TEMPERATURE COEFFICIENT OF THE PHYSICO-CHEMICAL INDEX

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SUMMARY

The temperature coefficients of the physico-chemical index (PCI) of more than 75 isoparaffins, cycloparaffins and aromatic hydrocarbons have been calculated, tabulated and compared with the experimentally found $\Delta I/\Delta T$ values. The discrepancy observed leads to errors of ± 0.5 i.u. or less and rarely to ± 1 i.u. when the temperature of the analysis is changed over the range $\pm 20°$.

INTRODUCTION

In two previous papers[1,2], we have shown that the relative retentions of hydrocarbons on non-specific phases (squalane) can be calculated from such established physical data as their vapour pressure (p) and molecular volume (V_{mol}). If the experimental retention value from the original KOVÁTS formula is replaced by one calculated on p and V_{mol} values, the magnitude of the index obtained will depend entirely on the values of the physical data of the hydrocarbons in question. This index, introduced by us as a physico-chemical index (PCI), could be corrected according to the geometrical structure of the respective hydrocarbon. The discrepancies between (PCI)$_{corr.}$ and the retention index, I(experimental), would lie within the limits of ± 1 i.u. (ref. 3). In this paper, the temperature coefficient of PCI is calculated and is compared with $\Delta I/\Delta T$ for hydrocarbons separated on squalane.

EXPERIMENTAL

The formula for the calculation of PCI is[2]:

$$PCI = 100z + 100 \frac{\log \left(p_z \cdot V_{mol_z}/p_i \cdot V_{mol_i} \right)}{\log \left(p_z \cdot V_{mol_z}/p_{z+1} \cdot V_{mol_{z+1}} \right)}$$

It is evident that PCI is dependent on the changes of the analysis temperature in a similar manner to I.

The PCI values at 30°, 60° and 90° are calculated by using the data reported in

refs. 4 and 5, and the $\Delta PCI/\Delta T$ values are determined from the values obtained. The magnitude of $\Delta PCI/\Delta T$ per degree is termed K_t. $\Delta I/\Delta T$ is taken as an average from published data[6-11], or was experimentally determined in our laboratory by analysing synthetic hydrocarbon mixtures on a 100-m capillary column with squalane and with an efficiency of more than 100,000 theoretical plates.

RESULTS AND DISCUSSION

In Tables I–IV are given K_t values for isoparaffins, cycloparaffins and aromatics compared with ΔI per degree. The tabulated data show that large discrepancies rarely occur. Among the isoparaffins, the greatest difference between K_t and ΔI per degree is 0.048 i.u. If K_t is used to calculate PCI or even I from one temperature to another, the inaccuracy in the calculated PCI or I value for a temperature interval of $\pm$ 20° would lie within $\pm$ 1 i.u. About 70% of 31 isoparaffins of up to C_9 studied have less than $\pm$ 0.5 i.u. discrepancy for the same temperature interval. The most significant error found by studying 25 cycloparaffins was 0.037 i.u. The discrepancy between the calculated PCI or I value in a temperature interval of $\pm$ 20° for 88%

TABLE I

TEMPERATURE COEFFICIENTS OF C_7–C_9 ISOPARAFFINS

Hydrocarbon	K_t	ΔI per degree	$\pm$ Discrepancy of I in the range $\pm$ 20°
2,2-Dimethylpentane	0.033	0.052	0.380
2,4-Dimethylpentane	0.008	0.028	0.400
3,3-Dimethylpentane	0.108	0.129	0.420
2,3-Dimethylpentane	0.067	0.069	0.040
2-Methylhexane	0.008	0.018	0.200
3-Methylhexane	0.017	0.028	0.220
3-Ethylpentane	0.050	0.062	0.240
2,2,3-Trimethylbutane	0.108	0.142	0.680
2,2-Dimethylhexane	0.018	0.057	0.780
2,5-Dimethylhexane	0.005	0.027	0.440
2,4-Dimethylhexane	0.025	0.053	0.560
3,3-Dimethylhexane	0.093	0.131	0.760
2,3-Dimethylhexane	0.050	0.067	0.340
3,4-Dimethylhexane	0.075	0.099	0.480
2-Methylheptane	0.008	0.020	0.250
3-Methylheptane	0.017	0.042	0.500
4-Methylheptane	0.012	0.022	0.200
3-Ethylhexane	0.033	0.061	0.560
3-Methyl-3-ethylpentane	0.175	0.197	0.440
2-Methyl-3-ethylpentane	0.083	0.125	0.840
2,2,4-Trimethylpentane	0.068	0.111	0.860
2,2,3-Trimethylpentane	0.118	0.156	0.760
2,3,4-Trimethylpentane	0.117	0.165	0.960
2,3,3-Trimethylpentane	0.175	0.211	0.720
2,3-Dimethylheptane	0.074	0.080	0.120
4-Ethylheptane	0.062	0.050	0.240
3,4-Dimethylheptane	0.104	0.080	0.480
4-Methyloctane	0.028	0.030	0.040
2-Methyloctane	0.010	0.030	0.400
3-Methyloctane	0.025	0.030	0.100
3-Methylheptane	0.058	0.050	0.160

