Journal of Chromatography, 217 (1981) 109–123
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,979

SCANNING ELECTRON MICROSCOPY AS AN AID IN GAS CHROMATOGRAPHY

STUDY OF POROUS POLYMERS COATED WITH STATIONARY PHASES

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SUMMARY

Scanning electron microscopy was used to study the appearance of Chromosorb 101 with different amounts of stationary phases Ethofat 60/25, squalane, Fractonitril VI, and also to reveal whether there exists any relationship between the surface appearance and the chromatographic behaviour of different solutes on these packings.

It can be concluded that the support does not remain completely covered until large amounts of liquid phase are present, and that the presence of uncovered zones is the cause of the observed adsorption. The percentage of the stationary phase at which the support becomes practically completely coated changes with the nature of the stationary phase, and corresponds to the value at which a change in the chromatographic behaviour is observed.

INTRODUCTION

In two previous reports[1,2] we have studied the solute–stationary phase–adsorbent interaction phenomena associated with the use of active Chromosorb 101 support in gas chromatography. In order to determine the influence of the nature of the support and the amount and the nature of the stationary phase in the chromatographic process, a series of compounds of different polarity were chromatographed on different columns, and their experimental partition constants K'_L and adsorption constants K_S were calculated. Ethofat 60/25, squalane, and Fractonitril VI were used as stationary phases, and Chromosorb 101 was the support. The values of K'_L are compared with those obtained for the same stationary phases on Chromosorb P HMDS.

0021-9673/81/0000–0000/$02.50

The value of K'_L can be obtained from the plot $V'_R/W_S = f(W_L/W_s)$ and according to the expression

$$V'_R/W_S = K'_L W_L/W_S + K_a A_L/W_S + K_S A_S/W_S$$

assuming that the mechanism of partition of the solute between the gas phase and the stationary liquid phase and the mechanism of adsorption on the gas–liquid and liquid–solid interfaces are essentially independent. (V'_R is the adjusted retention volume; W_S and W_L are the weights of the support and the stationary phase, respectively; and A_S and A_L are the surface areas of the support and the stationary phase, respectively. Three kinds of relationship between V'_R and the amount of stationary phase were obtained for the 26 studied compounds (Fig. 1).

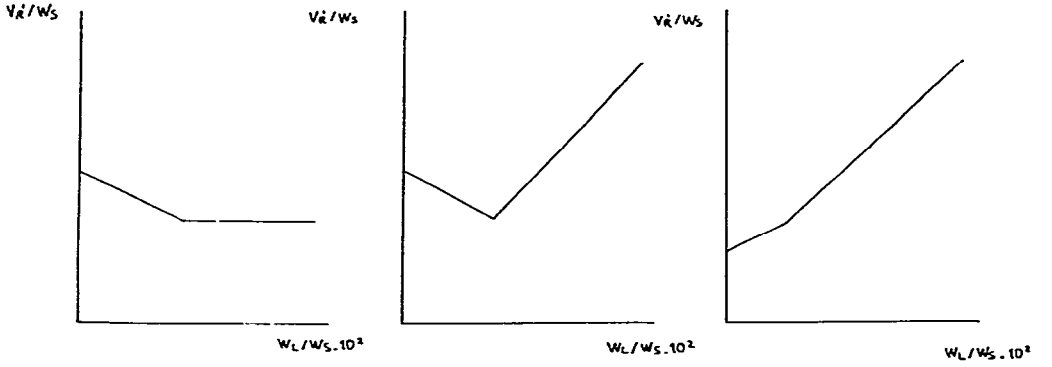

Fig. 1. Relationship between adjusted retention volume per gram of solid support V'_R/W_S and liquid loading $W_L/W_S \times 10^2$.

The shape of the graph obtained depends on the nature of the compound and of the stationary phase, but always for each stationary phase a common interval of change in slope is observed. Thus in the column of Ethofat 60/25 and Chromosorb 101 it corresponds to 10% of the liquid phase, and in the squalane and Fractonitril VI on Chromosorb 101 it corresponds to 20–25% of the liquid phase. From these observations we concluded that the support remains active until the amount of stationary phase is 10% or 20–25% higher than the amount necessary to form a uniform monolayer[2].

This observation of continued activity of the support may be due to incomplete covering of the support by the stationary phase, leaving some active points uncovered that would be responsible for the adsorption. The reason for poor covering could be the different chemical natures of the support and the stationary phase, which determine the type and strength of the interactions. Thus, if the polarities of the stationary phase and the support are very different, the latter will not be properly wetted and drops may form on the support, leaving uncovered zones that will be more or less numerous according to the amount of stationary phase added.

There is another possible explanation of these phenomena. This is that the stationary phase really does cover all the support, but that one with a strongly adsorbent power acts on the molecules of the solute that have crossed the liquid phase.

According to the thickness of the stationary liquid phase the effect of the support will be greater or lesser.

Therefore, it would be of interest to know the real state of the stationary phase on the support. A suitable technique for this purpose is scanning electron microscopy (SEM), and several authors have already used it. Drew and Bens[3,4] published scanning electron micrographs of several supports (PTFE, Chromosorbs P, W and G) with various stationary phases (SE-30 and Carbowax 4000). De Mets and Lagasse[5,6] studied supports such as Porapak Q, and Aue *et al.*[7] several kinds of silicones on Chromosorbs W and G. Berezkin *et al.*[8] also studied some polar and non-polar stationary phases on Chromaton N, and Gearhart and Burke[9] the supports Porapak Q and Chromosorbs 101 and 102. However, no information has been found of studies carried out by SEM of these last supports when covered with stationary phases. For this reason, we proceeded to study the surfaces of the different aforementioned packings by SEM in order to reveal whether there is any correlation with the observed chromatographic behaviour.

EXPERIMENTAL

Scanning electron microscopy

The samples of packing materials were mounted on specimen holders using a thin layer of adhesive. After they had thoroughly dried, the specimens were coated with a 400–600 Å layer of gold in a vacuum evaporator (pressure, 0.2 Torr) fitted with a sputtering diode. They were examined with a stereoscan Model S-4 scanning electron microscope, using an accelerator voltage between 5 and 10 kV and with a magnification of 5000.

Chromatographic packings

The samples observed by SEM were the supports Chromosorb P HMDS and Chromosorb 101 from Johns-Manville (Denver, CO, U.S.A.); their physical properties are listed in Table I. The following packings were used: Ethofat 60/25 (Carlo Erba, Milan, Italy); squalane (Merck, Darmstadt, G.F.R.); and Fractonitril VI (Merck).

