Surface Viscoelasticity of Hydroxypropylcellulose and Hydroxyethylcellulose Monolayers at the Air/Water Interface

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ABSTRACT: The surface viscoelastic properties of hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC), spread and adsorbed as monolayers at the air/water interface, have been determined using the electrocapillary wave diffraction (ECWD) technique over the wave frequency range 0.1–4.0 kHz. Evidence is presented to show that monolayers formed by adsorption from solution produce surface elasticities and surface viscosities that are essentially identical to those values obtained by spread monolayers at the same surface pressure. In all studies the more hydrophobic HPC exhibited greater surface elasticity and surface viscosity than HEC. Distinct changes in these parameters occur as the surface concentration exceeds values at which extensive looping of monomer segments into the underlying aqueous phase appears to take place. This suggests that the concentration and state of these monomer segments in the aqueous phase play the dominant role in the surface viscoelasticity of adsorbed monolayers which exist at these higher surface concentrations. Such conclusions are supported by the significant changes in viscoelasticity for HPC monolayers when the temperature is raised from 25 to 45 °C, conditions that cause a phase separation of HPC in solution. On the other hand, HEC, which does not exhibit a lower critical solution temperature in this temperature range, does not exhibit such changes in monolayer properties.

Introduction

Previous studies from this laboratory have reported on the interfacial properties of water-soluble cellulosics, such as hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC), and have shown that HPC, the more hydrophobic of the two, is much more surface active at various interfaces.[1,2] HPC also exhibits phase separation in aqueous solution over a wide concentration range as temperature is increased above about 40–45 °C at its lower critical solution temperature (LCST) and the ability to self-associate and form lyotropic liquid crystalline phases in water and other solvents at higher polymer concentrations.[3] HEC, in contrast, being more hydrophilic, exhibits no such tendencies in water up to very high temperatures and concentrations.[3]

Central to many of the interfacial properties and functionalities of water-soluble cellulosics is the manner in which the chain conformations of adsorbed layers are such as to effectively reduce interfacial energies and to act as protective barriers. An excellent indication of the ability of polymeric materials to act as interfacial barriers is the manner in which they respond to mechanical stress through their surface viscoelasticity. Previous studies from this laboratory, with a variety of lipids, proteins, and polymers spread as monolayers at the air/water interface, have reported their surface elasticities and surface viscosities using sensitive and relatively noninvasive techniques.[4–7] Other studies with HPC and HEC have recently demonstrated that stable monolayers of both polymers can be spread at the air/water interface and that the surface properties are seemingly the same as those exhibited by adsorbed monolayers at the same surface pressure.[1] Thus, it was of interest to closely study the surface viscoelastic properties of HPC and HEC monolayers spread and adsorbed at the air/water interface with particular attention to whether their relative tendencies to self-associate in solution at higher concentrations and temperatures would be reflected in their surface rheological properties and would carry over to when they exist as closely packed monolayers.

In this paper, therefore, we report the measurement of the static and dynamic properties of HPC and HEC monolayers spread and adsorbed at the air/water interface as a function of surface concentration and temperature. Surface longitudinal elasticity and viscosity values as a function of frequency have been determined by using electrocapillary wave diffraction (ECWD), a relatively noninvasive dynamic surface rheological technique previously reported from these laboratories with other systems.[7]

Experimental Section

Materials. Hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC) were obtained from Aqualon, Inc. (Wilmington, DE) with nominal molecular weight of 1×10^5 (HPC-L and HEC-L). They were treated by solvent extraction[8] and by precipitation,[9] respectively, for further purification and limited fractionation. Previous studies had shown that the surface tensions of aqueous solutions and spread monolayers of various molecular weight grades of HPC and HEC treated in this manner were essentially identical.[1] This would indicate, therefore, that the degree of any molecular weight polydispersity in such samples is not an important factor in their surface properties at the air/water interface. The water used throughout this study was first treated with a Sybron PBS system (Barnstead, Boston, MA) and then distilled twice using alkaline permanganate and dilute sulfuric acid.

Methods. Surface Tension and Spread Monolayers. All surface tension measurements were made by the Wilhelmy plate method using a roughened platinum plate attached to a Cahn 2000 electrobalance (Cahn Instruments, Cerritos, CA) as described previously.[10] For aqueous solutions of HPC and HEC, measurements were made in a jacketed vessel to allow for temperature control. All surface tension values reported for these polymer solutions represent those found to be independent of time and, therefore, reflect equilibrium adsorption. Results reported were reproducible to within 0.1 mN/m.

