Prediction of Polymer-Solvent Phase Equilibria by a Modified Group-Contribution EOS

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A new group-contribution lattice–fluid equation of state (GCLF-EOS), which is capable of predicting the equilibrium properties of polymer–solvent solutions, was developed by modifying the original GCLF-EOS of High and Danner. The GCLF-EOS is a group-contribution form of the Panayiotou–Vera equation of state based on the lattice-hole theory. Group contributions for the interaction energy and reference volume were developed based only on the saturated vapor pressures and liquid densities of low molecular weight compounds. For a mixture, a binary interaction parameter was introduced into the mixing rules. Group contributions for the binary interaction parameter were developed from the binary vapor–liquid equilibria of low molecular weight compounds. This modified GCLF-EOS model gives excellent predictions of solvent activity coefficients both at infinite dilution and at finite concentrations. It is significantly better than the original GCLF-EOS model in its prediction capability. The only input required for the model is the structure of the molecules in terms of their functional groups. No other pure component or mixture properties of the polymer or solvent are needed.

Introduction

Calculations involving phase equilibria behavior are required in the design and operation of many polymer processes such as polymerization, devolatilization, drying, extrusion, and heat exchange. A typical problem in polymer processing involves determining the thermodynamic properties of polymers, solvents, plasticizers, antiplasticizers, and diluents in a mixture. The most important of these thermodynamic properties is how a solvent will distribute itself between the polymer and solvent phases. Equation-of-state models are preferred over activity coefficient models for calculation of phase equilibria because equations of state can describe all phases and pressure dependency. We describe in this article an equation of state, which is capable of predicting pure component and mixture properties of low and high molecular weight compounds. A group-contribution approach has been used to develop a predictive model. The group-contribution approach assumes that the interaction energy between groups will be constant regardless of the overall structure of the molecule.

A group-contribution lattice–fluid equation of state (GCLF-EOS) for the prediction of vapor–liquid equilibria in polymer–solvent solutions was originally developed by High and Danner (High, 1990; High and Danner, 1989, 1990). Generally the model predicted well the activities of nonpolar solvents in various polymers. The model, however, was not adequate for some polymer–solvent systems. For example, the predictions of the original GCLF-EOS were consistently poor for a variety of solvents in polyisobutylene. High and Danner (1990) suggested that the poor predictions for polyisobutylene systems were due to the inaccurate group-contribution values used for the quaternary carbon atom found in polyisobutylene. They also reported that very poor predictions were obtained with the original GCLF-EOS for solutions of acetone or methyl ethyl ketone in polystyrene. They concluded that for polar solvents a nonzero binary interaction parameter was necessary. The original GCLF-EOS also systematically underpredicted solvent activities for many polymer–solvent systems, even with nonpolar solvents.

In this work, by modifying the original GCLF-EOS, we developed an improved model that is capable of predicting the equilibrium thermodynamic behavior of pure polymers and

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polymer solutions for a wider variety of polymer–solvent systems. Several modifications were made to improve the predictability of the model. New groups were added, thus expanding the applicability of the model. More accurate temperature dependencies for the interaction energy and reference volume parameters were developed. All the group contribution values were revised. For a mixture, a binary interaction parameter was introduced into the combining rule and a group-contribution mixing rule for this parameter was developed. All the group parameters were obtained using only pure component and binary mixture equilibrium properties of low molecular weight compounds.

In this article the performance of the modified GCLF-EOS is presented and compared with that of the original GCLF-EOS, the UNIFAC-free volume model (Oishi and Prausnitz, 1978), the revised group-contribution Flory EOS (Bogdanic and Fredenslund, 1994), and the entropic-free volume model (Kontogeorgis et al., 1993). The modified GCLF-EOS can be applied to the prediction of vapor–liquid equilibria in both dilute and concentrated polymer solutions and to any homopolymer, random copolymer, or alternating copolymer which can be constructed from the available group contributions.

Group-Contribution Lattice-Fluid Equation of State

Equation of state for pure components

Flory (1941) and Huggins (1941) independently developed a theory in which the polymer–solvent system was modeled as a lattice structure. The combinatorial contributions to the thermodynamic mixing functions were calculated from the number of ways the polymer and solvent molecules could be arranged on the lattice sites. Sanchez and Lacombe (1976) developed an EOS for pure fluids that was extended to mixtures (Lacombe and Sanchez, 1976). The Sanchez–Lacombe EOS is based on lattice-hole theory and assumes that a random mixing combinatorial term is sufficient to describe the fluid. Panayiotou and Vera (1982a,b) developed equations for both pure components and mixtures that correct for the nonrandom mixing arising from the interaction energies between molecules. In the Panayiotou–Vera theory the volume of a lattice site is arbitrarily fixed to be equal to 9.75×10^{-3} m^3/kmol, while in the Sanchez–Lacombe model the volume of a lattice site is a variable quantity regressed from experimental data.

The lattice-hole theory differs from the lattice model used in the Flory–Huggins theory because here the density of the mixture is allowed to vary by increasing the fraction of holes in the lattice. In the Flory–Huggins treatment every site is occupied by a solvent molecule or polymer segment. The holes in the lattice serve as a means of varying the density of the fluid and are analogous to the free volume in the generalized van der Waals models such as the Flory EOS (Flory et al., 1964), the group-contribution Flory EOS (Chen et al., 1990; Bogdanic and Fredenslund, 1994).

The development of the lattice-fluid EOS for a pure component is based on the well-established lattice statistics model of Guggenheim (1952). A detailed derivation of the EOS is given by Panaiotou and Vera (1982a) and High (1990). The EOS for a pure component in terms of reduced variables is

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

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

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

$$\tilde{v}_1 = \frac{v}{v_1^*} = \frac{v_h(N_h + r_1 N_1)}{v_1^* N_1} \tag{4}$$

$$\theta_1 = \frac{q_1 N_1}{N_q} \tag{5}$$

$$zN_q = z(N_h + q_1 N_1) \tag{6}$$

$$zq_1 = (z-2)r_1 + 2 \tag{7}$$

$$r_1 = \frac{v_1^*}{v_h} \tag{8}$$

$$N_h = r_1 N_1(\tilde{v}_1 - 1), \tag{9}$$

where ϵ_{11} is the molecular interaction energy, v_1^* is the molecular reference volume, z is the coordination number (10), v_h is the volume of a lattice site, r_1 is the number of lattice sites occupied by a molecule of type 1, N_1 is the number of molecules of type 1 in the system, zq_1 is the number of interaction sites available to molecules of type 1, θ_1 is the surface area fraction of pure component 1, N_h is the number of holes in the lattice, and zN_q is the total number of interaction sites in the lattice.

This EOS contains two adjustable parameters: molecular interaction energy, ϵ_{11}, and molecular reference volume, v_1^*. Once these two parameters are known, all of the remaining parameters in Eq. 1 can be determined from Eqs. 2 through 9 for a given temperature and pressure. Properties of a system can then be determined by solving Eq. 1 with respect to reduced volume. In the derivation of Eq. 1, it was assumed that the molecules and holes are randomly placed on the lattice. Panayiotou and Vera (1982a) found that the additional complexity of local compositions did not appreciably increase the accuracy of the EOS for pure components.

