Equations of State and Activity Coefficient Models for Vapor-Liquid Equilibria of Polymer Solutions

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Four noncubic equations of state (EOS) and five activity coefficient models are applied to binary polymer and solvent solutions. Solvent activities at intermediate concentrations and equilibrium pressures are predicted with the perturbed-soft-chain theory (PSCT), group-perturbed-soft-chain theory, (GPSCT), group-contribution-lattice fluid (GCLF) EOS, GC-Flory EOS, UNIFAC-FV, entropic-FV and GK-FV models, "new" UNIFAC, and modified Flory-Huggins model. Free-volume activity coefficient models (UNIFAC-FV, entropic-FV) are simpler and, when applied to polymer solutions, more accurate than the EOS. Activity coefficient models are restricted to low-pressure calculations and require accurate values of pure-component volumes. Mixture parameters for activity coefficient models and GC-Flory EOS have been previously evaluated from experimental vapor-liquid equilibrium data for mixtures with only low-molecular-weight compounds. The GC-Flory EOS, though more complicated than activity coefficient models, provides equally good or in some cases better predictions. The application of GC-Flory EOS developed as an activity coefficient model is restricted to low-pressure calculations. On the other hand, PSCT and GCLF developed as "true" EOS provide reliable equilibrium predictions using mixture parameters evaluated solely from pure-component properties together with standard mixing and combining rules. PSCT EOS performs generally better than GCLF EOS for polymer solutions considered in this study.

Introduction

Despite the continuously increasing interest in polymer solutions, most of the phase-equilibrium calculations have been carried out until rather recently with empirical and approximate models. Indeed, very little had been done until the last two decades since the famous activity coefficient expression was proposed and developed independently by Flory (1941, 1942) and Huggins (1941, 1942).

Flory and Huggins emphasized that, contrary to mixtures involving only low molecular weight compounds, the combinatorial and entropic effects in polymer solutions are especially pronounced, and often they are more important than the enthalpic effects. Using lattice statistics, Flory and Huggins derived independently their famous combinatorial expression, which in terms of the activity coefficient of component i is written:

$$\ln\gamma_i = \ln\frac{\phi_i^{\mathrm{vol}}}{x_i} + 1 - \frac{\phi_i^{\mathrm{vol}}}{x_i} \tag{1}$$

where ϕ_i^{vol} and x_i are the volume fraction and the mole fraction of component i, respectively. Note that the combinatorial expression proposed by Huggins is similar but not identical to Eq. 1. It has been, though, customary in the literature to

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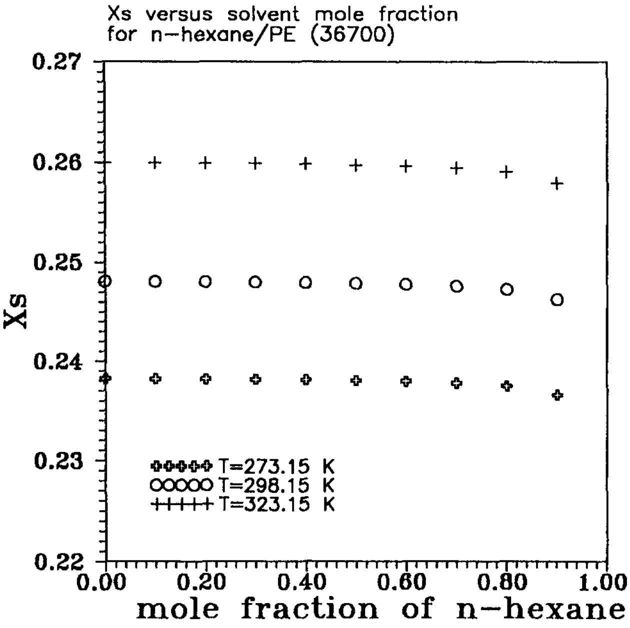

Figure 1. Entropic part of the FH parameter (χ_s) as calculated by the entropic-FV model vs. the mole fraction of the solvent for the system *n*-hexane/PE (36,700).

address Eq. 1 as the Flory-Huggins model, and the same practice will be followed here.

In order to apply Eq. 1 to real polymer solutions, an energy term must be added. Flory and Huggins used a van Laar heat of mixing term, which can be considered only a rough approximation of the energetic or the *residual* (other than combinatorial) contributions to the activity coefficient. The resulting equation for a binary solvent 1 /polymer 2 solution is:

$$\ln\gamma_1 = \ln\frac{\phi_1^{\text{vol}}}{x_1} + 1 - \frac{\phi_1^{\text{vol}}}{x_1} + \chi(\phi_2^{\text{vol}})^2 \qquad (2)$$

The parameter χ was initially considered to be a measure of the interchange energy between the molecules, but it was soon found to depend significantly on the temperature and the composition. It is often treated as a completely empirical free-energy term, which must be evaluated from experimental vapor-liquid equilibrium (VLE) data. The χ parameter includes in reality both free-volume and enthalpic effects and represents the major drawback of the Flory-Huggins theory. For nearly athermal polymer solutions, like hexane in polyethylene, excellent correlation can be achieved with a constant χ, which is for such solutions rather independent of temperature and composition. The χ-parameter for nearly athermal solutions is called the "entropic part" of the parameter (usually denoted as χ_s). For many solutions, this entropic part has a value between 0.2 and 0.3. Elbro et al. (1990) proposed recently a combined combinatorial/free-volume term, similar to Eq. 1, which uses free-volume instead of volume fractions (see Appendix B). Elbro's term represent the solvent activities in athermal polymer solutions much more accurately than the Flory-Huggins (FH) model with χ equal to zero (Eq. 1). Using Elbro's free-volume (FV) term, it is possible to estimate the χ_s parameter. It can be shown that the thus predicted χ_s values are almost constant over the entire composition range, relatively independent of temperature and have a typical value around 0.25, as shown in Figure 1 for the system *n*-hexane/PE (36,700) and discussed in some detail in Appendix A. This value is in agreement with what is reported in the literature (Brandrup and Immergut, 1989; Barton, 1990).

After the advent of group-contribution activity coefficient models for mixtures with low-molecular weight compounds, like the analytical solution of group theory (ASOG) (Derr and Deal, 1969, 1973) and UNIFAC (Fredenslund et al., 1975, 1977), various UNIFAC-based models have been proposed for polymer solutions. The most well-known is the *three-term* UNIFAC-FV model of Oishi and Prausnitz (1978). A different, also three-term, UNIFAC-FV expression has been recently developed and discussed in a series of publications by Iwai et al. (1985, 1989, 1990, 1991). Both UNIFAC-FV models include a combinatorial and a residual term taken from UNIFAC plus an additive free-volume term. In the Oishi-Prausnitz model, the free-volume term is calculated from the Flory EOS, while Iwai et al. derived their free-volume expression from a rather empirical partition function. The equations for these UNIFAC-FV models can be found in the original publications. The need for an additive free-volume term to the original UNIFAC combinatorial expression is evident, since the combinatorial term used in the original UNIFAC usually underestimates solvent activities in "athermal" polymer solutions.

A simpler *two-term* activity coefficient model (*entropic-FV*), also based on UNIFAC, has been recently proposed and developed by Elbro et al. (1990) and Kontogeorgis et al. (1993).

Both the entropic-FV and the UNIFAC-FV model of Oishi-Prausnitz will be considered here. Predictions will also be shown with other activity coefficient models:

- The GK-FV model, suggested by Kontogeorgis et al. (1993), which is a simple modification of the entropic-FV model;
- The "new" UNIFAC model, which uses the classical SG combinatorial term of the original UNIFAC and the new linear temperature-dependent parameter table developed by Hansen et al. (1992); and
- A modified FH model, proposed in this work, which is a combination of the FH combinatorial term (Eq. 1) with the residual term of UNIFAC (using the linear temperature-dependent parameters of Hansen et al., 1992).

An important difference should be noted. In the UNIFAC-FV model of Oishi and Prausnitz, the temperature-independent parameter table of the original UNIFAC model is used. In all the other (two-term) activity coefficient models (entropic-FV, GK-FV, modified FH, "new" UNIFAC), the recently developed linear temperature-dependent parameter matrix (Hansen et al., 1992) is used. These (two-term) models are discussed in some detail in Appendix B.

So far, mainly noncubic EOS have been proposed for polymer solutions. They can be divided into two categories:

(a) *The lattice-fluid EOS*, like the Panayiotou-Vera (1982) and its group-contribution version (GCLF) proposed by High and Danner (1990a). The GCLF EOS is discussed in Appendix C.

(b) *The van der Waals-type EOS*, that is, the EOS derived from different forms of the van der Waals partition function.

Various such equations exist, but the most important and by far more useful for polymer solutions are: the GC-Flory EOS (Chen et al., 1990; Bogdanic and Fredenslund, 1994), which is a simplification of the EOS of Holten-Andersen et al. (1987); the associated-perturbed-anisotropic-chain-theory (APACT) and its derivatives developed by Donohue and coworkers (Vimalchand and Donohue, 1985; Ikonomou and Donohue, 1986; Economou and Donohue, 1992).

In this work, we use the perturbed-soft-chain-theory (PSCT EOS, Morris et al., 1987), because its group-contribution version (GPSCT) can be easily applied to polymers. The PSCT is an improvement over the original perturbed-hard theory (PHCT) of Donohue and Prausnitz (1978).

The derivation and the final equations of the GC-Flory EOS are rather lengthy and the reader is referred to the original publications. The PSCT EOS is briefly presented and discussed in Appendix D.

It should be noted that simple cubic EOS have been recently proposed for polymer solutions, as well (Sako et al., 1989; Harismiadis et al., 1994; Kontogeorgis et al., 1994b). These EOS seem to perform very accurately for "athermal" and nonpolar polymer solutions, but they have not been investigated for solutions containing polar solvents yet.

The noncubic EOS mentioned above (GCLF, GC-Flory, PSCT, GPSCT) are derived from different forms of the partition function and they are rather complex. They are supposed to have a solid theoretical basis. GCLF and GC-Flory are group-contribution EOS, while PSCT is only semi-group contribution; it uses molecular parameters for the solvent and group parameters for the polymer, whose values are obtained from small molecules. A complete group-contribution version of PSCT (called GPSCT) exists, and is presented in Appendix D. GCLF and PSCT are *developed* as EOS, based on pure-component vapor pressure and saturated liquid molar volume data. The mixture parameters are evaluated from pure-component properties alone, using conventional mixing and combining rules. On the contrary, GC-Flory has been developed as an activity coefficient model, without using any vapor pressure data. VLE data for mixtures with only low molecular weight compounds have been used to evaluate the necessary group parameters for the GC-Flory model. Using these group parameters, GC-Flory can be used to predict solvent activities and pressures in polymer solutions. The application of the GC-Flory model as an EOS is currently under investigation (Berg, 1993; Bogdanic, 1993). GCLF and GC-Flory EOS have approximately the same number of group parameters. The PSCT EOS has molecular parameters for many solvents. All three EOS are equivalent from the range-of-applicability point of view. The UNIFAC-type activity coefficient models, however, can be used for a greater number of polymer solutions than the aforementioned EOS due to the large parameter table available for UNIFAC.

The purpose of this work is to present a comparison of the aforementioned activity coefficient models and EOS for the prediction of solvent activities at finite concentrations and equilibrium pressures in several athermal, nonpolar, and polar polymer solutions. Such comparisons exist in the literature (High and Danner, 1990b; Fried et al., 1992; Kontogeorgis et al., 1993), but they are either limited to infinite dilution activity coefficients or only few of the models discussed above are considered. No evaluation of the performance of the PSCT EOS for VLE calculations in polymer solutions has, to our knowledge, been published. In this work, we focus on some characteristic polymer solutions, which can reveal the advantages and the shortcomings of the various models.

The binary solvent-polymer solutions examined in this work are given in the next section of this article, along with the predictions of the EOS and the activity coefficient models. Correlations with the PSCT, the GPSCT EOS, and the classical FH model (Eq. 2) are also presented. We end with a thorough evaluation and discussion of the models, and conclude with some recommendations. The necessary equations for the models investigated here are presented in Appendixes B, C and D.

