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Interfacial Properties of Methylcelluloses: The Influence of Molar Mass

Pauline L. Nasatto [1,2,*], Frédéric Pignon [2,3], Joana L. M. Silveira [1], Maria Eugênia R. Duarte [1], Miguel D. Noseda [1] and Marguerite Rinaudo [4]

[1] Departamento de Bioquímica e Biologia Molecular, Federal University of Paraná, P.O. Box 19046, CEP 81531-980, Curitiba, Paraná, Brazil; E-Mails: jlms12@yahoo.com (J.L.M.S.); nosedaeu@ufpr.br (M.E.R.D.); mdn@ufpr.br (M.D.N.)

[2] Laboratoire rhéologie et procédés (LRP), University Grenoble Alpes, F-38000 Grenoble, France; E-Mail: frederic.pignon@ujf-grenoble.fr

[3] Centre National de la Recherche Scientifique (CNRS), LRP, F-38000 Grenoble, France

[4] Biomaterials Applications, 6, rue Lesdiguières, F-38000 Grenoble, France; E-Mail: marguerite.rinaudo@sfr.fr

* Author to whom correspondence should be addressed; E-Mail: pauline.nasatto@gmail.com; Tel.: +55-041-3361-1663; Fax: +55-041-3266-2041.

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Abstract: The interfacial interactions of four methylcelluloses having the same average degree of substitution and distribution of methyl groups, but different molar masses, are studied at ambient temperature and at very low polymer concentrations. Firstly, the surface tension σ at the water/air interface is determined for the progressive addition of methylcellulose up to 100 mg/L; σ starts to decrease over 1 mg/L up to the critical aggregation concentration (CAC) at 10 mg/L. The curves describing the influence of polymer concentration on σ are independent of the molar mass at equilibrium. Secondly, the adsorption of methylcellulose on silica particles is estimated from ζ-potential measurements. The data are interpreted in terms of an increase of the adsorbed layer thickness at the interface when the molar mass of methylcellulose increases. It is concluded that methylcellulose is adsorbed, forming trains and loops at the interface based on the equilibrium between surface free energy and solvent quality.

1. Introduction

The interfacial properties of amphiphilic polymers are interesting for many applications, especially to stabilize foams and emulsions, mainly in the food domain, or to stabilize liposomes and solid dispersions [1–4]. Amphiphilic polymers present some advantages compared with the small molecules of surfactants: the viscosity of the medium is increased, and the thickness of the adsorbed layer at the interface is larger (as well as the van der Waals interactions), depending on the polymer structure. The interfacial film at the air/water or oil/water interface when formed with polymers has greater mechanical properties, as shown for gum arabic, or Sonorean mesquite gum [5], or with alkyl chitosan [6–8].

The mechanism of the stabilization of colloidal systems is described in the HVO (Hessenlink, Vrij and Overbeek) and DLVO theories (Derjaguin, Landau, Verwey and Overbeek) [9,10]. The theories predict that the stability of a colloidal suspension results from the balance between two forces: electrostatic repulsion and van der Waals attraction. The DLVO theory explains the tendency of colloids to agglomerate or to separate by combining electrostatic repulsion and van der Waals attraction curves. The DLVO theory provides a good explanation of the interaction between two approaching particles having the same ionic potential, describing the potential distribution at the interface, electrical double layer and the slipping plane corresponding to the ζ-potential, which may be determined experimentally by electrophoresis.

The stability of colloidal particles may be controlled by polymer adsorption at the interfaces (oil/water, air/water or solid/water). Their net charges are particularly important to control the stability of the dispersion, playing an additional role on electrostatic repulsions or van der Waals interactions: neutral polymers coating the surface cause a steric stabilization; polyelectrolyte, having the opposite charge compared to that of the particles, reinforcing the electrostatic repulsive potential after the charge inversion [4].

In this work, the influence of neutral polysaccharides interacting at different interfaces is investigated. In that respect, especially surface active polymers have an important role on the formation and stability of food foams and emulsions. Among these polymers, non-ionic cellulose ethers (hydroxyethyl- (HEC), hydroxypropyl- (HPC), methyl- (MC), methyl hydroxyethyl- (MHEC) and hydroxypropyl methyl- (HPMC) cellulose were tested) showed a clear positive adsorption at the liquid/air and the other interfaces [11] and are good candidates, especially for stabilizing emulsion and foams. Mostly the role of methylcellulose and hydroxypropyl methylcellulose has been discussed in the literature, where the influence of the molar mass is mentioned [12–14]. They play a role, not only due to their amphiphilic character (which depends on the microstructure, such as the degree of substitution and the distribution of the substituents along the chains), but also by their water holding and viscosity enhancing properties [2,14,15].

