Thermodynamic and Dynamic Characteristics of Hydroxypropylmethylcellulose Adsorbed Films at the Air−Water Interface

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Surface pressure isotherms and structural and surface dilatational properties of three hydroxypropylmethycelluloses (HPMCs, called E4M, E50LV, and F4M) adsorbed films at the air−water interface were determined. In this work we present evidence that HPMC molecules are able to diffuse and saturate the air−water interface at very low concentrations in the bulk phase. As bulk concentration increased, structural changes at a molecular level occurred at the interface. These changes corresponded to transition from an expanded structure (structure I) to a condensed one (structure II). When the surface concentration of HPMC was high enough, the collapse of the monolayer was observed. The three HPMCs formed very elastic films at the air−water interface, even at low surface pressures. E4M showed features that make it unique. For instance it showed the highest surface activity, mainly at low bulk concentrations ($<10^{-4}$ wt %). The differences observed in surface activity may be attributed to differences in the hydroxypropyl molar substitution and molecular weight of HPMC. All three HPMCs formed films of similar viscoelasticity and elastic dilatational modulus, which can be accounted for by their similar degree of methyl substitution.

Introduction

Cellulose is the most common natural plant carbohydrate in which the basic repeating structure is an anhydroglucose unit. Although it is a highly hydrophilic biopolymer it is not soluble in water due to its highly crystalline nature. Solubility can be achieved by altering its ordered crystallite regions by chemical substitution, generating cellulose derivatives.[1] Among them, hydroxypropylmethylcellulose (HPMC), which has methyl and hydroxypropyl groups added to the anhydroglucose backbone, includes a family of cellulose ethers that differ principally in molecular weight, viscosity, degree of substitution (DS), and molar substitution (MS). To be precise, DS defines the average number of hydroxyl groups per anhydroglucose unit where hydrogen is replaced by methyl, and MS represents the average number of propylene oxide groups per anhydroglucose unit.[2]

HPMC is used in the food industry, printing technology, and has pharmaceutical applications because it is nontoxic and possesses good mechanical properties. In the pharmaceutical industry, HPMC is of special interest for controlled drug-release matrixes.[3,4] In the food industry, HPMC is used to improve the quality of baked products,[5,6] in gluten-free breads,[7] for innovative battered food manufacturing,[8] low-fat edible coatings,[9,10] etc. The usefulness of HPMC is essentially based upon four key attributes: efficient thickening, surface activity, film forming ability, and the capacity to form reversible thermal gels that melt upon cooling.

Methyl substitutes constitute hydrophobic zones along the cellulose backbone, whereas hydroxypropyl groups are more hydrophilic. The introduction of these hydrophobic groups allows HPMC to behave as a surfactant because the molecules preferentially adsorb at the liquid−air interface and lower the solution surface tension. Once adsorbed at the interface, biopolymer chains undergo structural rearrangements with segments in contact with the surface, called trains, and other segments completely immersed in solution, called loops and tails.[2,11]

Although several works have focused on certain properties of HPMC, such as water affinity[12−14] and gelling,[1,15] there is scarce literature referring to its interfacial properties, film formation dynamics, and structure.[16−19] This knowledge is very important from a technological point of view because of the potential applications of HPMC as a stabilizer in foams and emulsions.[11,20,21]

The present work is part of an integral study undertaken to characterize the behavior of HPMC in adsorbed monolayers. Important aspects regarding potential interfacial surface active molecules are (i) the capacity to lower interfacial tension and the rate of lowering, (ii) the extent of adsorption at the interface, (iii) their ability to desorbe, (iv) the possibility of changing conformation during and after adsorption, (v) the thickening of the adsorbed monolayer, and (vi) the interactions between the adsorbed molecules and their lateral mobility.[22] We now report surface pressure data at equilibrium (surface pressure isotherm), monolayer structural characteristics, and surface dilatational properties of three types of hydroxypropylmethycellulose (E4M, E50LV, and F4M) monolayers adsorbed at the air−water interface at pH 7 and ionic strength of 0.05 M, which are typical conditions for food formulations.[23] The temperature was maintained constant at 20 °C.

