Application of the Group Contribution Lattice-Fluid EOS to Polymer Solutions

A new group contribution lattice-fluid equation of state (GCLF-EOS) is described that can accurately predict the activities of solvents in polymer solutions. This equation of state is a modification of the equation of state derived by Panayioutou and Vera (1982), which is based on the lattice statistics developments of Guggenheim (1952). The group contribution modification permits the prediction of solvent activity, given only the structure of the polymer and solvent involved. The GCLF-EOS can accurately predict solvent activities in polystyrene, polyethylene, poly(ethylene oxide), poly(ethylene glycol), poly(propylene oxide), and poly(vinyl chloride). The model does not perform as well for solvent activities in polyisobutylene due to the inaccurate group contribution values for the quaternary carbon group.

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Introduction

Polymer processing involves many separation operations that are designed to remove impurities, solvents, and monomers. Phase equilibrium properties of polymer solutions affect how these processing steps can be carried out. If possible, equations of state are preferred over activity coefficient models for calculation of phase equilibria. Equations of state can provide an accurate, consistent model for all phases and conditions. The equation of state, however, must be able to describe all phases involved. It is a difficult task to derive a general equation of state that is applicable to a wide variety of molecules for both vapor and liquid phases.

Many types of equations of state are available. Correlative equations of state have been available since the early 1900's. Predictive equations, which do not require experimental data to correlate mixture parameters, are less common, but inroads into these developments have been made over the past 20 years. An equation of state that is capable of predicting both pure component and mixture properties has not been developed. We describe in this paper an equation of state that is based solely on pure component data of low molecular weight compounds, which are capable of predicting pure component and mixture properties of low and high molecular weight compounds. To develop an equation of state which is predictive, a group contribution approach can be used. It was shown by Lee and Haile (1988), Massobrio et al. (1988), and Haile and Lee (1988) that the group contribution approach, sometimes called the solution of groups approach, has strong theoretical ties to statistical mechanical theory. The group contribution approach assumes that the interaction energy between groups will be constant regardless of the overall structure of the molecule. At this stage of development in statistical mechanics, group contributions offer the only realistic hope of developing a predictive equation of state for polymer solutions.

Only in the mid 1980's has a group contribution equation of state been proposed for polymer solutions (Holten-Andersen, 1985), but this model has been shown to have a number of serious deficiencies (High and Danner, 1989). Since group contribution approaches are so successful in various activity coefficient models, the goal of developing a predictive equation of state for polymer solutions reduces to developing a group contribution equation of state.

The group contribution method developed in this research can be applied in principle to any homopolymer, random copolymer, or alternating copolymer that can be constructed from the available group contributions, although only systems involving homopolymers are presented in this paper. Block copolymers and cross-linked polymers cannot be treated with this method. Branching in a molecule such as polyethylene must be specified in terms of number of branches per 1,000 carbon atoms in the main chain to correctly assign the groups in the molecule.

Pure-Component Group Contribution Equation of State

The basis of the random hole group contribution lattice-fluid equation of state (GTCLF-EOS) is a lattice-fluid model previously developed by Panayiotou and Vera (1982). Several workers have developed an equation of state based on the lattice fluid, and all of these models are based on the well established lattice statistics model of Guggenheim (1952). The equation of state described in this paper is identical to the Panayiotou and Vera model. A detailed derivation of the lattice-fluid equation of state is presented elsewhere (High, 1990). The Panayiotou-Vera equation of state in terms of reduced variables is

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

$$\tilde{P}_1 = \frac{2Pv_h}{z\epsilon_{11}} \qquad (2)$$

$$\theta_1 = \frac{q_1 N_1}{N_q} \qquad (3)$$

$$zN_q = z(\mathrm{N}_h + q_1 N_1) \qquad (4)$$

$$r_1 = \frac{v_1^*}{v_h} \qquad (5)$$

$$zq_1 = (z-2)r_1 + 2 \qquad (6)$$

$$\tilde{T}_1 = \frac{2RT}{z\epsilon_{11}} \qquad (7)$$

$$\tilde{v}_1 = \frac{v}{v_1^*} = \frac{v_h(N_h + r_1 N_1)}{v_1^*} \qquad (8)$$

where

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
N_h = number of holes in the lattice

Once the parameters ϵ_{11} and v^* are known, all of the remaining parameters in Eq. 1 can be determined from Eqs. 2 through 8 for a given temperature and pressure. All that remains to solving the equation of state, Eq. 1, is to specify T and P and solve for molar volume, v, of the system. Since Eqs. 2 through 8 involve v, solution of the equation of state involves a numerical solution of these equations along with the equation of state, Eq. 1.

Equation 1 is derived assuming that the molecules and holes are randomly placed on the lattice. Panayiotou and Vera (1982) point out that the additional complexity of local compositions does not appreciably increase the accuracy of the equation of state for pure components.

