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EVALUATION OF THE SPECIFICITY OF THE STATIONARY PHASE IN GAS CHROMATOGRAPHY

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SUMMARY

It was empirically established previously that the relation γ_2/γ_1 in the basic equation of gas chromatography

$$r_{1,2} = \frac{p_2^0}{p_1^0} \cdot \frac{\gamma_2}{\gamma_1}$$

could be substituted in some cases by V_{mol_2}/V_{mol_1}. Difficulties in the calculation of γ_2/γ_1 have been overcome, as the new equation

$$r_{1,2} = \frac{p_2^0 \cdot V_{mol_2}}{p_1^0 \cdot V_{mol_1}}$$

involves only physicochemical parameters of the solutes.

The relation $r_{1,2}^{exp}/r_{1,2}^{calc}$ is used as a measure of the specificity of phases which is related to hydrogen bonding or structure, but not of that due to differences in V_{mol}. These properties of the phase could be evaluated by means of suitable standard solutes.

The specificity of some phases for *n*-paraffins, aromatic hydrocarbons and chlorinated hydrocarbons, and its application to some simple calculations are discussed.

INTRODUCTION

It has recently been suggested[1–3] that no more than twenty liquid phases should be designated as preferred phases in gas chromatography (GC) in order to restrict the number of liquid phases used. This suggestion led to consideration of the methods of choosing these liquid phases. None of the criteria already suggested could necessarily provide the correct set of liquid phases.

Recently, a thermodynamically formulated approach has been developed[4,5] for

evaluation of stationary phase polarity. Compromising between accuracy and practicality in a GC laboratory, we have also derived a criterion.

The relative retention is non-specific provided it can be calculated by[6]:

$$r_{1,2} = p^0_{2,1} \cdot V_{mol\,2,1} \tag{1}$$

where p^0 is the vapour pressure and V_{mol} is the molecular volume of substances 1 and 2.

The ratio of the experimental relative retention ($r^{exp}_{1,2}$) and the one calculated from eqn. 1 ($r^{calc}_{1,2}$) could be used to determine the criterion, which we have called specificity (S):

$$S = 1 - \frac{r^{exp}_{1,2}}{r^{calc}_{1,2}} \tag{2}$$

The value of specificity and its application will be discussed in this paper.

RESULTS AND DISCUSSION

Apolar solutes were used at the very beginning of our investigations. It is common in GC to consider the stationary phase as a boiling point separator, provided both solute and solvent are apolar. This is not exactly the situation observed when specificity is determined. Thus, on squalane, cycloparaffins are retained better and aromatic hydrocarbons less well than predicted by eqn. 1 (ref. 7). Applying the specificity to the numerous experimental data taken from GC literature showed that liquid phases manifest different behaviour to the apolar solutes, even when they belong to the same homologous series. For example, the retention of two adjacent normal paraffins on some phases is used to obtain data about their specificities. We first calculated S values of phases of the phthalates homologous series (Table I).

TABLE I

SPECIFICITY OF SOME PHTHALATES TOWARDS THE SEPARATION OF C_9 AND C_8 *n*-PARAFFINS AT 120° (REF. 8)

Phase	$r^{exp}_{1,2}$	$r^{calc}_{1,2}$	S
Ideal		1.895	0.00
Diphenyl phthalate	1.782	1.895	0.06
Dibenzyl phthalate	1.792	1.895	0.05
Di(β-phenylethyl) phthalate	1.892	1.895	0.03
Di(γ-phenylpropyl) phthalate	2.166	1.895	−0.14

A tendency towards better separation is observed with an increasing number of methylene groups in the molecule of the solvent.

The changes in retention of adjacent *n*-paraffins with a variation in methylene groups in the phase are more or less shown in the literature data available. Some typical examples are given in Table II.

TABLE II

DEPENDENCE OF S ON THE METHYLENE GROUPS IN THE PHASE

Stationary phase	S	*Remarks*
Neopentyl glycol sebacate[10]	0.04	Show the tendencies observed
Neopentyl glycol succinate[10]	0.10	
Dibutyl phthalate[8]	0.005	Show the tendencies observed
Didecyl phthalate[8]	−0.03	
Dinonyl sebacate[10]	−0.02	Show a reciprocal tendency
Dioctyl sebacate[10]	−0.03	
Dinonyl phthalate[10]	−0.02	Are equal
Dioctyl phthalate[10]	−0.02	
Ethylene glycol adipate*	−0.04	Show a maximum
1,3-Propanediol adipate*	−0.15	
1,5-Pentanediol adipate*	−0.25	
1,9-Nonanediol adipate*	−0.10	

* Specificity in the separation of pinene and cyclohexane[13].

