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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

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A revised group-contribution Flory equation of state (GC-Flory EOS) for predicting activity coefficients of polymer solutions is presented in this work. Three modifications are introduced: (a) the extra binary entropic interaction parameter, ΔS_{ij}^{hb} , which was used in the original model for corrections due to hydrogen bonding of the OH and H₂O groups is found not be needed in the present version; (b) the values attributed to the segmental volume parameters R_{OH} and R_{H_2O} and the surface area parameters Q_{OH} and Q_{H_2O} are those derived by Bondi; (c) new EOS parameters have been determined for 15 main groups and 32 subgroups from pure component and binary mixtures properties of low molar mass compounds only. Extensive comparison of the accuracy of the predictions of activity coefficients using the revised GC-Flory EOS with two other predictive models, UNIFAC-FV (Oishi and Prausnitz, 1978) and Entropic-FV (Elbro et al., 1990, Kontogeorgis et al., 1993) is carried out. It is shown that the revised GC-Flory EOS gives much better predictions of vapor-liquid equilibria than does the original model, and it performs now as well as the Entropic-FV model. It gives, in general, predictions of vapor-liquid equilibria (VLE) of the same quality as the Entropic-FV model for finite concentrations as well as for the dilute regions. Until now, the GC-Flory model is the only model tested which can reasonably predict VLE behavior for solutions with poly(vinyl chloride) and hydrocarbons.

Introduction

In recent years, the GC-Flory EOS (Holten-Andersen et al., 1987; Chen et al., 1990) has been used to calculate activity coefficients in polymer-solvent mixtures. It has been found that the method is capable of predicting infinite dilution activity coefficient of nonpolar solvents, not as accurately as the UNIFAC-FV model (Oishi and Prausnitz, 1978), but with the advantage of not requiring pure component densities. On the other hand, relatively poor agreement with experimental results was obtained for systems which contain hydroxyl, ketone, and diene groups and for strongly polar systems. So, reestimation of the parameter table and estimation of additional parameters, as well as revision of the model, were required to improve the accuracy of the predictions and to extend the applicability of the EOS to a wider range of solvents and polymers. The aim of this work is to report the revision of the model and reestimation of the parameter tables.

The GC-Flory EOS

Starting from the generalized van der Waals partition function and well-defined approximations (Vera and Prausnitz, 1972; Sandler, 1985), it is possible to derive many of the thermodynamic models presently in use, for both pure fluids and mixtures, as well as to provide a basis for the derivation of models tailored to specific types of fluid and mixtures.

The generalized van der Waals canonical partition function for a pure liquid of n molecules is factored into three terms, as

$$Z = \left(\frac{1}{n!}\right) \left(\frac{V^{fv}}{\Lambda^3}\right)^n (q_{r,v})^n \exp\left(-\frac{E}{2kT}\right) \quad (1)$$

where n is the number of molecules in the total volume

V at temperature T , k is the Boltzmann constant, E is the intermolecular (attractive) energy, Λ is the de Broglie wavelength, depending only on temperature and molecular mass, and V^{fv} is the free volume. The term $q_{r,v}$ represents the contribution from the rotational and vibrational degrees of freedom per molecule, whereas the contributions from translations degrees of freedom are given by the first bracketed term.

Following the Prigogine approach based on the cell model (Prigogine, 1957), Flory has formulated a partition function for long-chain molecules (Flory et al., 1964), given by

$$Z = (nv^*)^n (\bar{v}^{1/3} - 1)^{3Cn} \exp(-nq\epsilon/RT\bar{v}) \quad (2)$$

where $\bar{v} = v/v^*$; v^* is the molar hard core volume and ϵ is the average configurational potential energy per segment surface area, q . The configurational energy varies inversely with the volume over the comparatively small range of volume of the liquid. Account is taken of intermolecular constraints on the segments by expressing the number of external degrees of freedom per segment as $3C$, where C enters as a parameter. Based on this partition function, a reduced Flory EOS can be derived as

$$\frac{\bar{p}\bar{v}}{\bar{T}} = \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} - \frac{1}{\bar{v}\bar{T}} \quad (3)$$

where $\bar{p} = p/p^*$, $\bar{v} = v/v^*$, and $\bar{T} = T/T^*$ and p^* , v^* , and T^* are the characteristic pressure, volume, and temperature determined from pure component volumetric data.

The GC-Flory EOS is a group contribution extension of a modified form of the Flory equation, and like the EOS of Flory it is derived from the generalized van der Waals partition function. The GC-Flory EOS differs from the Flory EOS in two aspects. First, instead of the free volume term introduced by Flory

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$$Z^{fv} = (nv^*)^n (\bar{v}^{1/3} - 1)^{3C_n} \quad (4)$$

it employs a free volume term which reduces to the correct ideal gas limit (i.e. $Z^{fv} \rightarrow V^n$ as $V \rightarrow \infty$) as in the earlier version of the model derived by Holten-Andersen et al. (1986, 1987)

$$Z^{fv} = \left[nv^* (\bar{v}^{1/3} - 1)^3 \left(\frac{\bar{v}^{1/3} - 1}{\bar{v}^{1/3}} \right)^{3C} \right]^n \quad (5)$$

This means that both the liquid and the vapor phase can be described by the same EOS, whereas the Flory EOS model strictly applies only to the liquid phase. Second, the attractive energy term of the partition function, similar to the Flory expression is adopted

$$Z^{attr} = \exp \left[-\frac{znq\epsilon_0}{2RT\bar{v}} \right] \quad (6)$$

but a nonrandom UNIFAC-like group contribution approach for the molecular parameters has been applied instead of the random mixing expression of the Flory model, i.e.

$$Z^{attr} = \exp \left\{ -\frac{1}{2kT} \sum_i q_i n_i \left(\epsilon_{ii} - kT \ln \left[\sum_j \theta_j \exp \left(-\frac{\Delta\epsilon_{ij}}{kT} \right) \right] \right) \right\} \quad (7)$$

Applying the relationship

$$P = kT \left(\frac{\delta \ln Z}{\delta V} \right)_{T,n} \quad (8)$$

to the new partition function, the EOS in terms of free volume and attractive contributions is obtained. It contains a free volume and attractive energy term

$$P = \frac{nRT}{V} \left(\frac{\bar{v}^{1/3} + C}{\bar{v}^{1/3} - 1} \right) + \frac{E^{attr}}{V} \quad (9)$$

The reduced volume in eq 9 is

$$\bar{v} = v/v^* \quad (10)$$

and the attractive energy is given by

$$E^{attr} = \sum_i 1/2 z q_i n_i \left\{ \epsilon_{ii} + \frac{\sum_j \theta_j \exp(-\Delta\epsilon_{ji}/RT) \Delta\epsilon_{ji}}{\sum_k \theta_k \exp(-\Delta\epsilon_{ki}/RT)} \right\} \quad (11)$$

In these expressions m and n refer to groups m and n , and i and j refer to molecules i and j .

