# Vapor-Liquid Equilibrium of Polymer Solutions Using a Cubic Equation of State

**Nese Orbey**
Dept. of Chemical Engineering, Middle East Technical University, Ankara, Turkey

**Stanley I. Sandler**
Center for Molecular and Engineering Thermodynamics, Dept. of Chemical Engineering,
University of Delaware, Newark, DE 19716

*A recently proposed mixing rule has been combined with a cubic equation of state to correlate the vapor-liquid equilibria of various polymer + solvent and solvent + long chain hydrocarbon mixtures. We find that the two-parameter version of this model can correlate the solvent partial pressure in concentrated polymer solutions with high accuracy over a range of temperatures and pressures with temperature-independent parameters. For the solvent + long chain hydrocarbon systems, for which accurate vapor-phase concentrations are also important, the model is best used as a three-parameter correlation. Advantages of this approach are that it extends the application of cubic equations of state to polymer + solvent systems in a simple fashion and that generally only temperature-independent parameters are required which allow for accurate interpolation and extrapolation of available data.*

## Introduction

Phase equilibrium is important in the industrial processing of polymer solutions. For example, polymers are often dissolved in supercritical or liquid solvents, and devolatilization of a solvent from a polymer requires information on the partial pressure of the solvent as a function of its mole fraction in polymer-solvent mixture. If the molecular weight of a polymer or long-chain hydrocarbon is relatively low, then an appreciable amount of it will be present in the gas phase and this may be important in dewaxer design. These are two examples of processes that require a quantitative description of the vapor-liquid equilibrium of polymer-solvent systems.

The prediction of phase equilibria in polymer solutions is further complicated by their complex nature. Polymers are mixtures of homologous components, and the average molecular weight and the molecular weight distribution may significantly affect phase behavior. Also, at the temperature and pressure of a solution of interest, the pure polymer may exist as a crystalline, amorphous or rubbery solid rather than a melt. Consequently, models describing phase behavior of systems containing polymers are usually complex and difficult to implement in engineering calculations. On the other hand, for industrial calculations it is advantageous to have a simple model with a limited number of parameters.

In recent years both cubic equations of state and their mixing and combining rules have evolved so that their use for the description of the vapor-liquid equilibrium (VLE) behavior of highly nonideal mixtures has become possible (for example, Wong and Sandler, 1992; Wong et al., 1992; Orbey et al., 1993). These developments encouraged us to look at the description of polymer-solvent systems with these tools.

In this work we use a conventional cubic equation of state coupled with the recent Wong-Sandler (1992) mixing rule to describe the VLE behavior of binary polymer-solvent systems. The excess free energy of mixing is described by the Flory-Huggins model (Flory, 1942, 1953; Huggins, 1942). Two types of systems are considered: binary mixtures of some long-chain alkanes with ethylene; solutions of industrial polymers in conventional liquid solvents. The systems in the first category are well defined binary mixtures that imitate the behavior of low-molecular-weight polymers in supercritical solvents (de Loos et al., 1984), whereas the second group is concentrated polymer solutions in common solvents (Bonner and Prausnitz, 1973).

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Correspondence concerning this article should be addressed to S. I. Sandler.

Table 1. PR Equation of State Parameters for Polymers and Heavy Hydrocarbons

| Component | MW | $a$<br>Pa·m$^6$/mol$^2$<br>(Pa·m$^6$/g$^2$) | $b$<br>cm$^3$/mol<br>(cm$^3$/g) | Source* |
|---|---|---|---|---|
| Polystyrene | 290,000 | 9,600<br>($1.14\times10^{-7}$) | $2.30\times10^5$<br>(0.793) | Bawn and Wajid (1956) |
| Polystyrene | 97,200 | 2,550<br>($2.70\times10^{-7}$) | $7.50\times10^4$<br>(0.772) | Flory and Höcker (1971) |
| Polyisobutylene | 40,000 | 2,840<br>($1.18\times10^{-6}$) | $4.10\times10^4$<br>(1.025) | Eichinger and Flory (1968a) |
| Polyethyleneoxide | 5,700 | 260<br>($8.00\times10^{-6}$) | $4.64\times10^3$<br>(0.814) | Booth and Devoy (1971a) |
| Polypropyleneoxide | 500,000 | 18,200<br>($7.30\times10^{-8}$) | $4.35\times10^5$<br>(0.870) | Booth and Devoy (1971b) |
| *n*-Tetracontane | | | | de Loos et al. (1984) |
| $T=373.15$ K | | 53.982 | $6.7175\times10^2$ | |
| $T=423.15$ K | | 53.516 | $6.8813\times10^2$ | |
| *n*-Eicosane | | | | |
| $T=373.15$ K | | 21.184 | $3.4244\times10^2$ | |
| $T=423.15$ K | | 20.300 | $3.4919\times10^2$ | |

