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GAS-LIQUID CHROMATOGRAPHY IN QUALITATIVE ANALYSIS

XVIII^a. STUDY OF THE DEPENDENCE OF THE RETENTION BEHAVIOUR OF POLYOXYETHYLENE GLYCOL COLUMNS ON THE NATURE OF THE SUPPORT AND PHASE LOADING

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SUMMARY

The retention behaviour of fourteen solutes, possessing a wide range of polarity, and five *n*-alkanes was investigated using various percentage loadings of polyethylene glycol 400 as stationary phase on two diatomaceous supports of different adsorptivity. Retentions were measured as Kováts retention indices and specific retention volumes, in order to compare the dependences of absolute and relative retentions on phase loading. For all the solutes examined the values of the retention index decrease with a reduction in phase loading, suggesting a decrease in phase polarity. In contrast, the polar test solutes display slight increases in specific retention whereas those of the *n*-alkanes increase enormously as the phase loading is decreased and thereby giving rise to the observed large shifts in retention index. In order to explain the phase loading dependence of retention index with polar stationary phases an elution mechanism involving a significant contribution of gas-liquid interfacial adsorption is proposed.

INTRODUCTION

Whilst partition forms the basis of gas-liquid chromatography, it is widely appreciated that other phenomena frequently contribute to retention. In particular, the stationary phase supports, used for both packed and capillary columns, are never totally inert. Despite the use of sophisticated deactivation procedures, which generally result in a minimization of the most obvious effects, adsorption artefacts frequently cause difficulties.

Almost from the inception of the technique, adsorption was suggested to be a frequent contributor to retention and its effect was demonstrated clearly by Martin

^a For Part XVII, see *Chromatographia*, 15 (1982) 355.

in 1961^{1,2}. The influence of adsorptive effects has been investigated by a number of workers using static and dynamic gas chromatographic measurements³⁻⁵ and by the measurement of the surface tension of solute-solvent mixtures⁶⁻⁸.

Diatomaceous supports are characterized by relatively large surface areas and on coating with stationary phase the ratio of the support surface to the stationary phase volume is considerable. For instance, with a 10% (w/w) loading of stationary phase on a support of modest surface area, say 2 m²/g, the ratio is 20 m²/ml of stationary phase. Hence any differences between the coated and bulk liquid phase may be accentuated by the support. For the stationary phase concentrations used with conventional analytical columns, significant multi-molecular layer build-up occurs so that interactions due to support adsorptivity are transmitted with decreasing effect. However, at reduced phase loadings the latter effects would be expected to become more obvious, together with interactions associated with the gas-liquid interface.

Koro⁹ has provided a thermodynamic model for phase-support performance from which it is evident that the physical state of the stationary phase on the support surface is of prime importance. Without adequate wetting of the support, the stationary phase will tend to be present as discrete droplets, on the outside of the support particles, rather than with penetration into the porous matrix. With increased phase concentration coalescence gradually occurs, leading to the formation of a continuous film. The capacity to achieve wetting is dependent on the chemical composition of a phase and is often poorer with non-polar materials. It is pertinent to note that Conder *et al.*¹⁰ reported that with a silanized diatomaceous earth support the presence of 7.15% of squalane was necessary to form a continuous film. Clearly, this level of stationary phase is orders of magnitude greater than that required to form a monomolecular layer, which might be expected if perfect wetting occurred. Before coalescence with the presence of droplets, a large area of support and a small area of stationary phase are available for contact with the solute as manifested by the peak tailing of polar analytes.

Nikolov¹¹ developed a relationship that considers the stationary phase to consist of a structured layer in the proximity of the support surface and a bulk liquid layer. A simplified form of the relationship, which corresponds to phase loadings that are sufficiently high that the effects due to the structured layer are minimal, is

$$V_N^* = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \quad (1)$$

which can be rearranged to

$$\frac{V_N^*}{V_L} = K_L + \frac{1}{V_L} (A_{GL} K_{GL} + A_{LS} K_{GLS}) \quad (2)$$

where

- V_N^* = net retention volume per gram of column packing;
- V_L = volume of liquid phase per gram of packing;
- K_L = gas-liquid partition coefficient;
- A_{GL} = gas-liquid interfacial area per gram of packing;
- K_{GL} = adsorption coefficient at the gas-liquid interface;
- A_{LS} = liquid-solid interfacial area per gram of packing;
- K_{GLS} = coefficient of adsorption at the liquid-solid interface.

