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# Prediction of retention indices V. Influence of electronic effects and column polarity on retention index

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**Abstract**

The retention index increment for addition of a methylene group to an analyte molecule is shown for 1-halo-*n*-alkanes to be different from 100 i.u., a value that is customarily assigned according to the current convention in retention index prediction. In temperature-programmed gas chromatography using linearly interpolated retention index *I*, a linear regression equation, $I=AZ+$(GRF), with the number of atoms ($Z$) in the molecule as variable can describe the retention of 16 homologous series of organic compounds on non-polar and polar columns with characteristic $A$ (linear regression coefficient) and (GRF) (group retention factor) values. A molecular model of retention on the basis of electron density and electron density distribution relative to that of *n*-alkane is proposed. This model brings out the inter- and intramolecular electronic effects in the analyte molecule and its dipole–dipole interaction with the stationary liquid phases, as variations in the $A$ value. The (GRF) value varies with the connectivity ability of a functional group for extended conjugation, substitution, etc., but is most influenced by hydrogen bonding (H-bonding) with the stationary liquid phase. One can estimate the sequence of elution of a mixture of organic compounds from any two of the three parameters on the right-hand side of the above equation or retrieve the retention indexes of an entire homologous series from its $A$ and (GRF) values. The fact that each analyte molecule has its own $A$ value on different columns makes column difference ($\Delta I$) compound-specific rather than column-specific, a departure from previous assumptions. 

*Keywords:* Retention indices; Retention models; Group retention factors; Regression analysis; Alkanes

## 1. Introduction

Gas chromatographic retention is a very complex process. It involves the interaction of a multitude of intermolecular forces, known as dispersion (or London forces), orientation (dipole–dipole or Keesom forces), induction (dipole–induced dipole or Debye forces), and electron donor–acceptor complexation, including hydrogen bonding forces, leading to the partition of the solute between the gas and liquid phases [1–4]. Other factors, such as adsorption at the gas–liquid and liquid-support interfaces, steric hindrance of substituent groups within the solute molecule, etc., can also affect retention [5,6]. Numerous methods for calculation and prediction of

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various retention indexes have been extensively reviewed [7,8].

Our study of chemical structure–retention index relationship is to predict retention index ($I$)[1] from structures of organic molecules and to retrieve structure information from retention index. In a temperature-programmed chromatographic system, retention is a simple function of the number of atoms ($Z$) in the analyte molecule [6,9]. In such a system the retention indexes of all members of a homologous series of organic compounds can be directly represented by a linear regression equation of the general form $I=aZ+b$, where $a$ and $b$ are predefined constants. These constants reflect the interactions between the analyte molecule and the stationary liquid phase and are important in the prediction of the retention index. Since studies of structure–retention index relationship are generally carried out on columns of non-polar stationary liquid phase, it is not clear how an increase in column polarity in discrete steps will affect the intermolecular interactions and alter the equation or the constants. In addition to column polarity, the chemical nature of homologous series and the intermolecular forces essential to chromatographic retention can exert an effect on the constants. This report describes the study of retention of a number of homologous series on eight columns of different polarity graded between the most non-polar DB-1 and the most polar DB-Wax column. The results, when interpreted from the viewpoint of electron density and electron density distribution in the analyte molecule and its interaction with the stationary liquid phase, give a new meaning to the constants that are important in the prediction of retention index in gas chromatography.

## 2. Experimental

The materials and methods are essentially those previously described [6,10]. The chemicals were obtained from Aldrich (Milwaukee, WI, USA) and other commercial sources and were used as received. The chromatographic runs were carried out on Hewlett-Packard 5880A and 5890 Series II gas chromatographs, equipped with thermal conductivity detectors and adapted for use of fused-silica macrobore capillary columns with 0.53 mm inner column diameter. Both gas chromatographs are equipped with HP 7673 autosamplers for automatic sample injection and with electronic integrators.

The amount of sample injected was in the range of nanograms in 1.0 μl of solvent (*n*-pentane, *n*-hexane or methanol). The sample peak height was kept below the height of the chart to yield correct retention time for calculation. Injected samples consisted of single compounds, mixtures of compounds or an entire homologous series; the latter mode of operation eliminates the variations of injection time for retention index calculation. Fused-silica capillary columns (0.53 mm I.D.) were from J&W Scientific (Folsom, CA, USA) and Agilent Technologies (Wilmington, DE, USA). These were DB-1 (100% dimethylpolysiloxane), DB-35 (35% diphenyl–65% dimethylpolysiloxane), DB-17 (50% diphenyl–50% dimethylpolysiloxane), DB-608 [same as DB-17, but specifically designed for the separation of US Environmental Protection Agency (EPA) Method 608 compounds], DB-210 (50% 3,3,3-trifluoropropyl–50% methylpolysiloxane), DB-225 (25% 3-cyanopropyl–25% phenyl–50% dimethylpolysiloxane), DB-Wax (polyethylene glycol), and HP-Basic Wax (modified polyethylene glycol) columns. The columns were 15 m in length coated with a film thickness of 1.0 μm liquid phase, with the exception of DB-608 column with a film thickness of 0.83 μm. Average linear velocity of helium gas on HP-5890 was about 31.5 cm/min. This selection of columns, according to an early recommendation for chromatographic separation [11–13], embraces a full spectrum of polarity of stationary liquid phases.

All the runs were temperature-programmed. The oven temperature was programmed for (a) DB-1: to start from 40°C (3 min) at 8°C/min to 200°C (1 min), and then at 5°C/min to 300°C (25 min); (b) DB-35, DB-17 and DB-608: to start from 40°C (3 min) at 8°C/min to 200°C (1 min), and then at 5°C/min to 280°C (25 min); (c) DB-210: to start from 45°C (3 min) at 5°C/min to 220°C (40 min); (d) DB-225: to start from 40°C (3 min) at 5°C/min to 200°C (25 min); (e) DB-Wax and HP-Basic Wax: to start from 40°C (3 min) at 5°C/min to 220°C (30 min or longer). The injection port was kept at 250°C for polar columns and at 270°C for non-polar

[1]Retention index ($I$) in this paper refers to the temperature-programmed, linearly interpolated retention index.

columns and the detector at 300°C. A mixture of *n*-alkanes, from pentane ($C_5$) to hexatriacontane ($C_{36}$), excluding tricosane ($C_{23}$), heptacosane ($C_{27}$), hentriacontane ($C_{31}$) and pentatriacontane ($C_{35}$), were used as markers for retention index ($I$) determination. The retention index $I$ was computed by linear interpolation using the equation of van den Dool and Kratz [14], thus:

$$I = 100i \cdot \frac{X - M_{(n)}}{M_{(n+i)} - M_{(n)}} + 100n \quad (1)$$

where $n$ is the number of carbon atoms in the *n*-alkanes used as markers; $X$, $M_{(n)}$, and $M_{(n+i)}$ are the retention times of the analyte, the normal alkane markers with $n$ carbon atoms eluting before and with $(n+i)$ carbon atoms eluting after the analyte, respectively; $i$ is the interval and has the value of 1 or 2.

Linear graphs correlating the observed retention index ($I$) and the atom number ($Z$) of the homologues were produced using the software SigmaPlot, Version 5.05 (SSPS, Chicago, IL, USA). Linear regression analysis was carried out using the statistical software SigmaStat for Windows, Version 2.03 (SSPS) to obtain the $A$ and (GRF) values (see Eq. (3)) and the statistical errors.

## 3. Results and discussion

Mono- and bifunctional organic compounds and their homologues[2], were chromatographed on non-polar and polar columns to study their retention behavior. These columns span a wide range of polarity and are recommended for chromatographic separation [11–13]. The focus of the paper, to be discussed in sections, is on retention, polarity of stationary liquid phases, connectivity of functional groups, selective retention of organic molecules, column difference ($\Delta I$), and conclusion. The following section begins with *n*-alkanes and 1-halo-*n*-alkanes, electron density distribution and retention, molecular model of retention and continues with a selection of other homologous series.

### 3.1. Retention

#### 3.1.1. The n-alkane reference standards

*n*-Alkanes are the retention index markers in the Kováts retention index system. Their $I$ values are arbitrarily assigned to equal the number of carbon atoms ($n$) in the molecule multiplied by 100 [15], thus:

$$I = 100n \quad (2)$$

The Kováts retention index system uses logarithmic interpolation for calculation of the isothermal retention index of the analyte molecule bracketed by the retention times of two adjacent *n*-alkanes, while the temperature-programmed retention index system uses linear interpolation. In temperature-programmed chromatographic systems, Eq. (2) can be derived from an equation that equates the observed retention index ($I_{obs}$) to the summation of atom contribution and functionality contribution of the analyte molecule [6,9], thus:

$$I_{obs} = AZ + (GRF)_z \quad (3)$$

where $A$ is the linear regression coefficient or the retention index increment per atom addition, $Z$ the number of C, N and O atoms in the molecule, and $(GRF)_z$ the group retention factor or functionality constant for functional groups in the molecule, based on the atom number $Z$. Eq. (3) is reduced to Eq. (2) for *n*-alkanes, by setting the term of (GRF) to zero because of the absence of functionality in the molecule, and $A$ is arbitrarily assigned a value of 100 index units (i.u.). Thus the *n*-alkanes become the chromatographic reference markers naturally in the limiting case of the equation. The usefulness of Eq.

[2] A higher homologue is formed from a lower homologue by addition of a methylene ($CH_2$) group to lengthen the alkane chain. Insertion of the methylene group can be envisioned to occur between the carbon–carbon bond connecting two methylene groups so that the bond breaking and bond making involve no energy change. Addition of a $CH_2$ group to methyl group to form ethyl group or to formic acid to form acetic acid, etc. necessitates the breaking of a C–H bond. Addition of a $CH_2$ group to oxalic acid, or ethylene glycol, or ethylene diamine, etc., to form higher homologues in bifunctional series involves the scission of a carbon–carbon bond, which is not between two methylene groups. Such an insertion of a $CH_2$ group involves different energies of formation and may or may not yield the same incremental chromatographic retention for the $CH_2$ group. Early reports in the literature frequently mention that the lower members of a homologous series tend to deviate chromatographically from the retention linearity of the series. It is possible that the differences in bond energy may be one of the underlying causes.

(3) as the basis for the chemical structure–retention index relationship and for *I* prediction has been discussed [9]. In this report, it will be referred to as the retention index equation. Data presented in this report show that Eq. (3) is applicable to all homologous series on non-polar and polar columns.

Graphs of retention times or the emergence curves of the *n*-alkanes from hexane ($C_6$) to hexatriacontane ($C_{36}$) on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, DB-Wax and HP-Basic Wax columns are shown in Fig. 1. The retention times were not adjusted for the air peak. These graphs appear quasi-

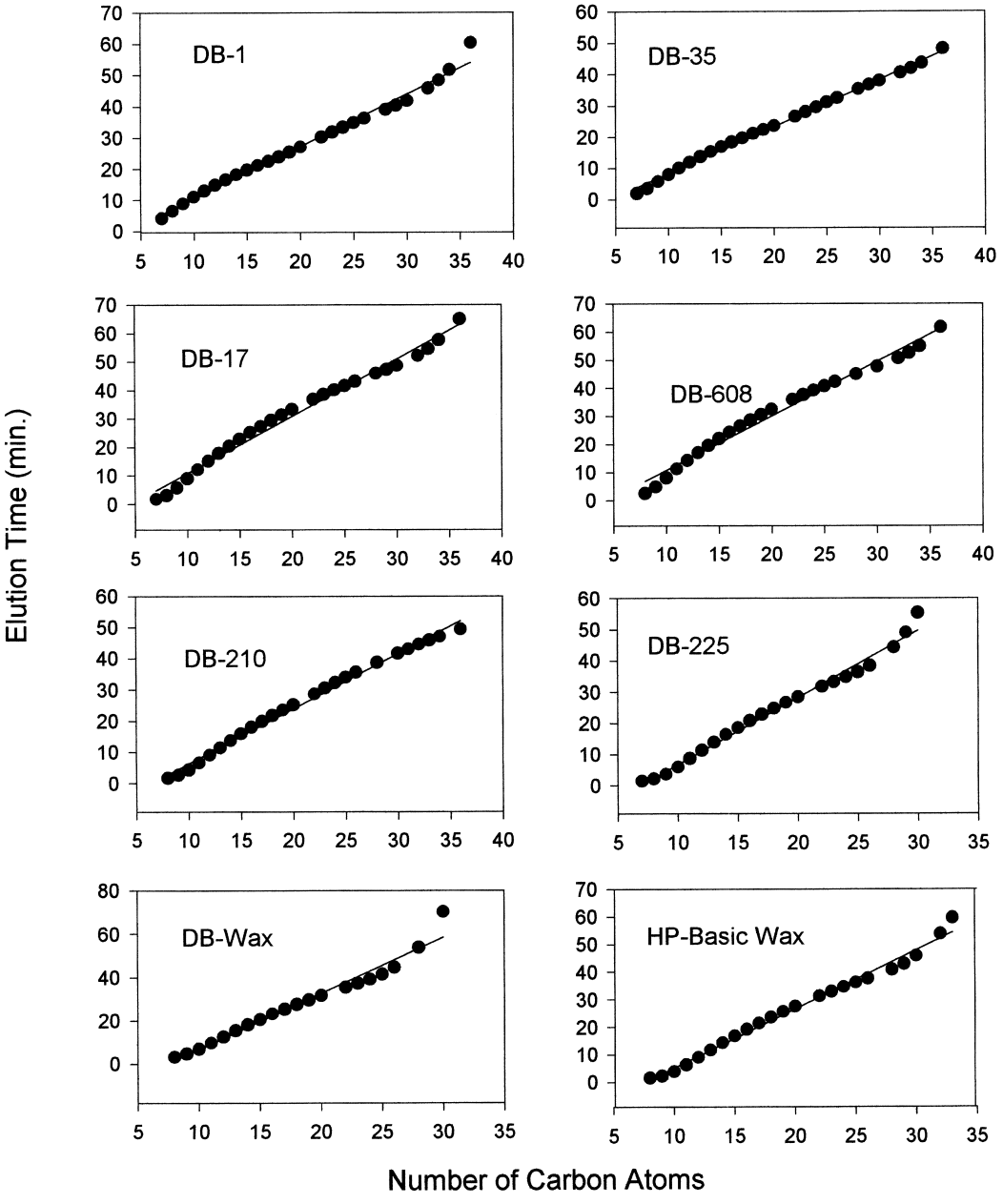



Fig. 1. Graphs of retention times of *n*-alkanes from hexane ($C_6$) to hexatriacontane ($C_{36}$) on eight different non-polar and polar columns.

linear, even though the runs on some columns are linearly and on others non-linearly temperature-programmed. The quasi-linearity of the emergence curve of *n*-alkanes does not affect the linearity of the *I* vs. *Z* plots of the homologous series on all columns, shown in Figs. 2–6. Automatic sample injection improves the reproducibility of the elution times of all peaks. The maximum operating column temperature is 200°C for the polar DB-225 column, 220°C for the polar DB-210 column, 240°C for the DB-Wax and HP-Basic Wax columns, 280°C for the non-polar DB-35, DB-17 and DB-608 columns, and 300°C for the non-polar DB-1 column. Octacosane ($C_{28}$) and higher alkanes are eluted isothermally from the polar columns. Elution of tetratriacontane ($C_{34}$) and hexatriacontane ($C_{36}$) may appear delayed on non-polar columns since they may be eluted isothermally at the maximum operating temperature. Compounds emerging from these columns in the high temperature isothermal region were included in the *I* vs. *Z* plots.