The parameters needed include the molecular hard core volume, v_i^* , the surface area, q_i , and the interaction energy, ϵ_{ij}^0 . The group-contribution expressions for these molecular parameters are as follows:

$$v_i^* = (1.448)(15.17) \sum_n \nu_n R_n \quad (12)$$

$$q_i = \sum_n \nu_n Q_n \quad (13)$$

$$\epsilon_{ji}^0 = \sum_m \theta_m^{(i)} \sum_n \theta_n^{(j)} \epsilon_{nm} \quad (14)$$

and

$$\epsilon_{nm} = -[\epsilon_{mm}\epsilon_{nn}]^{1/2} + \Delta\epsilon_{nm} \quad (15)$$

The normalization factor 15.17 is the one suggested by Abrams and Prausnitz (1975) and corresponds to a $-\text{CH}_2$ -unit in polyethylene. The factor 1.448 was introduced in order to obtain molar volumes which are in agreement with measured volumes for normal alkanes.

The energy interaction parameters ϵ_{ji} and $\Delta\epsilon_{ji}$ are given by

$$\epsilon_{ji} = \epsilon_{ji}^0 / \bar{v} \quad (16)$$

and

$$\Delta\epsilon_{ji} = \epsilon_{ji} - \epsilon_{ii} \quad (17)$$

where the normalized van der Waals volumes and surface areas R_n and Q_n are taken from UNIFAC (Fredenslund et al., 1977). It should be emphasized that in this revised model, the values attributed to the R_{OH} , $R_{\text{H}_2\text{O}}$, Q_{OH} , and $Q_{\text{H}_2\text{O}}$ are the "physical" ones as derived by Bondi (see Table 1).

The C -parameter correlation is the same as that introduced by Chen et al. Three group parameters $C_{T_0,n}$, $C_{T,n}$ and C_n^0 attributed to group n in molecule i are used to describe the temperature-dependent molecular external degrees of freedom parameter C

$$C_i = \sum_n \nu_n \left[C_{T_0,n} + C_{T,n} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \sum_n \frac{R_n}{\sum_m R_m} C_n^0 \right] \quad (18)$$

where ν_n is the number of groups n in molecule i and T_0 is an arbitrary reference temperature, here taken equal to 298.15 K.

The temperature dependence of the C parameter was introduced into the Helmholtz free energy expression, and the energy term from eq 9 becomes

$$E^{attr} = \sum_i 1/2 z q_i n_i \left\{ \epsilon_{ii} + \frac{\sum_j \theta_j \exp(-\Delta\epsilon_{ji}/RT) \Delta\epsilon_{ji}}{\sum_k \theta_k \exp(-\Delta\epsilon_{ki}/RT)} \right\} - 3R \ln \left(\frac{\bar{v}^{1/3} - 1}{\bar{v}^{1/3}} \right) \sum_i n_i \left[\frac{dC_i}{d(1/T)} \right] \quad (19)$$

where

$$\frac{dC_i}{d(1/T)} = -\frac{1}{T^2} \sum_n \nu_n C_{T,n} \quad (20)$$

It should be emphasized that in this revised model, the extra binary entropic interaction parameter, $\Delta S_{ij}^{\text{hb}}$, which was previously used (Holten-Andersen et al., 1987; Chen et al., 1990) for corrections due to hydrogen bonding when OH and H_2O groups are present was found not to be needed.

Simple linear mixing rules for the molar hard core volume, v^* , and the C parameter are used, i.e.

$$v^* = \sum_i n_i v_i^*/n \quad (21)$$

and

$$C = \frac{\sum_i n_i C_i}{n} \quad (22)$$

Expressions for the activity coefficients are derived from the EOS using classical thermodynamics. Writing the three contributions to the activity coefficients separately

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{fv}} + \ln \gamma_i^{\text{attr}} \quad (23)$$

combinatorial free volume attractive

then

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i} \quad (24)$$

$$\ln \gamma_i^{\text{fv}} = 3(1 + C_i) \ln \left(\frac{\bar{v}_i^{1/3} - 1}{\bar{v}^{1/3} - 1} \right) - C_i \ln \frac{\bar{v}_i}{\bar{v}} \quad (25)$$

$$\ln \gamma_i^{\text{attr}} = 1/2zq_i \left\{ \frac{1}{RT} [\epsilon_{ii}(\bar{v}) - \epsilon_{ii}(\bar{v}_i)] + 1 - \frac{\sum_j \theta_j \exp(-\Delta\epsilon_{ji}/RT) \Delta\epsilon_{ji}}{\sum_k \theta_k \exp(-\Delta\epsilon_{ki}/RT)} \right\} \quad (26)$$

where φ_i is the segment volume fraction

$$\varphi_i = \frac{x_i v_i^*}{\sum_j x_j v_j^*} \quad (27)$$

and θ_i is the surface area fraction

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (28)$$

Equation 9 can in principle be applied at all pressures and temperatures, but for normal-pressure applications, eq 9 can be simplified by solving for the volume roots at zero pressure instead of the pressure of the system.

Estimation and Reestimation of GC-Flory EOS Parameters and Parameter Tables

The GC-Flory EOS may be used to predict the molar activity coefficients γ_i for given values of the temperature T and the mole fractions x_i . The parameters needed are group sizes and surface areas R_n and Q_n and EOS parameters. The GC-Flory EOS parameters are related to pure component properties, C_i and ϵ_{ii}^0 , and to a mixture energy of interaction, ϵ_{ij}^0 . The values attributed to R_n

and Q_n are those derived from the van der Waals group volumes and surface areas, while EOS parameters have to be estimated from experimental data. As can be seen from eq 14 to 17 and eq 18, those parameters are defined in terms of the group parameters $C_{T,n}$, $C_{T,n}$, and C_n^0 , the interaction energies between like groups n , ϵ_{nn} , and $\Delta\epsilon_{nm}$, i.e. interaction energies between unlike groups n and m . The values used to determine the above group parameters are thermal expansivities of pure liquids, $\alpha = 1/V(\delta V/\delta T)_P$, heats of vaporization, ΔH^{vap} , and vapor-liquid equilibrium data for low molar mass binary mixtures.

The EOS parameters were estimated from pure component and binary mixtures data of low molar mass compounds only.

The new parameter tables for the GC-Flory EOS are based on PVT and enthalpy of vaporization, ΔH^{vap} , data for 300 pure compounds data and on vapor-liquid equilibrium (VLE) data for more than 600 low molar mass binary mixtures. For few parameter estimations it has been necessary to rely to some extent on liquid-liquid equilibrium (LLE) data. For the estimation of the model parameters, extensive use has been made of computerized data banks for pure low molar mass components (DIPPR) and VLE data (Dortmund). Most of the information in these data banks is available in book form also (See refs 6, 13-15, and 21).

The strategy of the estimation procedure was as follows: The C -parameter is determined at various temperatures from pure component information. In the next step, a correlation for the C -parameter is introduced (see eq 18) and parameters ϵ_{nn} and $\Delta\epsilon_{nm}$ are estimated from VLE information. In some cases it was necessary to iterate between these steps.