Surface pressure (π), the difference between the surface tension of water and a monolayer-covered surface, was measured for various surface concentrations (Γ) of spread monolayers of HPC and HEC. All measurements were performed with a Teflon trough having dimensions of 28.5 cm × 11.1 cm × 1.0 cm.

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Table I. Surface Pressure of HPC and HEC at Various Concentrations and Temperatures

concn, % w/v	temp, °C	surface pressure, mN/m HPC	surface pressure, mN/m HEC
0.0001	25	27.5	6.3
0.001	25	28.3	6.8
0.01	25	28.7	7.2
0.01	35	29.9	7.1
0.01	45	30.4	7.1

Temperature was controlled to ±0.1 °C by circulating water through a glass coil placed on the bottom of the trough and by heating lamps inside the box in which the trough was enclosed. Relative humidity within the box was maintained above 80% to minimize water evaporation from the trough during any experiment. The π–Γ isotherm was constructed either by successively adding HPC and HEC to the surface at constant surface area or by varying the surface area with a movable barrier at a fixed amount of deposited polymer. HPC and HEC were spread on the aqueous surface from a solution of 0.1–0.5 mg/ml in a mixture of water/methanol/chloroform in the ratio 5/10/35 by volume.

Surface Viscoelasticity. The surface longitudinal elasticity, ϵ, and corresponding viscosity, κ, for spread and adsorbed monolayers of HPC and HEC were carried out with the electrocapillary wave diffraction technique (ECWD), previously described.[7] In this technique surface capillary waves in the frequency range, ν, 0.1–4 kHz are produced at the air/liquid interface upon application of an ac electric field through a source needle positioned within about 100 μm of the interface. In this manner, we produce a circular ripple with a wavelength on the order of 0.3–3 mm and an amplitude of 10–100 nm by taking advantage of a difference in dielectric constants across the interface. Since this results in an amplitude-to-wavelength ratio on the order of 10^{-5}, we have a situation where the measurements are macroscopic in character, as is required in any viscoelastic measurement.

The spatial wave vector, k_0, and corresponding wave damping coefficient, β, for the capillary waves produced are determined by measuring the optical diffraction of a laser beam positioned at various distances from the source needle. The phase difference and amplitude ratio as a function of distance give rise to k_0 and β, and the two parameters are then used in the following dispersion equation to estimate ϵ and κ (11)

$$\left[\frac{\epsilon^* k^{*2}}{\omega} + i\eta(k^* + m) + i\eta'(k^* + m')\right] \times \left[i\eta(k^* + m) + i\eta'(k^* + m') + \frac{\sigma^* k^{*2}}{\omega} + \frac{g(\rho - \rho')}{\omega} - \frac{\omega(\rho + \rho')}{k^*}\right] + [\eta(k^* - m) - \eta'(k^* - m')]^2 = 0 \quad (1)$$

where $k^* \equiv k_0 - i\beta$, $m \equiv [k^{*2} + (i\omega\rho/\eta)]^{1/2}$, $m' \equiv [k^{*2} + (i\omega\rho'/\eta')]^{1/2}$, ω is angular frequency, g is the gravity constant, η and η' are the shear viscosities of air and subphase, respectively, ρ and ρ' are the densities of air and subphase, respectively, ϵ^* is $\epsilon - i\omega\kappa$, and σ^* is $\sigma - i\omega\mu$, where σ is the dynamic surface tension and μ is the transverse viscosity. The complex modulus, ϵ^*, and hence ϵ and κ are calculated from experimentally determined values of k_0 and β at fixed ω by assuming that μ, the transverse viscosity, is zero,[5] so that σ^* is equal to σ, which can, in turn, be equated to the static surface tension measured for the monolayer. The instrument was calibrated by determining the surface tension of water from eq 1, assumng ϵ^* equal to zero for pure liquids.[7]

Results

Surface Pressure of Solutions. The surface pressures for aqueous solutions of HPC and HEC as a function of concentration and temperature are given in Table I. Surface pressure in these experiments is defined as the difference between the surface tension of pure water and that of any aqueous polymer solution. For the concentration range of HPC used, the lower critical solution temperature was found to exist just above 45 °C, while no phase separation occurred when HEC was heated as high as 100 °C, in agreement with previous studies.[3] From Table I it can be seen that in the range 0.001–0.01% concentration (w/v) polymer at 25 °C both polymers exhibit very little difference in surface pressure but that the extent of surface pressure change at any concentration or temperature is much greater for HPC than HEC. Also, a very small but significant increase in surface pressure occurs going from 25 to 45 °C for HPC, while no such change occurs in this temperature range for HEC.