Systems, Methodology and Results

Solutions of various alkanes, aromatic solvents (like benzene), and other polar compounds (like acetone) with three polymers (PE, PIB, PS) are considered in this study. The exact description of these systems and the references of the experimental VLE data are given in Tables 1a and 1b.

Correlation with PSCT, GPSCT, classical Flory-Huggins

The PSCT, GPSCT, and FH models are in the next section used for prediction of VLE in polymer solutions. These models can also be used for correlation of experimental data using one adjustable parameter. The results of the correlations for some binary polymer solutions are given in Tables 1a and 1b.

The adjustable parameter in the FH model is the χ-parameter appearing in Eq. 2, while for the PSCT and GPSCT EOS it is the k_{ij} parameter (see Eq. D13 in Appendix D).

The χ parameter of the FH model has been estimated from experimental data by minimizing the following equation:

$$F=\frac{100}{N}\sum_{i=1}^{N}\left(\frac{\alpha_{1,i}^{\text{calc}}-\alpha_{1,i}^{\text{exp}}}{\alpha_{1,i}^{\text{exp}}}\right)^2 \tag{3}$$

where $\alpha_{1,i}$ is the activity of the solvent at data point i. N is the number of experimental VLE data points.

The k_{ij} parameter of the PSCT and GPSCT EOS has been estimated from experimental data by minimizing the following equation:

$$F=\frac{100}{N}\sum_{i=1}^{N}\frac{|P_{1,i}^{\text{calc}}-P_{1,i}^{\text{exp}}|}{P_{1,i}^{\text{exp}}} \tag{4}$$

where $P_{1,i}$ is the equilibrium (solvent) pressure at data point i, as taken from the bubble-point pressure calculations. Equations 3 and 4 are equivalent.

Using only one binary adjustable parameter for every isotherm (χ for the FH model, and k_{ij} for PSCT and GPSCT), excellent quantitative agreement is obtained with the experimental data for nearly athermal polymer solutions, as can be seen in Table 1a. No attempt was made to develop a temperature or composition dependent correlation for either χ or k_{ij}.

When using the FH model, both the solvent and the polymer volumes are required as a function of temperature. The correlation results presented in Table 1a were obtained using the

Table 1a. Correlation Results for Nearly Athermal Polymer Solutions

System	k_{ij} PSCT	% AAD PSCT	k_{ij} GPSCT	% AAD GPSCT	χ FH	% AAD FH
$nC6$/PE (50 K), 7 p., $T=353.15$ K	0.006	7.39	0.004	7.72	0.473	8.98
$nC6$/PE (50 K), 18 p., $T=410.15$ K	0.015	5.37	0.0125	5.43	0.566	8.03
$nC6$/PE (50 K), 6 p., $T=416.15$ K	0.0108	5.28	0.008	5.16	0.486	7.84
$nC6$/PE (50 K), 8 p., $T=430.15$ K	0.0087	4.07	0.0055	3.88	0.368	7.32
$nC10$/PE (50 K), 9 p., $T=458.15$ K	−0.0014	0.94	0.0012	1.07	0.142	1.11
$cC6$/PE (50 K), 6 p., $T=373.15$ K	0.0133	3.62	0.0133	3.62	0.404	3.95
$cC6$/PIB (100 K), 10 p., $T=298.15$ K	0.010	1.55	0.010	1.55	0.457	1.73
$cC6$/PIB (100 K), 10 p., $T=313.15$ K	0.0106	0.93	0.0106	0.93	0.414	0.78
$cC6$/PIB (100 K), 9 p., $T=338.15$ K	0.0117	2.37	0.0117	2.37	0.446	2.11

Percentage average absolute deviation in equilibrium pressures with the PSCT and GPSCT EOS using one binary adjustable parameter k_{ij}, and with the Flory-Huggins activity coefficient model (Eq. 2) using a single χ parameter. Experimental data: PE solutions (Wen et al., 1991); cyclohexane/PIB (Bawn and Patel, 1956). Molecular weight of the polymer is in parentheses; 50 K = 50,000; xp. = number of experimental VLE data points. % AAD = percentage average absolute deviation; $cC6$ = cyclohexane.

Table 1b. Correlation Results for PIB and PS Solutions

System	k_{ij} PSCT	% AAD PSCT	k_{ij} GPSCT	% AAD GPSCT
Benzene/PIB (45 K), 8 p., $T=298.15$ K	0.0158	3.08	0.0158	3.08
Benzene/PIB (45 K), 10 p., $T=313.15$ K	0.0168	4.26	0.0168	4.26
Benzene/PIB (45 K), 11 p., $T=338.15$ K	0.0170	2.98	0.0170	2.98
Acetone/PS (15.7 K), 8 p., $T=298.15$ K	0.0072	5.14	0.0790	14.18
Acetone/PS (15.7 K), 7 p., $T=323.15$ K	0.0088	3.89	0.1110	11.23
MEK/PS (290 K), 4 p., $T=298.15$ K	0.0046	1.25	−0.040	20.79
MEK/PS (290 K), 4 p., $T=343.15$ K	0.0043	3.17	0.056	13.33
Chloroform/PS (90 K), 6 p., $T=298.15$–323.15 K	−0.0055	3.97	ns	—
Chloroform/PS (290 K), 11 p., $T=298.15$ K	−0.0020	3.25	ns	—
Chloroform/PS (290 K), 12 p., $T=323.15$ K	−0.0058	4.49	ns	—
Toluene/PS (290 K), 11 p., $T=298.15$ K	−0.0013	1.89	—	—
Toluene/PS (290 K), 3 p., $T=333.15$ K	−0.0030	0.53	−0.010	40.89
Toluene/PS (290 K), 3 p., $T=353.15$ K	−0.0027	0.29	—	—
$cC6$/PS (25.1 K), 7 p., $T=297.15$ K	0.0043	9.14	0.0043	9.14
$cC6$/PS (25.1 K), 12 p., $T=307.15$ K	0.0057	17.47	0.0057	17.47
$cC6$/PS (25.1 K), 10 p., $T=307.15$ K	0.0048	7.63	0.0048	7.63
$cC6$/PS (25.1 K), 10 p., $T=317.15$ K	0.0050	10.38	0.0050	10.38
$cC6$/PS (154 K), 9 p., $T=303.15$ K	0.0020	1.76	0.0020	1.76
$cC6$/PS (154 K), 9 p., $T=318.15$ K	0.0015	1.53	0.0015	1.53
$cC6$/PS (154 K), 9 p., $T=338.15$ K	0.0012	1.47	0.0012	1.47
$cC6$/PS (440 K), 10 p., $T=307.15$ K	0.0017	4.47	0.0017	4.47
$cC6$/PS (440 K), 6 p., $T=317.15$ K	0.0032	6.55	0.0032	6.55

Percentage average absolute deviation in equilibrium pressures with the PSCT and GPSCT EOS using one binary adjustable parameter (k_{ij}). Experimental data: cyclohexane/PS solutions (Wen et al., 1991); benzene/PIB (Bawn and Patel, 1956); acetone/PS, chloroform/PS (Bawn and Wajid, 1956); MEK/PS, toluene/PS (Bawn et al., 1950). Molecular weight of the polymer is in parentheses; NS = the method cannot be used for this system due to lack of group and/or molecular parameters.

DIPPR equation (Daubert and Danner, 1989) for the estimation of the solvent's volume, the group-contribution volume (GCVOL) method (Elbro et al., 1991) for the estimation of the volume of polyethylene (PE), and an experimental correlation (Kontogeorgis et al., 1994a) for polyisobutylene (PIB).

The unrealistic value of $\chi=0.566$ obtained with the FH model for the system n-hexane/PE at 410.15 K reflects the need for the often used composition dependent χ-parameter, as well as the uncertainty in the data. Note that for this system the predictions obtained with the various models (Tables 2a and 2b) are significantly worse than for the other n-hexane/PE solutions. The uncertainty in the data and the weakness of the FH model are also reflected in the trends of the χ parameter with respect to temperature. Although theory suggests that χ should vary proportionally with $1/T$, this is often not the case when actual experimental data at different temperatures are used to evaluate the parameter. This conclusion, which is fully supported in the literature, is also made here.

When using either the PSCT or the GPSCT EOS, polymer molecules are treated as a sum of groups and, therefore, the group-contribution approach is used for the polymer with the group parameters given by Jin et al. (1986). In the case of the PSCT EOS, the solvent molecule is treated as a unique group with its properties calculated from the PSCT (see Table 6 in reference to Appendix D). On the other hand, calculations with the GPSCT EOS are performed by treating the solvent molecule in the same way as the polymer molecule, that is as a sum of different groups with their properties calculated from the GPSCT tables (Jin et al., 1986). Georgeton and Teja (1988) have developed a group-contribution version of the Simplified-PHCT (SPHCT) that gives accurate representation of VLE for mixtures of small molecules (nonpolymers). Other correlations for the molecular parameters of the PHCT EOS and its derivatives also exist (Wang and Whiting, 1988; Gasem and Robinson, 1990).

Prediction with all EOS and activity coefficient models

All the activity coefficient models investigated here (including the modified FH) and the GC-Flory EOS are purely predictive, since their mixture group parameters have been

Table 2a. Prediction Results for PE and PIB Solutions

System	% AAD PSCT	% AAD GPSCT	% AAD GC-Flory	% AAD GCLF
nC6/PE (50 K), 7 p., $T=353.15$ K	18.74	15.02	7.9	24.7
nC6/PE (50 K), 18 p., $T=410.15$ K	31.49	27.99	8.3	30.6
nC6/PE (50 K), 6 p., $T=416.15$ K	16.80	13.51	6.3	17.4
nC6/PE (50 K), 8 p., $T=430.15$ K	12.12	8.63	8.2	11.4
nC10/PE (50 K), 9 p., $T=458.15$ K	4.76	3.53	23.5	1.2
cC6/PE (50 K), 6 p., $T=373.15$ K	31.17	31.17	4.4	31.1
cC6/PIB (100 K), 10 p., $T=298.15$ K	12.50	12.50	1.7	11.4
cC6/PIB (100 K), 10 p., $T=313.15$ K	12.36	12.36	1.1	11.4
cC6/PIB (100 K), 9 p., $T=338.15$ K	12.01	12.01	1.9	11.7
Benzene/PIB (45 K), 8 p., $T=298.15$ K	23.95	23.95	2.7	25.0
Benzene/PIB (45 K), 10 p., $T=313.15$ K	24.93	24.93	3.2	25.9
Benzene/PIB (45 K), 11 p., $T=338.15$ K	20.54	20.54	2.4	21.8

Percentage average absolute deviation between experimental and predicted equilibrium pressures with four EOS (PSCT, GPSCT, GC-Flory, and GCLF) for PE and PIB solutions. No adjustable parameters are used. Molecular weight of the polymer is in parentheses.

estimated from VLE data for systems with only solvents (low molecular weight compounds). PSCT, GPSCT, and GCLF EOS are also purely predictive if the k_{ij} parameter is set equal to zero. Upon doing so, we have performed VLE predictions (equilibrium pressures and solvent activities) with all models (four EOS and five activity coefficient models) for various polymer solutions. The results are given in Tables 2 and 3, as percentage average absolute deviations between experimental and predicted equilibrium pressures. This is equivalent with using the percentage average absolute deviation between experimental and predicted solvent activities, as can be seen in Table 4, for the GCLF, GC-Flory, and UNIFAC-FV models. Predictions with some of the models for characteristic polymer solutions are also presented graphically in Figures 2-7. In these figures, the experimental and the predicted pressures are shown as a function of the weight fraction of the solvent.

Regarding Tables 1-3 there are several points to be noted:

(1) The predictions with the GC-Flory EOS presented in this work have been carried out with the new parameter table recently developed by Bogdanic and Fredenslund (1994).

(2) The GCLF and CPSCT EOS cannot be used for the chloroform/PS solutions, due to lack of the parameters for the chloroform group.