Equation of State for Binary Mixtures

The EOS for a binary mixture based on the same assumptions is

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v} - 1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v} + (q/r) - 1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}}. \tag{10}$$

The reduced variables in Eq. 10 are defined by

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv_h}{z\epsilon^*} \tag{11}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2RT}{z\epsilon^*} \tag{12}$$

$$\tilde{v} = \frac{v}{v^*} = \frac{v_h(N_h + rN)}{v^*N}. \tag{13}$$

For the other parameters, the following simple combining rules are used:

$$v^* = \sum x_i v_i^* \tag{14}$$

$$r = \frac{v^*}{v_h} = \sum x_i r_i \tag{15}$$

$$q = \sum x_i q_i \tag{16}$$

$$\theta = \sum \theta_i, \tag{17}$$

where x_i is the mole fraction of component i in a mixture and θ_i is the molecular surface fraction including holes in the mixture:

$$\theta_i = \frac{zq_iN_i}{z\left(N_h + \sum q_jN_j\right)} = \frac{q_iN_i}{N_h + qN}. \tag{18}$$

The interaction energy ϵ^* for a binary mixture is given by

$$\epsilon^* = \bar{\theta}_1\epsilon_{11} + \bar{\theta}_2\epsilon_{22} - \bar{\theta}_1\bar{\theta}_2\dot{\Gamma}_{12}\Delta\epsilon \tag{19}$$

where

$$\Delta\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}. \tag{20}$$

In Eq. 19, $\bar{\theta}_i$ is the molecular surface fraction on a hole-free basis, given by

$$\bar{\theta}_i = \frac{zq_iN_i}{z\sum q_jN_j} = \frac{q_iN_i}{qN} = \frac{x_iq_i}{q}. \tag{21}$$

Since $N_h = rN(\tilde{v} - 1)$ from Eq. 13, Eq. 18 becomes

$$\theta_i = \frac{x_iq_i}{q + r(\tilde{v} - 1)}. \tag{22}$$

As given by Panayiotou and Vera (1981), the nonrandomness parameters $\dot{\Gamma}_{ij}$ are related by

$$\bar{\theta}_1\dot{\Gamma}_{11} + \bar{\theta}_2\dot{\Gamma}_{12} = \bar{\theta}_2\dot{\Gamma}_{22} + \bar{\theta}_1\dot{\Gamma}_{12} = 1 \tag{23}$$

$$\dot{\Gamma}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1 - \dot{G})}} \tag{24}$$

$$\dot{G} = \exp\left(\frac{\theta(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}}{RT}\right) = \exp\left(\theta\frac{\Delta\epsilon}{RT}\right). \tag{25}$$

For the case where the molecules are randomly mixed, $\Delta\epsilon = 0$ and $\dot{\Gamma}_{11} = \dot{\Gamma}_{22} = \dot{\Gamma}_{12} = 1$. In a mixture the holes are assumed to mix randomly as in the pure component case; however, the molecules are not assumed to mix randomly. Local compositions of the molecules are calculated using the quasi-chemical theory of Guggenheim (1952).

Weight fraction activity coefficient

The expression for the pure component chemical potential, $\mu_i^{(P)}$, is given by (Panayiotou and Vera, 1982b; High, 1990)

$$-\frac{\mu_1^{(P)}}{RT} = \ln\frac{\delta_1}{\sigma_1} + \ln q_1 + \ln\frac{(1 - \theta_1)^{r_1}}{\theta_1} + \frac{\theta_1}{\tilde{T}_1}(q_1 + r_1\tilde{v}_1\theta_1), \tag{26}$$

where the subscript 1 in $\tilde{T}_1$ and $\tilde{v}_1$ represents a pure component. The chemical potential of component i in a binary mixture, $\mu_i^{(M)}$, is given by the following expression:

$$-\frac{\mu_i^{(M)}}{RT} = \ln\frac{\delta_i}{\sigma_i} + \ln q_i + \ln\frac{(1 - \theta)^{r_i}}{\theta_i} + q_i\theta\left(\frac{1}{\tilde{T}_i} + \frac{1}{\tilde{T}}\right) + \frac{\theta^2(r_i - q_i)}{\tilde{T}} - \frac{1}{2}zq_i\ln\dot{\Gamma}_{ii}, \tag{27}$$

where δ_i and σ_i are volume-independent parameters accounting for flexibility and symmetry of molecule i. Activity of a component i in a mixture is defined by

$$\ln a_i = \frac{\Delta\mu_i}{RT} = \frac{\mu_i^{(M)} - \mu_i^{(P)}}{RT} \tag{28}$$

and the weight fraction activity coefficient (WFAC) is

$$\Omega_i = \frac{a_i}{w_i}. \tag{29}$$

Thus, the WFAC of component i in a mixture can be shown to be

$$\ln\Omega_i = \ln\phi_i - \ln w_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i\ln\left(\frac{\tilde{v}}{\tilde{v} - 1}\frac{\tilde{v}_i - 1}{\tilde{v}_i}\right) + q_i\left(\frac{2\theta_{i,p} - \theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\dot{\Gamma}_{ii}. \tag{30}$$

Here ϕ_i and w_i are the volume and weight fractions of component i in the mixture, respectively, and $\theta_{i,p}$ is the surface area fraction of pure component i at the same temperature and pressure as the mixture.

Group-contribution mixing rules

High and Danner (1989, 1990) developed the GCLF-EOS by determining group contributions for the adjustable parameters in the Panayiotou–Vera EOS. The Panayiotou–Vera formulation provides a correlation method. The GCLF-EOS model, however, is capable of predicting polymer–solvent equilibria. The only input required in the GCLF-EOS is the structure of the polymer and solvent molecules.

The pure-component EOS (Eq. 1) has two adjustable parameters: molecular interaction energy, ϵ_{11}, and molecular reference volume, v_1^*. High (1990) has shown that the interaction energy and reference volume have a linear relationship with the carbon number of normal alkanes. Once the carbon number of a normal alkane is known, two molecular parameters for the pure component can be determined and the thermodynamic properties can be calculated from the EOS. This is a basis for using a group-contribution approach for determining the molecular parameters of the lattice–fluid model.

In order to calculate a group-contribution value, we need to provide mixing rules between the molecular parameters in the EOS and the group parameters. The molecular interaction energy between like molecules, ϵ_{ii}, is determined from the group interaction energies using the following mixing rule:

$$\epsilon_{ii} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (e_{kk} e_{mm})^{1/2} \tag{31}$$

where e_{kk} is the group interaction energy between like groups k. The group surface area fractions, $\Theta_k^{(i)}$, are expressed by

$$\Theta_k^{(i)} = \frac{n_k^{(i)} Q_k}{\sum_n n_n^{(i)} Q_n}, \tag{32}$$

where $n_k^{(i)}$ is the number of group k in component i, and Q_k is the dimensionless surface area parameter of group k, as used in the UNIFAC method (Fredenslund et al., 1975). The molecular reference volume, v_i^*, is calculated from the group reference volume parameter, R_k, using the following mixing rule:

$$v_i^* = \sum_k n_k^{(i)} R_k. \tag{33}$$

The two characteristic parameters are functions of temperature. In the original GCLF-EOS model, the interaction energy and reference volume parameters of a pure component were calculated by linearly interpolating or extrapolating between values determined at 300 and 400 K. The temperature range used in the original GCLF-EOS was limited. When the parameters are calculated over a wider range of temperatures, the temperature dependence is no longer linear. In this work, therefore, analytical and more accurate temperature dependencies for the pure component EOS parameters were developed. A quadratic form with respect to temperature was found to be adequate. Thus,

$$e_{kk} = e_{0,k} + e_{1,k}\left(\frac{T}{T_0}\right) + e_{2,k}\left(\frac{T}{T_0}\right)^2 \tag{34}$$

$$R_k = \frac{1}{10^3}\left[R_{0,k} + R_{1,k}\left(\frac{T}{T_0}\right) + R_{2,k}\left(\frac{T}{T_0}\right)^2\right], \tag{35}$$

where T is the system temperature in kelvins and T_0 was arbitrarily set to 273.15 K.

