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# Vapor−Liquid Equilibria of Water, Methanol, and Methyl Acetate in Poly(vinyl acetate) and Partially and Fully Hydrolyzed Poly(vinyl alcohol)

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ABSTRACT: A general procedure has been developed to predict the vapor−liquid equilibria (VLE) of solvent/copolymer systems with the Panayiotou and Vera equation of state (PV-EOS), using binary interaction parameters deduced from homopolymer VLE data. Mixing rules are proposed for the PV-EOS pure-component parameters and homopolymer−solvent binary interaction parameters in order to predict solvent solubilities in copolymer systems. This methodology has been evaluated with VLE data acquired in this study for water, methanol, and methyl acetate in poly(vinyl acetate), poly(vinyl alcohol), and a copolymer comprised of these two homopolymers containing 88% (molar) poly(vinyl alcohol) repeat units. The predictions from the PV-EOS of the copolymer VLE are in excellent agreement with our experimental data.

## Introduction

Poly(vinyl alcohol) (PVOH) is a semicrystalline, water-soluble commodity polymer of major industrial importance. Historically used in adhesives, textile fibers, paper products, and pervaporation membranes,[1] this versatile material has been more recently employed within drug release media[2] and is being applied in other biomedical applications.[3,4] PVOH is commercially produced through the hydrolysis of poly(vinyl acetate) (PVAc) since the vinyl alcohol monomer is not a stable compound. Consequently, all forms of PVOH are essentially poly(vinyl acetate−vinyl alcohol) copolymers of varying degrees of hydrolysis. Although solvent sorption in this family of copolymers has been studied,[5−10] many gaps still remain in our knowledge base for these systems. Unfortunately, few PVOH sorption studies in the literature adequately deal with the important issues of crystallinity and amorphous phase composition and are seldom conducted at the elevated temperatures of relevance to industrial processes.

In this work, the binary VLE of three solvents (water, methanol, and methyl acetate) with PVAc, PVOH, and an 88% hydrolyzed PVOH were studied with various techniques. In addition, a method is proposed for predicting the copolymer VLE with the PV-EOS. This method is general; once solvent + homopolymer VLE data are correlated, only the composition of the copolymer must be known to predict the copolymer VLE. All of the solvents studied in this work are important participants in the hydrolysis of PVAc. In the formation of PVOH, acetate groups in PVAc react with methanol (a process generally catalyzed by a strong base) to form vinyl alcohol units and methyl acetate as a byproduct. Water is formed as an intermediate compound during this reaction and also plays a key role in downstream separation and drying processes. These operations are commonly carried out at temperatures up to 130 °C. Therefore, it is desirable to conduct studies at elevated temperatures.

Crystallinity is an important issue that must be carefully considered in any sorption study involving PVOH. Solvent sorption is generally accepted to occur only in the amorphous region of polymers while the crystalline region is considered to be impenetrable to solvent. Fully hydrolyzed PVOH, however, is miscible in water at temperatures of 85−95 °C.[11] Consequently, crystal dissolution occurs under certain conditions. For the purpose of this study, where sorption is measured at elevated temperatures, it is crucial to the accuracy of the VLE data that the crystal content is well-defined. There are several studies of PVOH crystal behavior in the presence of water that appear in the literature. Peppas[12] reported that water sorption at 30 °C did not influence the crystal content of PVOH as measured by infrared spectroscopy and classic density measurements. In separate studies, Iwamoto et al.[13] and Hodge et al.[6] using laser Raman spectroscopy and X-ray diffraction, respectively, report that the presence of water in PVOH at room temperature does indeed dissolve crystals. The discrepancies between these findings likely have more to do with the pretreatment of the PVOH than the experimental techniques used in each of these studies. Hodge et al. pretreated their samples at temperatures far below the glass transition temperature of dry fully hydrolyzed PVOH, i.e., 85 °C,[14] while Iwamoto et al. pretreated their samples at higher temperatures (up to 150 °C) but for only 10 min. Peppas used a pretreatment regimen at temperatures up to 120 °C for up to 90 min, apparently beginning this process with a small amount of water contained in the polymer. The temperature exposure and presence of water during crystal formation may be the key to explaining why in some cases the crystals were found to dissolve and in other cases they were not. In a more recent study using X-ray diffraction

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measurements and computer modeling, Assender and Windle[15,16] report that PVOH crystal packing efficiencies increased (higher overall crystal density) with higher annealing temperatures. More importantly, they found that when water is present during the annealing process (at elevated temperature) even more perfect crystals with higher density are formed than could be obtained with heat treatment alone at any temperature. This evidence suggests that crystals formed solely with heat treatment (especially at lower temperatures) are more vulnerable to water dissolution because there are, as Assender and Windle describe it, some "unoccupied sites" within the crystal structure. Presumably, water can enter these defects, replace the vinyl alcohol−vinyl alcohol hydrogen bonds, and initiate crystal dissolution. These findings led us to employ a harsh annealing procedure for our PVOH and PVOH 88% samples that entails extended exposure to high water activity at high temperatures in order to form as stable a crystal structure as possible.

## Experimental Section

**Materials.** PVAc was purchased from Aldrich Chemical Co. and had a molecular weight of 113 000 g/mol. PVOH and PVOH 88% were obtained from Air Products and Chemicals, Inc. The fully (99%) hydrolyzed PVOH sample had a molecular weight of 116 000 g/mol. The 88% hydrolyzed PVOH had a molecular weight of 103 000 g/mol. Both the 99% hydrolyzed and 88% hydrolyzed PVOH samples had a polydispersity index of 1.8. For ease of further discussion, PVOH will refer to the 99% hydrolyzed material while PVOH 88% will refer to the partially hydrolyzed polymer.

