Effect of typical sugars on the viscosity and colloidal stability of apple juice

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ABSTRACT

Cloudy apple juice may be modeled as a dilute colloidal dispersion of solid particles in a solution of pectins, sugars, organic acids, and salts. In order to evaluate the effect of sugars on the viscosity and stability of the juice, it was diafiltered by ultrafiltration to remove the native soluble solids, and controlled amounts of sugars (glucose, sucrose, and maltose) were added afterwards. The addition of sugars produced a linear increase of the specific viscosity at decreasing water activities. The rates of increase (slopes) were proportional to the hydration capacity of each sugar. The specific viscosity of a colloidal dispersion of solid particles in sugar solution depends on three types of interactions: particle–particle (p–p), particle–water (p–w), and particle–sugar (p–s). P–p and p–w interactions were estimated from the extended DLVO theory in terms of the energy barrier between pairs of particles, and found to decrease at increasing sugar concentrations. Then, the increase of the specific viscosity was attributed to an increase of p–s interactions. The total energy barrier of the system (a measure of its stability) was modeled to be the sum of a p–p (including p–w) contribution plus a p–s contribution, and estimated from specific viscosity vs. particle volume fraction data at different sugar concentrations. The p–s contribution was estimated by difference. It was found to be positive (which was attributed to hydration repulsion) and higher than the p–p contribution at sugar concentrations $\geqslant 0.04$ mol/mol.

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1. Introduction

During the production of clarified juices the native pectin must be enzymatically degraded since it complicates the clarification process. After juice depectinization, only negatively charged colloidal particles smaller than 1 μm remain in suspension (Benítez, Genovese, & Lozano, 2007b), because bigger particulate material precipitates by gravity. Particles negative charge is attributed to degraded pectin molecules that remain bonded to the surface. These particles are mainly composed of carbohydrates and proteins, which are insoluble at the juice pH (Dietrich, Gierschner, Pecoroni, Zimmer, & Will, 1996). This system may then be considered to be a dilute solid–liquid colloidal dispersion (sol).

It has been reported (Dietrich et al., 1996) that cloudy apple juice concentration up to 45–50 °Brix (i.e. increasing the concentration of total soluble and insoluble solids) does not affect the colloidal stability of the system. Soluble solids of apple juice consist mainly of sugars, pectin, salts, and organic acids. Mensah-Wilson, Reiter, Bail, Neidhart and Carle (2000) found that the addition of pectin increased the cloud stability of pulp-containing fruit beverages. Furthermore, they claimed that added pectin formed a protective envelope around the particle, thus keeping the fine cloud (colloidal particles) in suspension. Benítez, Genovese and Lozano (2007a) found that increasing concentrations of salts and organic acids has no significant effect on the colloidal stability of depectinized apple juice. Since there was no pectin (or just pectin residues) around the particles, they concluded that particles were highly hydrated, each one coated with an immobilized water layer that provides its high stability.

The extended DLVO theory has been successfully applied to explain the stability of colloidal dispersions, including cloudy apple juice (Genovese & Lozano, 2006; Benítez et al., 2007a). This theory explains the tendency of colloidal particles to agglomerate or remain dispersed, combining interaction forces as a function of the distance between pairs of particles: the resulting curve is called the net interaction energy. The point of maximum repulsive energy is known as the energy barrier. To agglomerate two encountering particles due to their Brownian movement, they must have enough kinetic energy (due to their speed and mass) to overcome that barrier. Then, the flocculation degree will depend on the particles collision frequency and their energy respect to the energy barrier (Sennet & Olivier, 1965).

Genovese and Lozano (2006) found that cloudy juice concentration up to 50 °Brix increased the energy barrier between pairs of particles. Benítez et al. (2007a) found that reducing the pH and increasing the ionic strength of the liquid medium reduced particle hydration and consequently the energy barrier, but not enough to destabilize the turbidity of the system. The reduction of

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the hydration was attributed to a distortion of the hydration shells by hydrated cations attracted by the negative charge of the particles. This effect could be accompanied by an increase in the hydrophobicity promoted by the ionic strength rise, which reduced the pectin charge (Axelos & Thibault, 1991). The hydrophobic interactions are attributed to the attraction between the ester methyl groups of neighbor pectin molecules (Oakenfull & Scott, 1984). In the present work the juice was depectinized, and consequently hydrophobic interactions among pectin residues were considered to be negligible.

In short, the role of pectin, salts, and organic acids on the stability of apple juice particles has been studied in several works. However, no studies were found about the specific effect of the other major component of apple juice, sugars, on this subject. Consequently, the main objective of this work was to study the effect of sugars on the colloidal stability of apple juice particles.

1.1. Effect of sugars in aqueous systems

In food systems water may exist as free water and bound water. Bound water is generally defined as sorbent- or solute-associated water that differs thermodynamically from pure water (Berlin, 1981; Mathlouthy, 2001). It has been suggested (Rizvi, 1986) that water is bound to stronger hydrogen bonds acceptor than liquid water. According to Luck (1981) bound water exhibits a decrease in its diffusion coefficient with decreasing moisture content. Water activity in foods (a_W) is closely approximated as (Rizvi, 1986; Mathlouthy, 2001)

$$a_w = (P_w/P_w^0)_T \tag{1}$$

where P_w is the partial pressure of water vapor in the product and P_w^0 is the vapor pressure of pure water.