TABLE I

PHYSICAL PROPERTIES OF THE SUPPORTS CHROMOSORB P HMDS AND CHROMOSORB 101

	Chromosorb P HMDS	*Chromosorb 101*
Type	Calcined diatomite	STY-DVB
Free fall density (g cm^{-3})	0.38	0.30
Surface area (m^2 g^{-1})	4.0	< 50
Average pore diameter (μm)	< 5	0.3–0.4
Colour	Pink	White
Mesh size	80–100	80–100
Temp limit (isothermal) (°C)	–	300

RESULTS AND DISCUSSION

In this work a set of photographs from Chromosorb 101 support with Ethofat 60/25, squalane and Fractonitril VI stationary phases are shown. We have selected them according to the following criteria.

(1) The information that can be deduced, mainly from the viewpoint of comparing the supports with different amounts of stationary phase.

(2) How representative the pictures are. The packing particles are not homogeneous and, in fact, not uniformly covered. Therefore, in order to do an exhaustive study, it would be necessary to take photographs of a lot of particles or zones of particles of a certain packing. We have chosen the most representative samples, that is to say, the most frequently occurring ones for every percentage of stationary phase. Furthermore, in order to study the internal coating of the particles of Chromosorb 101, some of them have been cut and their appearance compared with the outer one. For the purpose of checking the effect of the column conditioning in the chromatograph, some packings have also been studied after that treatment.

The photograph of Chromosorb 101 without stationary phase (Fig. 2a) shows a very porous structure made up of microsized particles closely attached to one another. This model, according to Gearhart and Burke[9], is attributed to the polymerization process. The regions of high cross-linking become connected with less highly cross-linked material, and thus the pore structure results.

Comparing the photographs obtained for Chromosorb 101 without stationary phase with those of Chromosorb 101 with different amounts of Ethofat 60/25 (Fig. 2), it can be seen that the number of observable holes remarkably decreases as the amount of stationary phase increases. The extent of this decrease is significant even at 10% of stationary phase. This value of 10% of liquid phase agrees with the value of the percentage of stationary phase at which the slope changes in the plot of V'_R/W_S against W_L/W_S for a group of non-polar and semi-polar compounds[1].

When larger amounts of stationary phase are added, *ca.* 20–25%, the support appears to be fully covered, at least superficially (Fig. 2d, e). However, small holes can be detected even in these cases, which probably are the originators of the observed adsorption when columns with large amounts of stationary phase are used. Examination of the interior of the support confirms this idea; for instance, Fig. 2f represents a cut support grain with 30% of Ethofat. We can see a high degree of porosity, as we noted with 2.5% of Ethofat. This fact leads us to consider a non-uniform coating of the stationary phase on the support surface, in such a way that the stationary phase is not slowly filling the pores, but so that it has a certain tendency to lie on the external surface of the grain and it superficially coats the pores. Under this external surface there exists uncoated support which causes the adsorption effects.

This placing of the stationary phase on the external surface of the support grain may be due to the difficulty of introducing the polymer into the small pores or, as other authors pointed out[4], to solvent migration towards corners and edges of holes, resulting in transport of dissolved material to these regions. Whatever the reason, the column will work with the stationary phase unevenly distributed. This fact allows us to explain the adsorption effects. We can say that large changes in the distribution of the stationary phase have not been observed before even after a few hours of maintaining the column at work conditions, according to the results ob-

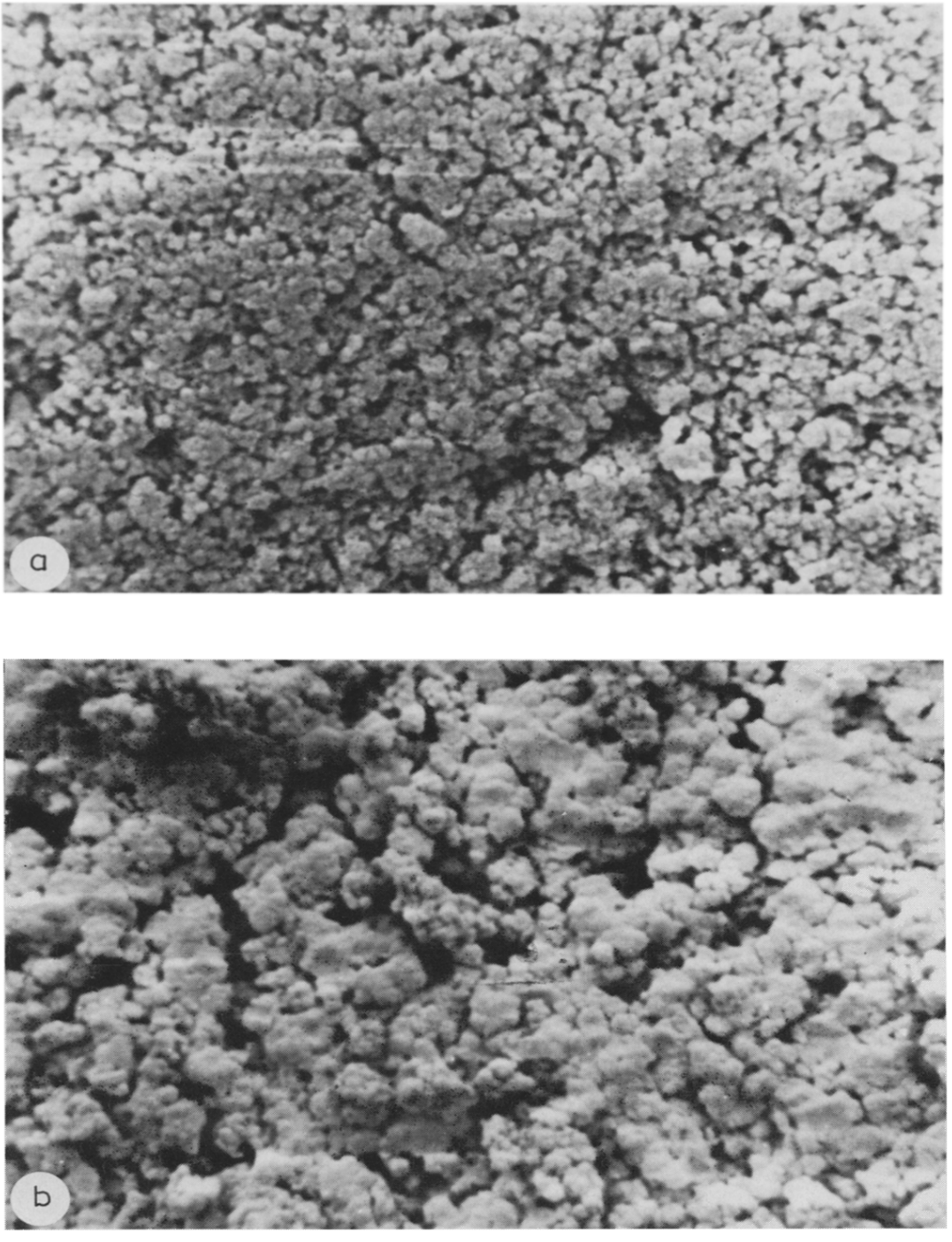

Fig. 2.

