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# Gas Chromatographic and Static Measurements of Solute Activity for a Polymeric Liquid-Crystalline Phase

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ABSTRACT: Inverse gas chromatographic methods allow measurements of solvent activity over polymeric liquid-crystalline phases. Aqueous solutions of hydroxypropyl cellulose form an ordered fluid phase at high polymer concentrations and also exhibit a lower critical solution temperature. Several gas chromatographic and static techniques were used to measure the activity of water in concentrated hydroxypropylcellulose solutions. The results are compared with osmotic pressure measurements in the literature. Within experimental precision, the activity appears to vary smoothly with concentration. It is suggested that in this system the polymer–solvent interaction parameter may have the same value at each end of the concentration range, but the entropy of mixing changes from that predicted by Flory's theory for rodlike mixing at high polymer concentrations to that for Flory–Huggins mixing in dilute solution.

Gas chromatography has proved useful for the examination of polymer physical properties and in particular for the measurement of the thermodynamics of polymer–solvent mixing at high polymer concentrations.[1,2] The fundamental relationship for GC measurements may be written as[1,3]

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

where $q$ (mol/g) is the concentration of solvent "probe" vapor in the polymer stationary phase, $c$ (mol/mL) is the corresponding concentration of solvent vapor in the vapor phase, and $w$ (g) is the mass of the polymer in the GC column. The value of $V_{R'}(c)$, the GC retention volume (mL) of a concentration $c$ of probe vapor, corrected for the column vapor phase volume, may be determined by several different finite concentration gas chromatographic methods.[3] At sufficiently low probe concentrations, in the so-called "infinite dilution" region, the concentration of vapor may obey a linear partition equation of the form $q = \beta c$, where $\beta$ (mL/g) is a partition coefficient per unit mass of stationary phase. In this limit, $V_{R'}(c)$ becomes independent of $c$, and comparison with eq 1 shows that the GC retention volume is simply related to the partition coefficient by $V_{R'} = \beta w$. The partition coefficient is often expressed as the specific retention volume $V_g = (273.2/T)\beta$, which corresponds to the volume of carrier gas, measured at 273.2 K, which is required to elute a small pulse of the probe vapor through a column at temperature $T$ (K) containing 1 g of stationary phase.

The specific retention volume may be related to weight- or volume-fraction activity coefficients at infinite dilution of vapor in the polymer phase.[4] Neglecting the minor effects of gas-phase imperfections and the volume changes on mixing, these activity coefficients are given by

$$\Omega_1^{\infty} = (a_1/w_1)^{\infty} = \frac{273.2R}{p_1^0 V_g M_1} \qquad (2)$$

$$\ln (a_1/\phi_1)^{\infty} = \ln (a_1/w_1)^{\infty} + \ln (v_2/v_1) \qquad (3)$$

where $a_1$ is the solvent activity, $w_1$ and $\phi_1$ are the solvent weight and volume fractions, respectively, $R$ is the gas constant, $p_1^0$ and $M_1$ are the saturated vapor pressure and molecular weight respectively of the probe, and $v_1$ and $v_2$ are the specific volumes of the probe and the polymer.

The activity of a solvent over a polymer solution according to the familiar Flory–Huggins theory is given by[4]

$$\ln (a_1/\phi_1) = (1 - 1/x)\phi_2 + \chi_{FH}\phi_2^2 \simeq 1 + \chi_{FH} (\phi_2 \rightarrow 1, x \rightarrow \infty) \qquad (4)$$

where $\phi_1$ and $\phi_2$ are the volume fractions of solvent and polymer, respectively, and $x$ is the number of segments in the polymer chain. The polymer–solvent interaction parameter, $\chi_{FH}$, quantifies the segment–solvent interaction, together with all other noncombinatorial contributions to the free energy of mixing. Combining eq 2, 3, and 4 gives[5]

$$\chi_{FH}^{\infty} \simeq \ln \frac{273.2Rv_2}{p_1^0 V_g V_1} - 1 \qquad (5)$$

where $V_1$ is the molar volume of the liquid probe, and $\chi_{FH}^{\infty}$ is the value of the interaction parameter at infinite dilution.

