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Gas chromatographic retention behaviour of some solutes on structurally similar polar and non-polar stationary phases

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ABSTRACT

A selection of 135 solutes, chosen to represent most chemical families, were characterized by *I*, the retention index of the solute on a pure polar phase and on a pure non-polar phase. Apart from the analysis of all the injected substances on the two pure extreme phases, a great number of the compounds were also measured on phases of variable polarity by modifying the mixtures of the two stationary phases available in well-defined proportions. Some correlations such as *I* as a function of the temperature and of the composition of the stationary phase were established.

INTRODUCTION

Alkanes are recognized as non-polar stationary phases in gas chromatography [1]. Their retention characteristics are the basis for the comparison of all other stationary phases. In order to obtain a non-polar model stationary phase, a high-molecular-weight branched hydrocarbon with very low polarity, $C_{78}H_{158}$, has already been synthesized [2].

Modification of the polarity of the reference stationary phase, 19,24-dioctadecyl dotetracontane (structure I), called hereafter "C_{78}", is achieved by replacing a methyl group with a unique hydroxyl group. This causes only a small change in the molecular weight and the global volume of the molecule [3].

Thus, the effect on the solute molecules of a change in only the polarity of the polar phase can be studied. The influence of molecular weight in the paraffin series of 1,1,6,6-tetraalkylhexane skeleton being already well documented [4], a single change in the structure of a molecule from this series changes only its polar part. In other words, having practically eliminated the effect of molecular weight, the effect of the polarity of the phase due to the one and only hydroxyl group of 19-(17′-hydroxy heptadecyl) 24-octadecyl dotetracontane (structure II), "C_{77}-OH", can be measured. Moreover, this –OH group, situated at the end of a chain, like a primary alcohol, is in an extremely

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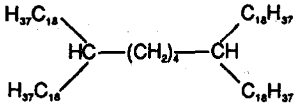
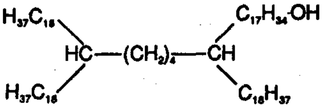
isolated situation, facing the rest of the molecule, represented by an enormous hydrocarbon ensemble.



I



II

The retention index [5] of a solute (j) is defined as:

$$I_j = 100 \cdot \frac{\log X_j - \log X_z}{\log X_{z+1} - \log X_z} + 100 \cdot z \tag{1}$$

where X represents any net retention value, j refers to the solute to be examined and X_z is the paraffin whose peak comes out before the solute and whose carbon atom number is z. X_{z+1} is the net retention value of the paraffin with $z + 1$ carbon atoms, which comes out after the solute.

The value of the retention index is affected by: (i) the solute; (ii) the stationary phase; and (iii) weakly by temperature.

EXPERIMENTAL

Materials

The solutes used for the chromatographic measurements were purchased either from Fluka (Buchs, Switzerland) or from Aldrich-Chemie (Steinheim, Germany). The compounds $C_{78}H_{158}$ [2] and $C_{77}H_{155}$-OH [3] were employed as stationary phases on Chromosorb G-HP (high performance), acid-washed and treated with dimethylchlorosilane, AW-DMCS, 80–100 mesh, from Supelco (Bellefonte, PA, USA). The commercial support was passed through a sieve and the fraction with particle diameter (d_p) 150–180 μm (between filters DIN Nos. 30 and 50) was dried overnight in an oven at 100°C.

Column packings

The columns were 370 cm long circular Pyrex tubes with a spiral diameter of 16.0 cm and an internal diameter of 0.40 cm.

The columns were filled with a support impregnated with 5.00% (w/w) liquid phase. This was measured by weighing both support and liquid phase with a precision of ±0.0001 g. (Preparation of the filling: the fine white crystals were dissolved in distilled cyclohexane and the homogeneous solution was added to an exact quantity of support. The solvent was evaporated under a slight vacuum in an argon stream at about 180°C.)

The Pyrex glass columns, washed, dried and weighed with a precision of ±0.01 g, were filled using a water pump and vibrations. They were kept overnight under argon.

The weight of packing in the column was measured as the difference between the

TABLE I

COLUMN PACKING CHARACTERISTICS

w is the ponderal fraction of C_{77}-OH in the stationary liquid, m_r is the packing mass, P_θ is the liquid internal weight (%) and $m_\theta = m_r \cdot P_\theta/100$ is the stationary liquid mass in the column.

w	m_r (g)	P_θ (%)	m_θ (g)
0.000	32.06	4.766	1.528
0.333	31.38	4.767	1.496
0.667	30.17	4.760	1.436
1.000	30.16	4.764	1.458

empty and packed columns (see Table I). The amount of liquid phase was calculated from the total weight of the packing. Since the two stationary phases were pure C_{78} and C_{77}-OH, two mixtures consisting of 33.3% and 66.7% C_{77}-OH could be precisely measured, to pack two further columns.

Apparatus

A Packard-Becker (Delft, Netherlands) Model 419 gas chromatograph was used for the retention data determination. This instrument was equipped with a platinum resistance thermometer, a flowmeter and a precision manometer for more precise measurements.

