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## CHARACTERIZATION OF POROUS POLYMER BEADS GAS CHROMATOGRAPHIC COLUMNS BY RETENTION INDEX VALUES OF ETHYLENE, ACETYLENE AND CARBON DIOXIDE

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### SUMMARY

Porapak N, P, Q, R, S and T and Chromosorb 101, 102, 103, 104, 105, 106, 107 and 108 porous polymer beads (PPBs) were characterized and listed in order of increasing "polarity" by determination of the retention index values of ethylene, acetylene and carbon dioxide with respect of the first terms of the alkane series. The values of  $\Delta I_Q(C_2H_2)$  (i.e. the difference in retention index of acetylene between any given PPB and the Porapak Q, taken as "less polar" reference term) increase in the following order: Porapak Q < Chromosorb 106 and 102 < Porapak P < Chromosorb 101 < Porapak S < Chromosorb 103 and 105 < Porapak K and N < Chromosorb 107 and 108 < Porapak T < Chromosorb 104 thus permitting a quantitative classification of the behaviour of PPB columns for the separation of gas mixtures. Values of  $\Delta I_Q(C_2H_4)$  and  $\Delta I_Q(CO_2)$  show similar trends, with small variations due to the chemical composition and structure of the beads.

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### INTRODUCTION

The gas chromatographic (GC) applications of porous polymer beads (PPBs) as synthetic sorbents are numerous and cover a wide variety of compounds having different polarities. The analysis of gas mixtures takes great advantages from the use of these stationary phases, which widely replace the "classical" packings such as silica gel and alumina and which, by the use of long columns or low analysis temperatures, permit the separation of oxygen from nitrogen and argon, previously restricted to molecular sieves. The possibility of fast temperature programming with a minimum of baseline drift due to column bleeding, allows the analysis of complex mixtures of gases to be accomplished in short times. The wide choice offered to the GC user by the numerous types of PPBs available from different producers is very useful because a column can be tailored for a given separation problem in order to perform the best resolution in the shortest time. However the wideness of the choice may be confusing as a general classification of the polarity of the various PPB has not yet been achieved.

In previous papers<sup>1,2</sup> the characterization of Porapak and Chromosorb "Century series" PPBs has been made by analysis of gaseous mixtures, and the values of

$\Delta H^0$  for the various compounds ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}_2$ ) were calculated. The use of the  $\alpha_{\text{C}_2\text{H}_4}$  values (retention time relative to ethylene), whose measurement is simple with respect of the determination of the thermodynamic functions, permitted the evaluation of the batch-to-batch reproducibility of the column behaviour, a semi-quantitative classification of the "polarity" of the various PPBs and a rough comparison between Porapak and Chromosorb sorbents. The use of a value relative to a unique reference substance (standard) is justified by its simplicity and by the fact that the retention time of ethylene depends less on temperature than those of other test substances (probes).

On the other hand, the validity of a unique reference standard decreases when the difference in retention times between the probes increases, and it must be taken into account that the change in  $\alpha_{\text{C}_2\text{H}_4}$  values can be due either to a real change in the retention of the probes or to a change in the retention of the standard<sup>3</sup>. The use of a homologous series of standard substances, e.g. linear alkanes as suggested by Kováts<sup>4</sup>, does not solve the latter problem, but gives a multiple reference for the determination of retention index values ( $I$ ) instead of retention relative to a unique standard ( $\alpha_{\text{C}_2\text{H}_4}$ ). The determination of the  $I$  values can also permit calculation of the  $\Delta I$  value with respect to a stationary phase taken as the "non-polar" reference and can give therefore a measure of the "polarity" of the various PPBs.

In order to obtain a common basis for the classification of the PPBs, the retention index values of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  with respect to the first members of the alkane homologous series were used, by employing a method similar to those suggested by Rohrschneider<sup>5</sup> and McReynolds<sup>6</sup> for the determination of the polarity of liquid stationary phases. The reference non-polar sorbent used was Porapak Q, because the retention index and  $\alpha$  values for this phase were the lowest for all the probes and sorbents tested. The classical non-polar reference term of Rohrschneider's and McReynold's method, squalane, obviously cannot be used as it does not separate the light hydrocarbons used and, in any case, its gas-liquid chromatographic interaction mechanism differs from those of porous sorbents, for which at low temperatures adsorption phenomena predominate over solution mechanisms.

