Prediction of thermodynamic properties of polymer solutions using the UNIFAC group-contribution method

G. J. Price*
Department of Chemistry, The City University, Northampton Square, London EC1V 0HB, UK

and A. J. Ashworth
School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

(Received 25 February 1987; revised 22 April 1987; accepted 24 April 1987)

The UNIFAC group-contribution method has been applied to solutions of polydimethylsiloxane in a number of solvents. In the region of high polymer concentration, the predicted Flory–Huggins interaction parameters are not in good agreement with experimental values and the predicted variation with molecular weight is the opposite to that measured. However, it has been shown that, if a single experimental result is available, the UNIFAC predictions can be improved to within a few per cent.

(Keywords: UNIFAC; polydimethylsiloxane; interaction parameter; molecular weight)

INTRODUCTION

The prediction and correlation of the thermodynamic properties of polymer solutions has attracted considerable attention from many workers. The basic theory of Flory and Huggins[1,2], even though dating from the 1940s, is still used as a basis for study. This treatment assumes two contributions to the activity, a_1, of a solvent in solution: a combinatorial or entropic component in terms of the volume fraction of solvent, ϕ_1, and a residual or enthalpic component in terms of a polymer–solvent interaction parameter, χ. The activity is then calculated from:

$$\ln a_1 = \ln \phi_1 + (1-\phi_1)(1-1/r) + (1-\phi_1)^2\chi \qquad (1)$$

where r is the size ratio of the polymer and solvent. This equation is now used with modifications to the meanings of the various terms, e.g. ϕ is usually regarded as a segment fraction and χ is usually regarded as a residual free-energy parameter[3] including non-combinatorial entropy effects. Many theories have been proposed to account for the measured values of χ. These include Flory's free-volume theory[3], the corresponding-states theory of Prigogine[4] and Patterson[5], the lattice-fluid theory[6] and others[7–9]. However, these have become increasingly complex and require a number of experimentally determined parameters for their application.

The UNIFAC treatment is a group-contribution method that allows ready prediction of solution thermodynamic properties. It was originally proposed[10,11] to correlate vapour–liquid equilibrium data but it has been extended by application to the prediction of enthalpies of mixing[12], gas solubilities[13] and phase equilibria[14].

The method was first applied to polymer solutions by Oishi and Prausnitz[15] who were able to predict solvent activities to within ~10% for solutions of a range of polymers including poly(vinyl acetate) and polyisobutylene. Gottlieb and Herskowitz[16] found good correlation of experimental χ values for polydimethylsiloxane with those predicted by UNIFAC. However, Tseng and Lloyd[17] applied the method to a range of polystyrenes of varying molecular weights and found that UNIFAC failed to predict the interaction parameter. Recently, Patwardhan and Belfiore[18] used UNIFAC to investigate the χ values and phase behaviour of a number of polymer–solvent pairs and found qualitative agreement.

In this work, the ability of UNIFAC to predict the Flory–Huggins interaction parameter and its variation with polymer molecular weight for a range of polydimethylsiloxane–solvent pairs has been investigated. In addition, a method to improve the predictions where a single experimental result is available is proposed.

THE UNIFAC METHOD

The UNIFAC method is a group-contribution method, i.e. it splits each component of a solution into a number of well defined functional groups and treats the solution as a mixture of these groups rather than of molecules. This allows treatment of a large number of solutions in terms of the properties of a relatively small number of groups.

The original method used for low-molecular-weight liquids assumed two contributions to the solvent activity as described above. The combinatorial contribution, a_1^C, is calculated using an expression derived from

---

* To whom correspondence should be addressed

0032-3861/87/122105-05$03.00

Staverman's statistical-mechanical method[19] as adapted by Abrams and Prausnitz[20]:

$$\ln a_1{}^{C} = \ln \phi_1 + \phi_2 + (zM_1q_1/2)[\ln(\theta_1/\phi_1) - 1 - (\phi_1/\theta_1)] \qquad (2)$$

where M_1 is the solvent molecular weight, z is a lattice coordination number (set to 10 in the current work to conform with recent practice)[15,17], and ϕ_1 and θ_1 are the UNIFAC segment and surface area fractions of the solvent, respectively, given for a weight fraction of solvent, W_1, by:

$$\phi_1 = W_1 r_1 \Big/ \sum_i W_i r_i \qquad \theta_1 = W_1 q_1 \Big/ \sum_i W_i q_i \qquad (3)$$

