

Structure–retention correlations of chlorobenzenes as a method for the comparison of the behaviour of gas–liquid–solid and gas–liquid capillary columns of various polarities

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Abstract

The structure–retention correlations of chlorobenzenes were investigated by using retention data measured on narrow-bore capillary columns: bonded-phase gas–liquid non-polar polydimethylsiloxane, polar polyglycol, carbon and graphite layer gas–liquid–solid modified by addition of various amount of polar liquid phase (polyglycols and terephthalic acid). The retention values obtained in various isothermal runs (ranging from 60 to 200°C) were correlated with the available physical properties data: boiling point, dipole moment, vapour pressure at the analysis temperature and the effect of the reciprocal position of the chlorine atoms on the aromatic ring was evaluated.

Keywords: Structure–retention relationships; Stationary phases, GC; Chlorobenzenes

1. Introduction

Structure–retention correlations of aromatic compounds having one or more substituent groups bonded to the benzene ring have been investigated by several authors on both packed and capillary gas–liquid columns. Chlorobenzenes [1–8], chlorophenols [7–9], alkylbenzenes [1,10–15], chlorophenylacetates [8,16], chloroanisoles [8] and variously substituted benzenes [17,18] were analysed on columns of different polarity and their retention times, retention indices, retention index increments and thermodynamic functions [1,3] were correlated with the positions of substitution. The non-polar liquid

phases used were squalane [11–14], various methyl- and phenylmethylsilicones [7–9,15–17] and some linear alkanes or Apiezon grease [13,14,17]. Polar columns were filled with Carbowax 20M [11,15], UCONs [11,15], *n*-octadecanol [10] and various esters [12–14].

Carbon- and graphite-layer capillary columns having different thickness and porosity of the support and various amounts of modifying polar liquid, designed as gas–liquid–solid (GLS) columns [19,20], are now available. By varying the type and thickness of the layer and the nature and amount of the modifier, the selectivity can be adjusted over a wide range. Changes in temperature also modify the selectivity and the polarity of these columns. Their characterization was carried out with the values of the capacity or

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partition ratio and the difference in apparent carbon number of linear alkanes and alcohols with the same retention, ΔC [21–24]. Two interaction mechanisms are simultaneously present in these columns, the importance of purely gas–liquid (GL) partitioning and gas–solid (GS) or gas–liquid–solid (GLS) absorption being dependent on the amount of liquid added to the carbon layer.

It has been reported that stationary phases containing graphitized carbon black and polar modifiers exhibit peculiar interactions with cyclic and aromatic compounds whose isomers can be separated [25–28]. Therefore, the elution order and the retention values of substituted benzenes may differ from those observed on gas–liquid columns.

The aim of the work described here was to investigate the different behaviour of GL and GLS capillary columns in the separation of chlorobenzenes, to measure the dependence of the retention on the number and position of the substituents and to verify if correlations can be found between retention, structure and physical properties which allow the classification of the columns through the analysis of some aromatic compound selected as polarity probes and the prediction of the retention of compounds belonging to the same class.

2. Experimental

The analyses were carried out with fused-silica capillary columns, 30 m \times 0.32 mm I.D. (nominal). The non-polar (polydimethylsiloxane) bonded-phase GL columns were SPB-1, 0.25 μm film thickness (Supelco, Bellefonte, PA, USA), and DB-1, 0.25 and 3 μm (J & W Scientific, Folsom, CA, USA). The polar columns were polyglycol Supelcowax-10 (Supelco), 0.25 μm , indicated in the figures and tables as WAX-10, and a DB-WAX (J & W), 0.25 μm . The GLS carbon layer capillary columns partially deactivated with polyglycol–terephthalic acid were obtained by courtesy of Supelchem, Milan, Italy (column CLOT), and the Istituto di Scienze Chimiche, University

of Urbino, Italy (column CL-U). The amount of liquid phase on the carbon layer was 16% for both CLOT and CL-U columns. The layer of the CL-U column was made of Carbograph 1 (Alltech) having a specific surface area of 90 m² g⁻¹. The true I.D. of the capillary tubing and the thickness of the stationary film deposited on the inner wall of the capillary was checked by scanning electron microscopy (SEM) using a Stereoscan Model 440 instrument (Leica Cambridge, UK). With this method the film thickness (carbon layer plus deactivating liquid phase) of the carbon layer columns was found to be 1.3 μm for CLOT and 0.7 μm for CL-U. For the bonded-phase columns, the nominal thickness of 0.25 μm was confirmed while an average value of 3.5 μm was found in the DB-1 column with a nominal thickness of 3 μm .

The columns were installed in a Varian (Palo Alto, CA, USA) Model 3600 gas chromatograph equipped with a capillary split–splitless injector, a constant inlet pressure flow control and a flame ionization detector. Helium was used as the carrier gas. The injector and detector temperatures were 250°C. Isothermal conditions of the column were set with an accuracy of $\pm 1^\circ\text{C}$. The analyses were carried out in the range 60–200°C at 5–10°C intervals.

