Prediction of compatibility in polymer–plasticizer systems

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(Received 14 August 1989; revised 21 November 1989; accepted 22 November 1989)

The UNIFAC group contribution method has been used to calculate the free energy of mixing *versus* composition curves for several polymer–plasticizer systems, including phthalates and stearates with poly(vinyl chloride). The solubility of the plasticizer has been calculated from the curves and compared with experimental results. Although the absolute values of the solubilities were underestimated, the relative solubilities amongst groups of compounds were predicted well, so that the method may be useful in the prediction of compatibility in these systems.

(Keywords: plasticizers; solubility; compatibility)

INTRODUCTION

Few polymers are used commercially in a pure state as they generally require some of their properties to be modified by the inclusion of plasticizers, antioxidants or other additives. Clearly, the solubility of these additives in the polymer is crucial to their use, and it is perhaps surprising that little quantitative work has appeared on these systems, certainly when compared to polymer–solvent mixtures or polymer blends. One explanation for this is that the experimental methods for the direct study of the thermodynamics of these systems are difficult[1], while the results from indirect studies such as vapour sorption or gas chromatography are often open to considerable doubt[2]. A method for the reliable prediction of the phase equilibria of polymer–plasticizer systems would be very useful, but those based on existing models such as the Flory–Huggins or solubility parameter treatments are of limited use in many cases[3].

A number of techniques that involve group contribution methods for predicting thermodynamic properties of solution have been proposed. Of these, perhaps the most useful has been UNIFAC, first applied to polymer solutions by Oishi and Prausnitz[4]. Gottlieb and Herskowitz[5] applied the method to solutions of poly(dimethylsiloxane) and found reasonable prediction of the Flory–Huggins interaction parameter χ. For the same polymer, Price and Ashworth[6] found that UNIFAC predicted the wrong variation of χ with molecular weight, but that the predictions could be much improved if a single experimental result were available. More recently, Patwardhan and Belfiore[7,8] have applied UNIFAC to a number of polymer–solvent and polymer–polymer mixtures, and have suggested explanations in some cases where the results did not agree with experiment.

In this paper, we present UNIFAC predictions for mixtures including a range of stearates or phthalates in poly(vinyl chloride) (PVC) and squalane in poly(dimethylsiloxane) of varying molecular weights, and compare their phase behaviour with experimental results.

THEORETICAL

The primary condition for two components to form a completely miscible system is that the free energy of mixing ΔG^{m} should be negative across the whole concentration range. However, this is not a sufficient condition since a mixture will split into two phases if this results in a lowering of the free energy, and it may be shown[1] that this implies that, for complete miscibility, the free energy–concentration curve must be concave downwards throughout, as shown in *Figure 1a*. If the curve has the form of *Figure 1b* then compositions between the two minima will be unstable with respect to phase separation and the system will be partially miscible.

The thermodynamic conditions for equilibrium between the phases is that the chemical potential, and hence the change in chemical potential on mixing, $\Delta\mu_i$, of each component (say 1 and 2) must be equal in each phase. Thus, for two phases, A and B:

$$\Delta\mu_1^{A} = \Delta\mu_1^{B} \quad \text{and} \quad \Delta\mu_2^{A} = \Delta\mu_2^{B} \tag{1}$$

Since

$$\Delta\mu_i = (\partial \Delta G^{m} / \partial x_i) \tag{2}$$

where x_i is the mole fraction concentration, it follows that the compositions where the chemical potentials are equal (and hence of the conjugate phases) are given where the curve has equal slope and therefore by the points of contact of a common tangent, as shown in *Figure 1b*, and not by the compositions of minimum free energy as are sometimes taken.

In many systems such as those studied here, the polymer is essentially insoluble in the lower-molecular-weight liquid. Thus the free energy–composition curve is as shown in *Figure 1c* with one minimum effectively

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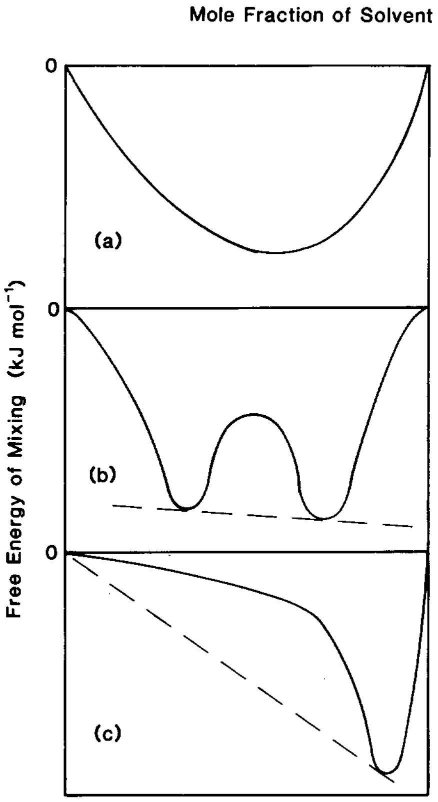

