

Rheological behavior and physical properties of aqueous solutions of carrageenan and acacia gum

ABSTRACT

Polysaccharides are widely used as thickening, stabilizing, and gelling agents for the control of the texture, flavor, microstructure, and shelf-life of foods. This work contributes to the study of the physical properties and rheological behavior of binary and ternary solutions of carrageenan and acacia gum. Experiments were performed to determine properties such as density, refractive index, and viscosity. The results showed that those properties studied increased with increasing biopolymer concentration and decreased with increasing temperature. Experimental data were modeled to describe the combined effects of temperature and biopolymer concentration on the density, refractive index, and dynamic viscosity of these solutions. The properties were measured in the temperature range from 298.15 to 308.15 K. Suitable polynomial functions were successfully fitted to the experimental data. Classical rheological models (Bingham, power law, Casson, and Herschel-Bulkley) were tested for binary and ternary aqueous solutions containing carrageenan. Pseudoplastic behavior was observed, and the solutions were accurately modeled through a power-law model.

KEYWORDS: Biopolymers; density; refractive index; non-newtonian behavior.

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INTRODUCTION

Knowledge of physical properties is of fundamental importance for engineering calculations involving selection, sizing of equipment, implementation of control process strategies and development of new products (McCABE; SMITH; HARRIOT, 1993). The physical properties are also an important aspect to ensure food quality and safety. They describe the unique, characteristic way a food material responds to physical treatments involving mechanical, thermal, electrical, optical, sonic, and electromagnetic processes and are the basis for instruments and sensors (WILHELM; SUTER; BRUSEWITZ, 2004).

Physical properties have been reported for polysaccharide-containing solutions (GUIMARÃES; JÚNIOR; ROJAS, 2005, ASSIS *et al.*, 2010, RAMOS; GARCIA-ROJAS; GIRALDO-ZUNIGA, 2013, COSTA *et al.*, 2014). In nature, polysaccharides are found in various forms with several functions. They may be extracted from plant roots, tubers, stalks, and seeds, wherein they act as energy reserves and contribute to the structural integrity and mechanical strength of the tissues (LAPASIN; PRICL, 1995). Polysaccharide solutions are scientifically and technologically important. Therefore, an understanding of the properties of these solutions is essential.

Polysaccharides are widely used as thickening, stabilizing, gelling agents for the control of the texture, flavor, microstructure and shelf-life of foods (KHOURYIEH *et al.*, 2015). The main polysaccharides used as emulsifiers in food applications are acacia gum, modified starches, modified celluloses, pectins, and galactomannans (DICKINSON, 2009). Hydrocolloids modify emulsion properties due to many factors, including their molecular characteristics (e.g., molar mass, branching, conformation, charge, hydrophobicity, concentration, and interactions) and their impact on bulk physicochemical properties (e.g., light scattering, thickening, gelling, and stability) (CHUNG; DEGNER; McCLEMENTS, 2013). Emulsions containing xanthan/locust bean gum mixtures were found to be effective at inhibiting lipid oxidation due to the enhanced viscosity from the synergistic interactions of the biopolymers, which resulted in the slow diffusion of oxidants to the oil droplet surface foods (KHOURYIEH *et al.*, 2015).

Carrageenans, sulfated linear polysaccharides of D-galactose and 3,6-anhydro-D-galactose, can be extracted as matrix components of red seaweed (GLICKSMAN, 1983). Carrageenans can be classified into five types, as lambda (λ), kappa (κ), iota (ι), mu (μ), and nu (η). The different types of carrageenan confer a broad spectrum of textures. For example, λ -carrageenan is a thickening agent that increases the viscosity of solutions. Other carrageenans act as thermoreversible gels that can vary in texture from soft and elastic (e.g., ι -carrageenan) to firm and brittle (e.g., κ -carrageenan) (PHILLIPS; WILLIAMS, 2009). Carrageenans are used mainly in the food, cosmetics, and textiles industries, where they are applied as stabilizing, gelling, thickening, and emulsifying agents (GLICKSMAN, 1987).

Acacia gum (also known as gum arabic) is a natural resin extracted from two acacia species from the sub-Saharan region, *Acacia senegal* and *Acacia seyal*. Acacia gum is found in nature as polysaccharide acid rich in calcium, magnesium, and potassium. Hydrolysis of acacia gum produces L-arabinose, D-galactose, D-glucuronic acid, and L-rhamnose and a small fraction of proteins. The highly branched structure, arabinogalactan-proteins (AGP), of gum from *A. senegal* gives rise to compact molecules with relatively small hydrodynamic volumes (GLICKSMAN, 1987, PHILLIPS; WILLIAMS, 2009, LOPEZ-TORREZ *et al.*, 2015).

