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GAS CHROMATOGRAPHIC BEHAVIOUR OF FRAGRANCES ON APIEZON L AND 1,2,3-TRIS(β-CYANOETHOXY)PROPANE

DETERMINATION OF ACTIVITY COEFFICIENTS

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SUMMARY

The gas chromatographic behaviour of fragrances has been studied on Apiezon L and 1,2,3-tris(β-cyanoethoxy)propane as stationary phases. The interaction of the sorbates with the stationary phases was evaluated using activity coefficients. The dependence of the activity coefficient on the molecular weight and on the structure of the compounds has been considered.

INTRODUCTION

The gas chromatographic (GC) behaviour of substances, in particular, the character of the interaction with the stationary phase, can be evaluated using the relevant activity coefficients which are calculated from the well-known equation including the saturated vapour pressures, P, and the specific retention volumes, V_g^0 (eqn. 1).

Having at our disposal the values of P^1 and having determined V_g^0 experimentally, we have calculated the activity coefficient at infinite dilution, γ^∞, on Apiezon L (ApL) and 1,2,3-tris(β-cyanoethoxy)propane (CEP) for alkyl-substituted cyclohexanols and their esters (Table I), certain terpenic compounds (Table II) and macrocyclic compounds (Table III). For heterocyclic oxygen compounds (Table IV), aromatic and aliphatic aldehydes and alcohols (Table V) on ApL, the relative activity coefficient, $\gamma_x^\infty / \gamma_{C_n}^\infty$, was also determined. The latter was calculated from the equation including the retention index, I_x, and the values of the saturated vapour pressure of the studied substance and of a standard (eqn. 2). This coefficient should be also useful in studies of the GC behaviour sorbates.

It should be mentioned that the role of adsorption phenomena in the present systems was not evaluated since we consider their contribution to retention sufficiently small.

EXPERIMENTAL

The GC analysis was performed on a Model 104 Tsvett chromatograph

equipped with a flame ionization detector. The column (1 m × 3 mm I.D.) was packed with 12.8% ApL or 12.9% CEP (determined by extraction after column conditioning) on Polychrom-1 having low absorbability[2]. The column oven temperature was 140°C, that of the injection port was 250°C; sensitivity 2 · 10^{-9} A. The retention time was measured by an I-02 integrator. Each determination was repeated 3–5 times. The accuracy of the measurements of γ^{∞} was about 2% (relative).

Calculations were carried out with the equation

$$\gamma^{\infty} = \frac{1.704 \cdot 10^7}{V_g^0 P_x M} \tag{1}$$

where V_g^0 is the specific retention volume, P_x is the saturated vapour pressure of the substance studied and M is the molecular weight of the liquid phase (for ApL, $M \approx 1300^3$). The relative activity coefficient was calculated from

$$\log \frac{\gamma_{C_n}^{\infty}}{\gamma_x^{\infty}} = C \cdot \frac{I_x - 100n}{100} - \log \frac{P_{C_n}}{P_x} \tag{2}$$

where I_x is the retention index of the substance studied, P_x and P_{C_n} are the saturated vapour pressures of the substance and of the standard (n-tetradecane), respectively, n is the number of carbon atoms in the molecule of the standard. C is a constant calculated from $\log (V_{n+1}'/V_n')$, where V_n' and V_{n+1}' are the adjusted retention volumes of the hydrocarbons with n and $n+1$ carbon atoms, respectively.

DISCUSSION

Our study of the GC behaviour of series of sorbates on two different stationary phases allows the following conclusions.

In general, the activity coefficient for homologous series of sorbates increases with increasing molecular weight independent of the nature of the stationary phase (Tables I, III and IV; groups I, II and IV–VII). The deviations from this tendency by some heterocyclic compounds can be explained by errors in the determination of the relative activity coefficient.

An inspection of sorbates in group II (Table I) shows that there is an influence of the column temperature on the value of γ^{∞}. A 20°C increase in the column temperature resulted in an ≈ 1.3-fold decrease in γ^{∞} on the polar phase (Table I) due to increasing solubility of the sorbates in the stationary phase.

