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Note

Unified retention indices for arenes in gas chromatography

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Arenes are of great practical importance and often the sole reason for an analysis is to determine their individual contents. That is why in many cases the phases used for gas chromatographic (GC) separation are polar[1–3] and sometimes extremely polar[4]. In the latter case all of the non-aromatic compounds are eluted first and almost as one peak, while the arenes are retained and eluted separately. The resolution of C_9^+ arenes, however, is very poor on such phases and a less polar or even apolar phase may be preferred. If the identification of the arene peaks is necessary, one needs accurate retention indices, I, this is better than using standards. There are enough I_{exp} data in the literature, but their comparison often shows very great differences.

Recently, Dimov[5] proposed the so-called unified retention index calculated from the available literature data. The aim of the present study is to examine the possibility of unifying the retention indices for arenes using the available experimental data obtained on different phases.

EXPERIMENTAL

The statistical treatment of the experimental data is based on the least-squares approach and leads to the equation

$$\mathrm{UI}_T = \mathrm{UI}_0 + (\mathrm{dUI}/\mathrm{d}T)T \pm s$$

where UI_T is the unified index at a given temperature T, UI_0 is a constant value at an accepted standard temperature, *e.g.*, 0°C, and s is the standard deviation.

It is considered that, in routine analysis, differences of ±1 index units (i.u.) between experimental indices from different laboratories are acceptable[6,7]. Any experimental data which differred from the calculated value of UI_T by more than ±1 i.u. were excluded from the regression analysis. The values of the unified index, UI_T, obtained and its temperature increment were considered as reliable if the data included in the regression matrix were from two authors and at three temperatures at least and no more than 33% of all data were excluded.

Experimental retention indices for arenes at different temperatures on squalane have been taken from eighteen sources[1,2,8–23]. Hively and Hinton[21] reported the retention of benzene, toluene, ethylbenzene and xylenes in the interval 27–86°C. Soják *et al.*[1,11,12,20] carried out a detailed study on the retention of arenes in the range 50–115°C. Švob and Deur-Šiftar[8] published experimental values at 100°C, while Kugucheva and Machinski[16] quoted data at 96 and 106°C. Papazova and Pankova[14] investigated the retention at 110°C.

Experimental retention indices for benzene and toluene on OV-101 at 50°C were reported by Johansen and Ettre[24]. Nabivach and co-workers[25,26] published retention indices for 56 alkylbenzenes on the same phase at 100, 120 and 140°C. Boneva *et al.*[27] investigated retention at 100°C.

Recently, experimental indices on Carbowax 20M have been reported by Tóth[28] at 70°C, by Döring *et al.*[3] at 90°C and by Engewald and Wennich[2] at 100°C.

The data on other phases are limited by the number of authors and do not meet the requirements for UI_T.

RESULTS AND DISCUSSION

A comparison of the literature data obtained by different authors using the same phase shows that even on the most apolar phase, squalane, the experimental data for arenes often differ greatly, in contrast to the retention of other classes of hydrocarbons. For example, the difference in the retention of benzene at 100°C is 4.6 i.u.[10,13], for toluene it is 5.0 i.u.[8,15] and for *p*-xylene it is 3.3 i.u.[17,19].

Much greater differences are found for the same hydrocarbons on polar phases. The interlaboratory reproducibility is so poor that it is impossible to use literature data for a reliable identification. In Table I we compare the values of UI_T calculated from all the available data with the values of I_{exp} from a given author. It is obvious that the I_{exp} value is of little use. The differences between UI_T and I_{exp} are less than ± 1 i.u. only on squalane. The more polar the phase, the greater are the differences: up to 3 i.u. on OV-101 and greater than 10 i.u. on Carbowax 20M.

