Prediction of retention in gas–liquid chromatography using the UNIFAC group contribution method

III. Recent developments in UNIFAC

Gareth J. Price

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY (UK)

ABSTRACT

Previous publications have described the application of the UNIFAC group contribution method to the prediction of retention in chromatographic systems via their thermodynamic properties but concluded that the basic method was of limited, if any, use for this purpose. This paper describes results from some recent developments in UNIFAC including modifications to the equations and newly calculated parameter sets applied to the retention of a range of solvents in squalane, dinonyl phthalate, N-methylpyrollidone, poly (isobutylene) and poly(ethylene oxide) stationary phases.

The best results obtained predicted the specific retention volumes to about 10%, although this model could only be applied to a few systems; predictions for a wide range of polar and non-polar systems in the phases could be correlated to approximately 20–25%. While this level of accuracy is sufficient to allow prediction of elution orders in some systems, none of the modifications to UNIFAC in current use are suitable for widespread application to chromatographic systems.

INTRODUCTION

The selection of an appropriate stationary phase for a particular analysis is an ever present problem for the chromatographer and a number of strategies such as the use of retention indices [1] or "window diagrams" [2] have been developed. Previous papers [3,4] in this series have explored the use of UNIFAC for this purpose. This is a "group contribution" method [5,6] which takes the components of a solution, splits them into a number of functional groups and sums their properties to arrive at the overall solution activity, from which activity coefficients, γ_1, can be calculated. Comparisons of the infinite dilution activity coefficient, γ_1^∞, with chromatographic data can then be made in terms of the measured specific retention volumes, V_g^0, of the solutes in the stationary phases using the well known relationship [7],

$$\gamma_1^\infty = 273.15 \; R/V_g^0 \; P_1^0 \; M_2 \qquad (1)$$

where R is the gas constant, M_2 is the molecular weight of the stationary phase liquid, P_1^0 is the saturated vapour pressure of the solute at the column temperature and V_g^0 is the retention volume of the solute per gram of stationary phase fully corrected to standard temperature and pressure. However, when considering polymeric stationary phases as are commonly used in current gas–liquid chromatography (GLC), this definition is often complicated by lack of an accurate value for M_2. Thus, the activity coefficients, Ω_1^∞, are usually defined on a weight fraction rather than mole fraction concentration basis [8]. Thus,

$$\Omega_1^\infty = 273.15 \; R/V_g^0 \; P_1^0 \; M_1 \qquad (2)$$

where M_1 is now the molecular weight of the volatile solute.

The UNIFAC method was developed by Fredenslund and co-workers [5,6] to allow the prediction of phase equilibria and other thermodynamic properties of solution in liquid mixtures and has been fully described in the previous papers [3,4]. The basic technique assumes two contributions to the thermodynamic activity in solution. The combinatorial (or entropic) part, a_1^C, accounting for differences in size and shape between the molecules in solution and a second, residual (or enthalpic) contribution to the activity, a_1^R, accounting for energetic interactions in solution. These two contributions were found to be adequate for small molecules solutions but, when working with polymer solutions, an extra contribution, a_1^{FV}, 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 [9]. The overall activity of the volatile solute in the solution is thus given by:

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{FV} \qquad (3)$$

Roth and Novak [10] applied the original UNIFAC method to a number of systems and concluded that "... (it) can be used merely to give a rough estimation of relative retentions". We have applied both the original and free volume modified versions to a number of stationary phases such as squalane, dinonyl phthalate and similar compounds [3] and found that, in most cases, although the absolute values of V_g^0 were not accurately predicted, the correct order of elution was obtained although very wide discrepancies were found with polar stationary phases such as N-methylpyrollidone. Similar results were found [4] with polymer stationary phases including "OV" silicones and Carbowax. It was thus concluded that, in its current state of development, UNIFAC was of limited, if any, use to the chromatographer.

In this paper, results using some of the more recent developments to the UNIFAC method to estimate V_g^0 are described to determine whether they will allow retention to be predicted with greater accuracy and hence assist with the selection of appropriate systems for analyses where little or no experimental data is available. To test the range of applicability of the methods (if any), calculations were performed for five representative stationary phases covering a range of properties. Three were low-molecular-weight phases: squalane (SQ, non-

polar), dinonyl phthalate (DNP, moderately polar) and N-methylpyrollidone (NMP, polar). Two polymeric phases, polyisobutylene (PIB, non-polar) and polyethylene oxide (PEO, polar) were also used. The experimental results were taken from the same sources as used previously [3,4] and were chosen from high-quality thermodynamic measurements made by GLC. As many solutes as possible were used, these having been described in our earlier papers [3,4]. From a chromatography point of view, studies of polydimethyl siloxane, the base material of the widely used OV series would have been useful but there are a very limited number of UNIFAC parameters available for silicones so that they were not considered here.