Consequently, these gum solutions become viscous only at high concentrations. At relatively low concentrations (<5%), acacia gum yields solutions that are essentially Newtonian in behavior (IDRIS, 2017). Acacia gum is mainly applied in the confectionery industry, where it is used in a wide variety of products including gums, tablets, candies, and marshmallows (toffees) (GLICKSMAN, 1987, VERBEKEN; DIERCKX; DEWETTINCK, 2003, PHILLIPS; WILLIAMS, 2009, LOPEZ-TORREZ *et al.*, 2015). Due to its low viscosity, acacia gum is constantly applied in combination with other polysaccharides (IDRIS, 2017). According to Srebernich *et al.* (2016), the use of acacia gum has several technological, nutritional and functional properties. In non-food applications, it is used as a suspending agent, emulsifier, adhesive, and binder in tableting and in demulcent syrup in the pharmaceutical industry. In cosmetics, it functions as a stabilizer in lotions and protective creams. It is still used as a dispersant in paints and insecticidal emulsions (VERBEKEN; DIERCKX; DEWETTINCK, 2003).

Studies of the physical properties and rheological behavior of aqueous mixtures of carrageenan and acacia gum are very important due to their wide application mainly in the food and pharmaceutical industries. Therefore, the objectives of this work were: i) to investigate the effects of temperature and biopolymer concentration on the thermophysical properties of binary and ternary aqueous solutions of carrageenan and/or acacia gum, ii) to model the thermophysical properties of these solutions with a general quadratic model, and iii) to study the rheological behavior of binary aqueous solutions of carrageenan and ternary aqueous solutions of carrageenan and acacia gum at different biopolymer concentrations.

MATERIALS AND METHODS

MATERIALS

Acacia gum (51198) and carrageenan (C1013) were purchased from Sigma Aldrich (St. Louis, MO, USA). All experiments employed ultrapure water (Master System MS 2000, Gehaka, Brazil; conductivity of $0.05 \mu\text{S}\cdot\text{cm}^{-1}$).

PREPARATION OF BINARY AND TERNARY SOLUTIONS

Aqueous solutions were prepared by gravimetrically dispersing the biopolymers in water with an analytical balance (AY220, Shimadzu, Japan; accuracy of 0.0001 g), followed by magnetic stirring (78 HW-1, Biomixer, Brazil) for 3 h. After that, ultrasound treatment (UP100H, Hielscher, Germany) was applied for 30 min for complete homogenization of the system. Compositions of the binary (carrageenan or acacia gum + water) and ternary (carrageenan + acacia gum + water) solutions are shown in Tables 1 to 3. The combined expanded uncertainty, $u(Y)$, of density, refractive indices and dynamic viscosities (Y) is given by Equation 1 (TAYLOR; KUYATT, 1994, DONG *et al.*, 2005).

$$u(Y)^2 = \sum_{i=1}^N \left(\frac{\partial Y}{\partial X_i} u(X_i) \right)^2 \quad (1)$$

Where N is the number of input parameters; $\mu(X_i)$ are the experimental all of the measured quantities (X_i).

DENSITY AND REFRACTIVE INDEX

The density of each solution was measured by an automatic U-tube density meter (DMA 4500M, Anton Paar, Austria) at atmospheric pressure with an accuracy of $5.0 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. The estimated combined expanded uncertainty of the density measurements at the 95% confidence level with a coverage factor of $k \approx 2$ is to be $0.02 \text{ kg}\cdot\text{m}^{-3}$ to $0.08 \text{ kg}\cdot\text{m}^{-3}$ depending on the mass fraction and temperature ranges.

The refractive index was measured with an automatic refractometer (Abbemat RXA170®, Anton Paar, Austria) with an accuracy of $4.0 \times 10^{-5} \text{ nD}$. Both instruments were connected to an automatic sample changer (Xsample 452®, Anton Paar, Austria). The temperature was monitored with a digital thermometer and the stability was 0.01 K. The apparatus was calibrated with ultrapure water and dry air. The estimated combined expanded uncertainty of the refractive indices measurements at the 95% confidence level with a coverage factor of $k \approx 2$ is to be $2 \cdot 10^{-5} \text{ nD}$ to $9 \cdot 10^{-5} \text{ nD}$ depending on the mass fraction and temperature ranges.

RHEOLOGICAL MEASUREMENTS

The rheological behavior of the binary and ternary solutions containing carrageenan were tested in a stress-controlled rheometer (Haake Mars III, Thermo Scientific, USA) using a cone (C 60/ 1° TIL) and plate (MPC 60) geometry. The temperature of the bottom plate was rapidly and precisely controlled at 298.15 K with a Peltier system and accessory solvent trap was used during measurements in order to prevent solvent evaporation. For each solution, the shear rate ($\dot{\gamma}$) values in the range of 0 to 500 s^{-1} were recorded. The measurement time was approximately 2 to 3 seconds per data point. The maximum allowable temperature deviation was $\pm 0.01 \text{ K}$. Power law (Eq. 2), Bingham (Eq. 3), Casson (Eq. 4), and Herschel-Bulkley (Eq. 5) classic rheological models were fitted to the experimentally obtained $\tau = f(\dot{\gamma})$ data.