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Table 1. Properties of E4M, E50LV, and F4M

HPMC	% methyl	% hydroxypropyl	methyl/ hydroxypropyl ratio	methyl substitution (DS)	hydroxypropyl substitution (MS)	total substitution (DS + MS)	viscosity (cp), 2 wt % solution, 20 °C	molecular weight
E4M	28.0	10.2	2.7	1.90	0.23	2.13	4965.0	90000
E50LV	29.1	9.2	3.2	1.90	0.23	2.13	41.0	18000
F4M	29.2	6.0	4.9	1.80	0.13	1.93	4.660	9500

Materials and Methods

Materials. Methocell E4M, E50LV, and F4M (food grade) from the Dow Chemical company were kindly supplied by Colorcon-Argentina and used without purification. Table 1 shows some characteristic properties, such as methyl and hydroxypropyl content (wt %), methyl/hydroxypropyl ratio, molar substitution, and the degree of substitution, viscosity (20°C) at 2 wt % solution, and molecular weight.

Surface Pressure Isotherm. Equilibrium surface tension (σ_{eq}) was registered by the Wilhelmy plate method, using a roughened platinum plate attached to a Sigma 701 digital tensiometer (KSV, Finland) as described elsewhere.[24] HPMC solutions in an increased range of concentrations from 5×10^{-7} to 2 wt % were allowed to age for 24 h at 4 °C prior to each measurement to achieve the HPMC adsorption. A device connected to the tensiometer recorded the reduction in surface tension, σ, continuously. Equilibrium was assumed when the pressure did not change by more than 0.1 mN/m in 30 min. The final surface pressure (π_{eq}) value was calculated as $\pi_{eq} = \sigma_0 - \sigma_{eq}$, where σ_0 is the subphase surface tension and σ_{eq} is the surface tension of the HPMC aqueous solution at equilibrium. The experiments were repeated four times. It was found that π_{eq} could be reproduced to ±0.5 mN/m.

Surface Film Balance. The surface pressure (π) measurements versus trough area (A) were performed on a fully automated Wilhelmy-type balance (KSV 3000, Finland), as described elsewhere.[25] The maximum area of the trough between the two barriers is 51.5×15 cm^2. HPMC powders were dissolved in a commercial buffer solution called Trizma ($(CH_2OH)_3$ CNH_2/$(CH_2OH)_3CNH_3Cl$, Sigma, >99.5%) and Milli-Q ultrapure water. The pH and buffer concentration in all the experiments were 7 and 0.05 M, respectively. The final concentration of HPMC in the subphase was 1×10^{-7} wt %

To allow the adsorption and penetration of HPMC at the interface, 30 min were allowed to elapse before the first isotherm was measured. The isotherms were measured again after different aging periods up to 24 h. The compression rate was 3.3 cm·min^{-1}, which is the highest value for which $\pi-A$ isotherms have been found to be reproducible in preliminary experiments with the same HPMC monolayers. The subphase temperature was maintained constant at 20 °C by water circulating from a thermostat, within an error range of ±0.5 °C. The standard deviation of the surface pressure results was better than ±0.4 mN/m.

Film Elasticity. The elasticity (E) was calculated from the slope of the $\pi-A$ isotherm at constant temperature as $E = -A(\partial\pi/\partial A)T$. The elasticity defined here is the elasticity at zero deformation rate. The film elasticity is a measure of the film resistance to a change in area.

Surface Dilatational Rheology. To obtain surface rheological parameters, such as surface dilatational modulus with its elastic and viscous components and loss angle tangent, a modified Wilhelmy-type film balance (KSV 3000) was used as described elsewhere.[25] In this method, the surface was subjected to small periodic sinusoidal compressions and expansions by means of two oscillating barriers at a given frequency (ω) and amplitude ($\Delta A/A$) and the response of the surface pressure (π) was monitored. Surface pressure was directly measured by means of two roughened platinum plates situated on the surface between the two barriers. The surface dilatational modulus derived from the change in surface tension (dilatational stress), σ (eq 1), resulting from a small change in surface area (dilatational strain), A (eq 2), may be described by eq 3.[26]