The present work concerns methylcellulose (MC), a neutral water-soluble cellulose derivative obtained by heterogeneous methylation of semi-crystalline cellulose, giving a blockwise distribution of

the methylated groups; the amorphous zones in cellulose being highly substituted (trimethylated zones, which form "cross-linking loci" upon heating [16]) are more hydrophobic than the other part of the chains. MCs are recognized as undergoing a two-step thermoreversible gelation upon heating, as found with other amphiphilic polymers, but this behavior, often studied in the literature, is original for MCs. The first step gives a loose and "clear gel" over 28–30 °C up to around 60 °C, followed by a second step, where a strong and "turbid gel" is formed [17,18].

In this paper, we firstly investigated the influence of methylcellulose molar mass on the air/water interface properties. Secondly, the adsorption on silica particles is investigated. These two series of experiments are performed with methylcellulose having the same microstructure, but different molar masses, allowing the establishment of the influence of molar mass on the interfacial properties.

2. Experimental Section

Commercial premium methylcelluloses from Dow Chemical Cy (Midland, MI, USA) were used as received: A15LV, A4C, A15C and A4M. The samples are obtained under heterogeneous conditions, producing blockwise methyl group distributions. They are dissolved by the following process: dispersion of the powder in hot water (around 80 °C) under magnetic stirring; then, after 15 min, the solution is kept at around 4 °C for 24 h, followed by stirring and then used at the desired temperature.

The molar mass is calculated from the intrinsic viscosity values of methylcellulose obtained from viscosity measurements on dilute solution as a function of polymer concentration after filtration on a 0.2-μm pore membrane. A capillary viscometer, Micro-Ubbelohde from Schott Instruments (Mainz, Germany), with a diameter of 0.66 mm linked with a semi-automatic chronometer, ViscoClock (Schott Instruments), and a thermo-bath at 20 °C were used. The data are given in Table 1. The M_W is an average-viscometric molar mass calculated using the relation given by Funami *et al.* [19]:

$$[\eta] = 0.102 \times M_v^{0.704} \tag{1}$$

The degree of substitution is determined by ^{13}C NMR (Nuclear Magnetic Resonance) in dimethyl sulfoxide (DMSO) at 80 °C and a concentration around 30 g/L on a Bruker Avance III 400 spectrometer (Billerica, MA, USA). Analyses of the spectra were performed after the identification of the different signals, following the literature [20,21]. The 3 signals in the range of 58–60 ppm correspond to the average substitution degree on the C2, C3 and C6 positions of the anhydroglucose repeat units, allowing the calculation of the average degree of substitution for each polymer (Table 1). Additionally, analysis of the samples after complete hydrolysis allows determining that 20% of the monomeric units are trisubstituted and should represent the maximum of hydrophobic blocks in the derivatives [22].

Table 1. Methylcellulose characteristics.

Polymer Reference	[η] (mL·g⁻¹) [a,b]	M_V (g·mol⁻¹) [c]	DS [d]
A15LV	193	42,100	1.8
A4C	573	212,000	1.7
A15C	740	304,600	1.8
A4M	933	423,400	1.7

[a] Measured at 20 °C; [b] intrinsic viscosity; [c] viscometric-average molar mass; [d] average degree of substitution.

Rheology on semi-dilute solutions up to gelation when the temperature increases was studied using a ARG2 rheometer from TA Instruments (New Castle, DE, USA) with a cone-plate geometry; the cone has a diameter of 60 mm, a 1°59'13" angle and a 54-μm gap. The temperature is controlled by a Peltier plate. The sample is left standing for 5 min before each experiment to attain thermal equilibrium. To prevent evaporation during the measurements, the system is isolated using a special cover, including a small cup filled with silicon oil. Steady-state flow experiments are performed in the rage of 0.03 to 10 s^{-1}. The dynamic oscillation measurements are performed for frequency sweeps between 0.05 to 10 Hz with 1% strain, where the MC solutions are in the linear viscoelastic region (LVR). Then, the Cox–Merz transformation [23] is used to obtain the viscosity (η expressed in Pa·s) as a function of the shear rate (expressed in s^{-1}).