*Reports volumes in the case of polymers, and *a* and *b* parameter values for *n*-eicosane and *n*-tetracontane.

### *Description of pure polymers by a cubic equation of state*

In this work, a modified version of the Peng-Robinson (PR) equation of state was used (Stryjek and Vera, 1986). This PRSV equation is:

$$P=\frac{RT}{V-b}-\frac{a}{V^2+2bV-b^2} \tag{1}$$

$$a=(0.457235R^2T_C^2/P_C)\alpha \tag{2}$$

$$b=0.077796RT_c/P_c \tag{3}$$

with

$$\alpha=[1+\kappa(1-T_R^{0.5})]^2 \tag{4}$$

$$\kappa=\kappa_0+\kappa_1(1+T_R^{0.5})(0.7-T_R) \tag{5}$$

and

$$\kappa_0=0.378893+1.4897153\omega-0.17131848\omega^2+0.0196554\omega^3 \tag{6}$$

The first problem to be addressed in the application of this cubic equation to polymer solutions is the description of the polymer by the equation of state. In the application of cubic equations of state to low-molecular-weight species, the pure component parameters are computed from the critical parameters as shown above. This approach is used for the solvents investigated here, but this is not possible for heavy alkanes and polymers since the critical point is not measurable. Consequently, for the heavy alkanes considered here P-V-T data at the temperature and pressure of the interest were used to obtain the parameters. Following the proposal of Joffe (1976), experimental saturation liquid volume and vapor pressure of the pure liquid at the temperature of interest were used to obtain parameters *a* and *b* of the EOS. The systems ethylene + *n*-eicosane ($C_{20}H_{42}$) and ethylene + *n*-tetracontane ($C_{40}H_{82}$) studied by de Loos et al. (1984) were used in this work. For *n*-eicosane and *n*-tetracontane PV isotherms are available (Doolittle, 1964), and de Loos et al. calculated values of the *a* and *b* parameters using these data. Their results are reported in Table 1.

For polymers, however, there is another problem: some of the polymers considered here are below their glass transition temperature so that they are glassy solids in their pure form at the temperature of the solution. Their sublimation pressures are too low to be measured, and their pure component "liquid" molar volumes are nonexistent. For the engineering model we develop here, in such cases we assumed that a very low fixed value ($10^{-7}$ MPa) can be used for the vapor pressure and the densities of the glassy polymers can be used as the "liquid" molar densities. For those polymers that are above their glass transition temperature and thus in a "liquid" form, the experimental melt densities were used with the hypothetical vapor pressure of $10^{-7}$ MPa to obtain the EOS parameters. For the polymer-solvent systems studied in this work, the polymers are well characterized in terms of their specific volumes over the temperature range in which polymer-solvent VLE data were available. We used this information and the above procedure to calculate the *a* and *b* values for each polymer in the temperature range of interest. These values are reported in Table 1.

It is interesting to note that although the value of *b* in cm$^3$/mol for the two polystyrene samples with different molecular weights are different, if *b* is reported in cm$^3$/g, the values are quite close (0.793 and 0.772 cm$^3$/g for PS with average molecular weights 290,000 and 97,200, respectively). This suggests that even if specific volume data for a particular polymer are not available, one can use generic specific volume data for that polymer to obtain a reasonable estimate for the *a* and *b* parameters needed in our model.

