CHROMATOGRAPHIC ANALYSIS OF METHYL(PROPYL)DIMETHYL-CYCLOSILOXANES

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SUMMARY

For some cyclosiloxanes it was found that a relationship exists between retention behaviour in gas chromatography and structure. A nomogram is proposed, based on data for some standard compounds, by means of which other compounds can be identified.

In order to determine the effect of substituent groups on the reactivity of the siloxane bond, we have synthesized a number of new compounds hitherto not described in the literature: cyclotrisiloxanes and cyclotetrasiloxanes containing various numbers of dimethyl- and methyl(propyl)siloxane groups in the cyclic structure.

In an earlier work[1,2] we carried out the synthesis and chromatographic analysis of the mixture of 3,3,3-trifluoropropyl(methyl)dimethylsiloxanes having the general formula F_mD_n, where F = the 3,3,3-trifluoropropylmethylsiloxane group; D = the dimethylsiloxane group; m = 0–5, n = 0–5, and $(m + n)$ = 3–6. Further analysis of the experimental chromatographic data for this mixture from the separation on methyltrifluoropropylsiloxane resin as the stationary phase showed that the logarithms of the retention volumes of cyclosiloxanes of the same homologous series were directly proportional to the number of groups D or F in the ring. Furthermore, a linear change in the logarithm of the retention volumes of cyclosilioxanes which were not part of a homologous series, was also observed for cyclotrisiloxanes: D_3, FD_2, F_2D, and F_3; cyclotetrasiloxanes: FD_3, F_2D, F_3D, F_4; cyclopentasiloxanes, FD_4, F_2D_3, F_3D_2, F_4D; and cyclohexasiloxanes, FD_5, F_2D_4, F_3D_3, F_4D_2, F_5D.

Fig. 1 shows the dependence of the logarithm of the retention volumes of F_mD_n cyclosiloxanes on the magnitude of $n(m)$. Each point lying at the intersection of three straight lines corresponds to an individual cyclosiloxane, the exception being cyclosiloxanes containing only dimethylsiloxane or only 3,3,3-trifluoropropyl-methyl siloxane groups: D_4, D_5, F_4, F_5 (these cyclosiloxanes correspond to points lying at the intersection of two straight lines). These differ qualitatively from mixed cyclosiloxanes. The homocyclics D_3 and F_3 behave analogously to mixed cyclosiloxanes, owing apparently to their good solubility in the stationary phase.

