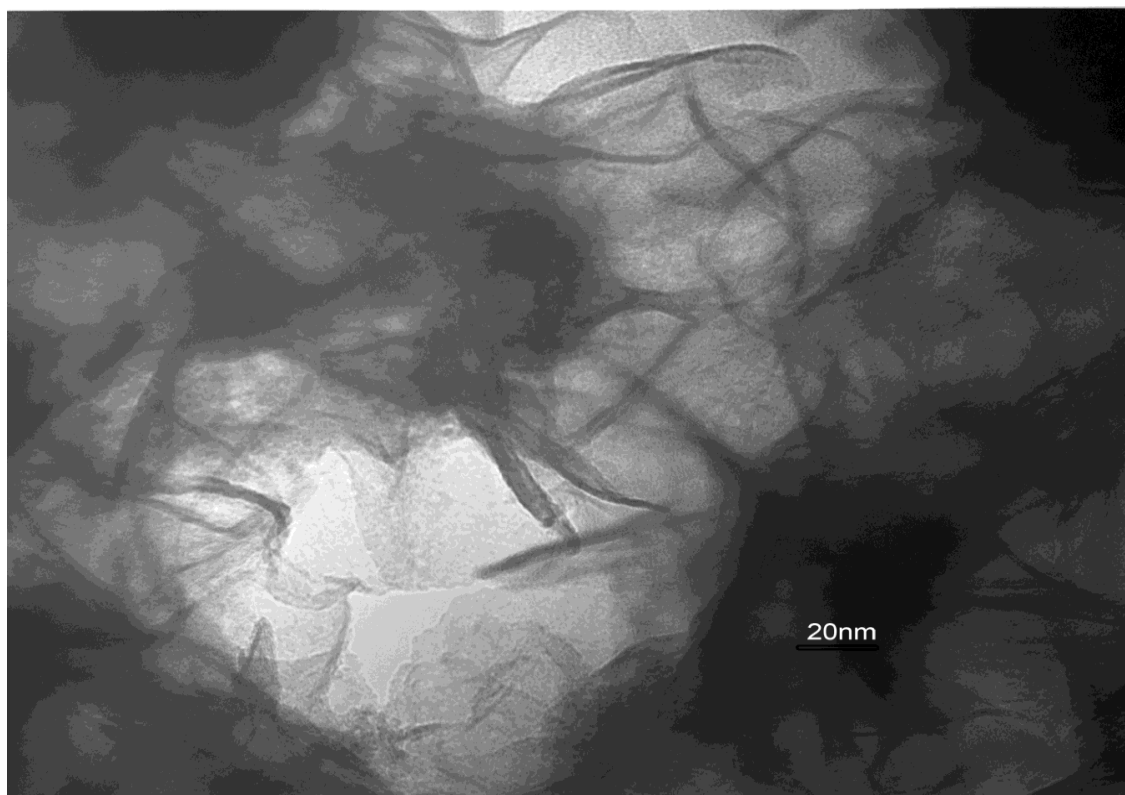
**Figure 1.** Sizes of mono- and disaccharide, polysaccharide, and higher MW components within sugar cane/beet juice.
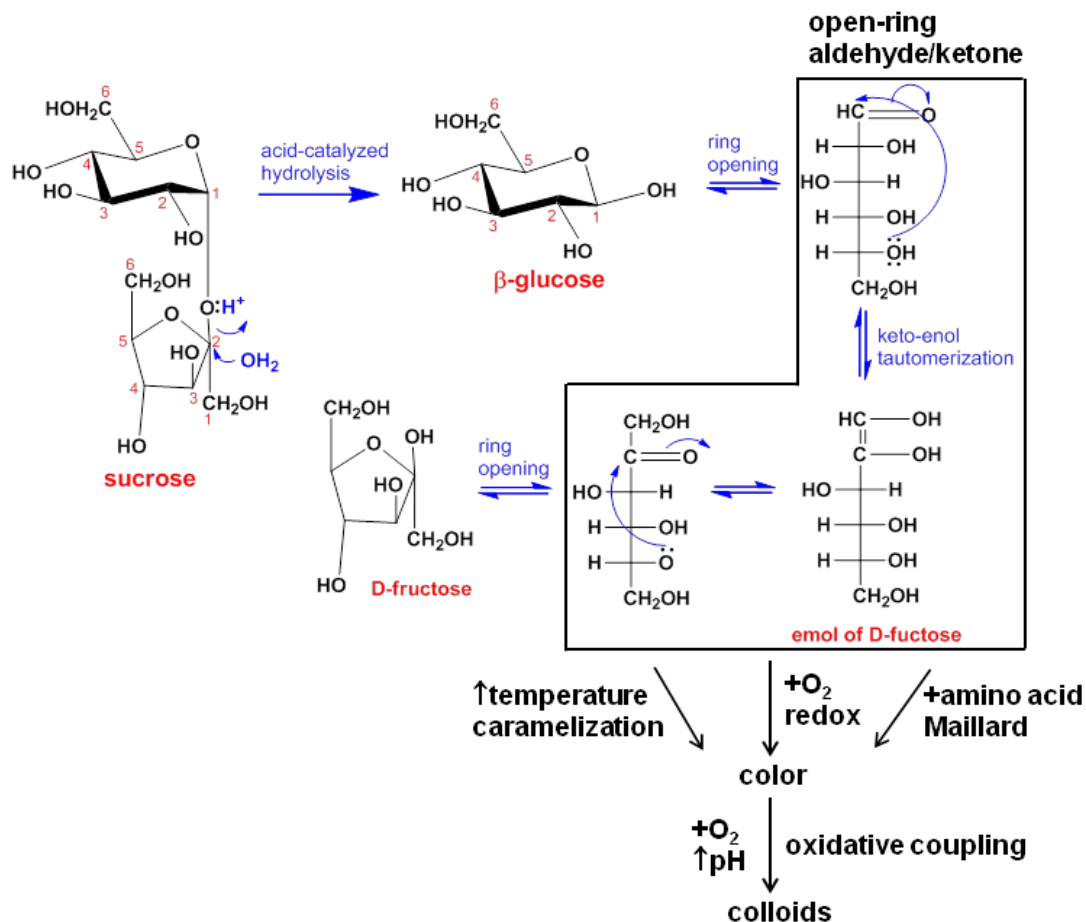
Figure 2. Chemical transformations of sucrose that produce colloids in sugar cane/beet juice.