### *Vapor-liquid equilibrium calculations*

To study vapor-liquid equilibrium, we used the recent Wong-

Sandler (W-S) mixing rule (Wong and Sandler, 1992). In this approach, the $a$ and $b$ parameters in a mixture are determined in such a way that while the low-density quadratic composition dependence of the second virial coefficient is satisfied, the excess Helmholtz free energy at infinite pressure from the equation of state is also equal to that of an appropriately chosen liquid activity coefficient model. This mixing rule for a two-parameter cubic equation is:

$$b_m = \frac{Q}{(1-D)} \tag{7}$$

$$\frac{a_m}{RT} = Q\frac{D}{(1-D)} \tag{8}$$

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{9}$$

with

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{10}$$

and

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A^{\text{ex}}}{cRT} \tag{11}$$

where $c$ is a constant equal to $[1/\sqrt{2}]\ln(\sqrt{2}-1)$ for the PRSV equation used in this study, and $A^{\text{ex}}$ is any suitable molar excess Helmholtz free energy model at infinite pressure or equivalently an excess Gibbs free energy model at low pressures (Wong et al., 1992). This mixing rule, used for correlation as to be described here, requires the parameters of the excess energy model and the interaction parameter $k_{ij}$ of Eq. 10.

The advantage of this mixing rule is that it incorporates excess energy models into equations of state in a theoretically correct way; as has been shown earlier (Wong et al., 1992; Orbey et al., 1993), it can be used for the very accurate correlation and/or prediction of vapor-liquid equilibrium for highly nonideal mixtures. Any excess free energy model, $A^{\text{ex}}$, can be used in this mixing rule, and it was hoped that the incorporation of an excess free energy model specifically developed to account for the free volume effect in polymer-solvent mixtures would allow the description of such mixtures with a conventional cubic equation of state. Thus, we chose the Flory-Huggins equation (Flory, 1942, 1953; Huggins, 1942) for this work. The Flory-Huggins model, which includes two contributions to the thermodynamics of binary polymer-solvent solutions—an entropy of athermal mixing due to the size difference between the species and an enthalpy of mixing due to the difference of the intermolecular forces—is:

$$\frac{A^{\text{ex}}}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \chi\Phi_1\Phi_2(x_1 + x_2 r) \tag{12}$$

Here, $\chi$ is the Flory interaction parameter, $\Phi$ is the volume fraction, and $r$ is the number of solvent-size segments that make up the polymer which is approximated by the ratio of hard-core volumes of the species involved: $r = v_{2*}/v_{1*}$, where $v^*$ is the hard-core volume. In Eq. 12, subscripts 1 and 2 denote the solvent and polymer, respectively, in a binary mixture.

Since the Flory-Huggins model is developed using a rigid, incompressible lattice, a PVT equation of state cannot be derived from it. However, since the excess Helmholtz energies from the equation of state and the Flory-Huggins theory are equated at infinite pressure, where the volume terms in the equation of state are replaced by the hard-core term $b$, the W-S mixing rule provides a way of combining the Flory-Huggins model with an equation of state. For some of the systems considered here, the parameters of the Flory-Huggins model were available in literature and it was hoped that those parameters could serve at least as satisfactory initial guesses in fitting the vapor-liquid equilibrium of the these systems with the new mixing rule.

With the selection of the PRSV equation of state and the W-S mixing rule, the fugacity coefficient of a species $i$ in a homogeneous binary mixture becomes (Wong and Sandler, 1992):

$$\ln\Phi_i = \ln\left[\frac{P(\underline{V}-b)}{RT}\right] + \frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\left(\frac{P\underline{V}}{RT} - 1\right) + \frac{1}{2\sqrt{2}}\left(\frac{a_m}{RTb_m}\right)\left[\frac{1}{a_m}\left(\frac{1}{n}\frac{\partial n^2 a_m}{\partial n_i}\right) - \frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\right]\ln\left[\frac{\underline{V} + b_m(1-\sqrt{2})}{\underline{V} + b_m(1+\sqrt{2})}\right] \tag{13}$$