(3) An arbitrary value for the molecular weight of polyethylene (equal to 50,000) was used for the calculations with all the models and for all the solutions involving this polymer. This was done because the exact molecular weight was not reported in the reference of the experimental data. Although the influence of the polymer's molecular weight on VLE cal-

Table 2b. Prediction Results for PE and PIB Solutions

System	% AAD Entr-FV	% AAD GK-FV	% AAD UNIFAC-FV	% AAD mod. FH	% AAD UNIFAC
nC6/PE (50 K), 7 p., $T=353.15$ K	16.7	13.3	26.9	34.0	44.1
nC6/PE (50 K), 18 p., $T=410.15$ K	19.9	16.7	36.9	38.4	51.0
nC6/PE (50 K), 6 p., $T=416.15$ K	11.9	9.8	26.3	24.5	35.3
nC6/PE (50 K), 8 p., $T=430.15$ K	7.5	6.5	22.4	18.6	30.5
nC10/PE (50 K), 9 p., $T=458.15$ K	5.9	8.6	10.6	12.1	25.1
cC6/PE (50 K), 6 p., $T=373.15$ K	18.6	18.6	30.3	31.4	40.3
cC6/PIB (100 K), 10 p., $T=298.15$ K	5.6	5.3	4.8	11.7	15.5
cC6/PIB (100 K), 10 p., $T=313.15$ K	4.5	4.2	4.3	11.1	15.3
cC6/PIB (100 K), 9 p., $T=338.15$ K	4.2	3.9	4.7	11.1	15.8
Benzene/PIB (45 K), 8 p., $T=298.15$ K	2.5	4.1	3.1	11.5	16.9
Benzene/PIB (45 K), 10 p., $T=313.15$ K	4.0	5.1	3.6	13.2	18.9
Benzene/PIB (45 K), 11 p., $T=338.15$ K	2.7	3.8	4.3	11.7	17.9

Percentage average absolute deviation between experimental and predicted equilibrium pressures with five activity coefficient models (entr(opic)-FV, GK-FV, UNIFAC-FV, mod(ified) FH, and (new) UNIFAC) for PE and PIB solutions. No adjustable parameters are used. Molecular weight of the polymer is in parenthesis.

culations for polymer solutions is small, the use of a completely erroneous value of the molecular weight may not lead to very accurate predictions especially for the solvent's activity or the equilibrium pressures. On the contrary, the weight fraction activity coefficients of the solvent ($\Omega_1 = \alpha_1/w_1$) are less influenced by the uncertainty in the knowledge of the molecular weight. The influence of the arbitrary molecular weight used for PE is reflected both in the fair correlation results with PSCT and FH (Tables 1a and 1b) as compared to the correlation achieved for the PIB solutions and in the predictions with almost all the models (with the exception of the GC-Flory EOS), as can be seen in Tables 2a and 2b. Note that, contrary to the excellent correlation and the very good predictions obtained with the generally very successful activity coefficient models for the similar PIB solutions, the results for the PE solutions are only fair.

(4) Predictions with the GPSCT EOS are given only for some of the solutions considered here, due to the large prediction errors obtained for most of them with this EOS. Even the correlation with the GPSCT (see Table 1b) is rather unsuccessful for many solutions. These problems with the GPSCT EOS are due to the inaccurate prediction of the pure solvent vapor pressures, as discussed later.

(5) The only difference between the entropic-FV and the GK-FV models is the inclusion in the latter of the Staverman-Guggenheim (SG) (Staverman, 1950) shape correction term. The exact equations are given in Appendix B. The SG correction is not important for most athermal solutions, but it may be significant for some polymer solutions containing polar solvents, like the PS/acetone system. This point is discussed later.

(6) The solutions of PE and PIB with *n*-alkanes and cyclohexane are treated by the UNIFAC-type activity coefficient models as purely athermal, that is, the value of the residual (energetic) part of the activity coefficient is unity. This is only approximately true, since there are no solutions that are athermal over a wide range of temperatures. The percentage deviation in solvent activities obtained from the different UNIFAC based models for these solutions reflect the differences between the various combinatorial and combined combinatorial and free-volume terms.

Discussion

Correlation with PSCT, GPSCT, classical Flory-Huggins

The correlation results with the PSCT, GPSCT EOS, and the classical Flory-Huggins model, as given by Eq. 2, are presented in Tables 1a and 1b. All three models are used with only one adjustable parameter, the k_{ij} parameter (PSCT and GPSCT) and the χ parameter (Flory-Huggins), as discussed previously. For the nearly athermal polymer solutions shown in Table 1a (PE, PIB with hydrocarbons), the correlative capabilities of PSCT, GPSCT, and FH are similar over the entire composition and temperature range. For some of the solutions shown in Table 1b, however, like PS/toluene, PS/acetone, and PS/methyl ethyl ketone (MEK), the GPSCT EOS *does not* correlate the equilibrium solvent pressures satisfactory with one adjustable parameter. However, the PSCT EOS correlates polar solutions as accurately as nonpolar or athermal solutions. The poor correlation obtained with the GPSCT EOS is probably due to the inaccurate predictions of the pure solvent vapor pressures with this EOS. It seems that the GPSCT EOS cannot describe accurately the properties of the solvents composed of different functional groups. We have tested both PSCT and GPSCT for calculating the vapor pressure of various pure solvents, and the results are shown in Table 5. In all cases, deviations between PSCT values and experimental data were less than 3% and for most systems less than 2%. On the other hand, deviations between GPSCT predictions and experimental values were often above 100%, as can be also seen in Table 5. For example, the experimental vapor pressure of toluene at 25°C is 0.038 bar. PSCT predicts a vapor pressure of 0.037 bar and GPSCT a value of 0.334 bar! These results contradict the claim by Jin et al. (1986) concerning the accuracy of GPSCT for vapor pressure prediction of pure components. GPSCT seems to work well for aliphatic hydrocarbons, since the PSCT molecular parameters for these compounds vary linearly with carbon number (or molecular size) and can be accurately correlated, as shown by Morris et al. (1987). However, the group-

Table 3a. Prediction Results for PS Solutions

System	% AAD PSCT	% AAD GPSCT	% AAD GC-Flory	% AAD GCLF
Acetone/PS (15.7 K), 8 p., $T = 298.15$ K	16.25	58.59	2.7	36.1
Acetone/PS (15.7 K), 7 p., $T = 323.15$ K	15.19	64.47	6.1	36.4
MEK/PS (290 K), 4 p., $T = 298.15$ K	12.40	32.57	1.4	21.9
MEK/PS (290 K), 4 p., $T = 343.15$ K	12.46	41.51	5.8	26.1
Chloroform/PS (90 K), 6 p., $T = 298.15$-323.15 K	7.57	ns	46.7	ns
Chloroform/PS (290 K), 11 p., $T = 298.15$ K	4.84	ns	60.0	ns
Chloroform/PS (290 K), 12 p., $T = 323.15$ K	9.87	ns	47.6	ns
Toluene/PS (290 K), 11 p., $T = 298.15$ K	3.37	228.95	1.4	9.1
Toluene/PS (290 K), 3 p., $T = 333.15$ K	8.67	44.89	1.2	10.9
Toluene/PS (290 K), 3 p., $T = 353.15$ K	3.03	—	0.5	5.2
*c*C6/PS (25.1 K), 7 p., $T = 297.15$ K	13.73	13.73	9.3	23.4
*c*C6/PS (25.1 K), 12 p., $T = 307.15$ K	21.85	21.85	17.5	30.3
*c*C6/PS (25.1 K), 10 p., $T = 307.15$ K	11.53	11.53	8.8	21.6
*c*C6/PS (25.1 K), 10 p., $T = 317.15$ K	13.42	13.42	10.9	23.9
*c*C6/PS (154 K), 9 p., $T = 303.15$ K	2.13	2.13	2.4	6.8
*c*C6/PS (154 K), 9 p., $T = 318.15$ K	1.73	1.73	2.6	6.0
*c*C6/PS (154 K), 9 p., $T = 338.15$ K	1.59	1.59	3.4	5.0
*c*C6/PS (440 K), 10 p., $T = 307.15$ K	6.07	6.07	5.1	16.8
*c*C6/PS (440 K), 6 p., $T = 317.15$ K	8.73	8.73	6.9	18.7

Percentage average absolute deviation between experimental and predicted equilibrium pressures with four EOS (PSCT, GPSCT, GC-Flory and GCLF) for PS solutions. No adjustable parameters are used. Molecular weight of the polymer is in parentheses.

Table 3b. Prediction Results for PS Solutions

System	% AAD Entr-FV	% AAD GK-FV	% AAD UNIFAC-FV	% AAD mod. FH	% AAD UNIFAC
Acetone/PS (15.7 K), 8 p., $T = 298.15$ K	12.9	7.2	5.3	23.4	15.4
Acetone/PS (15.7 K), 7 p., $T = 323.15$ K	14.7	6.5	5.8	26.5	19.5
MEK/PS (290 K) 4 p., $T = 298.15$ K	10.0	11.3	6.9	19.6	8.9
MEK/PS (290 K) 4 p., $T = 343.15$ K	13.2	11.0	4.7	25.5	16.3
Chloroform/PS (90 K), 6 p., $T = 298.15$-323.15 K	2.8	5.2	5.7	10.4	9.7
Chloroform/PS (290 K), 11 p., $T = 298.15$ K	5.0	7.2	7.5	8.8	7.8
Chloroform/PS (290 K), 12 p., $T = 323.15$ K	3.6	7.3	4.1	8.9	8.6
Toluene/PS (290 K), 11 p., $T = 298.15$ K	5.8	3.9	9.0	12.0	14.7
Toluene/PS (290 K), 3 p., $T = 333.15$ K	6.7	3.7	10.9	18.0	23.5
Toluene/PS (290 K), 3 p., $T = 353.15$ K	3.7	2.3	6.5	8.9	11.9
*c*C6/PS (25.1 K) 7 p., $T = 297.15$ K	15.8	10.5	16.2	21.9	20.9
*c*C6/PS (15.1 K) 12 p., $T = 307.15$ K	24.4	19.1	23.8	30.2	29.5
*c*C6/PS (25.1 K) 10 p., $T = 307.15$ K	15.7	10.4	15.0	21.6	20.9
*c*C6/PS (25.1 K) 10 p., $T = 317.15$ K	18.4	12.4	17.1	25.1	24.6
*c*C6/PS (154 K), 9 p., $T = 303.15$ K	3.9	1.8	3.8	6.6	6.2
*c*C6/PS (154 K), 9 p., $T = 318.15$ K	3.8	1.5	3.1	6.7	6.4
*c*C6/PS (154 K), 9 p., $T = 338.15$ K	3.7	1.3	2.7	6.7	6.7
*c*C6/PS (440 K), 10 p., $T = 307.15$ K	11.4	10.7	9.6	16.9	16.2
*c*C6/PS (440 K), 6 p., $T = 317.15$ K	14.0	13.7	11.8	20.1	19.7

Percentage average absolute deviation between experimental and predicted equilibrium pressures with five activity coefficient models (entr(opic)-FV, GK-FV, UNIFAC-FV, mod(ified) FH, and (new) UNIFAC) for PS solutions. No adjustable parameters are used. Molecular weight of the polymer is in parentheses.

