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A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions

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ABSTRACT: A new equation for an activity coefficient—a so-called free volume activity coefficient—which includes combinatorial *and* free volume contributions has been derived from a van der Waals free volume type of expression. The new expression is analogous to the Flory–Huggins combinatorial term. The free volumes of solvents and polymers are compared, and it is shown that even for mixtures of solvents the free volume effect cannot always be ignored. The new free volume activity coefficient is superior to the Flory–Huggins combinatorial in predicting solvent activities in polymer solutions without any energy interactions. For polymer solutions with energy interactions a UNIQUAC residual term is added. The energy parameters are obtained from small-molecule homologues. Again the new equation is superior to the Flory–Huggins equation in predicting the solvent activities of the polymer solution homologues. The results obtained with this new equation compare favorably with the Holten-Andersen equation of state and the UNIFAC-FV model by Oishi and Prausnitz.

Background

The Flory–Huggins expression, based on lattice theory, developed in the early 1940s has been used extensively in the description of the phase equilibria for polymer solutions (see, for instance, Flory[1]). The combinatorial molar activity coefficient for component i, γ_i^{comb} ($\gamma_i = a_i/x_i$), can be written as

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

where the volume fraction, φ_i^{vol}, can be calculated from the mole fraction, x_i, and the molar volume, v_i, using the following expression:

$$\varphi_i^{\text{vol}} = \frac{x_i v_i}{\sum_j x_j v_j} \tag{2}$$

The combinatorial entropy was derived by using segment fraction arguments but, since it was assumed that the volume differences were insignificant, the model was mainly implemented with volume fractions. Later Flory[2] used a form that depended on the segment fractions, φ_i^{seg}, instead of the volume fractions:

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\varphi_i^{\text{seg}}}{x_i} + 1 - \frac{\varphi_i^{\text{seg}}}{x_i} \tag{3}$$

where the segment fractions were based on hard-core volumes, v^*, which were calculated with Flory's equation of state from volumetric pure component properties. Other investigators (e.g., Fredenslund et al.[3]) have found the hard-core information directly from the van der Waals volume as tabulated by Bondi.[4] The latter approach is adopted in this paper. In order to describe systems with energy interactions, a van Laar heat of mixing term was added to the combinatorial entropy, resulting in the following equation for the activity of the solvent (1) in a binary polymer solution:

$$\ln a_1 = \ln \varphi_1^{\text{vol}} + 1 - \frac{\varphi_1^{\text{vol}}}{x_1} + \chi_1(\varphi_2^{\text{vol}})^2 \tag{4}$$

This equation is generally used in the reduction of experimental polymer solution data. In practice, the χ parameter exhibits considerable variation with temperature, pressure, and, unfortunately, also composition. Furthermore, even for nearly athermal polymer solutions, a nonzero χ parameter is obtained. This is commonly interpreted as being a result of not taking the free volume differences between the solvent and the polymer into consideration.

The composition dependence of the χ parameter can be avoided by adopting another energy interaction term. Heil and Prausnitz[5] used a local composition term by Wilson and correlated vapor–liquid equilibria data for 25 different polymer solutions with very good results.

The free volume effect can be taken into account by an equation of state (EOS). On a predictive basis, one of the few choices is the rather complicated Holten-Andersen et al.[6] group contribution EOS, which is a modification of the Flory equation of state. Another approach is employed in the UNIFAC free volume model (UNIFAC-FV) of Oishi and Prausnitz,[7] where two empirical parameters (b and c) have been optimized based on vapor–liquid equilibria data of approximately 30 systems. Even with the limited amount of data the UNIFAC-FV model does a very good job in predicting the solvent activities for a large number of polymer solutions (e.g., High and Danner[8]).

The purpose of this work is to develop a simple expression, similar to eq 4, where the free volume effects are taken into account and where the parameters of the energy interaction term are independent of composition and can be found from vapor–liquid equilibria of solvent mixtures only.

A New Equation for a Free Volume Activity Coefficient

In the following a new free volume activity coefficient equation is derived. The basic assumption is the generalized van der Waals partition function, Q. We use a form similar to that established by Sandler.[9] For a mixture containing N_i molecules of component i the generalized van der Waals partition function is

$$Q = \prod_i \left(\frac{q_{i,\text{int}}^{N_i}}{N_i! \Lambda_i^{3N_i}} \right) V^N \left(\frac{V_f}{V} \right)^N \exp\left(\frac{-\phi}{2kT} \right) \tag{5}$$

