

Contribution of colloidal forces to the viscosity and stability of cloudy apple juice

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Abstract

Cloudy apple juice (CAJ) was considered to be a dilute colloidal dispersion of electrically charged, hydrophilic particles in an electrolyte solution (serum). Experimental data of relative (CAJ/serum) viscosity as a function of particle volume fraction, $\eta_r(\phi)$, was modeled as the sum of a ‘hard-sphere’ contribution (η_r^{hs}) plus a ‘colloidal forces’ contribution (η_r^{cf}). Theoretical values of $\eta_r^{\text{hs}}(\phi)$ were obtained with Einstein’s equation for dilute suspensions of non-interacting, rigid spheres. Semi-empirical values of η_r^{cf} were found to be proportional to $\phi^{1.22}$, lower than the theoretical ϕ^2 . The difference was attributed to the effect of the energy barrier or activation energy between pairs of particles (U_{Max}). The value of U_{Max} at each ϕ was obtained from the maximum of total interaction potential curves as function of inter-particle distance, $U(x)$. In its turn, $U(x)$ was modeled with the extended DLVO theory as the balance between attractive Van der Waals, repulsive electrostatic, and repulsive hydration energies. The term U_{Max} was found to be a function of ϕ and the hydration pressure constant (P_0), which was unknown for CAJs particles. This function was introduced in an empirical model proposed in this work, $\eta_r^{\text{cf}} = \alpha(U_{\text{Max}}/k_B T)\phi$, and correlated with semi-empirical values, giving $\alpha=0.483$ and $P_0=2.45 \times 10^6 \text{ N m}^{-2}$. According to this result, hydration forces (even reduced by hydrophobic interactions between pectin molecules) played the main role in the stability of CAJ particles. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Cloudy apple juice (CAJ) may be considered as a colloidal dispersion of electrically charged particles in a complex aqueous solution (serum) of sugars, pectin, organic acids, and salts. This serum is an electrolyte solution of metal cations (mainly K^+) and a variety of organic and inorganic anions (Babsky & Lozano, 1986). Cloud particles are modeled to consist of negatively charged, partly demethoxylated pectin wrapped around a core of positively charged protein (cited in the review paper of Beveridge, 1997). Since proteins and polysaccharides (like pectin) are strongly hydrated in aqueous solution (cited in the review paper of Oakenfull, 1987), it is reasonable to assume that CAJ particles are hydrophilic in nature. When juice pectic enzymes are inactivated, the pectin coat acts as a protective

colloid, retarding particle aggregation. However, the detailed mechanism of particle stabilization in cloudy juices has not been completely described.

Shortly after juice extraction, coarse insoluble material settles out by gravity. Fine particles remaining in suspension are considered to be colloidal in nature. According to the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Overbeek, 1977), the stability of colloidal particles would depend on the balance between attractive van der Waals forces and repulsive electrostatic forces. Mobile cations reduce the net negative charge of apple juice particles, decreasing the electrostatic repulsion between them, and consequently increasing aggregation and instability. However, non-DLVO interaction forces have been found in aqueous suspensions of very hydrophobic or very hydrophilic particles (see, for example, Molina-Bolívar and Ortega-Vinuesa, 1999). Recently, Genovese and Lozano (In press) claimed that repulsive hydration forces might play a significant role in the stability of CAJ.

The rheological behavior of a solid–liquid dispersion depends on the characteristics of the continuous phase (the solvent or serum), the dispersed phase (the particles),

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and the interactions between them. It has been reported (Genovese & Lozano, 2000; Saravacos, 1970) that CAJ at soluble solids concentrations up to 50°Brix behave as a Newtonian fluid. Furthermore, Genovese et al. (2000) found that viscosities of CAJ were higher than theoretical values for dispersions of non-interacting particles, and that the effect of particles' non-sphericity was negligible. As a first hypothesis, that increment was attributed to the secondary electro-viscous effect produced by electrostatic repulsion forces between particles, as proposed by Russel (1980). However, the influence of the other colloidal interactions was ignored. For example, Berli, Deiber, and Añón (1999a) claimed that electrostatic repulsion yields viscosity values ~20 times greater than those expected for an equivalent suspension of neutral particles, but argued that this effect is also a consequence of the hydration repulsive forces. Durán, Ramos-Tejada, Arroyo, and González-Caballero (2000) studied the relation between the rheological behavior of sodium montmorillonite suspensions and the potential energy of interaction between particles (including Van der Waals attraction, and electrostatic and hydration repulsions).