The flow-rate was measured and regulated with a thermal flowmeter from Brooks (Veenendaal, Netherlands), composed of two essential units: a mass flow sensor Type 5850 TR and a regulator Model 4251-IA2B1E0. The flowmeter, originally calibrated at 2 Bars (1500.12 mmHg) and 20°C, was adjusted to give digital display of the volumic flow-rate of the carrier gas (helium) at 760 Torr and 0°C.

The column temperature was determined taking into account the temperature gradient inside the chromatograph oven. To measure this gradient, a cube-shaped wire skeleton was built smaller than the oven size. A chromel wire was fixed on the skeleton, and an alumel wire was soldered at each of its corners. The temperature differences between the corners of the cube were measured by means of a digital microvoltmeter, Type Trendicator 400A (Doric, San Diego, CA, USA). The absolute temperature was measured with a platinum resistance thermometer, which was calibrated by Dr. M. Wittwer (Eidg. Amt für Mass und Gewichte, Wabern/Berne, Switzerland) between 0°C and 400°C with a precision of ±0.1°C in absolute temperature. The column temperature ($\overline{T_c}$) was calculated as described in ref. 6, taking the gradient in the oven into consideration. A middle temperature value was calculated for the column centre, located at 1/4 and 3/4 of the total distance between the cube front and back sides.

The inlet pressure of the chromatographic system, $P_i' = \Delta P' + P_{atm}$, was measured via a Heise Type 710B digital manometer (Dresser Europe, Werk Baesweiler, Germany), where

$$\Delta P' = \Delta P + \Delta P_i + \Delta P_o \qquad (2)$$

was the pressure drop in the chromatographic system. The average pressure in the column was calculated considering the inlet resistance at the capillary tubes' injector

(R_i) and the outlet resistance at the detector (R_o). The inlet resistance (R_i) was determined at different temperatures and flow-rates by measuring the flow-rate, $\dot{V}_i$, after the injector and the pressure drop (ΔP_i), in the absence of column (NTP = normal temperature and pressure):

$$R_i = \Delta P_i / \dot{V}_i \qquad (3)$$

$$\dot{V}_i = (\dot{V}_c/\mathrm{NTP}) \cdot (\overline{T_c}/273.15)[760/(P_{atm} + \Delta P_i/2)] \qquad (4)$$

where $\dot{V}_c$ is the flow-rate in the column at NTP.

To measure the outlet resistance (R_o), an empty column was placed in the apparatus and the resistance was determined by measuring the carrier gas flow at the detector outlet ($\dot{V}_o'$).

$$R_0 = \Delta P_o / \dot{V}_o' \qquad (5)$$

$$\dot{V}_o' = (\dot{V}_c/\mathrm{NTP}) \cdot (\overline{T_c}/273.15) \cdot [760/(P_{atm} + \Delta P_o/2)] \qquad (6)$$

and

$$\Delta P_o = \Delta P' - P_i \qquad (7)$$

Both resistances (R_i and R_o) were constant with temperature. A mean value was therefore used [6].

The definition of the retention volume only becomes applicable if the flow at the column outlet, $\dot{V}_o$, is replaced by the average gas flow along the column [7], which is $\frac{2}{3}J \cdot \dot{V}_o$. The James and Martin factor ($\frac{2}{3}J$) [8], which depends on the inlet and the outlet pressures of the column, respectively P_i and P_o, is ($p = P_i/P_o$):

$$\tfrac{2}{3}J = 3/2\,(p^2 - 1)/(p^3 - 1) \qquad (8)$$

Practically, an average volumic flow of the carrier gas through the column, taking the charge loss into account, is defined by:

$$\overline{\dot{V}_c} = \tfrac{2}{3}J \cdot \dot{V}_o \qquad (9)$$

The gross retention time t_R was determined with two HP 3390A integrators (Hewlett-Packard) at a precision of ±0.001 min. The various regression coefficients listed in Table II were obtained by computer (Digital Equipment Corp., Maynard, MA, USA; Model Pro. 380). The data evaluation system RS/1 was conceived by the firm Bolt Beranek and Newmann (Cambridge, MA, USA). The tables were printed by an LA50 printer and the graphs traced with an LVP16 plotter (both Digital).

RESULTS

Using the retention time t_R and the "retention time of a non-retained compound" [7] such as neon, $\overline{t_R}$(Ne), we determined the net retention time, t_N:

$$t_N = t_R - \overline{t_R}(\mathrm{Ne}) \qquad (10)$$

Considering eqn. 1, the retention index can then be calculated by:

$$I_j = 100 \cdot \frac{\log t_N - \log t_N(z)}{\log t_N(z+1) - \log t_N(z)} + 100 \cdot z \tag{11}$$

The retention index I is determined at an experimental temperature, T_{exp}, which is near the column nominal temperature, *i.e.*, 90.0°C, 110.0°C, 130.0°C, 150.0°C and 170.0°C. The I average and T_{exp} average were determined at each experimental temperature. After regression of the experimental I, the slope was adjusted for I experimental to I at the nominal temperature.