RESULTS AND DISCUSSION

Since a value of zero concentration cannot be used in the UNIFAC equations, a solute weight fraction of $1 \cdot 10^{-6}$ was used to simulate infinite dilution, the usual situation pertaining to analytical gas chromatography. The use of lower concentrations was found to have negligible effect on the results. The UNIFAC activity of the solute was calculated using the appropriate equations as outlined above in a BASIC program written for the IBM-PC and converted to an activity coefficient by dividing by the mole or weight fraction as appropriate to the system. Values of the specific retention volume were then calculated from eqns. 1 or 2 using physical property data from literature sources [11–13].

Values have been calculated for each of the modifications considered using both the original treatment and with the free volume correction proposed for polymer solutions. These will be designated "uni" and "uni-fv", respectively. The deviation of the predictions from the experimental results was calculated according to

$$\Delta V_g^0(\%) = 100 \,\{[V_g^0(\text{UNIFAC}) - V_g^0(\text{Expt.})]/ \\ V_g^0(\text{Expt.})\} \qquad (4)$$

Modifications to UNIFAC

The combinatorial factor. One of the main features of UNIFAC is that it assigns a zero interaction parameter between groups of similar chemical nature, *e.g.*, methyl and methylene. This results in no contribution to the activity coefficient, and hence retention volume, from residual or energetic factors.

Thus in hydrocarbon mixtures, the activity coefficient is composed solely of combinatorial terms together with, for UNIFAC-FV, a free volume term. Since even in such mixtures, *e.g.*, hexane–squalane, V_g^0 is not predicted well by the basic methods, we first tried some of the suggested modifications to the equation for the combinatorial activity, a_1^C, given in the original treatment by

$$\ln a_1^C = \ln \phi_1 + \phi_2 + (z\, M_1 q_1/2)[\ln (\theta_1/\phi_1) - 1 - (\phi_1/\theta_1)] \qquad (5)$$

where M_1 is the solvent molecular weight, z is a "lattice coordination number", conventionally set to 10 to conform with recent practice [6,9] 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:

$$\phi_1 = W_1\, r_1 \Big/ \sum_i W_i\, r_i; \quad \theta_1 = W_1\, q_1 \Big/ \sum_i W_i\, q_i \quad (6)$$

the molecular parameters r_i and q_i are found by summing the volume and surface parameters for each group which are listed in the literature [6], having been calculated from Van der Waals properties as given by Bondi [12].

By optimizing activity coefficients for a large number of alkane and alcohol systems, Thomas and Eckert [14] suggested an empirical alteration to eqns. 5 and 6 where

$$\phi_1' = W_1\, r_1^{3/4} \Big/ \sum_i W_i\, r_i^{3/4} \qquad (6a)$$

and

$$\ln a_1^C = \ln \phi_1' + (1 - \phi_1') + (z\, M_1 q_1/2)[\ln (\theta_1/\phi_1) - 1 - (\phi_1/\theta_1)] \qquad (5a)$$

Other workers [6] have suggested that a 2/3 power term gives better results than the 3/4 power term. As a third altenative, particularly for the polymeric stationary phases, we have also calculated V_g^0 using a Flory–Huggins (F–H) [15,16] type combinatorial term as used in polymer solution thermodynamics,

$$\ln a_1^C = \ln \varphi_1 + (1 - V_2^0/V_1^0)\, \varphi_2 \qquad (6b)$$

where φ is the volume fraction of a species and V^0 its molar volume.

To compare these expressions, V_g^0 values were calculated for each solute-stationary phase system and the average absolute deviation for each phase is shown in Table I.

The final row of Table I shows the average percentage deviation for each of the modifications tested for all of the V_g^0 values calculated for each phase (58 systems in total). It can be seen that the free-volume corrected results give the best overall results except in the case of NMP, but none of these has a significant advantage over the original UNIFAC treatment. The individual results have not been included here for the sake of brevity, but even in the hydrocarbon mixtures there was no dramatic improvement in the results.

