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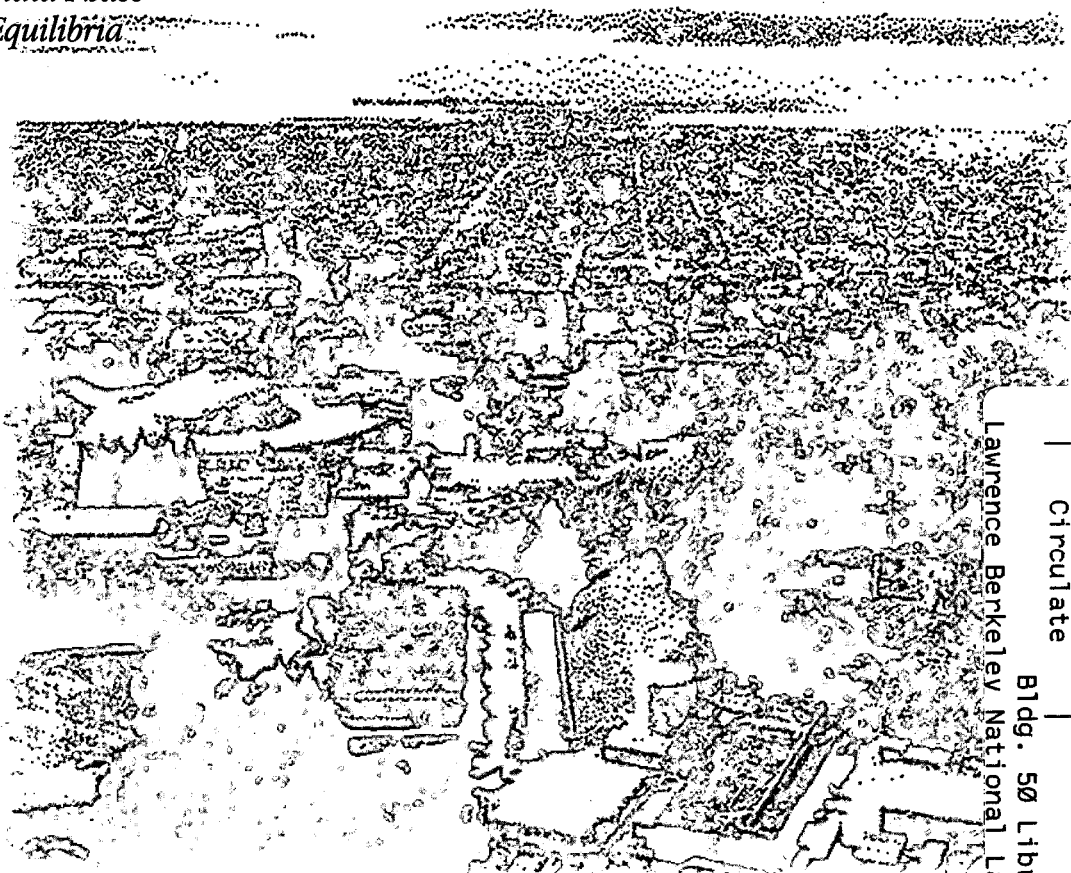


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ESTIMATION OF VAPOR-LIQUID EQUILIBRIA FOR POLYMER SOLUTIONS BY A GROUP-CONTRIBUTION METHOD

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ABSTRACT

A new group-contribution method is presented for prediction of vapor-liquid equilibria of polymer solutions. It is based on a close-packed lattice model developed previously; this model contains a revised Flory-Huggins entropy and a series expression for excess internal energy, as well as a double-lattice model to account for specific, oriented interactions. The group-contribution method includes three contributions: the combinatorial and free-volume contribution that is primarily responsible for entropy, the van der Waals energy contribution responsible for dispersion and polar forces, and the specific energy contribution from hydrogen bonding. Most of the model parameters can be estimated using pure-component properties either from experimental data or from group-contribution methods in the literature. The group-contribution method described in this work gives parameters for the cross specific interaction energy from hydrogen bonding between segments of polymers and segments of solvents. Parameters for pairs of groups are obtained by correlating experimental data for vapor pressures and infinite-dilution activity coefficients of solvents in polymer

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solutions. The method shown here gives improved results for prediction when compared with those of other group-contribution models.

