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A STUDY OF THE POLARITY OF SOME STATIONARY PHASES USED IN GAS–LIQUID CHROMATOGRAPHY

ESTERS OF PHTHALIC ACID AND THEIR ISOMERS

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SUMMARY

The relationship between the structure of the stationary phases and their gas chromatographic polarities is examined for a group of phthalic esters.

The dependence of the polarity on the structure of the phase is demonstrated by 25 esters of benzenedicarboxylic acids, their isomers and other similar compounds. It is found that lengthening the chain of the esterifying alcohol in the phthalic esters decreases the polarity of the phase.

The lowest polarities are found in the case of di-*n*-decylphthalate, di-*n*-hexylisophthalate and di-*n*-hexylterephthalate, and the highest in the case of di-*γ*-phenylpropylphthalate, diallylphthalate and di-*n*-butylphthalyl-bis-glycolate.

It is thought that the data obtained in this work might be of use in practical gas–liquid chromatography as a basis for the selection of a liquid phase from the group consisting of the phthalic esters.

INTRODUCTION

We have previously reported[1-3] the influence of the structure of phthalic acid esters on the activity coefficients of some paraffins, cyclohexanic and aromatic hydrocarbons. The activity coefficient, however, is a complex quantity depending on the properties of the molecules of the solute and the solvent. One of the most interesting properties of the stationary phases used in gas–liquid chromatography (GLC) is undoubtedly their polarity.

The present study is an attempt to ascertain the influence of the structure of the esters mentioned above on their gas chromatographic (GC) polarity. It is the authors' opinion that, apart from the theoretical interest, such an investigation would also be useful from the point of view of practical GLC.

Some years ago ROHRSCHNEIDER[4] suggested an empirical method for the determination of relative GC polarity of a stationary phase. This method, in spite of some weak points, is now the only method widely used in the field of GLC.

The polarity of the liquid phase, according to ROHRSCHNEIDER, could be calculated from the expression:

$$P = 100 - 100 \frac{q_1 - q_x}{q_1 - q_2} \tag{1}$$

where q_1 is the logarithm of the ratio of the specific retention volumes of butadiene: butane measured on a β, β'-oxydipropionitrile column at $70°$, q_2 is the logarithm of the ratio measured on a squalane column and q_x is that measured on the column with the liquid phase under investigation.

CHOVIN AND LEBBE[5], with the purpose of making the method more general, suggested a better standard pair, benzene/cyclohexane. These compounds are easily obtainable in every laboratory and with them it is possible to measure the polarity at higher temperatures than with the butadiene/butane pair.

EXPERIMENTAL

The specific retention volumes of benzene and cyclohexane on the liquid phases under investigation were measured with a "Fractovap" model B apparatus, produced by Carlo Erba, Italy.

Pure dry nitrogen was used as carrier gas at an outlet flow rate of 120 ml/min.

The stainless steel column was 2 m long and had an internal diameter of 6 mm. It was packed with ground unglazed tile (particle diameter 0.2–0.4 mm) and the stationary phase amounted to 15.3% (w/w) of the inert support.

Benzene and cyclohexane were used as the standard volatile compounds and β,β'-oxydipropionitrile and squalane were the standard stationary phases.

The polarity of the phases under investigation was measured at $120°$. The specific retention volumes of the standard compounds on β,β'-oxydipropionitrile and squalane are shown in Table I. The data in Table I are the arithmetic means from five measurements of every retention volume.

TABLE I

SPECIFIC RETENTION VOLUMES OF BENZENE AND CYCLOHEXANE ON β,β'-OXYDIPROPIONITRILE AND SQUALANE IN ml

No.	Standard compound	Squalane	β,β'-Oxydipropio- nitrile
1	Benzene	29.3	19.6
2	Cyclohexane	33.3	3.6

All the esters under investigation are shown in Table II. With exception of the dinonylphthalate (BDH Ltd.), all of them were synthesized by the authors as described earlier[1-3].

RESULTS AND DISCUSSION

Table II gives the values of the specific retention volumes of benzene and cyclohexane and the corresponding liquid phase polarity according to eqn. 1. On the

TABLE II

SPECIFIC RETENTION VOLUMES OF BENZENE AND CYCLOHEXANE AND POLARITY OF THE STATIONARY PHASES UNDER INVESTIGATION

No.	Stationary phase	Specific retention volume		Polarity
		Benzene	Cyclohexane	
1	Di-*n*-propylphthalate	18.0	35.2	44
2	Di-*n*-butylphthalate	19 2	35 2	40
3	Di-*n*-hexylphthalate	20.2	34.2	36
4	Di-*n*-octylphthalate	21.3	32.5	30
5	Di-*n*-decylphthalate	22.4	31.1	25
6	Diphenylphthalate	9.5	19.8	47
7	Dibenzylphthalate	9.9	21.3	49
8	Di-β-phenylethylphthalate	10.7	23.6	51
9	Di-γ-phenylpropylphthalate	10.9	25.2	53
10	Diisopropylphthalate	18.0	35.3	44
11	Diallylphthalate	14.4	32.8	52
12	Di-*sec.*-butylphthalate	18.7	35.2	42
13	Diisobutylphthalate	17.4	33 3	42
14	Dinonylphthalate	19.8	29.7	29
15	Di-*n*-hexylisophthalate	23.9	32.2	23
16	Di-*n*-hexylterephthalate	24 1	31.3	21
17	Dicyclohexylphthalate	15.4	27.4	38
18	Dibornylphthalate	9.1	18.8	47
19	Catecholdibutyrate	16.6	31.8	43
20	Catecholdibenzoate	11.5	21.8	42
21	Di-*n*-hexyl-4-nitrophthalate	17.0	32.4	42
22	Di-*n*-butyltetrachlorophthalate	17.9	33.7	42
23	Di-*n*-butylphthalyl-bis-glycolate	11.9	27.0	52
24	Di-*n*-hexyladipate	27.2	42.1	31
25	Di-*n*-hexylsuberate	27.5	41.4	30

basis of the data in the table some conclusions are possible about the influence of the structure of the phases on their GC polarity.

