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Note

Gas chromatographic study of grafted alkyl chains used as stationary phases

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In a previous paper[1], the adsorption of n-hexane on to alkyl chains chemically grafted on to silica was described in terms of thermodynamic parameters (heat and entropy of adsorption as a function of chain length and of surface coverage or grafting ratio).

Both the length of the grafted chains and the presence of residual hydroxyl groups of silica play an important role.

For short chains the hydroxyl groups greatly influence the mechanism of adsorption, whereas for the longer grafted chains the hydroxyl groups are shielded. In the latter situation, the interactions between n-hexane and the hydrocarbon grafted chains are similar to solution-type interactions.

The purpose of this study was to confirm the previous results by assuming that the longer grafts (C_{16} and C_{20}) behave like the usual stationary phases in gas chromatography (GC).

EXPERIMENTAL

Preparation of the stationary phases

The detailed procedure for the surface modification is given elsewhere[2,3]. Spherosil XOB 075 (Rhône Poulenc, Lyon, France) is a mesoporous silica with a specific surface area of 100 m²/g and a pore diameter of 30 nm. The silica is degassed at 350°C and reacted with thionyl chloride at 200°C. Finally, the sodium salt of the C_{16} and C_{20} alcohols is added and the grafted silica, after isolation from the reaction medium, is purified by alcohol extraction. Table I summarizes the relevant results.

TABLE I

CHARACTERISTICS OF C_{16} AND C_{20} GRAFTED CHAINS ON SPHEROSIL XOB 075

Bonded stationary phase	C (%)	Number of grafted chains per nm²
C_{16}	6.4	2.0
C_{20}	8.2	2.1

Chromatographic determinations

The modified silica with an average particle size between 40 and 100 μm is put into stainless-steel columns of length 50 cm and I.D. 0.217 cm (1/8 in.).

The experiments are carried out with a gas chromatograph employing a catharometric detection system (Intersmat IGC 12). The carrier gas is helium.

Before measurement the columns are conditioned at 100°C for 10 h.

Optimization of carrier gas flow-rate

The theoretical equations allowing the calculation of the thermodynamic parameters apply only at infinite dilution and at equilibrium. Therefore, optimal GC conditions were determined from Van Deemter curves measured systematically for all stationary phases. A typical plot for a C_{16} graft of height equivalent to a theoretical plate (HETP) versus measured flow-rate is shown in Fig. 1.
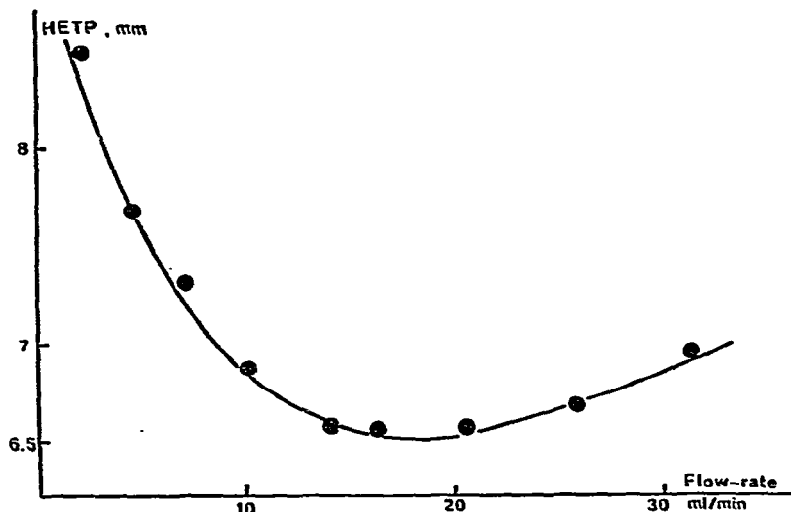

Fig. 1. Typical Van Deemter curve for C_{16} bonded stationary phase obtained at 47°C using *n*-hexane as solute.

The optimal flow-rates are between 15 and 20 ml/min. The retention times of *n*-hexane (or benzene) are then measured as a function of temperature. Next, the specific retention volumes, V_g, are calculated.

RESULTS AND DISCUSSION

Determination of ΔH, ΔG and ΔS

By definition, the heat (enthalpy) of evaporation is related to the heat of solution (ΔH_s) by the following equation:

$$\Delta H_v = \Delta H_s + \Delta H_e$$

where ΔH_e is the excess molar enthalpy of solution, which takes into account the non-ideality of the system. For non-polar stationary phases and non-polar solutes, ΔH_e can be considered to be negligible. Hence $\Delta H_v = \Delta H_s$ and

$$\log V_g = \frac{\Delta H_s}{2.3\, RT_c} + C^t$$

where R is the universal gas constant, T_c the temperature of the column and C^t a constant.

