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Group Contribution Methods for Predicting Polymer–Polymer Miscibility from Heats of Mixing of Liquids. 1. Comparison of the Modified Guggenheim Quasi-Chemical (MGQ) and UNIQUAC Models

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ABSTRACT: The abilities of two group contribution methods, the standard UNIQUAC method and a modified Guggenheim quasi-chemical, MGQ, method to fit and to predict the heats of mixing of a variety of ester, alkane, and chlorinated hydrocarbons are compared. The MGQ method is found, on average, to fit heats of mixing of polar compounds to within about 9% accuracy, while the UNIQUAC method is less accurate by a factor of about 2. The group interaction parameters obtained for the MGQ method are used to predict the heat of mixing and miscibility of poly(vinyl chloride) with a series of aliphatic polyesters. The predictions agree well with experiment.

Introduction

Because the combinatorial entropy of mixing is vanishingly small for mixtures of large molecules, a negative or exothermic heat of mixing, ΔH_{mix}, is required to obtain the negative free energy of mixing necessary for the spontaneous formation of a single phase, miscible, polymer solution.[1-6] In its simplest form, the heat of mixing can be written

$$\Delta H_{\text{mix}}/V = \sum_{i}\sum_{j\neq i} B_{ij}\Phi_i\Phi_j \qquad (1)$$

where V is the system volume, Φ_i is the volume fraction of species i in the multicomponent mixture, and B_{ij} is the binary interaction density between species i and species j. By identifying B_{ij} with the interaction per unit volume between polymer repeat unit i and polymer repeat unit j and by evaluating B_{ij} from liquid heats of mixing data obtained experimentally for mixtures of compounds which closely resemble the polymer repeat units, it is often possible to relate polymer–polymer miscibility to the presence of a negative B_{ij} interaction between the liquid analogues of the repeat units.

Interaction parameters, obtained from fitting ΔH_{mix} of liquid analogues of polymer repeat structures to a simple van Laar heat of mixing model, eq 1, agree reasonably well with the parameters obtained from the corresponding miscible polymer blends when the same heat of mixing model is used to thermodynamically analyze the melting point depression behavior,[7-11] sorption behavior,[7,8] and direct miscibility behavior[12,13] of the blends. These results, together with the observation that polymers are immiscible when their analogues mix endothermically,[7-9] seem to confirm the importance of nearest-neighbor enthalpic interactions to the thermodynamics associated with the phase behavior of binary polymer blends. Due to the simplified nature of these analyses, however, little insight is provided that would allow one to understand the contributions to the heat of mixing by the various species comprising each blend component, and it is often difficult to explain the nature of the interaction responsible for the exothermic, negative, B values obtained experimentally. Further, the use of analogue compounds to simulate the interactions between polymer repeat units is difficult, owing to the general lack of analogues whose structures precisely replicate those of the polymer repeat units.

The recent rediscovery by several investigators[14-18] that ΔH_{mix} can be calculated from the composition weighted sum of binary interactions between unlike molecular groups that comprise the polymer component repeat units seems to be a successful extension of the simple theory. This approach[14] properly considers the self-interactions between groups on the same molecule to obtain

$$\Delta H_{\text{mix}}/V = \sum_{i}\sum_{j>i} B_{ij}\Psi_i\Psi_j - \sum_{k}\Phi_k\sum_{i}\sum_{j>i} B_{ij}\Psi_i^{k}\Psi_j^{k} \qquad (2)$$

where Φ_k is the volume fraction of polymer k in the blend, Ψ_i^k is the volume fraction of group i in polymer k, and Ψ_i is the volume fraction of group i in the blend. Interestingly, eq 2 allows for the possibility that ΔH_{mix} can be negative, even though all B_{ij} parameters are positive. This situation can occur when the self-interactions, represented by the second terms in eq 2, are more endothermic that the interactions between groups on different polymers molecules in the blend, represented by the first terms. Equation 2 is important, in that it removes any conceptual difficulty associated with the presence of negative B parameters in the simpler model, eq 1. Equation 2 is also able to explain the miscibility of a copolymer with a polymer when none of the homopolymer forms of the copolymer constituents are miscible with that polymer[14] and "windows of miscibility" with polymer composition, as discussed below. Its practical application still suffers, however, from the need to evaluate the B parameters from experimental observations of analogue mixing heats.

The successes of both equations strongly suggest that a group contribution method, in which groups are chosen to closely approximate the multigroup structure of the blend components, should offer a comprehensive description of the effect of structure on the heat of mixing which could lead to a priori prediction of polymer-polymer miscibility. Provided the structural units are chosen to be small enough that they are well represented in a variety of small molecules, it should be possible to obtain the B parameters associated with interactions between groups from liquid heats of mixing data for a variety of compounds which are quite different from any particular polymer repeat unit. This would avoid the need to have close analogues to the polymer repeat units.

Basically, any thermodynamic model that calculates the heat of mixing in terms of group interactions could serve as a basis for a group contribution method, provided it is able to accurately fit the observed heats of mixing versus composition data with a minimum number of parameters. The most widely recognized group contribution methods in chemical engineering calculations are the universal quasi-chemical, UNIQUAC, method[19] and the related

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functional group activity method, UNIFAC.[20] These methods are well-known for accurately predicting vapor-liquid equilibria; however, they fail to accurately predict heats of mixing in the polar systems that are apt to be of most interest for predicting the miscibility of polymer blends. Several investigators have modified the UNIFAC method to obtain better correlations in polar and hydrogen bonding systems;[21–25] however, all modifications have required the addition of substantially more parameters to the model. An alternate, conceptually simpler, group contribution method can be based on the earlier quasi-chemical theory of Guggenheim.[26,27] The applicability of both models to the prediction of polymer–polymer miscibility from heats of mixing of low molecular weight liquids is examined in this paper.

Models for Heats of Mixing

Both the UNIQUAC and the Guggenheim models seek to obtain a better representation of the mixing process by recognizing that the distribution of interacting species in the equilibrium mixture is locally nonrandom as a result of the exchange energy associated with the interaction of unlike pairs in the mixture. The models differ by the way in which the nonrandom nature of the mixture is accounted. The Guggenheim model uses a "single fluid" approximation in which the number of i–j pairs, N_{ij}, and the exchange energy per pair, ΔE_{ij}, are considered to be the same as those associated with the j–i pairs in the system. The UNIQUAC model is a "two-fluid" model for which $N_{ij} \neq N_{ji}$. One of the goals of the comparison presented here is to determine whether the conceptual complexity associated with the two-fluid model is really necessary for the purpose of correlating and predicting heats of mixing data.

Guggenheim Model. Guggenheim[26,27] uses a quasi-chemical formula to describe the relationship between the numbers of the various types of contacts

$$(i\text{–}i) + (j\text{–}j) \xrightarrow{\Delta E} 2(i\text{–}j)$$

$$\frac{N_{ij}^2}{4N_{ii}N_{jj}} = \exp(-\Delta E/kT) = \exp(-2\Delta E_{ij}/kT) \qquad (3)$$

$$i, j = 1 \quad \text{to} \quad f, i \neq j$$

where f is the number of different types of interacting groups in the mixture and

$$\Delta E_{ij} = \Delta E/2 = E_{ij} - \tfrac{1}{2}E_{ii} - \tfrac{1}{2}E_{jj} \qquad (4)$$

is the exchange energy associated with the formation of an i–j contact on mixing of pure component i with contact energy E_{ii} and pure component j with contact energy E_{jj} to form an i–j contact pair with energy E_{ij}.