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Table I
Assumption on Zero Excess Volume and Its Influence on the Calculated Solvent Activity (Ω_1^{calc}) for Mixtures of Low Molecular Weight Alkanes and PIB[a]

solvent	T, K	w_1	$-10^2 v^E/\sum_j x_j v_j$	$\Omega_1^{calc}(v^E = 0)$	$\Omega_1^{calc}(v^E \neq 0)$	dev, %
n-hexane	298	0.316	0.822	2.56	2.58	1.1
n-hexane	298	0.412	0.857	2.15	2.17	0.9
n-hexane	298	0.470	0.842	1.95	1.97	0.7
n-heptane	273	0.424	0.474	2.07	2.08	0.5
n-heptane	298	0.424	0.615	2.06	2.07	0.7
n-heptane	323	0.424	0.804	2.04	2.06	0.9

[a] Experimental data on excess volumes are taken from Flory et al.[16]

where V is the total volume, $N = \sum_i N_i$, Λ_i depends on molar mass and temperature, (V_f/V) is the free volume correction, ϕ is the sum of attractive pair potentials, and $q_{i,\mathrm{int}}$ are the internal contributions, which are assumed to be functions of temperature only.

Notice that V^N cancels out in eq 5; however, this way of writing the generalized van der Waals partition function has been chosen so as better to identify three contributions to excess properties: the combinatorial, the free volume, and the attractive contributions (the three last terms of eq 5).

In Appendix 1 is shown how the Flory–Huggins equation for the combinatorial activity coefficient based on volume fractions (eq 1) can be derived from the combinatorial part of eq 5, the V^N term. In the derivation of the Flory equation of state (Flory[2]) the total hard-core volume, V^*, is factored out of the free volume term instead of the total volume. From this new combinatorial term, the V^{*N} term, and by using the same line of arguments as in the derivation of the volume-based Flory–Huggins equation one can arrive at a combinatorial activity coefficient identical with the segment-based Flory–Huggins equation (eq 3). In this paper, the combinatorial and the free volume terms are combined into a single term, V_f^N, causing the derived activity coefficient to include both combinatorial *and* free volume contributions. The advantage of deriving the Flory–Huggins combinatorial term and other similar equations from a generalized van der Waals (gvdW) equation is that, unlike the original derivation of the Flory–Huggins equation, the new derivation is independent of any lattice frame of reference. Furthermore, it is clear from the gvdW approach that the free volume differences should be taken into account.

Two simple assumptions are made in order to derive the free volume activity coefficient equation. One is that the total free volume is assumed to be what Bondi[4] labeled the empty volume:

$$V_f = n(v - v^*) \tag{6}$$

where v^* is the molar hard-core volume calculated from the van der Waals volumes given by Bondi,[4] v is the molar volume, and n is the number of moles. Other investigators have used other assumptions of the free volume: for instance, an expansion volume, where v^* is the molar volume at 0 K or where V_f is defined as a fluctuation volume calculated by a cell model. However, these models used together with the approach used in this work tend to overestimate the solvent activities.

The second assumption is that the mixture volumes are found from linear mixing rules:

$$v^*_{\mathrm{mix}} = \sum_i x_i v_i^* \tag{7}$$

$$v_{\mathrm{mix}} = \sum_i x_i v_i \tag{8}$$

From these two assumptions a new expression for the combined combinatorial and free volume contributions, the free volume activity coefficient (γ_i^{fv}), can be derived:

$$\ln \gamma_i^{fv} = \ln\left(\frac{\varphi_i^{fv}}{x_i}\right) + 1 - \frac{\varphi_i^{fv}}{x_i} \tag{9}$$

where φ_i^{fv} denotes the fraction of free volume associated with component i:

$$\varphi_i^{fv} = \frac{x_i(v_i - v_i^*)}{\sum_j x_j(v_j - v_j^*)} \tag{10}$$

Equations 9 and 10 are an essential result of this contribution. The derivation is straightforward but contrary to similar derivations of a free volume activity coefficient (for instance, by Flory[2]), the term $(\delta(v_{\mathrm{mix}}/v^*_{\mathrm{mix}})/\delta n_i)_{P,T,n_j}$ has not been neglected. The second assumption seems reasonable inasmuch as it has been shown in general[10] that a small v^E has a negligible effect on solvent activities. Furthermore, assuming a zero excess volume in this work does not change the results appreciably. This can be seen from Table I, where the calculated weight fraction activity coefficient ($\Omega_1 = a_1/w_1$) is given with and without this assumption.

The free volume activity coefficient (eq 9) is analogous to the simple Flory–Huggins combinatorial term and contains only pure component properties, which means that for polymer solutions without any energy interactions, solvent activities can be predicted from the molar volumes and the van der Waals volumes of the components. A similar equation for the total entropy of mixing, ΔS^{mix}, was derived by Hildebrand,[11] who argued that the probability of finding a molecule in a volume, V, was dependent on the free volume available.

