

Gas chromatographic comparative study of Superox 20M immobilized in different ways

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ABSTRACT

Three capillary columns of Superox 20M, two of them immobilized in different ways, were prepared. All columns showed a transition zone from adsorption of the solutes at low temperatures to absorption at higher temperatures. The minimum allowed operating temperature of the column was found to change from 64°C to 50°C when the polymer was immobilized. Partial molar enthalpies of mixing showed that alkanes are poor solvents of the stationary phase, while aromatics are good solvents, with little dependence on the degree of immobilization. It might be expected that Superox 20M will mix well with polymers with phenyl components, and will not mix with polymers of long hydrocarbon-type chains.

INTRODUCTION

Capillary columns have gained more importance in gas chromatography (GC) because of the high resolution which they offer. Immobilization of the polymer used as stationary phase produces additional advantages such as lower bleeding and consequently longer life and a higher maximum operating temperature (MOT) of the column. However, immobilization implies certain chemical reactions of the polymer, and this may lead to a modification of its behaviour as stationary phase. Differences may come to light by the estimation of the McReynolds' constants [1] of the polymer.

Superox 20M has been considered as one of the preferred liquid phases for GC [2,3], and it is for this reason that it has been chosen here to compare its behaviour under two different immobilization procedures.

Our interest has been focused on the effect of immobilization on two aspects: (a) the phase transition temperature (melting point) and (b) the change in the behaviour of a number of selected probes. The latter point might imply the possibility of prediction of the solubility of Superox 20M in other polymers as deduced from the values of the enthalpies of mixing of the solutes, depending on their functional groups. This would contribute to the understanding of the problem of the use of mixed stationary phases in GC.

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EXPERIMENTAL

The work described here refers to three different columns made of borosilicate glass. Columns were drawn on a Shimadzu GDM-1B drawing machine to a final internal diameter of 0.259 mm, as determined with the help of a NIKON micro-comparator. All three tubes were leached, washed and dehydrated in the same way, as described by Grob [4]. Once deactivated (see later) all three tubes were filled with the appropriate solution and evaporated by the static procedure described by Grob [5]. Column 1 was deactivated with Carbowax 20M [6–9], and then filled with a 0.425% (w/v) solution of Superox 20M on methylene chloride–pentane (50:50). Column 2 was deactivated in the same way, and then filled with the solution of Superox 20M to which dicumyl peroxide (DCP) had been added (20% of the Superox 20M content), according to the immobilization procedure described by Bystricky [10] for Carbowax-type stationary phases. Column 3 was deactivated with glycydoxypropyl trimethoxysilane (GPTMS) and immobilized with GPTMS and DCP, as described by Traitler [11]. Once prepared, all three columns were conditioned by passing nitrogen while slowly temperature programmed up to 150°C, at which temperature they were maintained for a few hours. Grob's test [12–14] was run on the three columns. Table I describes the physical characteristics of the columns.

TABLE I
CHARACTERISTICS OF THE GLASS CAPILLARY COLUMNS USED IN THIS WORK

	Column 1	Column 2	Column 3
Length (m)	23.36	22.0	25.0
Deactivation	Carbowax 20M	Carbowax 20M	GPTMS
Immobilization	None	DCP	GPTMS + DCP
Film thickness (μm)	0.275	0.261	0.264
Mass of stationary phase (mg)	5.23	4.67	5.35

Solutes used in this work to obtain the results described include: *n*-hexane, *n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, benzene, toluene and *n*-butanol. Other solutes were also used but results have not been included. Chromatograms were run at 16–18 temperatures between 35 and 150°C in each column. Carrier gas flow-rate was measured at the end of the column with a soap film flow meter at every temperature. Three gas chromatographs were used—two HP-9890 and a Varian 3300—all fitted with a flame ionization detector and split injection mode. Column head pressures were monitored with two pressure transducers calibrated in Torr (Felix Mateo Model 2900) and with a mercury manometer. Atmospheric pressure was checked several times during the day with a mercury barometer. The sample amount was always of the order of 0.02 μl , injected with a split ratio of about 1:20. Retention volumes used are always the average of at least three experiments. A mathematical dead time estimation method based on the retention of at least four *n*-alkanes [15] was used to find correct experimental retention volumes.