The partial derivatives of $a_m$ and $b_m$ are:

$$\frac{\partial nb_m}{\partial n_i} = \frac{1}{(1-D)}\left(\frac{1}{n}\frac{\partial n^2 Q}{\partial n_i}\right) - \frac{Q}{(1-D)^2}\left(1 - \frac{\partial nD}{\partial n_i}\right) \tag{14}$$

$$\frac{1}{RT}\left(\frac{1}{n}\frac{\partial n^2 a_m}{\partial n_i}\right) = D\frac{\partial nb_m}{\partial n_i} + b_m\frac{\partial nD}{\partial n_i} \tag{15}$$

with the partial derivatives of $Q$ and $D$ given by:

$$\frac{1}{n}\frac{\partial n^2 Q}{\partial n_i} = 2\sum x_j\left(b - \frac{a}{RT}\right)_{ij} \tag{16}$$

with

$$\frac{\partial nD}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln\gamma_i}{C} \tag{17}$$

and

$$\ln\gamma_i = \frac{1}{RT}\frac{\partial nA^{\text{ex}}}{\partial n_i} \tag{18}$$

The activity coefficient expressions for the Flory-Huggins model are obtained using Eqs. 12 and 18:

$$\ln\gamma_1 = \ln\frac{\Phi_1}{x_1} + \left(1 - \frac{1}{r}\right)\Phi_2 + \chi\Phi_2^2 \tag{19}$$

**Table 2. Hard-Core Volumes for Polymers and Solvents***

| Component | $v^*$, cm³/g |
|---|---|
| Polystyrene | 0.817 |
| Polyisobutylene | 0.949 |
| Polyethyleneoxide | 0.7532 |
| Polypropyleneoxide | 0.8424** |
| Chloroform | 0.546 |
| Cyclohexane | 1.02 |
| *n*-Pentane | 1.183 |
| Methyl ethyl ketone | 0.960 |
| Benzene | 0.895 |
| Ethylene | 0.851† |
| *n*-Eicosane | 0.748† |
| *n*-Tetracontane | 0.740† |

* Bonner and Prausnitz, 1973.
** From Booth and Devoy (1971b).
† From Bondi (1968).

and

$$\ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + (1-r)\Phi_1 + \chi \Phi_1^2 r \qquad (20)$$

respectively, for the solvent (1) and the polymer (2).

## Results

### *Concentrated polymer solutions in conventional solvents*

For this work we have selected seven systems studied earlier by Bonner and Prausnitz (1973). These systems are: chloroform + polystyrene (average molecular weight MW 290000) at 298.15 and 323.15 K (Bawn and Wajid, 1956); cyclohexane + polyisobutylene(PIB) (MW 40000) at 298.15 K (Eichinger and Flory, 1968c); *n*-pentane + PIB at 298.15 K (Eichinger and Flory, 1968d); benzene + PIB at 298.15 and 312.75 K (Eichinger and Flory, 1968b); methyl ethyl ketone (MEK) + polystyrene (MW 97200) at 283.15 and 323.15 K (Flory and Höcker, 1971); benezene + polypropylene oxide (MW500000) at 320.35, 333.35, 343.05 and 347.85 K (Booth and Devoy, 1971b); and benzene + polyethylene oxide (MW 5700) at 318.95 and 343.15 K (Booth and Devoy, 1971a).

For these systems we calculated the size parameter $r$ from the ratio of hard-core volumes of the species involved. The hard-core volumes were given by Bonner and Prausnitz (1973) and in the articles reporting the VLE data. The hard-core volumes used in this work are reported in Table 2, and the values of the size ratio $r$ are listed in Table 3. This leaves the parameter $\chi$ of the Flory-Huggins model and the binary interaction parameter $k_{ij}$ undetermined. We first used the reported, temperature-dependent values of $\chi$ reported in the literature, and fit $k_{ij}$ at each temperature. During these calculations, however, it became evident that if we used single values of both $\chi$ and $k_{ij}$, independent of temperature, we could obtain a very good correlation of the data. Therefore, we fitted these two temperature-independent parameters to experimental data with a bubble point pressure program using the simplex algorithm.