The coefficients of the C -parameter correlations are estimated from densities of pure components obtained from the DIPPR data bank (Danner and High, 1992). These were used to calculate thermal expansivities of the pure liquids, which again were used as input data. The size and temperature dependence of the C -parameter are thus determined by this information. A wide temperature range was used. The model utilizes UNIFAC group definitions for both subgroups and main groups, but the $C_{T,n}$ and C_n^0 coefficients in the correlation for C as well as interaction energies are estimated as single main group parameters, valid for all the subgroups of any given main groups. The obtained C -parameters are given in Table 1.

To illustrate the capability of the GC-Flory model to predict the properties of polymers from information on low molar mass components, the thermal pressure coefficients, $\beta = (\delta P/\delta T)_V$, of pure polymers were calculated. From Table 2, which presents a selection of experimental and predicted pure polymer properties, it may be seen that the model is able to predict the thermal pressure coefficients of polymers with good accuracy, and that the C correlation gives good temperature dependence.

The problem of fitting the GC-Flory EOS to experimental VLE data is now reduced to finding the values of parameters ϵ_{nn} and $\Delta\epsilon_{nm}$ that will predict activity coefficients which are as close as possible to the experimental values.

For aromatic hydrocarbon-water mixtures it was necessary to calculate experimental activity coefficients from LLE data. It should be mentioned that the interactions parameters $\Delta\epsilon_{nm}$ between the CH_2 and H_2O groups and the OH and H_2O groups are simultaneously determined from VLE data of water and alcohols.

The objective function for the parameter estimation may be defined in many ways. We have tried different

Table 1. Group R_n , Q_n , and C Values of the GC-Flory EOS

main no.	group name	subgroup		R_n	Q_n	C_{T_0n}	C_{T_n}	C_n^0
		no.	name					
1	CH ₂	1	CH ₃	0.9011	0.848	-0.0738	-3.570	0
		2	CH ₂	0.6744	0.540	0.1080	-3.570	0
		3	CH	0.4469	0.228	0.3442	-3.570	0
		4	C	0.2195	0.000	0.4779	-3.570	0
		5	cy-CH ₂	0.6744	0.540	0.0070	-3.570	0
2,2,4-trimethylpentane: 5(1), 1(2), 1(3), 1(4)								
cyclohexane: 6(5)								
2	ACH	6	ACH	0.5313	0.400	0.0152	-2.900	-0.013
		7	AC	0.3652	0.120	0.2640	-2.900	-0.013
toluene: 1(1), 5(6), 1(7)								
3	CH ₂ CO	8	CH ₃ CO	1.6742	1.488	0.1260	-4.117	0
		9	CH ₂ CO	1.4457	1.180	0.1300	-4.117	0
2-butanone: 1(1), 1(2), 1(8)								
3-pentanone: 2(1), 1(2), 1(9)								
4	COO	10	COO	1.0020	0.880	0.3682	6.139	0
		butyl acetate: 2(1), 3(2), 1(10)						
5	COOH	11	HCOOH	1.5280	1.532	0.4920	29.300	0
		12	COOH	1.3013	1.224	0.0212	29.300	0
formic acid: 1(11)								
acetic acid: 1(1), 1(12)								
6	CH ₂ O	13	CH ₃ O	1.1450	1.088	0.3130	28.830	0
		14	CH ₂ O	0.9183	0.780	0.4103	28.830	0
		15	CHO	0.6908	0.468	0.6710	28.830	0
diisopropyl ether: 4(1), 1(3), 1(15)								
diethyl ether: 2(1), 1(2), 1(14)								
7	C=C	16	CH ₂ =CH	1.3454	1.176	0.1503	-15.010	0
		17	CH=CH	1.1167	0.867	0.1762	-15.010	0
		18	CH ₂ =C	1.1173	0.988	0.4961	-15.010	0
		19	CH=C	0.8886	0.676	0.5010	-15.010	0
isoprene: 1(1), 1(16), 1(18)								
8	CCl	20	CH ₃ Cl	1.6921	1.572	-0.5177	-5.700	0
		21	CH ₂ Cl	1.4654	1.264	-0.2052	-5.700	0
		22	CHCl	1.2380	0.952	0.2310	-5.700	0
		23	CCl	1.0060	0.724	0.5849	-5.700	0
1,2,3-trichloropropane: 2(21), 1(22)								
9	CCl ₂	24	CH ₂ Cl ₂	2.2564	1.988	-0.4900	-5.700	0
		25	CHCl ₂	2.0606	1.684	-0.0980	-5.700	0
1,1,2-trichloroethane: 1(21), 1(25)								
10	CCl ₃	26	CHCl ₃	2.8700	2.410	-0.5030	-5.700	0
		27	CCl ₃	2.6401	2.184	0.5297	-5.700	0
1,1,1-trichloroethane: 1(1), 1(27)								
11	CCl ₄	28	CCl ₄	3.3900	2.910	-0.1480	1.700	0
tetrachloromethane: 1(28)								
12	ACCl	29	ACCl	1.1562	0.844	0.1590	-5.700	0
monochlorobenzene: 5(6), 1(29)								
13	CH ₃ OH	30	CH ₃ OH	1.4311	1.432	0.0360	6.900	-0.01
methanol: 1(30)								
14	OH	31	OH	0.5300	0.584	-0.4531	-20.900	-0.01
ethanol: 1(1), 1(2), 1(31)								
15	H ₂ O	32	H ₂ O	0.7567	0.892	-0.4141	-47.110	-0.04
water: 1(32)								

functions, and we have chosen to estimate the parameters that will minimize the following expression

$$F_{\min} = \sum_j \sum_i \left[\frac{Y_{ji}^{\text{exptl}} - Y_{ji}^{\text{calcd}}}{Y_{ji}^{\text{exptl}}} \right]^2 \quad (29)$$

where Y is a measured and calculated quantity, i is summed

Table 2. Prediction of Thermal Pressure Coefficients, $\beta = (\delta P / \delta T)_n$, for Polymers

component	T (K)	β_{exp} (MPa K ⁻¹)	β_{cal} (MPa K ⁻¹)	% error ^a
PE (MW = 180 000)	413	0.7163	0.6899	3.69
	433	0.6586	0.6368	3.31
	453	0.6075	0.5887	3.09
PE (MW = 10 000)	412	0.7328	0.6870	5.08
	431	0.6736	0.6364	5.52
	446	0.6268	0.5996	4.34
PIB (MW = 40 000)	273	1.2661	1.3598	7.40
	298	1.1360	1.1966	5.33
	323	1.0188	1.0615	4.19
PS (MW = 51 000)	353	0.8954	0.9268	3.51
	373	0.8230	0.8498	3.26
	423	0.6778	0.6925	2.17
	283	1.4970	1.4506	3.10
	298	1.3807	1.3447	2.61
	323	1.2177	1.1916	1.66
	373	0.9619	0.9527	0.96

^a 100 $(|\beta_{\text{exp}} - \beta_{\text{cal}}| / \beta_{\text{exp}})$.

over the number of measured variables in a data point, and j is summed over the total number of data points. The optimization algorithm used in the parameter estimation program (see Bogdanic and Berg, 1993) is the modified Levenberg-Marquard algorithm (Fletcher, 1980) from the IMSL program library.

