

Prediction of gas chromatographic retention indices of alkenes from the total solubility parameters

Zhide Hu* and Hongwei Zhang

Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000 (China)

(First received September 24th, 1992; revised manuscript received March 24th, 1993)

ABSTRACT

Gas chromatographic retention indices (I) for a large number of C_5 – C_{10} alkenes on different stationary phases at various temperatures were correlated with total solubility parameters (δ_T), molar volumes (V) and the number (N) of carbon atoms in the solute molecules. The correlation is a new three-parameter equation $I = aN + b\Delta(V\delta_T) + c\Delta V + d$, which is based on the expanded solubility parameter model. Two new parameters, $\Delta(V\delta_T)$ and ΔV , are introduced, accounting for the deviations of the $V\delta_T$ and the V values of the solutes from those of n -alkanes which have the same carbon number as the solutes. The empirically introduced constants a , b , c and d depend on the phase characteristics and column temperature. High correlation coefficients and low standard deviations were found in all instances. Especially for isomeric alkenes, the correlation between the I and δ_T and V values of the solutes, which is $I = bV\delta_T + cV + e$, is excellent. The above two equations could be used to predict retention indices of alkenes successfully.

INTRODUCTION

There have been many studies on the establishment of retention–structure relationships for alkene analysis [1–10]. Takács *et al.* [1] separated the retention index (I) into two additive components which represented molecular and interaction contributions. Sanz *et al.* [2] utilized the contributions of the different structural units of molecules. Bermejo and Guillen [3] studied the relationships between parameters related to electronic polarizability, such as molar refraction, refractive index, Van der Waals volume and molar volume, and the retention indices of alkenes. Papazova and Dimov [4,5] predicted I values with the help of a physico-chemical index and a structural number correction. Sojsk *et al.* [6] obtained the correlations between the structure and retention increments considering the position of the double bond and the geometrical

arrangement. Chrétien and Dubois [7,8] extensively analysed experimental retention indices of alkenes using the DARC topological system. Considering the influence of molecular parameters such as total energy and binding energy, Garcia-Raso *et al.* [9] studied the retention of n -alkenes with molecular orbital calculations. Rohrbaugh and Jurs [10] studied the relationships between I and different structure-based descriptors of alkenes and the correlation coefficient was 0.998.

A very different and simple approach to calculating retention indices of alkenes is proposed in this paper. The approach is more theoretical than pure empirical correlations because the equation is derived from Karger's expanded solubility model [11]. It is, however, empirical and practicable because the fundamental parameters employed are easily obtained and the relationship between the parameters in question and the retention is empirical.

In a recent study [12], we investigated the theoretical aspects of the solubility parameter

* Corresponding author.

model and found two equations for predicting retention indices of alkylbenzenes. We applied these equations to a large number of alkylbenzenes on different stationary phases at various temperatures and obtained satisfactory results.

The aim of this study was twofold: first, to establish whether the proposed method [12] could be used to calculate the retention data of alkenes, or in other words to support the usefulness of the model [12], and second, to obtain general expressions for alkenes that are analytically useful for the prediction of retention indices on different stationary phases at various temperatures.

DATA HANDLING

In a previous study [12], we applied the solubility parameter model to gas-liquid chromatography (GLC) and obtained the equation

$$I = aN + b\Delta(V\delta_T) + c\Delta V + d \quad (1)$$

where N refers to number of carbons atoms in the compound of interest, $\Delta(V\delta_T)$ is the difference between the product of V^i and δ_T^i , and that of V^{al} and δ_T^{al} :

$$\Delta(V\delta_T) = V^i\delta_T^i - V^{al}\delta_T^{al} \quad (2)$$

ΔV is the difference between V^i and V^{al} :

$$\Delta V = V^i - V^{al} \quad (3)$$

where the superscript i refers to the solute and the superscript al refers to the n -alkane with the same carbon atom number as the solute, and a , b , c and d are constants.