The effect of the relative orientation of the polymer segments is not considered in the Flory–Huggins theory. However, for rodlike molecules an additional factor becomes evident at higher concentrations, where parallel arrangements must be favored over random orientation of rods. Flory developed a lattice theory for semiflexible[6] and rodlike molecules which predicts the appearance of an anisotropic or ordered phase above a certain polymer concentration. The solvent activity above such a phase is given by[7,8]

$$\ln (a_1/\phi_1) = 2/y + \left(\frac{y-1}{x}\right)\phi_2 + \chi_R\phi_2^2 \qquad (6)$$

where the degree of orientation of the rods is given by $y$ ($1 < y \le x$) with $y = 1$ for perfect orientation. The subscript on the polymer–solvent interaction parameter, $\chi_R$, is used to indicate its origin in the rigid rod theory. For

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Table I
Comparison of Methods Used to Measure Sorption of Water onto HPC

| method | *a* | *b* | approx time required |
|---|---|---|---|
| elution by a characteristic point (ECP) | 0-0.03 | 0-0.4 | 1 day per isotherm |
| elution on a plateau (EP) | 0-0.06 | 0-0.6 | 1 day per point on an isotherm |
| static sorption (over $H_2SO_4$ soln) | 0-0.60 | 0-0.99 | 1 month per isotherm |
| static sorption (on microbalance) | 0-0.30 | 0-0.95 | 1 to 2 days per point on an isotherm |

[a] Volume fraction range of water. [b] Relative partial pressure range of water.

high polymer concentrations and sufficiently large $x$, $y \to 1$, and so eq 6 becomes

$$\ln (a_1/\phi_1) = 2 + \chi_R\phi_2^2 \tag{7}$$

Combining eq 7 and 2 gives

$$\chi_R^\infty \simeq \ln \frac{273.2Rv_2}{p_1^0 V_g V_1} - 2 \tag{8}$$

The value of the polymer-solvent interaction parameter at infinite dilution over an ordered solution of rods should thus be readily obtained from GC data. Treating the *same* GC data according to the Flory-Huggins theory would give a different value of $\chi$

$$\chi_{FH}^\infty = \chi_R^\infty + 1 \tag{9}$$

Hydroxypropylcellulose (HPC) is a water-soluble cellulose ether which forms a cholesteric liquid-crystalline phase at high polymer concentrations.[9] Aqueous solutions also show a sharp lower critical solution temperature at ~42 °C.[10] This system is more tractable than many mesogenic polymer-solvent systems. In this paper, we examine the sorption of water by HPC using infinite dilution and finite concentration gas chromatography. Precautions are required to minimize the surface and kinetic effects which often interfere with GC measurements of polymer-solvent substrates.[1] Few finite concentration GC measurements of polymer-solvent interactions have been made previously, so static sorption measurements for the HPC-water system at 25.0 °C are also presented for the sake of comparison.

## Experimental Section

The HPC sample used for the GC measurements was a Klucel "L" (Hercules, nominal $\bar{M}_w$ 100 000), while static measurements were done on a sample of HPC of the same nominal $\bar{M}_w$ from Aldrich. Bergmann and Sundelöf[11] have reported a value of $\bar{M}_n$ of 35 000 (osmometry) for their Klucel "L" sample. The HPC was coated onto a Teflon powder support by a slow evaporation from acetone solution. Supports with from 1 to 10 wt % loadings were packed into 1.8 m, 0.25 in. o.d. polypropylene columns. This choice of packing and column material minimized extraneous water-support interactions. Loadings on the supports were determined by Soxhlet extraction. Measurements at infinite dilution on these columns showed that the effect of column loading was small. The column used in subsequent experiments had a load of 0.646 g (2.39%) of HPC. The effect of flow rate was also shown to be small. Values of $V_g$ are reported to a precision of ±3%.

The gas chromatograph, a Hewlett-Packard 5722A, was equipped with a thermal conductivity detector. Temperatures of 30 °C and lower were controlled by an external circulating bath, while higher temperatures were controlled by the built-in air oven.