The group-interaction parameters have mainly been estimated one pair at a time. Based on the experimental activity coefficients for mixtures containing groups m and n , the parameters ϵ_{nn} and $\Delta\epsilon_{nm}$ that best fit the data have been found. In order to estimate, for example, the OH/CH₂CO group-interaction parameters from alcohol-ketone data, it is necessary to have available first the OH/CH₂ group-interaction parameters from alcohol-alkane data and the CH₂/CH₂CO parameters from alkane-ketone data. The determined group interaction parameters are given in the Table 3. As can be seen from Tables 1 and 3, each main group contains several subgroups with their own R_n and Q_n values. All subgroups, however, are assumed to have identical group-interaction parameters.

Table 4 shows experimental and calculated activity coefficients representing most of the systems in the data base. The examples given here are from the dilute regions. It should be noted that the agreement between calculated and experimental activity coefficients almost always is better in the middle of the concentration range than in the dilute regions.

A few comments are given below for some of the groups:

Hydrocarbons. The hydrocarbon main groups are CH₂ (alkanes), C=C (olefines), and ACH (aromatic compounds). Alkyl aromatic hydrocarbons are described by the CH₂ and ACH main groups.

Ketones. The ketones are described by one main group with two structural subgroups CH₃CO and CH₂CO plus hydrocarbon groups.

Ethers. The ethers are a large group of compounds, which are described by a single main group plus hydrocarbon group. The ether group is used to describe acyclic ethers. For cyclic ethers another group should be estimated. As in UNIFAC three subgroups are used for the description of ethers.

Esters. It was decided to describe the different esters by a single COO group and hydrocarbon groups.

Chlorinated Hydrocarbons. Four main groups are used for the description of the effect of chlorinated aliphatic compounds as in UNIFAC, ie. CCl, CCl₂, CCl₃, and CCl₄, according to the number of chlorine atoms on

Table 3. Group-Interaction Parameters ϵ_{mm} and ϵ_{mn} , J/q-unit

	CH ₂	ACH	CH ₂ CO	COO	COOH	CH ₂ O	C=C	CCl	CCl ₂	CCl ₃	CCl ₄	ACCl	CH ₃ OH	OH	H ₂ O
CH ₂	-2276	35	460	527	607	402	-68	452	76	56	39	238	392	1548	920
ACH		-3473	268	272	1201	213	-207	134	238	207	134	93	456	2531	351
CH ₂ CO			-4519	84	623	272	126	218	na	-473	356	418	-75	1079	326
COO				-6945	251	172	251	-335	418	180	469	-452	163	1502	-469
COOH					-5230	na	1590	163	na	1205	1665	na	-749	180	-732
CH ₂ O						-4268	146	205	-75	-130	251	-26	29	163	-987
C=C							-2636	-444	42	-96	-75	na	-247	2510	na
CCl								-2615	414	402	393	-678	159	1443	na
CCl ₂									-2573	na	38	na	na	na	na
CCl ₃										-188	na	na	na	1326	na
CCl ₄										-3381	na	na	na	1464	na
ACCl											-2510	na	na	1975	na
CH ₃ OH												-3452	na	12301	285
OH													-6569	-16799	540
H ₂ O															-10242

Table 4. Experimental and Calculated Activity Coefficients at Infinite Dilution Using the Revised GC-Flory EOS^a

system	T/K	$\gamma_2^{\infty}(\text{exp})$	$\gamma_2^{\infty}(\text{cal})$	% error ^b
<i>n</i> -Hexadecane (1) with (2)				
1. CHCl ₃	303.15	1.06	1.07	0.94
2. acetone	423.15	2.07	2.01	2.90
3. methyl acetate	413.15	1.51	1.36	9.93
4. 1-propanol	413.15	2.58	2.43	5.81
5. methyl ethyl ketone	423.15	1.76	1.71	2.84
6. 1-chlorobutane	324.45	1.12	1.22	8.93
7. 1-chloropentane	324.45	1.13	1.06	6.19
8. cyclohexane	323.15	0.76	0.76	0.00
9. 1-hexene	324.45	0.92	0.94	2.17
10. <i>n</i> -hexane	313.15	0.88	0.86	2.27
11. toluene	316.95	1.04	0.98	5.77
1-Octadecane (1) with (2)				
12. 1-chloropropane	342.65	0.98	1.08	10.20
13. benzene	343.25	0.86	0.97	12.79
14. <i>n</i> -hexane	343.25	0.90	0.89	1.11
15. toluene	343.25	0.86	0.85	1.16
16. ethylbenzene	334.15	0.90	0.85	5.56
1-Hexadecanol (1) with (2)				
17. 1-chlorobutane	326.35	1.43	1.54	7.69
18. cyclohexane	326.35	1.29	1.34	3.88
19. <i>n</i> -hexane	333.15	1.62	1.58	2.47
20. 1-heptene	326.35	1.63	1.79	9.82
21. propylbenzene	453.15	1.13	1.17	3.54
1-Chlorohexadecane (1) with (2)				
22. <i>n</i> -hexane	313.25	1.06	1.16	9.43
23. <i>n</i> -heptane	313.25	1.08	1.04	2.70
24. ethylbenzene	333.15	0.81	0.76	6.17
10-Nonadecanone (1) with (2)				
25. ethanol	343.25	2.79	2.74	1.79
26. 1-propanol	353.65	2.24	2.17	3.12
27. ethyl acetate	343.25	1.20	1.24	3.33
28. 1-butanol	363.65	1.75	1.80	2.86
29. 3-pentanone	343.25	1.05	0.94	10.47

^a Typical results from correlating the vapor-liquid equilibrium data included in the data base. ^b 100 $(|\gamma^{\text{exp}} - \gamma^{\text{cal}}|/\gamma^{\text{exp}})$.

the saturated carbon atom, and ACCl for chloro aromatic hydrocarbons.

Carboxylic Acids. The carboxylic acids contain the COOH main group. As in UNIFAC, formic acid is included among other carboxylic acids in the same main group.

Alcohols. Methanol is described by the structural group CH₃OH and all other alcohols are described by the OH structural group plus hydrocarbon groups. The structural parameters R and Q for OH have the "physical" value as derived by Bondi, i.e. $R_{\text{OH}} = 0.53$ and $Q_{\text{OH}} = 0.584$.

Water. The R and Q values are those as derived by Bondi, i.e. $R_{\text{H}_2\text{O}} = 0.7567$ and $Q_{\text{H}_2\text{O}} = 0.892$. Some water interaction parameters were derived from LLE data.