The resulting general equation of the retention index as a function of the temperature interval around 130°C, ΔT, and of the C_{77}-OH mass fraction, w, is therefore:

$$\begin{aligned} I = I_{130} &+ d_T \cdot \Delta T + d_{TT} \cdot \Delta T^2 + d_{TTT} \cdot \Delta T^3 + \\ &+ d_L \cdot w + d_{LL} \cdot w^2 + d_{LT} \cdot w \cdot \Delta T + \\ &+ d_{LLT} \cdot w^2 \cdot \Delta T + d_{LTT} \cdot w \cdot \Delta T^2 + d_{LLTT} \cdot w^2 \cdot \Delta T^2 \end{aligned} \tag{12}$$

where the coefficients for d_X are expressed by T for the temperature and L for the stationary phase composition, and where:

$$\Delta T = \{-40, -20, 0, +20, +40\} \tag{13}$$

and

$$w = \{0, 1/3, 2/3, 1\} \tag{14}$$

The stationary phase consisting of only pure C_{78} was taken as the reference, and thus I_{130} is the index at 130°C on C_{78} ($w = 0$).

An equation analogous to eqn. 12 can be put for I by considering, this time, the b_x coefficients of the orthogonal polynomials in P:

$$\begin{aligned} I = b_o &+ b_T \cdot P_T + b_{TT} \cdot P_{TT} + b_{TTT} \cdot P_{TTT} + \\ &+ b_L \cdot P_L + b_{LL} \cdot P_{LL} + b_{LT} \cdot P_L \cdot P_T + \\ &+ b_{LLT} \cdot P_{LL} \cdot P_T + b_{LTT} \cdot P_L \cdot P_{TT} + b_{LLTT} \cdot P_{LL} \cdot P_{TT} \end{aligned} \tag{15}$$

Considering that a five-temperature (T source) and four-phases composition (L source) system is available, the coefficient values of the orthogonal polynomials are defined [9] as follows:

$$P_T = \frac{\Delta T}{20} = \{-2, -1, 0, +1, +2\} \tag{16}$$

$$P_{TT} = P_T^2 - 2 = \{+2, -1, -2, -1, +2\} \tag{17}$$

$$P_{TTT} = P_T^3 - 3.4\, P_T = \frac{6}{5}\{-1, +2, 0, -2, +1\} \tag{18}$$

TABLE II

RETENTION INDICES ON STRUCTURALLY SIMILAR STATIONARY PHASES

The coefficients in eqn. 12 are evaluated by the orthogonal polynomials method applied to the measured chromatographic data. The values marked "—" are not calculable because measurements for these solutes were carried out only on the two extreme phases. On the other hand, "ϕ" means that the coefficient was not significant, and the values were therefore not retained. Δ_{95} is the confidence limit at the 95% confidence level.

Solute	Experimental conditions		I_{130}	$d_T \cdot 10$ (K^{-1})	$d_{TT} \cdot 10^3$ (K^{-2})	d_L	d_{LL}	$d_{LT} \cdot 10$ (K^{-1})	$d_{LLT} \cdot 10$ (K^{-1})	$d_{LTT} \cdot 10^3$ (K^{-2})	Δ_{95}
	T (°C)	L^a									
Isoalkanes											
2,2-Dimethylbutane	90–170	(2)	541.3	0.94	ϕ	−0.3	—	0.05	—	ϕ	1.08
2,2-Dimethylpentane	90–170	(2)	628.3	0.78	ϕ	−0.1	—	0.05	—	ϕ	0.77
2,4-Dimethylpentane	90–170	(2)	629.5	0.35	ϕ	−0.8	—	0.06	—	ϕ	0.85
2,2,3-Trimethylbutane	90–170	(2)	652.1	1.60	ϕ	−0.1	—	0.12	—	ϕ	0.82
2,2-Dimethylhexane	90–170	(2)	719.4	0.48	ϕ	−0.6	—	0.10	—	ϕ	0.69
2,4-Dimethylhexane	90–170	(2)	733.1	0.52	ϕ	−0.2	—	0.01	—	ϕ	0.55
3,4-Dimethylhexane	90–170	(2)	780.3	1.04	ϕ	0.2	—	0.03	—	ϕ	0.61
2,3,4-Trimethylpentane	90–170	(2)	764.8	1.45	ϕ	0.3	—	0.07	—	ϕ	0.53
2,2,4-Trimethylpentane	90–170	(2)	694.5	1.05	ϕ	−0.2	—	0.01	—	ϕ	0.50
2,2,4,6,6-Pentamethylheptane	90–170	(2)	989.7	2.08	ϕ	−0.5	—	−0.01	—	ϕ	1.08
Alkenes											
1-Hexene	90–170	(2)	588.1	0.88	ϕ	2.9	—	−0.37	—	ϕ	1.56
1-Heptene	90–170	(2)	686.5	0.58	ϕ	3.3	—	−0.26	—	ϕ	1.04
1-Octene	90–170	(2)	785.6	0.51	ϕ	3.7	—	−0.18	—	ϕ	0.69
1-Nonene	90–170	(2)	885.5	0.52	ϕ	4.0	—	−0.16	—	ϕ	0.44
1-Decene	90–170	(2)	985.2	0.50	ϕ	4.3	—	−0.25	—	ϕ	1.00
Alkynes											
1-Hexyne	90–170	(4)	589.7	0.67	ϕ	15.3	ϕ	−0.18	ϕ	ϕ	1.30
1-Heptyne	90–170	(4)	689.1	0.43	ϕ	15.6	ϕ	−0.17	ϕ	ϕ	1.03
1-Octyne	90–170	(4)	788.7	0.42	ϕ	16.0	ϕ	−0.08	ϕ	ϕ	0.87
1-Nonyne	90–170	(4)	889.0	0.47	ϕ	16.1	ϕ	−0.03	ϕ	ϕ	0.90
1-Decyne	110–170	(2)	988.9	0.54	ϕ	16.3	—	−0.10	—	ϕ	1.30
Cycloalkanes											
Cyclopentane	90–170	(2)	588.2	2.11	ϕ	2.1	—	−0.09	—	ϕ	0.90
Cyclohexane	90–170	(2)	694.0	3.08	ϕ	1.6	—	−0.13	—	ϕ	1.27
Cycloheptane	90–170	(2)	837.2	4.24	ϕ	3.0	—	−0.05	—	ϕ	0.59
Cyclooctane	90–170	(2)	965.2	5.25	ϕ	3.8	—	−0.10	—	ϕ	0.46