For any molecule i 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 the group surface and volume parameters, R_k and Q_k, which are found from Van der Waals properties as given by Bondi[21] and listed in the literature[22]:

$$r_i = \left(\sum_k n_k^{(i)} R_k\right) \Big/ M_i \qquad q_i = \left(\sum_k n_k^{(i)} Q_k\right) \Big/ M_i \qquad (4)$$

The residual contribution is defined in terms of intergroup interaction parameters calculated by minimizing the fit of UNIFAC to a large amount of literature data on the vapour–liquid equilibria of binary systems. Each pair of UNIFAC groups has two parameters, w_{jk} and w_{kj}, which account for energetic interactions between the groups and are tabulated in the literature. The residual contribution to the solvent activity, a_1^{R}, is given by:

$$\ln a_1^{R} = \sum_k n_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(1)}) \qquad (5)$$

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

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_j \theta_j \psi_{jk}\right) - \sum_j \left(\theta_j \psi_{kj} \Big/ \sum_m \psi_{jm}\right)\right] \qquad (6)$$

where at temperature T:

$$\psi_{jk} = \exp(-w_{jk}/T) \qquad (7)$$

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

When working with polymer solutions, an extra contribution to the solvent activity must be considered. This arises from differences in the free volume of the polymer and solvent and may be calculated from the expression of Flory[3]:

$$\ln a_1^{FV} = 3c_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] - c_1\{[(\tilde{v}_1/\tilde{v}) - 1](1 - \tilde{v}_1^{1/3})^{-1}\} \qquad (8)$$

The parameter $3c_1$ is the number of external degrees of freedom. Oishi and Prausnitz[15] give approximate expressions for the reduced volumes, $\tilde{v}_i$:

$$\tilde{v}_i = v_i/15.17br_i \qquad (9)$$

and for the solution by:

$$\tilde{v} = (W_1v_1 + W_2v_2)/[15.17b(W_1r_1 + W_2r_2)] \qquad (10)$$

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, a_1, is then calculated from:

$$\ln a_1 = \ln a_1^{C} + \ln a_1^{R} + \ln a_1^{FV} \qquad (11)$$

The value obtained may then be used in conjunction with equation (1) to obtain an estimate of the Flory–Huggins interaction parameter from UNIFAC, χ_{UNI}.

RESULTS AND DISCUSSION

A program to apply the UNIFAC method was written in the BASIC language for the Honeywell Multics system of the Avon Universities Computer Centre. Values for the various parameters needed were taken from literature sources and are shown in *Tables 1* and *2*. Since χ is much more sensitive to minor variations in experimental conditions, it was preferable to make comparisons in terms of χ rather than the solvent activity to give a more rigorous test of the predictive ability of UNIFAC. As part of another study, the authors had measured interaction parameters for several polydimethylsiloxane (PDMS)–solvent pairs so that this polymer was chosen for the comparison.

It was of interest to determine how well (i) the magnitude, (ii) the concentration variation and (iii) the molecular-weight variation of χ could be predicted using UNIFAC and also to see whether the predictions could be improved by using a minimal amount of experimental data.

In recent years, gas–liquid chromatography has become a useful technique for the rapid determination of activity coefficients and interaction parameters for polymer solutions[23]. The method as usually used yields a single result, effectively at infinite dilution of solvent in the polymer, χ^{∞}. Recent work[24] has shown that χ^{∞} values calculated from g.l.c. agree well with those extrapolated

Table 1 UNIFAC group volume and area parameters

Functional group	Main group[a]	R_k	Q_k	Ref.
SiO	SiO	1.1044	0.466	16
CH_3	CH_2	0.9011	0.848	15
CH_2	CH_2	0.6744	0.540	15
ACH	ACH	0.5313	0.400	15

[a] The main group includes all functional groups with similar structure and the same interaction parameter (ACH refers to a C–H group as found in benzene)

Table 2 UNIFAC group interaction parameters, w_{jk}

	Group k		
Group j	SiO	CH_2	ACH
SiO	0	109.3	293.8
CH_2	327.0	0	61.13
ACH	254.3	−11.12	0

from static equilibrium measurements. In previous studies, it has been noted that this is the concentration region where UNIFAC shows the largest deviation from experimental results. However, it is a range that is of considerable industrial importance for polymer processing.

In the current work, infinite-dilution interaction parameters, $\chi^{\infty}_{\text{expt}}$, were taken from several experimental vapour sorption studies on PDMS–solvent systems and compared with those predicted by UNIFAC, $\chi^{\infty}_{\text{UNI}}$. Since a concentration of zero cannot be used in the UNIFAC equations, $\chi^{\infty}_{\text{UNI}}$ were calculated by inserting a weight fraction of solvent of 1×10^{-6} in the above equations. It was found that using lower concentrations had negligible effect on the values obtained. The difference between these two values was then taken as a correction factor and added to the usual UNIFAC χ_{UNI} to give an 'adjusted' value, $\chi_{\text{U(adj)}}$:

$$\chi_{\text{U(adj)}} = \chi_{\text{UNI}} + (\chi^{\infty}_{\text{expt}} - \chi^{\infty}_{\text{UNI}}) \qquad (12)$$

Thus, the agreement at infinite dilution is exact and concentration effects are easily seen.

