A STUDY OF THE EVAPORATION OF THE STATIONARY PHASE FROM GAS-LIQUID CHROMATOGRAPHIC COLUMNS

ESTERS OF PHTHALIC ACID AND SOME OF THEIR ISOMERS

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SUMMARY

The present work is an attempt at more complete investigation of the evaporation of liquid phases from gas–liquid chromatographic columns. The validity of a general expression, found by the authors, is shown for 23 stationary phases, *viz.* phthalates and their isomers.

Some constants for the phases under investigation which might be useful in gas chromatography are tabulated.

The successful use of the gas–liquid chromatography for analytical and non-analytical purposes is only possible when a suitable stationary phase has been found. Besides a high selectivity, a fundamental requirement for such a phase is its low volatility under operating conditions.

Until recently, no good objective method for characterization of the phases was suggested from this view-point. The data published in the literature have been found empirically.

In our previous paper[1], in which di-*n*-propyl phthalate was used as a model stationary phase, it was shown that the quantity of phase evaporated from the column could be calculated from the equation:

$$\ln m = \frac{B}{T} + \ln V + C \tag{1}$$

where m is the quantity of the stationary phase evaporated from the column in g, V is the volume of the gas passed through it in ml, T is the temperature in °K and B and C are constants.

It was shown also that the evaporation of the stationary phase does not depend on the gas flow rate and on the nature and particle size diameter of the inert support.

Eqn. (1) may be used for several purposes.

In the first place it is possible to calculate the liquid phase losses from the

column and to make corrections in the values of the retention volumes if the phase has a high volatility.

From the quantity of the evaporated phase, the concentration of its vapour in the gas flow at a certain temperature may be found, or the temperature at which a certain concentration is reached. Such data are very important when it is necessary to estimate in advance whether the liquid phase volatility at a given temperature will permit the use of a more sensitive detector.

At the same time, from the value of the constant B, the molar latent heat of vaporization, ΔH_v, of the phase under investigation may be calculated from:

$$\Delta H_v = -RB + RT \tag{2}$$

Eqn. (1) permits the calculations mentioned above, if in addition to the experimental parameters T and V, the values of B and C are known.

The present study was undertaken as an attempt to demonstrate the validity and the application of eqn. (1). Some phthalic esters and their isomers were chosen as phases for investigation.

EXPERIMENTAL

Apparatus

All measurements were carried out with an apparatus which had good reproducibility for the experimental conditions in the gas chromatographic column (Fig. 1).

The inlet pressure of the inert gas was reduced by means of coarse (1) and fine (2) reducing valves before entering the column (4).
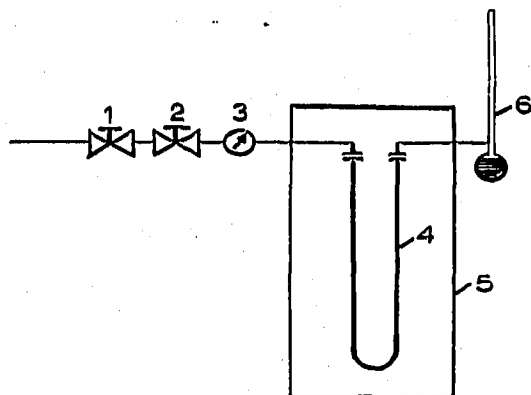

Fig. 1. Apparatus for liquid phase evaporation. 1 = Coarse reducing valve; 2 = fine reducing valve; 3 = manometer, 4 = column, 5 = air thermostat, 6 = soap flow meter.

The column was a 50 cm glass U-shaped tube with a 4 mm internal diameter. The inlet part of the column was always filled with glass spheres (1 mm diameter). In this way, the inlet gas was preheated to the column temperature before entering the chromatographic packing. The chromatographic column was enclosed in an air thermostat (5) with temperature control to within $\pm 1°$.

Pure dry nitrogen was used as inert gas. The outlet flow rate was measured with a soap flow meter (6) at the end of the column. The measurements were carried out

with gas flow rates of 60 to 120 ml/min. These rates were not corrected by the compressibility factor, because the column resistance was very low.

Ground unglazed tile, with a particle size diameter 0.2–0.4 mm was used as solid support. The weight of the liquid phase was 10 % of the weight of the chromatographic packing.