Alkylbenzenes											
Benzene	90–170	(4)	677.6	3.24	0.84	10.5	5.5	−0.08	φ	−1.13	1.01
Toluene	90–170	(4)	785.8	3.19	0.58	12.4	4.0	0.03	φ	−0.84	0.77
Ethylbenzene	90–170	(4)	875.4	3.52	0.63	12.9	3.4	−0.03	φ	−1.11	0.72
Propylbenzene	90–170	(2)	963.9	3.72	0.27	15.8	–	0.09	–	−0.89	1.56
1-Chloroalkanes											
1-Chlorobutane	90–170	(4)	639.7	1.93	0.75	13.7	2.7	−0.45	0.36	−1.09	0.75
1-Chloropentane	90–170	(4)	742.4	1.90	0.32	14.1	2.4	−0.42	0.44	−0.70	0.53
1-Chlorohexane	90–170	(4)	843.8	2.00	0.22	14.7	2.0	−0.44	0.46	−0.62	0.52
1-Chloroheptane	130–170	(2)	945.2	2.13	φ	16.8	–	−0.20	–	φ	0.88
1-Chlorooctane	130–170	(2)	1046.4	1.93	φ	16.2	–	0.00	–	φ	0.19
1-Bromoalkanes											
1-Bromopropane	90–170	(2)	628.8	2.67	0.36	17.1	–	−0.02	–	−0.29	1.33
1-Bromobutane	90–170	(2)	732.0	2.74	0.34	17.1	–	0.02	–	−0.30	1.13
1-Bromopentane	90–170	(2)	834.4	2.94	0.30	17.2	–	−0.03	–	−0.16	1.02
1-Bromohexane	130–170	(2)	935.4	3.28	φ	17.5	–	−0.15	–	φ	1.28
1-Bromoheptane	130–170	(2)	1036.3	3.38	φ	17.6	–	−0.20	–	φ	0.88
1-Cyanoalkanes											
1-Cyanopropane	90–170	(4)	593.8	1.24	φ	53.7	2.5	−1.40	4.16	φ	0.94
1-Cyanobutane	90–170	(4)	697.0	1.54	φ	53.7	4.4	−2.13	1.13	φ	1.34
1-Cyanopentane	90–170	(4)	798.8	1.67	φ	55.1	4.1	−2.18	1.26	φ	1.08
1-Cyanohexane	90–170	(4)	899.8	1.60	φ	55.0	4.2	−1.73	1.05	φ	1.13
1-Cyanoheptane	130–170	(2)	1000.7	1.80	φ	60.2	–	−1.17	–	φ	0.62
1-Nitroalkanes											
Nitroethane	90–170	(4)	571.9	1.62	φ	39.4	9.9	−0.88	0.36	φ	1.17
1-Nitropropane	90–170	(4)	664.6	1.98	φ	38.4	9.1	−1.40	0.87	φ	1.29
1-Nitrobutane	90–170	(4)	767.0	2.19	φ	39.7	8.3	−1.37	1.00	φ	1.15
1-Nitropentane	90–170	(4)	868.6	2.26	φ	41.8	6.7	−1.01	0.78	φ	1.42
1-Nitrohexane	130–170	(2)	970.1	2.38	φ	48.5	–	−0.55	–	φ	0.64
1-Acetoxyalkanes											
1-Acetoxypropane	90–170	(4)	639.8	−0.56	φ	45.8	−3.8	−2.12	1.14	φ	1.16
1-Acetoxybutane	90–170	(4)	741.0	−0.54	φ	46.7	−3.7	−2.21	1.28	φ	1.06
1-Acetoxypentane	90–170	(4)	841.3	−0.53	φ	47.8	−4.1	−1.88	0.97	φ	1.07
1-Acetoxyhexane	130–170	(2)	940.5	−0.28	φ	44.2	–	−1.17	–	φ	2.21
1-Acetoxyheptane	130–170	(2)	1040.4	−0.23	φ	44.1	–	−1.20	–	φ	2.47

(*Continued on p. 198*)

