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

II. Polymer stationary phases

Gareth J. Price*,☆

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

Michael R. Dent

Department of Chemistry, City University, Northampton Square, London EC1V 0HB (UK)

ABSTRACT

The UNIFAC group contribution method and its free volume modified version have been used to calculate thermodynamic activity coefficients and hence specific retention volumes for a number of solutes at infinite dilution in a range of polymeric gas–liquid chromatographic stationary phases including Carbowax and several of the OV series of methyl silicones. Specific retention volumes and partition coefficients have been calculated and used to predict relative retentions and the order of elution of the solutes, and these were compared to corresponding experimental values. However, although in some cases the results were predicted to within a few percent of their experimental values, in general the agreement is not good enough to give a reliable predictive method for a range of solvents and so reinforces the conclusions from work on low-molecular-weight stationary phases that the wider application of group contribution methods awaits future developments.

INTRODUCTION

In an attempt to develop a method for the prediction of retention in gas–liquid chromatography (GLC) stationary phases, a previous paper [1] described the application of the UNIFAC group contribution method to a number of low-molecular-weight phases such as squalane and dinonyl phthalate. The aim was to use the predictions to simplify the choice of a suitable system for a particular analysis from the vast number of available possibilities. Systems were characterised in terms of specific retention volumes [2], V_g^0, and it was found that, in most cases, although the absolute values of V_g^0 were

not accurately predicted, that the correct order of elution was obtained. However, very wide discrepancies were found with polar stationary phases such as N-methyl pyrollidone.

The majority of GLC analyses currently performed use stationary phases developed over the past decade or so based on polymeric materials. These have been found to give excellent results and allow the use of higher analysis temperatures due to their lower volatility. They have been widely used in capillary columns. This paper continues our earlier work by applying our methods to a range of polymer stationary phases including the OV and Carbowax series of materials.

The basis of the method arises from the use of GLC to measure thermodynamic properties of solution [2]. For instance, the activity coefficient of a

---

☆ Formerly of City University, London, UK.

volatile solute at infinite dilution in a low-molecular-weight liquid stationary phase, γ_1^∞, is given by:

$$\gamma_1^\infty = 273.15 \, R/V_g^0 P_1^0 M_2 \tag{1}$$

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 specific retention volume of the solute *i.e.* the retention volume per gram of stationary phase fully corrected to standard temperature and pressure. However, when considering polymers, this definition is often complicated by lack of an accurate value for M_2. Thus, the activity coefficients are usually defined on a weight fraction rather than mole fraction concentration basis. [3]. Thus,

$$\Omega_1^\infty = 273.15 \, R/V_g^0 P_1^0 M_1 \tag{2}$$

where M_1 is now the molecular weight of the volatile solute. The validity of GLC measurements of thermodynamics in polymer systems was not confirmed until well after that in low-molecular-weight systems, particularly with silicone polymers [4], but there is now ample evidence that, under the correct experimental conditions, GLC does provide valid results [5].

The UNIFAC method was developed by Fredenslund and co-workers [6,7] to allow the prediction of phase equilibria and other thermodynamic properties of solution in liquid mixtures. This is a group contribution method which splits the molecules comprising the solution into a number of well defined functional groups. The termodynamic activities of these groups are then summed using previously calculated and tabulated values of a selection of properties. Thus, only relatively few parameters are needed and, since only pure component properties such as densities and molecular weights are needed, this makes the method particularly attractive as it may be used in systems where little or no experimental data is available, as would be the case for a new GLC analysis. The full method has been described elsewhere and is merely summarized here.

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, is calculated using an expression derived from statistical mechanical treatments using tabulated values of parameters calculated from the Van der Waals volumes and surface areas. The second, residual (or enthalpic) contribution to the activity, a_1^R, accounting for energetic interactions in solution, 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. 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 [8].

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

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{FV} \tag{3}$$

Roth and Novak [9] 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" while Price and Ashworth [10] found that a single result from GLC could be used to improve the predictive ability of UNIFAC for polymer solutions. In the previous paper, this method was applied to stationary phases such as squalane, dinonyl phthalate and similar compounds. In this paper, we present a comparison of UNIFAC results for a number of volatile solutes with high quality thermodynamic measurements to gauge the accuracy of our method followed by a systematic approach to a number of analytical systems including methyl silicone polymers with varying phenyl substitution that comprise the OV series of phases and also, as a rather more polar phase, polyethylene oxide, often known as Carbowax.