The character of the interaction of the sorbates with the sorbent is dependent on the structure of the compounds. The values of γ^{∞} for cyclohexane compounds (groups I and II) at 140°C and terpenic compounds (group III) (responsible for fragrance of flowers) at 100°C are in the range 6–37 on the polar phase CEP (Tables I and II). This indicates week interaction with the stationary phase.

The esters of monosubstituted cyclohexanols (I) interacted more strongly with the polar stationary phase in comparison with disubstituted cyclohexanols (group II). For substances having molecular weights from 198 to 268, γ^{∞} ranges from 6 to 21 for substances in group I and from 10 to 30 in group II (Table I). It is interesting

TABLE I

ACTIVITY COEFFICIENTS, γ^∞, OF ALKYL-SUBSTITUTED CYCLOHEXANOLS AND THEIR ESTERS ON 1,2,3-TRIS(β-CYANOETHOXY)PROPANE AT 120 AND 140°C AND ON APIEZON AT 140°C

		R_1	R_2	R_3	R_4	R_5
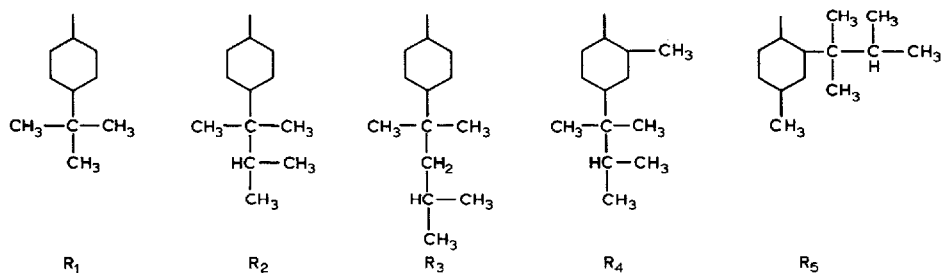
Group	Compound	γ^∞ CEP		γ^∞ ApL 140°C	Mol.wt.
		120°C	140°C		
I	R_1OCOCH_3		6.1	0.42	198
	$R_1OCOC_2H_5$		8.6	—	212
	$R_1OCOC_3H_7$		11	—	226
	R_2OCOCH_3		10	0.54	226
	$R_2OCOC_2H_5$		15	—	240
	$R_2OCOC_3H_7$		17	—	254
	R_3OCOCH_3		15	0.55	254
	$R_3OCOC_2H_5$		21	—	268
	$R_3OCOC_3H_7$		37	—	282
II	R_4OH	13	10	—	198
	R_4OCOCH_3	24	16	—	240
	$R_4OCOC_2H_5$	25	19	—	254
	$R_4OCOC_3H_7$	33	28	—	268
	$R_4OCOC_3H_7$-iso	38	30	—	268
	R_5OH	15	11	—	198
	R_5OCOCH_3	24	20	—	240
	$R_5OCOC_2H_5$	30	21	—	254
	$R_5OCOC_3H_7$	40	26	—	268
	$R_5OCOC_3H_7$-iso	44	29	—	268

that for isomeric cyclohexanes (group II) the ratios of the γ^∞ values for alcohols to those for the corresponding esters, $\gamma^\infty_{alc}/\gamma^\infty_{acet}$, are approximately equal. For acetates at 120°C this ratio is about 0.6, for propionates 0.5, for butyrates 0.4 and for iso-butyrates 0.3. The same value of $\gamma^\infty_{alc}/\gamma^\infty_{acet}$ (≈ 0.6) was obtained for the pair of terpenic compounds (group II): menthol/menthyl acetate and linalool/linalyl acetate (Table II).

The GC behaviour of cyclohexane compounds (groups I and II) on the non-polar phase shows that all the acetates have a great affinity for ApL, resulting in a small value of $\gamma^\infty \approx 0.5$. We could not measure γ^∞ an ApL for the other esters because of their high retention times.