The method of determination of the group parameters is given in the next section. Once the groups contained in a pure component are defined, the molecular properties at a given temperature can be calculated from the group parameters using the mixing rules, Eqs. 31 and 33, and finally the physical properties of the component can be obtained from the EOS and the chemical potential.

A combining rule for the cross interaction energy between unlike molecules 1 and 2, ϵ_{12}, given in Eq. 20, is also needed. To calculate ϵ_{12}, High and Danner (1989) used the geometric mean of the pure component interaction energies between like molecules, ϵ_{11} and ϵ_{22}.

$$\epsilon_{12} = (\epsilon_{11}\ \epsilon_{22})^{1/2}. \tag{36}$$

In this work, a binary interaction parameter, δ_{12}, was introduced:

$$\epsilon_{12} = (\epsilon_{11}\ \epsilon_{22})^{1/2}(1 - \delta_{12}). \tag{37}$$

The importance of the binary interaction parameter was discussed by High and Danner (1989). They suggested that the use of a binary interaction parameter could improve the capability of the GCLF-EOS as a correlative tool. Figures 1a and 1b show the binary vapor–liquid equilibrium calculations by the correlative GCLF-EOS model for n-hexane/benzene system at 1 atm. A WFAC calculation is shown in Figure 2 for polyisobutylene/n-pentane system. The δ_{12} values were obtained by correlation of the experimental data. The accuracy of the GCLF-EOS correlation is extremely sensitive to the value of the binary interaction parameter. To obtain an accurate predictive model, therefore, a group contribution for the δ_{12} parameter had to be developed. The molecular binary interaction parameter, δ_{12}, is calculated from the group binary parameter between groups m and n, α_{mn}, from

$$\delta_{12} = \sum_m \sum_n \Theta_m^{(M)} \Theta_n^{(M)} \alpha_{mn}, \tag{38}$$

where $\Theta_m^{(M)}$ is the surface area fraction of group m in the mixture:

$$\Theta_m^{(M)} = \frac{\sum_i n_m^{(i)} Q_m}{\sum_k \sum_i n_k^{(i)} Q_k} \tag{39}$$

where $n_m^{(i)}$ and Q_m are the number of group m in component i and the surface area parameter of group m, respectively.

Estimation of group parameters

The estimation of group interaction energy and reference volume parameters, e_{kk} and R_k, was carried out in three steps. The first step was to determine the two molecular parameters (ϵ_{11} and v_1^*) in the pure-component EOS (Eq. 1) for each pure compound. The two parameters were simultaneously determined by fitting the experimental vapor pressure and saturated liquid density data to the EOS. The molecular parameters at various temperatures were calcu-

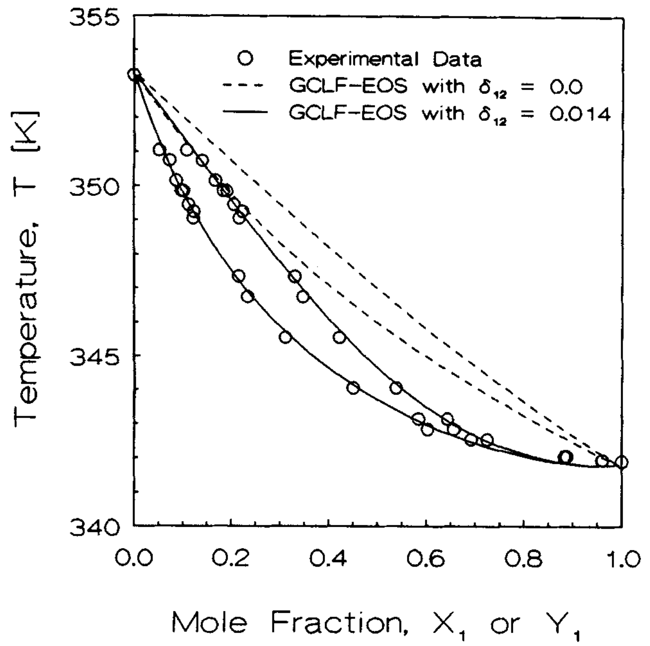

Figure 1a. Correlation of vapor–liquid equilibrium (T-XY diagram) by the GCLF-EOS for n-hexane(1)/benzene(2) system at 1 atm; the δ_{12} value was obtained by the correlation with experimental data.

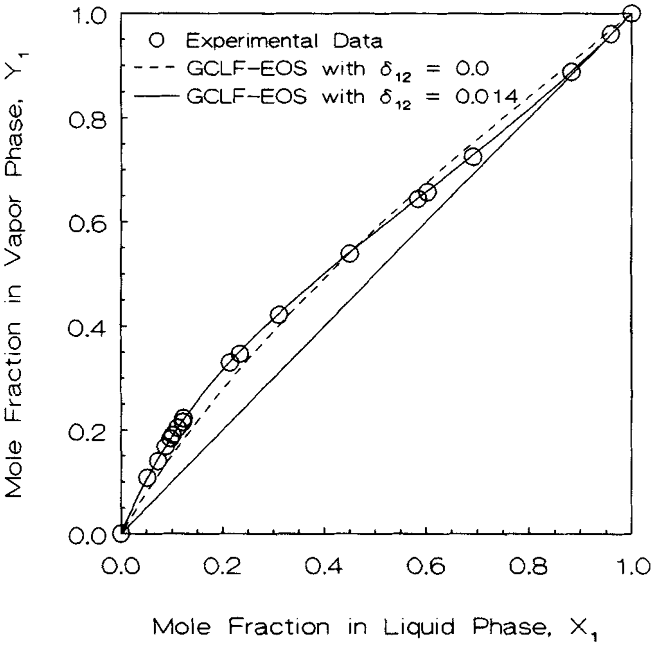

Figure 1b. Correlation of vapor–liquid equilibrium (XY diagram) by the GCLF-EOS for n-hexane(1)/benzene(2) system at 1 atm; the δ_{12} value was obtained by the correlation with experimental data.

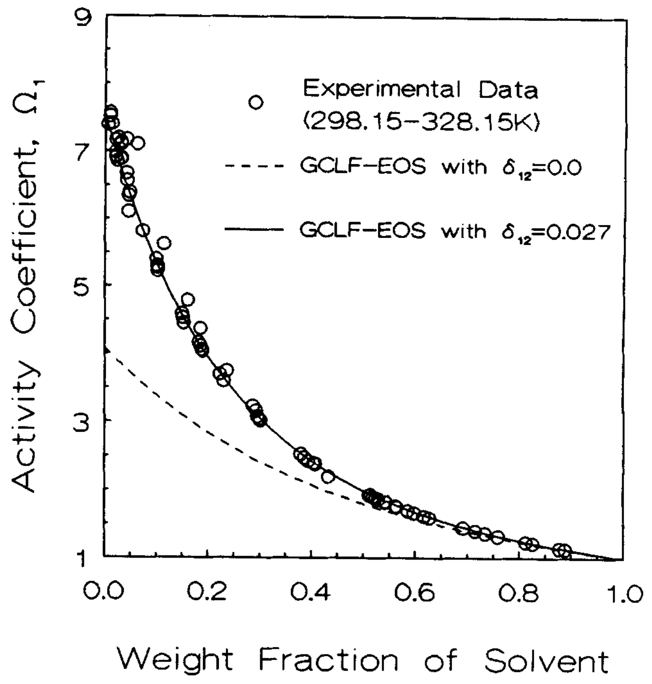

Figure 2. Correlation of weight fraction activity coefficient (WFAC) of n-pentane in polyisobutylene by the GCLF-EOS.

The δ_{12} value was obtained by the correlation with experimental data. Calculations were carried out at T = 308.15 K and MW = 1.0E5.

lated for a series of normal alkanes, branched alkanes, cycloalkanes, arenes, alkenes, chlorinated hydrocarbons, ethers, ketones, esters, acids, alcohols, water, and so on. Calculations were carried out in the range of 270 to 450 K. This temperature range is far enough away from the triple and critical points of all compounds included in the parameter estimation.

