

## CORRELATION BETWEEN THE STRUCTURE OF THE STATIONARY PHASE AND ACTIVITY COEFFICIENTS IN GAS-LIQUID CHROMATOGRAPHY: ESTERS OF BENZENEDICARBOXYLIC ACIDS AND SOME OTHER SIMILAR PHASES

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In the practical application of gas-liquid chromatography, the selection of the best liquid phase for a particular analytical purpose is fundamental. With regard to this, the investigation of the thermodynamics of solution of organic vapours in high-boiling solvents is a question of special interest in gas-liquid chromatography.

The data published up to now<sup>1-5</sup> have usually been concerned with stationary phases which are very different in their chemical nature and therefore do not give any opportunity for a systematic study of the influence of the structure on their thermodynamic properties.

An exception to this is a paper by CHOVIN AND DUCROS<sup>6</sup>. It is a thermodynamic study of the tartrates of *n*-butyl, *n*-amyl, *n*-hexyl and *n*-heptyl alcohols as phases in gas-liquid chromatography.

In our previous paper<sup>7</sup>, we pointed out the influence of the length and structure of the alcohol chain of phthalic acid esters on the activity coefficients of some aromatic hydrocarbons. It was found that the values of the activity coefficients decrease linearly with the increasing number of carbon atoms in normal aliphatic alcohols.

The present study is an attempt to establish more completely the influence of the nature of the alcohol chain and the position of the carboxylic acid groups in the benzene ring of benzenedicarboxylic acids, as well as the influence of some other structural changes on the values of activity coefficients. This would provide data which might be used as a reasonable basis for a quantitative approach to liquid phase selection.

The gas-chromatographic data are related to the activity coefficients by:

$$\gamma^{\circ} = \frac{RT}{MP^{\circ}V_{\sigma}^t} \quad (1)$$

where  $\gamma^{\circ}$  is the activity coefficient of the solute in the solvent at infinite dilution,  $R$  is  $6.236 \cdot 10^4$  ml.mm per mole per degree,  $T$  is the column temperature in  $^{\circ}\text{K}$ ,  $M$  is the molecular weight of the stationary phase,  $P^{\circ}$  is the vapour pressure of the pure solute in mm Hg and  $V_{\sigma}^t$  is the retention volume in ml (measured from the air peak, then corrected for compressibility) per gram of solvent at the column temperature.

On the other hand, according to thermodynamics, the value of the activity

coefficient depends on the value of the excess partial molar enthalpy and entropy at infinite dilution by:

$$\ln \gamma^{\circ} = \frac{\Delta H_e^{\circ}}{RT} - \frac{\Delta S_e^{\circ}}{R} \quad (2)$$

which may be employed for their estimation.

#### EXPERIMENTAL

All measurements were carried out, as in our previous work, with a "Fractovap" model B apparatus, produced by "Carlo Erba", Italy.

The stainless steel chromatographic column was 2 m long and had an internal diameter of 6 mm. Ground unglazed tile (particle size diameter 0.2–0.4 mm) was used as solid support. The amount of stationary phase was 17.6% w/w of the inert support.

Pure dry nitrogen was used as carrier gas. The outlet gas velocity in all experiments was 120 ml/min. In the calculations to follow it was corrected for the water vapour pressure in the soap flowmeter at its temperature.

All the phases were investigated at 120°, 130° and 140°.

The hydrocarbons employed as solutes were again benzene, toluene, ethylbenzene and *o*-, *m*- and *p*-xylenes. The samples were injected into the preheater (180°) with a Hamilton microsyringe. The sample size was 0.001 ml.

The vapour pressures of the pure hydrocarbons under investigation at the temperatures of the experiments were calculated from reference data<sup>8</sup>.

All the esters used for stationary phases (diphenyl phthalate<sup>9</sup>, dicyclohexyl phthalate<sup>10</sup>, dibenzyl phthalate<sup>11</sup>, di-( $\beta$ -phenylethyl) phthalate<sup>12</sup>, di-*n*-hexyl isophthalate<sup>12</sup>, di-*n*-hexyl terephthalate<sup>12</sup>, catechol dibenzoate<sup>13</sup>, catechol dibutyrate<sup>13</sup>, and di-*n*-butyl phthalyl-bis-glycolate<sup>14</sup>) were synthesized by the authors.

#### RESULTS AND DISCUSSION

The retention volumes of the aromatic hydrocarbons per gram of solvent at various column temperatures, and the corresponding activity coefficients are shown in Tables I and II.

It is evident from Table I, that the elution order of the hydrocarbons investigated on all the phases is in accordance with the order of the boiling points of the solutes.

The values of the activity coefficients are less than unity, or slightly greater than unity, but always less than two.