Figure 1 Typical free energy of mixing *versus* composition curves in binary systems: (a) miscible in all proportions; (b) partially miscible; (c) partially miscible with one polymer component

located at the origin[9]. In these cases, the concentration of the polymer-rich phase, i.e. the solubility of the plasticizer in the polymer, may be taken as the point of contact of a tangent to the curve which passes through the origin.

The usual Flory–Huggins treatment of polymer solution thermodynamics gives the following expression for the free energy of mixing for a polymer (component 2) and a solvent (component 1):

$$\Delta G^{\mathrm{m}} = RT(x_1 \ln \varphi_1 + x_2 \ln \varphi_2 + (x_1 + r x_2)\varphi_1 \varphi_2 \chi) \quad (3)$$

where φ represents the volume fraction of a component and r is the 'size ratio' given by the ratio of molar volumes of the polymer and solvent. The χ parameter was originally envisaged as an enthalpy parameter but is now usually interpreted as a free-energy function accounting for all contributions other than the combinatorial entropy of mixing.

The approach has several problems, such as the neglect of polydispersity, molecular-weight dependence of χ and volumes of mixing, but is commonly used to correlate results in polymer systems, largely because of its convenience in comparison to newer methods. The equation does not allow an analytical solution to its differential for the equilibrium phase limits as described above, although it can be solved numerically.

THE UNIFAC METHOD

UNIFAC is a group contribution technique, i.e. it splits each molecule being considered into a number of functional groups such as methyl, methylene, carbonyl, etc., and treats the solution as a mixture of these groups. The original method was developed by Fredenslund and coworkers[10,11] for the correlation and prediction of vapour–liquid equilibrium, although it has also been applied to a range of other properties[12,13]. It involved the assumption of two contributions to the thermodynamic activity of a solvent in solution. The combinatorial (or entropic) part a_1^{C} is calculated using an expression derived from Staverman's statistical mechanical treatment[4] as adapted by Abrams and Prausnitz[15]:

$$\ln a_1^{\mathrm{C}} = \ln \phi_1 + \ln \phi_2 + (zM_1 q_1/2)[\ln(\theta_1/\phi_1) - 1 - (\phi_1/\theta_1)] \quad (4)$$

where M_1 is the solvent molecular weight, z is a 'lattice coordination number', conventionally set to 10 to conform with recent practice[4–8], and ϕ_1 and θ_1 are the UNIFAC segment and surface area fractions, respectively, given for a weight fraction of solvent W_1 by:

$$\phi_1 = W_1 r_1 \Big/ \sum_i W_i r_i \qquad \theta_1 = W_1 q_1 \Big/ \sum_i W_i q_i \quad (5)$$

For any molecule containing $n_k^{(i)}$ groups of type k and having molecular weight M_i, the molecular parameters r_i and q_i are found by summing all group volume and surface parameters R_k and Q_k, which are listed in the literature[16], having been calculated from Van der Waals properties as given by Bondi[17]:

$$r_i = \left(\sum_k n_k^{(i)} R_k\right) \Big/ M_i \qquad q_i = \left(\sum_k n_k^{(i)} Q_k\right) \Big/ M_i \quad (6)$$

The second, residual (or enthalpic) contribution to the activity is defined in terms of inter-group interaction parameters, which have been calculated by minimizing differences between UNIFAC and experimental vapour–liquid equilibrium results for a large number of binary systems. Each pair of groups, say j and k, has two parameters, ψ_{jk} and ψ_{kj}, that account for energetic interactions between the groups and are tabulated in the literature[16]. The residual part of the activity, a_1^{R}, is given by:

$$\ln a_1^{\mathrm{R}} = \sum_k n_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(1)}) \quad (7)$$

Γ_k is the group residual activity in the solution while $\Gamma_k^{(1)}$ is that in the pure liquid solvent. These may be calculated by summing the interactions over all pairs of groups in the solution:

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_j \theta_j \psi_{jk}\right) - \sum_j \theta_j \psi_{kj} \Big/ \sum_m \psi_{jm} \right] \quad (8)$$

The same equation can be used for $\Gamma_k^{(1)}$ with appropriate assignment of j and m.

