

## LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

## VI. DEACTIVATED FLORISIL AS ADSORBENT

L. R. SNYDER

*Union Oil Company of California, Union Research Center,  
Brea, Calif. (U.S.A.)*

(Received March 22nd, 1963)

## INTRODUCTION

Preceding papers in this series have undertaken to develop a comprehensive and detailed theory of compound separation in linear elution adsorption chromatographic (LEAC) systems. Corresponding correlational equations have been derived from experimental retention volume data for the adsorbents alumina (Parts II-IV)<sup>1-3</sup> and silica (Part V)<sup>4</sup>. These equations permit the facile and systematic comparison of the separation possibilities in various LEAC systems<sup>5,6</sup>, and suggest approximate generalizations for related non-linear chromatographic separations. The extension of this treatment to additional adsorbent types is of obvious practical importance, since it permits us to take advantage of the unique features of each adsorbent. As additional adsorbents are included in this semi-empirical study we should also expect to achieve greater insight into the dependence of adsorption separation on the fundamental characteristics of the adsorbent, and hence come to better understand the adsorption process itself.

The choice of Florisil (a commercial coprecipitate of silica and magnesia) as the subject of the present study was suggested by several considerations. Florisil has been widely used<sup>7-11</sup> in chromatographic separation, particularly in the analysis of petroleum and related substances<sup>7-9</sup>. Its pronounced acidic properties<sup>12</sup> (similar to those of silica/alumina cracking catalysts) distinguish it from the relatively neutral alumina and silica samples studied in Parts II-V<sup>1-4</sup>, and suggest the possibility of unique separation capabilities. Finally, being composed largely of silica (82 % wt. %), it should be interesting to compare its adsorptive properties with those of silica.

## EXPERIMENTAL

Samples of Florisil as received from the manufacturer (Floridin Company, Tallahassee, Fla.) were treated in the usual manner<sup>1</sup> prior to use as chromatographic adsorbent, *i.e.*, atmospheric calcination at 400° for 16 h, followed by equilibration with added liquid water for a minimum of 48 h. It has been observed<sup>13</sup> that uncalcined Florisil samples are contaminated by an adsorbed oil which must be washed from the adsorbent prior to its use in separation procedures. No such contaminant could be detected in our Florisil samples after calcination, using the strongest eluent of the present study (methylene chloride) as a wash material.

In contrast to our experience with alumina and silica, where the above procedure gives closely similar final adsorbent samples<sup>1,4</sup>, two different shipments of Florisil showed markedly different adsorptive properties after calcination. This was traced to differences in the final surface area of calcined material, as summarized in Table I

TABLE I  
SURFACE AREA AND PORE DIAMETER OF SOME FLORISIL SAMPLES

Sample	Surface area* (m <sup>2</sup> /g)	Pore volume* (ml/g)	Average pore diameter* (Å)
Calcined No. 1	155	—	—
Calcined No. 2	247	—	—
Manufacturer's values	298	0.461	62

\* BET.

along with the manufacturer's values for original adsorbent. With the correction of retention volume data for these differing surface areas, as discussed in Part V<sup>4</sup> under "adsorbent standardization", the two adsorbents were then quite comparable. Whether these differences in final surface areas reflect corresponding differences in starting product or different sensitivities to the calcination procedure was not further investigated. This potential variability of the starting adsorbent restricts the usefulness of Florisil in *routine* analytical separation procedures<sup>4,14</sup>.

#### CHEMISORPTION ON FLORISIL

Chemisorption in adsorption chromatographic systems, when it occurs, is an important problem, since the recoveries of solute from the column tend to be incomplete, and the elution bands show pronounced tailing. The chemisorption of basic nitrogen compounds on silica was noted in Part V<sup>4</sup>, and attributed to the presence of acid groups on the adsorbent surface. The surface acidity of some commercial silicas has been related to the presence of free sulfuric acid<sup>12</sup> which can be removed by washing, so that chemisorption of basic compounds on silica may in principle be avoidable. The permanent acidity of Florisil<sup>12</sup> would be expected to lead to chemisorption of basic solutes, and ASATOOR AND DALGLIESCH<sup>10</sup> have noted that basic nitrogen compounds are strongly retained on Florisil. Reference also has been made to the semi-irreversible adsorption (chemisorption) of the hydrocarbon benzpyrene on Florisil<sup>9</sup>. Chemisorption on Florisil has since been confirmed in this laboratory, not only for basic nitrogen compounds such as the pyridines and quinolines, but also for such relatively non-basic substances as perylene and dimethyl terephthalate. The chemisorption of perylene on Florisil clearly involves an acid-base reaction, since adsorption bands develop the deep purple color associated with the dissolution of perylene in cold concentrated sulfuric acid. Chemisorption of dimethyl terephthalate on Florisil is illustrated in Table II and Fig. 1. Referring to Fig. 1, chemisorption of this solute in a chromatographic system using Florisil is shown to result in marked tailing of the elution band. At the same time, as seen in Table II, the recovery of solute from the column is incomplete and decreases markedly with

TABLE II  
CHEMISORPTION OF DIMETHYL TEREPHTHALATE ON FLORISIL;  
SOLUTE RECOVERIES FROM FLORISIL AND SILICA

Solute/adsorbent (g/g)	$R^{\circ}$		Recovery (%) <sup>*</sup>	
	Silica <sup>**</sup>	Florisil <sup>***</sup>	Silica <sup>**</sup>	Florisil <sup>***</sup>
$2 \cdot 10^{-5}$	18.7	—	83	< 5
$4 \cdot 10^{-5}$	18.0	14.4	84	18
$8 \cdot 10^{-5}$	18.2	16.0	91	15
$2 \cdot 10^{-4}$	—	14.2	—	38

<sup>\*</sup> In first 60 ml/g of eluate.

<sup>\*\*</sup> Elution by 40% methylene chloride-pentane from 16.0% H<sub>2</sub>O-SiO<sub>2</sub> (Davison Code 12).

<sup>\*\*\*</sup> Elution by methylene chloride from 3.5% H<sub>2</sub>O-Florisil (Sample No. 2).

decreasing sample size. Normal adsorption, by contrast, is shown (Table II, Fig. 2) for the elution of this same solute from a similar chromatographic system using silica rather than Florisil. The plot of Fig. 2 is typical of most LEAC systems, with the trailing edge of the elution band showing an exponential dependence of solute concentration on eluate volume. Table II shows the recovery of solute from the silica column as essentially complete, considering the probable purity of the solute, and independent of sample size. In view of the disadvantages of chemisorption in chromatographic separation, the apparently more frequent occurrence of chemisorption in separations using Florisil should be kept in mind when considering the use of this adsorbent.