### *3.1.2. 1-Halo-n-alkanes*

Halogen atoms are monovalent. The atom and functionality contributions from the halo atoms to chromatographic retention cannot be separated from each other, even though chlorine, bromine and iodine atoms have been tentatively assigned carbon atom equivalent values of 2, 3 and 4, respectively [6]. In this report, the (GRF) values of the halo atoms are inclusive of both contributions. Halogen atoms are electronegative, withdraw electrons by inductive effect and also donate electrons by mesomeric or resonance effect.

The observed retention indices ($I_{obs}$) of 1-chloro-, 1-bromo-, and 1-iodo-*n*-alkanes on all the columns are listed in Table 1. The polarity of the column increases from DB-1 column to DB-Wax column, thus:

$$\text{DB-1} < \text{DB-35} < \text{DB-17} \cong \text{DB-608} < \text{DB-210} < \text{DB-225} < \text{DB-Wax} \cong \text{HP-Basic Wax}$$

The $I_{obs}$ values of 1-halo-*n*-alkanes on these columns and their carbon numbers were used for plotting and for linear regression analyses. The *A* and (GRF) values are given in Table 2 together with the standard errors (S.E.s) and the number of data

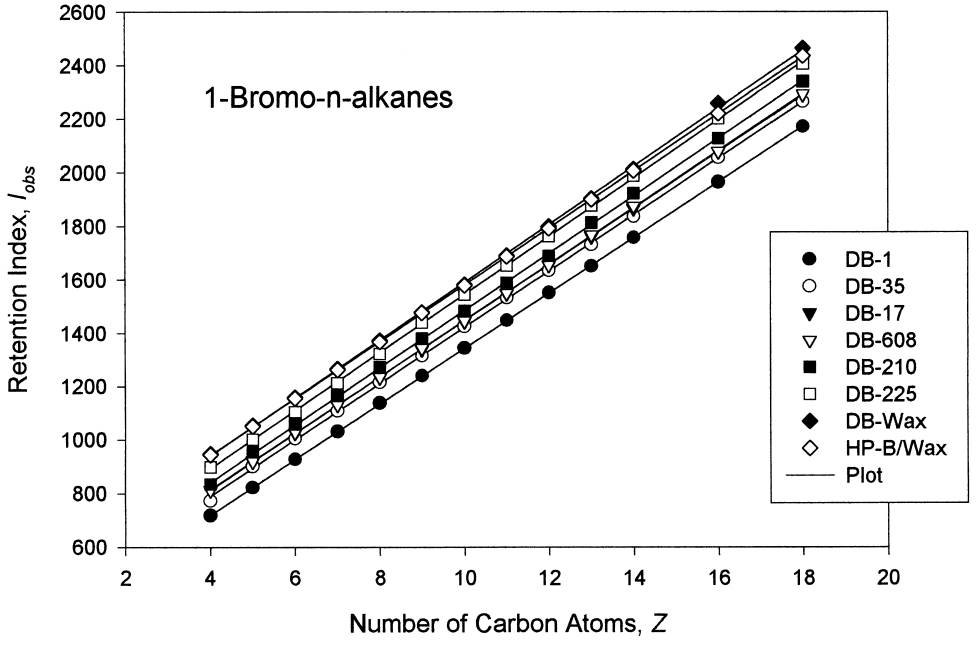



Fig. 2. Linear plots of $I_{obs}$ vs. *Z* of the homologous series of 1-bromo-*n*-alkanes on non-polar and polar columns. Plots from DB-17 and DB-608 columns and from DB-Wax and HP-Basic Wax columns are superposed.

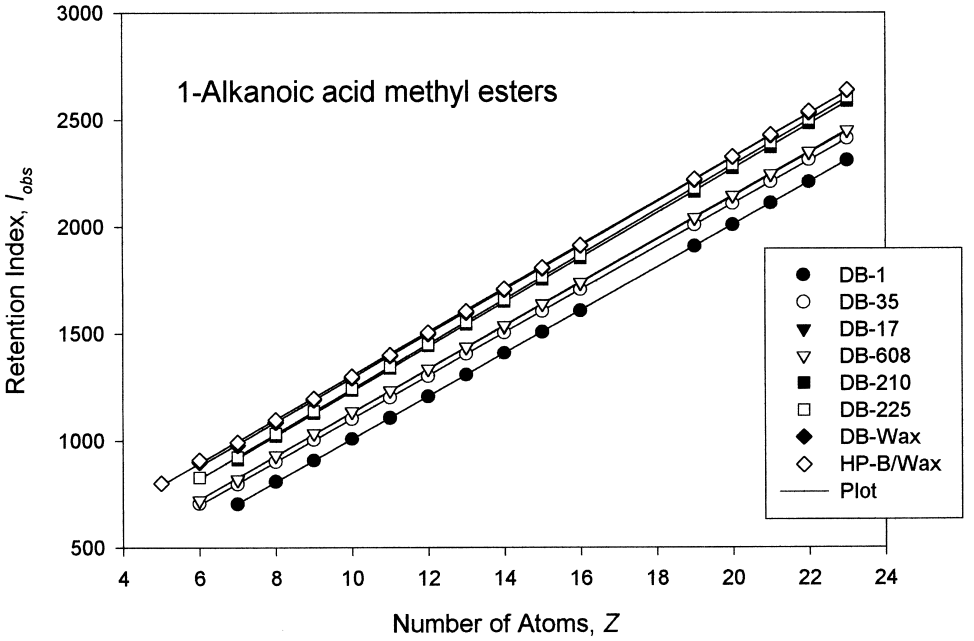



Fig. 3. Linear plots of $I_{obs}$ vs. $Z$ of 16 homologues of fatty acid methyl esters on non-polar and polar columns. Plots from DB-17 and DB-608, from DB-210 and DB-225, and from DB-Wax and HP-Basic Wax columns are superposed.

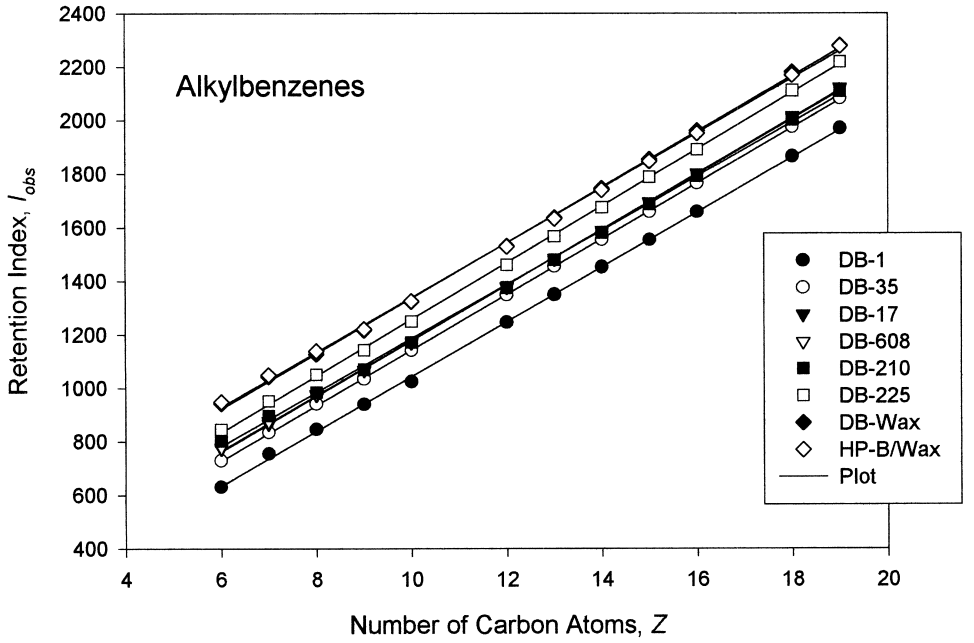



Fig. 4. Linear plots of $I_{obs}$ vs. $Z$ of 12 alkylbenzene homologues on non-polar and polar columns. Plots from DB-17 and DB-608, and from DB-Wax and HP-Basic Wax columns are superposed.

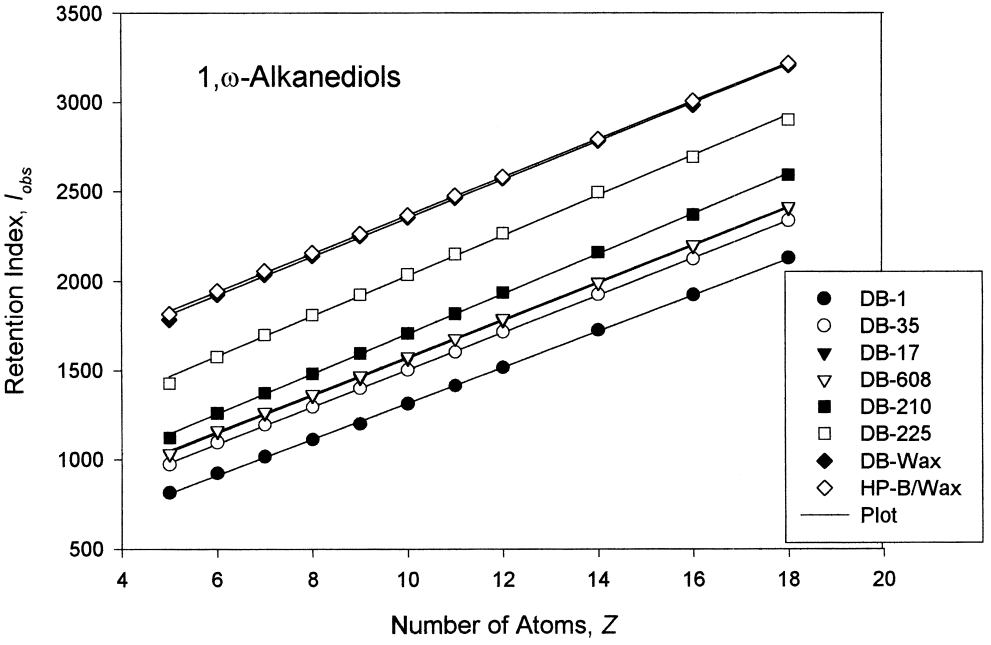



Fig. 5. Linear plots of $I_{obs}$ vs. $Z$ of 11 1,ω-alkanediols on non-polar and polar columns. Plots from DB-17 and DB-608, and from DB-Wax and HP-Basic Wax columns are superposed. Spacings between these plots indicate strong interactions between the diols and column stationary liquid phases.

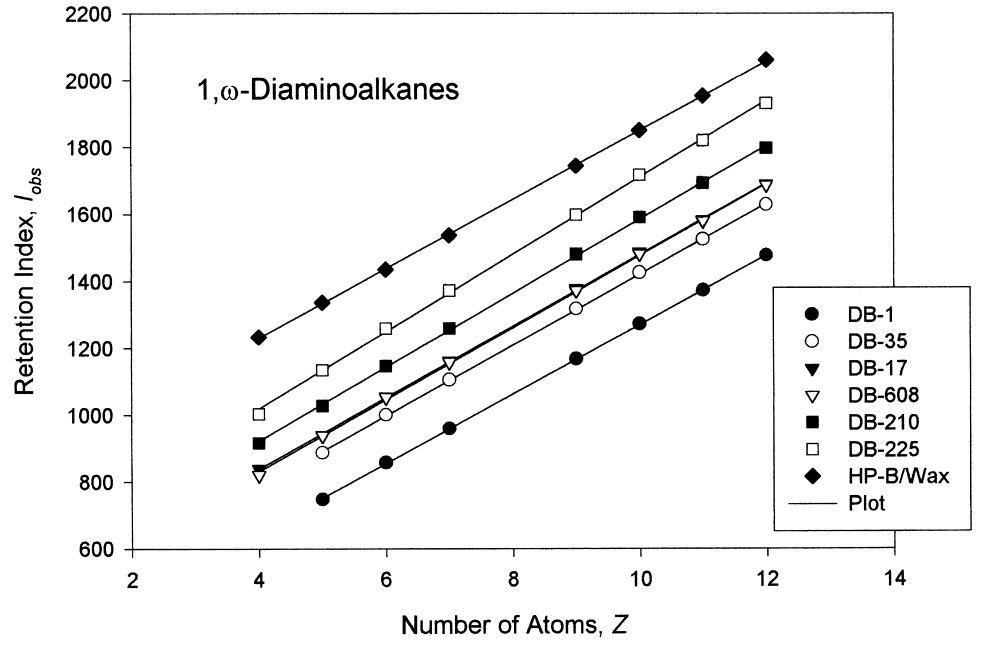



Fig. 6. Linear plots of $I_{obs}$ vs. $Z$ of 1,ω-diaminoalkanes on non-polar and polar columns. Plots from DB-17 and DB-608 columns are superposed.

