Influence of adsorption at the gas–liquid interface on the determination of gas chromatographic retention indices on open-tubular columns coated with cyanosilicones

A. BEMGÅRD and L. BLOMBERG*

Department of Analytical Chemistry, University of Stockholm, Arrhenius Laboratory, 106 91 Stockholm (Sweden)

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SUMMARY

The occurrence of adsorption of n-alkanes on the surface of polar stationary phases is demonstrated. The Kováts retention index in such instances is strongly dependent on the stationary phase film thickness. When using polar homologues as standards on a cyanosilicone-coated column, the retention index was only weakly dependent on film thickness.

INTRODUCTION

The Kováts retention index is widely used as a means for the uniform presentation of gas chromatographic retention data obtained in isothermal runs[1–3]. This index can be applied to all possible combinations of solutes and stationary phases; the reliability is, however, not equally acceptable in all situations. The reproducibility of retention indices between different laboratories is generally considered to be within one index unit for non-polar columns, whereas the reproducibility on polar columns may extended over several units. The relatively low reproducibility achieved on polar columns may be explained partly by poor reproducibility of the columns; the main problem, however, seems to be adsorption of the n-alkane standards at the gas–liquid interface. A high degree of gas–liquid adsorption leads to ill-defined retention times, and it is of course especially detrimental when this concerns the standard substances. By definition, true Kováts retention indices are obtained when retention is due only to dissolution of the solutes in the stationary phase. The use of more polar standards has been suggested to improve the precision of retention indices on polar stationary phases (*e.g.*, refs. 4–10). In a recent paper, we demonstrated the advantages of 2-ketones as standards for open-tubular columns coated with a cyanosilicone[11]. In this paper, the adsorption of n-alkanes on the surface of a polar stationary phase and the influence of such an adsorption on Kováts retention indices are demonstrated.

EXPERIMENTAL

A methyl(biscyanopropyl)silicone gum, 60-CN, synthesized in our laboratory[12], was used. The silicone is similar to polymer 60-CN-6 in ref. 12, and contains 60% cyanopropyl, 37% methyl and 3% vinyl substituents. This stationary phase has been extensively evaluated[11,13–15] and some further calculations based on data from these evaluations have been compiled in this work. In addition, retention data obtained on a dimethylsilicone gum, PS 264 (Petrarch Systems, Bristol, PA, U.S.A.), having 5% phenyl and 0.1–0.3% vinyl substitution[15,16], are included.

Data were obtained on various gas chromatographs. In ref. 13, normal-bore columns were evaluated on a Hewlett-Packard HP 5790 instrument and narrow-bore columns on some different instruments at the Laboratory of Instrumental Analysis, University of Technology, Eindhoven, The Netherlands. The HP instrument was used in ref. 14 and a Carlo Erba Mega instrument in refs. 11, 15 and 16.

Three test mixtures were used. In addition to the substances to be indexed, these contained n-alkanes, 2-ketones and fatty acid methyl esters (FAME). C_{13}–C_{20} n-alkanes were used for the polar columns and C_{10}–C_{16} n-alkanes for the columns coated with PS 264. For indexing in the 2-ketone system, C_{10}, C_{11}, C_{12} and C_{15} ketones were used. C_{10} was 2-decanone, and this substance was assigned a retention index of 1000 i.u. The FAME standard contained C_{10}, C_{11}, C_{12} and C_{14}, C_{10} being methyl decylate, to which a retention index of 1000 i.u. was assigned.

RESULTS

Three types of retention mechanisms are generally involved to different extents in gas–liquid chromatography: dissolution of the solutes in the stationary phase, adsorption at the gas–liquid interface and adsorption at the solid–liquid interface. The retention of a solute can be described by

$$V_N = (K_L V_L) + (K_{AL} A_L) + (K_L K_{AS} A_S) \tag{1}$$

where V_N is the net retention volume, K_L is the partition coefficient, V_L is the volume of stationary phase, K_{AL} is the coefficient of adsorption to the stationary phase surface, A_L is the surface area of the stationary phase, K_{AS} is the coefficient of adsorption to the liquid–support surface and A_S is the surface area of the support[17,18]. In the derivation of eqn. 1, it is assumed that the dissolution and adsorption isotherms are linear in the concentration interval studied, and that the stationary phase properties do not differ from the properties of the polymer in bulk.