Fig. 2 shows a chromatogram obtained from a mixture of methyl(propyl)-dimethylcyclosiloxanes having the general formula P_mD_n, taken on the same sta-
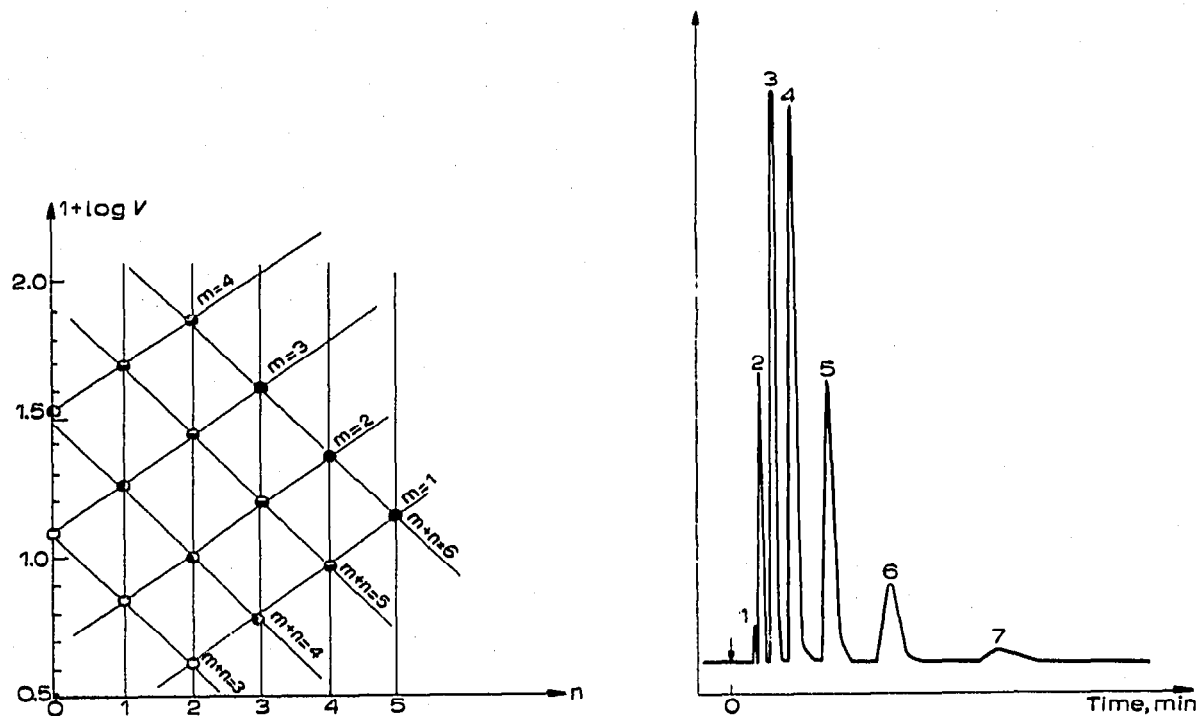
Fig. 1. Dependence of the logarithm of the retention volume on n for mixture F_mD_n. O = Cyclotrisiloxanes; ◑ = cyclotetrasiloxanes; ◓ = cyclopentasiloxanes; ● = cyclohexasiloxanes.

Fig. 2. Chromatogram for mixture P_mD_n. Chromatograph "Griffin"; katharometer; SF = 20 % SKTFT-50 on Celite-545; $l_{column.}$ = 1.87 m, t = 193°.
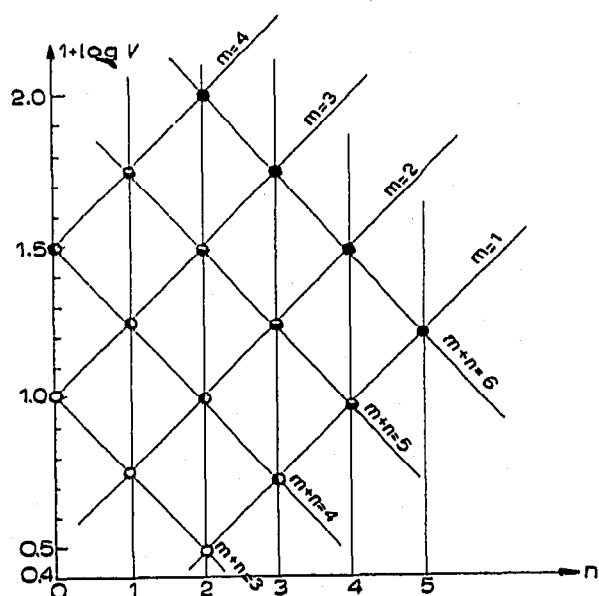

Fig. 3. Dependence of the logarithm of the retention volume on n for mixture P_mD_n.

tionary phase. The P_mD_n mixture was obtained by catalytic destruction of the cohydrolysis products of propylmethyldichlorosilane and dimethyldichlorosilane. By plotting the logarithm of the retention volume for these cyclosiloxanes as the function of n (Fig. 3) in a similar way to that for the above-mentioned dependence for the F_mD_n mixture, we were able to calculate the retention volume for cyclopentasiloxanes and cyclohexasiloxanes (Table I).