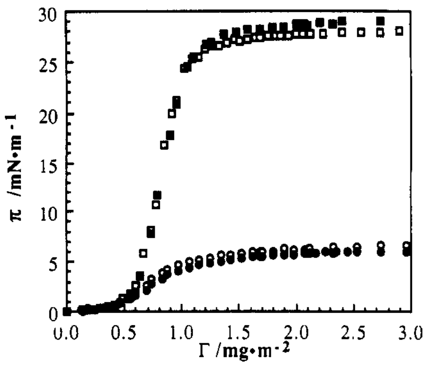

Figure 1. Surface pressure vs surface concentration for spread monolayers on water: HPC at 25 °C (□); HPC at 45 °C (■); HEC at 25 °C (○); HEC at 45 °C (●).

Surface Pressure vs Surface Concentration. The surface pressure, π, vs surface concentration, Γ, isotherms for spread monolayers of HPC and HEC at 25 and 45 °C are shown in Figure 1. It should be noted that both polymers exhibit a rise in surface pressure with surface concentration, followed by a plateau region. HPC produces a much sharper rise in surface pressure than HEC, indicative of a more condensed monolayer for HPC. This behavior is analogous to the formation of liquid-expanded vs liquid-condensed behavior noted for fatty acid monolayers of differing chain lengths and, hence, different hydrophobicities. Note the almost identical behavior for each polymer at 25 and 45 °C up to the plateau. However, with increasing temperature, at the plateau the surface pressure increases for HPC and decreases slightly for HEC.

It also should be noted that the surface pressures for HPC and HEC at the highest surface concentrations in the plateau region are essentially the same as those reported in Table I for adsorbed monolayers, as is the effect of temperature on π. Also of interest is the fact that the surface concentration at which HPC and HEC begin to exhibit a change in π is less than or equal to the point where all monomers would be expected to be situated at the interface in a closest packing arrangement, as estimated from CPK space-filling model projections. For HPC and HEC the limiting surface concentrations, Γ_0, estimated by extrapolating the linear portion of the π–Γ isotherm to zero surface pressure, are 0.55 and 0.36 mg/m^2, respectively, corresponding to 1.19 and 1.25 nm^2 per monomer segment, respectively, while the model-projected surface areas per monomer segment are 1.26 and 0.86 nm^2, respectively. This strongly suggests that at the higher values of Γ in the plateau region and presumably with adsorbed monolayers, as well, HPC and HEC exist with a significant proportion of the monomer segments extended into the underlying solution.

Surface Viscoelasticity. The dynamic surface longitudinal elasticity, ϵ, and corresponding viscosity, κ, of spread monolayers of HEC and HPC as a function of surface concentration at 25 °C and at the lowest frequency used are presented in Figures 2 and 3, respectively. Each value reported represents the average of at least three independent determinations. Included in Figures 2A and

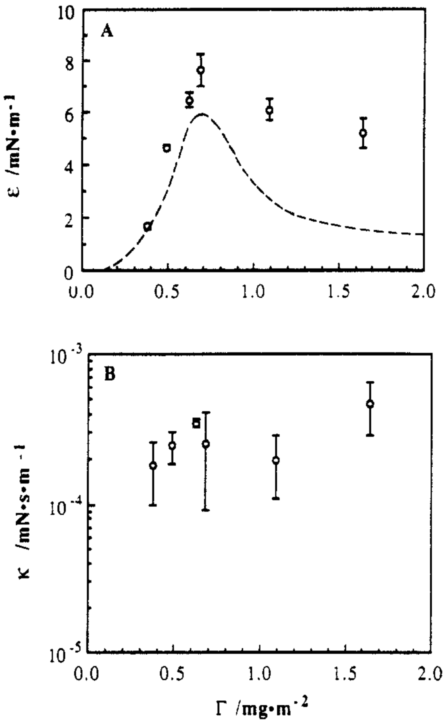

Figure 2. (A) Surface elasticity of HEC spread monolayers vs surface concentration at 24 °C: static elasticity, ϵ_{st} (- - -), and dynamic surface elasticity, ϵ at ν = 0.2 kHz (○). (B) Surface viscosity, κ, of HEC spread monolayers at 25 °C vs surface concentration at ν = 0.2 kHz (○).

