Note

The influence of the support material and liquid loading on retention indices in gas–liquid chromatography

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Retention indices are widely accepted in reporting gas chromatographic data. In comparison with absolute retention data, they can be determined easily and reproducibly using simple techniques, because relative retention values should not be influenced by instrumental parameters, *e.g.*, carrier gas flow-rate. Also, their temperature dependence is very small and is often linear.

The retention index of a test substance ("probe") increases as the "polarity" of the stationary phase is increased. Rohrschneider[1] introduced a characterization scheme for gas chromatographic liquid phases by measuring the retention indices of five selected probes. The magnitude of these values can be correlated with solubility parameters[2,3]. The measurement of retention indices may be the starting point in calculating thermodynamic data, *e.g.*, solution enthalpies[4]. However, in spite of their importance to the analyst and physical chemist and their widespread occurrence in the literature, the values cited for a particular stationary phase and column temperature often differ from worker to worker. The difference can sometimes be related to the use of incompletely specified stationary phases or to chemical modifications at the column temperature.

The application of different support materials and liquid loadings also causes variations in retention indices. The significance of these effects was not fully recognized until now and the interpretations given so far are contradictory. It was our intention to investigate the extent of variation of retention indices when the activity of the support material and the percentage of liquid loading are changed. Defined linear high polymers served as stationary liquids.

EXPERIMENTAL

A Perkin-Elmer F 6 gas chromatograph, equipped with a flame-ionization detector, was employed. The stationary phases were squalane (Merck, Darmstadt, G.F.R.) and some synthetic polymers: poly(ethylene oxide) ($\bar{M}_n$ 27,000, Hoechst, Frankfurt, G.F.R.), poly(vinyl acetate) ($\bar{M}_n$ 87,000, Wacker Chemie, München, G.F.R.), Solprene 303 (styrene–butadiene copolymer, 48% styrene, $\bar{M}_n$ 110,000, Philips Petroleum, Antwerp, Belgium). The support material was 60–80 mesh Chromosorb (Johns-Manville, Denver, Colo., U.S.A.); the activity of the various types was decreased by acid washing (AW) and dimethyldichloro silanization (DMCS) in the following order: A (NAW), W (AW), W (AW/DMCS), G (AW/DMCS).

The solutes injected were the probes suggested by Rohrschneider, namely benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine, with n-alkanes as reference substances. The injection volume was 0.01 μl.

A correction for gas hold-up was made by means of the retention of methane. The retention index, I, was calculated as follows:

$$I = 100\,x + (y - x)\frac{\log t_z - \log t_x}{\log t_y - \log t_x} \tag{1}$$

where t_x = net retention time of the n-alkane C_xH_{2x+2}, t_y = net retention time of the n-alkane C_yH_{2y+2} and t_z = net retention time of the probe.

The measured retention indices did not depend on instrumental parameters, e.g., column length, flow-rate and pressure. The reproducibility was within the limit of experimental error (± 3 index units).

RESULTS AND DISCUSSION

Gas chromatographic retention often cannot be explained by solution of the probe molecules in the liquid phase alone, but adsorption on the solid support and at the gas–liquid surface may contribute significantly to the retention. The net retention volume, V_n, then has to be expressed in the following form[5]:

$$V_n = \underset{\text{(term 1)}}{K_{SS}A_S} + \underset{\text{(term 2)}}{K_L V_L} + \underset{\text{(term 3)}}{K_{LS}A_L} \tag{2}$$

where K = partition coefficient, referring to sorption at the support surface (SS), at the liquid surface (LS) and in the bulk liquid (L); A = surface area of the support (S) and the liquid (L); and V_L = liquid phase volume.

If the net retention volume is determined by solution in the stationary liquid alone (term 2), relative retention data, like retention indices, do not depend on liquid loading, as $V_{n_1}/V_{n_2} = K_{L_1}/K_{L_2}$. However, if terms 1 and 3 are not negligible, variation of the retention index occurs when different support materials or liquid loadings (i.e., changing the surface to volume ratio) are used. This result follows from the fact that it is very unlikely that the non-polar reference substances (n-alkanes) will show the same adsorption behaviour as the selected probes.

The contribution of the individual terms in eqn. 2 to the overall retention is often discussed in the literature in a contradictory way. In most instances, different retention indices for the same stationary liquid are attributed to the use of supports of different activity[6]. This assumption seems to be valid only for non-polar liquids such as squalane. Indeed, for squalane we found a strong dependence on the support activity, even when a 20% liquid loading was used, as shown in Table I.

