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Gas chromatographic properties of immobilized poly(ethylene glycol) stationary phases

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ABSTRACT

Optimization of the preparation of immobilized poly(ethylene glycol) on Chromosorb W AW was carried out. The optimum concentration ratio of Carbowax 20M and Desmodur L75 in moles lies in the range 1:8 to 1:14. The effect of three different procedures of Chromosorb W AW treatment on the chromatographic properties of the packing material was investigated. Conditioning under a nitrogen stream at 240°C for 4 h appears to be the best. Carbowax 20M immobilized on the support prepared in this way also showed the best stability towards washing with different solvents. A new procedure was used for testing the thermal stability of the stationary phase, which also takes into consideration the extent of the phase immobilization on the support.

INTRODUCTION

Poly(ethylene glycol) (PEG) phases are used in gas chromatography (GC) for their selectivity, permitting separation of polar compounds with similar boiling points which cannot be separated on silicone phases [1]. Owing to their chemical structure, PEG phases have low thermal stability (about 220°C). However, their degradation occurs in chromatographic columns at substantially lower temperatures [2,3]. A high minimum working temperature (about 70°C) and a low oxidation stability are other disadvantages which result in a short service life of the stationary phases in the chromatographic column. These drawbacks can be eliminated by immobilizing PEG phases.

In capillary columns PEG phases have been immobilized by radical cross-linking with organic peroxides [4–6] or dibutyltin dilaurate [7] and by chemical reaction between the terminal OH groups of Carbowax 20M and NCO groups of isocyanates, producing urethane bonds [8,9]. The last reaction was also used by us to prepare immobilized Carbowax 20M on the chromatographic support.

In the present work the optimization of the preparation of immobilized Carbowax 20M on the chromatographic support is described. The influence of the concentration of the cross-linking agent, various procedures for the support surface treatment, extractability of the immobilized phase film with different solvents and thermal stability of the packing material depending on washing with solvents were studied.

EXPERIMENTAL

Chemicals and materials

The following major chemicals were used: Carbowax 20M (Carlo Erba, Italy), γ-glycidoxypropyltrimethoxysilane (Union Carbide, USA), Desmodur L75 (Plurisocyanate based on toluene diisocyanate, Bayer, Germany) and DABCO R-8020 [1,4-diazobicyclo-(2,2,2)-octane, Air Products, Chemical Group, Paulsboro, NJ, USA]. Other chemicals of analytical reagent grade were supplied by Lachema (Brno, Czechoslovakia). Acid-washed Chromosorb W (80–100 mesh) was supplied by Becker (Delft, Netherlands). The measurements were carried out with glass columns of 1.2 m × 3 mm I.D., using a Chrom 5 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia).

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Procedure

Chromosorb W AW was always first heated at 200°C for 4 h. Three procedures were used for the modification of the support surface.

AW: the chromatographic support (Chromosorb) was conditioned at 240°C under a nitrogen stream for 4 h.

AUE: the support was modified with a non-extractable layer of PEG film using the procedure described by Aue *et al.* [10].

S: the support was silylated with γ-glycidoxypropyltrimethoxysilane [11].

The S-type support was coated with solutions of various concentrations of Carbowax 20M, Desmodur L75 and DABCO R-8020 in dichloromethane to investigate the effects of the concentration of the cross-linking agent on the degree of immobilization. To study the influence of the modification of the support surface on the extractability of the immobilized PEG film with solvents, AW, AUE and S supports were coated with solutions containing 10% (w/w) Carbowax 20M, 3% (w/w) Desmodur L75 and DABCO R-8020 in dichloromethane (percentages relative to the mass of the support). The immobilization was performed using the procedure previously described [12].

The extractability of the stationary phase film was checked as follows. The packed column was gradually washed with a given volume of an organic solvent. After washing the column with distilled water the column was washed with 5 ml of acetone. After each column washing the remaining solvent was removed from the column by nitrogen flow and the column was conditioned at 200°C for 1 h at a nitrogen flow-rate of 25 ml/min. Changes in the capacity factors of solutes and in column efficiencies were followed.

The thermal stability test of the packing material was performed as follows. The capacity factors of the test solutes and the column efficiencies were measured first. The packed column was then heated at 200°C for 1 h and the capacity factors and the column efficiencies were again measured at a column temperature of 100°C. The column packing was then washed with 30 ml of dichloromethane, the column was conditioned at 200°C for 1 h and the capacity factors and the column efficiencies were again measured at a column temperature of 100°C. The same procedure was repeated at temperature intervals of 20°C up to 320°C.

n-Tridecane, *n*-tetradecane (evaluation of dispersion interactions), 1-heptanol and 1-nonanol (evaluation of interactions with etheric and hydroxyl groups of PEG) were used to test the chromatographic properties of the packing material.