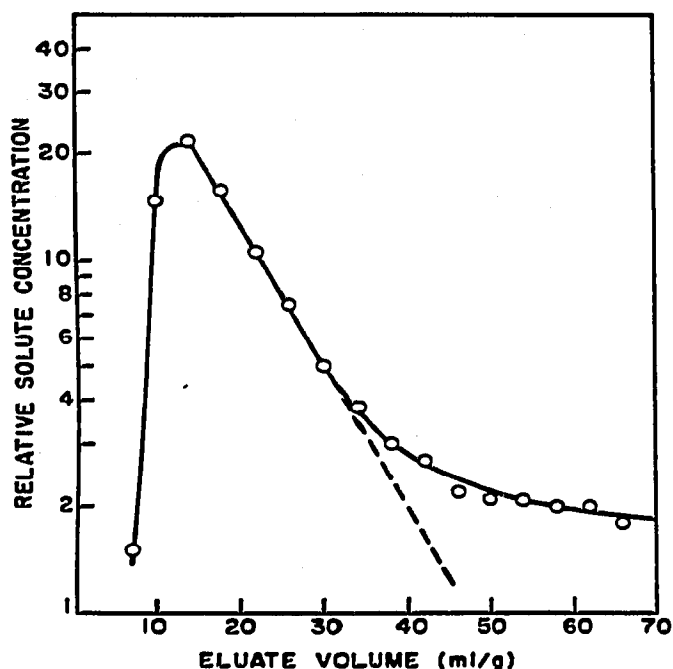


Fig. 1. Elution of dimethyl terephthalate from 3.5% H<sub>2</sub>O-Florisil by methylene chloride;  $2 \cdot 10^{-4}$  g/g column loading.

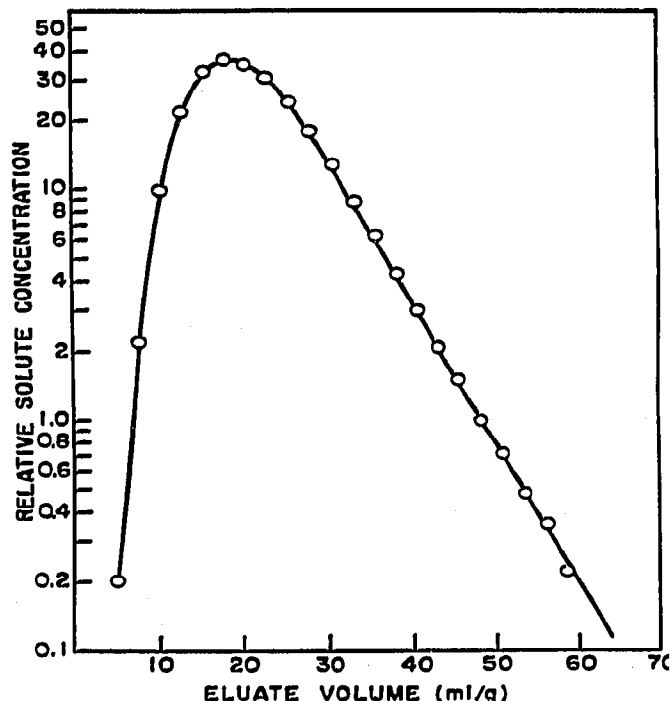


Fig. 2. Elution of dimethyl terephthalate from 16.0% H<sub>2</sub>O-SiO<sub>2</sub> (Davison Code 12) by 40% methylene chloride/pentane;  $1.0 \cdot 10^{-4}$  g/g column loading.

The theoretical problem of calculating a retention volume from bands such as that of Fig. 1 has been discussed previously<sup>4</sup>. The elution band may be regarded as the superposition of a "physically adsorbed" band on top of a "chemisorbed band". The retention volume of the physically adsorbed band may be desired both from the theoretical standpoint for comparison with "normal" retention volumes obtained with non-chemisorbed solutes, and for establishing minimum values of the retention volume for chemisorbable species. The physical adsorption  $\underline{R}^\circ$  value will of course always be less than the chemisorbed  $\underline{R}^\circ$  value. In the latter connection, it should be noted that chemisorption of the *strongest* adsorbing component (or group of components) in a sample does not limit the analytical usefulness of a particular chromatographic system. Extrapolation of the trailing edge of the elution band as in Fig. 1 (dashed line) permits the calculation of the physical adsorption band and the corresponding  $\underline{R}^\circ$  value. An essentially similar procedure was employed for the elution of aniline (chemisorbed) from silica<sup>4</sup>. This procedure has been shown to give  $\underline{R}^\circ$  values equal to the "non-chemisorbed"  $K^\circ$  values as required by theory. As seen in Table II,  $\underline{R}^\circ$  values calculated in this fashion for Florisil are independent of sample size at low column loadings, as required by theory.

#### THE PREDICTION OF LEAC RETENTION VOLUME DATA

Correlational equations were presented in Parts IV<sup>3</sup> and V<sup>4</sup> for the prediction of retention volume values in chromatographic systems using alumina or silica as adsorbent. By combining these separate equations into one general form, it is found that the resulting unified equation describes the retention volume data for Florisil as well. It is convenient to break up the overall expression for predicting retention volume values into smaller equations as follows. First, the dependence of a linear equivalent retention volume  $\underline{R}^\circ$  (ml/g) upon adsorbent surface volume  $V_a$ , adsorbent activity  $\alpha$ , solute adsorption energy  $S^\circ$ , eluent strength  $\varepsilon^\circ$ , and solute area  $A_s$  is given as:

$$\log \underline{R}^\circ = \log V_a + \alpha (S^\circ - \varepsilon^\circ A_s) \quad (1)$$