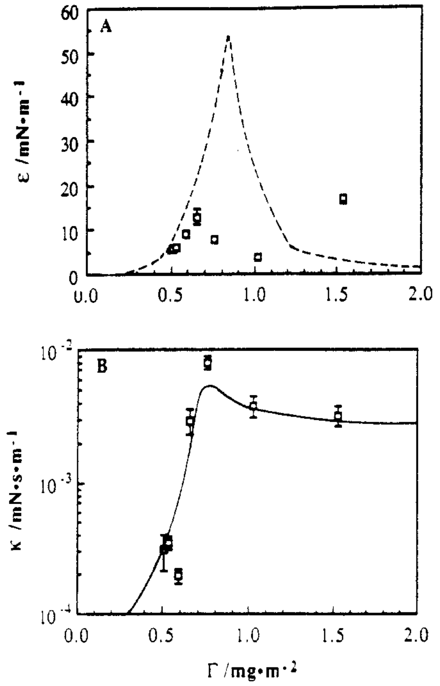

Figure 3. (A) Surface elasticity of HPC spread monolayers vs surface concentration at 25 °C: static elasticity, ϵ_{st} (- - - -), and dynamic surface elasticity, ϵ, at ν = 0.2 kHz (□). (B) Surface viscosity, κ, of HPC spread monolayers at 25 °C vs surface concentration at ν = 0.2 kHz (□). Solid line is drawn to guide the eye.

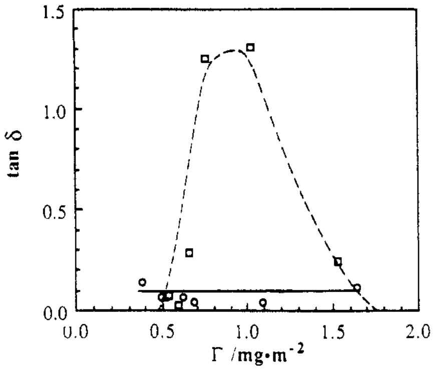

Figure 4. Loss tangent, tan δ, vs surface concentration for spread monolayers at 25 °C and ν = 0.2 kHz: HPC (□) and HEC (○). Lines are drawn to guide the eye.

3A also are plots of the static elasticities, ϵ_{st}, of these monolayers as a function of Γ, shown by dashed curves. Values of ϵ_{st} were obtained from the static π–Γ isotherms (Figure 1) by application of the equation

$$\epsilon_{st} = \Gamma(\partial\pi/\partial\Gamma)_T \qquad (2)$$

and by estimating the slope of the π–Γ isotherm as a function of Γ. Thus, we would expect values of ϵ, the dynamic elasticity, at very low frequency in a monolayer to approach ϵ_{st}, corresponding to the zero-frequency limit.

In Figure 2A we note that HEC exhibits good agreement between ϵ_{st} and ϵ over a wide concentration range. However, once the plateau region (Figure 1) is reached, or where the peak in ϵ_{st} vs Γ occurs, deviations appear between ϵ and ϵ_{st}. For HPC it may be noted in Figure 3A that values of ϵ are significantly lower than ϵ_{st} once the sharp rise in π with Γ occurs, except for the lowest surface concentration, but then they appear to increase at the higher surface concentrations. In Figures 2B and 3B, respectively, are the corresponding values of κ as a function of surface concentration. In Figure 2B we note that the viscosity of the HEC monolayer remains relatively constant at about 6 × 10^{-4} surface poise (mN s/m) as surface concentration increases to the plateau region, whereas in Figure 3B HPC exhibits a sharp rise, corresponding to the sharp increase in π, followed by a constant value of about 4 × 10^{-3} surface poise.

To further analyze the viscoelastic character of HPC and HEC monolayers as a function of surface concentration, we can gauge the relative contributions of storage and loss components, ϵ and $\omega\kappa$, through the loss tangent

$$\tan\delta = \omega\kappa/\epsilon \qquad (3)$$

In Figure 4 we present contrasting behaviors of HEC and HPC at 25 °C and 0.2 kHz. HPC shows loss at about 0.65 mg/m^2, the point where the surface pressure begins to increase significantly. The highest values of tan δ correspond to δ values of 45–56°, indicating a significant contribution from the loss component. Beyond this point of closest packing, the monolayer returns to an elastic film at around 1.5 mg/m^2. In contrast to this, the HEC monolayer at all surface concentrations exhibits tan δ values of less than 0.2, indicating a monolayer with very little viscoelastic character, rather purely elastic.