Prediction of interaction parameters

Figure 1 shows results for n-hexane, benzene and cyclohexane in PDMS (number-average molecular weight = 89 000) at 25°C. The data points are from experimental vapour sorption isotherms[25], the broken lines show the predictions from UNIFAC as usually used and the full lines show the adjusted UNIFAC values calculated from equation (12). Bearing in mind the large scale of the graph, the UNIFAC predictions are reasonable, although not as good as in some other PDMS systems studied by Gottlieb and Herskowitz[16]. However, in each case, they are considerably improved when adjusted using the single experimental data point. The predicted variation over the concentration range is also good. The results are quantified in *Table 3* which shows the percentage deviation of the two UNIFAC treatments from the experimental results at three concentrations.

Figure 2 and *Table 4* show the same treatment applied to five hydrocarbon solvents[24] in the same PDMS polymer at 30°C. The same general trend of results may be seen here.

Prediction of molecular-weight variation

Tseng and Lloyd[17] examined the ability of UNIFAC to predict the molecular-weight variation of the interaction parameters in polystyrene solutions but, within experimental error, found no variation so that no

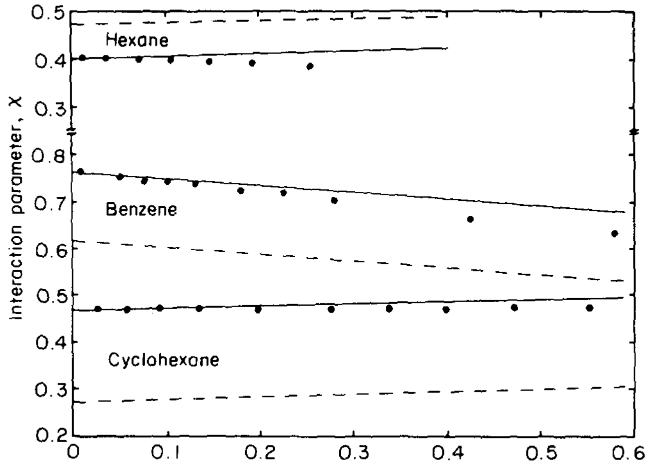

Figure 1 Prediction of PDMS interaction parameters at 25°C by the UNIFAC method: ●, experimental results[25]; -----, χ_{UNI}; ——, $\chi_{\text{U(adj)}}$