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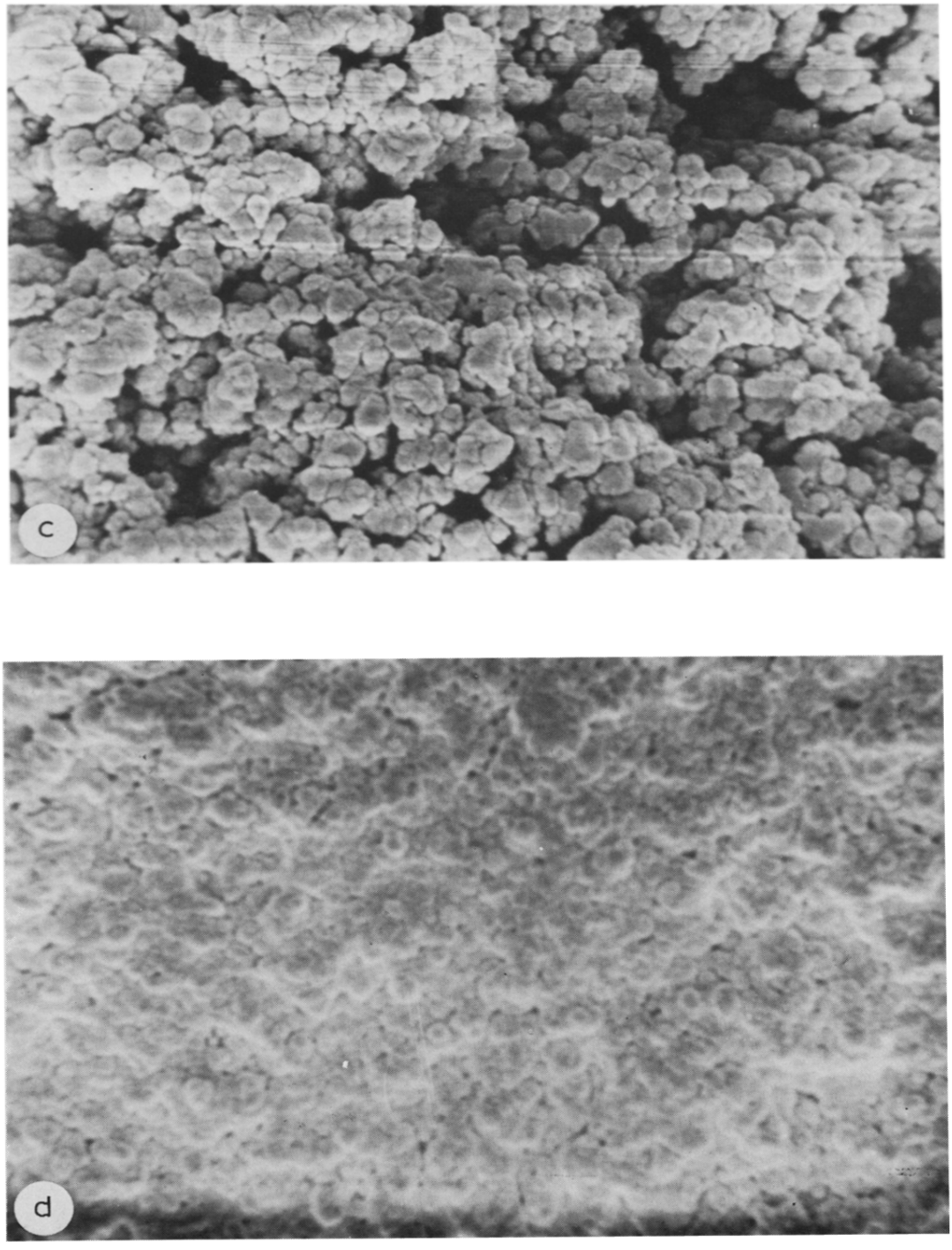


Fig. 2.