These two contributions were found to be adequate for small-molecule solutions but, when working with polymer solutions, an extra contribution to the solvent activity arising from the well known free-volume differences between polymers and solvents must be considered. As shown by Oishi and Prausnitz[4], this may be done using Flory's expression[18]:

$$\ln a_1^{\mathrm{FV}} = 3c_1 \ln[(v_1^{1/3} - 1)/(v^{1/3} - 1)] - c_1\{[(v_1/v) - 1](1 - v_1^{1/3})^{-1}\} \quad (9)$$

The parameter $3c_1$ is the number of external degrees of freedom. Oishi and Prausnitz[4] have given expressions for the reduced volumes υ_i of the solvent:

$$\upsilon_i = v_i/15.17br_i$$

and υ for the solution:

$$\upsilon = \left(\sum_i W_i v_i\right) \Big/ \left[15.17b\left(\sum_i W_i r_i\right)\right]$$

where v_i is the specific volume of a component. By comparison with experimental data, they set the factors $c_1 = 1.1$ and $b = 1.28$.

The overall activity of the solvent in the solution is thus given by:

$$\ln a_1 = \ln a_1^{\mathrm{C}} + \ln a_1^{\mathrm{R}} + \ln a_1^{\mathrm{FV}} \qquad (10)$$

RESULTS

A program was written to apply the UNIFAC method using the BASIC language on an IBM personal computer. A range of concentrations was entered and the activity of the components calculated according to equations (4)–(10). This activity was used to calculate the free energy of mixing of the solution. Differentiation of equation (3) gives:

$$\begin{aligned}\Delta\mu_1 &= (\partial \Delta G^{\mathrm{m}}/\partial x_1) = RT \ln a_1 \\ &= RT[\ln \varphi_1 + (1 - 1/r)\varphi_2 + \varphi_2^2 \chi] \qquad (11)\end{aligned}$$

so that the value of χ can be calculated at any concentration and this substituted in equation (3) to give the free energy of mixing per mole of mixture. Alternatively, the UNIFAC method can be applied to calculate the activities of both components in solution so that the free energy of mixing can be found from a version of the Gibbs–Duhem equation:

$$\Delta G^{\mathrm{m}} = RT(x_1 \ln a_1 + x_2 \ln a_2) \qquad (12)$$

Plots of the free energy of mixing *versus* concentration were constructed and the compositions of the conjugate phases were determined by graphical construction of the appropriate tangent lines as outlined above.

Poly(vinyl chloride)–n-alkyl stearates

Quantitative solubility results are available for relatively few systems. Ceccorulli and coworkers[19,20] measured the solubility of a series of n-alkyl stearates in PVC at 90°C using differential scanning calorimetry, viscosity and equilibrium swelling.

The UNIFAC prediction of the specific free energy of mixing for five stearates (methyl, ethyl, n-butyl, n-octyl and n-hexadecyl) in a PVC with molecular weight 50 000 at 90°C are shown in *Figure 2*. The plots are of the form displayed in *Figure 1c* and suggest the systems to be partially miscible with practically zero solubility of the polymer in the stearate. The composition of the equilibrium solution was estimated graphically as described above and is shown in *Table 1* along with experimental results for the solubility. The expected error from reading the UNIFAC plots is approximately 0.1–0.2 wt%. The UNIFAC predictions underestimate the solubility in each case except the n-hexadecyl stearate, where the solubility is very small. However, the trend of decreasing solubility with increasing chain length is reproduced. One factor that may help to explain these discrepancies is that the molecular weight of the polymer used in the experimental studies was not stated. In this type of system, the minimum value of the free energy is often taken as a measure of the compatibility, and it is interesting in this context that a plot of the minimum in the UNIFAC predictions varies linearly with the observed solubility, so that this gives an extra indication as shown in *Figure 3*.