Table 4. Percentage Average Absolute Deviation Between Experimental and Predicted Equilibrium Pressures and Solvent Activities with Three Models (GCLF, GC-Flory, and UNIFAC-FV) for Some Typical Polymer Solutions

Polymer Solution	GCLF EOS		GC-Flory EOS		UNIFAC-FV	
	% AAD pressure	% AAD activity	% AAD pressure	% AAD activity	% AAD pressure	% AAD activity
Acetone/PS (15.7 K), $T = 298.15$ K	36.1	35.4	—	—	5.3	5.4
MEK/PS (290 K), $T = 343.15$ K	26.1	28.1	—	—	4.7	3.6
Toluene/PS (290 K), $T = 298.15$ K	9.1	8.7	—	—	9.0	8.6
*c*C6/PIB (100 K), $T = 313.15$ K	11.4	11.3	1.1	1.1	4.3	4.2
*n*C10/PE (50 K), $T = 353.15$ K	24.7	23.8	7.9	8.2	26.9	26.0

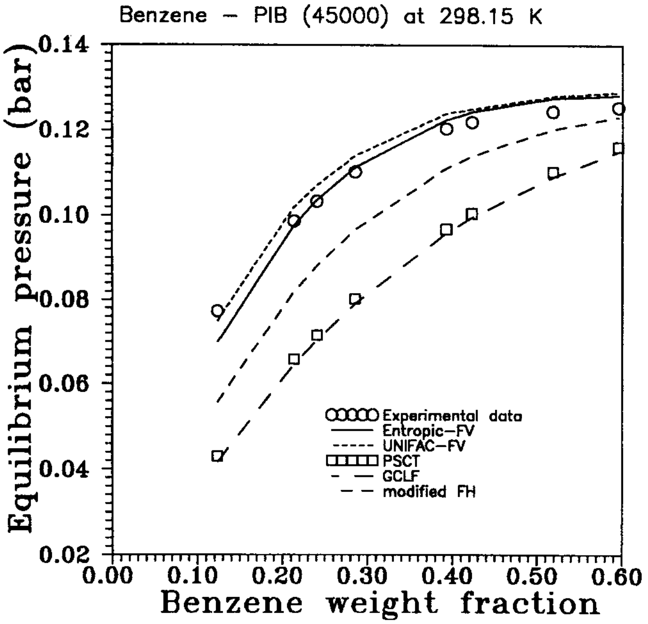

Figure 2. Experimental and predicted equilibrium pressures vs. weight fraction of the solvent for the system benzene/PIB (45,000) at $T = 298.15$ K.

PSCT results coincide with GPSCT results.

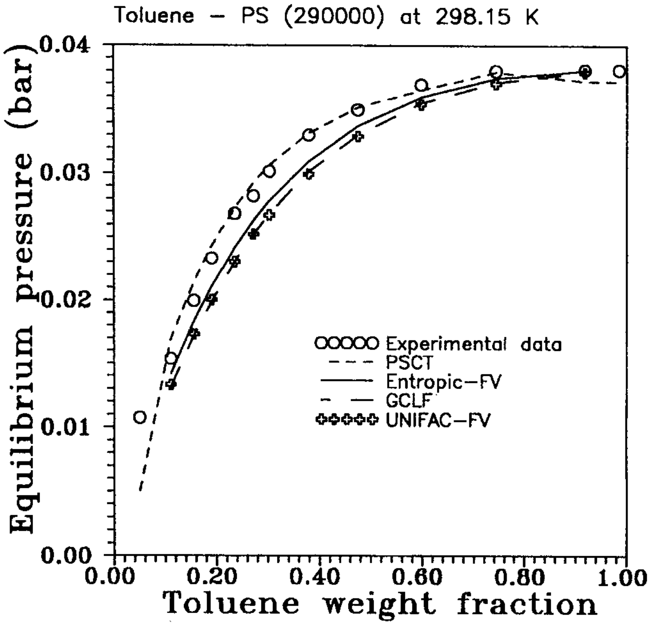

Figure 4. Experimental and predicted equilibrium pressures vs. the weight fraction of the solvent for the system toluene/PS (290,000) at $T = 298.15$ K.

contribution approach fails for the aromatics and ketones. The failure of the group-contribution approach for multifunctional molecules can easily be shown from the following test. Using the values for the PSCT parameters reported by Morris et al. (1987) for five aromatics (toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene), the parameter values given by Jin et al. (1986) for the $-CH_3-$, $-CH_2-$, and aromatic hydrocarbon groups and the combining rules (D8) through (D12) (see Appendix D), we back calculated the parameters for the aromatic R-C group. For all three group parameters (r_0^i, f_0^i, and q_0^i) the values obtained were very different. For example, f ranged from 0.1507

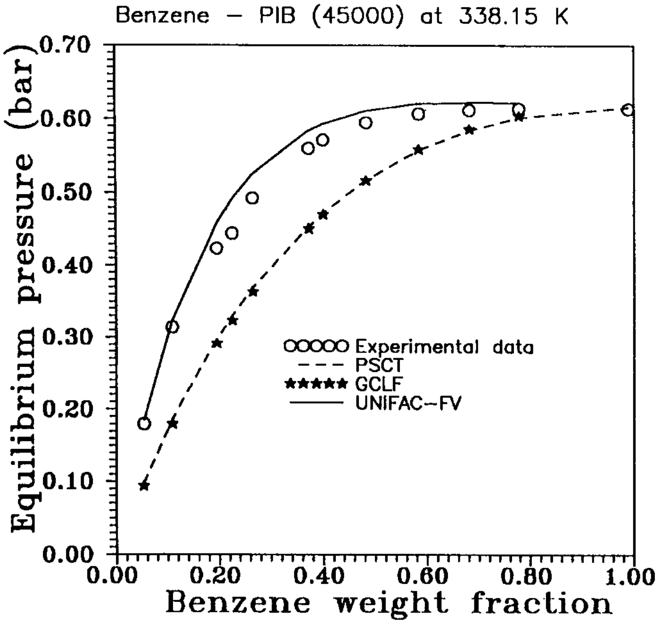

Figure 3. Experimental and predicted equilibrium pressures vs. the weight fraction of the solvent for the system benzene/PIB (45,000) at $T = 338.15$ K.

PSCT results coincide with GPSCT results.

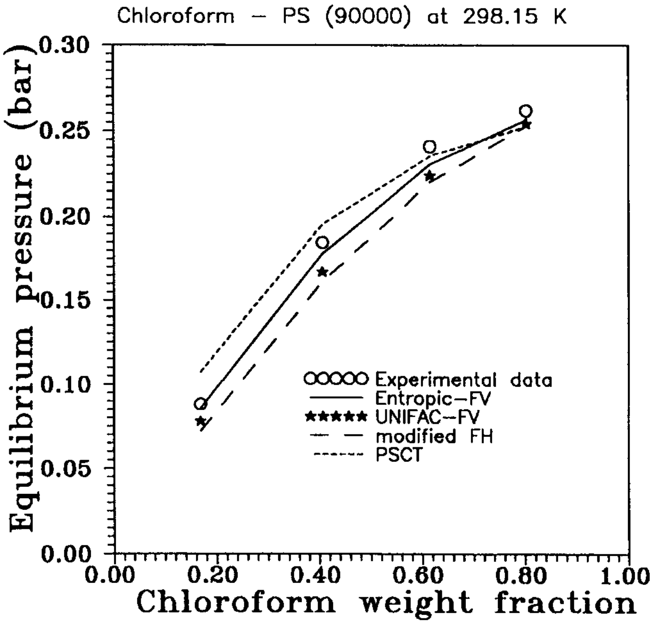

Figure 5. Experimental and predicted equilibrium pressures vs. the weight fraction of the solvent for the system chloroform/PS (90,000) at $T = 298.15$ K.

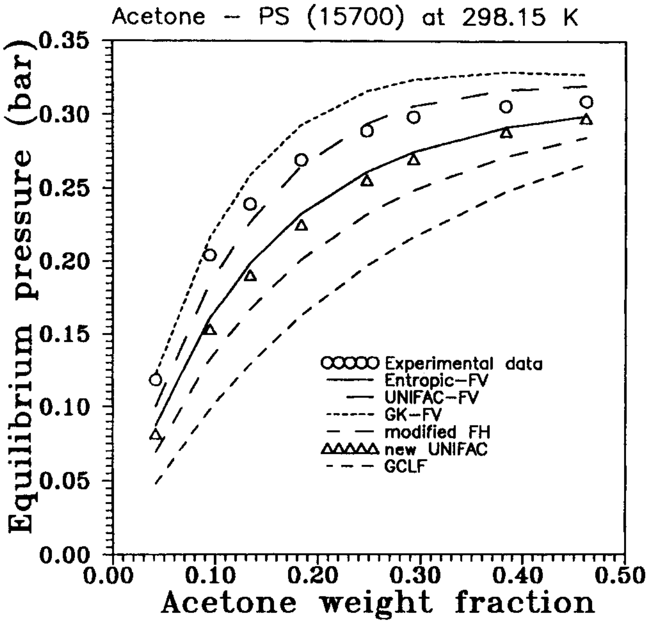

Figure 6. Experimental and predicted equilibrium pressures vs. the weight fraction of the solvent for the system acetone/PS (15,700) at $T = 298.15$ K.

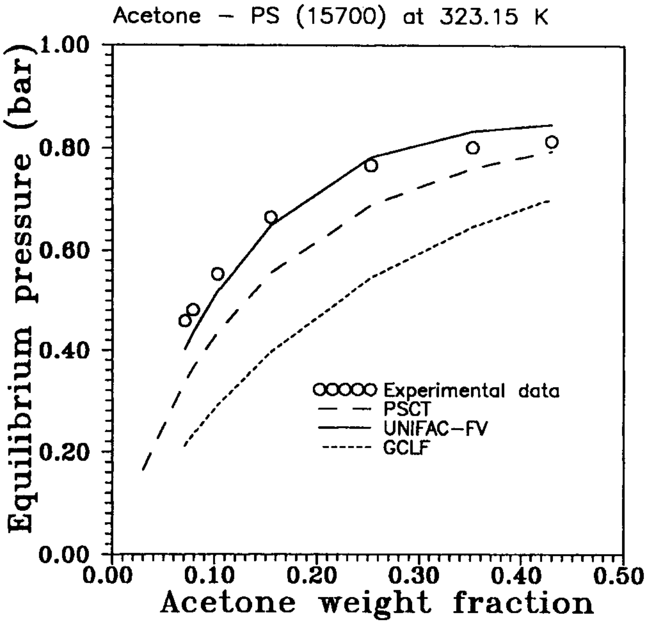

Figure 7. Experimental and predicted equilibrium pressures vs. the weight fraction of the solvent for the system acetone/PS (15,700) at $T = 323.15$ K.

for *p*-xylene to 0.2134 for toluene, while Jin et al. (1986) recommend a value of 0.12824. Similarly, *q* ranged from 0.1894 for ethylbenzene to 0.3387 for *m*-xylene, and the value reported by Jin et al. (1986) is 0.3262.

UNIFAC and other group-contribution methods have been applied for the prediction of pure component vapor pressures (Fredenslund and Rasmussen, 1979; Macknick and Prausnitz, 1979; Jensen et al., 1981). These methods have also been somewhat successful for straight chain compounds, like normal alkanes, but the prediction of the vapor pressures for cyclic and other branched compounds presents difficulties, as discussed by Fredenslund and Rasmussen (1979). It may be concluded that accurate prediction of pure-component vapor pressures is beyond the capabilities of current group contribution methods.

Prediction with all EOS and activity coefficient models

The predictions of the various models are, for all systems, given in Tables 2 and 3, and in graphical form for some typical solutions in Figures 2–7. The predictions for the PE and the PIB solutions are presented in Tables 2a and 2b, while the predictions for the PS solutions are shown in Tables 3a and 3b. The polymer solutions presented in Tables 2a, 2b, and in Figures 2 and 3 contain nonpolar polymers with hydrocarbon solvents and, therefore, the observed nonideality is mainly due to combinatorial and free-volume effects. These relatively nonpolar systems can serve as a test for the various combinatorial and free-volume terms used in the EOS and activity coefficient models. The systems shown in Tables 3a and 3b and in Figures 4–7 are relatively or strongly polar. The contribution, thus, of

Table 5. Experimental and Calculated Vapor Pressures for Pure Solvents from the PSCT and the GPSCT EOS

Solvent	T (°C)	P^{exp} (bar)	P^{PSCT} (bar)	% AAD PSCT	P^{GPSCT} (bar)	% AAD GPSCT
Acetone	25	0.3095	0.3184	2.86	0.6146	98.60
Acetone	50	0.8197	0.8496	3.67	1.6196	97.58
MEK	25	0.1190	—	—	0.5980	402.53
MEK	70	0.7320	—	—	2.2240	203.80
Toluene	25	0.0381	0.0372	2.37	0.3390	776.28
Toluene	60	0.1849	0.1839	0.52	0.9762	427.93
Toluene	80	0.3890	0.3880	0.26	1.6428	322.32
Chloroform	25	0.2630	0.2570	2.30	ns	—
Chloroform	50	0.6870	0.6880	0.17	ns	—
Benzene	25	0.1255	0.1278	1.86	0.1278	1.86
Benzene	40	0.2431	0.2438	0.27	0.2438	0.27
Benzene	65	0.6141	0.6166	0.41	0.6165	0.39
n-Hexane	137	5.762	5.750	0.21	6.7380	16.95
n-Decane	185	1.337	1.326	0.84	2.9380	119.73

the energetic (residual) term can be very significant and, sometimes, predominant.