RESULTS

Analytical GC is usually performed with the solute being analysed effectively at infinite dilution. 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 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 [1] in a BASIC program written for the IBM-PC and converted to an activity coefficient by dividing by the weight fraction. Values of the specific retention volume were calculated from Eqn. 2 using this Ω_1^∞ value and physical property data from literature sources [11]. Values have been calculated using both the original reatment 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

$$\Delta V_g^0(\%) = 100\{[V_g^0(\text{uni}) - V_g^0(\text{exptl.})]/V_g^0(\text{exptl.})\} \quad (4)$$

so that a negative value indicates that UNIFAC underestimates the specific retention volume. The results are also shown graphically by plots of the experimental retention volume *versus* the corresponding UNIFAC value which would, if the predictions were perfect, lie on the diagonal straight line on the graphs.

Poly(isobutylene) (PIB)

PIB, although little used as a GC stationary phase, has been used in a number of thermodynamic studies so that it gives a good basis of comparison with our UNIFAC results. Oishi and Prausnitz [8] applied the method to solutions of PIB in pentane, cyclohexane and benzene and found that solvent activities could be predicted to 24–38% with UNIFAC but to within 3–8% using the free volume correction. However, these results were at high solvent concentrations and any inaccuracies in the method would be expected to be magnified at infinite dilution. Table I lists the specific retention volumes [12] of a number of volatile solutes in PIB at 298 K together with the coresponding values from the UNIFAC treatments. The original UNIFAC gives very poor prediction of these values but, as would be expected, those from the version including the free volume treatment are much closer to experimental results although they are not as good as those found with solutions of higher concentrations. The values are plotted in Fig. 1 which clearly shows that there are large deviations from experimental.

Of perhaps more interest to the chromatographer than the absolute retention volumes are the relative retention volumes of a series of solutes. The values of the solutes considered here are shown in Table II along with the order in which they would elute. This shows that although the order of elution is reasonably well predicted there are some notable exceptions, hexane being swopped with chloroform and cyclohexane with benzene. Thus, it would appear that UNIFAC has limited usefulness with this stationary phase.

TABLE I

SPECIFIC RETENTION VOLUMES OF SOLUTES IN POLY(ISOBUTYLENE) AT 298 K

| Solute	V_g^0 (cm^3 g^{-1})			Deviation, ΔV_g^0 (%)	
	Expt.	uni	uni-fv	uni	uni-fv
Pentane	54.8	151.0	58.5	176.0	6.8
Hexane	184.0	439.9	204.1	139.0	10.9
Heptane	575.3	1263.6	596.6	119.6	3.7
Octane–	1781.1	3665.6	1849.0	105.8	3.8
Cyclohexane	338.8	756.5	440.3	123.3	29.9
Benzene	405.1	628.3	313.4	55.1	−22.6
Toluene	1062.1	1738.1	962.9	63.7	−9.3
Dichloromethane	137.2	172.5	80.2	20.5	−41.5
Chloroform	262.9	330.4	162.9	25.7	−38.0
Carbon tetrachloride	387.4	695.5	321.5	79.5	−17.0
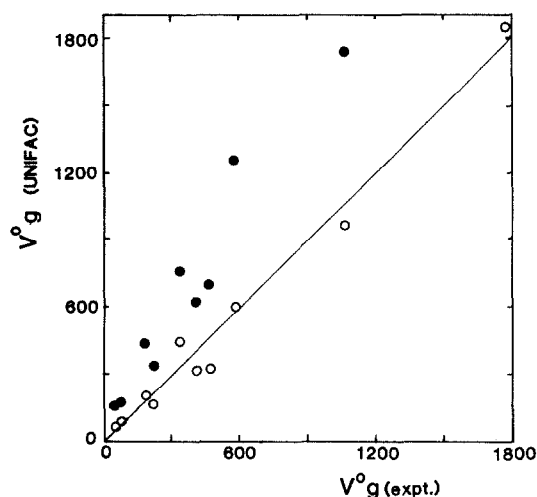
Fig. 1. Plot of experimental *versus* UNIFAC specific retention volumes for solutes in poly(isobutylene) at 298 K. ● = uni; ○ = uni-fv.

