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COMPARISON OF CHEMICALLY BONDED AND PHYSICALLY COATED POLYETHYLENE GLYCOL STATIONARY PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

Studies of the gas chromatographic behaviour of bonded and coated PEG 20M stationary phases showed that bonded PEG 20M has a liquid-type structure above room temperature. Retention diagrams for several solute molecules in the form of ln V_g *versus* the reciprocal of the absolute temperature show clear differences between bonded and coated PEG 20M on Chromosorb W. The absence of an inflection in the retention diagrams for bonded PEG 20M is observed, in contrast to the marked change in retention volumes for coated PEG 20M at or near the melting points. Both bonded and coated PEG 20M have almost identical enthalpies above the melting point of coated PEG 20M and the same holds for bonded PEG 20M at 80 °C and 35 °C. Peak asymmetry was calculated and marked differences between bonded and coated PEG 20M stationary phases were observed.

INTRODUCTION

New stationary phases chemically bonded to solid supports have recently been reviewed by Locke[1]. The main advantage of these packings in gas chromatography (GC) is that the stationary phases are thermally stable and their temperature limit is 80–90 °C higher than those for conventionally coated stationary phases. In addition, there may be rapid mass transfer between the bonded support and the mobile phase such that high carrier gas velocities can be used with little decrease in column efficiency[2]. The organic compounds attached to the solid support are oriented like bristles on the surface of the support, resulting in no pooling. Consequently, the speed of the mass transfer is considerably higher than with conventional stationary phases[3]. The term "brush" is used for silica esterified with aliphatic alcohols instead of esterified silica[4].

The bristles of the brushes are monomeric organic molecules bonded chemically[3]. The effect of rotation of the bristles bonded chemically on one end increases with increasing chain length and the crowding of the monomeric bristles may result in their bonding on two or more points of the support surface. The result may be that spatial order of the bristles decreases and their structure becomes more similar

to that of liquids. Polymerization of the chemically bonded molecules on the surface of the supports always results in liquid (or solid) type structures.

In stationary liquid phases bonded chemically, organic molecules with short chain lengths, such as triethylene glycol or octanol, form a monomolecular layer on an inactive support. As one end of the molecules is fixed on to the support, the area where these molecules can move freely is limited. Therefore, these stationary liquid phases behave as solids. However, the problem is to decide whether stationary liquid phases of larger molecular weight organic compounds such as polyethylene glycol 1000 behave as solids or liquids at column temperatures in GC. The question of whether a process is gas–solid or gas–liquid chromatography arises when chemically bonded stationary phases are used as column packing materials in GC. In this paper we will focus our attention on this point.

In polyamide stationary phases physically coated on Dia-solid M, the peak shapes and the separation factors for diesters of dibasic alkanoic acids below the melting points of the stationary liquid phases were nearly identical with those above the melting points[5]. Aue and Kapila[6], in their work with silica gels, commented that, judging from the chromatograms, there is no longer any difference between gas–solid and gas–liquid chromatography. Smidsrød and Guillet[7] found that a plot of the logarithm of the specific retention volume against the reciprocal of the absolute temperature showed a marked inflection at a temperature close to the transition temperatures for a polymer on using it as a stationary phase in a gas chromatograph.

This paper describes some results obtained by the GC analysis of both polymeric stationary phases chemically bonded and physically coated, with particular emphasis on transitions of the first order of the polymer. Polyethylene glycol 3900 and 20M were selected as polymers and were bonded to Chromosorb W. The elution behaviours of several solutes were observed at temperatures between room temperature and 150 °C, and were compared with those for the physically coated supports.

EXPERIMENTAL

Preparation of bonded and coated stationary phases

The inactive support used in this work was Chromosorb W, 80–100 mesh. Activation of the support surfaces was carried out by covering 100 ml of the support with 30 ml of concentrated hydrochloric acid, refluxing for 4 h and washing with distilled water until neutral and with acetone three times[8]. The support was then placed in a vacuum desiccator over silica gel, evacuated and kept at 100 °C for 6 h. Replacement of the surface hydroxyl groups with chloride was carried out with silicon tetrachloride[9]. To 50 ml (18 g) of activated Chromosorb W covered with 60 ml of dry n-hexane in a 500-ml flask were slowly added 30 ml (45 g) of silicon tetrachloride and the mixture was stirred under reflux for 1.5 h. The chlorinated Chromosorb W was then thoroughly washed with dry n-hexane.