From eqn. 2, it follows that a plot of V_N^*/V_L versus $1/V_L$ may be either linear or curved, giving K_L as the intercept at $1/V_L = 0$. The exact shape of the plot is dependent on the relative adsorption at the gas-liquid and liquid-solid interfaces. For solutes retained solely by gas-liquid partition, eqn. 2 predicts a zero slope. An evaluation of the above expressions using data obtained for Apiezon M and Carbowax 4000 columns was reported by the author¹¹. Related studies using polyhydric alcohols have included diethylene and triethylene glycols¹², ethylene glycol¹³ and glycerol¹⁴.

The present work reveals substantial differences between the retention behaviour of polar solutes and *n*-alkanes when chromatographed on polyoxyethylene glycol columns with phase loadings between 0.5 and 10%. Further, it is shown that these differences are dependent on the nature of the support phase. The significance of these results in terms of analytical applicability of Kováts retention index is discussed.

EXPERIMENTAL

Chromatography was carried out isothermally using a Pye Unicam 204 instrument equipped with a flame ionization detector and employing the following conditions: column temperature, 100°C; injection temperature, 120°C; detector temperature, 150°C; and carrier gas, nitrogen a flow-rate of at 40 ml/min. Glass columns (1.7 m × 4 mm I.D.) packed with mixtures of polyoxyethylene glycol (PEG) 400 (BDH, Poole, U.K.) and either 80-100 BS mesh Phasesep P or Phasesep W (Phase Separations, Queensferry, Clwyd, U.K.).

Acid-washed Phasesep P was prepared by washing the support continuously for 2 days with concentrated hydrochloric acid and then exhaustively washing with deionized water until approximately neutral. Phasesep P is prepared from Johns Manville Sil-o-cell C-22 insulation brick¹⁵ and is noted for its adsorptivity¹⁶. Phasesep W is a flux-calcined diatomaceous silica (Johns Manville Celite) with a relatively non-adsorptive surface and is widely used for polar solutes.

Fourteen probe solutes were used, including a number of those recommended by McReynolds for phase characterization with the notable exceptions of pyridine and *cis*-hydrindane. Additional alcohols were added as it was expected that hydroxylic solutes would be particularly sensitive to physico-chemical changes occurring in polar phases such as PEG 400.

Retentions, in specific retention volume¹⁷ and Kováts retention index units¹⁸, were obtained from chromatograms of calibration mixtures containing *n*-alkanes as internal standards. Retention times, measured between the point of injection and peak maxima by means of a Spectra-Physics SP4100 integrator, were corrected for the gas holdup by means of the retention of methane¹⁹. Values for V_g were calculated by means of the expression

$$V_g = \frac{273 V_N}{TW_L}$$

where V_N is the net retention volume, T the column temperature (K) and W_L the weight of stationary phase in the column, and values for the retention index were calculated using

$$I = 100N + 100n \left(\frac{\log R_x - \log R_N}{\log R_{N+n} - \log R_N} \right)$$

where R_x , R_N and R_{N+n} are the adjusted retentions of the analyte and n -alkanes possessing N and $N+n$ carbon atoms, respectively.

The volumetric flow-rate of carrier gas, required to determine V_N , was measured before and after each chromatogram by means of a soap-film bubble meter.

RESULTS AND DISCUSSION

For the Phasesep W columns, a reduction in phase loading was accompanied by substantial decreases in retention index for all the solutes examined, as shown in Table I.

Previously it has been found that the retention index is directly related to phase polarity²⁰ and that for polyoxyethylene glycols and related materials the retention indices of hydrogen bond donor and acceptor molecules increase with increasing hydroxyl content of the stationary phase^{21,22}. A similar observation was made with squalene-farnesol²³ and corn oil-castor oil²⁴ mixed phases in connection with oxidation studies by inverse gas chromatography. Therefore, it is possible that the dependence of retention index on phase loading is due to a concomitant reduction in effective polarity arising from the adsorption of the terminal hydroxyls of the polyoxyethylene glycol molecules by active sites on the support surface. It is envisaged that as the phase loading is increased a strongly adsorbed layer of orientated polyoxyethylene glycol molecules is formed initially, followed by the deposition of

TABLE I
DEPENDENCE OF RETENTION INDEX ON LIQUID PHASE LOADING FOR POLYOXYETHYLENE GLYCOL-PHASESEP W COLUMNS AT 100°C

Columns: A = 10.0%, B = 2.5%, C = 1.0%, D = 0.25% liquid phase loading.