Poly(dimethyl siloxane) (PDMS)

PDMS, in addition to being the first in the series of OV analytical stationary phases, has been well studied from a thermodynamic point of view by a number of workers [4,5,12]. Table II lists the specific retention volumes of a number of solutes in this polymer at 298 K together with the predicted values from the UNIFAC treatments. One point that should perhaps be noted is that the UNIFAC interaction parameter for the siloxane SiO group are

based on a rather limited data set [13] so that they carry a fair degree of uncertainty. In particular, UNIFAC interaction parameters are not available for SiO with several of the necessary functional groups such as those including the chloroalkanes. Thus, comparisons in terms of relative values will be more valid than the absolute results.

With this polymer, there is much less difference in the predicted retention volumes from the two UNIFAC variations, the average differences from experimental being 8.6% for the original UNIFAC and 6.6% if the free volume modification in included. The relative retention volumes and order of elution are shown in Table IV. In this case, both UNIFAC treatments predict the correct order of elution for the seven solutes involved. Fig. 2 also shows that the results for PDMS are much closer to experiment than was the case with PIB.

The OV series

The base polymer of this series of stationary phases is PDMS, originally known as OV-1 although a lower-molecular-weight version, OV-101 is now more common. Other phases have been prepared by replacing one or more of the methyl groups with other functionalities including phenyl, trifluoromethyl, cyanopropyl etc. to give a range of materials with varying polarity, basicity etc. It was of interest to apply UNIFAC to these phases since they are in common use. However, as noted above, there are a limited range of UNIFAC interaction

TABLE II

RELATIVE RETENTION VOLUMES OF SOLUTES IN POLY(ISOBUTYLENE) AT 298 K

Solute	Expt. V_g^0 (cm^3 g^{-1})	Relative retention volume			Elution order		
		Expt.	uni	uni-fv	Expt.	uni	uni-fv
Pentane	54.8	1	1	1	1	1	1
Hexane	184.0	3.3	2.9	3.5	3	4	4
Heptane	575.3	10.5	8.4	10.2	8	8	8
Octane	1781.1	32.5	24.3	31.6	10	10	10
Cyclohexane	338.8	6.2	5.0	7.5	5	7	7
Benzene	405.1	7.4	4.1	5.4	7	5	5
Toluene	1062.1	19.4	14.5	16.5	9	9	9
Dichloromethane	137.2	2.5	1.1	1.4	2	2	2
Chloroform	262.9	4.8	2.2	2.8	4	3	3
Carbon tetrachloride	387.4	7.1	4.6	5.5	6	6	6

TABLE III

SPECIFIC RETENTION VOLUMES OF SOLUTES IN POLY(DIMETHYL SILOXANE) AT 298 K

Solute	V_g^0 (cm^3 g^{-1})			Deviation, (%) ΔV_g^0	
	Expt.	uni	uni-fv	uni	uni-fv
Pentane	77.4	81.4	70.2	5.3	−9.3
Hexane	219.5	226.3	204.9	3.1	−6.6
Heptane	604.7	619.9	590.9	2.5	−2.3
Octane	1633.5	1714.9	1641.9	4.9	0.5
Cyclohexane	390.4	470.2	465.7	20.4	11.3
Benzene	359.1	434.5	414.7	20.9	15.5
Toluene	1053.4	1084.7	1064.2	3.0	1.0