$$\tau = K(\dot{\gamma})^n \quad (2)$$

$$\tau = \tau_0 + \eta_B(\dot{\gamma}) \quad (3)$$

$$\tau^{0.5} = \tau_0^{0.5} + K_C(\dot{\gamma})^{0.5} \quad (4)$$

$$\tau = \tau_0 + K(\dot{\gamma})^n \quad (5)$$

In Eqs. 2 to 5, τ is shear stress (Pa), τ_0 is yield stress (Pa; $\tau_0 = 0$ for Newtonian and power law fluids), η is a viscosity, K is the consistency index ($\text{Pa}\cdot\text{s}^n$), K_C is the Casson plastic viscosity ($\text{Pa}\cdot\text{s}^{0.5}$), and n is the dimensionless flow index ($n > 1$ for

dilatant fluids, $n < 1$ for pseudoplastic fluids, and $n = 1$, $K \equiv \eta$ for Newtonian fluids) (STEFFE, 1996).

DATA MODELING

All measurements were conducted in triplicate. Means and standard deviations of the experimental data were determined by the Statistical Analysis System (SAS®) software package, version 9.0 (SAS Institute Inc., Cary, NC, USA). Quadratic multiple regression models were adjusted according to the experimental data to describe how the studied properties were influenced by temperature and biopolymer concentration. The models were selected and the lack of parameter adjustments was evaluated by t-test and by analyzing differences between the observed and modeled data. A significance level of 5% ($p < 0.05$) was adopted as the criterion for the analysis of model parameters. The general quadratic model used in the current study was:

$$\psi = \beta_1 + \beta_2 T + \beta_3 w_1 + \beta_4 w_2 + \beta_5 T^2 + \beta_6 w_1^2 + \beta_7 w_2^2 + \beta_8 w_1 T + \beta_9 w_2 T + \beta_{10} w_1 w_2 \quad (6)$$

where Ψ is the thermophysical property, $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7, \beta_8, \beta_9$, and β_{10} are constants determined from experimental data adjustments, T is temperature, and w_1 and w_2 are the mass fraction of carrageenan and acacia gum respectively.

RESULTS AND DISCUSSION

DENSITY AND REFRACTIVE INDEX MEASUREMENTS

Densities and refractive indices of the binary and ternary solutions of carrageenan and acacia gum at different concentrations were measured at $T = 298.15$ to 308.15 K. Results for binary carrageenan solutions with w_1 of 0.0005 to 0.0100, binary acacia gum solutions with w_2 of 0.0005 to 0.0100, and ternary solutions of both biopolymers are listed in Tables 1 to 3, respectively.

Results indicate that density and refractive index values of the aqueous solutions decrease with an increase in the temperature and increase with an increase of concentration of biopolymers. The decrease in density with increasing temperature was due to the energy supplied to the system that increased the vibration and the distance among the molecules. This behavior of the refractive index with respect to increase of the polysaccharides concentration is due to the difficulty of light to propagate through a denser solution, resulting in an increase of this property (SANTOS *et al.*, 2012, RENGIFO *et al.*, 2015).

A temperature increase causes particle disorganization and decreases the refractive index due to increasing the amount of light that passes through the solution. The observed trends of these properties in this work are consistent with those reported by other authors (GUIMARÃES; JÚNIOR; ROJAS, 2005, ASSIS *et al.*, 2010, RAMOS; GARCIA-ROJAS; GIRALDO-ZUNIGA, 2013, COSTA *et al.*, 2014) for xanthan gum, carboxymethylcellulose, κ -carrageenan, and poly (ethylene glycol) 1500.

DINAMIC VISCOSITY MEASUREMENTS

Experimental viscosities for binary aqueous solutions of acacia gum with concentrations w of 0.0005 to 0.0100 were measured at $T = 298.15$ to 308.15 K (Table 1). As expected, the viscosity values decreased with increasing temperature and increased with increasing concentration of acacia gum. The viscosity of the solutions increased with increasing solute concentration because of the rise in intermolecular interactions and entanglements, such as hydrogen bonds with hydroxyl groups, and the distortion in the velocity pattern of the liquid by hydrated molecules in the solute (ASSIS *et al.*, 2010, GARCÍA-OCHOA *et al.*, 2000).

Table 1- Density (ρ) and refractive index (n) of carrageenan (w_1) in binary aqueous solutions at different temperatures (T) and concentrations^a