To obtain the optimum values of the parameters, a nonlinear least square regression (subroutine ZXSSQ of the IMSL Math Library) was used. The objective function (OF) minimized was

$$\mathrm{OF} = \left[\rho_{\mathrm{liq}}^{\mathrm{sat}}(\mathrm{calc}) - \rho_{\mathrm{liq}}^{\mathrm{sat}}(\exp)\right]^2 + \left[\mu^{\mathrm{liq}} - \mu^{\mathrm{vap}}\right]^2 \quad (40)$$

with

$$P^{\mathrm{sat}}(\mathrm{calc}) = P^{\mathrm{sat}}(\exp), \quad (41)$$

where $\rho_{\mathrm{liq}}^{\mathrm{sat}}(\mathrm{calc})$ and $\rho_{\mathrm{liq}}^{\mathrm{sat}}(\exp)$ are the calculated and experimental saturated liquid densities of a pure compound, respectively, and μ^{liq} and μ^{vap} are the chemical potentials of liquid and vapor phases, respectively. The $P^{\mathrm{sat}}(\mathrm{calc})$ and $P^{\mathrm{sat}}(\exp)$ are the calculated and experimental saturated vapor pressures, respectively. All the pure component properties were obtained from Daubert and Danner (extent 1993).

The second step was to determine the group parameters from the molecular parameters calculated in the first step. The group parameters, e_{kk} and R_k were independently determined by a nonlinear regression (SAS Statistics Package) using the mixing rules, Eqs. 31 and 33, at each temperature. The group parameters were determined in a sequential fashion. First, the parameters for groups CH_3 and CH_2 were regressed using only normal alkane data. These values were then used in conjunction with alcohol data to obtain the OH group, and so forth. In the final step, the parameter con-

Table 1. Group Interaction Energy and Reference Volume Parameters

Main Group	Subgroup	$e_{0,k}$	$e_{1,k}$	$e_{2,k}$	$R_{0,k}$	$R_{1,k}$	$R_{2,k}$	Q_k
1 CH_2	1 CH_3	642.019	10.186	−4.817	25.979	−0.388	0.814	0.848
	2 CH_2	919.390	−67.757	78.384	14.089	2.039	−0.963	0.540
	3 CH	1,300.351	331.832	391.739	2.522	3.362	−2.943	0.228
			n-hexane: 2 CH_3, 4 CH_2					
2 C	4 C	1,480.016	1,125.680	1,967.093	−11.793	7.681	−5.795	0.150
			2,2,4-trimethylpentane: 5 CH_3, 1 CH_2, 1 CH, 1 C					
3 cy-CH_2	5 cy-CH_2	899.910	−41.547	33.970	15.810	0.747	−0.168	0.540
	6 cy-CH	1,546.001	−381.152	472.951	3.432	5.248	−2.638	0.228
	7 cy-C	1,591.986	11.798	1,230.965	−8.931	10.852	−5.362	0.150
			cyclohexane: 6 cy-CH_2					
4 ACH	8 ACH	1,132.433	−209.906	78.217	12.189	1.834	−0.389	0.400
	9 AC	9,247.801	−7,299.508	2,824.623	3.062	0.806	0.000	0.120
			benzene: 6 ACH					
5 $ACCH_2$	10 $ACCH_3$	959.652	−11.693	33.812	26.370	3.136	−1.092	0.968
	11 $ACCH_2$	1,210.034	49.549	87.374	16.051	3.558	−1.907	0.660
	12 ACCH	2,134.993	−232.701	560.421	2.933	7.462	−4.174	0.348
			toluene: 5 ACH, 1 $ACCH_3$					
6 C=C	13 $CH_2=CH$	696.741	74.646	−17.603	35.587	1.550	−0.192	1.176
	14 $CH=CH$	982.211	6.384	44.321	20.234	7.337	−2.659	0.867
	15 $CH_2=C$	948.063	−33.316	64.267	19.593	7.767	−3.143	0.988
	16 $CH=C$	1,499.562	−66.818	136.874	9.821	6.231	−3.240	0.676
			1-hexene: 1 CH_3, 3 CH_2, 1 $CH_2=CH$					
7 CCl	17 CH_2Cl	1,289.876	−271.806	80.704	32.244	5.257	−0.599	1.264
	18 CHCl	1,319.789	−156.664	92.332	21.359	8.441	−3.179	0.952
	19 CCl	1,556.418	−176.378	233.935	12.810	9.171	−4.941	0.724
			1-chloropropane: 1 CH_3, 1 CH_2, 1 CH_2Cl					
8 CCl_2	20 CH_2Cl_2	1,354.956	−384.293	103.352	51.888	6.083	1.028	1.988
	21 $CHCl_2$	1,392.832	−349.566	113.018	39.812	14.427	−4.119	1.684
			dichloromethane: 1 CH_2Cl_2					
9 CCl_3	22 $CHCl_3$	1,173.525	−247.029	81.134	64.532	10.792	−1.937	2.410
	23 CCl_3	1,133.307	−174.685	84.569	55.461	11.675	−3.471	2.184
			chloroform: 1 $CHCl_3$					
10 CCl_4	24 CCl_4	1,007.887	−124.396	60.094	79.623	10.807	−2.673	2.910
			carbon tetrachloride: 1 CCl_4					
11 ACCl	25 ACCl	1,190.694	−25.681	34.993	23.688	4.975	−1.822	0.844
			monochlorobenzene: 5 ACH, 1 ACCl					
12 CH_2O	26 CH_3O	1,213.041	−440.261	123.117	31.624	1.853	0.721	1.088
	27 CH_2O	1,145.190	−86.586	41.257	17.426	7.991	−3.073	0.780
	28 CHO	1,762.751	−336.174	230.502	4.233	12.885	−6.215	0.468
			diethyl ether: 2 CH_3, 1 CH_2, 1 CH_2O					
13 CH_2CO	29 CH_3CO	1,623.704	−542.555	149.255	33.358	9.281	−1.182	1.488
	30 CH_2CO	2,004.018	−741.998	240.219	22.438	11.103	−3.557	1.180
			methyl ethyl ketone: 1 CH_3, 1 CH_2, 1 CH_3CO					
14 COO	31 COO	2,182.434	−782.011	226.335	14.091	10.712	−3.344	0.880
			n-butyl acetate: 2 CH_3, 3 CH_2, 1 COO					
15 COOH	32 HCOOH	2,510.362	−790.266	134.835	31.687	2.967	2.102	1.532
	33 COOH	3,963.163	−2,101.752	485.316	19.362	15.684	−3.114	1.224
			formic acid: 1 HCOOH; acetic acid: 1 CH_3, 1 COOH					
16 SiO	34 SiO	560.883	107.387	260.550	15.570	1.242	−3.836	0.4657
			octamethylcyclotetrasiloxane: 8 CH_3, 4 SiO					
17 CH_3OH	35 CH_3OH	2,727.987	−1,361.207	278.761	30.459	8.440	0.000	1.432
			methanol: 1 CH_3OH					
18 OH	36 OH	9,229.525	−7,980.168	2,105.795	4.862	14.325	−3.989	0.584
			ethanol: 1 CH_3, 1 CH_2, 1 OH					
19 H_2O	37 H_2O	5,447.490	−2,184.593	268.483	20.887	−6.280	3.400	1.400
			water: 1 H_2O					

stants ($e_{i,k}$ and $R_{i,k}$) were determined by fitting the group parameters obtained at the various temperatures to the quadratic temperature relations, Eqs. 34 and 35. The group parameter constants are given in Table 1. Once the molecular structure of a pure compound is known, the group parameters at a given temperature can be calculated from the constants in Table 1, and then the molecular parameters can be calculated using the mixing rules, Eqs. 31 and 33. In this work we added many groups such as alkene-, chloro-, and acid-groups that did not appear in the original GCLF-EOS model, thus extending the applicability of the model.

