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# Polymer Solutions with Specific Interactions: $\chi$ Parameter for Poly(4-hydroxystyrene) + Acetone

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ABSTRACT: The vapor pressure of poly(4-hydroxystyrene) + acetone has been measured at six temperatures between 298.15 and 318.15 K and for $0.35 \le w_1 \le 0.89$, $w_1$ being the weight fraction of acetone. The Flory–Huggins $\chi$ parameter has been calculated and found to increase with increasing $w_1$. A thermodynamic consistency test has been developed, and the data have been found to satisfy it. The local composition in the mixture has been discussed in terms of the Kirkwood–Buff–Zimm integrals and found to differ significantly from the bulk composition. Finally, a rigid-lattice model that incorporates the local composition concept has been tested. Differences between predicted and experimental results are larger than the uncertainty of the measurements.

## I. Introduction

An understanding of the thermodynamics of polymer solutions is important in many processes of technological interest.[1] Proper design and engineering of many polymer processes depend greatly upon accurate modeling of properties such as solvent activity; e.g., polymerization frequently takes place in solution, and demixing is not a rare phenomenon, even if the monomer serves as the solvent. The blending and compounding of polymers reveal emphatically the sensitivity toward phase separation, which, depending on application purposes, may or may not have to be avoided, since the mechanical properties of polymer blends, block copolymers, and composites are enormously dependent on phase relationships and morphology.[2]

Many theoretical approaches have been available for years for predicting the nonideal behavior of polymer solutions. Most of them can be considered as either generalized van der Waals (GVDW)[3-5] or lattice-like models,[6-11] and the most sophisticated of them currently give a correct qualitative behavior of the phase diagrams found in polymer systems. Two hypotheses are frequently assumed in the development of such theories: (i) that the intermolecular potential has an isotropic character and (ii) that the distribution of the molecules in the mixture is random. The existence of anisotropy of shape and/or multipolar moments either in the polymer(s) or in the solvent(s) make the first assumption a rather crude one. On the other hand, the existence of a nonrandom distribution of the molecules is a very well-known fact even for simple fluid mixtures,[12-14] and in polymer systems the behavior of the so-called preferential sorption has been extensively studied.[15-17]

The interest in the study of polymer blends has attracted much attention toward polymer systems in which there exist strong specific interactions, since their existence seems to be the reason for the miscibility of a majority of polymer pairs.[18-20] Specific interactions have a highly directional character, and it is well-known that hydrogen bonds can lead to phase diagrams that cannot be described by van der Waals like theories or with isotropic lattice-like models.[21,22] Directional interactions have been introduced in more or less empirical ways in the previous kind of models, most frequently, at the cost of introducing new adjustable parameters;[23-25] however, it still remains to be known whether they are able to describe experimental data in wide ranges of temperature, as needed in many practical cases.

Nonrandomness has also been introduced in GVDW and lattice models either empirically or based on the quasichemical hypothesis.[26-28] Even though in some cases improvement over the random distribution has been claimed, recent tests against computer simulation for simple fluids indicate that the most frequently used local expressions are not adequate.[29,30] Similar conclusions have been reached from experimental data on real mixtures of simple molecular fluids.[31]

Besides the difficulties imposed by both specific interactions and nonrandomness, it must be taken into account that the prediction of phase equilibria in polymer blends puts a strong quantitative exigence on any theoretical prediction. In effect, it is well-known that the compatibility of two polymers may depend on the solvent from which they are cast.[32-34] In general, when the interaction of the solvent with one polymer is different from that with the other, the polymers become less compatible.[35] Frequently, specific interactions between the two polymers exist when their chemical nature is different enough, and, in that case, also their interaction with the solvent could be different.