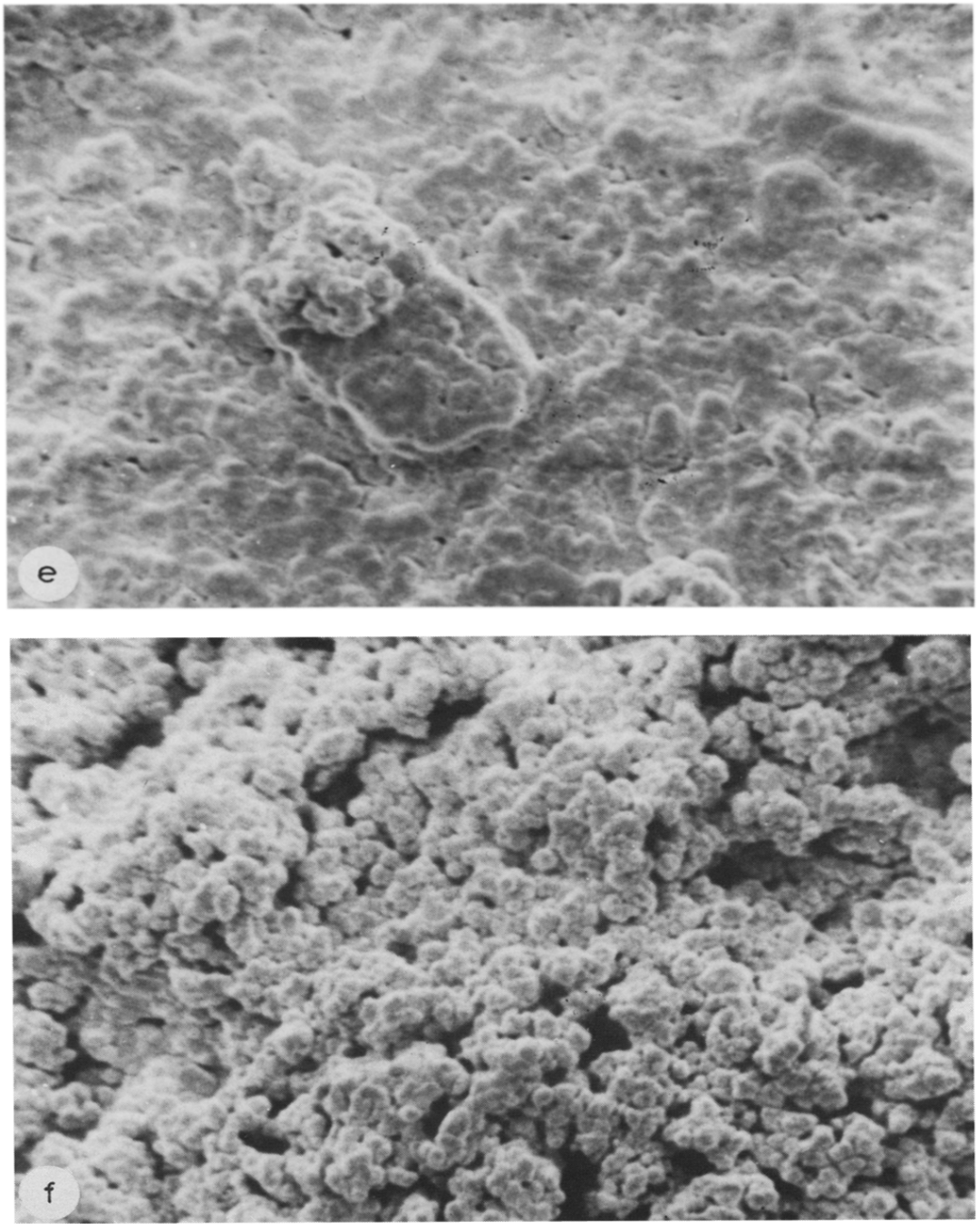


Fig. 2. Microphotographs of: (a) Chromosorb 101 (80–100 mesh); (b) 2.5% Ethofat 60/25 on Chromosorb 101 (80–100 mesh); (c) 10% Ethofat 60/25 on Chromosorb 101 (80–100 mesh); (d) 20% Ethofat 60 25 on Chromosorb 101 (80–100 mesh); (e) 30% Ethofat 60 25 on Chromosorb 101 (80–100 mesh); (f) 30% Ethofat 60/25 cut on Chromosorb 101 (80–100 mesh).

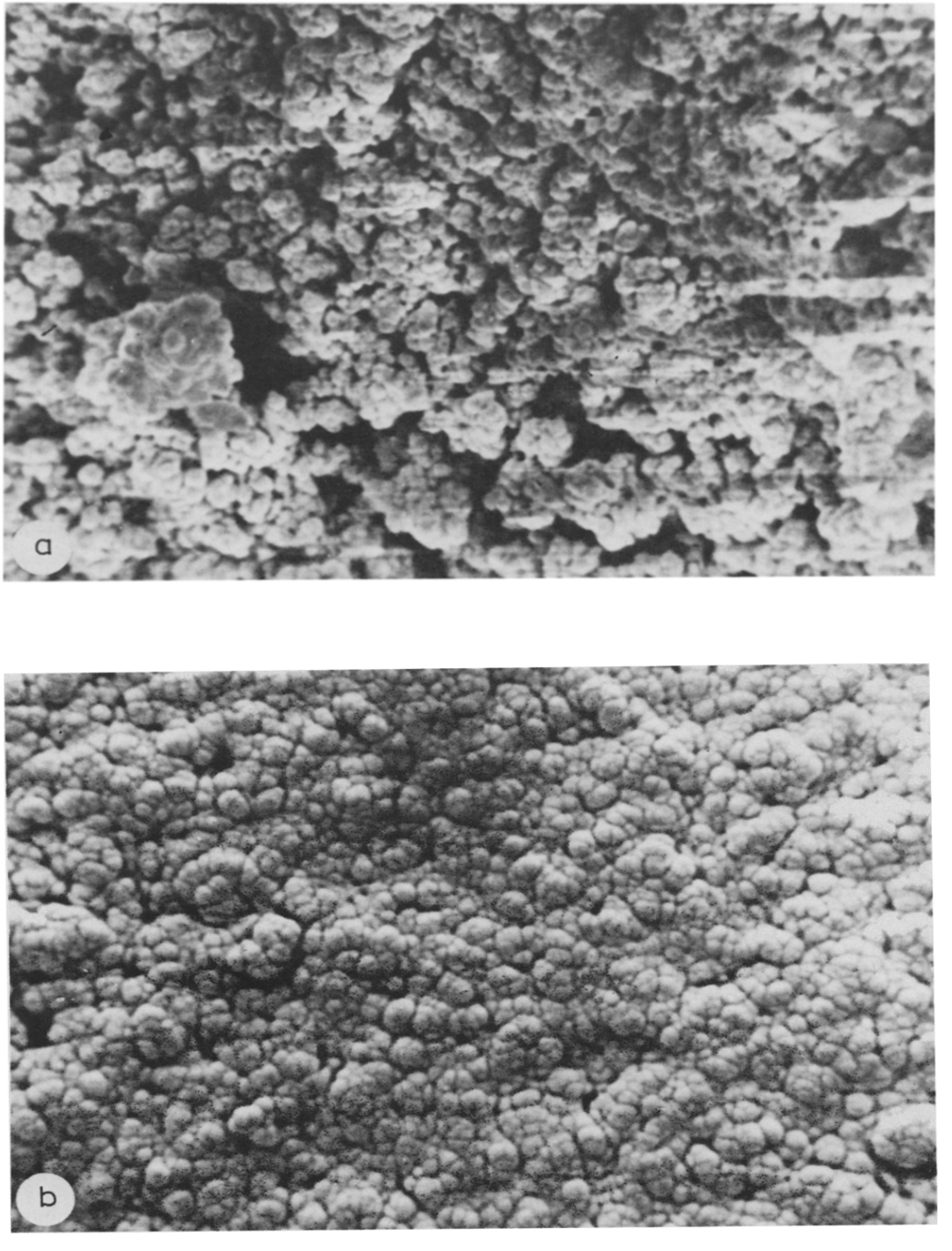


Fig. 3.

