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UTILIZATION OF THE SOLUTION-OF-GROUPS CONCEPT IN GAS-LIQUID CHROMATOGRAPHY

MICHAL ROTH* and JOSEF NOVÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Leninova 82, 61142 Brno (Czechoslovakia)

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SUMMARY

The possibilities of utilizing the UNIFAC group model of activity coefficients for the prediction of gas-liquid chromatographic retention data are discussed. Examples of the determination of the specific retention volumes of different types of solute compounds on both simple and mixed stationary phases, relative retentions, Kováts retention indices and differential sorption enthalpies are given. It appears that the original version of the UNIFAC model can be used merely to give a rough estimation of relative retentions, Kováts retention indices and sorption enthalpies.

INTRODUCTION

Since the advent of gas chromatography, considerable attention has been paid to relationships between the molecular structure of solutes and their chromatographic behaviour. In a number of papers, Kováts retention indices¹ were utilized to characterize the retention behaviour of solute compounds as well as the properties of chromatographic stationary phases. The retention indices predicted from the structure and/or topology of the solute molecules are often in good agreement with experimental values²⁻⁵. However, the applicability of these methods is usually limited to a very narrow range of compounds (*e.g.*, isoalkanes²⁻⁵). These methods also lack direct consistency with the thermodynamics of solutions, which restricts the possibilities of the interpretation of the results.

Another possibility of predicting and/or correlating retention behaviour is based on the relationship between the specific retention volume and the activity coefficient of the solute compound in a given chromatographic system. Provided the gaseous phase behaves ideally, this relationship is described by the equation⁶

$$V_g^0 = 273.15 R / (\gamma_D P_D^0 x_1 M_1) \quad (1)$$

where V_g^0 , R , γ_D , P_D^0 , x_1 and M_1 are the specific retention volume of the solute, molar gas constant, Raoult-law activity coefficient of the solute, saturation vapour

pressure of the solute, molar fraction of the stationary phase (solvent) in the solute-stationary phase mixture within the gas chromatographic zone and the molar mass of the solvent, respectively. Unless the molar mass of the solvent is significantly (more than about 100 times) larger than that of the solute, the quantity x_1 approaches unity under the usual conditions of elution gas chromatographic experiments, and eqn. 1 is simplified to

$$V_g^0 = 273.15 R / (\gamma_D^\infty P_D^0 M_1) \quad (2)$$

where γ_D^∞ is the solute activity coefficient at infinite dilution with the solvent. For mixed solvents composed of k pure components there holds under the conditions of infinite solute dilution

$$V_g^0 = 273.15 R / \left[\gamma_D^\infty P_D^0 \sum_{i=1}^k (x_i' M_i) \right] \quad (3)$$

where M_i and x_i' are the molar mass and molar fraction of an i th component of the mixed solvent $\left(\sum_{i=1}^k x_i' = 1 \right)$, respectively. Hence, if the values of M_1 (M_i), P_D^0 and γ_D^∞ are known, it is possible to estimate by eqn. 2 and/or eqn. 3 the value of V_g^0 for a given solute in a given solvent under given conditions. Vapour pressure data for a large number of compounds are available in the literature, so that the main problem of predicting V_g^0 by eqns. 2 and 3 is obtaining the value of the activity coefficient.

One of the possibilities of obtaining the activity coefficient is the use of the solution-of-groups model. This approximate model is based on the assumption that the excess chemical potential of each component of a liquid mixture of non-electrolytes is given by the sum of the contributions of the groups that constitute the molecule of the component. An exact formal derivation of the basic equation of this model was published by Hála⁷. The concept of solution-of-groups model is due to Langmuir (*c.f.* the respective quotation in ref. 9).