For instance, it is evident that the increase of the number of $-CH_2-$ groups in the alcoholic alkyl chains of the di-*n*-alkyl- and di-ω-phenylalkylphthalates leads to a linear change in the polarity. The difference between the polarity of the di-*n*-propyl- and di-*n*-decylphthalate is 19 units. If the phases are di-*n*-alkylphthalates (Fig. 1),
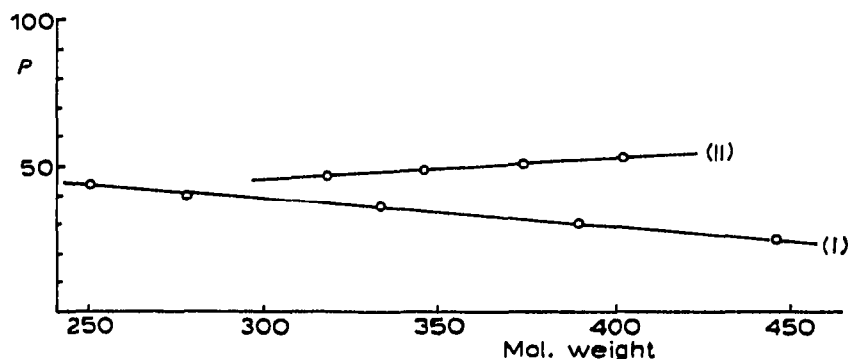

Fig. 1. Plot of the polarity of the phases under investigation *vs.* the molecular weight of the di-*n*-alkylphthalates (I) and of the di-ω-phenylalkylphthalates (II).

an increase in molecular weight causes a decrease in polarity, while in the case of di-ω-phenylalkylphthalates increasing molecular weight increases the polarity.

The nature of the carbon chain in the alcohol alkyl group has only a slight influence on the polarity. This can be seen by comparing the data for the esters of di-*n*-propyl- and diisopropylphthalate, and di-*n*-butyl-, di-*sec.*-butyl and diisobutylphthalate. Also if one compares the value for the dinonylphthalate (No. 14, Table II), which really is di-3,5,5-trimethylhexylphthalate, it corresponds to the polarity of the normal dinonyl ester, as it fits the relationship shown in Fig. 1.

Comparison of the data for the di-*n*-propylphthalate and diallylphthalate suggests that the presence of double bonds in the side chains of the ester leads to an appreciable increase in the polarity.

Comparison of the data for di-*n*-hexylphthalate with those for di-*n*-hexyliso-phthalate and di-*n*-hexylterephthalate shows that the polarity is highest for the *ortho* and lowest for the *meta* and *para* isomers. The difference between the last two is only 2 units according to ROHRSCHNEIDER's system. These data are in accordance with the values of the dipole moments for esters with similar structure. For example the dipole moments of the dimethyl esters of the isomeric phthalic acids are as follows: *ortho*, 2.75 D; *meta*, 2.46 D; and *para*, 2.40 D[6].

The difference in the polarity of the *m*- and *p*-isomers compared with that of the *o*-isomers is probably due to the steric arrangement of the carboxylic acid groups on the benzene ring: adjacent in the *o*-isomers and on opposite sides in the *p*-isomers.

If the properties of the di-*n*-hexyl-, dicyclohexyl- and diphenylphthalate are compared, it is found that the polarity increases slightly in the presence of a saturated ring structure. When the ring is aromatic, however, this increase is more definite. For example the difference between the polarities of the di-*n*-hexyl- and diphenylphthalate is 11 units.

On the other hand, it is interesting that substitution of the aromatic ring of the phthalic acid with a straight carbon chain with the same number of carbon atoms (total or linear between the ester groups) increases the polarity by about 10 units. (See the esters di-*n*-hexylterephthalate, di-*n*-hexyladipate and di-*n*-hexylsuberate.)

Dibornylphthalate is almost equal to the diphenylphthalate from the viewpoint of its polarity. It can be assumed that the aromatic rings of the latter together with the perpendicular π-orbitals are similar in their steric volume and influence to the bornyl groups.

Catecholdibutyrate does not much differ from its isomer di-*n*-propylphthalate. However with the other isomeric pair—catecholdibenzoate and diphenylphthalate— the difference in the polarities is 5 units.

The introduction of a nitro group in the phthalic ring (*cf.* di-*n*-hexylphthalate and di-*n*-hexyl-4-nitrophthalate) leads to an increase in the polarity of 6 units.

The influence of chlorine as a substituent in this respect is weaker. For instance, the presence of 4 chlorine atoms in di-*n*-butyltetrachlorophthalate increases the polarity only by 2 units with respect to the di-*n*-butylphthalate.

Di-*n*-butylphthalyl-bis-glycolate has a polarity of 12 units higher than that of the di-*n*-butylphthalate. It is thus possible to conclude that an increase in the number of carboxylic groups in the side chains is an effective way of obtaining phases with a high polarity.

The data presented in Table II show that the group of phthalic esters tested as

stationary phases have a low or medium polarity value. Di-*n*-decylphthalate, di-*n*-hexylisophthalate and di-*n*-hexylterephthalate have the lowest GC polarity, and di-γ-phenylpropylphthalate, diallylphthalate and di-*n*-butylphthalyl-bis-glycolate the highest.

The interchange of one phthalic ester for use as a stationary phase with another is possible only on the basis of their polarities.

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