THE APPLICATION OF PRECISION GAS CHROMATOGRAPHY TO THE IDENTIFICATION OF TYPES OF HYDROCARBONS

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SUMMARY

It appears that under precisely controlled conditions retention indices of apolar substances on apolar stationary phases can be reproduced to 0.03 units. This permits the accurate measurement of the temperature coefficients of the KOVÁTS index for different classes of hydrocarbons. In this way classes of compounds having similar ΔI values ($I_{polar} - I_{apolar}$) may be distinguished. This is of particular importance because of the lower precision of the index data on polar stationary phases.

INTRODUCTION

The importance of the characterization of volatile substances by accurate gas chromatographic retention data cannot be emphasized enough, particularly since the sample requirements differ by orders of magnitude from the amounts needed by spectroscopic techniques. The amount of information obtained increases if more accurate data become available (number of distinguishable peaks between two adjacent *n*-alkanes). Apart from an increase in precision identification can be enhanced by using different temperatures or stationary phases.

RETENTION INDICES ON TWO PHASES OF DIFFERENT POLARITY

The use of ΔI (the difference in the retention index on polar and apolar phases) has already been introduced by KOVÁTS[1] as an aid to recognizing types of compound. ΔI depends on both the polarity of the compounds and the polarity of the different stationary phases.

Retention indices of a number of hydrocarbons measured in our laboratory[2] on octadecene-1 and dimethylsulfolane at 25° are plotted in Fig. 1. Capillary columns of 50 m length and 0.25 mm I.D. were used. It should be noted that all the saturated

paraffins are scattered around the line $I_A = I_P$. The alkenes form groups of branching isomers on overlapping parallel lines (the Roofing tile effect according to WALRAVEN et al.[3]).

The scattering of point around isomer lines is real (not caused by inaccurate measurements) and gives a relationship between more detailed structure and retention behavior. The fine structure is demonstrated in Fig. 2 (WALRAVEN[3]).
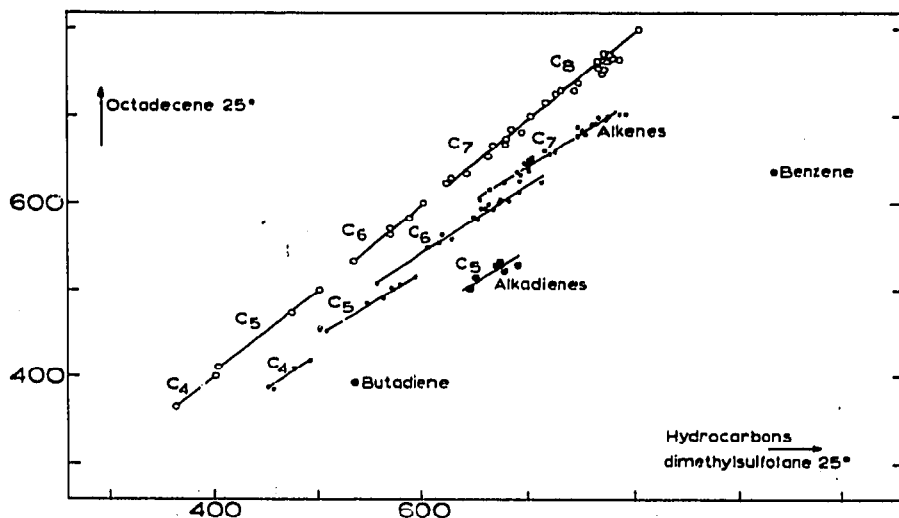