Unfortunately, the calculated values of UI_T have an unacceptably high standard deviation and could not be used for identification purposes. The only data that

TABLE I

UNIFIED RETENTION INDICES AND EXPERIMENTAL INDICES FOR SOME ARENES ON SQUALANE, OV-101 AND CARBOWAX 20M AT 100°C

Hydrocarbon	*Squalane*			*OV-101*			*Carbowax 20M*		
	UI	I^{8}_{exp}	*Δ*	*UI*	I^{26}_{exp}	*Δ*	*UI*	I^{2}_{exp}	*Δ*
Benzene	650.45	650.5	0.05	662.59	663.6	−1.01	940.25	947.2	−6.95
Toluene	757.63	758.0	−0.37	764.88	766.4	−1.52	1035.40	1043.2	−7.80
Ethylbenzene	847.51	847.7	−0.19	857.62	858.9	−1.28	1119.56	1127.1	−7.54
p-Xylene	861.93	861.8	0.13	866.37	867.7	−1.33	1127.27	1134.8	−7.53
m-Xylene	864.39	863.2	1.19	865.30	866.6	−1.30	1133.02	1140.7	−7.68
o-Xylene	883.97	883.7	0.27	888.75	890.3	−1.55	1175.50	1183.9	−8.40

TABLE II

VALUES OF THE CALCULATED UNIFIED INDEX (UI_0) AT 0°C ON SQUALANE, CALCULATED TEMPERATURE INCREMENT (dUI/dT), STANDARD DEVIATION, s, NUMBER OF EXPERIMENTAL INDICES USED IN THE CALCULATION, n, AND EXPERIMENTAL VALUES OF dI/dT FROM DIFFERENT AUTHORS

No.	*Hydrocarbon*	UI_0	s	n	dUI/dT	dI/dT
1	Benzene	623.01	0.41	13	0.2744	0.24[1]; 0.30[2]; 0.24[12]; 0.23[15]; 0.247[21]; 0.29[29]
2	Toluene	732.98	0.35	15	0.2465	0.245[1]; 0.32[2]; 0.22[12]; 0.22[15]; 0.25[29]
3	Ethylbenzene	821.76	0.24	16	0.2575	0.265[1]; 0.32[2]; 0.24[12]; 0.25[15]; 0.261[29]
4	*p*-Xylene	836.00	0.45	17	0.2593	0.251[1]; 0.34[2]; 0.23[12]; 0.25[15]; 0.26[29]
5	*m*-Xylene	839.42	0.54	14	0.2497	0.245[1]; 0.27[2]; 0.23[12]; 0.30[15]; 0.23[17]; 0.255[29]
6	*o*-Xylene	855.61	0.47	16	0.2836	0.284[1]; 0.34[2]; 0.27[12]; 0.24[15]; 0.27[17]; 0.295[29]
7	Isopropylbenzene	883.56	0.58	10	0.2389	0.264[1]; 0.30[2]; 0.25[12]; 0.26[15]; 0.253[29]
8	*n*-Propylbenzene	911.61	0.40	11	0.2470	0.282[1]; 0.31[2]; 0.26[12]; 0.27[15]; 0.272[29]
9	1-Methyl-3-ethylbenzene	923.99	0.67	10	0.2474	0.242[1]; 0.25[2]; 0.22[12]; 0.25[15]
10	1-Methyl-4-ethylbenzene	928.67	0.33	10	0.2279	0.269[1]; 0.36[2]; 0.24[12]; 0.27[15]
11	1-Methyl-2-ethylbenzene	939.69	0.65	10	0.2559	0.282[1]; 0.29[2]; 0.26[12]; 0.28[15]; 0.35[29]
12	1,3,5-Trimethylbenzene	948.27	0.51	8	0.1944	0.239[1]; 0.25[9]; 0.20[12]; 0.23[15]
13	*tert.*-Butylbenzene	950.93	0.53	7	0.2240	0.29[1]; 0.20[9]; 0.28[14]; 0.31[29]
14	Isobutylbenzene	954.95	0.49	7	0.3497	0.301[1]; 0.23[9]; 0.321[29]
15	1,2,4-Trimethylbenzene	959.06	0.48	8	0.2726	0.228[1]; 0.28[9]; 0.28[12]; 0.30[15]
16	*sec.*-Butylbenzene	959.89	0.48	8	0.3007	0.308[1]; 0.29[9]; 0.30[15]; 0.321[29]
17	1,2,3-Trimethylbenzene	978.19	0.51	8	0.3418	0.337[1]; 0.35[2]; 0.31[15]
18	1-Methyl-2-isopropylbenzene	987.19	0.68	8	0.2968	0.264[1]; 0.25[2]