The excess partial molar enthalpy and entropy found from the data of the activity coefficients at the temperatures of the experiments are positive in all cases. However, a more exact quantitative interpretation of the absolute values of  $\Delta H_e^{\circ}$  and  $\Delta S_e^{\circ}$  is impossible because of the experimental errors and insufficient number of measurements for a particular value.

If the data of the retention volumes of the six aromatic hydrocarbons on dicyclohexyl phthalate and diphenyl phthalate are compared with those on di-*n*-

TABLE I  
RETENTION VOLUMES,  $V_g^t$ , OF AROMATIC HYDROCARBONS

Hydrocarbons	Temperature (°C)	Phases								
		Diphenyl phthalate	Dicyclo- hexyl phthalate	Dibenzyl phthalate	Di-(β- phenyl- ethyl) phthalate	Di-n-hexyl isophthalate	Di-n-hexyl terephthalate	Catechol dibenzoate	Catechol dibutyrate	Di-n-butyl phthalyl bis- glycolate
Benzene	120	28.5	39.4	34.0	30.6	46.4	45.0	31.4	45.8	38.9
	130	25.4	33.8	28.2	26.4	38.8	38.8	27.2	39.3	32.4
	140	22.6	28.8	23.9	22.5	32.9	33.7	23.8	34.0	27.4
Toluene	120	55.5	77.5	64.9	59.3	96.5	92.9	61.6	86.1	70.9
	130	47.2	62.8	53.3	48.0	78.2	77.6	52.1	70.5	58.5
	140	40.5	51.2	43.6	39.3	63.2	63.5	43.3	57.0	48.3
Ethylbenzene	120	93.5	139.8	109.9	99.6	171.0	167.0	105.1	148.3	120.0
	130	79.0	110.0	88.5	80.0	135.0	136.0	85.1	119.9	96.5
	140	68.5	86.5	72.5	64.7	106.7	108.6	69.0	95.2	77.4
o-Xylene	120	130.6	176.8	147.5	137.0	227.8	229.0	145.0	193.0	158.9
	130	108.0	139.9	117.6	109.0	177.5	181.0	115.2	154.1	125.0
	140	87.7	109.0	95.5	86.6	139.5	141.2	91.2	123.0	99.4
m-Xylene	120	101.1	147.9	120.7	110.8	194.0	191.5	118.2	158.1	129.0
	130	84.5	119.0	96.4	88.0	152.5	153.2	95.5	127.3	102.2
	140	71.2	94.5	78.3	70.6	120.6	120.7	77.0	102.5	82.7
p-Xylene	120	99.9	144.0	118.0	107.6	191.1	189.9	112.8	153.5	128.3
	130	83.5	113.2	94.3	85.5	148.5	149.8	90.4	125.3	101.5
	140	70.4	89.5	76.1	68.4	116.6	119.2	73.8	101.0	80.2

hexyl phthalate<sup>7</sup>, it is evident that their values are lowest on diphenyl phthalate and highest on di-*n*-hexyl phthalate.

The values of the activity coefficients for the same phases are lowest on di-*n*-hexyl phthalate and highest on diphenyl phthalate. Moreover, the deviations from Raoult's law on di-*n*-hexyl phthalate are negative, while on diphenyl phthalate they are positive. The data for dicyclohexylphthalate have an intermediate position among them.

From the data for these three phases it follows that the hydrocarbons are retained best on di-*n*-hexyl phthalate and worst on diphenyl phthalate. According to eqn. (2) the interaction of the aromatic hydrocarbons with di-*n*-hexyl phthalate and of benzene and toluene with dicyclohexyl phthalate, when  $\gamma^\circ < 1$ ,  $\Delta H_e^\circ > 0$ ,  $\Delta S_e^\circ > 0$ , assumes the predominance of the entropy term. This assumption is supported by the fact that in the above mentioned cases the temperature has practically no effect on the activity coefficient.

The positive enthalpy indicates that the molecular interactions between the solute and the solvent are less than the interactions among the molecules of the pure solute. The positive value for the entropy shows that the molecules of the solute are able to come into contact with a greater number of molecules of the solvent than with their own molecules.

The interaction of ethylbenzene and the xylenes with dicyclohexyl phthalate and all of the hydrocarbons with diphenyl phthalate, when  $\gamma^\circ > 1$ ,  $\Delta H_e^\circ > 0$ ,  $\Delta S_e^\circ > 0$ , assumes that the influence of the enthalpy term upon the value of the activity coefficient is greater than that of the entropy term. The predominance of this term, however, over the entropy term, is probably not very great.