From all the above it seems clear that a good knowledge of the role of specific interactions in polymer–solvent systems is a necessary step for predicting the behavior of many polymer systems of interest. In this paper we present an experimental study of the $\chi$ interaction parameter for poly(4-hydroxystyrene) + acetone (P4HS + Ac) as a function of temperature and composition. Coleman et al.[36,37] have pointed out the formation of hydrogen bonds between hydroxyl groups of P4HS and carbonyl groups of poly(vinyl acetate) (PVA), which makes them miscible in all proportions. The P4HS + PVA blends are frequently cast from Ac, a common solvent for both polymers; hence a knowledge of the $\chi(T,\phi)$ surface for P4HS + Ac is a first step toward the understanding of the thermodynamics of P4HS + PVA + Ac and the calculation of the P4HS + PVA interaction parameter. In addition, the system P4HS

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Table I
**Vapor Pressures (Torr) for P4HS + Ac at Different Temperatures as a Function of the Weight Fraction of Acetone ($w_1$)**

| | $T$/K | | | | | |
|---|---|---|---|---|---|---|
| $w_1$ | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 | 318.15 |
| 0.3477 | 122.7 | 149.16 | 183.46 | 222.99 | 270.69 | 328.28 |
| 0.3852 | 133.1 | 165.11 | 200.08 | 246.98 | 299.56 | 363.15 |
| 0.4422 | | 182.17 | 225.76 | 276.18 | 334.59 | 404.69 |
| 0.4515 | 148.0 | 184.72 | 227.93 | 279.40 | 341.15 | 411.66 |
| 0.5077 | 159.9 | 199.86 | 246.19 | 301.49 | 365.9 | 441.40 |
| 0.5409 | 165.8 | 204.98 | 252.51 | 311.42 | 378.39 | 456.47 |
| 0.5598 | 167.3 | 207.86 | 256.07 | 315.17 | 384.04 | 464.37 |
| 0.5965 | 171.7 | 213.23 | 263.74 | 323.40 | 394.40 | 474.47 |
| 0.6372 | 175.3 | 217.70 | 268.98 | 329.67 | 402.53 | 485.18 |
| 0.6379 | 174.0 | 216.94 | 268.23 | 329.64 | 401.17 | 484.46 |
| 0.6890 | 178.3 | 220.55 | 274.67 | 336.50 | 408.66 | 493.12 |
| 0.7513 | 181.1 | 225.81 | 278.77 | 341.15 | 414.80 | 500.53 |
| 0.7807 | 182.5 | 226.86 | 280.51 | 343.54 | 416.60 | 503.52 |
| 0.8137 | 183.2 | 227.92 | 281.57 | 345.17 | 418.56 | 505.48 |
| 0.8561 | 183.7 | 228.80 | 282.93 | 346.13 | 420.79 | 508.19 |
| 0.8898 | 184.1 | 228.64 | 282.83 | 346.89 | 421.89 | 508.97 |

+ Ac has an intrinsic interest since P4HS has many applications in the photography and electronics industries.[38-40]

The rest of the paper is organized as follows: In section II a brief description of the experimental procedure is given. Section III gives the experimental data and their correlation. Section IV discusses the consistency of phase quilibria data in polymer–solvent systems. Section V discusses the local composition in the P4HS + Ac system, and finally in section VI the predictive ability of a recently proposed lattice model is tested.

## II. Experimental Section

The vapor pressures have been measured by using a technique of the static type, described in detail elsewhere.[41] The polymer was degassified by keeping it under high vacuum ($p \leq 10^{-6}$ Torr) for 24 h; afterward the cell was sealed and observed during a week for the appearance of any desorbed gas in the cell. Acetone was degassified according to the procedure described previously.[41]

The amounts of polymer in the cell and of acetone in each ampule were known to within ±0.03 mg. The temperature was kept constant within ±3 mK over 24-h periods and was measured with a thermistor calibrated against a platinum thermometer; the calibration was checked biweekly against a Ga melting point cell. The uncertainty in $T$ was <±8 mK, and the agreement with the IPTS-68 for $290 \leq T/\mathrm{K} \leq 323$ was ±0.01 K. The heights of the menisci in the manometers were read with a cathetometer precise to ±5 μm. Under the above conditions the precision in the vapor pressure was $\pm 2.2 \times 10^{-2}$ Torr for $p \leq 150$ Torr and $\pm 6.0 \times 10^{-2}$ Torr for higher pressures.

After each mixture was made, equilibrium was reached in a period of 15 h with the mixture continuously stirred, except for the mixtures with weight fraction of acetone $w_1 < 0.38$ for which 1-3 days was necessary. Each vapor pressure was the average of three measurements that agreed within the experimental error.