To prepare the semicrystalline polymer samples used in these experiments, the as-received PVOH and PVOH 88% were first dissolved in a solvent (either water or dimethyl sulfoxide) and then cast into films of different thicknesses to dry. After the sample films were dried at room temperature, they were annealed at 110 °C in the presence of water vapor at an activity of 0.7 in a quartz-spring gravimetric sorption column. The films were exposed to these conditions for 5 h and then placed in a vacuum oven to remove the residual water. This annealing process produced samples of PVOH and PVOH 88% with crystallinities of 64% and 39%, respectively. These values were obtained by modulated differential scanning calorimetry.

**Experimental Techniques.** The majority of the VLE data presented in this work were obtained using a gravimetric sorption balance that employs a quartz spring as the weight sensor.[17] Since the semicrystalline PVOH samples do not flow at the conditions of interest in this study, unconstrained films were suspended from the quartz spring and maintained at the experimental temperature of interest. The PVAc samples, however, were placed in a titanium sample holder. Before the gravimetric sorption experiments were conducted, the samples were devolatilized until no further weight loss was detectible. The polymer samples were subsequently exposed to pure vapors of water, methanol, and methyl acetate at different activities. PVOH and PVOH 88% are known to degrade if exposed to high temperatures for long periods of time. Consequently, the thickness of the polymer sheets was selected so that each sorption experiment could be completed during a working day to avoid this result. Residual catalyst in the PVOH 88% samples coupled with the presence of methanol was found to reinitiate the hydrolysis reaction. Thus, only samples devoid of catalyst were used in this study. The solubility of methyl acetate in PVOH was found to be so low that low-pressure gravimetric sorption was not a viable technique for taking these measurements. Instead, the gas-phase IR technique as developed by Zielinski et al.[18] was used. Finite concentration inverse gas chromatography[19] was used to obtain data for the methanol−PVAc system. The capillary column used in this study was furnished by Restek Corp. In this work, the activity of the solvent is reported as the ideal activity, $a_1 = P_1/P_1^{sat}$, where $P_1$ is the equilibrium pressure of the solvent and $P_1^{sat}$ is the vapor pressure of the solvent at the experimental temperature.

## Theory and Analysis

**The Panayiotou−Vera EOS.** Panayiotou and Vera[20] have developed an equation of state (PV-EOS) based on lattice−hole theory that corrects for the nonrandom local composition of a mixture due to the local interaction energies of the molecules. The PV-EOS for a pure component of type 1 takes the form

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln\left(\frac{\tilde{v}_1}{\tilde{v}_1 - 1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}_1 + (q_1/r_1) - 1}{\tilde{v}_1}\right) - \frac{\theta_1^{\,2}}{\tilde{T}_1} \quad (1)$$

$$\tilde{P}_1 = \frac{P}{P_1^*} = \frac{2Pv_h}{z\epsilon_{11}} \quad (2)$$

$$\tilde{T}_1 = \frac{T}{T_1^*} = \frac{2RT}{z\epsilon_{11}} \quad (3)$$

$$\tilde{v}_1 = \frac{v}{v_1^*} = \frac{v_h(N_h + r_1N_1)}{v_1^*N_1} \quad (4)$$

Here $r_1$ is the number of occupied lattice sites by a polymer molecule, $q_1$ is a surface area parameter, $\theta_1$ is the molecular surface area fraction including holes, $v_h$ is the volume of a lattice site ($9.75 \times 10^{-3}$ m$^3$/kmol), $P$ is the pressure, $T$ is the temperature, $v$ is the molar volume, $P_1$* and $T_1$* are the pure-component characteristic pressure and temperature, and $z$ is the coordination number set equal to 10. $N_1$ is the number of molecules in the system, and $N_h$ is the number of holes in the lattice. There are two characteristic parameters of a pure component: (1) $v_1$*, which is the hard-core contribution to the volume of the system, and (2) $\epsilon_{11}$, which is the molecular interaction energy. Since the molecular interaction energy represents an average energy over all of the possible configurations of the system, it may be considered as the free energy of interactions[21] with an enthalpic contribution, $\epsilon_{11h}$, and an entropic contribution, $\epsilon_{11s}$, such that

$$\epsilon_{11} = \epsilon_{11h} + T\epsilon_{11s} \quad (5)$$

Once $v$* and $\epsilon_{11}$ are determined, eq 1 can be solved for the molar volume of the system, $v$, at a given temperature and pressure.

The PV-EOS for a binary mixture takes the same general form as given in eq 1:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v} - 1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v} + (q/r) - 1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \quad (6)$$

But now the reduced parameters are defined as

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv_h}{z\epsilon^*} \quad (7)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2RT}{z\epsilon^*} \quad (8)$$

$$\tilde{v} = \frac{v}{v^*} = \frac{v_h(N_h + rN)}{v^*N} \quad (9)$$

The mixture variables are obtained from the following mixing rules:

$$v^* = x_1 v_1{}^* + x_2 v_2{}^* \tag{10}$$

$$r = x_1 \frac{v_1{}^*}{v_\mathrm{h}} + x_2 \frac{v_2{}^*}{v_\mathrm{h}} \tag{11}$$

$$q = x_1 q_1 + x_2 q_2 \tag{12}$$

$$\theta = \theta_1 + \theta_2 \tag{13}$$

Here, $x_i$ is the mole fraction of component $i$ in the mixture. The interaction energy of the binary mixture, $\epsilon^*$, is given as

$$\epsilon^* = \bar{\theta}_1\epsilon_{11} + \bar{\theta}_2\epsilon_{22} - \bar{\theta}_1\bar{\theta}_2\dot{\Gamma}_{12}(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) \tag{14}$$

where $\bar{\theta}_i$ is the surface area fraction of component $i$ on a hole-free basis, $\dot{\Gamma}_{12}$ is a nonrandomness term,[22] and $\epsilon_{12}$ is the interaction energy between two unlike molecules. A geometric mixing rule is used to obtain $\epsilon_{12}$ from the pure interaction energies between like molecules which includes a binary interaction energy parameter $k_{12}$:

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}(1 - k_{12}) \tag{15}$$

For the case of a binary mixture, there are five parameters needed to employ the equation of state: $v_i{}^*$ for each component, $\epsilon_{ii}$ for each component, and the binary interaction parameter of the mixture, $k_{12}$. In this work, the binary interaction parameters of the polymer–solvent mixtures are considered to be independent of temperature.