In Table 1 the compounds analysed are listed, with their boiling points, molecular masses, dipole moments and parameters of the Antoine equation used for the calculation of vapour pressures [29]. Dipole moments were calculated with the computer program MOPAC 6.0 by using the semi-empirical calculation by Hamiltonian AM1, which considers single molecules in the gas phase. Tabulated values obtained in the gas phase [29] agree with the calculated values, while those measured in solvents (mainly benzene) differ appreciably for tetrachlorobenzenes. Standard solutions in dichloromethane at concentrations ranging between 10 and 50 mg l⁻¹ were injected (amount 1 μl) with 1:20 splitting ratio. The retention times were measured with an accuracy of ± 0.005 min by using a Varian DS-650 data system. The carrier gas velocity and the gas hold-up time were obtained by using the inlet pressure (149.6 kPa) maintained constant at all

Table 1

Compounds analysed, abbreviations, boiling points, melting points, molecular masses, dipole moments and parameters *A* and *B* of the Antoine equation used to calculate the vapour pressure [29]

Compound	Abbreviation	B.p. (°C)	M.p. (°C)	<i>M</i>	Dipole moment Debye	<i>A</i>	<i>B</i>
Chlorobenzene	1CB	132	−45.6	112.5	1.30	10098.00	8.500
1,2-Dichlorobenzene	12CB	179	−17.0	147.0	1.97	10943.00	8.185
1,3-Dichlorobenzene	13CB	172	−24.7	147.0	1.23	10446.80	8.018
1,4-Dichlorobenzene	14CB	173	53.1	147.0	0.00	10611.00	8.074
1,2,3-Trichlorobenzene	123CB	218	53–54	181.4	2.06	11349.50	7.916
1,2,4-Trichlorobenzene	124CB	214	16.95	181.4	1.03	11425.10	8.031
1,3,5-Trichlorobenzene	135CB	208	63–64	181.4	0.00	11211.00	7.977
1,2,3,4-Tetrachlorobenzene	1234CB	254	47.5	215.9	1.61	12872.50	8.251
1,2,3,5-Tetrachlorobenzene	1235CB	246	54.5	215.9	0.83	11982.10	7.925
1,2,4,5-Tetrachlorobenzene	1245CB	243–246	139.5–140.5	215.9	0.00	12828.80	8.282
Pentachlorobenzene	5CB	276	86	250.3	0.79	15124.20	8.907
Hexachlorobenzene	6CB	322	230	284.8	0.00	15199.10	8.550

temperatures, the geometrical parameters of the columns and the Poiseuille equation [30,31].

3. Results and discussion

In order to permit a direct comparison of the performance under the same conditions, Table 2 shows capacity factor values, $k' = t'_R/t_M$, of all chlorobenzenes measured at 140°C on the columns tested. The elution order is the same and

the resolution is satisfactory except for 1,3- and 1,4-dichlorobenzene and 1,2,3,5- and 1,2,4,5-tetrachlorobenzene at some temperatures on non-polar columns with a 0.25- μ m film thickness. An example of the trend of $\ln k'$ values on gas-liquid non-polar and polar columns and carbon-layer columns as a function of the reciprocal of the absolute temperature (Arrhenius plots) is shown in Fig. 1. The perfect linearity of the Arrhenius plots, often reported for narrow temperature intervals, is not confirmed when

Table 2

Capacity factors, k' , at 140°C of chlorobenzenes on the columns tested

Compound ^a	SPB-1	DB-1 (0.25 μ m)	DB-1 (3 μ m)	WAX	CLOT	CL-U
1CB	0.239	0.209	1.850	0.291	0.595	0.447
12CB	0.472	0.436	4.507	0.703	2.014	1.246
13CB	0.422	0.388	3.922	0.536	1.470	0.934
14CB	0.422	0.388	3.992	0.585	1.638	1.033
123CB	0.978	0.937	10.346	1.650	5.846	3.294
124CB	0.834	0.799	8.790	1.190	4.117	2.339
135CB	0.710	0.668	7.239	0.753	2.446	1.434
1234CB	1.980	1.908	21.868	3.314	15.139	7.685
1235CB	1.630	1.568	17.831	1.990	8.653	4.455
1245CB	1.630	1.568	17.831	2.070	9.067	4.650
5CB	3.714	3.603	41.781	4.823	31.670	13.965
6CB	8.311	8.089	93.173	10.356	74.724	46.545

^a See Table 1.

