1546 *Macromolecules* 1981, *14*, 1546–1549

Mixing of Water with (Hydroxypropyl)cellulose Liquid Crystalline Mesophases

Joseph S. Aspler and Derek G. Gray*

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec H3A 2A7, Canada. *Received March 11, 1981*

ABSTRACT: Several gas chromatographic and static sorption techniques were used to measure the activity of water vapor over concentrated solutions of (hydroxypropyl)cellulose (HPC). Activities of water vapor measured from 15 to 55 °C show the effect of the lower critical solution temperature (LCST) at temperatures above 40 °C in the ordered liquid crystalline mesophase in that activities approach unity and the partial molar heats of mixing, calculated from the temperature dependence of the sorption isotherms, go to zero.

Introduction

(Hydroxypropyl)cellulose (HPC) is a cellulose ether, soluble in water and in many organic solvents. The commercial polymer is available in a variety of molecular weights, with an average substitution of four hydroxypropyl groups per anhydroglucose unit. It is believed that there may exist unsubstituted hydroxyl groups on the cellulose backbone as well as hydroxypropyl groups condensed upon other hydroxypropyl groups. HPC has been shown to form an ordered liquid crystalline mesophase with cholesteric structure in concentrated aqueous solution,[1] as well as in concentrated solutions of polar organic solvents.[2] Aqueous solutions show a lower critical solution temperature (LCST) at about 42 °C.[1,2] Above this temperature, the solutions precipitate, coalescing into a white gel at yet higher temperatures. For a given sample, the position of the LCST has been shown to be independent of concentration from a few ppm of polymer up to approximately 40% polymer by weight, the point at which the anisotropic phase starts to form.

In our previous paper,[3] we measured the activity of water vapor over concentrated aqueous solutions of HPC by inverse gas chromatographic and static methods at 25 °C and used GC to measure the activity coefficients at infinite dilution of water on the polymer from 15 to 85 °C. We found that our data at high water content and the data from the literature[4] were best fitted to the familiar Flory–Huggins equation

$$\ln (a_1/\phi_1) = (1 - 1/x)\phi_2 + \chi_{FH}\phi_2^2 \qquad (1)$$

while the results at very high polymer concentration were best fitted to Flory's equation for an ordered phase of rodlike molecules[5,6]

$$\ln (a_1/\phi_1) = 2/y + \left(\frac{y-1}{x}\right)\phi_2 + \chi_R\phi_2^2 \qquad (2)$$

where the degree of orientation of the rods is given by y ($1 < y \leq x$), with $y = 1$ for perfect orientation. The subscripts on the two interaction parameters χ_{FH} and χ_R show their origin in the Flory–Huggins and rodlike molecule theories, respectively. Recently, Flory has extended these calculations[7] and considered mixtures of rods of different lengths.[8]

Although an increasing number of papers are being published on lyotropic, polymeric liquid crystals, there have been few studies of the thermodynamics of mixing. The HPC–water system is attractive because of the benign nature of the components, the reasonable vapor pressure of the solvent, and the readily accessible lower critical solution temperature. We have therefore extended our previous measurements[3] to cover concentrations from 0 to 50% water by volume over a temperature range, 15 to 55 °C, which spans the LCST of the system. Various thermodynamic parameters have been calculated, in an attempt to elucidate the mesophase structure and mechanism of sorption in this composition range.