Acetone was Carlo Erba RPE and was used without further purification, except for being kept over 0.4-nm molecular sieves. P4HS was obtained from Polysciences (U.K.) ($M_w$ = 1000–7000). Vapor pressure osmometry of P4HS dissolved in 1,4-dioxane gave $M_n$ = 1500. HPLC experiments revealed a polydispersity $M_w/M_n \simeq 2$.

The density of acetone at 293.15 K was 0.791 g·cm$^{-3}$, which compares well with the value reported in the literature.[42]

## III. Results

The vapor pressures of the system P4HS + Ac were measured at six temperatures between 293.15 and 318.15 K over a wide composition range: $0.34 \leq w_1 \leq 0.89$. The results are shown in Table I. Figure 1 shows the data at the two temperatures. The solvent activity was calculated according to

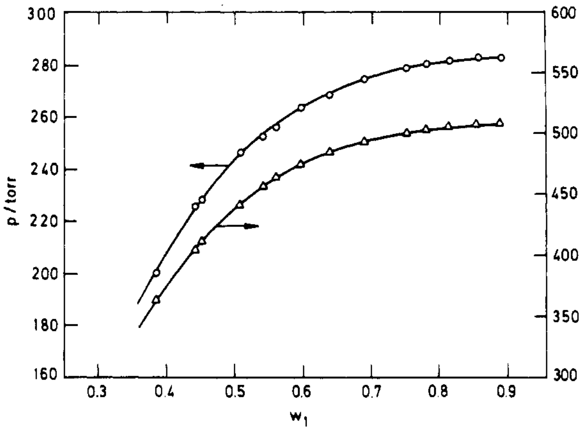

Figure 1. Vapor pressures of the system P4HS + Ac at two temperatures. The symbols are experimental data, while the lines represent the fit to eq 1: (○) 303.15 K; (△) 318.15.

$$a_1 = (p/p_1^\circ) \exp[-B_{11}(p_1^\circ - p)/RT] \qquad (1)$$

where $B_{11}$ and $p_1^\circ$ are the second virial coefficient and the vapor pressure of pure acetone, respectively. $B_{11}(T)$ was taken from ref 43 and $p_1^\circ(T)$ from ref 44. From the $a_1$ values the calculation of Flory's χ parameter is immediate. In general, it is difficult to obtain information on the temperature dependence of χ from phase equilibria experiments, since it is usually masked by the experimental uncertainty. However, for the very well studied polystyrene + cyclohexane system, a simple functional form has been proposed for $\chi = \chi(T,\phi)$:[45]

$$\chi = \chi_0 + \chi_1\phi_2 + \chi_2\phi_2^2; \qquad \chi_0 = \chi_{01} + \chi_{02}T^{-1} \qquad (2)$$

$\phi_2$ being the volume fraction of polymer. Once eq 2 is adopted, the parameters $\chi_i$ can be obtained from the vapor pressure data of Table I. $\phi_2$ was calculated from $w_1$ using the values for the density of acetone as a function of temperature taken from ref 42, and a density of 1.15 g·cm$^{-3}$ for P4HS obtained by pycnometry at 298.15 K (see also ref 46). The optimum values of the parameters were $\chi_{01}$ = 0.290, $\chi_{02}$ = 25.654 K, $\chi_1$ = −0.369, and $\chi_2$ = −1.983, which lead to a mean standard deviation (msd) of 0.68 Torr for the whole set of data. Figure 1 shows the calculated vapor pressures using eqs 1 and 2 and the $\chi_i$ parameters; as can be observed, the agreement is very good, supporting the validity of eq 2. It has to be remarked that the point corresponding to the most concentrated mixture, $w \simeq 0.35$, has been deleted since it was impossible to obtain an acceptable fit when it was included. Other empirical equations with up to 12 adjustable parameters were used instead of eq 2, and the points corresponding to $w \simeq 0.35$ always deviated by more than 5 times the msd of the fits. In addition, the points of $w_1 \simeq 0.35$ were found to be inconsistent from the thermodynamic point of view (see below).