The number of unlike contact pairs, N_{ij}, in the mixture are computed from the number of like pairs by eq 3. The number of like pairs in the mixture can be related to the number of molecules in the pure component liquids through a variety of assumptions. The simplest approach would be to relate the number of contact pairs with the number of molecular pairs in the mixture. For this simple case

$$N_{ii} = zN_i/2 - \tfrac{1}{2}\sum_{j\neq i} N_{ij} \qquad (5)$$

where z is the number of nearest neighbors and N_i is the number of molecules of pure component i in the mixture. The total number of contact pairs is just

$$N = \sum_i\sum_{j\geq i} N_{ij} = (z/2)\sum_i N_i \qquad (6)$$

The energy of the mixture, U_{mix}, is then

$$U_{\text{mix}} = \sum_i\sum_{j\geq i} N_{ij}E_{ij} = \sum_i U_i + \sum_i\sum_{j>i} N_{ij}\Delta E_{ij} \qquad (7)$$

where $U_i = zN_iE_{ii}/2$ is the energy of pure component i. The change in energy on mixing, ΔU_{mix}, is then

$$\Delta U_{\text{mix}} = \sum_i\sum_{j>i} N_{ij}\Delta E_{ij} \qquad (8)$$

The energy of the mixture, U_{mix}, and the pure component energies, U_i, are negative numbers by the usual convention that the potential energy of the ideal-gas state is zero. Since volume changes on mixing of liquids are usually small, the heat or enthalpy of mixing, ΔH_{mix}, is approximately equal to ΔU_{mix}.

The Guggenheim model, outlined by 2 through 8 above, accounts for local nonrandomness in a mixture of similarly sized spherical molecules. For mixtures of polysegmented molecules that differ in size and shape, however, N_{ij} is not simply related to composition, and more sophisticated relationships between molecular composition and contact sites need to be derived. Further improvements in the ability of the Guggenheim model to fit and predict heats of mixing in polar systems can be made by altering eq 3. These modifications lead to the modified Guggenheim quasi-chemical, MGQ, model discussed below.

Modified Guggenheim Quasi-Chemical, MGQ, Model. Two modifications are proposed to the simple theory presented above. The first considers the possibility that chemical equilibrium between i–j contacts is best described by a change in free energy instead of just potential energy. This empirical consideration has the effect of adding an additional characteristic constant, A_{ij}, for each i–j pair

$$\begin{aligned} N_{ij}^2/4N_{ii}N_{jj} &= \exp(-2\Delta F_{ij}/kT) = \\ &\qquad \exp(2\Delta S_{ij}/k)\exp(-2\Delta E_{ij}/kT) \\ &= A_{ij}\exp(-2\Delta E_{ij}/kT) \end{aligned} \qquad (9)$$

The second modification was proposed by Guggenheim[26] as an attempt to account better for the mixing of molecules of unlike sizes and shapes by considering contact sites instead of just molecular composition. This approach is used in one or another form in most modern theories, including UNIQUAC. Abrams and Prausnitz,[19] for example, consider each molecule of component i to have zq_i nearest neighbors, where q_i is a parameter proportional to the molecule's external surface area. The average area fraction of component i in the mixture is then given by

$$\Theta_i = q_iN_i/(\sum_j q_jN_j) \qquad (10)$$

where

$$\sum_i \Theta_i = 1 \qquad (11)$$

This average area fraction is equivalent to the local area fraction for athermal, noninteracting, random, mixtures. Guggenheim[26] has shown that the number of contacts between molecules i and j in a totally random mixture is given by

$$\mathcal{N}_{ij} = \mathcal{N}_{ji} = z(\sum_k q_kN_k)\Theta_i\Theta_j \qquad (12)$$

and

$$\mathcal{N}_{ii} = (z/2)(\sum_k q_kN_k)\Theta_i^2 \qquad (13)$$

To account for local nonrandomness in contact sites in non-athermal mixtures, Panayiotou and Vera[28] define a nonrandom factor, Γ_{ij}, to obtain N_{ij}. Thus

$$N_{ij} = N_{ji} = \Gamma_{ij}\mathcal{N}_{ij} = \Gamma_{ji}\mathcal{N}_{ji} \tag{14}$$

and

$$N_{ii} = \Gamma_{ii}\mathcal{N}_{ii} \tag{15}$$

The symmetry of eq 14 clearly requires that $\Gamma_{ij} = \Gamma_{ji}$. In addition, the number of contact sites for each component i must be conserved, so that

$$2N_{ii} + \sum_{j\neq i} N_{ij} = N_i z q_i \tag{16}$$

or

$$\sum_j \Theta_j \Gamma_{ji} = 1 \tag{17}$$

These authors point out the equivalency of their approach with the local surface fraction approach used in the UNIQUAC method.[28] The local, nonrandom, surface fraction of unit j available for contacts with a central unit of species i, Ψ_{ji}, is related to the nonrandom factors by

$$\Psi_{ji} = \Theta_j \Gamma_{ji} \tag{18}$$

$$\Psi_{ij} = \Theta_i \Gamma_{ij}$$

$$\Psi_{ii} = \Theta_i \Gamma_{ii}$$

The surface fractions are conserved for each component i as can be demonstrated by substituting eq 18 into (17)

$$\sum_j \Psi_{ji} = 1 \tag{19}$$

$$\Theta_i \Psi_{ji} = \Theta_j \Psi_{ij} \tag{20}$$

can be obtained from eq 18 and the requirement that $\Gamma_{ij} = \Gamma_{ji}$. Equations 10 through 19 are common to both the MGQ method presented here and the UNIQUAC method discussed below. Equation 20 is necessary for the MGQ method but is not used in the UNIQUAC method.

The energy change on mixing is then given by combining eq 8 with eq 12–15 for the multicomponent mixture

$$\Delta U_{\text{mix}} = (\sum_k z q_k N_k) \sum_i \sum_{j\neq i} \Gamma_{ij} \Delta E_{ij} \Theta_i \Theta_j \tag{21}$$

Provided ΔE_{ij} and A_{ij} are known, the nonrandom parameters, Γ_{ij}, can be evaluated by eliminating Γ_{ii} and Γ_{jj} through use of eq 17 and by combining eq 12 through 14 with eq 3 for each i–j pair

$$\frac{N_{ij}^2}{4N_{ii}N_{jj}} = \frac{\Gamma_{ij}^2 \Theta_i \Theta_j}{(1 - \sum_{j\neq i} \Theta_j \Gamma_{ij})(1 - \sum_{i\neq j} \Theta_i \Gamma_{ij})} = A_{ij} \exp(-2\Delta E_{ij}/kT) \tag{22}$$

For a simple binary mixture of groups 1 and 2, eq 22 becomes

$$\Theta_1 \Theta_2 (1 - F_{12}) \Gamma_{ij}^2 + F_{12} \Gamma_{12} - F_{12} = 0 \tag{23}$$

where

$$F_{12} = A_{12} \exp(-2\Delta E_{12}/kT) \tag{24}$$

Equation 23 has two roots. Since $\Gamma_{12} \to 1$ as $F_{12} \to 1$, the root with physical meaning is given by

$$\Gamma_{12} = \frac{-F_{12} + (F_{12}^2 + 4F_{12}\Theta_1\Theta_2(1 - F_{12}))^{1/2}}{2\Theta_1\Theta_2(1 - F_{12})} \tag{25}$$

For the simple binary mixture of groups 1 and 2, equation (21) reduces to

$$\Delta U_{\text{mix}} = z(q_1 N_1 + q_2 N_2) \Gamma_{12} \Delta E_{12} \Theta_1 \Theta_2 \tag{26}$$

The parameters z and q_i remain to be specified before solution of the simultaneous eq 22 for each i–j pair can occur. Following Abrams and Prausnitz[19] and Bondi,[29] we set $z = 10$ as the coordination number. The surface parameter, q_i, is

$$q_i = A_{wi}/(2.5 \times 10^9) \tag{27}$$

where the numerical factor in eq 27 is the standard segment area of a methylene group in units of cm^2/mol and A_{wi} is the area of the molecule given by Bondi. This choice permits a direct comparison between the model given here and the UNIQUAC model of Abrams and Prausnitz.