For isomers, N , $V^{al}\delta_T^{al}$ and V^{al} are constants, so rearranging eqn. 1 one obtains

$$I = bV\delta_T + cV + e \quad (4)$$

where i in $V^i\delta_T^i$ and V^i has been omitted, and b , c and e are constants for a given phase. Constants b and c stem from eqn. 1, so for the same system, b and c in eqn. 1 should be identical with b and c in eqn. 4. Constant e is given by

$$e = aN - bV^{al}\delta_T^{al} - cV^{al} + d \quad (5)$$

Eqns. 1 and 4 represent the basic equations of the retention indices in terms of solubility pa-

rameters. Constants a , b , c , d and e are dependent on the stationary phase characteristics and the column temperature; d and e are also related to specific interactions of the solute and stationary phase. In this paper, no further attention is paid to this phenomenon. These two equations can be formulated and statistically evaluated from regression analysis of experimental retention indices, total solubility parameters and molar volume data for a sufficient large set of compounds. The best correlations were found for alkenes on a series of non-polar and moderately polar stationary phases at several temperatures.

EXPERIMENTAL

Calculation of total solubility parameter

The total solubility parameter, δ_T , is the sum of a series of specific solubility parameters related to each other by the equation [13–15]

$$\delta_T^2 = \delta_d^2 + 2\delta_{in}\delta_a + \delta_0^2 + 2\delta_a\delta_b \quad (6)$$

where the specific solubility parameters δ_d , δ_0 , δ_{in} , δ_a and δ_b are measures of the ability of the substance to enter into selective interactions of the type dispersive, dipole orientation, dipole inductive and hydrogen bonding, respectively.

Sufficiently accurate data for the total solubility parameter are obtained from readily available and simple physical parameters, such as the molar volume, the heat of vaporization and the boiling point [13,14,16,17]. In this paper, total solubility parameters were calculated according to Sun *et al.*'s expression [18] from boiling points and densities of substances:

$$\delta_T^2 = -0.02085 \cdot \frac{T_b^2}{V} + 58.93 \cdot \frac{T_b}{V} - 6892.14 \cdot \frac{1}{V} - 26.76 \quad (7)$$

where T_b is the boiling point and V the molar volume of the solute. The equation was derived by regression analysis based on the systematic analysis of the relevant factors and had been employed to calculate total solubility parameters of more than 300 compounds with satisfactory results. Boiling points and densities were taken

from handbooks [19,20]. The molar volume is the ratio between molecular mass and density.

Data set

Retention indices of alkenes in different phases at several temperatures were taken from the literature [7,21–23]. The alkenes ranged from C₅ to C₁₀ compounds and included straight-chain and branched compounds. The 86 compounds are listed in Table I. The stationary phases and column temperatures used are given in Table II.

Regression analysis

Regression coefficients and statistics were calculated by a multiple regression linear program on a personal computer.

RESULTS

Regression coefficients a , b , c and d , correlation coefficients R and standard deviations S for eqn. 1 are given in Table II. The correlation coefficients are better than 0.9988 and the standard deviations are better than 3.9 i.u. Obviously, the proposed method has good accuracy.

Comparing constants a , b , c and d in Table II for the same stationary phases but different temperatures, such as SQ and OV-101, we found that a difference exists between each group of constants. For instance, for the stationary phase SQ at 80, 50 and 70°C, the corresponding constant $a = 97.21, 96.56, 97.13$, respectively, $b = 1.19, 1.19$ and 1.17 , $c = -3.44, -3.33$ and -3.23 and $d = 12.63, 16.45$ and 13.55 . This shows that a , b , c and d depend slightly on temperature. This can be explained by the expressions for constants a , b , c and d [12]. The expressions for b , c and d contain the term $(\Delta E^s)^{m/j}$, which is the solution energy of solute i in liquid stationary phase j . Further, the term is related to temperature, so b , c and d are dependent on temperature. The adjustable constant a should be related to b , c and d , so a also depends on temperature. Evidently, the model [12] is in agreement with the regression results.

One can expect the coefficient (a) of carbon atom number (N), which was proposed to be an adjustable constant in the original paper [12]

instead of 100, will be close to 100. The results in Table II confirm this, with a values ranging from 95.79 to 98.17.

Isomeric alkenes having the same molecular mass provide nearly the same molar refraction, molar volume or connectivity indices but widely different retention data. This always worsens the correlation, so it is necessary to propose a method for predicting the retention of isomers. Fortunately, eqn. 4 is good enough to distinguish the isomers. This is confirmed by the results for eqn. 4 in Table III. The best quantitative correlation is obtained within a series of isomeric compounds when we apply eqn. 4 to alkenes. We only list representatives of each kind of stationary phase in Table III as examples. The correlation coefficients are not as good as those from eqn. 1, but it is notable that the deviations are much smaller than those from eqn. 1 except for DB-1 and HP-PONA. The accuracy is good.