A remarkable advance has been the combination of the group model with semi-empirical relationships for the excess Gibbs function of a liquid mixture, based on the concept of local composition of the mixture. One of these relationships is Abrams and Prausnitz's⁸ universal quasi-chemical equation (UNIQUAC). Fredenslund *et al.*⁹ combined the UNIQUAC equation with the solution-of-groups concept. The resulting UNIFAC model (UNIQUAC Functional-Group Activity Coefficients) makes it possible to calculate activity coefficients in both binary and multi-component liquid mixtures by virtue of structural parameters and binary parameters characterizing the energy of mutual interaction of the functional groups present in the system. The structural parameters are derived from the Van der Waals volumes and surface areas of the functional groups. The interaction parameters were obtained by reducing a large volume of experimental data on vapour-liquid and liquid-liquid equilibria. The activity coefficient of a component is calculated as the product of a combinatorial and a residual contribution. The combinatorial contribution depends only on the

sizes and shapes of the molecules present in the system, whereas the residual contribution depends on the energy of interaction of pairs of functional groups and on the fraction of the surface of these groups that is available for mutual interaction. This approach partially takes into account the deviation of the actual molecular configuration in the mixture from the configuration corresponding to random mixing of the components. It is particularly this feature that makes the UNIFAC method attractive in view of its possible application in gas-liquid chromatography (GLC).

Scheller *et al.*¹⁰ published a group-model variant parameterized on the basis of GLC retention behaviour. The possibilities of using the group model in chromatography were outlined by Pierotti *et al.*¹¹, Langer¹² and, most recently, Rizzi and Huber¹³. The aim of this work was to try out these possibilities with regard to their utilization for predicting GLC retention data.

CALCULATION

A program in Fortran IV, for the calculation of the activity coefficients of solutes at infinite dilution was designed on the basis of the equations and group parameters quoted by Fredenslund *et al.*⁹. The saturation solute vapour pressures necessary to calculate specific retention volumes (*cf.*, eqns. 2 and 3) were calculated from tabulated¹⁴ Antoine-equation constants.

RESULTS

Simple stationary phases

The specific retention volumes were calculated, in the above-outlined way, for

TABLE I
COMPARISON OF CALCULATED SPECIFIC RETENTION VOLUMES WITH THE CORRESPONDING EXPERIMENTAL¹⁵ VALUES

$$\Delta (\%) = 100[(V_g^0)_{\text{exp.}} - (V_g^0)_{\text{calc.}}]/(V_g^0)_{\text{exp.}}$$

<i>Stationary phase</i>	<i>Solute</i>	<i>Temperature</i> (°C)	$(V_g^0)_{\text{calc.}}$ (ml/g)	$(V_g^0)_{\text{exp.}}$ (ml/g)	$\Delta (\%)$
Squalane	Toluene	80	192	226	14.9
	Heptanal	80	369	478	22.8
	<i>n</i> -Decane	80	1951	1508	29.4
Bis(2-ethylhexyl) sebacate	2-Octanone	120	333	341	2.4
	Ethyl propionate	120	49.4	40.8	21.0
Bis(2-ethylhexyl) adipate	2,3-Dimethylbutane	100	25.4	20.5	24.1
	Di- <i>n</i> -propyl ether	100	77.5	54.1	43.3
Dibutyl tetrachlorophthalate	3-Methyl-2-pentanol	120	54.9	77.1	28.9
Dioctyl phthalate	3-Pentanone	120	49.5	41.0	20.7
	<i>n</i> -Propyl acetate	120	59.2	36.1	64.0
Bis(2-ethoxyethyl) phthalate	<i>o</i> -Xylene	120	140	142	1.7
	<i>m</i> -Xylene	120	120	113	6.1
	<i>p</i> -Xylene	120	117	111	5.5
Docosanol	2-Propanol	100	53.0	35.5	49.2
Carbowax 400	1-Pentanol	100	449	269	67.0
	1,4-Dioxane	100	110	87.1	26.0
	3-Hydroxy-2-butanone	100	325	388	16.2
Diglycerol	1-Propanol	120	51.9	20.4	155
	1,3-Propanediol	120	4930	3895	26.6

