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CORRECTED PHYSICOCHEMICAL INDICES OF MONO- AND DIALKYL-AROMATIC HYDROCARBONS ON SQUALANE

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SUMMARY

A method is given for calculation of correction factors of the physicochemical indices (*PCI*) of mono- and dialkyl aromatic hydrocarbons. It was shown that the corrected *PCI* for the hydrocarbons are in agreement with the experimental retention indices *I* on squalane. Discrepancies observed are within the limits of the results obtained for the *I*, determined experimentally in different laboratories.

INTRODUCTION

We have proposed¹ a method for the calculation of the physicochemical index (*PCI*) correction factors of isoparaffins and cycloparaffins. The *PCI* obtained, duly corrected, agree with the experimental retention indices *I* within the limits of 1–2 index units (i.u.). These discrepancies do not affect the accuracy of a routine analysis with packed columns. The difference between the *PCI* and the *I* of olefins and aromatic hydrocarbons is regarded as a result of the properties of the C=C bond. The presence of an aromatic ring in a compound considerably reduces the retention of that compound on squalane compared with that of the normal paraffins on squalane, and the calculated *PCI* are bigger than the experimental *I*.

In the present paper the possibility of calculating the *PCI* correction factors of aromatic hydrocarbons separated on squalane is discussed. Investigations^{2–6} have shown that the experimentally obtained Kováts retention indices *I* of hydrocarbons separated on squalane differ and the greater the temperature dependence of *I*, the greater the difference. They usually vary from 2–3 i.u. for aromatic hydrocarbons. Substantial discrepancies in the calculated retention indices *I* are obtained if the latter have been treated according to the *PCI* method. Evidently, a method should be devised to accurately calculate *PCI* corrections. The flat aromatic ring is found to be the principal difference in the structures of squalane and aromatic hydrocarbons. Transition of a chain into a flat structure reduces the retention on squalane so that the magnitude of the *PCI* correction factors for the aromatics is negative. Linear and branched alkyl groups improve the retention, as already observed in isoparaffins and

cycloparaffins. As a result, the magnitude of the negative correction of mono- and dialkyl aromatic hydrocarbons decreases. Three times and more substituted aromatic hydrocarbons are not included in the method for calculating the corrected *PCI*.

METHOD

The following *PCI* correction factors of aromatic hydrocarbons separated on squalane were calculated:

- (1) Aromatic ring: -40 i.u.
- (2) The first methyl group alkylating the ring: $+2.5$ i.u.
- (3) The second methyl group: $+2.5$ i.u. if it elongates the first methyl group, but: $+5.0$ i.u. in *para* position, $+5.0$ i.u. in *meta* position, and 0.0 i.u. in *ortho* position.
- (4) The third and subsequent methyl groups of mono- and dialkyl aromatic hydrocarbons are located in the already available alkyl groups as set forth above. If elongated, the contribution is found to be $+2.5$ i.u., and if branched $+5.0$ i.u.

Examples

Calculation of the corrected PCI of 1-methyl-2-ethylbenzene. The *PCI* of 1-methyl-2-ethylbenzene at 100° is 1001.0 i.u. Correction: (1) for the aromatic ring, -40 i.u.; (2) for the first methyl group, $+2.5$ i.u.; (3) for the second methyl group in the *ortho* position, 0.0 i.u.; and (4) for the third methyl group, making the previous group longer, $+2.5$ i.u. Total correction is -35.0 i.u., so that the corrected *PCI* is 966.0 i.u. (experimental *I* is 965.8 i.u.).

Calculation of the corrected PCI of 1,4-diisopropylbenzene. The *PCI* of 1,4-diisopropylbenzene at 100° is 1175.9 i.u. Correction: (1) for the aromatic ring, -40.0 i.u.; (2) for the first methyl group, $+2.5$ i.u.; (3) for the second methyl group in the *para* position, $+5.0$ i.u.; (4) for the two methyl groups extending the chain, $+2 \times 2.5$ i.u.; and (5) for the two methyl groups as chain branches, $+2 \times 5.0$ i.u. Total correction is -17.5 i.u., so that the corrected *PCI* is 1158.4 i.u. (experimental *I* is 1159.0 i.u.).

RESULTS

In Table I the experimental *I* values determined in our laboratory at 100° and the corrected *PCI* values at the same temperature are given for 27 aromatic hydrocarbons. The same hydrocarbons were also chromatographed at 92° and their I_{exp} and PCI_{corr} calculated. These values were compared with those determined experimentally by Soják⁷. The chromatographic column was the same as used in a previous study¹.