It is evident, from the data for diphenyl phthalate, dibenzyl phthalate and di-( $\beta$ -phenylethyl) phthalate, that the retention volumes of the hydrocarbons are smallest on diphenyl phthalate and greatest on dibenzyl phthalate. The corresponding values of the activity coefficients are practically equal when the dibenzyl- and di-( $\beta$ -phenylethyl) phthalate phases are concerned and higher for the diphenyl phthalate phase. With the exception of benzene, which on dibenzyl- and on di-( $\beta$ -phenylethyl) phthalates has  $\gamma^\circ < 1$ , all hydrocarbons on the three phases give positive deviations from Raoult's law. Therefore the hydrocarbons are retained on dibenzyl phthalate and di-( $\beta$ -phenylethyl) phthalate better than on diphenyl phthalate. Di-( $\beta$ -phenylethyl) phthalate has one methylene group more than dibenzyl phthalate but this fact has not such a noticeable influence on the activity coefficient as is the case with diphenyl and dibenzyl phthalates.

Comparison of the data for di-*n*-hexyl phthalate with those for di-*n*-hexyl isophthalate and di-*n*-hexyl terephthalate shows that the activity coefficients are practically independent of the position of the ester groups in the benzene ring of the phthalate.

It is the authors' opinion that it would be interesting to be able to determine how the position of the functional groups and atoms influences the activity coefficient.

If the data for di-*n*-propyl phthalate<sup>7</sup> are compared with the corresponding data for its isomer, catechol dibutyrate, it can be seen that the retention volumes for the former phase are greater than the retention volumes for the latter. In di-*n*-propyl phthalate, the aliphatic radicals are attached to the carboxyl oxygen, while in the case of catechol dibutyrate they are attached to the carboxyl carbon atom. If the radicals

TABLE II

ACTIVITY COEFFICIENTS,  $\gamma^0$ , OF AROMATIC HYDROCARBONS

Hydrocarbons	Temperature (°C)	Phases								
		Diphenyl phthalate	Dicyclo- hexyl phthalate	Dibenzyl phthalate	Di-( $\beta$ - phenyl- ethyl) phthalate	Di-n-hexyl isophthalate	Di-n-hexyl terephthalate	Catechol dibenzoate	Catechol dibutyrate	Di-n-butyl phthalyl bis- glycolate
Benzene	120	1.20	0.84	0.93	0.95	0.70	0.73	1.09	0.95	0.71
	130	1.10	0.79	0.91	0.90	0.68	0.68	1.04	0.90	0.67
	140	1.01	0.77	0.88	0.86	0.66	0.65	0.98	0.86	0.67
Toluene	120	1.41	0.97	1.11	1.12	0.77	0.80	1.27	1.16	0.89
	130	1.31	0.95	1.07	1.10	0.75	0.76	1.19	1.12	0.86
	140	1.22	0.93	1.04	1.07	0.75	0.74	1.14	1.10	0.83
Ethylbenzene	120	1.71	1.10	1.34	1.36	0.89	0.91	1.52	1.37	1.08
	130	1.56	1.08	1.28	1.31	0.87	0.86	1.45	1.31	1.03
	140	1.46	1.07	1.22	1.27	0.86	0.84	1.40	1.29	1.00
o-Xylene	120	1.56	1.11	1.27	1.26	0.85	0.85	1.40	1.34	1.03
	130	1.43	1.07	1.21	1.21	0.83	0.82	1.34	1.28	1.00
	140	1.37	1.06	1.15	1.18	0.82	0.81	1.31	1.24	0.97
m-Xylene	120	1.72	1.14	1.33	1.34	0.86	0.87	1.48	1.40	1.09
	130	1.58	1.08	1.28	1.29	0.83	0.83	1.40	1.34	1.06
	140	1.47	1.07	1.23	1.26	0.83	0.83	1.36	1.30	1.02
p-Xylene	120	1.70	1.14	1.33	1.34	0.85	0.86	1.51	1.41	1.07
	130	1.57	1.11	1.28	1.30	0.84	0.83	1.45	1.33	1.04
	140	1.45	1.10	1.23	1.27	0.83	0.81	1.38	1.28	1.03

are aromatic instead of aliphatic (*e.g.*, the phases are catechol dibenzoate and diphenyl phthalate), the effect is reversed, the retention volumes on diphenyl phthalate being less than those on catechol dibenzoate.

The activity coefficients have lowest values with di-*n*-propyl phthalate and highest with diphenyl phthalate. The two catechol diesters have an intermediate position.

Investigation of the influence of the number of carboxyl groups in the side chains of the phthalic ester was performed on di-*n*-butyl phthalyl-bis-glycolate.

The values of the retention volumes on di-*n*-butyl phthalyl-bis-glycolate are less than those on di-*n*-butyl phthalate. The activity coefficients on these two phases are practically equal.

#### SUMMARY

The present work is an attempt to investigate the correlation between the stationary phases and the activity coefficients in gas-liquid chromatography. Nine esters of benzenedicarboxylic acids or their isomers were chosen as liquid stationary phases and aromatic hydrocarbons were used as solutes.

It was found that the most energetic interactions between solute and solvent take place with the phthalates, isophthalates and terephthalates of the aliphatic alcohols.

It is thought that the data obtained in this work might serve as a good basis for liquid phase selection.

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