The aim of this work was to model the total interaction energy between CAJ particles with the extended DLVO theory, and to predict its influence on juice viscosity at different concentrations.

2. Theory

2.1. Viscosity models

Quiescent suspensions are ordered structures and for flow to occur particles must be forced to move against the force field of the other particles. Under these conditions, the viscosity of a colloidal suspension (η) has been modeled as the sum of a 'hard-sphere' contribution (η^{hs}) and a colloidal forces contribution (η^{cf}) (Berli et al., 1999a,b; Ogawa, Yamada, Matsuda, & Okajima, 1997; Quemada & Berli, 2002):

$$\eta = \eta^{\text{hs}} + \eta^{\text{cf}} \quad (1)$$

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. (2)) predicts it, in terms of the volume fraction of particles (ϕ), and the viscosity of the continuous medium or solvent (ϕ_s) (Metzner, 1985; Rao, 1999):

$$\eta^{\text{hs}} = \eta_s(1 + 2.5\phi) \quad (2)$$

The effect of both hydrodynamic and thermodynamic particle–particle interactions has been introduced in the second term of the virial expansion of the viscosity of

suspensions (Quemada et al., 2002), thus:

$$\eta_{\text{cf}} = \eta_s k \phi^2 \quad (3)$$

where k was modeled in terms of electrostatic repulsive forces through the second electroviscous effect (Russel, 1980). For concentrated colloidal suspensions, Ogawa et al. (1997) modeled η_{cf} in terms of the energy barrier or activation energy (U_{Max}) between pairs of particles. However, the influence of attractive Van der Waals and hydration repulsive forces was ignored in both models.

2.2. Extended DLVO theory

Consider a system which consists of two cloudy apple juice particles of radius a at a surface-to-surface separation h (Fig. 1). According to the extended DLVO theory developed for very hydrophilic (or very hydrophobic) colloidal dispersions, the total potential energy of interaction (U_{T}) between a pair of particles (also called pair potential) is the sum of Van der Waals attractive energy (U_{A}), electrostatic repulsive energy (U_{E}), and hydration repulsive energy (U_{H}), thus

$$U_{\text{T}}(x) = U_{\text{A}}(x) + U_{\text{E}}(x) + U_{\text{H}}(x) \quad (4)$$

where x is the distance between the surfaces of the particles (see for example, Molina-Bolívar et al., 1999). Conventionally, attractive energies are considered to be negative, and vice versa.

Considering only non-retarded forces (small distances), Hamaker derived an expression for the energy of attraction

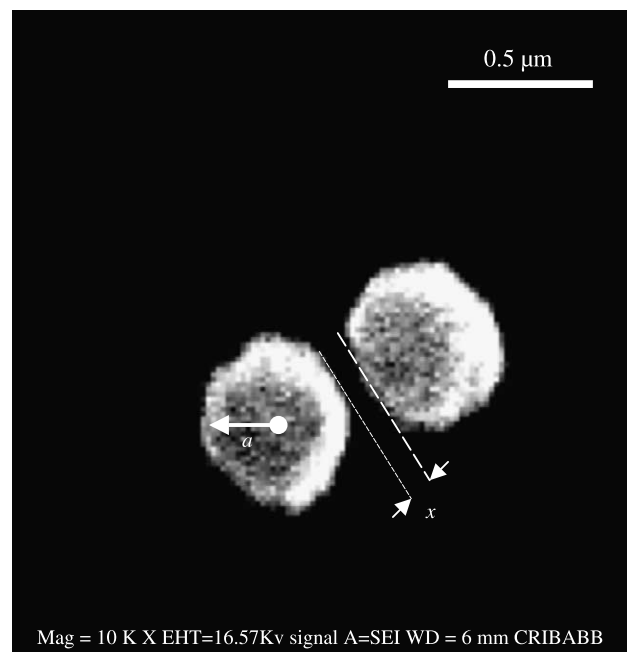


Fig. 1. Cloudy apple particle of radius a separated by a surface-to-surface separation x . Micrograph was obtained with a LEO EVO 40XVP (Extended pressure range) TEM (LEO Electron Microscopy Ltd, Cambridge, UK).