The results are shown in Figures 1 to 5, and the resulting parameters are given in Table 3. In all cases it was possible to obtain excellent correlations of the VLE data for these systems with the present model. Moreover, an inspection of the resulting parameters in Table 3 shows that the Flory-Huggins $\chi$ parameters used in the equation of state approach are temperature- and concentration-independent, in contrast to their counterparts in the original Flory theory, and that their numerical values fall within the range of Flory-Huggins parameters reported earlier. The $k_{ij}$ parameter used in our model for polymer solutions is also concentration- and temperature-independent (Table 3). Consequently, we have a two-parameter correlative equation of state model with a good initial estimate for the Flory $\chi$ parameter at a single temperature, and equally important, an accurate method of extrapolating VLE information to higher temperatures and pressures with constant parameters.

Bonner and Prausnitz (1973) also correlated data for the systems considered here using three parameters for each pure component and a binary interaction parameter that was temperature-dependent. This is to be compared with the present

**Table 3. Parameters Used in Equation of State Description**

| System | $r$ | $\chi$ | $\chi$ Range | Source | $k_{ij}$ |
|---|---|---|---|---|---|
| Chloroform + polystyrene | 3,635 | 0.19 | 0.15 to 0.4 | Bawn and Wajid (1956) | 0.84 |
| Cyclohexane + polyisobutylene | 442 | 0.46 | 0.45 to 0.5 | Eichinger and Flory (1968c) | 0.91 |
| *n*-Pentane + polyisobutylene | 445 | 0.61 | 0.5 to 0.9 | Eichinger and Flory (1968d) | 0.96 |
| Benzene + polyisobutylene | 547 | 0.80 | 0.5 to 1.1 | Eichinger and Flory (1968b) | 0.97 |
| Methyl ethyl ketone + polystyrene | 1,140 | 0.56 | 0.5 to 1.0 | Flory and Höcker (1971) | 0.49 |
| Benzene + polyethylene oxide | 61.4 | 0.21 | 0.15 to 0.3 | Booth and Devoy (1971a) | 0.78 |
| Benzene + polypropylene oxide | 6,022 | 0.16 | 0.1 to 0.2 | Booth and Devoy (1971b) | 0.77 |
| Ethylene + *n*-eicosane | | | | | |
| $T$ = 373.15 K | 5 | 0.71 | | | 0.81 |
| $T$ = 423.15 K | 5 | 0.71 | | | 0.83 |
| Ethylene + *n*-tetracontane | | | | | |
| $T$ = 373.15 K | 9 | 0.965 | | | 0.922 |
| $T$ = 423.15 K | 9 | 0.965 | | | 0.940 |

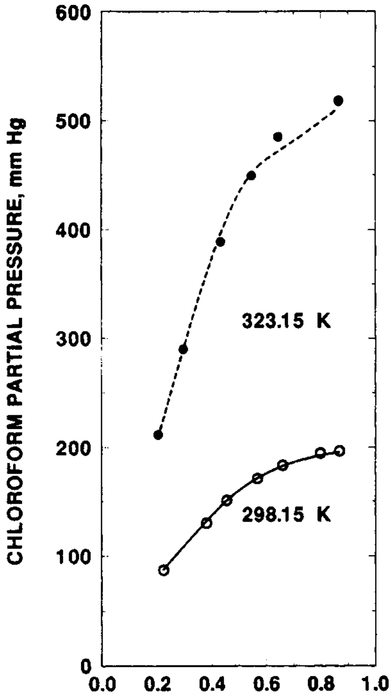

**Figure 1. Partial pressure of chloroform in polystyrene (MW = 290,000).**

o, •, experimental data (Bawn and Wajid, 1956); —, - - - -, our correlation with $r$ = 3,635, $\chi$ = 0.19, and $k_{ij}$ = 0.84.

model which uses fewer parameters, and parameters that are temperature- and concentration-independent, thus allowing prediction of VLE for a given system over a range of temperatures from knowledge of its behavior at only a single temperature.