Solutions of Polyethylene and Polyisobutylene. It seems that for these simple relatively nonpolar solutions the activity coefficient models (especially the entropic-FV and the GK-FV), and the GC-Flory EOS are the most accurate models for the prediction of equilibrium pressures and solvent activities at intermediate concentrations. The relatively large errors for the PE solutions with the activity coefficient models, as compared to the very good accuracy obtained with the same models for the similar PIB solutions, is probably due to the arbitrary value used for the molecular weight of polyethylene, as discussed previously.

Both the PSCT and GCLF EOS reveal some problems for these solutions, especially for the ones containing PIB. In the case of GCLF, the poor predictions for the PIB solutions may be attributed to the questionable group-contribution values for the quaternary carbon atom "*C*," as discussed further in Appendix C.

For the solutions with cyclohexane and benzene, calculations with the GPSCT and PSCT EOS are identical, since each one of the molecules of cyclohexane and benzene is composed of one functional group (-CH_2- for the cyclohexane and aromatic H-C for the benzene). The percentage average absolute deviation in pressure for the benzene/PIB solutions is almost twice that for the cyclohexane/PIB systems. Similar results are obtained with the GCLF EOS as well. In the case of the PSCT EOS, this is due to the fact that in the cyclohexane/PIB systems both components interact through nonpolar dispersion (Lennard-Jones) interactions, whereas in the benzene/PIB solutions, polar and induced polar interactions are present due to the quadrupole moment of the aromatic ring of benzene. PSCT and as a result GPSCT account explicitly only for Lennard-Jones interactions and polar effects such as the quadrupolar interactions are accounted implicitly through the three molecular parameters of the equation (T^*, v^*, and c). A more accurate model for polar compounds such as the perturbed-anisotropic-chain-theory (PACT) would improve the agreement between the calculated and the experimental results. Unfortunately, no accurate method exists for the estimation of molecular parameters of polymers for PACT, yet.

Finally, note that the predictions with both the PSCT and the GPSCT EOS are in reasonable agreement with the experimental data for PE solutions and similar to each other. In fact, for the systems with *n*-hexane and *n*-decane, GPSCT is systematically better by approximately 3%. This is surprising considering the inaccurate solvent vapor pressures calculated from the GPSCT and indicates the large cancellation of errors achieved, in some cases, with the GPSCT EOS.

Polystyrene Solutions. The UNIFAC-FV and the entropic-FV activity coefficient models are consistently more accurate than the PSCT and the GCLF EOS, while the GPSCT EOS is by far the worst model. The predictions with the GC-Flory EOS are, except for the chloroform containing solutions, comparable to those of the simpler activity coefficient models. The large predictive errors obtained with the GPSCT EOS are, as discussed previously, mainly due to the inaccurate predictions for the solvent vapor pressures. Unless these vapor pressure predictions can be improved, the GPSCT EOS *should not* be used for VLE calculations in polymer solutions.

UNIFAC-FV and especially the GC-Flory EOS are the most accurate models for the two ketone/PS solutions, while the entropic-FV is the best model for the chloroform/PS and toluene/PS solutions. The empirical GK-FV model seems to have the best overall behavior, although the performance of these three free-volume activity coefficient models and of the GC-Flory EOS is very similar. For some of these solutions (for example, chloroform/PS), even the modified Flory-Huggins and the "new" UNIFAC models can be used satisfactory. This is due to the importance and magnitude of the energetic effects for such polar solutions which are properly taken into account by the UNIFAC residual term. Note that, as known in the literature and also shown in Figure 2, the (modified) FH and (new) UNIFAC models usually underestimate to a significant degree the solvent activities and equilibrium pressures in nearly athermal and relatively nonpolar polymer solutions. This indicates the need of an additive free-volume correction, like the ones used in the UNIFAC-FV models (Oishi and Prausnitz, 1978; Iwai et al., 1990), or of a combined combinatorial/free-volume term, like the one used in the entropic-FV model.

Shape Effects in Polymer Solutions. The FH combinatorial term (as used in this work) is based on volume fractions. It gives in most cases better predictions than the classical combinatorial term (of the original and "new" UNIFAC models), which is based on segment fractions (see, for example, the results for the athermal polymer solutions). For some solutions, however, like acetone/PS, the predictions with the "new" UNIFAC are better than with the modified FH model. For these solutions the difference between the predictions obtained with the entropic-FV and GK-FV models is also rather significant. These differences are, in both cases, explained by the significant influence of the SG shape correction term for such polar, multifunctional group solutions. The influence of the SG correction term for athermal and nonpolar polymer solutions is very small.

Effect of the Polymer Molecular Weight. The effect of polymer molecular weight on the VLE predictions for the cyclohexane/PS solution was investigated. The various models were used to predict the cyclohexane equilibrium pressures in PS for various molecular weights of the polymer, and the results are shown in Tables 3a and 3b. All the models (even GPSCT) predict the equilibrium pressure for these solutions with good accuracy at all molecular weights. The percentage average absolute deviation is higher for the PS (25100), but this is because the experimental data are in a much broader composition range than in the other systems. It can be, therefore, concluded that the predictions of the various models at infinite dilution may be worse than the predictions at finite concentrations, presented in this work.

Similarities and differences of the various models

We summarize here the basic similarities and differences of the various models:

(a) *PSCT GPSCT GCLF input information: Structure of the Components, Molecular and/or Group Parameters.* These EOS are purely predictive (when k_{ij} is set equal to zero), see results in Tables 2a and 3a. No pressure limitation.

(b) *GC-Flory input information: Structure of the Components, Pure Component/Mixture Group Parameters.* This EOS has been developed as an activity coefficient model using low-pressure VLE data for mixtures with only low molecular weight compounds (a group-contribution table similar to UNIFAC table exists). No volume data required. Limited to low-pressure calculations.

(c) *Activity Coefficient Models: Purely Predictive Models.* Use of the "new" UNIFAC linear temperature dependent parameter table (Hansen et al., 1992) for the entropic-FV, GK-FV, modified FH, and (new) UNIFAC models. The old temperature independent UNIFAC parameter table is used in the UNIFAC-FV model of Oishi and Prausnitz (1978), as described in the original publication. The group-parameters (in both UNIFAC tables) are evaluated from low-pressure VLE data for mixtures with only solvents. Entropic-FV, GK-FV, UNIFAC-FV, and modified FH require, in addition, the densities of the solvent (usually from the DIPPR compilation) and the polymer (usually calculated from the Tait correlation or estimated from group-contribution methods). New UNIFAC requires the knowledge of only the structure of the components. All activity coefficient models are limited to low-pressure calculations.

Two important remarks:

(a) PSCT is a semimolecular model (molecular parameters are used for the solvent, group-parameters for the polymer). All other (EOS and activity coefficient models) use group-parameters for both solvents and polymers.

(b) PSCT is a three-parameter EOS, while GCLF has only two parameters. PSCT uses, in addition to the energy and hard-core volume parameters, a parameter to account for the external degrees of freedom, as well.

Recommendations

Considering the overall performance and other parameters, like simplicity and ease of use, the UNIFAC-FV and especially the entropic-FV (and the GK-FV) are the best models for low-pressure VLE calculations in polymer solutions. Unlike UNIFAC-FV, which has temperature independent parameters, the entropic-FV model contains linear-temperature dependent parameters obtained from the "new" UNIFAC parameter table (Hansen et al., 1992). The entropic-FV model can, thus, extrapolate more reliably at high temperatures. More specifically:

(a) For the PE and PIB solutions, the entropic-FV model is the best activity coefficient model and the GC-Flory is the best EOS at low pressures. Both GCLF and PSCT perform very similarly and have some problems, especially for PIB solutions.

(b) For the ketones/PS solutions, the UNIFAC-FV model is the best activity coefficient model and the GC-Flory and PSCT are the best EOS; the former being more accurate but restricted to low-pressure calculations. The entropic-FV model performs as accurately as the PSCT EOS. The error with the GCLF EOS is twice as large as that with the PSCT EOS, indicating probably the problems encountered when the lattice theory is extended to polymer solutions with polar solvents.

(c) For the chloroform/PS solutions, the entropic-FV is the best activity coefficient model and the PSCT the best *and only* EOS that can be used. The error in the equilibrium pressure with the PSCT EOS is comparable to that of the entropic-FV model. The GCLF *cannot* be applied to the chloroform containing polymer solutions, while the percentage error with the GC-Flory EOS is unacceptably high, especially as compared to the predictions of the model for the other systems.

(d) For the relatively simple solutions of toluene and cyclohexane in PS, the performance of most of the models (with the exception of the GCLF and GPSCT EOS) is very similar and the predictions are reasonably accurate. Any of the models can be used. The entropic-FV is the best activity coefficient model, while PSCT and GC-Flory perform similarly, the latter being slightly more accurate. Note that the PSCT EOS performs much better than the GCLF EOS for all the cyclohexane/PS solutions.

Conclusions

Various noncubic EOS and activity coefficient models were tested for VLE calculations at low and moderate pressures in some typical nonpolar and polar binary solvent/polymer solutions. Two kinds of models were considered: models which are connected with or derived from the generalized van der Waals theory (GC-Flory, PSCT, GPSCT, entropic-FV), and lattice models (GCLF, modified FH). All the models are purely predictive in the absence of any adjustable parameters. The pure component parameters are, for all models, obtained from data for low-molecular-weight compounds alone. The mixture parameters for the activity coefficient models are given by group contributions (UNIFAC parameter table), estimated from VLE data for systems with only low molecular weight compounds. The PSCT is a *semi-molecular three-parameter* EOS, while the GCLF is a *group-contribution two-parameter* EOS; they are both developed as equations of state, without use of any mixture data. On the other hand, the GC-Flory EOS is also based on the group-contribution approach, but is developed as an activity coefficient model using information about pure component volumetric behavior and VLE data for mixtures with low molecular weight solvents.

The best overall predictions are obtained with the UNIFAC-FV and entropic-FV (and GK-FV) models, which are simpler by far and more flexible than the EOS considered in this study. The predictions of the GC-Flory EOS are, with the exception of the chloroform/PS solutions, as accurate as those of the activity coefficient models. Reasonable estimates of the equilibrium pressures are obtained for *some polar polymer solutions* even with the "new" UNIFAC model, which may be used *only when* volumetric data for the solvent and/or the polymer are not available. No reasons for using the modified FH model could be established.

Excellent predictions for athermal polymer solutions are obtained with the GC-Flory EOS, indicating that the combinatorial/free-volume term of this EOS is, though far more complicated, as accurate as the simple terms used in the UNIFAC-FV and entropic-FV models. The extension of the GC-Flory EOS to low-pressure VLE calculations for polar polymer solutions is proven to be very successful using the new parameter table by Bogdanic and Fredenslund (1994), as can be seen by the results presented in this work and elsewhere (Bogdanic and Fredenslund, 1994). It still remains to be seen whether the GC-Flory model can be used as a *true EOS*, that is, to predict pure component liquid and vapor volumes, excess volumes, and especially vapor pressures.

The two *true EOS*, the PSCT and GCLF, reveal some predictive problems for the PIB and (to a smaller degree) PE solutions, thus indicating that further improvement in their repulsive/rotational term is needed. Such an improvement may be obtained with a more accurate theory for repulsive interactions (Honnell and Hall, 1989; Bokis et al., 1993). The PSCT can be used for VLE calculations in many solvent/polymer solutions with satisfactory accuracy. It is, moreover, far more accurate than the GCLF EOS for VLE calculations in polymer solutions containing cyclohexane and polar solvents like acetone. In addition, its predictive capability can be increased by inclusion of the polar interactions explicitly.