Substance	Retention index (<i>I</i>)				δI^a
	A	B	C	D	
2-Butanol	1135	1057	977	944	191
Chlorobenzene	1272	1164	1106	1037	235
2,3-Dimethyl-3-pentanol	1284	1179	1139	1085	199
2,4-Dimethyl-3-pentanol	1278	1177	1139	1076	202
1,4-Dioxane	1168	1083	1000	956	212
3-Hexanol	1300	1188	1148	1085	215
2-Hexanone	1168	1098	1033	979	189
1-Iodobutane	1115	1050	977	930	185
Methyl <i>n</i> -butyrate	1046	983	935	920	126
2-Methyl-2-pentanol	1204	1124	1070	1026	178
1-Nitropropane	1297	1182	1129	1058	239
2-Octyne	1079	1018	977	956	123
Toluene	1093	1018	935	928	165
2,2,3-Trimethyl-3-pentanol	1324	1269	1174	1124	200

^a $\delta I = I_A - I_D$.

bulk liquid containing hydroxyl groups available for partitioning with analyte molecules. Consistent with this hypothesis, the more polar analytes display the greater shifts in retention index. However, there are a number of inconsistencies, for instance, the lack of discrimination between the secondary and tertiary alcohols butan-2-ol and 2,2,3-trimethylpentan-3-ol, which suggest the occurrence of other retention processes.

Whereas Phasesep W is a relatively inert support, Phasesep P is moderately adsorptive and its use with apolar stationary phases is characterized by the peak tailing of polar solutes and in extreme cases on-column decomposition¹⁶. Such problems can be prevented by the addition of small amounts of polyols, which it is envisaged are strongly adsorbed as an orientated monolayer on the support surface²⁵. Because of its greater adsorptivity, Phasesep P would be expected to adsorb a higher proportion of a deposited layer of polyoxyethylene glycol, therefore reducing the effective concentration of bulk phase hydroxyl groups at a particular phase loading. Accordingly, the retention indices of polar solutes would be expected to be lower when examined on PEG 400-Phasesep P columns compared with those obtained using the equivalent loading on Phasesep W. As can be seen from the data in Tables I and II, the experimental results at first sight are consistent with this hypothesis.

The acid washing of diatomaceous supports generally leads to the removal of metallic impurities, such as iron, and a slight but significant increase in adsorptivity due to the exposure of surface silanol groups and the hydrolysis of siloxane groups:

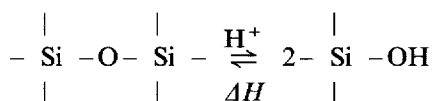


TABLE II

DEPENDENCE OF RETENTION INDEX ON LIQUID PHASE LOADING FOR POLYOXYETHYLENE GLYCOL-PHASESEP P COLUMNS AT 100°C

Columns: A = 10%, B = 2.5%, C = 1.0%, D = 0.5% PEG 400 on Phasesep P; E = 10%, F = 2.5% PEG 400 on acid-washed Phasesep P; G = 5% PEG 4000 on Phasesep P.

Substance	Retention index (I)							δI^a	δI^a	$\delta I'^a$	$\delta I''^a$
	A	B	C	D	E	F	G				
2-Butanol	1101	949	866	825	1079	959	907	276	22	-10	82
Chlorobenzene	1233	1051	939	879	1202	1059	1076	354	31	-8	197
2,3-Dimethyl-3-pentanol	1249	1108	1042	1005	1223	1114	1069	244	26	-6	64
2,4-Dimethyl-3-pentanol	1246	1109	1048	1020	1220	1114	1077	226	26	-5	57
1,4-Dioxane	1136	955	838	779	1105	967	948	357	31	-12	169
3-Hexanol	1266	1113	1046	1011	1235	1120	1074	255	31	-7	63
2-Hexanone	1137	987	921	900	1112	1000	979	237	25	-13	79
1-Iodobutane	-	940	-	833	1066	946	965	-	-	-6	132
Methyl <i>n</i> -butyrate	1026	889	809	790	1000	892	884	236	26	-3	94
2-Methyl-2-pentanol	1175	1039	974	947	1148	1048	990	228	28	-9	43
1-Nitropropane	1251	1050	958	896	1218	1077	1068	355	33	-27	172
2-Octyne	1059	955	913	896	1037	959	967	163	22	-4	71
Toluene	1070	912	838	779	1038	925	933	291	32	-13	154
2,2,3-Trimethyl-3-pentanol	1289	1152	1089	1059	1264	1159	1119	230	25	-7	60