## IV. Thermodynamic Consistency of Vapor–Liquid Equilibrium Data

As already said, it is difficult to obtain the temperature and composition dependence of $\chi$ from phase equilibrium experiments. This is especially true when, for a given system, data from different system sources are considered.[47] Hence, a test for checking the thermodynamic consistency of phase equilibrium data (and thus $\chi$ parameters) seems desirable. It is possible to develop such a test for $\chi$, and more especially for $(\partial\chi/\partial T)_\phi$ and $(\partial\chi/\partial\phi)_T$, from general conditions of phase equilibrium.[48,49] In effect, it is possible to show that (see Appendix)

$$0 \geq -\frac{\phi_2{}^2\left[-2\chi\frac{\phi_1}{x_2} + \left(\frac{\partial\chi}{\partial x_1}\right)_{T,p} x_1\right] + 1 - x_1 x_2 \frac{\beta^2}{(1-\beta x_1)^2}}{x_1\left(\ln\phi_1 + \left(1 - \frac{1}{r_2}\right)\phi_2 + \phi_2{}^2\left[\chi + T\left(\frac{\partial\chi}{\partial T}\right)_{x,p}\right]\right)} \tag{3}$$

with $\beta = (\gamma - 1)/\gamma$ and $\gamma = r_2/r_1 = \upsilon_2/\upsilon_1$.

The data presented in this paper for P4HS + Ac described by eq 2 have been analyzed in terms of eq 3 and have been found to be consistent within the experimental uncertainty for $w_1 \geq 0.44$. The data with $w_1 \leq 0.38$ showed negative values for the right-hand side of eq 3, although they were so small that they are almost within the experimental error of $(\partial t/\partial x)_p$. Two factors may be the cause of this behavior. On one hand, these experimental points are in the limit of the $p,\phi,T$ surface, and thus a spurious behavior of the fitted surface might exist as a purely numerical artifact. In fact, $(\partial\chi/\partial T)$ takes quite small values ($\simeq 2 \times 10^{-3}$), and assuming $(\partial\chi/\partial T)$ to be for $w_1 \leq 0.38$ the same as for $w_1 \geq 0.44$, the consistency test is satisfied. On the other hand, the mixtures with $w_1 \leq 0.38$ were very viscous, and although long equilibration times were allowed, systematic errors cannot be completely discarded. We can, therefore, conclude that a consistent $\chi(T,\phi)$ surface is available for P4HS + Ac for $w_1 \geq 0.35$ and $293 \leq T/\mathrm{K} \leq 318$.

The $\chi(T,\phi)$ surface previously proposed for PS + $C_6H_{12}$[45] has been tested according to the equality (3) and found to be consistent over the whole $\phi$ range and for the $T$ interval suggested by the authors.

Finally, it must be remarked that the right-hand side of equality (3) takes values closer to zero on the high-concentration side; thus small errors in the data can lead to a negative values, and thus equality (3) is an energy test for solvent absorption data.

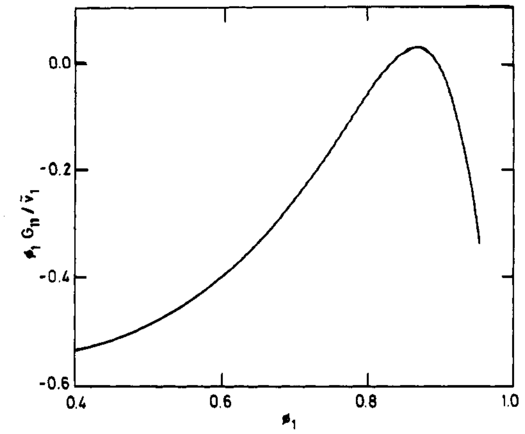

**Figure 2.** Cluster integrals, $\phi_1 G_{11}/\bar{\upsilon}_1$, of the system P4HS + Ac at 298.15 K for the whole range of solvent volume fraction, $\phi_1$.

## V. Kirkwood–Buff–Zimm Integrals

Kirkwood–Buff (KB) theory has been used during the past few years for discussing the tendency of a component to homo- or heterocoordination in binary mixtures.[50,51] Such a discussion can be done in terms of the Kirkwood–Buff–Zimm integrals, which are related to the pair correlation functions. $G_{11}$ is defined as[52,53]

$$G_{11} = \frac{4\pi}{\upsilon^2}\int_0^\infty F_2(i,j)\,\mathrm{d}r_i\,\mathrm{d}r_j \tag{4}$$