The group binary interaction parameters (α_{mn}) were estimated by the following procedure. First, the δ_{12} parameters were regressed from the experimental binary vapor–liquid equilibrium data of numerous low molecular weight binary mixtures. The OF minimized in the regression was

$$OF = \sum_{j=1}^{n} \sum_{i=1}^{NC} \left(\mu_i^{\mathrm{liq}} - \mu_i^{\mathrm{vap}} \right)_j^2 \qquad (42)$$

where n is the number of data points and NC is the number of components in the mixture, and μ_i^{liq} and μ_i^{vap} are the chemical potentials of component i in liquid and vapor phases at equilibrium, respectively. In this work the δ_{12} parameter is considered to be independent of temperature. The experimental binary VLE data were obtained from DECHEMA Chemistry Data Series (Gmehling et al., 1977–1993).

Once the δ_{12} parameters were calculated for binary mixtures, the α_{mn} parameters between unlike groups m and n were determined by a nonlinear regression of the mixing rule, Eq. 38. There is not adequate binary VLE data available to calculate values for all the subgroups. Thus, as in the UNIFAC method, values were obtained only for the main groups as defined in Table 1. The group binary interaction parameters, α_{mn}, are given in Table 2. The group binary interaction parameters between like groups, α_{mm}, are set to zero and α_{mn} is equal to α_{nm}. Using the group contribution mixing rules (Eqs. 31, 33, and 38) and group parameters (Tables 1 and 2), one can predict the vapor–liquid equilibria of polymer solutions as well as of low molecular weight compounds.

Table 2. Group Binary Interaction Parameters (α_{mn})*

Main Groups	CH_2	C	cy-CH_2	ACH	$ACCH_2$	C = C	CCl	CCl_2	CCl_3	CCl_4	ACCl	CH_2O	CH_2CO	COO	COOH	SiO	CH_3OH	OH	H_2O
CH_2	0.0000	0.2033	0.0000	0.0363	−0.0064	0.0000	0.0407	0.0701	0.0290	0.0000	−0.0074	0.0333	0.1490	0.0211	0.1020	0.0349	0.1732	0.3994	0.0000
C		0.0000	0.0000	0.0202	−0.3946	N.A.**	N.A.**	N.A.**	N.A.**	0.8948	N.A.**	N.A.**	−0.4285	N.A.**	N.A.**	N.A.**	1.8040	1.2601	N.A.**
cy-CH_2			0.0000	0.0226	0.0183	0.0000	0.0390	N.A.**	0.0285	0.0000	0.0322	0.1688	0.1272	0.2029	0.1091	0.0349	0.2037	0.3662	N.A.**
ACH				0.0000	0.0116	−0.0126	0.0138	0.0216	−0.0206	0.0000	0.0000	−0.2003	−0.1259	−0.1408	0.1294	−0.1178	0.1698	0.1031	N.A.**
$ACCH_2$					0.0000	0.0375	0.0295	N.A.**	−0.0415	0.0000	−0.0509	0.1632	0.1050	0.0415	0.0656	N.A.**	0.2687	0.3770	N.A.**
C = C						0.0000	0.1365	0.0000	−0.0411	0.0000	−0.0990	N.A.**	−0.1114	0.4554	0.1176	N.A.**	0.0158	−0.0484	N.A.**
CCl							0.0000	0.0000	0.0000	0.0555	−0.3350	−0.1277	−0.1775	N.A.**	0.1094	N.A.**	0.1516	0.0750	N.A.**
CCl_2								0.0000	0.0000	0.0435	N.A.**	−0.5183	−0.3259	−0.5160	0.0053	N.A.**	0.0928	−0.1656	0.0754
CCl_3									0.0000	0.0000	N.A.**	−0.5444	−0.2919	−0.4515	0.1218	N.A.**	0.0952	−0.1398	N.A.**
CCl_4										0.0000	0.0000	0.1593	0.0071	0.0302	0.1041	N.A.**	0.1616	0.2819	N.A.**
ACCl											0.0000	N.A.**	−0.0738	0.1722	−0.4201	N.A.**	0.4054	0.3059	N.A.**
CH_2O												0.0000	−0.8271	−0.7928	N.A.**	N.A.**	−0.5642	−1.0634	−1.2774
CH_2CO													0.0000	−0.7579	N.A.**	N.A.**	−0.2303	−1.3451	−0.3778
COO														0.0000	−0.9330	N.A.**	−0.3211	−1.4501	−0.6527
COOH															0.0000	N.A.**	−0.2754	−1.9989	−0.1690
SiO																0.0000	0.0000	0.0000	N.A.**
CH_3OH																	0.0000	−1.4001	−0.0520
OH																		0.0000	−0.7455
H_2O																			0.0000

*$\alpha_{mm} = 0.0$ and $\alpha_{mn} = \alpha_{nm}$.
**N.A. = not available due to the lack of binary VLE data.

Results and Discussion

The WFACs at infinite dilution and finite concentrations of solvents have been predicted for many polymer–solvent systems. In these calculations no pure component or mixture properties of the solvent or polymer are used other than the molecular structures of the solvent and polymer repeating unit. The results have been compared against those of the original GCLF-EOS model of High and Danner (1990). Calculations have also been made with the UNIFAC-free volume model (UNIFAC-FV; Oishi and Prausnitz, 1978), the revised group-contribution Flory EOS (GC-Flory EOS; Bogdanic and Fredenslund, 1994), and the entropic-free volume model (entropic-FV; Kontogeorgis et al., 1993). The detailed derivations and final equations of these models can be found in the cited publications.

The UNIFAC-FV method is a group-contribution activity coefficient model based on the UNIFAC model (Fredenslund et al., 1975). The free-volume contribution, derived from the Flory EOS, was added to the combinatorial and residual terms of the UNIFAC model to account for the free-volume differences between the polymer and solvent molecules. This model, however, requires the liquid densities of the pure solvent and pure polymer at the temperature of the mixture.

The revised GC-Flory EOS is a revision of the GC-Flory EOS originally developed by Chen et al. (1990). The original GC-Flory EOS is a group-contribution extension of a modified form of the Flory equation of state (Flory et al., 1964). In the revised model, the extra binary entropic interaction parameter, ΔS_{ij}^{HB}, which was included in the original model to account for hydrogen bonding, was not used. All the parameters were reestimated to improve the accuracy of predictions and some group parameters were added. Although the revised GC-Flory EOS was derived from an EOS, it is in effect an activity coefficient model, because the parameters were determined from liquid density at the zero pressure limit of the equation and no vapor pressure data were used. Thus, the model cannot predict any pressure dependency.

The entropic-FV method is an activity coefficient model consisting of two terms, the combined combinatorial and free-volume term by Elbro et al. (1990) and the residual term of the UNIFAC. The combined combinatorial and free-volume term was derived by replacing the volume fraction in the Flory–Huggins combinatorial term with the free-volume fraction. The free volume was defined as the difference between the liquid molar volume and the van der Waals volume of the molecule. In this model the liquid densities of the pure solvent and pure polymer are needed.

