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OBSERVATIONS WITH HIGH-MOLECULAR-WEIGHT POLYETHYLENE GLYCOL STATIONARY PHASES IN CAPILLARY GAS CHROMATOGRAPHY

I. ADSORPTION *VERSUS* PARTITIONING CHROMATOGRAPHY

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SUMMARY

Fused-silica open-tubular capillary columns coated with high-molecular-weight polyethylene glycols of different origins have been evaluated. The chromatographic behaviour below and above the solid–liquid transition temperature was studied through measurements of the column efficiency, resolution and capacity factors as a function of the column temperature and the nature of the solutes.

INTRODUCTION

One of the five basic phases employed in capillary gas chromatography (CGC) is polyethylene glycol (PEG) with a high molecular weight[1,2]. PEGs have an unique selectivity and polarity and are particularly useful for the analysis of medium polar and polar compounds with molecular weights ranging from 20 to 300. High-molecular-weight PEG can be modified into an acidic form by reaction with nitroterephthalic anhydride (FFAP, free fatty acid phase) for the analysis of fatty acids from C_1 to C_{24} (ref. 3), and into an alkaline form for example by reaction with isocyanates for the analysis of free amines[4]. They are, therefore, intensively used in everyday CGC.

Nevertheless, as polyglycols and derivatives, the polymers nowadays used to manufacture PEG-coated capillary columns leave much to be desired. In many cases, industrial products are used, not synthesized for chromatography. Depending on the origin and on the batch, the molecular weight distribution varies and traces of cata-

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lysts from the polymerization process are present in various amounts and moreover may differ in nature. Therefore in CGC, the reproducibility of the efficiency, inertness, useful temperature range, maximum allowable operating temperature and even the selectivity and polarity is poor.

On the occasion of The Fourth International Symposium on Capillary Chromatography, Hindelang, May 1981 a round robin test was organized[5] to evaluate the (qualitative and quantitative) performance of capillary columns coated with apolar phases of the methyl silicone type and polar phases of the high-molecular-weight PEG type. For the apolar columns, interlaboratory data were excellent, whereas for the polar columns, interlaboratory and even intralaboratory data were poor.

Since then, we at the University of Gent and Virginia Polytechnic have continuously investigated PEG phases in CGC[6–9] and also evaluated the properties of commercial PEG columns. Developments with PEGs include the purification of industrial polyoxiranes[3], stabilization of the PEG film by adding antioxidants[4] and the evaluation of different immobilization and/or cross-linking procedures[10–16]. PEG substitutes with a polysiloxane structure were introduced[2,17]. The overall polarity of PEG, as measured by the Rohrschneider–McReynolds standards, can be approached but never its specific selective interactions.

This is Part I of a series of papers[18,19] to summarize our observations. It focuses on the solid–liquid transition of PEGs and on the implications for the chromatographic properties of columns. The chromatographic behaviour below and above the transition temperature of the different PEGs was studied by measuring the number of theoretical plates per metre (N/m), the resolution (TZ) and the capacity factors, k, as functions of the column temperature and nature of the solutes.

EXPERIMENTAL

The following columns were used.

Column 1: PEG NXL. 25 m × 0.25 mm I.D. fused-silica open-tubular (FSOT), coated with 0.5 μm of Bondable PEG (Innophase, Portland, CT, U.S.A.). The fused-silica tubing was flushed with dichloromethane and dried under nitrogen before static coating. The column was conditioned to 100°C only, to avoid cross-linking of the phase.

Column 2: PEG XL-200. Similar to column 1, but cross-linking was achieved by heating the column rapidly to 200°C after coating for 8 h, which gives the highest chromatographic efficiency[18].

Column 3: FFAP XL-200. Similar to column 2, but coated with Bondable FFAP (Innophase).

Column 4: PEG HM-2500. 10 m × 0.25 mm I.D. FSOT, coated with 0.2 μm of laboratory made cross-linkable PEG-2500. The polymer was obtained by condensation of PEG-2500 with triethoxysilylpropyl isocyanate. The FS tubing was leached with 3% HCl and dehydrated at 220°C. Deactivation was performed by coating the column dynamically with a 1% solution of PEG-1500 in dichloromethane and heat treatment at 280°C for 15 h. After flushing the column with dichloromethane, it was statically coated with the polymer. The column was then installed in a GC instrument and connected to a split–splitless vaporizing inlet system. *In situ* cross-linking was carried out by injecting splitless 3 × 1 μl distilled water (steam) at intervals of 5 min at

a column temperature of 150°C. By this treatment the ethoxy groups are hydrolyzed and polycondensation takes place.