between two particles of radius a (Overbeek, 1977)

$$U_A(x) = -\frac{A}{6} \left[\frac{2a^2}{x(4a+x)} + \frac{2a^2}{(2a+x)^2} + \ln \frac{x(4a+x)}{(2a+x)^2} \right] \quad (5)$$

where A is the Hamaker constant, whose value depends on the properties of the particles and the dispersing medium. At close separations ($x \ll a$), the above equation may be simplified considerably (McClements, 1999):

$$U_A(x) = -\frac{aA}{12x} \quad (6)$$

Electrically charged particles in aqueous media are surrounded by ions of opposite charge (counterions) and electrolyte ions, namely, the electrical double layer. The quantity U_E represents the energy of repulsion due to the interaction of the electrical double layers. The expression for U_E depends on the ratio between a , and the thickness of the electrical double layer (κ^{-1}) called the Debye length. At $\kappa a > 10$, and particle's surface potentials (ψ_0) independent of x and lower than ≈ 25 mV (McClements, 1999; Quemada et al., 2002)

$$U_E(x) = 2\pi\epsilon\psi_0^2 a \ln[1 + \exp(-\kappa x)] \quad (7)$$

where $\epsilon = \epsilon_0\epsilon_r$ is the permittivity of the medium, ϵ_0 is the permittivity in vacuum, and ϵ_r is the relative permittivity or dielectric constant. The value of ψ_0 is often unknown. In most cases, the nearest practical approximation to ψ_0 is the potential at the shear plane (the distance from the charged surface below which the counterions remain strongly attached), known as the zeta-potential (ξ) (Durán et al., 2000; McClements, 1999; Overbeek, 1977). The Debye length is given by the expression

$$\kappa^{-1} = \sqrt{\frac{\epsilon k_B T}{2eFI}} \quad (8)$$

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

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (9)$$

where z_i and c_i are the valence and molar concentration of ions i in the bulk, respectively (Overbeek, 1977). Increasing the concentration of counterions is expected to reduce the net surface charge and the thickness of the double layer, reducing the electrostatic repulsion, and vice versa.

In the case of hydrophilic particles in aqueous media, the dipolar or ionic groups (e.g. $-\text{OH}$, $-\text{COO}^-$, and NH_3^+) on particle's surface may get hydrated via hydrogen bonding with the surrounding water molecules. The structuring of water molecules around these groups produces a restriction in their motion referred as hydration pressure. The pressure of the water in the boundary layer increases as surfaces approach one another (because hydrogen bonds must be disrupted) resulting in a short-range repulsive interaction

(Grasso, Subramaniam, Butkus, Strevett, & Bergendahl, 2002; McClements, 1999). Some of the dipolar and/or ionic groups are also capable of binding hydrated ions (e.g. $-\text{COO}^- + \text{K}^+ \rightarrow -\text{COO}^- \text{K}^+$). Genovese et al. (In press) proposed different hydration mechanisms of CAJ particles. The repulsive hydration energy U_H decreases exponentially from the surface to the bulk of the solution (Grasso et al., 2002; Molina-Bolívar et al., 1999)

$$U_H(x) = \pi a \lambda^2 P_0 \exp(-x/\lambda) \quad (10)$$

where λ is the decay length (usually in the range 0.2–1.1 nm for 1:1 electrolytes), and P_0 is the hydration pressure constant, which increases with materials' hydrophilicity.

It should be noted that for high-methoxyl pectins (like apple pectin), hydrophobic interactions take place between the ester methyl groups of the different molecules, leading to strong attractions between them. Since hydrophobic interactions and hydration forces are antagonistic (Axelos & Thibault, 1991), the formers are expected to decrease the value of the hydration pressure constant (P_0). For simplification, it was considered in this work that P_0 includes the effects of both hydration forces and hydrophobic interactions.

Overall, the function $U(x)$ typically shows a primary maximum at some critical inter-particle distance x^* , followed by a secondary minimum (Chang & Chang, 2002). That maximum or energy barrier, U_{Max} , acts as an activation energy decreasing the rate of coagulation (Overbeek, 1977).