Figures 3 through 7 are the predictions of WFACs at infinite dilution of solvents by the models described earlier as well as the modified GCLF-EOS for various polymer–solvent systems. The experimental and predicted WFACs are shown as a function of temperature. The experimental data are the solvent WFACs measured at different temperatures and polymer molecular weights and carried out by different researchers. All the experimental data used were obtained from

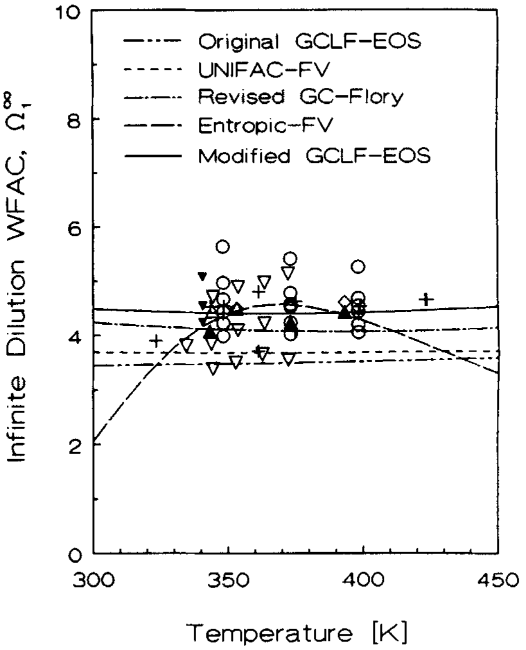

Figure 4. Prediction of infinite dilution weight fraction activity coefficient of benzene in poly(ethylene oxide).

Calculations were carried out at MW = 3.5E3. The sources of experimental data are as follows: + Cheng and Bonner, 1974; ▲ Klein and Jeberien, 1980; ◇ Fernandez-Berridi et al., 1982; ▼ Kawakami et al., 1976; ▲ Galin, 1983; ○ Ratzsch et al., 1980; and ▽ Sorensen, 1988.

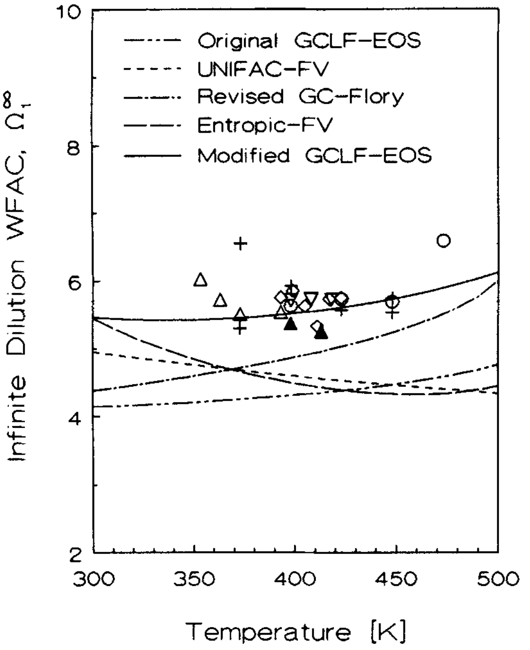

Figure 3. Prediction of infinite dilution weight fraction activity coefficient of benzene in poly(vinyl acetate).

Calculations were carried out at MW = 8.35E4. The sources of experimental data are as follows: ○ Newman and Prausnitz, 1973; + Lichtenthaler et al., 1974a; ▽ DiPaola-Baranyi and Guillet, 1978; DiPaola-Baranyi et al., 1980; △ Deshpande and Tyagi, 1978; ▲ Merk et al., 1980; ◇ Castells and Mazza, 1986.

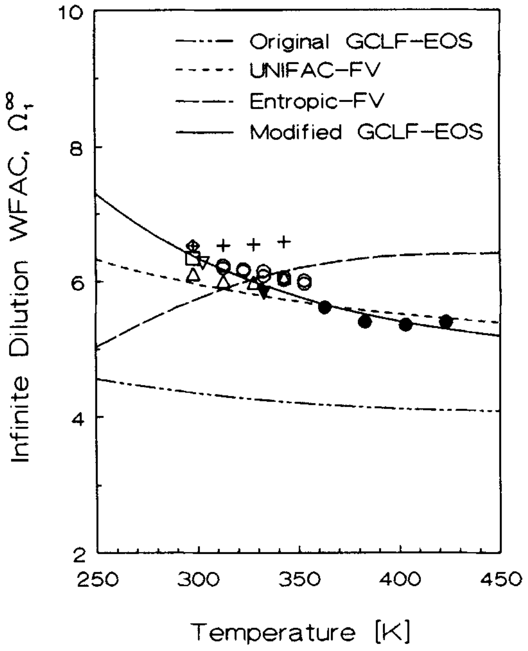

Figure 5. Prediction of infinite dilution weight fraction activity coefficient of *n*-octane in poly(dimethyl siloxane).

Calculations were carried out at MW = 9.25E4. The sources of experimental data are as follows: ▽ Ashworth et al., 1984; + Summers et al., 1972; ◇ Price et al., 1986; △ Lichtenthaler et al., 1974b; ▼ Deshpande et al., 1974; □ Hammers and De Ligny, 1974; ○ Roth and Novak, 1986; ● Becerra et al., 1981.

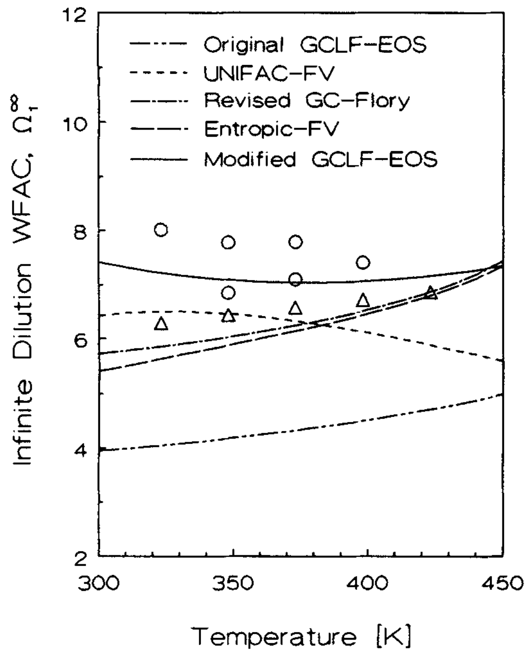

Figure 6. Prediction of infinite dilution weight fraction activity coefficient of *n*-hexane in polyisobutylene.

Calculations were carried out at MW = 5.3E4.

The sources of experimental data are as follows: ○ Lichtenthaler et al., 1974a; △ Newman and Prausnitz, 1974.

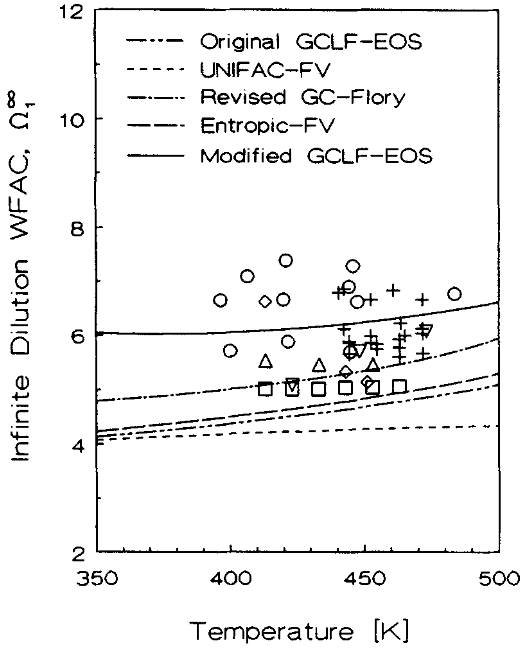

Figure 7. Prediction of infinite dilution weight fraction activity coefficient of ethylbenzene in polystyrene.