Equation 21 describes only the energy of mixing associated with mixing pure, simple, sites i and j. Generally, the description of an actual experiment of mixing two or more real fluids, each of which contains several different groups or sites, requires recognition of the self-interactions that exist between the different sites in each real, pure, fluid.[14-18] That is, each real fluid in the experimental mixture must also be considered as a mixture of interacting sites which follows eq 3–27. The heat of mixing of real, multisited, fluids is then given by

$$\Delta U_{\text{mix}} = \sum_i \sum_{j>i} [\sum_m z q_m N_m] \Gamma_{ij} \Delta E_{ij} \Theta_i \Theta_j - \sum_k \sum_i \sum_{j>i} [\sum_m z q_m N_m^{(\mathrm{k})}] \Delta E_{ij} \Gamma_{ij}^{(\mathrm{k})} \Theta_i^{(\mathrm{k})} \Theta_j^{(\mathrm{k})} \tag{28}$$

where $\Theta_i^{(\mathrm{k})}$ is the surface fraction of group i in molecule k, $\Gamma_{ij}^{(\mathrm{k})}$ is the nonrandom factor estimated from the composition of molecule k, and $N_m^{(\mathrm{k})}$ is the number of groups of type m associated with molecule k.

Equation 28 can be easily reorganized to the form of the binary interaction model,[14] by defining the group interaction densities as

$$B_{ij}' = S \Gamma_{ij} \Delta E_{ij} \tag{29}$$

$$B_{ij}'^{(\mathrm{k})} = S^{(\mathrm{k})} \Gamma_{ij}^{(\mathrm{k})} \Delta E_{ij}$$

where S is the number of contact sites per unit volume

$$S = (\sum_m z q_m N_m)/V \tag{30}$$

$$S^{(\mathrm{k})} = (\sum_m z q_m N_m^{(\mathrm{k})})/V^{(\mathrm{k})}$$

Equation 28 then becomes

$$\Delta H_{\text{mix}}/V = \sum_i \sum_{j>i} B_{ij}' \Theta_i \Theta_j - \sum_k \sum_i \sum_{j>i} \phi_k B_{ij}'^{(\mathrm{k})} \Theta_i^{(\mathrm{k})} \Theta_j^{(\mathrm{k})} \tag{31}$$

where $\Phi_k = V^{(\mathrm{k})}/V$ is the volume fraction of type k molecules in the system. Equation 31 is identical in form to the binary interaction model, eq 2; however, the interaction densities, B, are now functions of both composition and temperature, through eq 29 and 30, and the compositions, Θ, are area fractions.

UNIQUAC Model. While not derived strictly in accordance with the following, the UNIQUAC model[19] essentially assumes that the contact energy changes on mixing are different, depending on whether i or j is the central atom in the cluster. In essence, this assumption is equivalent to writing

$$(i\text{–}i) + (j\text{–}j) \xrightarrow{\Delta E} (i\text{–}j) + (j\text{–}i)$$

where

$$\Delta E = (E_{ij} - E_{jj}) + (E_{ji} - E_{ii}) = \Delta u_{ij} + \Delta u_{ji} \tag{32}$$

Table I
Summary of UNIQUAC Parameters

groups *i*/*j*	systems studied	data pts	sources	$\Delta u_{ij}/k$, K	$\Delta u_{ji}/k$, K	pct rms error
CH_2/CH_2COO	9	123	30–32	519.4	232.4	29
CH_2/CH_2CH_2OH	15	136	46, 47	2146	736.5	23
$CH_2/CHCl$	8	73	33–36	510.3	145.2	19
CH_2/CH_2CN	7	92	40, 41	563.6	207.2	29
CH_2/CH_2Cl	7	83	34, 35, 37–39	314.5	204.3	9
$CH_2/PhCH$	5	91	42–45	109.5	53.4	5

Table II
Summary of MGQ Parameters

groups *i*/*j*	systems studied	data pts	sources	A_{ij}	ΔE_{ij}, cal/mol	pct rms error
CH_2/CH_2COO	9	123	30–32	1.000	137.4	10
CH_2/CH_2CH_2OH	15	136	46, 47	9.26	3888	9
$CH_2/CHCl$	8	73	33–36	0.752	148.8	13
CH_2/CH_2CN	7	92	40, 41	0.312	185.4	11
CH_2/CH_2Cl	7	83	34, 35, 37–39	0.501	88.3	11
$CH_2/PhCH$	5	91	42–45	0.935	28.8	6
CH_2COO/CH_2CH_2OH	5	85	48–49	0.120	215.3	5
CH_2Cl/CH_2COO	2	12	Table III	2.11	6.55	5
$CHCl/CH_2COO$	2	17	Table III	8.07	23.3	22
*$CH_2/CHCl$[a]	3	23	Table III	0.438	78.3	4
*$CHCl/CH_2COO$[a]	3	23	Table III	2.14	−0.90	4

[a] Parameters with an asterisk simultaneously correlated from data.

The quasi-chemical equilibrium expression, analogous to eq 3, is then

$$\frac{N_{ij}N_{ji}}{4N_{ii}N_{jj}} = \frac{N_{ij}}{2N_{jj}}\,\frac{N_{ji}}{2N_{ii}} = \exp(-\Delta E/kT) = \tau_{ij}\cdot\tau_{ji} \quad (33)$$

where

$$\tau_{ij} = \exp(-\Delta u_{ij}/kT) \quad (34)$$

$$\tau_{ji} = \exp(-\Delta u_{ji}/kT)$$

$$\tau_{ii} = \tau_{jj} = 1$$

Each *i*–*j* pair in the mixture is thus characterized by two parameters; Δu_{ij} and Δu_{ji} or, equivalently, τ_{ij} and τ_{ji}. By substituting eq 12 and 13 into eq 33, it is easy to show that

$$\Gamma_{ij}/\Gamma_{jj} = \tau_{ij} \qquad \Gamma_{ji}/\Gamma_{ii} = \tau_{ji} \quad (35)$$

The continuity of sites, eq 18, further requires that

$$\Gamma_{ii} = 1/\sum_j \tau_{ji}\Theta_j \qquad \Gamma_{ji} = \tau_{ji}/\sum_j \tau_{ji}\Theta_j \quad (36)$$

The potential energy of the mixture, U_{mix}, is given by the expression[19]

$$U_{mix} = (z/2)\sum_i q_iN_i\sum_j \Psi_{ji}E_{ji} = (z/2)\sum_i q_iN_i\sum_j \Theta_j\Gamma_{ji}E_{ji} \quad (37)$$

The energy of pure component *i* is $U_i = zN_iE_{ii}/2$, as before, so that the change in energy on mixing of pure components of the type *i*–*i*, *j*–*j*, etc., is

$$\begin{aligned}\Delta U_{mix} &= U_{mix} - \sum_i U_i = (z/2)\sum_i q_iN_i\sum_j \Psi_{ji}(E_{ji} - E_{ii}) \\ &= (z/2)\sum_i q_iN_i\sum_j \Psi_{ji}\Delta u_{ji} \\ &= (z/2)\sum_i q_iN_i\sum_j \Gamma_{ji}\Theta_j\Delta u_{ji} \\ &= (z/2)(\sum_k q_kN_k)\sum_i\sum_j \Gamma_{ji}\Delta u_{ji}\Theta_i\Theta_j \quad (38)\end{aligned}$$

Provided each real fluid in an experimental mixture can be considered to be a mixture of component sites, one form of the energy of mixing for real fluids is, by analogy with the procedure leading to eq 28

$$\Delta U_{mix} = (z/2)[\sum_m q_mN_m\sum_i\sum_j \Gamma_{ji}\Delta u_{ji}\Theta_i\Theta_j - \sum_k\sum_m q_mN_m^{(k)}\sum_i\sum_j \Gamma_{ji}^{(k)}\Delta u_{ji}\Theta_i^{(k)}\Theta_j^{(k)}] \quad (39)$$

Further rearrangements, along the lines indicated by eq 29 through 31 are possible. There is little apparent difference in the general functional forms of the two models, eq 28 and 39. Both models require two parameters to characterize the *i*–*j* interaction, and both can be placed in a form containing pseudo-binary interaction coefficients. The primary difference between the models is the way in which the local surface fractions of interacting sites are computed. The only way to determine relative superiority is to carefully examine these models by using the same data base. Some comparisons are shown in the following section.

Application to Liquid Heats of Mixing

Heats of mixing for a variety of liquid systems, including esters with alkanes, esters with alcohols, alkanes with chlorinated hydrocarbons, esters with chlorinated hydrocarbons, and alkanes with nitriles are examined below to demonstrate the relative abilities of the MGQ and UNIQUAC models to describe specific systems. These systems are chosen for study because they contain structural elements important to the prediction of polymer–polymer miscibility, discussed in the following section, and because the data are judged to be of high quality.