Surface tension σ (expressed in mN/m) is measured at 20 °C using a digital K-10 ST tensiometer from Krüss (Hamburg, Germany) by the du Noüy ring method. The ring is washed with water and flamed before each series of experiments. The solutions tested are prepared using bidistilled and deionized water added progressively to a methylcellulose solution (at 0.2 g/L and 10 g/L, depending on the polymer concentration needed). The initial methylcellulose solutions are filtrated through 0.2-μm pore membranes. The average polymer concentration varies from 0.01 to 100 mg/L of aqueous solution. All of the experiments were performed three times with a precision of ±1.0 mN/m.

The adsorption of methylcellulose onto silica particles is characterized by the electrokinetic potential ζ (expressed in mV) measured at 20 °C using a Zetasizer 2000 Malvern Instrument (Worcestershire, UK). For that purpose, the electrophoretic mobility is transformed into ζ-potential according to the Smoluchowski equation and averaged over ten repeated measurements (μ = ε ζ/η with η and ε being the viscosity and the permittivity of the external solution, respectively). Different amounts of methylcellulose solution were added to each 10-mL sample of the initial dispersion of silica particles to the desired concentration and tested after equilibrium at 20 °C. The methylcellulose concentration is expressed in mg/L of suspension (at 0.023 g/L of silica) and varies from 0.05 up to 100 mg/L. All of the experiments are performed with a precision of ±1.0 mV.

The solid-liquid interface is studied using silica particles adsorbing methylcellulose. Thermo Scientific™ 8000 Series Silica Particle Size Standards (ref. CD8050), with an average 0.5-μm diameter dispersed in water were obtained from Thermofisher Scientific (Waltham, MA, USA). The silica density is around 2 g/cm^3; 0.3 g of the commercial suspension (at around 20 g/L of silica) was dispersed in 250 mL of distilled and deionized water, corresponding to 0.023 g/mL of silica in the suspension with the methylcellulose solution progressively added.

3. Results and Discussion

Methylcellulose is a lower critical solution temperature (LCTS) polymer in water; the LCST is located at 29 ± 2 °C [17]. Then, the polymer is soluble at a low temperature, but it starts to form chain aggregates progressively when the temperature increases, progressing to gel formation and concomitant phase separation at high temperatures. The aqueous solutions of methylcellulose are Newtonian at ambient temperature, as shown in Figure 1, indicating that the methylcellulose coiled chains are well solvated and dispersed in the solvent. These data are determined from dynamic rheometry using the Cox–Merz transformation. In Figure 2, the viscosities determined in steady-state flow

experiments are compared with those obtained from dynamic measurement using the Cox–Merz transformation. It is demonstrated that the agreement is good for the two series of values, validating the use of this transformation in a domain where only loose interchain interactions exist. When the temperature increases over 35 °C, the solutions become non-Newtonian, the shear rate becoming more effective when the temperature increases in relation to the local structure formed (Figure 1).

Figure 1. Influence of viscosity obtained from dynamic measurements using Cox–Merz transformation as a function of shear rate at different temperatures of methylcellulose A4M solution at 10 g/L.