The activity coefficient of water, γ_w, is a measure of the deviation of water behavior in real solution from its behavior in ideal solution, and is defined as

$$\gamma_w = a_w/X_w \tag{2}$$

where X_w is the molar fraction of water.

Carbohydrates have the ability to fix water. Carbohydrate–water interactions produce not only a special arrangement of water molecules around the solute, but also affect the solute conformation (Grigera, 1994). In practical experience, the effects of water on carbohydrates and of carbohydrates on water are complex and become even more complex in the presence of other materials, such as salts. Water competes for carbohydrates intramolecular and intermolecular hydrogen bonds, which will certainly determine the carbohydrate flexibility and preferred conformation (Kirschner & Woods, 2001). At increasing sugar concentrations this complex carbohydrate–water interaction reduces the free energy of the system (Sato, Kawabuchi, Irimoto, & Miyawaki, 2004), and consequently not all the water is available to hydrate the particles.

For sugar solutions, the activity coefficient of water may be described by the following single parameter equation (Kozak, Knight, & Kauzmann, 1968; Miyawaki, Saito, Matsuo, & Nakamura, 1997):

$$\gamma_w = \exp(\delta X_s^2) \tag{3}$$

where X_s is the molar fraction of sugar. The parameter δ is the expansion coefficient, generally temperature dependent (Starzak & Mathlouthi, 2006), and represents the excess free energy caused by the solute–solvent and solute–solute interactions (Sato et al., 2004).

The viscosity of a colloidal dispersion in a liquid medium with sugar is subjected to six kinds of intermolecular interactions: (I) water–water, (II) water–sugar, (III) sugar–sugar, (IV) water–particle, (V) sugar–particle, and (VI) particle–particle (p–p) (Sato et al., 2004). The first three effects are reflected in the viscosity of sugar solutions without particles and could be excluded using the specific viscosity, η_{sp}, calculated as

$$\eta_{sp} = (\eta - \eta_s)/\eta_s \tag{4}$$

where η is the viscosity of the colloidal dispersion with sugar, and η_s is the viscosity of a sugar solution without particles. The specific viscosity is expected to represent mainly the interactions between particles (VI), although same effects of water–particle (IV) and sugar–particle (V) interactions are expected (Fig. 1).

1.2. Extended DLVO theory

This theory was used to estimate the p–p interactions (VI), at different sugar concentrations in the juice. The total interaction energy (U_T) between pairs of particles for this system is (Genovese & Lozano, 2006; Benítez et al., 2007a)

$$U_T(x) = U_A(x) + U_E(x) + U_H(x) \tag{5}$$

where x is the distance between particles surfaces, U_A is the Van der Waals attractive energy, U_E the electrostatic repulsive energy, and U_H the hydration repulsive energy.

It should be noted that steric interactions (typically between polymeric chains covering the external surface of the particles) were considered to be negligible or null in the dispersions studied in this work, because the treatment of the apple juice with pectinolytic enzymes is expected to eliminate the pectin chains surrounding the particles, as shown by Sorrivas, Genovese and Lozano (2006) in TEM images.
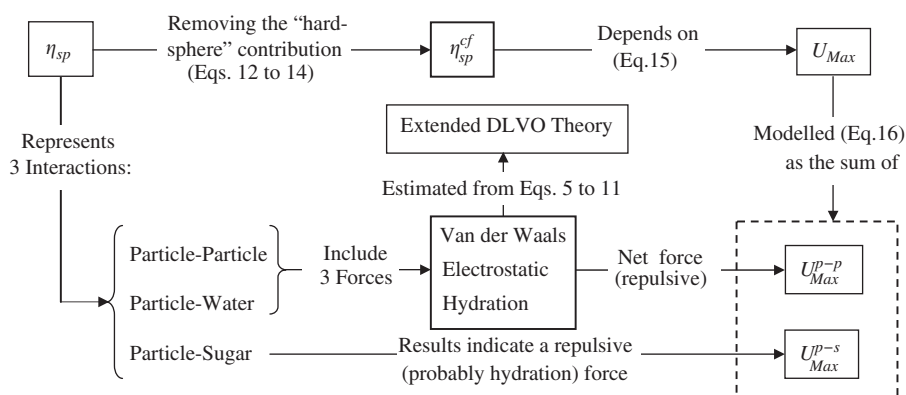

Fig. 1. Schematic representation of the relationships between the specific viscosity (η_{sp}), the contribution of colloidal forces to the specific viscosity (η_{sp}^{cf}), the total energy barrier (U_{Max}), and the contribution of particle–particle and particle–sugar interactions to the energy barrier (U_{Max}^{p-p} and U_{Max}^{p-s}, respectively).