The energetic factor. Clearly then, modification of the combinatorial terms alone using the existing set of interaction parameters is insufficient to give a better prediction of chromatographic behaviour. The parameters were calculated by minimising the deviation of UNIFAC derived activity coefficients from the corresponding experimental values from a large number of vapour–liquid equilibrium systems over a range of concentrations. More recently, several tables of results derived exclusively from experimental data at infinite dilution have been compiled so that it seemed a potentially useful approach to investigate these. Two such parameter tables have been used here. However, it must be stressed that, as yet, these values are only available for a restricted range of systems so that any conclusions must, of necessity, be narrow.

Bastos *et al.* [17] used 11 500 results for vapour-liquid equilibria at infinite dilution covering 40

TABLE I

PERCENTAGE DEVIATION OF UNIFAC V_g^0 VALUES FROM EXPERIMENTAL FOR MODIFICATIONS TO THE COMBINATORIAL TERMS

See text for explanation of column headings.

	Original		$r^{3/4}$		$r^{2/3}$		F–H	
	uni	uni-fv	uni	uni-fv	uni	uni-fv	uni	uni-fv
SQ	17.8	14.4	19.5	18.4	20.2	19.0	29.9	19.5
DNP	19.9	8.7	22.6	11.5	27.0	16.1	35.3	12.9
NMP	41.1	55.0	38.4	53.0	35.4	50.7	92.3	52.9
PIB	99.9	16.3	90.6	15.8	83.4	15.2	61.8	22.5
PEO	32.1	14.0	33.2	22.5	35.9	27.6	22.2	32.7
All	40.4	18.7	34.4	19.2	58.5	23.2	44.6	25.3

groups to calculate values which allowed them to correlate most of the data with an average error of 20%. The original UNIFAC and UNIFAC-FV equations were used with these new parameters and the results are shown in Table II.

It can be seen by comparing values from Table II with those for the original UNIFAC model in Table I that this data set does not significantly improve the predictive value of the method. The "uni" results give a somewhat worse fit to the experimental data. While the free-volume corrected values are slightly closer to experiment using these interaction parameters, the improvements are not significant in terms of using the method to predict chromatographic behaviour. In particular, the new interaction parameter for "CH$_2$O" as in PEO seems to be unsuitable for use with polymers.

The final modification to the UNIFAC method used here is to employ the set of parameters derived by Weidlich and Gmehling [18]. These workers changed the original UNIFAC model by incorporating a $r_i^{3/4}$ term into the expression for the combinatorial term as described above in addition to deriving a new set of interaction parameters that they claimed greatly improved prediction of infinite dilution activity coefficients and enthalpies of mixing. Rather than a single parameter to describe interactions between groups, three new constants for each group were calculated to take account of temperature, T, dependence,

$$\Psi_{ij} = \exp - (a_{ij}/T + b_{ij} + c_{ij}T)$$

where Ψ represents the UNIFAC interaction energy of group i with group j and a_{ij}, b_{ij} and c_{ij} are the tabulated interaction parameters. With this model, the average error in predicted γ_1^∞ for a wide range of

small molecule systems was reduced from 21.1% to 5.3%.

Unfortunately, a number of groups needed for the systems studied here, e.g., the ester group in DNP were not included in the new parameter table so that only a limited range of results could be obtained and these are shown in Table III. For each of SQ and PIB phases, values were calculated for nine solvents and the average deviation from experiment calculated.

As can be seen, this model does give somewhat improved predictions for the systems considered and gives the best fit to experimental results of all the models examined here. However, the best predictions give errors that are of the order of 10% and perhaps it is worth stressing that SQ is a somewhat "ideal" phase in which the best results would be expected. More detailed consideration awaits further development of the parameter sets.

Further discussion

The results presented here have only considered deviations from experimental results. Our previous work [3,4] has shown that, in general, the order of elution of a series of compounds can be reasonably well predicted using UNIFAC. The closest predictions show differences of around 10% from experimental and this is sufficient to lead to reversal of predicted elution order for compounds of different chemical nature and hence to limited application to chromatography.

The reasons for the deviation of the predictions of the UNIFAC models from experimental results can be ascribed to a number of sources. Firstly, any group contribution method must, by its nature, be approximate since it assumes that all functional groups will behave in the same manner irrespective of the molecule in which it occurs and that there are no proximity effects. Clearly, with more groups included, a larger number of environments could be

TABLE II

PERCENTAGE DEVIATION OF UNIFAC V_g^0 VALUES FROM EXPERIMENTAL FOR MODIFICATIONS TO THE UNIFAC INTERACTION PARAMETERS

	uni	uni-fv
SQ	20.5	11.7
DNP	22.1	7.4
NMP	41.1	35.1
PIB	94.6	14.6
PEO	108.2	53.3

TABLE III

PERCENTAGE DEVIATION OF UNIFAC V_g^0 VALUES FROM EXPERIMENTAL FOR METHOD OF WEIDLICH AND GMEHLING [18]

	uni	uni-fv
SQ	10.6	9.4
PIB	74.9	14.3

described but this would lead to an increasing number of parameters needed, reducing the flexibility of the technique.