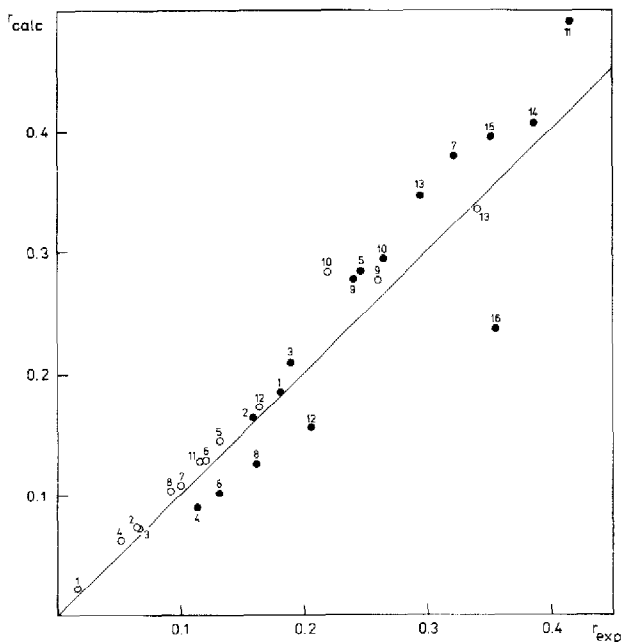


Fig. 1. Comparison of calculated and experimental¹⁵ relative retention volumes at 120°C. (O) Ketones—dioctyl phthalate (relative to 2-nonanone): 1 = acetone; 2 = 2-pentanone; 3 = 3-pentanone; 4 = 3-methyl-2-butanone; 5 = 2-hexanone; 6 = 3-hexanone; 7 = 3-methyl-2-pentanone; 8 = 4-methyl-2-pentanone; 9 = 2-heptanone; 10 = 4-heptanone; 11 = 2,4-dimethyl-3-pentanone; 12 = cyclopentanone; 13 = cyclohexanone. (●) Alcohols—diglycerol (relative to 1-nonanol): 1 = methanol; 2 = ethanol; 3 = 1-propanol; 4 = 2-propanol; 5 = 1-butanol; 6 = 2-butanol; 7 = 1-pentanol; 8 = 2-pentanol; 9 = 2-methyl-1-butanol; 10 = 3-methyl-1-butanol; 11 = 1-hexanol; 12 = 2-hexanol; 13 = 2-methyl-1-pentanol; 14 = 3-methyl-1-pentanol; 15 = 4-methyl-1-pentanol; 16 = 2-octanol.

140 compounds (hydrocarbons, alcohols, ketones, esters and ethers) on nine stationary phases [bis(2-ethoxyethyl) phthalate, Carbowax 400, dibutyl tetrachlorophthalate, bis(2-ethylhexyl) sebacate, bis(2-ethylhexyl) adipate, dioctyl phthalate, diglycerol, *n*-docosanol and squalane]. As is shown by several examples in Table I, the differences between the calculated and measured¹⁵ V_g^0 values reach tens percent of the value measured.

It is possible from the calculated V_g^0 values to express the respective relative retention data ($r_{\text{calc.}}$) and compare them with the corresponding measured relative retention data ($r_{\text{exp.}}$). Fig. 1 shows a comparison of the $r_{\text{calc.}}$ and $r_{\text{exp.}}$ values for ketones on dioctyl phthalate and alcohols on diglycerol. As would be expected (see Discussion), with the alcohol—diglycerol systems there are marked differences between the calculated and measured r values.

The calculated V_g^0 values were further processed to express the Kováts retention indices ($I_{\text{calc.}}$). Fig. 2 shows a comparison of these data with the corresponding measured values ($I_{\text{exp.}}$) for alkyl esters of lower carboxylic acids on bis(2-ethylhexyl) sebacate and for alcohols on *n*-docosanol. With the esters on bis(2-ethylhexyl) sebacate the differences $|I_{\text{calc.}} - I_{\text{exp.}}|$ usually do not exceed 10, whereas with the alcohols on *n*-docosanol these differences are as high as 50 or more.

Mixed stationary phases

In recent years, considerable attention has been devoted to the utilization of GLC with mixed stationary phases (mixed solvents) for studying the thermodynamics of molecular associations in solutions¹⁶⁻²⁴. Until now, essentially two models of liquid mixtures were applied in the interpretation of the retention behaviour of solutes on mixed solvents: (1) a model^{16,17,21-23} based on the combination of Scatchard-Hildebrand's theory of regular solutions and the Flory-Huggins equation, involving the assumption of *random mixing* of the components of the mixture; and (2) Purnell and co-workers' "microscopic partitioning" model^{18,19}, according to which a liquid mixture of two solvents is looked upon as a *microscopically two-phase liquid*, consisting of microscopic aggregates of the molecules of the individual pure components. The distribution constant $K_{R(M)}$ of a solute in a gas-mixed solvent system is, in the context of this model, given by the simple equation

$$K_{R(M)} = \varphi_S K_{R(S)} + \varphi_A K_{R(A)} \quad (4)$$

where $K_{R(S)}$ and $K_{R(A)}$ are the distribution constants of the solute in the pure components S and A of the mixed solvent, respectively, and φ_S and φ_A are the volume fractions of these components in the mixed solvent ($\varphi_S + \varphi_A = 1$).