When adsorption occurs at both the gas–liquid and the liquid–solid interfaces in open-tubular columns, it may be difficult to distinguish between the two. In this work, the intention was to study the adsorption of n-alkanes at the gas–liquid interface, and a system where other types of adsorption can be neglected was therefore selected here. For polar stationary phases, it is reasonable to assume that adsorption at the gas–liquid interface predominates and that adsorption at the liquid–support surface can be neglected[19,20]. Further, 2-methylnaphthalene was chosen as a probe, because it has a negligible adsorption at the gas–liquid and liquid–solid interfaces in the system used here. Observed shifts in retention indices would therefore be due, in principle,

TABLE I

VALUES OF K_L AND K_{AL}, WITH THE 90% CONFIDENCE LIMITS FOR 60-CN AT 100°C, CALCULATED FROM $k (V_m)/A_L = K_L (V_L/A_L) + K_{AL} (n = 10)$

Compound	K_L	K_{AL}	K_L/K_{AL} (sign)	r^2
2-Methylnaphthalene	2635 ± 145	0.040 ± 0.061	$\pm$	0.993
C_{17}	670 ± 109	0.085 ± 0.046	$+$	0.942
C_{20}	2541 ± 666	0.489 ± 0.283	$+$	0.863

only to surface adsorption of n-alkanes. However, when an extremely thin film of stationary phase has been applied, an active support surface may attract polar moieties in the stationary phase, thereby decreasing the observed polarity[21]. The extent of such an orientation depends on the nature of the support surface. The different batches of fused-silica capillary tubing used in this work may have shown some variations in surface properties. These variations, however, were probably evened out by the surface deactivation that was applied here.

By use of eqn. 1, and making the assumption that adsorption occurs only at the gas–liquid interface, it is possible to calculate the adsorption and partition coefficients from[22]

$$V_N/A_L = K_L(V_L/A_L) + K_{AL} \tag{2}$$

and

$$(kV_m)/A_L = K_L(V_L/A_L) + K_{AL} \tag{3}$$

where k is the retention factor and V_m the column dead volume. The pressure correction factor according to James and Martin[23] was assumed to be 1 in all calculations. For open-tubular columns, $V_L/A_L \approx d_f$ when $r \gg d_f$ (d_f = film thickness, r = column radius).

In Table I, the partition and adsorption coefficients at 100°C are listed for
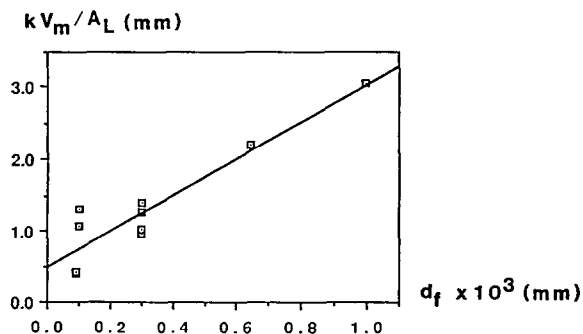

Fig. 1. Plot of $k V_m/A_L$ versus d_f for eicosane (C_{20}) at 100°C on the columns listed in Table II.

TABLE II

DATA FROM DIFFERENT COLUMNS COATED WITH 60-CN (T = 100°C)

Column length (m)	I.D. (mm)	d_f (µm)	Ref.	k			I: 2-MN[a]	$(1/d_f) \cdot 10^{-3}$ (mm^{-1})
				2-MN[a]	C_{17}	C_{20}		
20	0.32	1.00	11	32.8	9.5	38.4	1964	1.00
20	0.32	0.3	14	10.0	3.1	12.8	1948	3.33
19	0.32	0.64	14	22.4	6.5	27.5	1956	1.56
20	0.32	0.09	14	3.6	1.2	4.9	1935	11.1
11	0.10	0.09	14	10.7	3.8	17.3	1905	11.1
20	0.32	0.3	13	11.7	4.2	15.8	1932	3.33
10	0.32	0.3	13	11.9	3.8	17.6	1923	3.33
26	0.32	0.3	13	9.7	2.9	11.9	1953	3.33
4	0.05	0.1	13	21.1	16.4	85.8	1746	10.0
4.5	0.05	0.1	13	19.4	18.2	104.8	1708	10.0

[a] 2-Methylnaphthalene.

2-methylnaphthalene, n-heptadecane and n-eicosane, and in Fig. 1 is shown the plot of eqn. 3 for n-eicosane on the columns listed in Table II. It is worth noting that on the 60-CN coated columns, the adsorption coefficient, K_{AL}, increases more rapidly than the partition coefficient, K_L, with an increase in length of the hydrocarbon chain. Moreover, the value of K_{AL} for 2-methylnaphthalene includes the origin within the 90% confidence limit, which indicates that this compound has a non-adsorptive character on this stationary phase. Experimental factors certainly introduced some errors here, the data being obtained on different instruments and in different laboratories. The results indicate, however, that the adsorption effects are more pronounced with the n-alkanes than with 2-methylnaphthalene. A presupposition for the validity of eqn. 1 is that the adsorption isotherm should be linear in the concentration interval studied. The lack of such a linearity for immobilized 60-CN was demonstrated in ref. 14; the columns evaluated here were, however, coated with non-immobilized stationary phase, and retention times for n-alkanes were found not to vary with amount injected within the concentration range studied.