In Figures 5 and 6 are given plots of surface longitudinal elasticity, ϵ, and the corresponding viscosity, κ, for spread and adsorbed monolayers of HPC and HEC at 25 °C and surface pressures of 28.3 and 6.8 mN/m, respectively, as a function of frequency, over the range 0.1–4.0 kHz. The data for adsorbed monolayers shown in Figures 5 and 6 were obtained with 0.001% (w/v) HPC and HEC, and, though not shown, measurements at 0.0001% and 0.01% were essentially identical. Each value reported represents the average of at least three independent determinations, and the error bars represent one standard deviation. Two specific observations are made. First, for both polymers the adsorbed and spread monolayers at the same surface pressure and, presumably, therefore, at the same surface concentration exhibit the same viscoelastic properties and follow the same wave frequency dependence. Second,

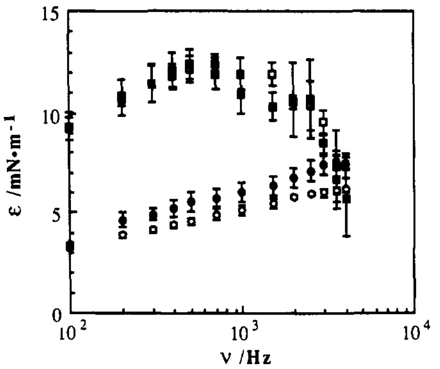

Figure 5. Surface elasticity, ϵ, vs wave frequency for spread and adsorbed monolayers at 25 °C: HPC spread (□) and HPC adsorbed (■) at a surface pressure of 28.3 mN/m; HEC spread (○) and HEC adsorbed (●) at a surface pressure of 6.8 mN/m.

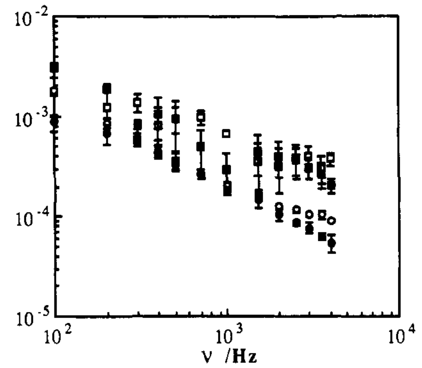

Figure 6. Surface viscoity, κ, vs wave frequency, ν, for spread and adsorbed monolayers at 25 °C: HPC spread (□) and HPC adsorbed (■) at a surface pressure of 28.3 mN/m; HEC spread (○) and HEC adsorbed (●) at a surface pressure of 6.8 mN/m.

HPC, the more hydrophobic polymer, exhibits greater elasticities than HEC, except at the highest frequency region, and similarly greater surface viscosities, particularly at the higher frequencies.

We now turn to the frequency dispersions of the elasticity and viscosity. Briefly summarizing, it appears that we may be probing some intermediate region between the low- and high-frequency limits with our available frequency range of 0.1–4 kHz. If the polymer films at the interface were to be represented by a generalized Maxwell element for their viscoelastic behaviors, we should expect that

$$\epsilon = \sum_i \epsilon_i \frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2} \quad \text{and} \quad \kappa = \sum_i \kappa_i \frac{\tau_i}{1+\omega^2\tau_i^2} \tag{4}$$

since

$$\epsilon^* \equiv \epsilon - i\omega\kappa$$

where ϵ_i and κ_i are the elastic and viscous components of the ith dilational mode and τ_i is the corresponding relaxation time. Thus, the two frequency limits should be

$$\epsilon \propto \omega^2 \quad \text{and} \quad \kappa \propto \omega^0 \text{ (low } \omega \text{ limit)} \tag{5}$$

and

$$\epsilon \propto \omega^0 \quad \text{and} \quad \kappa \propto \omega^{-2} \text{ (high } \omega \text{ limit)} \tag{6}$$

Our findings, as shown in Figures 5 and 6, are clearly not in these two limiting behaviors. Rather, the results can be represented as

$$\epsilon \propto \omega^0 \quad \text{and} \quad \kappa \propto \omega^{-1} \text{ (0.1–4.0 kHz)} \tag{7}$$

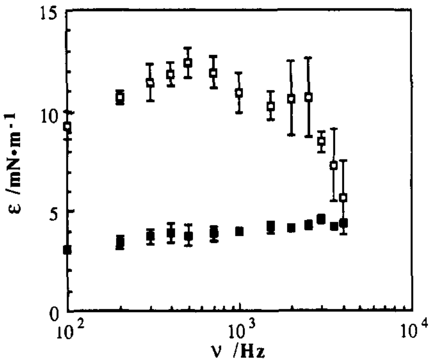

Figure 7. Surface elasticity, ϵ, vs wave frequency, ν, for adsorbed monolayers of a 0.001% solution of HPC at 25 (□) and 45 °C (■).