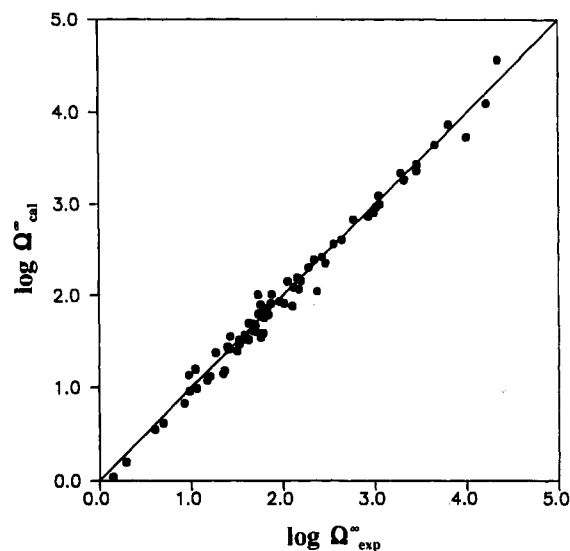


Figure 1. Calculated activity coefficients at infinite dilution using the revised GC-Flory EOS, $\Omega_{\text{cal}}^{\infty}$, versus experimental data, $\Omega_{\text{exp}}^{\infty}$, for polymer solutions.

Results

The purpose of this section is to present an extensive evaluation of the capability of the revised GC-Flory EOS in predicting activity coefficients for mixture with polymers. We do so by showing extensive examples of predicted solvent activity coefficients, both at infinite dilution and finite concentrations. These are compared with the corresponding experimental values and with the other two predictive models, UNIFAC-FV (Oishi and Prausnitz, 1978) and Entropic-FV (Kontogeorgis et al., 1993). In part 2 of this work, predicted LLE results for polymer-solvent systems will be shown.

Tables 5 and 6, together with Figure 1, summarize the results for solvent activity coefficients at infinite dilution for many polymer solutions using the original GC-Flory EOS (Chen et al., 1990), the revised GC-Flory EOS with the new parameter tables (this work), the UNIFAC-FV (Oishi-Prausnitz, 1978), and the Entropic-FV (Kontogeorgis et al., 1993) model. Note that none of the mixtures listed in Tables 5 and 6 were included at all in the data base for estimating parameters in this work. Table 6 shows the results of comparison in the prediction of solvent activities at infinite dilution for polymer solutions which contain hydroxyl, ketone, and diene groups, i.e. for previously "difficult systems", where the original GC-Flory model gives poor results and when other models fail. Figures 2-6 show predictions of solvent activities in poly(propylene oxide), polybutadiene, polystyrene, poly(vinyl chloride), and poly(ethylene oxide).

Table 5. Experimental and Predicted Solvent Activity Coefficients at Infinite Dilution for Polymer Solutions *

polymer solution	T (K)	Ω^{exp}	$\Omega^{\text{GC-Flory(old)}}$	$\Omega^{\text{GC-Flory(new)}}$	$\Omega^{\text{UNIFAC-FV}}$	$\Omega^{\text{Entropic-FV}}$
LDPE(35000) + <i>n</i> -hexane	383.2	5.65	6.06	6.06	4.26	5.07
			7.26%	7.26%	24.60%	10.27%
LDPE(35000) + <i>n</i> -heptane	383.2	5.08	5.46	5.46	3.94	4.64
			7.48%	7.48%	22.44%	8.67%
HDPE(82000) + <i>n</i> -dodecane	393.2	4.02	4.21	4.21	3.28	3.73
			4.73%	4.73%	18.41%	7.21%
PIB(40000) + CCl ₄	298.2	2.53	2.10	2.29	2.93	2.74
			17.00%	9.49%	15.81%	8.30%
PIB(860000) + cyclohexane	313.1	4.81	4.61	4.57	4.60	3.62
			4.17%	4.99%	4.37%	24.74%
PIB(40000) + toluene	298.2	6.15	6.92	5.96	6.29	6.07
			12.52%	3.09%	2.28%	1.30%
PIB(40000) + <i>n</i> -octane	298.2	5.98	4.90	4.90	5.41	4.82
			18.06%	18.06%	9.53%	19.40%
PBD(22600) + CCl ₄	373.0	1.82	1.96	1.73	1.77	1.87
			7.96%	4.95%	2.75%	2.75%
PBD(22600) + CHCl ₃	373.0	2.00	2.97	1.85	2.34	2.68
			48.50%	7.50%	17.00%	34.00%
PBD(22600) + acetone	373.0	10.40	33.62	10.94	9.53	11.36
			<i>e</i>	5.19%	8.37%	9.23%
PBD(93000) + 1-propanol	349.2	26.80	203.86	28.28	26.07	22.39
			<i>e</i>	5.52%	2.72%	16.46%
PBD(22600) + methyl ethyl ketone	373.0	8.36	24.25	8.04	7.44	8.92
			<i>e</i>	3.83%	11.00%	6.70%
PBD(22600) + ethyl acetate	353.0	6.02	12.83	5.81	5.59	5.90
			<i>e</i>	3.49%	7.14%	1.99%
PBD(22600) + benzene	353.0	3.65	7.92	3.11	3.84	3.93
			<i>e</i>	14.79%	5.21%	7.67%
PBD(22600) + cyclohexane	353.0	4.15	6.82	4.72	3.61	4.13
			64.34%	13.73%	13.01%	0.48%
PBD(22600) + <i>n</i> -hexane	353.0	6.31	9.22	5.99	4.97	5.49
			46.12%	5.07%	21.24%	12.99%
PBD(22600) + ethylbenzene	353.0	3.36	7.71	3.06	3.19	15.77
			<i>e</i>	8.93%	5.06%	<i>e</i>
PS(20000) + CHCl ₃	445.0	4.47	2.18	4.02	2.78	3.08
			51.23%	10.07%	37.81%	31.10%
PS(20000) + CH ₂ Cl ₂	492.9	4.12	2.64	4.11	3.46	3.06
			35.92%	0.24%	16.02%	25.73%
PS(20000) + acetic acid	445.0	31.82	333.41	29.00	15.37	15.53
			<i>e</i>	8.86%	51.70%	51.19%
PS(20000) + 1-propanol	445.0	18.80	16.21	17.65	24.20	12.99
			13.78%	6.12%	28.72%	30.90%
PS(96200) + methyl ethyl ketone	420.0	7.13	14.32	6.93	7.91	6.87
			<i>e</i>	2.81%	10.94%	3.65%
PS(96200) + monochlorobenzene	420.0	3.55	na ^c	3.96	3.40	4.15
				11.55%	4.23%	16.90%
PS(120000) + benzene	403.4	4.61	6.51	4.35	4.41	4.97
			41.21%	5.64%	4.34%	7.81%
PS(50660) + <i>n</i> -hexane	423.0	11.36	11.30	11.30	11.24	8.99
			0.53%	0.53%	1.06%	20.86%
PS(76000) + toluene	433.2	5.34	8.35	5.42	4.25	4.92
			56.37%	1.50%	20.41%	7.87%
PS(97000) + ethylbenzene	448.2	5.47	7.41	5.32	4.27	4.79
			35.47%	2.74%	21.94%	12.43%
PS(50660) + <i>n</i> -octane	418.0	9.80	9.68	10.05	10.75	7.23
			1.22%	2.55%	9.69%	26.22%
PS(20000) + water	492.9	76.84	83.89	96.58	9.71	86.54
			9.17%	25.69%	87.36%	12.62%
PVC(41000) + CCl ₄	393.2	8.22	3.54	6.57	3.97	3.63
			56.93%	20.01%	51.70%	55.84%
PVC(35000) + CHCl ₃	393.2	8.84	4.24	7.91	3.83	4.33
			52.04%	10.52%	56.67%	51.02%
PVC(41000) + acetone	393.2	11.80	3.64	10.55	10.17	9.98
			69.15%	10.59%	13.81%	15.42%
PVC(40000) + 1-butanol	383.0	31.80	95.85	30.57	20.32	20.39
			<i>e</i>	3.87%	36.10%	35.88%
PVC(40000) + toluene	413.0	10.80	4.44	7.74	4.39	6.22
			58.89%	28.33%	59.35%	42.41%
PEO(1000) + CCl ₄	343.4	3.25	3.21	2.93	2.21	2.70
			1.23%	9.85%	32.00%	16.92%
PEO(10700) + CHCl ₃	373.2	1.16	0.14	1.04	0.73	1.18
			87.93%	10.34%	37.07%	1.72%
PEO(1400) + CH ₂ Cl ₂	340.5	1.33	0.50	1.22	0.91	1.13
			62.41%	8.27%	31.58%	15.04%
PEO(1000) + ethanol	373.2	6.13	0.89	6.02	10.14	6.61
			<i>e</i>	1.79%	65.42%	7.83%