where $(1/\upsilon^2)F_2(i,j)\,\mathrm{d}r_i\,\mathrm{d}r_j$ is the probability that molecules $i$ and $j$ are each at the positions specified by the coordinates $r_i$ and $r_j$ in the range of these coordinates $\mathrm{d}r_i$ and $\mathrm{d}r_j$. Inversion of the KB theory allows $G_{11}$ to be calculated from experimental data. For noncompressible fluids $G_{11}$ is given by

$$G_{11}/\bar{\upsilon}_1 = -\phi_2\left(\frac{\partial(a_1/\phi_1)}{\partial a_1}\right)_p - 1 \tag{5}$$

where $\bar{\upsilon}_1$ is the partial molar volume of the solvent. Considering the compressibility of the fluids would add a term to the right-hand side of eq 5, but it turns out to be negligible, especially if one considers that $G_{11}$ is affected by the relatively large uncertainty associated with $[\partial(a_1/\phi_1)/\partial a_1]_p$.[50,51]

At a molecular level, $\phi_1 G_{11}/\bar{\upsilon}_1$ represents the average number of molecules of solvent around a solvent molecule in excess over the number corresponding to the case where the solvent molecule is absent. As has been pointed out,[31] due to the size difference between the molecules of components 1 and 2, $G_{11}$ does not allow one to make a quantitative discussion of the local composition; nevertheless it is very useful for visualizing the variation of the local composition with composition. This way, increasing $\phi_1 G_{11}/\bar{\upsilon}_1$ corresponds to increasing the solvent tendency to homocoordination. As a reference one must consider that $\phi_1 G_{11}/\bar{\upsilon}_1 = -\phi_1$ for an ideal solution for which $a_1/\phi_1$ = constant (notice that this does not correspond to $\chi = 0$ unless $r_2/r_1 = 1$!).

In terms of eq 2

$$\phi_1 G_{11}/\bar{\upsilon}_1 = \frac{\phi_2\Delta - \phi_1/r_2}{\phi_1/r_2 + \phi_2 - \phi_2\Delta} \tag{6}$$

with $\Delta = 2\chi_0 + (3\chi_1 - 2\chi_0)\phi_2 + (4\chi_2 - 3\chi_1)\phi_2{}^2 - 4\chi_2\phi_2{}^3$.

Figure 2 shows $G_{11}$ for P4HS + Ac at 298.15 K. Due to the large uncertainty in $G_{11}$, its temperature dependence cannot be discussed. As can be observed, $\phi_1 G_{11}/\bar{\upsilon}_1$ increases with $\phi_1$ until $\phi_1 \simeq 0.6$ and then decreases. A similar behavior was found by Saeki et al. for some polyisoprene solutions.[54,55] It is possible to give a naive qualitative explanation for the observed curve. For low $\phi_1$ the acetone molecules are mainly used in forming hydrogen bonds with the hydroxyl groups of P4HS. For high enough $\phi_1$, most of the OH groups are already surrounded by Ac molecules, and then the Ac molecules can only interact either with Ac molecules or with the backbone of the P4HS chain. However, the P4HS backbone is essentially the same as that of PS, and it is well-known that Ac is a nonsolvent for PS;[56] thus one should expect a nonfavorable interaction and therefore an increase in the tendency of Ac to homocoordination. For dilute enough solutions there are so many molecules that most of them do not participate in interactions with the polymer, and the local composition tends to the bulk, i.e., to a random distribution.

We may conclude that for the P4HS + Ac system the distribution of the molecules is clearly nonrandom, a fact that has to be considered by any theory that attempts to describe the data.

## VI. Rigid-Lattice Models

Rigid-lattice models have been shown to be able to correlate thermodynamic properties of mixtures with hydrogen bonds.[57,58] On the other hand, the introduction of nonrandomness, even in the quasichemical approach, has improved the description of polymer–solvent 1–solvent 2 systems.[59] Hence, in this section we will test the ability of the variable-size ASOG model,[60,61] which uses a modified Flory–Huggins lattice model for the combinatorial contribution and a group contribution model, ASOG,[62] for the accounting of the energetic contributions.