Figure 2. Comparison of viscosity obtained by Cox–Merz transformation (CM) and viscosity from steady-state experiments at 45 and 50 °C of methylcellulose A4M solution at 10 g/L.
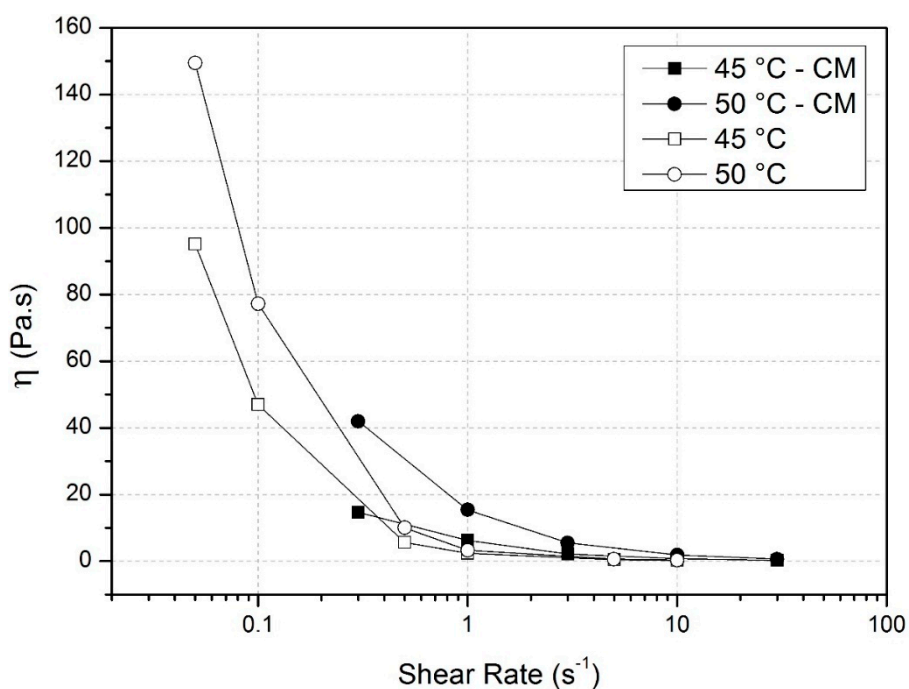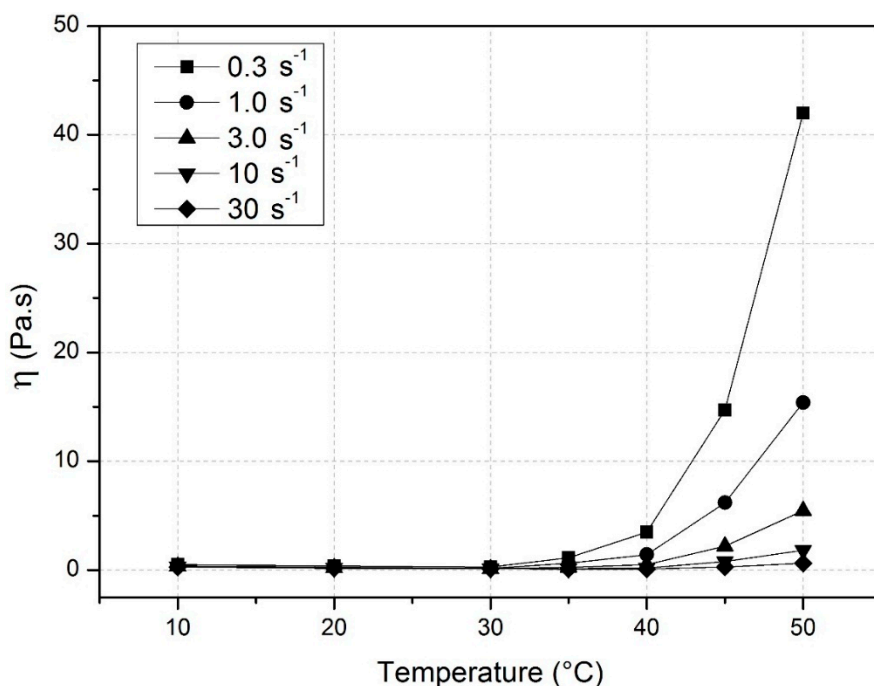
Figure 3 shows the variation of the viscosity of methylcellulose A4M solution as a function of temperature at fixed shear rates. It is Newtonian up to 30 °C, but over 30 °C, the viscosity depends on the shear rate of measurement when entering the first step of association, called also "clear gel": the lower the shear rate, the higher the viscosity showing the formation of a loose connected network based on hydrophobic zone interactions [17,21]. These results indicate that methylcellulose is water soluble and molecularly dispersed at a temperature lower than 30 °C (loose interactions occurring only at a temperature higher than 30 °C), as used in the following experiments.