3. Materials and methods

3.1. Preparation of cloudy apple juice

Cloudy apple juice (CAJ) was obtained as follows. Granny Smith apples bought in a local market were milled and pressed in our pilot plant. The juice extracted was steam heated up to 80 °C and hold during 5 min at that temperature before cooling, to inhibit further enzymatic and microbial activity (Yemenicioglu, Ozkan, & Cemeroglu, 1997). After cooling, the juice was centrifuged ($4200g \times 15$ min) and filtered (Whatman No. 1 filter paper) to remove the coarse-unstable particulate material.

3.2. Phase separation

In order to isolate its continuous phase (serum), part of the CAJ was micro-filtered through 0.45 μm cellulosic membrane (E04WP04700, MSI, Westboro, MA), obtaining a crystal-clear filtrate. Both CAJ and the filtrate were vacuum-concentrated to more than 50°Brix in a rotary evaporator (Rotavapor R-151, Büchi, Switzerland) and each one re-diluted to 10, 20, 30, 40 and 50°Brix by reconstitution with distilled water. Soluble solids

concentration (X) and refractive index (n) were measured in a bench refractometer (Abbe Mark II, Reichert, USA).

Particle size distribution (PSD) of the 10°Brix CAJ was determined by photon correlation spectroscopy in a Malvern Zetasizer 3000 (Malvern Instruments, Inc., London, UK). PSD of the 10°Brix filtrate could not be determined with this technique, due to its extremely low concentration of particles.

To check the efficiency of micro-filtration to remove the suspended particles, turbidity of CAJ and the filtrate (both at 10°Brix) were measured in a PC Compact Turbidimeter (Aqualitic, Germany) in Nephelos Turbidity Units (NTU). It was found that micro-filtration reduced the turbidity of CAJ from ≈ 1100 NTU to ≈ 3 NTU, the latter being in the order of a clarified apple juice. Consequently, the filtrate was considered an acceptable approximation to the ideal serum.

3.3. Characterization of CAJ and its serum

Particle volume fraction was determined by micro-filtrating 20 ml of 10°Brix CAJ. Particles retained in the filter were vacuum dried at 55–60 °C until constant weight. Particles' weight was converted to volume applying a particle density of $\delta_p = 1.2$ g/ml (cited in the review paper of Beveridge, 2002).

Density (δ) of CAJ and its serum at all concentrations were determined in a pycnometer of 45.70 ml capacity, calibrated with distilled water. Kinematics viscosity ($\nu = \eta/\delta$) of CAJ and its serum at all concentrations were determined in Cannon-Fenske glass capillary viscometers (efflux times > 150 s), calibrated with distilled water and sugar solutions (Liley, Thomson, Friend, Daubert, & Buck, 1999; Wolf, Brown, & Prentiss, 1990;).

Electrophoretic mobility (μ_E) measurements of CAJ at all concentrations were performed in the Malvern Zetasizer 3000 (Malvern Instruments, Inc., London), and internally converted to Zeta-potential (ξ) values by means of the Smoluchowsky equation, valid for $\kappa a \gg 1$:

$$\xi = \frac{\eta_s}{\epsilon_r} \mu_E \quad (11)$$

At high concentrations, measurement of ξ became increasingly difficult. In order to obtain repeatable values, the 40°Brix CAJ had to be diluted 1:3 (v/v) with serum at the same concentration. Unfortunately, it was not possible to obtain reliable values of the 50°Brix CAJ, even at high dilutions. All physical properties were determined at 25 °C, at least by triplicate.

4. Results and discussion

4.1. Particle volume fraction (ϕ)

Particle volume fraction of 10°Brix CAJ was found to be $\phi_0 = 2.14 \times 10^{-3}$, which is very close to the value

determined by Genovese et al. (2000) with an electron microscopy technique. Genovese et al. (2000) found that the dominant metal cation in CAJ was potassium (94.2%, w/w), followed by calcium (5.5%, w/w), while iron, copper, and zinc represented less than 0.4% (w/w) altogether. Since valence and concentration of anions in CAJ were unknown, electrolyte concentration (C) and ionic strength (I) were estimated assuming a symmetric $z-z$ electrolyte for each cation. Results obtained by Genovese et al. (In press) for a 10°Brix CAJ were $I_0 = 20.6$ mol/m³, and $C_0 = 17.5$ mol/m³. Assuming that each of these properties, namely ϕ , I , and C (generalized in Eq. (12) as Y), is directly proportional to the concentration of soluble solids (X , °Brix) in the juice, the following expression is valid

$$Y = Y_0 \frac{X\delta}{X_0\delta_0} \quad (12)$$

where δ is CAJs density (Table 1), and sub-index 0 indicates reference (10°Brix) juice. It should be noted that Eq. (12) is valid to calculate particle volume fractions of dilute suspensions ($\phi < 0.2$) (Metzner, 1985), where particle deformability, asymmetry, and conformation effects may be neglected.