Free Volume Effect

The free volume effect can be quantified by looking at the difference between the two activity coefficient equations, the new free volume and the Flory–Huggins combinatorial:

$$\ln \gamma_i^{fv} - \ln \gamma_i^{\mathrm{comb}} = \ln \frac{(\mathrm{FV}\ \%)_i}{(\mathrm{FV}\ \%)_{\mathrm{mix}}} + \frac{v_i}{v_{\mathrm{mix}}}\left(1 - \frac{(\mathrm{FV}\ \%)_i}{(\mathrm{FV}\ \%)_{\mathrm{mix}}}\right) \tag{11}$$

where $(\mathrm{FV}\ \%)_i$ and $(\mathrm{FV}\ \%)_{\mathrm{mix}}$ denote free volume percent for a pure component and a mixture, respectively, and are given by expressions similar to eq 6:

$$(\mathrm{FV}\ \%)_i = \frac{v_i - v_i^*}{v_i} \times 100 \tag{12}$$

$$(\mathrm{FV}\ \%)_{\mathrm{mix}} = \frac{v_{\mathrm{mix}} - v^*_{\mathrm{mix}}}{v_{\mathrm{mix}}} \times 100 \tag{13}$$

From eq 11 it can be seen that the free volume contribution

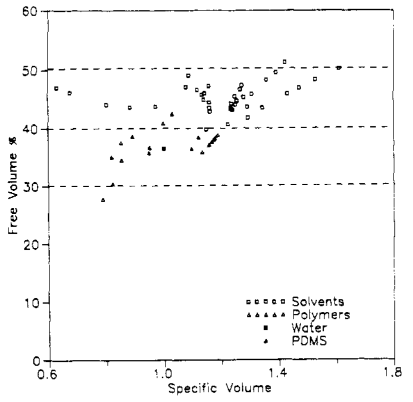

Figure 1. Calculated free volume percent for amorphous polymers (Δ) and solvents (□) at 25 °C. Polymer densities are from van Krevelen and Hoftyzer.[37]

to the activity coefficient can only be ignored if all components in a mixture have equal free volume percentages. The combinatorial activity coefficient equation used here is the one based on volume fractions, but similar conclusions can be drawn by using the activity coefficient based on segment fractions.

In Figure 1 the free volume percent, $(\mathrm{FV}\ \%)_i$, for approximately 20 polymers and 40 common solvents at 25 °C is plotted against the specific volume. The free volume percent of solvents ranges between 40 and 50, excluding water, which has a free volume percent of approximately 36. Polymers, on the other hand, generally have a free volume percent between 30 and 40. This demonstrates that polymers and solvents have different free volume percentages, which compares nicely with the discussion by Patterson[12] on the importance of free volume considerations in phase equilibria calculations for polymer solutions. The new free volume activity coefficient equation is capable of describing these differences.

Aqueous polymer solutions and poly(dimethylsiloxane) (PDMS) solutions with organic solvents both have components with similar free volume percentages, and consequently free volume considerations are not necessary for these systems. This has been demonstrated by Rasmussen and Rasmussen,[13] who used the UNIFAC model without any free volume corrections to predict the activity of water in various polymer solutions. Gottlieb and Herskowitz[14] also used the original UNIFAC model to estimate χ-parameters for PDMS solutions with good results.

However, Figure 1 also shows that even for mixtures of low molecular weight solvent systems free volume differences can reach the same magnitude as in polymer solutions. Consequently if a free volume contribution is necessary in order to describe phase equilibria for polymer solutions, it should also be included in models for solvent mixtures. Most of the activity coefficient models for solutions of small molecules have been derived under the assumption that the free volume percent is constant, independent of component and composition. The energy interaction term in these models must therefore incorporate some contributions from free volume differences. Consequently extrapolation of these models from small-molecule systems to polymer solutions is likely to lead to large errors.

In Figure 2 the deviations between calculated and experimental pressures are shown for a series of hydrocarbon mixtures. The activities have been calculated by the two forms of the Flory–Huggins combinatorial equation (one based on volume fractions and one based on segment fractions, eq 1 and 3, respectively) and by the new free volume activity coefficient, eq 9. For mixtures where the components are similar in size and free volume differences, the three equations result in nearly the same deviations between the calculated and experimental pressures. As the size and free volume differences increase, there is a marked improvement in using eq 9. This tendency is further demonstrated in Figure 3, where the molar activity coefficients at infinite dilution of two pentane isomers in mixtures with higher straight-chain hydrocarbons are shown. The best predictions are given by eq 9. These results demonstrate that free volume differences are also important for solvent mixtures as, for example, those commonly described by the UNIFAC model.