## Analysis of Copolymer

The underlying principle for the application of PV-EOS to a copolymer system in this study is that the $v^*$ and $\epsilon_{11}$ of the copolymer can be obtained from volume and energy characteristics of the monomer repeat units in the homopolymers. In this work, we seek to determine the applicability of the PV-EOS to these strongly associating copolymer–solvent systems by taking information only from the homopolymer PVT and VLE data. From homopolymer density behavior, the $v^*$ and $\epsilon_{11}$ for the repeat unit in the polymer can be determined. To obtain these characteristic values for the copolymer, however, we propose mixing rules for the pure polymer parameters. It is assumed that the molar reference volume of the copolymer, $v^*_\mathrm{CoP}$, is the mole fraction sum of the hard-core volumes of the monomer repeat units:

$$v^*_\mathrm{CoP} = x_\mathrm{A}\hat{v}^*_\mathrm{A}\frac{\mathrm{MW}_\mathrm{CoP}}{\mathrm{MW}_\mathrm{RUA}} + x_\mathrm{B}\hat{v}^*_\mathrm{B}\frac{\mathrm{MW}_\mathrm{CoP}}{\mathrm{MW}_\mathrm{RUB}} \tag{16}$$

where $\hat{v}^*_\mathrm{A}$ and $\hat{v}^*_\mathrm{B}$ are the hard-core volume of the repeat unit in homopolymers A and B, $\mathrm{MW}_\mathrm{CoP}$ is the molecular weight of the copolymer, and $\mathrm{MW}_\mathrm{RUA}$ and $\mathrm{MW}_\mathrm{RUB}$ are the molecular weight of the A and B repeat units.

The mixing rule for $\epsilon_{11}$ is less straightforward because it not only involves the number of the different types of repeat units in the copolymer but also includes information regarding the surface area available for interactions. The surface area parameter, $q_\mathrm{A}$, of a polymer is given as

$$q_\mathrm{A} = \frac{(z-2)r_\mathrm{A} + 2}{z} \tag{17}$$

and represents the surface area parameter for the entire polymer. To determine the surface area of a repeat unit, $\hat{q}_\mathrm{A}$, the surface area must be divided by the degree of polymerization of homopolymer A, $D_\mathrm{P,A}$:

$$\hat{q}_\mathrm{A} = \frac{q_\mathrm{A}}{D_\mathrm{P,A}} \tag{18}$$

The surface area fraction of repeat unit A in a copolymer, $Q_\mathrm{CoP,A}$, made up of repeat units A and B is

$$Q_\mathrm{CoP,A} = \frac{x_\mathrm{A}\hat{q}_\mathrm{A}}{x_\mathrm{A}\hat{q}_\mathrm{A} + x_\mathrm{B}\hat{q}_\mathrm{B}} \tag{19}$$

The mixing rule employed to calculate the copolymer interaction energy, $\epsilon_\mathrm{11,CoP}$, from the interaction energies of the homopolymers ($\epsilon_\mathrm{11,A}$ and $\epsilon_\mathrm{11,B}$) is

$$\epsilon_\mathrm{11,CoP} = Q_\mathrm{CoP,A}{}^2\epsilon_\mathrm{11,A} + Q_\mathrm{CoP,B}{}^2\epsilon_\mathrm{11,B} + 2Q_\mathrm{CoP,A}Q_\mathrm{CoP,B}(\epsilon_\mathrm{11,A}\epsilon_\mathrm{11,B})^{1/2} \tag{20}$$

This mixing rule is based on the probability of finding two adjacent monomer units of the relevant composition.

Before applying this analysis to the copolymer VLE problem, we can test the applicability of the mixing rules (eqs 16 and 20) for the pure component parameters $v^*_\mathrm{CoP}$ and $\epsilon_\mathrm{11,CoP}$ by predicting copolymer PVT behavior with the PV-EOS using parameters obtained from the PVT behavior of the pure homopolymers. Kim and Paul[23] have measured PVT behavior over a range of pressures and temperatures for styrene–methyl methacrylate copolymers. Values given by Panayiotou and Vera for $v_1{}^*$, $\epsilon_\mathrm{11h}$, and $\epsilon_\mathrm{11s}$ for polystyrene and poly(methyl methacrylate) homopolymers were used to obtain $v^*_\mathrm{CoP}$ and $\epsilon_\mathrm{11,CoP}$ for a copolymer composed of 20.5 wt % methyl methacrylate repeat units. Figure 1 depicts the prediction of the copolymer PVT behavior plotted alongside the experimental data. The average absolute relative deviation (AARD) of the model from the experimental data was calculated as

$$\mathrm{AARD} = \frac{1}{n}\sum\frac{\left|\frac{1}{\rho_\mathrm{exp}} - \frac{1}{\rho_\mathrm{pred}}\right|}{\frac{1}{\rho_\mathrm{exp}}} \tag{21}$$

where $\rho_\mathrm{exp}$ is the experimentally measured density, $\rho_\mathrm{pred}$ is the predicted density, and $n$ is the number of data points in each data set. The AARD was calculated at each pressure and appears in Figure 1. The predicted values are found to be accurate over a wide range of temperature and pressure.