1. INTRODUCTION

For engineering design, it is often necessary to estimate vapor-liquid equilibria in polymer solutions. Because experimental data for such solutions are not plentiful, it is desirable to use a group-contribution method. Such methods have been proposed previously, notably by Oishi and Prausnitz (1978) and later variations (Holten-Anderson and Fredenslund, 1987, 1988, Chen, Fredenslund and Rasmussen's, 1990, Elbro, Fredenslund and Rasmussen, 1990, Kontogeorgis, Fredenslund and Tassios, 1993, Bogdanic and Fredenslund, 1994). These methods are based on the UNIFAC correlation that is often successful for estimating vapor-liquid equilibria in mixtures containing ordinary (nonpolymer) liquids.

The fundamental basis for existing group-contribution methods for polymer solutions is the lattice theory of Flory (1942) and Huggins (1942) with variations (e.g. Guggenheim, 1952; Orifino and Flory, 1957; Koningsveld and Kleintjens 1980). However, it is well known that the Flory-Huggins theory is based on severe simplifying assumptions which have happily been overcome (at least in part) in the much-improved lattice-cluster theory of Freed and coworkers (Bawendi and Freed, 1988; Dudowicz and Freed, 1991a,b,c). Freed's theory is mathematically complicated but the results can be well approximated using a mathematical simplification introduced by Hu, Liu, Soane and Prausnitz (1991).

Freed's theory is for a mixture of athermal chains and monomers; it contains only a single binary parameter ε_{12} . However, Freed's theory does not take into account orientation as found in hydrogen-bonding liquids nor does it take into account compressibility (free-volume effects). To include the effect of oriented forces into Freed's theory, Hu et al (1991) use a secondary lattice which, in effect, assigns a theoretical temperature dependence to the binary parameter ε_{12} . This extended theory of Freed is the basis of the group-contribution correlation presented here.

As shown by Hu, Liu and Shi (1996), for a binary, the Helmholtz function of mixing $\Delta_{\text{mix}}A$ is:

$$\frac{\Delta_{\text{mix}} A}{N_r kT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \frac{1.2}{9} (r_1^{-1} - r_2^{-1})^2 \phi_1 \phi_2 + \left(2 + \frac{\phi_1}{r_2} + \frac{\phi_2}{r_1} \right) \phi_1 \phi_2 \tilde{\varepsilon}_{12} - 1.611 \phi_1^2 \phi_2^2 \tilde{\varepsilon}_{12}^2 \quad (1)$$

where N_r is the total number of sites in the lattice; r_i and ϕ_i are the chain length and the volume fraction of component i , respectively; $\tilde{\varepsilon}_{12}$ is the reduced interchange energy defined by:

$$\tilde{\varepsilon}_{12} = \varepsilon_{12} / kT \quad (2)$$

where ε_{12} is the interchange energy. Eq.(1) shows that for an athermal mixture ($\varepsilon_{12}=0$), the equation does not reduce to the athermal Flory-Huggins equation except for the trivial case when $r_1=r_2$.

As shown earlier (Hu et al, 1991, 1993), to account for specific, oriented interactions, a secondary lattice gives a temperature dependence for the energy parameter:

$$\varepsilon_{12} = \left(\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^* \right) + \left(-\Delta A_{\text{sec},11} / N_{11} - \Delta A_{\text{sec},22} / N_{22} + 2\Delta A_{\text{sec},12} / N_{12} \right) \quad (3)$$

where ε_{11}^* , ε_{22}^* , ε_{12}^* are van der Waals-energy interaction parameters. $\Delta A_{\text{sec},11}$, $\Delta A_{\text{sec},22}$ and $\Delta A_{\text{sec},12}$ are the additional Helmholtz functions for the corresponding secondary lattice; N_{11} , N_{22} and N_{12} are the numbers, of 1-1, 2-2 and 1-2 segment-segment pairs, respectively. Terms $\Delta A_{\text{sec},ij} / N_{ij}$ are given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij} kT} = \frac{1}{3} \left[\eta_{ij} \ln \eta_{ij} + (1 - \eta_{ij}) \ln(1 - \eta_{ij}) - 3\delta\tilde{\varepsilon}_{ij} \eta_{ij}^2 - 1.5\delta\tilde{\varepsilon}_{ij}^2 \eta_{ij}^2 (1 - \eta_{ij})^2 - 0.04\delta\tilde{\varepsilon}_{ij}^3 \eta_{ij}^3 (1 - \eta_{ij})^3 \right] \quad (4)$$

where η_{ij} is a geometric constant; it is the fraction of the segment surface that can participate in oriented interactions for an i - j segment-segment pair. As before, we set $\eta_{ij}=0.3$; final results are insensitive to that choice. The reduced additional energy parameter $\delta\tilde{\varepsilon}_{ij}$ is defined by

$$\delta\tilde{\varepsilon}_{ij} = \delta\varepsilon_{ij} / kT \quad (5)$$

where $\delta\varepsilon_{ij}$ is the energy beyond the van der Waals energy due to specific oriented interactions between segment i and segment j .