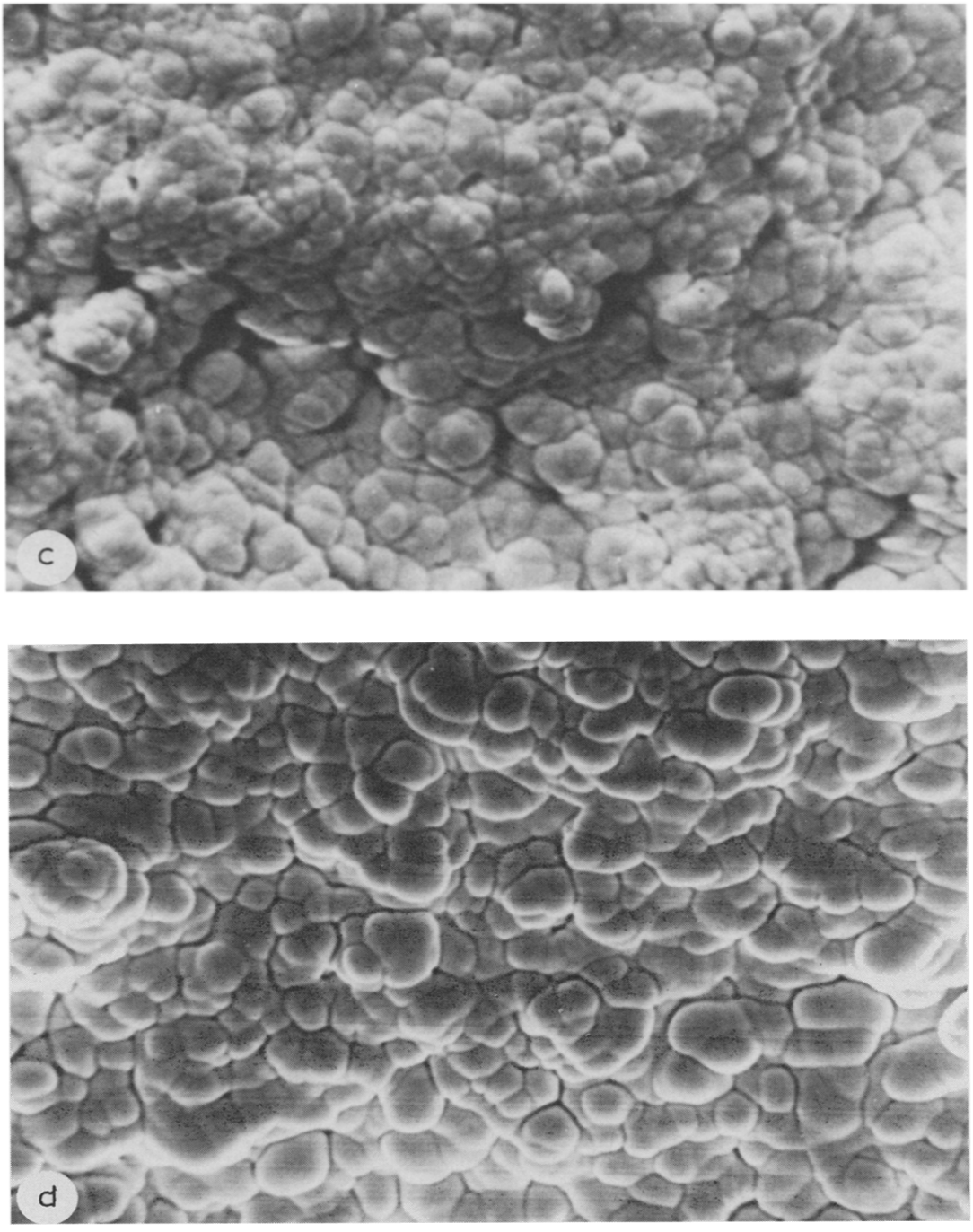
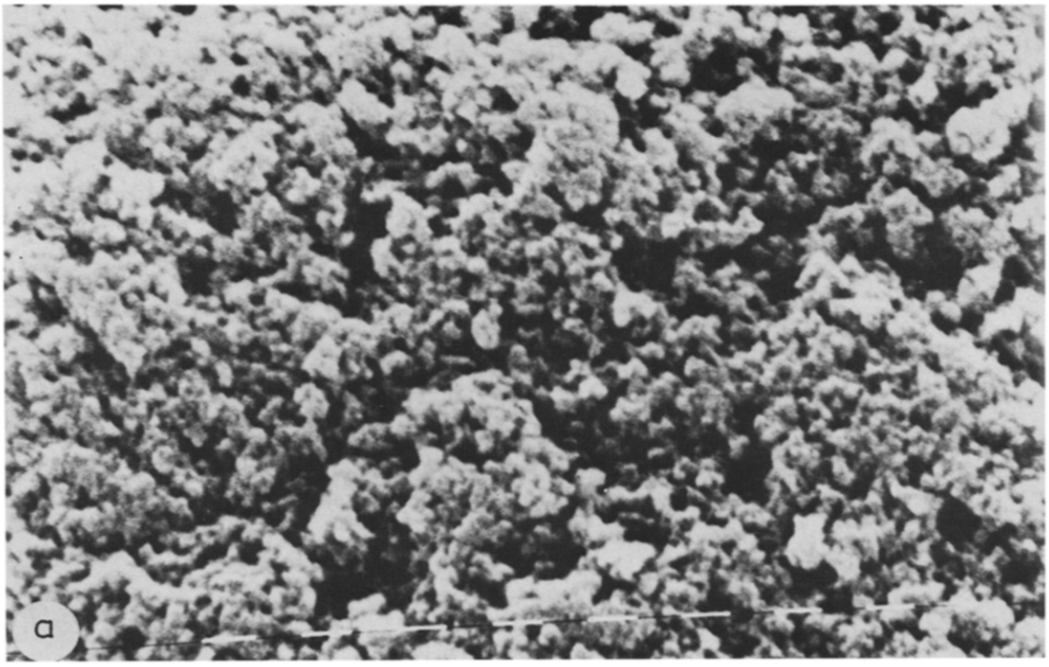


Fig. 3. Microphotographs of: (a) 3.4% squalane on Chromosorb 101 (80–100 mesh); (b) 15.3% squalane on Chromosorb 101 (80–100 mesh); (c) 23% squalane on Chromosorb 101 (80–100 mesh); (d) 40% squalane on Chromosorb 101 (80–100 mesh).