The solute apparent area  $A_s$  is in turn given as the sum of solute group area contributions  $\delta_i$  and group localization functions  $c_1 L_1 (Q^\circ_i)$ :

$$A_s = \sum^i [\delta_i + c_1 L_1 (Q^\circ_i)] \quad (2)$$

Finally, the solute adsorption energy  $S^\circ$  is related to solute group adsorption factors  $Q^\circ_i$ , for various groups  $i$ , to geometry factors  $q^\circ_j$  for various critical solute geometries  $j$ , to a localization function  $c_2 L_2 (Q^\circ_k)$  characteristic of the single strongest adsorbing group  $k$  in the solute, to the number of atoms or groups  $n$  contained in aromatic ring systems, and to the number of such aromatic ring systems  $r$  not directly connected by aromatic carbon-carbon bonds (*e.g.*,  $r = 2$  in the diphenyl alkanes):

$$S^\circ = \sum^i Q^\circ_i + \sum^j q^\circ_j - c_2 L_2 (Q^\circ_k) \sum^{i \neq k} Q^\circ_i - c_3 (n - 6r) \quad (3)$$

Certain of the above terms have been noted to be zero for alumina or for silica. The overall situation for alumina, silica, and Florisil is summarized in Table III, which

TABLE III  
SUMMARY OF THE FORM OF THE TERMS OF EQUATIONS (1)-(3) WITH  
REFERENCE TO TABULATED VALUES FOR VARIOUS ADSORBENTS\*

Term	Alumina	Silica	Florisil
$V_a, \alpha$	II-2 <sup>a</sup>	V-5 <sup>a</sup>	VI-4 <sup>b</sup> , VI-(Fig. 3)
$\varepsilon^\circ$	III-2, III-(Eqn. 2)	V-7, III-(Eqn. 2)	VI-9
$[\delta_i + c_1 L_1 (Q^\circ_i)]$	III-1 <sup>b</sup>	V-12 <sup>c</sup>	VI-9
$\delta_i$	III-1	III-1	III-1
$c_1 L_1 (Q^\circ_i)$	Zero	14.6 $f(Q^\circ_i)$ <sup>e</sup>	10 $f(Q^\circ_i/1.6)$ <sup>e</sup>
$Q^\circ_i$	IV-1, IV-4, VI-11	V-6 <sup>f</sup>	VI-11, VI-12 <sup>g</sup>
$q^\circ_j$	IV-3, VI-11, II-3 <sup>h</sup> (refs. 15, 16)	VI-11	VI-11
$c_2 L_2 (Q^\circ_k)$	$f(Q^\circ_k)$ <sup>e</sup>	0.4 $f(Q^\circ_k)$ <sup>e</sup>	0.65 $f(Q^\circ_k)$ <sup>e</sup>
$c_3$	Zero	0.11 <sup>i</sup> , 0.14 <sup>j</sup>	Zero

\* Roman numerals refer to the Part number in the present series (Part II = ref. 1; Part III = ref. 2; Part IV = ref. 3; Part V = ref. 4). Arabic numerals refer to the table number in the paper concerned.

<sup>a</sup>  $V_a$  calculable as 0.00035 (surface area in m<sup>2</sup>/g) — 0.01 % H<sub>2</sub>O.

<sup>b</sup>  $\delta_i$  equal  $[\delta_i + c_1 L_1 (Q^\circ_i)]$

<sup>c</sup>  $\delta_i'$  equal  $[\delta_i + c_1 L_1 (Q^\circ_i)]$

<sup>d</sup> To be used only if experimental value of  $[\delta_i + c_1 L_1 (Q^\circ_i)]$  unavailable.

<sup>e</sup>  $f(Q^\circ_k)$  tabulated in IV-2.

<sup>f</sup> and IV-1, where  $(Q^\circ_i)_{sil} \cong (Q^\circ_i)_{alum}$ .

<sup>g</sup> and IV-1, V-6, where  $(Q^\circ_i)_{flor} \cong 1.6 (Q^\circ_i)_{sil} \cong 1.6 (Q^\circ_i)_{alum}$ .

<sup>h</sup>  $q^\circ_j$  values for aliphatic substituents on aromatic ring calculated on different basis than in VI-11.

<sup>i</sup> Small pore diameter gel (22 Å).

<sup>j</sup> Large pore diameter gel (170 Å).

notes the excludable terms in each case, and gives references for the location of the best tabulation of chromatograph parameters for each adsorbent (Roman numerals referring to paper number in present series, Arabic number referring to table number in that paper).

One change in Table III relative to Part V<sup>4</sup> should be noted. In Part V the coefficient  $c_2$  for silica was postulated as zero. It has since been observed that a value of 0.4 for this coefficient significantly improves the accuracy of eqn. (3) in correlating experimental data (average deviation between experimental and calculated  $S^\circ$  values for solutes of Table XVII, Part V, reduced from  $\pm 0.33$  to  $\pm 0.24$  log units). The significance of this change is discussed further in a later section.

As indicated in the experimental section, values of  $V_a$  cannot be tabulated as a function of water content for Florisil because of the variability of the surface area of starting calcined adsorbent. Consequently, the surface area of calcined adsorbent should be measured for each batch of adsorbent in order to calculate  $V_a$ . An analogous situation exists for silica samples, and Part V provides a detailed discussion of both the problem and its solution. For both alumina and silica, it has been possible to calculate the strength  $\varepsilon^\circ$  of binary eluents from the  $\varepsilon^\circ$  values of the constituent solvents. Application of this same equation to some binaries used as eluents with Florisil shows poorer reliability. Consequently, for accurate calculations it is necessary to experimentally determine the  $\varepsilon^\circ$  values of binaries to be used with Florisil, following the procedure outlined in Part III<sup>2</sup>.

As previously, a few examples of the calculation of retention volume using

Florisil as adsorbent will be given. In a first example, consider the elution of the hydrocarbon picene from a 1% H<sub>2</sub>O-Florisil (whose initial calcined surface area was 155 m<sup>2</sup>/g) by benzene. The value of  $V_a$  for this adsorbent may be calculated as 0.044 (*i.e.*,  $0.00035 \times 155 - 0.01$ ). The value of  $\alpha$  is given in Table IV of the present paper (or Fig. 3) as 0.63. The value of  $A_s$  can be calculated from eqn. (2) and Table IX of the present paper as 14 ( $6 + 0.5 \times 16$ ). The eluent parameter  $\varepsilon^\circ$  for benzene is given as 0.28 from Table IX. Substituting these values into eqn. (1):

$$\log \underline{R}^\circ = \log 0.044 + 0.63 (S^\circ - 0.28 \times 14)$$

Now  $S^\circ$  must be calculated.  $Q_i^\circ$  for an aromatic carbon atom is 0.28 (Table XII), there are no  $q_j^\circ$  terms for the unsubstituted aromatic hydrocarbons, the strongest adsorbing group K is the aromatic carbon atom so ( $Q_i^\circ/1.6$ ) is 0.17, and  $f(0.17)$  from Table II of Part IV<sup>3</sup> is zero, and  $c_3$  for Florisil is zero (Table III). Thus, from eqn. (3):

$$\begin{aligned} S^\circ &= (14 \times 0.28) + 0 - 0 - 0 \\ &= 6.16 \end{aligned}$$

Substituting the value 6.16 for  $S^\circ$  in the above expression for  $\underline{R}^\circ$ , it is calculated that  $\log \underline{R}^\circ$  equals 0.05. The experimental value was 0.16.