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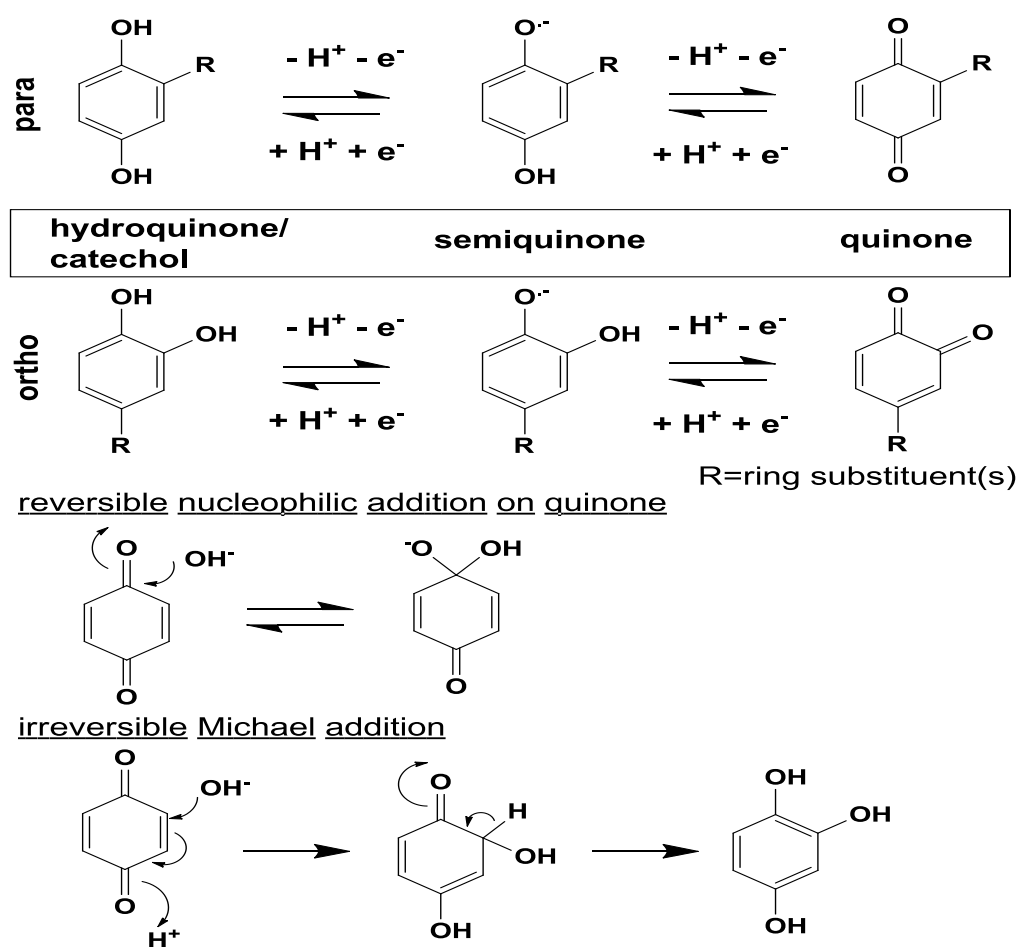
Figure 3. Redox and addition reactions of phenolic impurities in sugar crops. Reprinted with permission from (Uchimiya and Stone, 2006, 2009).