Calculations were carried out at MW = 2.75E5. The sources of experimental data are as follows: ○ Covitz and King, 1972; ▽ Newman and Prausnitz, 1972; ◇ Vrentas et al., 1983; △ Grater et al., 1985; ▲ Galin and Rupprecht, 1978; + Inoue et al., 1986; and □ Schuster et al., 1984.

the data base provided by Danner and High (1993). The experimental WFACs at infinite dilution were measured using inverse gas chromatography technique. Normally at high molecular weights, the polymer molecular weight has a negligible influence on the solvent activity coefficients for most of polymer–solvent systems. Thus, the predictions were carried out at the average value of the polymer molecular weights given in the experimental data. The temperature dependence of the experimental and predicted activity coefficients is also very small over a wide range of temperature.

Figure 3 shows the predictions of the infinite dilution WFACs for poly(vinyl acetate)-benzene system. Significant scatter is obvious in these data. Unfortunately this is typical of the infinite dilution data for most systems. Furthermore, there is no objective method of ascertaining which data are more accurate. Thus, we have elected to show all the data collected by Danner and High (1993). Temperature generally has a negligible effect on the activity coefficients. The modified GCLF-EOS gave an excellent prediction, while the other models underpredicted the experimental values. The predictions of infinite dilution WFACs for poly(ethylene oxide)-benzene system are shown in Figure 4. This experimental data from a number of different researchers show even more scatter. The modified GCLF-EOS gave good predictions following the mean values of the experimental WFACs. All the models except the entropic-FV model predicted no significant change in the WFAC with respect to temperature. The entropic-FV model, however, showed an unusual behavior at low and high temperatures. This behavior of the entropic-FV model has also been found in the predictions of infinite dilution WFACs of toluene and *n*-butyl acetate in poly(ethylene oxide). The predictions of infinite dilution WFACs of *n*-octane in poly(dimethyl siloxane) are shown in Figure 5. The UNIFAC-FV and the modified GCLF-EOS gave good predictions. Temperature had an influence on the activity coefficients for this system. Similar temperature dependencies in the experimental data were also observed for the systems of poly(dimethyl siloxane) with a number of other solvents. Figures 6 and 7 show the predictions of the WFACs of *n*-hexane and ethylbenzene in polyisobutylene and polystyrene, respectively. The modified GCLF-EOS predicted the experimental data well, although the experimental data are scattered. For the systems shown in Figures 3 to 7, the modified GCLF-EOS model gave consistently good predictions, while the original GCLF-EOS underpredicted the experimental data.

Figures 8 through 13 are the predictions of activity coefficients of solvents in polymers at finite solvent concentrations. The temperature and polymer molecular weight are included in each figure. The experimental data at finite concentrations were measured by the gravimetric sorption technique, and were also obtained from the data base of Danner and High (1993). The prediction of the WFACs of *n*-pentane in polyisobutylene is illustrated in Figure 8. The modified GCLF-EOS gave excellent predictions and is much better than the original model. The predictions of the other three models are reasonably good as well. Figure 9 is the prediction results for polystyrene-toluene system. The modified GCLF-EOS and the revised GC-Flory models show good agreements with the experimental data. Figure 10 shows the predictions of the WFACs of benzene in poly(vinyl acetate). Most of the models give good predictions for this system.

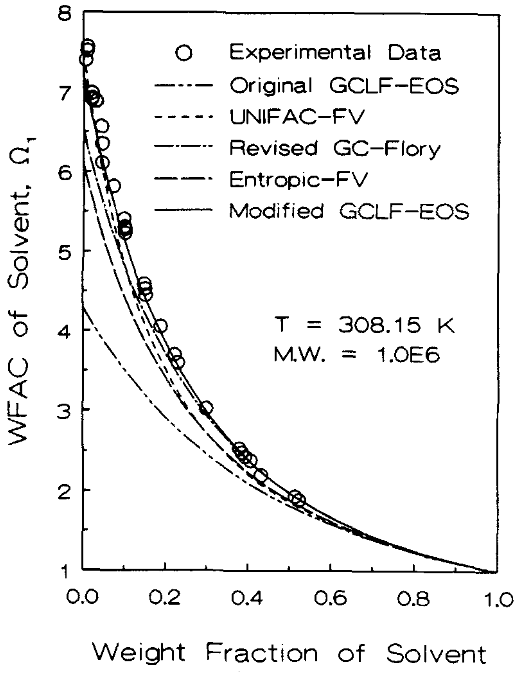

Figure 8. Prediction of weight fraction activity coefficient of *n*-pentane in polyisobutylene; experimental data are from Prager et al. (1953).

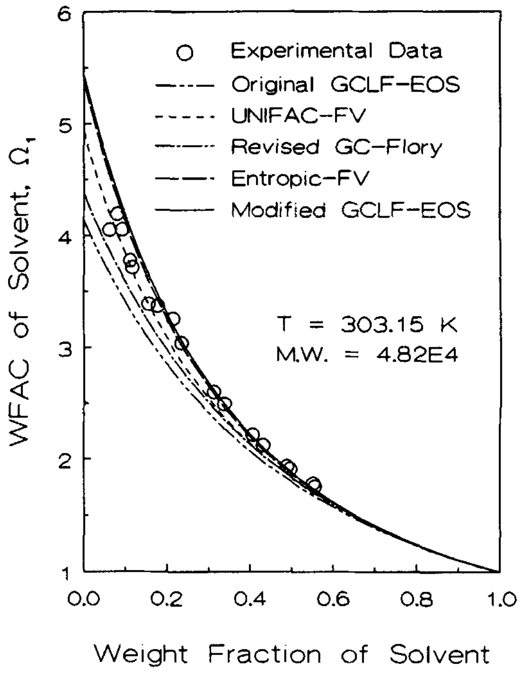

Figure 10. Prediction of weight fraction activity coefficient of benzene in poly(vinyl acetate); experimental data are from Nakajima et al. (1959).

The predictions of the WFACs of methyl ethyl ketone in poly(methyl methacrylate) are shown in Figure 11. All the models except the original model and the UNIFAC-FV model predicted the experimental values very well. The UNIFAC groups for poly(methyl methacrylate) should be 2CH_3, 1CH_2, 1C, and 1COO. In their paper defining the UNIFAC-FV method, Oishi and Prausnitz (1978) listed the group CH_3COO as $COOCH_3$ (their Table 1), in contradiction to the UNIFAC definition as discussed by Macedo et al. (1983). This is note-

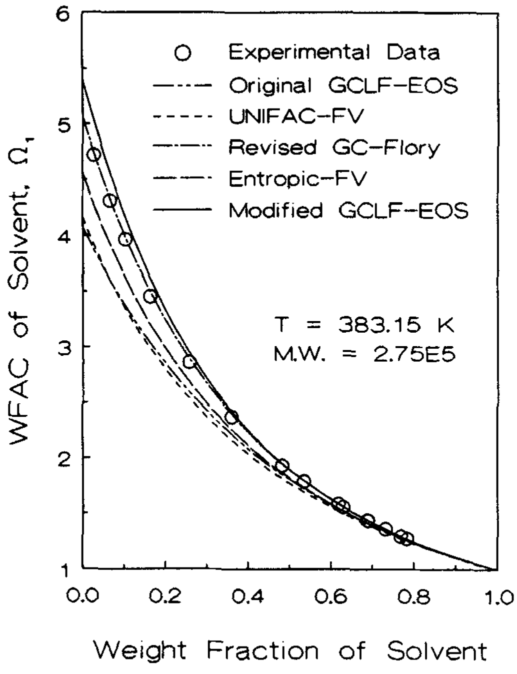

Figure 9. Prediction of weight fraction activity coefficient of toluene in polystyrene; experimental data are from Vrentas et al. (1983).