Although Eq. 1 is not cubic, it behaves numerically as a cubic equation of state as it should to accurately describe both the liquid and vapor phases. The equation of state contains two adjustable parameters for each molecule: a characteristic segmental interaction energy, ϵ_{11}, that describes the average interaction energy between the segments of two molecules and a reference volume, v^*.

The characteristic interaction energy, ϵ_{11}, is an average interaction energy over the length of the molecule. Structural elements of the molecule with large interaction energies are averaged with other structural elements with less or zero interaction energy. Averaging the interaction energy over the length of the molecules does not correspond to the exact statistical mechanical definition of the mean field approximation. Regardless of the definition of the type of approximation, averaging the interaction energy over the length of the molecule will most likely cause poor prediction for strongly associating systems. The definition of the average interaction energy has implications regarding the functional forms of the group contribution equations used later.

The above equation of state is used with the chemical potential expression to regress the two molecular parameters ϵ_{11} and v^* for each molecule. Once these parameters are found, a group contribution technique can be constructed to calculate the molecular parameters from the structure of the molecule. The expression for the pure component chemical potential is given by (Panayiotou and Vera, 1982; High, 1990):

$$-\frac{\mu_1}{RT} = \ln\frac{\delta_1}{\sigma_1} + \ln q_1 + \ln\frac{(1-\theta_1)^{r_1}}{\theta_1} + \frac{\theta_1}{\tilde{T}_1}(q_1 + r_1\tilde{v}_1\theta_1) \qquad (9)$$

Pressure and volume are implicitly involved in the parameters θ_1, q_1, r_1, and $\tilde{v}$, which must be determined by solving the equation of state, Eq. 1, simultaneously with Eq. 9 when calculating the chemical potential. This expression for the chemical potential was derived assuming that the molecules and holes are distributed randomly throughout the lattice. δ_i and σ_i are volume-independent parameters accounting for flexibility and symmetry of the molecule. Since these parameters are not volume-dependent, they do not appear in the equation of state and will not influence equilibrium calculations.

Calculation of the Molecular Parameters through Group Contributions

The two molecular parameters, ϵ_{11} and v^*, have been determined by fitting the saturated liquid density and the vapor pressure calculated from the equation of state to the experimental values at several temperatures. From the two equations

$$\rho_{\mathrm{exp}}^{\mathrm{sat,liq}} = \rho_{\mathrm{pred}}^{\mathrm{sat,liq}} \qquad (10)$$

$$P_{\mathrm{exp}}^{\mathrm{sat}} = P_{\mathrm{pred}}^{\mathrm{sat}} \qquad (11)$$

the two parameters for each molecule, the characteristic interaction energy ϵ_{11} and the reference volume v^* can be determined. High (1990) has shown that the interaction energy and reference volume vs. carbon number for the normal alkanes are linear. Once the carbon number of a normal alkane is known, the molecular parameters can be determined and the thermodynamic properties for the pure components can be calculated from the equation of state. This is the basis for using a group contribution approach for determining the molecular parameters of the lattice-fluid model.

The reference volume, v^*, is a very weak function of temperature. The characteristic interaction energy, ϵ_{11}, however, is a strong function of temperature; therefore, temperature dependence of the characteristic interaction energy must be taken into account in a group contribution approach (High, 1990).

The molecular parameters ϵ_{11} and v^* were determined for a series of n-alkanes, branched alkanes, cycloalkanes, arenes, ethers, ketones, monochlorinated alkanes, and water. These molecular parameters were determined at 300 and 400 K. The two temperatures provide a means for determining the temperature dependence of the group interaction energies and the reference volume. The molecular interaction energy is determined from the group interaction energies from

$$\epsilon_{ij,T} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(j)} \sqrt{e_{kk,T}\, e_{mm,T}} \qquad (12)$$

where the group surface area fractions, $\Theta_k^{(i)}$ and $\Theta_m^{(i)}$, are calculated from the UNIFAC dimensionless surface area parameters, Q_k and Q_m (Fredenslund et al., 1975):

$$\Theta_k^{(i)} = \frac{\nu_k^{(i)} Q_k}{\sum_m \nu_m^{(i)} Q_m} \qquad (13)$$

The surface area fractions $\Theta_k^{(i)}$and $\Theta_m^{(j)}$used to calculate the energy parameters should not be confused with the surface area parameter θ_1 used in the equation of state. The surface area fractions $\Theta_k^{(i)}$ and $\Theta_m^{(i)}$ are calculated using the surface area parameters Q_k taken from the UNIFAC method. The surface area parameters are then used to calculate the interaction energy, ϵ_{ij}. The lattice fluid model surface area parameter, θ_1, is calculated from Eq. 3 and used in the equation of state and chemical potential expressions.