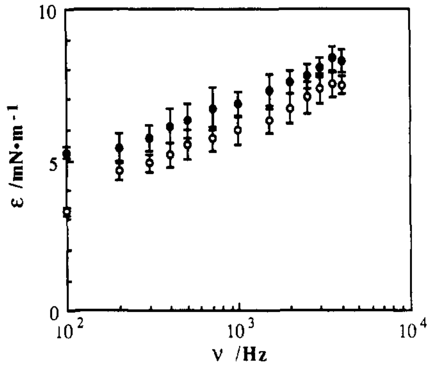

Figure 8. Surface elasticity, ϵ, vs wave frequency, ν, for adsorbed monolayers of a 0.001% solution of HEC at 25 (○) and 45 °C (●).

Hence, we propose that a collective mean relaxation time $\langle\tau_i\rangle$ of the dilation–compression surface mode of these polymer films, as linear viscoelastic objects, may be in the range 40 μs –1.6 ms since $\langle\tau_i\rangle \approx 1/\omega = 1/2\pi\nu$, where $0.1 \leq \nu \leq 4$ kHz. We note parenthetically that such an estimate of the mean relaxation time is based on the hypothesis that the polymer films are linearly viscoelastic, undergoing long wavelength deformations of dilation–compression mode, and the meaning of the collective mean relaxation time is rather ill-defined since we do not have any estimate of the spectral density profile. Of particular interest is a qualitative difference in the frequency dispersions of HPC and HEC, as we will shortly discuss below, rather than what frequency regime of the linear viscoelastic spectrum is being probed.

Since the region of surface concentration of most practical interest is that where HPC and HEC form adsorbed monolayers from solution, it was of further interest to compare values of ϵ and κ as a function of frequency, for HPC and HEC solutions over the temperature range 25–45 °C. In Figures 7 and 8 are given the ϵ values of HPC and HEC for a 0.001% solution at 25 and 45 °C, while the κ values are given in Figures 9 and 10. We note in Figure 7 that for HPC a very significant decrease occurs in ϵ with an increase in temperature, as well as a complete loss of frequency dependence. However, with HEC (Figure 8) a small but detectable increase in ϵ occurs in going from 25 to 45 °C with no apparent change in frequency dependence. Correspondingly, HPC exhibits a sizable decrease of 1–2 orders of magnitude in κ as the temperature is raised, while no such change in κ occurs with HEC.

Discussion

Surface Pressure vs Surface Concentration. By being able to use spread monolayers of HPC and HEC, where π vs Γ relationships can be measured, and by providing evidence that the properties of adsorbed and

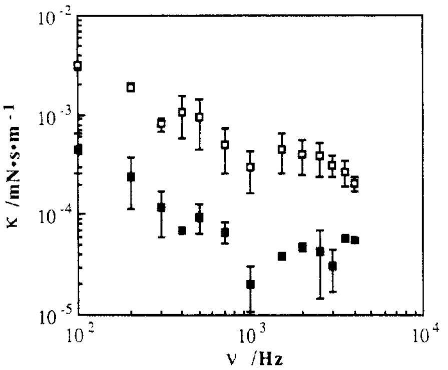

Figure 9. Surface viscosity, κ, vs wave frequency, ν, for adsorbed monolayers of a 0.001% solution of HPC at 25 (□) and 45 °C (■).