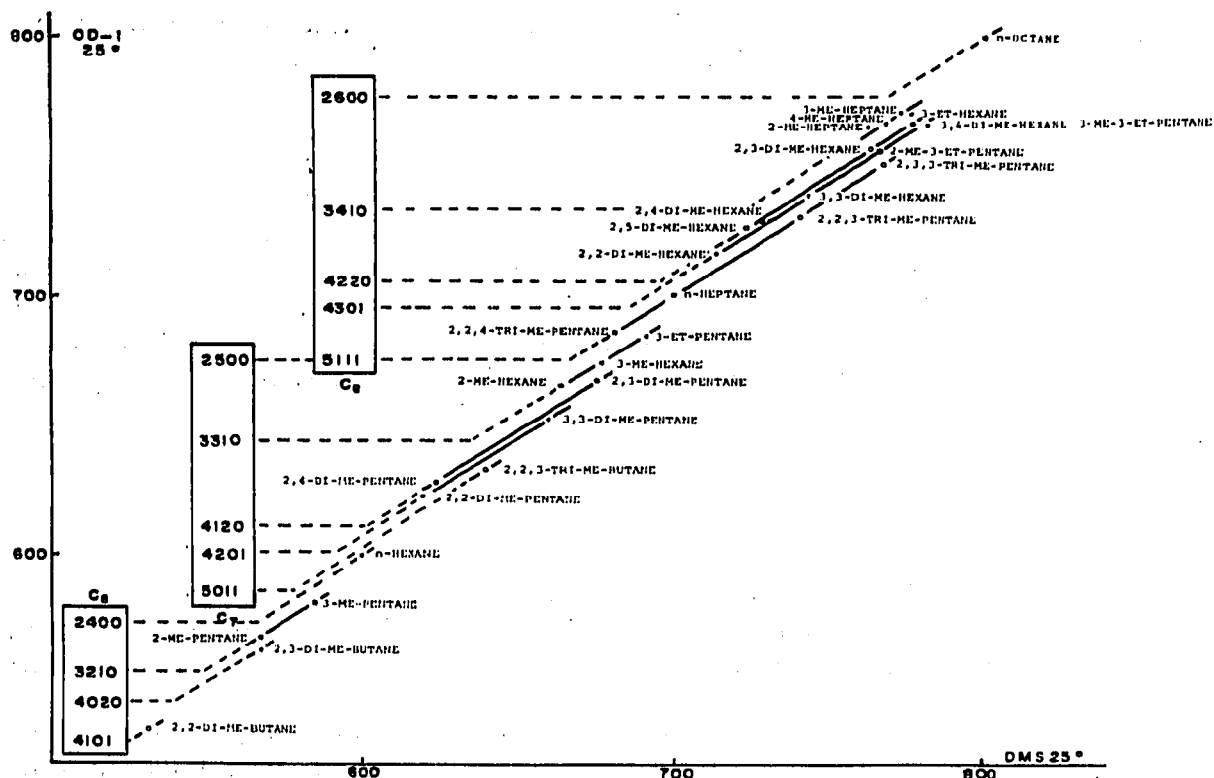Fig. 1. Retention index plot on two phases of different polarity.

Fig. 2. Fine structure of retention index plot.

THE TEMPERATURE DEPENDENCE OF THE RETENTION INDEX

One of the reasons favoring the use of the retention index in the collection of retention data is its weak temperature dependence. However, if extreme care is taken in the measurements of retention indices, at two not too distant temperatures, the value of dI/dT appears to given some additional analytical information.

This offers promising possibilities[4], particularly in the analysis of complex mixtures of apolar substances (like petroleum fractions). With a small temperature change, peak inversion is unlikely to occur and dI/dT values are relatively easy to collect. The opposite is true for ΔI values, where quantisation of the peaks involved is essential for identification.

COLLECTION OF RETENTION DATA

For future work, sets of collected retention data will be essential for identification purposes. A review of the literature, however, reveals a lack of agreement between different sources. For instance $I_{cyclohexane}$ on squalane as the stationary phase at 100[b] shows a discrepancy of 60 units! On this basis KOVÁTS was right in not expecting decimal places in his index system.