Column 5: PEG HM-10000. 15 m × 0.32 mm I.D. FSOT, coated with 0.25 μm laboratory made cross-linkable PEG-10000. PEG-10000 was modified with triethoxysilylpropyl isocyanate. Column deactivation, coating and immobilization was as for column 4.

Column 6: PEG Comm.-1. 15 m × 0.32 mm I.D. FSOT, coated with 0.5 μm of chemically bonded PEG. Commercial column of relatively low MW.

Column 7: PEG Comm.-2. 25 m × 0.32 mm I.D. FSOT, coated with 1.3 μm of chemically bonded PEG. Commercial column of higher MW than column 6.

The columns were tested in an Hewlett-Packard 5890 GC instrument equipped with split injection and flame ionization (FID) detection. The carrier gas was nitrogen. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a DuPont 900 thermal analyzer. Superox 20 M for TGA comparison was obtained from RSL (Eke, Belgium).

RESULTS AND DISCUSSION

The useful temperature range is an important characteristic of a stationary phase for capillary GC. The minimum allowable operating temperature is the temperature at which the phase is in the liquid state so that partitioning (liquid–gas) chromatography occurs. The phase transition (solid to liquid) temperature is thus of upmost importance. This transition temperature can be measured by DSC analysis. As an illustration, Fig. 1 depicts the scan of commercial bondable PEG. The first heating (H_1) has the highest transition temperature (60°C) and a "shoulder" at the base of the peak is observed, which is most likely due to the cross-linking agent. The cooling transition (C) to solid occurs at a much lower temperature (34°C). Finally, the transition for the second heating (H_2) is slightly lower and the band is narrower than for the first heating. The "shoulder" has disappeared through reaction of the cross-linking agent during the first heating. The explanation for the difference in transition temperatures should be a combination of two factors: crystallization and cross-linking. High-molecular-weight PEGs exist for 60–70% as small crystallites which form large crystalline areas called spherulites. The large difference between the heating transition temperatures and the cooling transition temperature can be explained by a time lag due to crystallization. Generally, PEG crystallizes from its melted form in two stages. First nucleation occurs followed by growth of the crystalline nuclei to form macroscopic spherulites. The half-life for crystallization of PEG 20000 at 58°C is 80 min. During the crystallization time the observed melting point varies until the polymer is in equilibrium. The rapid heating and cooling rates (10°C/min) do not allow the polymer to achieve its lowest energy state at each point. Consequently, there is a reduced transition temperature upon cooling and an increased transition temperature upon heating. The rapid cooling rate applied has resulted in a very low degree of crystallinity. Cooling rates in CGC however are rapid, so the same phenomena will be observed in practical CGC. The difference between H_1 and H_2 is mainly due to cross-linking of the phase, which has the effect of delaying (or in some cases destroying at room temperature) the crystallinity of the polymer and thus lowering the melting point. The chromatographic interpretation of the DSC data explains some anomalies observed in practical work with PEG phases.