TABLE II

I (EXPERIMENTAL), PCI, ΔI PER DEGREE AND K_t VALUES OF SOME C_{10} ISOPARAFFINS

Hydrocarbon	I^{80}	PCI^{80}	I^{a}	ΔI per degree	K_t
2-Methylnonane	964.0	965.7	964.0	0.02	−0.01
3-Methylnonane	970.4	970.6	971.1	0.01	0.02
4-Methylnonane	960.4	959.5	959.2	0.05	0.03
5-Methylnonane	957.4	956.8	958.6	0.04	0.03
3-Ethyloctane	964.4	964.6	955.8	0.04	0.06
4-Ethyloctane	950.0	950.0	954.8	0.06	0.06
2,2-Dimethyloctane	917.9	916.6	915.2	0.01	−0.03
2,3-Dimethyloctane	953.1	952.0	953.5	0.06	0.07
2,4-Dimethyloctane	916.0	916.3	917.3	0.01	−0.03
2,5-Dimethyloctane	922.8	922.4	923.4	0.02	0.01
2,6-Dimethyloctane	932.8	931.8	933.9	0.02	0.01
2,7-Dimethyloctane	929.5	930.5	931.5	0.02	−0.02

a Calculated from the experimental data after TAKÁCS et al.[16].

TABLE III

TEMPERATURE COEFFICIENTS OF C_6–C_8 CYCLOPARAFFINS

Hydrocarbon	K_t	ΔI per degree	± Discrepancy of I in the range ± 20°
Methylcyclopentane	0.142	0.165	0.460
Cyclohexane	0.208	0.205	0.060
1,1-Dimethylcyclopentane	0.150	0.184	0.680
1-trans-3-Dimethylcyclopentane	0.142	0.166	0.480
1-cis-3-Dimethylcyclopentane	0.142	0.163	0.420
1-trans-2-Dimethylcyclopentane	0.150	0.169	0.380
1-cis-2-Dimethylcyclopentane	0.192	0.218	0.520
1,1,3-Trimethylcyclopentane	0.175	0.200	0.500
1,1,2-Trimethylcyclopentane	0.192	0.229	0.740
Methylcyclohexane	0.242	0.247	0.100
Ethylcyclopentane	0.192	0.196	0.080
1-trans-2-cis-4-Trimethylcyclopentane	0.150	0.172	0.440
1-cis-2-trans-4-Trimethylcyclopentane	0.200	0.214	0.280
1-Ethyl-cis-2-methylcyclopentane	0.235	0.231	0.080
Ethylcyclohexane	0.282	0.270	0.240
1-trans-4-Dimethylcyclohexane	0.234	0.234	0.00
1-cis-4-Dimethylcyclohexane	0.267	0.272	0.100
1-trans-3-Dimethylcyclohexane	0.242	0.245	0.060
1-cis-3-Dimethylcyclohexane	0.225	0.230	0.100
1-trans-2-Dimethylcyclohexane	0.284	0.284	0.00
1-cis-2-Dimethylcyclohexane	0.294	0.311	0.340
1,1-Dimethylcyclohexane	0.270	0.276	0.120
1-Methyl-1-ethylcyclopentane	0.200	—	—
n-Propylcyclopentane	0.195	0.195	0.00
Isopropylcyclopentane	0.250	0.235	0.360

of these naphthenes was found to be ± 0.5 i.u. and below. The $\Delta I/\Delta T$ ratios for aromatic hydrocarbons were mostly determined in our laboratory. The influence of the temperature as well as the capacity of the column on the retention of the aromatics is greater than for other hydrocarbons, which causes a more significant random error. However, only two aromatic hydrocarbons, p-xylene and m-xylene, showed a deviation of more than ± 1 i.u. The discrepancy between the calculated and mea-