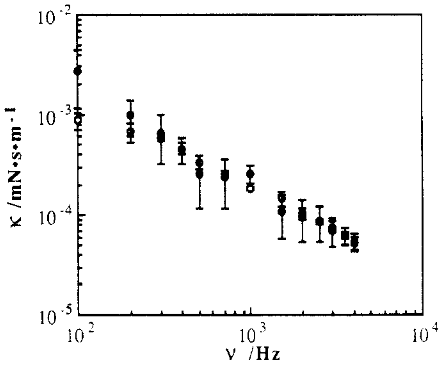

Figure 10. Surface viscosity, κ, vs wave frequency, ν, for adsorbed monolayers of a 0.001% solution of HEC at 25 (○) and 45 °C (●).

spread monolayers at the same surface pressure appear to be identical, we can estimate that the surface concentrations of HPC and HEC monolayers formed by adsorption from aqueous solution at 25 °C in the concentration range 0.0001–0.01% are about 3.2 and 3.1 mg/m^2 for HPC and HEC, respectively. From the molecular weight of a monomer unit and CPK space-filling models of a monomer unit and hence a projected cross-sectional area per monomer unit, we estimate that the total number of monomer segments of HPC and HEC adsorbed is in large excess of that expected for a situation where all monomer segments are located at the interface as a closely packed monolayer. Since polymer chains are forced to be at surface concentrations above this close-packed value, we would expect that they might be forced to move into either the upper or lower bulk phases, remaining as a single monolayer, or to accumulate as distinct multiple layers above or below the interface. In view of the significant water solubility of HPC and HEC in the temperature range of interest, it appears most likely that these polymers would adsorb as monolayers, rather than as multiple layers, and that they would prefer monomer segment distribution into the aqueous phase. In short, there would be many loops and tails in the bulk aqueous phase relative to trains at the air/water interface. Indeed, some direct evidence of this has been obtained in this laboratory by surface ellipsometric measurements.[12]

Surface Viscoelasticity. When a monolayer-covered surface experiences wave motion and the surface expands and contracts, the monolayer will require some time to respond to the resulting variation in surface tension. Generally, the relaxation time for a response to deformation can be affected by two processes: (1) a molecular diffusional interchange between the surface and subphase and (2) molecular rearrangement within the surface. For the types of monolayers envisioned for HPC and HEC, we would expect only local segmental rearrangements to be a major factor in controlling their surface viscoelastic properties as opposed to desorption/adsorption of the entire polymer chain. In particular, we would expect that upon deformation, the major rheological responses with HPC and HEC at the higher surface concentration exhibited by adsorbed monolayers (or in the plateau region for spread monolayers) would be governed by the interchange process of trains and loops.

From what we have found with ϵ and κ at 25 °C with HPC and HEC, we can state that these two systems are indeed different. On the basis of the tan δ values given in Figure 4, we can conclude that both HPC and HEC are dominated by their elastic properties in a state consistent with that of an adsorbed monolayer, i.e., Γ in the region of 3 mg/m^2, both exhibiting relatively low values of tan δ. Much more complex behavior appears to occur at the lower concentrations wherein, with HPC, there is an initial increase in tan δ values, due to a significant increase in κ followed by a decrease to some constant value. With HEC this initial increase in κ must have already occurred at Γ values below 0.3 mg/m^2, and we now are only observing the decrease in tan δ because of the significant increase in ϵ. The exact molecular interpretation of these results is not possible with what we know, but it does indicate the sensitivity of ϵ and κ to the changes taking place once the plateau region is reached. We may note about 1 order of magnitude higher values of ϵ and κ HPC than HEC, presumably tied to the differences in the ratio of loops to trains, HPC having a smaller ratio than HEC.

Effect of Temperature. It is well established that HPC in aqueous solution over a wide concentration range exhibits a lower critical solution temperature in the range 40–45 °C[3] and forms liquid crystalline mesophases in concentrated solution.[13] In contrast, no such tendency exists for HEC under corresponding conditions. It has also been shown that ethyl(hydroxyethyl)cellulose, a polymer showing the hydrophobic tendencies of HPC, exhibits properties at the solid/liquid interface that are very sensitive to temperature and its effects on solvent quality.[14] Thus, the hydrophilic properties of HEC are clearly linked to a low degree of substitution and the availability of free hydroxy groups. Focusing only on changing the temperature from 25 to 45 °C so as to approach the LSCT of HPC closely, we have found the surface viscoelasticity to be very sensitive to such changes. Whereas π–Γ isotherms (Figure 1) and hence ϵ_{st} values (not shown) over the entire isotherm change very little with an increase in temperature for both HPC and HEC and no temperature dependence is noted for adsorbed or spread HEC monolayers as far as ϵ and κ values (see Figures 8 and 10), we see a roughly 2-fold decrease in ϵ and a 10-fold decrease in κ for HPC (Figures 7 and 9). The lack of temperature dependence for HEC and the significant decreases in ϵ and κ for HPC over this relatively narrow temperature range suggest some relationship between the surface and bulk properties of these polymers and that their surface viscoelastic properties are in large part affected by the state of the monomer segments in the underlying aqueous phase. Just as might occur in aqueous solution, the increase in temperature for HPC most likely has a significant effect on the relative solvent–segment and segment–segment interactions giving rise to a greater tendency for local "phase separation", as schematically represented in Figure 11. Such a change could then alter the tendency for lateral motion within the monolayer, as well as segmental motion in and out of the interface, thus giving rise to a reduced elasticity and viscosity. The greater hydrophilic nature of HEC and less tendency for self-