4.2. Relative viscosity (η_r)

Newtonian viscosities measured on CAJ (η) and its serum (η_s) at different concentrations are listed in Table 1. The viscosity of a suspension is usually related to the viscosity of the continuous medium in terms of the relative viscosity:

$$\eta_r = \eta/\eta_s \quad (13)$$

Relative (CAJ/serum) viscosity (η_r) values at different juice concentrations were calculated and represented as a function of ϕ (Fig. 2). It can be observed that in terms of particle volume fraction, CAJ up to 50°Brix fell in the very dilute region ($\phi < 0.013$), where Eqs. (2) and (12) are applicable. Theoretical 'hard-sphere' contribution to relative viscosity (η_r^{hs}) calculated from Eqs. (2) and (13) was found to be much lower than η_r , and practically invariant (Fig. 2). The difference was attributed to the contribution of colloidal forces to relative viscosity (η_r^{cf}). Combining Eqs. (1) and (13):

$$\eta_r^{cf} = \eta_r - \eta_r^{hs} \quad (14)$$

Table 1

Effect of juice soluble solids concentration (X) on refractive index (n), density (δ), and Newtonian viscosity (η) of cloudy apple juice (CAJ) and serum (η_s), an aqueous solution of sugars, pectin, organic acids, and salts

X (°Brix)	n (–)	δ (g/ml)	η (mPa s)	η_s (mPa s)
10	1.347	1.037	1.709	1.405
20	1.363	1.081	3.647	2.353
30	1.380	1.127	8.385	4.372
40	1.399	1.178	22.31	9.488
50	1.419	1.232	74.50	25.38

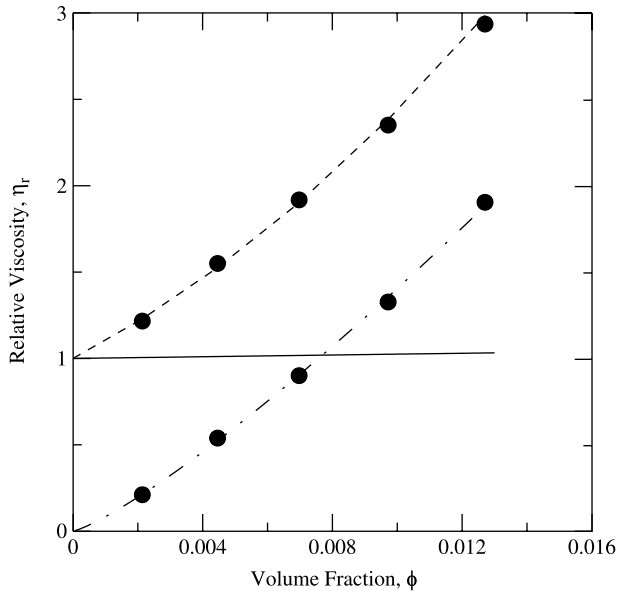


Fig. 2. Relative (CAJ/serum) viscosity vs. particle volume fraction: (●) Experimental, (- - -) predicted with Eq. (21), (—) theoretical hard-sphere contribution; considered to be the viscosity of an ideal suspension of rigid, non-interacting (inert), spherical particles. Colloidal-forces contribution: (○) semi-empirical values, and (- · - ·) fitted with the general model to predict the viscosity of a dilute colloidal dispersion in terms of the viscosity of the continuous phase, the volume fraction of particles, and the activation energy between pairs of particles (Eq. (15)).

