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PETROCHEMICAL ANALYTICAL PROBLEMS

III*. GAS CHROMATOGRAPHIC CONTROL OF ACETATE ESTER PRODUCTION USING POROUS POLYMER BEAD COLUMNS

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SUMMARY

H_2O–ROH–ROAc–AcOH (R=Me, Et, *n*-Pr, iso-Pr, *n*-Bu, *sec.*-Bu, iso-Bu, *tert.*-Bu) mixtures in the presence and absence of sodium chloride were successfully analysed using Porapak Q and T columns. The separation achieved permits the analytical control of the production by either intermittent or continuous sampling.

INTRODUCTION

The increasing outputs and quality demanded in the solvent industry (see, *e.g.*, refs. 2 and 3) have led to the need for rapid and simple analytical procedures that can be utilized as sensors in automation. If gas chromatography (GC) is to be used as an analytical tool, good resolution and possibly low tailing are necessary for this purpose.

Our aim was to develop a GC method for use in the control of acetate ester production. From the analytical viewpoint, the problem was to analyze H_2O–ROH–ROAc–AcOH (R=Me, Et, *n*-Pr, iso-Pr, *n*-Bu, *sec.*-Bu, iso-Bu and *tert.*-Bu) mixtures over a wide concentration range of each component. As the esterification is catalysed by hydrochloric acid, the crude product samples could contain hydrochloric acid or (after neutralization) 1–2% of sodium chloride.

Several papers have dealt with the GC and GLC analysis of systems of similar composition, but the following considerations excluded most of the reported possibilities:

(1) because of the presence of water as well as the simultaneous presence of alcohol and acetic acid, all methods based on the analysis of derivatives were excluded;

(2) as the ester:alcohol ratio was a crucial aspect of the problem it did not seem advisable to use acid-deactivated silica supports; and

(3) as the samples could contain hydrochloric acid and/or water, deactivation of the support by water did not seem suitable.

These considerations and our previous favourable results obtained with analogous very polar substrates[4] prompted us to use columns with microporous cross-

* For Part II, see ref. 1.

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linked polymer beads. Although these excellent packing materials have been reported by other workers [5-17] to be particularly suitable for use with highly polar mixtures, systematic work on the system of interest to us was lacking. Our results concerning this problem are reported in this paper.

EXPERIMENTAL

Analytical-grade reagents were used for the systematic experiments. Industrial samples were taken from the ester production plant of the Egyesült Vegyimüvek (United Chemical Works), Budapest, Hungary.

Gas chromatographic measurements were performed using a Fractovap GT chromatograph (Carlo Erba, Milan, Italy) with a thermal conductivity detector and 2 m × 0.4 cm glass columns*. Porapak Q and T were of commercial origin (Waters Ass., Framingham, Mass., U.S.A.). Hydrogen was used as the carrier gas.

RESULTS AND DISCUSSION

Preliminary experiments showed Porapak Q and T to be the most suitable microporous polymer packings.

Optimal conditions were selected on the basis of log t_R' *versus* $1/T$ plots, which were linear, as can be seen for example in Fig. 1.

The working temperatures listed in Table I were found to be advantageous for the systems investigated.