The characteristic interaction energy can be calculated at temperatures other than 300 and 400 K by linearly interpolating between these two temperatures (High, 1990). The characteristic molecular volume, v^*, is calculated from the reference volume parameters, R_k,

$$v^*_{i,T} = a_T + \sum \nu_k^{(i)} R_{k,T} \qquad (14)$$

A nonzero intercept is necessary in the above equation, particularly for the low molecular weight compounds in a homologous series. Even though the temperature dependence of the reference volume is small, this temperature dependence was included for completeness. The reference volume can be determined by linearly interpolating with the group values at 300 and 400 K. The value of the intercept at 300 K, a_{300}, is 0.02123 and a_{400} is 0.02237. This parameter becomes negligible for high molecular weight compounds and polymers. The group contributions calculated using this technique are given in Table 1.

Pure Component Predictions

As a first test of the capabilities of the group contribution lattice-fluid equation of state, the vapor pressure and saturated liquid densities of the n-alkanes were predicted. In the calculations for the n-alkane data, only experimental data at 300 and 400 K were used in determining the molecular parameters. At a given temperature, the pressure of the system must be adjusted to equate the chemical potentials in the vapor and liquid phases. The densities of the vapor and liquid phases are also a function of temperature and pressure.

Table 1. Group Contributions for the Group Contribution Lattice Fluid Equation of State

	$e_{kk,300}$	$e_{kk,400}$	$R_{k,300}$	$R_{k,400}$	
Group	kJ · kmol^{-1}		m^3 · kmol^{-1}		Q_k
CH_3	640.87	640.79	0.01596	0.01628	0.848
CH_2	943.33	987.68	0.01524	0.01498	0.540
CH	2,209.38	2,708.76	0.01311	0.01175	0.228
C	5,378.38	7,731.24	0.01071	0.08463	0.150
cy-CH_2	895.44	911.40	0.01260	0.01256	0.540
cy-CH	1,727.56	2,043.28	0.01255	0.01199	0.228
cy-C	4,069.49	5,993.67	0.01242	0.01126	0.150
AC-H	975.38	971.62	0.01059	0.01073	0.400
AC-CH_3	994.41	1,022.68	0.02465	0.02456	0.968
AC-CH_2	1,471.59	1,581.80	0.02351	0.02302	0.660
AC-CH	2,780.93	3,281.53	0.02220	0.02060	0.348
AC-C	5,452.73	6,771.48	0.01985	0.01700	0.270
-O-	868.47	679.56	0.00760	0.00798	0.240
H_2O	949.12	1,154.31	0.07611	0.07544	1.400
$CH_3C{=}O$-	1,237.10	1,171.50	0.03117	0.03254	1.488
-$CH_2C{=}O$-	1,542.00	1,509.50	0.02968	0.03039	1.180
-CHCl-	1,364.40	1,387.30	0.04865	0.05036	0.952

High (1990) showed that the prediction of the vapor pressures and saturated liquid densities for a series of low molecular weight n-alkanes using the GCLF-EOS is excellent. Most equations of state are not able to accurately represent both

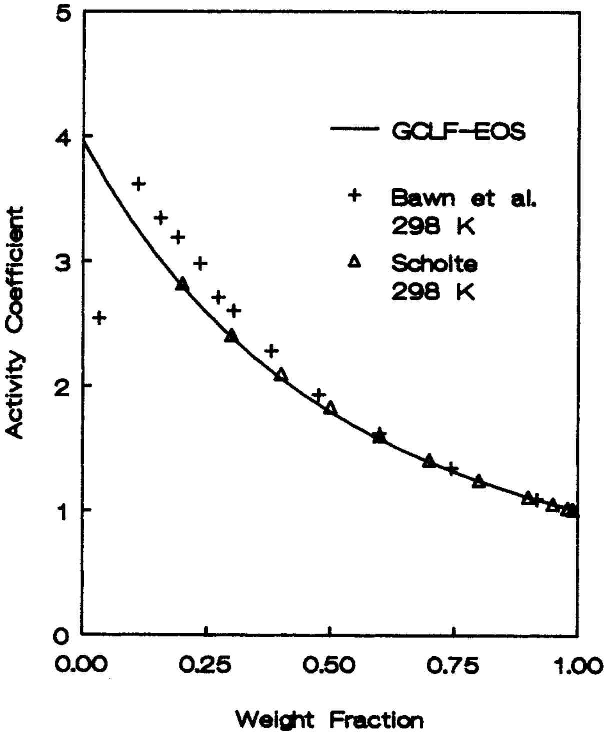

Figure 1. Prediction of the weight fraction activity coefficient of toluene in polystyrene.

Data of Bawn et al. (1950) (M_n = 290,000) and Scholte (1970) (M_n = 154,000) liquid- and vapor-phase properties simultaneously. Prediction of the vapor pressure is a significant test of the ability of the model to describe the interaction energies between molecules. The saturated liquid density provides a good test of the accuracy of the reference volume in the model.

The only group parameters that were used to calculate the vapor pressure and liquid density for the entire series of n-alkanes were the characteristic interaction energies between CH_3 groups and CH_2 groups, $e_{CH_3,T}$ and $e_{CH_2,T}$, and the reference volume of the two groups, R_{CH_3} and R_{CH_2}. The temperature dependence of the interaction energies must be taken into account as discussed previously. Although the temperature dependence of the reference volume is usually insignificant, it was accounted for in the same way.