The extended DLVO theory derives expressions for U_A, U_E, and U_H (Eqs. 6, 7 and 10, respectively) based on the assumption of spherical particles. Sorrivas et al. (2006) studied the shape of depectinized apple juice particles and concluded that they look like vesicles and agglomerates. Since the extended DLVO theory does not provide expressions for these particle shapes, it was considered a good approximation to use their average hydrodynamic radius for calculations.

For spheres of radius a at close separations ($x \ll a$) the Van der Waals energy may be simplified to the expression (McClements, 1999):

$$U_A(x) = -aA/12x \tag{6}$$

where A is the Hamaker constant, whose value depends on the properties of the particles and the dispersing medium, and the negative sign is used for attractive energies.

The term U_E represents the energy of repulsion due to the interaction of the electrical double layers around the particles (Genovese & Lozano, 2006; Benítez et al., 2007a). For $\kappa a > 10$, the electrostatic energy is given by the expression (Quemada & Berli, 2002):

$$U_E(x) = 2\pi\varepsilon a\psi_0^2 \ln[1 + \exp(-\kappa x)] \tag{7}$$

where ε is the permittivity of the medium, ψ_0 the particles surface potential, and κ^{-1} is the thickness of the electrical double layer surrounding the particles, or Debye's length:

$$\kappa^{-1} = (\varepsilon k_B T/2Ie F)^{1/2} \tag{8}$$

where k_B is the Boltzmann constant, T is the absolute temperature, e is the electronic charge, F is Faraday's constant, and I is the ionic strength calculated as

$$I = 1/2\Sigma c_i z_i^2 \tag{9}$$

where z_i and c_i are the valence and molar concentration of ions i in the bulk, respectively (Overbeek, 1977).

The structuring of water molecules around the particle surface produces a restriction in their motion known as hydration pressure. When two particles approach each other this pressure increases, resulting in a repulsive interaction, named hydration repulsion, U_H (Genovese & Lozano, 2006; Benítez et al., 2007a). The hydration energy could be described by an exponentially empirical function (Israelachvili, 1992):

$$U_h(x) = aP_0\lambda \exp(-x/\lambda) \tag{10}$$

where P_0 is the hydration pressure constant which depends on the degree of hydration of the surface (typically between 3 and 30 mJ/m²), and λ is the characteristic decay length of the interaction (typically between 0.6 and 1.1 nm) (Israelachvili, 1992).

The energy barrier between particles, U_{Max}^{p-p}, is defined as the primary maximum of the energy curve, $U_T(x)$. This maximum can be obtained at the point where the derivative of the curve with respect to x becomes zero:

$$\left.\frac{dU_T}{dx}\right|_{x^*} = \frac{-2\pi\varepsilon a\psi_0^2\kappa \exp(-\kappa x^*)}{1 + \exp(-\kappa x^*)} + \frac{aA}{12x^{*2}} - aP_0 \exp(-x^*/\lambda) = 0 \tag{11}$$

x^* being the interparticle distance where the energy barrier is located, such that: $U_T(x^*) = U_{Max}^{p-p}$ (Fig. 1).

1.3. Specific viscosity of colloidal dispersions

The energy barrier of a dilute colloidal dispersion could be determined from specific viscosity–particle volume fraction data (Genovese & Lozano, 2006). The viscosity of a colloidal dispersion (η) has been modeled as the sum of a "hard-sphere" contribution (η^{hs}) and a "colloidal forces" contribution (η^{cf}) (Ogawa, Yamada, Matsuda, & Okajima, 1997; Berli, Deiber, & Añón, 1999a, b; Quemada & Berli, 2002):

$$\eta = \eta^{hs} + \eta^{cf} \tag{12}$$

The term η^{hs} is considered to be the viscosity of an ideal suspension of rigid, non-interacting (inert), spherical particles. In the dilute regime, the well-known Einstein's equation (Eq. (13)) predicts it in terms of the volume fraction of particles (ϕ), and the viscosity of the continuous medium or solvent (η_s) (Metzner, 1985; Rao, 1999):

$$\eta^{hs} = \eta_s(1 + 2.5\phi) \tag{13a}$$

Rearranging, the hard-sphere specific viscosity, η_{sp}^{hs}, is obtained:

$$\eta^{hs}/\eta_s - 1 = 2.5\phi = \eta_{sp}^{hs} \tag{13b}$$

Combining Eqs. (4), (12) and (13b), the contribution of colloidal forces to the specific viscosity, η_{sp}^{cf}, may be determined from viscosity data of the solvent and the dispersion at different volume fractions:

$$\eta_{sp}^{cf} = \eta_{sp} - \eta_{sp}^{hs} = \eta/\eta_s - 1 - 2.5\phi \tag{14}$$