Table 1
Observed retention indexes ($I_{obs}$) of 16 homologous series of organic compounds on non-polar and polar columns

| Homologous series | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| 1-Chloro-*n*-alkanes | | | | | | | | | |
| 1-Chlorobutane | $C_4H_9Cl$ | | | | | | | | 832 |
| 1-Chloropentane | $C_5H_{11}Cl$ | 739 | 811 | 829 | 823 | 880 | 906 | 946 | 941 |
| 1-Chlorohexane | $C_6H_{13}Cl$ | 844 | 914 | 933 | 929 | 984 | 1008 | 1047 | 1049 |
| 1-Chloroheptane | $C_7H_{15}Cl$ | 948 | 1017 | 1036 | 1036 | 1088 | 1113 | 1152 | 1155 |
| 1-Chlorooctane | $C_8H_{17}Cl$ | 1051 | 1121 | 1138 | 1138 | 1193 | 1220 | 1257 | 1260 |
| 1-Chlorononane | $C_9H_{19}Cl$ | 1154 | 1224 | 1241 | 1241 | 1296 | 1327 | 1363 | 1364 |
| 1-Chlorodecane | $C_{10}H_{21}Cl$ | 1257 | 1327 | 1343 | 1343 | 1401 | 1434 | 1469 | 1468 |
| 1-Chlorotetradecane | $C_{14}H_{29}Cl$ | 1668 | 1740 | 1757 | 1757 | 1823 | 1860 | 1890 | 1886 |
| 1-Chlorohexadecane | $C_{16}H_{33}Cl$ | 1873 | 1945 | 1964 | 1964 | 2031 | 2079 | 2104 | 2099 |
| 1-Chlorooctadecane | $C_{18}H_{37}Cl$ | 2079 | 2152 | 2172 | 2173 | 2244 | 2293 | 2312 | 2307 |
| 1-Bromo-*n*-alkanes | | | | | | | | | |
| 1-Bromobutane | $C_4H_9Br$ | 719 | 773 | 813 | 813 | 835 | 898 | 948 | 944 |
| 1-Bromopentane | $C_5H_{11}Br$ | 823 | 902 | 923 | 920 | 954 | 1001 | 1055 | 1052 |
| 1-Bromohexane | $C_6H_{13}Br$ | 927 | 1005 | 1026 | 1027 | 1059 | 1105 | 1160 | 1156 |
| 1-Bromoheptane | $C_7H_{15}Br$ | 1031 | 1109 | 1130 | 1130 | 1165 | 1213 | 1266 | 1262 |
| 1-Bromooctane | $C_8H_{17}Br$ | 1138 | 1216 | 1235 | 1234 | 1271 | 1322 | 1373 | 1368 |
| 1-Bromononane | $C_9H_{19}Br$ | 1240 | 1314 | 1339 | 1343 | 1381 | 1439 | 1478 | 1476 |
| 1-Bromodecane | $C_{10}H_{21}Br$ | 1344 | 1426 | 1444 | 1446 | 1483 | 1544 | 1583 | 1579 |
| 1-Bromoundecane | $C_{11}H_{23}Br$ | 1448 | 1531 | 1549 | 1550 | 1589 | 1653 | 1692 | 1687 |
| 1-Bromododecane | $C_{12}H_{25}Br$ | 1552 | 1636 | 1655 | 1655 | 1689 | 1764 | 1800 | 1793 |
| 1-Bromotridecane | $C_{13}H_{27}Br$ | 1652 | 1731 | 1762 | 1768 | 1814 | 1878 | 1905 | 1900 |
| 1-Bromotetradecane | $C_{14}H_{29}Br$ | 1758 | 1837 | 1867 | 1876 | 1924 | 1989 | 2013 | 2007 |
| 1-Bromohexadecane | $C_{16}H_{33}Br$ | 1965 | 2055 | 2079 | 2078 | 2128 | 2201 | 2258 | 2220 |
| 1-Bromooctadecane | $C_{18}H_{37}Br$ | 2172 | 2265 | 2291 | 2292 | 2340 | 2405 | 2465 | 2436 |
| 1-Iodo-*n*-alkanes | | | | | | | | | |
| 1-Iodoethane | $C_2H_5I$ | | | 724 | | | | 881 | |
| 1-Iodopropane | $C_3H_7I$ | 700 | 795 | 826 | 821 | | | 971 | |
| 1-Iodobutane | $C_4H_9I$ | 798 | 900 | 929 | 923 | 920 | 1000 | 1062 | 1063 |
| 1-Iodopentane | $C_5H_{11}I$ | 903 | 1004 | 1032 | 1031 | 1026 | 1109 | 1164 | 1166 |
| 1-Iodohexane | $C_6H_{13}I$ | 1008 | 1110 | 1137 | 1134 | 1132 | 1218 | 1275 | 1272 |
| 1-Iodoheptane | $C_7H_{15}I$ | 1114 | 1218 | 1243 | 1241 | 1241 | 1330 | 1384 | 1381 |
| 1-Iodooctane | $C_8H_{17}I$ | 1221 | 1324 | 1350 | 1348 | 1349 | 1441 | 1493 | 1487 |
| 1-Iodononane | $C_9H_{19}I$ | 1327 | 1431 | 1457 | 1455 | 1457 | 1552 | 1600 | 1596 |
| 1-Iododecane | $C_{10}H_{21}I$ | 1433 | 1538 | 1563 | 1562 | 1562 | 1663 | 1706 | 1705 |
| 1-Iodoundecane | $C_{11}H_{23}I$ | 1539 | 1646 | 1671 | 1670 | 1671 | 1774 | 1816 | 1813 |
| 1-Iodododecane | $C_{12}H_{25}I$ | 1644 | 1753 | 1778 | 1778 | 1779 | 1885 | 1926 | 1922 |
| 1-Iodohexadecane | $C_{16}H_{33}I$ | 2064 | 2180 | 2209 | 2208 | 2213 | 2332 | 2362 | (see text) |
| 1-Iodooctadecane | $C_{18}H_{34}I$ | 2272 | 2390 | 2422 | 2421 | 2427 | 2548 | 2576 | |
| 1-Alkanoic acid methyl esters | | | | | | | | | |
| Methyl acetate | $C_3H_6O_2$ | | | | | | | | 801 |
| Methyl propionate | $C_4H_8O_2$ | | 705 | 721 | 721 | | 828 | 899 | 908 |
| Methyl butyrate | $C_5H_{10}O_2$ | 704 | 797 | 818 | 819 | 912 | 924 | 979 | 993 |
| Methyl valerate | $C_6H_{12}O_2$ | 808 | 901 | 931 | 931 | 1022 | 1032 | 1086 | 1096 |
| Methyl caproate | $C_7H_{14}O_2$ | 907 | 1002 | 1034 | 1035 | 1129 | 1137 | 1189 | 1197 |
| Methyl enanthate | $C_8H_{16}O_2$ | 1007 | 1102 | 1134 | 1136 | 1236 | 1242 | 1292 | 1299 |
| Methyl caprylate | $C_9H_{18}O_2$ | 1106 | 1202 | 1234 | 1235 | 1338 | 1345 | 1394 | 1400 |
| Methyl nonanoate | $C_{10}H_{20}O_2$ | 1206 | 1302 | 1334 | 1335 | 1442 | 1449 | 1496 | 1503 |

Table 1. Continued

| Homologous series | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| Methyl decanoate | $C_{11}H_{22}O_2$ | 1307 | 1403 | 1434 | 1436 | 1543 | 1553 | 1597 | 1603 |
| Methyl undecanoate | $C_{12}H_{24}O_2$ | 1407 | 1503 | 1534 | 1537 | 1649 | 1659 | 1703 | 1710 |
| Methyl laurate | $C_{13}H_{26}O_2$ | 1506 | 1604 | 1638 | 1637 | 1751 | 1763 | 1805 | 1810 |
| Methyl tridecanoate | $C_{14}H_{28}O_2$ | 1606 | 1705 | 1736 | 1738 | 1852 | 1866 | 1911 | 1913 |
| Methyl palmitate | $C_{17}H_{34}O_2$ | 1908 | 2008 | 2039 | 2042 | 2163 | 2181 | 2218 | 2223 |
| Methyl heptadecanoate | $C_{18}H_{36}O_2$ | 2009 | 2107 | 2144 | 2146 | 2273 | 2290 | 2325 | 2329 |
| Methyl stearate | $C_{19}H_{38}O_2$ | 2111 | 2211 | 2244 | 2247 | 2371 | 2392 | 2426 | 2431 |
| Methyl nonadecanoate | $C_{20}H_{40}O_2$ | 2210 | 2313 | 2348 | 2350 | 2483 | 2503 | 2534 | 2539 |
| Methyl eicosanoate | $C_{21}H_{42}O_2$ | 2311 | 2414 | 2450 | 2452 | 2589 | 2606 | 2638 | 2640 |
| *n*-Alkyl ethers | | | | | | | | | |
| Propyl ether | $C_6H_{14}O$ | 680 | 712 | | | | 788 | | |
| Butyl ether | $C_8H_{18}O$ | 876 | 918 | 944 | 932 | 926 | 961 | 974 | 968 |
| Pentyl ether | $C_{10}H_{22}O$ | 1070 | 1116 | 1139 | 1131 | 1123 | 1162 | 1172 | 1173 |
| Hexyl ether | $C_{12}H_{26}O$ | 1265 | 1311 | 1331 | 1324 | 1317 | 1358 | 1367 | 1368 |
| Octyl ether | $C_{16}H_{34}O$ | 1657 | 1702 | 1722 | 1716 | 1705 | 1752 | 1761 | 1760 |
| Alkylbenzenes | | | | | | | | | |
| Benzene | $C_6H_6$ | 630 | 729 | 774 | 778 | 801 | 845 | 943 | 947 |
| Toluene | $C_7H_8$ | 754 | 834 | 867 | 876 | 897 | 951 | 1043 | 1049 |
| Ethylbenzene | $C_8H_{10}$ | 846 | 941 | 975 | 978 | 984 | 1051 | 1127 | 1138 |
| *n*-Propylbenzene | $C_9H_{12}$ | 939 | 1036 | 1068 | 1067 | 1069 | 1142 | 1217 | 1221 |
| *n*-Butylbenzene | $C_{10}H_{14}$ | 1024 | 1141 | 1172 | 1171 | 1172 | 1249 | 1324 | 1325 |
| 1-Phenylhexane | $C_{12}H_{18}$ | 1246 | 1349 | 1379 | 1378 | 1376 | 1461 | 1531 | 1529 |
| 1-Phenylheptane | $C_{13}H_{20}$ | 1350 | 1455 | 1485 | 1484 | 1479 | 1567 | 1638 | 1634 |
| 1-Phenyloctane | $C_{14}H_{22}$ | 1453 | 1554 | 1589 | 1588 | 1581 | 1676 | 1746 | 1741 |
| 1-Phenylnonane | $C_{15}H_{24}$ | 1554 | 1660 | 1696 | 1694 | 1688 | 1789 | 1854 | 1847 |
| 1-Phenyldecane | $C_{16}H_{26}$ | 1659 | 1766 | 1802 | 1800 | 1792 | 1892 | 1962 | 1953 |
| 1-Phenyldodecane | $C_{18}H_{30}$ | 1866 | 1977 | 2015 | 2014 | 2002 | 2111 | 2180 | 2169 |
| 1-Phenyltridecane | $C_{19}H_{32}$ | 1971 | 2083 | 2123 | 2121 | 2109 | 2219 | 2280 | 2277 |
| Cycloalkanes | | | | | | | | | |
| Cyclopentane | $C_5H_{10}$ | 559 | | | | | | | |
| Cyclohexane | $C_6H_{12}$ | 665 | 624 | 707 | 700 | | 708 | | |
| Cycloheptane | $C_7H_{14}$ | 786 | 822 | 843 | 844 | 812 | 858 | 899 | 878 |
| Cyclooctane | $C_8H_{16}$ | 910 | 960 | 988 | 985 | 945 | 1005 | 1036 | 1023 |
| Cyclodecane | $C_{10}H_{20}$ | 1127 | 1193 | 1219 | 1215 | 1168 | 1238 | 1271 | 1261 |
| Cyclododecane | $C_{12}H_{24}$ | 1316 | 1400 | 1434 | 1433 | 1377 | 1471 | 1521 | 1510 |
| Cycloalkane carboxylic acids | | | | | | | | | |
| Cyclopropane carboxylic acid | $C_4H_6O_2$ | 900 | 1022 | 1067 | 1071 | 1146 | 1359 | 1811 | (see text) |
| Cyclobutane carboxylic acid | $C_5H_8O_2$ | 987 | 1115 | 1163 | 1167 | 1248 | 1465 | 1885 | |
| Cyclopentane carboxylic acid | $C_6H_{10}O_2$ | 1070 | 1207 | 1257 | 1260 | 1332 | 1568 | 1989 | |
| Cyclohexane carboxylic acid | $C_7H_{12}O_2$ | 1157 | 1297 | 1348 | 1352 | 1434 | 1685 | 2117 | |
| 1-Alkanoic acids | | | | | | | | | |
| Formic acid | $CH_2O_2$ | | | | | | | | |
| Acetic acid | $C_2H_4O_2$ | | | | | | 1033 | 1484 | (see text) |
| Propionic acid | $C_3H_6O_2$ | 711 | | 830 | 814 | 924 | 1140 | 1574 | |
| 1-Butanoic acid | $C_4H_8O_2$ | 814 | 900 | 943 | 943 | 1027 | 1239 | 1666 | |