Further, in order to illustrate the predictive ability of eqn. 4, we used it to estimate the retention indices of solutes not included in the original regression analysis. First, we selected some alkenes at random and, using their experimental retention index values, we could obtain the regression coefficient of eqn. 4. Then we used the regression equation to calculate the retention indices of other alkenes. Finally, we compared the calculated retention indices with the experimental values. Here we only list a representative group of results as an example. For the stationary phase 1-octadecene (25°C), there are sixteen isomeric alkenes whose carbon number is 6. We selected eight of the alkenes at random. To illustrate the random selection, we selected three times, in other words, there are three different group selections for the same system. For the first group, the serial numbers (No.) of the selected alkenes, for which the names are given in Table I, are 6, 9, 10, 14, 16, 17, 19 and 20. The following regression equation is obtained:

$$I = 1.0776V\delta_T - 4.4725V + 116.01 \quad (8)$$

$$R = 0.999, S = 1.4$$

For the second group, the selected alkenes are Nos. 7, 9, 13, 14, 16, 18, 20 and 21. The following regression equation is obtained:

TABLE I
VALUES OF PARAMETERS UTILIZED IN THIS STUDY

No.	Compound	V	δ_T	$\Delta(V\delta_T)$	ΔV
1	1-Pentene	109.51	7.48	-30.04	-5.71
2	<i>cis</i> -2-Pentene	106.99	7.80	-14.65	-8.23
3	<i>trans</i> -2-Pentene	109.05	7.68	-11.67	-6.17
4	2-Methyl-1-butene	107.84	7.60	-29.59	-7.38
5	2-Methyl-2-butene	105.90	7.91	-11.50	-9.32
6	1-Hexene	125.03	7.61	-27.42	-5.49
7	<i>cis</i> -2-Hexene	122.52	7.85	-17.12	-8.00
8	<i>trans</i> -2-Hexene	124.06	7.76	-16.19	-6.46
9	<i>cis</i> -3-Hexene	123.84	7.73	-21.62	-6.68
10	<i>trans</i> -3-Hexene	124.28	7.73	-18.22	-6.24
11	3-Methyl-1-pentene	126.08	7.34	-53.47	-4.44
12	2-Methyl-1-pentene	123.78	7.63	-34.46	-6.74
13	4-Methyl-1-pentene	126.71	7.31	-52.65	-3.81
14	2-Methyl-2-pentene	122.63	7.81	-21.16	-7.89
15	<i>cis</i> -3-Methyl-2-pentene	120.47	7.91	-25.18	-10.05
16	<i>cis</i> -4-Methyl-2-pentene	125.80	7.40	-47.98	-4.72
17	<i>trans</i> -4-Methyl-2-pentene	125.88	7.45	-41.09	-4.64
18	2-Ethyl-1-butene	122.08	7.77	-30.34	-8.44
19	2,3-Dimethyl-1-butene	123.71	7.48	-53.55	-6.81
20	2,3-Dimethyl-2-butene	118.87	8.12	-13.68	-11.65
21	3,3-Dimethyl-1-butene	128.90	6.98	-79.18	-1.62
22	<i>trans</i> -3-Methyl-2-pentene	121.44	7.93	-15.88	-9.08
23	1-Heptene	140.88	7.61	-24.17	-5.68
24	<i>cis</i> -2-Heptene	138.69	7.79	-15.87	-7.87
25	<i>trans</i> -2-Methyl-3-hexene	143.28	7.35	-43.16	-3.28
26	<i>trans</i> -2-Heptene	140.03	7.73	-13.84	-6.53
27	<i>cis</i> -3-Heptene	138.82	7.73	-23.19	-7.74
28	5-Methyl-1-hexene	142.78	7.36	-45.41	-3.78
29	<i>trans</i> -3-Heptene	140.65	7.66	-18.89	-5.91
30	4-Methyl-1-hexene	141.44	7.44	-43.96	-5.12
31	<i>trans</i> -5-Methyl-2-hexene	142.66	7.42	-37.73	-3.90
32	2,3-Dimethyl-1-pentene	139.26	7.48	-54.60	-7.30
33	<i>cis</i> -5-Methyl-2-hexene	140.88	7.52	-36.85	-5.68
34	2,4-Dimethyl-1-pentene	141.42	7.33	-59.66	-5.14
35	4,4-Dimethyl-1-pentene	143.83	7.05	-82.27	-2.73
36	2-Ethyl-1-pentene	138.71	7.70	-28.20	-7.85
37	2,3-Dimethyl-2-pentene	134.93	7.93	-26.27	-11.63
38	3-Ethyl-1-pentene	141.95	7.37	-50.10	-4.61
39	3-Ethyl-2-pentene	136.30	7.84	-27.68	-10.26
40	<i>trans</i> -3,4-Dimethyl-2-pentene	137.83	7.68	-37.73	-8.73
41	<i>cis</i> -4,4-Dimethyl-2-pentene	141.26	7.31	-63.66	-5.30
42	2,3,3-Trimethyl-1-butene	139.28	7.34	-73.95	-7.28
43	2-Ethyl-3-methyl-1-butene	137.33	7.65	-45.69	-9.23
44	3,3-Dimethyl-1-pentene	140.79	7.27	-72.73	-5.77
45	3,4-Dimethyl-1-pentene	141.61	7.31	-61.10	-4.95
46	2,4-Dimethyl-2-pentene	141.20	7.38	-54.21	-5.36
47	<i>trans</i> -4,4-Dimethyl-2-pentene	142.53	7.19	-71.48	-4.03
48	<i>cis</i> -4-Methyl-2-hexene	141.24	7.44	-45.44	-5.32
49	<i>trans</i> -4-Methyl-2-hexene	141.79	7.45	-39.93	-4.77
50	<i>trans</i> -3-Methyl-3-hexene	139.28	7.67	-27.99	-7.28
51	<i>trans</i> -3-Methyl-2-hexene	138.30	7.74	-25.83	-8.26
52	<i>cis</i> -3,4-Dimethyl-2-pentene	138.45	7.61	-42.66	-8.11