In a second example, we have the elution of methyl *m*-nitrobenzoate from a 3.5% H<sub>2</sub>O-Florisil (initial calcined surface area equal 247 m<sup>2</sup>/g) by methylene chloride.  $V_a$  is calculated as 0.051 ( $0.00035 \times 247 - 0.035$ ), and  $\alpha$  is 0.51 (Table IV or Fig. 3).  $A_s$  is calculable from eqn. (2) and Table IX as 17.0 ( $6 \times 1 + 6.0 + 5.0$ ).  $\varepsilon^\circ$  for methylene chloride is 0.37, from Table IX. Substituting these values into eqn. (1):

$$\log \underline{R}^\circ = \log 0.051 \pm 0.51 (S^\circ - 0.37 \times 17)$$

In the calculation of  $S^\circ$ , there are 6 aromatic carbon atoms, 1 aromatic nitro group, and one aromatic ester group with respective  $Q_i^\circ$  values of 0.28, 4.88, and 5.47 (Table XII), no important geometry factors exist for this solute, the strongest adsorbing group K is the ester group so  $f(5.47/1.6)$  is given as 0.41 from Table II in Part IV<sup>3</sup>, and again  $c_3$  is zero. Inserting these values into eqn. (3):

$$\begin{aligned} S^\circ &= (6 \times 0.28 + 4.88 + 5.47) + 0 - 0.65 \times 0.41 \times (1.68 + 4.88) - 0 \\ &= 10.28 \end{aligned}$$

Inserting this value of  $S^\circ$  into the previous expression for  $\log \underline{R}^\circ$  gives a value of  $\log \underline{R}^\circ$  equal 0.74. The experimental value was 0.94.

In a final example, consider the elution of indole from the same 1% H<sub>2</sub>O-Florisil of example one by 15% methylene chloride-pentane. The  $V_a$  and  $\alpha$  values have already been obtained,  $A_s$  is calculable as previously ( $6 \times 1 + 2 \times 0.5 + 10.4 = 17.4$ ), and an experimental value of  $\varepsilon^\circ$  for this eluent and 1% H<sub>2</sub>O-Florisil has been measured (0.123). Thus, from eqn. (1):

$$\log \underline{R}^\circ = \log 0.044 + 0.63 S^\circ - (0.123 \times 17.4)$$

To calculate  $S^\circ$ , the 8 aromatic carbon atoms have  $Q_i^\circ$  values of 0.28 and the nitrogen

group has a  $Q^\circ_i$  value of 4.84, there are no  $q^\circ_j$  terms, and the strongest adsorbing group K is the  $-\text{NH}-$  group.  $f(4.84/1.6)$  is 0.34, and  $c_3$  is zero, so:

$$\begin{aligned} S^\circ &= (3 \times 0.28 + 4.84) + 0 - 0.65 \times 0.34 \times 0.56 - 0 \\ &= 6.96 \end{aligned}$$

Substituting into the above expression the calculated value of  $\log R^\circ$  is 0.89. The experimental value was 0.96.

If an experimental value of  $\alpha\varepsilon^\circ$  had been unavailable, the  $\varepsilon^\circ$  values of pentane (0.00) and methylene chloride (0.37) could have been used to estimate an  $\alpha\varepsilon^\circ$  value according to eqn. (2) of Part III<sup>2</sup>. This calculated  $\alpha\varepsilon^\circ$  value (0.099) is sufficiently in error to give a distinctly poorer final value of  $\log R^\circ$  (1.24).

#### THE ROLE OF ADSORBENT ACTIVITY AND SURFACE VOLUME

The effect of adsorbent activity  $\alpha$  and surface volume  $V_a$  on retention volume is given in eqn. (1), which has been previously verified for alumina<sup>1</sup> and silica<sup>4</sup>. Assuming the applicability of eqn. (1) to Florisil as adsorbent, values of  $V_a$  can be calculated from BET surface area data and the amount of water added to calcined adsorbent as in Part V<sup>4</sup> (eqn. 3). Values of  $\alpha$  for given adsorbent samples can in turn be calculated from  $R^\circ$  values for a standard solute and eluent (naphthalene-pentane in previous work) if the value of  $\alpha$  for calcined adsorbent is defined as 1.00. Fig. 3 and Table IV

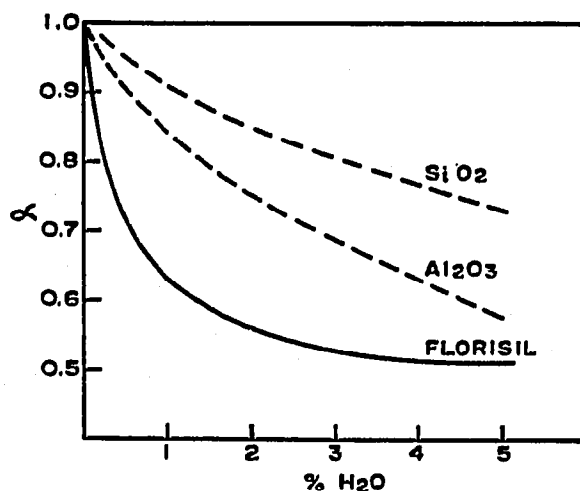


Fig. 3. Adsorbent activity functions  $\alpha$  for Florisil, alumina, and silica *versus* percent added water.

summarize values of  $\alpha$  for the two Florisil samples studied in the present investigation, using both naphthalene and fluoranthene as standard solutes, and pentane as standard eluent. The abrupt initial decline in  $\alpha$  with added water is believed to result from the Florisil strong acid sites, which are preferentially covered by the first 1% or so of added water. Fig. 3 contrasts the behavior of Florisil in this regard with the adsorbents alumina and silica (dashed lines).