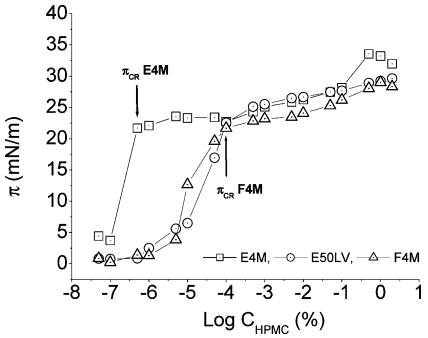

Figure 1. Surface pressure isotherm for E4M, E50LV, and F4M at the air−water interface. Temperature 20 °C, pH 7, and $I = 0.05$ M. π_{cr} indicates the surface pressure corresponding to the transition from structure I to structure II.

$$\sigma = \sigma_0 \sin(\omega t + \theta) \tag{1}$$

$$A = A_0 \sin(\omega t) \tag{2}$$

$$E = \frac{\partial\sigma}{\partial A/A} = -\frac{\partial\pi}{\partial(\ln A)} \tag{3}$$

where t is the time, σ_0 and A_0 are the stress and strain amplitudes, respectively, θ is the phase angle between stress and strain, $\pi = \sigma_0 - \sigma$ is the surface pressure, and σ_0 is the surface tension in the absence of polysaccharide.

The dilatational modulus is a complex quantity and is composed of real and imaginary parts (eq 4). The real part of the dilatational modulus or storage component is the dilatational elasticity, $\mathrm{Ed} = |E| \cos\theta$. The imaginary part of the dilatational modulus or loss component is the surface dilatational viscosity, $\mathrm{Ev} = |E| \sin\theta$. The ratio ($\sigma_0/A_0$) is the absolute modulus, $|E|$, a measure of the total unit material dilatational resistance to deformation (elastic + viscous). For a perfectly elastic material the stress and strain are in phase ($\theta = 0°$), and the imaginary term is zero. In the case of a perfectly viscous material, $\theta = 90°$, and the real part is zero. The loss angle tangent can be defined by eq 5. If the film is purely elastic, the loss angle tangent is zero.

$$E = (\sigma_0/A_0)(\cos\theta + \mathrm{i}\sin\theta) = \mathrm{Ed} + \mathrm{iEv} \tag{4}$$

$$\tan\theta = \mathrm{Ev}/\mathrm{Ed} \tag{5}$$

Measurements were made at least three times. The reproducibility of the results was better than 5%.

Results and Discussion

Surface Pressure Isotherms. The surface behavior of three different types of hydroxypropylmethylcellulose (E4M, E50LV, and F4M) at the air−water interface was studied by means of tensiometry. Figure 1 shows the effect of HPMC concentration (C_{HPMC}) on the equilibrium surface pressure. As for proteins,[24,27,28] true equilibrium adsorption does not seem to be possible with these biopolymers. Therefore, we considered the

surface pressure measured after 24 h as the pseudoequilibrium value. The observed behavior was sigmoidal, which is typical for biopolymers and surfactants. The surface pressure increased with HPMC concentration and tended to a pseudoequilibrium in the case of E4M and F4M, while E50LV surface pressure continuously increased over the range of concentrations studied.

At low bulk concentrations (C_{HPMC} $<10^{-4}$ wt %), E4M showed the highest surface activity, this polymer being the most surface active. At bulk concentrations between 10^{-4} and 10^{-1} wt %, E4M and E50LV showed similar surface pressure, higher than that displayed by F4M. When the bulk concentration was higher than 10^{-1} wt % F4M and E50LV displayed similar surface activity but lower than that displayed by E4M.

The adsorption efficiency, defined as the lowest amount of an emulsifier able to saturate the interface, was higher for E4M. E4M caused a strong increase in surface pressure at the beginning of saturation of the interface, at very low concentrations in the bulk phase (5×10^{-6} wt %), while a concentration 2 orders of magnitude higher was required for E50LV and F4M to provoke the same effect. Wollenweber et al.[11] working with three types of HPMC of different chemical characteristics reported that, at equilibrium, the interface was saturated when the HPMC concentration in solution was around 0.1 wt % Nahringbauer[2] working with a different cellulose derivative (ethylhydroxyethylcellulose), reported that the interface saturation occurred at 5×10^{-4} wt %. Melzer et al.[29] established this concentration as 0.25 wt % for ethylcellulose, and Guillot et al.[30] showed that the methylcellulose concentration had to be equal or higher than 1×10^{-4} wt % to saturate the air−water interface.