Using the same approach, tests were made at 125°C, the data taken from refs. 11

TABLE III

DATA FROM DIFFERENT COLUMNS COATED WITH 60-CN (T = 125°C)

Column length (m)	I.D. (mm)	d_f (µm)	k					I: 2-MN[a]	$(1/d_f) \cdot 10^{-3}$ (mm^{-1})
			2-MN[a]	C_{17}	C_{20}	K_{12}[a]	E_{12}[a]		
20	0.32	2.0	23	5.7	19	15	15	2053	0.50
20	0.32	1.0	12	3.0	10	7.6	8.0	2042	1.00
26.5	0.22	0.16	2.8	0.9	3.6	1.8	2.0	1947	6.29
26.5	0.25	0.20	2.9	0.8	2.8	1.9	2.0	2010	5.00
26.5	0.25	0.20	2.9	0.8	2.8	1.9	2.0	2011	5.00

[a] 2-MN = 2-Methylnaphthalene; K_{12} = 2-decanone; E_{12} = methyl dodecylate.

TABLE IV

VALUES OF K_L AND K_{AL}, WITH THE 90% CONFIDENCE LIMITS FOR 60-CN AT 125°C, CALCULATED FROM $k\ (V_m)/A_L\ =\ K_L\ (V_L/A_L)\ +\ K_{AL}\ (n\ =\ 5)$

Compound	K_L	K_{AL}	K_L/K_{AL} (sign)	r^2
2-Methylnaphthalene	925 ± 36	0.009 ± 0.040	$\pm$	0.9992
C_{17}	218 ± 10	0.012 ± 0.010	$+$	0.9988
C_{20}	723 ± 47	0.055 ± 0.050	$+$	0.9977
2-Decanone	254 ± 12	0.005 ± 0.010	$\pm$	0.9988
2-Dodecanone	572 ± 24	0.009 ± 0.020	$\pm$	0.9991
Methyl decylate	269 ± 10	0.005 ± 0.010	$\pm$	0.9993
Methyl dodecylate	603 ± 21	0.010 ± 0.020	$\pm$	0.9993

and 15 being listed in Tables III and IV. The effect of adsorption is more significant for the n-alkanes than for the 2-ketones and the FAME. No significant adsorption could be detected with the latter compounds on the 60-CN stationary phase at 125°C.

For comparison, data were obtained from tests made on a non-polar stationary phase. The columns used were the same as those used in refs. 15 and 16. In Table V the column dimensions and k values are listed, and in Table VI the calculated values of the adsorption and partition coefficients are given. The retention index for 2-methyl-naphthalene, with the n-alkane standards, was found to be independent of film thickness, $1305.1 \pm 0.11\ (n\ =\ 5)$ at 125°C.

For the non-polar columns, the adsorption coefficients are significant only for the polar solutes, e.g., 2-ketones and FAME. The adsorption coefficients for these compounds are, however, much lower than those observed for the n-alkanes on the polar cyano phase. The partition coefficient seems to increase more rapidly than the adsorption coefficient with increasing chain length, which indicates that the contribution to retention from adsorption effects will be less pronounced for higher homologues. Possibly, the adsorption in this instance can be attributed to adsorption on the fused-silica surface, rather than at the gas–liquid interface.

TABLE V

DATA OBTAINED ON DIFFERENT COLUMNS COATED WITH PS 264 ($T\ =\ 125$°C)

Column length (m)	I.D. (mm)	d_f (μm)	$2-MN^a$	C_{12}	C_{14}	$E_{10}{}^a$	$E_{12}{}^a$	$K_{10}{}^a$	$K_{12}{}^a$	$(1/d_f) \cdot 10^{-3}$ (mm^{-1})
20	0.32	4.14	54.0	29.9	92.2	–	–	–	–	0.24
20	0.32	2.00	26.3	14.6	45.0	–	–	–	–	0.50
20	0.32	0.93	12.2	6.8	20.8	12.8	39.6	6.2	19.2	1.07
20	0.32	0.49	–	3.7	11.2	–	–	–	–	2.04
20	0.32	0.24	–	1.8	5.4	–	–	–	–	4.16
18	0.32	0.49	6.2	–	–	6.8	21.0	3.3	10.2	2.04
17	0.32	0.24	3.1	–	–	3.4	10.5	1.6	5.1	4.16

The k column header spans: $2-MN^a$, C_{12}, C_{14}, $E_{10}{}^a$, $E_{12}{}^a$, $K_{10}{}^a$, $K_{12}{}^a$.