2. THE MOLECULAR-THERMODYNAMIC MODEL

The group-contribution method developed here is based on a molecular-thermodynamic model wherein the Helmholtz function of mixing includes three contributions: the combinatorial and free-volume contribution that is primarily responsible for entropy of mixing, the van der Waals-energy contribution from dispersion and polar forces, and the specific energy contribution from hydrogen bonding.

2.1 COMBINATORIAL AND FREE-VOLUME CONTRIBUTION

A lattice model (without holes) does not allow a volume change upon mixing; there is no change in free volume. However, changes in free volume may have a profound influence on the entropy of mixing. Therefore, we rewrite eq.(1):

$$\begin{aligned} \frac{\Delta_{mix}A}{N_r kT} = & \frac{\phi_1}{r_1} \ln \phi_1^{FV} + \frac{\phi_2}{r_2} \ln \phi_2^{FV} + \frac{1.2}{9} (r_1^{-1} - r_2^{-1})^2 \phi_1 \phi_2 \\ & + \left(2 + \frac{\phi_1}{r_2} + \frac{\phi_2}{r_1} \right) \phi_1 \phi_2 \tilde{\varepsilon}_{12} - 1.611 \phi_1^2 \phi_2^2 \tilde{\varepsilon}_{12}^2 \end{aligned} \quad (6)$$

where the free-volume fraction ϕ_i^{FV} is calculated by

$$\phi_i^{FV} = N_i V_{mi}^{FV} / \sum_i N_i V_{mi}^{FV} \quad (7)$$

$$V_{mi}^{FV} = V_{mi} - V_{mi(vdW)} \quad (8)$$

$$r_i = V_{mi(vdW)} / 15.17 \times 10^{-6} \text{ m}^3 \text{ mol} \quad (9)$$

$$\phi_i = N_i r_i / \sum_i N_i r_i \quad (10)$$

Here V_{mi} and $V_{mi(vdW)}$ are the molar volume and the van der Waals volume of component i , respectively. The molar volume V_{mi} depends on temperature, while

the hard-core volume $V_{mi(\text{vdW})}$ is temperature-independent by assumption; it can be estimated by an existing group-contribution method, as shown, for example, by Van Krevelen (1990). Chain length r_i and volume fraction ϕ_i are calculated using hard-core volumes; it is a hard-core volume fraction. The constant $15.17 \times 10^{-6} \text{m}^3 \text{mol}^{-1}$ is the molar hard-core volume of a CH_2 group. In eq.(6), free-volume fractions are used only in the first two terms because it is these terms which are primarily responsible for the entropy of mixing, whereas the third term is a correction to the close-packing entropy; the remaining terms are responsible for the energy of mixing.

If the solvent of a polymer solution is designated as component 1, the solvent activity is

$$\begin{aligned} \ln a_1 = & \ln \phi_1^{\text{FV}} + \left(1 - \frac{V_{\text{ml}}^{\text{FV}}}{V_{\text{m2}}^{\text{FV}}}\right) \phi_2^{\text{FV}} + \frac{1.2}{9} r_1 (r_1^{-1} - r_2^{-1})^2 \phi_2^2 \\ & + r_1 \phi_2^2 \left[2 + r_1^{-1} + 2(r_2^{-1} - r_1^{-1}) \phi_1\right] \tilde{\varepsilon}_{12} + 3.222 r_1 \phi_1 \phi_2^2 (1 - 1.5 \phi_1) \tilde{\varepsilon}_{12}^2 \end{aligned} \quad (11)$$