The observed discrepancies may be due to imperfect instrumentation (inaccuracies in temperature and flow control). Other reasons are the use of not very well defined stationary phases, or chemical changes in the stationary phase during use. Adsorption on the solid support is also an important source of error, especially if polar substances are run on a non-polar column.

Nonlinearity in the chromatographic process, caused by overloading or adsorption, results in concentration dependant retention times. Therefore, retention times obtained from asymmetric peaks were discarded in our work and the measurements were repeated with smaller samples. Another important factor is that, for several reasons, shifting of peak maxima will occur in the case of incomplete resolution.

For many of the reasons listed below, the use of capillary columns is becoming more and more important. (High resolution, low concentrations, no solid support, sharp peaks, easier thermostating and flow control.)

PRECISE MEASUREMENT OF RETENTION INDICES

Instrument conditions:
Capillary column: 100 m, stainless steel, I.D. 0.25 mm
Stationary phase: squalane
Plate number $\simeq$ 300 000
Temperature: 50–70° ± 0.05°
Pressure: 2 atm ± 0.002 atm
Sample size: < 0.02 μg/component
Retention times are measured with a stop watch with an accuracy of 0.3 sec. (The use of digital electronic integrators for this purpose appeared to be unsuccessful.) More accurate time measurements by means of an on-line process computer is in progress.

The retention time of an unretarded component must be accurately known for

the calculation of the KOVÁTS index as shown under the index definitions. With ionization detectors methane is usually used; however, methane is, to some extent, soluble in all stationary phases and thus a definite error is introduced in the calculations.
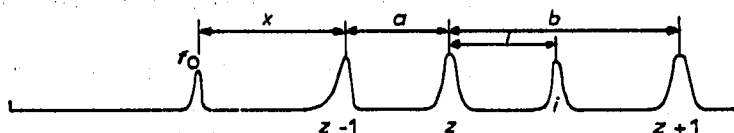
INDEX DEFINITIONS

KOVÁTS:
$$I = 100\ Z + \frac{\log \dfrac{i + a + x}{a + x}}{\log \dfrac{a + b + x}{a + x}} \cdot 100$$

using $\log \dfrac{a + b + x}{a + x} = \log \dfrac{a + x}{x}$ yields:

GROENENDIJK–WALRAVEN: $I = 100\ Z + \dfrac{\log\,(1 + i/a - i/b)}{\log\,b/a} \cdot 100$

GROENENDIJK, VAN KEMENADE AND WALRAVEN of this laboratory have proposed a new definition of the retention index, utilizing the linear relationship that exists between the logarithms of the adjusted retention times and the number of carbon atoms in a homologous series of n-alkanes. They realize that this relationship is in fact non-linear, but *define* a linear plot between three alkanes $Z - 1$, Z, and $Z + 1$.

As may be seen from the index definitions, the two higher n-alkanes should bracket the component i, if I_i is to be calculated. However, following a suggestion of HALÁSZ, we succeeded in measuring t_0 directly with a flame ionization detector by introducing a relatively large sample of H_2 (or He). For this purpose the hydrogen flow to the FID must be diminished to about 60 % of its normal value.

Table I shows the retention data obtained by the different methods of t_0-estimation. It is clear that for capillary columns the use of methane gives a better approximation to the ideal value than does the use of extrapolation methods.
Using $t_{CH_4} \equiv t_0$ retention indices of a number of hydrocarbons on squalane at 50–60° and 70° were measured.

Table II shows the repeatability on one instrument (over a period of three months) to be better than 0.03 I units!

Comparison of our data with similar work done by different workers[4] reveals deviations larger than can be explained by the confidence limits of the respective measurements. This can only partly be explained by systematic deviations in absolute temperatures or different methods in estimating t_0. In our opinion, the main factor contributing to the discrepancies in the literature data is the slight dependency of the retention times upon the sample size (peak asymmetry). A comparison of literature data is given in Table III. By definition the dI/dT for n-alkanes is zero.