Changes in retention of adjacent n-paraffins are observed less on polyethylene glycols with different molecular weights[10] (see Table III).

Esterification of the hydroxyl group in PEG results in a decrease in S: Triton X-305, $S = 0.07$; Ethofat 60/25, $S = 0.04$ (ref. 10).

The density of the molecular packing of the phases might be a possible explanation of the specificity. This assumption is confirmed by further examples: PEG 1000, $S = 0.12$; Polypropylene glycol 2000, $S = 0.03$; Polypropylene glycol sebacate, $S = 0.06$; Neopentyl glycol sebacate, $S = 0.04$ (ref. 10).

TABLE III

SPECIFICITY OF DIFFERENT PEG's TOWARDS SEPARATION OF n-PARAFFINS

Stationary phase	S
PEG 600	0.12
PEG 1000	0.12
PEG 4000	0.11
PEG 6000	0.11
PEG 20M	0.11
PEG 20M TPA	0.11

Branching of the chain minimizes the density of molecular packing, which is followed by a reduction in specificity. The same effect is observed on comparing o- and m-phthalates: the specificity of ethylene glycol o-phthalate is 0.17 and that of ethylene glycol m-phthalate 0.12 units.

In our investigations on silicones, we found that even apolar methylsilicones, such as SE-30, OV-101, E-301, etc., have a specificity about 0.10 units higher than have apolar hydrocarbon stationary phases like squalane, liquid paraffin, n-$C_{36}H_{74}$, and so on. The higher specificity of the methylsilicones could be explained by the presence of –Si–O–Si– groups that contribute, like –C–O–C– groups in PEG, to a denser packing of molecules.

The examples mentioned show that the specificity of the phases towards the

n-paraffins depends to a great extent on their structure. The specificity calculated by this method relates effectively to the chromatographic properties of the phases and was applied to other solutes.

We next studied the specificity of a phase towards further members of a single homologous series. C_6–C_{12} aromatic hydrocarbons and phases with different polarity were checked. The results are shown in Fig. 1.

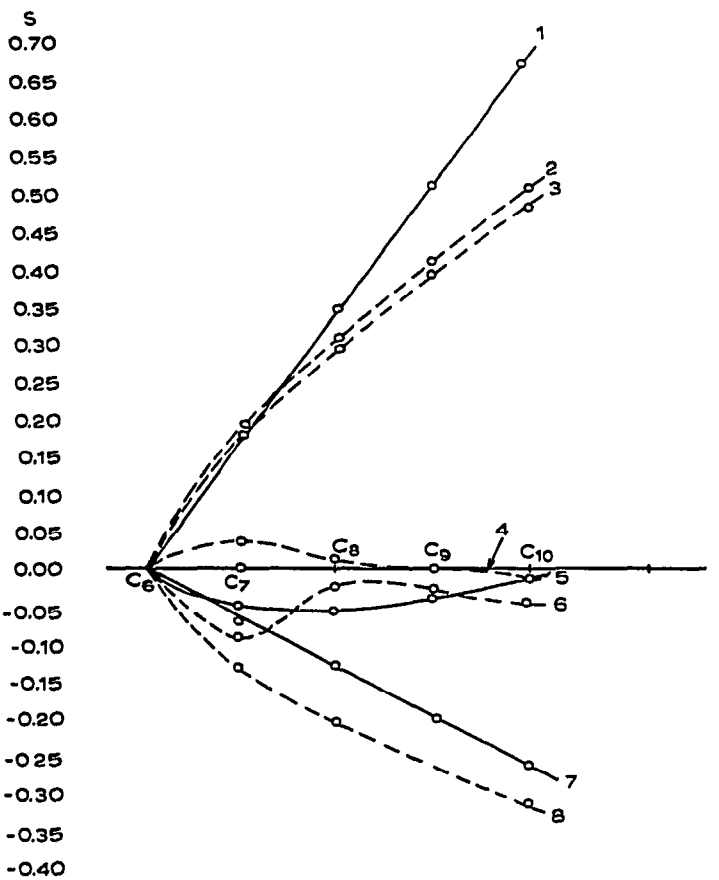

Fig. 1. Group specificity of some phases towards aromatic hydrocarbons. 1 = TCEP; 2,3 = PEG; 4 = 7,8-benzoquinoline; 5 = polypropylene glycol; 6 = di-*n*-propyl tetrachlorophthalate; 7 = squalane; 8 = phenanthrene.