2.2 VAN DER WAALS-ENERGY CONTRIBUTION

The energy parameter ε_{ij}^* in eq.(3) is due to van der Waals forces (dispersion and polar forces). For a pure component i , ε_{ii}^* can be estimated using the square of the pure-component van der Waals solubility parameter of Hansen (Barton, 1991; van Krevelen, 1990), which is the sum of a dispersion contribution and a polar contribution: $\delta_{\text{vdW}}^2 = \delta_{\text{d}}^2 + \delta_{\text{p}}^2$. To relate ε_{ii}^* to δ_{vdW}^2 , we note that the number of i - i segment-segment pairs for a pure component i is $N_{ii} = zN_i r_i / 2 = 3N_i r_i$, where $z=6$ is the coordination number of a cubic lattice. Therefore,

$$\delta_{\text{vdW},i}^2 = 3L\varepsilon_{ii}^* r_i / V_{\text{mi}} \quad (12)$$

where L is the Avogadro number and where δ_{vdW} and $V_{\text{m},i}$ are at 25°C . If Hansen's solubility parameter is not available, we use a group-contribution method (Hoftyzer and Van Krevelen, 1976) to estimate it. For a pure component, the effect of temperature on ε_{ii}^* is given by

$$\varepsilon_{ii}^* = \varepsilon_{ii}^+ / V_{\text{mi}} \quad (13)$$

where $V_{m,i}$, depends on temperature. The temperature-independent parameter ε_{ii}^+ can be estimated by

$$\varepsilon_{ii}^+ = \delta_{vdW}^2 V_{mi}^2 (25^\circ \text{C}) / 3Lr_i \quad (14)$$

Parameter ε_{ii}^* is then calculated by eq.(13) with the molar volume at the system temperature.

The cross interaction van der Waals energy parameter ε_{ij}^* is estimated by the geometric mean of the corresponding pure-component parameters:

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*} \quad (15)$$

2.3 SPECIFIC-ENERGY CONTRIBUTION

Toward obtaining better agreement with experimental data, we redefine $\delta\varepsilon_{ij}$, $\delta\varepsilon_{ij}^2$, $\delta\varepsilon_{ij}^3$ in eq.(4) as three independent new parameters $\delta\varepsilon_{ij(1)}$, $\delta\varepsilon_{ij(2)}$, $\delta\varepsilon_{ij(3)}$. When we substitute eq.(4) into eq.(3), we obtain the interchange energy in eqs (1) and (2):

$$\begin{aligned} \varepsilon_{ij} = & (\varepsilon_{ii}^* + \varepsilon_{jj}^* - 2\varepsilon_{ij}^*) + \eta^2 (\delta\varepsilon_{ii(1)} + \delta\varepsilon_{jj(1)} - 2\delta\varepsilon_{ij(1)}) \\ & + 0.5\eta^2 (1 - \eta)^2 (\delta\varepsilon_{ii(2)} + \delta\varepsilon_{jj(2)} - 2\delta\varepsilon_{ij(2)}) / kT \\ & + 0.04\eta^3 (1 - \eta)^3 (\delta\varepsilon_{ii(3)} + \delta\varepsilon_{jj(3)} - 2\delta\varepsilon_{ij(3)}) / 3k^2 T^2 \end{aligned} \quad (16)$$

where $\eta=0.3$.

To obtain pure-component parameters $\delta\varepsilon_{ij(1)}$, $\delta\varepsilon_{ij(2)}$, and $\delta\varepsilon_{ij(3)}$, we use Hansen's hydrogen-bonding solubility parameter δ_h ; it is related to the additional specific energy $\Delta U_{sec,ii}$ by

$$\Delta U_{sec,ii} (25^\circ \text{C}) = -\delta_h^2 V_{mi} (25^\circ \text{C}) \quad (17)$$

For the temperature dependence of $\Delta U_{sec,ii}$, we again assume

$$\Delta U_{\text{sec},ii} = \Delta U_{\text{sec},ii}^+ / V_{mi} \quad (18)$$

where $\Delta U_{\text{sec},ii}^+$ is independent of temperature. We then obtain from eqs.(17) and (18),

$$\Delta U_{\text{sec},ii}(T) = -\delta_h^2 V_{mi}^2(25^\circ\text{C}) / V_{mi}(T) \quad (19)$$

For a pure component i , upon inserting eqs.(4) and (10) into the thermodynamic relation $[\partial(\Delta A/T) / \partial(1/T)] = \Delta U$, we have

$$\Delta U_{\text{sec},ii} = N_i r_i \left[-3\eta_{ii}^2 \delta\epsilon_{ii(1)} - 3\eta_{ii}^2 (1 - \eta_{ii})^2 \frac{\delta\epsilon_{ii(2)}}{kT} - 0.12\eta_{ii}^3 (1 - \eta_{ii})^3 \frac{\delta\epsilon_{ii(3)}}{k^2 T^2} \right] \quad (20)$$

Selecting molar volumes at three different temperatures for pure component i , three parameters $\delta\epsilon_{ii(1)}$, $\delta\epsilon_{ii(2)}$, $\delta\epsilon_{ii(3)}$ can be calculated from eq.(20).