Table 1. Continued

| Homologous series | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| 1-Pentanoic acid | $C_5H_{10}O_2$ | 894 | 980 | 1027 | 1011 | 1141 | 1355 | 1780 | |
| 1-Hexanoic acid | $C_6H_{12}O_2$ | 983 | 1076 | 1116 | 1118 | 1238 | 1463 | 1889 | |
| 1-Heptanoic acid | $C_7H_{14}O_2$ | 1074 | 1170 | 1216 | 1211 | 1337 | 1568 | 1997 | |
| 1-Octanoic acid | $C_8H_{16}O_2$ | 1162 | 1266 | 1312 | 1305 | 1445 | 1674 | 2106 | |
| 1-Nonanoic acid | $C_9H_{18}O_2$ | 1256 | 1363 | 1409 | 1400 | 1542 | 1780 | 2211 | |
| 1-Decanoic acid | $C_{10}H_{20}O_2$ | 1354 | 1465 | 1515 | 1501 | 1654 | 1882 | 2318 | |
| Lauric acid | $C_{12}H_{24}O_2$ | 1545 | 1661 | 1703 | 1695 | 1849 | 2100 | 2529 | |
| Myristic acid | $C_{14}H_{28}O_2$ | 1739 | 1863 | | 1896 | 2052 | 2313 | 2734 | |
| Palmitic acid | $C_{16}H_{32}O_2$ | 1941 | 2067 | 2109 | 2104 | 2273 | 2524 | 2954 | |
| 1-Alkyl aldehydes | | | | | | | | | |
| Propionaldehyde | $C_3H_6O$ | | | | | | | 807 | 801 |
| Butyraldehyde | $C_4H_8O$ | | | | | | 837 | 899 | 891 |
| Valeraldehyde | $C_5H_{10}O$ | 668 | 769 | 814 | 805 | 943 | 945 | 1003 | 999 |
| Hexanal | $C_6H_{12}O$ | 777 | 886 | 919 | 911 | 1049 | 1051 | 1106 | 1101 |
| Heptaldehyde | $C_7H_{14}O$ | 880 | 987 | 1017 | 1015 | 1153 | 1156 | 1210 | 1204 |
| Octylaldehyde | $C_8H_{16}O$ | 981 | 1088 | 1117 | 1118 | 1261 | 1262 | 1315 | 1307 |
| Nonylaldehyde | $C_9H_{18}O$ | 1082 | 1180 | 1218 | 1219 | 1364 | 1369 | 1419 | 1411 |
| Decylaldehyde | $C_{10}H_{20}O$ | 1184 | 1290 | 1319 | 1320 | 1470 | 1477 | 1523 | 1514 |
| Undecylic aldehyde | $C_{11}H_{22}O$ | 1287 | 1390 | 1422 | 1425 | 1578 | 1585 | 1630 | 1618 |
| Dodecylaldehyde | $C_{12}H_{24}O$ | 1388 | 1494 | 1524 | 1526 | 1686 | 1693 | 1735 | 1724 |
| 1-Alkanols | | | | | | | | | |
| Propanol | $C_3H_7O$ | | | 705 | | | 868 | 1091 | 1073 |
| Butanol | $C_4H_9O$ | 647 | 738 | 781 | 781 | 827 | 969 | 1191 | 1172 |
| Pentanol | $C_5H_{12}O$ | 760 | 843 | 875 | 866 | 925 | 1075 | 1296 | 1294 |
| Hexanol | $C_6H_{14}O$ | 860 | 944 | 976 | 970 | 1028 | 1179 | 1398 | 1375 |
| Heptanol | $C_7H_{16}O$ | 959 | 1045 | 1076 | 1074 | 1132 | 1284 | 1501 | 1476 |
| Octanol | $C_8H_{18}O$ | 1058 | 1146 | 1177 | 1175 | 1240 | 1384 | 1603 | 1578 |
| Decanol | $C_{10}H_{22}O$ | 1259 | 1349 | 1380 | 1379 | 1441 | 1597 | 1805 | 1779 |
| Dodecanol | $C_{12}H_{26}O$ | 1462 | 1553 | 1584 | 1583 | 1649 | 1810 | 2010 | 1981 |
| Tetradecanol | $C_{14}H_{30}O$ | 1664 | 1759 | 1791 | 1788 | 1858 | 2022 | 2217 | 2186 |
| Hexadecanol | $C_{16}H_{34}O$ | 1866 | | 1998 | 1994 | 2071 | 2235 | 2421 | 2391 |
| Heptadecanol | $C_{17}H_{36}O$ | 1968 | 2066 | 2104 | 2099 | 2177 | 2342 | 2518 | 2496 |
| Octadecanol | $C_{18}H_{38}O$ | 2070 | 2169 | 2205 | 2200 | 2281 | 2444 | 2612 | 2598 |
| 1,ω-Alkanediols | | | | | | | | | |
| 1,3-Propanediol | $C_3H_8O_2$ | 814 | 973 | 1029 | 1034 | 1122 | 1427 | 1786 | 1818 |
| 1,4-Butanediol | $C_4H_{10}O_2$ | 922 | 1095 | 1157 | 1165 | 1261 | 1577 | 1925 | 1945 |
| 1,5-Pentanediol | $C_5H_{12}O_2$ | 1016 | 1195 | 1258 | 1268 | 1374 | 1699 | 2037 | 2058 |
| 1,6-Hexanediol | $C_6H_{14}O_2$ | 1111 | 1295 | 1359 | 1365 | 1483 | 1810 | 2143 | 2161 |
| 1,7-Heptanediol | $C_7H_{16}O_2$ | 1201 | 1400 | 1460 | 1471 | 1596 | 1926 | 2253 | 2265 |
| 1,8-Octanediol | $C_8H_{18}O_2$ | 1313 | 1503 | 1568 | 1579 | 1709 | 2038 | 2357 | 2369 |
| 1,9-Nonanediol | $C_9H_{20}O_2$ | 1414 | 1604 | 1678 | 1678 | 1818 | 2152 | 2464 | 2475 |
| 1,10-Decanediol | $C_{10}H_{22}O_2$ | 1518 | 1716 | 1783 | 1791 | 1937 | 2269 | 2574 | 2583 |
| 1,12-Dodecanediol | $C_{12}H_{26}O_2$ | 1725 | 1926 | 1995 | 1991 | 2163 | 2496 | 2786 | 2795 |
| 1,14-Tetradecanediol | $C_{14}H_{30}O_2$ | 1924 | 2125 | 2198 | 2203 | 2370 | 2695 | 2985 | 3009 |
| 1,16-Hexadecanediol | $C_{16}H_{34}O_2$ | 2130 | 2338 | 2409 | 2415 | 2593 | 2903 | 3209 | 3219 |

Table 1. Continued

| Homologous series | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| 1,2-Alkanediols | | | | | | | | | |
| Ethylene glycol | $C_2H_6O_2$ | | | | | | | | |
| 1,2-Propanediol | $C_3H_8O_2$ | 722 | 850 | 903 | 903 | 988 | 1264 | 1581 | (see text) |
| 1,2-Hexanediol | $C_6H_{14}O_2$ | 1017 | 1159 | 1205 | 1206 | 1299 | 1584 | 1888 | |
| 1,2-Octanediol | $C_8H_{18}O_2$ | 1214 | 1360 | 1409 | 1409 | 1510 | 1803 | 2098 | |
| 1,2-Decanediol | $C_{10}H_{22}O_2$ | 1419 | 1570 | 1621 | 1622 | 1731 | 2030 | 2316 | |
| 1,2-Dodecanediol | $C_{12}H_{26}O_2$ | 1621 | 1778 | 1827 | 1827 | 1944 | 2254 | 2530 | |
| 1,2-Tetradecanediol | $C_{14}H_{30}O_2$ | 1826 | 1987 | 2039 | 2040 | 2163 | 2476 | 2740 | |
| 1,2-Hexadecanediol | $C_{16}H_{34}O_2$ | 2031 | 2198 | 2251 | 2252 | 2379 | 2684 | 2945 | |
| 1-Aminoalkanes | | | | | | | | | |
| Ethylamine | $C_2H_7N$ | | | | | | | | |
| Propylamine | $C_3H_9N$ | 545 | | | | | | | |
| Butylamine | $C_4H_{11}N$ | 608 | 695 | 738 | | 816 | 837 | (see text) | |
| Amylamine | $C_5H_{13}N$ | 726 | 788 | 830 | 819 | 906 | 933 | | 1029 |
| Hexylamaine | $C_6H_{15}N$ | 830 | 900 | 935 | 927 | 997 | 1031 | | 1123 |
| Heptylamine | $C_7H_{17}N$ | 930 | 1002 | 1035 | 1030 | 1097 | 1135 | | 1218 |
| Octylamine | $C_8H_{19}N$ | 1032 | 1104 | 1134 | 1131 | 1194 | 1235 | | 1316 |
| Nonylamine | $C_9H_{21}N$ | 1133 | 1206 | 1235 | 1233 | 1295 | 1339 | | 1416 |
| Decylamine | $C_{10}H_{23}N$ | 1236 | 1308 | 1337 | 1335 | 1397 | 1446 | | 1517 |
| Dodecylamine | $C_{12}H_{27}N$ | 1442 | 1513 | 1546 | 1538 | 1604 | 1658 | | 1724 |
| Tetradecylamine | $C_{14}H_{31}N$ | 1640 | 1719 | 1749 | 1744 | 1803 | 1863 | | 1925 |
| Octadecylamine | $C_{18}H_{39}N$ | 2048 | 2125 | 2158 | 2157 | 2216 | 2287 | | |
| 1,ω-Diaminoalkanes | | | | | | | | | |
| Ethylene diamine | $C_2H_8N_2$ | | | 839 | 821 | 917 | 1004 | (see text) | 1233 |
| 1,3-Diaminopropane | $C_3H_{10}N_2$ | 748 | 888 | 941 | 939 | 1028 | 1132 | | 1337 |
| 1,4-Diaminobutane | $C_4H_{12}N_2$ | 858 | 1001 | 1055 | 1053 | 1147 | 1259 | | 1434 |
| 1,5-Diaminopentane | $C_5H_{14}N_2$ | 960 | 1105 | 1161 | 1158 | 1259 | 1372 | | 1537 |
| 1,7-Diaminoheptane | $C_7H_{18}N_2$ | 1168 | 1318 | 1377 | 1372 | 1480 | 1598 | | 1744 |
| 1,8-Diaminooctane | $C_8H_{20}N_2$ | 1273 | 1425 | 1486 | 1480 | 1590 | 1717 | | 1850 |
| 1,9-Diaminononane | $C_9H_{22}N_2$ | 1373 | 1524 | 1582 | 1579 | 1692 | 1820 | | 1954 |
| 1,10-Diamindecane | $C_{10}H_{24}N_2$ | 1476 | 1628 | 1689 | 1686 | 1798 | 1931 | | 2061 |
| ω-Amino-1-alkanols | | | | | | | | | |
| 3-Amino-1-propanol | $C_3H_9NO$ | 785 | 949 | 1023 | 1020 | 1170 | 1272 | (see text) | 1555 |
| 4-Amino-1-butanol | $C_4H_{11}NO$ | 904 | 1077 | 1138 | 1148 | 1293 | | | 1687 |
| 5-Amino-1-pentanol | $C_5H_{13}NO$ | 988 | 1156 | 1214 | 1228 | 1361 | 1534 | | 1799 |
| 6-Amino-1-hexanol | $C_6H_{15}NO$ | 1094 | 1256 | 1314 | 1327 | 1465 | 1646 | | 1902 |
| Trichloroacetic alkyl esters | | | | | | | | | |
| Hexyl ester | $C_8H_{13}Cl_3O_2$ | 1353 | 1476 | 1515 | 1510 | 1601 | 1651 | 1741 | (see text) |
| Heptyl ester | $C_9H_{15}Cl_3O_2$ | 1455 | 1576 | 1610 | 1609 | 1709 | 1758 | 1844 | |
| Octyl ester | $C_{10}H_{17}Cl_3O_2$ | 1557 | 1678 | 1717 | 1711 | 1815 | 1863 | 1947 | |
| Nonyl ester | $C_{11}H_{19}Cl_3O_2$ | 1660 | 1781 | 1819 | 1814 | 1921 | 1970 | 2054 | |
| Decyl ester | $C_{12}H_{21}Cl_3O_2$ | 1760 | 1884 | 1922 | 1917 | 2028 | 2081 | 2160 | |
| Undecyl ester | $C_{13}H_{23}Cl_3O_2$ | 1864 | 1986 | 2026 | 2022 | 2137 | 2188 | 2263 | |
| Dodecyl ester | $C_{14}H_{25}Cl_3O_2$ | 1966 | 2090 | 2133 | 2128 | 2244 | 2296 | 2369 | |
| Myristyl ester | $C_{16}H_{29}Cl_3O_2$ | 2174 | 2300 | 2341 | 2336 | 2460 | 2514 | 2580 | |
| Palmityl ester | $C_{18}H_{33}Cl_3O_2$ | 2381 | 2511 | 2553 | 2546 | 2678 | 2717 | 2788 | |
| Stearyl ester | $C_{20}H_{37}Cl_3O_2$ | 2588 | 2721 | 2765 | 2756 | 2891 | 2932 | 2987 | |

Table 2
Linear regression coefficients (*A*) and intercepts (GRF) with standard errors (S.E.) for 16 homologous series of organic compounds on non-polar and polar columns and the number of data points (*n*) used for linear regression analysis[a]

| Homologous series | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-Basic Wax |
| 1-Chloro-*n*-alkanes | | | | | | | | |
| *A*±S.E. | 102.94±0.09 | 103.14±0.34 | 103.23±0.083 | 103.56±0.14 | 104.91±0.12 | 106.92±0.22 | 105.27±0.15 | 105.10±0.18 |
| (GRF)±S.E. | 226.61±1.00 | 295.41±0.39 | 312.56±0.93 | 308.09±1.57 | 353.71±1.31 | 366.26±2.41 | 416.24±1.52 | 416.67±1.91 |
| *n* | 9 | 9 | 9 | 9 | 9 | 9 | 8 | 10 |
| Goodness of fit | a | a | a | a | a | a | a | a |
| 1-Bromo-*n*-alkanes | | | | | | | | |
| *A*±S.E. | 103.76±0.10 | 105.37±0.46 | 105.35±0.13 | 105.63±0.20 | 107.25±0.40 | 108.81±0.39 | 106.04±2.61 | 106.42±0.11 |
| (GRF)±S.E. | 305.29±1.08 | 368.10±5.11 | 392.47±1.38 | 391.07±2.21 | 412.88±4.35 | 456.95±4.30 | 530.21±28.83 | 514.42±1.19 |
| *n* | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 |
| Goodness of fit | a | a | a | a | a | a | m | a |
| 1-Iodo-*n*-alkanes | | | | | | | | |
| *A*±S.E. | 105.27±0.16 | 106.60±0.11 | 106.39±0.26 | 106.92±0.17 | 107.78±0.11 | 110.88±0.12 | 107.10±0.64 | 107.63±0.29 |
| (GRF)±S.E. | 379.08±1.62 | 472.46±1.07 | 502.41±2.54 | 494.78±1.69 | 486.59±1.10 | 554.46±1.26 | 640.62±6.23 | 628.38±2.40 |
| *n* | 12 | 12 | 13 | 12 | 11 | 11 | 13 | 9 |
| Goodness of fit | a | a | a | a | a | a | a | a |
| 1-Alkanoic methyl esters | | | | | | | | |
| *A*±S.E. | 100.30±0.064 | 100.73±0.11 | 101.40±0.16 | 101.52±0.16 | 104.12±0.19 | 104.78±0.13 | 103.03±0.27 | 102.41±0.27 |
| (GRF)±S.E. | 3.18±1.00 | 94.67±1.61 | 116.03±2.44 | 115.86±2.37 | 189.72±2.98 | 193.08±2.02 | 262.91±4.06 | 278.78±4.01 |
| *n* | 15 | 16 | 16 | 16 | 15 | 16 | 16 | 17 |
| Goodness of fit | a | a | a | a | a | a | a | a |
| *n*-Alkyl ethers | | | | | | | | |
| *A*±S.E. | 97.65±0.10 | 98.76±0.59 | 97.20±0.23 | 97.87±0.30 | 97.30±0.23 | 97.05±1.20 | 98.31±0.15 | 98.76±0.68 |
| (GRF)±S.E. | −3.60±1.23 | 25.97±7.00 | 69.00±2.91 | 52.36±3.81 | 51.50±2.91 | 97.78±14.27 | 89.57±1.91 | 82.79±8.78 |
| *n* | 5 | 5 | 4 | 4 | 4 | 5 | 4 | 4 |
| Goodness of fit | a | a | a | a | a | b | a | a |
| Alkylbenzenes | | | | | | | | |
| *A*±S.E. | 102.48±0.30 | 103.78±0.25 | 104.02±0.47 | 103.47±0.58 | 101.02±0.88 | 105.81±0.59. | 103.74±0.93 | 102.44±0.96 |
| (GRF)±S.E. | 19.69±3.92 | 106.23±3.18 | 137.80±6.07 | 144.97±7.45 | 175.06±11.43 | 199.91±7.65 | 299.61±12.02 | 314.33±12.42 |
| *n* | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Goodness of fit | a | a | a | a | c | a | c | c |
| Cycloalkanes | | | | | | | | |
| *A*±S.E. | 109.56±2.50 | 125.72±8.68 | 120.44±4.02 | 121.20±4.19 | 112.17±3.38 | 125.78±4.23 | 123.27±1.92 | 125.02±2.65 |
| (GRF)±S.E. | 17.36±20.89 | -81.35±76.98 | −1.68±35.61 | −6.91±37.18 | 37.93±31.91 | −25.67±37.48 | 41.49±18.15 | 11.59±25.01 |
| *n* | 6 | 5 | 5 | 5 | 4 | 5 | 4 | 4 |
| Goodness of fit | f | s | g | k | f | h | b | c |
| Cycloalkane carboxylic acids | | | | | | | | |
| *A*±S.E. | 85.40±0.57 | 91.70±0.48 | 93.70±0.79 | 93.60±0.65 | 94.80±2.55 | 108.10±2.11 | 102.20±8.55 | (see text) |
| (GRF)±S.E. | 388.00±4.29 | 472.50±3.64 | 506.00±6.02 | 510.50±4.91 | 579.00±19.30 | 708.50±16.03 | 1184.00±64.82 | |
| *n* | 4 | 4 | 4 | 4 | 4 | 4 | 4 | |
| Goodness of fit | a | a | a | a | d | c | t | |