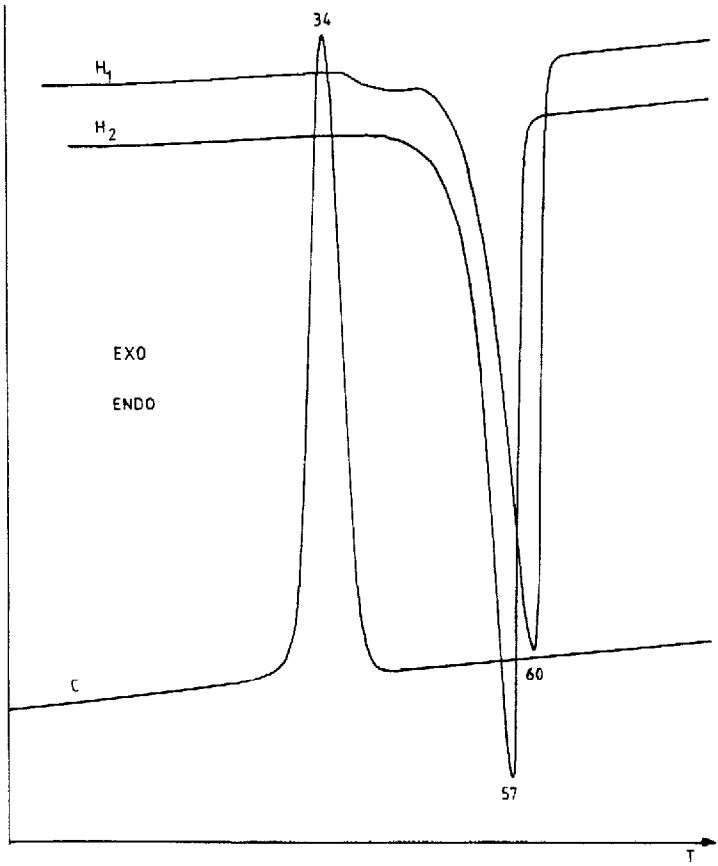

Fig. 1. DSC analysis of Bondable PEG. The analysis was performed in the following way: scan H_1, from −10 to 180°C, which is above the cross-linking temperature; scan C, cooling to −10°C; scan H_2, second heating to 180°C.

For a cross-linked column to work in the partitioning mode the minimum allowable operating temperature is 57°C. When an analysis is performed in a temperature programmed mode (for example from 60 to 180°C at 3°C/min) all compounds are eluted with narrow band widths (high efficiency). On cooling, however, the minimum allowable operating temperature shifts to a lower temperature dependent on the cooling rate, on the temperature reached and on the time interval before the next injection. It is thus possible for the second analysis to take place in the partitioning mode starting from 40°C! However, when the same analysis is then performed after a long delay (for example the next morning), complete PEG crystallization has occurred and compounds eluting between 40 and 60°C are only separated by an adsorption mechanism. It is obvious that the state of crystallization is all important and for the bondable PEG, to obtain reproducible k values, a minimum allowable operating temperature of 60°C is recommended. The phase becomes more homogeneous through cross-linking and displays a narrower transition range. The reaction of the cross-linking agent can also be deduced from a thermogravimetric analysis. The TGA

curve for Superox 20M (a linear polyoxirane) is flat to 320°C. This should correspond to the maximum allowable operating temperature of the phase. In CGC practice, however, such an high temperature stability can be reached only in a completely oxygen-free system. This is very difficult to achieve. Antioxidants can be added to the phase to delay decomposition but this then has an influence on the selectivity of the phase. The curve for a bondable high-molecular-weight PEG phase, on the other hand, shows a decrease from the movement the cross-linking agent starts to react at about 200°C. The cross-linked phase is then stable up to a temperature even higher (340°C) than the maximum allowable operating temperature of the Superox 20M phase. A very similar pattern is obtained when the TGA curve of Superox FA, the terephthalic acid derivative of Superox 20M, is recorded. Starting from 230–240°C, the terephthalic acid group is released and the phase loses its acidic properties. This is evidenced by tailing of free fatty acids after this heat treatment whereas other polar compounds are eluted with perfect peak shapes.

Fig. 2A shows plots of *N*/m *versus* temperature for *n*-undecane on the columns PEG NXL, XL-200 and FFAP XL-200. The curves are very similar in shape and there is a tremendous efficiency increase over a small different temperature range for each. This reflects the difference between a separation based on adsorption and one based on partitioning. The transition from adsorption to partitioning corresponds very well to the phase transition temperature deduced from the DSC analysis. The

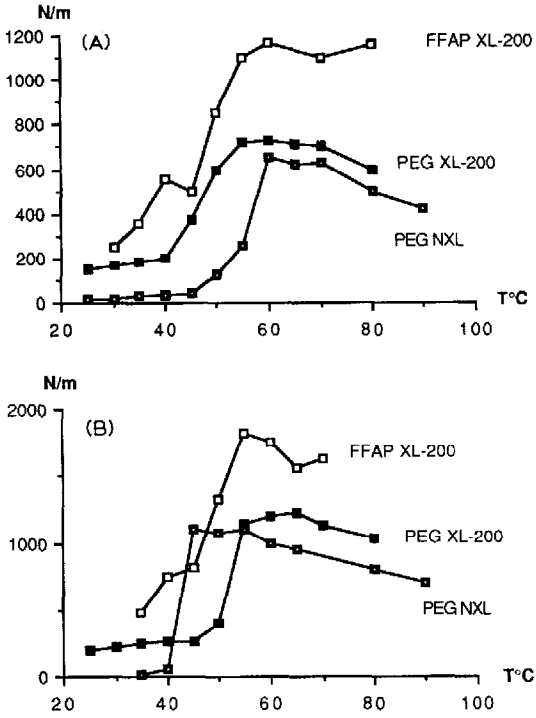

Fig. 2. Plots of *N*/m (plates per metre) *versus* temperature for *n*-undecane (A) and for *n*-butanol (B) on columns PEG NXL, XL-200 and FFAP XL-200.