As it allows, to some extent, for deviations from random mixing of the components of mixtures, the UNIFAC model probably offers a more realistic picture of the situation than the above two models can do, and therefore seems to be a plausible compromise between the rather extreme views of the situation with the other¹ two models. Eqn. 3 makes it possible to utilize the UNIFAC model to establish the course of the dependence of $K_{R(M)}$ on the composition of the mixed solvent.

Meyer and Meyer²⁴ studied the retention behaviour, of *n*-alkanes, 1-chloroalkanes and α,ω -dichloroalkanes on *n*-eicosane-dinonyl ketone (DNK) mixed stationary phases at 60°C. The volume fractions of the components of the stationary phase were calculated with the (experimentally checked) assumption of zero excess volume of mixing. The distribution constant, $K_{R(X)}$, of a solute in a gas-solvent X system at temperature *T* is related to the specific retention volume of the solute on solvent X as a stationary phase by

$$K_{R(X)} = V_g^0 T \rho_X / 273.15 \quad (5)$$

where ρ_X and *T* are the stationary phase density and column temperature, respectively. Fig. 3 shows a comparison of the measured and calculated courses of the dependences of the distribution constant of *n*-heptane on the volume fraction of DNK in the liquid phase. Similar dependences are shown for 1-chlorobutane and 1,2-dichloroethane in Figs. 4 and 5, respectively. It is apparent from Figs. 4 and 5 that the UNIFAC method considerably overestimates the deviations of the $K_{R(M)}$ versus φ_{DNK} dependence from linearity with the solutes employed.

Dependence of retention on temperature

It is also possible to predict the temperature dependence of retention by means of the UNIFAC method. The dependence of the specific retention volume on temperature is described by

$$d \ln V_g^0 / dT = \Delta H_s^0 / (RT^2) \quad (6)$$

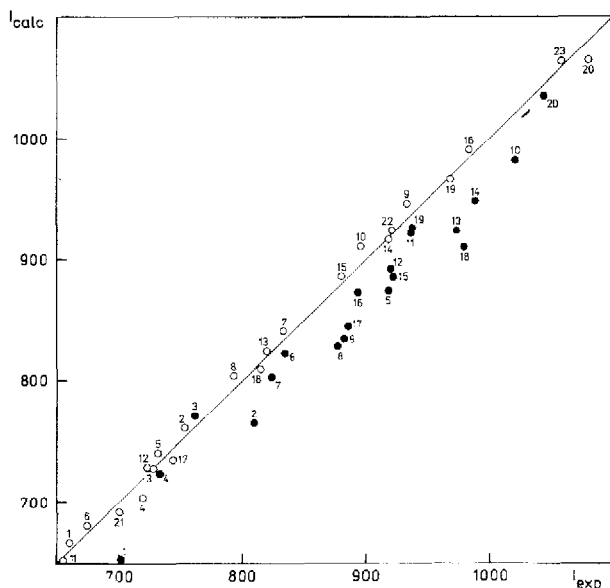


Fig. 2. Comparison of calculated and experimental^{11,5} Kováts retention indices. (O) Esters bis(2-ethylhexyl) sebacate at 120°C: 1 = propyl formate; 2 = butyl formate; 3 = isobutyl formate; 4 = *sec.*-butyl formate; 5 = *n*-propyl acetate; 6 = isopropyl acetate; 7 = *n*-butyl acetate; 8 = isobutyl acetate; 9 = *n*-pentyl acetate; 10 = isopentyl acetate; 11 = methyl propionate; 12 = ethyl propionate; 13 = *n* propyl propionate; 14 = *n*-butyl propionate; 15 = isobutyl propionate; 16 = isopentyl propionate; 17 = methyl *n*-butyrate; 18 = ethyl *n*-butyrate; 19 = isobutyl *n*-butyrate; 20 = isopentyl *n*-butyrate; 21 = methyl isobutyrate; 22 = isobutyl isobutyrate; 23 = ethylene diacetate. (●) Alcohols-*n*-docosanol at 100°C: 1 = 1-propanol; 2 = 1-butanol; 3 = isobutanol; 4 = *sec.*-butanol; 5 = 1-pentanol; 6 = 2-pentanol; 7 = 3-pentanol; 8 = 2-methyl-1-butanol; 9 = 3-methyl-1-butanol; 10 = 1-hexanol; 11 = 2-hexanol; 12 = 3-hexanol; 13 = 2-methyl-1-pentanol; 14 = 4-methyl-1-pentanol; 15 = 3-methyl-2-pentanol; 16 = 4-methyl-2-pentanol; 17 = 2-methyl-3-pentanol; 18 = 2-ethyl-1-butanol; 19 = cyclopentanol; 20 = cyclohexanol.