TABLE IV

RELATIVE RETENTION VOLUMES OF SOLUTES IN POLY(DIMETHYL SILOXANE) AT 298 K

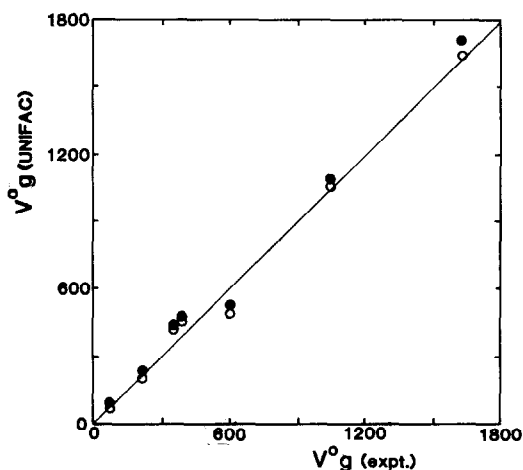| Solute	Expt. V_g^0 (cm^3 g^{-1})	Relative retention volume			Elution order		
		Expt.	uni	uni-fv	Expt.	uni	uni-fv
Pentane	77.4	1	1	1	1	1	1
Hexane	219.5	2.8	2.8	2.9	2	2	2
Heptane	604.7	7.8	7.6	8.4	5	5	5
Octane	1633.5	21.1	21.0	23.4	7	7	7
Cyclohexane	390.4	5.0	5.8	6.6	4	4	4
Benzene	359.1	4.6	5.3	5.9	3	3	3
Toluene	1053.4	13.6	13.3	15.2	6	6	6

Fig. 2. Plot of experimental *versus* UNIFAC specific retention volumes for solutes in poly(dimethyl siloxane) at 298 K. ● = uni; ○ = uni-fv.

parameters available so that only a series with varying phenyl content could be considered. The compounds studied were OV-101, OV-3, OV-7, OV-11 and OV-17 having 0, 10, 20, 35 and 50% phenyl substitution respectively.

Parcher *et al.* [14] measured the retention of five solutes in these stationary phases at 66, 100 and 150°C and the results, along with the UNIFAC predictions, are shown in Tables V–VII. The densities of the polymers at 20°C were taken from the manufacturers' data sheets and those at higher temperatures estimated from the thermal expansion coefficient of PDMS.

In these systems, the free volume modified UNIFAC yields considerably less accurate predictions of retention volume than the original treatment and hence the relative retention volumes are also further away from experiment. However, it is noticeable

TABLE V

RELATIVE RETENTION VOLUMES FOR SOLUTES IN OV PHASES AT 66°C

Solute	Expt. V_g^0 (cm^3 g^{-1})	Deviation, ΔV_g^0 (%)		Relative retention volume			Elution order		
		uni	uni-fv	Expt.	uni	uni-fv	Expt.	uni	uni-fv
OV-101 (0% phenyl)									
Pentane	21.4	5.7	−24.7	1	1	1	1	1	1
Hexane	48.4	4.8	−18.1	2.3	2.2	2.4	2	2	2
Heptane	108.2	4.0	−12.9	5.1	5.0	5.6	4	4	4
Octane	240.4	3.5	−9.8	11.3	11.0	2.8	5	5	5
Benzene	75.2	24.6	13.5	3.5	4.4	5.1	3	3	3
OV-3 (10% phenyl)									
Pentane	18.8	12.0	−17.2	1	1	1	1	1	1
Hexane	43.3	9.2	−13.4	2.3	2.2	2.4	2	2	2
Heptane	98.8	6.5	−10.6	5.3	5.0	5.6	4	3	3
Octane	222.8	4.3	−9.3	11.9	10.9	12.7	5	5	5
Benzene	83.7	26.3	15.1	4.5	5.3	6.2	3	4	4
OV-7 (20% phenyl)									
Pentane	17.3	11.9	−20.8	1	1	1	1	1	1
Hexane	40.3	7.6	−18.5	2.3	2.2	2.4	2	2	2
Heptane	92.6	3.5	−6.9	5.4	4.9	5.5	4	3	3
Octane	211.0	−0.5	−7.3	12.2	10.7	12.6	5	5	5
Benzene	92.4	24.4	10.8	5.3	6.2	7.2	3	4	4
OV-11 (35% penyl)									
Pentane	13.9	19.4	−18.5	1	1	1	1	1	1
Hexane	32.9	13.1	−18.8	2.4	2.2	2.4	2	2	2
Heptane	75.5	7.8	−18.8	2.4	4.8	5.4	4	4	4
Octane	171.6	3.0	−19.4	12.3	10.2	12.2	5	5	5
Benzene	97.9	23.8	5.4	7.0	7.5	8.8	3	3	3
OV-17 (50% phenyl)									
Pentane	11.5	24.5	−21.9	1	1	1	1	1	1
Hexane	26.6	19.4	−20.3	2.3	2.2	2.3	2	2	2
Heptane	60.1	14.7	−18.5	5.2	4.6	5.4	4	4	4
Octane	135.8	9.4	−20.2	11.8	9.8	11.9	5	5	5
Benzene	93.8	28.4	4.0	8.1	8.6	10.3	3	3	3

that the free volume results underestimate V_g^0 while the uncorrected values are overestimated. The two treatments give the same elution order and this in general agrees with experiment, although in some cases benzene is predicted to elute in the wrong place. The results are also displayed in Fig. 3.