To predict the VLE between a copolymer and a solvent, we must also define a mixing rule for the binary interaction energy, $k_{12}$. Since the binary interaction parameter is related to the energy of interaction, the following mixing rule based on the surface area fraction was used to obtain the binary interaction parameter between a solvent (2) and the copolymer, $k_\mathrm{CoP,2}$:

$$k_\mathrm{CoP,2} = Q_\mathrm{CoP,A}k_\mathrm{A,2} + Q_\mathrm{CoP,B}k_\mathrm{B,2} \tag{22}$$

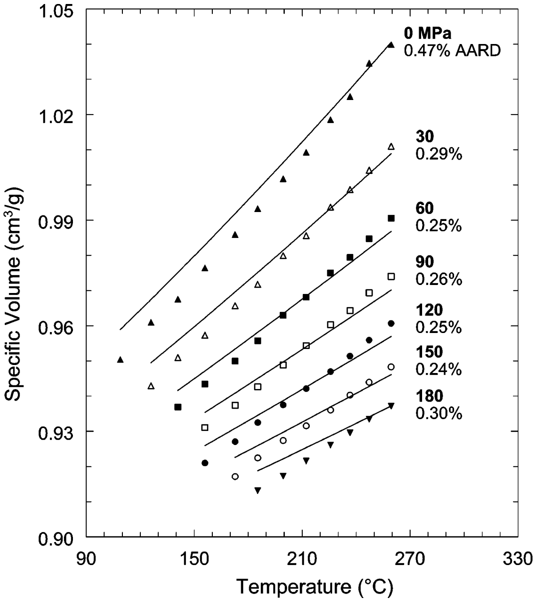

**Figure 1.** PVT data[23] for styrene–methyl methacrylate copolymer containing 20.5 wt % methyl methacrylate repeat units compared with predicted values (solid lines).

where $k_{A,2}$ and $k_{B,2}$ are the binary interaction parameters of solvent (2) in each of the homopolymers.

## PV-EOS Parameter Estimation

**Correlation of Homopolymer PVT Data.** The ultimate goal of the present study is to apply the PV-EOS to predict the phase equilibrium behavior of binary mixtures of partially hydrolyzed PVOH with water, methanol, and methyl acetate. The first step in performing this analysis entails determining $v_i$* and $\epsilon_{ii}$ from the parent homopolymers and the individual solvents. For a semicrystalline homopolymer, however, this analysis is complicated because of the presence of the crystals. Since it is generally assumed that solvent sorption occurs exclusively in the amorphous phase of a polymer, $v_i$* and $\epsilon_{ii}$ must be obtained specifically for the amorphous phase of the polymer. For this reason, total volumetric data (measured below the crystal melting temperature) cannot be used directly due to the presence of crystals. In a recent publication, Zoller[24] reports PVT data for PVOH over a temperature range of 25–253.8 °C and a pressure range of 0–200 MPa. No crystallinity information, however, is included. The crystallinity of the sample can be estimated from a total density measurement if the densities of the crystalline and amorphous phases are known.[14] Todakaro[25] reports values for the density of the amorphous and crystalline phases to be 1.270 and 1.340 g/cm$^3$, respectively, at ambient temperature. A crystallinity value of 54% is obtained for Zoller's data when Todakaro's density values are applied at 25 °C. For the present study, estimates of the PVOH amorphous phase density are required at appreciably higher temperatures, where the experimental VLE data are measured. In their work, Assender and Windle[16] used X-ray diffraction to measure the thermal expansion coefficients of a PVOH crystal unit cell. These expansion coefficients of the unit crystal can be used to determine the volume change of the crystalline phase with temperature. With this information it is now possible to isolate the volumetric behavior of the amorphous region of PVOH in the presence of crystals. Figure 2 illustrates Zoller's total volumetric data along with the density at zero pressure of the amorphous phase calculated by (1) neglecting the thermal expansion of the crystals and (2) including the dimension change of the crystals. Since the dependence of the amorphous phase density on temperature in the presence of the crystals has been estimated, the characteristic parameters $v_1$*, $\epsilon_{11h}$, and $\epsilon_{11s}$ can be regressed for the PV-EOS (Table 1).

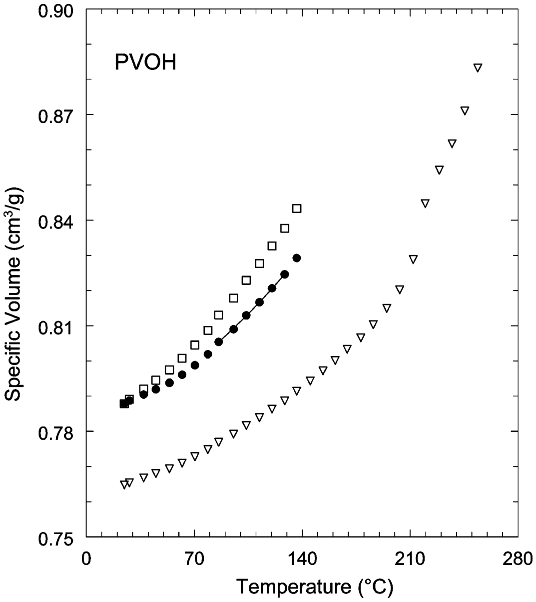

**Figure 2.** Total volumetric data[24] at vacuum for PVOH (▽) compared with specific volume of the amorphous phase neglecting the thermal expansion of the crystalline phase (□) and the specific volume of the amorphous phase considering the change in dimension of the crystals with temperature (●). The solid line is the density from the PV-EOS using the regressed parameters.

**Table 1. Polymer Pure Component Parameters for the PV-EOS[a]**

| polymer | $v^*_{1,sp}$ (cm$^3$/g) | $\epsilon_{11h}$ (J/mol) | $\epsilon_{11s}$ (J/(mol K)) | temp range (°C) |
|---|---|---|---|---|
| PVOH | 0.765 | 1579 | −0.714 | 85.8–128.6 |
| PVAc | 0.786 | 938.0 | 0.180 | 64–120 |
| PVOH 88% | 0.770[b] | 1343[b] | −0.380[b] | 85.8–120 |

[a] Note that the specific hard-core volume, $v^*_{1,sp}$, is given for these polymers. [b] Values obtained using the mixing rules given in eqs 16 and 20.