^a $\delta I = I_A - I_D$; $\delta I' = I_A - I_E$; $\delta I'' = I_B - I_F$; $\delta I''' = I_G - I_D$.

Consistent with the proposed model for the retention behaviour of polyoxyethylene glycol-packed columns, the 10% loaded columns show a reduction in apparent phase polarity on acid washing. On the other hand, the situation is reversed in the case of the 2.5% loading.

There is clear evidence from electron microscopic studies of chromatographic supports that the surface is less cluttered with debris after acid washing, leading to a higher effective surface area²⁶. As a result, the gas-liquid interfacial area also might be expected to be greater, at a particular phase loading, thereby accentuating the effect on relative retention data of differences in the interfacial adsorption behaviour between *n*-alkanes and polar solutes. This in part may account for the inconsistency between the results obtained with the various acid-washed packings.

Further evidence that the hydroxyl content of polyoxyethylene glycol columns is not solely responsible for their retention behaviour is provided by a comparison of the data for columns D and G. These were prepared using polyoxyethylene glycol samples with average molecular weights of 400 and 40 000, respectively, at loadings designed to yield the same weight of hydroxyl groups per gram of packing. Consistently the retention indices on column D are significantly lower than those on column G, suggesting a marked difference in polarity. Clearly, it is necessary to implicate a factor in addition to hydroxyl content to account for the retention behaviour of these columns.

In an attempt to compensate for the effects of instrumental variables on absolute

TABLE III

DEPENDENCE OF SPECIFIC RETENTION VOLUMES ON LIQUID PHASE LOADING FOR POLYOXYETHYLENE GLYCOL-PHASESEP W COLUMNS AT 100°C

Columns: A = 10.0%, B = 2.5%, C = 1.0%, D = 0.50% liquid phase loading

Substance	Specific retention volume ($\text{cm}^3 \text{g}^{-1}$)			
	A	B	C	D
<i>n</i> -Octane	73.0	174.8	225.3	393.9
<i>n</i> -Nonane	121.7	274.7	477.0	840.3
<i>n</i> -Decane	309.5	536.9	927.6	1392
<i>n</i> -Undecane	563.4	961.3	1656	2600
<i>n</i> -Dodecane	1005	2171	3034	4674
2-Butanol	695.5	749.1	821.5	1050
Chlorobenzene	1513	1623	1723	1786
2,3-Dimethyl-3-pentanol	1607	1835	2080	2337
2,4-Dimethyl-3-pentanol	1558	1798	2067	2311
1,4-Dioxane	838.1	873.9	980.6	1077
3-Hexanol	1767	1973	2226	2390
2-Hexanone	834.6	948.9	1153	1208
1-Iodobutane	619.0	711.6	795.0	971.6
Methyl <i>n</i> -butyrate	410.4	474.4	649.3	911.6
2-Methyl-2-pentanol	1029	1174	1391	1654
1-Nitropropane	1732	1885	1974	1970
2-Octyne	497.3	611.8	808.3	1077
Toluene	546.0	599.3	662.5	945.4
2,2,3-Trimethyl-3-pentanol	2031	2297	2637	3046

TABLE IV

DEPENDENCE OF SPECIFIC RETENTION VOLUMES ON LIQUID LOADING FOR POLYOXYETHYLENE GLYCOL-PHASESEP P COLUMNS AT 100°C

Columns: A = 10%, B = 2.5%, C = 1.0%, D = 0.5% PEG 400 on Phasesep P; E = 10%, F = 2.5% PEG 400 on acid-washed Phasesep P; G = 5% PEG 4000 on Phasesep P.