Twenty grams of PEG 20M or 10 g of PEG 3900 were dissolved in 90 ml of dry benzene and the solution was added slowly to the chlorinated Chromosorb W in the flask, followed by refluxing for 6 h. The PEG–Chromosorb W was then extracted with dry benzene for 8 h in a Soxhlet extractor to remove all traces of non-bonded PEG and dried in vacuo at 100 °C for 4 h.

Esterification of the chlorinated support with PEG resulted in polymer con-

tents of 4.2% for PEG 20M and 2.0% for PEG 3900. The polymer contents were determined by carbon and hydrogen elemental analysis of the surface. Conventionally coated stationary phase was prepared by dissolving a weighed amount of PEG 20M in benzene, mixing the solution with a weighed amount of inactive Chromosorb W AW and evaporating the solvent. The polymer concentration on the support was 4.2%.

Determination of gas chromatograms

The columns were 1.5 m × 3 mm I.D. stainless-steel tubes and were packed under reduced pressure with vibration. A Yanagimoto Model G80 gas chromatograph equipped with a flow meter, pressure gauge and a flame-ionization detector was used. A trap, containing anhydrous calcium chloride, was placed in the carrier gas (nitrogen) line in order to remove trace amounts of water.

All sample solutes used in this study were of reagent grade. To prevent chemical attack of the bonded phases (*i.e.*, hydrolysis), the solutes were dried and redistilled before injection. Volumes of 2 μl of sample solutes were injected on to the column using a Hamilton 10-μl syringe. The flow-rate of the carrier gas was 16 ml/min for all temperatures. The temperature at the injection port was 20 °C higher than either the solute boiling point or the column temperature, whichever was the greater.
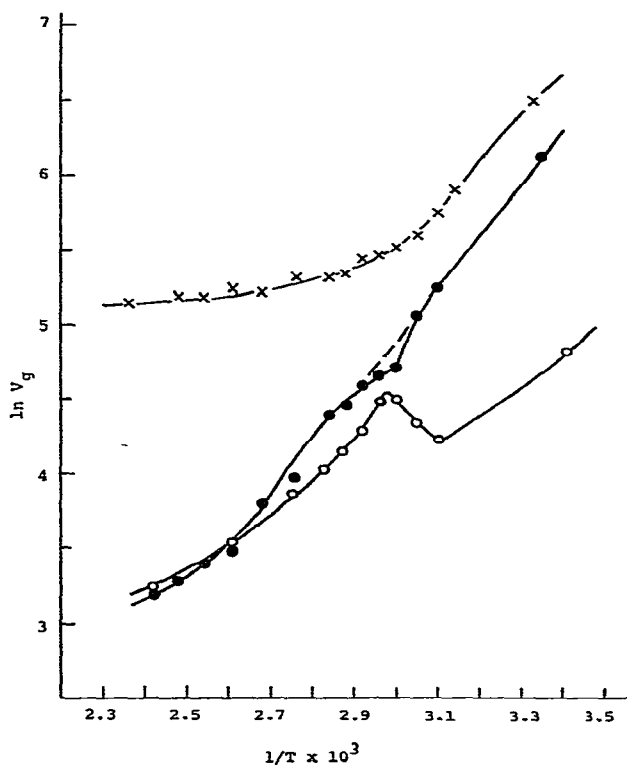

Fig. 1. Retention diagrams for acetone. ●, Bonded PEG 20M; ○, coated PEG 20M; ×, bonded PEG 3900.

Calculation

Specific retention volumes, V_g, were calculated from the following equation:

$$V_g = \frac{J(V_R - V_M)}{W} \cdot \frac{273}{T_R}$$

where $J = 1.5(P^2 - 1)/(P^3 - 1)$ is the compressibility factor; P is the ratio of the inlet to the outlet pressure ($P = P_i/P_o$); V_R is the measured retention volume for the solute; V_M is the measured retention volume for the non-interacting reference sample; W is the mass of the stationary phase; and T_R is the room temperature (in °K) when the flow meter is checked. The specific retention volume, V_g, is conventionally reported as millilitres of carrier gas (measured at 273 °K) per gram of stationary phase.