The differences found in both adsorption efficiency and in surface activity of the mentioned cellulose derivatives and those found for E4M, F4M, and E50LV in the present work may be related to differences in the molecular characteristics of these polymers, as will be discussed in the next section.

Structural Characteristics. Figure 2 shows the π-trough area isotherms for HPMC adsorbed films from a biopolymer solution at 1×10^{-7} wt % This biopolymer concentration was selected from previous data of the surface pressure isotherms (Figure 1). At this biopolymer concentration in solution the surface pressure at equilibrium is zero (E4M adsorbed films are an exception). In fact, after 24 h the surface pressure (π) at the maximum area of the trough was practically zero. It is known that under dynamic adsorption conditions at the air−water interface the onset of the surface pressure increase lagged well behind the increase of surface concentration.[31] For each biopolymer there may exist a critical surface concentration only above which it can engage in intermolecular cohesive interactions at the interface and cause an increase in surface pressure. The critical surface concentration at which the surface pressure started to increase was in the range of 0.5−1.2 mg·m^{-2} for proteins.[31] Below this concentration, where no measurable surface pressure is detected, the biopolymer molecules at the interface might exist as individual molecules and are probably in a gaseous state. As for proteins,[32,33] for adsorbed biopolymer films the maximum biopolymer concentration in the aqueous bulk phase should be selected in order to obtain a reasonable rate of adsorption at the interface but maintaining the equilibrium surface pressure as zero. In fact, at low biopolymer concentrations in the aqueous bulk phase the adsorption rate is extremely low.

Thus, in these experiments we have selected optimum conditions in order to obtain the $\pi-A$ isotherm of the adsorbed film, from the more expanded monolayer (at the higher areas) to the more condensed monolayer, at the collapse point (at the lower areas). These isotherms were assessed at 30 min, 3, 6, and 24 h after the beginning of the adsorption process (Figure 2). The displacement of the isotherm to higher areas and surface pressures with time was due to the time required by HPMC to adsorb at the interface, especially given their low concentration in the aqueous phase (at 1×10^{-7} wt %). Just to clarify, one can consider that the increase in surface pressure with time due to the adsorption of polymer molecules must involve an increase in the number of adsorbed segments per unit of area with time, as pointed by Lankveld and Lyklema.[34] The formation of an interfacial layer requires first the diffusion of the polymer from the aqueous solution to the interface, and second, its adsorption at the interface. The results of Figure 2 show the importance of undertaking further studies on the adsorption kinetics of HPMC at the air−water interface, which will be discussed in a future paper.