The optimum values of the solvent and homopolymer PV-EOS parameters were regressed from PVT data with a nonlinear least squares regression package that used a modified Levenberg–Marquardt algorithm (subroutine DUNLSF of the IMSL Math Library). The objective function (OBJF) that was minimized was

$$\mathrm{OBJF} = [\rho_{\mathrm{calc}}(T_{\mathrm{exp}}) - \rho_{\mathrm{exp}}(T_{\mathrm{exp}})]^2 \qquad (23)$$

Here, $\rho_{\mathrm{calc}}(T_{\mathrm{exp}})$ is the calculated density of the polymer at the temperature of the experimental data point. The temperature range over which this analysis could be conducted, however, was limited. Since we are regressing for equilibrium amorphous phase values, the data employed must be above the glass transition temperature ($T_g$) of PVOH, which is known to be about 85 °C for fully hydrolyzed PVOH. Consequently, density values in the range 85.8–128.6 °C in a vacuum were used to estimate the PVOH homopolymer parameters because no information about the volume change of the

**Table 2. Pure Solvent Parameters for the PV-EOS**[a]

| solvent | $v_2^*$ (cm$^3$/mol) | $\epsilon_{22h}$ (J/mol) | $\epsilon_{22s}$ (J/(mol K)) | density error av/max | vapor press. error av/ max |
|---|---|---|---|---|---|
| water | 18.5 | 4591 | −4.31 | 0.96%/1.87% | 0.94%/1.95% |
| methanol | 41.2 | 2002 | −1.59 | 1.55%/2.51% | 0.55%/0.96% |
| methyl acetate | 74.9 | 1022 | −0.133 | 0.80%/1.67% | 0.44%/0.72% |

[a] Values given with average and maximum errors for the vapor pressure and density data.

crystals with pressure is available. The regression of the $v_1$*, $\epsilon_{11h}$, and $\epsilon_{11s}$ parameters for PVAc can be done directly due to the absence of crystals. The PVT data of Beret and Prausnitz[26] in the temperature range of 64−120 °C were used for this purpose.

Table 1 contains the values of the pure-component parameters obtained for each of the polymers. One of the assumptions made for estimation of these parameters for PVOH 88% is that the crystals are comprised exclusively of vinyl alcohol repeat units.[27,28] The regressed values agree well with the values given by Panayiotou and Vera for PVAc. For example, there is a 0.2% difference for $v_1$* and 0.78% difference for $\epsilon_{11}$ at 100 °C between the values obtained in this study and the value reported by Panayiotou and Vera[20] even though they used a different set of PVT data taken over a slightly different temperature range.

**Correlation of Pure Solvent Data.** The parameter calculation method for $v_2$* and $\epsilon_{22}$ for the solvents used differs from that employed for the homopolymers since both liquid density and vapor pressure data are available for these compounds. For each of the solvents in this study, the optimum values for $v_2$*, $\epsilon_{22h}$, and $\epsilon_{22s}$ were determined for the temperature range 40−110 °C, which is the temperature range of the data used in this study. The optimum values for these parameters were obtained through the simultaneous regression of both liquid density and vapor pressure data with the following objective function:

$$\mathrm{OBJF} = \left[\frac{\rho_{\mathrm{calc}}(T_{\mathrm{exp}}) - \rho_{\mathrm{exp}}(T_{\mathrm{exp}})}{\rho_{\mathrm{exp}}(T_{\mathrm{exp}})}\right]^2 + \left[\frac{P^{\mathrm{sat}}_{\mathrm{calc}}(T_{\mathrm{exp}}) - P^{\mathrm{sat}}_{\mathrm{exp}}(T_{\mathrm{exp}})}{P^{\mathrm{sat}}_{\mathrm{exp}}(T_{\mathrm{exp}})}\right]^2 \quad (24)$$

Table 2 lists the values of the PV-EOS parameters with the associated errors from the experimental data.

**Regression of the Binary Interaction Parameter.** To determine the binary interaction parameters for the homopolymer−solvent systems, the binary polymer−solvent data were regressed using the following objective function:

$$\mathrm{OBJF} = [\omega_{\mathrm{calc}} - \omega_{\mathrm{exp}}]^2 \quad (25)$$

Here $\omega_{\mathrm{calc}}$ is the weight fraction of solvent (in the amorphous phase) calculated by the equation of state, and $\omega_{\mathrm{exp}}$ is the experimental weight fraction. Table 3 provides the regressed values of the binary interaction parameters. The $k_{12}$ parameters for the copolymer (PVOH 88%) given in Table 3 were obtained using the mixing rule given in eq 22. The binary interaction parameters were regressed using all of the data and therefore are the best fit over the entire range of temperature. In the case of water−PVAc, data were collected only at activities up to 0.6; however, water sorption in PVOH 88% was studied up to an activity of 0.9. Since the regressed values of $k_{12}$ for water in both PVAc and PVOH are used to predict the $k_{12}$ of water in the copolymer, it is desirable to evaluate this parameter over as large an activity range as possible. Long and Thompson[8] obtained data for water in PVAc using quartz-spring gravimetric sorption that cover a broader activity range than examined in this study. Their data were used along with the data obtained in this work for the regression of the water−PVAc binary interaction parameter.

**Table 3. Binary Interaction Parameters, $k_{12}$, for PVAc, PVOH 88%*, and PVOH Obtained by Regression of Experimental Data with the Number of Data Points Used Given in Brackets**

| solvent | PVAc | PVOH 88% | PVOH |
|---|---|---|---|
| water | −0.00754[a] [17] | −0.0309[b] | −0.0433 [18] |
| methanol | 0.0689 [10] | 0.0503[b] | 0.0405 [6] |
| methyl acetate | 0.0187 [8] | 0.0481[b] | 0.0636 [3] |

[a] Simultaneously regressed on the data of Long and Thompson[8] and the data obtained in this work. [b] Values obtained using the mixing rule given in eq 22.