Prediction of Vapor–Liquid Equilibria for Polymer Solutions

Systems without Energy Interactions. A mixture of polymer and solvent where the chemical structure of the solvent is close to the repeat unit of the polymer is not expected to show any energy interactions. Examples of such systems are PE and PIB + various hydrocarbons, PS + ethylbenzene, PαMS + cumene, PVAc + ethyl acetate, and PDMS + HMDS. Experimental data for such systems have been compared with predictions of the three activity coefficients: the two forms of the Flory–Huggins equation, one based on segment fractions and the other based on volume fractions (eqs 3 and 1, respectively), and the new free volume activity coefficient (eq 9).

In Figure 4 the experimental and calculated solvent weight fraction activity coefficients at infinite dilutions, Ω^∞, for PE, PIB, PS, PVAc, and PDMS systems (some of them at variable temperatures) are shown. Details are given in Table II, where the results of the Holten-Andersen EOS and the UNIFAC-FV also are given for comparison.

For all the systems studied the solvent activity is underestimated. This might be a consequence of ignoring the energy interaction. A positive contribution from the energy interaction (which is to be expected for these systems) would increase the predictions toward the experimental data.

The Ω^∞ is seen to increase with increasing temperature. The Flory–Huggins equation based on segment fractions does not have any temperature dependency. Equations 1 and 9, on the other hand, both show an increase in Ω^∞ with increasing temperature. The UNIFAC-FV cannot reproduce this trend for all of the systems studied, which reflects the empirical nature of this model.

The Ω^∞ values for all the systems calculated by the Flory–Huggins equation based on segment fractions are nearly constant, obtaining the value e. This is a consequence of the close chemical similarity of the repeat unit and the solvent. The variation in Ω^∞ from system to system for the two other versions of the Flory–Huggins equation comes into play via the molar volume data.

The predictions of the weight fraction activity coefficient at infinite dilution, Ω^∞, for all systems studied rank as follows: Equation 9 predicts Ω^∞'s closer to the experimental data than eq 1, which again is better than eq 3.

In Figure 5 the mean percent deviations between calculated and experimental solvent activities are given for PIB, PS, PαMS, PDMS, and PVAc systems, with different molecular weights of the polymers for some of the systems. In Figures 6 and 7 are given two examples of solvent activity predictions by the three equations. Details are given in Table III, where the results of the Holten-Andersen EOS and the UNIFAC-FV also are given for comparison.

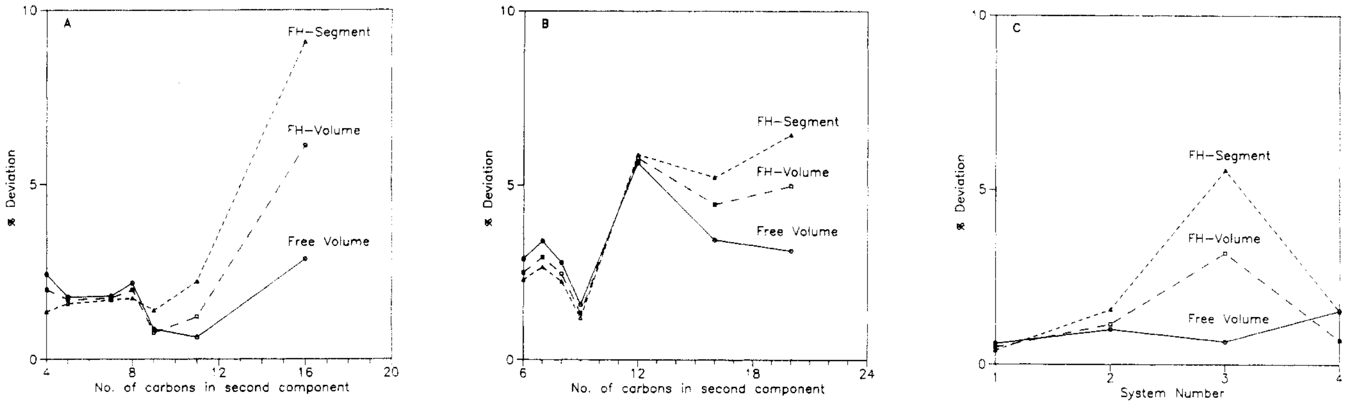

Figure 2. Mean pecent deviations (AMD) between calculated and experimental pressures for hydrocarbon mixtures. (A) *n*-Hexane + $n\text{-}C_nH_{2n+2}$ at 10–55 °C. (B) Cyclohexane + $n\text{-}C_nH_{2n+2}$ at 25–40 °C. (C) Binary mixtures of cyclic compounds at 25 °C: (1) cyclopentane + cyclohexane; (2) cyclohexane + *cis*-decalin; (3) cyclopentane + *cis*-decalin; (4) cyclopentane + *trans*-decalin. Experimental data are taken from the Dortmund data bank (Gmehling and Onken[28]) and cover the entire range of molar compositions. % AMD $= (1/n_{\text{data}})\sum[|p^{\text{calc}} - p^{\text{exp}}|/p^{\text{exp}}] \times 100$.