Substance	Specific retention volume ($\text{cm}^3 \text{g}^{-1}$)						
	A	B	C	D	E	F	G
<i>n</i> -Octane	95.0	254.3	570.2	961.3	105.6	285.4	152.2
<i>n</i> -Nonane	263.1	611.8	1416	2320	249.7	660.1	369.0
<i>n</i> -Decane	573.7	1279	2969	4840	509.0	1356	764.6
<i>n</i> -Undecane	1111	2510	5859	9750	974.9	2658	1521
<i>n</i> -Dodecane	2064	4847	11500	19020	1801	5102	2948
2-Butanol	1118	874.1	1022	1160	845.2	999.0	384.2
Chlorobenzene	2543	1804	1868	1923	1825	2007	1297
2,3-Dimethyl-3-pentanol	2799	2654	3972	5005	2079	2098	1233
2,4-Dimethyl-3-pentanol	2744	2670	4090	5536	2907	1305	
1,4-Dioxane	1393	921.7	786.5	795.6	1004	1070	521.1
3-Hexanol	3111	2749	4050	5237	2233	3015	1278
2-Hexanone	1400	1160	1632	2320	1047	1356	658.1
1-Iodobutane	—	826.0	—	1260	778.0	927.6	593.4
Methyl <i>n</i> -butyrate	679.6	556.0	609.5	861.9	509.0	624.4	323.3
2-Methyl-2-pentanol	1761	1661	2477	3248	1306	1855	715.1
1-Nitropropane	2828	1788	2163	2188	2012	2266	1225
2-Octyne	844.0	922.0	1573	2188	644.0	1008	604.8
Toluene	908.0	659.5	786.7	828.7	653.0	784.9	464.1
2,2,3-Trimethyl-3-pentanol	3592	3520	5427	7293	2670	3889	1727

retention data, Littlewood *et al.*¹⁷ introduced the specific retention volume, which is defined as the net retention volume of a solute at 0°C per unit weight of stationary phase. Clearly, for a purely gas-liquid partition system values of the specific retention volume, V_g , would be expected to be independent of phase loading. For all the solutes examined, the values for V_g increased as the phase loading was reduced with Phasesep W as the support, as shown in Table III. The increases in V_g are not uniform and are most pronounced with the less polar compounds. Thus, 2-methyl-2-pentanol and *n*-dodecane have almost identical retentions at the 10% loading but for the 0.5% loading the specific retention volume of the *n*-alkane is almost three times that of the alcohol. Similar trends are apparent for the other polar solutes when compared with the *n*-alkanes, which consistently display the greater shifts in specific retention volume. A consequence of these shifts is that the corresponding values for retention index are distorted. Data which appear to suggest a reduction in selectivity with reduced phase loading are in fact due to the selective retention of the *n*-alkane internal standards used to measure retention index.

A possible explanation of the observed phase loading dependence of specific retention volume is that for polyoxyethylene glycol there is a significant contribution to the overall retention by adsorption at the gas-liquid interface. As pointed out previously, this contribution would be expected to be greater for the less polar solutes.

TABLE V

DEPENDENCE OF RELATIVE RETENTION RATIOS ON LIQUID PHASE LOADING AND THE FUNCTIONALITY OF THE INTERNAL STANDARD

 R_{xn} , *n*-undecane as internal standard; R_{xs} , 2-hexanone as internal standard; $R_{xs'}$, 3-hexanol internal standard.