Group Contribution Lattice Fluid EOS for Mixtures

The equation of state for the mixture is derived in a similar manner as the pure component equation of state. The holes in the mixture are assumed to mix randomly as in the pure component case. For the mixture, however, the molecules are not assumed to mix randomly. Local compositions of the molecules are calculated through Guggenheim's quasichemical theory. The resulting mixture equation of state is:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+(q/r)-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \tag{15}$$

where

$$\tilde{T} = \frac{T}{\dfrac{z\epsilon^*}{2R}} \tag{16}$$

$$\tilde{P} = \frac{P}{\dfrac{z\epsilon^*}{2v_h}} \tag{17}$$

$$\epsilon^* = \bar{\theta}_1\epsilon_{11} + \bar{\theta}_2\epsilon_{22} - \bar{\theta}_1\bar{\theta}_2\dot{\Gamma}_{12}\Delta\epsilon_{12} \tag{18}$$

$$v^* = \sum x_i v_i^* \tag{19}$$

$$r = \sum x_i r_i \tag{20}$$

$$q = \sum x_i q_i \tag{21}$$

$$\theta = \sum \theta_i \tag{22}$$

$$\dot{\Gamma}_{12} = \frac{2}{1+\sqrt{1-4\bar{\theta}_1\bar{\theta}_2(1-\dot{G})}} \tag{23}$$

$$\dot{G} = \exp\left[\frac{\theta(\epsilon_{11}+\epsilon_{22}-\epsilon_{12})}{RT}\right] = \exp\left[\theta\frac{\Delta\epsilon}{RT}\right] \tag{24}$$

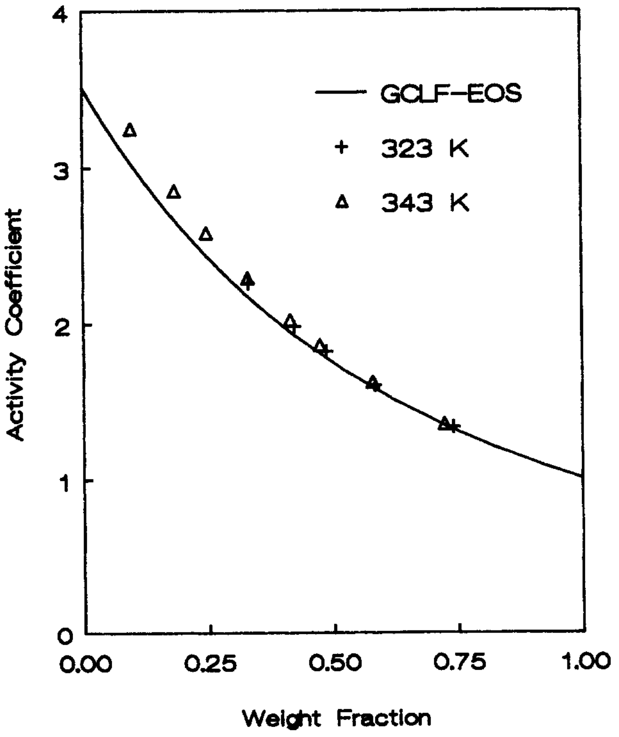

Figure 2. Prediction of the weight fraction activity coefficient of benzene in poly(ethylene oxide) (M_n = 600,000).
Data of Booth and Devoy (1971a)

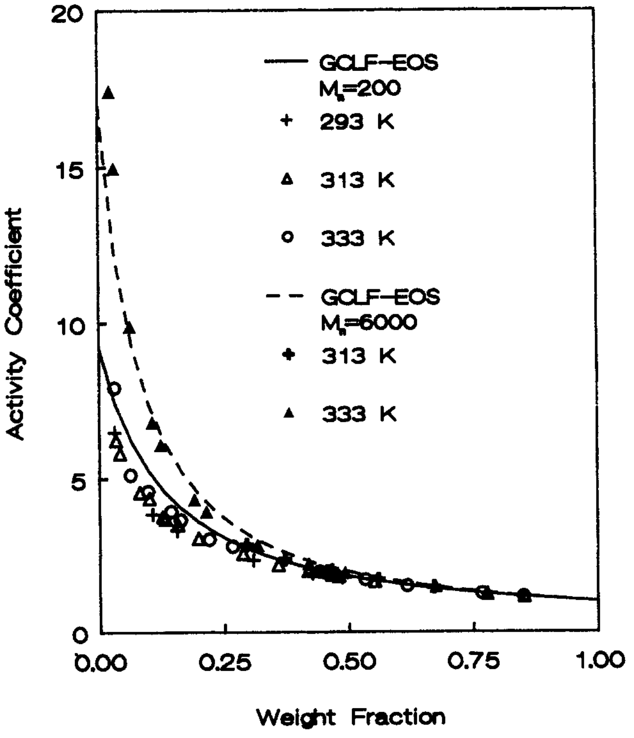

Figure 3. Prediction of the weight fraction activity coefficient of water in poly(ethylene glycol) (M_n = 200 and 6,000).
Data of Herskowitz and Gottlieb (1985)