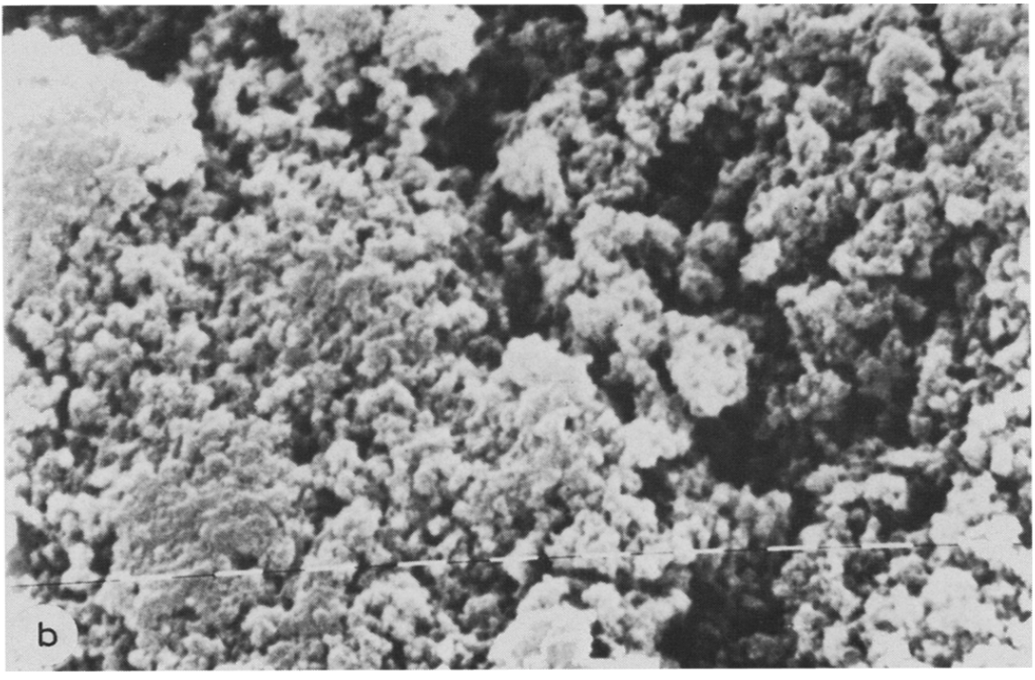


Fig. 4.

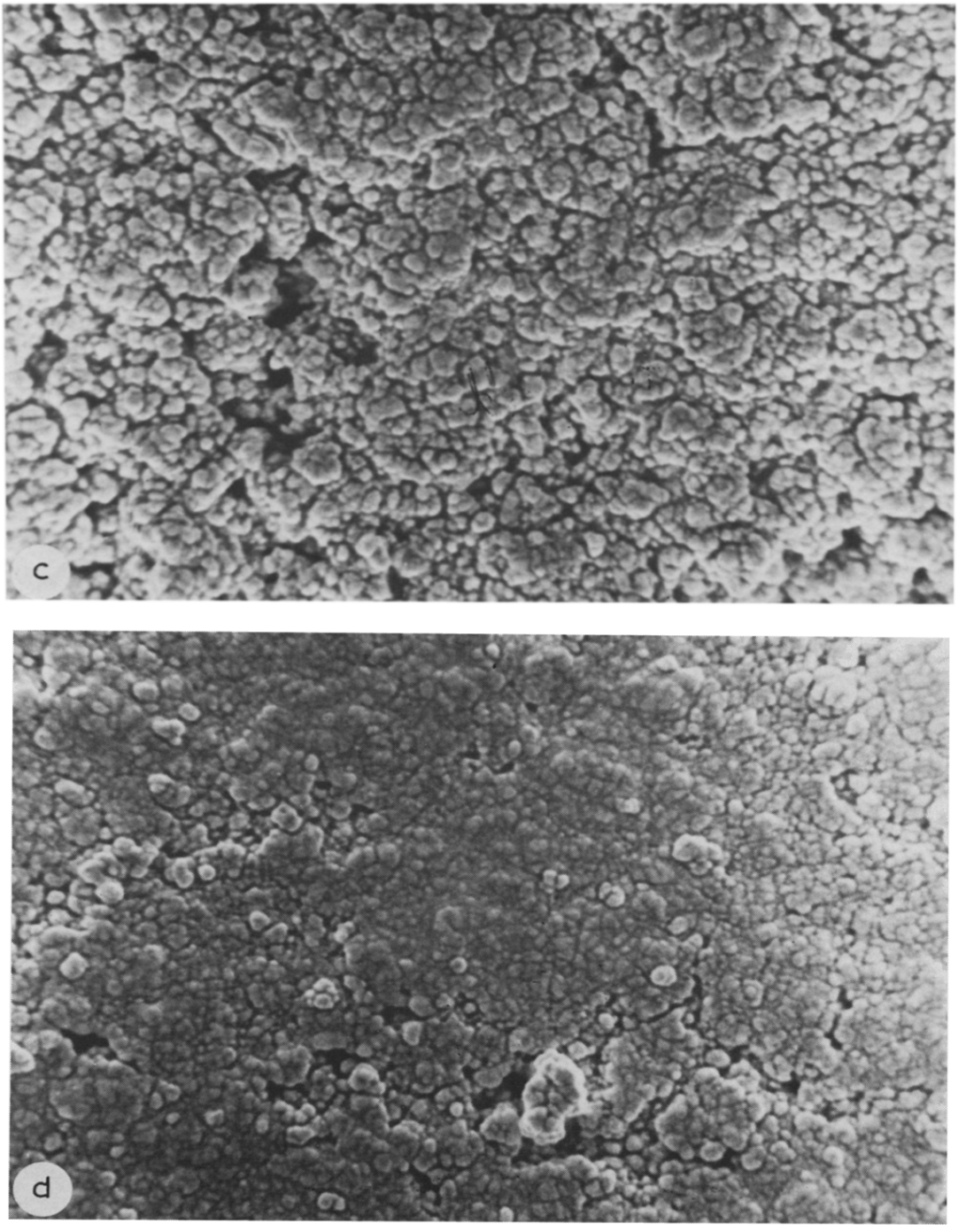


Fig. 4. Microphotographs of: (a) 8% Fractonitril VI on Chromosorb 101; (b) 21% Fractonitril VI on Chromosorb 101; (c) 40% Fractonitril VI on Chromosorb 101; (d) 40% Fractonitril VI plus 0.8% Zonyl A on Chromosorb 101.