RESULTS AND DISCUSSION

Effect of the cross-linking agent

In earlier work [12] we showed that it is possible to prepare column packings with immobilized PEG. The stoichiometric ratio of Carbowax 20M to Desmodur L75 cross-linking agent is 1:0.5 mol (or 1:0.02 g for the cross-linking reaction.

TABLE I

EFFECT OF CROSS-LINKING AGENT CONCENTRATION

n/m = efficiency per 1 m of the column; k' = capacity factor.

Column packing	Ratio Carbowax 20M/Desmodur		*n*-Tetradecane		1-Heptanol	
	w/w (%)	mol/mol	k'	n/m	k'	n/m
1	6:4	1:18	13.6	1870	17.2	1120
2	7:3	1:12	15.8	2460	20.8	1900
3	8:2	1:7	14.3	2240	19.2	1840
4	9:1	1:3	15.0	1460	18.4	1540
5	10:3	1:8	17.5	2600	21.1	2080
6	10:5	1:14	18.5	2450	25.9	1960
7	10:10	1:27	18.3	1720	26.3	370

The capacity factors (k') and the column efficiencies are listed in Table I for the packings prepared from solutions of different concentrations of Carbowax 20M and cross-linking agent (packing 1–4) and from solutions containing a constant concentration of Carbowax 20M (10%, w/w) and different concentrations of the cross-linking agent (packing 5–7). The ratios of the solution concentrations expressed in weight per cent relative to the mass of support are listed in the second column. The same data expressed in moles are listed in the third column (the value 1800 was taken as an average molecular weight of Carbowax 20M). It follows that the optimum ratio of the components of the liquid phase expressed in moles ranges from 1:8 to 1:14. The concentration of the cross-linking agent is about twenty-fold that given by the stoichiometric ratio. A large excess of the cross-linking agent, packings 1 and 7 in Table I, results in a decrease in the column efficiency, particularly for 1-heptanol. An almost six-fold decrease in the column efficiency was observed for packing 7. It is interesting that the optimum concentration ratio of only about 1:6.6 mol [9] was found for similar immobilization in the capillary column.

Column packings 1, 2, 5 and 6 are the most stable against washing. If a large decrease in the capacity factors occurs after washing, the column efficiency usually increases (compare packing materials 3 and 4). A larger decrease in the capacity factors and the column efficiencies occurs with 1-heptanol. On packing material 7 the alcohol peak is asymmetric and broad (already the efficiency of the column which was not washed is very low —see Table I).

Effect of support surface modification

The properties of the support before being coated with the liquid stationary phase substantially affect the chromatographic properties of the obtained packing material.

The capacity factors, the column efficiencies and asymmetry factors (TF) for our three different types of support treatment are listed in Table II. *n*-Tetradecane shows the lowest retention on Chromosorb W AW that was only thermally conditioned (type AW) and the highest on the silylated surface (Type S). At 100°C 1-heptanol does not elute from support AW even within 1 h. At higher temperatures the alcohol peak tails and retention times of peak maxima depend on the amount of alcohol injected. This is because of interaction between the alcohol molecules and the active sites on the support surface. If the support surface is treated with PEG at a high temperature (Type AUE), deactivation of its surface occurs. 1-Heptanol therefore elutes from the column as a narrow peak (compare the column efficiencies and TF). Silylation of the support surface (type S) leads to higher 1-heptanol retentions (more than two-fold) in comparison with the AUE-type support. *n*-Tetradecane retention is similar. The peak tailing intensified and the efficiency decreased. This is obviously because of poorer deactivation of the support surface.

The best deactivation of the support surface is achieved with the AUE support. This agrees with previous observations that a homogeneous inextractable film of PEG decomposition products [10] is created. It was however found that the film formed in this way is not stable at temperatures

TABLE II

EFFECT OF SUPPORT SURFACE MODIFICATION

For AW, AUE, S see text; TF = asymmetry factor (calculated from front and rear halves of the tailing peak, both halves measured at 10% of the peak height above the baseline); x = does not elute (see text).