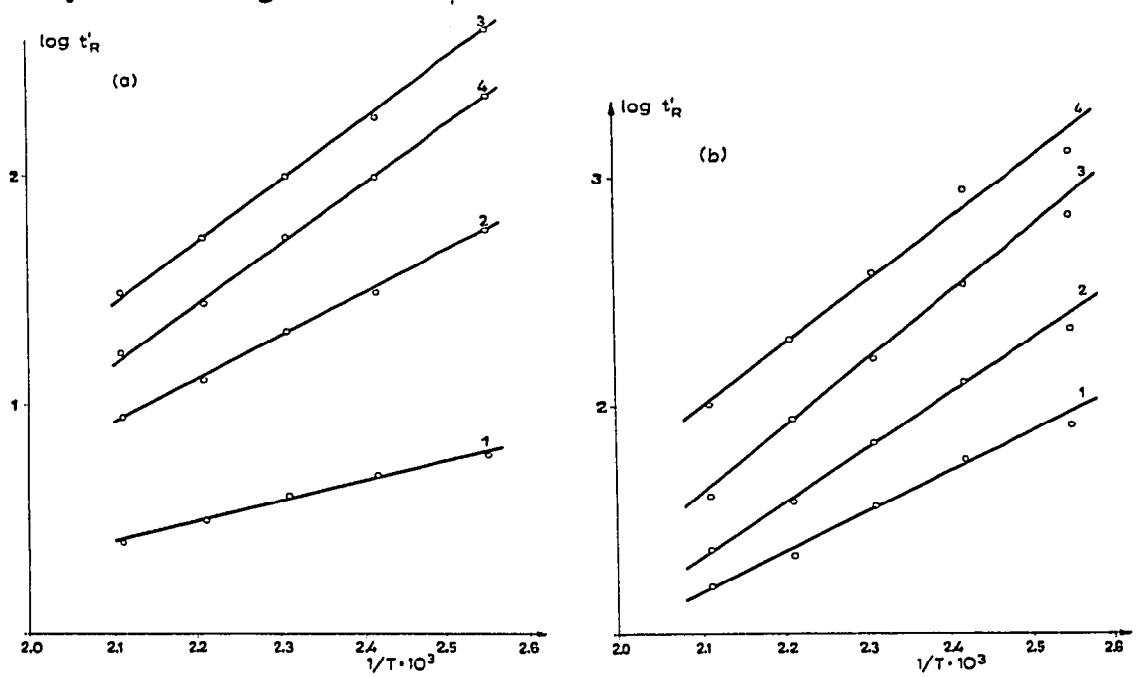

Fig. 1. log t_R' *versus* $1/T$ plots for the system H_2O (1)–EtOH (2)–EtOAc (3)–AcOH (4) on 2 m × 0.4 cm columns of (a) Porapak Q and (b) Porapak T. Carrier gas (hydrogen) flow-rate, 150 ml/min.

* The use of metal tubing (aluminium, steel) caused more tailing and influenced the retention time of water and acetic acid in an irregular manner, as expected[4,18].

TABLE I

ADJUSTED RETENTION VALUES OF THE COMPOUNDS INVESTIGATED

Columns as in Experimental; carrier gas (hydrogen) flow-rate, 150 ml/min; chart speed, 0.75 m/h.

Substance	*Column temp.* (°C)	t_R' (*mm*)	
		Porapak Q	*Porapak T*
H_2O	140	7	–
H_2O	160	2.3	–
H_2O	180	1.0	19
AcOH	140	126	914
AcOH	160	52	362
AcOH	180	29	192
MeOH	140	18	32
MeOAc	140	105	167
EtOH	160	19	65
EtOAc	160	100	158
n-PrOH	160	52	134
n-PrOAc	160	254	230
iso-PrOH	160	40	82
iso-PrOAc	160	190	217
n-BuOH	180	73	156
n-BuOAc	180	251	280
sec.-BuOH	180	59	111
sec.-BuOAc	180	206	223
iso-BuOH	180	63	131
iso-BuOAc	180	226	253
tert.-BuOH	180	40	69
tert.-BuOAc	180	210	178

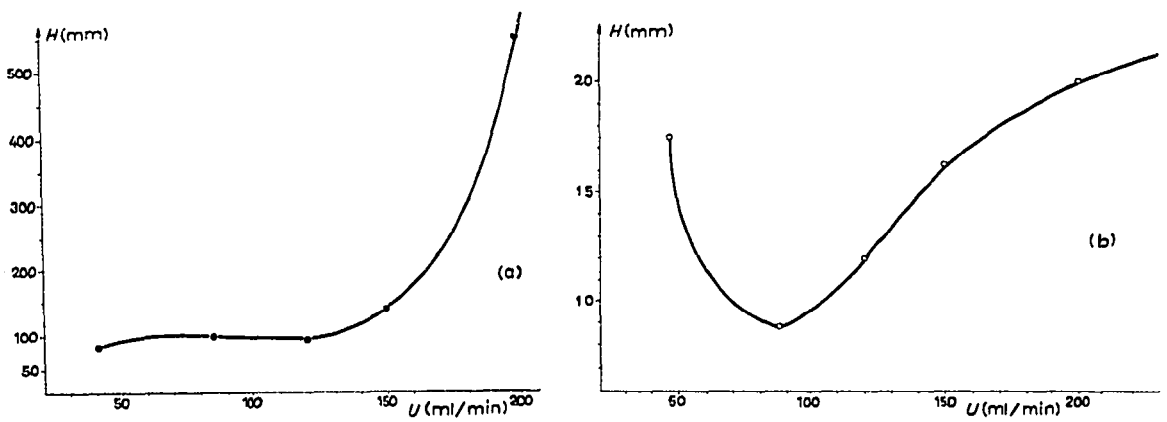

Fig. 2. Van Deemter plots of (a) methanol on Porapak Q and (b) ethanol on Porapak T at 120°.

The best range for the carrier gas velocity was determined from the Van Deemter curves. These showed a generally regular shape (see for example Fig. 2b) but sometimes did not show well defined minima (see for example Fig. 2a). The facts that the Van Deemter minima were not at the same flow-rate (u) value for all substances containing a given R group and that sometimes the minima were absent enabled only an approximate determination of the optimal u value to be made, which was 120–170 ml/min for all systems.