Excepting cross specific energy parameters $\delta\epsilon_{12(1)}$, $\delta\epsilon_{12(2)}$ and $\delta\epsilon_{12(3)}$, we now have all parameters in the model: r_i , V_{mi}^{FV} , ϵ_{11}^* , ϵ_{22}^* , ϵ_{12}^* , $\delta\epsilon_{11(1)}$, $\delta\epsilon_{11(2)}$, $\delta\epsilon_{11(3)}$, $\delta\epsilon_{22(1)}$, $\delta\epsilon_{22(2)}$ and $\delta\epsilon_{22(3)}$ have all been fixed by pure-component properties obtained either from experimental pure-component data or from published group-contribution methods. The group-contribution method in this work gives cross specific energy parameters. They are calculated from pair-interaction group parameters.

$$L^l \delta\epsilon_{ij(l)} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn(l)} \quad (l=1,2,3) \quad (21)$$

where N_s and N_p are numbers of groups in solvents and polymers; ϕ_m and ϕ_n are the volume fraction of group m in a solvent and that of group n in a polymer, respectively; $g_{mn(1)}$, $g_{mn(2)}$ and $g_{mn(3)}$ are pair interaction parameters between group m in a solvent and group n in a polymer. In this work, they are estimated by fitting experimental vapor pressures and infinite-dilution solvent activity coefficients of polymer solutions. These cross parameters, shown in Table 1, are independent of temperature.

To improve the accuracy of prediction, we assume that a functional group in a polymers is different from that in a solvent. Pair-interaction parameters between groups are estimated successively, one pair at a time.

3. RESULTS

Altogether 110 pair interaction parameters between 11 solvent groups and 10 polymer groups have been obtained. Those groups cover most common polymers and solvents in the coating and paint industry. Table 1 lists pair-interaction parameters. Figures 1 to 4 show predicted solvent activities for the PPO(5.e5)/benzene system at 320.35K, the PS(1.03e4)/2-butanone system at 321.65K, the PS(2.9e5)/propyl acetate system at 298K, and the PIB(1170)/Pentane system at 298K. The experimental results are also shown for comparison. Table 2 shows some representative results for deviations of calculated infinite-dilution solvent activity coefficients of polymer solutions covering a wide temperature range as high as one hundred degrees K. Shown also are some results by other group-contribution methods which were reported for a much narrower temperature range. Using the method described here, for vapor-pressure calculations, most of the deviations from experiment are less than 3%. For infinite-dilution solvent activity coefficients, most of the deviations are less than 5%, while the deviations by other methods are notably larger.

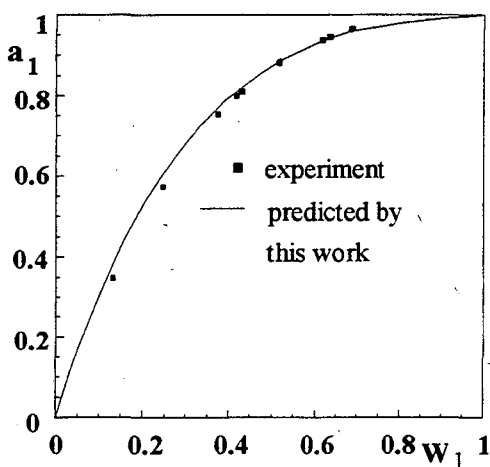


Figure 1. Solvent activities for PPO/Benzene at 320.35K, $M_w = 5 \times 10^5$.

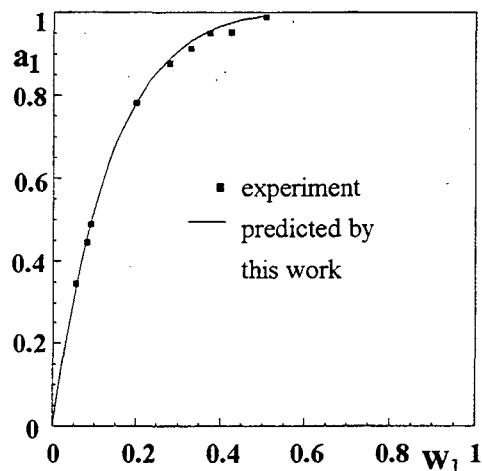


Figure 2. Solvent activities for PS/2-Butanone at 321.65K, $M_w = 1.03 \times 10^4$.

