CORRELATION BETWEEN THE STRUCTURE OF THE STATIONARY PHASE AND ACTIVITY COEFFICIENTS IN GAS-LIQUID CHROMATOGRAPHY: ESTERS OF PHTHALIC ACID WITH ALIPHATIC ALCOHOLS

N. PETSEV AND CHR. DIMITROV

Department of Chemistry, University of Sofia (Bulgaria)

(Received March 8th, 1965)

Gas-liquid chromatography, first used about thirteen years ago, has been found to be very effective in the field of analytical practice.

In spite of the large amount of accumulated experimental data it is very often difficult to find a suitable stationary phase for some particular purpose. Usually these difficulties are overcome empirically.

The relationship of chromatographic data to the thermodynamic quantities for solution of organic vapours in high boiling liquids provides a basis for the theoretical interpretation of the problem of solute-solvent interactions.

A qualitative and quantitative evaluation of these interactions would also be a reasonable basis for liquid phase selection.

LANGER AND PURNELL showed in their paper[1], that the retention volume $V_g{}^t$ in ml (measured from the air peak, then corrected for compressibility) per gram of solvent, at the column temperature, is related to the activity coefficient by

$$V_g{}^t = \frac{RT}{MP^\circ \gamma^\circ} \tag{1}$$

where R is 82 ml.atm per mole per degree, T is the column temperature in $^\circ K$, M is the molecular weight of the liquid stationary phase, P° is the vapour pressure of the pure solute in atm, and γ° is the activity coefficient of the solute in the solvent at infinite dilution.

In this way, the need for a solvent density measurement, as is required by the classical method of PORTER, DEAL AND STROSS[2] is eliminated.

The activity coefficient is a criterion for the deviation of the system from the ideal solution state if the measurement is made in the region of validity of Henry's law *i.e.* at infinite dilution.

The activity coefficient, on the other hand, may be employed as a starting quantity for the estimation of the excess partial molar free energy, the partial molar enthalpy and the partial molar entropy of mixing at infinite dilution.

As is evident from the literature[1-5], gas-liquid chromatography has so far only been used to obtain thermodynamic data with stationary phases that were very different in their chemical nature.

It is the authors' opinion that it would be interesting to make an analogous

investigation, but with a class of organic compounds that have shown good qualities as stationary phases.

This would disclose some correlation between the structure of the stationary phases and their behaviour, from the thermodynamic point of view, in the gas-chromatographic process.

The esters of phthalic acid with aliphatic alcohols, which have a wide application as liquid phases, were chosen for this investigation, and aromatic hydrocarbons which are very common in analytical practice, were used as solutes.

EXPERIMENTAL

Apparatus

All measurements were carried out with a "Fractovap" model B apparatus, produced by "Carlo Erba", Italy. The detector was of the through-flow type with thermistors and, together with the chromatographic column, it was enclosed in an air thermostat, the temperature being controlled to $\pm$ 0.1°.

Carrier gas

Pure nitrogen, dried with "blaugel" was used as carrier gas. The outlet gas velocity in all experiments was 120 ml/min, and the pressure drop through the column was about 450 mm Hg.

The outlet pressure was atmosphere pressure, corrected for the water vapour in the soap flowmeter at its temperature.

Column

The stainless steel chromatographic column had an internal diameter of 6 mm, and was 2 m long. Column packing was weighed with accuracy to $\pm$ 0.01 g. During the work the weight of the packing was periodically checked and corrected for the evaporation of the stationary phase. In spite of this control, all columns had a working time of not more than 10 h.

The density of packing was about 1.24 g/ml. Ground unglazed tile (particle size diam. 0.2–0.4 mm) was used as solid support. The amount of stationary phase was 15 % w/w of the inert support and varied from 10.70 to 10.90 g for all columns.

All the esters under investigation as stationary phases were synthesized by the authors, and after purification they had the physical constants shown in Table I.

TABLE I

PHYSICAL CONSTANTS OF THE ESTERS

Esters	d_4^{20}	n_D^{20}	Ref. No.
1. Di-n-propyl phthalate	1.0725	1.4980	6
2. Diisopropyl phthalate	1.0472	1.4918	6
3. Diallyl phthalate	1.1174	1.5211	7
4. Di-n-butyl phthalate	1.0489	1.4940	6
5. Di-sec.-butyl phthalate	1.0425	1.4915	6
6. Diisobutyl phthalate	1.0383	1.4920	6
7. Di-n-hexyl phthalate	1.0044	1.4885	6
8. Di-n-octyl phthalate	0.9756	1.4860	6

With the exception of diallyl phthalate, all the esters were investigated at 120°, 130° and 140°. Diallyl phthalate polymerizes easily with rise of temperature and because of this it was only employed at the lowest temperature, 120°.