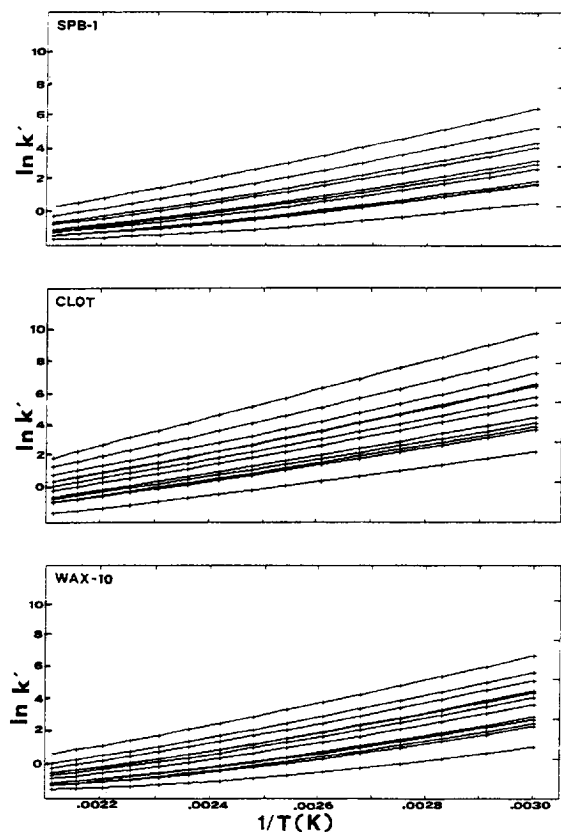


Fig. 1. Typical values of the capacity factor, k' , for a non-polar and a polar GL columns and for a carbon-layer GLS column, as a function of the reciprocal of absolute column temperature.

greater ranges are investigated. The exact retention of a given compound at any temperature can therefore be predicted only when experimental values are known at temperatures relatively close to that to be predicted.

Fig. 2 shows for all columns the ranges of $\ln k'$ values covered by the chlorobenzenes (monochloro at the left and hexachloro at the right of each line) at the lowest (60°C) and at the highest (200°C) temperatures tested. The absolute retention values and their spread as a function of the number of chlorine atoms in the molecule are greater on carbon-layer columns. The difference between gas-liquid columns with the same film thickness and different polarity is small, owing to the lack of hydrogen bonding that mainly in-

fluences the interaction of polar solutes with the polyglycol liquid phase used for Supelcowax-10 and as a modifying liquid for carbon layer columns. The different behaviour of isomeric compounds can therefore be investigated as a function of their dipole moment, the parameter that mainly influences the vapour pressure and the boiling point (i.e., the interaction between identical molecules in the pure liquid) and the retention (i.e., the solute-solvent interaction in the chromatographic column). The retention does not depend on the vapour pressure of the compounds only, as the influence of the dipole moments (Table 1) increases the interaction of the solute with the stationary phase with respect of the interaction in the liquid. This effect is also present, although more weakly, with non-polar stationary phases. Within each series of isomers with the same number of Cl atoms, symmetrical compounds having dipole moments equal to zero show the lowest retention values. A similar behaviour is also observed when carbon- or graphite-layer open-tubular columns are used.

In order to investigate the influence of the non-hydrogen-bonding polarity of isomers on their retention, the Fig. 3 the $\ln k'$ values of trichlorobenzenes at 140°C are plotted as a function of their dipole moment, and a nearly linear relationship is found. The lines for non-polar GL columns with the same thickness of the liquid phase (0.25 μm) are coincident (lowest lines), and are parallel to the highest line of the graph that shows the behaviour of the non-polar column with a film thickness of 3 μm . The slope for the polar GL column (WAX-10) is greater, as the effect of the dipole moment of the solute increases with the polarity of the stationary phase. The slope for the carbon-layer GLS columns deactivated with polyglycol is the same as the slope for pure polyglycol GL column.

In order to permit a comparison between the columns used, all the other parameters (length, flow-rate, liquid phase, etc.) being the same, the results can be normalized with respect of the thickness of the stationary phase layer by means of the fundamental equation [32]