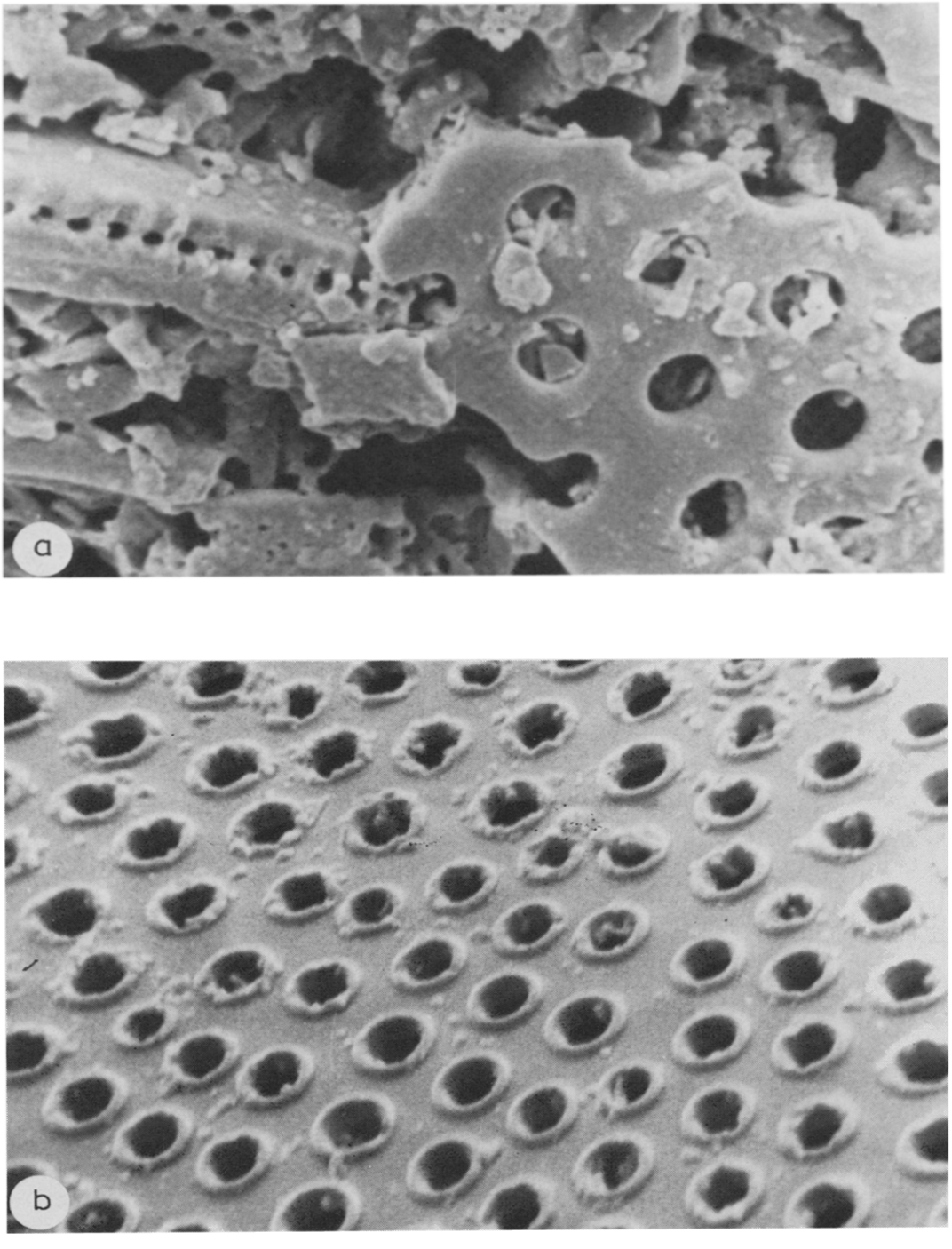


Fig. 5.

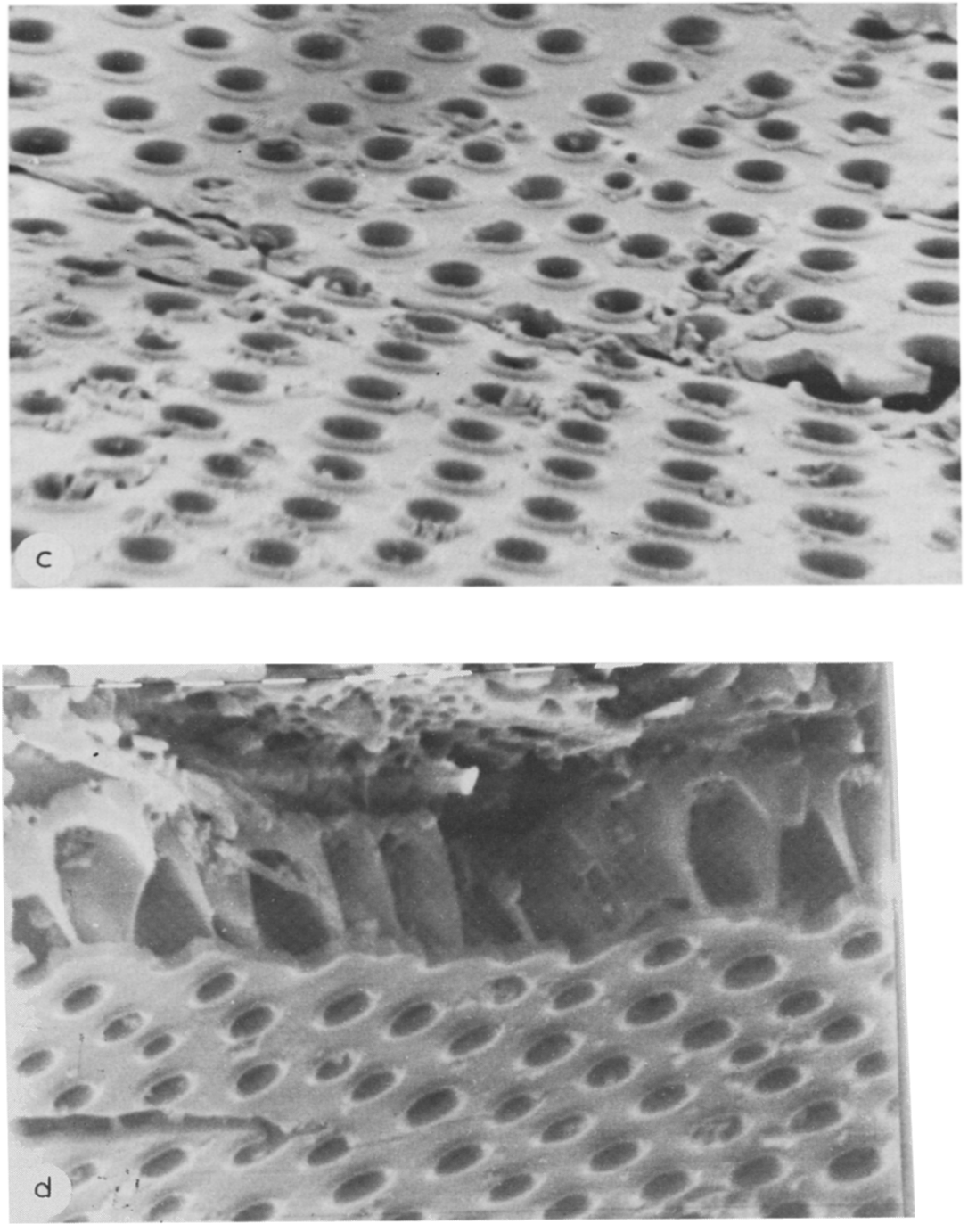


Fig. 5. Microphotographs of: (a) Chromosorb P HMDS (80–100 mesh); (b) 8.5% squalane on Chromosorb P HMDS (80–100 mesh); (c) 13% Ethofat on Chromosorb P HMDS (80–100 mesh); (d) 11.8% Fractonitril VI on Chromosorb P HMDS (80–100 mesh).