## Results and Discussion

Table 4 provides all of the experimental VLE data obtained in this study. The PV-EOS provides excellent correlations for the PVAc and PVOH VLE data with the single adjustable binary interaction parameter. This is particularly noteworthy for the strongest of the associating systems where one might expect the model to do poorly. Figure 3 shows the correlation with the PV-EOS for the water−PVOH system at 100 °C with the experimental data taken in this study at 90, 100, and 110 °C. Even though the crystal content of these samples is fairly high, the PV-EOS captures the VLE behavior of the data well. The case of water−PVOH is also the best opportunity to examine the assumption that crystal dissolution does not take place if the crystals are formed with the extreme annealing process used in this work. The VLE data exhibit no bias with temperature, as would be expected if one of these samples (most likely at the highest temperature) had undergone a change in crystallinity. The only hint of any morphology change is at the highest temperature (110 °C) and highest activity (0.87). This data point shows a lower solubility in the amorphous phase than the solubility trend at lower temperatures. It is possible that the annealing process could have caused further densification under these conditions, causing the apparent solubility in the amorphous phase to drop. DSC experiments were conducted on several of the samples after being removed from the gravimetric apparatus. No crystallinity change of the samples during the experiments could be detected.

There is wide disagreement in the literature on sorption data for methanol in PVAc. Figure 4 shows the data obtained in this work compared with other data from the literature that were taken with a variety of experimental techniques. One reason for the wide differences could be the hydrolysis reaction that takes place between PVAc and methanol. The plot in Figure

**Table 4. VLE Data for Water, Methanol, and Methyl Acetate in PVAc, PVOH 88%, and PVOH**

| $T$ (°C) | $a_1$ | $\omega_{1a}$ | $T$ (°C) | $a_1$ | $\omega_{1a}$ |
|---|---|---|---|---|---|
| PVAc−Water[a] | | | | | |
| 40 | 0.265 | 0.0050 | 40 | 0.351 | 0.0061 |
| 40 | 0.265 | 0.0048 | 40 | 0.485 | 0.0101 |
| 40 | 0.263 | 0.0038 | 40 | 0.623 | 0.0153 |
| 40 | 0.351 | 0.0060 | | | |
| PVAc−Methanol[a,b] | | | | | |
| 65 | 0.128 | 0.0099[b] | 90 | 0.330 | 0.0334 |
| 65 | 0.215 | 0.0174[b] | 100 | 0.037 | 0.0026 |
| 65 | 0.132 | 0.0085[b] | 100 | 0.099 | 0.0062 |
| 65 | 0.335 | 0.0273[b] | 100 | 0.061 | 0.0046 |
| 90 | 0.137 | 0.0108 | 100 | 0.238 | 0.0184 |
| PVAc−Methyl Acetate[a] | | | | | |
| 65 | 0.739 | 0.2600 | 65 | 0.344 | 0.0901 |
| 65 | 0.628 | 0.197 | 65 | 0.280 | 0.0722 |
| 65 | 0.519 | 0.149 | 65 | 0.206 | 0.0470 |
| 65 | 0.423 | 0.117 | 65 | 0.110 | 0.0271 |
| PVOH 88%−Water[a] | | | | | |
| 90 | 0.222 | 0.0237 | 90 | 0.467 | 0.0701 |
| 90 | 0.461 | 0.0523 | 100 | 0.221 | 0.0228 |
| 90 | 0.701 | 0.1037 | 100 | 0.490 | 0.0623 |
| 90 | 0.891 | 0.189 | 100 | 0.675 | 0.112 |
| 90 | 0.295 | 0.0373 | 100 | 0.849 | 0.208 |
| 90 | 0.623 | 0.1170 | 110 | 0.244 | 0.0222 |
| 90 | 0.909 | 0.219 | 110 | 0.442 | 0.0506 |
| 90 | 0.224 | 0.0273 | 110 | 0.621 | 0.0930 |
| PVOH 88%−Methanol[a] | | | | | |
| 90 | 0.147 | 0.0180 | 110 | 0.083 | 0.0090 |
| 90 | 0.145 | 0.0183 | 110 | 0.164 | 0.0191 |
| 90 | 0.297 | 0.0406 | 110 | 0.179 | 0.0245 |
| 90 | 0.385 | 0.0573 | 110 | 0.224 | 0.0315 |
| 90 | 0.148 | 0.0185 | 110 | 0.089 | 0.0119 |
| 90 | 0.295 | 0.0367 | 110 | 0.160 | 0.0207 |
| 90 | 0.389 | 0.0526 | 110 | 0.207 | 0.0271 |
| 100 | 0.106 | 0.0141 | 110 | 0.091 | 0.0106 |
| 100 | 0.208 | 0.0278 | 110 | 0.164 | 0.0163 |
| 100 | 0.278 | 0.0384 | 110 | 0.207 | 0.0254 |
| PVOH 88%−Methyl Acetate[a] | | | | | |
| 90 | 0.118 | 0.0081 | 100 | 0.177 | 0.0152 |
| 90 | 0.231 | 0.0178 | 110 | 0.088 | 0.0065 |
| 100 | 0.087 | 0.0081 | 110 | 0.163 | 0.0143 |
| PVOH−Water[a] | | | | | |
| 90 | 0.215 | 0.0404 | 90 | 0.885 | 0.373 |
| 90 | 0.483 | 0.0989 | 100 | 0.193 | 0.0335 |
| 90 | 0.714 | 0.197 | 100 | 0.551 | 0.122 |
| 90 | 0.869 | 0.338 | 100 | 0.717 | 0.202 |
| 90 | 0.152 | 0.0272 | 100 | 0.876 | 0.296 |
| 90 | 0.272 | 0.0475 | 110 | 0.229 | 0.0409 |
| 90 | 0.425 | 0.0828 | 110 | 0.491 | 0.107 |
| 90 | 0.548 | 0.120 | 110 | 0.723 | 0.228 |
| 90 | 0.700 | 0.188 | 110 | 0.844 | 0.336 |
| PVOH−Methanol[a] | | | | | |
| 90 | 0.106 | 0.0115 | 110 | 0.107 | 0.0160 |
| 100 | 0.157 | 0.0183 | 110 | 0.153 | 0.0205 |
| 100 | 0.239 | 0.0313 | 110 | 0.232 | 0.0297 |
| PVOH−Methyl Acetate[c] | | | | | |
| 100 | 0.1188 | 0.0062 | 100 | 0.9484 | 0.0602 |
| 100 | 0.5037 | 0.0292 | | | |

[a] Gravimetric sorption. [b] IGC. [c] Gas-phase IR.