The retention behaviour of the substances investigated under the above conditions is shown in Table I. A considerable difference in the behaviour of the two types of Porapak towards substances containing active H atoms can be seen. The fact that acetic acid is eluted before any of the esters except for methyl acetate on Porapak Q was utilized in practical work: this column was used for samples with a low acetic acid content, and thus more exact results could be obtained. The large differences between the retention values of the alcohols on the two polymers, while the differences are considerably lower for the corresponding acetates, seems to be of theoretical interest.

The resolution factors[19] (R_s) were determined for the neighbouring peaks and are listed in Table II. It can be seen that the resolution is good, as a result of the low

TABLE II

PEAK RESOLUTION FACTORS (R_s) FOR THE NEIGHBOURING PEAKS OF THE SYSTEMS INVESTIGATED

Columns as in Experimental, carrier gas (hydrogen) flow-rate, 150 ml/min.

Column temp. (°C)	*Substance pair*	R_s *(Porapak T)*	*Substance pair*	R_s *(Porapak Q)*
140	H_2O–MeOH	0.4	H_2O–MeOH	0.7
140	MeOH–MeOAc	3.2	MeOH–MeOAc	3.0
140	MeOAc–AcOH	5.8	MeOAc–AcOH	0.4
160	H_2O–EtOH	1.6	H_2O–EtOH	1.5
160	EtOH–EtOAc	1.7	EtOH–AcOH	1.4
160	EtOAc–AcOH	2.8	AcOH–EtOAc	1.5
160	H_2O–*n*-PrOH	3.8	H_2O–*n*-PrOH	1.9
160	*n*-PrOH–*n*-PrOAc	1.1	*n*-PrOH–AcOH	0.1
160	*n*-PrOAc–AcOH	2.1	AcOH–*n*-PrOAc	2.0
160	H_2O–iso-PrOH	2.8	H_2O–iso-PrOH	2.3
160	iso-PrOH–iso-PrOAC	2.6	iso-PrOH–AcOH	0.2
160	iso-PrOAc–AcOH	1.8	AcOH–iso-PrOAc	2.2
180	H_2O–*n*-BuOH	5.8	H_2O–AcOH	1.0
180	*n*-BuOH–AcOH	0.8	AcOH–*n*-BuOH	1.5
180	AcOH–*n*-BuOAc	1.9	*n*-BuOH–*n*-BuOAc	3.8
180	H_2O–*sec.*-BuOH	3.8	H_2O–AcOH	1.7
180	*sec.*-BuOH–AcOH	2.1	AcOH–*sec.*-BuOH	0.9
180	AcOH–*sec.*-BuOAc	0.7	*sec.*-BuOH–*sec.*-BuOAc	3.1
180	H_2O–iso-BuOH	3.4	H_2O–AcOH	1.7
180	iso-BuOH–AcOH	1.0	AcOH–iso-BuOH	0.8
180	AcOH–iso-BuOAc	1.0	iso-BuOH–iso-BuOAc	2.8
180	H_2O–*tert.*-BuOH	2.0	H_2O–AcOH	2.0
180	*tert.*-BuOH–*tert.*-BuOAc	3.1	AcOH–*tert.*-BuOH	0.3
180	*tert.*-BuOAc–AcOH	0.6	*tert.*-BuOH–*tert.*-BuOAc	4.3

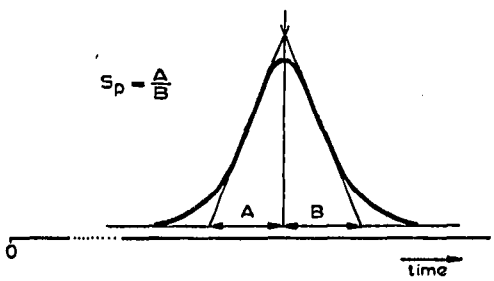

Fig. 3. Definition of S_p according to Fuchs[20].

tailing of the peaks. We characterized the symmetry of the peak by the S_p values suggested by Fuchs[20]. The definition of the S_p peak symmetry is shown in Fig. 3, and the S_p values of the peaks obtained are shown in Table III.

For the more polar components, the S_p values are generally higher on Porapak T, which results in a better separation generally being achieved on this column. The results indicate some structural effect on S_p, but the explanation of this effect requires further study.

TABLE III

PEAK SYMMETRY VALUES (S_p) FOR THE SUBSTANCES INVESTIGATED

Columns as in Experimental, carrier gas (hydrogen) flow-rate, 150 ml/min. S_p is given as the main value for sample sizes from 0.5 to 2 l*.