As would be expected slightly branched hydrocarbons have only small values

TABLE I

RETENTION INDICES ON A SQUALANE CAPILLARY COLUMN AT 70° WITH DIFFERENT t_0

Solute	t_0 measured		t_0 calculated			According to Groenendijk
	CH_4	H_2	$C_4C_5C_6$	$C_5C_6C_7$	$C_6C_7C_8$	
1t2DiMeCPr	479.76	479.69	479.25	479.08	479.04	—
ECPr	511.53	511.51	511.38	511.33	511.31	511.38
22DiMeBu	538.46	538.41	538.13	538.02	537.98	538.13
112TriMeCPr	550.33	550.29	550.00	549.88	549.85	550.00
CPe	568.49	568.46	568.22	568.12	568.10	568.22
3MePe	585.14	585.12	584.99	584.94	584.92	584.99
ECBu	623.43	623.42	623.33	623.29	623.28	623.29
MeCPe	630.96	630.95	630.84	630.80	630.79	630.80
223TriMeBu	642.59	642.58	642.46	642.41	642.40	642.41
CHex	667.10	667.09	666.99	666.95	666.94	666.95
3MHex	676.94	676.93	676.86	676.82	676.81	676.82
1t2DiMeCPe	692.38	692.37	692.34	692.33	692.33	692.33
22DiMeHex	720.47	720.47	720.43	720.42	720.41	720.41
MeCHex	730.63	730.63	730.59	730.57	730.56	730.56
ECPe	737.49	737.49	737.44	737.42	737.42	737.42
223TriMePe	740.11	740.10	740.06	740.04	740.03	740.03
112TriMeCPe	767.88	767.87	767.83	767.82	767.81	767.81
3MeHept	772.92	772.91	772.88	772.86	772.86	772.86

TABLE II

REPEATABILITY OF MEASUREMENTS OVER A PERIOD OF THREE MONTHS

Operating conditions: column immersed in the silicone oil bath at 70° ± 0.05°; pressure: 2.00 atm; split ratio: 1:200, using Hamilton splitter inlet system; heated FID; sample: 0.1 μl liquid sample + 6 μl of methane and n-butane. Number of measurements: 6.

Compound	a_{i,nC_6}			I	
	Average	σ	$\sigma\%$	Average	σ
n-Bu	0.1544	0.0002	0.15	400.00	0.00
1t2DiMeCPr	0.3307	0.0003	0.10	479.76	0.12
n-Pe	0.4012	0.0004	0.11	500.00	0.00
ECPr.	0.4458	0.0003	0.08	511.53	0.08
22DiMeBu	0.5701	0.0005	0.08	538.45	0.08
112TriMeCPr	0.6354	0.0003	0.04	550.33	0.03
CPe	0.7500	0.0003	0.05	568.49	0.04
3MePe	0.8731	0.0002	0.02	585.14	0.04
n-Hex	1.0000	0.0000	0.00	600.00	0.00
ECBu	1.2323	0.0006	0.05	623.43	0.04
MeCPe	1.3179	0.0005	0.04	630.96	0.03
CHex	1.8188	0.0007	0.04	667.10	0.02
3MeHex	1.9856	0.0006	0.03	676.94	0.01
1t2DiMeCP	2.2784	0.0008	0.04	692.38	0.01
n-Hep	2.4387	0.0010	0.04	700.00	0.00
22DiMeHex	2.9213	0.0012	0.04	720.47	0.01
MeCHex	3.1953	0.0013	0.04	730.63	0.01
ECPe	3.3946	0.0012	0.03	737.49	0.01
223TriMePe	3.4738	0.0020	0.04	740.11	0.01
112TriMeCPe	4.4380	0.0020	0.04	767.88	0.01
3MeHep	4.6396	0.0017	0.04	772.92	0.01
n-Oct	5.8916	0.0026	0.04	800.00	0.00
1t2DiMeCHex	6.2742	0.0027	0.04	806.21	0.00