The GC behaviour of macrocyclic compounds (responsible for musk odour) was studied on the non-polar phase. Except for heptamethylene sebacinate, all the

TABLE II

ACTIVITY COEFFICIENTS, γ^{∞}, OF SOME TERPENIC COMPOUNDS ON 1,2,3-TRIS(β-CY-ANOETHOXY)PROPANE AT 100°C

Group	Compound	γ^{∞}	Mol.wt.
III	Linalool	6.5	154
	Linalyl acetate	11.0	196
	Menthol	7.7	156
	Methyl acetate	12.0	198
	Nerol	5.8	154
	cis-Citral	5.0	152
	Geraniol	5.9	154
	trans.-Citral	4.0	152
	Citronellol	10.0	156
	Citronellal	7.0	154

values of γ^{∞} are less than unity (Table II) and are in the same range for C_5–C_{10} n-hydrocarbons on squalane[4]. This indicates that these compounds have considerable affinity for the non-polar phase.

The most polar of all the macrocyclic compounds are the diesters (group V): these substances with molecular weights in the range of 228–284 have γ^{∞} values of

TABLE III

ACTIVITY COEFFICIENTS, γ^{∞}, OF MACROCYCLIC LACTONES, OXALACTONES AND DIESTERS ON APIEZON L

Lactone   Oxalactone   Diester
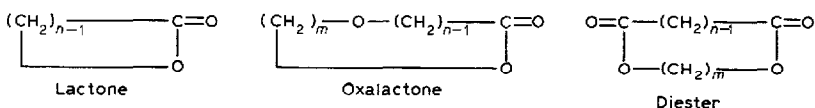
Group	Compound	m	n	γ^{∞}	Mol.wt.
IV	Tridecanolide-1,13	—	13	0.39	212
	Pentadecanolide-1,15	—	15	0.32	240
	Hexadecanolide-1,16	—	16	0.40	254
	Heptadecanolide-1,17	—	17	0.49	268
	12-Oxatetradecanolide-1,14	2	11	0.37	228
	10-Oxapentadecanolide-1,15	5	9	0.41	244
	10-Oxapentadecanolide-1,16	6	9	0.49	260
	12-Oxaheptadecanolide-1,17	5	11	0.59	272
	12-Oxaoctadecanolide-1,18	6	11	0.69	284
V	Tetramethyleneazelainate	4	9	0.85	242
	Hexamethyleneazelainate	6	9	0.66	270
	Ethylenesebacinate	2	10	0.51	228
	Tetramethylenesebacinate	4	10	0.71	256
	Heptamethylenesebacinate	6	10	1.09	284
	Ethylenedodecanedioate	2	12	0.63	256
	Tetramethylenedodecanedioate	4	12	0.93	284
	Ethylenebrassilate	2	13	0.71	270

TABLE IV

RELATIVE ACTIVITY COEFFICIENTS, $\gamma_x^\infty/\gamma_{\bar{C}_n}^\infty$, OF HETEROCYCLIC OXYGEN COMPOUNDS ON APIEZON L AT 100°C

Group	Compound	$\gamma_x^\infty/\gamma_{\bar{C}_n}^\infty$	Mol.wt.
VI	3-Amyl-4-hydroxytetrahydropyran	6.3	172
	3-Hexyl-4-hydroxytetrahydropyran	7.1	186
	3-Heptyl-4-hydroxytetrahydropyran	5.9	200
VII	3-Amyl-4-acetoxytetrahydropyran	2.2	214
	3-Hexyl-4-acetoxytetrahydropyran	1.9	228
	3-Heptyl-4-acetoxytetrahydropyran	2.4	242
	4-Hexyl-1,3-dioxane	1.1	172
	4-Heptyl-1,3-dioxane	1.3	186
	4-Octyl-1,3-dioxane	1.2	200
	2-Hexyl-1,3-dioxalane	0.7	158
	2-Heptyl-1,3-dioxalane	0.8	170
	2-Octyl-1,3-dioxalane	1.0	186
	4,5-Dimethyl-2-hexyl-1,3-dioxalane	0.8	186
	4,5-Dimethyl-2-heptyl-1,3-dioxalane	0.8	200
	4,5-Dimethyl-2-octyl-1,3-dioxalane	1.7	214
	2-Butyl-1,3-dioxepane	0.5	158
	2-Hexyl-1,3-dioxepane	0.7	186
	2-Heptyl-1,3-dioxepane	0.7	200
	2-Octyl-1,3-dioxepane	0.7	214
	2-Butyl-4,7-dihydro-1,3-dioxepine	0.8	156
	2-Hexyl-4,7-dihydro-1,3-dioxepine	0.9	184