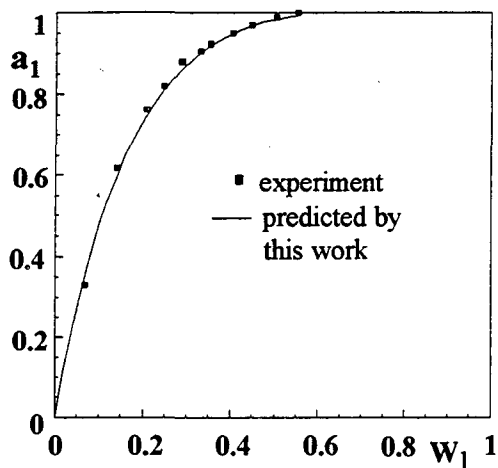


Figure 3. Solvent activities for PS/Propyl acetate at 298K
 $M_w = 2.9 \times 10^5$.

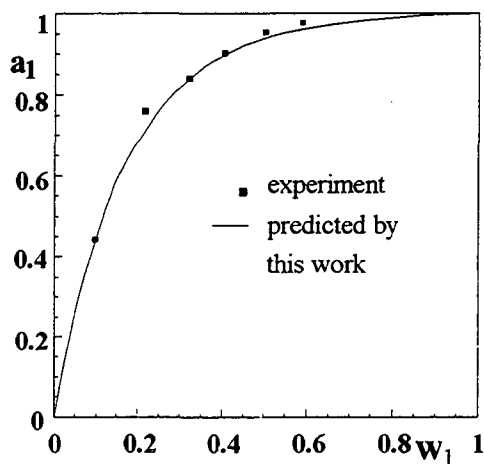


Figure 4. Solvent activities for PIB(1170)/Pentane at 298K
 $M_w = 1170$.

4. DISCUSSION AND CONCLUSION

The success of a group-contribution method depends primarily on the molecular-thermodynamic model. As shown in our previous work (Hu et al, 1996), the model used here gives critical temperatures and critical volume fractions for polymer solutions with $r_1=1-10,000$ and $r_2=1-10,000$ in good agreement with those predicted by Freed's theory. Prediction of spinodal and binodal curves for binary polymer solutions with chain length $r_1=1$ and $r_2=1-200$ are excellent compared with computer-simulation results, much better than those by Flory-Huggins theory and better than those by Freed's theory. By incorporating a double lattice, the model can account for specific oriented interactions because it gives a temperature dependence for the energy parameter.

On the other hand, the accuracy of the method also depends on the data used to obtain the group parameters. In this work, most of the parameters are calculated from pure-component properties, either from experimental data or from published estimation methods. For establishing a useful group-contribution method, the most important part is the cross specific-interaction parameters for pairs between segments of polymers and segments of solvents; some of these are given here. To obtain those group parameters, we correlated not only experimental vapor pressures of polymer solutions near ambient temperature, but also infinite-dilution solvent activity coefficients over a wide temperature range. We distinguish the groups in polymers from those in solvents.

The model can be extended to multicomponent systems. The corresponding Helmholtz function of mixing can be written:

$$\begin{aligned} \frac{\Delta_{\text{mix}}A}{N_r kT} = & \sum_i \frac{\phi_i}{r_i} \ln \phi_i^{\text{FV}} + \frac{1.2}{9} \sum_i \sum_j \phi_i \phi_j (r_i^{-1} - r_j^{-1})^2 \\ & + \sum_i \sum_j \phi_1 \phi_2 a_{ij} - (\sum_i \sum_j \phi_1 \phi_2 a_{ij}^*)^2 \end{aligned} \quad (22)$$

where a_{ij} and a_{ij}^* are functions of $\tilde{\varepsilon}_{ij}$, r_i and r_j (Hu et al, 1996).

However, the list of group parameters is not complete. More experimental data are required to improve and extend the method to a larger variety of systems.

A computer program is available upon request. This program includes a data base for pure-component parameters that covers most common polymers and solvents.