where ΔH_s^0 is the standard differential molar enthalpy of sorption (enthalpy change associated with the transition of 1 mole of solute from a standard state in the gaseous phase to a standard state in the stationary phase). Provided that the gaseous phase can be assumed to behave as an ideal gas, the value of ΔH_s^0 is virtually equal to the differential molar heat of sorption as measured under the actual conditions of the GLC experiment. If, in addition, the value of ΔH_s^0 can be assumed to be invariant within the temperature interval (T_1 , T_2), it is possible to write

$$\Delta H_s^0 = RT_1 T_2 [\ln V_g^0(T_2) - \ln V_g^0(T_1)] / (T_2 - T_1) \quad (7)$$

Employing eqn. 7, the ΔH_s^0 values for 28 solute compounds on *n*-hexadecane and its derivatives were calculated from the respective specific retention volumes at 40 and 60°C, calculated by eqn. 2. These data are summarized and compared with the corresponding measured data^{2,5} in Table II. The mean relative error is less than 10% of the measured ΔH_s^0 value.

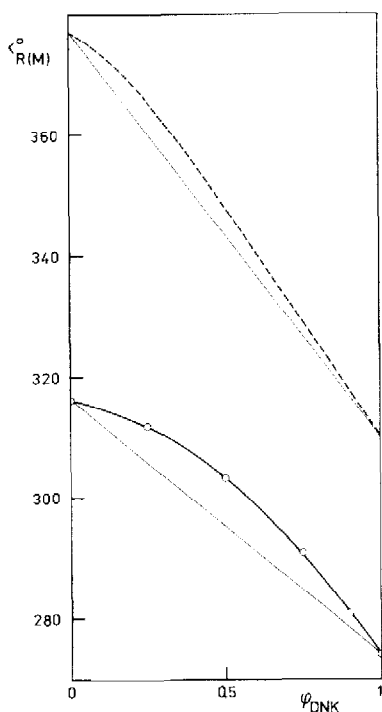


Fig. 3. Partition coefficient of *n*-heptane at 60°C as a function of the volume fraction of DNK in a mixed solvent (DNK-*n*-icosane). —○—, Experimental curve²⁴; ----, calculated curve.

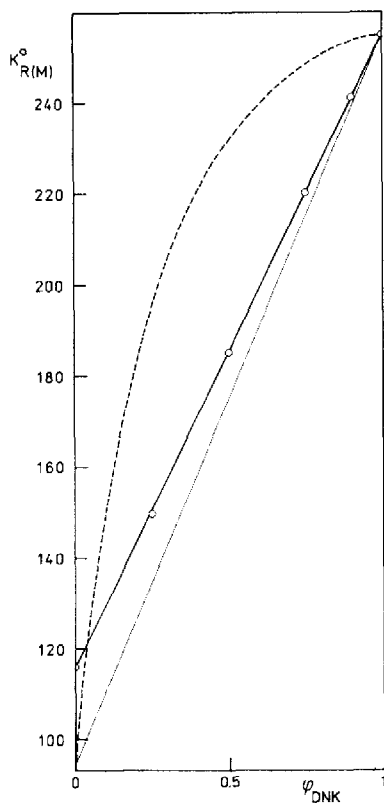


Fig. 4. Partition coefficients of 1-chlorobutane at 60°C as a function of the volume fraction of DNK in a mixed solvent (DNK-*n*-icosane). —○—, Experimental curve²⁴; ----, calculated curve.

DISCUSSION

If the less significant errors introduced by the assumption of ideal behaviour of the gaseous phase and by calculating the saturation solute vapour pressures by the Antoine equation are disregarded, the causes of the discrepancies between measured and calculated retention data can be divided into two groups: (1) errors brought about by the fact that the experimental retention data do not represent "exact" solution of the solute in the solvent and (2) errors due to the method used for calculating the activity coefficients.