[a] 2-MN = 2-Methylnaphthalene; E_{10} = methyl decylate; E_{12} = methyl dodecylate; K_{10} = 2-decanone; K_{12} = 2-dodecanone.

TABLE VI

VALUES OF K_L AND K_{AL}, WITH THE 90% CONFIDENCE LIMITS FOR PS 264 AT 125°C, CALCULATED FROM k $(V_m)/A_L = K_L (V_L/A_L) + K_{AL}$ (n = 5 FOR THE n-ALKANES AND 2-METHYLNAPHTHALENE AND n = 3 FOR THE 2-KETONES AND FAME)

Compound	K_L	K_{AL}	K_L/K_{AL} (sign)	r^2
2-Methylnaphthalene	1009 ± 27	0.026 ± 0.060	±	0.9996
C_{12}	550 ± 14	0.029 ± 0.030	±	0.9997
C_{14}	1703 ± 42	0.080 ± 0.090	±	0.9997
2-Decanone	518 ± 1	0.006 ± 0.001	+	1.0000
2-Dodecanone	1618 ± 8	0.015 ± 0.005	+	1.0000
Methyl decylate	1083 ± 1	0.012 ± 0.001	+	1.0000
Methyl dodecylate	3342 ± 31	0.034 ± 0.020	+	1.0000

Berezkin[24,25] developed from eqn. 1 an equation for the calculation of an invariant retention index, I_0:

$$I_i = I_0 + a_{1Li}(1/V_L) \tag{4}$$

where I_i is the retention index for compound i, I_0 is the independent retention index for compound i, arising from pure partitioning, and a_{1Li} is a constant including, *inter alia*, the adsorption coefficient for compound i at the stationary phase surface. A presupposition for eqn. 4 is that the standards should show no adsorption on the surface of the stationary phase used. For polar phases, it is therefore necessary to use polar standards. The constant a_{1Li} in eqn. 4 also contains the stationary phase surface area A_L, and for columns having different values of A_L, I should be plotted against A_L/V_L, which is *ca.* $1/d_f$ when the column radius $r \gg d_f$. Plots of I vs. $1/d_f$ for 2-methylnaphthalene at 100 and 125°C using n-alkanes as standards are shown in Figs. 2 and 3. It seems that column radius would be of no importance here. It should be noted, however, that narrow-bore columns have much smaller sample capacities than normal-bore columns. In order to remain in the solute concentration region applied
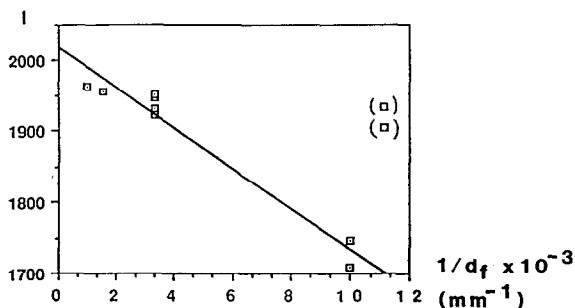

Fig. 2. Dependence of the retention index for 2-methylnaphthalene on $1/d_f$. Conditions: split injections on the columns listed in Table II, isothermal at 100°C. $I = 2019 - 29 \cdot 10^{-3} (1/d_f)$; correlation coefficient 0.98, n = 8.
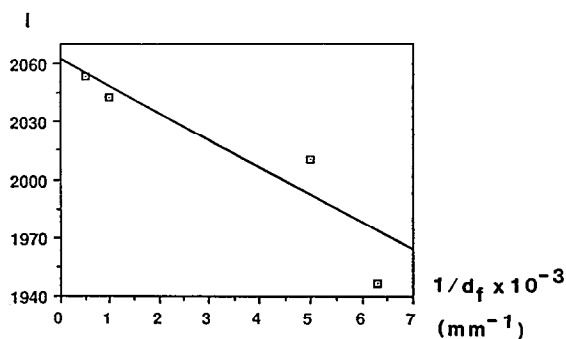
Fig. 3. Dependence of the retention index for 2-methylnaphthalene on $1/d_f$. Conditions: split injections on the columns listed in Table III, isothermal at 125°C. $I = 2063 - 14 \cdot 10^{-3} (1/d_f)$; correlation coefficient 0.89, $n = 5$.

for normal-bore columns, only small sample amounts should be injected on the narrow-bore columns.