### *Mixtures of ethylene and long-chain alkanes*

Mixtures of ethylene and long-chain alkanes have been studied by de Loos et al. (1984), and can be considered as prototypes for low-molecular-weight polymers in supercritical solvents. The systems we consider here are ethylene + $n$-eicosane at 373.15 and 423.15 K and ethylene + $n$-tetracontane at 373.15 and 423.15 K. Unlike the polymer + solvent systems considered above, for these mixtures complete VLE data are available over a broad range of temperatures and pressures, including near the critical point.

de Loos et al. used the Peng Robinson equation of state and the van der Waals one-fluid mixing rules with two binary interaction parameters to correlate their experimental data. While their correlations were good for the ethylene + $n$-eicosane mixture, they had to make their parameters a function of temperature for accurate correlations. Also, they were not able to predict accurate VLE behavior near the critical point for the ethylene + $n$-tetracontane mixture.

We initially tried the approach described above for these systems: we obtained the parameter $r$ from the ratio of hard-core volumes of the pure components (as reported by Bondi, 1968) and correlated the other two parameters by fitting VLE data. The values of $r$ obtained this way are 8.85 and 17.45 for

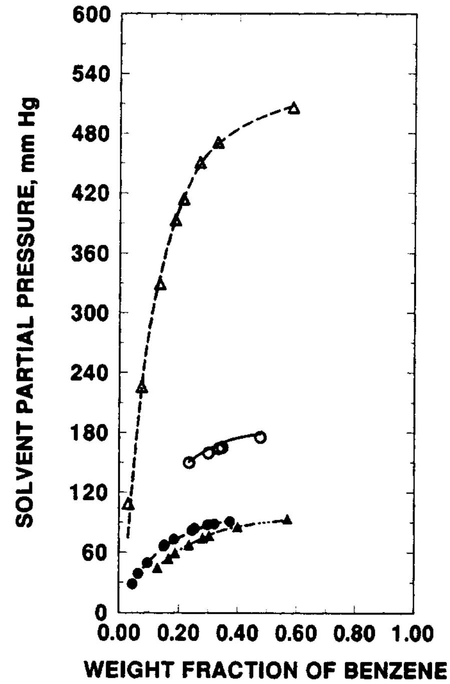

**Figure 2. Partial pressure of various solvents in polyisobutylene (MW = 40,000).**

(a) ▲, experimental data (Eichinger and Flory, 1968c) for cyclohexane in PIB at 298.15 K; —· · ·—, our correlation with $r$ = 442.3, $\chi$ = 0.46, and $k_{ij}$ = 0.91.

(b) △, experimental data (Eichinger and Flory, 1968d) for $n$-pentane in PIB at 298.15 K; - - - -, our correlation with $r$ = 445, $\chi$ = 0.61, and $k_{ij}$ = 0.96.

(c) •, o, experimental data (Eichinger and Flory, 1968b) for benzene in PIB at 298.15 and 312.75 K, respectively; —, our correlation with $r$ = 547, $\chi$ = 0.80, and $k_{ij}$ = 0.97.

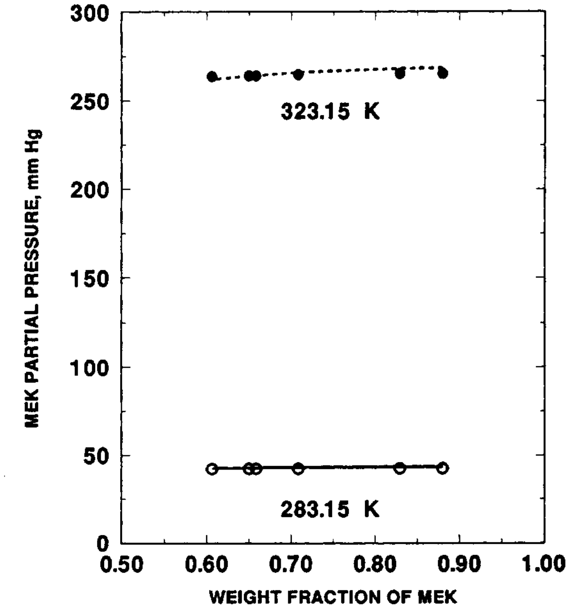

**Figure 3. Partial pressure of methyl ethyl ketone in polystyrene (MW = 97,200).**

o, •, experimental data (Flory and Höcker, 1971); —, - - - -, our correlation with $r$ = 1,140, $\chi$ = 0.56, and $k_{ij}$ = 0.49.