TABLE III

COMPARISON OF OUR RESULTS WITH DATA GIVEN IN LITERATURE

Solute	I-50				
	Our results	TOURRES	HIVELY	KEME-NADE	Δ_{max}
22DiMePr	412.30	411.7	412.6	—	0.9
2MeBu	475.32	474.0	474.9	—	1.3
22DiMeBu	536.81	536.6	537.1	—	0.5
CPe	565.74	565.7	566.5	—	0.8
2MePe	569.66	569.5	569.7	—	0.2
3MePe	584.24	584.0	584.6	—	0.6
22DiMePe	625.64	625.9	625.9	625.63	0.3
MeCPe	627.90	628.5	628.8	—	0.9
223TriMeBu	639.70	639.8	640.3	639.58	0.7
33DiMePe	658.85	658.9	659.2	658.72	0.5
CHe	666.62	666.5	666.9	666.58	0.4
11DiMeCPe	673.45	674.3	674.2	—	0.8
3MeHe	676.21	676.2	676.4	676.16	0.2

TABLE IV

VARIATION OF RETENTION INDICES WITH TEMPERATURE

Temperature: 25°. See also ref. 2

Solute	I_{50}	I_{70}	dI/dt	$\Delta I_{DMS-OCTAD}$
n-Bu	400.00	400.00	—	—
22DiMePr	412.30	412.91	0.030	− 14.1
2MeBu	475.32	475.47	0.007	− 2.1
1t2DiMeCPr	479.20	479.76	0.028	—
n-Pe	500.00	500.00	—	—
ECPr	510.20	511.53	0.066	—
1c2DiMeCPr	515.01	516.15	0.057	—
22DiMeBu	536.81	538.45	0.082	− 3.3
112TriMeCPr	549.24	550.33	0.054	—
CPe	565.74	568.49	0.137	55.3
2MePe	569.66	570.01	0.017	− 2.1
3MePe	584.24	585.14	0.045	3.9
n-Hex	600.00	600.00	—	—
1122TetraMeCPr	619.85	621.75	0.095	—
ECBu	620.99	623.43	0.122	—
22DiMePe	625.64	626.95	0.065	− 4.2
MeCPe	627.90	630.96	0.153	42.9
223TriMeBu	639.70	642.59	0.144	6.8
33DiMePe	658.85	661.50	0.132	6.9
CHex	662.73	667.10	0.218	50.0
2MeHex	666.62	666.96	0.017	− 2.8
1c3DiMeCPe	682.65	685.92	0.163	25.8
1t3DiMeCPe	686.78	690.10	0.166	27.4
1t2DiMeCPe	689.20	692.38	0.159	31.1
n-Hep	700.00	700.00	—	—
22DiMeHex	719.44	720.47	0.051	− 5.0
113TriMeCPe	723.64	727.47	0.191	15.7
MeCHex	725.78	730.63	0.242	37.9
ECPe	733.83	737.49	0.183	42.1
223TriMePe	737.15	740.11	0.148	8.6

TABLE IV (continued)

Solute	I_{50}	I_{70}	dI/dt	$\Delta I_{DMS-OCTAT}$
1t2c3TriMeCPe	747.81	751.11	0.165	19.8
112TriMeCPe	763.24	767.88	0.232	35.2
2MeHep	764.86	765.16	0.015	− 4.4
3MeHep	772.29	772.92	0.031	0.3
1c2t4TriMeCPe	773.06	777.42	0.218	25.5
1c3DiMeCHex	785.04	789.89	0.242	24.6
11DiMeCHex	786.97	792.80	0.291	38.3
n-Oct	800.00	800.00	—	—
1t2DiMeCHex	801.80	807.54	0.287	31.4
1c2c3TriMeCPe	802.20	807.75	0.277	36.0
1t3DiMeCHex	805.61	810.84	0.261	39.7
223TriMeHex	821.56	824.33	0.138	—
1c2DiMeCHex	829.27	835.41	0.307	47.5
ECHex	834.28	839.66	0.269	40.9
113TriMeCHex	840.39	846.03	0.282	—
2233TetraMePe	852.11	857.61	0.257	—
n-Non	900.00	900.00	—	—