By comparing the data shown in Table I and Fig. 2 it is possible to assume that peak I is due to pure compound D_3; peak II—to compound PD_2 containing a trace of D_4; peak III—to the main component P_2D containing some D_5 and PD_3; peak IV—to the main component P_2D_2 admixed with PD_4 in front and P_3 behind; peak V—to the main compound P_3D and an admixture of PD_5 and P_2D_3 in front, which do not become separated; peak VI—to the simultaneous appearance of P_2D_4, P_3D_3 and P_4; peak VII—to overlapping of P_4D and P_3D_3 components.

TABLE I

THE RELATIVE RETENTION VOLUME FOR COMPONENTS OF THE P_mD_n MIXTURE

Component	V_R relative*	Component	V_R relative**
D_3	0.0785	D_5	0.511
PD_2	0.306	PD_4	0.934
P_2D	0.574	P_2D_3	1.718
P_3	1.083	P_3D_2	3.09
D_4	0.259	P_4D	5.51
PD_3	0.527	PD_5	1.585
P_2D_2	1.0	P_2D_4	3.08
P_3D	1.753	P_3D_3	5.47
P_4	3.04		

    * Values determined from chromatogram (Fig. 2).
  ** Values calculated from the graph (Fig. 3).

As may be seen from Fig. 2, the P_mD_n mixture does not become completely separated on SKTFT-50 phase; however, this does not make it impossible to calculate from the plot the retention volume for all the components of the mixture. The most complete separation of this mixture was obtained with diphenylene oxide siloxane resin as the stationary phase (Fig. 4).
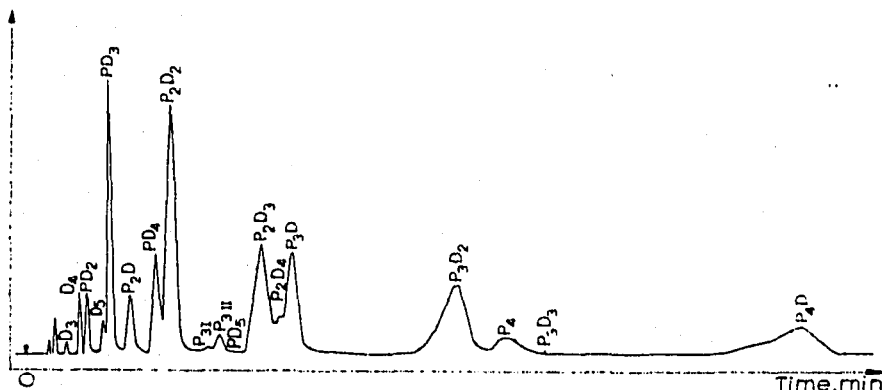

Fig. 4. Chromatogram for mixture P_mD_n. SF = siloxane resin containing diphenylene oxide group; $t = 190°$.

The analysis of F_mD_n and P_mD_n cyclosiloxanes was carried out on the "Griffin" chromatograph utilizing a detector of the heat-conductivity type. Various siloxane resins were used as the stationary phases. The amount of the phase was 20 % of the weight of the solid support (Celite-545). Helium was used as the carrier gas ($v = 30$ cm^3/min).

In gas chromatographic analysis of F_mD_n and P_mD_n cyclosiloxanes using siloxane phases of different polarities[3], we observed the same regularities in the changes in the retention volume of these compounds.

The established regularity is apparently common for cyclosiloxanes having different siloxane groups in the ring, since it was observed both for polar (F_mD_n) and nonpolar (P_mD_n) compounds when the polarities of the siloxanes were different.

It is known[4-6] that in the cohydrolysis or catalytic destruction of cohydrolysis products of diorganodichlorosilanes, mixed cyclosiloxanes are formed having different siloxane groups in the ring. As a rule, such a reaction mixture contains a large amount of closely boiling components that are difficult to separate by distillation. The proposed method makes it possible, on the basis of several known reference cyclosiloxanes, to identify all the components of such mixtures, even when they are not well separated.

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