tained by other authors[4]. We should also comment that this observation of the stationary phase on the surface would probably be due to the sample treatment during the preparation, when it was introduced into the microscope under conditions of high vacuum (10^{-6} Torr). At any rate, the fact that the covering process with the gold layer is done under slight vacuum (0.2 Torr) and that the thickness (400–600 Å) of this gold layer is important, leads us to suppose that microscopic treatment will not seriously affect the appearance of the packing material observed.

In our study of the appearance of the support coated with different amounts of Ethofat 60/25, it appears that the Ethofat settles on the support surface and wets it, without forming isolated drops. This can be explained if we take into consideration the nature of the stationary phase (a polyoxyethylene monostearate of an average relative molecular mass of 938), which contains ester and ether groups with dipole moments which can produce induction interactions with the benzenic groups or with the unreacted vinyl groups, that are formed in a noticeable concentration on the surface of the supports[10,11], slight specific adsorbents according to the Kiselev's classification[12].

In the case of Chromosorb 101 with squalane, the surface of the support when coated with different amounts of stationary phase has a globular appearance that shows up perfectly with large amounts of stationary phase (Fig. 3d). This appearance leads us to suppose that the stationary phase does not properly wet the support and that it settles in such a way that isolated drops are formed. The fact that the stationary phase does not properly wet the support can be explained by taking into account that it is a non-polar compound (a saturated hydrocarbon of 30 carbon atoms) and will not have specific interactions with the support surface. Furthermore, if the dispersion interactions between the hydrocarbon molecules are greater than those between the support and the hydrocarbon, the result will be aggregation of the hydrocarbon molecules, leading to the observed globular appearance.

Comparing the photographs of Chromosorb 101 with different amounts of this stationary phase (Fig. 3) it seems as if the number of drops of the stationary phase increases and the cracks between the drops decrease. However, the number of cracks is large even with large amounts of stationary phase (Fig. 3c). This again agrees with the plots of V_R/W_S against the amount of stationary phase W_L/W_S (ref. 2), because only from 30% of stationary phase does the usual partition effect take place with an increase of the retention volumes as the amount of stationary phase increases. If the amount of stationary phase is lower than 30%, the support effect is important, particularly at 10% of stationary phase. At this percentage, a great number of holes can be observed in the surface of the packing material.

Comparing by SEM the surface of Chromosorb 101 with Fractonitril (Fig. 4) and those of Chromosorb 101 with Ethofat 60/25 and squalane a considerable difference is apparent. This is because of poor covering of the support by the stationary phase so that a great number of holes can be seen, even with large amounts of stationary phase (Fig. 4c). In this case the poor wetting can be easily interpreted, because a polar phase such as 1,2,3,4,5,6-hexakis-(2-cyanoethoxy)hexane has only a slight tendency to wet a support of low specific adsorbance, such as Chromosorb 101. The addition of small amounts of Zonyl A, a surface-active agent (Fig. 4d), results in a better coating of the support and a considerable decrease in the number of pores.

We have also taken SEM photographs of the studied stationary phases on

Chromosorb P HMDS. In Fig. 5, photographs of each of these stationary phases are shown. There is no essential difference in the appearance of the packing material when the stationary phase is changed; nor is it possible to detect significant differences with the amount of stationary phase. This is probably due to the bigger size of the pores in the Chromosorb P HMDS (2–3 μm) than in Chromosorb 101 (0.3–0.4 μm), so that the stationary phase can get into the pores and not accumulate on the periphere. This results in superficial layers so thin that we cannot detect any difference between them, which would be visible only with a great excess of stationary phase. This argument agrees with different authors[4,7,8], who suggest that the stationary phase gradually fills the pores in this kind of support. On the other hand, we have pointed out that when Chromosorb 101 is used a completely different effect occurs, and the stationary phase is basically placed on the periphery of the support grain even though a certain amount goes into it.

CONCLUSION

The SEM studies carried out do not lead to a definite conclusion about the behaviour of the packing. However, they yield information that agrees with the experimental chromatographic values and that leads us to think that, at least for packing with amounts of stationary phase less than 10 or 20%, the presence of uncovered zones of the support is the cause of the observed adsorption.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the skilful technical assistance from the Servei de Microscopia of the Universitat de Barcelona, and especially from Mr. Font Arnau.

REFERENCES

1 D. Barceló, M. T. Galcerán and L. Eek, *Chromatographia*, 12 (1979) 725.
2 D. Barceló, M. T. Galcerán and L. Eek, *Chromatographia*, 14 (1981) 73.
3 E. M. Bens and C. M. Drew, *Nature (London)*, 216 (1967) 1046.
4 C. M. Drew and E. M. Bens, in C. L. A. Harbourn (Editor), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 3.
5 M. De Mets and A. Lagasse, *Chromatographia*, 2 (1969) 401.
6 M. De Mets and A. Lagasse, *J. Chromatogr. Sci.*, 8 (1970) 272.
7 W. A. Aue, C. R. Hastings, J. M. Augl, M. K. Norr and J. V. Larsen, *J. Chromatogr.*, 56 (1971) 295.
8 V. G. Berezkin, E. Ju. Sorokina, G. F. Shaligin, I. A. Litvinov and M. N. Budantseva, *J. Chromatogr.*, 193 (1980) 132.
9 H. L. Gearhart and M. F. Burke, *J. Chromatogr. Sci.*, 15 (1977) 1.
10 W. Hertl and M. G. Neumann, *J. Chromatogr.*, 60 (1971) 319.
11 C. I. Barta and A. S. Gordon, *J. Chromatogr. Sci.*, 8 (1970) 63.
12 A. V. Kiselev and Ya. I. Yashin, *La Chromatographie Gaz-Solide*, Masson, Paris, 1969, p. 69.