TABLE IV

TEMPERATURE COEFFICIENTS OF SOME C_9-C_{10} AROMATIC HYDROCARBONS

Hydrocarbon	K_t	ΔI per degree	$\pm$ Discrepancy of I in the range $\pm$ 20°
Benzene	0.220	0.247[a]	0.540
Toluene	0.280	0.250	0.760
		0.242[a]	
Ethylbenzene	0.305	0.261	0.880
		0.280[a]	
n-Propylbenzene	0.315	0.272	0.860
Isopropylbenzene	0.280	0.253	0.540
n-Butylbenzene	0.350	0.350	0.00
sec.-Butylbenzene	0.340	0.321	0.380
Isobutylbenzene	0.330	0.321	0.180
tert.-Butylbenzene	0.305	0.310	0.100
p-Xylene	0.320	0.260	1.040
m-Xylene	0.305	0.255	0.820
o-Xylene	0.385	0.295	1.500
1-Methyl-4-ethylbenzene	0.340	—	—
1-Methyl-3-ethylbenzene	0.310	—	—
1-Methyl-2-ethylbenzene	0.345	0.350	0.100
1,4-Diethylbenzene	0.350	0.362	0.240
1,3-Diethylbenzene	0.305	0.300	0.100
1,2-Diethylbenzene	0.350	0.362	0.240

[a] From ref. 7.

sured index for 50% of the aromatic hydrocarbons studied was less than $\pm$ 0.5 i.u.

Different investigations[6-8,10-12] have shown that the KovÁTS[13,14] retention indices, I, of the hydrocarbons separated on squalane differed in their values. It was reported[8] that cyclohexane has shown a discrepancy of 60 i.u. at 100°, but the accuracy of the data usually varies within $\pm$ 1 index unit and less[7,11]. The same disparity also exists among the data for $\Delta I/\Delta T$[6,7,9,11]. This makes the exact indentification of the peaks from a wide-boiling chromatogram very difficult. ROBINSON AND ODELL[15] have recently proposed a "standard index" calculated from the boiling-point of the hydrocarbons, but such an index cannot express the influence of the temperature of analysis on the separation. At present, the difficulty in identifying the hydrocarbons is overcome by analysing a standard mixture under the same conditions or, when pure compounds are not available, by changing the temperature of the analysis. In the latter case, the method of TAKÁCS et al.[16] could be usefully applied. Both of these methods, however, are time-consuming.

The precision of our method for the calculation of PCI or I values at different temperatures is similar to the accuracy of the routine analysis, and produces differences of the same order as those in published data. An advantage of our method is the possibility of predicting not only the peak position between two n-paraffins, but also its movement by changing the temperature. The choice of the analysis temperature and peak identification is facilitated to a great extent. When chromatography is carried out on a non-specific phase and there are no data in the literature for the calculation of PCI, then $\Delta I/\Delta T$ can be estimated and its value compared with K_t from Tables I–IV. This permits the class to which the hydrocarbon in question belongs to be determined. For slightly branched isoparaffins, the magnitude of K_t lies between

0.01 and 0.15 i.u., for cycloparaffins between 0.15 and 0.25–0.30 i.u., and for aromatic hydrocarbons above 0.25–0.35 i.u.

As a physico-chemical characteristic of the hydrocarbon, the PCI value is proposed as a possible "standard" index. In the ideal case, the retention value I(experimental) would approximate to the PCI values. In separations on a non-specific stationary phase, the differences between PCI and I(experimental) as well as between K_t and $\Delta I/\Delta T$ are caused by the different structures of the hydrocarbons analysed. If the hydrocarbons prove to be of known structure, the differences observed can be used for studying the specificity of the phase[17] or the influence of the experimental conditions.

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