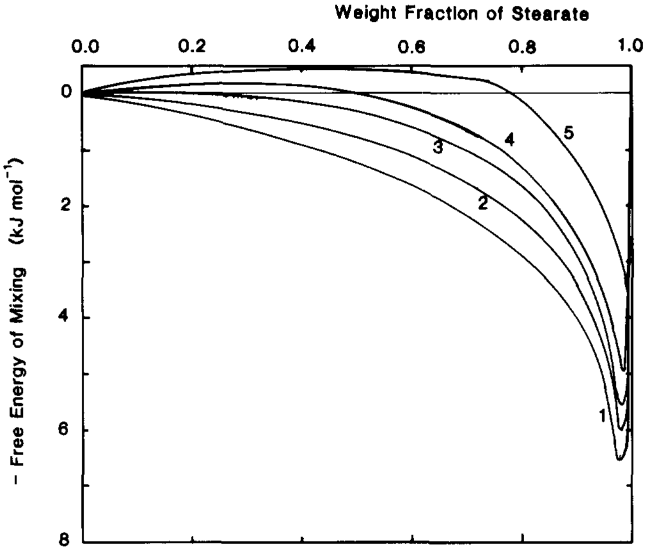

Figure 2 Free energy of mixing *versus* composition curves for n-alkyl stearates in PVC at 90°C predicted by the UNIFAC method: 1, methyl; 2, ethyl; 3, n-butyl; 4, n-octyl; 5, n-hexadecyl

Table 1 Comparison of predicted with experimental solubilities for n-alkyl stearates in PVC (experimental results from ref. 19)

	Solubility (wt%)	
Plasticizer	Experiment	UNIFAC
Methyl	6.1	2.4
Ethyl	4.9	2.1
n-Butyl	4.2	1.8
n-Octyl	2.6	1.3
n-Hexadecyl	0.3	0.8

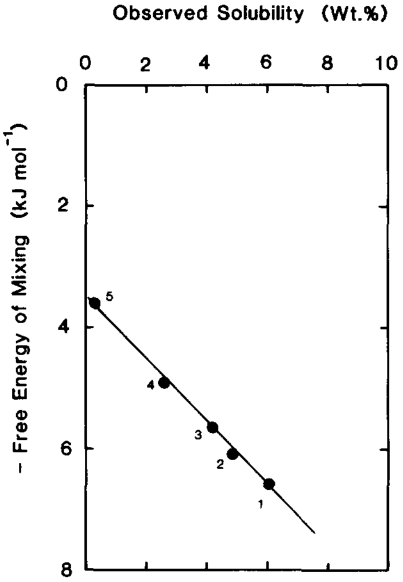

Figure 3 Plot of minimum of UNIFAC free energy of mixing *versus* observed solubility of stearate: 1, methyl; 2, ethyl; 3, n-butyl; 4, n-octyl; 5, n-hexadecyl

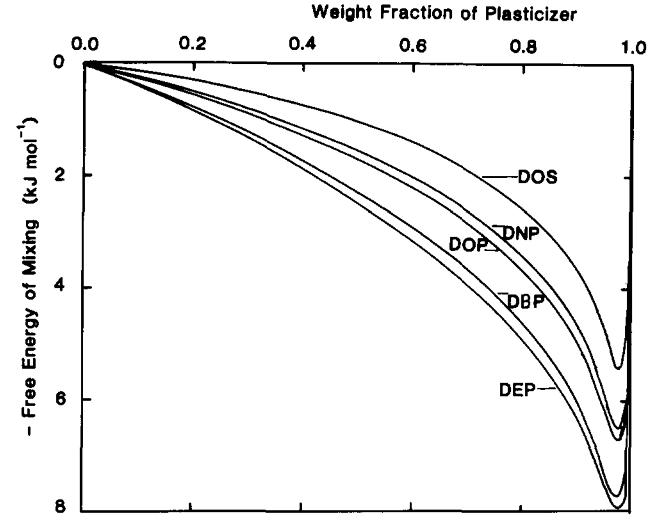

Figure 4 Free energy of mixing *versus* composition curves for alkyl phthalates in PVC at 25°C predicted by the UNIFAC method: DOS, dioctyl sebacate; DNP, dinonyl phthalate; DPO, dioctyl phthalate; DBP, dibutyl phthalate; DEP, diethyl phthalate

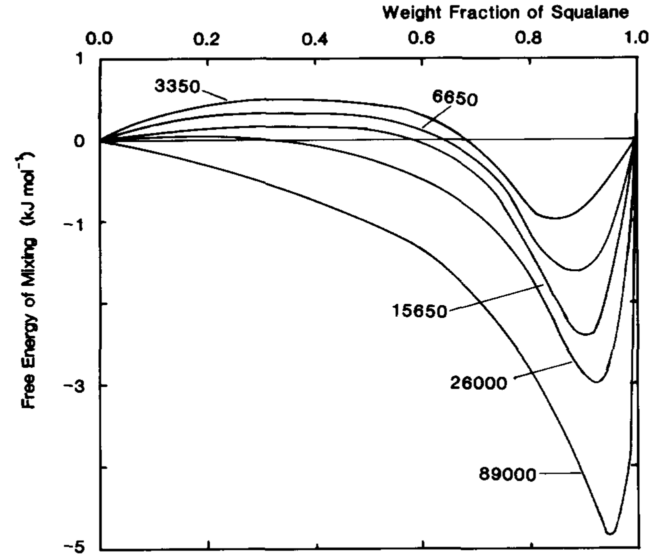

Figure 5 Free energy of mixing *versus* composition curves for squalane in PDMS predicted by the UNIFAC method: values on curves refer to polymer molecular weight