Experimental Section

The HPC samples used for these measurements were the same as those used previously.[3] The GC sample was a Klucel "L" (Hercules, nominal $\bar{M}_w$ = 100 000). Static measurements were done on a sample of HPC of the same nominal $\bar{M}_w$ from Aldrich, reported to have a value of $\bar{M}_n$ = 35 000.[4] The column used in the GC measurements on HPC was that used in the previous work and had a load of 0.646 g (2.39%) of HPC. The HPC was coated onto the Teflon powder support by slow evaporation from acetone solution and the support packed into 1.8-m, 0.25-in. o.d. polypropylene columns. Octakis(2-hydroxypropyl)sucrose (HPS) is a water-soluble, highly viscous fluid and is obtainable from Chromatographic Specialties Ltd. under the trade name Hyprose SP80. An elemental analysis was performed by Schwarzkopf Microanalytical Laboratory to confirm its purity. Anal. Calcd for $(CH_2CH(OH)CH_3)_8$, $C_{12}H_{14}O_{11}$: C, 53.58; H, 8.74. Found: C, 53.04; H, 8.83. A value of 1.187 g mL^{-1} was used for the density.[9] The column used for the GC measurements was prepared in the same manner as the HPC column and had a load of 0.480 g (2.16%) of HPS.

The gas chromatograph, a Hewlett-Packard Model 5722A, was equipped with a thermal conductivity detector. For the finite-concentration work, temperatures were controlled to within ±0.05 °C by an external circulating bath; for the work done at infinite dilution, temperatures above 30 °C were controlled to within 0.1 °C by the built-in air oven. Flow rates of the helium carrier gas were measured with a soap bubble flowmeter and were corrected for water vapor content of the carrier gas in the flowmeter and for column pressure drop.

At low water content, sorption isotherms of water and HPC were measured by the GC method of "elution by a characteristic point" or ECP, to which was added at 25 °C measurements by the "elution on a plateau" or EP method.[3] Two static methods were also used. In the first static method, a sample of HPC was suspended from a Cahn vacuum microbalance, and the equilibrium vapor pressure of water and weight of sorbed water were measured with stepwise addition of water vapor to the system. This method was used in the range 15–30 °C and only gave reproducible results at relative partial pressures of water of less than 90%. In the second method, sealed sample bottles containing HPC suspended over aqueous H_2SO_4 were submerged in a constant-temperature bath. The uptake of water by the HPC was followed gravimetrically until equilibrium was attained. The concentration of H_2SO_4 was then determined by titration, and the corresponding partial pressure of water was obtained from the literature.[10] This method gave the sorption isotherms at high water content in the 15–30 °C range and the complete isotherms in the range 35–55 °C.

The fundamental relationship between the corrected GC retention volume, $V_{R'}$,[11,12] and the corresponding sorption isotherms is

$$q = \frac{1}{w}\int_0^c V_{R'}(c)\,dc \qquad (3)$$

where q (mol g^{-1}) is the concentration of solvent "probe" vapor

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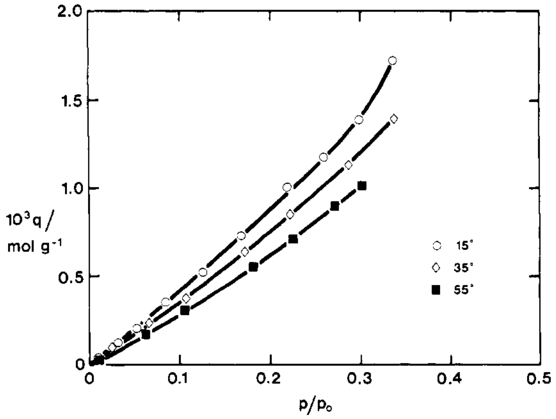

Figure 1. Sorption isotherm at 15, 35, and 55 °C for low concentrations of water on HPC. The amount of water adsorbed, in mol g^{-1}, is plotted as a function of the relative partial pressure with data from GC (ECP) measurements.