Peak asymmetry was calculated by the ratio of the back to front sides of the base-line band width. These half-widths were obtained as follows: the base-line band width was found from the intersections of the tangents to the inflection points with the base-line; the dividing point between the front and back sides was found by the intersection of the perpendicular from the peak maximum with the base-line. The number of theoretical plates was also calculated by the usual method.
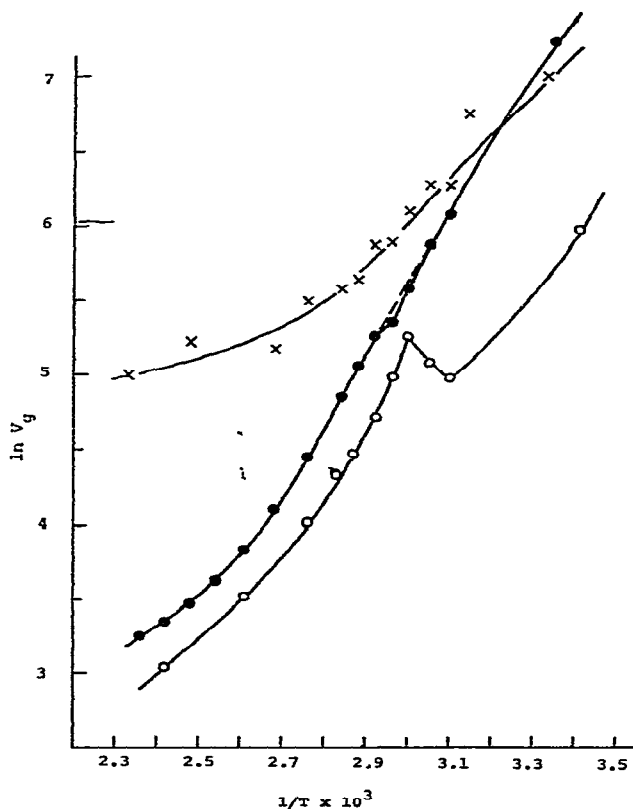

Fig. 2. Retention diagrams for methanol. Symbols as in Fig. 1.

Differential thermal analysis

Differential thermal analysis traces were obtained on a Shimadzu instrument at a scan rate of 20 °C/min and $\pm 10\ \mu$V full scale.

RESULTS AND DISCUSSION

Retention diagrams for several solute molecules in the form of plots of ln V_g against the reciprocal of the absolute temperature $(1/T)$ are shown in Figs. 1–6. The retention diagrams on coated PEG 20M for all solutes show the expected sharp maxima and minima near the melting point of the polymer. The maxima correspond to the melting point of the polymer[10,11] and the values were 62–64 °C (60 °C for methanol), which are in good agreement with the values determined with a hot-plate melting-point apparatus (60 °C).

The retention diagrams on bonded PEG 20M are linear or slightly curved plots, indicating the absence of phase transition. This suggests that bonded PEG 20M and coated PEG 20M have different properties near the melting point. A generalized plot of the ln V_g versus the reciprocal of the absolute temperature is shown in Fig. 7. At temperatures above the melting point, the retention diagram (II–III) should be linear, as predicted by theory, and retention volumes obtained by extrapolation (II–IV) of this straight line to below the melting point correspond to those obtained
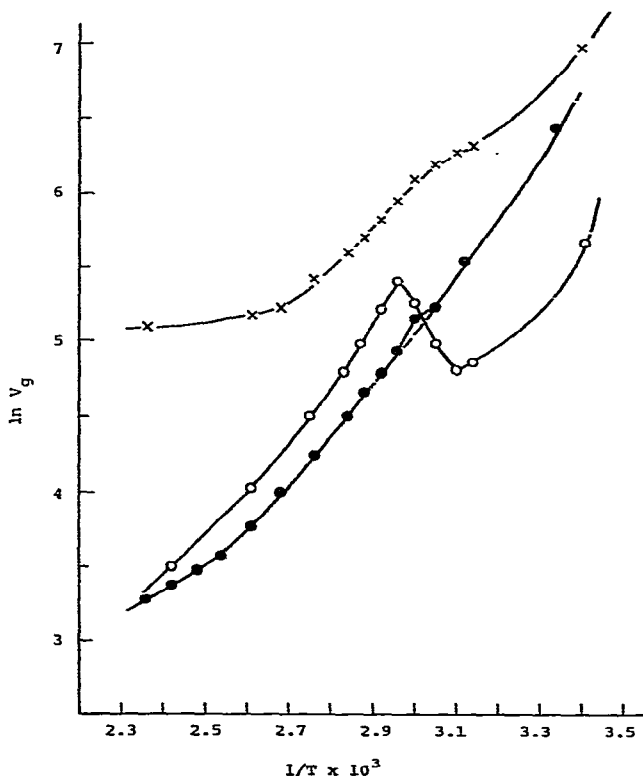