Substance	10% PEG 400-Phasesep W			1% PEG 400-Phasesep W			Percentage change ^a		
	R_{xn}	R_{xs}	$R_{xs'}$	R_{xn}	R_{xs}	$R_{xs'}$	R_{xn}	R_{xs}	$R_{xs'}$
<i>n</i> -Dodecane	1.784	1.204	0.569	1.832	2.631	1.363	+ 2.7	+11.8	+139
2-Butanone	1.234	0.833	0.394	0.496	0.712	0.369	-59.8	-14.5	- 6.3
Chlorobenzene	2.685	1.813	0.856	1.040	1.494	0.774	-61.2	-17.6	- 9.6
2,3-Dimethyl-3-pentanol	2.852	1.925	0.909	1.256	1.804	0.934	-56.0	- 6.3	- 2.7
2,4-Dimethyl-3-pentanol	2.765	1.866	0.882	1.248	1.793	0.928	-54.9	- 3.9	+ 5.2
1,4-Dioxane	1.488	1.004	0.474	0.592	0.850	0.440	-60.2	-15.3	- 7.2
1-Iodobutane	1.099	0.742	0.350	0.480	0.690	0.357	-56.3	- 7.0	+ 2.0
Methyl <i>n</i> -butyrate	0.728	0.492	0.232	0.392	0.563	0.291	-46.1	+14.4	+25.4
2-Methyl-2-pentanol	1.826	1.233	0.582	0.840	1.206	0.625	-54.0	- 2.2	+ 7.4
1-Nitropropane	3.074	2.075	0.908	1.192	1.712	0.887	-61.2	-17.5	- 9.5
2-Octyne	0.883	0.596	0.281	0.488	0.701	0.363	-44.7	+17.6	+29.2
Toluene	0.969	0.654	0.309	0.400	0.574	0.298	-58.7	-12.2	- 3.5
2,2,3-Trimethyl-3-pentanol	3.605	2.433	1.149	1.592	2.287	1.032	-55.8	- 6.0	-10.2

$$^a \text{Percentage change} = \frac{R_{xs}(1\%) - R_{xs}(10\%)}{R_{xs}(10\%)} \cdot 100.$$

Also, for a particular solute retention due to gas-liquid adsorption would be expected to increase with increase in the gas-liquid interfacial area.

Not only is Phasesep P more adsorptive, but also it has a surface area per gram that is approximately four times that of Phasesep W²⁷. Therefore, at a particular phase loading the Phasesep P columns would be expected to possess larger gas-liquid interfacial areas and in turn give rise to increased values for V_g . As can be seen from the data in Table IV, for all the solutes examined the specific retention volumes are greater than the values on the corresponding Phasesep W columns. Again, the *n*-alkanes show the greater shifts which, on comparison with those of the polar solutes, are more marked than with the Phasesep W columns, an observation that is consistent with the retention indices given in Tables I and II.

The retention volumes obtained for columns A, B, C and D (see Table IV) are consistent with a retention mechanism involving partition together with an adsorption phenomenon, probably gas-liquid interfacial adsorption. Consistent with this view, the V_g data for the 2.5% loading on acid-washed Phasesep P show marked increases, particularly for the more hydrophobic solutes, compared with the non-acid-washed material. The converse occurs with the 10% loading, where the changes in support adsorptivity might be expected to outweigh the effects of the concomitant increase in surface area.

The results for columns D and G are particularly interesting insofar as these columns contain the same weight-percentage of hydroxyl groups. As a 5% loading the PEG 4000 column would be expected to possess a greater average film thickness of stationary phase but a lower gas-liquid interfacial area. Consistent with the thesis put

forward to explain the loading dependence of retention index with polar phases, the 0.5% PEG 400 column yields the higher V_g values.

The results of these studies provide strong evidence to suggest that the phase loading dependence of retention index is due in part to the preferential adsorption of *n*-alkanes at the gas-liquid interface of polar stationary phases, a conclusion that is borne out by independent observations by Kersten *et al.*²⁸.

Because *n*-alkanes are sparingly soluble in polar phases, such as the lower molecular weight polyoxyethylene glycols, several alternative standards have been proposed for retention index measurements, including alkanolic acid methyl esters²⁹, 2-alkanones³⁰ and *n*-alkanols³¹. Relative retention ratios determined using 2-hexanone and 3-hexanol as internal standards for a series of PEG 400-Phasesep W columns were compared with the corresponding R_{xII} values in Table V. As can be seen, the R_{xs} values obtained with the polar internal standards are distinctly less dependent on phase loading. However, with apolar solutes the converse applies, thereby presenting the analyst with a dilemma.

Recently, 1-nitroalkanes have been recommended as alternatives to *n*-alkanes as retention index standards for drug identification³². These compounds were shown to be suitable for use with polar stationary phases with the added attraction of sensitivity towards selective detector systems and correlation with reversed-phase liquid chromatographic retention indices³³. In view of these attributes, a more severe test was applied using a series of Phasesep P columns. The relative retention ratios obtained, which are summarized in Table VI, indicate that with respect to phase loading dependence the 1-nitroalkanes offer no significant advantages over the *n*-alkanes as standards for retention index measurements.