w_1	T (K)	ρ (kg·m ⁻³)	$n \cdot 10^{-3}$ (nD)
0.0005	298.15	997.31 ± 0.01	1332.58 ± 0.01
0.0005	300.15	996.64 ± 0.01	1332.26 ± 0.00
0.0005	303.15	995.91 ± 0.01	1331.91 ± 0.00
0.0005	305.65	995.13 ± 0.01	1331.59 ± 0.00
0.0005	308.15	994.30 ± 0.01	1331.21 ± 0.01
0.0020	298.15	998.04 ± 0.02	1332.70 ± 0.03
0.0020	300.65	997.38 ± 0.02	1332.45 ± 0.01
0.0020	303.15	996.65 ± 0.02	1332.10 ± 0.03
0.0020	305.65	995.87 ± 0.02	1331.76 ± 0.03
0.0020	308.15	995.03 ± 0.02	1331.42 ± 0.03
0.0040	298.15	998.61 ± 0.03	1332.71 ± 0.03
0.0040	300.65	997.95 ± 0.03	1332.46 ± 0.02
0.0040	303.15	997.23 ± 0.03	1332.12 ± 0.03
0.0040	305.65	996.44 ± 0.03	1331.79 ± 0.02
0.0040	308.15	995.60 ± 0.03	1331.51 ± 0.02
0.0060	298.15	998.87 ± 0.02	1332.80 ± 0.07
0.0060	300.65	998.21 ± 0.02	1332.55 ± 0.06
0.0060	303.15	997.48 ± 0.02	1332.22 ± 0.07
0.0060	305.65	996.69 ± 0.02	1331.88 ± 0.06
0.0060	308.15	995.85 ± 0.02	1331.58 ± 0.04
0.0080	298.15	1000.23 ± 0.03	1332.85 ± 0.09
0.0080	300.65	999.55 ± 0.03	1332.59 ± 0.08
0.0080	303.15	998.82 ± 0.03	1332.28 ± 0.10
0.0080	305.65	998.03 ± 0.03	1331.93 ± 0.10
0.0080	308.15	997.20 ± 0.03	1331.63 ± 0.09
0.0100	298.15	1000.75 ± 0.05	1332.83 ± 0.06
0.0100	300.65	1000.07 ± 0.05	1332.58 ± 0.05
0.0100	303.15	999.33 ± 0.05	1332.27 ± 0.07
0.0100	305.65	998.54 ± 0.05	1331.93 ± 0.07
0.0100	308.15	997.70 ± 0.04	1331.63 ± 0.09

NOTE: ^aThe combined expanded uncertainties U_c are $U_c(\rho) = 0.02$ to 0.08 kg·m⁻³; $U_c(n) = 2 \cdot 10^{-5}$ to $9 \cdot 10^{-5}$ nD and with a 0.95 level of confidence ($k \approx 2$).

force of cohesion between the molecules. Therefore, the shear stress and viscosity are mainly dependent on the magnitude of the cohesive forces, such that the adjacent molecules tend to be maintained in a fixed position and to resist movement. As these forces decrease rapidly with increases of temperature, the viscosity of the fluid decreases (ASSIS *et al.*, 2010).

MODELS FOR DENSITY, REFRACTIVE INDEX, AND DINAMIC VISCOSITY

Density, refractive index, and dynamic viscosity were modeled by a general quadratic model (Eq. 6) to analyze the influence of temperature and biopolymer concentration. The values of the fitted coefficients for each property for the binary and ternary aqueous solutions were determined by regression (Table 2 and 3).

Table 2- Density (ρ), refractive index (n) and, dynamic viscosity (η) of acacia gum (w_2) in binary aqueous solutions at different temperatures (T) and concentrations^b

w_2	T (K)	ρ (kg·m ⁻³)	$n \cdot 10^{-3}$ (nD)	η (mPa·s)
0.0005	298.15	997.27 ± 0.00	1332.55 ± 0.01	0.70 ± 0.01
0.0005	300.65	996.61 ± 0.01	1332.26 ± 0.02	0.67 ± 0.01
0.0005	303.15	995.88 ± 0.01	1331.92 ± 0.02	0.64 ± 0.01
0.0005	305.65	995.10 ± 0.01	1331.59 ± 0.02	0.62 ± 0.01
0.0005	308.15	994.26 ± 0.00	1331.22 ± 0.02	0.60 ± 0.00
0.0020	298.15	997.84 ± 0.01	1332.72 ± 0.01	0.82 ± 0.00
0.0020	300.65	997.18 ± 0.01	1332.46 ± 0.01	0.78 ± 0.00
0.0020	303.15	996.45 ± 0.01	1332.13 ± 0.01	0.74 ± 0.00
0.0020	305.65	995.67 ± 0.01	1331.79 ± 0.01	0.72 ± 0.00
0.0020	308.15	994.83 ± 0.01	1331.45 ± 0.02	0.70 ± 0.00
0.0040	298.15	998.61 ± 0.02	1332.99 ± 0.01	0.89 ± 0.01
0.0040	300.65	997.93 ± 0.05	1332.71 ± 0.01	0.85 ± 0.01
0.0040	303.15	997.22 ± 0.02	1332.42 ± 0.01	0.82 ± 0.01
0.0040	305.65	996.42 ± 0.04	1332.06 ± 0.00	0.79 ± 0.01
0.0040	308.15	995.59 ± 0.02	1331.71 ± 0.01	0.77 ± 0.00
0.0060	298.15	999.37 ± 0.06	1333.28 ± 0.01	0.94 ± 0.00
0.0060	300.65	998.71 ± 0.05	1332.99 ± 0.01	0.90 ± 0.00
0.0060	303.15	997.98 ± 0.05	1332.68 ± 0.01	0.87 ± 0.00
0.0060	305.65	997.19 ± 0.05	1332.36 ± 0.02	0.83 ± 0.00
0.0060	308.15	996.35 ± 0.07	1331.98 ± 0.02	0.80 ± 0.00
0.0080	298.15	1000.10 ± 0.01	1333.53 ± 0.02	0.96 ± 0.00
0.0080	300.65	999.44 ± 0.01	1333.27 ± 0.04	0.96 ± 0.00
0.0080	303.15	998.71 ± 0.01	1332.93 ± 0.04	0.88 ± 0.00
0.0080	305.65	997.92 ± 0.01	1332.61 ± 0.03	0.84 ± 0.00
0.0080	308.15	997.08 ± 0.01	1332.26 ± 0.05	0.81 ± 0.00
0.0100	298.15	1000.92 ± 0.06	1333.82 ± 0.02	1.00 ± 0.02
0.0100	300.65	1000.26 ± 0.06	1333.55 ± 0.02	0.95 ± 0.02
0.0100	303.15	999.52 ± 0.06	1333.24 ± 0.02	0.91 ± 0.03
0.0100	305.65	998.73 ± 0.06	1332.88 ± 0.02	0.87 ± 0.02
0.0100	308.15	997.89 ± 0.06	1332.55 ± 0.02	0.83 ± 0.02