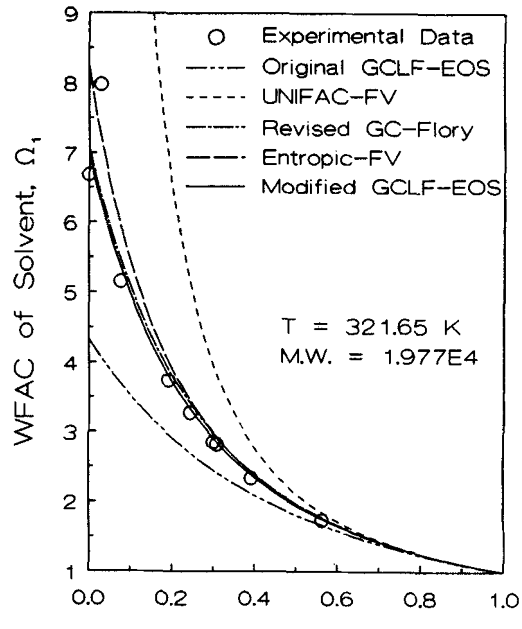

Figure 11. Prediction of weight fraction activity coefficient of methyl ethyl ketone in poly(methyl methacrylate); experimental data are from Tait and Abushihada (1977).

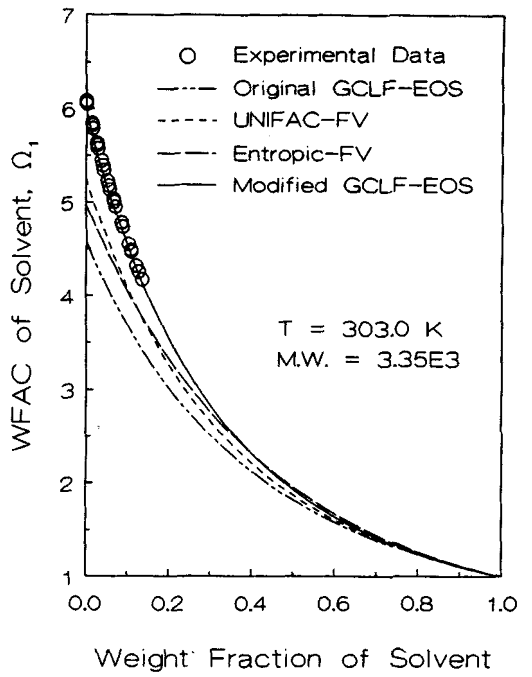

Figure 12. Prediction of weight fraction activity coefficient of benzene in poly(dimethyl siloxane); experimental data are from Ashworth and Price (1986).

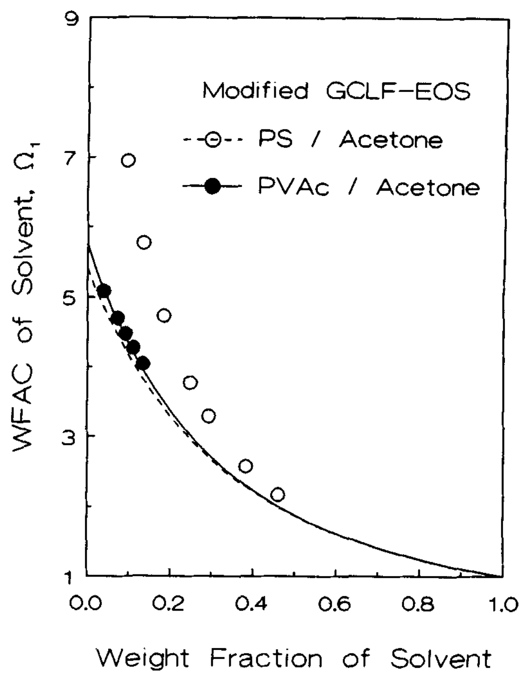

Figure 13. Prediction of weight fraction activity coefficients of acetone in polystyrene and poly(vinyl acetate) by the modified GCLF-EOS.

Polystyrene data ($T = 298.15$ K, MW = 1.57E4) are from Bawn and Wajid (1956), and poly(vinyl acetate) data ($T = 303.15$ K, MW = 1.72E4) from Kokes et al. (1953).

worthy because using 1CH_3, 1CH_2, 1C, and 1CH_3COO (as if it were $COOCH_3$) for poly(methyl methacrylate) significantly improves the prediction. There appears, however, to be no justification for the use of the CH_3COO group in the definition of poly(methyl methacrylate).

Figure 12 is the prediction results for poly(dimethyl siloxane)-benzene system. The modified GCLF-EOS showed excellent agreement with the experimental values. Figure 13 shows the predictions of the WFACs of a polar solvent, acetone, in polystyrene and poly(vinyl acetate) by the modified GCLF-EOS. The model gave excellent results for the poly(vinyl acetate) system (the more polar case), but it underpredicted the experimental values for the polystyrene system. Evaluation of the available systems revealed no identifiable tendency with respect to the polarity of the components.

For the systems shown in Figures 8 to 12, the original GCLF-EOS underpredicted the experimental activity coefficients at finite concentrations, as it did for the infinite dilution WFACs. More systems have been tested to see the prediction capability of the modified and original GCLF-EOS models at finite concentrations. The modified GCLF-EOS gave consistently good predictions for many systems, although only a few examples were shown in this article. Addition of the binary interaction parameter is the key to these improved predictions.

Conclusions

A modified GCLF-EOS has been developed that is capable of predicting accurately the activity coefficients of solvents in polymers. Group contributions for the interaction energy and reference volume have been developed based only on the saturated vapor pressures and liquid densities of low molecular weight compounds. Analytical and more accurate temperature dependencies for the interaction energy and reference volume parameters have been developed. For a mixture, a binary interaction parameter (δ_{12}) has been added into the combining rule for calculating the interaction energy in the mixture. Group-contribution values of the binary interaction parameter have been determined using the binary vapor–liquid equilibria of low molecular weight compounds.

The binary interaction parameter in the modified GCLF-EOS was found to be an important and necessary parameter to give good predictions. The modified GCLF-EOS gave excellent predictions of solvent activity coefficients both at infinite dilution and at finite concentrations. It was significantly better than the original GCLF-EOS in its prediction capacity. For the polymer–solvent systems investigated in this work, the modified GCLF-EOS provided more accurate predictions than the UNIFAC-FV, the revised GC-Flory EOS, and the entropic-FV models.

The only information required for the GCLF-EOS is the structure of the molecules in the polymer and solvent in terms of their functional groups. No other pure component or mixture properties of polymer and solvent are needed.

A computer program for this model is available and can be obtained by contacting R. P. Danner.

Acknowledgment

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Notation

a_i = activity of component i in a mixture

P = pressure, Pa

P_i^*, P^* = characteristic pressures of a pure component i and a mixture, respectively, Pa

$\tilde{P}_i, \tilde{P}$ = reduced pressures of a pure component i and a mixture, respectively

q_i, q = effective chain length or surface area parameter for a component i and for a mixture, respectively

r = number of lattice sites for a mixture

R = gas constant, $J \cdot kmol^{-1} \cdot K^{-1}$

T_i^*, T^* = characteristic temperatures of a pure component i and a mixture, respectively, K

$\tilde{T}$ = reduced temperature of a mixture

v = molar volume, $m^3/kmol$

v^* = reference volume of a mixture, $m^3/kmol$

$\tilde{v}_i, \tilde{v}$ = reduced volume of a pure component i and a mixture, respectively

Greek letters

θ = molecular surface fraction of a mixture

$\mu_i^{(M)}$ = chemical potential of a component i in a mixture, J/kmol

$\Delta \mu_i$ = chemical potential change upon mixing for component i, J/kmol

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