## EXPERIMENTAL

Stainless-steel columns (3 m  $\times$  2.4 mm I.D.) were packed with known amounts of Porapak or Chromosorb "Century series" PPBs, 80-100 mesh. The types of PPBs tested are listed in Table I, with the chemical composition, surface area and pore sizes, when available<sup>7-9</sup>.

A thermal conductivity detector (Varian 3760) was used, with helium as the carrier gas (flow-rate, 22 ml min<sup>-1</sup>). The column temperature was set at temperatures ranging between  $30 \pm 0.1$  and  $70 \pm 0.2^\circ\text{C}$  and monitored by digital and precision mercury thermometers. Samples of gas mixtures were prepared in glass syringes and injected by using a gas-sampling valve directly connected to the column inlet, in order to reduce the dead volume. Dilution of the sample with helium split from the carrier gas line permitted the introduction of very small amounts of each test compound, in order to give small and symmetrical peaks. Fig. 1 shows the layout of the sampling system. Retention times and peak areas were measured with a Varian CDS-111 C data system. The dead time was taken as being equal to the retention time of hydro-

gen, corresponding to that of helium within the accuracy limit of the data system ( $\pm 0.01 \text{ min}$ )<sup>10</sup>.

## RESULTS AND DISCUSSION

Figs. 2 and 3 show the behaviour of the  $I$  values on the various PPB columns over the temperature range 30–70°C. The dependence of  $I$  values on temperature was found to be linear, as a consequence of the linear dependence of  $\ln V_N$  values\* on temperature<sup>1,2</sup>. Table II shows the slope  $h$  and the intercept  $k$  of the equation

$$I = h \cdot \frac{1}{T} + k \quad (1)$$

from which the values of  $I$  at any temperature can be deduced. The intersection points, *i.e.* the temperatures at which two given compounds have the same retention index, can be calculated by solving a system of equations of the same type as eqn. 1. Of course, depending on the efficiency of the column, *i.e.* on the peak width at a given retention time ( $t'_R$ ), satisfactory resolution can only be achieved when the retention index values of two compounds differ more than 5–10 index units.

The  $I$  values of the probes fall within 150 and 200, except for  $C_2H_2$  on Porapak N, R and T and Chromosorb 104, 107 and 108 and for  $CO_2$  on Chromosorb 104. While  $C_2H_2$  on Porapak R and  $CO_2$  on Chromosorb 104 are eluted so close to  $C_2H_6$  that extrapolation of the retention index formula used (eqn. 2) gives suitable values, with the results having a deviation smaller than one index unit, the  $I$  values for  $C_2H_2$  on Porapak N and T and on Chromosorb 104, 107 and 108 may be correctly calcu-

TABLE I

CHEMICAL COMPOSITION, SURFACE AREA AND PORE SIZE OF THE TESTED PPBS (FROM REFS. 7-9 AND FROM MANUFACTURERS' CATALOGUES)

Sty = Styrene; DVB = divinylbenzene; EVB = ethylvinylbenzene; EGDMA = ethylene glycol dimethacrylate; ACN = acrylonitrile.

PPB	Composition	Surface area ( $m^2/g$ )	Average pore diameter ( $\text{Å}$ )
Porapak N	Vinylpyrrolidone	225–350	—
Porapak P	Sty-DVB	100–200	—
Porapak Q	EVB-DVB	500–600	75
Porapak R	Vinylpyrrolidone	450–600	76
Porapak S	Vinylpyridine	300–450	76
Porapak T	EGDMA	250–350	91
Chromosorb 101	Sty-DVB	< 50	3500
Chromosorb 102	Sty-DVB	300–400	85
Chromosorb 103	Polystyrene	15–25	3500
Chromosorb 104	ACN-DVB	100–200	700
Chromosorb 105	Acrylic ester	600–700	500
Chromosorb 106	Polystyrene	700–800	50
Chromosorb 107	Acrylic ester	400–500	80
Chromosorb 108	Crosslinked acrylic	100–200	250

\*  $V_N$  is the net retention volume calculated by multiplying the pressure gradient correction factor of James and Martin by the adjusted retention volume  $V'_R$ .