19	1-Methyl-3-isopropylbenzene	987.56	0.52	8	0.1521	0.216[1]; 0.22[2]; 0.15[9]
20	1-Methyl-4-isopropylbenzene	992.21	0.50	5	0.1824	0.267[1]; 0.22[2]
21	1,3-Diethylbenzene	1002.94	0.38	10	0.2584	0.244[1]; 0.18[2]; 0.23[12]
22	1-Methyl-4-*n*-propylbenzene	1007.63	0.54	5	0.3222	0.282[1]; 0.27[12]; 0.30[29]
23	1-Methyl-3-*n*-propylbenzene	1008.37	0.43	8	0.2522	0.255[1]; 0.23[12]
24	1,4-Diethylbenzene	1010.12	0.64	7	0.3063	0.277[1]; 0.27[12]; 0.362[29]
25	1,2-Diethylbenzene	1011.19	0.47	9	0.2816	0.289[1]; 0.362[29]
26	*n*-Butylbenzene	1012.67	0.54	12	0.2351	0.284[1]; 0.24[12]; 0.35[29]
27	1-Methyl-2-*n*-propylbenzene	1015.06	0.37	10	0.3104	0.298[1]; 0.25[2]; 0.29[12]
28	1,3-Dimethyl-5-ethylbenzene	1023.45	0.23	3	0.2493	0.218[1]
29	*tert.*-Pentylbenzene	1030.86	0.73	4	0.3985	0.369[1]
30	1,4-Dimethyl-2-ethylbenzene	1032.46	0.29	4	0.2745	0.26[1]; 0.32[2]
31	1,2-Dimethyl-4-ethylbenzene	1035.71	0.51	4	0.3677	0.286[1]; 0.31[2]
32	1,3-Dimethyl-4-ethylbenzene	1036.61	0.14	5	0.2979	0.281[1]; 0.24[2]
33	*sec.*-Pentylbenzene	1045.35	0.07	3	0.3280	0.286[1]
34	1-Methyl-4-*tert.*-butylbenzene	1045.50	0.71	4	0.3022	0.292[1]
35	1,2,4,5-Tetramethylbenzene	1071.14	0.32	4	0.3605	0.341[1]; 0.31[2]; 0.31[9]
36	1,2,3,5-Tetramethylbenzene	1077.48	0.37	5	0.3563	0.338[1]; 0.33[2]
37	1,2,3,4-Tetramethylbenzene	1083.84	0.18	5	0.5254	0.395[1]; 0.41[2]; 0.35[9]
38	1-Ethyl-4-*n*-propylbenzene	1093.94	0.07	3	0.3251	0.336[1]
39	1,3-Diisopropylbenzene	1095.19	0.35	4	0.2497	0.195[1]; 0.22[2]
40	*n*-Pentylbenzene	1102.29	0.52	3	0.3326	0.286[1]; 0.27[2]
41	1,3,5-Triethylbenzene	1161.79	0.86	3	0.3252	0.167[1]; 0.17[9]
42	Pentamethylbenzene	1241.75	0.20	4	0.4555	0.452[1]; 0.41[2]

might be used for UI_T calculation with an acceptable variance are those obtained on squalane.

Using the least-square approach, we evaluated the experimental retention indices of 42 arenes on squalane. The values of UI_0, dUI/dT, s and n are given in Table II. The hydrocarbons are arranged in order of increasing values of UI_0. The values of dUI/dT are compared with some of the most similar values of dI/dT cited in the literature.

Comparing the values of UI_0 and dUI/dT for C_6–C_8 aromatic hydrocarbons given here and in ref. 5, it can be concluded that in spite of the different number of input data, the results are adequate. Thus there is a real possibility to check the separation and identification properties of every squalane column for arenes, using the UI_T concept.