TABLE V

RELATIVE ACTIVITY COEFFICIENTS, $\gamma_x^\infty/\gamma_{\bar{C}_n}^\infty$, OF AROMATIC AND ALIPHATIC ALDEHYDES AND ALCOHOLS ON APIEZON L AT 100°C

Group	Compound	$\gamma_x^\infty/\gamma_{\bar{C}_n}^\infty$	Mol.wt.
VIII	Cinnamic aldehyde	2.4	132
	α-Methylcinnamic aldehyde	1.7	146
	α-Ethylcinnamic aldehyde	1.5	160
	Hydrocinnamic aldehyde	1.8	134
	α-Methylhydrocinnamic aldehyde	1.6	148
	α-Ethylhydrocinnamic aldehyde	1.8	162
	α-Ethylidenehydrocinnamic aldehyde	2.2	160
	β-Ethylcinnamic alcohol	3.3	162
	β-Methylhydrocinnamic alcohol	2.8	150
	β-Ethylhydrocinnamic alcohol	3.0	164
	5-Phenylpentanol	3.5	164
IX	3-(3,4-Methylenedioxyphenyl)propanaol	3.5	192
	3-(3,4-Methylendioxyphenyl)propanol	6.3	194
	2,2,5-Trimethylhexen-4-al*	0.8	140
	2,2,5-Trimethylhexen-4-ol*	1.4	142
	2-Ethyl-5-butyl-5-methylhexen-4-al*	1.1	196
	2-Ethyl-5-butyl-5-methylhexen-4-ol*	1.9	198
	2,2,5,9-Tetramethyldecadien-4,8-al*	1.5	208
	2,2,5,9-Tetramethyldecadien-4,8-ol*	2.4	210

* Temperature was 80°C.

0.51–1.09. The macrocyclic oxalactones having the same molecular weights exhibit γ^∞ = 0.37–0.69 (Table III). The introduction of an oxygen atom into the macrocyclic chain of the lactone also leads to a slight increase in polarity.

From Table IV it can be concluded that of all the heterocyclic compounds studied the tetrahydropyran derivatives (group IV) —some of which give rise to the jasmine fragrance— have the lowest affinity for the non-polar phase. For substances, γ^∞ decreases when alcohols are converted into the respective acetates, despite the increase in molecular weight: $\gamma^\infty_{alc}/\gamma_{acet}$ is about 3.

The heterocyclic compounds (group VII, Table IV) containing two oxygen heteroatoms differ in their polarity depending on the position of substituents and on the ring size. The influence of the two oxygen atoms on the polarity is most masked for 1,3-dioxanes with an alkyl in the 4-position: these compounds have rather high values of γ^∞: 1.0–1.2, assuming the value of γ^∞ for tetradecane is about 0.9 (calculated by us using data from ref. 4). These values are in good agreement with those given for 1,3-dioxane on a non-polar phase[4].

For 2-alkyl-substituted dioxalanes and dioxepanes the values of γ^∞ decrease with increasing ring size. The introduction of one double bond in dioxepane exerts the opposite effect. So, it can be concluded that aromatic (group VIII) and aliphatic (group IX) alcohols and aldehydes have low affinity for the non-polar sorbent. Thus, the absolute value of γ^∞ should be greater than unity ($\gamma^\infty_{C_n} \approx 0.9$) (Table V). For these series of compounds the ratio of $\gamma^\infty_{alc}/\gamma^\infty_{ald}$ is about 1.7.

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