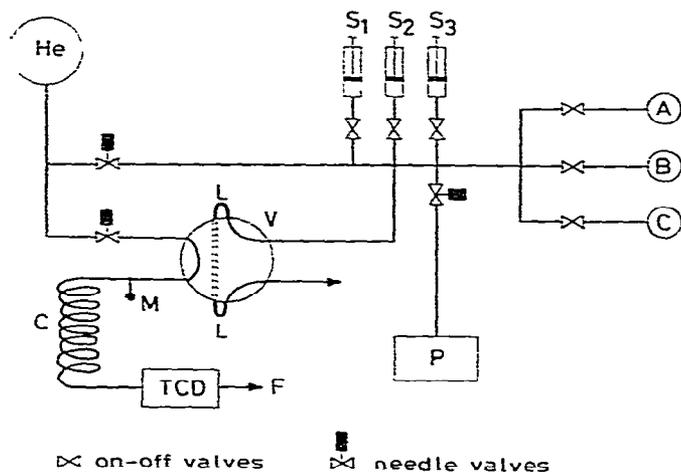


Fig. 1. Schematic diagram of the manifold used for preparation and injection of samples. He = carrier gas; V = rotary-type gas-sampling valve; LL = calibrated loop; M = connection point of the measure of inlet pressure; C = column; TCD = detector; F = carrier gas outlet to flow meters; A, B, C = reservoirs of standard gases; S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> = gas-tight and calibrated glass syringes for preparation and dilution of standard mixtures; P = vacuum pump. Thermostating ovens and electronic modules are not shown.

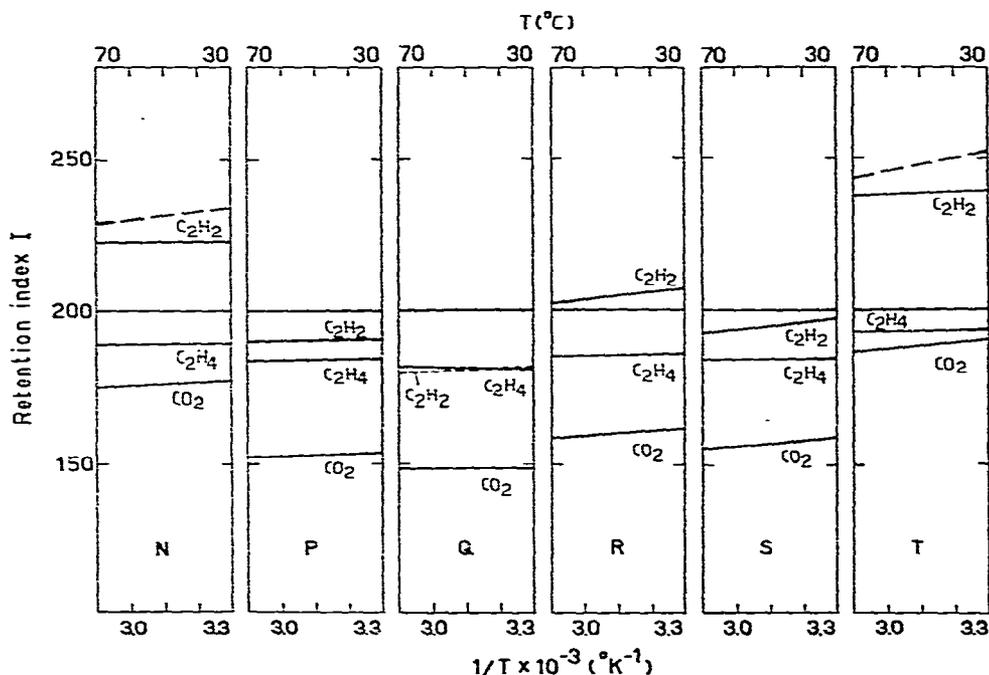


Fig. 2. Retention index values (interpolated between CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> as a function of temperature on various Porapak PBs (80–100 mesh). Column 3 m × 1/8 in. I.D.; helium flow-rate, 22 ml min<sup>-1</sup>; dashed lines, *I* values of C<sub>2</sub>H<sub>2</sub> interpolated between C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>.