In this work, mixture calculations were performed only at low and moderate pressures (up to a few bar). For high-pressure phase equilibria, activity coefficient models fail and therefore an equation of state should be used. In addition, at extreme conditions such as high temperatures and high pressures, the GC-Flory EOS fails, since it does not account for pressure variation (Chen et al., 1990). As a result, for high-pressure VLE calculations in polymer solutions, the PSCT EOS is preferable over the other models tested.

Acknowledgment

The authors wish to thank Dr. Grozdana Bogdanic for performing the VLE calculations with the GC-Flory EOS for the benzene/PIB and the PS solutions investigated in this work using the new group-parameter table.

After this work was accepted for publication, Orbey and Sandler (*AIChE J.*, **40**, 1203, 1994) reported their calculations on "Vapor-Liquid Equilibrium of Polymer Solutions Using a Cubic Equation of State." In their work, they used two binary adjustable parameters for each binary mixture, whereas for all of our EOS correlations only one binary parameter was used.

Notation

c = parameter equal to one-third the number of the external degrees of freedom
k = interaction parameter (in PSCT, GPSCT EOS)
M = molecular weight
N = number of points
P = pressure
q = surface area parameter
T = temperature
V = volume
w = weight fraction
x = molar fraction
z = coordination number
Z = compressibility factor

Greek letters

α = activity
γ = molar activity coefficient
ϵ = molecular energy parameter
θ = surface area fraction
ϕ = volume/segment fraction
χ = FH interaction (free-energy) parameter

Superscripts

$*$ = characteristic/hard-core property
∞ = infinite (dilution)
$\sim$ = reduced property
calc = calculated
comb = combinatorial term/part
exp = experimental
fv = free volume
LJ = Lennard-Jones
rep = repulsive
res = residual term/part
s = segment
vol = volume

Subscripts

1 = first component in a binary mixture (solvent)
2 = second component in a binary mixture (polymer)
att = attractive
h = enthalpic part of the FH parameter
i = component i
i = data point index (in Eqs. 3 and 4)
ij = property of the mixture of components i and j
n = number average
p = polymer
r = reduced property
s = solvent
S = entropic part of the FH parameter

Literature Cited

Abrams, D., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Alder, B. J., D. A. Young, and M. A. Mark, "Studies in Molecular Dynamics: X. Corrections to the Augmented van der Waals Theory for the Square-Well Fluid," *J. Chem. Phys.*, **56**, 3013 (1972).

Barton, A. F. M., *Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Boca Raton, FL (1990).

Bawn, C. E. H., R. F. J. Freeman, and A. R. Kamaliddin, "High Polymer Solutions: I. Vapor Pressure of Polystyrene Solutions," *Trans. Faraday Soc.*, **46**, 677 (1950).

Bawn, C. E. H., and R. D. Patel, "High Polymer Solutions: 8. The Vapor Pressure of Solutions of Polyisobutylene in Benzene and Cyclohexane," *Trans. Faraday Soc.*, **52**, 1664 (1956).

Bawn, C. E. H., and M. A. Wajid, "High Polymer Solutions: 7. Vapor Pressure of Polystyrene Solutions in Acetone, Chloroform, and Propyl Acetate," *Trans. Faraday Soc.*, **52**, 1658 (1956).

Beret, S., and J. M. Prausnitz, "Perturbed Hard Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules," *AIChE J.*, **21**, 1123 (1975).

Berg, L. P., personal communication (1993).

Bogdanic, G., personal communication (1993).

Bogdanic, G., and Aa. Fredenslund, "Revision of the Group-Contribution Flory Equation of State for Phase Equilibria Calculations in Mixtures with Polymers: 1. Prediction of Vapor-Liquid Equilibria for Polymer Solutions," *Ind. Eng. Chem. Res.*, **33**(5), 1331 (1994).

Bokis, C. P., Y. Cui, and M. D. Donohue, "Thermodynamic Properties of Hard-Chain Molecules," *J. Chem. Phys.*, **98**(6), 5023 (1993).

Bondi, A., *Physical Properties of Molecular Crystals, Liquids, and Glasses*, Wiley, New York (1968).

Brandrup, J., and E. H. Immergut, *Polymer Handbook*, Wiley, New York (1989).

Carnahan, N. F., and K. E. Starling, "Equation of State for Non-attracting Rigid Spheres," *J. Chem. Phys.*, **51**(2), 635 (1969).

Carnahan, N. F., and K. E. Starling, "Intermolecular Repulsions and the Equation of State for Fluids," *AIChE J.*, **18**(6), 1184 (1972).

Chen, F., Aa. Fredenslund, and P. Rasmussen, "Group-Contribution Flory Equation of State for Vapor-Liquid Equilibria in Mixtures with Polymers," *Ind. Eng. Chem. Res.*, **29**(5), 875 (1990).

Daubert, T. E., and R. P. Danner, *Physical and Thermodynamic Properties of Pure Compounds: Data Compilation*, Hemisphere, New York (1989).

Derr, E. L., and C. H. Deal, *J. Chem. Eng. Symp. Ser.*, **3**(32), 40 (1969).

Derr, E. L., and C. H. Deal, *Adv. in Chemistry Ser.*, 124, 11 (1973).

Donohue, M. D., and J. M. Prausnitz, "Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**(5), 849 (1978).

Donohue, M. D., and P. Vimalchand, "The Perturbed-Hard-Chain Theory. Extensions and Application," *Fluid Phase Equilibr.*, **40**, 185 (1988).

Economou, I. G., and M. D. Donohue, "Equation of State with Multiple Associating Sites for Water and Water-Hydrocarbon Mixtures," *Ind. Eng. Chem. Res.*, **31**, 2388 (1992).

Elbro, H. S., Aa. Fredenslund, and P. Rasmussen, "A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions," *Macromolecules*, **23**, 4707 (1990).

Elbro, H. S., Aa. Fredenslund, and P. Rasmussen, "Group-Contribution Method for the Prediction of Liquid Densities as a Function of Temperature for Solvents, Oligomers, and Polymers," *Ind. Eng. Chem. Res.*, **30**(12), 2576 (1991).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **9**, 660 (1941).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **10**, 51 (1942).

Fredenslund, Aa., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC. A Group-Contribution Method*, Elsevier Scientific, Amsterdam (1977).

Fredenslund, Aa., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**, 1086 (1975).

Fredenslund, Aa., and P. Rasmussen, "Correlation of Pure Component Gibbs Energy Using UNIFAC Group Contribution," *AIChE J.*, **25**(1), 203 (1979).

Fried, J. R., J. S. Jiang, and E. Yeh, "Group-Contribution Methods in Polymer Thermodynamics," *Computational Polymer Sci.*, **2**, 95 (1992).

Gasem, K. A. M., and R. L. Robinson, "Evaluation of the Simplified Perturbed Hard Chain Theory (SPHCT) for Prediction of Phase Behavior of *n*-Paraffins and Mixtures of *n*-Paraffins with Ethane," *Fluid Phase Equilibr.*, **58**, 13 (1990).

Georgeton, G., and A. S. Teja, "A Group Contribution Equation of State based on the Simplified Perturbed Hard Chain Theory," *Ind. Eng. Chem. Res.*, **27**, 657 (1988).

Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford (1952).

Hansen, H. K., B. Coto, and B. Kuhlmann, "UNIFAC with Linearly Temperature-Dependent Group-Interaction Parameters," Technical Report (SEP 9212), IVC-SEP Research Engineering Center, Institut for Kemiteknik, The Technical Univ. of Denmark, Lyngby (1992).

Harismiadis, V. I., G. M. Kontogeorgis, Aa. Fredenslund, and D. P. Tassios, "Application of the van der Waals Equation of State to Polymers: II. Prediction," *Fluid Phase Equilibr.*, **96**, 93 (1994).

High, M. S., "Prediction of Polymer-Solvent Equilibria with a Group Contribution Lattice-Fluid Equation of State," PhD Thesis, Pennsylvania State Univ., University Park (1990).

High, M. S., and R. P. Danner, "Application of the Group Contribution Lattice-Fluid EOS to Polymer Solutions," *AIChE J.*, **36**(11), 1625 (1990a).

High, M. S., and R. P. Danner, "Comparison of Recent Group Contribution Equations of State for Polymer Solutions," AIChE Meeting, Chicago (1990b).

Hildebrand, J., *J. Chem. Phys.*, **15**, 225 (1947).

Hildebrand, J. H., and R. L. Scott, *The Solubility of Nonelectrolytes*, Dover Publication, New York (1964).

Holten-Andersen, J., P. Rasmussen, and Aa. Fredenslund, "Phase Equilibria of Polymer Solutions by Group Contribution. 1. Vapor-Liquid Equilibria," *Ind. Eng. Chem. Res.*, **26**(7), 1382 (1987).

Honnell, K. G., and C. K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**(3), 1841 (1989).

Huggins, M. L., "Solutions of Long Chain Compounds," *J. Chem. Phys.*, **9**, 440 (1941).

Huggins, M. L., "Thermodynamic Properties of Solutions of High Polymers: the Empirical Constant in the Activity Equation," *Ann. N.Y. Acad. Sci.*, **43**, 431 (1942).

Ikonomou, G. D., and M. D. Donohue, "Thermodynamics of Hydrogen-Bonded Molecules: the Associated-Perturbed-Anisotropic-Chain Theory," *AIChE J.*, **32**, 1716 (1986).

Iwai, Y., and Y. Arai, "A Semiempirical Equation of State for Molten Polymers and Hydrocarbon Liquids," *Macromol.*, **18**, 2775 (1985).

Iwai, Y., and Y. Arai, "Measurement and Prediction of Solubilities of Hydrocarbon Vapors in Molten Polymers," *J. Chem. Eng. Japan*, **22**(2), 155 (1989).

Iwai, Y., T. Ishidao, S. Miyamoto, H. Ikeda, and Y. Arai, "Solubilities of Nonane Vapors in Styrene-Butadiene Copolymers at 100 and 130°C," *Fluid Phase Equilibr.*, **68**, 197 (1991).

Iwai, Y., S. Miyamoto, K. Nakano, and Y. Arai, "Measurement and Prediction of Solubilities of Ethylbenzene Vapor in Styrene-Butadiene Rubbers," *J. Chem. Eng. Japan*, **23**(4), 508 (1990).

Jensen, T., Aa. Fredenslund, and P. Rasmussen, "Pure-Component Vapor Pressures Using UNIFAC Group Contribution," *Ind. Eng. Chem. Res.*, **20**(3), 238 (1981).

Jin, G., J. M. Walsh, and M. D. Donohue, "A Group-Contribution Correlation for Predicting Thermodynamic Properties with the Perturbed-Soft-Chain-Theory," *Fluid Phase Equilibr.*, **31**, 123 (1986).

Kontogeorgis, G. M., Aa. Fredenslund, and D. P. Tassios, "Simple Activity Coefficient Model for the Prediction of Solvent Activities in Polymer Solutions," *Ind. Eng. Chem. Res.*, **32**(2), 362 (1993).

Kontogeorgis, G. M., V. I. Harismiadis, Aa. Fredenslund, and D. P. Tassios, "Application of the van der Waals Equation of State to Polymers: I. Correlation," *Fluid Phase Equilibr.*, **96**, 65 (1994b).

Kontogeorgis, G. M., P. Coutsikos, D. P. Tassios, and Aa. Fredenslund, "Improved Models for the Prediction of Activity Coefficients in Nearly Athermal Mixtures," *Fluid Phase Equilibr.*, **92**, 35 (1994a).

Macknick, A. B., and J. M. Prausnitz, "Vapor Pressures of Heavy Liquid Hydrocarbons by a Group-Contribution Method," *Ind. Eng. Chem. Fundam.*, **18**(4), 348 (1979).

Morris, W. O., P. Vimalchand, and M. D. Donohue, "The Perturbed-Soft-Chain-Theory: An Equation of State Based on the Lennard-Jones Potential," *Fluid Phase Equilibr.*, **32**, 103 (1987).

Oishi, T., and J. M. Prausnitz, "Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method," *Ind. Eng. Chem. Process Des. Dev.*, **17**(3), 333 (1978).