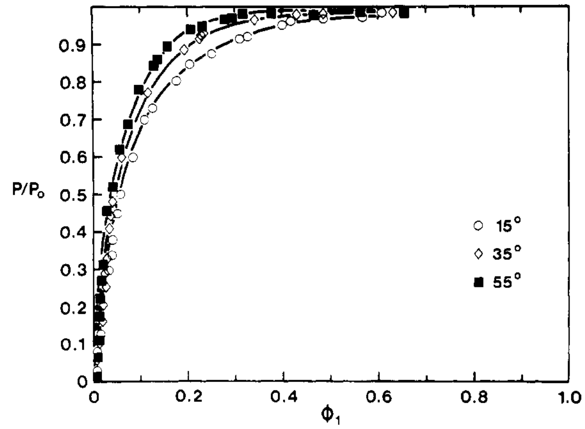

Figure 2. Sorption isotherms at 15, 35, and 55 °C for water on HPC. The activity is plotted as a function of the volume fraction of water with data from both GC and static measurements.

in the stationary phase (polymer), c (mol mL^{-1}) is the corresponding concentration of solvent vapor in the vapor phase, and w (g) is the mass of polymer loading in the GC column. The isotherms were calculated from the peak shapes of injected water by means of the above basic equation, but with various standard corrections for gas-phase compressibility and the sorption effect.[11,12] The volume fractions, ϕ_1, of water sorbed were calculated assuming zero volume change upon mixing.

Results

The appearance of the HPC samples observed during static measurements was similar to that reported previously,[2] progressing from the original white powder to a clear film to a gel, with the cholesteric colors developing as water content increased. Results from various sorption methods agreed within experimental error up to the useful limits of each method. The experimental error was greatest at the lowest GC concentrations (ϕ_1 = 0.005–0.015), due to the error inherent in the calibration of the GC detector at low partial pressures of water, and in the range $0.03 \lesssim \phi_1 \lesssim 0.07$, above the limits of the GC measurements but at the lowest limits of the static methods.

Typical GC sorption isotherms measured by the ECP technique are shown in Figure 1, while Figure 2 shows isotherms measured over the entire concentration range. No hysteresis was seen in the sorption/desorption curves measured on the vacuum microbalance.

In order to determine the partial molar heats of mixing, the activities of water, $a_1 = p_1/p_1{}^\circ$, were first obtained at regular intervals by interpolation of the isotherms from a volume fraction of 0.005–0.030 in steps of 0.005, and above 0.030 in steps of 0.01. The average values of the activities were computed by polynomial regression over small portions of the isotherms encompassing five experimental points. While this did not provide any great advantage over the hand-fitted curve, it did help to determine the precision of the interpolation. A complete tabulation of the experimental data is available as supplementary material.

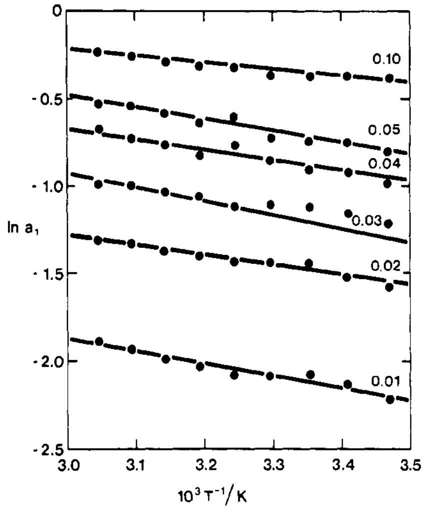

Figure 3. Natural logarithm of the activity of water vapor plotted as a function of inverse absolute temperature for volume fractions of water from 0.01 to 0.10, as indicated.

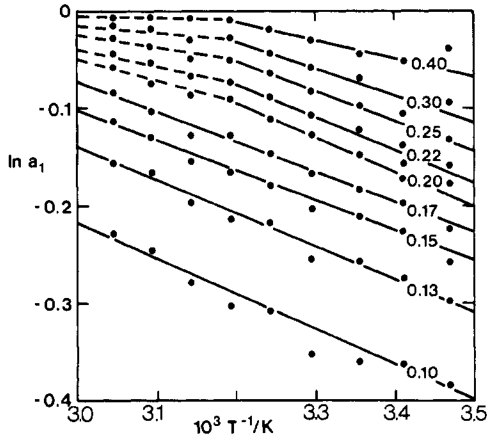

Figure 4. Natural logarithm of the activity of water vapor plotted as a function of inverse absolute temperature for volume fractions of water from 0.10 to 0.40, as indicated.