It was found that semi-empirical data obtained with Eq. (14) (Fig. 1) followed a power law relationship

$$\eta_r^{cf} = b\phi^d \quad (15)$$

with $b = 391$ and $d = 1.22$ ($R^2 = 0.999$). The deviation from the theoretical value $d = 2$ (see Eq. (3)) was attributed to the effect of attractive Van der Waals and repulsive hydration forces, which were not considered in the derivation of Eq. (3). Therefore, the concept of maximum net repulsion energy (U_{Max}) was introduced for dilute systems like CAJ, and its effect on the viscosity was analyzed.

4.3. Energy barrier or activation energy (U_{Max})

The value of U_{Max} is obtained from the maximum of the total interaction energy curve, $U_T(x)$. The expression for $U_T(x)$ of CAJ was obtained by replacing Eqs. (6), (7), and (10) into Eq. (4):

$$U_T(x) = -\frac{aA}{12x} + 2\pi\epsilon\psi_0^2 a \ln[1 + \exp(-\kappa x)] + \pi a \lambda^2 P_0 \exp\left(-\frac{x}{\lambda}\right) \quad (16)$$

Dielectric permittivity (ϵ) of foods is known to be strongly influenced by water content. In the particular case of sugar solutions, ϵ decreases with increasing sugar concentration. In this context, CAJs serum may be modeled as a solution of fructose, sucrose and glucose. Genovese

Table 2

Effect of juice concentration (X) refractometrically determined as °Brix, on dielectric constant (ϵ_r), Debye's screening length (κ^{-1}), Hamaker constant (A), and activation energy (U_{Max})

X (°Brix)	ϵ_r (-)	κ^{-1} (nm)	A ($k_B T$)	U_{Max} ($k_B T$)
10	76.2	2.09	3.287	217
20	72.5	1.41	2.878	239
30	67.4	1.09	2.476	262
40	60.8	0.88	2.066	290
50	52.8	0.71	1.677	318

et al. (In press), combined dielectric constant (ϵ_r) data of apple juice (11.5°Brix) and sucrose solutions (20, 40, and 60°Brix) at 25 °C, and found the correlation $\epsilon_r = \epsilon_r^w - 1.58 \times 10^{-1} X - 7.13 \times 10^{-3} X^2$ ($R^2 = 0.998$), where ϵ_r^w is the dielectric constant of water. Calculated values of ϵ_r at the five juice concentrations were listed in Table 2.

Particle size analysis of 10°Brix CAJ showed a bimodal distribution, as reported in the review paper of Beveridge (2002). Since viscosity of diluted suspensions ($\phi < 0.2$) is not affected by modest changes in particles size (Metzner, 1985), the average of the distribution was used for calculations. Particle average radius was determined to be $a = 331 \pm 2$ nm, and it was considered to be independent of juice concentration. Consequently, Eq. (6) is valid for CAJ inter-particle distances lower than ≈ 30 nm.

Since values of the Hamaker constant (A) for CAJ have not been experimentally determined yet, they were estimated with the theoretical expression (Israelachvili, 1992)

$$A = \frac{3}{4} k_B T \left(\frac{\epsilon_p - \epsilon}{\epsilon_p + \epsilon} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_p^2 - n^2)^2}{(n_p^2 + n^2)^{3/2}} \quad (17)$$

where sub-index p indicates particle, h is Planck's constant, and ν_e is the main electronic absorption frequency in the UV. Measured values of serum's refractive index (n) at different concentrations were listed in Table 1. Particle's properties were assumed to be constant in this range of concentrations, and approximately equal to the properties of pure protein: $\epsilon_p = 4.43 \times 10^{-11}$ F/m, $n_p = 1.56$, and $\nu_e = 2.9 \times 10^{-15}$ s $^{-1}$ (McClements, 1999). Although it is not clear why calculated A values decreased at increasing juice concentrations (Table 2), they are in the range of values reported for other biological systems (Chang et al., 2002; Molina-Bolívar et al., 1999). Following Eq. (6), the decrease in the Hamaker constant produced a decrease (in absolute values) of the attractive Van der Waals energy at increasing juice concentrations (not-shown). The curve $U_A(x)$ corresponding to a 10°Brix CAJ is shown in Fig. 3.

Calculated values of κ^{-1} (Eq. (8)) decreased at increasing values of C (Table 2), because of the increasing compression of the electrical double layer surrounding the particles. The product κa (being a the average particle radius) resulted higher than 158 for all juice concentrations, fulfilling the conditions required by Eqs. (7) and (11).