$$K_D = k'\beta$$

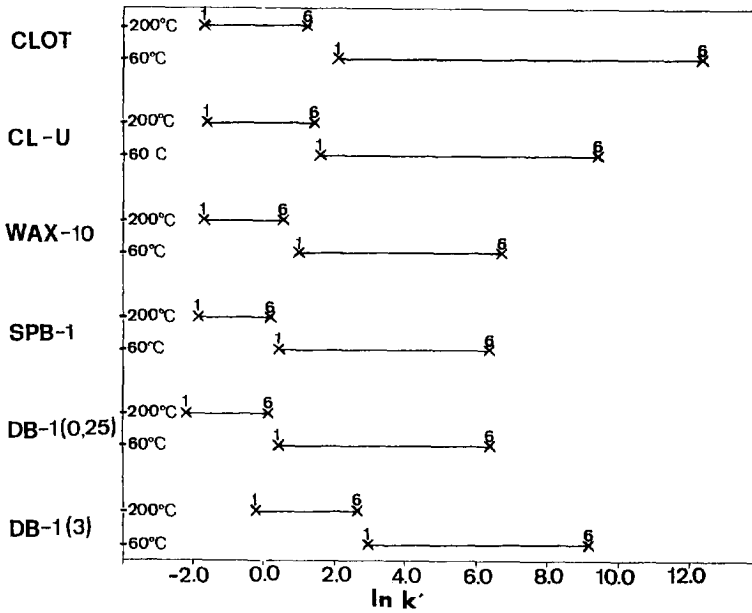


Fig. 2. Ranges of $\ln k'$ values covered by the chlorobenzenes for monochloro (1) at the left and for hexachloro (6) at the right of each line at the lowest (60°C) and at the highest (200°C) temperature on the GL and GLS columns tested.

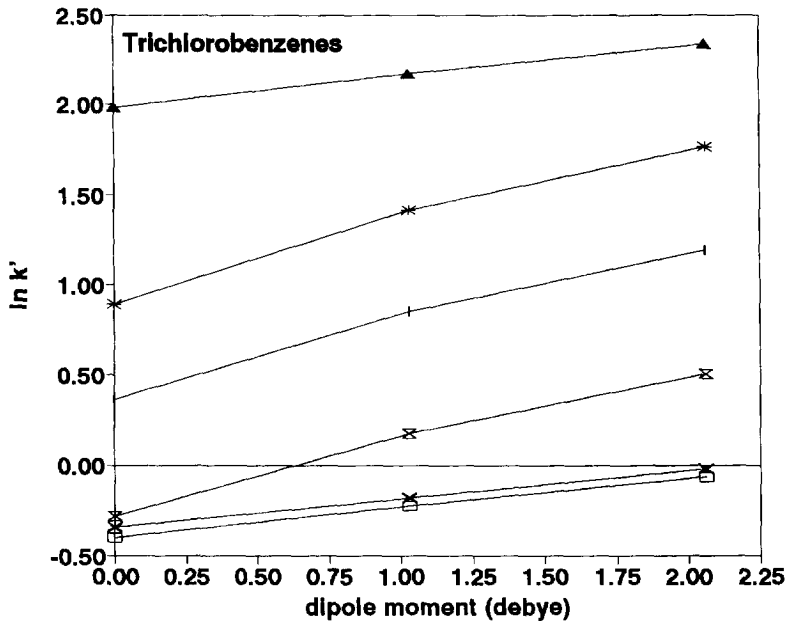


Fig. 3. Dependence of the capacity factors, k' , of trichlorobenzenes on their dipole moments, on the columns tested at 140°C. Carrier gas velocity: 59.5 cm s⁻¹. Columns: x = SPB-1; □ = DB-1 (0.25 μm); ▲ = DB-1 (3 μm); ⊗ = WAX-10; * = CLOT; ■ = CL-U.

where K_D = partition (distribution) coefficient and β = phase ratio:

$$\beta = V_G/V_L = r/2d_f$$

where V_G = volume of mobile phase (void volume of the column), V_L = volume of stationary phase [liquid layer or liquid + carbon (see below)]. r = inner radius of the column and d_f = thickness of the phase layer.

The V_L value can be calculated by measuring the true thickness of the layer and the internal diameter of the capillary tubing by SEM examination. When a carbon layer with added liquid phase is the stationary phase of the column, its total volume (carbon plus modifying liquid) or the volume of liquid obtained by taking into account the percentage of modifying agent (16% in this case) can be considered. Table 3 shows the results of this calculation. The two last rows refer to CLOT and CL-U columns where the data are calculated by using the total volume of stationary phase (carbon + liquid). The normalization for LC columns having different thicknesses of the same stationary phase (3 against 0.25 μm) leads to similar values (the difference is of the same order of magnitude as that obtained with columns from different producers having the same layer thickness: SPB-1 and DB-1 or DB-WAX

and Supelcowax-10). Therefore, the K values for GL columns depend on the type and polarity of the liquid phase only: the difference between the K values of two columns with a similar stationary phase (polar or not polar) is comparable to the small difference in polarity expressed by ΔC [23,33].

When GLS carbon-layer columns modified with 16% polyglycol are used, their K values should correspond to that of polyglycol GL columns if the solute–solvent interaction is due only to liquid–liquid partitioning. The K values of CLOT and CL-U columns are much greater than those of GL polyglycol columns if the liquid amount only is considered and confirm that the liquid–solid interaction plays an important role in the mechanism of GLS columns. On the other hand, the K values calculated for GLS columns by taking into account the total thickness of stationary layer (liquid plus carbon) are smaller than those of GL columns with polyglycol phase. The ratio between the average K values of GL polyglycol columns (about 450) and the k' measured on CLOT and CL-U columns yields “equivalent” β values of 109 and 193, respectively, corresponding to a theoretical thickness of polyglycol of 0.73 and 0.41 μm for CLOT and CL-U, respectively.