Table 5. (Continued)

polymer solution	<i>T</i> (K)	$\Omega_{\text{exp}}^{\infty}$	$\Omega_{\text{GC-Flory(old)}}^{\infty}$	$\Omega_{\text{GC-Flory(new)}}^{\infty}$	$\Omega_{\text{UNIFAC-FV}}^{\infty}$	$\Omega_{\text{Entropic-FV}}^{\infty}$
PEO(1000) + acetone	352.4	6.17	6.54	5.99	5.20	4.16
PEO(10700) + ethyl acetate	373.2	5.33	6.00%	2.92%	15.72%	32.58%
			4.36	5.03	4.32	4.70
			18.20%	5.63%	18.96%	11.82%
PEO(4000) + benzene	353.5	4.08	4.31	4.12	3.67	4.53
			5.64%	0.98%	10.05%	11.03%
PEO(7500) + <i>n</i> -hexane	345.0	27.86	28.83	26.25	16.28	22.38
			3.48%	5.78%	41.56%	19.67%
PEO(1000) + toluene	373.2	4.86	5.11	4.80	4.14	4.43
			5.14%	1.23%	14.81%	8.85%
PEO(7500) + water	358.2	20.00	10.99	18.40	19.90	9.23
			45.05%	8.00%	0.50%	53.85%
PBMA(73500) + CCl ₄	413.2	2.68	2.79	2.61	2.11	3.05
			4.10%	2.61%	21.27%	13.81%
PBMA(73500) + CH ₂ Cl ₂	413.2	2.90	2.26	2.68	2.23	2.98
			22.07%	7.59%	23.10%	2.76%
PBMA(8716) + acetone	413.0	8.66	13.71	8.99	8.44	9.48
			58.31%	3.81%	2.54%	9.47%
PBMA(73500) + 1-chlorobutane	403.2	5.10	3.50	4.56	3.92	4.75
			31.37%	10.59%	23.14%	6.86%
PBMA(73500) + benzene	403.2	4.58	6.26	4.52	3.79	3.64
			36.68%	1.31%	17.25%	20.52%
PMA(63200) + benzene	383.2	5.65	7.05	4.76	58.15 ^d	5.75 ^d
			24.78%	15.75%	^e	1.77%
PMA(63200) + toluene	383.2	7.50	10.05	6.79	72.88 ^d	6.59 ^d
			34.00%	9.47%	^c	12.13%
PEMA(144000) + acetone	417.7	9.04	13.11	8.67	16.23 ^d	10.44 ^d
			45.02%	4.09%	79.54%	15.49%
PEMA(144000) + monochlorobenzene	417.7	3.92	na ^c	3.26	5.63 ^d	3.11 ^d
				16.84%	43.62%	20.66%
PEMA(144000) + toluene	417.7	5.88	9.00	6.15	11.25 ^d	4.31 ^d
			53.06%	4.59%	91.33%	26.70%
PMMA(6107) + CH ₂ Cl ₂	423.0	3.86	2.17	3.16	6.45	3.36
			43.78%	18.13%	67.10%	12.93%
PMMA(6107) + acetic acid	448.0	5.82	51.93	6.69	17.94	7.72
			^e	14.95%	^e	32.65%
PVAC(83350) + ethyl acetate	473.2	6.21	na ^b	6.44	4.46	6.36
				3.71%	28.18%	2.42%
PVAC(83350) + toluene	448.2	6.57	na ^b	7.49	6.11	5.80
				14.00%	7.00%	11.72%
PVAC(86000) + <i>n</i> -nonane	418.2	31.78	na ^b	31.05	34.04	15.98
				2.30%	7.11%	49.72%

^a GC-Flory(old) is the original GC-Flory EOS (Chen et al., 1990). GC-Flory(new) is the revised GC-Flory EOS (this paper). Percentage values represent absolute mean percent deviations, $100(|\Omega_{\text{exp}}^{\infty} - \Omega_{\text{calc}}^{\infty}|/\Omega_{\text{exp}}^{\infty})$. ^b Temperature is higher than the critical temperature. ^c The group parameters are not available. ^d The density of the polymer is predicted by GCVOL method (Elbro et al., 1991). ^e The percent error is greater than 100.

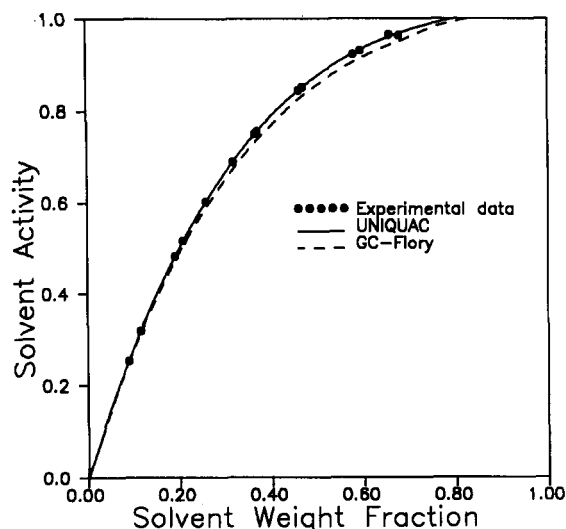


Figure 2. Activity of benzene in poly(propylene oxide) ($M_n=500\,000$) as predicted by the revised GC-Flory EOS (---) and correlated by UNIQUAC (—) at 347.85 K. Experimental data (●) are taken from Hao et al. (1991).