The partial molar heat of solution, $\Delta\bar{H}_m$, was calculated from the activities according to

$$\Delta\bar{H}_m = R\left(\frac{\partial \ln a_1}{\partial(1/T)}\right)_{\phi_1} \qquad (4)$$

The corresponding free energy of mixing with respect to a standard state of liquid water is

$$\Delta\bar{G}_m = RT \ln a_1 \qquad (5)$$

and the corresponding entropy of mixing

$$\Delta\bar{S}_m = (\Delta\bar{H}_m - \Delta\bar{G}_m)/T \qquad (6)$$

Figures 3 and 4 show the natural logarithm of the activities as a function of inverse absolute temperature at low water content (ϕ_1 = 0.01–0.10) and high water content (ϕ_1 = 0.10–0.40), respectively. At volume fractions of water

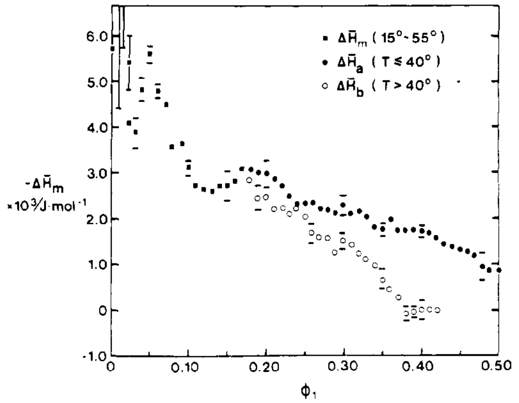

Figure 5. Partial molar heats of mixing measured from adsorption isotherms in various temperature ranges: $\Delta\bar{H}_m$, 15–55 °C; $\Delta\bar{H}_a$, 25–40 °C; $\Delta\bar{H}_b$, 45–55 °C.

less than 0.2, the relationship between ln a_1 and $1/T$ is linear within experimental error, indicating constant heats of mixing over the temperature range. However, at temperatures above 40 °C and water contents $\phi_1 \gtrsim 0.20$, there is an inflection clearly visible in the curves of Figure 4, with the slope and hence $\Delta\bar{H}_m$ above the LCST approaching zero as the water content increases. The point of the inflection is drawn with prior knowledge of the dilute-solution LCST of 42 °C. With this in mind, if the portions of these curves above and below the inflection point are taken as linear, then two heats of mixing may be inferred: one ($\Delta\bar{H}_a$) below the LCST and one ($\Delta\bar{H}_b$) above the LCST.

Figure 5 shows the partial molar heats of mixing from 0 to 50% water by volume per mole of water. Typical precisions estimated from the least-squares analysis of the data are given.

Discussion

In common with other lyotropic polymeric mesophases, a two-phase isotropic–anisotropic region exists at intermediate concentrations of HPC in water below the LCST.[2] This requires that a plateau should exist in the sorption isotherms, since for the two phases to coexist, the water activity should remain constant with increasing HPC concentration and the amount of anisotropic phase should increase at the expense of the isotropic material.[5] However, the two-phase region is narrow and the experimental activities are close to unity, and so the measurements are insufficiently precise to detect the region of constant water vapor pressure.

Above the LCST, the dilute solutions separate into a polymer-rich precipitate and a very dilute aqueous phase. When the water content drops below about 60% (by volume), the liquid crystalline mesophase forms. Even in the mesophase region, the samples turn white on heating, indicating that separation of a dispersed phase still occurs, but over a much more extended temperature range than for the dilute solutions.[2] This effect provides an explanation for the variation in the heats of mixing with temperature shown in Figures 4 and 5.