The difference between the actual k' values

Table 3

Layer thickness, d_f , capacity factor, k' , volume of phase, V_L , phase ratio, β , partition coefficient, K , and ΔC at 140°C for 1,2,4-trichlorobenzene

Column	d_f (μm)	k'	V_L (mm^3)	β	K	ΔC
SPB-1	0.25	0.858	7.53	320	274	2.69
DB-1 (0.25 μm)	0.25	0.802	7.69	320	257	2.49
DB-1 (3 μm)	3.00	8.827	86.76	26.7	235	2.39
DB-WAX	0.25	1.430	7.69	320	458	7.44
WAX-10	0.25	1.358	7.53	320	435	7.53
CLOT (liquid only)	0.22 ^a	4.128	6.72	363	1498	6.27
CL-U (liquid only)	0.11 ^b	2.330	3.37	727	1694	6.93
CLOT (liquid + solid)	1.40	4.128	42.02	57	238	6.27
CL-U (liquid + solid)	0.70	2.330	21.05	114	266	6.93

^a Equivalent layer thickness of pure liquid (16% concentration).

^b Actual thickness of liquid plus carbon layer.

and those calculated above can be considered as a measure of the contribution of the carbon layer to the total interaction of the columns.

The dependence of the k' values on the number of chlorine atoms in the molecule is shown in Fig. 4. The values for isomeric compounds are shifted along the vertical axis and this behaviour will be discussed below. All the values obtained on GL columns are still strictly grouped, independent on the wide range of polarity and thickness of the liquid phases, while the values for the two carbon-layer columns lie in the upper region of the graph, show a greater slope and are nearly coincident owing to the comparable amount of modifying liquid (about 16%) and notwithstanding the different thickness of the layer. The different behaviours of bonded-phase and carbon-layer columns and the vertical shift between the values for the two types of columns are correlated with the gas–solid interaction, which increases with increasing number of chlorine atoms in the molecule.

While the ratios are nearly the same for isomers, and do not depend on the polarity and

producer of the GL columns with the same film thickness, the ratios between columns with different thickness of the same phase and between pure polyglycol and carbon–polyglycol columns differ appreciably for compounds having an increasing number of chlorine atoms. The vertical spreading of the points is small (about 10%) on changing from chlorobenzene to hexachlorobenzene for GL columns having a 0.25- μm film thickness, independent of the polar or non-polar liquid phase; the ratio between 3- and 0.25- μm GL columns differs by about 30%, whereas the ratio between CLOT and WAX-10 increases by more than 250%; this means that the carbon layer increases the retention of compounds having a greater number of chlorine atoms more than the increase in liquid phase amount. A ratio increase of 190% is found on the CL-U column, having the same percentage of polyglycol (16%) as the CLOT column, but a thickness of 0.7 instead of 1.4 μm .

The position of the substituent atoms in the benzene ring has the same effect on both vapour pressure and retention, which are also correlated

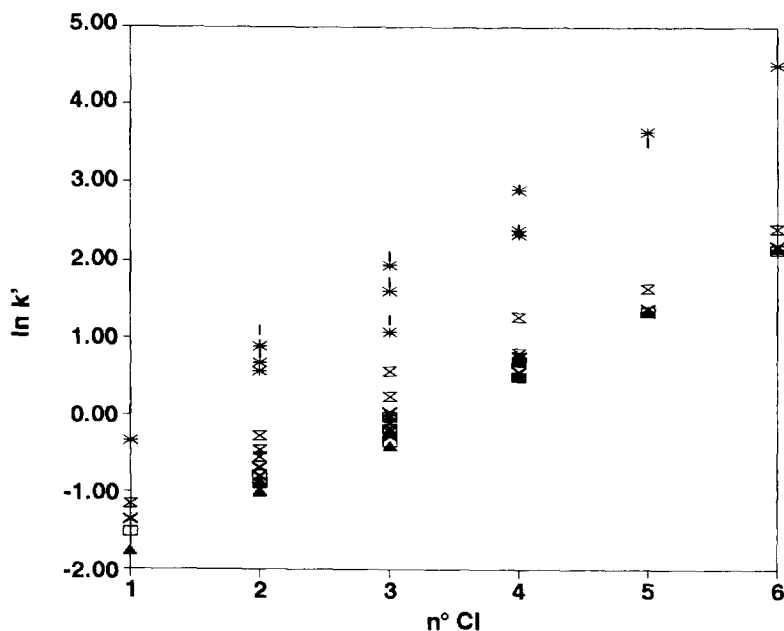


Fig. 4. Dependence of $\ln k'$ of chlorobenzenes at 140°C on the number of chlorine atoms in the molecules. Symbols for columns as in Fig. 4.