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LIST OF SYMBOLS

a_i	activity of component i
$\Delta_{\text{mix}}A$	Helmholtz function of mixing
$\Delta A_{\text{sec},ij}$	additional Helmholtz function for specific interaction of i - j segment pair
g_{mn}	group interaction parameter of m - n pair
k	Boltzman constant
L	Avogadro constant
M_w	relative weight-average molar mass
N_r	total number of sites of the lattice
N_i	number of molecules of component i
N_{ij}	number of i - j segment pairs
r_i	chain length, number of segments of a molecule i

T	temperature
$\Delta U_{\text{sec},ij}$	additional internal energy for specific interaction of i - j segment pair
V_{mi}^{FV}	molar free volume of component i
W_i	weight fraction of component i

Greek letters

ϕ_i	volume fraction of component i
ϕ_i^{FV}	free volume fraction of component i
ϕ_m	volume fraction of group m in a component
$\delta\tilde{\varepsilon}_{ij}$	reduced specific contribution energy of i - j segment pair
$\delta\varepsilon_{ij}$	specific energy of i - j segment pair
$\tilde{\varepsilon}_{ij}$	reduced interchange energy of i - j segment pair
ε_{ij}	interchange energy of i - j segment pair
ε_{ij}^*	van der Waals energy parameter
η_i	surface fraction of segment i participating in oriented interaction
δ_d	dispersion contribution of Hansen's solubility parameter
δ_p	polar contribution of Hansen's solubility parameter
δ_h	hydrogen-bonding contribution of Hansen's solubility parameter
δ_{vdw}	van der Waals contribution of Hansen's solubility parameter

Subscripts

i, j	component or segment
m, n	group
vdw	van der Waals
h	hydrogen-bonding
mix	mixture

superscripts

FV	free volume
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Table 1. Group-interaction parameters: $g_{mn(1)}/\text{Jmol}^{-1}$, $10^{-3} g_{mn(2)}/\text{J}^2\text{mol}^{-2}$ and $10^{-4} g_{mn(3)}/\text{J}^3\text{mol}^{-3}$




polymer		CH3	CH2	CH	C		C=C	SiO	COO	-O-	Cl
CH3	$g_{mn(1)}$	81.566	-71.794	-4121.4	1956.6	2033.3	11.424	-431.16	7375.9	5845.5	8428.9
	$g_{mn(2)}$	0.0	-669.52	0.0	0.0	-2216.7	0.0	182.89	-1464.8	-8817	-9007.
	$g_{mn(3)}$	0.0	2439.3	12983.	-8909.2	-622.36	0.0	1072.5	-19720	0.0	0.0
CH2	$g_{mn(1)}$	0.0	663.25	1693.2	-2115.6	225.34	-405.56	1066.9	-793.9	-113.9	323.56
	$g_{mn(2)}$	0.0	-1088.4	-1243.6	0.0	0.0	0.0	-1454.9	3403.3	0.0	3112.1
	$g_{mn(3)}$	1614.5	0.0	-6338.7	-9250	0.0	-2061.5	-1593.5	0.0	0.0	0.0
CH	$g_{mn(1)}$	1213.2	991.03	-46539.	-14700	-5150.8	-999.41	3064.8	4971.6	-14056	38201
	$g_{mn(2)}$	0.0	0.0	32765	0.0	0.0	0.0	-6342.6	0.0	0.0	-47004
	$g_{mn(3)}$	0.0	-5020.8	115364	0.0	0.0	0.0	29.2	0.0	0.0	0.0
	$g_{mn(1)}$	-438.84	519.19	854.06	-699.32	-86.96	-360.01	637.43	1357.1	-703.6	1003.0
	$g_{mn(2)}$	788.95	-617.35	-521.23	-491.25	176.55	873.26	-987.4	231.0	2940.1	658.5
	$g_{mn(3)}$	0.0	-478.67	-1701.1	-2777.4	0.0	0.0	-146.01	0.0	0.0	0.0
C=O	$g_{mn(1)}$	-3524.5	3597.8	13783.	-16579	-777.25	0.0	613.03	-11443	42224	-2339
	$g_{mn(2)}$	0.0	-6210.6	0.0	17853	2862.4	0.0	0.0	23878.	0.0	0.0
	$g_{mn(3)}$	10092.	-1058.6	-47784	2045	-33.85	4812.2	0.0	0.0	-2000	0.0
	$g_{mn(1)}$	333.08	288.87	-689.99	-3629.2	586.58	79.12	-230.3	4552.6	827.12	4542.5
	$g_{mn(2)}$	0.0	-403.98	0.0	0.0	-436.57	0.0	0.0	-5312.7	-1639.1	-3575.7
	$g_{mn(3)}$	0.0	0.0	631.82	1150	-125.92	0.0	-379.01	0.0	0.0	-2573.5
COO	$g_{mn(1)}$	263.68	3372.4	2848.5	-71529.	-2043.9	-609.96	278.9	0.0	-6994.4	-1059.3
	$g_{mn(2)}$	0.0	-3498.4	-8808.9	260.48	4842.7	0.0	0.0	8464.2	16135	5199.9
	$g_{mn(3)}$	0.0	0.0	0.0	119844	0.0	0.0	0.0	0.0	0.0	0.0
OH	$g_{mn(1)}$	2898.3	-7.599				7797.1			25089	
	$g_{mn(2)}$	0.0	0.0				-7452.8			0.0	
	$g_{mn(3)}$	0.0	0.0				0.0			15377	
Cl	$g_{mn(1)}$	114.71	518.95	10898	-17832	4765.1	845.6	274.88	3060.3	1520.9	-4157.2
	$g_{mn(2)}$	0.0	-873.13	-17633	28300	-8126.8	0.0	0.0	-1964.4	7154.0	6581.6
	$g_{mn(3)}$	0.0	0.0	0.0	0.0	-949.1	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	$g_{mn(1)}$	-1941.4	4006.9	15998		8806.6	-9872.9			-8973.1	
	$g_{mn(2)}$	0.0	-3858.2	-9432.1		-18499	15000			8299.8	
	$g_{mn(3)}$	0.0	0.0	-378.3		0.0	0.0			23095	