Table 2. Continued

| Homologous series | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-Basic Wax |
| 1-Alkanoic acids | | | | | | | | |
| *A*±S.E. | 93.93±0.78 | 97.89±0.76 | 97.66±0.68 | 97.77±0.79 | 102.98±0.43 | 106.61±0.21 | 105.88±0.51 | (see text) |
| (GRF)±S.E. | 234.93±8.82 | 294.52±8.85 | 341.43±7.29 | 332.44±8.86 | 412.37±4.80 | 606.50±2.29 | 1044.73±5.48 | |
| *n* | 11 | 10 | 10 | 11 | 11 | 12 | 12 | |
| Goodness of fit | c | b | a | c | a | a | a | |
| 1-Alkylaldehydes | | | | | | | | |
| *A*±S.E. | 102.42±0.38 | 102.33±0.88 | 101.10±0.26 | 102.77±0.27 | 105.95±0.25 | 106.82±0.19 | 103.72±0.45 | 103.06±0.40 |
| (GRF)±S.E. | 57.92±3.67 | 163.33±8.60 | 208.35±2.55 | 191.02±2.66 | 306.45±2.46 | 302.54±1.76 | 383.12±4.06 | 381.04±3.60 |
| *n* | 8 | 8 | 8 | 8 | 8 | 9 | 10 | 10 |
| Goodness of fit | a | b | a | a | a | a | a | a |
| 1-Alkanols | | | | | | | | |
| *A*±S.E. | 101.06±0.21 | 102.06±0.10 | 101.32±0.60 | 102.08±0.31 | 104.05±0.23 | 105.40±0.18 | 101.86±0.20 | 101.33±0.37 |
| (GRF)±S.E. | 148.90±2.58 | 228.35±1.25 | 273.17±7.28 | 258.47±3.86 | 300.94±2.88 | 441.36±2.13 | 684.82±2.41 | 668.57±4.46 |
| *n* | 11 | 10 | 12 | 11 | 11 | 12 | 12 | 12 |
| Goodness of fit | a | a | a | a | a | a | a | a |
| 1,ω-Alkanediols | | | | | | | | |
| *A*±S.E. | 101.17±0.51 | 104.26±0.40 | 105.36±0.49 | 104.97±0.56 | 112.17±0.75 | 112.55±1.44 | 107.64±0.90 | 106.72±0.54 |
| (GRF)±S.E. | 304.73±5.70 | 461.44±4.52 | 515.65±5.47 | 525.80±6.35 | 583.17±8.44 | 903.26±16.18 | 1275.66±10.08 | 1301.50±6.04 |
| *n* | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 |
| Goodness of fit | a | a | a | a | a | d | c | a |
| 1,2-Alkanediols | | | | | | | | |
| *A*±S.E. | 100.83±0.42 | 103.67±0.31 | 103.84±0.47 | 103.89±0.48 | 107.31±0.47 | 110.04±0.55 | 105.52±0.43 | (see text) |
| (GRF)±S.E. | 211.61±5.24 | 328.25±3.89 | 376.64±5.88 | 376.59±6.00 | 433.91±5.96 | 708.78±6.86 | 1048.57±5.42 | |
| *n* | 7 | 7 | 7 | 7 | 7 | 7 | 7 | |
| Goodness of fit | a | a | a | a | a | a | a | |
| 1-Aminoalkanes | | | | | | | | |
| *A*±S.E. | 101.45±0.64 | 102.51±0.21 | 101.79±0.30 | 102.56±0.18 | 100.46±0.64 | 103.90±0.46 | (see text) | 99.97±0.66 |
| (GRF)±S.E. | 119.53±6.83 | 180.33±2.44 | 221.30±3.31 | 207.07±2.10 | 297.81±7.14 | 306.21±5.10 | | 421.30±6.75 |
| *n* | 11 | 11 | 10 | 9 | 10 | 10 | | 8 |
| Goodness of fit | a | a | a | a | a | a | | a |
| 1,ω-Diaminoalkanes | | | | | | | | |
| *A*±S.E. | 103.75±0.41 | 105.52±0.61 | 106.68±0.59 | 107.47±0.82 | 110.38±0.79 | 115.23±1.24 | (see text) | 103.37±0.42 |
| (GRF)±S.E. | 233.00±3.61 | 365.43±5.44 | 412.78±4.99 | 401.27±6.95 | 480.81±6.64 | 557.26±10.45 | | 816.82±3.55 |
| *n* | 7 | 7 | 8 | 8 | 8 | 8 | | 8 |
| Goodness of fit | a | a | a | a | a | c | | a |
| ω-Amino-1-alkanols | | | | | | | | |
| *A*±S.E. | 101.70±4.32 | 98.80±8.12 | 94.90±5.05 | 100.10±6.59 | 95.30±7.10 | 125.57±4.70 | (see text) | 115.30±4.65 |
| (GRF)±S.E. | 275.70±28.47 | 468.80±53.53 | 555.40±33.29 | 530.10±43.49 | 702.80±46.84 | 646.86±31.89 | | 986.30±30.67 |
| *n* | 4 | 4 | 4 | 4 | 4 | 3 | | 4 |
| Goodness of fit | k | n | l | n | p | e | | h |
| Trichloroacetic alkyl esters | | | | | | | | |
| *A*±S.E. | 102.93±0.15 | 103.87±0.28 | 104.46±0.32 | 104.10±0.25 | 107.61±0.13 | 106.93±0.30 | 104.35±0.27 | (see text) |
| (GRF)±S.E. | 527.40±2.08 | 535.72±4.12 | 567.17±4.64 | 567.13±3.69 | 631.14±1.90 | 689.24±4.32 | 906.27±3.73 | |
| *n* | 10 | 10 | 10 | 10 | 10 | 10 | 10 | |
| Goodness of fit | a | a | a | a | a | a | a | |

[a] For the designation of the goodness of fit, see text.

points ($n$) used for linear regression analysis. The precision and goodness of fit, as measured by the correlation coefficient ($R$), the coefficient of determination ($R^2$), and the model fitness (adjusted $R^2$) for different homologous series on different columns, are listed in parentheses in that order in Table 2 as: a (1.000, 1.000, 1.000), b (1.000, 1.000, 0.999), c (1.000, 0.999, 0.999), d (0.999, 0.999, 0.998), e (0.999, 0.999, 0.997), f (0.999, 0.998, 0.997), g (0.998, 0.997, 0.996), h (0.998, 0.997, 0.995), k (0.998, 0.996, 0.995), l (0.997, 0.994, 0.992), m ((0.997, 0.993, 0.993), n (0.996, 0.991, 0.987), p (0.994, 0.989, 0.984), s (0.993, 0.986, 0.981), and t (0.993, 0.986, 0.979).

In retention index prediction the conventional procedure is to assume the $A$ value for each atom in the analyte molecule to be 100 i.u. for calculating the base value ($100Z$) of the molecule and then add to it the interaction or functionality contribution, i.e., the (GRF) value, according to Eq. (3) [6,9,10]. In the case of 1-halo-$n$-alkanes, such a procedure produces a predicted $I$ value a few index units smaller than the observed $I$ value. In order to minimize the discrepancy between the predicted and the observed $I$ values, the (GRF) value (based on $A=100$), i.e., $(GRF)^{100}$, for the halo atom has to be repeatedly adjusted upward by a few index units from a lower homologue to the next higher homologue. The need for upward incremental adjustment of the $(GRF)^{100}$ values persists throughout for all three 1-halo-$n$-alkane series. The cumulative effect of the adjustment is large. To cite an example: the $(GRF)^{100}$ value for 1-iodo-$n$-octadecane, obtained from the observed retention index ($I_{obs}$) minus the base value, exceeds the $(GRF)^{100}$ value for 1-iodo-$n$-butane by more than 100 i.u. on polar columns. This readjustment of the $(GRF)^{100}$ value for the halo atom is contrary to the definition of Eq. (3) that the (GRF) value should be constant. On the other hand, when one plots the observed retention indexes against the carbon numbers of 1-halo-$n$-alkanes, one obtains straight lines. Linear regression analysis yields constant (GRF) values for the Cl, Br, and I atoms, but the $A$ values for the 1-halo-$n$-alkane series are all above 100. Table 2 shows that the $A$ value for 1-iodo-$n$-alkanes varies from 105 on DB-1 column to 111 on DB-225 column, for 1-bromo-$n$-alkanes from 104 on DB-1 column to 109 on DB-225 column, and for 1-chloro-$n$-alkanes from 103 on DB-1 column to 107 on DB-225 column. Among all the columns DB-225 column gives the highest $A$ values and DB-Wax column the highest (GRF) values for all three series. These clearly indicate that an accurate value of $A$ is essential for retention index prediction. To assign an $A$ value of 100 to 1-halo-$n$-alkanes in retention index prediction as if they were $n$-alkanes, irrespective of the presence of the electronegative halo atom in the molecule, is not justified.

Linear plots of $I_{obs}$ vs. $Z$ for 13 1-bromo-$n$-alkanes on all eight columns are given in Fig. 2 to show the consistent degree of linearity throughout the entire homologous series. The minor differences in the $A$ values on different columns are obscured by the large scale of the ordinate axis.

It should be pointed out that the higher homologues of 1-iodo-$n$-alkanes, such as 1-iodo-$n$-hexadecane and 1-iodo-$n$-octadecane, are retained on HP-Basic Wax but not on DB-Wax column. Their retention by the modified stationary liquid phase of the HP-Basic Wax column may be caused by on-column deiodination reaction.

### *3.1.3. Electron density distribution and retention*

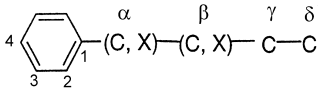
The retention index increment per atom addition (i.e., the linear regression coefficient $A$) is arbitrarily assigned by definition a value of 100 i.u. for each addition of a methylene group to a $n$-alkane molecule on all non-polar and polar columns. This convention, according to Kováts [15], is also applied to analytes in the prediction of their retention indexes. Partition and adsorption of solute between gas–liquid and liquid–solid phases in gas chromatographic retention are interactions involving a multitude of intermolecular forces, bringing into play the inter- and intramolecular interaction with the electron density and electron density distribution of the analyte molecule. Conceivably, molecules with higher or lower electron densities than $n$-alkanes will have longer or shorter retention times accordingly. Determination of electron density distribution in a molecule is difficult but shielding of a nucleus such as a carbon atom by electrons in a magnetic field can be measured by carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectroscopy [16–18]. Electron shielding of a nucleus is influenced by its chemical environment, electron density, and contributions

from other sources and is expressed in terms of chemical shift ($\delta$) in parts per million (ppm) in reference to tetramethylsilane (TMS). According to Wehrli and Wirthlin [16], the chemical shift is the spectral parameter that ''directly reflects the distribution of electrons surrounding the observed nucleus''. A small chemical shift means that the nucleus is highly shielded (i.e., in the high field and rich in shielding electrons) and a large chemical shift means that it is deshielded (i.e., in the low field and poor in shielding electrons). According to $^{13}$C-NMR measurement, the carbon atoms in methane and ethane with $\delta_c$ equal to $-2.3$ ppm and 1.6 ppm, respectively, are thus highly shielded. Higher *n*-alkane molecules, from propane to *n*-decane, have $^{13}$C chemical shifts ($\delta_c$) from 13 ppm to 32 ppm, depending on the position of the carbon atom in the molecule, with the terminal carbon atoms being highly shielded and the secondary, tertiary and quarternary carbon atoms deshielded. In branch-chain alkanes the terminal carbon atoms are highly shielded, and the carbon atom where branching occurs is deshielded. The effect of a substituent group can extend to three adjacent $\alpha$, $\beta$, and $\gamma$ carbon atoms. The $^{13}$C chemical shift values for *n*-hexane, 1-chloro-, 1-bromo-, and 1-iodohexane, and other aliphatic compounds and the $\delta_c$ values for aromatic compounds, taken from the literature, are given in Tables 3 and 4, respectively [18,19]. The pattern of $^{13}$C chemical shifts in the presence of an

Table 3
$^{13}$C chemical shifts ($\delta_c$ in ppm) of selected aliphatic compounds [18,19]

| Compound | Chemical shift (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7/C-α | C-8/C-β |
| Methane | −2.30 | | | | | | | |
| Ethane | 7.26 | 7.26 | | | | | | |
| *n*-Butane | 13.10 | 24.90 | | | | | | |
| Isobutane | 24.30 | 25.00 | | | | | | |
| *n*-Hexane | 13.70 | 22.80 | 31.90 | | | | | |
| | | | | | | | | |
| *n*-Hexane | 14.2 | 23.1 | 32.2 | 32.2 | 23.1 | 14.2 | | |
| Iodohexane | 7.0 | 34.0 | 30.7 | 31.3 | 23.1 | 14.2 | | |
| Bromohexane | 33.9 | 33.3 | 28.4 | 31.5 | 23.1 | 14.2 | | |
| | | | | | | | | |
| Chlorohexane | 45.2 | 33.1 | 27.1 | 31.7 | 23.1 | 14.2 | | |
| Dipropyl ether | 73.7 | 24.4 | 11.8 | | | | | |
| Dibutyl ether | 71.6 | 33.5 | 20.8 | 15.1 | | | | |
| | | | | | | | | |
| 1,2-Propanediol | 71.60 | 72.70 | 22.95 | | | | | |
| 1,4-Butanediol | 65.50 | 31.70 | | | | | | |
| 1-Butanol | 61.40 | 35.00 | 19.10 | 13.60 | | | | |
| 1-Hexanol | 61.9 | 32.8 | 25.8 | 32.0 | 22.8 | 14.2 | | |
| 1-Octanol | 61.90 | 32.90 | 26.10 | 29.70 | 29.60 | 32.10 | 22.80 | 13.90 |
| 2-Octanol | 23.40 | 67.20 | 39.60 | 26.10 | 29.70 | 32.20 | 22.80 | 14.00 |
| 3-Octanol | 10.00 | 30.30 | 72.60 | 37.20 | 25.70 | 32.30 | 22.90 | 13.90 |
| 4-Octanol | 14.00 | 19.10 | 40.00 | 70.90 | 37.50 | 28.20 | 23.00 | 14.00 |
| 5-Nonanol | 14.00 | 23.00 | 28.30 | 37.50 | 71.10 | | | |
| | | | | | | | | |
| Hexylamine | 42.65 | 34.6 | 27.1 | 32.35 | 23.15 | 14.2 | | |
| | | | | | | | | |
| Formic acid | 165.70 | | | | | | | |
| Acetic acid | 177.05 | 19.10 | | | | | | |
| Hexanoic (caproic) acid | 180.6 | 34.2 | 31.4 | 24.5 | 22.4 | 13.8 | | |
| Methyl butanoate | 172.2 | 35.6 | 18.9 | 13.8 | | | 51.9 | |
| | | | | | | | | |
| Pentanal | 202.3 | 43.7 | 24.3 | 22.3 | 13.8 | | | |