Whenever several chromatograms were run at different temperatures, the

sequence was always from low to high temperature to prevent any recrystallization of the stationary phase upon cooling of the column. Columns were left at 35°C overnight.

DATA REDUCTION

Specific retention volumes were calculated according to the expression:

$$V_g = \frac{F_0 j}{w_1} \cdot t'_R \cdot \frac{273}{T} \cdot \frac{(p_0 - p_w)}{p_0} \quad (1)$$

where V_g is the specific retention volume of the substance; F_0 is the carrier gas flow-rate, as measured at the column outlet, at ambient temperature (T) and atmospheric pressure (p_0); j is James and Martin's correction factor; w_1 is the mass of the stationary phase in the column; t'_R is the adjusted retention time of the solute; T is the absolute temperature of the carrier gas in the flow meter; p_0 is the pressure of the carrier gas in the flow meter, in our case atmospheric pressure; and p_w is the vapour pressure of the water at the flow meter temperature (T).

Activity coefficients at infinite dilution based on weight fraction, Ω^∞ , were calculated [16–23] according to the expression:

$$\ln \Omega^\infty \equiv \ln \frac{a_1}{w_1} = \ln \frac{273.15R}{P_1^0 V_g M_1} - \frac{P_1^0}{RT} (B_{11} - V_1^0) \quad (2)$$

which has the advantage of ignoring the molecular mass of the polymer. In this equation, a_1 and w_1 are the activity and weight fraction of the solute in the polymer, respectively, and M_1 , P_1^0 , B_{11} and V_1^0 are the molecular masses, saturated vapour pressure, second virial coefficient and molar volume of the solute at the column temperature T , respectively. R is the gas constant.

Vapour pressures were deduced using Antoine coefficients from Boublik *et al.* [24]. Second virial coefficients of n -alkanes were calculated by the method of O'Connell and Prausnitz [25]; for other substances, values were interpolated or extrapolated from literature values corresponding to other temperatures [26]. Densities were calculated according to the pertinent equation [27,28].

Partial molar enthalpy of sorption, ΔH_s , was deduced in each case from experimental values according to the expression:

$$\Delta H_s = -R \frac{\partial(\ln V_g)}{\partial(1/T)} \quad (3)$$

Partial molar enthalpy of mixing of the solute at infinite dilution, ΔH_1 , was calculated from:

$$\Delta \bar{H}_1^\infty = R \frac{\partial(\ln \Omega^\infty)}{\partial(1/T)} \quad (4)$$

The molar enthalpy of vaporization of the solutes was calculated as the difference:

$$\Delta H_v = \Delta \bar{H}_1^\infty - \Delta H_s \quad (5)$$

The activity coefficients at infinite dilution are related to the partial molar free energy of mixing by the expression:

$$\Delta G_m = RT \ln \Omega^\infty \quad (6)$$

Partial molar free energies of sorption at infinite dilution can be calculated from:

$$\Delta G_s = RT \ln(M_1 V_g / 273.15) \quad (7)$$

RESULTS AND DISCUSSION

The melting point of the polymer

Fig. 1 shows values of $\log V_g$ versus $1/T$ for *n*-octane, benzene, toluene and *n*-butanol, obtained on column 1 (not immobilized). The three typical temperature zones of polymers showing a phase transition are clearly seen in all cases. Between 35 and 55°C a zone is defined where adsorption of the solutes takes place. From 55 to 64°C, the values of V_g increase with temperature in a transition zone of non-equilibrium where two phenomena coexist: adsorption and absorption of the solutes in the polymer. From 64°C, upwards, we have the normal temperature zone of use of Superox 20M with reproducible chromatographic results. The temperature 64°C is the minimum allowable operating temperature of the column (MAOT). The value of 64°C is the same as that found by Sandra and co-workers [29,30] for other Superoxes of higher molecular mass.