$$\overline{\theta}_i = \frac{zq_i\,N_i}{zqN} \qquad (25)$$

Equation 15 is exactly the same expression that is used for the pure component case. The change in chemical potential between the species *i* in the mixture and pure component *i* is given by

$$\frac{\Delta\mu_i}{RT} = \ln\phi_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i\ln\left(\frac{\tilde{v}}{\tilde{v}-1}\,\frac{\tilde{v}_i-1}{\tilde{v}_i}\right) + q_i\left(\frac{2\theta_{i,p}-\theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\dot{\Gamma}_{ii} \qquad (26)$$

The volume fraction of component *i*, ϕ_i, is calculated based on the reference volumes of the components in the mixture. A detailed derivation of the equation of state and chemical potential expression can be found in High (1990). The weight fraction activity coefficient of component *i* is calculated from

$$\ln\Omega_i = \ln a_i - \ln w_i = \frac{\Delta\mu_i}{RT} - \ln w_i \qquad (27)$$

The equation of state, Eq. 15, is used in conjunction with the chemical potential expression, Eq. 26, for general phase equilibria calculations. In the polymer-solvent cases discussed later, the equation of state must be solved for the pure solvent, the pure polymer, and the solvent-polymer mixture. Since the solvent is the only component present in the vapor phase, the isochemical potential condition does not have to be solved. Equation 27 is used to calculate the weight fraction activity coefficient of the solvent directly.

Mixture Predictions

Although the GCLF-EOS was developed primarily for the prediction of polymer-solvent equilibria, the group parameters are based on low molecular weight compounds; and the model should be able to predict the phase equilibria of small molecular systems. Application to a number of low molecular weight systems yielded satisfactory predictions (High, 1990).

The true test for the GCLF-EOS is to see how well it can predict polymer-solvent equilibria. In this paper we present a summary of the prediction results for the GCLF-EOS for various solvents in polystyrene, poly(ethylene glycol), poly(propylene oxide), poly(vinyl chloride), polyethylene, and polyisobutylene. More examples and details of these predictions are given by High (1990).

As an example of the prediction capability of the GCLF-EOS, predictions of the weight fraction activity coefficients of toluene in polystyrene are illustrated in Figure 1. It is evident that the predictions are quite good. At the high molecular weights given in Figure 1, molecular weight has a negligible influence on activity coefficients. The model results are essentially identical for these two molecular weights.

The GCLF-EOS prediction of the benzene-poly(ethylene oxide) system is given in Figure 2. The prediction for this system is only fair since there is deviation at the infinite dilute region. The predictions for the system containing water and poly(ethylene glycol)—the low molecular weight analog of poly(ethylene

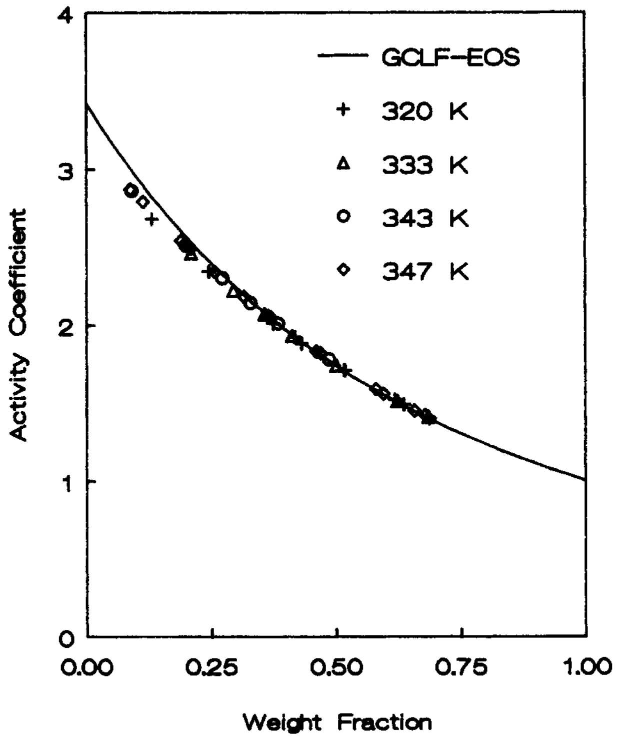

Figure 4. Prediction of the weight fraction activity coefficient of benzene in poly(propylene oxide) (M_n = 500,000).
Data of Booth and Devoy (1971b)