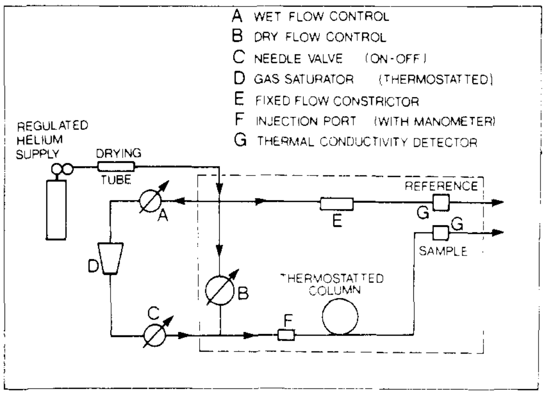

Figure 1. GC apparatus modified to give constant water vapor pressure in carrier gas.

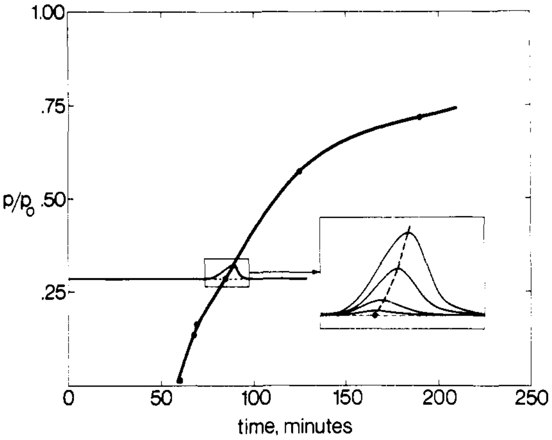

Figure 2. Typical results for EP method. The dotted line in the insert extrapolates to the retention time at the plateau water vapor concentration (solid point). The sorption isotherm is calculated from the line through the solid points at different plateau concentrations.

Injections were made with a Hamilton microlitre syringe, with retention times for infinite dilution studies obtained by extrapolation of the peaks of small injections to zero peak height. Typical injection sizes were 0.05 to 0.001 μL. The smallest injections were obtained by inserting a syringe from which solvent had previously been expelled into the injection port and injecting the resulting air/solvent vapor mixture. Flow rates of the helium carrier gas were measured with a soap bubble flowmeter and corrected for column pressure drop and water vapor content.

The sorption of water onto HPC at finite concentration was measured by the two gas chromatographic and two static methods summarized in Table I. The modification of the carrier gas flow system for finite concentration GC measurements is shown in Figure 1. The "elution by a characteristic point" (ECP) method utilizes the peak shapes of a series of discrete injections of different amounts of vapor to measure $V_R(c)$ and has been described in detail elsewhere.[3,1] The amount of water sorbed at each partial pressure, formally given by eq 1, was calculated according to the more complete equation of Conder and Purnell (eq 16 of ref 3). The ECP method requires rapid equilibration between the stationary and mobile phases. In the "elution on a plateau" (EP) method, a fixed concentration of water vapor is introduced into the helium carrier gas. At each concentration of water, which corresponds to a vapor pressure plateau, the retention times for peaks resulting from small additional injections are measured. The retention times vary with peak height, and so an extrapolation is required to determine the retention time at zero peak height on each plateau. The process is illustrated in Figure 2. The variation in retention time at zero peak height with plateau height has the same form as the characteristic experimental isotherm in the ECP method, and the sorption isotherm is calculated in a similar way.[3,12,13] One advantage of the EP method is that the gas saturator allows a higher partial pressure of water to be achieved than is possible by discrete injection. Second, at each

Table II
Activity Coefficient and Heats of Mixing of HPC at Infinite Dilution of Water

| $T$, °C | ln $V_g$ ±0.03 | ln $(a_1/\phi_1)^\infty$ ±0.03[a] | $-\Delta\bar{H}_m^\infty$ ±1.0,[a] kJ mol$^{-1}$ |
|---|---|---|---|
| 15.0 | 8.67 | 2.38 | 2.6 |
| 19.7 | 8.30 | 2.40 | 3.2 |
| 25.0 | 7.91 | 2.43 | 3.8 |
| 29.3 | 7.66 | 2.45 | 4.3 |
| 34.2 | 7.34 | 2.47 | 4.9 |
| 40.3 | 7.05 | 2.51 | 5.6 |
| 45.1 | 6.74 | 2.54 | 6.1 |
| 49.9 | 6.41 | 2.57 | 6.6 |
| 54.8 | 6.25 | 2.60 | 7.2 |
| 59.6 | 5.92 | 2.64 | 7.7 |
| 64.9 | 5.62 | 2.68 | 8.2 |
| 69.0 | 5.37 | 2.72 | 8.6 |
| 74.7 | 5.11 | 2.76 | 9.2 |
| 79.5 | 4.84 | 2.80 | 9.7 |
| 84.5 | 4.65 | 2.84 | 10.2 |