Poly(ethylene oxide)

Two determinations of V_g^0 in poly(ethylene oxide) have been published, one on a low-molecular-weight ($1 \cdot 10^4$) sample [15] and the other on a higher-molecular-weight polymer ($4 \cdot 10^6$) [16]. The results are shown in Table VIII and a considerable molecular weight dependence can be seen. This is reflected in the UNIFAC calculations through the density of the polymer and the values of this parameter were those used in the expirimental work. Resulted from the two UNIFAC treatments are compared with experimental in Tables VIII and IX. The agreement with experimental results is very variable with some excellent prediction for some probes such as toluene and xylene but very poor for others such as chloroform and cylcohexane. This is also shown by the scatter of the results in Fig. 4. In general, the free volume corrected results are superior but even these are not in sufficient agreement with experi-

TABLE VI

RELATIVE RETENTION VOLUMES FOR SOLUTES IN OV PHASES AT 100°C

Solute	Expt. V_g^0 (cm^3 g^{-1})	Deviation, ΔV_g^0 (%)		Relative retention volume			Elution order		
		uni	uni-fv	Expt.	uni	uni-fv	Expt.	uni	uni-fv
OV-101 (0% phenyl)									
Pentane	9.9	0.1	−45.3	1	1	1	1	1	1
Hexane	20.2	−2.7	−39.0	2.0	2.0	2.1	2	2	2
Heptane	38.4	−0.2	−26.9	3.9	3.9	4.4	4	4	4
Octane	74.4	−0.3	−21.9	7.5	7.5	8.9	5	5	5
Benzene	29.0	21.9	4.0	2.9	3.7	4.3	3	3	3
OV-3 (10% phenyl)									
Pentane	8.4	10.2	−31.6	1	1	1	1	1	1
Hexane	16.9	8.2	−25.1	2.0	2.0	2.1	2	2	2
Heptane	33.6	6.2	−19.5	4.0	3.8	4.4	4	3	3
Octane	65.9	4.7	−16.6	7.9	7.4	8.9	5	5	5
Benzene	30.4	27.0	9.8	3.6	4.5	5.3	3	4	4
OV-7 (20% phenyl)									
Pentane	7.9	8.5	−38.5	1	1	1	1	1	1
Hexane	16.1	4.9	−33.5	2.0	2.0	2.1	2	2	2
Heptane	32.3	1.0	−29.7	4.1	3.8	4.4	3	3	3
Octane	64.6	−3.4	−29.8	8.2	7.3	8.8	5	5	5
Benzene	33.8	23.9	3.5	4.3	5.2	6.2	4	4	4
OV-11 (35% penyl)									
Pentane	6.5	14.8	−39.1	1	1	1	1	1	1
Hexane	13.3	9.8	−35.9	2.0	1.9	2.1	2	2	2
Heptane	26.4	5.8	−31.7	4.1	3.7	4.3	3	3	3
Octane	53.1	−0.3	−33.9	8.2	7.0	8.5	5	5	5
Benzene	34.5	25.6	0.5	5.3	6.1	7.4	4	4	4
OV-17 (50% phenyl)									
Pentane	5.5	18.2	−47.9	1	1	1	1	1	1
Hexane	11.5	10.6	−48.5	2.0	1.9	2.1	2	2	2
Heptane	22.4	7.4	−41.5	4.1	3.6	4.2	3	3	3
Octane	44.1	2.2	−42.0	8.0	6.7	8.3	5	4	4
Benzene	34.3	27.2	7.3	6.2	7.0	8.6	4	5	5

mental to allow their use in a predictive manner. Table IX shows this in terms of the predicted relative retention volumes and the generally poor predicted elution order of the solutes.