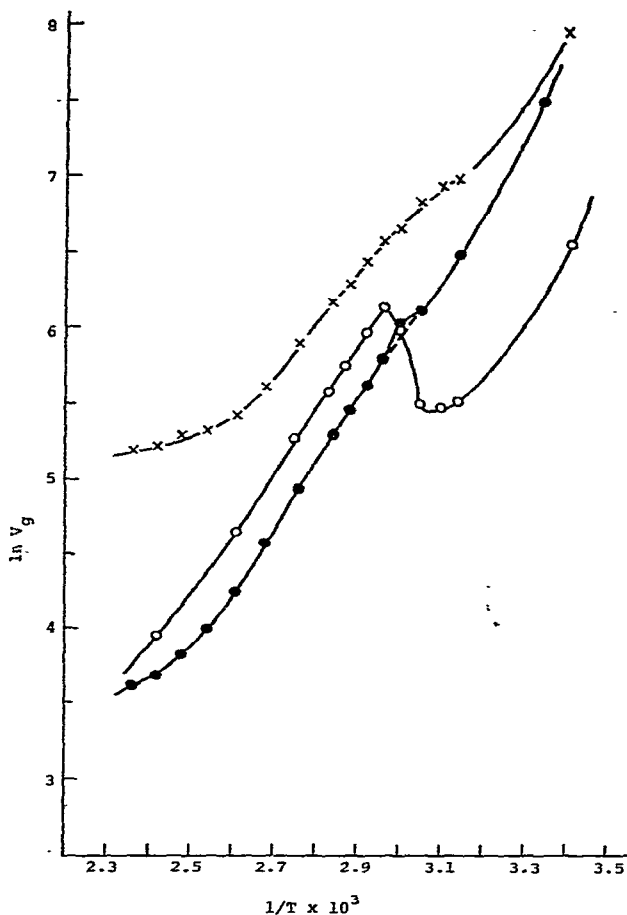Fig. 3. Retention diagrams for benzene. Symbols as in Fig. 1.

Fig. 4. Retention diagrams for toluene. Symbols as in Fig. 1.

when the stationary phase is completely amorphous. Similarly, the line I–IV is the region at temperatures below the melting point, where the retention time is directly proportional to the amount of amorphous material, as penetration of the probe into the bulk of the crystalline phase is precluded. Hence, the retention diagrams shift from the line IV–I–II–III to the line IV–II–III with the crystallinity of the stationary phase at temperatures below the melting point.

In general, the retention volume above a glass transition can be divided into surface and bulk contributions[11]:

$$V_g = (1-C)\,V_g^b + V_g^s$$

where C is the fraction of the polymer crystallized and V_g^b and V_g^s are the bulk and surface retention volumes. If a non-polar stationary phase is used with non-polar solutes, the contribution of V_g^s is neglected, because there is no need to consider surface adsorption of solutes on the stationary phase.
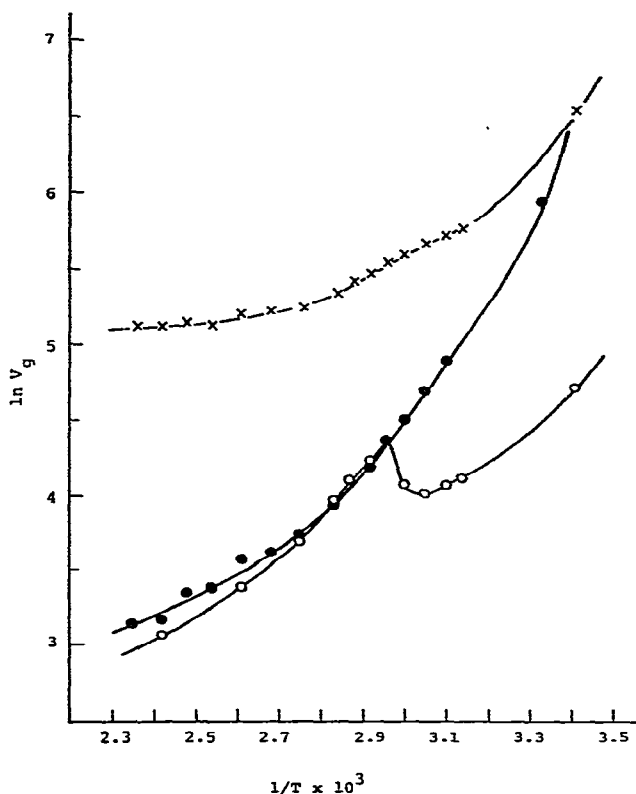
Fig. 5. Retention diagrams for cyclohexane. Symbols as in Fig. 1.