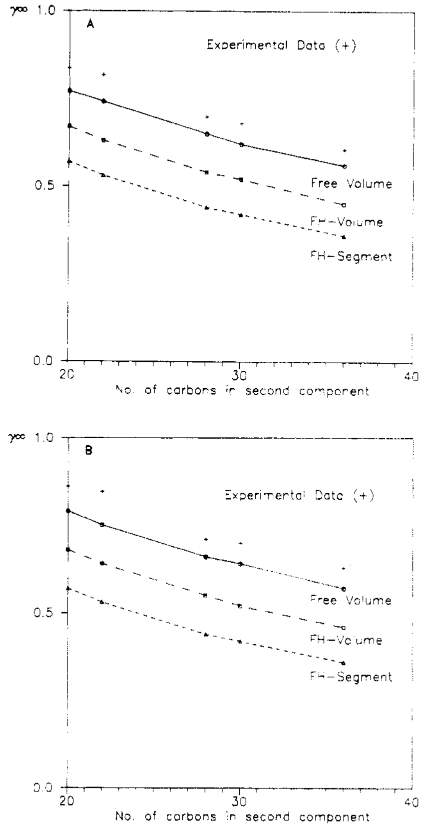

Figure 3. Molar activity coefficients for hydrocarbons at infinite dilution at 100 °C: (A) *n*-pentane + $n\text{-}C_nH_{2n+2}$; (B) isopentane + $n\text{-}C_nH_{2n+2}$. Experimental data are taken from Parcher et al.[38]

For the systems with low molecular weight PDMS polymers, the three equations perform similarly in predicting the solvent activities, but as the molecular weight is increased, eq 9 is better.

For all three versions of the Flory–Huggins equation the tendency of underestimating solvent activities seen at infinite dilution is repeated in the predictions on the finite polymer solution data (not evident in Table III or Figure 5).

The average absolute percent errors for all the infinite dilute systems studied (Figure 4) are 9.7%, 11%, and 14% for eq 9, the Holten-Andersen EOS, and the UNIFAC-FV, respectively. The average absolute percent errors for all finite polymer systems studied (Figure 5) are 5.4%, 5.4%, and 3.5% for eq 9, the Holten-Andersen EOS, and the UNIFAC-FV, respectively. This demonstrates that for polymer solutions without energy interactions the simple free volume activity coefficient model compares favorably with other predictive models.

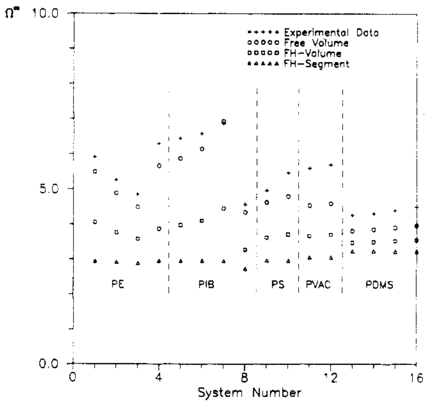

Figure 4. Solvent weight fraction activity coefficients ($\Omega_1^\infty = a_1/w_1$) for polymer solutions without energy interactions at infinite dilution. System description is given in Table II.

Systems with Energy Interactions. There is a lack of dependable experimental data for mixtures of polymers and solvents. Hence, in order for an activity coefficient model for polymer solutions to be of value one needs to be able to obtain the energy parameters from low molecular weight systems. One way of doing this is by a group contribution approach. For some polymer solutions, however, the energy parameters can be obtained on a molecular basis also. This is the case if the repeat unit of the polymer has a low molecular weight homologue with similar energy characteristics. Examples of such polymer solution systems are polystyrene solutions, where the repeat unit is nearly identical with ethylbenzene.

In order to study polymer solutions with energy interactions a UNIQUAC (Abrams and Prausnitz[15]) residual term (γ_i^{res}) has been adopted:

$$\ln \gamma_i^{\text{res}} = q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_j q_i\left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} + \frac{\tau_{ij}}{\theta_i\tau_{ij} + \theta_j}\right) \tag{14}$$

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{RT}\right)$$

where γ_i^{res} is written for a binary system, θ_i is the surface area fraction calculated from the van der Waals surface