DISCUSSION

Taken overall, the predicted retention volumes from the free volume modified UNIFAC method are closer to the experimental results suggesting that it is indeed useful for polymer solutions. However, the deviations of the infinite dilution results discussed here in most cases are wider than those at higher solvent concentrations discussed by other workers. For the poly(isobutylene) values, it is interesting that the compounds where the biggest differences between the two treatments occur are with the alkane solutes. In solutions of PIB (a polyalkane) with these compounds, there is assumed to be zero enthalpic interaction in UNIFAC whereas there is a small mixing enthalpy in these system [17]. Thus, there are clearly deficiencies in the UNIFAC model even for these straightforward solutions. It also suggests that, as would be expected from current usage [18], the expression for the combinatorial (entropic) contribution to the solvent activity does

TABLE VII

RELATIVE RETENTION VOLUMES FOR SOLUTES IN OV PHASES AT 150°C

Solute	Expt. V_g^0 (cm^3 g^{-1})	Deviation, ΔV_g^0 (%)		Relative retention volume			Elution order		
		uni	uni-fv	Expt.	uni	uni-fv	Expt.	uni	uni-fv
OV-101 (0% phenyl)									
Pentane	3.9	2.4	−70.4	1	1	1	1	1	1
Hexane	6.6	1.4	−50.5	1.7	1.8	1.9	3	3	2
Heptane	11.1	−1.6	−40.5	2.9	3.0	3.5	4	4	4
Octane	18.5	2.2	−32.8	4.8	5.0	6.2	5	5	5
Benzene	9.0	−12.9	−211.1	2.3	1.1	1.3	2	2	3
OV-3 (10% phenyl)									
Pentane	3.5	1.4	−66.0	1	1	1	1	1	1
Hexane	6.0	3.7	−48.0	1.7	1.8	1.9	2	3	3
Heptane	10.3	2.5	−40.4	2.9	3.0	3.5	4	4	4
Octane	17.4	1.2	−35.1	5.0	5.0	6.2	5	5	5
Benzene	9.4	−114.4	−196.2	2.7	1.3	1.5	3	2	2
OV-7 (20% phenyl)									
Pentane	3.1	−3.7	−67.4	1	1	1	1	1	1
Hexane	5.5	4.0	−53.2	1.8	1.8	1.9	2	3	3
Heptane	9.5	1.3	−46.7	3.0	3.0	3.4	3	4	4
Octane	16.2	−1.7	−43.3	5.2	4.9	6.1	5	5	5
Benzene	9.8	−113.4	−205.3	3.2	1.4	1.7	4	2	2
OV-11 (35% penyl)									
Pentane	2.6	9.0	−71.2	1	1	1	1	1	1
Hexane	4.6	7.8	−58.8	1.7	1.8	1.9	2	3	2
Heptane	8.0	3.3	−55.0	3.1	2.9	3.4	3	4	4
Octane	13.7	3.3	−53.1	5.2	4.7	5.9	5	5	5
Benzene	9.9	−107.3	−218.6	7.0	7.5	8.8	4	2	3
OV-17 (50% phenyl)									
Pentane	2.4	5.8	−98.4	1	1	1	1	1	1
Hexane	4.2	5.4	−80.9	1.7	1.7	1.9	2	2	2
Heptane	7.1	1.1	−75.6	2.9	2.8	3.3	3	4	4
Octane	12.1	4-0	−73.7	5.0	4.5	5.7	5	5	5
Benzene	10.0	−107.8	−252.3	4.2	1.9	2.3	4	3	3

not completely describe the situation in polymer solutions. These points have been addressed in a number of modifications to the UNIFAC combinatorial and free volume model [7,13,19,20] and we intend to investigate these in a forthcoming paper.

Many of the results showing greatest deviation from experimental are those involving polar solvents such as alcohols. This may well be due to the inability of the UNIFAC interaction parameters to describe such polar intermolecular forces. Additionally, doubts have been expressed [21] as to use of small molecule interaction parameters for polymer solutions since the restricted conformations of

the chain may prevent some interactions. A related factor may be that these interaction parameters may not describe infinite dilution conditions with sufficient accuracy for use in chromatography. Recently, parameters have been derived solely from infinite dilution data [22,23] and it is intended to explore the use of these for predicting retention volumes.