temperatures are respectively 60°C for PEG NXL and FFAP XL-200, and 55°C for PEG XL-200. If the columns are operated in the adsorption mode, *i.e.*, below the minimum allowable operating temperature, the non-cross-linked column has the lowest efficiency. This is due to the high degree of crystallinity at low temperatures and, consequently, the slowest exchange of the solutes between the stationary phase and the mobile phase. In the partitioning mode, above 60°C PEG NXL and XL-200 have similar efficiencies. The FFAP XL-200 column, on the other hand, gives much higher plate numbers and much higher efficiencies than the corresponding PEG phases. The slope of the FFAP curve in the adsorption mode below 60°C is much steeper than the slope for the PEG phases. There is a "nod" in the curve around 45°C. The nitroterephthalic acid group most probably is responsible for this.

The efficiency and very surprisingly the transition temperature are strongly dependent on the nature of the solute. Fig. 2B depicts the N/m *versus* temperature curves for *n*-butanol as the solute on the same columns. The minimum allowable operating temperature values for PEG XL-200 and FFAP XL-200 are a few degrees lower than for the analysis of *n*-undecane (Fig. 2A) and surprisingly butanol seems to be separated in the partitioning mode at as low as 45°C on the PEG NXL column! On the three columns, much higher plate numbers are found for *n*-butanol than for *n*-undecane. On the PEG XL-200 column, 1200 plates per metre are calculated for butanol ($k = 5$) at 60°C but only 750 plates per metre for undecane ($k = 3$) at the same temperature. This is due to *n*-butanol having a lower diffusion coefficient than of *n*-undecane in PEG. Plots of N/m *versus* temperature were also constructed on the columns PEG Comm.-1 and Comm.-2. The curve for PEG Comm.-2 had the same shape as that for the columns in Fig. 2A but with a transition at 70°C. On the other hand, the curve for PEG Comm.-1 was nearly flat and decreased with temperature. This phase seems not to have any solid–liquid transition in the temperature range 20–100°C and the efficiency is nearly independent of the temperature! A possible explanation can be found in Fig. 3 where the N/m plot for PEG HM-10000 shows an increase in efficiency with temperature up to the maximum at 60°C corresponding to the maximum for the columns PEG NXL and FFAP XL-200. PEG HM-2500, on the other hand, has no visible transition temperature like PEG Comm.-1. The lower the molecular weight of the PEG, the lower is the solid–liquid transition temperature.

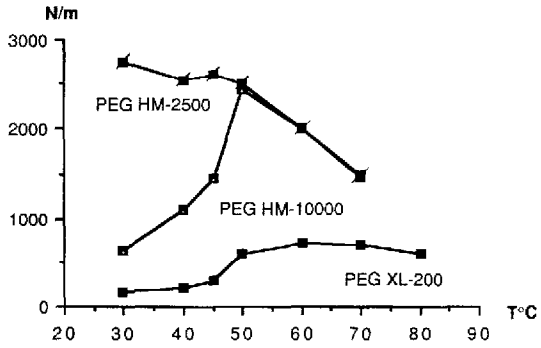

Fig. 3. Plots of N/m *versus* temperature for *n*-tridecane on PEG HM-2500 and HM-10000 and, for comparison, for *n*-undecane on PEG XL-200.

That this is valid for cross-linked phases is surprising. The starting phase in the PEG Comm.-1 column most likely also has a low molecular weight. PEG HM-2500 shows a dramatic decrease in efficiency as the temperature increases, but the PEG Comm. 1 column does not. An higher degree of cross-linking, resulting in a more homogeneous film at elevated temperatures in PEG Comm. 1 may be the reason.

The resolution (TZ value) between different solute pairs (*n*-decane–*n*-undecane, *n*-propanol–*n*-butanol, benzene–toluene) *versus* temperature was measured on several columns. For cross-linked columns, the plots are very similar in shape and the transition points differ only by a few degrees for the different solute pairs. A remarkable shift however was observed for the non-cross-linked film (Fig. 4). Obviously, there is a tremendous resolution increase over a small temperature range for all solute pairs, particularly alcohols. The use of these phases just above their melting temperature gives the best resolution. For the alkanes and aromatics, the maximum TZ value is obtained at 60°C, a temperature corresponding to the DSC value (Fig. 1). For the alcohols, however, a maximum TZ value is reached at 42–43°C. Are alcohols separated in the partitioning mode on a solid surface rich in hydroxyl groups through hydrogen bonding? The fact that this does not occur on cross-linked phases, where hydroxyl groups are no longer available, is support for this hypothesis.