It can be seen that the revised GC-Flory model is capable of solving all the troublesome cases previously described

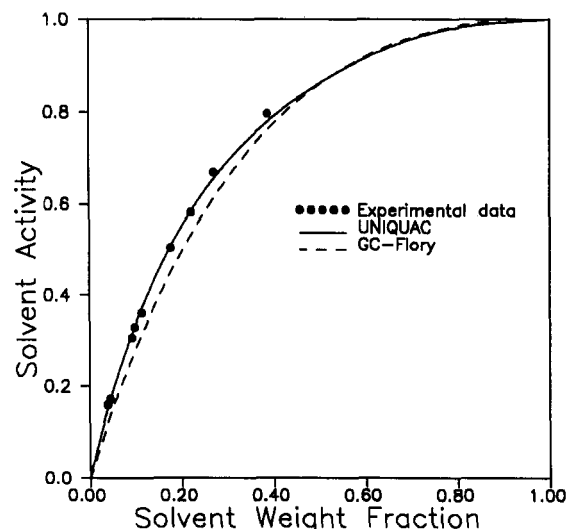


Figure 3. Activity of ethylbenzene in polybutadiene ($M_n=250\,000$) as predicted by the revised GC-Flory EOS (---) and correlated by UNIQUAC (—) at 373.15 K. Experimental data (●) are taken from Hao et al. (1991).

(PVC solutions, alcohol-polymer solutions, mixture containing diene, and ketone groups). The GC-Flory EOS

Table 6. Experimental and Predicted Solvent Activity Coefficients at Infinite Dilution for Polymer Solutions^a (Difficult Cases)

polymer solution	T (K)	$\Omega^{\infty}_{\text{exp}}$	$\Omega^{\infty}_{\text{GC-Flory(old)}}$	$\Omega^{\infty}_{\text{GC-Flory(new)}}$	$\Omega^{\infty}_{\text{UNIFAC-FV}}$	$\Omega^{\infty}_{\text{Entropic-FV}}$
PBD(93000) + methyl ethyl ketone	339.2	7.80	23.32 <i>b</i>	8.65 10.70%	7.96 2.05%	9.61 23.21%
PBD(93000) + toluene	339.2	2.85	8.64 <i>b</i>	3.32 16.49%	3.29 15.44%	4.14 45.26%
PBD(22600) + 1-butanol	353.0	20.50	72.76 <i>b</i>	19.56 4.59%	18.18 11.32%	17.42 15.02%
PVC(40000) + methyl isobutyl ketone	383.2	12.90	4.56 64.65%	13.05 1.16%	6.84 46.98%	9.98 22.64%
PVC(40000) + <i>n</i> -octane	383.0	68.00	13.56 <i>b</i>	60.31 11.31%	14.59 78.54%	14.86 78.15%
PVC(41000) + <i>n</i> -pentane	393.2	38.80	5.98 84.59%	38.41 1.01%	15.51 60.03%	16.46 57.58%
PVC(41000) + <i>n</i> -hexane	393.2	54.60	7.70 85.90%	41.91 23.24%	14.59 73.28%	15.04 72.45%
PVC(41000) + <i>n</i> -heptane	393.2	45.00	10.37 76.96%	48.07 6.82%	14.19 68.47%	15.64 65.24%
PVC(41000) + methanol	298.2	21.36	88.78% <i>b</i>	20.15% 5.66%	54.58% <i>b</i>	80.67% <i>b</i>
PBMA(8716) + methanol	393.0	21.10	62.36 <i>b</i>	22.12 4.83%	24.15 14.45%	24.78 17.44%
PMMA(6107) + methanol	448.0	14.10	19.25 36.52%	13.69 2.91%	45.85 <i>b</i>	17.69 <i>b</i>
PMMA(85100) + methanol	373.5	15.97	56.74 <i>b</i>	17.06 6.83%	82.12 <i>b</i>	19.36 21.22%
PVAC(83400) + 2-propanol	448.2	6.50	6.80 4.62%	6.75 3.85%	10.03 54.31%	6.09 6.31%
PEO(2000) + 1-butanol	348.2	5.52	0.26 95.29%	4.96 10.14%	9.26 67.75%	6.50 17.75%
PEO(10700) + 1-propanol	393.2	5.81	0.66 88.64%	4.67 19.62%	8.01 37.86%	5.74 1.20%

^a GC-Flory(old) is the original GC-Flory EOS (Chen et al., 1990). GC-Flory(new) is the revised GC-Flory EOS (this paper). Percentage values represent absolute mean percent deviation, $100(|\Omega^{\infty}_{\text{exp}} - \Omega^{\infty}_{\text{cal}}|/\Omega^{\infty}_{\text{exp}})$. ^b The percent error is greater than 100.

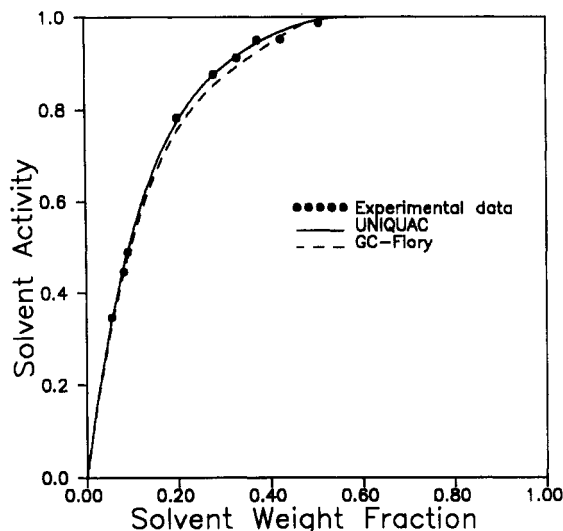


Figure 4. Activity of methyl ethyl ketone in polystyrene ($M_n=10\,300$) as predicted by the revised GC-Flory EOS (---) and correlated by UNIQUAC (—) at 321.65 K. Experimental data (●) are taken from Hao et al. (1991).