Support type	*n*-Tetradecane			1-Heptanol		
	k'	n/m	TF	k'	n/m	TF
AW	4.3	1220	123	x	x	x
AUE	6.4	1710	139	7.2	1110	161
S	7.4	730	262	16.7	460	475

TABLE III

EFFECT OF SUPPORT SURFACE MODIFICATION ON EXTRACTABILITY OF IMMOBILIZED CARBOWAX 20M

Solvent: dichloromethane; for CW-AW, CW-AUE, CW-S, see text.

Column packing	Solvent volume (ml)	*n*-Tetradecane		1-Heptanol	
		k'	n/m	k'	n/m
CW-AW	0	18.3	2620	23.2	1960
	30	18.8	2460	23.5	2130
	60	18.7	2510	23.9	2130
	90	18.6	2470	23.1	2120
	120	18.4	2500	22.9	2240
CW-AUE	0	20.8	1260	29.5	1130
	30	20.6	1380	28.1	910
	60	20.1	1700	27.5	960
	90	21.1	1370	29.8	1060
	120	18.8	1620	26.3	1440
CW-S	0	18.0	2500	25.0	1840
	30	18.2	2780	23.3	1530
	60	17.2	2430	22.9	1630
	90	17.2	2630	23.3	1580
	120	16.2	2510	21.6	1340

above 300°C and is very sensitive to oxygen traces in both carrier gas and injected sample [13].

The influence of support surface modification on the extractability with dichloromethane of the immobilized PEG is obvious from Table III. A simultaneous decrease in retention and column efficiency does not occur only on the CA-AW packing. Reduction in the retention of 1-heptanol and *n*-tetradecane to 90% occurs on the CW-AUE packing only after washing with 120 ml of dichloromethane. The column efficiencies remain unchanged. On the CW-S packing, the k' value for *n*-tetradecane decreases to 90% and the efficiency remains unchanged; for 1-heptanol k' decreases to 86% and the efficiency to 70%. The best column efficiency is achieved for 1-heptanol on the CW-AW packing and the worst on CW-AUE. Hence the modifed AW- and S-types supports seem to be suitable for the preparation of the packing with the polar phase. The stabilities of the immobilized phase films towards washing with different solvents are listed in Table IV. The packings were gradually washed with 30 ml of each solvent. Neither retention nor efficiency decreased significantly for CW-AW type (except for acetone and ethanol for *n*-tetradecane). With the CW-S-type support the k' value decreases for *n*-tetradecane to 87% and the efficiency remains unchanged: for 1-heptanol the k' value decreases to 80% and the efficiency to 64% of the original value. The CW-AW packing again seems to be the best.

Thermal stability

Immobilization of the liquid stationary phase contributes significantly to the increase in the thermal stability of the packing. The thermal stability of the stationary phase is usually evaluated with the aid of the so-called maximum operating temperature limit (MAOT) [14]. This procedure has also been used in all known procedures for the evaluation of thermal stabilities of immobilized phases. However, the described procedure does not consider the changes in the phase cross-linking during the time when the column temperature is increased. That is why we have used for the evaluation of the thermal stability the procedure which also takes into account the changes in the immobilization due to thermal stress. We found that the immobilized PEG phases can withstand relatively high temperatures

TABLE IV

EXTRACTABILITY OF IMMOBILIZED CARBOWAX 20M WITH DIFFERENT SOLVENTS

For CW-S, CW-AW, see text.

Solvent	Solvent volume (ml)	*n*-Tetradecane		1-Heptanol	
		CW-S	CW-AW	CW-S	CW-AW
Capacity factors					
Dichloromethane	0	18.0	18.3	25.0	23.2
	30	18.2	18.8	23.3	23.5
	60	17.2	18.7	22.9	23.9
	90	17.2	18.6	23.3	23.1
	120	16.2	18.4	21.6	22.9
Acetone	30	16.3	18.3	21.4	23.3
	60	16.8	18.9	21.9	24.6
Ethanol	30	16.8	18.5	22.1	23.6
	60	16.8	19.11	20.4	24.5
Water	30	16.0	17.8	19.8	22.6
	60	15.6	18.3	19.9	22.6
Column efficiency					
Dichloromethane	0	2500	2620	1840	1960
	30	2780	2460	1530	2130
	60	2430	2510	1630	2130
	90	2630	2470	1580	2120
	120	2510	2500	1340	2240
Acetone	30	2250	2350	1350	1850
	60	2680	2310	1590	1780
Ethanol	30	2540	2160	1310	2050
	60	2440	2300	1390	2430
Water	30	2220	2860	1210	2300
	60	2510	2610	1180	2060

without significant changes in the values of k' and the column efficiencies, but, after washing with the solvent, some phase destruction occurs. This fact is demonstrated by Table V. After heating the packing at 310°C for 30 min, the value of k' did not change for *n*-tridecane and 1-nonanol, and the efficiencies even increased. However, after washing the column with the solvent, the value of k' for *n*-tridecane decreased to 80% and the efficiency remained unchanged. For 1-nonanol the k' value decreased to 75% and the efficiency to 60%. After heating the column at 330°C for the next 30 min the situation was similar. Further decrease in the k' value and in the column efficiency only occurred after washing with solvent. The column efficiency decreased to 32% of the original value for 1-nonanol.