Calculational Procedures. The general approach for comparing the UNIQUAC and MGQ models was to fit the models to the same good quality heats of mixing data from the literature. Heats of mixing information that could be derived by fitting UNIFAC to vapor–liquid equilibrium data were not used. Model parameters were obtained by fitting the models to the same data sets with a FORTRAN, International Mathematical and Statistical Library, IMSL, nonlinear parameter estimation subroutine called ZXMWD. No preference weights were applied to the data, prior to fitting with the models. The parameters obtained

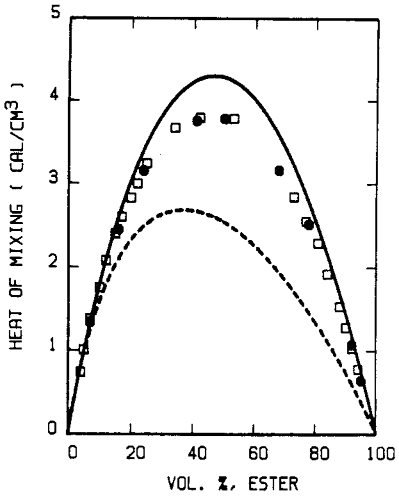

Figure 1. Heats of mixing of methyl acetate with alkanes at 25 °C: □, methyl acetate with *n*-heptane;[32] ●, methyl acetate with *n*-octane;[30] —, estimate by MGQ; ---, estimate by UNIQUAC.

by curve fitting were then used to predict the heats of mixing for systems outside the data set used for parameter estimation. See the Appendix for a sample calculation that shows the procedures used to predict ΔH_{mix} with the MGQ model and previously established parameters.

Comparison of Models. Tables I and II contain the parameter estimates for the UNIQUAC and MGQ models, eq 39 and 28, respectively. The i/j group assignments used, the data sources, and the average root-mean-squared (rms) deviation between the calculated heats of mixing from the listed parameters and the experimental data for each set of systems examined are also summarized in these tables. The first six systems in Tables I and II are common to both models and were deliberately chosen to explore the models' abilities to accurately fit mixtures of polar with nonpolar molecules while the number of interacting groups to be considered were minimized. For example, the first system is heats of mixing for aliphatic esters with alkanes. This system requires determination of only the CH_2/CH_2COO group interaction, since UNIQUAC considers that CH_3 is equivalent to CH_2, a convention which is followed for both models in the present work. The second system similarly uses heats of mixing of alkanes with aliphatic alcohols to obtain the CH_2/CH_2CH_2OH group interaction. This general strategy is employed to obtain the remaining group interactions for the first six systems in Tables I and II.

A direct comparison of the two models can be made by examining the rms error for the first six systems in Table I and II. Both models describe weakly interacting systems equally well, as evidenced by the generally good fits obtained for $CH_2/PhCH$ and CH_2/CH_2Cl containing systems. The relatively low magnitudes of their energy parameters confirm that these systems are weakly interacting, and the local area fractions are close to the random fractions determined solely from system compositions, regardless of the model employed. As the energy parameters become larger in magnitude, suggesting more energetic interactions, the MGQ model appears to fit better the heats of mixing data. This may suggest that the MGQ model more properly accounts for local nonrandomness in mixtures of polar with nonpolar fluids. Conversely, it may do so by simply being mathematically more relaxed than the UNIQUAC model. That is, no constraint is placed on the parameter A_{ij} in the MGQ model, but the UNIQUAC model requires that eq 32 be satisfied during the parameter estimating process.

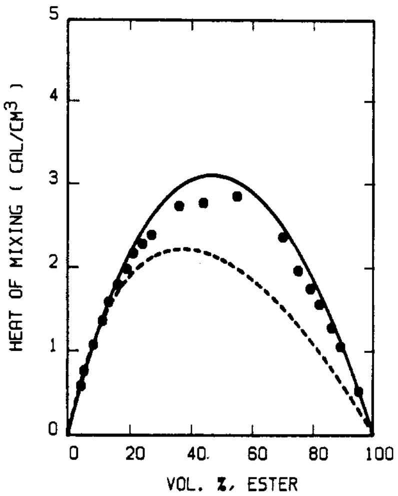

Figure 2. Heats of mixing of ethyl acetate with *n*-dodecane at 25 °C: ●, data from ref 30; —, estimate by MGQ; ---, estimate by UNIQUAC.

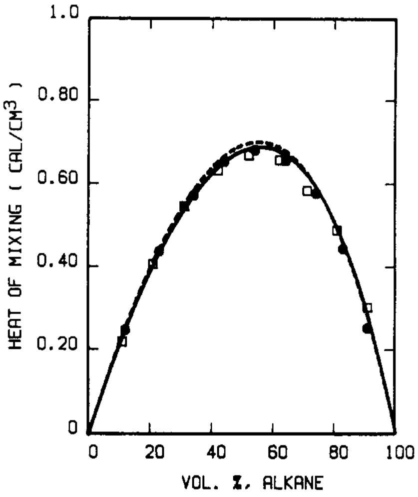

Figure 3. Heats of mixing of 1-chlorohexane with alkanes at 25 °C: ●, 1-chlorohexane with octane;[39] □, 1-chlorohexane with heptane;[39] —, estimate by MGQ; ---, estimate by UNIQUAC.

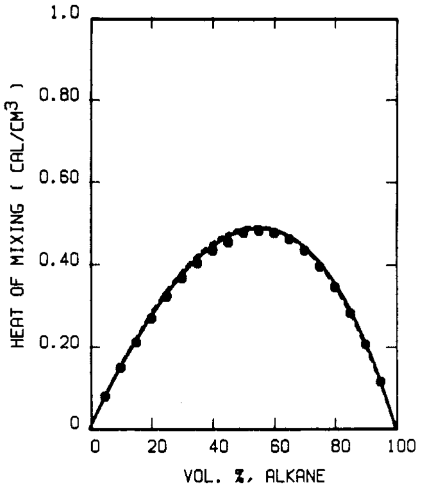

Figure 4. Heats of mixing of 1-chlorooctane with octane at 25 °C: ●, data from ref 38; —, estimate by MGQ; ---, estimate by UNIQUAC.

Figures 1–5 show the relative abilities of the two models to predict heats of mixing for systems outside the data bases used to generate the parameters in Table I and II. The MGQ model seems to be generally superior to UNIQUAC or UNIFAC as a predictive model for the systems

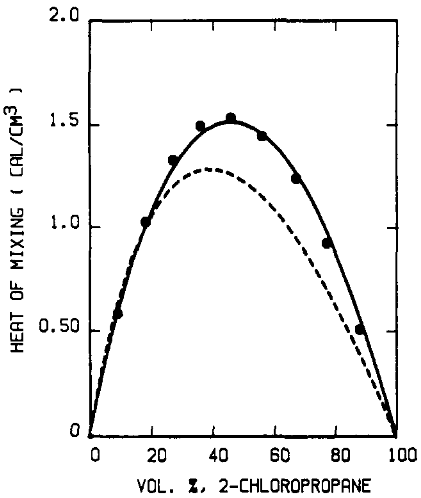

Figure 5. Heats of mixing of 2-chloropropane with cyclohexane at 10 °C: ●, data from ref 33; —, estimate by MGQ; ---, estimate by UNIQUAC.