For diluted systems, Genovese and Lozano (2006) proposed the following model to predict η_{sp}^{cf} in terms of ϕ and the energy barrier, U_{Max} (normalized with Brownian thermal energy, $k_B T$):

$$\eta_{sp}^{cf} = \alpha(U_{Max}/k_B T)\phi \tag{15}$$

where α is a numerical constant. The term U_{Max} is considered to include the three interactions involved in the specific viscosity of this system: p–p, particle–water (p–w), and particle–sugar (p–s) (Fig. 1). Assuming that p–w is included in p–p interaction through the hydration energy (Eq. 10), it is proposed that the energy barrier obtained from Eq. (15) is the sum of a p–p contribution, U_{Max}^{p-p}, and a p–s contribution, U_{Max}^{p-s} (Fig. 1):

$$U_{Max} = U_{Max}^{p-p} + U_{Max}^{p-s} \tag{16}$$

In the absence of sugar ($X_s = 0$), $U_{Max}^{p-s} = 0$, then $U_{Max} = U_{Max}^{p-p}$. It should be noted that the "sum of contributions" criterion used in Eq. (16) is valid if p–p and p–s interactions are not coupled (McClements, 1999). Although this condition was not demonstrated in the present work, this approach was considered to give a good first approximation.

As mentioned, the aim of this study was to determine the effect of major apple juice sugars on the colloidal stability of the suspended particles. This stability is considered to depend on the p–p and p–s interactions, which in turn are expected to govern the specific viscosity of the dispersion. Then, the first objective was to determine the effect of sugar type and concentration on the specific viscosity of aqueous dispersions with a fixed concentration of apple juice particles. The second objective was to determine, for a given type of sugar, the combined effect of particle and sugar concentration on the specific viscosity of the dispersions, and to estimate the total (p–p+p–s) interaction potential from this data. The third objective was to estimate the p–p interaction potential from the extended DLVO theory, and the p–s interaction potential by difference.

2. Materials and methods

2.1. Sample preparation

Cloudy apple juice (cv. Granny Smith) was obtained from a juice factory (Jugos S.A., Río Negro, Argentina). The juice was depectinized with a commercial pectolytic enzyme (Solvay 5XLHA; 20 mg/l, 2 h a 50 °C), the supernatant was separated from

the degraded pectin sediment, and subjected to diafiltration in a lab-scale equipment Osmonic Sepa® CF (Osmonics, Minnetonka, MN, USA) with 100 kDa cut off polysulfone membranes. The juice (1000 ml) was diafiltered with distilled water until reaching a constant conductivity of 0.06 mS/cm. The objective of the diafiltration process was to eliminate the natural solutes of apple juice, thus isolating the insoluble solids in almost pure water. The final concentration of particles in water was $C_0 = 628.4$ mg/l.

From this sample, another four dispersions with different particle concentrations were obtained by dilution: 125.7, 251.4, 377.1, and 502.8 mg/l. Glucose was added to each one of these samples at six concentrations, $X_S = 0.02, 0.04, 0.06, 0.08, 0.10,$ and 0.12 mol/mol, thus obtaining 30 different samples (5 particle concentrations × 6 glucose concentrations). Besides glucose, sucrose and maltose at five concentrations, $X_S = 0.02, 0.04, 0.06, 0.08,$ and 0.10 mol/mol, were also separately added to the original ($C_0 = 628.4$ mg/l) particle dispersion (0.12 mol/mol was not added due to the lower solubility of sucrose and maltose in water). The ionic strength of all samples was adjusted with KCl to a constant value of $I = 2 \times 10^{-3}$ M. All samples were prepared in duplicate.

Glucose, sucrose, and maltose were chosen because of the significant difference in their hydration capacities (Chen & Joslyn, 1967; Oakenfull & Scott, 1984; Sato et al., 2004; Aeberhardt, Saint Laumer, & Bouquerand, 2005). Fructose and glucose have a similar behavior, but glucose has a smaller hydration capacity (Gharsallaoui, Rogé, Génotelle, & Mathlouthi, 2008), which is better for comparison with the other two sugars used in this work.

2.2. Zeta potential, electric conductivity, and size distribution measurements

Zeta potential (ζ), electric conductivity (C), and size distribution were measured at 25 °C in a Malvern Zetasizer 3000 particle analyzer (Malvern Instrument Inc., London, UK), with 10 replicates per sample.

2.3. Viscosity measurements and particle volume fraction determination

Kinematic viscosity ($v = \eta/\rho$) of all samples was measured at 25 °C in Cannon-Fenske glass capillary viscometers (No. 100, 150, 200, and 400), calibrated with sugar solutions with efflux times >360 s. Measurements were done in triplicate. The kinematic viscosities were converted to viscosity using the sugar solutions densities obtained from the literature (Wolf, Brown, & Prentiss, 1987).

The particle volume fractions (ϕ) of the dispersions were determined as described in Benítez et al. (2007a). Basically, 25 ml of diafiltered juice was lyophilized in a Heto FD 8.0 freeze dryer (Heto-Holten, Denmark) during 48 h. Afterwards apple juice particles were stored under vacuum in desiccators with P_2O_5 during 24 h. Particles weight was converted to volume using a particle density of $\delta_P = 1.2$ g/ml. Determinations were done in duplicate.