TABLE V

THERMAL STABILITY

Packing: CW-S.

Treatment	*n*-Tridecane		1-Nonanol	
	k'	n/m	k'	n/m
–	7.5	2170	51.0	1800
310°C	8.0	2550	50.5	2230
20 ml	6.5	2600	38.7	1320
330°C	5.8	2700	24.0	1310
20 ml	5.5	1250	30.9	570

Based on the above findings, the test of thermal stability of the immobilized phase was performed as follows. After heating the column at the given temperature and after testing its chromatographic properties, the column was washed with 30 ml of dichloromethane and retested. The results of the test are illustrated in Fig. 1 for all packings. The values of k' decrease with increasing test temper-

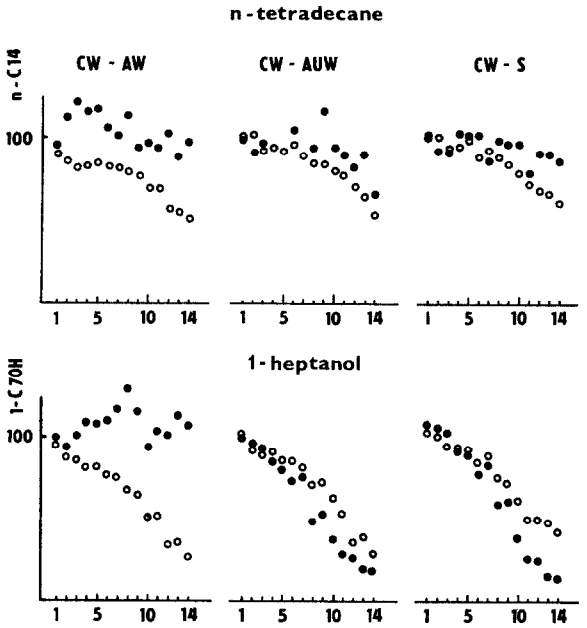

Fig. 1. Stationary phase thermal stability. (○) z_k and (●) z_n designated the ratio (%; of, respectively, the capacity factors and column efficiencies for solutes after washing with dichloromethane to their values before the washing (for *n*-tetradecane and 1-heptanol). 1 = 200°C; 2 = 200°C and 30 ml of dichloromethane; 3 = 220°C; 4 = 220°C and 30 ml; 5 = 240°C; 6 = 240°C and 30 ml; 7 = 260°C; 8 = 260°C and 30 ml; 9 = 280°C; 10 = 280°C and 30 ml; 11 = 300°C; 12 = 300°C and 30 ml; 13 = 320°C; 14 = 320°C and 30 ml.

ature for all packing types. The decrease occurs at temperatures between 260 and 280°C. The decrease in the k' value for 1-heptanol is greater than for *n*-tetradecane. With the packings of CW-AUE and CW-S types there is also a decrease in efficiency. This is obvious first of all from the comparison of z_n values for 1-heptanol. While the efficiency decreased to 14 and 18% of the original value at the end of the test for CW-S and CW-AUE, respectively, it remained unchanged for the CW-AW packing. The results of the thermal stability test of the immobilized PEG suggest that, under given chromatographic conditions, the maximum temperature at which no destruction of immobilized PEG occurs with this packing is 260–280°C. It follows from the above experiments that it is necessary to differentiate two types of thermal stability test of the column packing. One evaluates the packing by the phase bleeding only. The other simultaneously also evaluates the state of the phase immobilization on the support.

CONCLUSIONS

The procedure by which Chromosorb W AW is thermally treated at 240°C for 4 h and then coated with a mixture of 10% (w/w) of Carbowax 20M, 3% of Desmodur 75L and 0.02% (w/w) DABCO R-8020 in dichloromethane is the optimum technique for the preparation of immobilized PEG on the support. This fact is confirmed by the results of the tests of the thermal stability of the phase and its extractability with a solvent.

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