Table II
Observed and Predicted Weight Fraction Activity Coefficients at Infinite Dilution for Some Polymer Solutions without Energy Interactions[a]

					act. coeff eq				
no.	system	T, K	expt	ref	(9)	(1)	(3)	H-A EOS	UNIFAC-FV
1	PE + n-hexane	423	5.91	17	5.49	4.05	2.94	5.81	4.18
2	PE + n-heptane	423	5.26	17	4.88	3.76	2.91	5.10	3.88
3	PE + n-octane	423	4.85	17	4.49	3.58	2.88	4.67	3.66
4	PIB + n-hexane	323	6.29	17	5.66	3.87	2.95	4.91	6.61
5	PIB + n-hexane	348	6.44	17	5.87	3.97	2.95	5.05	6.45
6	PIB + n-hexane	373	6.58	17	6.14	4.10	2.95	5.27	6.33
7	PIB + n-hexane	423	6.86	17	6.92	4.45	2.95	6.61	6.15
8	PIB + cyclohexane	323	4.56	17	4.34	3.27	2.72	5.48	4.67
9	PS + ethylbenzene	423	4.96	18	4.63	3.62	2.96	5.28	4.22
10	PS + ethylbenzene	448	5.47	18	4.80	3.71	2.96	6.46	4.25
11	PVAC + ethyl acetate	353	5.6	19	4.54	3.66	3.05	5.34	4.19
12	PVAC + ethyl acetate	373	5.7	19	4.59	3.70	3.05	5.51	4.12
13	PDMS + HMDS	298	4.26	20	3.80	3.47	3.22	na	4.71
14	PDMS + HMDS	313	4.30	20	3.85	3.49	3.22	na	4.65
15	PDMS + HMDS	328	4.39	20	3.90	3.52	3.22	na	4.60
16	PDMS + HMDS	343	4.50	20	3.96	3.55	3.22	na	4.56

[a] The results by the UNIFAC-FV model for the siloxane systems have been calculated by using parameters given by Herskowitz and Gottlieb.[21]

Table III
Mean Percent Deviations (AMD) between Calculated and Experimental Solvent Activities for Some Polymer Solutions without Energy Interactions[a]

					act. coeff eq				
no.	system	T, K	polym mol wt	ref	(9)	(1)	(3)	H-A EOS	UNIFAC-FV
1	PIB + n-pentane	298	40000	22	14.1	28.3	38.1	15.9	8.1
2	PIB + cyclohexane	298	40000	23	7.3	17.9	24.5	7.7	4.8
3	PS + ethylbenzene	283	82000	24	0.9	1.5	1.9	0.6	0.9
4	PαMS + cumene	338	236	25	1.0	2.3	3.4	2.5	0.2
5	PαMS + cumene	338	17000	25	4.7	11.6	16.5	2.7	1.1
6	PDMS + HMDS	298	594	26	2.3	1.0	1.0	na	5.8
7	PDMS + HMDS	298	958	26	4.3	6.0	7.5	na	1.1
8	PDMS + HMDS	298	1540	26	3.5	5.6	7.4	na	1.7
9	PDMS + HMDS	298	4170	26	2.9	5.4	7.4	na	3.0
10	PVAC + ethyl acetate	303	8600	27	10.3	20.1	27.0	5.7	7.4
11	PVAC + ethyl acetate	303	110000	27	7.7	18.3	25.8	2.9	4.8

[a] The results by the UNIFAC-FV model for the siloxane systems have been calculated by using parameters given by Herskowitz and Gottlieb.[21] % AMD = $(1/n_{\mathrm{data}})\sum[|a^{\mathrm{calc}} - a^{\mathrm{exp}}|/a^{\mathrm{exp}}] \times 100$.

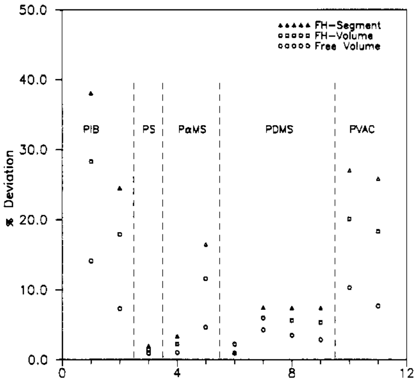

Figure 5. Mean percent deviations between calculated and experimental activities for polymer solutions without energy interactions. System description is given in Table IV.

areas (q_i)

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{15}$$

and the interaction parameters a_{ij} are to be optimized from experimental data. The total activity coefficient can now be calculated from

$$\ln \gamma = \ln \gamma' + \ln \gamma^{\mathrm{res}} \tag{16}$$

where the activity coefficient, γ', is calculated by either of the two forms of the Flory–Huggins equation (eqs 1 and 3) or by the new free volume activity coefficient (eq 9).

Table IV
Optimization of UNIQUAC Parameters for Mixtures of Low Molecular Weight Compounds[a]

polym homologue	no.	system	T, K	thermodynamic consistency test
PIB	1	benzene + TMP	308	consistent
PIB	2	TMP + toluene	373	consistent
PVAc	3	ethyl acetate + benzene	323	consistent
PVAc	4	ethyl acetate + 1-propanol	328	consistent
PDMS	5	hexane + HMDS	303	consistent
PDMS	6	HMDS + toluene	338	consistent
PS	7	tetrachloromethane + ethylbenzene	293	consistent
PS	8	toluene + ethylbenzene	298	only PTx data
PS	9	MEK + ethylbenzene	328	consistent
PS	10	cyclohexane + ethylbenzene	303	only PTx data
PS	11	dipropyl ether + ethylbenzene	323	not consistent
PH	12	heptane + toluene	303	consistent

[a] Experimental data are from the Dortmund data bank (Gmehling and Onken[28]); this reference also describes the criteria for consistency.