Panayiotou, C., and J. H. Vera, "Statistical Thermodynamics of r-Mer Fluids and Their Mixtures," *Polymer J.*, **14**, 681 (1982).

Prausnitz, J. M., R. N. Lichtenthaler, and G. d. E. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1986).

Sako, T., A. H. Wu, and J. M. Prausnitz, "A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids," *J. of Appl. Polymer Sci.*, **38**, 1839 (1989).

Staverman, A. J., *Rec. Trav. Chim.*, Pays-Bas, **69**, 163 (1950).

Vimalchand, P., and M. D. Donohue, "Thermodynamics of Quadrupolar Molecules: the Perturbed-Anisotropic-Chain-Theory," *Ind. Eng. Chem. Fundam.*, **24**, 246 (1985).

Wang, S. H., and W. B. Whiting, "Parameters for the Perturbed-Hard-Chain Theory from Characterization Data for Heavy Fossil Fuel Fluids," *Ind. Eng. Chem. Res.*, **27**(6), 1058 (1988).

Wen, H., H. S. Elbro, and P. Alessi, *Data Collection on Polymer Containing Solutions and Blends*, DECHEMA Chemistry Data Series, Frankfurt (1991).

Appendix A: Method for Evaluation of the Entropic Part of Flory-Huggins Free-Energy Parameter Using the Entropic-FV Model

A reliable procedure of evaluating the entropic part of the FH parameter, denoted in the literature as χ_s, is presented. The proposed approach is based on a recently developed activity coefficient model which combines in a single term both combinatorial and free-volume contributions (Elbro et al., 1990).

For nearly athermal polymer solutions, the Flory-Huggins equation for the activity coefficient of component 1 (solvent) in a binary polymer solution is:

$$\ln\gamma_1^{FH} = \ln\frac{\phi_1^{vol}}{x_1} + 1 - \frac{\phi_1^{vol}}{x_1} + \chi_s(\phi_2^{vol})^2 \tag{A1}$$

where ϕ_1^{vol} is the volume fraction of the solvent, defined as:

$$\phi_1^{vol} = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2} \tag{A2}$$

For nearly athermal polymer solutions ($\gamma_1^{res} = 1$), the entropic-FV model can be written as (see Appendix B):

$$\ln\gamma_1^{Entr-FV} = \ln\frac{\phi_1^{fv}}{x_1} + 1 - \frac{\phi_1^{fv}}{x_1} \tag{A3}$$

where ϕ_1^{fv} is the free-volume fraction of the solvent. The free-volume fractions are similar to the volume fractions, but free-volumes are used instead of molar volumes in the relevant equations (see Eq. B7 in Appendix B).

It is, thus, possible to evaluate the χ_s-parameter by equating Eqs. A1 and A3. The accuracy of the estimated entropic parameter evidently depends on the accuracy of the prediction of solvent activities in athermal polymer solutions with the combinatorial/free-volume term of the entropic-FV model (Eq. A3).

After some algebra, the final expression for χ_s is:

$$\chi_s = \left(\frac{x_1 V_1 + x_2 V_2}{x_2 V_2}\right)^2 A \tag{A4}$$

where:

$$A = \ln \frac{V_{fv,1}}{x_1 V_{fv,1} + x_2 V_{fv,2}} - \ln \frac{V_1}{x_1 V_1 + x_2 V_2} + \frac{V_1}{x_1 V_1 + x_2 V_2} - \frac{V_{fv,1}}{x_1 V_{fv,1} + x_2 V_{fv,2}} \tag{A5}$$

where $V_{fv,i}$ is the free-volume of component i.

It seems, from Eqs. A4 and A5, that χ_s is a function of both temperature and composition.

At infinite dilution of the solvent ($x_1 = 0.0$), Eqs. A4 and A5 can be simplified:

$$\chi_s^\infty = \ln \frac{V_{fv,1}}{V_{fv,2}} - \ln \frac{V_1}{V_2} + \frac{V_1}{V_2} - \frac{V_{fv,1}}{V_{fv,2}} = \ln \frac{V_{fv,1}\%}{V_{fv,2}\%} + \frac{V_1}{V_2}\left[1 - \frac{V_{fv,1}\%}{V_{fv,2}\%}\right] \tag{A6}$$

where $V_{fv,i}\%$ is the free-volume percentage of component i and is simply defined as the ratio of the free-volume to the molar volume ($V_{fv,i}\% = 100\ V_{fv,i}/V$).

The χ_s-values calculated from Eqs. A4, A5, and A6 are for typical athermal solutions, like *n*-hexane in polyethylene, practically independent of composition and temperature. These values are comparable to the ones reported in the literature. The χ_s parameter is sometimes regarded as a physically meaningful quantity, approximately equal to the inverse coordination number (Hildebrand, 1947; Hildebrand and Scott, 1964).

Appendix B: Two-Term Activity Coefficient Models

Several simple activity coefficient models are investigated in this work. Some of them combine both combinatorial and free-volume contributions (entropic-FV, GK-FV), and others take explicitly into account only combinatorial effects (modified FH, "new" UNIFAC). It is evident that for polymer solutions the former (free-volume) models are expected to perform more accurately. It is, however, important to investigate the influence of the free-volume effects for VLE calculations in polymer solutions.

All the two-term activity coefficient models studied here are based on UNIFAC (Fredenslund et al., 1975, 1977) and are given by the general equation:

$$\ln\gamma_i = \ln\gamma_i^{comb} + \ln\gamma_i^{res} \tag{B1}$$

where the superscripts comb and res denote the combinatorial (and free-volume) and the residual (or energetic) contributions, respectively. The residual term for all the models is given by UNIFAC. The group-interaction parameters used, however, are *not* the temperature independent parameters used in the first versions of UNIFAC (Fredenslund et al., 1975, 1977). The interaction parameters used in this work are assumed to be temperature dependent through a simple linear relationship:

$$\alpha_{mn} = \alpha_{mn,1} + \alpha_{mn,2}(T - T_0) \tag{B2}$$

where α_{mn} is the interaction parameter between groups m and n, and T_0 is a reference temperature, equal to 298.15 K.

The group-interaction parameters (α_{mn}) used in this work *with all four two-term activity coefficient models* investigated here (entropic-FV, GK-FV, modified FH, "new" UNIFAC) have been previously estimated by Hansen et al. (1992). These group-parameters were estimated exclusively from experimental VLE data for mixtures with only low molecular weight compounds using the "new" UNIFAC model (Eqs. B1, B2, and B3 later). Like the original UNIFAC, the "new" UNIFAC (Hansen et al., 1992) contains the standard combinatorial term (Staverman, 1950) given by Eq. B3, shown later in this Appendix. The only difference is that the "new" UNIFAC uses linear temperature dependent parameters, contrary to the temperature independent parameters used in the original UNIFAC model.

The same parameter matrix of "new" UNIFAC has been used with all four different combinatorial and combined combinatorial/free-volume terms. The differences, thus, between the various activity coefficient models correspond to the different combinatorial and free-volume terms used. The terms investigated in this work are hereafter briefly presented.

Combinatorial terms

"New" UNIFAC. The Staverman-Guggenheim term of "new" (and original) UNIFAC is the sum of the FH term, based on segment fractions and the SG shape correction term (second term of the righthand side of the following equation):

$$\ln\gamma_i^{comb} = \ln \frac{\phi_i^s}{x_i} + 1 - \frac{\phi_i^s}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\phi_i^s}{\theta_i} + 1 - \frac{\phi_i^s}{\theta_i}\right) \tag{B3}$$

where

z = coordination number, an essentially empirical parameter, which is usually set equal to ten

θ_i, ϕ_{is} = segment and surface area fractions of component i, respectively

The segment and the surface area fractions of component 1 in a binary solution are defined as:

$$\phi_1^s = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \tag{B4}$$

where r_i and q_i are the (normalized) van der Waals volume and external surface area parameters of component *i*. They are calculated from the group-increments given by Bondi (1968).

Combinatorial Terms: Flory-Huggins. The FH term based on volume fractions can be written:

$$\ln\gamma_i^{\text{comb}} = \ln\frac{\phi_i^{\text{vol}}}{x_i} + 1 - \frac{\phi_i^{\text{vol}}}{x_i} \tag{B5}$$

where ϕ_i^{vol} is the volume fraction of component *i* (Eq. A2). In this work we combine Eq. B5 with the residual term of UNIFAC using the new linear temperature dependent parameter matrix (Eq. B2). We refer to this combination as the *modified Flory-Huggins* model.

Combined combinatorial/free-volume terms

The entropic-FV and GK-FV models have been proposed and developed by Elbro et al. (1990) and Kontogeorgis et al. (1993). The entropic-FV model is a simple modification of the FH term given by Eq. B5, where free-volume fractions are used instead of volume fractions. The GK-FV model is simply the sum of the entropic-FV term and the SG correction term. The exact equations are:

Entropic-FV:

$$\ln\gamma_i^{\text{Entr-fv}} = \ln\frac{\phi_i^{\text{fv}}}{x_i} + 1 - \frac{\phi_i^{\text{fv}}}{x_i} \tag{B6}$$

where ϕ_i^{fv} is the free-volume fraction of component *i*. The free-volume fraction of component 1 in a binary solution is defined as:

$$\phi_1^{\text{fv}} = \frac{x_1 V_{\text{fv},1}}{x_1 V_{\text{fv},1} + x_2 V_{\text{fv},2}} \tag{B7}$$

GK-FV:

$$\ln\gamma_1^{\text{GK-FV}} = \ln\frac{\phi_i^{\text{fv}}}{x_i} + 1 - \frac{\phi_i^{\text{fv}}}{x_i} - \frac{z}{2} q_i \left(\ln\frac{\phi_i^s}{\theta_i} + 1 - \frac{\phi_i^s}{\theta_i}\right) \tag{B8}$$

The free volume is defined (Elbro et al., 1990) as the difference between the molar volume and the van der Waals volume, as calculated by Bondi (1968). The molar volumes for the low-molecular-weight compounds (solvents) are calculated from the correlations given by Daubert and Danner (1989). The empirical but very accurate Tait equation is used for the estimation of the volume for the three polymers used in this work.

Appendix C: Group-Contribution Lattice Fluid (GCLF) EOS

High and Danner (1990a) proposed a lattice-fluid EOS for polymers and polymer solutions. Their EOS is a revised and group-contribution version of the EOS by Panayiotou and Vera (1982). Both EOS, and most of the work done recently on lattice models, is based on the well established lattice statistics developments of Guggenheim (1952). A lattice model containing holes is a convenient way of representing a polymer solution. The holes of the lattice represent a way of varying the density of the fluid and they are analogous to the free-volume used in the generalized van der Waals models, like the PSCT EOS (Appendix D), the GC-Flory EOS, and the entropic-FV model. Use of the lattice approach often eliminates the need of an "external degree of freedom" parameter, used in various FV-models, like the UNIFAC-FV models of Oishi-Prausnitz (1978) and Iwai et al. (1985, 1989, 1990, 1991).

The GCLF EOS in terms of reduced variables is:

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln\frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{z}{2}\ln\frac{\tilde{v}_1 + \left(\frac{q_1}{r_1}\right) - 1}{\tilde{v}_1} - \frac{\theta_1^2}{\tilde{T}_1} \tag{C1}$$

where:

$$\tilde{P}_1 = \frac{2Pv_h}{z\epsilon_{11}} \tag{C2}$$

$$\theta_1 = \frac{q_1 N_1}{N_q} \tag{C3}$$

$$zN_q = z(N_h + q_1 N_1)$$

$$r_1 = \frac{\overset{*}{v_1}}{v_h} \tag{C4}$$

$$zq_1 = (z-2)r_1 + 2$$

$$\tilde{T}_1 = \frac{2RT}{z\epsilon_{11}} \tag{C5}$$

$$\tilde{v}_1 = \frac{v}{\overset{*}{v_1}} = \frac{v_h(N_h + r_1 N_1)}{\overset{*}{v_1}} \tag{C6}$$

Pure-component parameters used in Eqs. C2–C6 are:

q_i = number of interaction sites available to a molecule
N_i = number of molecules of type *i* in the system
r_i = number of lattice sites occupied by one molecule of type *i*
zN_q = total number of interaction sites in the lattice
v_h = volume of a lattice site, arbitrarily fixed to be equal to the volume of a methylene group in polyethylene
N_h = number of holes in the lattice

Equation C1 is derived assuming that the molecules and the holes are randomly placed on the lattice in the pure component case. Panayiotou and Vera (1982) point out that the additional complexity introduced if the local composition concept is used does not affect significantly the accuracy of the EOS, at least for the pure components. For the mixture, only the holes are assumed to mix randomly. Local compositions of the molecules in the mixture are calculated through Guggenheim's quasi-chemical theory.