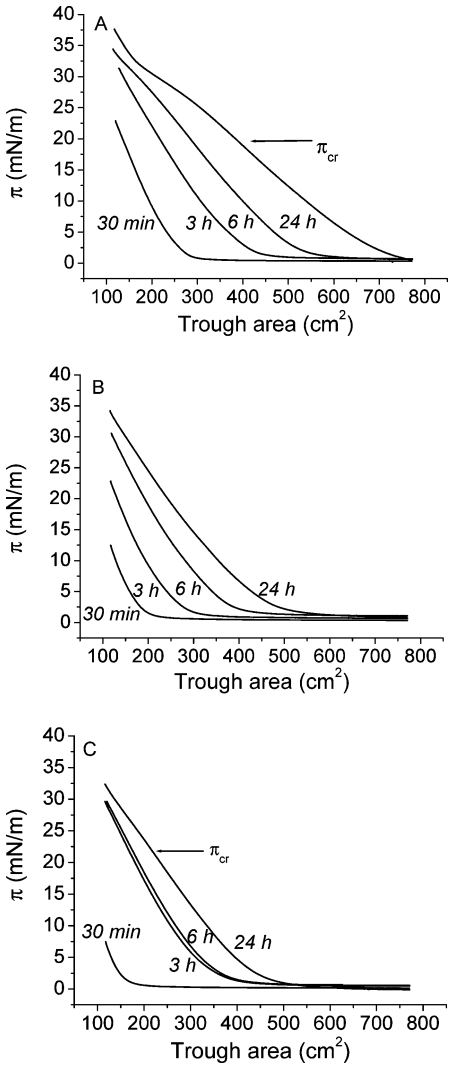

Figure 2. π-Trough area isotherms from 30 min to 24 h of adsorption for (A) E4M, (B) E50LV, and (C) F4M monolayers at the air−water interface and at 20 °C, pH 7, and $I = 0.05$ M. π_{cr} indicates the surface pressure corresponding to the transition from structure I to structure II.

HPMCs have a strong tendency to accumulate at the water−air interface, as can be deduced from the results shown in Figures 1 and 2. This phenomenon can be explained in terms of their molecular structure, which is a consequence of the manufacturing process, which involves a heterogeneous reaction. The presence of crystalline and amorphous regions, in the solid

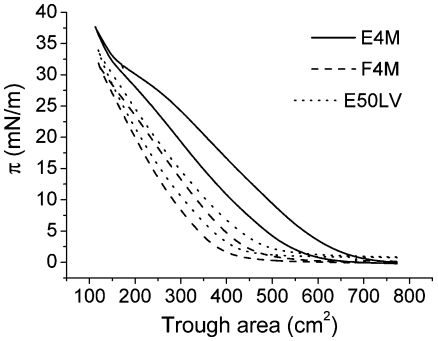

Figure 3. π-Trough area isotherms after a compression and expansion cycle for E4M, E50LV, and F4M monolayers at the air−water interface after 24 h of aging. Temperature 20 °C, pH 7, and $I = 0.05$ M.

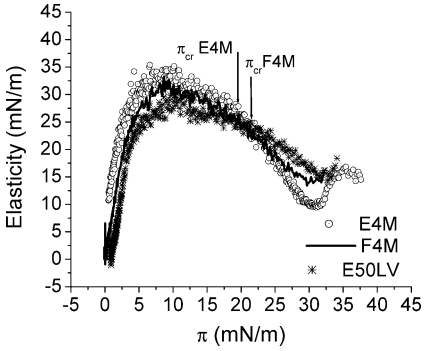

Figure 4. Elasticity dependence on the surface pressure for E4M, E50LV, and F4M monolayers at the air−water interface after 24 h of aging. Temperature 20 °C, pH 7, and $I = 0.05$ M. π_{cr} indicates the surface pressure corresponding to the transition from structure I to structure II.

state of cellulose, causes a nonuniform distribution of constituents along the backbone of the cellulose molecule.[2] As a result, there might be sequences of glucose units, which are hydrophilic in nature, and other sequences of glucose, which are hydrophobic. Once at the interface the biopolymer chains would suffer structural rearrangements or structural changes in accordance with the nature of the sequences.[11,17,35]

The $\pi-A$ isotherms (Figure 2) show that monolayers formed by HPMC adopt different structures as the surface pressure increases and finally collapse at the lowest surface area. These structural patterns in the monolayer are the consequence of the conformation of biopolymer molecules adsorbed at the air−water interface that appear as trains (structure I) and loops and tails (structure II).[2] The transition from structure I to structure II represents the rearrangement of an expanded monolayer to a more condensed one. The collapse of the HPMC film is associated with multiple interfacial layers (multilayers), as was concluded by Wollenweber et al.[11] The transition from structure I to structure II occurs at a defined value of pressure called the critical pressure (π_{cr}). The collapse of the film occurs at the collapse pressure (π_C).