In the Flory–Huggins model

$$\ln a_1 = \ln a_1^{c} + \ln \gamma_1^{G} \tag{7}$$

with

$$\ln a_1^{c} = \ln \phi_1 + (1 - 1/r_2)\phi_2 \tag{8}$$

and

$$\ln \gamma_1^{G} = \chi \phi_2^{2} \tag{9}$$

The variable-size hypothesis is introduced through the variable $R_1$, defined as

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})(1 - w_1)} \tag{10}$$

where $w_1$ is the weight fraction of solvent, $\gamma_1^{G\infty}$ is the enthalpic contribution to the activity coefficient at infinite dilution, which, as we will see, will be calculated with the ASOG model, and $\Omega_1^{\infty}$ is the weight fraction activity coefficient at infinite dilution, which will be the only adjustable parameter of the model. According to the variable-size model, the combinatorial contribution to ln $a_1$ is given by eq 8 but with the $\phi_1$ substituted by $R_1$.

According to the ASOG method

$$\ln \gamma_1^{G} = \sum_k \nu_{k1}(\ln \Gamma_k - \ln \Gamma_k^{*}) \tag{11}$$

$$\ln \Gamma_k = -(\ln \sum_l X_l A_{kl}) + 1 - \sum_l \frac{X_l A_{lk}}{\sum_m X_m A_{lm}} \tag{12}$$

$$\ln \Gamma_k^{*} = \ln \Gamma_k(x_1{=}1) \tag{13}$$

$$X_k = \sum_i x_i \nu_{ki} / \sum_j \sum_l x_j \nu_{lj} \tag{14}$$

$$\ln \gamma_1^{\infty} = \ln \gamma_1^{G}(x_1{=}0) \tag{15}$$

In eqs 11–15 $\nu_{ki}$ is the number of $k$ groups in a molecule of component $i$, $X_k$ is the mole fraction of group $k$, and $\Gamma_k$ is the activity coefficient of group $k$. Indices $i$ and $j$ refer to the components in the mixture, while indices $k$, $l$, and $m$ refer to functional groups. $A_{kl}$ ($\neq A_{lk}$) are parameters that characterize the interactions between groups $k$ and $l$ and are usually expressed as

$$A_{kl} = \exp(a_{kl} + b_{kl}/T) \tag{16}$$

**Table II**
**Number of Groups $\nu_{kl}$ and Molecular Weight $M_w$ per Repeating Unit for the P4HS + Ac System**

| | $\nu_{ki}$ | | | | |
|---|---|---|---|---|---|
| | $CH_3$[a] | CO | ArCH | ArOH | $M_w$ |
| acetone | 2 | 1 | 0 | 0 | 58.081 |
| P4HS | 2 | 0 | 6 | 1 | 120.152 |

[a] $CH_3$, $CH_2$, and CH are considered equivalent. $\nu_{ki}' = \nu_{ki}$(acetone), $\nu_{ki} = \nu_{ki}'M_w$(polymer).

**Table III**
**ASOG Coefficients $a_{kl}$ for the P4HS + Ac System Groups[a]**

| | $CH_3$ | CO | ArCH | ArOH |
|---|---|---|---|---|
| $CH_3$ | 0 | 2.6172 | –0.7457 | –6.5482 |
| CO | –1.7588 | 0 | –0.4021 | –0.3283[b] |
| ArCH | 0.7297 | 0.9273 | 0 | 0.6483 |
| ArOH | 3.5403 | –0.7262[b] | –2.0123 | 0 |

[a] Reference 62. [b] OH has been used instead of ArOH because of the lack of data.

**Table IV**
**ASOG Coefficients $b_{kl}$ for the P4HS + Ac System Groups[a]**

| | $CH_3$ | CO | ArCH | ArOH |
|---|---|---|---|---|
| $CH_3$ | 0 | –865.1 | 146.0 | 2719.5 |
| CO | 169.6 | 0 | –216.8 | 1.3[b] |
| ArCH | –176.8 | –185.8 | 0 | –252.0 |
| ArOH | –2282.8 | 2.9[b] | –478.0 | 0 |

[a] Reference 62. [b] OH values used because of lack of data.

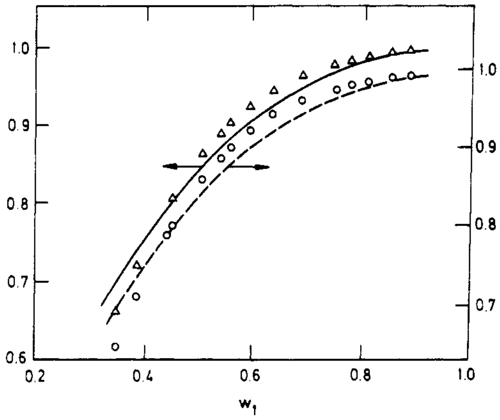

**Figure 3.** Solvent activities: symbols, experimental values; lines, calculated with the variable-size ASOG model. (○, - - -), 298.15 K; (△, —), 293.15 K.