Thus, on the basis of these results, the same conclusion must be drawn as was the case with low-molecular-weight stationary phases, that at its present stage of refinement, the UNIFAC methods cannot be used to predict chromatographic behaviour
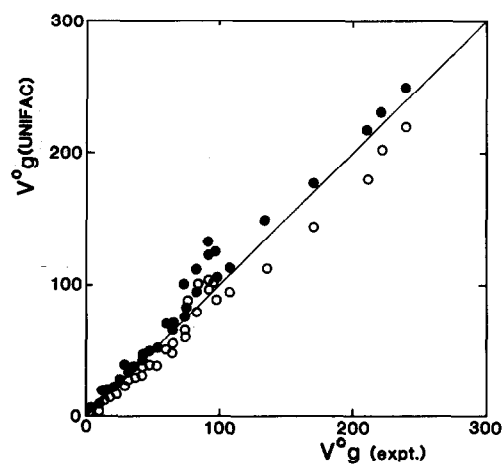
Fig. 3. Plot of experimental *versus* UNIFAC specific retention volumes for solutes in OV polymers at 66 and 100°C. (Some points have been omitted for clarity.) ● = uni; ○ = uni-fv.
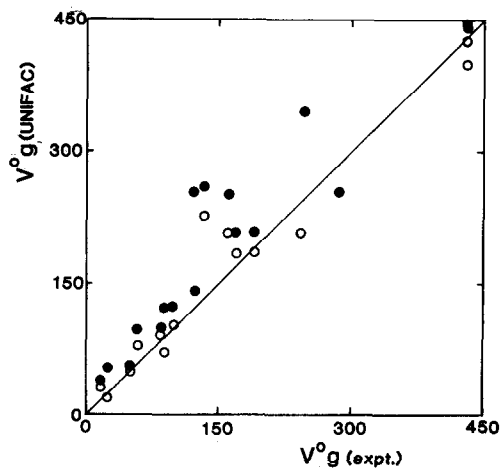
Fig. 4. Plot of experimental *versus* UNIFAC specific retention volumes for solutes in poly(ethylene oxides) at 343 K. ● = uni; ○ = uni-fv.

TABLE VIII

SPECIFIC RETENTION VOLUMES OF SOLUTES IN POLY(ETHYLENE OXIDE) AT 70°C

	Solute	V_g^0 (cm^3 g^{-1})			Deviation, ΔV_g^0 (%)	
		Expt.	uni	uni-fv	uni	uni-fv
A[a]	Water	283.9	254.8	0.1	− 10.3	−
	1-Butan-ol	431.6	444.4	401.3	3.0	− 7.0
	Chloroform	124.0	253.6	141.0	104.5	13.7
	1,1,2-Trichloroethane	643.2	322.8	300.6	− 49.8	− 53.3
	Benzene	89.4	123.2	70.1	37.8	− 21.2
	Toluene	173.6	209.2	185.8	20.5	7.0
	O-Xylene	430.6	448.0	426.9	4.0	− 0.8
	Acetone	50.4	56.3	48.9	11.8	− 2.8
	Butanone	86.7	101.4	90.5	16.9	4.3
	Butyl acetate	246.0	346.4	209.2	40.8	− 14.9
B[b]	Heptane	17.9	37.1	30.0	107.7	68.0
	Decane	134.6	261.8	233.1	94.5	73.2
	Benzene	100.0	123.2	102.9	23.2	2.9
	Toluene	192.6	209.2	185.5	8.6	− 3.7
	Cyclohexane	22.9	53.2	20.8	132.1	− 9.2
	Chloroform	162.1	253.6	208.4	56.4	28.6
	Ethyl acetate	62.7	95.8	77.4	52.7	23.4

[a] Results from ref. 16. Polymer molecular weight = 4 · 10^6, density = 1.175 g cm^{-3}.
[b] Results from ref. 15. Polymer molecular weight = 10 000, density = 1.085 g cm^{-3}.