3. Results and discussion

The samples studied in this work may be considered basically as sugar solutions with a very small concentration (<0.1% v/v) of suspended particles, i.e. dilute colloidal dispersions. Fig. 2 shows that the addition of sugars (keeping constant the concentration of particles) produced a linear increase of the specific viscosity at decreasing water activities. This increase was sugar type dependent.
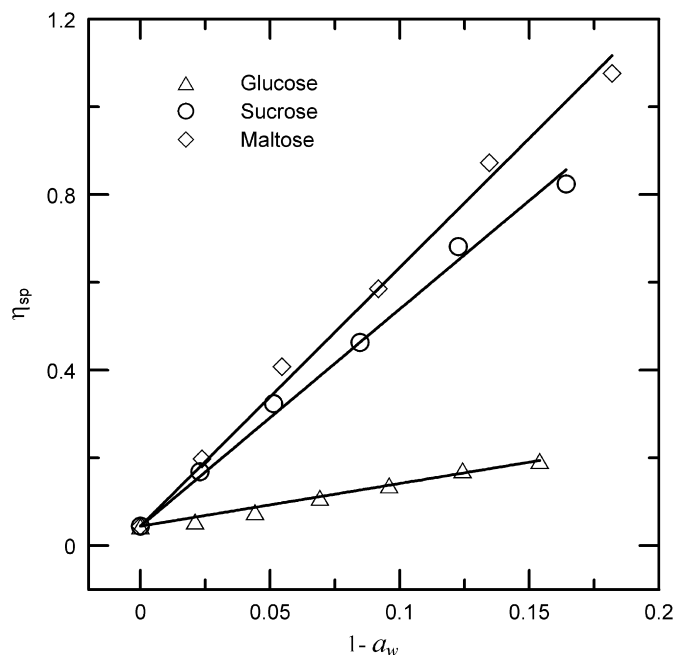
Fig. 2. Effect of water activity and sugar type on the specific viscosity of apple juice particle dispersion. $C_0 = 628.4$ mg/l.

Table 1
Expansion coefficient (δ), slope of η_{sp} vs. a_W, and Eq. (17) fitting regression coefficient for the three types of sugar used in this work

Sugar	$-\delta$	$-(\mathrm{d}\eta_{sp}/\mathrm{d}a_w)$	R^2
Glucose	2.734	0.973	0.987
Sucrose	7.405	4.947	0.994
Maltose	9.549	5.894	0.994

It is known that for most sugars the viscosity follows a linear relationship with water activity in the range $a_w = 0.8$–1.0 (Anese, Shtylla, Torreggiani, & Maltini, 1996). A similar behavior was reported in pectin (2%)–sugar solutions (Sato et al., 2004), but the slopes were 3–4 orders of magnitude higher than that in the present work. This was attributed to gel formation due to the cross-linking of pectin chains (produced by hydrophobic interactions and hydrogen bondings), favored by the presence of sugars. In this work, juice depectinization hindered the gelation process. The samples studied were viscous Newtonian liquids with absolute viscosity values lower than 0.5 Pa s. Chen and Joslyn (1967) measured the effect of sugars on the intrinsic viscosity of pectin solutions and found similar effects in the association of pectin molecules, but the solutions were too diluted to cause gelation.

Based on the previous considerations, the following equation was proposed to fit the experimental values:

$$\eta_{sp} = \eta_{sp_W} + (-\mathrm{d}\eta_{sp}/\mathrm{d}a_W)(1 - a_w) \tag{17}$$

where $\eta_{sp_W} = 0.0443$ is the measured specific viscosity of particles in water. As inferred from Eq. (4), this term represents the p–p (including p–w) interactions without sugar in the solution. Therefore, the second term would represent the p–p and p–s interactions in the presence of sugar. Consequently, the increase in the specific viscosity at increasing amounts of sugar molecules in the juice (Fig. 1) was produced by a proportional increase in (p–p+p–s) interactions. Table 1 shows the calculated slopes ($-\mathrm{d}\eta_{sp}/\mathrm{d}a_w$) and fitting regression coefficients for the different

types of sugar, and the corresponding δ values (Eq. 3) reported by Sato et al. (2004).

The parameter δ is an index of the sugar–water (II) interaction, and the negative value represents the sugar hydration or solvent ordering. Sugars interact with water to an extent which depends upon their molecular structure (Franks, Ravenhill, & Reid, 1972; Tait, Suggett, Franks, Ablett, & Quickenden, 1972). Tait et al. (1972) have proposed a "specific hydration model" to explain these effects. Sugar molecules induce structuring in the water molecules surrounding them if the orientation of OH groups is such that some of the O–O spacings correspond with the O–O distance of the water lattice (4.86 Å). Thus, each type of sugar has a different spatial arrangement of –OH groups, and consequently interacts with water in a different way.

In agreement, a good correlation ($R^2 = 0.983$) was found between ($-\mathrm{d}\eta_{sp}/\mathrm{d}a_w$) and $-\delta$ (Fig. 3). This means that the rate of increase of the specific viscosity was proportional to the hydration capacity of each sugar. This result suggests that in the presence of sugars, specific viscosity is governed by the interactions between particles and hydrated molecules of sugar, while p–p interactions seem to play a secondary role. This hypothesis was supported by the results obtained in the next section.