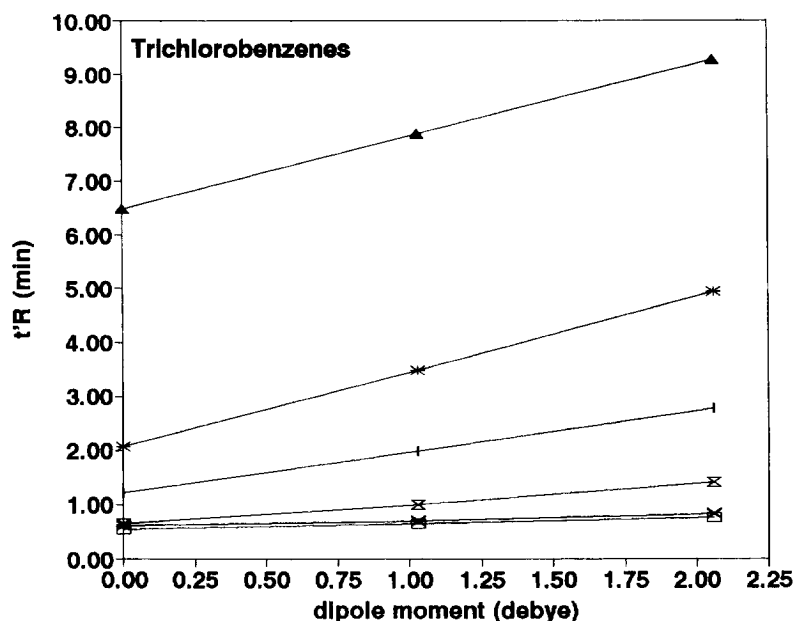


Fig. 5. Linear dependence of the adjusted retention times of trichlorobenzene, t'_R , on their dipole moment at 140°C. Symbols for columns as in Fig. 4.

with the dipole moment (see Fig. 3). The correlation between t'_R and dipole moment is strictly linear for trichlorobenzenes (Fig. 5). The extrapolation of the lines in Fig. 5 shows that they intersect the x -axis ($t'_R = 0$) at a value depending on the type and not on the thickness of the phase: at ca. -5 for non-polar columns, ca. -1.75 for pure polyglycol (WAX-10 and DB-WAX) and -1.48 and -1.58 for CLOT and CL-U, respectively (Table 4).

The linearity as a function of the dipole moment is not verified for di- and tetrachlorobenzenes: boiling points (Table 1) and k' values (Table 2) greater than those expected on the basis of their absence of dipole moment are observed for 1,3-dichlorobenzene and 1,2,4,5-tetrachlorobenzene. An explanation of this behaviour can be found in the *para* position of the substituents in these compounds, whose molecules have an elongated shape that influences the solute–solvent interaction due to a dispersion-type mechanism. This is confirmed by the greater molecular volume of 1,4-dichlorobenzene, which shows a liquid density at 20°C of 1.528, smaller

than that of its isomers (1.546 and 1.552 for 1,3- and 1,2-dichlorobenzene, respectively) [29].

The regular behaviour of k' values observed on all the columns tested allows one to predict the retention of a given compound by extrapolation of the values measured for other components of the same homologous series (the extended definition of homologous series is consid-

Table 4

Value of the intercept with x -axis ($t'_R = 0$) of the lines in Fig. 7 for isomeric compounds with an increasing number of chlorine atoms analysed on different columns

Column	Dichloro	Trichloro	Tetrachloro
SP-1	-5.02	-5.44	-2.80
DB-1 (0.25 μm)	-4.85	-5.11	-2.76
DB-1 (3 μm)	-3.72	-4.80	-2.62
WAX-10	-1.15	-1.72	-0.34
DB-WAX	-1.21	-1.77	-0.35
CLOT	-0.77	-1.48	-0.21
CL-U	-0.99	-1.58	-0.25

Temperature 140°C. Retention time of three trichloro and of two di- and tetrachlorobenzenes were used for regression.

ered here, taking into account the linear relationship between many parameters, such as $\log p^\circ$ and $\log c$, and the number of structural units in the molecule: carbon atoms, methylene groups, chlorine atoms, etc.) [34,35]. Previously published papers [36,37] have shown that the retention and some physical properties of halo-methanes, -ethanes and -ethenes can be deduced by linear inter- or extrapolation, because straight lines can be drawn connecting those compounds that are formed by adding an increasing number of chlorine atoms to the hydrocarbon backbone. A fine structure of parallel lines, where compounds belonging to different homologous series or “families” are plotted, permits one to identify the crossing points occupied by compounds not available as standard samples and to calculate their retention or some physical properties.

In aromatic compounds, however, a further chlorine atom may be added in different positions on the benzene ring, and therefore a given compound can be generated by two or more “parents” and hence belong to different families. Benzene (no chlorine atom) and hexachloroben-

zene (no hydrogen atom) are the two extreme configurations. The replacement of a hydrogen with a chlorine or vice versa results in a constant increase and decrease, respectively, in the logarithm of t'_R and k' values, that must be coincident for trichlorobenzenes, obtained by adding three chlorine atoms to benzene or three hydrogen atoms to hexachlorobenzene.