With exception of the dinonyl phthalate (BDH Ltd.), all of the stationary phases were synthesized by the authors, as described in other papers[2,3].

Calculations

The evaporation of the stationary liquid phase was checked by weighing the column.

TABLE I

CONCENTRATION OF STATIONARY PHASE VAPOUR IN THE CARRIER GAS AT DIFFERENT TEMPERATURES

No.	Phase	$A \cdot 10^8$ g/ml at the following temperatures (°C)								
		80	100	120	140	160	180	200	220	240
1	Di-n-propyl phthalate	0.9	2.8	7.0	16.5	—	—	—	—	—
2	Di-n-butyl phthalate	0.3	1.5	4.5	10.8	—	—	—	—	—
3	Di-n-hexyl phthalate	—	—	0.8	2.5	7.8	16.6	—	—	—
4	Di-n-octyl phthalate	—	—	—	0.6	2.1	6.4	18.0	—	—
5	Di-n-decyl phthalate	—	—	—	—	0.3	1.1	4.2	9.3	—
6	Diphenyl phthalate	—	—	—	0.6	2.7	5.3	10.0	—	—
7	Dibenzyl phthalate	—	—	—	0.8	1.8	3.6	8.4	—	—
8	Di-β-phenylethyl phthalate	—	—	—	—	0.9	2.2	4.6	8.4	—
9	Di-γ-phenylpropyl phthalate	—	—	—	—	—	1.7	4.3	7.7	25.5
10	Diisopropyl phthalate	1.4	4.7	17.3	46.3	—	—	—	—	—
11	Diallyl phthalate	0.4	1.8	8.4	30.2	—	—	—	—	—
12	Di-sec.-butyl phthalate	0.6	1.8	5.2	14.0	—	—	—	—	—
13	Diisobutyl phthalate	0.5	2.0	5.1	15.8	—	—	—	—	—
14	Dinonyl phthalate	—	—	—	0.8	2.2	7.9	19.8	—	—
15	Di-n-hexyl isophthalate	—	—	0.9	2.8	6.4	14.5	—	—	—
16	Di-n-hexyl terephthalate	—	—	0.5	1.2	4.1	10.0	—	—	—
17	Dicyclohexyl phthalate	—	—	0.2	0.9	3.3	11.0	—	—	—
18	Dibornyl phthalate	—	—	—	0.9	1.6	3.4	8.8	—	—
19	Catechol dibutyrate	0.9	3.3	9.9	26.8	—	—	—	—	—
20	Catechol dibenzoate	—	—	—	0.7	2.5	6.0	16.8	—	—
21	Di-n-hexyl 4-nitrophthalate	—	—	—	0.4	1.3	3.6	10.7	—	—
22	Di-n-butyl tetrachlorophthalate	—	—	0.4	1.5	5.3	17.5	—	—	—
23	Di-n-butyl phthalyl-bis-glycolate	—	—	—	0.6	2.4	7.7	28.2	—	—

The concentration of the liquid phase vapour in the carrier gas at different temperatures was calculated from the liquid phase losses at a certain gas velocity and for a constant time.

The concentration of the liquid phase in the carrier gas depending on the temperature is shown in Table I.

Fig. 2. shows the relationship between concentration of the liquid phase in the carrier gas at different temperatures and is represented by the function ln A = f $(1/T)$, where A is the concentration of the liquid phase, di-n-hexyl phthalate, in the carrier gas.

From the function $\ln A = f(1/T)$ it is easy to calculate, or to find graphically the values of B and C, as well as the temperature at which a concentration limit will be reached.
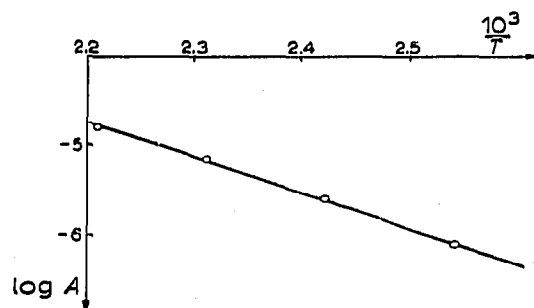

Fig. 2. Plot of the logarithm of the phase vapour concentration in the carrier gas *vs.* the inverse of the temperature. Liquid phase: di-*n*-hexyl phthalate.