Table 4
$^{13}$C chemical shifts ($\delta_c$ in ppm) of selected aromatic compounds [18,19]




| Compound | Chemical shift (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-α | C-β | C-γ | C-δ |
| Benzene | 128.5 | | | | | | | |
| Toluene | 137.8 | 129.2 | 128.4 | 125.5 | 21.3 | | | |
| Ethylbenzene | 144.3 | 128.1 | 128.6 | 125.9 | 29.7 | 15.8 | | |
| Butylbenzene | 143.3 | 129.0 | 128.2 | 125.7 | 36.0 | 34.0 | 22.9 | 14.9 |
| *sec*.-Butylbenzene | 148.4 | 127.9 | 129.3 | 126.8 | 42.3 | 31.7 | 12.2 | 22.2 (β′) |
| Isobutylbenzene | 141.1 | 128.7 | 127.6 | 125.3 | 45.3 | 30.1 | 22.2 | |
| *tert*.-Butylbenzene | 150.9 | 125.4 | 128.3 | 125.7 | 34.6 | 31.4 | | |
| Iodobenzene | 96.2 | 138.4 | 131.1 | 128.1 | | | | |
| Bromobenzene | 122.6 | 131.5 | 130.0 | 127.0 | | | | |
| Chlorobenzene | 134.9 | 128.7 | 129.5 | 126.5 | | | | |
| Fluorobenzene | 163.6 | 114.2 | 129.4 | 124.1 | | | | |
| Benzoic acid | 131.4 | 129.8 | 128.9 | 133.1 | 168 | | | |
| Phenol | 155.1 | 115.7 | 130.1 | 121.4 | | | | |
| Anisol | 159.9 | 114.1 | 129.5 | 120.7 | | 54.8 | | |
| Aniline | 148.7 | 114.4 | 129.1 | 116.3 | | | | |
| *N*-Methylaniline | 150.4 | 112.1 | 129.1 | 115.9 | | 29.9 | | |
| *N*,*N*-Dimethylaniline | 150.7 | 112.7 | 129 | 116.7 | | 40.3 | | |

electronegative or electropositive functional group strongly suggests that a substituted molecule will have a different electron density distribution from that of an *n*-alkane molecule. If this is the case, the validity of applying the same retention index increment of 100 i.u. per atom addition for *n*-alkanes to compounds containing functional groups in the currently accepted convention of retention index prediction should be reexamined.

Proton chemical shifts are correlated with chromatographic retention. Linear correlation between the chemical shifts of the α protons of methanol, ethanol, and 2-propanol and their retention indexes and also that between the chemical shifts of protons α to the oxygen atom in methyl, ethyl, and isopropyl propionates and their retention indexes have been reported [6]. Deviations of retention index increment varying within a wide range of 100 i.u. were reported for fatty acid esters [20], dibasic acid esters [21], phenyl alkanes [22] and derivatized analytes [23]. This shows that different *A* values are specific to different classes of compounds and can be correlated with their different electron densities.

### *3.1.4. Limitations of Eq. (3) and the meaning of A*

Eq. (3) is an empirical equation, expressing the linear relationship in a homologous series between *I* and *Z* values. In such a series individual members differ from near neighbors by methylene groups, which allows the same retention mechanism to prevail for all members of the series, leading to a simple linear relationship. The constants *A* and (GRF) in Eq. (3) are empirical and mutually compensatory. The accuracy of these values is crucially dependent upon the quality of the data, the linearity of the plot, and the number of data points used in linear regression analysis. It should be pointed out that one or two out-of-range data points can distort the slope and the intercept, leading to a large standard error. The numerical values of *A* and (GRF)

may change slightly from run to run or from column to column but, in general, will converge to true values for a given stationary liquid phase on a large number of data points with a small standard error. The trend is unmistakable.

As shown in Table 2, many compounds such as alcohols, aldehydes, amines, esters, ethers, etc., have *A* values near 100 on the non-polar DB-1 column, and their retention indexes can be correctly predicted to within the range of ±3% error by assuming *A* to be 100 i.u., as previously reported [6]. For compounds with *A* values deviating significantly from 100, such as 1-alkanoic acids and 1-halo-*n*-alkanes, *I* values are difficult to predict correctly with the same assumption.

Based on Eq. (3) and the results of this study, it is plausible to propose a simple molecular model of retention for the purpose of discussion. The model should consist of an alkane-like backbone structure as part of the molecular configuration of the analyte molecule to represent retention allowed for by the *AZ* term and also a polar or polarizable functionality portion to represent retention allowed for by the (GRF) term. In this model, both *A* and (GRF) values are affected by intermolecular forces, electron density and column polarity, *A* only weakly and (GRF) more strongly. The interactions are dependent on the nature of the functional groups. A larger or smaller *A* value than 100 i.u., is interpreted to mean that the electron density distribution in the molecule is such as to allow the backbone structure of the analyte molecule to be retained longer or shorter than the corresponding *n*-alkane molecule. In other words, a larger *A* value than 100 indicates a higher electron density in the backbone structure of the analyte molecule than that of an *n*-alkane; the analyte molecule will be retained longer. The converse will also be true. This simple model can explain the long retention times of analytes that are multi-functional or have extended double-bond conjugation and the short retention times of derivatized and highly branched analytes. The introduction of an electronegative or electropositive group to a neutral alkane molecule will undoubtedly change the electron density and electron density distribution of the molecule. The substituent group will remain the center of reaction in the molecule, but the rest of the molecule may or may not resemble an *n*-alkane molecule in electron density distribution. In view of this retention model, the less polarizable carbon chain of 1-halo-*n*-alkanes will show only a slight increase in its *A* value while the more polarizable halo atom will substantially increase its (GRF) value with increasing column polarity. This proposed molecular model of retention, based on electron density and electron density distribution, appears to be in line with the current ''cavity'' theory that the solute free energy is separated into a cavity term and an interaction term for the size of the solute and its solute–solvent interaction [24].

The halo atoms are electronegative with an electronegativity ranking of Cl>Br>I. This effect should be manifest in their *A* values. The Cl atom, the Br atom and the I atom in 1-halo-*n*-alkanes are progressively withdrawing fewer electrons away from the carbon atoms of the alkane backbone structure and yield progressively larger *A* values, i.e., $A_{Cl} < A_{Br} < A_{I}$, for all columns, as shown in Table 2. The relative magnitude of the *A* values of 1-halo-*n*-alkanes on non-polar and polar columns lends support to the proposed molecular model of retention.

Tables 1 and 2 also contain, respectively, the $I_{obs}$ values and the *A* and (GRF) values of additional homologous series for discussion in the following.

### *3.1.5. Alkanoic acid methyl esters*

Esterification masks the carboxylic function of fatty acids and changes their polarity. The methyl esters of 1-alkanoic acids behave chromatographically as *n*-alkanes on DB-1 column [6]. The *A* values for the methyl esters are 100.30, 100.73, 101.40, 101.52, 103.01, 104.65, 103.03, and 102.41 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, DB-Wax, and HP-Basic Wax columns, respectively. The (GRF) values increase from 3.18 on DB-1, to 94.67 on DB-35, 116.03 on DB-17, 115.86 on DB-608, 189.72 on DB-210, 193.08 on DB-225, 262.91 on DB-Wax, and 278.78 on HP-Basic Wax column (see Table 2). The large (GRF) value on the polar columns is attributed to the residual polarizability of the acid ester group.

Fig. 3 shows the linear *I* vs. *Z* plots of 16 homologues of fatty acid methyl esters on all eight columns. The small differences between their slopes (*A*) are obscured by the large magnitude of the scale of the ordinate axis.

Our earlier data show that replacing the methyl group in the alcohol moiety of the ester group with ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, or *n*-hexyl causes a decrease in the *A* value accordingly from 99.25 to 95.94, 92.11, 89.57, 87.26, and 85.97 on DB-1 column [6]. In the proposed molecular model of retention this decrease can be explained on the basis that the long-chain alkyl groups branching off from the ester backbone structure can withdraw more electrons than the short-chain alkyl groups. This results in lowered retention and smaller *A* values. According to the chemical shift in $^{13}$C-NMR spectroscopy, the terminal C atom of large alkyl groups in acid esters is more shielded, and the carboxyl C atom less shielded than the corresponding carbon atoms in esters with small alkyl groups. Ashes and Haken [20] detailed the changes of structure–retention increments of aliphatic esters with column polarity and came essentially to the same conclusion that increasing the size of the alkyl group in acid esters causes a decrease in the value of *A*.

### *3.1.6. Alkyl ethers*

Alkyl ethers have structures consisting of an electronegative oxygen atom linked to two alkyl groups. The oxygen atom tends to withdraw electrons from the alkyl groups. The overall effect is a lowering of the electron density in the backbone structure. Alkyl ethers appear to be less responsive to the increase in column polarity and are unique in this respect. The *A* value of alkyl ethers remains essentially unchanged between 97 and 98 on all non-polar and polar columns. The (GRF) value for the ether function shows only a slight increase with increasing column polarity. These are unique properties and may qualify alkyl ethers for potential use as secondary retention index markers.

### *3.1.7. Alkylbenzenes*

Benzene, alkylbenzenes and 1-phenylalkanes are homologous. Alkylbenzenes have *A* values of 102.48, 103.78, 103.96, 103.47, 101.02, 105.81, 103.74, and 102.44 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, DB-Wax, and HP-Basic Wax columns, respectively. The (GRF) value for the ring function increases steadily from 20 on DB-1 column to 314 on HP-Basic Wax column. Fig. 4 shows the linear *I* vs. *Z* plots of 12 alkylbenzene homologues on different columns.

The functionality of alkylbenzenes resides in the benzene ring. The *I* values of the series may be represented by either of two linear regression equations depending on how the *Z* value is selected, which can be the total number of C atoms in the molecule (Eq. (4)) or the number of C atoms in the alkyl chain (Eq. (5)). These two equations will differ in the (GRF) value. For example, on DB-1 column these equations are represented as follows:

$$I = 102.48Z + 19.69 \quad (4)$$

$$I = 102.48Z' + 634.57 \quad (5)$$

where $Z' = Z - 6$. That these two equations have identical *A* values, suggests that *A* is a property of the solute molecule and will not be influenced by contributions from the functionality term.

Branched alkyl chains vary widely in electron density distribution. Isomeric alkylbenzenes with branched alkyl chains have *I* values different from those with straight-chained alkyl groups. An early report on the retention of isomeric 1-$(alkyl)_m(alkyl)_n$benzenes, where $m+n=10$, 11, 12, 13, show that these alkylbenzenes can be grouped into homologous series on the basis of a fixed short chain (such as 1-methyl, 1-ethyl, 1-propyl or 1-butyl) or a fixed long chain (such as 1-octyl, 1-nonyl or 1-decyl) [22]. These homologous series have different *A* and (GRF) values.

Based on the retention data of the above alkylbenzenes, Haken [25] discussed the retention and molecular configuration of the branch-chained alkylbenzenes, from the viewpoint of dispersion and selectivity indexes. Heinzen and Yunes [26] also correlated the retention and structures of these isomeric alkylbenzenes using connectivity indices. Both approaches arrive at the same conclusion; more compact and symmetric isomers have lower retention. From the point of view of electron density distribution, a branched chain in an isomeric alkylbenzene withdraws electrons away from the alkane backbone structure. The connection of a benzene ring to a terminal or center or any carbon atom in the alkyl chain can affect the electron density distribution in the molecule (cf. the $\delta_c$ values for different

octanols in Table 3). These considerations for electron density and electron density distribution lead to the same conclusion; a symmetric isomeric alkylbenzene molecule has a lower retention than the one that is not.

*3.1.8. Cycloalkanes*

Cycloalkanes are cyclic aliphatic hydrocarbons, forming 5, 6, 7, 8, 10, and 12-membered rings with no aromaticity. The addition of a methylene group enlarges the ring forming a higher homologue. The *A* value for the cycloalkanes is anomalously high and is 109.56 on DB-1, 125.72 on DB-35, 120.44 on DB-17, 121.20 on DB-608, 112.17 on DB-210, 125.78 on DB-225, 123.27 on DB-Wax, and 125.02 on HP-Basic Wax column. The *I* vs. *Z* plot is linear but the negative (GRF) value is anomalous. Perhaps the early retention times of lower homologues near the solvent peak may cause distortion of the *A* and (GRF) values; in addition, the small number of data points tends to limit the precision of the linear regression analysis. The addition of a methylene group to enlarge a cycloalkane ring can affect the energy of ring formation. If this occurs, the linear relationship between the *I* and *Z* values will change.

*3.1.9. Cycloalkane carboxylic acids*

The carboxylic acid group is directly attached to the alicyclic ring in cycloalkane carboxylic acids. Higher homologues are formed by ring enlargement. The acids are eluted as highly unsymmetrical peaks but the *I* vs. *Z* plot is linear. The *A* value is 85.01, 91.70, 93.70, 93.60, 94.80, 108.10, and 102.20 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, and DB-Wax columns, respectively. The *A* values on less polar columns are lower than those of 1-alkanoic acids indicating that the carboxyl group is withdrawing more electrons away from the backbone structure. For that reason the carboxyl group will have a higher electron density and a smaller tendency to ionize which will make cyclohexane carboxylic acid a weaker acid than acetic acid (see Section 3.3). The *A* and (GRF) values for the four cycloalkane carboxylic acids on all columns are given in Table 2.