If one assumes that the crystalline regions of bonded PEG 20M exist below 60 °C (melting point of unbonded PEG 20M) ($C > 0$), the values of V_g decrease with increasing column temperature through the path VI–I–V in Fig. 7. If $C = 0$ for bonded PEG 20M below 60 °C, then the retention diagram lies on the path IV–II–III. From the results shown in Figs. 1–6, it is indicated that bonded PEG 20M is in the completely amorphous state. The absence of a melting transition in bonded PEG 20M is evident from the differential thermograms for both bonded and coated PEG 20M stationary phases shown in Fig. 8.

It is still uncertain from the above results whether bonded PEG 20M at temperatures below 60 °C is in a liquid state or in a completely amorphous form. Bonded PEG 20M is essentially solid, because one end of the PEG molecules is fixed to the surface of the stationary support and free movement of the molecules is not possible. The presence of a slight inflection at or near 60 °C in the retention diagrams for bonded PEG 20M might suggest the presence of any phase transition.

From theoretical considerations, the slope of the ln V_g versus $1/T$ graph is $(\Delta H_v - \Delta H_m - \Delta H_a)/R$, where ΔH_v is the enthalpy of vaporization of the solute molecules, ΔH_m is the enthalpy of mixing of the solute molecule and the stationary phase and ΔH_a is the enthalpy of adsorption of the solute molecules at the stationary phase–vapour interface[7]. The adsorption of the solute molecules at the stationary
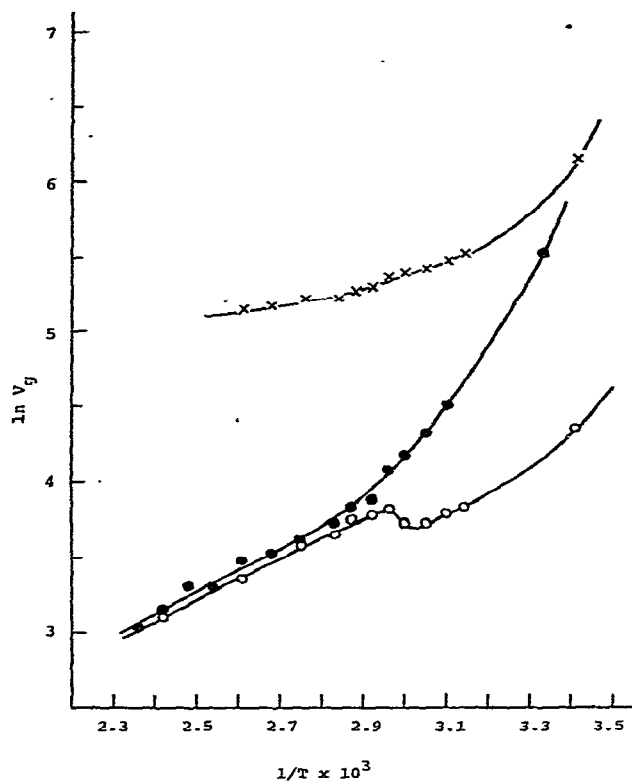
Fig. 6. Retention diagrams for *n*-hexane. Symbols as in Fig. 1.
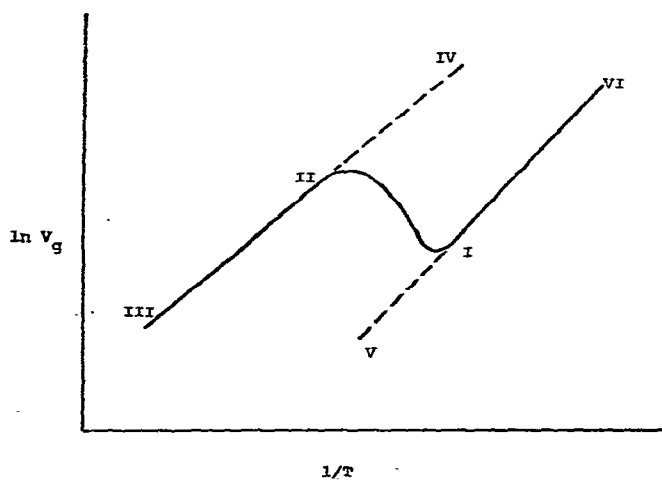