NOTE: ^b The combined expanded uncertainties Uc are $Uc(\rho) = 0.02$ to 0.08 kg·m⁻³; $Uc(n) = 2 \cdot 10^{-5}$ to $9 \cdot 10^{-5}$ nD and $Uc(\eta) = 0.01$ to 0.02 mPa·s, with a 0.95 level of confidence ($k \approx 2$)

The p-value of each coefficient for all parameters in Eq. 6 was used as one test of significance. An equation with a set of coefficients providing p-values of less than 0.05 for all parameters was accepted. All fitted equations presented coefficient of determination (R^2) values exceeding 0.98. The quadratic model presented in this paper was previously used in the literature. Ramos *et al.* (2013) and Costa *et al.* (2014) built general quadratic models to express the effects of temperature and concentration on the thermophysical properties of aqueous solutions of κ -carrageenan and poly (ethylene glycol) 1500, respectively.

Table 3- Density (ρ) and refractive index (n) of carrageenan (w_1) and acacia gum (w_2), in ternary aqueous solutions at different temperatures (T) and concentrations^c

w_1	w_2	T (K)	ρ ($\text{kg}\cdot\text{m}^{-3}$)	$n\cdot 10^{-3}$ (nD)
0.0020	0.0020	298.15	998.76 \pm 0.03	1333.00 \pm 0.01
0.0020	0.0020	300.65	998.09 \pm 0.02	1332.71 \pm 0.00
0.0020	0.0020	303.15	997.36 \pm 0.03	1332.43 \pm 0.00
0.0020	0.0020	305.65	996.58 \pm 0.02	1332.07 \pm 0.01
0.0020	0.0020	308.15	995.74 \pm 0.03	1331.72 \pm 0.00
0.0030	0.0040	298.15	1000.00 \pm 0.01	1333.39 \pm 0.05
0.0030	0.0040	300.65	999.34 \pm 0.01	1333.10 \pm 0.06
0.0030	0.0040	303.15	998.60 \pm 0.01	1332.77 \pm 0.05
0.0030	0.0040	305.65	997.82 \pm 0.01	1332.49 \pm 0.03
0.0030	0.0040	308.15	996.99 \pm 0.02	1332.13 \pm 0.01
0.0040	0.0060	298.15	1001.21 \pm 0.01	1333.68 \pm 0.04
0.0040	0.0060	300.65	1000.54 \pm 0.01	1333.42 \pm 0.04
0.0040	0.0060	303.15	999.81 \pm 0.01	1333.11 \pm 0.06
0.0040	0.0060	305.65	999.01 \pm 0.01	1332.82 \pm 0.08
0.0040	0.0060	308.15	998.16 \pm 0.01	1332.65 \pm 0.05
0.0060	0.0080	298.15	1002.97 \pm 0.01	1334.02 \pm 0.03
0.0060	0.0080	300.65	1002.30 \pm 0.01	1333.74 \pm 0.01
0.0060	0.0080	303.15	1001.56 \pm 0.01	1333.45 \pm 0.01
0.0060	0.0080	305.65	1000.76 \pm 0.01	1333.12 \pm 0.01
0.0060	0.0080	308.15	999.89 \pm 0.01	1332.88 \pm 0.02

NOTE: ^c The combined expanded uncertainties U_c are $U_c(\rho) = 0.02$ to $0.08 \text{ kg}\cdot\text{m}^{-3}$; $U_c(n) = 2\cdot 10^{-5}$ to $9\cdot 10^{-5}$ nD, with a 0.95 level of confidence ($k=2$).