Substance	*Column temp. (°C)*	S_p	
		Porapak Q	*Porapak T*
H_2O	140	0.21	0.35
H_2O	160	0.22	0.33
AcOH	140	0.22	0.50
AcOH	160	0.23	0.52
AcOH	180	0.55	0.51
MeOH	140	0.20	0.29
MeOAc	140	0.60	0.71
EtOH	160	0.44	0.40
EtOAc	160	0.42	0.50
n-PrOH	160	0.33	0.56
n-PrOAc	160	0.47	0.60
iso-PrOH	160	0.46	0.36
iso-PrOAc	160	0.38	0.50
n-BuOH	180	0.15	0.50
n-BuOAc	180	0.60	0.40
sec.-BuOH	180	0.20	0.27
sec.-BuOAc	180	0.50	0.45
iso-BuOH	180	0.22	0.76
iso-BuOAc	180	0.50	0.62
tert.-BuOH	180	0.46	0.28
tert.-BuOAc	180	0.62	0.52

* Relative standard deviation, ±8–9%.

The quality of the chromatograms can be seen from the curves shown in Fig. 4. The hydrochloric acid content of the samples did not cause interference. Samples containing sodium chloride in amounts up to 5% (in practice the sodium chloride content does not exceed 1.5%) were successfully analyzed by filling a 5–6-cm length of the starting end of the column with glass-wool and injecting the sample directly into the column. The glass-wool should be changed after 20–25 h operation of the column (*i.e.*, after 100–150 samples).

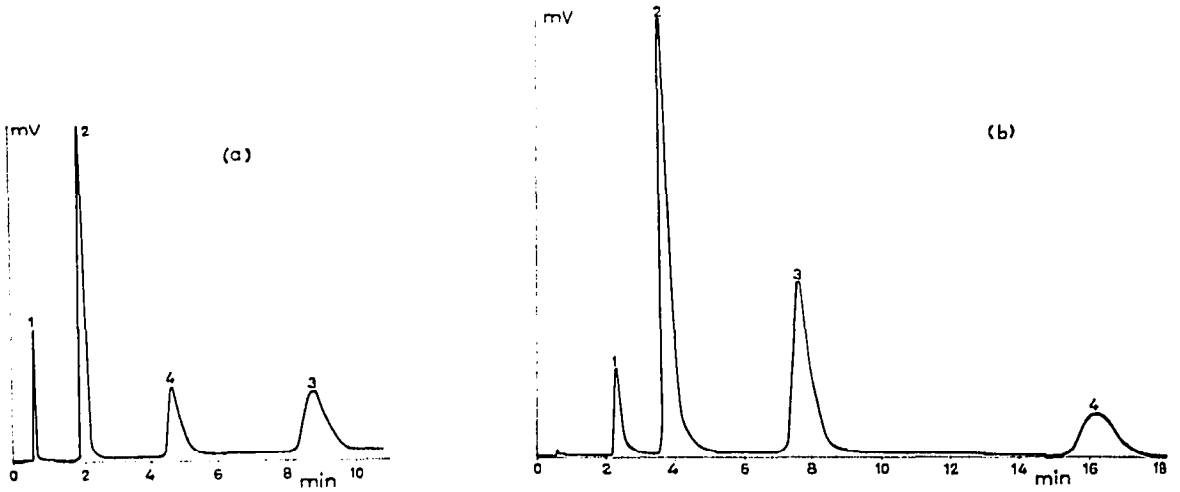

Fig. 4. Chromatograms of the system H_2O (1)–EtOH (2)–EtOAc (3)–AcOH (4) on 2 m × 0.4 cm columns of (a) Porapak Q at 160° and (b) Porapak T at 180°. Carrier gas (hydrogen) flow-rate, 150 ml/min.

We found that both retention times (adjusted) and the shape of the peaks depended on the amount of sample introduced (*i.e.*, in practical work on the sample composition). This is in agreement with the observations of Eek and Galcerán[14]. The variation of the retention times did not exceed ±5.6% (relative standard deviation), which did not cause problems in the analytical work. The change in the peak shape influenced the formal response factor (f_r) of the substances. The variation of the f_r values could not be neglected and therefore it was necessary to determine them for all possible compositions.

If calibration was made using changes of 20% in the amounts of the individual components, quantitative analysis could be carried out with a mean relative standard deviation of ± 10.8% for components of 1–10%, while for components under 1% the results are of only an orientative (approximate) character.

Serial analyses with intermittent sampling for a period of over 1 year (more than 3000 analyses) showed that the method can be used advantageously in industrial control work. In the case of automation with continuous sampling, the above precautions should be built into the program of an on-line computer.

We found in practice that the short analysis times, good resolution and the steady quality of the columns over a long period compensate well for the special precautions that are necessary in the calibration work.

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