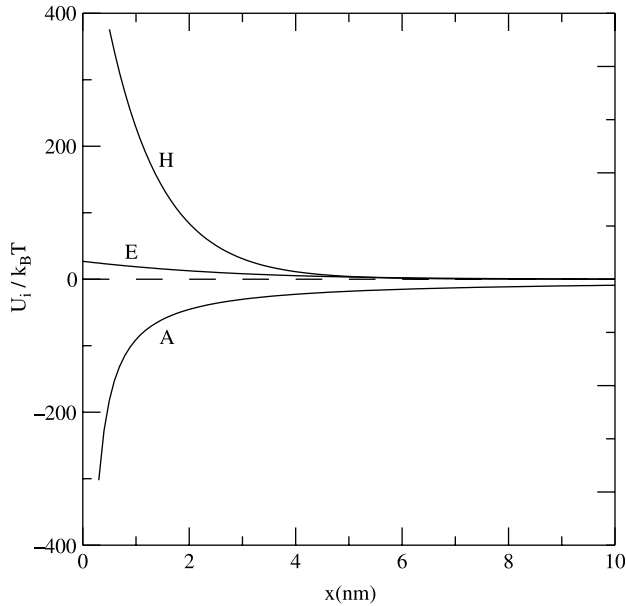


Fig. 3. Pair interaction energies normalized with the Brownian thermal energy $k_B T$ as a function of the inter-particle distance x for a 10°Brix CAJ. Full lines refer to the contribution of attractive Van der Waals forces (A), electrostatic repulsive forces (E) and hydration repulsive forces (H), predicted with the extended DLVO theory.

As previously mentioned, the surface potential is often represented by the zeta potential, i.e. $\psi_0 \approx \xi$ (Chang et al., 2002). Values of η_s (Table 1) and ε_r (Table 2) were used in Eq. (11) to calculate zeta potential at different concentrations. Although it was not possible to determine ξ of the highly concentrated 50°Brix CAJ, with the analyzer used in this work, statistical analysis did not find significant differences between the values measured at 10, 20, 30, and 40°Brix ($P > 0.05$). Consequently, particle surface potential was considered to be independent of juice concentration, and the global average $\xi = -10.7 \pm 0.9$ mV was used for calculations. Since the absolute value of ξ was lower than 25 mV, then Eq. (7) is applicable. The electrostatic repulsive energy (Eq. (6)) decreased at increasing juice concentrations (Genovese et al. (In press)) due to the decrease in ε (see Table 2). The curve $U_E(x)$ obtained for a 10°Brix CAJ is also shown in Fig. 2.

The decay length of CAJ was assumed to be $\lambda \approx 1$ nm (Berli et al., 1999a,b; Durán et al., 2000; Quemada et al., 2002). Since λ is known to be almost independent of ionic strength, it was considered approximately constant in the range of juice concentrations studied in this work. The hydration pressure constant (P_0) has been claimed to either increase (Molina-Bolívar et al., 1999) or decrease (Chang et al., 2002) with electrolyte concentration (C). Furthermore, in this work P_0 was considered to be affected also by hydrophobic interactions between pectin molecules. Since $P_0(C)$ of CAJ has not been determined yet, it was assumed as a first approximation that its value was constant in the range of concentrations studied. It was observed that at any arbitrary value of P_0 , the values of U_{Max} (normalized with

the Brownian thermal energy, $k_B T$) followed a power law relationship with ϕ ($R^2 > 0.92$)

$$\frac{U_{Max}}{k_B T} = f\phi^g \quad (18)$$

where parameters f and g varied with P_0 . For P_0 values in the range $1.5 \times 10^6 - 1.0 \times 10^7 \text{ N m}^{-2}$, $f = 260 + 2.24 \times 10^{-4} P_0$ ($R^2 = 0.995$), and $g = 4.31 \times 10^4 P_0^{-0.828}$ ($R^2 = 0.994$).

4.4. Modeling $\eta_r(\phi, U_{Max})$

It is proposed in this work, on an empirical basis, that in this very dilute regime η_r^{cf} is proportional to U_{Max} and ϕ , thus:

$$\eta_r^{cf} = \alpha \left(\frac{U_{Max}}{k_B T} \right) \phi \quad (19)$$

where α is a dimensionless proportionality constant.