Figure 4. High-resolution TEM image of a model redox reaction between phenolic impurities and iron present in sugar crops. Biofilm-like polymeric coatings (dark shade) are observable on the amorphous Fe^{III} hydroxide product. The image was obtained at 300000 magnification. Initial conditions: 50 μM p-benzoquinone, 250 μM Fe^{II}, 50 mM MES buffer (pH 5.9), and 0.10 M NaCl (Uchimiya, 2005).
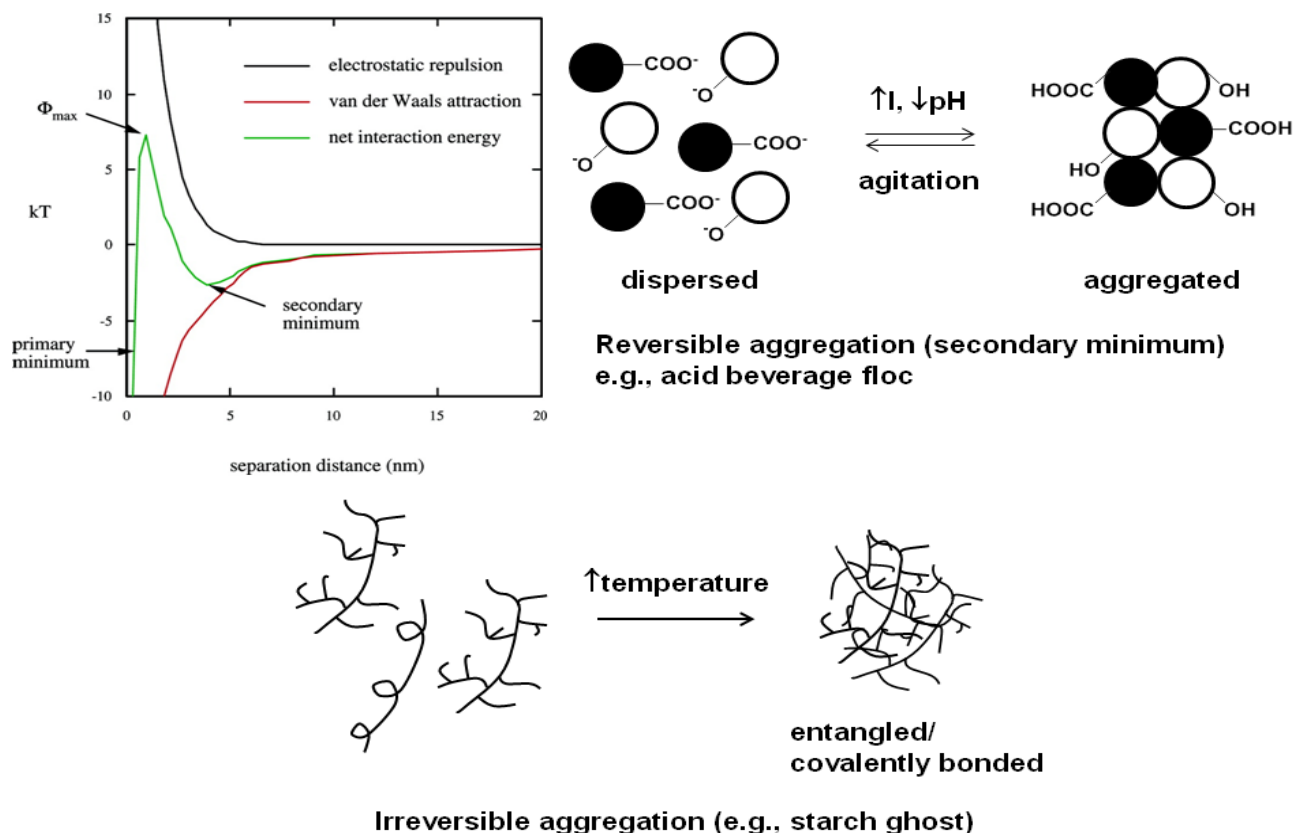
Figure 5. Hypothesis of reversible and irreversible aggregation processes in juice. Typical repulsive, attractive, and net interaction energy curves (between a sphere and a flat plate based on DLVO theory; far left figure) were obtained from (Hahn and O'Melia, 2004).