TABLE II *(continued)*

Solute	Experimental conditions		I_{130}	$d_T \cdot 10$ (K^{-1})	$d_{TT} \cdot 10^3$ (K^{-2})	d_L	d_{LL}	$d_{LT} \cdot 10$ (K^{-1})	$d_{LLT} \cdot 10$ (K^{-1})	$d_{LTT} \cdot 10^3$ (K^{-2})	Δ_{95}
	T (°C)	L^a									
1-Alkanols											
1-Butanol	90–170	(4)	596.7	0.97	1.32	57.6	12.0	−6.43	ϕ	4.59	2.84
1-Pentanol	90–170	(4)	700.0	0.85	0.76	60.6	10.7	−6.39	ϕ	5.29	2.75
1-Hexanol	90–170	(4)	801.6	0.98	0.77	63.5	9.1	−6.46	ϕ	5.37	2.78
1-Heptanol	130–170	(2)	903.2	1.33	ϕ	73.2	–	−4.51	–	ϕ	4.19
1-Octanol	130–170	(2)	1004.1	1.35	ϕ	73.5	–	−4.55	–	ϕ	4.34
2-Alkanols											
2-Butanol	90–170	(4)	549.7	0.75	0.20	46.7	12.3	−5.38	ϕ	4.94	3.40
2-Pentanol	90–170	(4)	647.8	0.87	0.38	50.3	9.5	−5.67	ϕ	4.63	3.10
2-Hexanol	90–170	(4)	747.3	0.90	0.31	53.6	8.0	−5.73	ϕ	4.74	3.00
2-Heptanol	90–170	(4)	837.2	0.99	0.33	55.7	6.9	−5.80	ϕ	4.82	2.94
2-Octanol	110–170	(2)	948.8	1.01	ϕ	63.6	–	−4.46	–	ϕ	3.58
2-Methylalkan-2-ols											
2-Methylbutanol-2	90–170	(4)	600.2	1.19	1.20	50.2	5.9	−5.30	ϕ	3.38	3.11
2-Methylpentanol-2	90–170	(4)	691.9	0.92	1.10	51.4	5.4	−5.22	ϕ	3.21	3.07
2-Methylhexanol-2	90–170	(4)	787.0	0.94	1.05	53.3	4.6	−5.26	ϕ	3.28	2.92
2-Methylheptanol-2	90–170	(4)	884.7	0.97	1.05	55.1	3.4	−5.31	ϕ	3.15	3.04
Thiols											
Butanethiol	90–170	(2)	722.5	3.15	−1.11	19.3	–	0.23	–	2.05	5.52
Pentanethiol	90–170	(2)	823.8	3.22	−0.89	18.1	–	0.59	–	2.25	2.00
Hexanethiol	130–170	(2)	924.7	2.83	ϕ	17.7	–	1.57	–	ϕ	1.00
Heptanethiol	130–170	(2)	1024.5	3.00	ϕ	18.5	–	1.45	–	ϕ	2.29
2-Alkanones											
2-Pentanone	90–170	(4)	631.6	0.77	0.66	47.9	ϕ	−3.32	1.98	−0.92	1.05
2-Hexanone	90–170	(4)	732.8	0.79	0.63	49.5	ϕ	−3.34	2.04	−0.93	0.99
2-Heptanone	90–170	(4)	832.8	0.88	0.68	50.2	ϕ	−3.57	2.27	−0.98	1.06
2-Octanone	130–170	(2)	932.6	1.25	ϕ	50.6	–	−1.75	–	ϕ	1.03
2-Nonanone	130–170	(2)	1032.7	1.23	ϕ	50.8	–	−1.78	–	ϕ	0.76
Ethers											
Dipropyl ether	90–170	(4)	657.1	0.29	0.58	17.1	0.8	−2.65	1.67	−0.79	1.08
Dibutyl ether	90–170	(4)	854.5	0.10	0.30	20.4	−2.1	−1.87	1.22	−0.64	0.61
Dipentyl ether	130–170	(2)	1051.1	0.20	ϕ	18.9	–	−0.85	–	ϕ	0.50