Generally, the capacity factor, k, of a solute decreases with increasing solute volatility when the activity coefficients remain constant. The plots for *n*-undecane as a solute on the columns coated with the highest-molecular-weight PEGs (PEG NXL and XL-200 in Fig. 5A) show an obvious discontinuity at about 55°C. Around this transition temperature the adsorption plot changes to the one corresponding to partitioning. As the solid–liquid phase transition is approached from lower temperatures, the retention suddenly becomes longer due to the increasing liquid property of the PEG. The curves for PEG HM-2500 and Comm.-1 do not show this effect and only an exponential decrease can be noted (Fig. 5B). A very slight plateau may be seen for the PEG HM-10000 column between 50 and 60°C.

The crystallization delay time observed in the DSC analysis can also be demonstrated chromatographically. Column PEG NXL was heated to 70°C for 2 h, then cooled to 30°C with the oven closed and after 30 min dodecane was injected. The value of N was over 6000. 30 min later the number of plates had dropped to only 1500

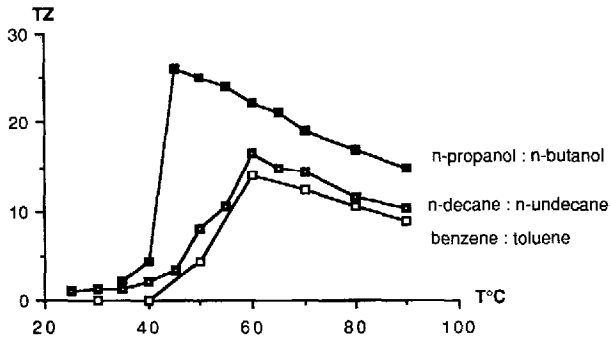

Fig. 4. Plots of TZ (resolution) *versus* temperature for *n*-decane–*n*-undecane, *n*-propanol–*n*-butanol and benzene–toluene on PEG NXL.

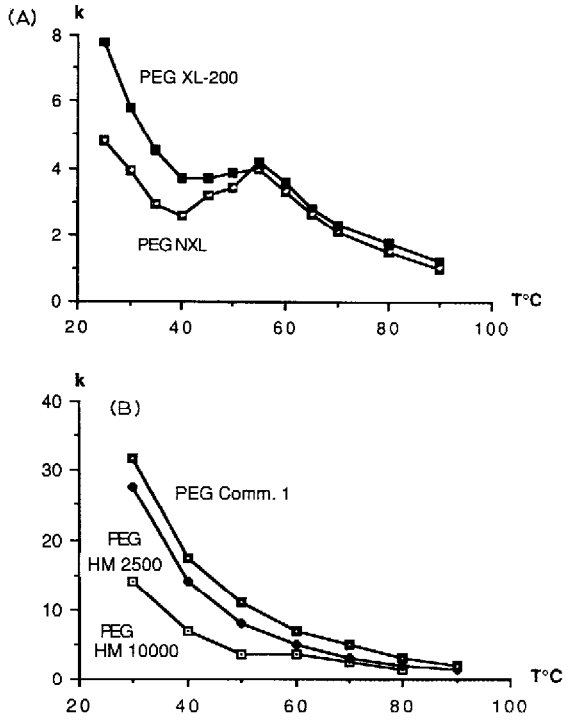

Fig. 5. Plots of the capacity factor, k, *versus* temperature (A) for *n*-undecane on PEG NXL and XL-200 and (B) for *n*-tridecane on PEG HM-2500 and HM-10000 and for *n*-dodecane on PEG Comm.-1.

and to about 1300 after 100 min. The capacity factor, k, decreased accordingly. The following day a slightly lower efficiency and capacity factor were recorded. The more crystallization that is achieved, the lower is the efficiency and the retention of dodecane. The crystallization delay time is important to obtain reproducible data where working below the phase transition temperature, although this must present a risk of poor results.

CONCLUSION

PEGs definitively have to be used above the solid–liquid transition temperature to obtain reproducible results. Above this minimum allowable operating temperature the highest efficiency is obtained. The transition temperature depends strongly on the chain length of the PEG: the shorter the chain length, the lower is the transition temperature. This behaviour remains valid for cross-linked PEGs.

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