The free energy of evaporation is given by

$$\Delta G_s = RT \log V_g$$

and the corresponding entropy can be calculated from

$$\Delta S_s = \frac{\Delta H_s - \Delta G_s}{T_c}$$

Fig. 2 relates log V_g to the reciprocal of the absolute temperature. Straight lines are obtained, from which values of ΔH_s can be calculated.
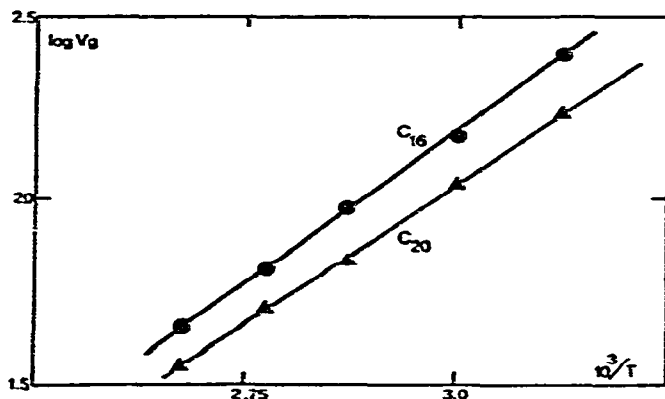

Fig. 2. Plot of specific retention volume (V_g) of n-hexane versus reciprocal of temperature for C_{16} and C_{20} bonded stationary phases.

Table II summarizes the results and compares them with previous values obtained from adsorption isotherms[1,3]. (Application of Clausius–Clapeyron equation for the calculation of the isosteric heat of adsorption and computation of the spreading pressure, using Gibb's equation, for the determination of the free enthalpy of adsorption. The entropy was calculated knowing both the free energy and enthalpy.)

The values of the heat of solution of n-hexane in the bonded phase or in pure n-hexadecane (taken from the literature) are identical. It follows that n-hexane exchanges solution-type interactions with the silica-grafted hydrocarbon chain.

TABLE II

HEATS OF SOLUTION (ΔH_s) AND ENTROPIES OF SOLUTION (ΔS_s) OF n-HEXANE IN DIFFERENT STATIONARY PHASES AT 47°C

Stationary phase	Reference	$-\Delta H_s$ (kcal/mole)		$-\Delta S_s$ (cal/mole·°K)	
		Clausius–Clapeyron	GC	Calculated	GC
C_{16} (grafted)		7.7 ± 0.2	7.5 ± 0.1	22.2 ± 0.7	18.7 ± 0.3
n-Hexadecane (non-grafted)	4		7.4		28.8
C_{20} (grafted)		7.6 ± 0.2	7.6 ± 0.1	21.9 ± 0.7	19.2 ± 0.3
Eicosane (non-grafted)	5		7.1		20.2

The values of ΔS_s are also close to those measured previously. However, GC gives more reliable data corresponding to a direct determination of ΔS, whereas in the previous case it was necessary to make a supplementary hypothesis about the morphology of the absorbed molecule (cross-sectional area required for the calculation of the coverage of the solid surface by the adsorbent).

Determination of the activity coefficient at infinite dilution

The specific retention volume, V_g, is related to the activity coefficient, γ^∞, by

$$V_g = \frac{273\,R}{\gamma^\infty\,Mp^0}$$

where M is the molecular weight of the grafted phase and p° the saturation vapour pressure at the column temperature. Calculated values of γ^∞ are collected in Table III.

TABLE III

ACTIVITY COEFFICIENT (γ^∞) OF n-HEXANE IN DIFFERENT STATIONARY PHASES
Values for n-hexadecane are taken from the literature.

Stationary phase	Temperature (°C)	Solute			
		n-Hexane	Reference	Benzene	Reference
C$_{16}$ (grafted)	47	0.85		1.03	
n-Hexadecane (non-grafted)	40	0.87	6	0.985	7
		0.91	7		
	50	0.86	6	0.995	10
		0.891	8		
		0.892	9		
		0.902	9		

The activity coefficients of n-hexane in the grafted phase are compared with values given in the literature[7] for n-hexadecane. Again, the values are very similar. Moreover, benzene behaves in a similar manner, confirming that the interactions of the non-polar solutes with non-polar stationary phases are of a solution type.

CONCLUSION

Stationary phases chemically bonded at the surface of silica behave thermodynamically, as do the usual stationary phases in GC.

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