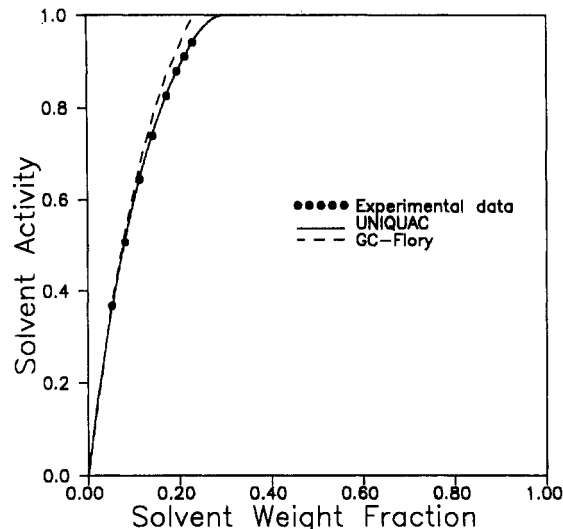


Figure 5. Activity of CCl_4 in poly(vinyl chloride) ($M_n=39\,600$) as predicted by the GC-Flory EOS (---) and correlated by UNIQUAC (—) at 338.15 K. Experimental data (●) are taken from Hao et al. (1991).

now performs as accurately as the Entropic-FV model for finite concentrations as well as for the dilute region. As a whole, the results of these predictions are highly encouraging.

All the models investigated here are based on the group contribution approach; the GC-Flory model is an equation of state while the UNIFAC-FV and Entropic-FV models are activity coefficient models. The advantages and disadvantages of equations of state and activity coefficient models have been discussed elsewhere (Prausnitz et al., 1989; Danner and High, 1992; Fried et al., 1992; Harismadis et al., 1993) and we will not repeat this here, except to underline that an equation of state does not require pure

component and mixture densities. The major drawback of using activity coefficient models is finding accurate density data for the polymer at the temperature of the system, and the predictions from these models are rather sensitive to the pure component and mixture densities. The major drawback of GC-Flory EOS is that only a relatively small number of group parameters have been determined comparing to the activity coefficient models.

Over the whole spectrum of polymer-solvent systems investigated here, there is not one model that is superior to the revised GC-Flory EOS. Each model has its advantages and shortcomings for different types of systems. Our intention was not to compete with other

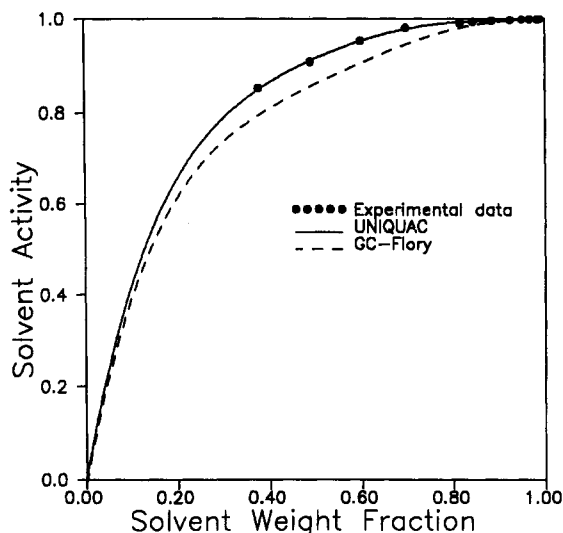


Figure 6. Activity of water in poly(ethylene oxide) ($M_n=1460$) as predicted by the GC-Flory EOS (---) and correlated by UNIQUAC (—) at 297.75 K. Experimental data (●) are taken from Hao et al. (1991).

models but to provide a model which can quantitatively predict VLE and also qualitatively represent and predict LLE for polymer-solvent systems. It can be seen from Table 6 that the GC-Flory EOS is the only model tested which can reasonably well predict the VLE behavior for PVC with hydrocarbons. In part 2 of this work we will show that LLE for polymer-solvent systems may be predicted qualitatively well.

Conclusions

The GC-Flory EOS has been revised and new EOS parameter tables have been derived from VLE data for systems with low molar mass components only. Sample results for prediction of pure component liquid phase properties and VLE predictions for mixtures with polymers are presented, as well as extensive comparison with the UNIFAC-FV and the Entropic-FV models. The results obtained with the revised model using the new parameter tables are of the same quality as the results obtained by the Entropic-FV model. It is encouraging that the model can predict LLE for solutions containing polymers, which will be shown in part 2 of this series of papers.

Acknowledgment

The authors wish to thank Dr. Fei Chen Fredenslund for useful discussions during this work and Mr. Georgios Kontogeorgis for the calculations with the Entropic-FV model presented in Tables 5 and 6.

Nomenclature

C_i = the number of external degrees of freedom associated with component i
 $C_{T,n}$ = degree of freedom parameter
 $C_{T,n}$ = degree of freedom parameter
 C_n^o = degree of freedom parameter
 E = energy parameter, J
 n = total number of moles in the system, kmol
 n_i = number of moles of component i , kmol
 P = pressure of the system, P
 R = gas constant, 8314 J kmol⁻¹ K⁻¹
 R_n = hard core volume of group n
 Q_n = surface area of group n
 q_i = surface area of component i
 T = temperature of polymer solution, K

T_0 = 298.15 K (reference temperature)
 v_i^* = hard core volume of component i , m³/kmol
 v = molar volume of the system, m³/kmol
 v_i = reduced volume of pure component i determined from the equation of state, at temperature and pressure of mixture
 \bar{v} = reduced volume of polymer solution mixture determined from the equation of state, at temperature and pressure of the mixture
 z = 10 (coordination number)
 x_i = mole fraction of component i

Abbreviations

CCl₄ = carbon tetrachloride
 CHCl₃ = chloroform
 EOS = equation of state
 FV = free volume
 GC = group contribution
 HDPE = high density polyethylene
 LDPE = low density polyethylene
 LLE = liquid-liquid equilibria
 PBD = polybutadiene
 PBMA = poly(*n*-butyl methacrylate)
 PEMA = poly(ethyl acrylate)
 PEO = poly(ethylene oxide)
 PIB = polyisobutylene
 PMA = poly(methyl acrylate)
 PMMA = poly(methyl methacrylate)
 PS = polystyrene
 PVAC = poly(vinyl acetate)
 PVC = poly(vinyl chloride)
 VLE = vapor-liquid equilibria

Greek Letters

α = thermal expansivity, K⁻¹
 β = thermal pressure coefficient, J m⁻³ K⁻¹
 $\Delta\epsilon_{ji}$ = interaction energy parameter, J/kmol of contact sites
 $\Delta\epsilon_{nm}$ = interaction energies between unlike groups n and m , J/kmol of interaction sites
 ϵ_{mm} = interaction energies between like groups m , J/kmol of interaction sites
 γ_i = activity coefficient of component i at temperature T
 γ_i^{comb} = combinatorial contribution to the activity coefficient
 γ_i^{attr} = attractive contribution to the activity coefficient
 γ_i^{fv} = free volume contribution to the activity coefficient
 $\nu_n^{(i)}$ = the number of groups of type n in component i
 θ_i = surface area fraction of component i
 Φ_i = the molecular volume fraction of component i
 Ω_i = weight fraction activity coefficient of component i

Superscripts

attr = attractive
 comb = combinatorial
 fv = free volume
 ∞ = infinite dilution

Subscripts

cal = calculated (value)
 exp = experimental (value)
 i = component i
 j = component j
 m = group of type m
 n = group of type n

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