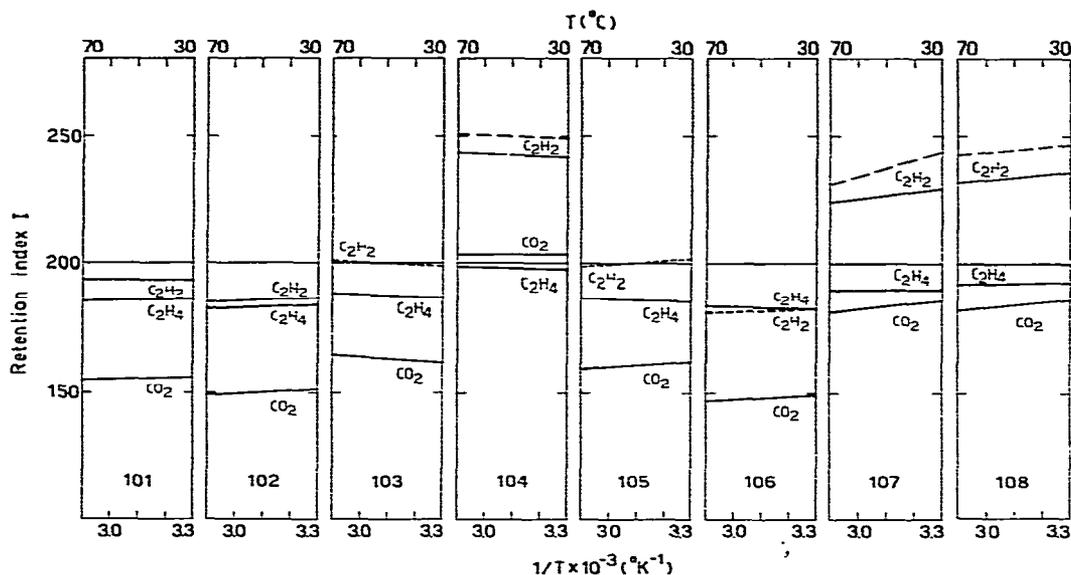


Fig. 3. Retention index values of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  as a function of temperature on various Chromosorb "century series" PPBs. Conditions and symbols as in Fig. 2.

lated by using  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  as standard compounds. The linearity of the plot of  $\ln I'_R$  as a function of the number of C atoms in a homologous series of compounds often shows deviations when the lowest members on the series are considered; this phenomenon was also previously observed for *n*-alcohols of PPB columns<sup>7</sup>. The deviation

TABLE II

VALUES OF THE SLOPE ( $h$ ) AND INTERCEPT ( $k$ ) OF THE EQUATION  $I = h \cdot 1/T + k$ , FOR  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  AND  $\text{C}_2\text{H}_2$ , ON VARIOUS PORAPAK AND CHROMOSORB COLUMNS, IN THE RANGE 30–70°C

Carrier gas, helium; flow-rate, 22 ml min<sup>-1</sup>.

Column	$\text{CO}_2$		$\text{C}_2\text{H}_4$		$\text{C}_2\text{H}_2$	
	$h$	$k$	$h$	$k$	$h$	$k$
Porapak N	7.7	152.6	0.047	189.7	10.9	187.7
Porapak P	7.2	130.7	4.3	171.0	2.9	181.7
Porapak Q	0.1	148.4	-5.5	199.2	4.3	168.2
Porapak R	8.8	132.2	0.0	186.1	10.9	171.0
Porapak S	9.0	128.8	3.4	173.7	9.8	165.3
Porapak T	12.3	150.5	0.0	193.3	0.0	238.5
Chromosorb 101	4.4	141.9	2.2	178.8	1.4	189.3
Chromosorb 102	0.0	150.4	1.8	177.7	-2.8	194.9
Chromosorb 103	-8.6	190.4	-4.2	200.5	-4.4	213.5
Chromosorb 104	-0.08	203.8	-2.2	204.9	-4.7	257.3
Chromosorb 105	7.9	136.3	-3.5	196.8	7.9	175.7
Chromosorb 106	0.02	147.6	-1.7	188.3	4.9	166.6
Chromosorb 107	0.16	181.5	0.13	189.6	0.13	185.5
Chromosorb 108	11.05	149.4	9.12	196.3	-9.37	205.6

from linearity of the  $\ln t'_R$  values of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  is very small over the temperature range considered (Fig. 4 shows the dependence on temperature and on number of carbon atoms for Porapak N and T and Chromosorb 104, 107 and 108) but large enough to cause appreciable differences in the  $I$  values for  $\text{C}_2\text{H}_2$ , depending on the reference compounds used as standards.

$$I(x) = \frac{\ln t'_R(x) - \ln t'_R(\text{CH}_4)}{\ln t'_R(\text{C}_2\text{H}_6) - \ln t'_R(\text{CH}_4)} \cdot 100 + 100 \quad (2)$$

The dashed lines in Figs. 2 and 3 show the  $I$  values of  $\text{C}_2\text{H}_2$  calculated by interpolation between  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ .

A correct application of the Kovats' retention index concept requires the interpolation between two members of the alkane series, and therefore the  $I(\text{C}_2\text{H}_2)$  values calculated by using  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  should be chosen for Porapak N and T and for Chromosorb 104, 107 and 108, but, owing the long retention time of  $\text{C}_3\text{H}_8$ , only reference to  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  is rapid and precise enough for practical purposes.

From the  $I$  values, values of  $\Delta I_Q$  (the difference between the  $I$  value of a particular PPB and that of Porapak Q) were calculated. These are shown (at 30 and 70°C) in Table III, in order of increasing  $\Delta I_Q(\text{C}_2\text{H}_2)$ , and correspond reasonably well with the empirical order of polarity given by the manufacturers and found by several authors for the two series of PPBs.

Except for Porapak R and Chromosorb 103, 105, 107 and 108, which have very similar values,  $\Delta I_Q(\text{CO}_2)$  follows the same order as  $\Delta I_Q(\text{C}_2\text{H}_2)$  while  $\Delta I_Q(\text{C}_2\text{H}_4)$  shows fluctuations at lower values and is generally smaller than the  $\Delta I_Q$  value of other probes. This is in accord with the small influence that changing the analytical param-

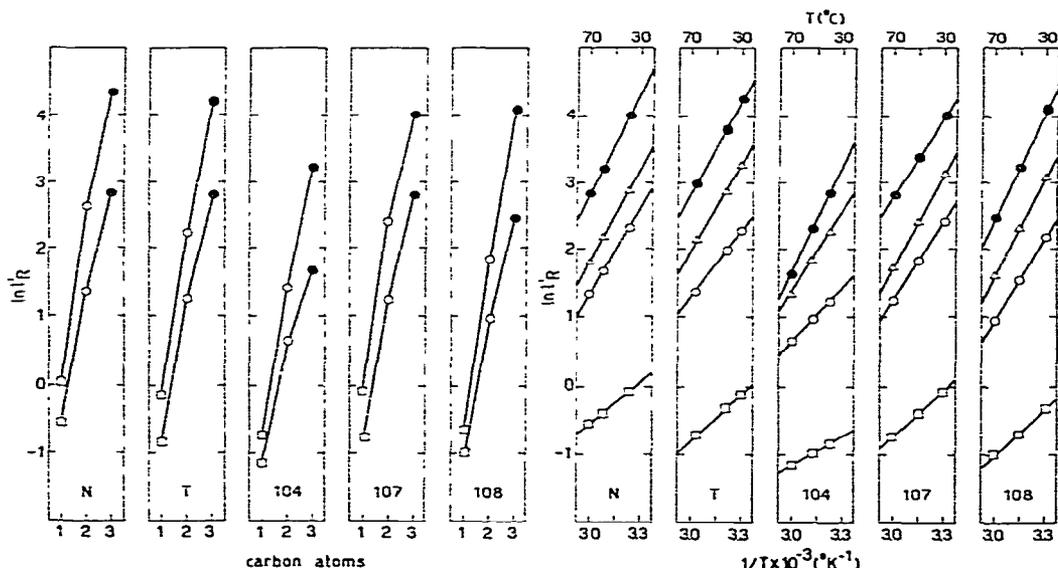


Fig. 4. Linearity of  $\ln t'_R$  (min) values as a function of the number of carbon atoms for light paraffins (left) and as a function of temperature for light paraffins and acetylene (right). Conditions as in Fig. 2. Plots:  $\square$  = methane;  $\circ$  = ethane;  $\bullet$  = propane;  $\triangle$  = acetylene.

TABLE III

$\Delta I_Q$  VALUES WITH RESPECT TO PORAPAK Q (REFERENCE "LESS POLAR" COLUMN) FOR  $C_2H_2$ ,  $C_2H_4$  AND  $CO_2$  AT 30 AND 70°C

All  $I$  values calculated by reference to  $CH_4$  and  $C_2H_6$  retention times. In parentheses are the  $\Delta I_Q(C_2H_2)$  values referred to  $C_2H_6$  and  $C_3H_8$ .