The application of UNIFAC to chromatographic systems modifies two of the basic situations for which it was developed. The current application requires infinite dilution of solvent while the combinatorial expression and, with the exception of those of Bastos *et al.*, the interaction parameters are derived from results at finite concentrations. An alternative expression to eqns. 5 and 5a may be more appropriate at infinite dilution. However, even when used with interaction parameters derived solely from data measured at infinite dilution, UNIFAC does not yield satisfactory predictions of solution behaviour.

The largest source of error lies in the use of parameters derived using small molecule solutions for polymers. In solutions of low-molecular-weight components, all of the functional groups will be relatively accessible to each other so that it is valid to sum interactions over all groups in solution. However, it is well known that polymer chains can adopt a range of conformations so that a solvent molecule may not be able to interact with all polymer segments. Other reasons for the inability of UNIFAC to describe polymer solutions have been suggested [19–21]. While squalane and dinonyl phthalate are not polymers, they are relatively large molecules so that the same arguments may apply, albeit to a lesser extent. NMP is a much more polar molecule than the others considered and the large deviations found with this system are clearly indicative of the inability of UNIFAC to accurately deal with highly polar interactions which, due to specific interactions, can greatly influence a_1^C as well as a_1^R.

Clearly then, as it stands UNIFAC is unable to predict the retention behaviour of chromatographic systems with sufficient accuracy to justify its widespread use. Future developments that may change this would include the derivation of a parameter set exclusively from polymer systems. Although relatively few have been studied in detail, sufficient studies have been published to allow a preliminary test of this approach. To be useful, we estimate that UNIFAC, or a derivative of the approach, would have to predict V_g^0 to within 5% for a wide range of solvents. If this can be achieved, it would be a relatively straightforward extension to the computer program to calculate the amount of stationary phase or length of capillary column necessary to perform the separation assuming a reasonable efficiency. This seems some way in the future.

REFERENCES

1 W. McReynolds, *J. Chromatogr.*, 8 (1970) 685.
2 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 799.
3 G. J. Price and M. R. Dent, *J. Chromatogr.*, 483 (1989) 1.
4 G. J. Price and M. R. Dent, *J. Chromatogr.*, 585 (1991) 83.
5 A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, 21 (1975) 1086.
6 A. Fredenslund, J. Gmehling and P. Rasmussen, *Vapour–Liquid Equilibria using UNIFAC*, Elsevier, Amsterdam, 1977.
7 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1977.
8 D. Patterson, Y. Tewari, H. P. Schreiber and J. E. Guillet, *Macromolecules*, 4 (1971) 356.
9 T. Oishi and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, 17 (1978) 333.
10 M. Roth and K. Novak, *J. Chromatogr.*, 258 (1983) 23.
11 *Selected Values of the Properties of Hydrocarbons*, T.R.C. Data Project, Texas A&M University, College Station, TX, 1967.
12 A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, 1968.
13 S. Ohe, *Computer Aided Data Book of Vapour Pressures*, Data Publ. Co., Tokyo, 1976.
14 E. R. Thomas and C. A. Eckert, *Ind. Eng. Chem. Process Des. Dev.*, 23 (1984) 194.
15 P. J. Flory, *J. Chem. Phys.*, 9 (1941) 660.
16 M. L. Huggins, *J. Am. Chem. Soc.*, 64 (1942) 1712.
17 J. C. Bastos, M. E. Soares and A. G. Medina, *Ind. Eng. Chem. Res.*, 27 (1988) 1269.
18 U. Weidlich and J. Gmehling, *Ind. Eng. Chem. Res.*, 26 (1986) 1372.
19 A. Bekker, D. E. Knox and S. E. Sund, *J. Solution Chem.*, 16 (1987) 435.
20 G. J. Price and M. R. Dent, *Polymer*, 31 (1990) 1745.
21 L. A. Belfiore, A. A. Patwardhan and T. G. Lenz, *Ind. Eng. Chem. Res.*, 27 (1988) 284.