

## Short Communication

# Dispersion and selectivity indices of *n*-alkyl- and 1-(alkyl)alkylbenzenes

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(First received June 9th, 1992, revised manuscript received July 21st, 1992)

### ABSTRACT

The dispersion and selectivity indices of a series of *n*-alkyl- and 1-(alkyl)<sub>m</sub>(alkyl)<sub>n</sub>benzenes were determined using retention index values determined on a non-polar (DB-1) and a polar (DB-wax) fused-silica capillary column. The effect of the individual groups and the multiple alkyl substituents and their position on the alkyl chain are discussed in terms of the relevant polar interactions.

### INTRODUCTION

The effect of the solute–solvent interactions in chromatography on the retention of a substance in chromatography is conveniently determined as the retention index value, this being a summation of both non-polar and polar forces, moderated by steric factors. Evans *et al* [1] have expressed the retention index (*I*) as the sum of two factors

$$I = I_m + I^*$$

where *I<sub>m</sub>* the dispersion index is defined as the retention index of a hypothetical *n*-alkane having the same molecular mass as the solute and *I\** is the selectivity index, which reflects the combined effects of molecular shape and functionality.

Since an *n*-alkane has a molecular formula of C<sub>*i*</sub>H<sub>2*i*+2</sub> or (CH<sub>2</sub>)<sub>*i*</sub> + 2H its molecular mass is

$m = 14.026i + 2.016$  Therefore *I<sub>m</sub>* can be calculated from

$$I_m = \frac{m - 2.016}{0.14026}$$

where *m* is the molecular mass of the solute.

The scheme has been applied to a study of the homologous carboxyl and carboxyl compounds [2,3], alkyl, chlorinated and alkenyl benzoate esters [4], *n*-alkylbenzenes [5] and chlorinated derivatives of cyclohexane, benzene and anisole [6]. This paper extends the analyses of *n*-alkylbenzenes by the use of a wider range of alkyl chain lengths than previously reported [5] and includes homologous branched chain alkylbenzenes.

### DATA

The retention data used in this paper are reproduced from work reported by Peng *et al* [7] who used Hewlett-Packard Model 5890 and 5880 A gas chromatographs, equipped with thermal conductivity detectors using non-polar and polar fused-silica

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capillary columns (30 m × 0.53 mm I.D., film thickness 1.0 μm of DB-wax and 1.5 μm of DB-1 (J & W Scientific, Folsom, CA, USA). The temperature was linearly programmed, the initial oven temperature of 40°C was held for 4 min and then increased at a rate of 8°C/min to 280°C for DB-1 and to 200°C for the DB-wax column. The maximum oven temperature was maintained for 20 min. The retention index values were calculated using the equation of Van der Dool and Kratz [8].

## RESULTS

Table I shows retention data of C<sub>1</sub>-C<sub>7</sub> *n*-alkylbenzenes determined by Engewald *et al* [9] on packed OV-1 and UCON LB550 columns and similar data of C<sub>1</sub>-C<sub>13</sub> *n*-alkylbenzenes determined by Peng *et al* [7] on capillary columns coated with a comparable dimethylsiloxane and DB-wax. The earlier values on the OV-1 column are essentially identical with those of Peng *et al* [7] indicating that the works should be generally comparable. With C<sub>1</sub>-C<sub>7</sub> *n*-alkylbenzenes it was shown that the value

of the selectivity indices *I*\* gradually decreased indicating a reduction in polar character as the alkyl chain length increased. With the longer chain length homologues the trend is reversed and the values increase due evidently to alteration of the configuration of the alkyl chain.

This effect was not as expected or as observed in the earlier works [4-6] where the *I*\* values tended to approach a constant value. However, this work differs from the earlier studies in that a much wider range of homologues was considered. A variation in the trend of properties of homologues which pass through a minimum is well known with many systems. One of the earliest studies of homologue properties considers the polyalkyl acrylates and the polyalkyl methacrylates. The brittle point and the hardness of the first eight *n*-alkyl acrylates and the first twelve *n*-alkyl methacrylates follow a linear function with the logarithm of the carbon number of the alkyl groups but with increased alkyl chain length the relationship does not continue as the values dramatically alter and the previous trend is reversed [10]. The systems which find considerable

TABLE I  
RETENTION (*I*), DISPERSION (*I*<sub>m</sub>) AND SELECTIVITY (*I*\*) INDICES OF *n*-ALKYLBENZENES

<i>n</i> -Alkylbenzenes	<i>I</i> <sub>m</sub>	OV-100			DB-1			LB550X			DB-wax		
		<i>I</i>	<i>I</i> *	<i>I</i> * - <i>I</i> * <sub>B</sub> <sup>a</sup>	<i>I</i>	<i>I</i> *	<i>I</i> * - <i>I</i> * <sub>B</sub>	<i>I</i>	<i>I</i> *	<i>I</i> * - <i>I</i> * <sub>B</sub>	<i>I</i>	<i>I</i> *	<i>I</i> * - <i>I</i> * <sub>B</sub>
Benzene	542	664	122		654	112		759	217		947	405	
Toluene	642	767	125	3	764	122	10	862	220	3	1051	409	4
Ethylbenzene	742	859	117	-5	858	116	4	950	208	-9	1129	382	-18
<i>n</i> -Propylbenzene	842	950	108	-14	945	103	-9	1037	185	-22	1206	364	-41
<i>n</i> -Butylbenzene	942	1047	105	-17	1047	105	-7	1134	192	-25	1306	364	-41
<i>n</i> -Pentylbenzene	1042	1146	104	-18	-	-	-	1233	191	-26	-	-	-
<i>n</i> -Hexylbenzene	1142	1244	102		1254	112	0	1332	190	-27	1515	373	-32
<i>n</i> -Heptylbenzene	1242	1342	100		1348	106	-6				1611	369	-36
<i>n</i> -Octylbenzene	1342				1456	114	2				1715	373	-32
<i>n</i> -Nonylbenzene	1442				1560	118	6				1821	379	-26
<i>n</i> -Dccylbenzene	1542				1664	122	10				1928	386	-19
<i>n</i> -Dodecylbenzene	1742				1870	128	16				2141	399	-6
<i>n</i> -Tridecylbenzene	1842				1958	136	24				2265	423	18