The GCLF is a two-parameter EOS. The only parameters that need to be estimated are the characteristic segmental interaction energy ϵ_{11} and the reference (hardcore) volume ν^*. These parameters have been determined from experimental data of vapor pressures and saturated liquid volumes. Although GCLF is not a cubic EOS, it behaves numerically like one and it is obviously developed in a way similar to classical EOS. Most other EOS proposed for polymers, like the Flory (Prausnitz et al., 1986), the Holten-Andersen et al. (1987), and the GC-Flory EOS (Chen et al., 1990; Bogdanic and Fredenslund, 1994) have been developed as activity coefficient models, that is, using only volumetric data, and other liquid-phase properties.

The detailed derivation of the GCLF EOS is given by High (1990). In the same reference it is shown that the interaction energy parameter ϵ_{11} is a strong function of temperature, while the reference volume is almost temperature independent, and it is for *n*-alkanes a linear function of the number of carbon atoms.

After evaluating the molecular parameters, High and Danner estimated group parameters for several groups (mainly hydrocarbons, aromatics, water, and a few polar groups) at the temperature range 300–400 K. The EOS is, evidently, more accurate in this rather narrow temperature range.

They have shown that the prediction of pure-component properties (*both* vapor pressures and liquid densities) for a series of *n*-alkanes is excellent.

High and Danner have applied the GCLF EOS to VLE calculations for binary polymer solutions as well. Using conventional mixing rules and (a small value of) one binary interaction parameter k_{ij} (in the combining rule for the molecular cross interaction parameter ϵ_{ij}) excellent correlation of the solvents' activity over the entire composition range is achieved for many different solvent/polymer solutions, like pentane in PIB or cyclohexane in PS. The accuracy of the correlation with the GCLF EOS is, however, found to be extremely sensitive to the value of the binary interaction parameter and an accurate value is required for good results.

Using no interaction parameters, the GCLF EOS can be used to predict VLE in polymer solutions. High and Danner (1990a) report very good predictions for the activities at intermediate concentrations for some *mainly nonpolar* solvents (like toluene, benzene, heptane) in several polymers, like polystyrene (PS), PE, poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO). Very good predictions are also reported for some water/poly(ethylene glycol) (PEG) and dipropyl ether/PVC solutions. On the other hand, High and Danner report without any examples that very poor predictions are obtained with the GCLF EOS for solutions of acetone and MEK in PS. They conclude that for polar solvents a nonzero binary interaction parameter is necessary. This is in agreement with the predictions for the GCLF EOS obtained by Kontogeorgis et al. (1993) and Fried et al. (1992) for polar (especially alcohol and ketone-containing) polymer solutions. It seems that the GCLF EOS often underestimates systematically the solvent activities, and, thus, a single interaction parameter usually improves significantly the results.

Consistently poor predictions with the GCLF EOS are obtained for PIB solutions, even with nonpolar solvents. High and Danner state that this is probably due to the inaccurate group-contribution values used for the quaternary carbon atom "*C*." If the reference volume for PIB is estimated from pure polymer volumetric data, improved predictions for the solvent activities are obtained. Significant underestimation of the experimental activities is, however, still observed.

Appendix D: Perturbed-soft-chain-theory

The perturbed-soft-chain-theory (PSCT) developed by Morris et al. (1987) is an improvement over the perturbed-hard-chain-theory (PHCT) introduced by Beret and Prausnitz (1975) and Donohue and Prausnitz (1978). The main difference between the two EOS is in the term used to take into account the energetic effects: the PHCT uses the square-well potential in the attractive (perturbation) term (Alder et al., 1972), whereas the PSCT uses the more realistic Lennard-Jones (LJ) intermolecular potential. Both the PHCT and the PSCT EOS use the chain-Carnahan Starling expression (Carnahan and Starling, 1969, 1972) in their repulsive (reference) term. The PSCT is given in terms of the compressibility factor from the equation:

$$Z = 1 + Z^{\mathrm{rep}} + Z_{\mathrm{att}}^{\mathrm{LJ}} \tag{D1}$$

where the repulsive and the attractive parts are given by the equations:

$$Z^{\mathrm{rep}} = c\,\frac{4\tau \dfrac{V_d^*}{V} - 2\left(\tau \dfrac{V_d^*}{V}\right)^2}{\left(1 - \tau \dfrac{V_d^*}{V}\right)^3} \tag{D2}$$

$$Z_{\mathrm{att}}^{\mathrm{LJ}} = \frac{Z_1^{\mathrm{LJ}} + Z_2^{\mathrm{LJ}} - 2Z_1^{\mathrm{LJ}} \dfrac{A_2^{\mathrm{LJ}}}{A_1^{\mathrm{LJ}}}}{\left(1 - \dfrac{A_2^{\mathrm{LJ}}}{A_1^{\mathrm{LJ}}}\right)^2} \tag{D3}$$

The terms Z_i^{LJ} and A_i^{LJ} are given as:

$$Z_1^{\mathrm{LJ}} = c\,\frac{T^*}{T} \sum_m^6 m A_{1m} \left(\frac{V_d^*}{V}\right)^m \tag{D4}$$

$$Z_2^{\mathrm{LJ}} = c\left(\frac{T^*}{T}\right)^2 \sum_m^4 \left(\frac{m}{2} C_{1m} \left(\frac{V_d^*}{V}\right)^m + (m+1)C_{2m}\left(\frac{V_d^*}{V}\right)^{m+1} + \frac{m+2}{2} C_{3m}\left(\frac{V_d^*}{V}\right)^{m+2}\right) \tag{D5}$$

$$\frac{A_1^{\mathrm{LJ}}}{NkT} = c\,\frac{T^*}{T} \sum_m^6 A_{1m} \left(\frac{V_d^*}{V}\right)^m \tag{D6}$$

$$\frac{A_2^{\mathrm{LJ}}}{NkT} = c\left(\frac{T^*}{T}\right)^2 \sum_m^4 \left(\frac{C_{1m}}{2} \left(\frac{V_d^*}{V}\right)^m + C_{2m}\left(\frac{V_d^*}{V}\right)^{m+1} + \frac{C_{3m}}{2} \left(\frac{V_d^*}{V}\right)^{m+2}\right) \tag{D7}$$

where A_{1m}, C_{1m}, C_{2m}, and C_{3m} are universal constants.

The PSCT is a three parameter equation of state. The three parameters are the energy parameter T^*, the size parameter v^*, and the shape parameter c which is unity for spherical molecules like methane and always greater than one for long-chain and nonspherical molecules. The v^* parameter is the

Table 6. Pure Component Parameters for the PSCT EOS

Component	T^* (K)	100 v^* (lt/mol)	c	r	ϵ/k (K)	q
n-Hexane	326.4	7.398	1.8224	6.915	105.0	5.665
n-Decane	357.7	11.393	2.6454	10.649	105.0	9.012
Cyclohexane	371.3	6.411	1.5487	5.992	118.0	4.873
Benzene	380.2	5.368	1.5275	5.017	127.0	4.573
Toluene	384.2	6.386	1.7347	5.969	123.8	5.384
Acetone	341.6	4.229	1.6882	3.953	140.0	4.119
MEK	352.3	5.185	1.7916	4.847	140.0	4.508

For a more extensive table, see Morris et al. (1987).

temperature independent soft-core volume, whereas v_d^* is the temperature dependent hard-core volume. There are four additional parameters that need to be estimated for mixture calculations: the segmental dispersion energy ϵ, the number of segments per molecule r, the normalized external surface area q, and the segmental diameter σ. For pure components these parameters are intercorrelated using the expressions: $T^* = \epsilon q/ck$ and $v^* = N_A r\sigma^3/2^{0.5}$. For mixtures, the expressions for the repulsive and the attractive part of the compressibility factor, Z^{rep} and $Z^{\text{LJ}}_{\text{att}}$ are slightly more complicated and are given by Donohue and Vimalchand (1988).

The three molecular parameters for the PSCT (T^*, v^*, and c) are calculated by fitting the equation of state to experimental liquid density and vapor pressure data from the triple point to the critical point for the pure components. These parameters have been calculated for a number of various compounds and are presented by Morris et al. (1987).

Jin et al. (1986) developed a group-contribution version of the PSCT EOS, the Group-PSCT (GPSCT). In GPSCT, it is assumed that each molecule is composed of several functional groups and the properties of the molecule can be calculated through the respective properties of its constituent groups. As a result, in the GPSCT each group is characterized by five parameters that are calculated by correlating a large number of molecular parameters with the PSCT. These parameters are:

- The number of segments of group o in molecule i, r_o^i
- The normalized external surface area of group o in molecule i, q_o^i
- The dispersion energy between segments of group o in molecule i and segments of group p in molecule j per unit external surface area, ϵ_{op}^{ij}
- The density-dependent rotational and vibrational degrees of freedom of group o in molecule i, $3f_o^i$
- The soft-core diameter of a segment of group o in molecule i, σ_o^i.

In PSCT and in GPSCT EOS as well as in the other PHCT-derivatives (PACT, APACT, and so on) the size of a segment is arbitrarily taken as that of a -CH$_2$- group. The same assumption is used in classical activity coefficient models, like UNIQUAC (Abrams and Prausnitz, 1975) and UNIFAC (Fredenslund et al., 1975, 1977). In addition, based on the definition of f, it is: $f = c - 1$.

The GPSCT is given from Eqs. D1 through D7 with the molecular parameters calculated from the following mixing and combining rules:

$$\langle V^* \rangle_i = \frac{N_A \sum_o^G n_o^i r_o^i (\sigma_o^i)^3}{\sqrt{2}} \tag{D8}$$

with:

$$\langle T^* \rangle_i = \frac{\sum_o^G \sum_p^G n_o^i n_p^i \epsilon_{op}^{ii} q_o^i r_p^i (\sigma_{op}^{ii})^3}{\left(1 + \sum_o^G n_o^i f_o^i\right) \sum_o^G n_o^i r_o^i (\sigma_o^i)^3} \tag{D9}$$

$$\langle c \rangle_i = 1 + \sum_o^G n_o^i f_o^i \tag{D10}$$

$$\epsilon_{op}^{ii} = \sqrt{\epsilon_{oo}^{ii} \epsilon_{pp}^{ii}} \tag{D11}$$

$$\sigma_{op}^{ii} = \frac{\sigma_o^i + \sigma_p^i}{2} \tag{D12}$$

where n_o^i refers to the number of groups of type o in molecule i, and G is the total number of distinct groups in molecule i.

A binary interaction parameter k_{ij} may be introduced for mixture calculations to yield improved correlation results:

$$\epsilon_{op}^{ij} = \sqrt{\epsilon_{oo}^{ii} \epsilon_{pp}^{jj}}(1 - k_{ij}) \tag{D13}$$

where i and j refer to the two different molecules.

The mixing and combining rules of Eqs. D8 through D13 are used both for small molecules and polymers. To calculate the molecular parameters of a polymer, one has to identify the functional groups in the repeating unit of the polymer and then multiply the number of each specific group per repeating unit with the number of units per polymer molecule. For mixtures, the equation is slightly more complicated since the combining rules (Eqs. D8 to D13) are coupled with the mixing rules of the model. These expressions are presented and discussed by Jin et al. (1986) and, therefore, they are not repeated here.

Table 6 presents the molecular parameters used with the PSCT EOS for the solvents studied in this work, while the group parameters for the GPSCT EOS used here are presented by Jin et al. (1986).

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