Porapak or Chromosorb type	$C_2H_2$		$C_2H_4$		$CO_2$	
	30°C	70°C	30°C	70°C	30°C	70°C
Q	0	0	0	0		0
106	0.46	0.44	1.77	0.92	0.04	0.02
102	4.52	4.80	2.83	0.33	2.51	0.31
P	8.62	9.77	4.01	1.81	5.72	3.56
101	11.3	13.2	5.08	2.77	8.07	6.19
S	14.9	12.4	3.70	1.93	9.99	6.12
103	16.5	20.8	5.56	6.04	13.4	16.1
105	19.4	18.4	4.53	3.90	13.9	10.6
R	24.8	22.2	5.37	3.04	12.8	9.4
N	40.0	42.1	8.74	7.18	29.3	26.4
	(51.6)	(48.5)				
107	47.0	43.5	8.33	7.52	37.6	32.6
	(57.1)	(49.3)				
108	51.5	51.7	10.6	9.44	36.8	32.7
	(63.3)	(61.8)				
T	57.4	57.1	12.5	10.8	42.2	38.1
	(69.6)	(62.5)				
104	59.3	63.0	16.9	15.9	55.0	54.7
	(66.6)	(70.5)				

ters has on the retention behaviour of  $C_2H_4$ , as has been previously observed, and justifies the choice of this hydrocarbon as reference compound for the calculation of the  $\alpha_{C_2H_2}$  values<sup>1,2,10</sup>.

Fig. 5 shows the  $\Delta I(C_2H_2)$  and  $\Delta I_Q(C_2H_4)$  values plotted at 30°C as a function of  $\Delta I_Q(CO_2)$ .

Linear correlation were also found by plotting  $\Delta I_Q(C_2H_2)$  as a function of  $\Delta I_Q(C_2H_4)$ . Table IV shows the intercept  $a$  and the angular coefficient  $b$  of eqns. 3–5

$$\Delta I_Q(C_2H_2) = a_1 + b_1 \cdot \Delta I_Q(CO_2) \quad (3)$$

$$\Delta I_Q(C_2H_4) = a_2 + b_2 \cdot \Delta I_Q(CO_2) \quad (4)$$

$$\Delta I_Q(C_2H_2) = a_3 + b_3 \cdot \Delta I_Q(C_2H_4) \quad (5)$$

at 30 and 70°C, and the corresponding values of the correlation coefficient  $r$ , calculated by using the  $\Delta I_Q$  values of the Porapak, the Chromosorb and all the PPBs together. Values in parentheses are obtained by using in the least-squares calculation the  $I(C_2H_2)$  values interpolated between  $C_2H_6$  and  $C_3H_8$ . Notwithstanding the small number of experimental points, the linearity of the plots, as shown by the values of the correlation coefficient  $r$ , is good and does not change appreciably with temperature. The values of  $r$  calculated when the  $\Delta I_Q$  values obtained from both types of PPB

TABLE IV  
VALUES OF INTERCEPT (*a*), SLOPE (*b*) AND CORRELATION COEFFICIENT (*r*) OF EQNS. 3-5  
In parentheses are values calculated with  $M_0$  values interpolated between  $C_2H_6$  and  $C_3H_8$ .

Parameter	Parapak		Chromosorb		Parapak + Chromosorb	
	30°C	70°C	30°C	70°C	30°C	70°C
$a_1$	3.56 (0.22)	6.04 (5.07)	1.23 (1.41)	4.66 (4.04)	2.72 (1.54)	4.88 (4.20)
$b_1$	1.28 (1.68)	1.36 (1.55)	1.17 (1.36)	1.16 (1.35)	1.19 (1.45)	1.23 (1.42)
$r_1$	0.99 (0.996)	0.995 (0.995)	0.98 (0.97)	0.98 (0.97)	0.98 (0.97)	0.98 (0.97)
$a_2$	2.05	0.54	1.93	0.82	1.66	0.60
$b_2$	0.24	0.26	0.24	0.26	0.25	0.27
$r_2$	0.99	0.997	0.96	0.98	0.97	0.99
$a_3$	-6.71 (-13.15)	3.38 (2.09)	-3.69 (-5.30)	2.01 (1.10)	-3.06 (-4.90)	2.29 (1.93)
$b_3$	5.23 (6.86)	5.11 (5.84)	4.30 (5.06)	4.27 (4.92)	4.43 (5.32)	0.99
$r_3$	0.98 (0.99)	0.990 (0.990)	0.93 (0.90)	0.96 (0.94)	0.94 (0.92)	0.96 (0.95)