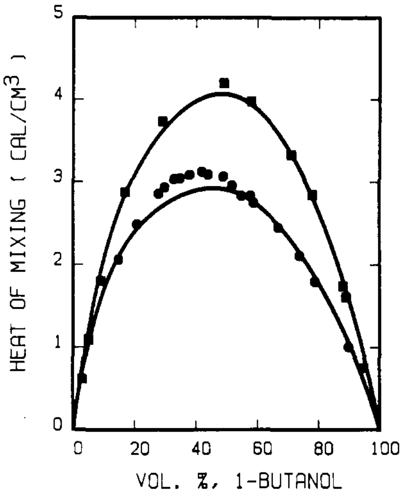

Figure 6. Heats of mixing of aliphatic esters with alcohol at 25 °C: ■, ethyl acetate with 1-butanol;[56] ●, butyl acetate with 1-butanol;[48] —, estimate by MGQ.

examined. Figures 1 and 2 show that the MGQ model tends to overpredict, somewhat, the heats of mixing of alkanes with esters; however, the model more closely predicts these systems than does UNIQUAC that greatly underpredicts the response. Both models accurately predict the heats of mixing of chlorinated alkanes with alkanes, Figure 3 and 4; however, the MGQ model is again superior to UNIQUAC when predicting the heat of mixing for chlorinated alkanes with cyclohexane (Figure 5). The inability of UNIQUAC or UNIFAC to accurately fit or predict heats of mixing of polar species is well recognized, and several improvements to the original model have been made.[24,50,51] Generally, these modifications require additional parameters to account for the assumed effects of solvation, hydrogen bonding, etc. The MGQ model compares well with these modified versions of UNIQUAC without the need for additional parameters.

The ability of the MGQ model to successfully predict heats of mixing of complex molecules is illustrated in Figure 6. Prediction of heats of mixing of aliphatic alcohols with aliphatic esters requires three interaction parameters corresponding to the CH_2/CH_2COO, CH_2/CH_2CH_2OH, and CH_2COO/CH_2CH_2OH pairs in the system. Once again, the interaction parameters (Table II), used to predict the lines in Figure 7, were evaluated from experiments other than the butanol/ester data in this figure. Agreement between prediction and experiment is quite good. A similar comparison using UNIQUAC was not attempted due to the poor fit of that model to the ester/alkane and alkane/alcohol data bases (Table I).

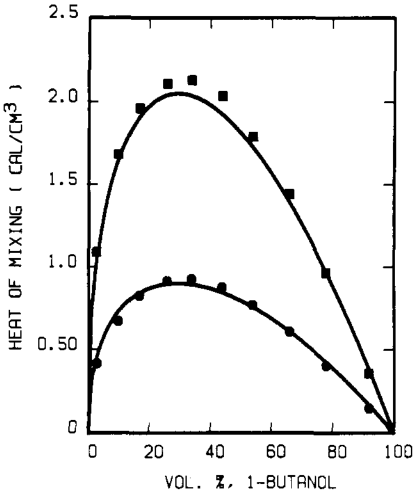

Figure 7. Effect of temperature on heats of mixing of 1-butanol with heptane:[47] ■, data at 15 °C; ●, data at 55 °C; —, estimates by MGQ.

The MGQ model seems to be able to predict the temperature dependency of the heat of mixing of alcohols with alkanes, as illustrated in Figure 7. This may be a fortuitous result, as we have not extensively explored this aspect of the model with many different systems, but it is certainly encouraging. As discussed below, the reason for this success may be related to the dominating influence of the hydrogen bond between alcohol molecules. By contrast, the UNIQUAC calculation for this system underpredicts the observed change in ΔH_{mix} with temperature by more than a factor of 2, a situation which causes or results from an overprediction of ΔH_{mix} at 15 °C and an underprediction at 55 °C.

To permit as fair a comparison as possible, the choice of interacting groups follows UNIQUAC or UNIFAC where possible. One change from this strategy is noted by the separate identification of CHCl and CH_2Cl moieties in Table I and II. Analysis of the data for chlorinated hydrocarbon mixtures with alkanes by either UNIQUAC or MGQ model suggests that simply assigning CH_xCl is insufficient to describe the apparently different dependency of heat of mixing on CHCl versus CH_2Cl groups. This suggests that the UNIQUAC classification of groups should be modified to account for this difference. Thomas and Ekerdt[52] have also observed thermodynamic differences that seem to depend on whether the halogen is substituted as CHCl or CH_2Cl.

Experimental Heats of Mixing. Heats of mixing of esters with 1,3-dichlorobutane[10] were recently examined by this laboratory for the purpose of predicting the range of aliphatic polyester compositions which are miscible with poly(vinyl chloride), PVC, and binary interaction parameters corresponding to CH_x/COO, $CH_x/CHCl$, and CHCl/COO interactions were evaluated. Since evidence exists to suggest that CHCl and CH_2Cl units interact differently with alkanes and since 1,3-dichlorobutane contains both units, it was considered important to reexamine these mixtures with halocarbons that contain either CHCl or CH_2Cl units but not both. Virtually no data with sufficient quality were available in the literature. Consequently, an experimental program was established to obtain these measurements for 2,3-dichlorobutane/ester mixtures and for mixtures of esters with 1,5-dichloro-

Table III
Experimental Heats of Mixing

1,5-dichloropentane[a] and propyl butyrate (25 °C)		1,4-dichlorobutane[b] and diethyl adipate (25 °C)	
a, mol %	ΔH_{mix}, J/mol	**b**, mol %	ΔH_{mix}, J/mol
30.7	-159	47.0	-255
37.4	-162	54.5	-269
41.0	-159	63.9	-248
44.2	-158	73.7	-169
50.4	-146		
58.1	-135		
63.0	-123		
69.2	-104		

2,3-dichlorobutane[c] and propyl butyrate (25 °C)		2,3-dichlorobutane[d] and ethyl heptanoate (25 °C)	
c, mol %	ΔH_{mix}, J/mol	**d**, mol %	ΔH_{mix}, J/mol
34.4	-318	33.5	-251
41.2	-344	39.0	-270
45.7	-351	46.6	-278
50.6	-348	54.7	-272
61.2	-328	60.7	-259
66.7	-303	66.8	-228
74.6	-252	72.6	-201

2,3-dichlorobutane[e] and diethyl adipate (30 °C)		2,3-dichlorobutane[f] and diethyl sebacate (30 °C)	
e, mol %	ΔH_{mix}, J/mol	**f**, mol %	ΔH_{mix}, J/mol
82.1	-289	80.6	-371
79.7	-315	77.8	-399
74.9	-354	68.2	-482
69.4	-388	62.4	-492
64.2	-414	58.1	-493
53.3	-417	52.1	-488
46.8	-393	46.2	-466
45.6	-388	37.2	-416
41.4	-372		

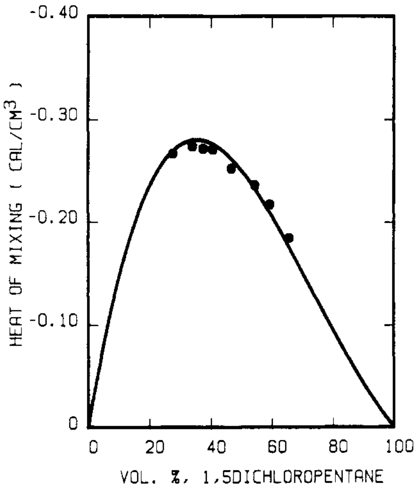

Figure 8. Heats of mixing of 1,5-dichloropentane with propyl butyrate at 25 °C: ●, data from Table III; —, estimate by MGQ.

pentane and with 1,4-dichlorobutane.

An LKB Model 2107 batch calorimeter was used to obtain heats of mixing. This calorimeter is able to measure heats of mixing to within an estimated relative error of about 3%. Most of this error appears to result from the vapor space present in the mixing cell. With the exception of diethyl sebacate, which was obtained from Kodak, all of the chemicals listed in Table III, were obtained from Aldrich Chemical Co. The purity of all chemicals used in the study was at least 98%, and all materials were used without further purification.

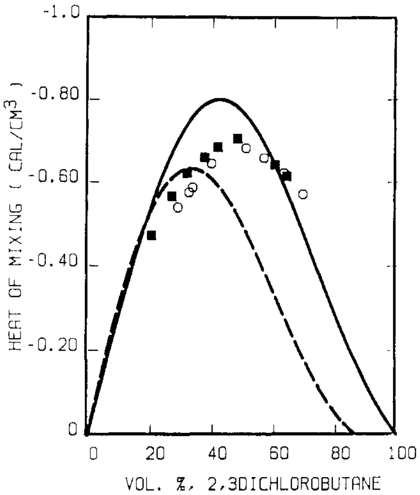

Figure 9. Heats of mixing of 2,3-dichlorobutane with diethyl adipate (○, —) and with diethyl sebacate (■, - - -). Data are from Table III, and lines are estimated by MGQ.