TABLE I (continued)

No.	Compound	V	δ_T	$\Delta(V\delta_T)$	ΔV
53	2-Methyl-1-hexene	140.27	7.58	-33.02	-6.29
54	2-Methyl-2-hexene	139.51	7.70	-22.04	-7.05
55	3-Methyl-1-hexene	142.91	7.33	-48.74	-3.65
56	cis-3-Methyl-2-hexene	130.68	8.10	-37.76	-15.88
57	cis-3-Methyl-3-hexene	138.71	7.73	-24.04	-7.85
58	1-Octene	156.97	7.53	-24.58	-5.64
59	cis-2-Octene	154.94	7.68	-16.63	-7.67
60	trans-2-Octene	155.88	7.64	-15.64	-6.73
61	trans-4-Octene	157.15	7.55	-20.08	-5.46
62	2,3,4-Trimethyl-2-pentene	150.96	7.66	-50.21	-11.65
63	2,4,4-Trimethyl-2-pentene	155.47	7.28	-74.74	-7.14
64	2,4,4-Trimethyl-1-pentene	156.95	7.16	-82.80	-5.66
65	2,5-Dimethyl-2-hexene	156.24	7.40	-50.39	-6.37
66	2,3-Dimethyl-2-hexene	151.53	7.75	-32.21	-11.08
67	cis-2,2-Dimethyl-3-hexene	158.37	7.19	-67.89	-4.24
68	2,3-Dimethyl-1-hexene	156.47	7.35	-56.51	-6.14
69	trans-2-Methyl-3-heptene	159.86	7.26	-45.98	-2.75
70	trans-4-Methyl-2-heptene	157.61	7.38	-43.40	-5.00
71	2-Methyl-1-heptene	157.97	7.46	-28.11	-4.64
72	2-Methyl-2-heptene	155.86	7.60	-22.03	-6.75
73	cis-4-Octene	155.60	7.60	-24.01	-7.01
74	trans-3-Octene	156.91	7.57	-18.76	-5.70
75	cis-3-Octene	156.10	7.59	-21.77	-6.51
76	trans-4-Methyl-2-heptene	157.61	7.38	-43.40	-5.00
77	2-Methyl-1-Octene	171.92	6.92	-30.94	-6.81
78	1-Nonene	172.93	7.42	-25.16	-5.80
79	trans-3-Nonene	172.46	7.46	-21.75	-6.27
80	2-Methyl-1-nonene	189.25	7.27	-25.41	-5.64
81	2,3-Dimethyl-2-heptene	172.69	7.41	-28.67	-6.04
82	1-Decene	189.35	7.30	-19.00	-5.54
83	cis-5-Decene	188.41	7.32	-22.10	-6.48
84	trans-4-Decene	189.45	7.30	-18.27	-5.44
85	cis-4-Decene	189.45	7.30	-18.27	-5.44
86	trans-5-Decene	189.53	7.29	-19.59	-5.36