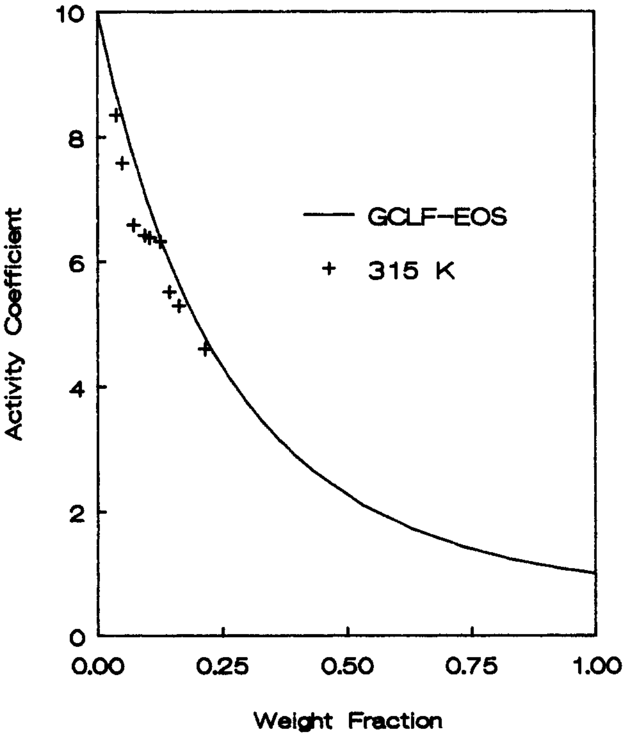

Figure 5. Prediction of the weight fraction activity coefficient of dipropyl ether in poly(vinyl chloride) (M_n = 34,000).
Data of Tait and Abushihada (1977)

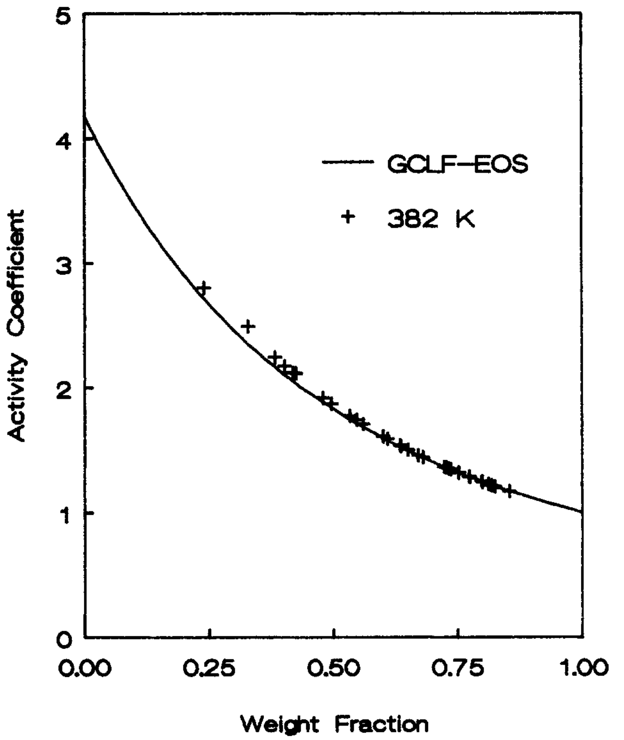

Figure 6. Prediction of the weight fraction activity coefficient of heptane in polyethylene (M_v = 26,300).
Data of van der Waals and Hermans (1950)

oxide)—are given in Figure 3 for the two molecular weights of PEG. The results for these systems are excellent.

An example of the GCLF-EOS prediction for the benzene-poly(propylene oxide) system is given in Figure 4. The temperature dependence of the experimental and predicted activity coefficients is very small over the experimental temperature range of 320 to 348 K. The GCLF-EOS prediction of dipropyl ether in poly(vinyl chloride) is given in Figure 5. The predictions for these systems containing a chlorinated polymer are excellent.

In this work polyethylene is modeled as having no branches, so polyethylene is simply a string of —CH_2— groups. If branching information is available in terms of the number of branches per 1,000 carbon atoms in the main chain and the average length of those branches, then branching can be included in the calculations by including the proper number of C_2H groups in the structure. The results of the GCLF-EOS prediction assuming no branching are given in Figure 6.

The GCLF-EOS model does a very good job of predicting the benzene, cyclohexane, ethylbenzene, and toluene systems in polystyrene, but does poorly for acetone and methyl ethyl ketone in polystyrene (High, 1990). This is understandable since the ketones are polar, and a binary interaction parameter has not been used for these predictions. In addition, the poor results of acetone could arise from the group contribution method used to calculate the interaction energy and reference volume since group contributions tend to fail for the low molecular weight members of a structural family.

The prediction of the activity of pentane in polyisobutylene is given in Figure 7. The prediction results for the GCLF-EOS are consistently poor in a variety of solvents in PIB. The most likely explanation for poor results involving polyisobutylene is that the "C" group (i.e., a carbon atom with four nonhydrogen covalent bonds) has poor group contribution values. The group contributions for the "C" group were calculated from only a few low molecular weight compounds and therefore may be regarded as suspect. A larger number of compounds should help improve the results with compounds containing the "C" group.