Halogenomethanes											
Dichloromethane	90–170	(4)	508.0	1.70	ϕ	15.9	9.9	0.05	ϕ	ϕ	1.87
Trichloromethane	90–170	(4)	610.1	2.57	ϕ	16.4	9.2	−0.47	ϕ	ϕ	1.25
Tetrachloromethane	90–170	(4)	680.2	3.07	ϕ	3.1	5.5	−0.02	ϕ	ϕ	0.91
Aldehydes											
Pentanal	90–170	(2)	651.6	1.12	−0.84	40.5	–	−2.17	–	1.80	3.50
Hexanal	90–170	(2)	751.8	1.17	−0.36	42.4	–	−1.98	–	1.13	1.41
Heptanal	90–170	(2)	852.7	1.26	−0.21	43.2	–	−1.89	–	1.04	0.93
Octanal	110–170	(2)	953.3	1.36	ϕ	43.8	–	−1.60	–	ϕ	0.67
Halogenobenzenes											
Fluorobenzene	90–170	(2)	666.4	2.49	ϕ	17.7	–	−0.07	–	ϕ	1.76
Chlorobenzene	90–170	(2)	865.7	4.46	ϕ	19.8	–	−0.04	–	ϕ	1.29
Bromobenzene	90–170	(2)	960.9	5.63	ϕ	21.5	–	0.04	–	ϕ	0.91
Alkylpyridines											
Pyridine	90–170	(4)	725.5	3.47	0.82	66.9	−1.3	−6.17	2.90	ϕ	2.22
2-Picoline	90–170	(4)	803.4	2.99	1.04	72.9	−6.6	−6.98	3.33	ϕ	1.93
3-Picoline	90–170	(4)	846.0	3.73	1.04	76.6	−3.1	−7.25	3.34	ϕ	2.16
4-Picoline	90–170	(4)	845.1	3.79	1.21	81.1	−4.0	−8.02	3.83	ϕ	2.49
2,3-Lutidine	130–170	(2)	936.6	3.70	ϕ	70.6	–	−3.85	–	ϕ	0.36
2,4-Lutidine	130–170	(2)	921.8	3.03	ϕ	76.7	–	−4.48	–	ϕ	0.88
2,5-Lutidine	130–170	(2)	921.3	3.30	ϕ	71.9	–	−4.05	–	ϕ	2.46
2,6-Lutidine	130–170	(2)	873.8	2.25	ϕ	62.6	–	−3.68	–	ϕ	2.46
3,4-Lutidine	130–170	(2)	988.1	4.55	ϕ	86.0	–	−4.98	–	ϕ	1.41
3,5-Lutidine	130–170	(2)	966.1	3.88	ϕ	80.7	–	−4.61	–	ϕ	3.34
2-Ethylpyridine	130–170	(2)	888.5	3.35	ϕ	57.2	–	−2.95	–	ϕ	1.05
3-Ethylpyridine	130–170	(2)	928.9	4.18	ϕ	73.0	–	−3.83	–	ϕ	1.23
4-Ethylpyridine	130–170	(2)	943.4	4.10	ϕ	76.9	–	−4.07	–	ϕ	0.71
2-Propylpyridine	130–170	(2)	976.8	3.35	ϕ	56.4	–	−2.87	–	ϕ	3.51
4-Propylpyridine	130–170	(2)	1033.6	4.38	ϕ	76.0	–	−3.90	–	ϕ	2.64
sym-Collidine	130–170	(2)	988.2	2.30	ϕ	72.3	–	−4.23	–	ϕ	1.41
2,3,6-Collidine	130–170	(2)	1002.2	2.80	ϕ	66.3	–	−3.95	–	ϕ	0.36
4-*t*-Butylpyridine	130–170	(2)	1069.8	4.78	ϕ	76.7	–	−3.98	–	ϕ	0.19
3-Chloropyridine	110–170	(2)	886.7	4.57	ϕ	47.9	–	−1.59	–	ϕ	0.93
Silane derivatives											
Hexamethyldisilane	90–170	(2)	686.2	0.27	ϕ	−0.3	–	−0.07	–	ϕ	1.82
Hexamethyldisiloxane	90–170	(2)	597.8	−2.49	ϕ	0.2	–	−0.11	–	ϕ	2.54

(*Continued on p. 200*)

TABLE II *(continued)*

Solute	Experimental conditions		I_{130}	$d_T \cdot 10$ (K^{-1})	$d_{TT} \cdot 10^3$ (K^{-2})	d_L	d_{LL}	$d_{LT} \cdot 10$ (K^{-1})	$d_{LLT} \cdot 10$ (K^{-1})	$d_{LTT} \cdot 10^3$ (K^{-2})	Δ_{95}
	T (°C)	L^a									
Primary amines											
Butylamine	90–170	(2)	610.4	0.84	0.57	71.4	–	−5.36	–	−3.52	19.96
Pentylamine	90–170	(2)	713.8	0.76	0.14	68.1	–	−5.83	–	2.36	8.18
Hexylamine	90–170	(2)	815.6	0.89	0.41	66.7	–	−5.83	–	4.18	4.58
Heptylamine	130–170	(2)	917.5	0.95	ϕ	66.2	–	−3.85	–	ϕ	2.22
Secondary amines											
Diethylamine	90–170	(2)	555.8	−0.25	−1.27	55.1	–	−5.51	–	4.98	1.78
Dipropylamine	90–170	(2)	743.6	0.19	−0.75	42.5	–	−4.26	–	3.02	1.03
Dibutylamine	130–170	(2)	943.0	0.18	ϕ	44.4	–	−3.61	–	ϕ	4.35
Tertiary amines											
Triethylamine	90–170	(2)	676.4	0.47	−0.64	29.6	–	−3.28	–	1.77	1.66
Tripropylamine	110–170	(2)	918.5	0.68	ϕ	10.2	–	−0.76	–	ϕ	1.03
Miscellaneous											
Tetrahydrofuran	90–170	(4)	611.3	1.99	ϕ	43.5	−4.9	−1.45	ϕ	ϕ	1.80
1,4-Dioxane	90–170	(4)	670.8	2.31	ϕ	50.1	−2.3	−1.20	ϕ	ϕ	1.59
Thiophene	90–170	(2)	685.6	3.57	ϕ	18.6	–	−0.11	–	ϕ	1.89
1,1,1-Trifluorodecane	110–170	(2)	922.1	−2.44	ϕ	9.5	–	0.01	–	ϕ	2.11
Miscellaneous cyclic compounds											
Cyclopentanone	90–170	(2)	743.5	3.00	ϕ	60.0	–	−1.59	–	ϕ	0.98
Cyclohexanone	90–170	(2)	857.2	4.52	ϕ	61.5	–	−1.77	–	ϕ	0.36
Cyclohexanol	110–170	(2)	855.3	4.05	ϕ	68.2	–	−4.72	–	ϕ	4.48
Cyclohexylamine	110–170	(2)	863.2	4.23	ϕ	72.1	–	−5.69	–	ϕ	3.74
Pyrrolidine	90–170	(2)	679.5	2.08	−1.21	78.3	–	−10.18	–	8.77	1.98
Piperidine	90–170	(2)	766.4	3.35	−0.96	72.1	–	−7.32	–	4.86	1.86
Miscellaneous aromatics											
Aniline	110–170	(2)	939.4	4.98	ϕ	59.1	–	−1.75	–	ϕ	0.95
Nitrobenzene	130–170	(2)	1053.9	5.48	ϕ	46.1	–	−0.53	–	ϕ	1.06
Benzylic alcohol	130–170	(2)	981.4	4.33	ϕ	89.7	–	−4.86	–	ϕ	5.38
2-Phenylethanol	130–170	(2)	1060.4	4.93	ϕ	85.2	–	−4.50	–	ϕ	3.28
Anisol	130–170	(2)	910.7	3.00	ϕ	28.3	–	−0.20	–	ϕ	2.12
Phenetol	130–170	(2)	979.6	2.43	ϕ	27.1	–	−0.25	–	ϕ	2.52