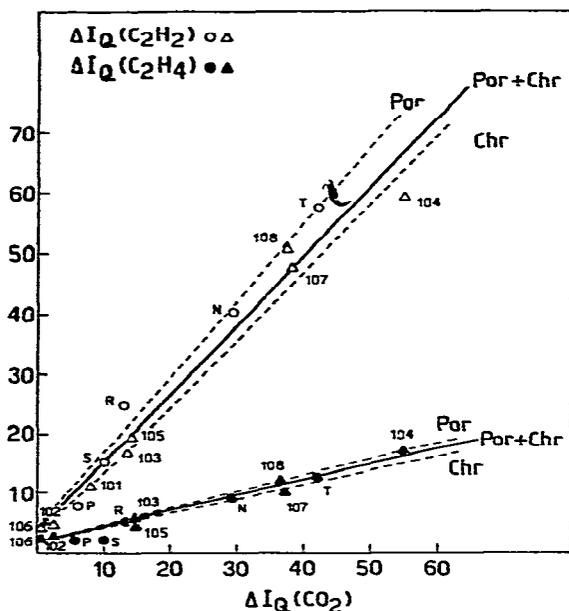


Fig. 5.  $\Delta I_Q(\text{C}_2\text{H}_2)$  and  $\Delta I_Q(\text{C}_2\text{H}_4)$  values at  $30^\circ\text{C}$  plotted as a function of the  $\Delta I_Q(\text{CO}_2)$  values. Straight lines are calculated by the method of least squares [eqns. (3) and (4)]. Dashed lines, calculated from  $\Delta I_Q$  values obtained on Porapak (O, ●) and Chromosorb ( $\Delta$ ,  $\blacktriangle$ ); full lines, calculated from  $\Delta I_Q$  values obtained on both PPBs.

are fitted together are lower, owing to the slight difference between the slopes on the Porapak and Chromosorb beads.  $\text{C}_2\text{H}_2$  is in fact better retained by Porapak-type beads than by the equivalent Chromosorb ones, in respect of  $\text{CO}_2$ . Use in the calculations of the values of  $\Delta I_Q(\text{C}_2\text{H}_2)$  obtained by interpolation yields greater slopes, as a consequence of the slight deviation from linearity of the plot of retention time vs. number of carbon atoms (see Fig. 4).

Comparison of Tables I and II shows that the lowest values of the retention index and, as a consequence, of  $\Delta I_Q$ , are shown by EVB-DVB polymers (Porapak Q). In the field of aromatic polymers, EVB-DVB beads are followed by Sty-DVB (Porapak P and Chromosorb 101 and 102) and cross-linked polystyrene (Chromosorb 103 and 106). When similar chemical compositions are given by the manufacturer, as in the case of Sty-DVB Chromosorb 101 and 102, of Polystyrene Chromosorb 103 and 106, and of acrylic Chromosorb 105, 107 and 108, the  $\Delta I_Q$  values increase with decreasing surface area and, except for Chromosorb 105, with increasing pore diameter.

No regular correlation was found between the  $\Delta I_Q$  values and the amount of crosslinking, equivalent to DVB content, as determined by pyrolysis gas chromatography of some Sty-DVB and crosslinked polystyrene polymers<sup>11</sup>: this gave the following values for copolymerized divinylbenzene: Chromosorb 101, 3%; Chromosorb 102, 3.5%; Porapak P, 4%; Chromosorb 103, 5%. The nitrogen-containing polymers show increasing  $\Delta I_Q$  values in the order Porapak S (vinylpyridine) < Porapak R and N (vinylpyrrolidone) < Chromosorb 104 (ACN-DVB). Also the two vinylpyrrolidone polymers show increasing  $\Delta I_Q$  values with decreasing surface area.

The two most polar PPBs (Porapak T and Chromosorb 104) have very similar behaviour, notwithstanding the different chemical composition, from the point of view of elution of acetylene and ethylene, while Chromosorb 104 is the only PPB which elutes CO<sub>2</sub> after ethane and ethylene.

#### CONCLUSIONS

Taking into account the fact that the calculation of the retention index values of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> can be accomplished easily at room temperature, the use of  $\Delta I_Q$  values permits the "polarity" of the various PPBs, previously known in a non-quantitative way, to be expressed with numerical values, in order to give a reproducible classification of the packings belonging to the same series or to different commercial types. Moreover, the similarities and differences between the Chromosorb and Porapak PPBs can be quantitatively measured and used for choosing the best packing for the analysis of a given gas mixture and for the calculation of mixed columns.

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