Errors of the first type

The calculation of retention data is based on the relationship between the specific retention volume and the activity coefficient of the solute compound. Hence, it is assumed that there is sorption equilibrium in the solute-concentration maximum of the chromatographic zone and that the retention of the solute is due exclusively

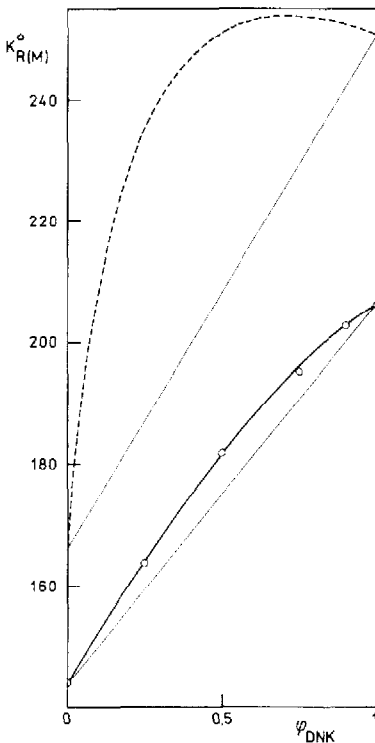


Fig. 5. Partition coefficient of 1,2-dichloroethane at 60°C as a function of the volume fraction of DNK in a mixed solvent (DNK *n*-eicosane). ---○---, Experimental curve²⁴; -----, calculated curve.

to its dissolution in the bulk liquid stationary phase. As the stationary phase is spread in the form of an effectively very thin layer over a large surface area of the support, the first assumption is fairly well met; possible exceptions may be systems with high-molecular-weight stationary phases. However, the second assumption is more important. If the polarity of the solute differs appreciably from that of the stationary phase, the adsorption of solute at the gas solvent phase interface^{26,27} can significantly contribute to the retention of the solute. With polar solutes, also the adsorption of solute at the solvent-support phase interface²⁸ may play an important role. Part of the discrepancy between calculated and measured data is undoubtedly due to the above adsorption effects.

Errors of the second type

As the solution-of-groups model is a generalized method²⁹, no concentration region is preferred in selecting the data base of the model. This results in the fact that the discrepancy between the measured and calculated activity coefficients of a given component in the system is usually largest at infinite dilution of the component^{13,29}. With most applications of the group model in chemical engineering, from the needs of which the model has developed, the above fact does not matter.

With regard to the potential utilization of the solution-of-groups model in

TABLE II

COMPARISON OF CALCULATED STANDARD DIFFERENTIAL MOLAR ENTHALPIES OF SORPTION ($\Delta H_{s, \text{calc.}}^0 \equiv \Delta H_c$) WITH THE CORRESPONDING EXPERIMENTAL VALUES^{2,5} ($\Delta H_{s, \text{exp.}}^0 \equiv \Delta H_m$).

$$\Delta(\%) = |100(\Delta H_{s, \text{exp.}}^0 - \Delta H_{s, \text{calc.}}^0) / \Delta H_{s, \text{exp.}}^0|$$