Table V summarizes data on a number of chromatographic systems designed to test the applicability of eqn. (1) to Florisil as adsorbent. Values of  $V_a$  and  $\alpha$  were

TABLE IV  
 ADSORBENT PARAMETERS FOR PRESENT TWO FLORISIL SAMPLES

Sample		$\alpha$	$V_a$
No. 1	Calcined	1.00	0.054
	1 % H <sub>2</sub> O	0.63	0.044
	5 % H <sub>2</sub> O	0.52	0.013*
No. 2	Calcined	1.00	0.086
	0.5 % H <sub>2</sub> O	0.73	0.081
	1.0 % H <sub>2</sub> O	0.62	0.076
	3.5 % H <sub>2</sub> O	0.51	0.051
	7.0 % H <sub>2</sub> O	0.50	0.022*

\* Chromatographically evaluated<sup>1,4</sup> since surface coverage by water is near complete<sup>4</sup>.

TABLE V  
 TEST OF EQUATION (1) FOR FLORISIL AS ADSORBENT;  
 FLORISIL SAMPLE NO. 2 USED

Chromatographic system	$\log R^0$					$(S^0 - 6^0 A_2)$
	0 % H <sub>2</sub> O	0.5 % H <sub>2</sub> O	1.0 % H <sub>2</sub> O	3.5 % H <sub>2</sub> O	7.0 % H <sub>2</sub> O	
Benzene-pentane						
(Exptl.)	0.62	0.27	—0.05	—0.40		1.75
(Calc.)	0.68	0.19	—0.04	—0.40		
Naphthalene-pentane						
(Exptl.)	1.77	1.00	0.64	0.17	0.16	2.86
(Calc.)	1.79	1.00	0.65	0.17	0.23	
Fluoranthene-pentane						
(Exptl.)		2.19	1.69	1.06	0.60	4.60
(Calc.)		2.29	1.73	1.06	0.64	
Perylene-pentane						
(Exptl.)			2.26	1.65	1.20	5.76
(Calc.)			2.45	1.65	1.22	
<i>p</i> -Xylene-pentane						
(Exptl.)	1.63	0.91	0.17	0.30		1.94
(Calc.)	0.87	0.33	0.08	0.30		
Phenyl ethyl sulfide-pentane						
(Exptl.)		1.52	1.26	0.76	0.39	4.02
(Calc.)		1.84	1.37	0.76	0.35	
Picene-benzene						
(Exptl.)	0.45	0.41	0.26	—0.01	—0.24	2.51
(Calc.)	1.44	0.74	0.44	—0.01	—0.41	
1-Nitronaphthalene-benzene						
(Exptl.)			1.16	0.40	—0.02	3.31
(Calc.)			0.93	0.40	—0.01	
<i>o</i> -Nitroaniline-benzene						
(Exptl.)		1.96	1.80	1.15	0.73	4.78
(Calc.)		2.40	1.84	1.15	0.73	
Acetophenone-methylene chloride						
(Exptl.)			1.20	0.42	0.06	3.35
(Calc.)			0.96	0.42	0.12	
$\alpha^*$	1.00	0.73	0.62	0.51	0.50	
$V_a^*$	0.086	0.081	0.076	0.051	0.022	

\* Data of Table IV.



evaluated as above. Values of  $(S^\circ - \varepsilon^\circ A_s)$  for each system were calculated from the  $R^\circ$  value for elution from 3.5 % H<sub>2</sub>O-Florisil, and values of  $R^\circ$  for other adsorbent activities derived from this value of  $(S^\circ - \varepsilon^\circ A_s)$  and eqn. (1). It is apparent that the calculated and derived  $R^\circ$  values are not in good agreement. The overall average deviation is  $\pm 0.13$  log units, and several values disagree by more than 0.5 log units. If the data are divided into two sets, one including data for calcined and 0.5 % H<sub>2</sub>O-Florisil, and the other set including the remaining data for Florisil deactivated by one or more percent water, the data for the less deactivated adsorbent samples show an average deviation between experimental and calculated  $R^\circ$  values equal to  $\pm 0.33$  log units, while the more highly deactivated adsorbents show a corresponding average deviation of only  $\pm 0.06$  log units. It may be concluded that eqn. (1) is unreliable for Florisil samples containing less than 1 % added water, but that data for other adsorbent activities are correlated with reasonable accuracy. The reason for the failure of eqn. (1) in the present connection is not difficult to discover. The fundamental basis of eqn. (1) has been discussed elsewhere<sup>1,16</sup>. Briefly, eqn. (1) assumes adsorption sites of continuously varying energy and basically similar character. That is, eqn. (1) would not be expected to apply when the strong sites on an adsorbent surface are of fundamentally different character (*e.g.*, involving bonding of varying type, as electrostatic polarization in one case, charge transfer in another, or covalent bonding in a third case). Evidence has already been presented, however, to indicate that precisely this situation characterizes the Florisil surface; that is, coverage by strong (acid) sites which are fundamentally different from the "normal" sites (which presumably form simple electrostatic polarization bonds with the solute<sup>16</sup>). Fig. 3 suggests that the strong acid sites are largely covered up after the addition of 1 % water to calcined Florisil, with the remaining surface being more nearly "normal" by comparison with the surfaces of alumina and silica. The applicability of eqn. (1) to moderately deactivated Florisil samples similarly suggests that the removal of acid sites by the first 1 % added water leaves a "normal" adsorbent surface.

The failure of eqn. (1) to apply to calcined and lightly deactivated Florisil does not necessarily limit the usefulness of calcined adsorbent. The separation possibilities with calcined Florisil are in fact actually expanded over the case where eqn. (1) is applicable to an adsorbent. Thus, in "normal" chromatographic systems such as those using alumina, silica, and moderately deactivated Florisil, separation order is not a function of adsorbent activity, and in general separation will be unimproved by changes in activity so long as the necessary cut points occur at reasonably large eluate volumes (greater than 1 ml/g). Failure to obtain a desired separation using deactivated Florisil, however, may well be overcome on changing to calcined or near calcined adsorbent. Unfortunately, the data of Table V offer no obvious clues as to when such a change will be advantageous.