Poly(vinyl chloride)–alkyl phthalates

The alkyl phthalates are a class of compound that has found extensive use as plasticizers for PVC. The predicted free-energy curves at 25°C from UNIFAC for a series of phthalates together with dioctyl sebacate are shown in *Figure 4*. The methods of drawing tangents or taking the composition at the free-energy minimum do not allow any correlation of solubility for these mixtures since all systems are predicted to have virtually the same solubility, approximately 2.5 wt%. However, there is a distinct trend in the value of the minimum free energy, with the shorter alkane chain compounds having more negative values, and this correlates well with the observed compatibility[21].

Squalane–poly(dimethylsiloxanes)

Both squalane and poly(dimethylsiloxane) (PDMS) have found extensive use for the measurement of thermodynamic properties by a number of methods and this has included their phase equilibrium[9]. The predicted free energy–composition curves at 30°C for five polymers with molecular weights ranging from 3350 to 89 000 are shown in *Figure 5*. Significantly, the predicted curves for the lower-molecular-weight polymers start off in a positive direction, as was observed experimentally[9]. The predicted and observed solubilities are compared in *Table 2*. Again the actual solubilities are underestimated to a large degree although the correct trend of values is seen. It should, however, be noted that the interaction parameters for the siloxane groups are based on a rather small data set[5,6] and so an extra element of uncertainty will be introduced in this case. In this case, the changing molecular weight of the polymer precludes comparison of the molar free energies of mixing but, as shown in *Table 2*, calculation of ΔG^m per gram of mixture shows a correlation of increased squalane solubility with larger values of the minimum free energy.

DISCUSSION

The results show that UNIFAC can be used to predict the relative equilibrium compositions in systems that are typical of polymer–plasticizer mixtures. The predicted values underestimate the plasticizer solubility in each case but the trends within groups of compounds agree with experimental work.

The reasons for the underestimation lie in the UNIFAC method, since any group contribution theory must of necessity be approximate. Patwardhan and Belfiore[7,8] have discussed possible areas where the UNIFAC method might be erroneous in polymer systems. First, the expression for the combinatorial activity may need modification, for example by the use of the Flory–Huggins equation, although this would have a small effect on the overall result. The interaction parameters used to determine the residual activity are based on vapour–liquid equilibrium of small molecules and so may not be the optimum values for use here, as groups will not interact in the same way in polymers due to restricted conformations, etc. Calculations based on a data set derived from results on polymer systems may well yield better results. In addition to inaccuracies in the Flory–Huggins treatment mentioned earlier, there are other features that it, as well as UNIFAC, fails to take into account. Among these are the polydispersity of the polymer, the methods being assumed to give number-average quantities, as well as polymer microstructure such as tacticity or crystallinity.

Despite these considerable drawbacks, the UNIFAC method offers a straightforward method for predicting phase equilibria in systems where little or no experimental data are available. The only values needed for its application are the pure component densities. Clearly,

Table 2 Comparison of predicted with experimental solubilities for squalane in PDMS (experimental results from ref. 9)

PDMS molecular weight	Solubility (wt%)		Free energy of mixing	
	Experiment	UNIFAC	($J g^{-1}$)	($J mol^{-1}$)
3350	32.5	18.8	−0.339	−950
6650	21.7	12.5	−0.256	−1480
15650	16.5	8.9	−0.167	−2370
26000	12.2	7.2	−0.124	−3000
89000	9.7	4.8	−0.057	−4820

no conclusions as to the behaviour of single systems should be drawn but calculation of relative values in a series of compounds is possible. It may therefore be used as a preliminary tool to identify likely candidates for study and therefore remove the need for costly and time-consuming experimental work, especially since calculations can be performed for systems over a range of temperatures. Additionally, it is relatively straightforward to use the method for mixtures of two or more additives with a polymer, greatly extending its range of applicability. Hopefully, current work to modify the method[22,23] will result in a more useful method that will allow the prediction of more accurate solubilities.

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