Poor values of the contributions for the "C" group would lead to poor P-V-T predictions for polyisobutylene. To determine whether poor polyisobutylene density is responsible for poor mixture predictions, specific volumes of polyisobutylene at various temperatures and pressures were predicted and compared to the experimental values measured by Beret and Prausnitz (1975). This prediction is shown by the solid line in Figure 8. It is clear that the GCLF-EOS severely overpredicts the experimental values. To determine the effect of this poor pure polymer P-V-T prediction on the mixture properties, new group contributions for the "C" group in polyisobutylene were regressed from the experimental P-V-T data. Only the group contribution for the "C" group reference volume was regressed, since the liquid density of a component depends strongly on the value of the reference volume, not the characteristic interaction energy. Therefore, it is impossible to get improved group contributions for the characteristic interaction energy from P-V-T data for polymers. The dashed line in Figure 8 shows that there is a considerable improvement in the results from the GCLF-EOS using the regressed values of the reference volume.

Figure 7 is an example of the GCLF-EOS prediction for the pentane-polyisobutylene with the reference volume regressed from pure polyisobutylene data (modified GCLF-EOS). The

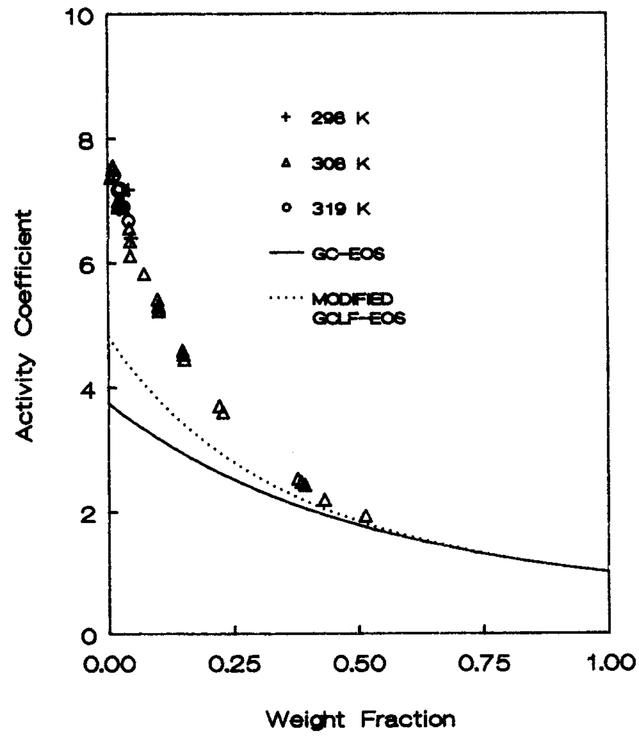

Figure 7. Prediction of the weight fraction activity coefficient of pentane in polyisobutylene (M_v = 1,000,000).
Data of Prager et al. (1953)

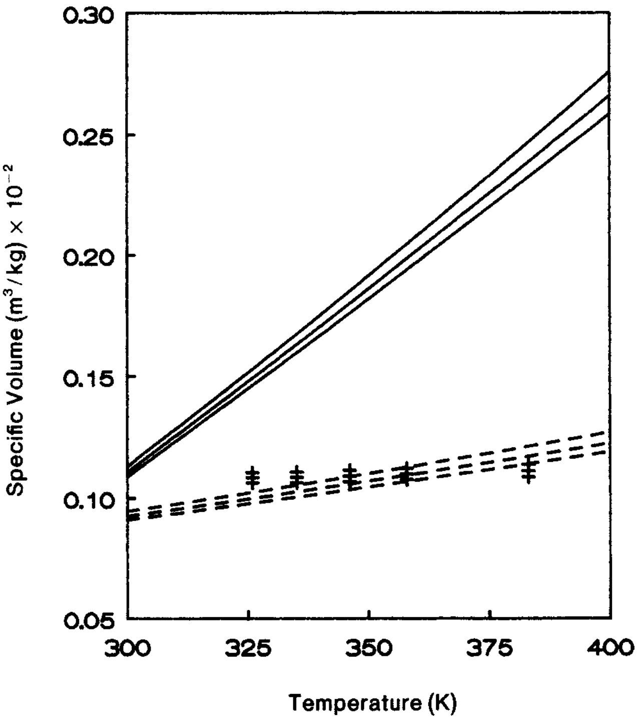

Figure 8. Prediction of the specific volume of polyisobutylene with the GCLF-EOS and the modified GCLF-EOS.

Data of Beret and Prausnitz (1975)

reference volume group contribution for the "C" group regressed from the P-V-T data for polyisobutylene (dotted line) improves the results considerably, but the prediction still underpredicts the activity of the solvent as shown in Figure 7. If a more accurate value of the interaction energy group contribution for the "C" group were available, the slope of the pure component P-V-T prediction for polyisobutylene would match that of the experimental data and should lead to improved mixture results.