Table2. Calculations of solvent activity coefficients at infinite dilution for polymer solutions by this group-contribution method

System	T/K	Dev%	T/K	Dev% GC -Flory ¹	Dev% UNIFAC -FV ²	Dev% Entropic -FV ³
PB(2.36e4)/benzene	353-373	0.45	353.0	14.79	5.21	7.67
PEO(4.e6)/benzene	343-424	4.97	353.5	0.98	10.05	11.03
PS(8.2e4)/benzene	413-473	3.23	403.4	5.64	4.34	7.81
PE(2.35e5)/hexane	398-423	4.77	383.15	7.26	24.60	10.27
PE(2.35e5)/heptane	383-473	3.11	383.15	7.48	22.44	8.67
PE(8.2e4)/dodecane	393.2	3.71	393.15	4.73	18.41	7.21
PB(2.26e4)/ethylbenzene	353-373	3.68	353.0	8.93	5.06	
PIB(4.e4)/octane	298.15	0.00	298.15	18.06	9.53	19.40
PIB(1.e4)/toluene	298-423	3.03	298.15	3.09	2.28	1.30
PB(9.3e4)/acetone	339-369	0.75	373.0	5.19	8.37	9.23
PB(9.3e4)/2-butanone	339-369	5.40	339.2	10.70	2.05	23.21
PS(9.7e4)/2-butanone	423.15	1.82	420.0	2.81	10.94	3.65
PS(7.6e4)/toluene	413-453	2.71	433.2	1.50	20.41	7.87
PS(2.e4)/hexane	445.0	4.18	423.0	0.53	1.06	20.86
PS(7.6e4)/ethylbenzene	433-473	2.46	448.2	2.74	21.94	12.43
PB(2.26e4)/cyclohexane	353-373	1.30	353.0	13.73	13.01	0.48
PIB(5.e4)/cyclohexane	323-423	2.91	313.15	4.99	4.37	24.74
PMA(6.32e4)/toluene	363-383	5.33	383.2	9.47		12.13
PVAc(8.35e4)/toluene	373-423	5.27	448.2	14.00	7.00	11.72
PVAc(5.e5)/ethylbenzene	393-423	4.81	473.2	3.71	28.18	2.42
PVAc(4.35e5)/nonane	363-433	3.42	418.2	2.30	7.11	49.72
PVAc(1.5e6)/nonane	374-385	4.24	418.2	2.30	7.11	49.72
PEO(4.e6)/toluene	343-423	5.37	373.2	1.23	14.81	8.85
PB(2.26e4)/ethyl acetate	353-373	2.51	373.2	5.63	18.95	11.82
PEO(2000)/1-butanol	343-398	1.84	348.2	10.14	67.75	17.75
PEO(4.e6)/chloroform	343-423	1.00	373.2	10.34	37.07	1.72
PVC(3.5e4)/chloroform	393.2	4.40	393.2	10.52	10.17	15.42

Note:

1. Dev%: average percentage error of solvent activity coefficients at infinite dilution.

$$\text{Dev}\% = \sum \left| (\gamma_{\text{calc}} - \gamma_{\text{expt}}) / \gamma_{\text{expt}} \right| \times 100$$

2. References: 1 -- Chen et al, 1990.

2 -- Oishi et al, 1978.

3 -- Elbro et al, 1990; Kontgeogis et al, 1993.

All data from *Polymer Solution Data Collection* (Wen, Elbro and Alessi, 1992b)

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