RESULTS AND DISCUSSION

According to the data in the literature[4], detectors with a low sensitivity tolerate a concentration of liquid phase vapour in the carrier gas up to 10^{-6} g/ml, while those with a higher sensitivity have a concentration limit of 10^{-8} g/ml.

TABLE II

MAXIMAL OPERATING TEMPERATURES AND VALUES OF B, C AND $\varDelta H_v$ FOR THE PHASES UNDER INVESTIGATION

No.	Phase	Max. operating temperature (°C)		$B \cdot 10^{-3}$	C	$\varDelta H_v$ (kcal/mole)
		10^{-6} g/ml	10^{-8} g/ml			
1	Di-*n*-propyl phthalate	86	21	—2.989	2.427	14.4
2	Di-*n*-butyl phthalate	95	33	—3.642	3.868	17.4
3	Di-*n*-hexyl phthalate	130	60	—4.092	4.277	19.6
4	Di-*n*-octyl phthalate	148	87	—4.980	5.815	23.8
5	Di-*n*-decyl phthalate	178	120	—6.238	7.832	29.4
6	Diphenyl phthalate	135	49	—3.062	1.493	14.9
7	Dibenzyl phthalate	146	65	—3.363	2.026	16.3
8	Di-*β*-phenylethyl phthalate	163	87	—3.899	3.997	18.7
9	Di-*γ*-phenylpropyl phthalate	169	99	—4.550	4.274	22.8
10	Diisopropyl phthalate	79	18	—3.699	4.666	17.6
11	Diallyl phthalate	92	42	—4.688	6.841	22.2
12	Di-*sec*-butyl phthalate	89	28	—3.279	3.062	15.7
13	Diisobutyl phthalate	90	28	—3.455	3.514	16.5
14	Dinonyl phthalate	145	80	—4.767	5.400	22.8
15	Di-*n*-hexyl isophthalate	118	43	—3.627	3.119	17.5
16	Di-*n*-hexyl terephthalate	135	69	—4.242	4.393	20.3
17	Dicyclohexyl phthalate	141	82	—5.073	6.246	24.1
18	Dibornyl phthalate	151	75	—3.849	3.081	18.5
19	Catechol dibutyrate	82	24	—3.541	3.997	16.9
20	Catechol dibenzoate	146	94	—3.723	2.994	18.0
21	Di-*n*-hexyl 4-nitrophthalate	157	92	—4.832	5.259	23.0
22	Di-*n*-butyl tetrachloro-phthalate	134	76.5	—4.933	6.129	26.4
23	Di-*n*-butyl phthalyl-bis-glycolate	148	94	—5.592	7.282	26.5

In the following text "maximal operating temperatures" will be the name given to the temperatures at which the concentration of the liquid phase vapour in the carrier gas is 10^{-6} or 10^{-8} g/ml. The data for the maximal operating temperatures of the liquid phases under investigation are shown in Table II.

The determination of the maximal operating temperatures was carried out graphically, while the values of the constants B and C and the molar latent heats of vaporization ΔH were calculated.
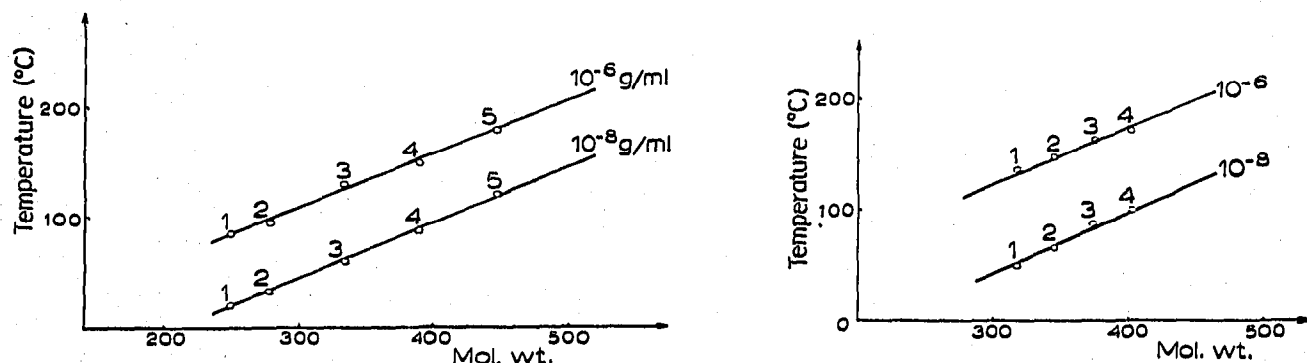