Different structures for HPMC can be deduced from the (pseudo) equilibrium $\pi-A$ isotherms (after 24 h of adsorption) as a shift in the slope (data not shown), according to the method applied by Rosenholm et al.[36] (Figure 3). It was possible to notice that π_{cr} for E4M and F4M were 19.6 and 21.3 mN/m, respectively. In contrast to E4M and F4M, E50LV monolayers only adopted structure I, but this structure was more condensed as the surface pressure increased. The collapse of E4M, F4M, and E50LV monolayers must be produced at surface pressures (π_C) higher than 29.0, 27.0, and 32 mN/m, respectively, which are the maximum surface pressures observed in these experiments at the minimum molecular area.

These structural transitions were corroborated by the adsorption isotherms (Figure 1), where arrows indicate the π-values corresponding to the structural transitions of the HPMCs. The effects of HPMC bulk concentration on surface pressure reached a well-defined plateau over the range from 10^{-6} to 10^{-4} wt % for E4M and from 10^{-4} to 10^{-2} wt % for F4M, indicating that the monolayer became saturated. The hydrophobicity and molecular flexibility of HPMC would cause more molecules to be adsorbed and packed into the interface, causing a further increase in surface pressure, up to the monolayer collapse. Graham and Phillips[37] related the inflections observed in the adsorption isotherms with structural changes. That is, the inflections in Figure 1 would mark the points at which loop and tail formation (structure II) becomes dominant in the adsorbed HPMC film. Related to this fact, Nahringbauer [2] stated that a change in the conformation of the adsorbed HPMC molecules could cause a drastic effect both on the fraction of the segments directly in contact with the surface (i.e., on the surface pressure) and on the thickness of the adsorbed biopolymer layer, as we have observed with these films (unpublished results). However, the surface pressure increased monotonically with E50LV concentration in aqueous bulk solution, denoting the absence of any change in the structure of the adsorbed monolayer (Figure 1).

Figure 3 shows the 24 h aged $\pi-A$ isotherms after a compression and expansion cycle for the three cellulose derivatives. It has already been shown that E4M displayed the highest surface activity and more expanded structure in comparison with those of E50LV and F4M, even during expansion. The $\pi-A$ isotherm for E50LV was between those of E4M and F4M, F4M being the HPMC derivative with a more condensed structure at the air−water interface. A remarkable hysteresis between the compression and expansion cycles is apparent for the celluloses, E4M being the cellulose that showed the highest hysteresis area.

This behavior is associated with the different rearrangement and reorganization of the biopolymer molecules at the interface as the expansion occurs. The biopolymer segments situated at the surface can interact, generating networks among the molecules. As a consequence, the rapid recovery of the initial structure is hindered. Film compression would increase film thickness, which would be higher than the initial value.[38] The reproducibility of compression−expansion cycles in time was proof that the observed hysteresis is not due to a loss of HPMC molecules when the monolayer is compressed but rather the consequence of a molecular rearrangement. The molecular rearrangement is in fact a reversible process, since the monolayer was able to recover its initial state when enough time between compression−expansion cycles has elapsed.

The elasticity of a film is a way to quantify the film resistance to area changes, and it can be directly calculated from the $\pi-A$ isotherm at equilibrium (this is the elasticity at zero deformation rate). Therefore, a high value of elasticity means a film with a very cohesive structure. Figure 4 shows the evolution of the elasticity deduced from the slope of the $\pi-A$ isotherm for E4M, E50LV, and F4M as a function of π. In general, the elasticity of the three HPMCs displayed similar behavior with a strong dependence on surface pressure. The behavior of the elasticity started with a sharp increase followed by a less-pronounced decrease to finally rise again at the higher surface pressures. The surface pressure evolution of the film elasticity is similar to that observed for disordered proteins[39] and may be associated