4 also shows the correlation of the experimental data obtained in this work (open symbols) with the PV-EOS. The correlations each use the same binary interaction parameter that was obtained with the fit of all these data, as found in Table 3. The PV-EOS correlation shows a significant influence of temperature on the solubility of methanol in PVAc. This trend is generally exhibited by the experimental data, but again, wide disagreement exists.

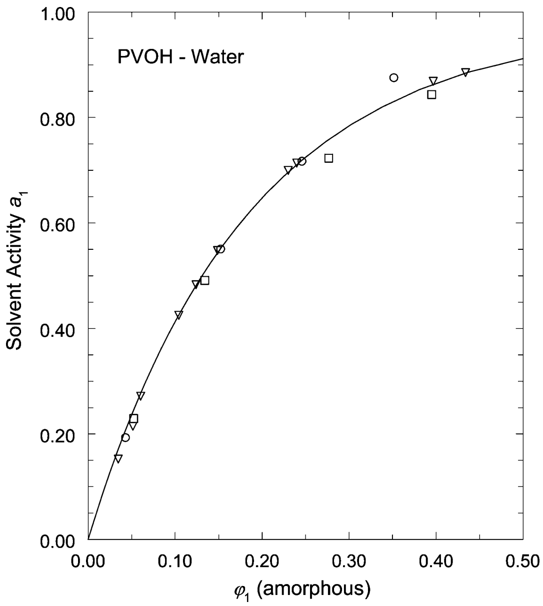

**Figure 3.** Volume fraction of water at equilibrium with PVOH at 90 (▽), 100 (□), and 110 °C (○). The solid line is the correlation of the data with the PV-EOS at 100 °C.

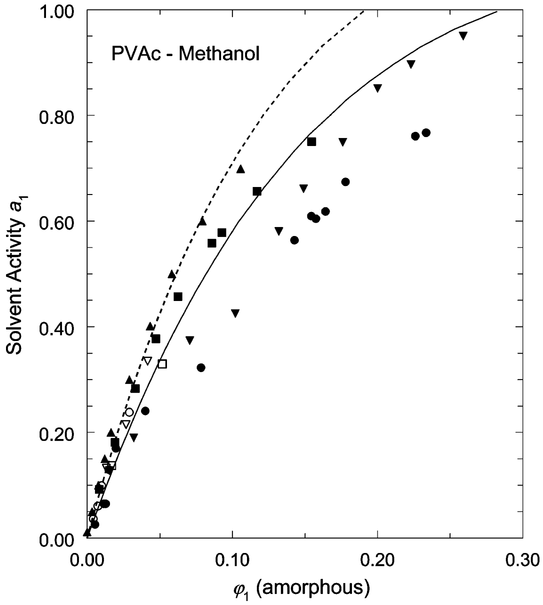

**Figure 4.** Volume fraction of methanol at equilibrium with PVAc at 65 (▽), 90 (□), and 100 °C (○). The solid line is a PV-EOS correlation at 100 °C, and the dashed line is the PV-EOS correlation at 65 °C (with the same binary interaction parameter). The data of Saure and Schlunder at 60 °C (▲),[30] Wibawa et al. at 65 (▼) and 80 °C (■),[31] and Zielinski et al. at 100 °C (●)[18] are plotted for comparison.

The solubility of each solvent in PVAc, PVOH, and PVOH 88% are shown in Figures 5, 6, and 7, respectively. For convenience, the data obtained in this work for each system are given the same symbol regardless of the experimental temperatures. The average absolute deviation (AAD) and the AARD reported in Table 5 were calculated as follows:

$$\mathrm{AAD} = \frac{1}{n}\sum|\omega_{\mathrm{exp}} - \omega_{\mathrm{pred}}| \qquad (26)$$

$$\mathrm{AARD} = \frac{1}{n}\sum\frac{|\omega_{\mathrm{exp}} - \omega_{\mathrm{pred}}|}{\omega_{\mathrm{exp}}} \qquad (27)$$

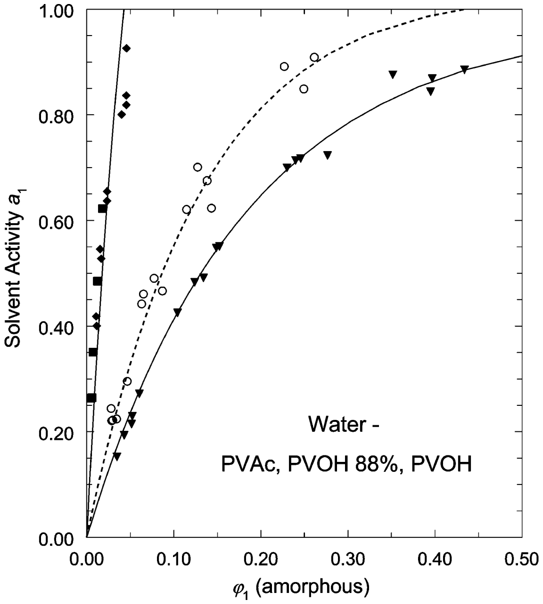

**Figure 5.** Volume fraction of water at equilibrium with PVAc at 40 °C (■), PVOH at 90, 100, and 110 °C (▼), and PVOH 88% at 90, 100, and 110 °C (○). The data of Long and Thompson at 40 °C (◆)[8] were used in the fit of the binary interaction parameter for water−PVAc. The solid lines are the correlations of the PV-EOS to the data at 40 °C for PVAc and 100 °C for PVOH. The dashed line is the prediction of water solubility in PVOH 88% at 100 °C.