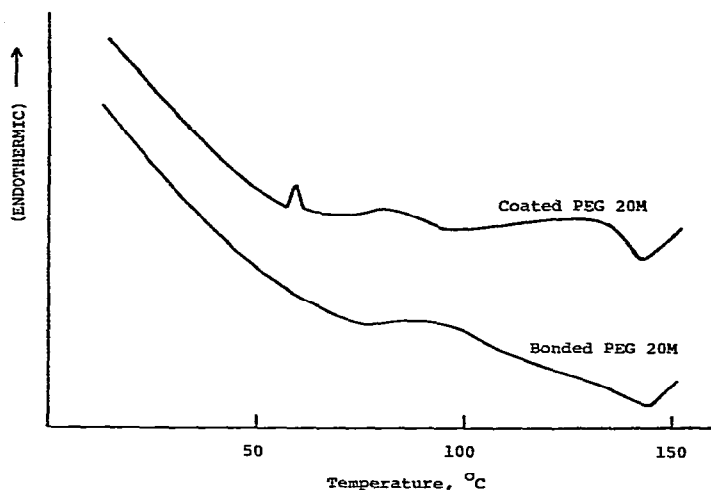Fig. 7. Generalized retention diagram.

Fig. 8. Differential thermograms for bonded and coated PEG 20M.

phase–support interface is neglected. Table I gives the values of the slope at 80 °C and 35 °C for several solutes. The slopes at 80 °C for both bonded and coated PEG 20M are similar, which indicates that the thermodynamic functions at temperatures above 60 °C (melting point for coated PEG 20M) are equal. The same effect occurs for bonded PEG 20M at 80 °C and 35 °C. These results seem to suggest that the state of bonded PEG 20M at temperatures below 60 °C is identical with that above 60 °C. Because of a deviation from linearity and possible errors in interpolation, the slopes for coated PEG 20M at 35 °C were not calculated.

Peak asymmetry on PEG 20M stationary phases is shown in Table II. The values from room temperature to 150 °C for bonded PEG 20M were higher than unity (results for temperatures higher than 100 °C are not shown), and the ratio of the maximum and minimum values was less than 2. The values for coated PEG 20M, on the other hand, varied from 0.02 in some instances to as much as 11.6 in others. At temperatures below the solute melting points the values were less than unity, and above the solute melting points the values were higher than unity, indicating that solute melting points affect peak asymmetry. Little difference in the solute–polymer

TABLE I

SLOPES OF THE RETENTION DIAGRAMS FOR DIFFERENT SOLUTES

Solute	35 °C		80 °C		
	Bonded PEG 20M	Bonded PEG 3900	Coated PEG 20M	Bonded PEG 20M	Bonded PEG 3900
Acetone	3.7	3.4	3.0	3.5	1.3
Methanol	4.6	2.9	4.8	4.6	2.6
Benzene	4.2	2.6	4.6	3.9	2.9
Toluene	4.9	3.6	4.4	4.3	3.5
Cyclohexane	4.5	2.9	3.1	3.1	1.6
n-Hexane	4.4	2.3	1.5	2.1	0.8

TABLE II

PEAK ASYMMETRY ON PEG 20M CALCULATED FROM THE RATIOS FOR THE BACK TO FRONT SIDES OF THE BASELINE BAND WIDTH (b/a)