Tourres (ref. 4)

Solute	I_{50}	I_{70}	dI/dt	$\Delta I_{DMS-OCTAT}$
24DiMePe			−0.032	− 5.8
23DiMePe			−0.101	8.1
3EtPe			−0.062	9.50
25DiMeHex			−0.030	− 6.0
24DiMeHex			−0.053	− 2.4
33DiMeHex			−0.130	3.2
234TriMePe			−0.150	10.2
23DiMeHex			−0.072	5.5
2Me3EtPe			−0.160	9.4
4MeHept			−0.027	− 0.4
34DiMeHex			−0.112	9.4
3Me3EtPe			−0.199	13.7
3EtHex			−0.037	4.4
2244TetraMePe			−0.190	0.5
225TriMeHex			−0.065	−10.3
224TriMeHex			−0.135	− 2.1
2234TetraMePe			−0.225	15.8
244TriMeHex			−0.160	1.6
235TriMeHex			−0.085	2.0
1c2DiMeCPe			−0.230	44.5
1t2c4TriMeCPe			−0.167	13.1
1t4DiMeCHex			−0.277	21.9
1Me1ECHex			−0.250	40.1
1c4DiMeCHex			−0.295	37.6
IsoPrCHex			0.265	38.3
PrCPe			0.198	40.0

of dI/dT. The numerical value of dI/dT increases with the degree of branching, the largest values are found for cyclic compounds (5 and 6 rings). HIVELY AND HINTON[5] correlated the magnitude of dI/dT to the increase in the minimum cross sectional area of the molecule. From dI/dT values only, it does not appear to be possible to distinguish highly branched paraffins and C_5 cyclic compounds. If, however, dI/dT for several components is plotted against ΔI values for the same components a distinction can be made because of the appreciably larger ΔI value for C_5 cyclic compounds. (This of course is in fact a three-dimensional plot.)