Solute	Stationary phase								
	<i>n</i> -Hexadecane			1-Chlorohexadecane			Palmitonitrile		
	$-\Delta H_m$ (kJ/mole)	$-\Delta H_c$ (kJ/mole)	$\Delta(\%)$	$-\Delta H_m$ (kJ/mole)	$-\Delta H_c$ (kJ/mole)	$\Delta(\%)$	$-\Delta H_m$ (kJ/mole)	$-\Delta H_c$ (kJ/mole)	$\Delta(\%)$
Isopentane	21.92	25.52	16.41	24.77	25.36	2.36	22.43	24.81	10.63
<i>n</i> -Pentane	26.86	26.78	0.31	26.36	26.61	0.95	23.51	26.11	11.03
2-Methylpentane	29.00	29.71	2.45	28.79	29.46	2.33	26.90	28.87	7.31
3-Methylpentane	30.00	30.00	0.00	28.91	29.75	2.89	27.03	29.20	8.05
<i>n</i> -Hexane	31.09	31.13	0.13	30.21	30.88	2.22	28.37	30.33	6.93
2,4-Dimethylpentane	30.50	31.13	2.06	30.21	30.88	2.22	27.99	30.21	7.92
3-Methylhexane	33.68	34.23	1.61	33.64	33.97	1.00	31.38	33.26	6.00
<i>n</i> -Heptane	35.06	35.56	1.43	35.40	35.31	0.24	32.55	34.64	6.43
1-Pentene	25.02	26.48	5.85	24.98	26.44	5.86	22.93	25.65	11.86
2-Methyl-2-butene	26.32	27.74	5.41	26.48	27.70	4.58	24.52	26.78	9.22
1-Hexene	29.58	30.71	3.81	30.04	30.63	1.95	27.36	29.75	8.72
1-Heptene	34.27	35.06	2.32	34.43	34.98	1.58	32.09	34.02	6.00
Cyclohexane	31.30	32.80	4.81	31.05	32.59	4.99	28.49	32.13	12.78
Benzene	30.79	32.09	4.21	31.71	33.14	4.49	32.47	32.55	0.26
Diethyl ether	26.90	27.20	1.09	24.94	—	—	26.19	—	—
Di- <i>n</i> -propyl ether	33.39	34.56	3.51	34.35	—	—	33.39	—	—
Methanol	27.91	25.48	8.70	23.22	28.45	22.52	29.66	30.08	1.41
Ethanol	26.02	33.05	27.01	27.28	34.94	28.07	32.26	36.61	13.49
<i>n</i> -Propanol	27.87	38.07	36.64	28.66	40.04	39.71	37.32	41.59	11.43
<i>n</i> -Butanol	28.58	43.89	53.59	33.30	45.77	37.44	41.34	47.28	14.37
Methyl formate	20.71	23.81	14.95	20.92	—	—	23.30	—	—
Ethyl formate	23.93	26.23	9.62	26.02	—	—	27.49	—	—
Ethyl acetate	28.24	30.71	8.74	30.21	—	—	32.05	—	—
Methyl ethyl ketone	27.23	25.90	5.21	30.21	32.93	9.00	31.00	34.77	12.15
Propionaldehyde	20.50	25.02	22.04	26.48	—	—	26.78	—	—
<i>n</i> -Butyraldehyde	27.57	28.66	3.95	29.92	—	—	30.67	—	—
<i>n</i> -Propyl chloride	25.10	27.20	8.33	27.41	28.37	3.51	27.07	29.08	7.42
Ethyl cyanide	24.48	29.20	19.32	29.29	32.84	12.14	32.47	34.43	6.06
<i>n</i> -Propyl cyanide	28.87	32.68	13.19	33.64	36.28	7.84	32.47	37.78	16.37
Average relative error (%)			9.89			9.00			8.90

chromatography, Rizzi and Huber¹³ recently tested the capability of four different variants of the model of predicting accurately activity coefficients in binary mixtures. Five different groups, namely CH₂, C-OH, CO, aromatic CH and H₂O, occurred in the mixtures investigated. The ASOG (*cf.*, ref. 13) and UNIFAC⁹ models yielded the most accurate reproduction of limiting activity coefficients. Rizzi and Huber¹³ found a marked improvement in the reproduction of activity coefficients at low concentrations of the components studied if the data base of the model consisted exclusively of infinite dilution activity coefficients. The aim of our work was to try out the possibilities of predicting GLC retention data by means of the UNIFAC model. Use was made of a large compilation of retention data and the original values of UNIFAC interaction parameters⁹, which were not optimized for the reproduction of infinite dilution activity coefficients. The UNIFAC method expresses the activity coefficient as the product of the combinatorial and residual contributions, the former being independent of temperature⁹. The calculated specific retention volumes generally suffer from errors in the calculation of both contributions to the activity coefficients. On the other hand, the standard differential molar enthalpies of sorption are influenced only by the error made in the description of the temperature dependence of the residual contribution. With alkane-alkane systems, the relative error of the calculation of V_g^0 is about an order of magnitude larger than that of the calculation of ΔH_s^0 , while the calculated V_g^0 values with these systems are influenced only by the error of the calculation of the combinatorial contribution, in the context of the UNIFAC model. Hence it seems that it is especially the error in the calculation of the combinatorial contribution to the value of γ_D^∞ that makes the differences between calculated and measured V_g^0 values so large. This finding is in agreement with Rizzi and Huber's conclusions¹³. The expression for the combinatorial contribution to the activity coefficient in the UNIFAC model has recently been modified by Kikic *et al.*³⁰.