[a] Calculated from smoothed data (eq 10).

vapor pressure plateau, retention times are measured for very small injections, eliminating problems due to slow equilibration of large injections in the ECP method. The thermal conductivity detector was maintained at a temperature well above 100 °C. Detector response was measured by injecting large samples of water vapor into an empty column held at a series of temperatures. The height of the resultant plateau on the chart recorder corresponds to the vapor pressure of water at the column temperature. The calibration was checked for the EP method by passing the wet carrier gas stream from the column through a drying tube for a known length of time and weighing the water uptake.

The sorption of water on HPC was also measured by two static methods. Sealed sample bottles containing HPC suspended over aqueous $H_2SO_4$ were submerged in a constant temperature bath. The uptake of water by 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.[14] In the second method, a sample of HPC was suspended from a Cahn vacuum microbalance, and the equilibrium vapor pressure of water and weight of water sorbed were measured with stepwise addition of water vapor to the system.

## Results and Discussion

**Infinitely Dilute Region.** The results for the interaction of water with hydroxypropylcellulose as the amount of water approaches zero are shown in Table II. The experimental values for $V_g$ as a function of $1/T$ between 288 and 338 K are conveniently expressed as a second degree polynomial

$$\ln V_g = A + B(1/T) + C(1/T)^2 \qquad (10)$$

where $A = -15.99$, $B = +8540$, $C = -417700$, and the standard error in $V_g = \pm 0.038$. The partial molar heats of mixing at infinite dilution were calculated from the smoothed $V_g$ values (eq 10) using

$$\Delta\bar{H}_m^\infty = -R\left(\frac{\mathrm{d}\ln p_1^0}{\mathrm{d}(1/T)} + \frac{\mathrm{d}\ln V_g}{\mathrm{d}(1/T)}\right) \qquad (11)$$

where the first term represents the latent heat of vaporization of water, and the second term represents the heat of vaporization of water at a very small concentration in hydroxypropylcellulose. The data in Table II show a very marked increase in $-\Delta\bar{H}_m^\infty$ as the temperature increased. The term d ln $V_g$/d$(1/T)$ in eq 11 is almost constant over the temperature range investigated, but the latent heat of vaporization of water changes markedly, resulting in the increase in the enthalpy of mixing. Extrapolation suggests that the solution process would become athermal at about −4 °C, at which point the energy of formation of polymer–water contacts is considered to balance the energy required to break polymer–polymer and water–water contacts. The increasingly exothermic heat may plausibly be attributed to the greater ease of disrupting the hydrogen-bonded water structure as the temperature is increased.

Values for $\chi$ at infinite dilution of water in HPC are in principle readily derived from the GC data in Table II. Thus, if the entropy of mixing is given by the Flory–Huggins theory, $\chi_{FH}$ at any temperature is obtained according to eq 4 by simply subtracting 1 from the tabulated values of ln $(a_1/\phi_1)$. The $\chi_{FH}$ values would then range from 1.38 at 15 °C to 1.84 at 84.5 °C, with a value of 1.51 at 40 °C. However, the assumption of random mixing seems unreasonable for this polymer. Hydroxypropylcellulose film exhibits some crystallinity.[15] If, as previously indicated for water at infinite dilution in poly(ethylene oxide),[16] the water only mixes with the amorphous fraction, then the retention volume in eq 5 should be replaced by $V_g(1 - C)$, where $C$ is the fractional crystallinity of the stationary phase. The crystallinity may be evaluated if GC data are available above and below the melting point,[16,17] but HPC has too high a melting point for this method to be useful. However, a value of 14.9% for the crystallinity of water-cast HPC film has been deduced from calorimetry, X-ray, and density measurements.[15] This value corresponds to a change in $\chi_{FH}^\infty$ of ln (1 − 0.149) = −0.16. Thus, assuming that the crystallinity remains constant from 15 to 85 °C, the values of $\chi_{FH}^\infty$ corrected for crystallinity are given by