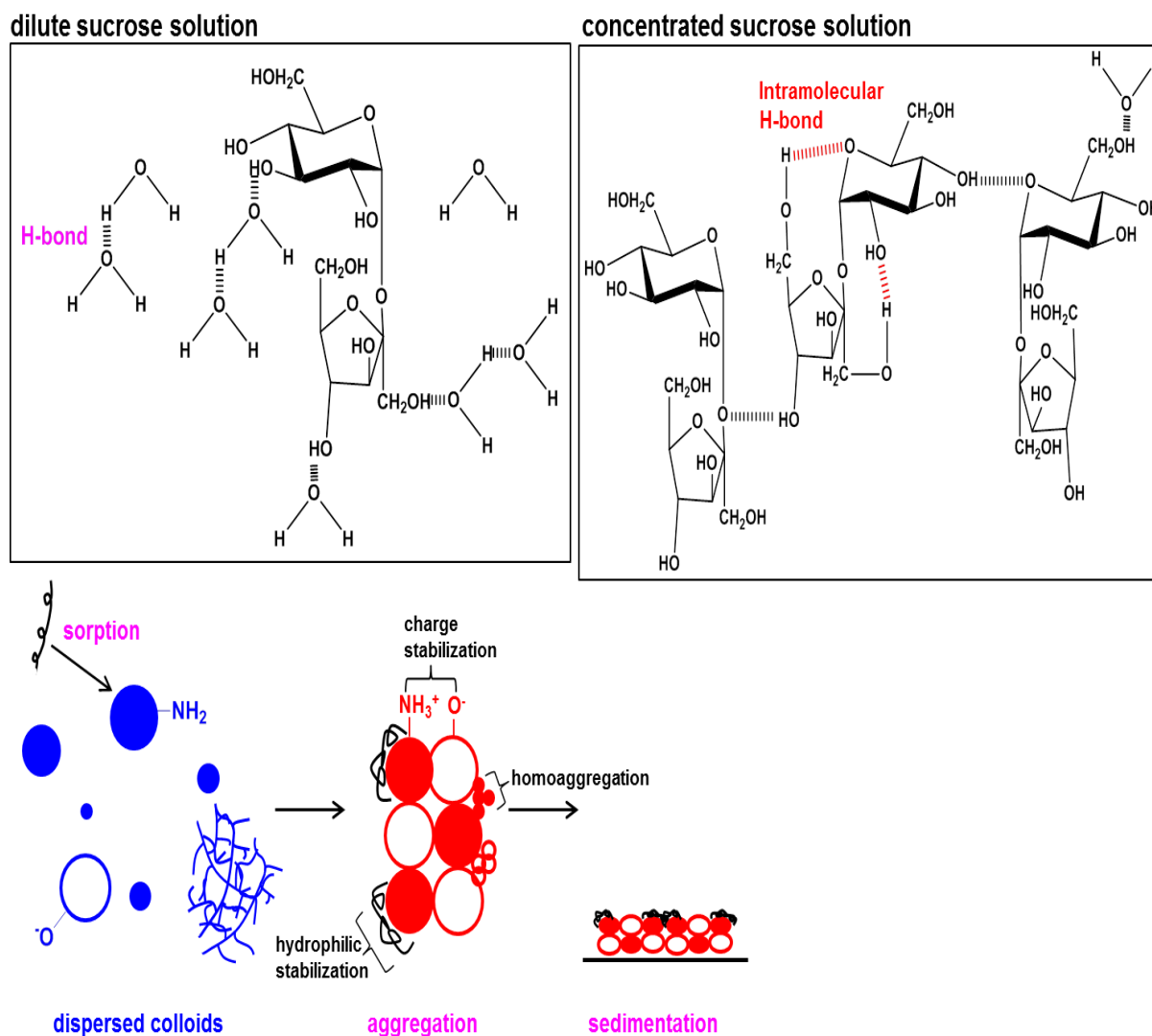
Figure 6. Dispersed colloids (blue) form aggregates (red) in dilute and concentrated sucrose solutions.