Fig. 6 shows an example of the application of this method to the $\ln k'$ values of chlorobenzenes analyzed on a DB-1 3- μm column at 100 and 140°C. Straight lines with different slopes connect benzene (B), chlorobenzene (1CB), 12CB, 123CB (*ortho* replacement of a hydrogen with a chlorine, upper full line: average slope 0.85); chlorobenzene, 1,3CB, 135CB (*meta* substitution, lower dotted line: average slope 0.68). Compounds formed by two different kinds of substitution (e.g., 124CB, that is obtained by *ortho* addition to chlorobenzene followed by *meta* addition to 12CB or by *meta* addition to chlorobenzene followed by *ortho* addition to 13CB) lie at a point identified by two consecutive segments having, respectively, the slope of the *ortho* and

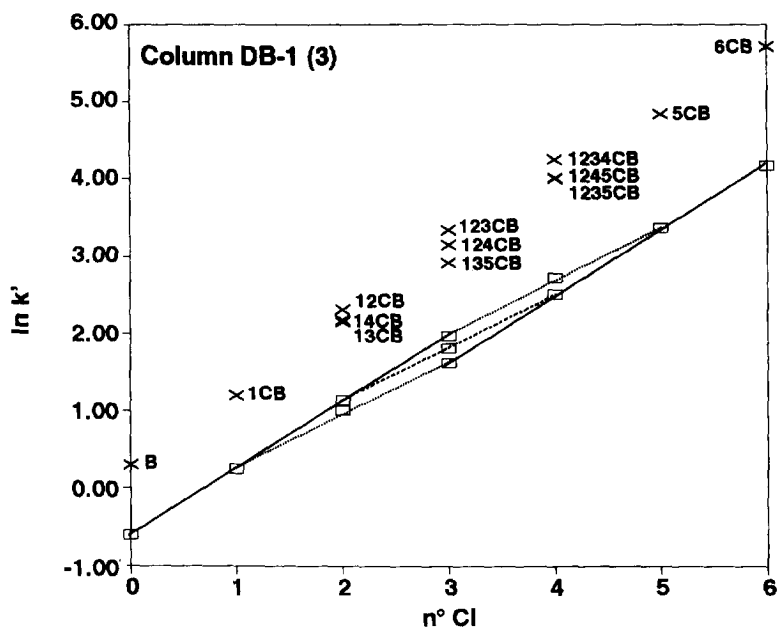


Fig. 6. Regular behaviour of $\ln k'$ of chlorobenzenes as a function of the number of chlorine atoms in the molecule. \times = 100°C; \square = 140°C. Straight lines show *ortho* or *meta* replacement of hydrogen with chlorine atoms. See text.

that of the *meta* substitution (see dashed line). Another example is 1235CB, coming from chlorobenzene by *ortho-ortho-meta* or *ortho-meta-ortho* addition of chlorine atoms.

A mirror-like behaviour with different slopes for *ortho* or *meta* replacement of a chlorine atom with a hydrogen is observed on starting from hexachlorobenzene and moving toward trichlorobenzenes. The lower full line connecting hexachlorobenzene, pentachlorobenzene, 1235CB and 135CB (*meta* replacement of chlorine with hydrogen) has an average slope of 0.85, and is therefore parallel to the *ortho* replacement of hydrogen with chlorine, and that connecting pentachlorobenzene, 1234CB and 123CB (*ortho* replacement of chlorine with hydrogen, upper dotted line) has an average slope of 0.70. Many different combinations of segments with *ortho* and *meta* slopes can lead to the same compound.

A similar behaviour is observed at other temperatures and other film thicknesses. For non-polar phases at a thickness of 0.25 μm , the vertical spreading of the isomers is less evident, and a straight line can be drawn which, within the range of experimental fluctuations, seems to connect all the *ortho*-substituted compounds from benzene to hexachlorobenzene. On polar or carbon-layer columns some deviations from the regular behaviour described above are found, mainly when *para* substitution is considered. This is probably due to the simultaneous influence of steric hindrance and dipole moment on the interaction with polar stationary phases.

4. Conclusions

Linear relationships between retention and structure are observed for compounds with increasing chlorine contents on all the columns tested. Constant increments are correlated with the replacement of a hydrogen with a chlorine atom in the *ortho*- or *meta*-position. Linear behaviour is found at all temperatures and for many groups of homologous compounds, and can therefore allow one to predict the retention value or the boiling point of a compound belonging to a group and not available as an authentic sample,

by interpolation of the corresponding values of other compounds of the same series.