The low molecular weight systems for which the energy parameters have been optimized are given in Table IV, where the result of a thermodynamic consistency test also is given. The parameter optimization has been done for each of the three versions of eq 16, resulting in three sets of energy parameters (a_{ij}) for each set of finite solvent

Table V
Mean Percent Deviations (AMD) between Calculated and Experimental Solvent Activities for Polymer Solutions with Energy Interactions[a]

				act. coeff eq				
no.	system	T, K	ref	(9)	(1)	(3)	H-A EOS	UNIFAC-FV
1	PIB + benzene	298	29	8.3	11.9	24.0	16.1	3.7
2	PIB + toluene	338	29	14.5	22.6	34.5	34.6	12.4
3	PVAc + benzene	303	30	2.8	8.5	14.2	19.8	3.9
4	PVAc + 1-propanol	313	31	6.4	26.2	35.8	17.2	11.7
5	PDMS + hexane	303	32	10.4	18.7	25.0	na	7.3
6	PDMS + toluene	313	26	2.6	4.3	8.7	na	5.3
7	PS + tetrachloromethane	293	33	1.1	11.0	18.7	na	4.9
8	PS + toluene	298	34	0.9	2.9	5.1	0.9	1.0
9	PS + MEK	298	35	11.3	20.9	27.2	5.9	4.3
10	PS + cyclohexane	303	34	2.3	4.5	6.2	2.4	2.3
11	PS + dipropyl ether	293	33	20.6	31.6	38.8	11.7	8.3
12	PH + toluene	303	36	12.2	8.8	14.3	62.0	9.2

[a] $\%\ \text{AMD} = (1/n_{\text{data}})\sum[|a^{\text{calc}} - a^{\text{exp}}|/a^{\text{exp}}] \times 100$.

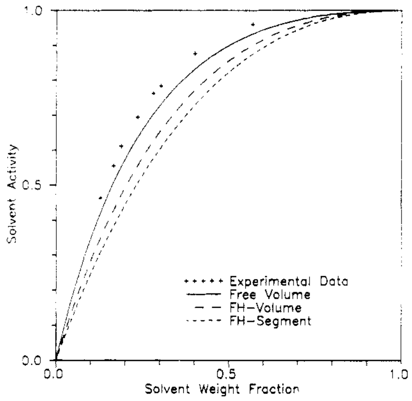

Figure 6. Comparison of the three activity coefficient expressions for the prediction of cyclohexane activities in PIB (system no. 2 in Table III).

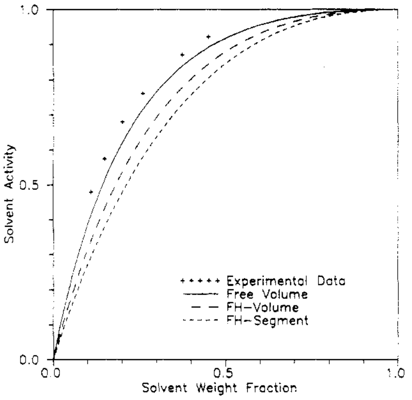

Figure 7. Comparison of the three activity coefficient expressions for the prediction of ethyl acetate in PVAc (system no. 11 in Table III).

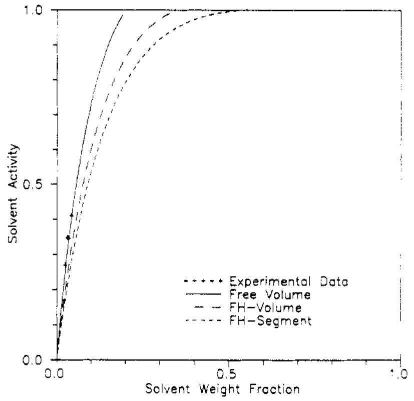

Figure 8. Comparison of the three versions of the UNIQUAC activity coefficient model for the prediction of 1-propanol activities in PVAc (system no. 4 in Table V).