CONCLUSIONS

The original UNIFAC model can be used merely to give a rough estimation of relative retentions and retention indices of solutes in GLC systems. Absolute retention data calculated by means of this model suffer from too large an error, but the differential enthalpies of sorption, derived from the dependence of the calculated absolute retention data on temperature, may in many instances be fairly reliable. Rather than predicting GLC retention data by the UNIFAC model, it appears that GLC can advantageously be used to refine this model by providing for its data base infinite dilution activity coefficients. Such an application of activity coefficients determined from GLC retention data has recently been described by Alessi *et al.*³¹. However, it can hardly be expected that even a refined solution-of-groups model will offer the analytical chromatographer retention data as reliable as those obtained experimentally with modern chromatographic instrumentation.

REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 T. S. Lombosi, E. R. Lombosi, I. Bernát, Zs. Sz. Bernát, E. C. Takács and J. M. Takács, *J. Chromatogr.*, 119 (1976) 307.

- 3 N. Dimov and D. Papazova, *Chromatographia*, 12 (1979) 443.
- 4 N. Dimov and D. Papazova, *Chromatographia*, 12 (1979) 720.
- 5 D. Papazova, N. Dimov and D. Bonchev, *J. Chromatogr.*, 188 (1980) 297.
- 6 D. E. Martire, *Anal. Chem.*, 46 (1974) 626.
- 7 E. Hála, *Collect. Czech. Chem. Commun.*, 43 (1977) 10.
- 8 D. S. Abrams and J. M. Prausnitz, *AIChE J.*, 21 (1975) 116.
- 9 A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, 21 (1975) 1086.
- 10 W. A. Scheller, J. L. Petricek and G. C. Young, *Ind. Eng. Chem., Fundam.*, 11 (1972) 53.
- 11 G. J. Pierotti, C. H. Deal, E. L. Derr and P. E. Porter, *J. Amer. Chem. Soc.*, 78 (1956) 2989.
- 12 S. H. Langer, *Anal. Chem.*, 39 (1967) 524.
- 13 A. Rizzi and J. F. K. Huber, *Ind. Eng. Chem., Process Des. Develop.*, 20 (1981) 204.
- 14 J. Dykyj and M. Repáš, *Tlak Nasýtenej Pary Organických Zlúčenín (Saturated Vapour Pressures of Organic Compounds)*, Veda, Bratislava, 1979.
- 15 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Company, Evanston, IL, 1966.
- 16 Hsueh-Liang Liao, D. E. Martire and J. P. Sheridan, *Anal. Chem.*, 45 (1973) 2087.
- 17 D. E. Martire, *Anal. Chem.*, 46 (1974) 1712.
- 18 J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 97 (1975) 3585.
- 19 R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 98 (1976) 30.
- 20 D. E. Martire, *Anal. Chem.*, 48 (1976) 398.
- 21 P. F. Tiley, *J. Chromatogr.*, 179 (1979) 247.
- 22 M. W. P. Harbison, R. J. Laub, D. E. Martire, J. H. Purnell and P. S. Williams, *J. Phys. Chem.*, 83 (1979) 1262.
- 23 P. F. Tiley, *Faraday Symposium No. 15, Brighton, 1980*, Royal Society of Chemistry, London, 1980, pp. 93-102.
- 24 E. F. Meyer and J. A. Meyer, *J. Phys. Chem.*, 85 (1981) 94.
- 25 A. B. Littlewood, *Anal. Chem.*, 36 (1964) 1441.
- 26 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
- 27 R. L. Martin, *Anal. Chem.*, 35 (1963) 116.
- 28 R. A. Keller and G. H. Stewart, *Anal. Chem.*, 34 (1962) 1834.
- 29 T. Magnussen, P. Rasmussen and A. Fredenslund, *Ind. Eng. Chem., Process Des. Develop.*, 20 (1981) 331.
- 30 I. Kikic, P. Alessi, P. Rasmussen and A. Fredenslund, *Can. J. Chem. Eng.*, 58 (1980) 253.
- 31 P. Alessi, I. Kikic, A. Fredenslund and P. Rasmussen, *Can. J. Chem. Eng.*, 60 (1982) 300.