RHEOLOGICAL BEHAVIOR

Figures 1-a and 1-b show the relationship between the shear stress and shear rate (flow curves) of binary and ternary aqueous solutions of carrageenan and acacia gum, respectively, at 298.15 K.

Shear stress increased with increasing polysaccharide concentration. The increase in fluid viscosity due to the increased polysaccharide concentration caused higher energy, which increased the frictional forces and, consequently, led to the production of “shear”, as is always the case when a fluid is physically moved or distributed (LEWIS, 1993). High concentrations enhance the entanglement and aggregation of macromolecule chains. Accordingly, the viscosity increases significantly with an increasing degree of entanglement (XU *et al.*, 2015).

Regression analyses were performed to aid in accurately determining the best-fitting model (Newton, Bingham, power law, Casson, or Herschel-Bulkley) for

mathematically representing the data of the binary and ternary aqueous solutions of carrageenan and acacia gum. Table 4 shows the adjusted equations, together with their corresponding R^2 and chi-square (X^2) values. A preliminary analysis of the R^2 values suggested that all models (except the Newton model) fitted well to the linear data. However, in the Herschel-Bulkley, Casson, and Bingham models, the yield stress was nearly equal to zero ($\tau_0 \approx 0$). Thus, these three models were assumed to be unsuitable for the studied solutions. The power-law model was chosen to describe the rheological behavior of ternary aqueous solutions of carrageenan and acacia gum. The high R^2 and low X^2 values supported the good fit to the experimental data.

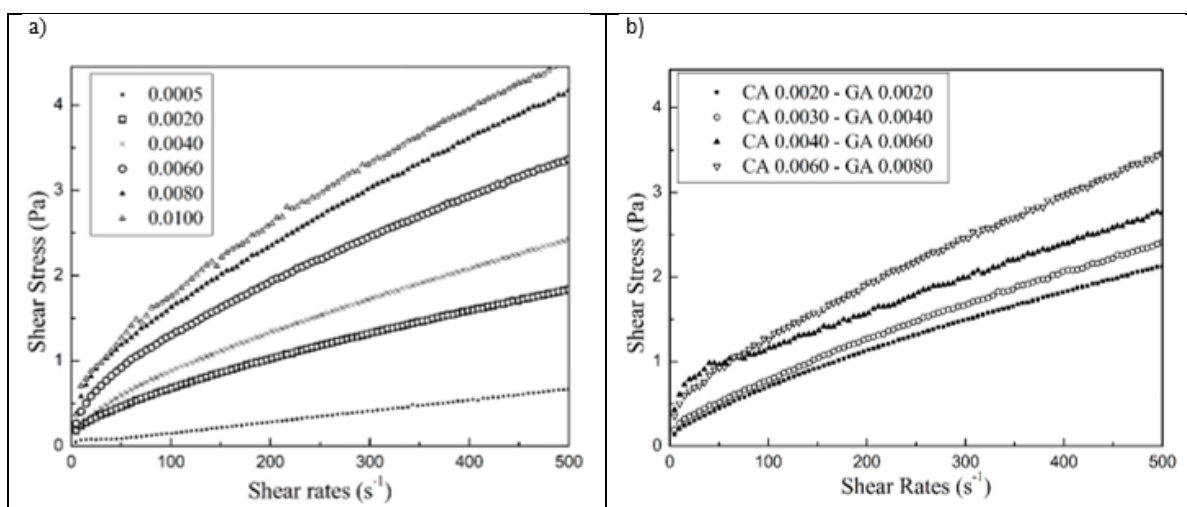


Figure 1 - (a) Flow curves of binary aqueous solutions of carrageenan (CA) and (b) flow curves of ternary aqueous solutions of carrageenan-acacia gum (CA-GA).

Table 4- Adjusted parameters (β_1 to β_{10}) for general quadratic model (Eq. 7) of the binary and ternary aqueous solutions of carrageenan and acacia gum ($p < 0.05$) for all studied thermophysical properties (Ψ)

Aqueous solution	Ψ	β_1	β_2	β_3	β_4	β_5
Binary solution of carrageenan	ρ (kg·m ⁻³)	671.74	2.44	286.20	-	-0.00452
	n (10 ⁻³ nD)	1245.60	0.703	-291.84	-	-0.00138
Binary solution of acacia gum	ρ (kg·m ⁻³)	659.27	2.522	-	374.19	-0.00466
	n (10 ⁻³ nD)	1.1786	0.00114	-	-	-0.0000021
	η (mPa·s)	32.50	-0.19684	-	61.10	0.0003025
Ternary solution of carrageenan and acacia gum	ρ (kg·m ⁻³)	652.41	2.549	3024.46	-435.52	-0.0047
	n (10 ⁻³ nD)	1265.90	0.557	504.21	-216.68	-0.00112
Aqueous solution	β_6	β_7	β_8	β_9	β_{10}	R^2
Binary solution of carrageenan	6478.96	-	-	-	-	0.98
	-4447.78	-	1.23	-	-	0.99
Binary solution of acacia gum	-	666.07	-	-	-	0.99
	-	-	-	0.00045	-	0.99
Ternary solution of carrageenan and acacia gum	-	-3382.23	-	-	-	0.98
	-	1145.85	0.09	-0.47658	95493.00	0.99
	274833.00	392.06	-1.126	1.24	-2079.10	0.99
	-14897.00					

Figures 2-a and 2-b show the relationships between the apparent viscosity and shear rate for binary and ternary aqueous solutions of carrageenan and acacia gum, respectively, at 298.15 K.