TABLE IX

SPECIFIC RETENTION VOLUMES OF SOLUTES IN POLY(ETHYLENE OXIDE) AT 70°C

Solute	Expt. V_g^0 (cm^3 g^{-1})	Relative retention volume			Elution order		
		Expt.	uni	uni-fv	Expt.	uni	uni-fv
[a] Water	283.9	5.6	4.5	–	7	6	–
1-Butan-ol	431.6	8.6	7.9	8.2	9	9	8
Chloroform	124.0	2.5	4.5	2.9	4	5	4
1,1,2-Trichloroethane	643.2	12.8	5.7	6.1	9	7	7
Benzene	89.4	1.8	2.2	1.4	3	3	2
Toluene	173.6	3.4	3.7	3.8	5	4	5
O-Xylene	430.6	8.5	7.9	8.7	8	10	9
Acetone	50.4	1	1	1	1	1	1
Butanone	86.7	1.7	1.8	1.8	2	2	3
Butyl acetate	246.0	4.9	6.1	4.7	6	8	6
[b] Heptane	17.9	1	1	1.4	1	1	2
Decane	134.6	7.5	7.1	11.2	5	7	7
Benzene	100.0	5.6	3.3	5.0	4	4	4
Toluene	192.6	10.8	5.6	8.9	7	5	5
Cyclohexane	22.9	1.3	1.4	1	2	2	1
Chloroform	162.1	9.1	6.8	10.0	6	6	6
Ethyl acetate	62.7	3.5	2.6	3.7	3	3	3

[a] Results from ref. 16. Polymer molecular weight = $4 \cdot 10^6$, density = 1.175 g cm^{-3}.
[b] Results from ref. 15. Polymer molecular weight = 10000, density = 1.085 g cm^{-3}.

with any degree of certainty. Whether the adaptations developed will improve its predictive use will be the subject of a future communication.

REFERENCES

1 G. J. Price and M. R. Dent, *J. Chromatogr.*, 483 (1989) 1.
2 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1977.
3 D. Patterson, Y. Tewari, H. P. Schreiber and J. E. Guillet, *Macromolecules*, 4 (1971) 356.
4 R. Lichtenthaler, J. M. Prausnitz, C. Su, H. P. Schreiber and D. Patterson, *Macromolecules*, 7 (1984) 136.
5 A. J. Ashworth, C. Chien, D. Furio, D. M. Hooker, M. Kopecni, R. J. Laub and G. J. Price, *Macromolecules*, 17 (1984) 1090.
6 A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J*, 21 (1975) 1086.
7 A. Fredenslund, J. Gmehling and P. Rasmussen, *Vapour–Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, 1977.
8 T. Oishi and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, 17 (1978) 333.
9 M. Roth and K. Novak, *J. Chromatogr.*, 258 (1983) 23.

10 G. J. Price and A. J. Ashworth, *Polymer*, 28 (1987) 2105.
11 *Selected Values of the Properties of Hydrocarbons*, TRC Data Project, Texas A&M University, College Station, TX 1967.
12 G. J. Price, J. E. Guillet and J. H. Purnell, *J. Chromatogr.*, 369 (1986) 273.
13 M. Gottlieb and M. Herskowitz, *Macromolecules*, 14 (1981) 1468.
14 J. F. Parcher, J. R. Hansborough and A. M. Koury, *J. Chromatogr.*, 16 (1978) 183.
15 M. Galin, *Polymer*, 24 (1983) 865.
16 Y. H. Chang and D. C. Bonner, *J. Appl. Polym. Sci.*, 19 (1975) 2439.
17 A. Rodrigues and D. Patterson, *J. Chem. Soc. Faraday II.*, 78 (1982) 501.
18 P. J. Flory, *Discuss. Faraday Soc.*, 49 (1970) 7.
19 A. Bekker, D. E. Knox and S. E. Sund, *J. Solution Chem.*, 16 (1987) 435.
20 U. Weidlich and J. Gmehling, *Ind. Eng. Chem. Res.*, 26 (1987) 1372.
21 L. A. Belfiore, A. A. Parwardhan and T. G. Lenz, *Ind. Eng. Chem. Res.*, 27 (1988) 284.
22 A. Sarius, K. Gerstenberger, F. Hradsky, W. Hauthal and H. Freydank, *Chem. Tech. (Leipzig)*, 36 (1984) 159.
23 J. C. Bastos, M. E. Soares and A. G. Medina, *Ind. Eng. Chem. Res.*, 27 (1988) 1269.