The data tabulated show that large discrepancies rarely occur. Of all the aromatic hydrocarbons examined only four showed deviations of more than ± 3.0 i.u. between the corrected *PCI* and the experimental *I*. These discrepancies may be due to the different sources of data for vapour pressure and are comparable with those recently mentioned in the literature⁹.

Significant disparities seen in Table I might result from the experimental *I* being determined in different laboratories. The agreement observed between PCI_{corr} and

TABLE I
I VALUES OF AROMATIC HYDROCARBONS

Hydrocarbon	$I_{\text{exp}}^{100^\circ}$	$PCI_{\text{corr}}^{100^\circ}$	I^{92° (Ref. 7)	$I_{\text{exp}}^{92^\circ}$	$PCI_{\text{corr}}^{92^\circ}$
Benzene	655.0	655.9	650	653.0	654.0
Toluene	757.1	757.7	758	755.2	754.8
Ethylbenzene	847.4	849.5	847	845.1	847.4
<i>p</i> -Xylene	862.0	860.5	861	860.0	857.6
<i>m</i> -Xylene	864.0	864.5	863	862.0	862.3
<i>o</i> -Xylene	883.0	885.7	883	880.6	882.8
Isopropylbenzene	906.7	907.9	907	903.7	905.5
<i>n</i> -Propylbenzene	936.3	935.9	935	935.8	933.4
<i>m</i> -Ethyltoluene	949.5	951.3	948	946.2	948.8
<i>p</i> -Ethyltoluene	951.9	952.3	950	950.0	949.6
<i>o</i> -Ethyltoluene	965.8	966.0	964	963.0	963.3
<i>tert.</i> -Butylbenzene	974.6	973.4	973	972.2	970.9
Isobutylbenzene	990.1	984.5	989	987.7	981.7
<i>sec.</i> -Butylbenzene ^a	990.0	989.0	989	987.7	986.3
<i>n</i> -Butylbenzene	1036.4	1037.2	1035	1033.6	1034.5
<i>m</i> -Isopropyltoluene	1002.1	1000.0*	1002	1001.9	997.3*
<i>p</i> -Isopropyltoluene	1016.5	1018.6	1010	1012.4	1015.9
<i>o</i> -Isopropyltoluene	—	1011.7*	1015	1015.2	1009.4*
<i>m</i> -(<i>n</i> -Propyl)toluene	1033.8	1034.5*	1033	1031.4	1031.8*
<i>p</i> -(<i>n</i> -Propyl)toluene	1040.5	1038.5*	1039	1036.8	1035.5*
<i>o</i> -(<i>n</i> -Propyl)toluene	1046.9	1045.2*	1045	1043.6	1042.2*
<i>m</i> -Diethylbenzene	1029.0	1033.2	1028	1026.6	1030.8
<i>p</i> -Diethylbenzene	1040.5	1043.0	1039	1036.8	1040.3
<i>o</i> -Diethylbenzene	1040.5	1040.4	1039	1036.8	1037.8
<i>m</i> -Diisopropylbenzene	1126.0	1126.1	—	—	1125.3
<i>p</i> -Diisopropylbenzene	1159.0	1158.4	—	—	1155.4
<i>o</i> -Diisopropylbenzene	1132.0	1129.7	—	—	1124.7

* Calculated from the data for vapour pressure at 92° after ref. 8.

I_{exp} shows the advantages of the method proposed with regard to a preliminary orientation for the separation of hydrocarbons at a given temperature, as well as for peak identification.

REFERENCES

- 1 N. Dimov and D. Shopov, *J. Chromatogr.*, 63 (1971) 223.
- 2 L. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 1.
- 3 L. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 12.
- 4 D. A. Tourres, *J. Chromatogr.*, 30 (1967) 357.
- 5 C. A. Cramers, J. A. Rijks, V. Pacáková and I. Ribreiro de Andrade, *J. Chromatogr.*, 51 (1970) 13.
- 6 L. Soják, J. Hrivňák, P. Majer and J. Janák, *Anal. Chem.*, 45 (1973) 293.
- 7 L. Soják and J. Hrivňák, *Ropa Uhlíe*, 11 (1969) 364.
- 8 J. Krupčík, O. Lipska and L. Soják, *J. Chromatogr.*, 51 (1970) 119.
- 9 J. M. Takács, *J. Chromatogr. Sci.*, 11 (1973) 210.