Replacing Eq. (18) into Eq. (19) and comparing with Eq. (15), the following values were obtained for CAJ: $\alpha = 0.483$ and $P_0 = 2.45 \times 10^6 \text{ N m}^{-2}$. This value of P_0 lies within the range where correlations for $b(P_0)$ and $d(P_0)$ are valid, and within the range $1 \times 10^6 - 5 \times 10^8 \text{ N m}^{-2}$ reported for hydrophilic materials (Molina-Bolívar et al., 1999). The hydration repulsive energy $U_H(x)$ calculated with Eq. (10) (and here considered to be independent of juice concentration, and affected by hydrophobic interactions) was also plotted in Fig. 3. It was observed that at short distances ($x < 5$ nm) U_H exceeded both U_E and U_A , being thus responsible for the stability of the suspension, as found in other systems (see, for example, Berli et al., 1999b; Molina-Bolívar et al., 1999).

The total interaction energy curves obtained with Eq. (16) at different CAJ concentrations were plotted in Fig. 4.

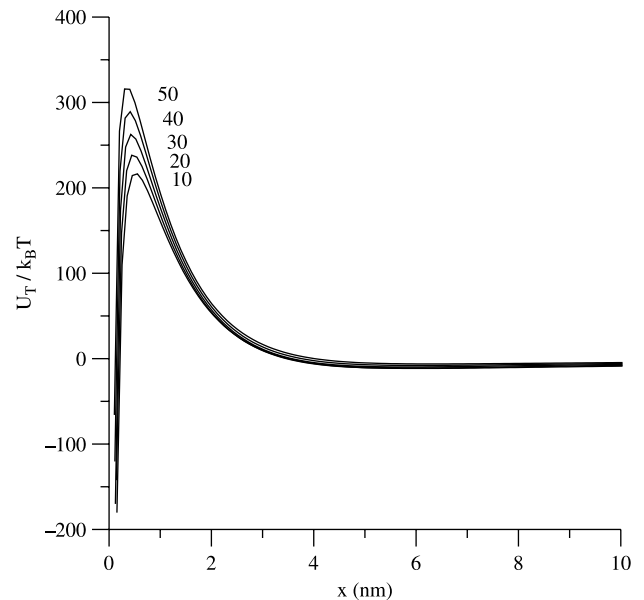


Fig. 4. Total pair interaction energies (U_T) normalized with the Brownian thermal energy $k_B T$ as a function of the inter-particle distance x , for CAJ at different concentrations (10, 20, 30 40 and 50°Brix), predicted with the extended DLVO theory.

Calculated values of U_{Max} increased with X (Table 2), suggesting that stability increases at increasing juice concentrations.

Combining Eqs. (1), (2) and (19), a general model to predict the viscosity of a dilute colloidal dispersion was obtained in terms of the viscosity of the continuous phase, the volume fraction of particles, and the activation energy between pairs of particles:

$$\frac{\eta}{\eta_s} = 1 + 2.5\phi + \alpha \left(\frac{U_{\text{Max}}}{k_B T} \right) \phi \quad (20)$$

Or in its reduced form:

$$\eta_r = 1 + \left(2.5 + \alpha \frac{U_{\text{Max}}}{k_B T} \right) \phi \quad (21)$$

Calculated values of α and U_{Max} were introduced in Eq. (21) to predict $\eta_r(\phi)$ of CAJ, showing very good correlation ($R^2=0.999$) with experimental data (Fig. 2).

5. Conclusions

Colloidal forces between pairs of particles produced a significant increase in the relative viscosity of CAJ, compared to the values expected for equivalent suspensions of non-interacting particles. This effect was found to be proportional to the volume fraction of particles and the activation energy between them. The activation energy was also a function of the volume fraction of particles, and at short distances it was governed by the hydration repulsion energy, which was higher than electrostatic repulsion and attractive Van der Waals energies. This suggests that hydration forces (even reduced by hydrophobic interactions) played the main role in the stabilization of CAJs particles. Since the Hamaker constant of CAJ was determined theoretically, and the hydration pressure constant was determined indirectly from rheological data, future studies will be focused on the experimental determination of both constants.

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