At a sharp LCST, one would expect that the activity of water over the very dilute aqueous phase would go to unity. The heat of mixing would be expected to go to zero at the same time since the excess heat of mixing of water with water is zero. The polymeric mesophase is a more complicated case, since the phase separation does not yield precipitate plus water but instead a still-ordered phase apparently containing a dilute dispersed phase. The nonlinearity in the activity plots of Figure 4 at high water content can be attributed to the separation of a dilute dispersed phase above the LCST. For ϕ_1 greater than about 0.38, the activities above the LCST are close to unity, as expected for very dilute solution mixing, and $\Delta\bar{H}_b$ is zero within experimental error (Figure 5). As the amount of water decreases, the magnitude of $\Delta\bar{H}_b$ increases until it coincides with $\Delta\bar{H}_a$ at $\phi_1 \simeq 0.20$. At lower concentrations of water, there is a single heat of mixing, $\Delta\bar{H}_m$.

The enthalpic interactions between water and the liquid crystalline phase are given by $\Delta\bar{H}_a$ and $\Delta\bar{H}_m$. The mixing process is exothermic, with the magnitude of $\Delta\bar{H}_m$ decreasing as the volume fraction of water increases. However, the decrease is not smooth, apparent maxima occurring at $\phi_1 \simeq 0.05$ and $\phi_1 \simeq 0.17$. Such discontinuities have been observed in the past for water adsorption on the polymers collagen,[13] poly(*N*-vinylpyrrolidone),[14] amylose,[15] and cellulose,[16] and in poly(hydroxyethyl methacrylate) and its copolymer with poly(*N*-vinylpyrrolidone)[17] and have been interpreted in terms of specific states of water in the swollen adsorbate. The volume fractions at which the discontinuities occur correspond approximately to one ($\phi_1 = 0.053$) and three ($\phi_1 = 0.145$) water molecules per substituted anhydroglucose unit. As each unit contains three hydroxyl groups, the maxima may be associated with interactions between these groups and water. The second maximum near three water molecules per unit is also close to the point where the effect of the LCST is first seen in the activities of water vapor.

A second contribution to the enthalpy of mixing may result from the disruption of the partially crystalline regions of the dry polymer to give the aqueous liquid crystalline phase. The magnitude of the effect is uncertain, ΔH_c for the transition from the semicrystalline polymer to the isotropic state being 4 J/g of polymer.[18] This effect may contribute to the high value of $\Delta\bar{H}_m$ at very low water content.

Acknowledgment. J.S.A. thanks the Pulp and Paper Research Institute of Canada for a scholarship. We thank the Natural Sciences and Engineering Research Council of Canada and Hercules Inc. for partial support of this work.

Appendix. $\Delta\bar{H}_m^\infty$ Values for (Hydroxypropyl)cellulose and for a Dimeric Analogue

In a previous paper[3] we tabulated the partial molar heats of mixing at infinite dilution, $\Delta\bar{H}_m^\infty$, as a function of temperature for water in (hydroxypropyl)cellulose. The values were calculated from

$$\Delta\bar{H}_m^\infty = -R\left(\frac{\partial \ln p_1^\circ}{\partial(1/T)} + \frac{\partial \ln V_g}{\partial(1/T)}\right) \qquad (7)$$

where p_1° is the vapor pressure of water at temperature T and V_g is the specific retention volume at infinite dilution. The first term on the right side of eq 7 corresponds to the latent heat of vaporization of water, and the second term represents the partial molar heat of solution of water at very low concentration in the polymeric stationary phase. The tabulated values were obtained by fitting each term on the right to a second-degree polynomial in $1/T$ and taking the difference between the curves at each temperature. The values for $-\Delta\bar{H}_m^\infty$ increased from ~3 kJ/mol at 15 °C to ~10 kJ/mol at 85 °C.