<sup>a</sup> *I*\*<sub>C</sub> = *I*\*<sub>compound</sub>, *I*\*<sub>B</sub> = *I*\*<sub>benzene</sub>

TABLE II  
RETENTION ( $I$ ), DISPERSION ( $I_m$ ) AND SELECTIVITY ( $I^*$ ) INDICES OF 1-(ALKYL)ALKYLBENZENES

Compound	$I_m$	DB-1			DB-wax		
		$I$	$I^*$	$I_C^* - I_B^*$	$I$	$I^*$	$I_C^* - I_B^*$
Benzene, (1-butylhexyl)	1542	1526	-16	-128	1729	187	-30
(1-propylheptyl)	1542	1534	-8	-120	1743	201	-16
(1-ethyloctyl)	1542	1553	11	-101	1767	225	-2
(1-methylnonyl)	1542	1588	46	-66	1833	291	74
<i>n</i> -decyl	1542	1664	122	10	1928	306	169
(1-pentylhexyl)	1642	1620	-22	-134	1820	178	-39
(1-butylheptyl)	1642	1626	-16	-128	1828	186	-31
(1-propyloctyl)	1642	1636	-6	-118	1843	201	-16
(1-ethylnonyl)	1642	1656	14	-98	1873	231	14
(1-methyldecyl)	1642	1692	50	-62	1933	291	74
(1-pentylheptyl)	1742	1719	-23	-135	1918	176	-41
(1-butylloctyl)	1742	1723	-19	-131	1928	188	-29
(1-propylnonyl)	1742	1735	-7	-119	1943	201	-16
(1-ethyldecyl)	1742	1755	13	-99	1972	230	13
(1-methylundecyl)	1742	1791	49	-63	2036	294	77
<i>n</i> -dodecyl	1742	1870	128	16	2140	398	181
(1-pentylloctyl)	1842	1814	-28	-140	2015	173	-44
(1-butylloctyl)	1842	1821	-21	-133	2026	184	-33
(1-propyldecyl)	1842	1836	-9	-121	2046	204	-13
(1-ethylundecyl)	1842	1856	14	-63	2079	237	20
(1-methyldodecyl)	1842	1894	50	-62	2143	301	84
<i>n</i> -tridecyl	1842	1978	164	52	2275	433	216

industrial application have been extensively studied and other physical properties show the same trends [11]

Most of the contribution to the  $I^*$  value is due to the aromatic ring, the effect of the alkyl chain may be estimated by subtraction of  $I^*$  for benzene. The values decrease due to the reduction in polar forces with increasing chain length then increase as the end of the alkyl chain comes closer to the aromatic ring.

A comparison of the  $I^*$  values on the dimethyl polysiloxanes, on UCON LB550X and on DB-wax shows the increasing polar character of the stationary phases. The values of  $I^*$  on DB-wax show the same decrease and then an increase as the chain length is increased. The contribution of the alkyl chain similarly varies the negative values showing that the effect is small compared to the contribution of the aromatic ring.

Several examples of the retention of isomers are

evident, isopropylbenzene exhibiting a lower retention value than the *n*-alkyl homologue due to the more compact shape, diethylbenzene showing minimally lower values than *n*-alkylbenzene and cyclopropylbenzene and cyclohexylbenzene showing greater retention than the *n*-alkyl isomers due to the increased rigidity of the ring system.

Table II shows retention indices, together with dispersion and selectivity indices of several series of 1-(alkyl)<sub>m</sub>(alkyl)<sub>n</sub>benzenes where  $m$  varies from 1 to  $(n - 1)$  while the value of  $m + n$  remains constant.

Movement of a methylene group from the  $m$  or long alkyl chain to the short alkyl chain makes the molecule more symmetrical. The more symmetrical isomer exhibits the lower retention. The trend continues with all of the series and the isomer in each case where the two alkyl chains are closest in size has the lowest retention.

The selectivity indices on the polysiloxane station-

ary phase increase as the symmetry of the alkyl chains is reduced, the values showing the greater influence of the aromatic ring as the interference of the aliphatic structure is reduced. The effect is more apparent by subtraction of  $I^*$  for benzene from the  $I^*$  value of the compound where the polar interactions are reduced as the proximity of the alkyl groups are increased from the aromatic ring. With the DB-wax stationary phase the  $I^*$  values of the compounds are greatly enhanced while the values less the contribution due to the aromatic ring are reduced, the interactions of the aromatic structure and the more polar phase overshadowing the effect of the alkyl substituents.

#### CONCLUSIONS

The retention of a larger range of alkyl chain lengths of *n*-alkylbenzenes than previously available have been examined. It is evident that while the  $I^*$  (selectivity index) values decrease with increased alkyl chain length they then increase as the polar character of the extremity of the chain increases due to its configuration and increasing proximity of the aromatic ring.

With 1-(alkyl)<sub>m</sub>(alkyl)<sub>n</sub>benzenes the selectivity indices increase as the symmetry of the alkyl chains is reduced, the values showing the greater influence of the aromatic ring as the interference of the aliphatic structure is reduced. The  $I^*$  values show the greater influence of the aromatic ring with the stationary phase of increased polar character.

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