Evidently, polarity and specificity of a phase are not different terms for one phenomenon. For example, squalane according to Rohrschneider[9] or McReynolds[10] appears apolar, but it has a well determined specificity towards the hydrocarbons chosen. By plotting S against the number of carbon atoms (Fig. 1), a curve is obtained which expresses the phase group specificity towards all of the solutes studied —in our case the aromatic hydrocarbons. It might be a straight line for some phases and can be characterized by the slope (tg α). In our example, the slope of the squalane curve

is negative. This means that every alkyl aromatic hydrocarbon would be retained better than eqn. 1 predicts when benzene is used as standard.

Polyethylene glycol and polypropylene glycol are polar phases, but the first has a group specificity with positive tg α while the second has a group specificity with tg α almost equal to zero.

An approximate picture of the separation of different groups of substances can only be obtained when based on polarity. If known, the value of the group specificity (tg α) might be used for various simple calculations.

Calculation of separation before the experiment

Compared to other phases, polypropylene glycol appears almost non-specific towards aromatic hydrocarbons. The slope of the curve is approximately zero (Fig. 1) so that the separation can be calculated by eqn. 1. Table IV shows the calculated relative retentions of some aromatic hydrocarbons at 80° compared with those experimentally obtained on polypropylene glycol[11].

The small discrepancies between $r_{1,2}^{calc}$ and $r_{1,2}^{exp}$ allow a precise prediction.

TABLE IV

COMPARISON OF r^{calc} AND r^{exp} OF AROMATIC HYDROCARBONS SEPARATED ON POLYPROPYLENE GLYCOL

Hydrocarbon	$r_{1,2}^{calc}$	$r_{1,2}^{exp}$
Benzene	1	1
Toluene	2.17	2.31
Ethylbenzene	4.34	4.62
p-Xylene	4.55	5.00
m-Xylene	4.83	5.12
o-Xylene	5.87	6.25
Cumene	6.65	6.85
n-Propylbenzene	8.42	8.80
m-Ethyltoluene	9.31	9.56
p-Ethyltoluene	9.35	9.56
Mesitylene	10.70	10.50
o-Ethyltoluene	10.80	11.08
Isobutylbenzene	11.90	12.30
sec.-Butylbenzene	12.06	12.60
1,2,4-Trimethylbenzene	12.50	13.05
1,2,3-Trimethylbenzene	16.35	16.75
n-Butylbenzene	18.20	18.35

Selection of a suitable phase for separation

Fig. 1 shows that in the separation of aromatic hydrocarbons, 1-phenylhexane, for example, would appear from a tris(cyanoethoxy)propane (TCEP) column earlier than predicted according to eqn. 1 and much quicker than it would leave a squalane column under the same conditions. Evidently, a TCEP column saves time. This was proved experimentally by the separation of C_8–C_{14} *n*-paraffins on Apiezon L and TCEP columns, as the slopes of the curves of their group specificities are also very different. The chromatograms obtained are given in Fig. 2. C_8–C_{14} *n*-paraffins appear on an Apiezon L column at 80° over 30 min, while on a TCEP column C_8–C_{12} *n*-paraffins are separated in 10 min. A temperature programme of 10°/min is necessary to achieve the same effect on the Apiezon L column (Fig. 2c).