These experiments were repeated with octakis(2-hydroxypropyl)sucrose (HPS) as the stationary phase. HPS is composed of two monosaccharide residues with four hydroxypropyl substituent groups on each and is thus a reasonable dimeric analogue of the hydroxypropyl-substituted anhydroglucose units in HPC. For HPS, the retention data are given by

$$\ln V_g = -5.728 + 2493(1/T) + 490600(1/T)^2 \qquad (8)$$

in the temperature range 15–75 °C, and the values for $-\Delta\bar{H}_m^\infty$ decreased from $\sim$5 kJ/mol at 15 °C to $\sim$2 kJ/mol at 75 °C. Thus the temperature dependence of $-\Delta\bar{H}_m^\infty$ for HPS apparently differs from that of HPC. We note that, unlike aqueous HPC solutions, HPS solutions in water showed no signs of phase separation when heated to 100 °C.

In comparing the HPS retention data with those for HPC,[3] we noted that the HPC measurements showed much greater experimental variation. This was due to the dependence of the measured retention volumes on sample size and to the consequent extrapolations to zero water peak height. (The HPS retention volumes were virtually independent of water concentration, as should be the case in the infinitely dilute region.) We now think that extrapolating to zero peak height and taking the difference between two fitted curves may have introduced errors which contribute to the apparent temperature dependence of $\Delta\bar{H}_m^\infty$ for water in HPC. Table II and the associated discussion in ref 3 should therefore be treated with caution; the trend is still thought to be correct, but the errors in $\Delta\bar{H}_m^\infty$ are larger than those listed. (We note that this problem only concerns the measurement of the partial molar heats of mixing of water with HPC at effectively zero water content reported in the previous paper.[3] The finite-concentration measurements in the present paper showed negligible kinetic effects, and, of course, no extrapolation to zero concentration was necessary.)

Supplementary Material Available: Experimental activities of water over HPC solutions (4 pages). Ordering information is given on any current masthead page.

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Miscibility of Acrylic Polymers in Polystyrene by Melt Titration

R. H. Somani and M. T. Shaw*

Department of Chemical Engineering and Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06268.

Received March 16, 1981

ABSTRACT: The melt titration technique was used to determine the extent of miscibility in several polystyrene/polyacrylate (PMA, PEA, PBA) and polystyrene/polymethacrylate (PnBMA, PMMA) blends. The results were used in the Flory–Huggins theory of polymer solutions to calculate the interaction energy density. A theoretical value of the interaction energy density was obtained from the components' solubility parameters and the two values were compared. The Flory theory and Sanchez's lattice fluid theory, based on statistical thermodynamic principles, were used to predict the miscibility of the polystyrene/acrylic blends. The use of experimental values of the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient was found to affect the miscibility predictions considerably. Finally, results from the melt titration technique were compared with predictions of these theories. The Flory treatment offered the best ranking of the experimental miscibilities, while the Sanchez theory correctly predicted the very low miscibilities (10^{-5} to 10^{-6}) found for all pairs.

Introduction

Miscibility in a two-component polymer system is required to obtain a homogeneous product, which is highly desirable for superior and predictable performance. Various theories have been developed to aid in predicting polymer–polymer miscibility[2,9] and its dependence on temperature, pressure, and concentration. For better appreciation of the performance of these theories, experimental miscibility data are essential. Unfortunately, very few data are available at present, which has led many scientists to investigate new methods for determining miscibility in polymer–polymer systems. We reported[1] earlier a melt titration technique for measuring the extent of miscibility in polymer blends.

In this work, polystyrene (PS) was chosen as one component and the extent of miscibility of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), poly(*n*-butyl methacrylate) (PnBMA), poly(methyl methacrylate) (PMMA), and poly(dimethylsiloxane) (PDMS) in polystyrene was determined by melt titration. From the known phase behavior of the polymer blends, the "Tompa interaction parameter" χ and "interaction energy density" $B = RT\chi/V_1$ were calculated. For comparison purposes, the interaction energy density was obtained from the difference in solubility parameters δ_i calculated from group contributions: $B = (\delta_1 - \delta_2)^2$.

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