As illustrated by Figure 8, heats of mixing of aliphatic chlorides containing CH_2Cl with esters can be well represented by using the CH_2Cl/CH_2 and the CH_2/CH_2COO parameter values previously obtained from other experiments (Table II), and curve fitting to determine CH_2Cl/CH_2COO parameter values. While the data set is somewhat limited, ΔE_{ij} = 6.55 cal/mol and A_{ij} = 2.112 are found to describe the CH_2Cl/CH_2COO interaction and to fit, to within 5% error, the heats of mixing of selected esters with either 1,5-dichloropentane or 1,4-dichlorobutane.

Similar attempts to obtain the $CHCl/CH_2COO$ interaction parameter values from heats of mixing of the esters in Table III with 2,3-dichlorobutane and from the prescribed parameters for the $CHCl/CH_2$ and CH_2/CH_2COO interactions (Table II), were not very successful. Figure 9 shows typical comparisons between model and experiments using the best fit $CHCl/CH_2COO$ parameter values, ΔE_{ij} = 23.3 cal/mol and A_{ij} = 8.07. Clearly, the model does not fit the data well, a fact also indicated by the 22% rms error associated with the $CHCl/CH_2COO$ parameter values in Table II. The reason for this failure seems to be that the model with these parameters requires the maxima in the heats of mixing to occur at ester contents greater than 50% by volume while the experimental data show maxima near 50% by volume. By contrast, mixtures containing CH_2Cl units (Figure 8) have experimental maxima at ester contents greater than 50% and are consequently well fit by the MGQ model.

The failure of the model to describe the heats of mixing of 2,3-dichlorobutane with esters may be associated with incorrect parameter values obtained from literature data. That is, the values found for CH_2/CH_2Cl interactions are distinctly different from those found for $CH_2/CHCl$, see Table II, and one could question whether such differences should exist. Of course, the error could also reside in the parameter values obtained for the CH_2/CH_2COO interaction; however, the differences in the ability of the model to fit the halocarbon/ester systems cited above suggest that the problem may indeed be with the parameter values assigned to the $CH_2/CHCl$ interaction. One way to examine the validity of parameter values is to fit the 2,3-dichlorobutane/ester data by prescribing only the CH_2/CH_2COO interaction values, thereby simultaneously evaluating the parameters for both the $CH_2/CHCl$ and the $CHCl/CH_2COO$ interactions from the data in Table III. This approach yields the parameter values $*CH_2/CHCl$ and $*CHCl/CH_2COO$ in Table II. As shown there, simultaneously evaluating two sets of parameters does lead to a better fit of the data and reduces the rms error to about 4%. Interestingly, the $*CH_2/CHCl$ parameter value is quite similar to the CH_2/CH_2Cl interaction obtained by fitting literature data with the first strategy described above. This suggests that the UNIQUAC assertion that CH_xCl is sufficient to describe chlorocarbon structure is correct and that some portion of the data set in references[33-36] is simply in error. Also of interest is the suggestion of a weak exothermic complex between CHCl and CH_2COO moieties, as indicated by the small negative ΔE_{ij} value for the $*CHCl/CH_2COO$ parameter. This is discussed in greater detail below.

Interpretation of Parameters. With the limited number of parameters available for study, it is probably premature to place too strong a physical interpretation on their relative values. Nonetheless there are some indications that the parameters in Table II may have physical meaning.

Both A_{ij} or ΔS_{ij}, see eq 9, and ΔE_{ij} are large and positive for alcohol/alkane mixtures. This is consistent with the well-known hydrogen bonding between alcohol molecules in the pure state which causes that pure state to be more highly ordered than the solution, viz. $S_{ij} > (S_{ii} + S_{jj})/2$. Substantial energy must be added to create i/j pairs in this system, and the ΔE_{ij} parameter, though a bit low, is close to the 4500–6500 cal/(g·mol) range normally cited for hydrogen-bond formation.[53]

The chlorinated hydrocarbon/ester systems also show relatively large positive ΔS_{ij} values, although solutions containing these groups are nearly athermal, as judged by the small ΔE_{ij} parameters associated with the CH_2Cl/CH_2COO and $*CHCl/CH_2COO$ pairs. Since the ester portion of these pairs does not seem to be associated in the pure state (ΔS_{ij} is zero for alkane/ester interactions in Table II), the positive values of ΔS_{ij} must be the result of organization in the pure states of the chlorinated hydrocarbons. Local dipoles in the halogenated hydrocarbons may be responsible for this behavior. Interaction of these dipoles with the ester carbonyl have been held responsible for the miscibility of poly(vinyl chloride) with aliphatic polyesters.[54,55] Since the heats of mixing of esters with chlorinated hydrocarbons are exothermic (see Table III) whereas the mixing heats for mixtures of chlorinated hydrocarbons with alkanes are endothermic, it is not surprising that the ΔE_{ij} parameters for the formation of the halocarbon/ester pairs are less positive than for the halocarbon/alkane pairs. What is not understood is why the ΔS_{ij} for formation of halocarbon/ester pairs is so much larger than that for halocarbon/alkane pairs.

Further work is obviously necessary to establish the physical meaning, if any, of the two parameters in the MGQ model. Regardless of the outcome, however, the MGQ model still seems to be superior to UNIQUAC for predicting heats of mixing of liquids. Its ability to use group contribution parameters, obtained from liquid heats of mixing, to predict polymer–polymer miscibility is demonstrated in the following section.

Prediction of Polymer–Polymer Miscibility

A series of linear aliphatic polyesters having CH_2/COO ratios in their repeat structures from 2 to 14 were recently examined for miscibility with poly(vinyl chloride), PVC, by this laboratory.[10] In that study, the binary interaction model, eq 2, was used to obtain B_{ij} parameters from heats of mixing of esters, chosen to have CH_2/COO ratios in the same range as those of the polyesters, with 1,3-dichlorobutane. This information was then augmented with heats of mixing information for hexane with several chlorinated hydrocarbons and for the esters with hexane to obtain the three parameters, corresponding to CH_x/COO, $CH_x/CHCl$, and COO/CHCl interactions, considered important. These parameters were found to be all positive. The pseudobinary interaction coefficient for mixing of ester with 1,3-dichlorobutane was then computed via

$$B = \Delta H_{mix}/V\Phi_1\Phi_2 \qquad (40)$$

where Φ_1 is the volume fraction ester, Φ_2 is that of the halogenated hydrocarbon, and $\Delta H_{mix}/V$ was calculated by using eq 2 and the B_{ij} parameters mentioned above. These results were compared with experimental B values obtained from analysis of the melting point depressions of the polyesters in blends with PVC. While the variation of B with CH_x/COO ratio was found to be similar for both experiments, the B values from analogue calorimetry were less negative than those from melting point depression studies by a factor of approximately 2.

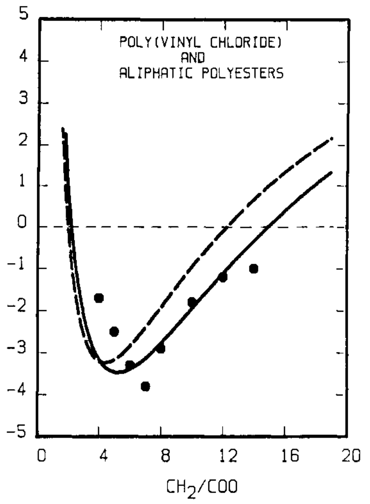

Figure 10. Comparison of binary interaction parameters for PVC with aliphatic polyesters which contain various CH_2/COO ratios: ●, data from ref 10; —, MGQ estimate at 60 °C for PVC volume fraction = 0.10; ---, MGQ estimate at 60 °C for PVC volume fraction = 0.50.