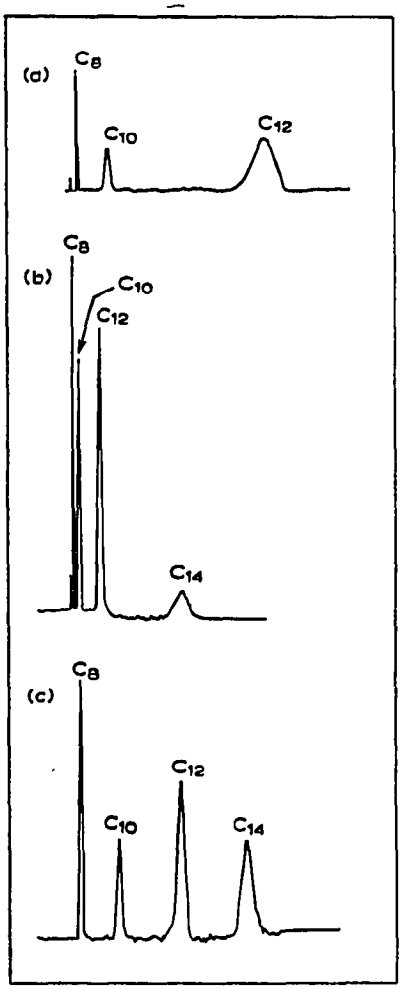

Fig. 2. Chromatogram of C_8–C_{14} *n*-paraffins on Apiezon L and TCEP columns. (a) Apiezon L; (b) TCEP; (c) Apiezon L–PTGC.

Vapour pressure calculation

The group specificities of PEG and TCEP towards aromatic hydrocarbons are seen to be almost straight lines (Fig. 1). The vapour pressure of 1-phenylpentane is calculated by interpolation when a TCEP column is used and by extrapolation with a PEG column, after eqn. 3.

$$p^0_{C_{11}} = \frac{(1 - S) \cdot p^0_{C_6} \cdot V_{\text{mol } C_6}}{r^{\text{exp}}_{C_{11}/C_6} \cdot V_{\text{mol } C_{11}}} \tag{3}$$

The results are given in Table V.

Suppose the curve of the group specificity is not a straight line, an extremum would mean a special behaviour of the phase towards the solute at this point. The real

TABLE V

CALCULATED AND LITERATURE DATA FOR VAPOUR PRESSURE OF 1-PHENYLPENTANE AT 80 AND 100°

Phase used to determine group specificity	*Vapour pressure (p°)*			
	80°		*100°*	
	Calc.	*Lit.*	*Calc.*	*Lit.*
TCEP	10.4	9.82	23.4	24.86
PEG-400	10.8	9.82	24.3	24.86

reason for the extremum observed could easily be found out, provided that the standard had been suitably chosen. Our example is based on the data of Little[12] (Table VI).

The higher specificity of PEG towards $CHCl_3$ and CH_2Cl_2 observed in comparison with those of *n*-octane could be considered a result of hydrogen bonding. Besides, $CHCl_3$ is better retained because of its more strongly polarized hydrogen atom.

TABLE VI

SPECIFICITY OF PEG-400 AND *n*-OCTANE, CHEMICALLY BONDED ON THE SUPPORT, TOWARDS CHLORINATED HYDROCARBONS

Solute	*Specificity*	
	PEG-400	*n-Octane*
CCl_4	0	0
$CHCl_3$	−1.0	−0.25
CH_2Cl_2	−0.63	−0.38
$ClCH_2CH_2Cl$	−0.10	−0.21

The method for evaluation of the specificity of the phases can only be applied when p^0 and V_{mol} of the substances are known. Nevertheless, specificity is a very chromatographic term, it is not connected with a strong set of standards, and the examples given for different calculations show that it could be a useful parameter of wide application.

REFERENCES

1 S. T. Preston, *J. Chromatogr. Sci.*, 8 (1970) 18A.
2 R. A. Keller, *J. Chromatogr. Sci.*, 11 (1973) 188.
3 J. R. Mann and S. T. Preston, *J. Chromatogr. Sci.*, 11 (1973) 216.
4 J. Novák, *J. Chromatogr.*, 78 (1973) 269.
5 J. Novák, J. Růžičková, S. Wičar and J. Janák, *Anal. Chem.*, 45 (1973) 1365.
6 D. Shopov and N. Dimov, *BAN, Commun. Dep. Chem.*, 2 (1969) 159.
7 N. Dimov and D. Shopov, *C.R. Acad. Bulg. Sci.*, 22 (1969) 285.
8 N. Petsev and Chr. Dimitrov, *J. Chromatogr.*, 42 (1969) 311.
9 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
10 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
11 N. G. McTaggart and J. V. Mortimer, *J. Inst. Pet.*, 50 (1964) 255.
12 J. Little, *J. Chromatogr. Sci.*, 8 (1970) 647.
13 B. V. Bapat, B. V. Chatge and S. C. Bhattacharyya, *J. Chromatogr.*, 23 (1966) 363.