Figs. 2 and 3 show results obtained with the same set of solutes on columns 2 and 3, both immobilized. Column 2 presents the three temperature zones of the polymer,

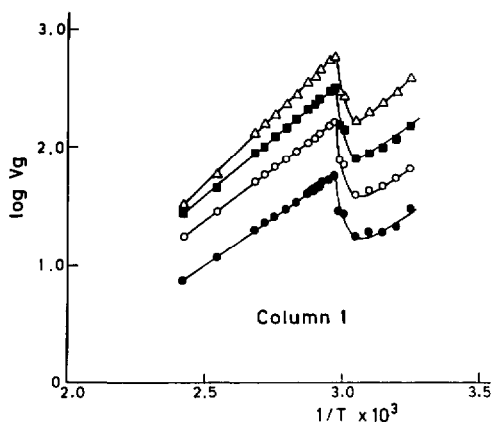


Fig. 1. Representation of $\log V_g$ versus $1/T$ on column 1 (not immobilized): ● = *n*-octane; ○ = benzene; ■ = toluene; △ = *n*-butanol.

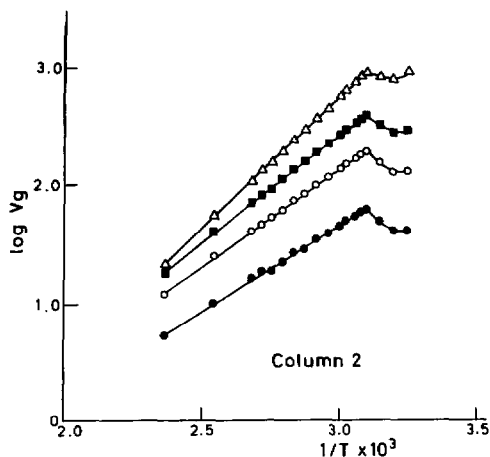


Fig. 2. Representation of $\log V_g$ versus $1/T$ on column 2 (immobilized with DCP): ● = *n*-octane; ○ = benzene; ■ = toluene; △ = *n*-butanol.

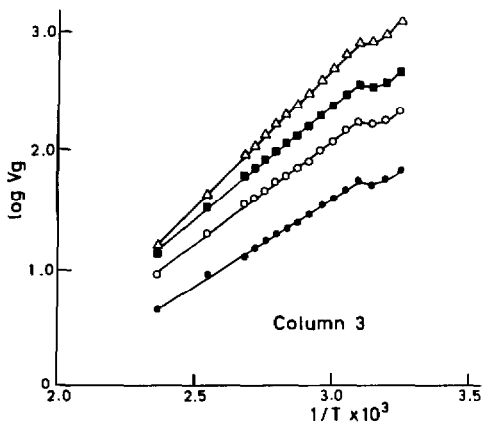


Fig. 3. Representation of $\log V_g$ versus $1/T$ on column 3 (immobilized with GPTMS and DCP): ● = *n*-octane; ○ = benzene; ■ = toluene; △ = *n*-butanol.

but now the melting point appears at about 40°C and the MAOT is found to be 50°C, 14°C lower than in the case of non-immobilized Superox 20M. Fig. 3 shows plots with shapes that again differ from the previous ones. The non-equilibrium zone appears here between 45 and 50°C as a zone with a slightly different slope. The MAOT of the column is again about 50°C. Sandra *et al.* [31] mention that the minimum useful temperature of a cross-linked polyethylene glycol column is 57°C in the case of a normal run, although it might be as low as 40°C if the column is heated and then cooled very quickly.

The different behaviour of column 1 from that exhibited by columns 2 and 3 with respect to the melting point of the polymer may be explained if we admit that the immobilization process introduces the effect of altering the crystallization of the polymer, decreasing the melting point. In the case of immobilized Superox 20M columns, the MAOT is found to be about 50–52°C. The transition zone of the polymer shows differences that depend on the immobilization procedure followed. It may be observed from Fig. 3 that, as immobilization with GPTMS produces a bonding between the polymer chains and the column surface through the coupling agent (GPTMS), this gives rise to a lower degree of crystallization than that produced with DCP alone (column 2) where only cross-linking of the polymer is supposed to occur. We measured the percentage of crystallinity according to the expression of Stein and Guillet [32]:

$$\text{Crystallinity (\%)} = 100 \left(1 - \frac{V_g}{V'_g} \right) \quad (8)$$

where V_g is the experimental specific retention volume of a solute at a temperature below the melting point of the stationary phase and V'_g is the hypothetical value for the

TABLE II
PERCENTAGE OF CRYSTALLINITY OF THE STATIONARY PHASES

	Column 1		Column 2		Column 3	
	35°C	40°C	35°C	40°C	35°C	40°C
<i>n</i> -Octane	81	83	59	53	27	24
Benzene	86	86	61	54	32	30
Toluene	86	86	60	53	32	31
<i>n</i> -Butanol	85	85	53	47	27	26

same solute at the same temperature, assuming the polymer to be in a 100% amorphous state. V_g' is found by extrapolation from the values of V_g of the solute above the MAOT. The percentage of crystallinity should not depend on the solute chosen to measure it. Table II lists the values obtained for the three columns. Values are independent of the solute used.