In order to estimate the effect of sugars on p–p interactions using the extended DLVO theory, the (particles and liquid medium) properties involved in Eqs. (6–10) were determined at different concentrations of glucose (X_s). Particle radius (a) data (Eqs. 6, 7, and 10) were obtained from a previous work (Benítez et al., 2007b), and listed in Table 2. The decrease of a at increasing sugar concentrations was attributed to either a conformational change and/or hydration of the particles.

The Hamaker constant involved in the calculation of Van der Waals energy (Eq. 6) was estimated from Lifshitz theory (Israelachvili, 1992):

$$A = \frac{3}{4}k_B T \left(\frac{\varepsilon_p - \varepsilon}{\varepsilon_p + \varepsilon}\right)^2 + \frac{3hv_e}{16\sqrt{2}}\frac{(n_p^2 - n^2)^2}{(n_p^2 + n^2)^{3/2}} \qquad (18)$$

where sub-index "$_p$" indicates particle, h is Planck's constant, v_e is the main electronic absorption frequency in the UV, and n is the
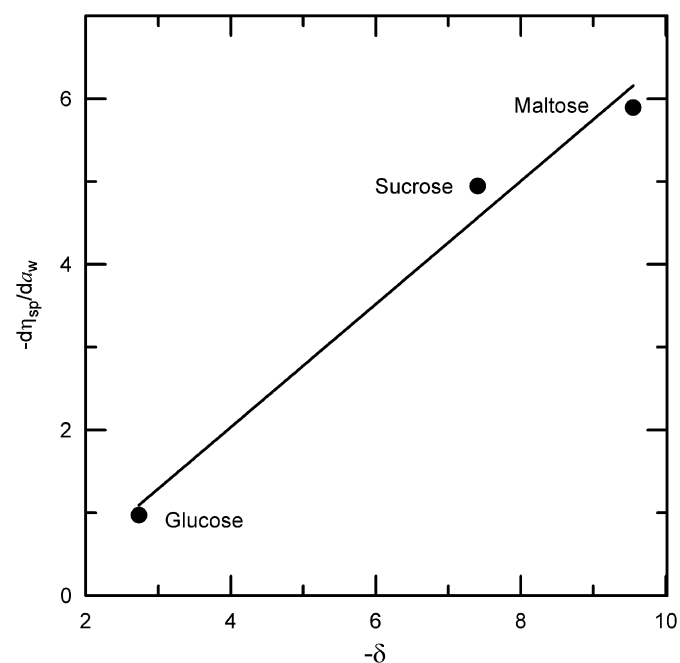
refractive index. The values $\varepsilon_p = 4.43 \times 10^{-11}$ F/m, $v_e = 2.9 \times 10^{15}\,\mathrm{s}^{-1}$ (Benítez et al., 2007a), and the particle refractive index $n_p = 1.487$ recently reported for apple juice (Benítez et al., 2007b) were used for calculations, and assumed to be constant within the range of sugar concentrations used in this work. Values of the refractive index (n) and the electric permittivity (ε) of the liquid medium were obtained from data of glucose solutions (Liley, Thomson, Friend, Daubert, & Buck, 1999). The calculated A values are shown in Table 2. The Hamaker constant decrease at increasing sugar concentrations was attributed to a change in the polarization of the water molecules induced by the presence of sugar. This change reduces the attraction between water molecules, because the sugar modifies the spatial arrangement of water molecules around the solute (Grigera, 1994).

Zeta potential (ζ) is the potential at the shear (or slipping) plane, and is considered to be the nearest practical approximation to the particle surface potential (ψ_0) (Overbeek, 1977; McClements, 1999). The value $\zeta = -32$ mV obtained for $X_s = 0.02$ mol/mol was considered to be constant within the range of sugar concentrations used in this work (Genovese & Lozano, 2006; Benítez & Lozano, 2006), and used to calculate the electrostatic energy (Eq. 7). Debye's length (κ^{-1}) was calculated (Eq. 8) for each glucose concentration and reported in Table 2. The values $P_0 = 9.22$ mJ/m^2 and $\lambda = 1$ nm (Benítez et al., 2007a) were used for the calculation of the hydration energy (Eq. 10) at $X_s = 0$ and $I = 2 \times 10^{-3}$ M.

The properties of the colloidal dispersion determined at $X_s = 0$ (Table 2) were used in Eq. (11) to calculate the interparticle distance of net maximum repulsion energy, $x^* = 0.33$ nm. This is about the size of 1 or 2 water molecules. Since apple juice particles are supposed to be covered by an immobilized water layer (Benítez et al., 2007a), the result suggests that two hydrated particles may approach each other until a minimum distance, x^*, where their water layers come in contact, at which point the repulsion energy reaches a maximum. In this case x^* would be the minimum contact distance between the hydrated surfaces of the two particles (no polymer chains adsorbed on the surface), then it might be considered to be independent of particle size and shape. This result also indicates that p–p interactions in apple juice dispersions are governed by the hydration repulsive forces, as previously reported (Genovese & Lozano, 2006; Benítez et al., 2007a).