Figure 10 compares the observed B values with those calculated by the MGQ model and the parameters corresponding to $*CHCl/CH_2COO$, $*CH_2/CHCl$, and CH_2/CH_2COO interactions, given in Table II. For purposes of this comparison, binary interaction parameters for the mixture of PVC and polyester structural units are computed from eq 40 and 31 for various CH_2/COO ratios. Qualitatively, the MGQ model seems to predict both the general shape and the magnitude of the B response to polyester composition and to correctly suggest that miscible PVC/polyester blends are probable when the CH_2/COO ratio in the polyester is between 2 and 14.

As can be seen from the parameter values, Table II, the MGQ model also seems to verify previous suggestions[10,14] that relatively strong endothermic interactions between structural groups on the pure components are an important factor which can help to cause the exothermic heat of mixing required to form a miscible high polymer blend. The PVC/polyester system is especially interesting in this regard because the overall exothermicity is driven by the replacement of endothermic $*CH_2/CHCl$ and CH_2/CH_2COO pure component interactions with essentially athermal $*CHCl/CH_2COO$ interactions on mixing.

Since the interaction densities in eq 31 are complex functions of composition and temperature, the calculated B must generally be a function of these variables. The interaction energy ratios, $\Delta E_{ij}/RT$, are all quite small in this particular system, however, and the calculated variation of B with temperature is less than 3% in 100 °C, a change which is too small to be displayed in Figure 10. Calculated B values do vary substantially with changes in the volume fraction of PVC in the blend, as illustrated by the two curves in Figure 10. This variation with PVC fraction should cause the polyester melting points in the blends to decrease nonlinearly in a concave-up manner when plotted against the increasing square of the PVC volume fraction, and the observation of such nonlinear behavior could be considered to be a partial proof of the MGQ model. The equilibrium melting points[57] have been examined and could be interpreted to vary with PVC volume fraction in the manner suggested by the model; however, data precision is too poor to reach a definite conclusion.

Summary and Conclusions

The ultimate purpose of the research described in this paper is to improve methods for predicting polymer–polymer miscibility by finding heats of mixing models that can accurately fit experimental data for a broad range of liquids and that require a minimum number of group contribution parameters. In principle, the availability of such models and of catalogs of parameters for group interactions corresponding to the models could provide a way to numerically screen atactic polymer pairs for potential miscibility from knowledge of only their repeat structures.

Both the MGQ and the UNIFAC/UNIQUAC models require two parameters per interacting group and are substantially better able to fit a wide range of data than is a van Laar model with only one parameter per group. Both models achieve this additional flexibility through the assumption of local nonrandomness, but they differ somewhat in their formulation of this assumption. Both models are undoubtedly empirical, however, and users should not become overly concerned with the physical interpretations of the models or their parameters. The MGQ model seems to be superior to the UNIQUAC model for predicting heats of mixing where at least one of the components in the binary is polar. Since many polymer blends are comprised of polar polymers, the MGQ model should prove to be superior to UNIQUAC for predicting polymer–polymer miscibility from liquid heats of mixing data.

This paper indicates that it is possible to predict polymer–polymer miscibility through use of a group contribution based model for the heat of mixing. A flexible model, such as the MGQ model, and very high quality heats of mixing data are required to do this successfully. Models that are able to fit and predict liquid heats of mixing to within 5% relative error will generally yield group interaction parameters which are sufficiently accurate to permit reasonable prediction of polymer–polymer miscibility for atactic systems. Subsequent papers in this series will use the MGQ model to characterize additional systems and to broaden the base of group contribution parameters.

The MGQ model seems to describe the heat of mixing between polymer repeat units, and the apparent binary interaction parameter, B, calculated from this model is also a function of temperature. Some preliminary work suggests that the MGQ model, like the simpler Flory–Huggins theory, is still not able to predict lower critical solution temperature, LCST, behavior. The temperature variation of B is simply too small to explain phase splitting by purely enthalpic considerations. We are presently attempting to combine aspects of the MGQ model with "equation of state" theories to provide the additional information required to predict LCST behavior.[58-62]

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Appendix

The calculational steps associated with using the MGQ model to estimate heats of mixing are shown below for a mixture of 1,5-dichloropentane (1) with propyl butyrate (2) at 298.15 K. The solution contains $\phi_1 = 0.2746$, where ϕ_1 is the volume fraction of material 1. Pure component 1 has a density, $\rho_1 = 1.106$ g/mL, and a molecular weight, $M_1 = 141$ g/mol. The density and molecular weight for component 2 are $\rho_2 = 0.873$ g/mL and $M_2 = 134$ g/mol.

It is convenient to define a structural coefficient, ν_{ik}, to express the number of groups i per molecule k. The compositional quantities of interest can then be easily determined by the equations

$$N_i/V = \sum_k \phi_k \rho_k \nu_{ik}/M_k \tag{41}$$

$$N_i^{(k)}/V^{(k)} = \rho_k \nu_{ik}/M_k \tag{42}$$

$$\Theta_i = \frac{\sum_k \phi_k \rho_k \nu_{ik} q_i/M_k}{\sum_i \sum_k \phi_k \rho_k \nu_{ik} q_i/M_k} \tag{43}$$

$$\Theta_i^{(k)} = \frac{\nu_{ik} q_i}{\sum_i \nu_{ik} q_i} \tag{44}$$

The structural groups and associated surface parameters, q_i, are obtained from Bondi[29] and are assigned as follows: class 1, CH_2 group, $q_1 = 0.54$ and CH_3 group, $q_2 = 0.85$; class 2, CH_2COO group, $q_3 = 1.420$; class 3, CH_2Cl group, $q_4 = 1.264$. The structural coefficients, ν_{ij}, are then as follows: Dichloropentane ($k = 1$): $\nu_{11} = 3$, $\nu_{21} = 0$, $\nu_{31} = 0$, $\nu_{41} = 2$. Propyl butyrate ($k = 2$): $\nu_{12} = 3$, $\nu_{22} = 2$, $\nu_{32} = 1$, $\nu_{42} = 0$. From eq 43, the fraction of each class of groups in the mixture is calculated to be $\Theta_1 = 0.6136$, $\Theta_2 = 0.2161$, and $\Theta_3 = 0.1703$. From eq 44, the fraction of each class of groups in pure component 1 is calculated to be $\pm_1^{(1)} = 0.3905$, $\Theta_2^{(1)} = 0$, and $\Theta_3^{(1)} = 0.6095$, and the fractions of classes in pure component 2 are $\Theta_1^{(2)} = 0.7002$, $\Theta_2^{(2)} = 0.2998$, and $\Theta_3^{(2)} = 0$.

Three binary interaction parameters are required to describe both the inter- and intramolecular interactions between classes of groups on materials 1 and 2. These are taken from Table II to be $\Delta E_{12} = 137.4$ cal/mol and $A_{12} = 1.00$, $\Delta E_{13} = 88.3$ cal/mol and $A_{13} = 0.501$, and $\Delta E_{23} = 6.55$ cal/mol and $A_{23} = 2.112$.

The nonrandom parameters associated with the intramolecular interactions between classes of groups in the pure components can be easily determined from equations, similar in form to eq 24 and 25, because each pure component in this example calculation can be considered a simple binary mixture. For pure component 1, containing classes 1 and 3

$$F_{13} = A_{13} \exp(-2\Delta E_{13}/RT) = 0.3719$$

$$\Gamma_{13}^{(1)} = \frac{-F_{13} + (F_{13}^2 + 4F_{13}\Theta_1^{(1)}\Theta_3^{(1)}(1 - F_{13}))^{1/2}}{2\Theta_1^{(1)}\Theta_3^{(1)}(1 - F_{13})}$$

$$\Gamma_{13}^{(1)} = 0.7648$$

Similarly, for pure component 2, $F_{12} = 0.6289$ and $\Gamma_{12}^{(2)} = 0.8997$.