$$I = 1.0780V\delta_T - 4.5465V + 125.09 \quad (9)$$

$$R = 0.999, S = 1.6$$

For the third group, the selected alkenes are Nos. 6, 8, 10, 13, 15, 17, 19 and 21. The following regression equation is obtained:

$$I = 1.1120V\delta_T - 4.2073V + 50.51 \quad (10)$$

$$R = 0.999, S = 1.9$$

Using the above equations, we calculated the retention indices of the remaining eight alkenes for each group. Comparisons of the predicted and measured I values are given in Table IV.

There is good agreement between the experimental and predicted retention data.

The good results suggest that $V\delta_T$ is a promising parameter for describing the retention behaviour of alkenes. As we have already noted in Table I, the difference between the δ_T values of a group isomers is small and also V does not change significantly from compound to compound in isomers, but the difference between the $V\delta_T$ values of isomers obtained by multiplying V and δ_T becomes large, so $V\delta_T$ may be an important parameter for distinguishing the isomers in eqn. 4.

Comparing the regression coefficients b and c

TABLE II

REGRESSION COEFFICIENTS AND STANDARD DEVIATIONS IN VARIOUS PHASES FOR THE EQUATION
 $I = aN + b\Delta(V\delta_T) + c\Delta V + d$

n = number of the alkene (see Table I); R = regression coefficient; S = standard deviation; SQ = squalane; DB-1 is a cross-linked and bonded methylsilicone phase; DB-5 is similar to DB-1 with 5% phenyl substitution; HP-PONA is a cross-linked methylsiloxane phase.

No.	Phase	Temperature (°C)	a	b	c	d	n	R	S
1	SQ	80	97.21	1.19	-3.44	12.63	39	0.9990	3.9
2	1-Octadecene	25	95.79	1.21	-3.77	20.10	35	0.9991	2.7
3	OV-101	50	96.84	1.19	-3.19	23.23	46	0.9989	3.5
4	SQ	50	96.56	1.19	-3.33	16.45	46	0.9990	3.3
5	OV-101	70	96.97	1.17	-3.26	21.74	46	0.9988	3.7
6	SQ	70	97.13	1.17	-3.23	13.55	46	0.9988	3.6
7	OV-101	40	97.71	1.24	-3.61	16.16	61	0.9996	3.8
8	OV-101	60	97.87	1.21	-3.74	13.75	61	0.9996	3.7
9	OV-101	80	98.05	1.18	-3.91	10.91	61	0.9996	3.8
10	DB-1	40	98.11	1.26	-3.27	18.13	69	0.9991	3.7
11	HP-PONA	40	98.10	1.26	-3.27	18.27	69	0.9991	3.7
12	DB-5	40	98.17	1.29	-3.33	20.90	67	0.9990	3.8

TABLE III

REGRESSION COEFFICIENTS AND STANDARD DEVIATIONS OF ALKENES ISOMERS FOR THE EQUATION
 $I = bV\delta_T + cV + e$

See Table II for n , R and S . N = No. of carbon atoms in the molecule.

No. ^a	N	b	c	e	n	R	S
2	6	1.09	-4.45	97.47	16	0.999	1.5
	7	1.26	-3.38	-192.64	15	0.999	1.9
3	6	1.12	-4.23	53.73	12	0.998	1.5
	7	1.19	-3.16	-139.45	23	0.993	3.6
	8	1.33	-3.27	-273.97	8	0.998	1.9
4	6	1.04	-4.80	194.90	12	0.998	1.6
	7	1.20	-3.20	-155.06	23	0.995	3.0
	8	1.33	-3.46	-249.07	8	0.999	1.2
10	6	1.10	-4.30	80.18	17	0.999	1.7
	7	1.28	-3.13	-243.37	35	0.991	3.8
	8	1.32	-4.61	-41.79	11	0.994	2.4
11	6	1.10	-4.30	81.15	17	0.999	1.7
	7	1.29	-3.14	-243.59	35	0.991	3.8
	8	1.32	-4.56	-48.71	11	0.993	2.4
12	6	1.12	-4.39	74.15	17	0.999	1.7
	7	1.31	-3.2	-255.70	35	0.992	3.8
	8	1.36	-4.45	-110.57	10	0.993	2.5

^a See stationary phases and column temperatures in Table II.