The standard error of the *A* value for the four cycloalkane carboxylic acids is small ($<\pm 2.6$) on less polar columns but large ($\pm 8.6$) on DB-Wax column. One explanation is that if there are small differences in (GRF) values for different ring size formation, such differences can become accentuated on more polar columns. When that occurs, a large number of data points should be provided for linear regression analysis.

*3.1.10. 1-Alkanoic acids*

The carboxylic acid group of 1-alkanoic acids is electronegative and withdraws electrons from the alkyl chain. The *A* values are, respectively, 93.93, 97.87, 97.66, and 97.77 on DB-1, DB-35, DB-17, and DB-608 columns. On polar DB-210, DB-225 and DB-Wax columns, the *A* values are all above 100. The HP-Basic Wax column is not useful for separating alkanoic acids. The (GRF) value for the acid functionality increases from DB-1 column to DB-Wax column by more than fourfold, as given in Table 2. The retention indexes of 1-alkanoic acids on DB-1 column cannot be correctly predicted by assuming the *A* value to be 100 [6].

1-Alkanoic acids with less than 11 or 12 carbon atoms are eluted as extremely unsymmetrical peaks on DB-210 column and as unsymmetrical peaks on DB-1, DB-35, DB-17, and DB-608 columns. Higher homologues with more than 12 carbon atoms are eluted as symmetrical peaks. On polar DB-225 and DB-Wax columns, the entire series from acetic acid to palmitic acid are eluted as narrow, symmetrical peaks. This clearly demonstrates the need for matching the polarity of the analyte molecule with the polarity of the column. In general, a symmetrical elution peak is a manifestation of normal, unbiased partition and sorption–desorption processes in chromatographic retention. Our observation shows that a balanced lipophilic–lipophobic property in the analyte molecule is essential for a symmetrical peak. Higher homologues of hydroxylic compounds are eluted as more symmetric peaks than lower homologues.

On DB-225 column, formic acid (*I*: 997) appears close to acetic acid (*I*: 1026), and on DB-Wax, formic acid (*I*: 1539) has a higher *I* value than acetic acid (*I*: 1485) (cf. Footnote 2). On other non-polar columns formic acid is eluted too near the solvent peak for its *I* value to be reliably determined. As explained in Footnote 2, formic acid may not be considered as the first homologue of the series.

*3.1.11. 1-Alkanols*

Alcohols have a mild polar character. The *A* values for 1-alkanols are 101.06, 102.06, 101.32, 102.08, 104.05, 105.04, 101.86, and 101.33 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, DB-Wax, and HP-Basic Wax columns, respectively. The (GRF) value for the alcoholic function is 148.90 on DB-1 column and increases to 684.82 on DB-Wax column and to 668.57 on HP-Basic Wax column, with increase in column polarity. The retention indexes of 1-alkanols were correctly predicted to within a margin of ±3% error on DB-1 and DB-Wax columns by assuming *A* to be 100 [6,10].

*3.1.12. 1,ω-Alkanediols*

1,ω-Alkanediols are straight-chain aliphatic alcohols with two terminal hydroxyl groups. The *A* values for the diols are 101.17, 104.26, 105.36, 104.97, 112.17, 112.55, 107.64, and 106.72 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, DB-Wax, and HP-Basic Wax columns, respectively. The high *A* values on DB-210 and DB-225 columns suggest high electron densities in the backbone structure of the diols, possibly from an electron current established between the two terminal hydroxyl groups. The (GRF) value for the hydroxyl groups increases with an increase in column polarity. The linear *I* vs. *Z* plots of 1,ω-alkanediols on different columns are given in Fig. 5. These plots depict more distinctly the intermolecular interaction of the bifunctional compounds with the stationary liquid phase of the column.

According to the rule of additivity from thermodynamic considerations, two functional groups far separated from each other in a molecule can act independently with no interference [15]. Our data show that this rule applies only to non-polar DB-1 column with a normal *A* value of 100 or close to it; for polar columns, the high value of *A* complicates the additivity rule. It is difficult, in the absence of a known *A* value, to deconvolute a composite (GRF) value of a multi-functional compound into individual component (GRF) values.

*3.1.13. 1,2-Alkanediols*

In 1,2-alkanediols the two –OH groups are nested together at one end of the alkane chain with one hydroxyl group attached to a secondary C atom. The adjacency of the two functional groups curtails the electron current between the two –OH groups along the backbone structure of the molecule, and as a result, the 1,2-diols have lower *A* and (GRF) values than 1,ω-alkanediols on all the columns. 1,2-Alkanediols are completely retained on the HP-Basic Wax column. The retention index *I* values and the *A* and (GRF) values for 1,2-alkanediols are given in Tables 1 and 2, respectively.

*3.1.14. 1-Aminoalkanes*

1-Aminoalkanes have about the same polar character as 1-alkanols. The *A* values are 101.45, 102.51, 101.79, 102.56, 100.46, 103.90, and 99.97 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, and HP-Basic Wax columns, respectively. The DB-Wax columns are not base-deactivated and can completely retain the aliphatic amines but not the aromatic amines. The (GRF) value for the amino group increases with increasing column polarity, but the increase is less when compared with the (GRF) value of 1-alkanols.

*3.1.15. 1,ω-Diaminoalkanes*

The presence of the two terminal amino groups increases the electron current in the alkane backbone of the 1,ω-diaminoalkanes. The *A* values for 1,ω-diaminoalkanes are substantially higher than those for 1-aminoalkanes or 1,ω-alkanediols. They are 103.75 on DB-1, 105.52 on DB-35, 106.68 on DB-17, 107.47 on DB-608, 110.38 on DB-210, 115.23 on DB-225, and 103.37 on HP-Basic Wax column. The high *A* value makes it difficult to resolve the bifunctional (GRF) value into two single amino functionality (GRF) values. Fig. 6 shows the linear *I* vs. *Z* plots of 1,ω-diaminoalkanes on non-polar and polar columns.

*3.1.16. ω-Amino-1-alkanols*

ω-Amino-1-alkanols contain one hydroxyl and one amino group in the molecule. The *A* values are 101.70, 98.80, 94.90, 100.10, 95.30, 125.57, and 115.30 on DB-1, DB-35, DB-17, DB-608, DB-210, DB-225, and HP-Basic Wax columns, respectively. The *A* values on these columns are comparable to those of 1-alkanols and 1-aminoalkanes. On DB-225 column, the *A* value is extremely high with a high standard error. Contrary to that observed in 1,ω-

alkanediols and 1,ω-diaminoalkanes, there is little or no electron current between the two dissimilar functional groups in ω-amino-1-alkanols. It should be pointed out that the results on aminoalkanols are based on only four data points, one of which, 4-amino-1-butanol, is consistently higher than the linear plots for all columns.

#### *3.1.17. Trichloroacetic alkyl esters*

Trichloroacetic alkyl esters have been recommended for use as retention index markers for electron capture detector [27]. In contrast to fatty acid methyl esters, the presence of three Cl atoms in the molecule increases the *A* value on all columns, as shown in Table 2. The highest *A* value is on DB-210 rather than on DB-225 column. The (GRF) value includes both the atom contribution from the three Cl atoms and the functionality contribution from the trichloracetyl group. With an increase in column polarity, both contributions will increase proportionately to give the (GRF) its final value. It should be noted that the presence of the electronegative trichloroacetyl group enables the HP-Basic Wax column to retain this homologous series of alkyl esters on column.

#### *3.1.18. The uniqueness of A and (GRF) values*

The above study shows that the temperature-programmed gas chromatography can analyze 16 homologous series of mono- and bifunctional organic compounds on eight columns of graded polarity. The retention indices of all the homologous series on all stationary liquid phases obey the retention index equation, Eq. (3). Both *A* and (GRF) values are characteristic of the homologous series and the stationary liquid phase. Bifunctional compounds with identical functional groups have higher *A* values and larger (GRF) values than the monofunctional ones. Although the polarizability forces interact between the analyte molecule and the stationary liquid phase to affect both *A* and (GRF) values, the *A* value is particularly affected by the dipole–dipole interaction and the (GRF) value by the H-bonding in the intermolecular interactions (see below). These constants can define and aid in the retrieval of retention indexes of members of a homologous series.

### *3.2. The stationary liquid phase*

The structure of the stationary liquid phase is important for the retention of the analyte. Both *A* and (GRF) values in Eq. (3) increase with the polarity of the stationary liquid phase, *A* only weakly and (GRF) strongly. In Table 2, the *A* values of all the homologous series peak on DB-225 column with the exceptions of *n*-alkyl ethers and alkyl trichloroacetate esters, while the (GRF) values for all the homologous series reach their highest values on the most polar DB-Wax and HP-Basic Wax columns with no exception. This implies that *A* and (GRF) values represent different aspects of intermolecular interaction between the analyte and the stationary liquid phase and show accordingly different variations.

The stationary liquid phases of DB-1, DB-35, DB-17, DB-608, DB-210, and DB-225 columns are substituted polysiloxanes. The liquid phase on DB-1 column is the non-polar (100%) dimethylpolysiloxane polymer. DB-35, DB-17, and DB-608 liquid phases incorporate, respectively, 35%, 65%, and 65% of diphenyl groups in the dimethylpolysiloxane polymer, and are increasingly more polarizable. DB-17 and DB-608 columns differ in film thickness. The liquid phase on DB-210 column incorporates 50% of trifluoropropyl groups in the dimethylpolysiloxane polymer, and that on DB-225 column 25% cyanopropyl and 25% phenyl groups in the polymer. Both are increasingly more polar. DB-Wax and HP-Basic Wax liquid phases, being the most polar stationary liquid phase used in this study, are unmodified and modified polyethylene glycol polymers, respectively.

#### *3.2.1. Analyte–stationary liquid phase structure correlation*

The backbone of the polysiloxane polymers contains Si–O and Si–C linkages, but there are methyl, phenyl, diphenyl, trifluoropropyl, and cyanopropyl groups attached to the Si atoms as side chains in different polymers [11–13]. The methyl group is inert; phenyl and diphenyl groups are polarizable; and the trifluoropropyl and cyanopropyl groups have very high dipole moments in the range of 3–4 Debye units. Conceivably, the *A* value changes according to the extent of interactions between the backbone structure of the analyte molecule and the different

polysiloxane polymer molecules. Since the *A* values of all homologous series, with the exception of the trichloroacetic alkyl esters and the *n*-alkyl ethers, show peak values on DB-225 column, it is reasonable to assume that the peak increase in the *A* value may be attributed to the dipole–dipole interaction (or Keesom forces). The *A* value of trichloroacetic alkyl esters shows its peak value on DB-210 column rather than on DB-225 column. The trichloroacetyl moiety of the substituted alkyl esters, namely, the analyte molecules, can match better for dipole–dipole interaction with the trifluoropropyl group in the DB-210 stationary liquid phase than with the cyanopropyl group in the DB-225 liquid phase. The *n*-alkyl ethers can orient their linear molecules alongside the backbone structure of different polysiloxane polymers (i.e, a string of Si–O linkages in coiled conformations)[3] and avoid interaction with any of their side chains. This explains why this homologous series is unique in that that it has approximately the same *A* and (GRF) values on all different stationary liquid phases. The bifunctional analyte molecules, such as 1,2- and 1,ω-alkanediols and 1,ω-diaminoalkanes, when compared with their monofunctional counterparts, have higher *A* values on all the columns except on DB-1 column. The DB-1 column is the most non-polar liquid phase and contains only Si–O and Si–C linkages with no polarizable and polar side chains and with only minimum capability and polarity for intermolecular interactions with the analyte molecules. It confirms again that the increase in the *A* value is predominantly dependent upon the dipole–dipole interaction between the analyte molecule and the polymeric stationary liquid phase.

The backbone of the polyethylene glycol polymer on the DB-Wax column contains a string of (–C–C–O–) groups that interact by hydrogen bonding with the functional group(s) of the analyte molecule to contribute to long retention. For this reason, the (GRF) values of all the homologous series are at their highest on DB-Wax column with no exception. DB-Wax columns retain aliphatic amines but not aromatic amines. The modified polyethylene glycol polymer of the HP-Basic Wax column retains 1-alkanoic acids, cycloalkane carboxylic acids, trichloroacetic alkyl esters, and 1,2-alkanediols. The basic reagent used for modifying the polymer can cause on column deiodination of higher 1-iodo-*n*-alkanes.

Thus, interactions between analyte molecules and stationary liquid phases result in the chromatographic retention of the backbone structure and the functional groups. These interactions are dominated by the dipole–dipole and H-bonding forces and are represented as variations of the *A* and (GRF) values, respectively.

### *3.3. Connectivity*

The (GRF) value of a functional group varies with its connectivity ability (i.e., connection to atoms or to groups of atoms) and electron density. When connected to a primary, secondary or tertiary carbon atom, the same functional group will have a different (GRF) value decreasing in that order because the carbon atom to which the functional group is attached is increasingly deshielded and will have a larger chemical shift ($\delta_e$) and lower electron density. The same functional group, when connected to a phenyl ring, will have a larger (GRF) value than that connected to an alkyl group. The larger (GRF) value is attributed especially to the extended conjugation of the phenyl ring through resonance stabilization. Examples are given below.

#### *3.3.1. The halogen atoms*

The halogen atoms are electronegative and monovalent. The halo atom connected to the phenyl ring has a smaller (GRF) value than that connected to an alkyl group [cf. the aliphatic and aromatic (GRF) values for the halo atoms in Table 5]. The halo atom donates electrons to the phenyl ring by electromeric or resonance effect, but being univalent it cannot

[3]The polysiloxane macromolecules have ''coiled'' structures. The structures of the polysiloxane elastomers are less rigid and are randomly coiled at high temperatures. The unique properties of polysiloxanes are: (i) the unusual flexibility of the large Si–O–Si bond angles (140±10°), (ii) the large Si–O bond length (1.62 Å), (iii) the large difference in sizes of the alternating Si and O atoms in the chain, (iv) the relatively free rotation of the organic substituents around Si–C bond, (v) the relatively large free volume between neighboring chain segments, and (vi) the very small activation energies for viscous flow (<10 kcal/mol; 1 cal=4.184 J), etc. [28]. With these properties, it is highly probable that small molecules, such as *n*-alkyl ethers, will find a place in the vicinity or in the center of the helix of polysiloxane macromolecules, thus avoiding interaction with the pendant groups or side chains.