Some deviation from linearity can be correlated with the molecular structure and shape of the compounds. The use of capacity factors and partition coefficients permits one to obtain values correlated with the nature of the liquid phase only, independent on column length, diameter and layer thickness. The behaviour of gas-liquid and gas-liquid-solid capillary columns can be classified on the basis of different slopes and absolute values of the capacity factor as a function of the position and number of chlorine atoms.

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References

- [1] A.N. Korol, J. Chromatogr., 129 (1976) 125.
- [2] M.L. Lanhorst and T.J. Nestruck, Anal. Chem., 51 (1979) 2018.
- [3] A.N. Korol and N.V. Novorusskaya, J. Chromatogr., 169 (1979) 73.
- [4] B.G. Oliver and K.D. Bothen, Anal. Chem., 52 (1980) 2066.
- [5] F.W. Crow, A. Bjorseth, K.T. Knapp and R. Bennet, Anal. Chem., 53 (1981) 619.
- [6] J.K. Haken and I.O.O. Korhonen, J. Chromatogr., 205 (1983) 323.
- [7] I.O.O. Korhonen, Chromatographia, 17 (1983) 195.
- [8] I.O.O. Korhonen, J. Chromatogr., 321 (1985) 115.
- [9] H.B. Lee, Y.D. Stokker and A.S.Y. Chau, J. Assoc. Off. Anal. Chem., 70 (1987) 1003.
- [10] V. Pacakova, H. Ullmannova and E. Smolkova, Chromatographia, 7 (1974) 171.
- [11] W. Engewald and L. Wenrich, Chromatographia, 9 (1976) 540.
- [12] L. Soják, J. Janák, and J.A. Rijks, J. Chromatogr., 142 (1977) 177.
- [13] V.M. Nabivach and A.V. Kirilenko, Chromatographia, 13 (1980) 29.
- [14] V.M. Nabivach and A.V. Kirilenko, Chromatographia, 13 (1980) 93.
- [15] N. Dimov and Ov. Mekenyan, J. Chromatogr., 471 (1989) 227.

- [16] J.K. Haken and I.O.O. Korhonen, *J. Chromatogr.*, 257 (1983) 267.
- [17] L.E. Cook and F.M. Raushel, *J. Chromatogr.*, 65 (1972) 556.
- [18] F. Yugi, Z. Pengling and H. Zhide, *Chromatographia*, 25 (1988) 382.
- [19] H. Purnell, *Gas Chromatography*, Wiley, New York, 1962.
- [20] A. di Corcia and A. Liberti, *Adv. Chromatogr.*, 4 (1976) 346.
- [21] L.M. Sidisky and M.V. Robillard, in P. Sandra and M.L. Lee (Editors), *Proceedings of the 14th International Symposium on Capillary Chromatography*, Baltimore, 1992, p. 110.
- [22] G. Castello and S. Vezzani, in P. Sandra (Editor), *Proceedings of the 15th International Symposium on Capillary Chromatography*, Riva del Garda, Italy, 1993, Hüthig, Heidelberg, 1993, p. 68.
- [23] G. Castello, G. D'Amato and S. Vezzani, *J. Chromatogr.*, 646 (1993) 361.
- [24] G. Castello, S. Vezzani and P. Moretti, *J. High. Resolut. Chromatogr.*, 17 (1994) 31.
- [25] G.C. Goretti, A. Liberti and G. Nota, *Chromatographia*, 8 (1975) 486.
- [26] C. Vidal-Madjar, S. Bekassy, M.F. Gonnard, P. Arpino and G. Guiochon, *Anal. Chem.*, 49 (1977) 768.
- [27] W. Engewald, J. Porschmann and T. Welsch, *Chromatographia*, 30 (1990) 537.
- [28] E. Forgács and T. Cserhádi, *Chromatographia*, 33 (1992) 356.
- [29] R.C. Weast (Editor), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 69th ed., 1989.
- [30] G. Castello, S. Vezzani and P. Moretti, *J. Chromatogr. A*, 677 (1994) 95.
- [31] S. Vezzani, P. Moretti and G. Castello, *J. Chromatogr. A*, 677 (1994) 331.
- [32] L.S. Ettre and J.W. Hinshaw, *Basic Relationships of Gas Chromatography*, Advanstar, Cleveland, OH, 1993, p. 60.
- [33] G. Castello and G. D'Amato, *J. Chromatogr.*, 623 (1992) 289.
- [34] G.J. Pierotti, C.H. Derr and P.E. Porter, *J. Am. Chem. Soc.*, 78 (1956) 2989.
- [35] D.A. Leathard and B.C. Shurlock, in J.H. Purnell (Editor), *Progress in Gas Chromatography*, Wiley, New York, 1968.
- [36] T.C. Gerbino and G. Castello, *J. Chromatogr.*, 537 (1991) 305.
- [37] T.C. Gerbino, G. Castello and G. D'Amato, *J. Chromatogr.*, 609 (1992) 289.