$$\chi_{FH}^\infty = \ln (a_1/\phi_1) - 1.16 \qquad (12)$$

The values for $\chi_{FH}^\infty$ are very high, considering that hydroxypropylcellulose is readily dissolved in water below 42 °C. If, however, the random mixing implied in the Flory–Huggins theory becomes impossible at high polymer concentrations because of chain stiffness,[6,18] an alternative model for the mixing entropy term is required. Flory's model for rodlike mixing gives eq 7 and 8 at infinite dilution; the corresponding values for $\chi$ are obtained by subtracting 2 from the ln $(a_1/\phi_1)^\infty$ data in Table II. Thus at 40 °C, $\chi_R = 0.51$, a not unreasonable value when it is remembered that dilute aqueous HPC solutions show a lower critical solution temperature at 42 °C. This suggests that polymer–solvent interaction parameter might remain relatively constant with concentration but that the combinatorial entropy of mixing might change from "Flory–Huggins" to "Flory rodlike" across the concentration range.

**Finite Concentration Region.** The obvious way to test this suggestion is to examine the solvent activity as a function of concentration. Recently, Bergmann and Sundelöf published comprehensive osmotic pressure data for aqueous solutions of Klucel L.[11] These authors discussed their data in terms of a virial expansion, but the Flory–Huggins theory should also be applicable for the relatively high concentrations examined. The volume fraction interaction parameter $\chi$ may be calculated from the osmotic pressure data according to[4]

$$\chi = -\frac{[\pi\bar{V}_1/RT + \ln\phi_1 + \phi_2(1 - 1/\bar{x}_n)]}{\phi_2^2} \qquad (13)$$

where $\chi$ (without subscripts) is the Flory–Huggins interaction parameter derived from osmotic pressure measurements, $\pi$ is the osmotic pressure, $\bar{V}_1$ is the molar volume of water, and $\bar{x}_n$ is the number average molar

Table III
Values for $\chi_1$ and $\chi_2$, Calculated[a] from the Osmotic Pressure Data of Bergmann and Sundelöf

| temp, °C | $\chi_1$ | $\chi_2$ |
|---|---|---|
| 25 | 0.482 | 0.371 |
| 30 | 0.486 | 0.372 |
| 35 | 0.492 | 0.357 |
| 40 | 0.500 | 0.333 |

[a] Calculated from eq 13 and 14. Values are linear least-squares fit.

volume ratio for water and polymer. Taking $\bar{M}_n$ 35 000 and 1.23 as the density of HPC, $\bar{x}_n \simeq 1600$. Volume fractions were calculated from component densities, assuming no volume change on mixing. A marked concentration dependence in the calculated values of $\chi$ was evident, with $\chi$ varying linearly with $\phi_2$ over the experimental concentration range. The data were therefore fitted to the empirical equation[19]

$$\chi = \chi_1 + \chi_2\phi_2 \qquad (14)$$

where $\chi_2$ is the slope and $\chi_1$ is the intercept at $\phi_2 = 0$ of a plot of $\chi$ vs. $\phi_2$. Values for $\chi_1$ and $\chi_2$ are presented in Table III. The values for $\chi_1$ reach the expected value of 0.50 as the temperature approaches the observed cloud point of 42 °C. Furthermore $\chi_2$ is 0.33 at this point. Flory and Daoust[19] indicate that a value of $\chi_2 \leq {}^1/_3$ is a necessary condition for a critical point at $\phi_2 = 0$, whereas a finite critical concentration requires $\chi_2 > {}^1/_3$. While precise phase data are not yet available for this system, preliminary measurements[20] on a similar sample of HPC give a virtually constant cloud point temperature for aqueous solutions from 2% down to a few ppm, in accord with values of $\chi_2$ close to ${}^1/_3$.

The value of $\chi$ at $\phi_2 = 1$ may be estimated from an extrapolation of these data. From eq 14, $\chi = 0.83$ at 40 °C. The value from infinite dilution GC, assuming Flory–Huggins mixing and correcting for crystallinity, is 1.35 according to eq 12. On the other hand the value of $\chi_R$ at 40 °C, assuming rodlike mixing at $\phi_2 = 1$, is the same as that for $\chi_{FH}$ from osmometry at $\phi_2 = 0$. This agreement may be fortuitous, because the values for $\chi$, calculated from osmotic pressure data according to eq 13, are rather sensitive to the value for $\bar{x}_n$. However, it seems noteworthy that with appropriate models for mixing, the same polymer–solvent interaction parameter is obtained at the extremes of the concentration range.