Table 5
Retention indexes of halobenzenes, differences ($\Delta$'s) between aliphatic and aromatic (GRF) values, and selectivity in retention

| Compound | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| *(a) Aliphatic halo atoms* | R-X | | | | | | | | |
| 1-Halo-*n*-alkanes | $C_nH_{2n+1}X$ | | | | | | | | |
| Aliphatic $(GRF)_{Cl}$ | | 227 | 295 | 313 | 308 | 354 | 366 | 416 | 417 |
| Aliphatic $(GRF)_{Br}$ | | 305 | 368 | 392 | 391 | 413 | 457 | 530 | 514 |
| Aliphatic $(GRF)_{I}$ | | 379 | 472 | 502 | 495 | 487 | 554 | 641 | 628 |
| *(b) Aromatic halo atoms* | Φ-X | | | | | | | | |
| Benzene | $C_6H_6$ | 642 | 731 | 765 | 760 | 801 | 845 | 950 | 947 |
| Chlorobenzene | $C_6H_5Cl$ | 829 | 943 | 985 | 976 | 989 | 1070 | 1240 | 1228 |
| Bromobenzene | $C_6H_5Br$ | 913 | 1044 | 1087 | 1083 | 1078 | 1186 | 1381 | 1359 |
| Iodobenzene | $C_6H_5I$ | 1010 | 1175 | 1227 | 1221 | 1176 | 1342 | 1520 | 1527 |
| Aromatic $(GRF)_{Cl}$ | | 187 | 212 | 220 | 216 | 188 | 225 | 290 | 281 |
| Aromatic $(GRF)_{Br}$ | | 271 | 313 | 322 | 323 | 277 | 341 | 431 | 412 |
| Aromatic $(GRF)_{I}$ | | 368 | 444 | 462 | 461 | 375 | 497 | 570 | 580 |
| $\Delta_{Cl}$ | | 40 | 83 | 93 | 92 | 166 | 141 | 126 | 136 |
| $\Delta_{Br}$ | | 34 | 55 | 70 | 68 | 136 | 116 | 99 | 102 |
| $\Delta_{I}$ | | 11 | 28 | 40 | 34 | 112 | 57 | 71 | 48 |

form extended conjugation with the phenyl ring to enlarge the backbone structure to increase its (GRF) value. The halogen atoms are the only exceptions among the functional groups that form extended ring conjugation.

The difference ($\Delta$) between the aliphatic and aromatic (GRF) values of the halo atoms should show the relationship of $\Delta_{Cl} > \Delta_{Br} > \Delta_{I}$, to reflect the electronegativity scale of the halo atoms: Cl>Br>I. The more electronegative halo atoms attract more electrons by inductive effect and should be capable also of donating more electrons by resonance effect. The aliphatic (GRF) values for the halo atoms are from Table 2. The aromatic (GRF) value for each halo atom is obtained as the difference between the *I* values of benzene and chloro- or bromo-, or iodobenzenes on all non-polar and polar columns. The difference ($\Delta$) value for each halo atom is then obtained from the corresponding aliphatic and aromatic (GRF) values to substantiate the above inequality, as shown in Table 5.

### *3.3.2. The carboxyl and hydroxyl groups*

When connected to the phenyl ring, the carboxyl group donates electrons to the ring and ionizes readily. It makes benzoic acid a stronger acid ($pK_a$ 4.2 at 25°C) than acetic acid ($pK_a$ 4.734 at 25°C) [29]. By comparison, the cycloalkane carboxylic acids have a lower *A* value than 1-alkanoic acids. The carboxylic group when connected to a cycloalkane ring withdraws more electrons from the backbone structure and will ionize less, making cyclohexane carboxylic acid a weaker acid ($pK_a$ 4.88 at 25°C) than acetic acid [30]. Applying the same reasoning to the hydroxyl group leads to the prediction that phenol will be a stronger acid ($pK_a$ 9.89) than ethanol ($pK_a$ ~16) [31]. Both carboxyl and hydroxyl groups can dissociate, forming ions. These ions, unlike the halogen atoms, can form extended conjugation with the phenyl group and are stabilized by resonance so that their backbone structures have a larger flat area for interaction with intermolecular forces to give a longer retention and a larger (GRF) value than one with a smaller area. In comparison with the halo atoms, the (GRF) values of the carboxyl and hydroxyl groups connected to the phenyl groups are larger than those connected to the *n*-alkyl groups.

### *3.4. Selective retention*

According to Eq. (3), the values of *Z*, (GRF), and

*A* determine the retention of an analyte molecule. One can predict the retention index if all three values are given. Or, one can predict the elution sequence if only two of the values are known. In a homologous series, for example, members share the same (GRF) and *A* values, and the sequence of elution is determined by the *Z* value. When compounds have the same *Z* and *A* values, the sequence of elution is determined by the (GRF) values of the functional groups. In isomeric compounds with the same *Z* and (GRF) values, the highly branched or symmetric isomers will be eluted earlier because of their smaller *A* values.

Columns of different polarities can influence the sequence of elution by influencing *A* and (GRF) values. Some examples are given below.

### *3.4.1. Peak overlap and peak reversal*

A mixture of different compounds of comparable structures can appear as a single or an overlapping peak on one column and as separate peaks on another column, due to the influence of column polarity on the *A* and (GRF) values. For example, α-chlorotoluene and *o*-bromotoluene appear as a single or an overlapping peak when co-chromatographed on DB-35, DB-17, DB-608, and DB-210 columns, since their retention indices differ by only a few i.u. and as two separate peaks on DB-1 column with α-chlorotoluene leading and on DB-225, DB-Wax, and HP-Basic Wax column with *o*-bromotoluene leading. The *I* values of these two compounds on non-polar and polar columns are given in Table 6.

The above observation can be explained as follows: because of their connectivity, the aliphatic Cl atom and the aromatic Br atom have approximately the same (GRF) values on DB-35, DB-17, DB-608, and DB-210 columns. On DB-1 column, the aromatic Br atom has larger a (GRF) value than the aliphatic Cl atom, and on DB-225, DB-Wax, and HP-Basic Wax columns the opposite is true. This is caused by differential column polarity and dipole–dipole interaction. Since the (GRF) value of a halo atom includes both atom and functionality contributions, it is difficult to separate these interactions.

### *3.4.2. Substitution*

Functional groups contain oxygen or nitrogen atom or both. Substitution at the O atom converts alcohols into ethers, acids into esters, etc., changing one functionality neatly into another. Substitution at the N atom is more complicated because the decrease

Table 6
Effects of connectivity of substituent groups on retention index[a]

| Compound | Formula | Column | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DB-1 | DB-35 | DB-17 | DB-608 | DB-210 | DB-225 | DB-Wax | HP-B/Wax |
| *(a) Peak overlap and peak reversal* | | | | | | | | | |
| Toluene | $C_7H_8$ | 753 | 835 | 867 | 871 | 897 | 951 | 1059 | 1049 |
| α-Chlorotoluene | α-$C_6H_5CH_2Cl$ | 992 | 1152 | 1199 | 1195 | 1179 | 1354 | 1509 | 1529 |
| *o*-Bromotoluene | *o*-$CH_3C_6H_4Br$ | 1021 | 1156 | 1195 | 1188 | 1182 | 1293 | 1430 | 1449 |
| *(b) Substitution* | | | | | | | | | |
| Aniline | $C_6H_5NH_2$ | 947 | 1136 | 1196 | 1197 | 1257 | 1476 | 1779 | 1770 |
| *m*-Toluidine | $(CH_3)C_6H_4NH_2$ | 1050 | 1240 | 1305 | 1304 | 1361 | 1581 | 1850 | 1856 |
| *N*-Methylaniline | $C_6H_5NH(CH_3)$ | 1037 | 1226 | 1287 | 1285 | 1325 | 1526 | 1716 | 1737 |
| *N*,*N*-Dimethylaniline | $C_6H_5N(CH_3)_2$ | 1069 | 1234 | 1287 | 1285 | 1325 | 1439 | 1539 | 1557 |
| 2,4-Dimethylaniline | $(CH_3)_2C_6H_3NH_2$ | 1135 | 1331 | 1395 | 1391 | 1435 | 1570 | 1877 | 1885 |
| *N*-Ethylaniline | $C_6H_5NH(C_2H_5)$ | 1099 | 1280 | 1340 | 1338 | 1395 | 1568 | 1724 | 1743 |
| *N*,*N*-Diethylaniline | $C_6H_5N(C_2H_5)_2$ | 1199 | 1362 | 1416 | 1414 | 1451 | 1559 | 1623 | 1640 |
| 2-Ethylaniline | $(C_2H_5)C_6H_4NH_2$ | 1122 | 1320 | 1391 | 1390 | 1429 | 1648 | 1886 | 1875 |
| 4-Ethylaniline | $(C_2H_5)C_6H_4NH_2$ | 1134 | 1327 | 1403 | 1402 | 1442 | 1664 | 1938 | 1926 |

[a] Examples of peak overlap and peak reversal and of substitution on non-polar and polar columns.

of the (GRF) value of the amine function from conversion of primary to secondary to tertiary amine is compensated by an increase in atom contribution (*AZ*) of the incoming substituent group. As *A* and (GRF) values increase at different rates with an increase in column polarity, the outcome of these competing processes determines the *I* value of the substituted product. Prediction of retention index can be difficult without the knowledge of *A* and (GRF) values of the compounds before and after the substitution. Amides have a greatly depressed *A* value because their functional group containing both electronegative oxygen and nitrogen atoms, can attract more electrons from the backbone structure more easily than one electronegative atom acting alone [10].

Aromatic amines are substituted anilines. In aromatic substitutions the position of the substituent group in the ring or its connectivity to C or N atom can affect the atom contribution and influence the *A* value of the substituent group. As shown in Table 6, 2,4-dimethylaniline, 2-ethylaniline and 4-ethylaniline have higher *I* values than *N*,*N*-dimethylaniline and *N*-ethylaniline, even though all five compounds have the same number of C and N atoms in the molecule. The first three compounds have intact amino groups, and the last two compounds have substituted amino groups.

*N*-Methylaniline and *N*,*N*-dimethylaniline appear as two adjacent peaks with the former compound leading on DB-1 and DB-35 columns and as a single peak on DB-17, DB-608 and DB-210 columns and as two adjacent peaks on DB-225, DB-Wax, and HP-Basic Wax columns with the latter compound leading, as given in Table 6. Without any knowledge of the *A* and (GRF) values for these aromatic amines, this phenomenon can be explained as follows: emergence of *N*,*N*-dimethylaniline and *N*-methylaniline as a single peak implies that the decrease in the amine (GRF) value from conversion of secondary to tertiary amine is exactly balanced by the gain in retention index of the substituted molecule from the addition of a methylene group. Since *A* increases weakly and (GRF) strongly with increase in column polarity, the above phenomenon regarding the sequence of elution becomes understandable on the basis that on DB-1 and DB-35 columns, $A >$ (GRF); on DB-17, DB-608, and DB-210 columns, $A =$ (GRF); and on DB-225, DB-Wax, and HP-Basic Wax, $A <$ (GRF). Another example is represented by the substituted ethylanilines. *N*-Ethylaniline and *N*,*N*-diethylaniline elute as two adjacent peaks, with the secondary amine preceeding the tertiary amine on DB-1, DB-35, DB-17, DB-608, and DB-210 columns. On DB-225, DB-Wax, and HP-Basic Wax columns, reversal of the peak appearance occurs with *N*,*N*-diethylaniline leading *N*-ethylaniline. The *AZ* value for the ethyl group is anomalous and varies from 175 to 125 i.u. or thereabout, depending upon the electronegativity of the atom to which the ethyl group is attached. It rarely approaches the anticipated value of about 200 i.u. The possible cause for the low *AZ* value for the methylene group in ethyl group is mentioned in Footnote 2.

### *3.5. The column difference (ΔI)*

The column difference ($\Delta I$) is defined as the difference between two *I* values of the same compound on two columns of different polarities [9], thus:

$$\Delta I = I_{\text{more polar}} - I_{\text{less polar}} \tag{6a}$$

$$= I_1 - I_2 \tag{6b}$$

The subscripts ''more polar'' and ''less polar'' in Eq. (6a) are changed for brevity to ''1'' and ''2'', respectively. Substituting Eq. (3) with appropriate subscripts ''1'' and ''2'' into Eq. (6b) followed by rearrangement gives:

$$\Delta I = (A_1 - A_2)Z + \{(\text{GRF})_1 - (\text{GRF})_2\} \tag{7}$$

Eq. (7) shows that the value of the column difference ($\Delta I$) is compound-specific, depending not only upon the differences between the *A* and (GRF) values of the same compound on the two columns, but also upon the *Z* value. When the retention index increments of the same compound on the two columns are equal, i.e., $A_1 = A_2$, Eq. (7) is reduced to Eq. (8), thus:

$$\Delta I = (\text{GRF})_1 - (\text{GRF})_2 \tag{8}$$

The $\Delta I$ value becomes only column-specific, when the difference between the two *A* values vanishes.

The $\Delta I$ value in our early publication is based on Eq. (8) because the significance of different $A$ values on different columns was not fully known [9]. The validity of Eq. (7) can be verified by the $I$, $A$, and (GRF) values given in Tables 1 and 2 for the different homologues on different columns.

## 4. Conclusion

In temperature-programmed gas chromatography using linearly interpolated retention index, the retention of a homologous series of organic compounds on non-polar and polar columns can be described by the retention index equation with characteristic $A$ and (GRF) values. The equation is the basis for correlation of chemical structure with retention index. The proposed molecular model of retention based on electron density and electron density distribution divides the analyte molecule structurally into two domains, the backbone structure and the functionality of functional groups. The $A$ value reflects the dipole–dipole and the (GRF) value the H-bonding interactions between the analyte molecule and the stationary liquid polysiloxane phase. The $A$ value is influenced by both inter- and intramolecular electronic effects.

Functional groups are variably retained according to their connectivity and ability to undergo extended conjugation, substitutions, and H-bonding. A general criterion of retention is the relative increase or decrease in the electron density of the functional groups. A higher electron density tends to promote a longer retention.

The four parameters in the retention index equation, namely, $I$, $Z$, $A$, and (GRF), are interrelated. The retention index of an analyte molecule can be precisely predicted if all three parameters $Z$, $A$, and (GRF) are given. The sequence of elution can be determined from any two of the above three parameters. The retention indexes of all the members of a homologous series on a given column can be determined from the two parameters $A$ and (GRF). The elution sequence of a mixture of organic compounds is generally predictable from their chemical structure, provided that the $A$ and (GRF) values for different functional groups and related homologous series can be estimated or have been pre-determined. The molecular model of retention, based on electron density and electron density distribution, gives a new meaning to the $A$ and (GRF) values for defining the retention of an entire homologous series.

The fact that the retention index increment for the addition of a methylene group in an analyte molecule has its own characteristic $A$ value rather than the arbitrarily assigned value of 100 i.u. that a $n$-alkane assumes, may complicate our customary understanding of the term ‘‘column difference’’. The column difference ($\Delta I$) for an analyte with different $A$ values on two different columns is compound-specific. Only when the analyte molecule has identical $A$ values on both columns, is the column difference column-specific. The column differences, often referred to in the literature as phase constants by many authors for defining the polarity or the selectivity of non-polar and polar columns, were originally conceived to be column-specific but in fact are compound-specific.

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