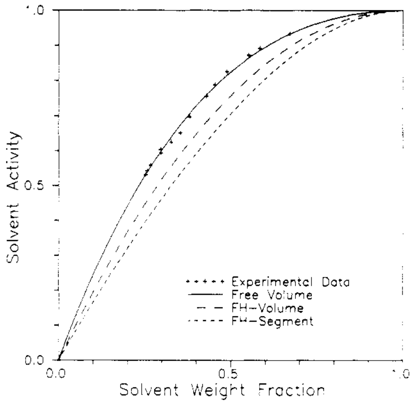

Figure 9. Comparison of the three versions of the UNIQUAC activity coefficient model for the prediction of tetrachloromethane activities in PS (system no. 7 in Table V).

mixture data. These energy parameters are used to predict solvent activities for the homologous polymer solutions. In Figures 8 and 9 are given two examples of solvent activity predictions by the three equations. For all systems studied the mean percent deviations between calculated and experimental solvent activities for the three versions of eq 16 are given in Table V. For these systems there is no tendency for the solvent activities to be underestimated as that seen in the systems without any energy interaction. The results from the Holten-Andersen EOS and the UNIFAC-FV are given for comparison. There is a tendency for the UNIFAC-FV model to make predictions that are somewhat better than the ones obtained with eq 9. This should not be taken as a final argument that the free volume contribution used in the UNIFAC-FV model is more theoretically sound than the one used here, since 5 of the 12 systems studied here also went into the optimization of the two empirical parameters in the UNIFAC-FV model.

Of the three activity coefficients, eq 9 is found to be clearly superior in extrapolating low molecular weight data to the homologous polymer solutions.

For all systems studied, except the dipropyl ether solution, the simple free volume activity coefficient approach compares favorably to other predictive models. The explanation for this inconsistency could be that the vapor–liquid equilibria data for the corresponding low molecular weight systems are not thermodynamically consistent.

Conclusion

A new approximate expression for a free volume activity coefficient, taking into account both the combinatorial and free volume contributions, has been developed. The expression is similar to the Flory–Huggins expression replacing the volume or segment fraction with a free volume fraction. The free volume fraction is calculated empirically using Bondi's empty volume concept and assuming zero excess volumes of mixing.

The model can explain why free volume effects in aqueous polymer solutions and solutions of PDMS in organic solvents can be neglected, which tends to support the underlying assumptions.

The new model is first used to model vapor–liquid equilibria in polymer solutions without energy interactions, where it is shown to be far superior to the Flory–Huggins expression (which neglects free volume effects). For polymer systems with energy interactions, the new free volume activity coefficient expression is combined with a UNIQUAC residual term. It is shown that when the residual UNIQUAC energy interaction parameters are obtained from phase equilibrium data on mixtures with the low molecular weight homologues, excellent predictions of solvent activities in polymer solutions result.

The results obtained with this new equation compare favorably to two other predictive models: the rather complicated Holten-Andersen model[6] and the empirically based UNIFAC-FV model.[7]

List of Abbreviations

MEK	methyl ethyl ketone
HMDS	hexamethyldisiloxane
PE	polyethylene
PIB	polyisobutylene
PS	polystyrene
PαMS	poly(α-methylstyrene)
PDMS	poly(dimethylsiloxane)
PH	poly(1-heptene)
PVAc	poly(vinyl acetate)
TMP	2,2,4-trimethylpentane

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Appendix 1. Derivation of the Flory–Huggins Combinatorial Term and Similar Activity Coefficient Equations

The Flory–Huggins combinatorial term is derived from the combinatorial part of the generalized van der Waals partition function:

$$Q^{\text{comb}} = V^N \tag{A1}$$

Using the relationship $A = -kT \ln Q$, the combinatorial contributions to the molar Helmholz energy for a pure component and a mixture are

$$a_i^{\text{comb}}/RT = -\ln (n_i v_i) \tag{A2}$$

and

$$a^{\text{comb,mix}}/RT = -\ln (n v_{\text{mix}}) \tag{A3}$$

where v_i and v_{mix} are the pure component and mixture molar volumes. Upon summation of eq A2 over all pure components and subtraction of eq A3, the combinatorial contribution to the Helmholz energy change of mixing is

$$\Delta a^{\text{comb}}/RT = -\ln v_{\text{mix}} + \sum x_i \ln v_i + \sum x_i \ln x_i \tag{A4}$$

Assuming linear mixing rules for the mixture volume, we end up with an equation that corresponds to the Flory–Huggins combinatorial entropy of mixing:

$$\begin{aligned} g^{\text{E,comb}}/RT &= -\ln v_{\text{mix}} + \sum x_i \ln v_i \\ &= \sum x_i \ln (v_i/v_{\text{mix}}) \\ &= \sum x_i \ln (\varphi_i^{\text{vol}}/x_i) \end{aligned}$$

where

$$\varphi_i^{\text{vol}} = x_i v_i / \sum x_j v_j \tag{A5}$$

By interchanging all volumes with either a hard-core volume or a free volume in the derivation, we end up with the Flory–Huggins combinatorial term based on segment fraction (eq 3) and the new free volume activity coefficient equation (eq 9), respectively.

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