Figure 3. Viscosity obtained at different shear rates plotted as a function of temperature using Cox–Merz transformation of methylcellulose A4M solution at 10 g/L.
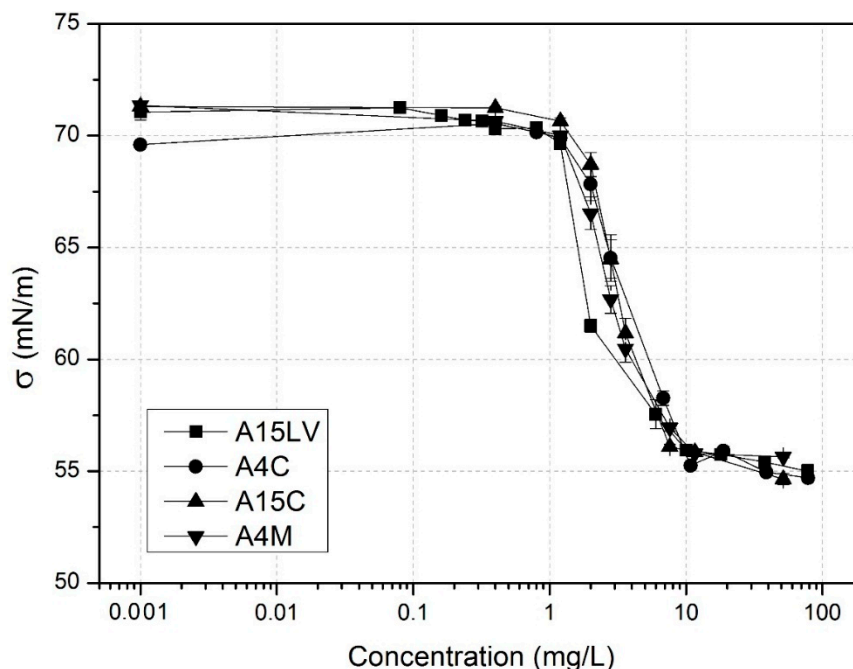

The Newtonian methylcellulose solutions are used at a low concentration and a temperature lower than 30 °C to test the interactions at different interfaces: (1) the air/water interface is investigated from the surface activity (σ); and (2) the silica surface/water interaction is tested by the ζ-potential of silica particles. All of the experiments are performed using methylcelluloses with different molar masses, so as to point out the role of molar mass on the interfacial properties.

3.1. Surface Activity of Methylcelluloses

The data obtained are represented in Figure 4. From our data, it seems to be clear that the molar mass has no influence on the surface activity of methylcelluloses at equilibrium; the same conclusion was given for hydroxypropyl methylcelluloses by Gaonkar [13], but a minor role is mentioned for hydroxylpropyl methylcelluloses by Sarkar [12]. The surface activity is mainly influenced by the chemical modification of cellulose and the distribution of hydrophobic groups along the polymeric chains [12]. To our knowledge, the influence of molar mass on surface activity was never tested before on methylcellulose.
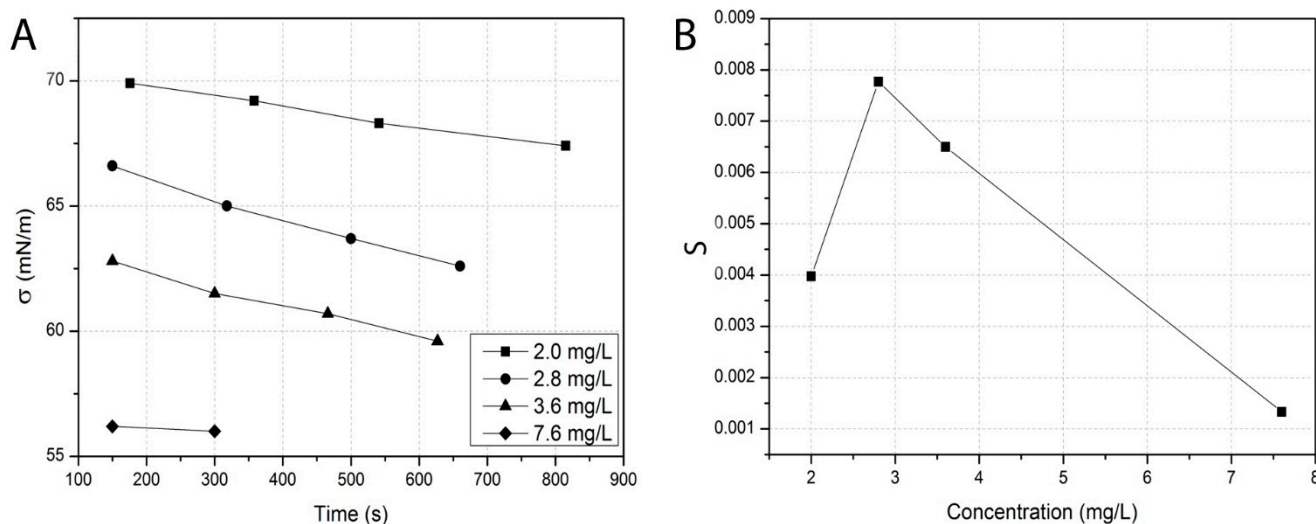
Figure 4. Influence of the molar mass on the tensio-active properties (σ in mN/m) of methylcellulose as a function of polymer concentration expressed in mg/L at 20 °C.