The studied aqueous solutions exhibited the shear-thinning behavior that is typical of pseudoplastic fluids (STEFFE, 1996). Graphically, the shear-thinning region is where the apparent viscosity of a dilute polysaccharide solution gradually decreases with increasing shear rate.

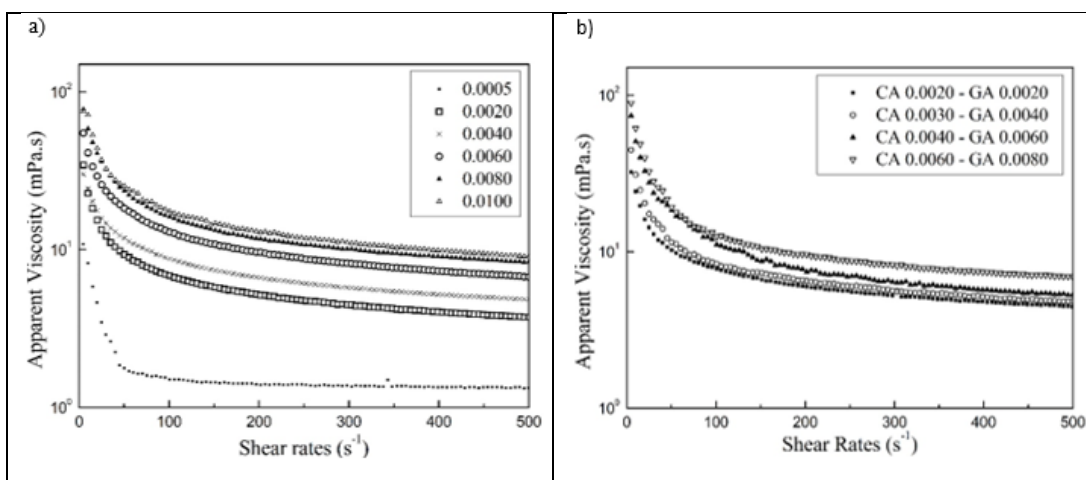


Figure 2- (a) Apparent viscosity (η_a) versus shear rate (s^{-1}) of binary aqueous solutions of carrageenan and (b) apparent viscosity (η_a) versus shear rate (s^{-1}) of ternary aqueous solutions of carrageenan-acacia gum.

A power-law model can be used to describe the rheological behavior of these solutions within the considered range of shear rate, as these solutions behave as pseudoplastic fluids. This finding was further corroborated by the observation that the values of n (behavior index) ranged between 0 and 1 in the corresponding adjusted equations (Table 5). The power-law model is a two-parameter model that is widely used to describe the flow properties of non-Newtonian fluids in theoretical and practical engineering applications (BARNES; HUTTON; WALTERS, 1989). In fluids that follow a power-law model, the unit distance of the flow behavior index measures the degree of deviation of the fluid from Newtonian behavior (STEFFE, 1996). Other authors reported a power-law behavior for locust bean gum (HADDARAH, *et al.*, 2014), *Acacia tortuosa* gum (MUÑOZ *et al.*, 2007), basil seed gum (HOSSEINI-PARVAR *et al.*, 2010), diluted avocado puree (BI *et al.*, 2015), several food hydrocolloids (carrageenan, pectin, gelatin, starch, and xanthan) (MARCOTTE; HOSHAHILI; RAMASWAMY, 2001), modified xanthan gum (EREN; SANTOS; CAMPANELLA, 2015), and tara gum (WU *et al.*, 2015).

Table 5- Parameters for rheological models of binary and ternary aqueous solutions of carrageenan (w_1) and acacia gum (w_2), at 298.15K