The partial molar enthalpies and the free energies of sorption and mixing

Table III presents the partial molar enthalpies of sorption, mixing (adsorption and absorption) and vaporization, as found with eqns. 3–5, for the four solutes in the

TABLE III
PARTIAL MOLAR ENTHALPIES OF SOLUTION (ΔH_s), MIXING (ΔH_{ad} OR ΔH_{ab}) AND VAPORIZATION (ΔH_v) (kcal/mol⁻¹)

	<i>n</i> -Octane	Benzene	Toluene	<i>n</i> -Butanol
Column 1 (not immobilized)				
Adsorption zone (35–55°C)				
ΔH_s	-4.79	-5.14	-6.27	- 8.49
ΔH_{ad}	4.95	2.89	2.68	4.23
ΔH_v	9.74	8.03	8.95	12.72
Absorption zone (64–140°C)				
ΔH_s	-7.40	-8.06	-8.97	-10.62
ΔH_{ab}	1.79	-0.33	-0.38	0.77
ΔH_v	9.20	7.73	8.60	11.35
Column 2 (immobilized with DCP)				
Absorption zone (50–150°C)				
ΔH_s	-6.56	-7.44	-8.27	-10.17
ΔH_{ab}	2.71	-0.33	0.37	1.35
ΔH_v	9.27	7.76	8.63	11.52
Column 3 (immobilized with GPTMS and DCP)				
Adsorption zone (35–45°C)				
ΔH_s	-4.80	-4.87	-5.79	- 8.32
ΔH_{ad}	5.01	3.19	3.21	4.57
ΔH_v	9.81	8.06	9.00	12.89
Absorption zone (50–150°C)				
ΔH_s	-6.66	-7.83	-8.66	-10.50
ΔH_{ab}	2.57	-0.06	-0.04	0.97
ΔH_v	9.25	7.76	8.62	11.47

three columns. Columns 1 and 3 show enthalpies of adsorption for all solutes which are higher than the corresponding enthalpies of sorption. Column 2 has an ill-defined adsorption zone, with fewer experimental points and, consequently, values of the partial molar enthalpies cannot be deduced for that zone. In the low-temperature region, when the stationary phase acts as an adsorbent solid, the values of the partial molar enthalpies of solution do not depend much on the degree of immobilization of the polymer. Considering the values of the partial molar enthalpy of mixing in the absorption zone, at temperatures above the phase transition zone, it may be said that *n*-alkane is in all cases the compound that mixes worst with the polymer, but it mixes slightly better with the non-immobilized stationary phase. The aromatic solutes mix better with the polymer than does *n*-butanol, but in this case differences with respect to the immobilization procedure cannot be observed.

With respect to the values of the enthalpies of sorption found in the zone of temperatures above the melting point of the polymer, it may be observed that in the three columns the most negative value is that of the alcohol, followed by those of the aromatics and the least negative value corresponding to the hydrocarbon. The sorption phenomenon implies that the molecules of the solute have transferred from the vapour phase into the polymer. This process depends to a great extent on the interaction of the solute with the Superox 20M, and therefore the enthalpy associated with this process will depend on this interaction. In the case we are considering here, we may deduce that the solute-polymer interaction decreases in the order alcohols > aromatics > hydrocarbons. It may also be observed from the table that the values obtained for the non-immobilized stationary phase are somewhat more negative than those of the other two columns. The values of the partial molar free energies of mixing and sorption (Tables IV and V) confirm this.