Sample injection

Samples were injected through a silicone rubber membrane into a preheater (180°) with a Hamilton microsyringe.

The use of small samples obviated the need of extrapolation to zero sample sizes. By varying sample sizes, it was found that their influence on the values of the retention volumes is negligible if the samples are less than 0.003 ml. As a precautionary measure all the investigations were carried out with a sample size of 0.001 ml.

The hydrocarbons before injection into the test columns were carefully purified and their purity checked gas chromatographically on a column of Reoplex-400 and commercial dinonyl phthalate.

EXPERIMENTAL ACCURACY

The most important part in this investigation was the precise determination of retention volumes, since all thermodynamic quantities depend on them.

ADLARD, KHAN AND WHITHAM[8] have described a very accurate technique and the determination of retention volumes and activity coefficients under conditions of infinite dilution from the resulting data. These authors pass the sample through the column several times, and the arithmetic mean of all the retention volumes is used. In this way the error is about 1 %. This technique is not altogether possible when the investigation involves several compounds or phases; thus a compromise had to be made while maintaining the principle of the "arithmetic mean", and good accuracy was dependent on the constancy of the experimental parameters.

On the other hand, the first results showed that the differences between the activity coefficients of the phases under investigation were quite sufficient for a comparative interpretation.

The retention volumes were determined with an accuracy of about $\pm$ 2 %. This accuracy gave $\pm$ 2 % error in the values of the activity coefficients, which was an error of about $\pm$ 0.03 abs. units. The values of partial molar enthalpy and entropy at infinite dilution were lower than the experimental accuracy and only a qualitative interpretation of them was possible. It should be emphasized that this is the usual sort of accuracy in gas–liquid chromatography.

RESULTS AND DISCUSSION

The retention volumes $V_g{}^t$ (Table II) of the aromatic hydrocarbons per gram of solvent at the various column temperatures show a tendency to decrease with the increase of the number of C-atoms in the esterifying alcohol. An exception to this was observed only for the retention volumes of *m*- and *p*-xylene, which increase a little with the increase of the number of C-atoms in the esterifying alcohol.

The esters of alcohols with *iso*- and *sec.*-alkyl radicals gave lower retention volumes (for one and the same solute) than the esters of normal alcohols with the same number of C-atoms.

8

18 N. PETSEV, C. DIMITROV

TABLE II

RETENTION VOLUMES V_g^t OF AROMATIC HYDROCARBONS

Hydrocarbons	Temperature °C	Phases							
		Di-n-propyl phthalate	Diisopropyl phthalate	Diallyl phthalate	Di-n-butyl phthalate	Di-sec.-butyl phthalate	Diisobutyl phthalate	Di-n-hexyl phthalate	Di-n-octyl phthalate
Benzene	120	50.7	50.8	45.5	50.7	50.7	47.9	49.2	46.8
	130	42.1	42.3	—	41.9	42.2	39.9	40.7	38.7
	140	35.4	35.6	—	35.2	35.5	33.4	34.1	32.5
Toluene	120	99.3	98.8	82.4	98.1	95.5	94.5	97.2	95.6
	130	80.3	80.2	—	78.8	77.2	76.0	78.2	77.0
	140	66.3	65.9	—	64.5	63.5	62.4	63.8	62.8
Ethylbenzene	120	174.8	173.1	141.1	174.1	169.0	168.5	172.0	171.5
	130	137.0	138.0	—	138.6	132.6	132.6	135.5	135.2
	140	110.8	110.0	—	109.7	106.3	106.0	108.4	107.8
o-Xylene	120	224.0	219.9	185.7	223.8	214.5	218.0	219.0	218.0
	130	176.1	171.5	—	176.0	167.5	170.0	170.3	168.0
	140	142.1	136.8	—	138.1	133.2	134.5	135.4	132.0
m-Xylene	120	183.0	173.1	146.2	184.7	175.2	174.0	187.5	188.5
	130	144.8	136.8	—	145.6	138.2	137.0	146.0	148.8
	140	114.2	109.1	—	114.9	109.7	108.8	115.0	117.5
p-Xylene	120	178.0	173.8	142.8	179.1	174.5	175.8	181.5	184.3
	130	140.2	137.7	—	140.7	137.2	138.0	142.5	144.1
	140	112.0	110.2	—	112.3	109.6	111.0	114.2	115.0