The nonrandom parameters for the mixture of classes of groups are obtained by simultaneously solving the following equations

$$\frac{\Gamma_{12}^2}{\Gamma_{11}\Gamma_{22}} = A_{12}\exp(-2\Delta E_{12}/RT)$$

$$\frac{\Gamma_{13}^2}{\Gamma_{11}\Gamma_{33}} = A_{13}\exp(-2\Delta E_{13}/RT)$$

$$\frac{\Gamma_{23}^2}{\Gamma_{22}\Gamma_{33}} = A_{23}\exp(-2\Delta E_{23}/RT)$$

$$\Theta_1\Gamma_{11} + \Theta_2\Gamma_{21} + \Theta_3\Gamma_{31} = 1.0$$

$$\Theta_1\Gamma_{12} + \Theta_2\Gamma_{22} + \Theta_3\Gamma_{32} = 1.0$$

$$\Theta_1\Gamma_{13} + \Theta_2\Gamma_{23} + \Theta_3\Gamma_{33} = 1.0$$

$$\Gamma_{12} = \Gamma_{21} \qquad \Gamma_{13} = \Gamma_{31} \qquad \Gamma_{23} = \Gamma_{32}$$

The FORTRAN subroutine HYBRJ1 from the MINPAC FORTRAN library has been used to solve the above equations with a CDC dual cyber computer. The equations can also be quickly solved with an IBM PC/AT using a Newton iteration method described elsewhere.[63,64] The Γ_{ij} values for this example are $\Gamma_{12} = 0.8394$, $\Gamma_{13} = 0.7237$, and $\Gamma_{23} = 1.5932$. With use of a coordination number, z, equal to 10, the contacts per unit volume, S, $S^{(1)}$, and $S^{(2)}$ are estimated from eq 30, 41, and 42 to be $S = 0.3197$ mol/cm^3, $S^{(1)} = 0.3253$ mol/cm^3, and $S^{(2)} = 0.3176$ mol/cm^3. The heat of mixing is then calculated by eq 29 and 31 to be

$$\Delta H_{\text{mix}}/V = S(\Gamma_{12}\Delta E_{12}\Theta_1\Theta_2 + \Gamma_{13}\Delta E_{13}\Theta_1\Theta_3 + \Gamma_{23}\Delta E_{23}\Theta_2\Theta_3) - \phi_1 S^{(1)}\Gamma_{13}{}^{(1)}\Theta_1{}^{(1)}\Theta_3{}^{(1)} - \phi_2 S^{(2)}\Gamma_{12}{}^{(2)}\Theta_1{}^{(2)}\Theta_2{}^{(2)}$$

$$\Delta H_{\text{mix}}/V = 7.1468 - 1.4358 - 5.9786$$

$$\Delta H_{\text{mix}}/V = -0.2676\ \text{cal/cm}^3$$

The experimental heat of mixing for this composition is observed to be $\Delta H_{\text{mix}}/V = -0.2669$ cal/cm^3.

Nomenclature

A_{ij}	quasi-chemical parameter related to exchange entropy, ΔS_{ij}
A_{wi}: cm^2/mol	Bondi area of structural group i
B_{ij}: J/m^3, cal/cm^3	interaction energy density between components i and j
E_{ij}: J, cal/mol	energy per i–j contact pair
ΔE_{ij}: J, cal/mol	exchange energy for formation of i–j pair
ΔF_{ij}: J, cal/mol	change in Helmholz free energy for formation of i–j pair
ΔH_{mix}: J, cal	enthalpy of mixing
k: J/K, cal/K	Boltzmann constant
N_i: mol	numbers or moles of i groups
N_{ij}: mol	numbers or moles or i–j contacts
$\mathcal{N}$: mol	numbers or moles of i–j contacts in a random, athermal, mixture
q_i	surface area parameter for group i
S: 1/m^3, mol/cm^3	contact sites per unit volume
S_{ij}: J/(mol K), cal/(mol K)	entropy per i–j contact pair
ΔS_{ij}: J/(mol K), cal/(mol K)	exchange entropy for formation of i–j contact pairs
T: K	absolute temperature
U_{mix}: cal, J	potential energy of mixture
U_i: cal, J	potential energy of component i
ΔU_{mix}: cal, J	potential energy of mixing
Δu_{ji}: cal, J	UNIQUAC energy parameter
V: cm^3, m^3	system volume
z	coordination number
Γ_{ij}	nonrandom parameter
Θ_i	surface fraction of group i in mixture
$\Theta_i{}^{(k)}$	surface fraction of group i in molecule k
τ_{ij}	UNIQUAC parameter
Φ_i	volume fraction of species i in multicomponent mixture
$\Psi_i{}^k$	volume fraction unit i on polymer k
Ψ_{ji}	local surface fraction of j available for contact with central unit i
Ψ_i	volume fraction unit i in the blend

Registry No. PVC, 9002-86-2; 1,5-dichloropentane, 628-76-2; propyl butyrate, 105-66-8; 2,3-dichlorobutane, 7581-97-7; diethyl adipate, 141-28-6; 1,4-dichlorobutane, 110-56-5; ethyl heptanoate, 106-30-9; diethyl sebacate, 110-40-7; methyl acetate, 79-20-9; heptane, 142-82-5; ethyl acetate, 141-78-6; dodecane, 112-40-3; 1-chlorohexane, 544-10-5; 1-chlorooctane, 111-85-3; octane, 111-65-9; 2-chloropropane, 75-29-6; cyclohexane, 110-82-7; 1-butanol, 71-36-3.

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Static and Dynamic Light Scattering Studies of Poly(terephthalic acid–4-aminobenzohydrazide) in Dimethyl Sulfoxide

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ABSTRACT: Eleven narrow fractions between 3.78×10^3 and 2.62×10^5 g/mol of poly(terephthalic acid–4-aminobenzohydrazide) were studied in dimethyl sulfoxide. The molecular weight dependence of the intrinsic viscosity, molecular anisotropy, radius of gyration, and the diffusion coefficient, D_0, was used to derive a persistence length, q, of 105 ± 10 Å. The trend found in D_0, being less sensitive to chain expansion in a good solvent, supports the neglect of correcting molecular dimensions for the excluded-volume effect. An application of the Yamakawa–Stockmayer treatment for the expansion factor, α_s, for wormlike chains shows that the Kuhn limit is reached at nearly 6×10^4 g/mol while α_s^2 does not exceed 1.05 at a molecular weight of 2×10^5 g/mol.

Introduction

Workers at Monsanto developed a high modulus, heat-resistant fiber, X-500, by wet-spinning the poly(terephthalic acid–4-aminobenzohydrazide) from dimethyl acetamide (DMAC) or dimethyl sulfoxide (DMSO) with and without LiCl.[1] Even though the X-500 fibers attained high strength, their performance did not attain, much less exceed, that of Du Pont's Kevlar and X-500 was hence never commercialized.

An important distinction between these two materials exists with regard to their phase behavior in concentrated solution. Poly(*p*-phenylenediamine–terephthalic acid) (PPTA) forms a nematic liquid crystal at approximately 8% by weight in 96% sulfuric acid at 25 °C.[2] Optimum fiber properties result when spinning from 20% (wt/wt) solutions at 80 °C.[2] The ordered nematic phase assists in producing fibers having polymer chains highly oriented along the fiber direction. In contrast, a mesophase for the X-500/DMSO or DMAC systems (with or without added salt) is not observed even up to 27% (w/w) at 25 °C.[3] The solubility of X-500 decreases with increasing temperature.[3]

Table I
Literature Values Reported for the Persistence Length of X-500 in DMSO or DMAC at 25 °C

method	q, Å	ref
birefringence techniques	240–400	6–8
SLS	35–60 (70–80)	9
[η]	49 (70)	3
SAXS[a]	71–88 (90–98)[b]	10
SLS, [η]	100–120	11
flow birefringence	125	12
SLS, [η]	112	13

[a] Small-angle X-ray scattering. [b] DMAC.

X-500 is soluble in sulfuric acid but degrades in that solvent at room temperature. However, Morgan[4] observed a liquid crystal solution at a concentration of 10% (w/w) for X-500 in sulfuric acid at 0 °C. We are not aware of X-500 fiber produced under these conditions.

The difference in phase behavior between X-500 in DMSO at 25 °C and in H_2SO_4 at 0 °C suggests a more flexible chain in DMSO. The characterization of chain flexibility of X-500 in DMSO or DMAC at 25 °C has been

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