Calculation of I_0 at 125°C in the n-alkane, 2-ketone and FAME retention index systems from plots of I vs. $1/d_f$ resulted in $I_0 = 2063$, 1318 and 1309, respectively[11].

The adsorption coefficients given in Tables I, IV and VI are relatively small, and they do not directly indicate the practical situation. Using eqn. 1 and the data given in Tables I–IV, the contribution of adsorption to the retention can be calculated (Table VII). The percentage contributions given in Table VII show tendencies rather than absolute figures. When the film thickness is increased, the stationary phase volume is increased, but the stationary phase surface area is almost unaffected. The

TABLE VII

PERCENTAGE CONTRIBUTIONS TO THE RETENTION FROM ADSORPTION EFFECTS

Column length (m)	I.D. (mm)	d_f (μm)	Ref.	Contribution to retention from adsorption effects (%)		T (°C)
				C_{17}	C_{20}	
20	0.32	1.00	11	11	16	100
20	0.32	0.3	14	30	39	100
19	0.32	0.64	14	17	23	100
20	0.32	0.09	14	58	68	100
11	0.10	0.09	14	58	68	100
20	0.32	0.3	13	30	39	100
10	0.32	0.3	13	30	39	100
26	0.32	0.3	13	30	39	100
4	0.05	0.1	13	56	66	100
4.5	0.05	0.1	13	56	66	100
20	0.32	2.0	11	3	4	125
20	0.32	1.0	11	5	7	125
26.5	0.22	0.16	11	26	32	125
26.5	0.25	0.20	11	22	28	125
26.5	0.25	0.20	11	22	28	125

role of gas–liquid adsorption is thus decreased for increased values of d_f. For polar packed columns, a strong influence of column loading on Kováts retention index was demonstrated by Fritz et al.[26].

The relationship in eqn. 4 can also be expressed as[25,27]

$$I_i = I_0 + a_{lKi}(1/k_{st})$$ (5)

where k_{st} is the retention factor of a standard compound. Use of this equation was proposed for measurement of the retention index on capillary columns. The factor a_{lKi} includes $1/r$, and eqn. 5 is therefore relevant only for constant column radius.

I_0 can also be expressed as[25]

$$I_0 = 100 z + 100 \cdot \frac{\log (K_{li}/K_{lz})}{\log [K_{l(z+1)}/K_{lz}]}$$ (6)

where K_{li} is the partition coefficient of the substance to be indexed and $K_{l(z+1)}$ and K_{lz} are the partition coefficients of the standards, whose molecules contain $z + 1$ and z carbon atoms, respectively[25]. Insertion of the data in Table IV into eqn. 6 gives the invariant retention index for 2-methylnaphthalene at 125°C in the three different retention index systems tested. I_0 in the n-alkane, 2-ketone and FAME systems were 2062, 1318 and 1306, respectively. Good agreement with the I_0 values calculated from plots of I vs. $1/d_f$ can be observed. The I_0 value for 2-methylnaphthalene at 100°C in the n-alkane system was 2008 when calculated from eqn. 6. The same I_0 calculated from Fig. 2 was 2019 when the two points at $1/d_f = 11.1$ were excluded. Excluding instead the two points at $1/d_f = 10.0$ resulted in a line $I = 1956 - 3.45 \cdot 10^{-3} (1/d_f)$; correlation coefficient 0.71 and $n = 8$. The I_0 and correlation coefficient values and the slope of the line indicate that the data obtained on the two columns having $1/d_f = 11.1$ are anomalous.

When using n-alkanes as standards on a polar column, the conditions for the calculation of I_0 are not strictly followed, i.e., that the standard should show no adsorption at the gas–liquid interface. In this work, the probe, 2-methylnaphthalene, is not adsorbed, and here the strong adsorption of n-alkanes is demonstrated by the variation in Kováts retention index for 2-methylnaphthalene with $1/d_f$. The unsuitabilty of n-alkanes as retention index standards on polar columns is thus demonstrated. It has been shown that when using 2-ketones or FAME as standards, the slope of plots of I for 2-methylnaphthalene vs. $1/d_f$ was approximately ten times lower than when n-alkanes were used as standards[11]. A comparison of Tables I and IV shows that the adsorption effects decrease, at least for n-alkanes, as the temperature increases. This was observed also by Martin[22].

The concept of invariant retention index has been used to demonstrate the adsorption of n-alkanes at the gas–liquid interface when using a polar column. Polar standards show only a slight degree of surface adsorption, and, therefore, they would give more precise indexing on than n-alkane standards polar columns.

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