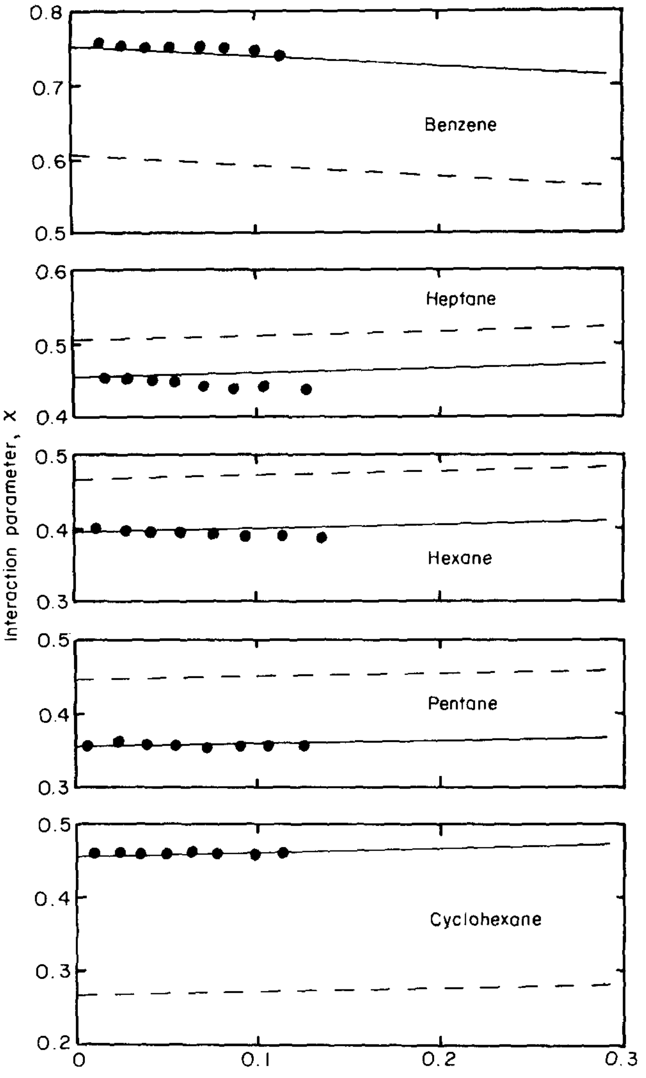

Figure 2 Prediction of PDMS interaction parameters at 30°C by the UNIFAC method: ●, experimental results[24]; -----, χ_{UNI}; ——, $\chi_{\text{U(adj)}}$

Table 3 Percentage deviation of UNIFAC treatments for PDMS interaction parameters at 25°C for three solvents at volume fractions shown

	Cyclohexane			Benzene			Hexane		
	$\phi_l = 0$	0.2	0.5	0	0.2	0.5	0	0.2	0.5
χ_{UNI}	−41.4	−39.6	−36.3	−19.7	−19.3	−17.4	17.8	24.3	36.4
$\chi_{\text{U(adj)}}$	0	1.7	2.3	0	1.7	5.8	0	5.9	17.0

Table 4 Percentage deviation of UNIFAC treatments for PDMS interaction parameters at 30°C for five solvents at volume fractions shown

	Cyclohexane		Benzene		Pentane		Hexane		Heptane	
	$\phi_1=0$	0.2	0	0.2	0	0.2	0	0.2	0	0.2
χ_{UNI}	−49.5	−39.5	−20.3	−20.9	19.6	27.9	17.9	25.2	10.9	22.2
$\chi_{\mathrm{U(adj)}}$	0	−1.5	0	0.5	0	2.4	0	6.6	0	10.5

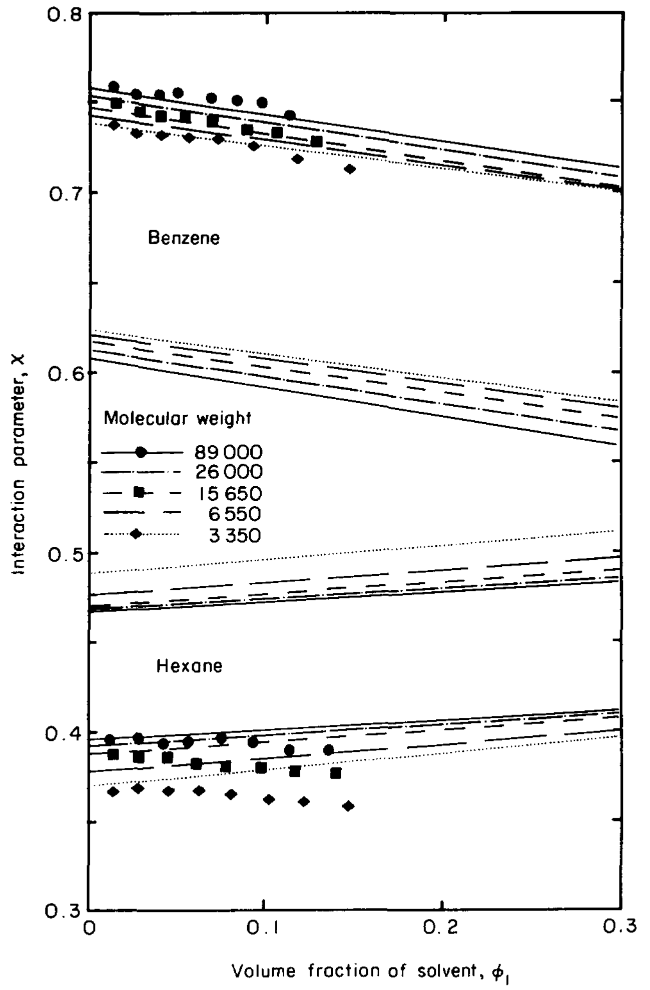

Figure 3 Prediction of PDMS interaction parameters for various molecular weights at 30°C by the UNIFAC method: ●, ■, ◆, experimental results[26]. The middle two sets refer to the normal UNIFAC treatment and the top and bottom sets are derived from the use of equation (12)

conclusion was reached. In the current work, the basic UNIFAC method and that adjusted as above was applied to five PDMS polymers with molecular weights ranging from 3350 to 89000 using n-hexane and benzene as solvents at 30°C. These may be compared with experimental results[26] in *Figure 3* where, for clarity, only the results for three samples are shown. The basis of UNIFAC is that the group parameters are independent of the molecule in which the group occurs so that no adjustment to these values was necessary for the different polymers.