CONCLUSIONS

A systematic study of the retention behaviour of polyoxyethylene glycol-packed columns has revealed a marked dependence of retention index data on the nature of the support and stationary phase loading. Polar solutes in particular show large shifts of retention index with reduction in phase loading, which suggests the occurrence of a significant reduction in the polarity of the bulk liquid phase. On the other hand, specific retention volumes are found to increase with reduction in phase loading. Here the *n*-alkanes display the greatest shifts with phase loading, which are interpreted in terms of selective retention at the gas-liquid interface through Gibbs surface adsorption. It is the selective retention of the *n*-alkanes that is in large part responsible for the shifts in retention index rather than changes in stationary phase polarity.

The results of this work indicate that retention indices measured using polar phases supported on diatomaceous materials should be viewed with caution. Clearly, in order that compilations of data may be used for peak identification by retention coincidence, not only should the nature of the support be defined but also the exact phase loading. Moreover, as the Gibbs surface adsorption is dependent on sample size³⁴, the use of small, well defined solute and *n*-alkane samples would seem to be prudent. Further, the present observations indicate that stationary phase polarity scales based on retention index measurements, as exemplified by those introduced by Rohrschneider³⁵, McReynolds³⁶ and Evans and Haken³⁷, could yield misleading results and should be used with caution.

TABLE VI
DEPENDENCE ON PHASE LOADING, WITH PHASESEP P AS SUPPORT, OF RELATIVE RETENTION RATIOS DETERMINED WITH *n*-ALKYL AND 1-NITROALKANE INTERNAL STANDARDS

R_{sm} , *n*-undecane as internal standard; R_{ss} , 1-nitropropane as internal standard.

Substance	10% PEG 400-Phasesep P		2.5% PEG 400-Phasesep P		1% PEG 400-Phasesep P		Percentage change ^a	
	R_{sm}	R_{ss}	R_{sm}	R_{ss}	R_{sm}	R_{ss}	R_{sm}	R_{ss}
<i>n</i> -Decane	0.516	0.203	0.509	0.715	0.506	1.373	-1.94	+576
2-Butanol	1.006	0.395	0.348	0.488	0.174	0.472	-82.7	+19.5
Chlorobenzene	2.289	0.899	0.719	1.009	0.319	0.864	-86.1	-3.9
2,3-Dimethyl-3-pentanol	2.519	0.990	1.057	1.484	0.678	1.836	-73.1	+85.4
2,4-Dimethyl-3-pentanol	2.470	0.970	1.064	1.493	0.698	1.891	-71.7	+95.0
1,4-Dioxane	1.254	0.493	0.367	0.515	0.134	0.364	-89.3	-26.2
3-Hexanol	2.800	1.100	1.095	1.537	0.691	1.872	-75.3	+70.2
2-Hexanone	1.264	0.496	0.462	0.648	0.278	0.754	-78.0	+52.0
Methyl <i>n</i> -butyrate	0.612	0.240	0.222	0.310	0.104	0.281	-83.0	+17.1
2-Methyl-2-pentanol	1.585	0.623	0.661	0.929	0.422	1.145	-73.4	+83.8
2-Octyne	0.760	0.298	0.367	0.515	0.268	0.727	-64.7	+143
Toluene	0.817	0.321	0.263	0.369	0.134	0.364	-83.6	+13.4
2,2,3-Trimethyl-3-pentanol	3.233	1.270	1.402	1.968	0.926	2.509	-71.4	+95.6

$$^a \text{Percentage change} = \frac{R_{ss}(1\%) - R_{ss}(10\%)}{R_{ss}(10\%)} \cdot 100.$$

Relative retention ratios obtained with oxygenated internal standards are found to be less susceptible than *n*-alkanes to changes in phase loading with hydroxylic phases. However, it is likely that these standards will be equally inappropriate with apolar phases owing to the interfacial adsorption of sparingly soluble standards. Therefore, rather than embark on a new quest for a unified system of phase characterization, which is probably unattainable, it is recommended that scales based on Kováts retention index should be retained, notwithstanding the problems identified herein.

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