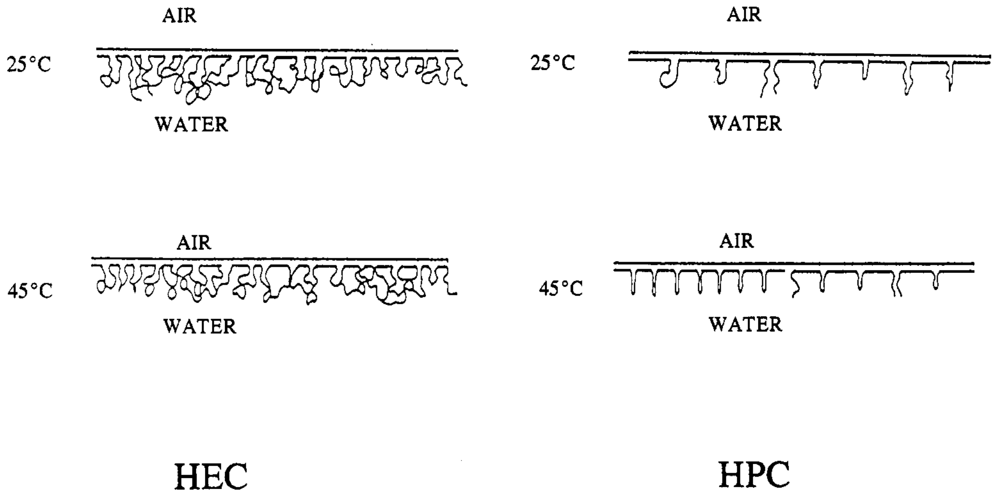

Figure 11. Schematic illustration of adsorbed polymer films at 25 and 45 °C. We intend to highlight here two points. At 25 °C, HEC is proposed to be different from HPC by having many more segments not adsorbed at A/W but involved in chain looping, whereas HPC segments are predominantly adsorbed at A/W. At 45 °C, however, HEC chain conformations are proposed to be only slightly different from those at 25 °C, whereas HPC chain conformations may be classified by two different types, each in separate surface phases, with one much more aggregated laterally than the other one. Such is our hypothesis, although we cannot prove it at this stage.

association at these temperatures would preclude any strong effect on its loop characteristics and hence on its surface viscoelasticity.

Conclusions

It has been possible to prepare adsorbed and spread monolayers of two water-soluble macromolecules, hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC), and to determine their surface pressure (π) vs surface concentration (Γ) isotherms and their dynamic surface longitudinal elasticities (ϵ) and corresponding viscosities (κ) as a function of frequency and temperature using the electrocapillary wave diffraction (ECWD) technique. These studies confirm that spread and adsorbed monolayers of HPC and HEC at the same surface pressure are identical and that adsorbed monolayers, exhibiting the same surface pressure over a very wide range of solution concentrations, exist at surface concentrations of about 3.2 and 3.1 mg/m^2, respectively. Analysis of π–Γ isotherms and use of molecular models support the conclusion that a very large proportion of the monomer segments of the adsorbed monolayer are extended into the aqueous phase.

Generally speaking, the surface viscoelastic properties of HPC and HEC spread and adsorbed as monolayers are quite different from each other, with HPC, the more hydrophobic polymer, exhibiting greater overall viscoelasticity, presumably, in part, because of a greater number of monomer segments actually located at the interface. In view of the large proportion of monomer segments that are associated with the underlying solution for adsorbed monolayers of both HPC and HEC, it is not surprising that HPC, with a lower critical solution temperature in aqueous solution just above 45 °C, exhibits a corresponding significant change in viscoelasticity when the temperature is increased from 25 to 45 °C, whereas no such effects are noted with HEC, which shows no such tendencies in solution.

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