In addition to the error in predicting the magnitude of the interaction parameters, the wrong trend with changing molecular weight is predicted. The experimental results show an increase of χ with rising molecular weight whereas the reverse is true of the UNIFAC results. However, if the UNIFAC results are adjusted using equation (12), not only are the magnitudes of the χ parameters significantly improved, but the correct trend of increase with rising molecular weight is also seen.

Thus, this work has shown that UNIFAC is a useful method for the prediction of solvent activities and interaction parameters for polymer solutions, although it is probably more accurate at low polymer concentrations. The region of high polymer concentration is important in many industrial applications such as the removal of volatiles from polymers. In this range, the improvement of the UNIFAC method by the inclusion of a single experimental result is particularly marked. In principle, a value of a_1 or χ at any concentration could be used. However, most techniques for measuring these parameters are applicable over a wide concentration range so that the actual values could be measured, removing the need for the use of UNIFAC. The most applicable experimental method for this use would appear to be g.l.c. Alternatively, other forms of adjustment could be used. For instance, a concentration-dependent adjustment was tried in equation (11) but was found to show negligible difference from that described above. Several workers[16,17] have discussed theoretical reasons for differences between UNIFAC and experimental values and suggested ways of improving the fit. However, while improvements have been made to individual systems, none has found general applicability and it should be remembered that UNIFAC was designed simply as a method to obtain an estimate of properties for systems where no experimental data were available. In this regard, it remains an attractive and potentially useful technique but no conclusions as to fundamental thermodynamic behaviour should be based on its use.

REFERENCES

1 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660; 1942, **10**, 51
2 Huggins, M. L. *J. Am. Chem. Soc.* 1942, **64**, 1712
3 Flory, P. J. *Disc. Faraday Soc.* 1970, **49**, 7
4 Prigogine, I. 'The Molecular Theory of Solutions', North-Holland, Amsterdam, 1957
5 Patterson, D. D. *Macromolecules* 1969, **2**, 672
6 Sanchez, I. and Lacombe, R. H. *Macromolecules* 1978, **11**, 1145
7 Dayantis, J. *J. Phys. Chem.* 1972, **76**, 1600; 1973, **77**, 2977
8 Huggins, M. L. *Polymer* 1971, **12**, 389
9 Renuncio, J., Canovas, A. and Rubio, R. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 841
10 Fredenslund, A., Jones, R. L. and Prausnitz, J. M. *AIChE J.* 1975, **21**, 1086
11 Fredenslund, A., Gmehling, J. and Rasmussen, P. 'Vapour-Liquid Equilibrium using UNIFAC', Elsevier, Amsterdam, 1977
12 Nagata, I. and Ohta, T. *Chem. Eng. Sci.* 1982, **33**, 177
13 Nocon, G., Weidlich, U., Gmehling, J., Menke, J. and Oriken, U. *Fluid Phase Equilibria* 1985, **13**, 381
14 Skjold-Jorgensen, S., Rasmussen, P. and Fredenslund, A. *Chem. Eng. Sci.* 1982, **37**, 536
15 Oishi, T. and Prausnitz, J. M. *Ind. Eng. Chem., Process Des. Dev.* 1978, **17**, 333
16 Gottlieb, M. and Herskowitz, M. *Macromolecules* 1981, **14**, 1468
17 Tseng, H. S. and Lloyd, D. R. *Polymer* 1984, **25**, 670
18 Patwardhan, A. A. and Belfiore, L. A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2473

19 Staverman, A. J. *Rec. Trav. Chim. Pays-Bas* 1950, **69**, 163
20 Abrams, D. S. and Prausnitz, J. M. *AIChE J.* 1975, **21**, 116
21 Bondi, A. 'Physical Properties of Molecular Crystals, Liquids and Glasses', Wiley, New York, 1968
22 Skjold-Jorgensen, S., Kolbe, B., Gmehling, J. and Rasmussen, P. *Ind. Eng. Chem., Process Des. Dev.* 1979, **18**, 714
23 Conder, J. R. and Young, C. L. 'Physicochemical Measurement by GLC', Wiley, Chichester, 1977
24 Ashworth, A. J., Chien, C. F., Furio, D. L., Hooker, D. M., Laub, R. J. and Price, G. J. *Macromolecules* 1984, **17**, 1090
25 Ashworth, A. J. and Price, G. J. *Thermochim. Acta* 1984, **82**, 161
26 Ashworth, A. J. and Price, G. J. *Macromolecules* 1986, **19**, 358