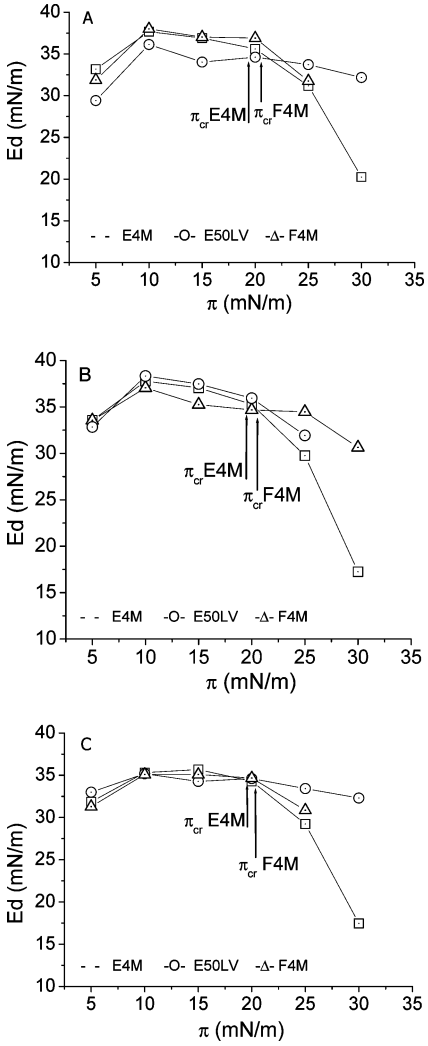

Figure 5. Elastic component of surface dilatational modulus as a function of surface pressure for E4M, E50LV, and F4M at a frequency of (A) 20, (B) 50, and (C) 100 mHz. Temperature 20 °C, pH 7, and $I = 0.05$ M. π_{cr} indicates the surface pressure corresponding to the transition from structure I to structure II.

with the structural changes in the monolayer. The pressures corresponding to transition from structure I to structure II (π_{cr}) of E4M and F4M are indicated by arrows in Figure 4. When films adopted structure I the most elastic film was that of E4M followed by E50LV and F4M, the latter being the most condensed film. It is interesting to point out that E50LV films, which always retained an expanded structure, were more elastic than the other HPMC derivatives when they adopted a condensed structure (structure II) or even at higher surface pressures.

Surface Dilatational Characteristics. Figure 5 shows the effect of surface pressure on the elastic component of the surface dilatational modulus, Ed, at three representative frequencies. The values of the surface dilatational modulus (data not shown) were very similar to those of the dilatational elasticity, indicating the elastic character of the film. The π_{cr} corresponding to the transitions from structure I (more expanded monolayer) to structure II (more condensed) of E4M and F4M films are marked in the figure with arrows but not the collapse because it occurred at pressures higher than the maximum surface pressure considered.

In general, it could be said that the differences in Ed values of the three HPMC films decreased as frequency increased, mainly at pressures lower than 20 mN/m, this value being close to π_{cr}. At low frequencies (at 20 and 50 mHz) (Figure 5, parts A and B), F4M and E4M formed the most elastic films. At pressures above 20 mN/m, where E4M and F4M attain structure II, Ed greatly decreased. E50LV, which never attained structure II, retained a strong solid character with higher Ed values.

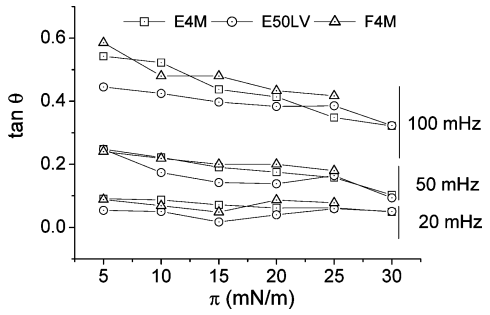

Figure 6. Loss tangent angle (tan θ) as a function of surface pressure for E4M, E50LV, and F4M monolayers at the air−water interface at frequencies of 20, 50, and 100 mHz. Temperature 20 °C, pH 7, and $I = 0.05$ M.

It is noticeable that the behavior of the elastic component of the surface dilatational moduli at every frequency is similar to that shown by the elasticity at zero deformation rate deduced from $\pi-A$ isotherms (Figure 4) at surface pressures close to the film collapse, where both greatly drop. However, the elasticity showed a well-defined maximum close to 10 mN/m, which began to decrease as the monolayer became more condensed, but Ed persisted relatively constant from 10 to 20 mN/m. An explanation of this phenomenon could be that a certain number of HPMC molecules, lower than the quantity needed to saturate the interface, are enough for surface gelation to occur leading to the formation of a very elastic film.[40−42] The elastic character of films is little changed up to the transition of the monolayer to a more condensed structure (II), which occurs around 20 mN/m. The behavior of film elasticity with surface pressure indicates that an optimum film resistance to area changes (i.e., the maximum elasticity) is related to the formation of an elastic film (i.e., high Ed values), but requires the molecules to be in a high expanded conformation so that they can rapidly rearrange when the film is subjected to a deformation.