Over 1 mg/L, up to around 10 mg/L, the surface tension decreases in relation to the progressive packing of amphiphilic molecules at the interface with the orientation of highly hydrophobic blocks.

In this region, a kinetic process takes place, but only A15LV attained equilibrium rapidly. The evolution of the surface tension in this concentration regime is tested as a function of time, after mixing of methylcellulose in water. An example of the results is given in Figure 5A in which, in a short delay, a quasi-linear variation of the surface tension with time is obtained, allowing the drawing of the curve relating the slopes S (with σ in mN/m and time in seconds) as a function of A15C methylcellulose concentration (Figure 5B).

Figure 5. Influence of polymer concentration on the surface tension in the intermediate regime on the solution of methylcellulose A15C at 20 °C. (**A**) Kinetics of variation of the surface tension; (**B**) Slope S as a function of polymer concentration.
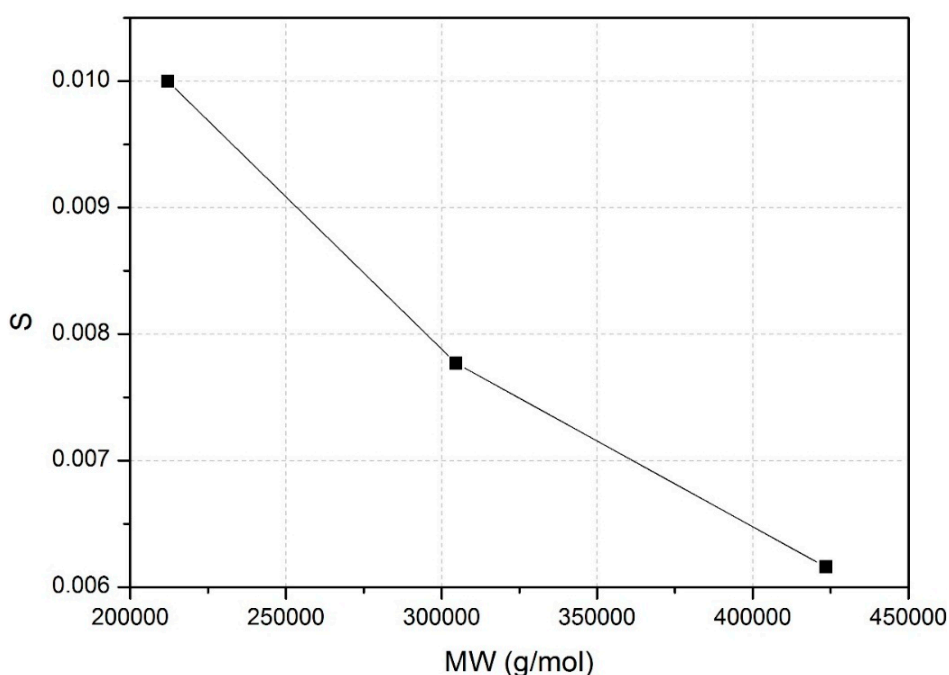
The curve obtained in Figure 5B passes through a maximum at 2.8 mg/L, corresponding approximately to the inflexion point of the curve of Figure 4. Considering the same curves as Figure 5B for methylcelluloses A4C, A15C and A4M, it is shown that the optimum rate (expressed by *S* values) decreases when the molar mass increases (Figure 6); this effect may be attributed to the influence of MW on the diffusion of molecules from the bulk to the interface.

Concerning the diffusion of molecules from the bulk, it is estimated that the medium viscosity, which may play a role, is only slightly modified by the presence of the polymers (less than a 1% increase compared to pure water). Then, the diffusion is mainly controlled by the hydrodynamic volume of the molecules (Figure 6). This kinetic process was also mentioned previously by Sarkar [12].