J. Chromatog., 20 (1965) 15–22

TABLE III

ACTIVITY COEFFICIENTS, γ°, OF AROMATIC HYDROCARBONS

Hydrocarbons	Temperature °C	Phases							
		Di-n-propyl phthalate	Diisopropyl phthalate	Diallyl phthalate	Di-n-butyl phthalate	Di-sec.-butyl phthalate	Diisobutyl phthalate	Di-n-hexyl phthalate	Di-n-octyl phthalate
Benzene	120	0.77	0.77	0.87	0.74	0.74	0.78	0.63	0.57
	130	0.75	0.75	—	0.72	0.72	0.76	0.62	0.56
	140	0.74	0.73	—	0.71	0.70	0.75	0.61	0.55
Toluene	120	0.90	0.90	1.10	0.87	0.89	0.91	0.73	0.64
	130	0.88	0.88	—	0.86	0.87	0.89	0.72	0.63
	140	0.85	0.86	—	0.84	0.85	0.87	0.71	0.61
Ethylbenzene	120	1.05	1.05	1.32	1.01	1.04	1.04	0.85	0.73
	130	1.03	1.02	—	0.98	1.01	1.01	0.82	0.71
	140	0.99	1.00	—	0.96	0.99	0.99	0.81	0.70
o-Xylene	120	1.03	1.06	1.27	0.99	1.03	1.02	0.84	0.73
	130	1.00	1.03	—	0.96	1.01	0.99	0.82	0.72
	140	0.96	1.00	—	0.95	0.98	0.97	0.80	0.71
m-Xylene	120	1.09	1.15	1.38	1.03	1.09	1.09	0.84	0.72
	130	1.05	1.12	—	1.00	1.06	1.07	0.83	0.70
	140	1.04	1.09	—	0.99	1.03	1.04	0.82	0.69
p-Xylene	120	1.09	1.12	1.38	1.04	1.06	1.06	0.85	0.72
	130	1.06	1.08	—	1.01	1.04	1.03	0.83	0.71
	140	1.04	1.06	—	0.99	1.01	1.01	0.81	0.69

The retention volumes of benzene on diisopropyl phthalate and on di-*sec.*-butyl phthalate deviate from the rule, and it is supposed that this is due to experimental errors.

The values of the activity coefficients also change regularly (Table III) and in most cases they are less than unity, while the rest are equal to or slightly greater than unity. As the activity coefficients are close to unity, the peaks will be almost symmetrical.

Negative deviations from Raoult's law occur when the components of a mixture possess a great attraction for one another. Then the solute is strongly retained by the liquid phase. On the other hand, a negative deviation occurs when solute and solvent have similar polarities, but differ in their molar volumes.

The order of elution of the hydrocarbons found by the authors is in accordance with the similarity in polarities mentioned above. For instance, according to their polarities, the order of elution should be: *p*-xylene, *m*-xylene, ethylbenzene and *o*-xylene. The polarity of the phases, as well as the polarity of solutes is low and is not sufficient to ensure this order and the above-mentioned hydrocarbons leave the column according to their boiling points: ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene.

Diallyl phthalate gives a positive deviation from Raoult's law which is due to the increased difference between the polarities of the solute and the solvent. But this difference is still not very great, and the solutes maintain the previous order of elution.

It is possible to draw some conclusions from Table III:

1. The ideality of the system is as high as the molecular weight of the esterifying alcohol is low. The lower the molecular weight of the solute, the more valid this rule.

2. Activity coefficients decrease for one and the same solute with the increase in the number of C-atoms in the normal alcohols. This change is practically linear and means that the interactions between the solute and the solvent become stronger.
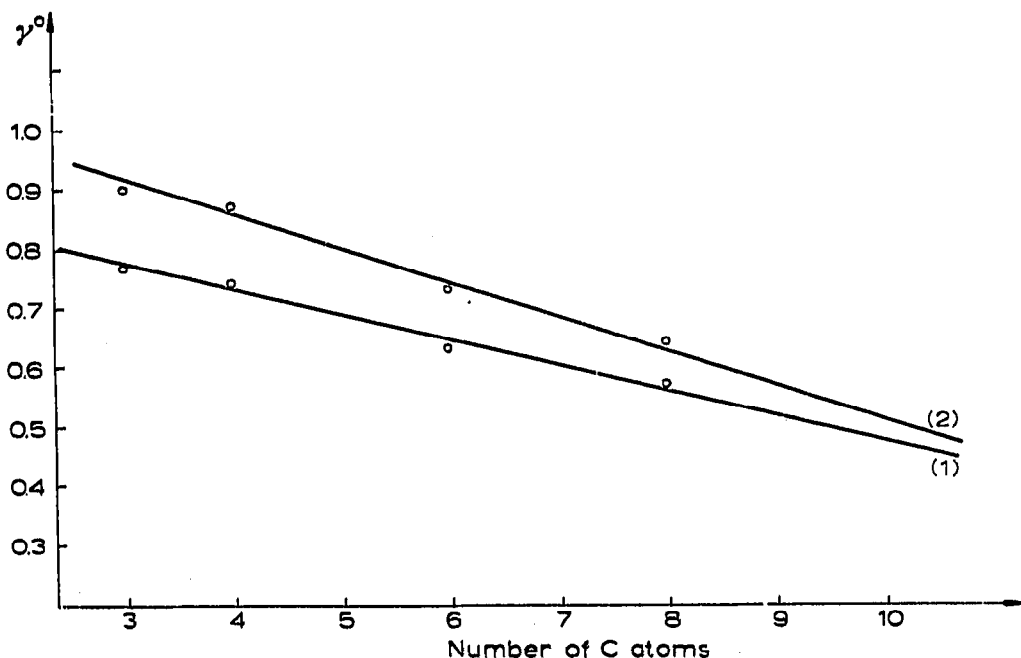