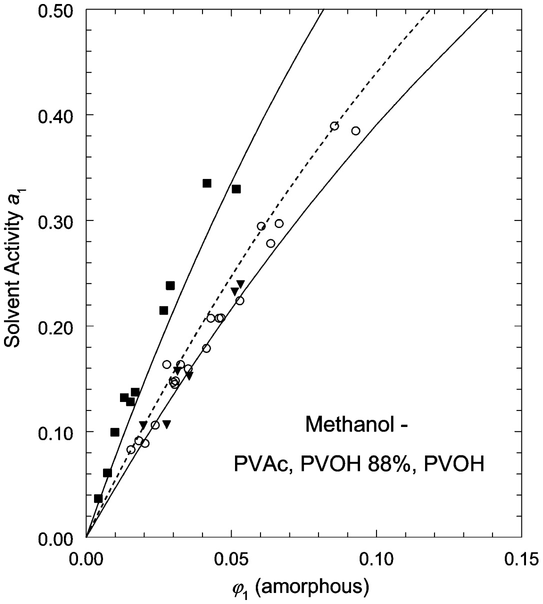

**Figure 6.** Volume fraction of methanol at equilibrium with PVAc at 65, 90, and 100 °C (■), PVOH at 90, 100, at 110 °C (▼), and PVOH 88% at 90, 100, and 110 °C (○). The solid lines are the correlations of the PV-EOS to the data at for PVAc and PVOH at 100 °C. The dashed line is the prediction of methanol solubility in PVOH 88% at 100 °C.

The weight fractions appearing in eqs 26 and 27 are expressed as weight fraction of solvent in the amorphous phase of the semicrystalline PVOH 88%. The VLE data, fits, and prediction of water in PVAc, PVOH, and PVOH 88% copolymer are plotted in Figure 5. There appears to be no systematic bias in the prediction of water solubility in the copolymer. This is particularly impressive when one considers the complex nature of this strongly associating, semicrystalline system. As shown in Figure 6, there is much less difference in the solubility of methanol in PVAc and PVOH than in the case of water or methyl acetate. In fact, the experimental data for PVOH and PVOH 88% are indiscernible. Unfortunately, the quartz-spring gravimetric sorption column used in this study is not able to withstand pressures much over ambient, so we were unable to study higher activities of methanol at the temperatures of interest. The data for PVOH and PVOH 88% are expected to show some differences at higher activities. The vapor pressure behavior of methyl acetate is similar to that of methanol, so a similar activity limitation was encountered on the highest activity attainable. Gas-phase IR was used to circumvent the problem of pressure limitation for the methyl acetate case. As seen in Figure 7, the prediction of the copolymer VLE does well for the small number of data obtained over the limited activity range. Table 5 provides an evaluation of the predictions for water, methanol, and methyl acetate. The mixing rules used to predict the solvent−PVOH 88% VLE proposed in this work were found to successfully represent the experimental data.

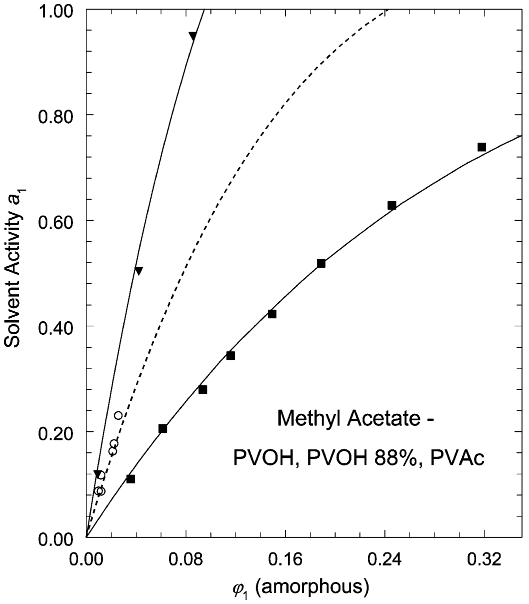

**Figure 7.** Volume fraction of methyl acetate at equilibrium with PVAc at 65 °C (■), PVOH at 100 °C (▼), and PVOH 88% at 90, 100, and 110 °C (○). The solid lines are the correlations of the PV-EOS to the data at 65 °C for PVAc and 100 °C for PVOH. The dashed line is the prediction of methyl acetate solubility in PVOH 88% at 100 °C.

**Table 5. Evaluation of the Prediction of the Solubilities of Water, Methanol, and Methyl Acetate in PVOH 88%**

| solvent | temp range (°C) | data points | solvent wt fraction (amorphous) | AAD | AARD |
|---|---|---|---|---|---|
| water | 90−110 | 16 | 0.022−0.219 | 0.008 | 0.115 |
| methanol | 90−110 | 20 | 0.009−0.057 | 0.003 | 0.120 |
| methyl acetate | 90−110 | 6 | 0.006−0.018 | 0.002 | 0.236 |

## Conclusions

VLE were obtained for water, methanol, and methyl acetate in PVAc, PVOH, and a copolymer made up of vinyl acetate and vinyl alcohol monomer units. The PV-EOS was found to correlate the homopolymer VLE with each solvent well using a single binary interaction parameter when the pure component parameters are regressed from density and vapor pressure (for the solvents) data. Mixing rules were proposed to obtain the copolymer parameters, $v^*_{\mathrm{CoP}}$ and $\epsilon_{11,\mathrm{CoP}}$, used in the PV-EOS from the corresponding homopolymer values. The application of this technique was demonstrated by using the mixing rules to predict the PVT behavior of a styrene−methyl methacrylate copolymer. This analysis was then extended to predict the PVOH 88% VLE for the solvents investigated in this study. The PV-EOS, using the mixing rules developed in this study, was found to predict the copolymer VLE with small ARD and AARD values with respect to the experimental data.

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