The critical aggregation concentration (CAC) located around 10 mg/L is also insensitive to the molar mass, as well as the minimum surface tension obtained (55–56 mN/m). This value agrees with that given on methylcellulose A4M (52 mN/m on 3 g/L solution at 20 °C after 20 min) by Gaonkar [13]. The CAC was given at 10 mg/L and 50 mN/m for Methocel A15 (M_W = 14 kDa) previously [14]. This value is higher than that obtained usually for a surfactant or for the surfactant-polyelectrolyte complex tested previously (values obtained between 35 and 45 mN/m) [6–8].

Figure 6. Influence of the molar mass on the maximum of the slope *S* as a function of polymer concentration for A4C, A15C and A4M, respectively, at 20 °C. All of the maximums are located at 2.8 mg/L.

In different papers, it is suggested that the polymers adsorbed at the interfaces forming loops and trains on the basis of the hydrophobic group blocks the distribution, which is orientated toward the air at the water/air interface [12]. In other papers, it has been suggested that adsorption of hydrocolloids occurs with two consecutive or simultaneous stages: firstly, a slow diffusion of the coiled macromolecules from the bulk phase to the subsurface region is followed by adsorption of polymer segments at the surface with conformational change [14,24]. This allows interpreting our data, in which only the fraction of hydrophobic zones (substitution degree around three being insoluble in water)
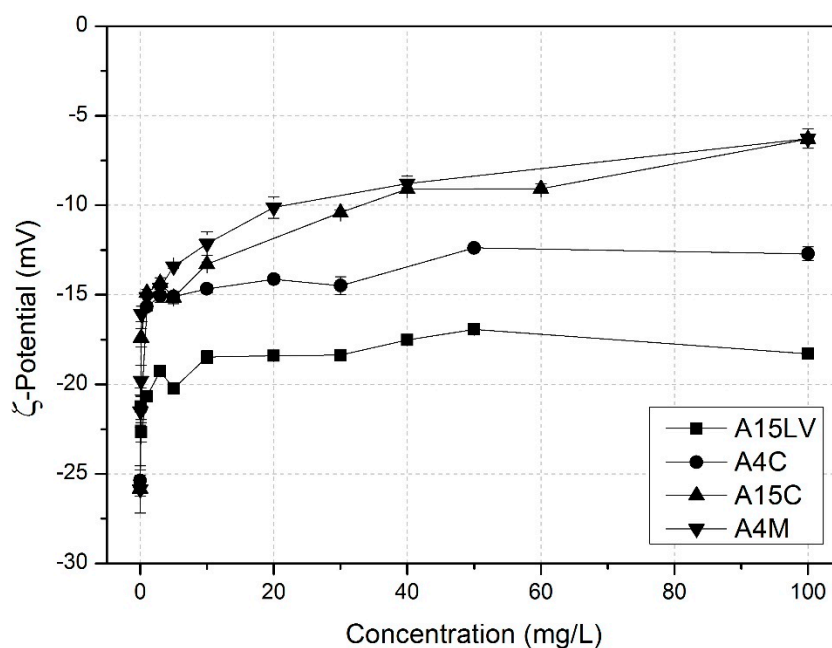
independently of the molar mass is involved in this process. It is necessary to recognize that the surface free energies corresponding to the two media (water/air) involved are largely different, causing a great orientation of the hydrophobic groups at the interface.

3.2. Adsorption Isotherm

Different methods have been proposed to study the adsorption of a polymer at a solid interface [25–31]. The technique has to be chosen in dependence of the system studied (the nature of the neutral or charged polymer, the bulk concentration of the polymer, the external salt concentration). One of the techniques used in our previous work is the zeta potential measurement; especially this method, chosen for the present work, previously allowed the study of the mechanism of adsorption of chitosan on liposomes formed by zwitterionic lipids [3,4]. As usually, in dilute solution, when neutral polymers are adsorbed on charged solid particles, the ζ-potential decreases and tends to zero, due to the increase of the thickness of the adsorbed layer, which displaces the slipping plane and reduces the measured ζ-potential. Then, the ζ-potential levels off progressively to zero for larger molar masses and larger amounts of methylcellulose added [25,26].