Fig. 3. Plot of the maximal operating temperatures vs. the molecular weight of the phases. $1 =$ Di-n-propyl phthalate; $2 =$ di-n-butyl phthalate; $3 =$ di-n-hexyl phthalate; $4 =$ di-n-octyl phthalate; $5 =$ di-n-decyl phthalate.
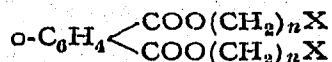
Fig. 4. Plot of the maximal operating temperatures vs. the molecular weight of the phases. $1 =$ Diphenyl phthalate; $2 =$ dibenzyl phthalate; $3 =$ di-β-phenylethyl phthalate, $4 =$ di-γ-phenyl-propyl phthalate.

It is necessary to stress that the maximal operating temperatures at the concentration of 10^{-8} g/ml were found by extrapolation.

The data in Table II are in good agreement with those published for some of the phases investigated. For instance, NABIVACH AND DAL[5] give the maximal operating temperatures (10^{-6} g/ml) as follows for: di-n-butyl phthalate $= 80$–$100°$; di-n-octyl phthalate $= 140°$; dinonyl phthalate $= 130°$; di-n-decyl phthalate $= 175°$; diphenyl phthalate $= 130°$; and di-n-butyl tetrachlorophthalate $= 125 °C$.

The phases whose structure changes regularly show a regular change in the corresponding maximal temperatures.

For example in Figs. 3 and 4 the dependence between the molecular weight and the maximal operating temperature for phthalic esters with general formula

$$o\text{-}C_6H_4\Big\langle\begin{matrix}COO(CH_2)_nX\\COO(CH_2)_nX\end{matrix}$$

is shown graphically in Fig. 3 for $X = CH_3$ and in Fig. 4 for $X = C_6H_5$. It is evident that the values of the maximal operating temperatures are a linear function of the molecular weight.

In accordance with the known data for the boiling points of organic compounds with normal and iso structure, the esters of the alcohols with iso chains have lower maximal operating temperatures than those of alcohols with normal chains.

The maximal operating temperature of the unsaturated diallyl phthalate shows a considerable rise in comparison with the maximal operating temperature of di-n-

propyl phthalate. Comparing the three isomeric di-*n*-hexyl esters of phthalic acid, di-*n*-hexyl isophthalate has the lowest volatility and di-*n*-hexyl terephthalate the highest.

The phases di-*n*-propyl phthalate and its isomer catechol dibutyrate have practically identical temperatures of operation. However, there is a difference between diphenyl phthalate and its isomer catechol dibenzoate. The values of the maximal operating temperatures of the diphenyl phthalate are lower than those of the catechol dibenzoate.

If one compares the maximal operating temperatures of di-*n*-butyl tetrachlorophthalate (mol. wt. 416) and di-*n*-nonyl phthalate* (mol. wt. 418), it can be seen that the second phase has higher maximal operating temperatures. This fact shows that a better decrease in volatility might be achieved if the ester molecule is made heavier by esterifying with a higher alcohol than by chlorination of the benzene ring.

The introduction of a nitro group into the benzene ring of di-*n*-hexyl 4-nitrophthalate (mol. wt. 379) in comparison with the di-*n*-octyl phthalate (mol. wt. 390) has a more sensitive influence than the chlorination.

The accumulation of the ester groups in the molecule of the ester, as is the case with di-*n*-butyl phthalyl-bis-glycolate (ml. wt. 394) does not give any advantage from the view-point of the liquid phase evaporation, if one compares its maximal operating temperatures with those of di-*n*-octyl phthalate.

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* The maximal operating temperature is found from Fig. 3. The commercial dinonyl phthalate used in this work is usually di-3,5,5-trimethylhexyl phthalate.