The results of static and GC measurements of water vapor activity at 25 °C across the intermediate concentration range are shown in Figure 3, along with values for water activity calculated from the osmotic pressure measurements. The agreement between the four sorption methods is good, with deviation only at the highest water contents, where the measurement of small changes in vapor pressure with large changes in water content becomes more difficult. The solid curve in Figure 3 is calculated from eq 14, with the values for $\chi$ at 25 °C shown in Table III. The broken curve was calculated from eq 7, with a value of 0.43 for $\chi_R$ from Table II. At the high water side, the results thus are in accord with Flory–Huggins mixing, while at high polymer concentrations the system follows the rigid-rod theory. Scatter in the experimental points inhibits any attempts at precise interpretation. Optical observations[20] indicate that the anisotropic mesophase is found at water concentrations less than $\phi_1 = 0.62$. This is a lower concentration of water than that predicted by Flory's theory[7] for rodlike molecules and is most readily rationalized by noting that HPC, like most cellulosics, is moderately flexible in dilute solution.[21,22] The experimental points for water vapor pressure over the mesophase deviate from the line for rodlike molecules when $\phi_1$ is greater than ~0.05. This again may be due to molecular flexibility. Values for activity as a function of concentration are given in Table IV, along with values of $y$ calculated from eq 6 with $\chi_R = 0.48$ and $x \gg y$. The value of $y$ indicates the disorder in the mesophase, although its significance is questionable if the molecules are not rigid. There is no evidence of a discontinuity or plateau in the variation of water activity with volume fraction; for monodisperse rods, the activity should remain constant over the concentration range where the isotropic phase and mesophase coexist. This must occur around $\phi_1 \simeq 0.6$, but the water activity is too close to that of pure water for the detection of a plateau by direct sorption measurements.

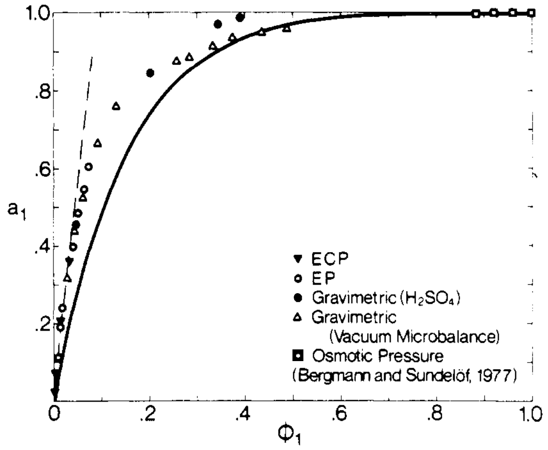

**Figure 3.** Sorption isotherm for water on HPC at 25 °C. Experimental points measured as indicated on figure. Solid and broken lines are calculated for normal and rodlike mixing, respectively (see text).

Table IV
Experimental Activities and Order Parameters for an Aqueous Hydroxypropylcellulose Mesophase at 25 °C

| $a_1$ | $a_1/\phi_1$ | $y$[a] |
|---|---|---|
| 0.0 | 11.30[b] | 1.0 |
| 0.025 | 14.86 | 0.9 |
| 0.070 | 12.80 | 1.0 |
| 0.113 | 12.42 | 1.0 |
| 0.239 | 11.24 | 1.0 |
| 0.317 | 11.53 | 1.0 |
| 0.356 | 10.61 | 1.0 |
| 0.392 | 9.89 | 1.1 |
| 0.486 | 9.23 | 1.1 |
| 0.527 | 8.72 | 1.1 |
| 0.548 | 8.75 | 1.1 |
| 0.606 | 8.29 | 1.2 |
| 0.668 | 7.24 | 1.3 |
| 0.758 | 5.83 | 1.4 |
| 0.847 | 4.17 | 1.8 |
| 0.877 | 3.40 | 2.0 |
| 0.885 | 3.12 | 2.2 |
| 0.920 | 2.74 | 2.4 |
| 0.934 | 2.48 | 2.7 |
| 0.951 | 2.18 | 3.1 |
| 0.960 | 1.96 | 3.6 |
| 0.972 | 2.82 | 2.4 |
| 0.990 | 2.53 | 2.6 |

[a] Order parameter given by eq 6. See text. [b] Limiting value at infinite dilution.