[a] $L = 2$: tested with the two pure phases. $L = 4$: tested with the two pure phases, as well as with the two mixtures (1:3; 2:3).

$$P_{\mathrm{L}} = 3\left(w - \frac{1}{2}\right) = \frac{1}{2}\{-3, -1, +1, +3\} \tag{19}$$

$$P_{\mathrm{LL}} = P_{\mathrm{L}}^2 - \frac{5}{4} = \{+1, -1, -1, +1\} \tag{20}$$

Substituting eqns. 16–20 into eqn. 15, and comparing with eqn. 12, we then obtain the d_x conversion coefficients, connected algebraically by the calculation method of the orthogonal polynomials, to b_x:

$$I_{130} = b_{\mathrm{o}} - 2\, b_{\mathrm{TT}} - \frac{3}{2}\, b_{\mathrm{L}} + b_{\mathrm{LL}} + 3\, b_{\mathrm{LTT}} - 2\, b_{\mathrm{LLTT}} \tag{21}$$

$$d_{\mathrm{T}} = \frac{1}{2}\, b_{\mathrm{T}} - 1.7\, b_{\mathrm{TTT}} - \frac{3}{4}\, b_{\mathrm{LT}} + \frac{1}{2}\, b_{\mathrm{LLT}} \tag{22}$$

$$d_{\mathrm{TT}} = \frac{1}{4}\, b_{\mathrm{TT}} - \frac{3}{8}\, b_{\mathrm{LTT}} + \frac{1}{4}\, b_{\mathrm{LLTT}} \tag{23}$$

$$d_{\mathrm{TTT}} = \frac{1}{8}\, b_{\mathrm{TTT}} \tag{24}$$

$$d_{\mathrm{L}} = 3\, b_{\mathrm{L}} - 9\, b_{\mathrm{LL}} - 6\, b_{\mathrm{LTT}} + 18\, b_{\mathrm{LLTT}} \tag{25}$$

$$d_{\mathrm{LL}} = 9\, b_{\mathrm{LL}} - 18\, b_{\mathrm{LLTT}} \tag{26}$$

$$d_{\mathrm{LT}} = \frac{3}{2}\, b_{\mathrm{LT}} - \frac{9}{2}\, b_{\mathrm{LLT}} \tag{27}$$

$$d_{\mathrm{LLT}} = \frac{9}{2}\, b_{\mathrm{LLT}} \tag{28}$$

$$d_{\mathrm{LTT}} = \frac{3}{4}\, b_{\mathrm{LTT}} - \frac{9}{4}\, b_{\mathrm{LLTT}} \tag{29}$$

$$d_{\mathrm{LLTT}} = \frac{9}{4}\, b_{\mathrm{LLTT}} \tag{30}$$

The treatment by orthogonal polynomials gives us a variance analysis. Each coefficient of eqn. 12 is thus examined separately for the significance of its effect. Although all the solutes are considered individually, the coefficients with a significant effect are taken into consideration with regard to a global analysis at the chemical family level. The coefficient is accepted as long as the significance level is within 5% of the maximum for each source and for at least half the solutes of a single family. The variance of each source is tested not against the total residue after the elimination of ten

b_x coefficients, but on the residual variance of the LT source having still $8 = [(4 - 1) \times (5 - 1)] - 4$ degrees of freedom. The test allows a b_x effect to be retained when the $F_{1/8}$ is greater or equal to 5.