A binary interaction parameter can be used in the calculation for the characteristic interaction energy between molecules i and j, ϵ_{ij}, using the standard expression:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}\,(1 - \delta_{ij}) \tag{28}$$

This binary interaction parameter can be regressed from the experimental data and the resulting correlation reproduces the data accurately. Even though a correlative model for solvent activities is not the goal of this research, it is useful to note that the GCLF-EOS can be used as a correlative tool.

Conclusions

A group contribution lattice-fluid equation of state has been developed that accurately predicts the activities of solvents in polymers with reasonable accuracy.

The GCLF-EOS was developed by calculating group contributions from the saturated liquid density and vapor pressure of low molecular weight compounds. Seventeen groups for the alkanes (CH_3, CH_2, CH, C), cycloalkanes (cy—CH_2, cy—CH, cy–C), arenes (AC—H, AC—CH_3, AC—CH_2, AC—CH, AC—C), ethers (—O—), water (H_2O), ketones, ($CH_3C{=}O$—, —$CH_2C{=}O$—), and monochlorinated alkanes (—CHCl—) were calculated. These groups, which were calculated from low molecular weight properties, were used to calculate the properties of polymer solutions.

The GCLF-EOS model requires only the structure of the molecules in the mixture. No other pure component or mixture data are needed.

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Notation

a_i = activity of component i in a mixture, dimensionless
a_T = reference volume intercept in the GCLF theory at temperature T, m^3/kmol
C = degree of freedom parameter, dimensionless
$e_{km,T}$ = group characteristic interaction energy between groups k and m at temperature T, kJ · $kmol^{-1}$
n_i = number of moles of component i, kmol
N = number of molecules in the ensemble, dimensionless
N_h = number of holes in the lattice, dimensionless
N_i = number of molecules of type i in the system, dimensionless
N_q = total number of interaction sites available in the system, dimensionless
N_{av} = Avogadro's number, $kmol^{-1}$
P = pressure, Pa
P^* = characteristic pressure, Pa
$\tilde{P}$ = reduced pressure of the mixture, dimensionless
$\tilde{P}_i$ = reduced pressure of component i, dimensionless
P_o = athermal contribution to the pressure, Pa
P^{sat} = vapor pressure, Pa
q = effective chain length or surface area parameter for the mixture, dimensionless
q_i = effective chain length or surface area parameter for component i, dimensionless
Q_k = UNIFAC surface area parameters, dimensionless
r = number average chain length for the mixture, dimensionless
r_i = number of segments in a molecule of type i, dimensionless
R = gas constant, J · $kmol^{-1}$ · K^{-1}
$R_{k,T}$ = reference volume of group k at temperature T, m^3 · $kmol^{-1}$
T = temperature, K
T^* = characteristic temperature, K
$\tilde{T}$ = reduced temperature of the mixture, dimensionless
$\tilde{T}_i$ = reduced temperature of component i, dimensionless
v = molar volume, m^3/kmol; volume per segment, m^3
$\tilde{v}$ = reduced volume of the mixture, dimensionless
v_h = volume of a lattice site, m^3/kmol
$\tilde{v}_i$ = reduced volume of component i (v/v^*), dimensionless
v_i^* = characteristic volume of component i, m^3/kmol
V^* = reference volume, m^3/kmol
ΔV = volume change of mixing, m^3
w_i = weight fraction of component i
x_i = mole fraction of component i
z = coordination number, dimensionless

Greek letters

α_h = characteristic surface area of a lattice site, dimensionless
β = $1/kT$, J^{-1}
γ_i = mole fraction activity coefficient of component i, dimensionless
Γ_{km} = nonrandomness parameter for k-m contacts on a hole-free basis, dimensionless
δ_i = flexibility parameter for component i, dimensionless
δ_{ij} = binary interaction parameter for the interaction between molecule i and j, dimensionless

ϵ_{ij} = characteristic energy of interaction between a segment of molecule i and a segment of molecule j, kJ · kmol^{-1}

θ = surface area fraction of the mixture, dimensionless

θ_i = surface area fraction of component i, dimensionless

$\theta_{i,p}$ = surface area fraction of pure component i at the same temperature and pressure as the mixture, dimensionless

$\Theta_k^{(i)}$ = surface area fraction of group k in component i using UNIFAC surface area parameters, dimensionless

μ^L = liquid phase chemical potential, J · kmol^{-1}

μ^V = vapor phase chemical potential, J · kmol^{-1}

μ_i = chemical potential of component i, J · kmol^{-1}

$\Delta\mu_i$ = change in chemical potential upon mixing for component i, J · kmol^{-1}

$\nu_k^{(i)}$ = number of groups of type k in molecules of type i, dimensionless

$\rho^{\text{sat,liq}}$ = saturated liquid molar density, kmol/m^3

ρ_l = liquid phase density, kmol/m^3

ρ_v = vapor phase density, kmol/m^3

σ_i = symmetry parameter for component i, dimensionless

ϕ_i = volume or segment fraction of component i, dimensionless; fugacity coefficient of component i, dimensionless

Ω_i = weight fraction activity coefficient of component i, dimensionless

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