Considering that x^* is not significantly affected by changes in the liquid medium (Benítez et al., 2007a), the value obtained was used for the calculation of the hydration pressure constant (P_0) at the other sugar concentrations (Table 2). The decrease of P_0 at increasing sugar concentrations was attributed to the reduction of water available for particle hydration (Aeberhardt et al., 2005).

Using the values of Table 2 in Eqs. 6, 7, and 10, the Van der Waals, electrostatic, and hydration p–p interaction energies were determined as a function of the interparticle distance (x), for the different sugar concentrations. Fig. 4 shows the curves obtained

Table 2
Particle radius (a), Hamaker constant (A), Debye's length (κ^{-1}), and hydration pressure constant (P_0) values for each glucose concentration

X_S (mol/mol)	a (nm)	A (k$_B$T)	κ^{-1} (nm)	P_0 (mJ/m^2)
0.00	524.8	2.18	9.71	9.22
0.02	426.7	1.70	9.44	7.12
0.04	358.5	1.36	9.06	5.67
0.06	324.6	1.12	8.65	4.64
0.08	264.7	0.95	8.24	3.89
0.10	253.5	0.82	7.84	3.33
0.12	253.8	0.72	7.46	2.90

Fig. 3. Correlation between the specific viscosity increment and the hydration capacity of the three sugars used in this work.
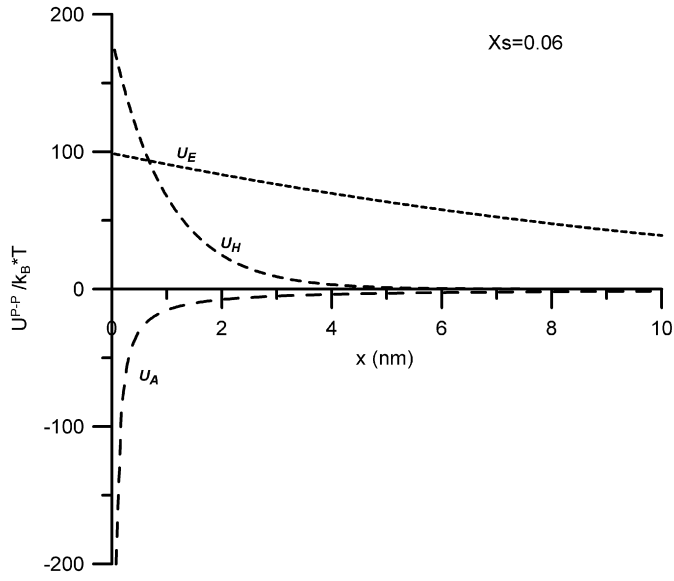
Fig. 4. Hydration (H), electrostatic (E), and Van der Waals (A) interaction energies (normalized with Brownian thermal energy) as a function of interparticle distance, for $X_s = 0.06$ mol/mol.
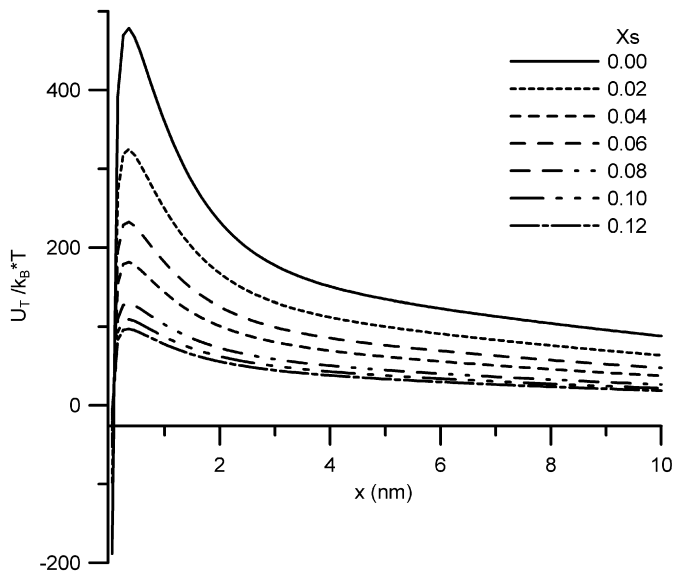

Fig. 5. Total interaction energies (normalized with Brownian thermal energy) as a function of interparticle distance, at different glucose concentrations.