For the cases of the incompletely measured solutes, that is on only two phases and at three temperatures (130.0–170.0°C) or four temperatures (110.0–170.0°C), only the treatment on each of the two phases taken separately was considered. The variance analysis considered only the T source effects. Consideration of the complete chemical family assumes that the effects of the T and LT sources are the same for each of its members. In this case, the coefficient $d_{LT} = d_T(C_{77}\text{-OH}) - d_T(C_{78})$ and $d_{LTT} = d_{TT}(C_{77}\text{-OH}) - d_{TT}(C_{78})$. Only the LL and LLT sources are not accessible for these incomplete situations (Table II).

DISCUSSION

From the measurements of the indices, some examples can be extracted. In Fig. 1, the difference in behaviour of solutes on the two pure stationary phases is compared. The retention index of 1-cyanopropane, a rather non-polar solute, increases linearly with temperature, whereas I values are higher on C_{77}-OH, because of the interactions, as expected. For a polar solute like 1-butanol, I is similar to that of the cyano compound on C_{78}, but on C_{77}-OH its behaviour is quite different, because I decreases with temperature.

At a constant temperature such as $T = 130°C$, as shown in Fig. 2, I increases going from a non-polar to a polar stationary phase. I of both of the two solutes increases as the polar phase concentration increases.

The two graphs in Figs. 3 and 4 show that the solutes can have very different behaviour when the phase composition is modified. If the solute is 1-cyanopropane (Fig. 3), I increases linearly with the temperature whatever the stationary phase composition w may be.

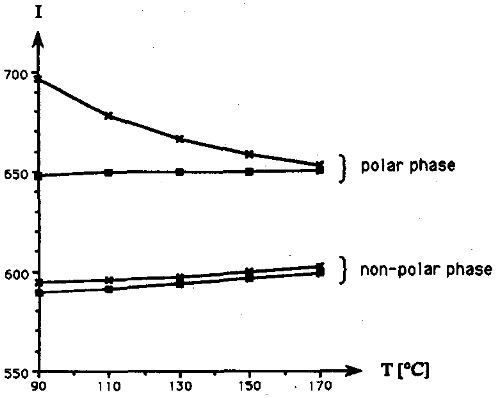


Fig. 1. I values as a function of column temperature (90, 110, 130, 150 and 170°C) on the pure stationary phases. Solutes: ■ = 1-cyanopropane; x = 1-butanol.

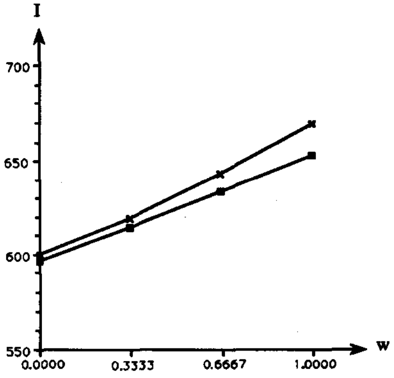
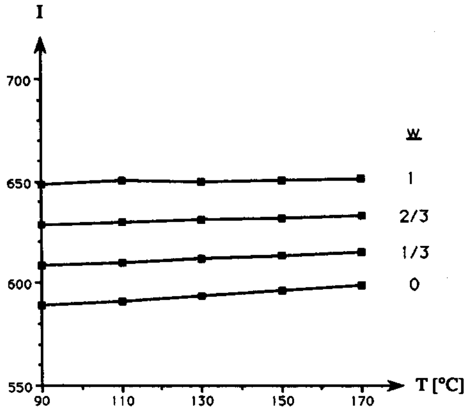


Fig. 2. I values as a function of w = stationary phase composition, at constant temperature $T = 130°C$. Solutes: ■ = 1-cyanopropane; x = 1-butanol.



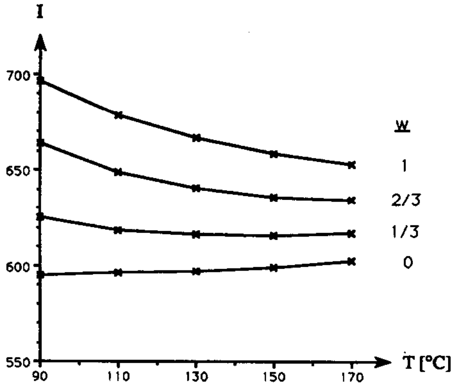


Fig. 3. *I* values as a function of column temperature (90, 110, 130, 150 and 170°C). *w* is the stationary phase composition. Solute: 1-cyanopropane.

Fig. 4. *I* values as a function of column temperature (90, 110, 130, 150 and 170°C). *w* is the stationary phase composition. Solute: 1-butanol.

For 1-butanol as the solute (Fig. 4), *I* increases linearly with the temperature on C_{78} but decreases as *w* increases, *i.e.*, with increased polarity of the stationary phase.

In conclusion, we can say that the *I* values are well adapted for a comparison between two stationary phases.

All the above data can also be compressed and reduced to an explicit three-dimensional diagram [10] using *I*, *T* and *w* as coordinates.

CONCLUSIONS

It should be noted that the results of the investigation on column packings prepared with two pure substances combined in different proportions allow the characterization of these two phases.

Finally, the retention indices obtained in this study will allow the determination of thermodynamic parameters useful for a further explanation of molecular interactions in gas chromatography [11].

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