Figure 6 displays the behavior of the loss angle tangent (tan θ) that represents the relationship between the viscous and elastic component of the surface dilatational modulus. This rheological parameter gives information about the relative viscoelasticity of HPMC films. It can be seen that HPMC monolayers behaved as viscoelastic at every frequency, but the viscoelasticity decreased with frequency owing to the increase of Ev to higher values (data not shown). Moreover, E50LV generated the most viscoelastic film over a wide range of surface pressures, while E4M and F4M showed a more similar and less-viscoelastic behavior at any frequency studied.

Surface Behavior−Molecular Structure Relationship. The results obtained in this work show that E4M, E50LV, and F4M displayed different interfacial activity. E4M showed features that make it singular; for instance, this biopolymer showed the highest surface activity, mainly at low bulk concentrations ($<10^{-4}$ wt %), as was observed by tensiometry (Figure 1) and by $\pi-A$ isotherms (Figure 3). The differences observed in the surface activity may be attributed to differences in the hydroxypropyl molar substitution and molecular weight of the three HPMCs. In fact, all these HPMC have a similar degree of methyl substitution (Table 1), which is the highest among the methocel series products. The degree of substitution, close to 2, accounts for a high degree of hydrophobicity, necessary for surface

activity. E4M and E50LV also have similar hydroxypropyl molar substitution (MS = 0.23), which is higher than the degree of MS of F4M. The hydroxypropyl groups are more hydrophilic than methyl groups and more likely to form hydrogen bonds to the water molecules as determined by NMR.[43] Nevertheless, both the methyl and the hydroxypropyl groups render the cellulose hydrophobic.[44] Thus, the lower surface activity of F4M may be attributed to its lower degree of total substitution as compared to that of E4M and E50LV. The lower surface activity of E50LV as compared to that of E4M, mainly at bulk concentrations lower than 10^{-4} wt %, should be attributed to the higher molecular weight of E4M. The surface tension decrease is not dependent on the molar adsorption of the polymer, but it depends on the number of polymer segments, which are in actual contact with the surface.[2] This means that the surface properties of a polymer depend on the length and distribution of trains, loops, and tails. The average degree of polymerization of E4M is 4 times higher than that of E50LV (data supplied by the Dow Chemical Co.), which involves an increase in the number of segments that potentially could be adsorbed per mol of polymer.

Another factor, which is not usually easy to measure and can have a significant effect on the behavior of HPMC, is the uniformity of substitution. The presence of crystalline and amorphous regions in the solid state of cellulose causes a nonuniform distribution of substituents along the backbone of the cellulose molecule, caused by heterogeneous reactions.[2] An unevenly substituted molecule has areas of the backbone without side units, which are hydrophilic in nature, and sequences of glucose units where all the side units are crammed together, which are hydrophobic. This nonuniform substitution has been shown to be necessary for gelation and the surface activity of cellulose derivatives.[45]

Thermal gelation of HPMC is thought to be primarily caused by the hydrophobic interaction between glucose sequences with a high methoxyl substitution.[15] The molecular weight of the particular HPMC has little effect on the gel temperature. However, an increase in concentration not only decreases the gel temperature, but also, at significantly high concentrations, some HPMC can gel at room temperature.[1] HPMC films have a strong gel character as demonstrated by surface dilatational rheology in this work (Figures 5 and 6). Surface gelation would arise from the hydrophobic interaction of methyl groups of adsorbed HPMC molecules, even at very low bulk concentrations.[40−42] All three HPMC formed films of similar viscoelasticity and elastic dilatational modulus, which can be accounted for by their similar degree of methyl substitution. Minor differences among the elastic behavior of films would reflect the differences in molecular weight among HPMCs and the role of hydroxypropyl groups, which have been reported to alter gelation due to steric reasons.[44]

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