Fig. 1. Plot of the activity coefficients of benzene (1) and toluene (2) at 120° *vs.* number of C-atoms in the chain of normal alcohols in the esters of phthalic acid.

Fig. 1 shows the linearity of the values of the activity coefficients of benzene and toluene depending on the number of C-atoms in the normal aliphatic alcohols.

It can be found by extrapolation from Fig. 1 that at $120°$ the activity coefficient of the system benzene/di-n-nonyl phthalate should be 0.52. The same coefficient for the system benzene/di-3,5,5-trimethylhexyl phthalate at $110°$ had the values 0.526 and 0.514 (from two measurements)[8].

It can be seen from the data on the change of the activity coefficient of toluene at $120°$ that on di-n-decyl phthalate as a stationary phase, $\gamma°$ should be 0.51. PORTER, DEAL AND STROSS[2] reported a value for the activity coefficient of toluene on diisodecyl phthalate at $115°$ of 0.48.

The two examples described above are in good agreement with the data published in the literature if we take into consideration that there are some differences due to the different temperature and to the structure of the alcohol chain.

Since

$$\ln\gamma° = \frac{\Delta H_e°}{RT} - \frac{\Delta S_e°}{R} \qquad (2)$$

the change of the values of the activity coefficients may depend on the change of $\Delta H_e°$, or on the change of $\Delta S_e°$, or on the change of both of them.

$\Delta H_e°$ is a measure of the energy excess, which arises when the molecules of the solute pass from the sphere of their own molecules into the sphere of the solvent molecules.

For one and the same solute, but with different phases, the activity coefficients are practically independent of the temperature. This is an indication that the energy excess mentioned above does not depend on the structure of the esterifying alcohol, and that the deviation from ideal state is mainly due to the entropy term.

The entropy term is a measure of the ability of the molecules of the solute to penetrate among the molecules of the solvent. The decrease of the activity coefficients due to the entropy term when $\gamma° \leqslant 1$ means that the process of aggregation between the molecules of the solute and the molecule of the solvent increases.

SUMMARY

In an investigation of the correlation between the structure of the stationary phase and activity coefficients in gas–liquid chromatography, the aliphatic esters of phthalic acid were chosen for study as the liquid stationary phase and aromatic hydrocarbons were used as solutes.

The dependence of the activity coefficients of the aromatic hydrocarbons on the structure of the stationary phase was demonstrated, and the effect of the length of the chain of the esterifying alcohol in the phthalic esters on the chromatographic behaviour was also shown.

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

REFERENCES

1 S. H. LANGER AND J. H. PURNELL, *J. Phys. Chem.*, 67 (1963) 263.
2 P. E. PORTER, C. H. DEAL AND F. H. STROSS, *J. Am. Chem. Soc.*, 78 (1956) 2999.
3 C. J. HARDY, *J. Chromatog.*, 2 (1959) 490.
4 A. KWANTES AND G. W. A. RIJNDERS, in D. H. DESTY (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, pp. 125–135.
5 G. L. PIEROTTI, C. H. DEAL, E. L. DERR AND P. E. PORTER, *J. Am. Chem. Soc.*, 78 (1956) 2989.
6 *Organic Syntheses*, Russian Edition, Vol. 4, p. 447.
7 D. A. KARDASHEV, N. S. LEZNOV AND V. P. NUZHDINA, *Khim. Prom.*, No. 2 (1945) 5.
8 E. R. ADLARD, M. A. KHAN AND B. T. WHITHAM, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 251.