TABLE IV

PARTIAL MOLAR FREE ENERGIES OF MIXING (kcal/mol)

	Adsorption zone				Absorption zone						
	35°C	40°C	45°C	50°C	70°C	80°C	90°C	100°C	120°C	140°C	150°C
Column 1 (not immobilized)											
<i>n</i> -Octane	3.24	3.34	3.31	3.20	2.24	2.24	2.24	2.24	2.27	2.34	—
Benzene	1.87	1.89	1.90	1.85	0.72	0.76	0.78	0.80	0.89	0.93	—
Toluene	1.98	2.01	2.01	1.98	0.84	0.89	0.91	0.95	1.05	1.08	—
<i>n</i> -Butanol	2.32	2.32	2.29	2.25	1.08	1.10	1.09	1.08	1.17	1.16	—
Column 2 (immobilized with DCP)											
<i>n</i> -Octane	<i>a</i>	2.96	<i>b</i>	<i>b</i>	2.43	2.40	2.47	2.39	2.40	—	2.44
Benzene	<i>a</i>	1.39	<i>b</i>	<i>b</i>	0.92	0.93	0.97	0.98	0.99	—	1.11
Toluene	<i>a</i>	1.50	<i>b</i>	<i>b</i>	1.06	1.07	1.13	1.13	1.16	—	1.25
<i>n</i> -Butanol	<i>a</i>	1.73	<i>b</i>	<i>b</i>	1.24	1.22	1.25	1.24	1.23	—	1.29
Column 3 (immobilized with GPTMS and DCP)											
<i>n</i> -Octane	2.79	2.76	2.72	<i>b</i>	2.58	2.56	2.53	2.58	2.51	—	2.60
Benzene	1.17	1.17	1.12	<i>b</i>	1.06	1.06	1.08	1.08	1.17	—	1.34
Toluene	1.30	1.30	1.24	<i>b</i>	1.18	1.19	1.20	1.23	1.31	—	1.49
<i>n</i> -Butanol	1.62	1.60	1.52	<i>b</i>	1.39	1.37	1.36	1.36	1.42	—	1.53

^a No data available.

^b Temperature does not correspond to the adsorption zone.

TABLE V
PARTIAL MOLAR FREE ENERGIES OF SORPTION, ΔG_s (kcal/mol)

	Temperature (°C)						
	70	80	90	100	120	140	150
Column 1 (not immobilized)							
<i>n</i> -Octane	-1.56	-1.39	-1.23	-1.07	-0.73	-0.36	-
Benzene	-2.02	-1.83	-1.66	-1.51	-1.09	-0.79	-
Toluene	-2.58	-2.39	-2.21	-2.05	-1.55	-1.29	-
<i>n</i> -Butanol	-2.83	-2.58	-2.37	-2.16	-1.65	-1.25	-
Column 2 (immobilized with DCP)							
<i>n</i> -Octane	-1.31	-1.23	-1.00	-0.92	-0.60	-	-0.10
Benzene	-1.82	-1.66	-1.44	-1.31	-1.10	-	-0.48
Toluene	-2.36	-2.20	-1.99	-1.84	-1.51	-	-0.98
<i>n</i> -Butanol	-2.67	-2.46	-2.20	-2.00	-1.59	-	-0.93
Column 3 (immobilized with GPTMS and DCP)							
<i>n</i> -Octane	-1.16	-1.07	-0.94	-0.73	-0.52	-	+0.05
Benzene	-1.68	-1.53	-1.37	-1.22	-0.84	-	-0.24
Toluene	-2.25	-2.09	-1.92	-1.74	-1.42	-	-0.73
<i>n</i> -Butanol	-2.53	-2.31	-2.10	-1.88	-1.40	-	-0.68

The results just cited might indicate that Superox 20M will mix well with polymers with aromatic rings or an alcoholic function in their chain, while mixing would be difficult with those polymers of long hydrocarbon-type chains [33,34]. Further experimentation with selected solutes would be needed to confirm the generality of this conclusion.

CONCLUSIONS

The MAOT for columns of Superox 20M has been found to be 64°C, the same as that reported for Superoxes of higher molecular weight. When Superox 20M is immobilized in some way, the MAOT changes to about 50°C. The immobilization method used does not affect the value of the MAOT but has a considerable effect on the intensity of the phase transition of the polymer.

According to the values of the partial molar enthalpy of mixing, it is seen that all solutes are better solvents of the non-immobilized stationary phase, with the solubility decreasing for all columns in the order: aromatics > alcohols > *n*-alkanes, the last being non-solvents of the polymer.

A study of the type presented here, based on a selected set of solutes, will allow us to predict polymer-polymer solubilities and is applicable to the problem of the use of mixed stationary phases in GC.

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