Using a limited set of arenes, the I_{exp} values are calculated and compared with UI_T. If they are coincident within ± 1 i.u. the I_{exp} values can be used for a reliable identification. In this case the values of UI_T could be used as a data bank and with the aid of suitable software a compouter-assisted identification might be possible.

Comparing dUI/dT with the experimental values of dI/dT obtained by different authors, it is evident that there are sometimes large differences. We consider the value of dUI/dT as the most reliable and should be used to calculate the optimum analysis temperature for separation of a given mixture of arenes. The I_{exp} values obtained from a given squalane column should be compared with the values of UI_T. We propose also a preliminary test of the column with a limited number of standards in order to determine whether it yields I_{exp} values that are statistically equal to UI_T. If this is not the case, the use of literature data may lead to an incorrect identification.

REFERENCES

1 L. Soják and J. A. Rijks, *J. Chromatogr.*, 119 (1976) 505.
2 W. Engewald and L. Wennrich, *Chromatographia*, 9 (1976) 540.
3 C. Döring, D. Estel and R. Fischer, *J. Prakt. Chem.*, 316 (1974) 1.
4 C. L. Stuckey, *J. Chromatogr. Sci.*, 7 (1969) 177.
5 N. Dimov, *J. Chromatogr.*, 347 (1985) 366.
6 T. Bellas, *Chromatographia*, 8 (1975) 38.
7 L. Soják, V. Berezkin and J. Janák, *J. Chromatogr.*, 209 (1979) 15.
8 V. Švob and D. Deur-Šiftar, *J. Chromatogr.*, 91 (1974) 677.
9 J. Macák, V. Nabivach, P. Buryan and Š. Sinder, *J. Chromatogr.*, 234 (1982) 285.
10 L. Hála, R. Lacko and K. Hegedüsova, *Ropa Uhlie*, 18 (1976) 140.
11 L. Soják and J. Hrivnak, *Ropa Uhlie*, 11 (1969) 361.
12 L. Soják, A. Bucinska and P. Skalák, *Ropa Uhlie*, 12 (1970) 1357.
13 N. Dimov, T. Petkova and D. Shapov, *J. Chromatogr.*, 91 (1974) 691.
14 D. Papazova and M. Pankova, *J. Chromatogr.*, 105 (1975) 411.
15 G. Mitra, G. Mohan and A. Sinha, *J. Chromatogr.*, 91 (1974) 633.
16 E. Kugucheva and V. Machinski, *Zh. Anal. Khim.*, 38 (1983) 2023.
17 G. Schomburg, in J. A. Rijks (Editor), *Thesis*, Eindhoven University of Technology, Eindhoven, 1973, p. 116.
18 J. Rijks and C. Cramers, *Chromatographia*, 7 (1974) 99.
19 J. Loewenguth and D. Tourres, *Fresenius' Z. Anal. Chem.*, 236 (1968) 170.
20 L. Soják and A. Bučinská, *J. Chromatogr.*, 51 (1970) 75.
21 R. Hively and R. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.
22 C. Döring, D. Estel, J. Weber, G. Zimmerman and D. Zschummel, *J. Prakt. Chem.*, 313 (1971) 1081

23 D. Desty, A. Goldup and W. Swanton, in N. Breuner *et al.*(Editors), *Gas Chromatography*, Academic Press, New York, 1962, p. 105.
24 N. Johansen and L. Ettre, *Chromatographia*, 15 (1982) 625.
25 V. Gerasimenko, A. Kirilenko and V. Nabivach, *J. Chromatogr.*, 208 (1981) 9.
26 V. Gerasimenko and V. Nabivach, *Zh. Anal. Khim.*, 37 (1982) 110.
27 S. Boneva, D. Papazova and N. Dimov, *God. Vissh. Khim. Tekhnol. Inst. Burgas, Bulg.*, 18 (1983) 143.
28 T. Tóth, *J. Chromatogr.*, 279 (1983) 157.
29 N. Dimov, T. Petkova and D. Shopov, *J. Chromatogr.*, 74 (1972) 165.