The values of $a_{kl}$ and $b_{kl}$ are usually determined from excess property data of mixtures of solvents. Tables II–IV collect the necessary parameters for the P4HS + Ac system.[62] Due to the lack of data, we have not distinguished between aromatic and aliphatic OH groups. From the $a_1$ data obtained from eqs 1 and 2 we have obtained $\Omega_1^{\infty}$ = 2.281 for the present system (mean standard deviation 0.024). Figure 3 shows the predictions of the variable-size ASOG model for 293.15 and 298.15 K; as can be observed, the model is not able to reproduce quantitatively the composition dependence of the data. The predictions for other temperatures are similar. Even though one could be tempted to say that the ASOG model does not describe correctly the nonrandomness in solutions with hydrogen bonds, similar discrepancies between experimental and predicted $a_1$'s have been found for the PVA + Ac system,[63] and, of course, no hydrogen bonds are present in that system. Thus perhaps, contrary to the case of solvent mixtures, the free volume contributins can by no way be neglected in polymer associated solutions, and models including both effects must be used. A test of some of those models and an experimental study of the PVA + Ac and P4HS + PVA + Ac systems are in progress.

## VII. Conclusions

The vapor pressure of P4HS + Ac as a function of composition has been measured at temperatures between 298.15 and 318.15. The dependence of the $\chi$ parameter can be described by a relatively simple function. The results have been found to be thermodynamically consistent according to a test developed in this paper.

The Kirkwood–Buff–Zimm integrals indicate that the solvent molecules have a clear tendency to homocoordination through most of the composition range.

The variable-size ASOG model is not able to describe the experimental data. It is suggested that although the thermodynamics of solvent mixtures is mainly determined by the hydrogen bonds, the free volume contribution cannot be neglected in the present mixture.

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## Appendix. Thermodynamic Consistency Test

Along the vapor–liquid locus[48,49] it holds that

$$(\partial T/\partial x_1^{I})_p = -(x_1^{I} - x_1^{II})RT^2/(S_{cc}^{I}L^{II}) \qquad \text{(A1)}$$

where $x_1$ is the mole fraction of solvent and I and II refer to the liquid and vapor phases, respectively (hence $x_1^{II} = 1$!).

In addition

$$L^{II} = (1 - x_1^{II})L_2 + x_1^{II}L_1 \qquad \text{(A2)}$$

with

$$\frac{L_1}{T} = \left[\frac{\partial \mu_1^{II}(T,x_1^{II})}{\partial T}\right]_{x_1^{II},p} - \left[\frac{\partial \mu_1^{I}(T,x_1^{I})}{\partial T}\right]_{x_1^{I},p} \qquad \text{(A3)}$$

$\mu_1$ being the chemical potential of the solvent. Similar equations hold for $(\partial T/\partial x^{II})_p$, $L^{I}$, and $L_2$. Considering that $x_1^{II} = 1$ and for most polymer–solvent systems the difference between the equilibrium vapor pressure and that of the pure solvent is small, one can finally write

$$\frac{L_1}{T} = S^{\text{comb}} - \left(\frac{\partial(\mu_1 - \mu_1^{\circ})^{\text{res}}}{\partial T}\right)_{x_1^{I},p} \qquad \text{(A4)}$$

where the terms "comb" and "res" refer to combinatorial and residual contributions to $\mu_1 - \mu_1^{\circ}$.

On the other hand, the long-wave limit of the concentration–concentration correlation function, $S_{cc}^{I}$, can be written as[64]

$$S_{cc}^{I} = (1 - x_1^{I})\left(\frac{\partial \ln a_1}{\partial x_1^{I}}\right) \qquad \text{(A5)}$$

Using the Flory–Huggins expression for $\mu_1 - \mu_1^{\circ}$ [65] and eq 2 and after substitution in eqs A1–A5, it is possible to arrive at eq 3.

## References and Notes

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