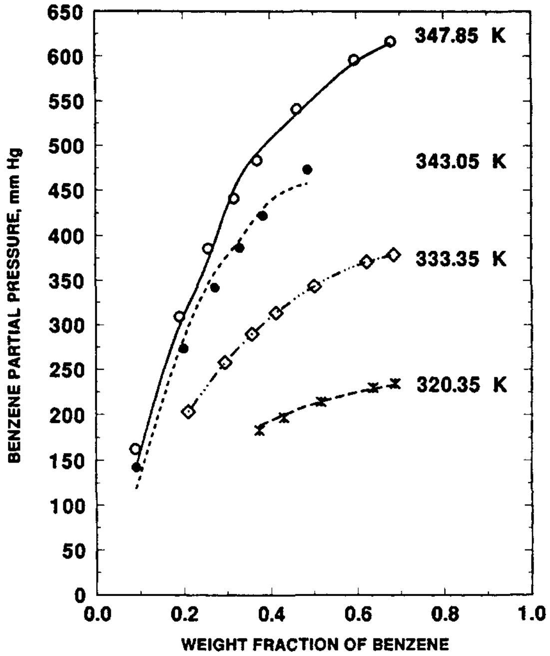

**Figure 4. Partial pressure of benzene in polypropylene oxide (MW = 500,000).**

○, ●, ◇, *, experimental data (Booth and Devoy, 1971b); —, ----, —···—, our correlation with $r$ = 6,022, $\chi$ = 0.16, and $k_{ij}$ = 0.77.

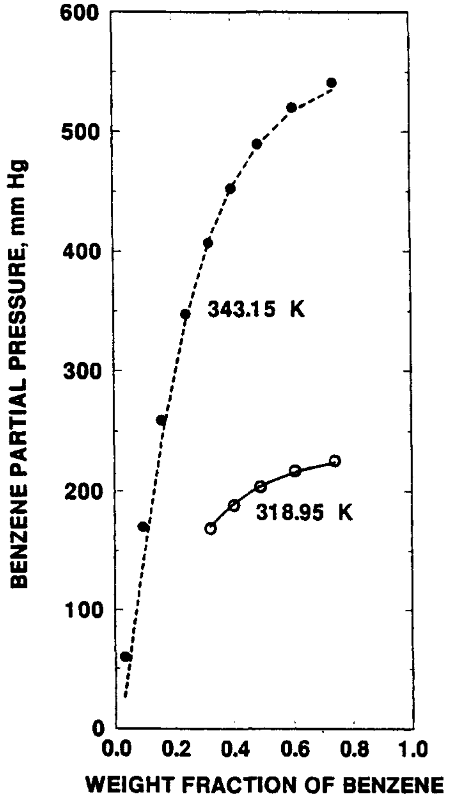

**Figure 5. Partial pressure of benzene in polyethylene oxide (MW = 5,700).**

○, ●, experimental data (Bawn and Wajid, 1956); —, ----, our correlation with $r$ = 61.4, $\chi$ = 0.21, and $k_{ij}$ = 0.78.