Table 3
Total energy barrier (U_{Max}) of the system, and the contribution of particle–particle interactions (U_{Max}^{p-p}) and particle–sugar interactions (U_{Max}^{p-s}), at different glucose concentrations

X_S (mol/mol)	U_{Max}^{p-p} (k_BT)	U_{Max} (k_BT)	U_{Max}^{p-s} (k_BT)
0.00	475	(475)[a]	0
0.02	325	564	239
0.04	233	802	569
0.06	182	1136	954
0.08	129	1423	1294
0.10	109	1812	1703
0.12	97	2028	1931

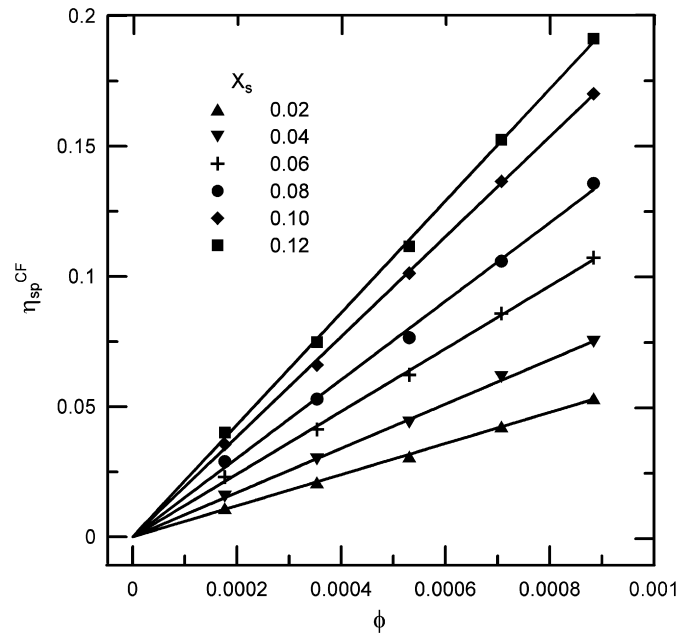[a] $U_{Max} = U_{Max}^{p-p}$ is considered for $X_s = 0$

Fig. 6. Effect of particle volume fraction on the colloidal forces contribution to specific viscosity, at different glucose concentrations.

concentrations (X_s) was determined with Eq. (14), and the are results shown in Fig. 6. As predicted by Eq. (15), η_{sp}^{cf} increased linearly at increasing values of ϕ ($R^2 > 0.998$). The slopes also increased at increasing values of X_s.

The values corresponding to the sugar-free ($X_s = 0$) dispersion: $\eta_{sp_W} = 0.0443$, $\phi = 8.84 \times 10^{-4}$ ($C_0 = 628.4$ mg/l), and $U_{Max} = U_{Max}^{p-p} = 475$ k_BT were applied in Eq. (15) to calculate the proportionality constant $\alpha = 0.106$. Assuming that α is independent of the sugar concentration (Genovese & Lozano, 2006), this value and the slopes of the η_{sp}^{cf} vs. ϕ curves (Fig. 5) were used to calculate U_{Max} at the different glucose concentrations (Table 3). With the values of U_{Max} and U_{Max}^{p-p}, the contribution of p–s interactions to the energy barrier, U_{Max}^{p-s}, was calculated by difference (Eq. 16) at the different glucose concentrations.

It can be noted (Table 3) that calculated U_{Max}^{p-s} values were positive (>0), suggesting that the interaction force between particles and sugar molecules was repulsive. What is the nature of this force? One possibility is that it arises from hydration repulsion, analogously to the force between pairs of hydrated particles, and may be explained as follows. The structured orientation of water molecules around the particle does not allow the approaching glucose molecule (with bipolar orientation) to accommodate in the vicinity of the particle, generating a repulsive

for $X_s = 0.06$ mol/mol. It can be observed that when the particles are very close (<1 nm) the short-distance hydration force is higher than the electrostatic force, indicating that hydration is the main contribution to the colloidal stability of the system, as observed in other works (Berli et al., 1999b; Genovese & Lozano, 2006; Benítez et al., 2007a). The curves obtained for the other sugar concentrations followed a similar behavior (not shown).

Then, the total p–p interaction energy, $U_T(x)$, was calculated using Eq. (5). Fig. 5 shows how the $U_T(x)$ curves shift down at increasing sugar concentrations. Consequently, the maximum of each curve or p–p energy barrier, U_{Max}^{p-p}, also decreased at increasing glucose content in the juice (Table 3).

The contribution of colloidal forces to the specific viscosity, η_{sp}^{cf}, at different particle volume fractions (ϕ) and sugar

force. The same phenomenon is expected for hydrated sugar molecules.

It can also be observed (Table 3) that both U_{Max} and U_{Max}^{p-s} increased at increasing sugar concentrations, in opposition to the trend followed by U_{Max}^{p-p}. Furthermore, at sugar concentrations $X_s \geqslant 0.04$ mol/mol, U_{Max}^{p-s} resulted to be higher than U_{Max}^{p-p}. This is in agreement with the results obtained in the previous sections, and indicates that above a critical sugar concentration, the interactions between particles and sugar molecules (hydrated or not) become more important than the interactions between particles themselves, governing the specific viscosity and probably the colloidal stability of the system.

4. Conclusions

The extended DLVO theory alone (including Van der Waals, electrostatic, and hydration forces) does not seem to explain satisfactorily the interactions involved in the specific viscosity of sols in the presence of sugars. The interactions between particles and sugar molecules (hydrated or not) have to be taken into consideration, as proposed in the present work. The particle–sugar interactions may be deduced combining the extended DLVO theory with specific viscosity vs. particle volume fraction data, at various sugar concentrations.

Acknowledgment

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