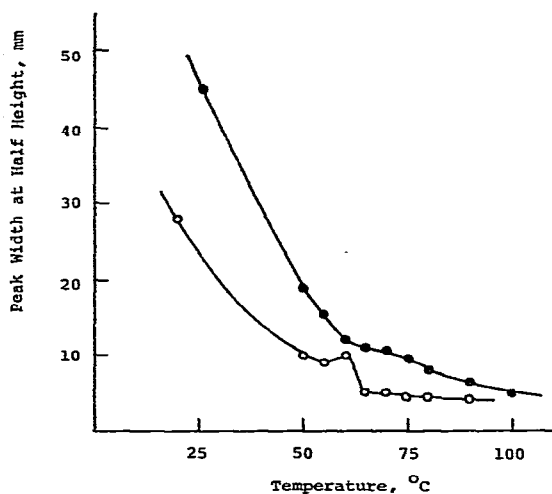| Temp. (°C)	Acetone		Methanol		Benzene		Toluene		Cyclohexane		n-Hexane	
	Bonded	Coated	Bonded	Coated	Bonded	Coated	Bonded	Coated	Bonded	Coated	Bonded	Coated
20		0.07		0.02		0.07		0.02		0.06		0.15
23	10.0						2.2		0.1		1.5	
26			8.8		3.2							
45	10.4	0.26	11.7	0.08	4.5	0.08	2.0	0.04	0.4	0.19	6.6	0.39
50	8.5	0.48	12.4	0.12	4.4	0.09	2.2	0.04	0.5	0.19	7.3	0.69
55	8.0	0.74	11.9	0.13	5.5	0.08	1.6	0.04	0.8	0.29	3.5	0.92
60	6.3	3.0	12.4	0.40	5.7	0.09	1.6	0.03	0.9	0.36	2.6	1.5
65	9.4	5.4	11.0	1.4	6.5	0.15	1.5	0.04	1.7	0.39	6.0	2.2
70	7.5	6.2	14.2	6.5	6.2	0.21	1.8	0.06	1.1	0.70	6.9	2.8
75	6.4	6.0	11.4	8.0	5.3	0.46	2.2	0.05	2.7	1.15	3.3	3.6
80	8.8	4.7	16.0	11.6	5.0	1.22	4.2	0.09	3.0	2.82	3.3	4.1
90	10.0	6.2	14.4	8.7	4.0	4.6	4.2	0.15	6.0	3.15	2.8	3.6
100		5.0		8.2		5.9		0.4		2.5		3.7

Fig. 9. Relationship between peak width at half-height and column temperature for methanol. ●, Bonded PEG 20M; ○, coated PEG 20M.

interactions on bonded PEG 20M for the whole temperature range is confirmed by these results. The differences in the b/a values (Table II) for bonded and coated PEG 20M above 60 °C indicate that the properties of both stationary phases are essentially different, even in the liquified state.

From the above discussion, it is concluded that bonded PEG 20M has a liquid rather than an amorphous solid character, even below 60 °C. Hence, gas–liquid chromatography on bonded PEG 20M for the whole temperature range studied is confirmed by these results, in contrast to coated PEG 20M, on which gas–liquid chromatography takes place above the melting point and gas–solid chromatography below the melting point.
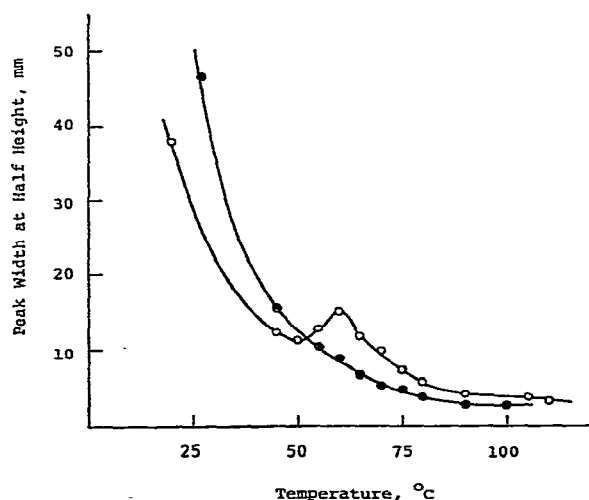

Fig. 10. Relationship of peak width at half-height and column temperature for toluene. Symbols as in Fig. 9.

Figs. 9 and 10 show the relationships between peak width at half-height and column temperature for methanol and toluene. The shapes of the curves are similar to those for ln V_g versus $1/T$. The number of theoretical plates on coated PEG 20M attained a maximum value near the solute boiling points and is nearly constant over the boiling point range. Although the relationships between the number of theoretical plates and column temperature on bonded PEG 20M for several solutes vary widely, it can be said that the number of theoretical plates on bonded PEG 20M was not greater than that on coated PEG 20M. This observation was different from that for bonded stationary phases of low-molecular-weight materials.

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