#### THE ROLE OF THE ELUENT

Retention volume data are presented in Tables VI and VII for the elution of a number of hydrocarbons from Florisil samples of varying activity and from both of the batches described in Table I, by several eluents. The assumption that  $A_s$  is given as  $6 + \frac{1}{2}(n - 6)$ , as for elution from alumina and silica, gives an excellent fit of these data to eqn. (1),  $\pm 0.05$  log units, when the indicated values of  $S^\circ$  for each solute and

TABLE VI  
EFFECT OF ELUENT ON ELUTION OF AROMATIC HYDROCARBONS FROM FLORISIL  
(SAMPLE NO. 1)

Solute	Water on adsorbent $\alpha^*$ $V_a^*$	$\log R^o$								$S^o$
		0.0%		1.0%		5%		5%		
		$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	
Eluent**	P	P	5% M-P	15% M-P	50% M-P	10% B-P	25% B-P	B	P	
		0.000	0.000	0.066	0.123	0.195	0.094	0.132	0.177	0.000
Benzene	(Exptl.)	0.17	—0.11							1.71
	(Calc.)	0.44	—0.28							
Naphthalene	(Exptl.)	1.59	0.46						—0.51	2.88
	(Calc.)	1.61	0.45						—0.39	
Acenaphthylene	(Exptl.)		0.78	0.19						3.39
	(Calc.)		0.78	0.19						
Phenanthrene	(Exptl.)		1.11	0.45			0.10		0.13	3.88
	(Calc.)		1.08	0.42			0.17		0.13	
Fluoranthene	(Exptl.)		1.40	0.70	0.04		0.34			4.47
	(Calc.)		1.45	0.72	0.10		0.43			
1,2-Benzanthracene	(Exptl.)		1.78	0.94	0.22		0.46	0.06	0.63	4.83
	(Calc.)		1.68	0.89	0.20		0.55	0.10	0.63	
Perylene	(Exptl.)			1.18	0.51		0.87	0.26		5.40
	(Calc.)			1.18	0.44		0.82	0.32		
Picene	(Exptl.)			1.69	0.89	—0.02	1.53	1.07	0.16	6.46
	(Calc.)			1.79	0.99	—0.02	1.39	0.86	0.23	

\* Data of Table IV.

\*\* Symbols defined as follows: P, pentane; B, benzene; M, methylene chloride.

TABLE VII  
EFFECT OF ELUENT ON ELUTION OF AROMATIC HYDROCARBONS FROM FLORISIL  
(SAMPLE NO. 2)

Solute	Water on adsorbent $\alpha^*$ $V_a^*$	$\log R^o$				$S^o$
		3.5%				
		$\alpha^o$	$\alpha^o$	$\alpha^o$	$\alpha^o$	
Eluent**	P	10% M-P	20% M-P	30% M-P		
		0.000	0.059	0.097	0.127	
Naphthalene	(Exptl.)	0.17				2.88
	(Calc.)	0.18				
Phenanthrene	(Exptl.)	0.68				3.88
	(Calc.)	0.69				
1,2-Benzanthracene	(Exptl.)	1.25	0.46	0.01	—0.41	4.83
	(Calc.)	1.17	0.46	0.01	—0.35	
Picene	(Exptl.)		1.18	0.67	0.29	6.46
	(Calc.)		1.18	0.64	0.22	

\* Data of Table IV.

\*\* Symbols defined as follows: P, pentane; M, methylene chloride.

TABLE VIII  
EFFECT OF ELUENT ON ELUTION OF NON-HYDROCARBONS FROM FLORISIL

Solute	Water on adsorbent Sample $\alpha^*$ $V_a^*$	$\log R^b$												$S^\circ$	
		P	5% M	15% M	50% M	10% B	10% B	M	B	10% M	20% M	30% M	B		M
Phenyl ethyl sulfide	(Exptl.)	8.5	0.41	0.05	0.15	0.15	0.177	0.233	0.146	0.059	0.097	0.127	0.143	0.188	3.78
	(Calc.)	(8.5)	1.02	-0.02	0.22	0.094	0.177	0.233	0.146	0.059	0.097	0.127	0.143	0.188	
Phenetole	(Exptl.)	10.3	0.82	0.41	0.57	0.57	-0.50	0.43	0.06	0.06	0.06	-0.17	0.43	0.06	4.59
	(Calc.)	(10.3)	1.53	0.26	0.56	0.56	-0.27	0.44	0.05	0.05	0.05	-0.26	0.44	0.05	
Nitrobenzene	(Exptl.)	12.0	1.52	0.74	0.76	0.76	0.16	0.16	-0.41	1.28	0.87	0.59	0.19	-0.43	6.59
	(Calc.)	(12.0)	1.31	0.45	0.67	0.67	-0.01	-0.21	1.36	0.91	0.55	0.35	0.18	-0.18	
Methyl benzoate	(Exptl.)	11.0	1.23	1.01	1.30	1.30	0.72	0.72	0.12	1.68	1.01	0.73	0.12	0.12	7.18
	(Calc.)	11.0	1.01	1.01	1.22	1.22	0.60	0.60	0.23	1.72	0.97	0.80	0.30	0.30	
Acetophenone	(Exptl.)	14.2	0.17	2.16	1.77	1.77	1.46	1.06	0.42	8.57	0.42	0.41	0.42	8.57	7.58
	(Calc.)	14.2	0.50	2.24	1.70	1.70	1.28	1.05	0.41	0.41	0.41	0.41	0.41	0.41	
<i>p</i> -Diethoxybenzene	(Exptl.)	14.2	-0.23	0.85	-0.23	-0.23	0.85	0.85	1.65	1.65	1.65	1.65	1.65	10.02	10.02
	(Calc.)	14.6	-0.08	0.76	-0.08	-0.08	0.76	0.76	1.53	1.53	1.53	1.53	1.53	0.44	
<i>m</i> -Dinitrobenzene	(Exptl.)	17.4	0.96	1.34	1.34	1.34	-0.08	1.34	-0.08	6.96	6.96	6.96	6.96	6.96	6.96
	(Calc.)	18.0	0.89	1.40	1.40	1.40	-0.05	1.40	-0.05	6.96	6.96	6.96	6.96	6.96	
Indole	(Exptl.)	17.7	0.96	1.34	1.34	1.34	-0.08	1.34	-0.08	6.96	6.96	6.96	6.96	6.96	6.96
	(Calc.)	17.7	0.89	1.40	1.40	1.40	-0.05	1.40	-0.05	6.96	6.96	6.96	6.96	6.96	

\* Data of Table IV.

\*\* Symbols defined as follows: P, pentane; B, benzene; M, methylene chloride; % M, % B refer to M/P and B/P binaries; % refers to volume percent

for each eluent are assumed. The behavior of the eluent in the elution of hydrocarbons from all three of the adsorbents so far studied is therefore essentially identical, and eqn. (1) applies without comment.