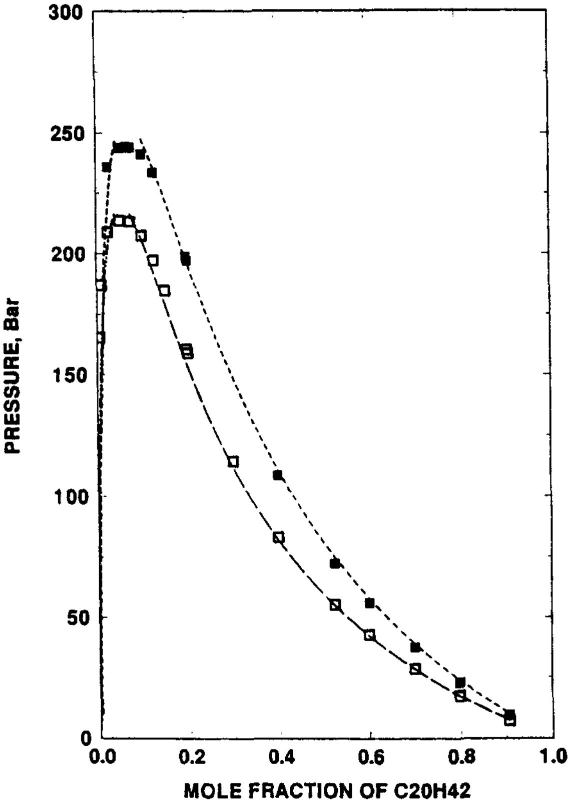

**Figure 6. Partial pressure of ethylene in *n*-eicosane.**

□, ■, experimental data at 373.15 and 423.15 K, respectively (de Loos et al., 1984); —, ----, our correlation with the parameters of Table 3.

the ethylene + *n*-eicosane and ethylene + *n*-tetracontane mixtures, respectively. The correlations with these values of $r$ were good in the low- and moderate-pressure regions, but not in the vicinity of the critical point. To correlate better the VLE over the entire pressure range with one set of parameters, it was necessary to determine $r$ along with $\chi$ and $k_{ij}$. The optimized values of $r$ are reported in Table 3. In this way, we found that it was possible to obtain a set of three parameters that were essentially temperature- and composition-independent. For best results, however, we allowed a slight variation of $k_{ij}$ with temperature. The values of the parameters are given in Table 3, and the correlations are shown in Figures 6 and 7. In this way a very good correlation of the compositions in both phases from low pressures to the critical point is possible with the present model.

## Conclusions

A mixing rule recently proposed by Wong and Sandler (1992) for cubic equations of state has been used to correlate the vapor-liquid equilibria of various polymer + solvent systems. We have shown that a two-parameter version of this model can correlate the solvent partial pressure in concentrated polymer solutions with high accuracy over a range of temperatures and pressures with temperature-independent parameters. For solvent + long-chain hydrocarbon and polymer + solvent systems for which accurate vapor-phase concentrations are important, the model is best used as a three-parameter correlation.

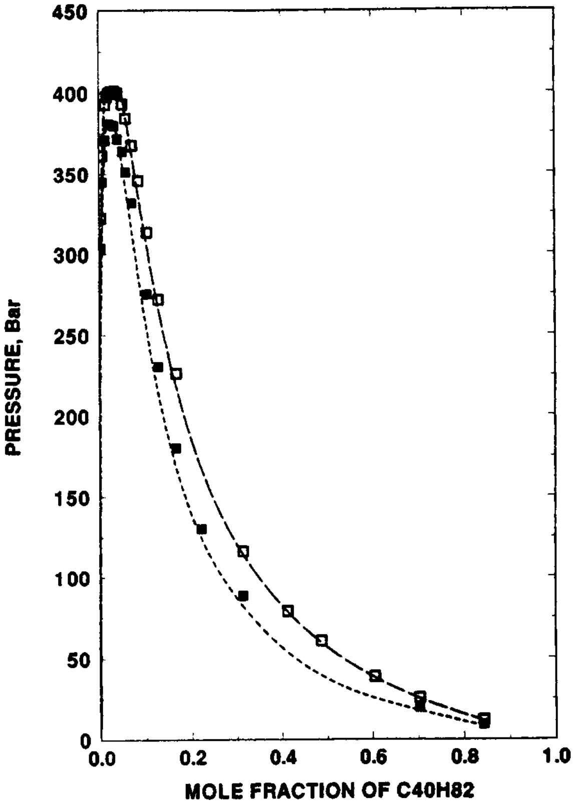

**Figure 7. Partial pressure of ethylene in *n*-tetracontane.**

■, □, experimental data at 373.15 and 423.15 K, respectively (de Loos et al., 1984); —, - - - -, our correlation with the parameters of Table 3.

Advantages of this approach are that it extends the application of cubic equations of state to polymer + solvent systems in a simple fashion by including the free volume effect in the excess free energy and that generally only temperature-independent parameters are required which allow for accurate interpolation between or extrapolation of existing experimental data.

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