The SiOH groups of the Chromosorb material lead to a strong adsorption at the support surface for polar probes that are capable of interacting with hydroxyl groups. This effect is manifested by an increase in the retention indices with enhanced support activity. It is well known that this adsorption is suppressed to a great extent if the SiOH groups are silanized (Table I).

If the percentage of liquid loading is increased (i.e., lowering the surface to volume ratio), the solution in the liquid phase becomes increasingly important, so

TABLE I

DEPENDENCE OF RETENTION INDICES ON SUPPORT ACTIVITY

20% squalane, 100°.

Chromosorb	Benzene	Ethanol	Methyl ethyl ketone	Nitromethane	Pyridine
A (NAW)	651	550	650	550	—
W (AW)	649	425	554	465	725
W (AW/DMCS)	649	377	531	460	695

TABLE II

RETENTION INDICES USING SOLPRENE 303 COATED ON CHROMOSORB W (AW) AT 100°

Loading (%)	Benzene	Nitromethane
5	753	731
10	755	678
20	756	669

that the retention indices of polar probes will decrease. This effect is shown in Table II for a non-polar styrene–butadiene copolymer as the stationary liquid and nitromethane as the probe.

Benzene and the *n*-alkanes do not interact with the hydroxyl groups of the support and thus the retention index is constant. According to eqn. 2, this result is possible only if term 2 dominates and therefore adsorption at the gas–liquid interface (term 3) is negligible for non-polar stationary liquids.

However, this conclusion is not valid for polar stationary liquids. Our results for these systems can be explained only by assuming a considerable adsorption at the gas–liquid interface. This interpretation contradicts other explanations given in the literature, relating the variation in retention index solely to the support activity[6].

If polar liquid phases are used, apparently the active centres (SiOH groups) are saturated by the functional groups of the stationary liquid. The activity of the diatomaceous earth supports used in this investigation has only a minor influence on the overall retention, as indicated by the fact that the retention indices are nearly identical for stationary phases that have very different support activities but similar liquid surface structures[7] (Table III).

Now, when the strongly deactivated support Chromosorb G (AW/DMCS) was used, which is assumed to be nearly inert, a dependence of the retention index on the percentage of liquid loading for all probes investigated, including benzene, was found (Table IV).

TABLE III

DEPENDENCE OF RETENTION INDICES ON SUPPORT ACTIVITY

15% poly(vinyl acetate), 100°.

Chromosorb	Benzene	Ethanol	Methyl ethyl ketone	Nitromethane	Pyridine
A (NAW)	986	940	980	1202	1240
W (AW/DMCS)	988	940	980	1206	1245

TABLE IV

DEPENDENCE OF RETENTION INDICES ON LIQUID LOADING

Poly(vinyl acetate) coated on Chromosorb G (AW/DMCS).

Loading (%)	Benzene	Ethanol	Methyl ethyl ketone	Nitromethane	Pyridine
2	964	919	954	1175	1230
4	992	949	981	1205	1242
5	996	953	985	1215	1246

From the above arguments, it is clear that the variation in retention indices in this instance is not related to the support activity, but should be attributed to adsorption at the gas–liquid interface of the polar liquid, corresponding to term 3 in eqn. 2. If the K_{LS}/K_L value is higher for the n-alkanes than for the polar molecules, the retention index increases with increasing liquid loading, as shown in Table IV. The major importance of the interfacial adsorption of alkanes on polar stationary liquids has been discussed by Martire[8].

To summarize our results, including additional experimental evidence reported elsewhere[3], the behaviour of retention indices can be related to the "polarity" of the stationary liquid in the following way:

(a) For non-polar stationary liquids, one has to evaluate the contribution of the adsorption on the solid support (term 1 in eqn. 2). Inert support materials are needed ($K_{SS} \rightarrow 0$), otherwise the retention index may decrease with increasing liquid loading.

(b) For polar liquids, the adsorption at the support surface is negligible, but the adsorption at the liquid surface should be taken into account (term 3). High liquid loadings are advantageous ($V_L \gg A_L$). The retention index increases with increasing liquid loading.

In most instances, terms 1 and 3 are active alternatively, not simultaneously. Thus the variation of retention index with liquid loading provides useful information about retention mechanisms in the system being investigated.

It should be noted, however, that the assumptions made in this investigation are valid only for diatomaceous earth supports. If, for example, a PTFE support is used, the adsorption of the polar probes on the support surface is considerably reduced, but there absorption of the n-alkanes in the PTFE matrix probably occurs[9], which makes the behaviour of the reference substances rather complex. This may lead to another type of variation of retention index which can be discussed in a similar manner using eqn. 2.

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