The evaluation of  $\alpha\epsilon^\circ$  for the eluent-adsorbent combinations of Tables VI and VII from these hydrocarbon  $\bar{R}^\circ$  data permits in turn the evaluation of  $A_s$  values for the non-hydrocarbons, as was done in the case of silica (Part V)<sup>4</sup>. In Table VIII, data for the elution of several non-hydrocarbons from various Florisil samples by several eluents are summarized. The  $\alpha\epsilon^\circ$  values of the eluent systems described in Tables VI and VII are taken from those tables. The other values of  $\alpha\epsilon^\circ$  are the averages of extrapolating  $\log \bar{R}^\circ$  values *versus*  $\alpha\epsilon^\circ$  from known to unknown eluents. Finally, the experimental values of  $A_s$  shown are the best (least squares) fit to all of the data for a given solute.

The best experimental values of  $A_s$  for the monosubstituted benzenes were used to calculate values of  $[\delta_i + c_1 L_1(Q^\circ_i)]$  for each substituent group (equal  $A_s$  — 6), and the values of  $A_s$  for the polysubstituted benzenes then calculated as the sum of group contributions. The overall agreement between experimental and calculated  $\bar{R}^\circ$  values, using these resulting  $A_s$  values, was  $\pm 0.11$  log units, which is reasonable agreement. As in the case of elution from silica, it is apparent that the non-hydrocarbon  $A_s$  values are considerably larger than would have been expected from their actual areas ( $\sum \delta_i$ ), and that the  $c_1 L_1(Q^\circ_i)$  term of eqn. (2) is non-zero for Florisil. In this respect, Florisil resembles silica rather than alumina. Table IX summarizes

TABLE IX  
SOLUTE GROUP APPARENT AREAS ON FLORISIL

Group	$[\delta_i + c_1 L_1(Q^\circ_i)]$	
	Exptl.	Calc.*
-CH=	0.5-1.0**	0.5-1.0**
-SR	2.5	2.7
-OR	4.3	3.3
-NO <sub>2</sub>	6.0	6.1
-CO <sub>2</sub> R	5.0	7.1
-COR	8.2	6.5
-NH-	10.4	(4.0)

\*  $\delta_i + 10 f(Q^\circ_i/1.6)$ .

\*\* See ref. 2.

*Eluent parameter values*

Solvent	$s^\circ$		
	Florisil	Alumina	Silica
Pentane	0.00	0.00	0.00
Carbon tetrachloride*	0.07	0.18	0.14
Benzene	0.28	0.32	0.25
Chloroform*	0.31	0.40	—
Methylene chloride	0.37	0.42	0.32
Di-ethyl ether*	0.49	0.46	—

\* Florisil values based on limited unreported data.

experimental values of  $[\delta_i + c_1 L_1 (Q^\circ_i)]$  for the various solute groups of Tables VI-VIII. With the exception of the  $-\text{NH}-$  group, which differs from the other strong groups in forming part of an aromatic ring, these apparent group area values are well represented by the relationship:

$$\text{Group area} = \delta_i + 10 f(Q^\circ_i/1.6) \quad (4)$$

$f(x)$  refers to the localization function previously defined for alumina in Part IV<sup>3</sup>. The form of this latter expression, specifically the factor 1/1.6, will be rationalized in the following section.

Eluent strength values  $\varepsilon^\circ$  for the three solvents presently studied, as well as values from limited unreported data on other solvents, are also summarized in Table IX. Comparison with corresponding  $\varepsilon^\circ$  values for alumina and silica shows reasonable agreement.

#### THE ROLE OF SOLUTE STRUCTURE

The preceding discussion and data provide a basis for evaluating experimental  $S^\circ$  values and hence arriving at the dependency of solute  $R^\circ$  values on solute structure, as in Part V<sup>4</sup>. The relationship between  $R^\circ$  values and molecular structure for unsubstituted aromatic hydrocarbons has been shown to be of one form (linear) with alumina<sup>1,15</sup> and another (non-linear) with silica<sup>4,17</sup>. This behavior has been related to the way strong sites are distributed on the adsorbent surface<sup>17</sup>. In the case of alumina, it is believed that the strongest sites are randomly distributed, while for silica it appears that the strongest sites occur in clumps roughly the size ( $40 \text{ \AA}^2$ ) of a benzene molecule. This grouping of sites on silica gives rise to the  $c_2(n - 6r)$  term of eqn. (3).  $S^\circ$  values for the elution of various unsubstituted aromatic hydrocarbons from Florisil have been derived from the data of Tables VI and VII, and tabulated therein. These  $S^\circ$  values are plotted *versus* carbon number  $n$  in Figure 4. It is evident

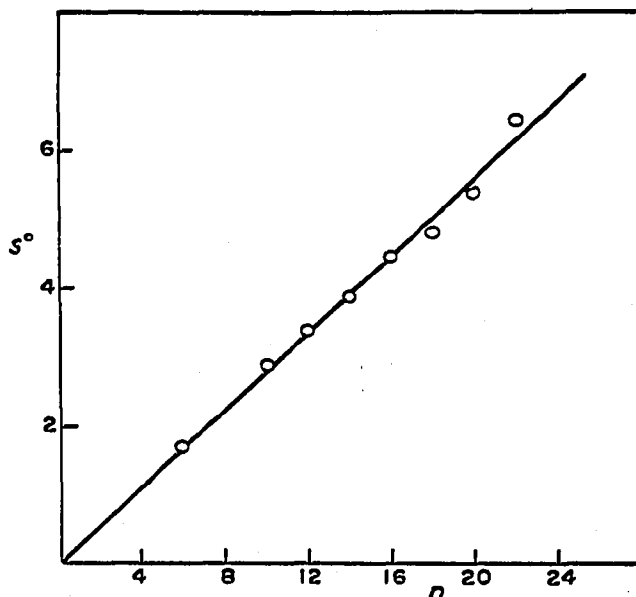


Fig. 4. Dependence of  $S^\circ$  on carbon number for unsubstituted aromatic hydrocarbons; Florisil adsorbent.

that these Florisil  $S^\circ$  values are linear in  $n$  for  $n \leq 22$ , and Florisil resembles alumina rather than silica in this respect. Consequently, the term  $c_2(n - 6r)$  may be neglected in the correlation and prediction of Florisil  $R^\circ$  values.