TABLE IV
COMPARISONS OF I_{exp} WITH I_{calc} ACCORDING TO EQNS. 8, 9 AND 10

No. ^a	Eqn. 8		Eqn. 9		Eqn. 10	
	Standard ^b	ΔI ^c	Standard ^b	ΔI ^c	Standard ^b	ΔI ^c
6	*			-2.0	*	
7		0.5	*			0.6
8		-0.3		-0.1	*	
9	*		*			0.4
10	*			1.9	*	
12		-1.6		-1.3		-1.7
13		-2.7	*		*	
14	*		*			0.4
15		0.8		1.3	*	
16	*		*			-0.8
17	*			0.3	*	
18		-1.1	*			-1.6
19	*			1.2	*	
20	*		*			-1.4
21		1.9	*		*	
22		-2.5		-2.0		-2.6

^a For compound numbers see Table I.

^b Standard = alkenes used to obtain the regression coefficients (constants b , c and e in eqn. 4).

^c $\Delta I = I_{\text{calc}} - I_{\text{exp}}$.

in Tables II and III for the same system, it can be seen that the values of b and c obtained by regressing I in eqn. 1 are approximately equal to the values obtained in eqn. 4 for a given system. Evidently, the results are in agreement with our model. The small disagreement is probably due to the fact that some small approximations were involved in formulating eqns. 1 and 4 [12].

The model is based on a non-polar and weakly polarizable system [12], so for more polar stationary phases and more polar solutes, such as organic compounds containing nitrogen, oxygen and halogen atoms, the regression results for eqns. 1 and 4 are not so good. Further investigations on the relationship between the chromatographic behaviour of more polar solutes on the more polar stationary phases and solubility parameters are being carried out.

ACKNOWLEDGEMENT

We thank the National Science Foundation of China for financial support.

REFERENCES

- 1 J. Takács, Zs. Tálas, I. Bernáth, Gy. Czako and A. Fisher, *J. Chromatogr.*, 67 (1972) 203.
- 2 J. Sanz, J. Calderon and M.V. Dabrio, *An. Quim.*, 75 (1979) 408.
- 3 J. Bermejo and M.D. Guillen, *Int. J. Environ. Anal. Chem.*, 23 (1985) 77.
- 4 D. Papazova and N. Dimov, *J. Chromatogr.*, 137 (1977) 259.
- 5 N. Dimov and D. Papazova, *Chromatographia*, 12 (1979) 720.
- 6 L. Sojsk, J. Krupzik and J. Jansk, *J. Chromatogr.*, 195 (1980) 43.
- 7 J.R. Chrétien and J.E. Dubois, *Anal. Chem.* 49 (1977) 747.
- 8 J.R. Chrétien and J.E. Dubois, *J. Chromatogr.*, 158 (1978) 43.
- 9 A. Garcia-Raso, F. Saura-Calixto and M.A. Raso, *J. Chromatogr.*, 302 (1984) 107.
- 10 R.H. Rohrbaugh and P.C. Jurs, *Anal. Chem.* 57 (1985) 2770.
- 11 B.L. Karger, L.R. Snyder and C. Eon, *Anal. Chem.* 50 (1978) 2126.
- 12 H. Zhang and Z. Hu, *Chromatographia*, 33 (1992) 575.
- 13 B.L. Karger, L.R. Snyder and C. Eon, *J. Chromatogr.*, 125 (1976) 71.

- 14 P.H. Shetty, P.J. Youngberg, B.R. Kersten and C.F. Poole, *J. Chromatogr.*, 411 (1987) 61.
- 15 P. Laffort and F. Patte, *J. Chromatogr.*, 126 (1976) 625.
- 16 D.D. Lawson and J.D. Ingham, *Nature*, 223 (1969) 614.
- 17 A. Munafò, M. Buchman, H. Nam-Tram and U.W. Kesselring, *J. Pharm. Sci.*, 77 (1988) 169.
- 18 Z. Sun, M. Lui and Z. Hu, *Fenxi Ceshi Tongbao*, 7 (1988) 15.
- 19 R.C. Weast and M.J. Astle (Editors), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 63rd ed., 1982–83.
- 20 R.C. Weast and M.J. Astle (Editors), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 69th ed., 1988–89.
- 21 S. Boneva and N. Dimov, *Chromatographia*, 21 (1986) 149.
- 22 R.J. Laub and J.H. Purnell, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 649.
- 23 A.J. Lubeck and D.L. Sutton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 542.