The value of the volume fraction activity coefficient, $a_1/\phi_1$, increases with decreasing water content, except at the lowest water contents, where a slight decrease occurs. Although this effect is too slight to be apparent on the adsorption isotherm (Figure 3), the raw ECP data show clearly that the retention volumes increase with decreasing

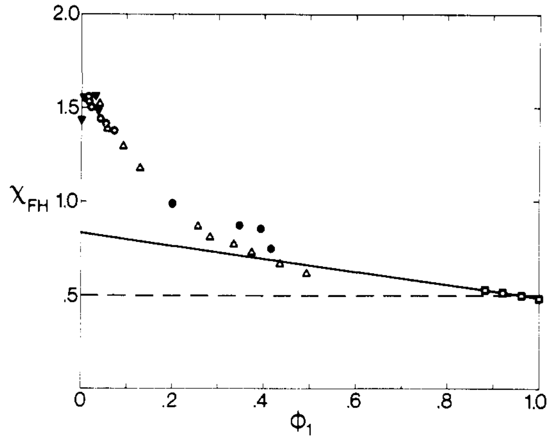

**Figure 4.** Values for $\chi_{FH}$ calculated according to eq 4. Symbols as in Figure 3. Solid line for $\chi$ calculated from eq 14 with $\chi_1$ = 0.482 and $\chi_2$ = 0.371.

water content at very low relative humidities, and the effect is also evident when the data are plotted as $\chi_{FH}$ vs. $\phi_1$ (Figure 4). Possible explanations include an initial hydration of the polymer or disruption of crystalline regions.

In their examination of the activity of organic solvents over liquid-crystalline solutions of poly($\gamma$-benzyl glutamate), Flory and Leonard[8] found that the Henry's law slope, $a_1/\phi_1$ at $\phi_1 = 0$, was much less than expected. They obtained a better fit to their experimental data by introducing a new volume fraction term for the mixing of solvent with only the side chains of the helical polymer molecules. In our case, no such assumption was needed to fit the rigid rod theory with a plausible value of $\chi$.

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# Crystalline Poly(organophosphazene) Blends and Copolymers

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ABSTRACT: The thermal transition behavior of a number of one-to-one aryloxy poly(phosphazene) copolymers with varied para and meta substituted phenoxy repeat units and several related homopolymer blends has been studied. From DSC experiments on the blends, it is concluded that the crystalline phases, and in some cases the amorphous phases as well, are incompatible. All the copolymers are crystalline and exhibit the $T(1)$ transition to a mesomorphic state typical of poly(phosphazene) homopolymers. Based on the thermal transition behavior, the copolymers can be divided into two classes. Class I copolymers, with similar meta or para substituted repeat units, exhibit $T(1)$ transitions close to homopolymer values and enthalpies at least 75% of theoretical. Class II copolymers, with mixed meta/para substituted phenoxy repeat units, exhibit $T(1)$ values lower than either homopolymer and enthalpies less than one-half the rule-of-mixtures value. The crystalline behavior is attributed to isomorphism. X-ray results on the *p*-chlorophenoxy/*p*-cresoxypoly(phosphazene), a class I copolymer, show that only a single unit cell occurs, while in a typical class II copolymer two unit cells are present. This suggests that class I copolymers exhibit type I and class II type II isomorphism in the sense defined by Natta and by Wunderlich.

Most poly(organophosphazene) homopolymers, with a single type of alkoxy or aryloxy substituent, are semicrystalline materials. These polymers generally exhibit two first-order transitions.[2-5] The lower transition, which is marked by a prominent enthalpy change, is now recognized as representing the transition to a partially ordered state.[5-10] The upper transition represents the true melting point which occurs at 350 to 400 °C in the aryloxy homopolymers and is close to the decomposition temperature.[3-5,9]

Poly(phosphazene) copolymers involving the use of mixed substituents to inhibit the development of crystallinity received early attention.[11] The use of mixed fluoroalkoxy substituents at near equimolar proportions