w_1	w_2	Power Law ^b (Eq. 2)					Bingham ^c (Eq. 3)				
		K	n	τ_0	X^2	R^2	K	τ_0	η_B	X^2	R^2
0.0005	-	0.0022	0.9172	*	0.0144	0.9979	*	0.0273	0.0013	0.0072	0.9990
0.0020	-	0.0408	0.6108	*	0.0327	0.9992	*	0.3374	0.0026	0.3559	0.9918
0.0040	-	0.0486	0.6267	*	0.0306	0.9996	*	0.4145	0.0042	0.6641	0.9913
0.0060	-	0.0885	0.5858	*	0.0947	0.9993	*	0.6694	0.0057	1.5095	0.9892
0.0080	-	0.1283	0.5812	*	0.3387	0.9983	*	0.8569	0.0070	2.0170	0.9895
0.0020	0.0020	0.0310	0.6842	*	0.0311	0.9995	*	0.2992	0.0038	0.4018	0.9937
0.0030	0.0040	0.0361	0.6808	*	0.0803	0.9990	*	0.3459	0.0043	0.3985	0.9949
0.0040	0.0060	0.1179	0.5022	*	0.9312	0.9877	*	0.7061	0.0042	0.7363	0.9901
0.0060	0.0080	0.0727	0.6173	*	1.8534	0.9877	*	0.6189	0.0058	2.4706	0.9835
w_1	w_2	Casson ^d (Eq. 4)					Herschel-Bulkley ^e (Eq. 5)				
		τ_0	n	K_C	X^2	R^2	τ_0	k	n	X^2	R^2
0.0005	-	0.0008	0.5	0.0012	0.0167	0.9976	0.0293	0.0012	0.5314	0.0070	0.9990
0.0020	-	0.1457	0.5	0.0019	0.0470	0.9989	0.0767	0.0285	0.6629	1.6304	0.9591
0.0040	-	0.0855	0.5	0.0041	2.6039	0.9701	0.0605	0.0390	0.6585	0.0186	0.9998
0.0060	-	0.3051	0.5	0.0034	0.2569	0.9982	0.1261	0.0646	0.6305	0.0541	0.9996
0.0080	-	0.4104	0.5	0.0041	0.3610	0.9981	0.2439	0.2587	0.6517	0.1952	0.9990
0.0020	0.0020	0.0661	0.5	0.0035	0.9741	0.9837	0.0460	0.0249	0.7130	0.0203	0.9997
0.0030	0.0040	0.1289	0.5	0.0029	0.0606	0.9993	0.1068	0.0226	0.7457	0.0393	0.9995
0.0040	0.0060	0.3741	0.5	0.0022	0.3646	0.9926	0.4709	0.0223	0.7438	0.4532	0.9939
0.0060	0.0080	0.2639	0.5	0.0036	1.6706	0.9889	0.2342	0.0380	0.7112	1.6715	0.9889

NOTE: ^a η = mPa·s;

^b K = mPa·s ^{n} ; n = dimensionless;

^c τ_0 = mPa; η_B = mPa·s;

^d τ_0 = mPa; K_C = mPa·s^{0.5};

^e τ_0 = mPa; K = mPa·s ^{n} ; n = dimensionless

* Parâmetro definido não pertence a essa equação

CONCLUSIONS

Carrageenan and acacia gum are currently used in the food industry and the knowledge of their physical properties is very important for the study and design of industrial processes. In this work, density (ρ), refractive index (n), and viscosity (η) of binary and ternary aqueous solutions of carrageenan and acacia gum were determined experimentally and mathematically modeled as functions of concentration and temperature. A general quadratic model was adjusted to the data, obtaining good fitting with high coefficients of determination. Properties such as density, refractive index, and viscosity increased with increasing biopolymer concentration and decreased with increasing temperature. The dependence of the apparent viscosity on the composition was more pronounced for ternary aqueous solutions than for binary aqueous solutions of carrageenan. Examination of the rheological behaviors at 298.15 K revealed that binary and ternary aqueous solutions containing carrageenan are pseudoplastic fluids that

can be accurately modeled through a power-law model. These results are satisfactory because of the small standard deviation and their consistency with the literature. The mathematical models obtained in this study have high determination coefficients and can be used in engineering calculations.

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Comportamento reológico e propriedades físicas de soluções aquosas de carragenina e goma arábica

RESUMO

Os polissacarídeos são amplamente utilizados como agentes espessantes, estabilizadores e gelificantes para o controle da textura, sabor, microestrutura e prazo de validade dos alimentos. Este trabalho contribui para o estudo das propriedades físicas e do comportamento reológico de soluções binárias e ternárias de carragenina e goma arábica. Foram realizadas experiências para determinar propriedades como densidade, índice de refração e viscosidade. Os resultados mostraram que essas propriedades estudadas aumentaram com o aumento da concentração de biopolímeros e diminuíram com o aumento da temperatura. Dados experimentais foram modelados para descrever os efeitos combinados da temperatura e da concentração de biopolímeros na densidade, índice de refração e viscosidade dinâmica dessas soluções. As propriedades foram medidas na faixa de temperatura de 298,15 a 308,15 K. Funções polinomiais adequadas foram ajustadas com sucesso aos dados experimentais. Modelos reológicos clássicos (Bingham, lei de potência, Casson e Herschel-Bulkley) foram testados para soluções aquosas binárias e ternárias contendo carragenina. O comportamento pseudoplástico foi observado e as soluções foram modeladas com precisão por meio de um modelo de lei de potência.

PALAVRAS-CHAVE: Biopolímeros; densidade; índice de refração; comportamento não-newtoniano.

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