Experimental data are given in Figure 7. These data are in agreement with the first results obtained for methylcellulose A4M adsorbed on the same silica particles [26]. It is demonstrated that the interaction is very great for the smaller amounts of added methylcellulose (lower than 5 mg/L). In addition, it is shown that the behavior depends on the molar mass, as is usual for the adsorption of the molecule at the interface forming loops and trains in dependence of the surface free energy [27]. In this model, large loops are formed and a few units adsorbed for small adsorption free energies, but small loops and more units are adsorbed for larger adsorption free energies when the chains are sufficiently flexible.

Figure 7. ζ-potential (expressed in mV) of silica particles dispersed in water at 20 °C in the presence of the increased amount of methylcellulose with different molar masses. Concentrations from 0 to 100 mg/L.

The trains are probably the more hydrophobic zones when the loops develop in the aqueous medium, a good solvent for methylcellulose with a lower average degree of substitution than the average. Our conclusions agree with those obtained for the adsorption of hydroxypropyl cellulose on laponite from different experiments, with respect to surface tension (a comparison of the surface tension in the presence and absence of laponite), isothermal calorimetric titration and dynamic light scattering [28]. The same type of mechanism was proposed previously for amylose and amylopectin adsorption on calcite based on electron spin resonance using labeled polysaccharides [29], on the determination of the amount of polymer adsorbed on calcite and on zeta potential measurements [30]. It was clearly demonstrated that the amount of adsorbed polymer increases when the molecular weight increases [30].

This result is in opposition to those obtained when polyelectrolytes are adsorbed on particles having the opposite ionic charge; in this case, the ζ-potential variation is independent of the molar mass of the polymer adsorbed on the flat surface [3,4].

Considering Figure 5, it is assumed that around 1 mg/L of methylcellulose is strongly adsorbed onto a particle dispersion containing 23 mg/L of silica (corresponding to the sharp variation of the ζ-potential); the estimation of the first adsorption layer may be roughly calculated. Knowing the radius, density and weight of solid particles, the total silica area per liter of suspension is determined ($S = 0.138$ m^2). Then, it is concluded that the degree of coverage equals 7.2 mg/m^2 of the methylcellulose adsorbed. In the second step, it is supposed that a monolayer is formed by side-by-side repeat units in a compact coverage (0.25 nm^2 per unit); then, the maximum degree of methylcellulose coverage should be equal to 1.25 mg/m^2, as proposed before [3,4]. From the comparison of these two numerical values, it is proposed that the methylcelluloses are adsorbed, forming loops and trains at the interface; the higher molar mass corresponds to the thicker layer adsorbed and, then, the lower ζ-potential.

In the present case, the surface free energies of water and silica particles [31] are relatively close, and water is a good solvent for moderately-modified methylcelluloses (average degree of substitution (DS) of the water soluble blocks <1.8). In these conditions, fewer hydrophobic trains are adsorbed, counterbalanced by larger loops and larger adsorbed layer thickness when the molar mass increases.

4. Conclusions

The influence of the molar mass of methylcellulose, having the same degree of substitution on interfacial interactions, is investigated at ambient temperature and very low polymer concentrations in aqueous solution. Firstly, the surface tension σ at the water/air interface is determined (the initial value for water is around 72 mN/m) for the progressive addition of methylcellulose: σ starts to decrease over 1 mg/L up to 10 mg/L; a kinetic process is observed in this domain, as mentioned previously. The rate of evolution of the surface tension is estimated and shown to decrease when the M_W increases in relation to the free diffusion of the molecules from the bulk. Then, the CAC obtained is located around 10 mg/L. At equilibrium, the curves describing the influence of polymer concentration on σ are independent of the molar mass. From these results, it is concluded that the most efficient stabilization of foams and emulsions should be obtained with the lower molar mass methylcellulose based on the diffusive process.

Secondly, the adsorption of methylcellulose on silica particles is discussed: the absolute value of the ζ-potential decreases in relation to the increase of the adsorbed layer thickness at the interface, this layer being larger for higher M_w methylcellulose. It is concluded that methylcellulose is adsorbed, forming trains and loops at the interface based on the equilibrium between the surface free energy and solvent quality. The larger loops formed with larger molar mass methylcellulose, which should cause the greater entropic stabilization of dispersed silica particles.

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Author Contributions

Pauline L. Nasatto, Frédéric Pignon and Marguerite Rinaudo have performed the experimental work. The team from Brasil contributed to the writing of the paper.

Conflicts of Interest

The authors declare no conflicts of interest.

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