Values of dI/dT measured in our laboratory and some additional values of
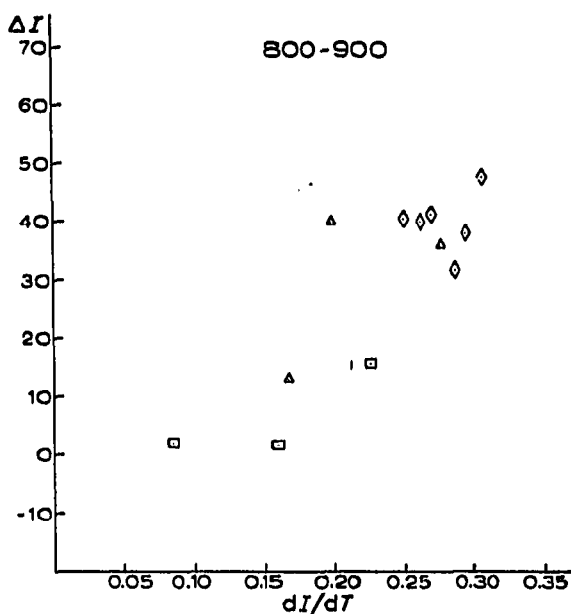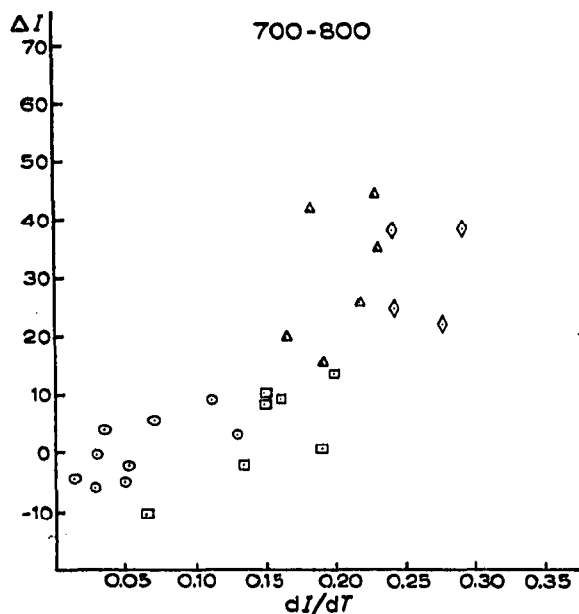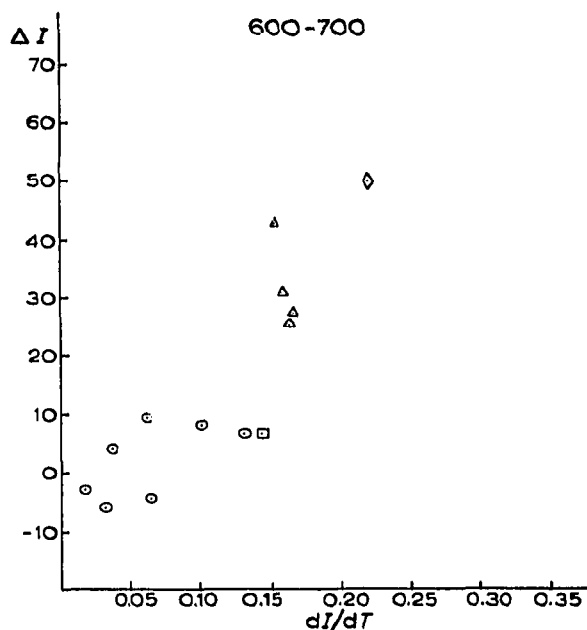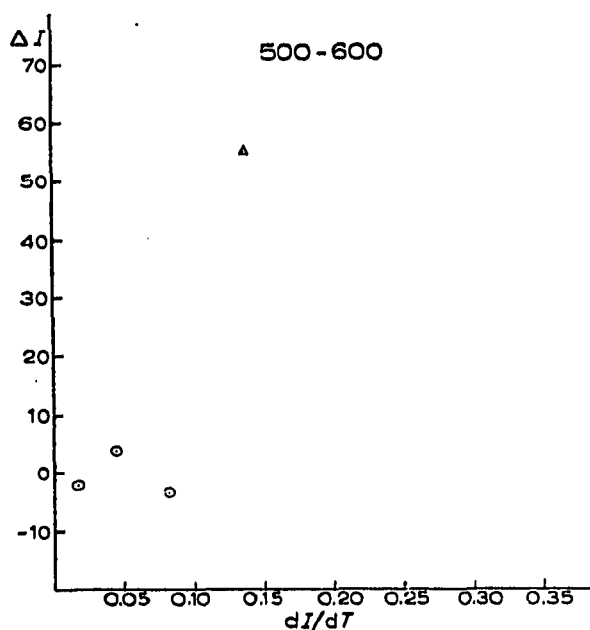
Figs. 3–6. Plot of the temperature coefficient of the retention index (on squalane) against ΔI ($I_{\text{dimethylsulfolane}} - I_{\text{octadecene-1}}$). $\odot$ = slightly branced paraffins; $\square$ = highly branched paraffins; $\triangle$ = C_5 cyclic compounds; $\diamondsuit$ = C_6 cyclic compounds.

TOURRES[4] are collected in Table IV, together with ΔI data ($I_{\text{dimethylsulfolane}} - I_{\text{octadecene-1}}$ at 25°, see Ref. 2). The same data are presented in Figs. 3, 4, 5 and 6.

It can be concluded that this method offers the possibility of identifying different types of hydrocarbon in oil fractions, although further experiments have to be done, especially in the higher molecular weight range.

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