The effect of alkyl substitution on the  $R^\circ$  values of the aromatic hydrocarbons eluted from Florisil is summarized in Tables X and XI. The experimental  $R^\circ$  data

TABLE X  
RETENTION VOLUMES OF THE ALKYL-SUBSTITUTED BENZENES; PENTANE ELUTION FROM  
1.0% H<sub>2</sub>O-FLORISIL (SAMPLE NO. 2)

Solute	log $R^\circ$	
	Exptl.	Calc.*
Benzene	-0.05	-0.05
Toluene	+0.03	+0.05
Ethylbenzene	+0.02	+0.04
<i>n</i> -Butylbenzene	+0.04	+0.05
<i>n</i> -Dodecylbenzene	+0.10	+0.10
<i>o</i> -Xylene	+0.26	+0.25
<i>p</i> -Xylene	+0.17	+0.15
<i>o</i> -Diethylbenzene	+0.26	+0.23
<i>p</i> -Diethylbenzene	+0.17	+0.13
Pentamethylbenzene	+0.94	+0.96
Hexamethylbenzene	+1.17	+1.16
Tetralin	+0.42	+0.42

\* Using parameters of Table XI.

of Table X for various alkyl-substituted benzenes were used to derive the Florisil  $Q^\circ_t$  and  $q^\circ_j$  values of Table XI for alkyl substituent groups and geometries. These values were then used in the calculation of the  $R^\circ$  data of Table X, assuming the value for benzene. The average deviation between experimental and calculated values of log  $R^\circ$  is only  $\pm 0.02$  units. The Florisil alkyl substitution parameters of Table XI are also compared with corresponding alumina and silica values from Parts II<sup>1</sup> and V<sup>4</sup>. The  $Q^\circ_t$  values for Florisil are in the same order as for alumina, but smaller. The various Florisil geometry effects ( $q^\circ_j$  values) parallel those for alumina and silica, and tend to be 2-3 times larger.

Table XII summarizes the Florisil  $Q^\circ_t$  values for the various solute groups so

TABLE XI  
HYDROCARBON SOLUTE PARAMETERS FOR FLORISIL, ALUMINA, AND SILICA

Parameter	Florisil	Alumina	Silica
$Q^\circ_t$ , -CH <sub>2</sub> - (alkyl)	+0.013	+0.02	-0.05
$Q^\circ_t$ , -CH <sub>2</sub> - (aromatic)	+0.16	+0.07	+0.01
$Q^\circ_t$ , -CH <sub>3</sub> (alkyl)	-0.02	-0.03	+0.05
$Q^\circ_t$ , -CH <sub>3</sub> (aromatic)	+0.16	+0.06	+0.11
<i>Ortho</i> alkyl substitution	+0.16	+0.09	+0.09
<i>Cyclo</i> alkyl ring closure	+0.24	+0.08	+0.14

TABLE XII  
SOLUTE GROUP ADSORPTION FACTORS ( $Q^{\circ}_i$ ) ON FLORISIL

Group	$Q^{\circ}_i$			
	Florasil		Silica <sup>a</sup>	1% H <sub>2</sub> O-Florasil
	Exptl.	Calc.*		
-CH=	0.28	0.4	0.25	0.18
Ar)-SR	2.07	2.1	1.29	1.30
Ar)-OR	2.88	2.9	1.83	1.81
Ar)-NO <sub>2</sub>	4.88	4.4	2.77	3.07
Ar)-CO <sub>2</sub> R	5.47	5.6	3.45	3.45
Ar)-COR	6.86	7.5	4.69	4.32
Ar)-NH-(Ar	4.84	4.8	3.00	3.05
R)-CH <sub>2</sub> -(R	0.013			

\* 1.6 ( $Q^{\circ}_i$ )<sub>sil</sub>.

far studied. These are definitely larger than the corresponding alumina or silica values. The relationship:

$$(Q^{\circ}_i)_{\text{flor}} = 1.6 (Q^{\circ}_i)_{\text{sil}}$$

gives a good fit of the Florasil values (average deviation,  $\pm 0.2$  units), with only the aromatic carbon group showing a relatively poor calculated value. This suggests that the surface energy of calcined silica is comparable to a Florasil surface with  $\alpha$  equal to  $1/1.6$  or  $0.63$ . This corresponds to a 1% H<sub>2</sub>O-Florasil sample, and it is tempting to relate this observation to our preceding remarks on the coverage of strong acid sites by the first 1% of added water in the case of starting calcined Florasil. Thus, the calcined Florasil surface may be regarded (in one sense) as a calcined silica surface on which are superimposed strong acid sites. This is perhaps not unreasonable when it is recalled that Florasil is largely silica. The strong sites are for the most part covered by

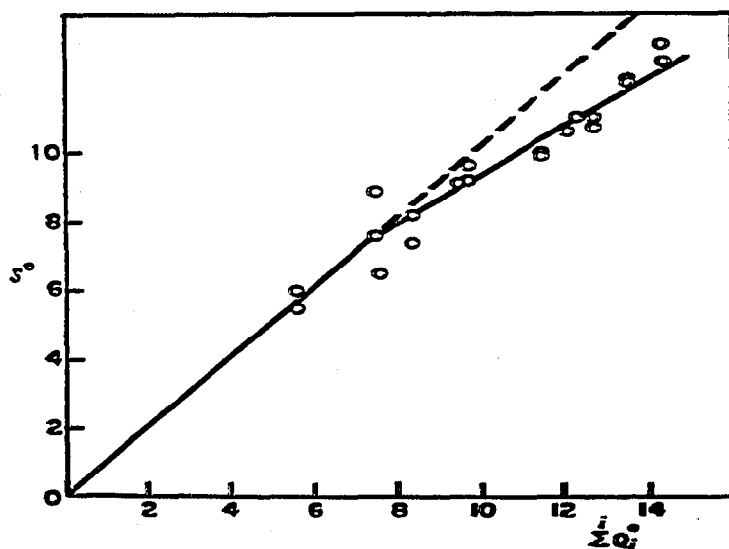


Fig. 5. Localization as a factor in determining the  $S^{\circ}$  values of strongly adsorbed solutes; Florasil adsorbent.

the first 1% added water, leaving essentially a calcined silica surface. This view of the Florisil surface must of course represent only a crude approximation.)

Table XIII summarizes experimental Florisil  $S^\circ$  values for a range of solutes,  $R^\circ$  for most of which have been given in preceding tables. In Fig. 5 these  $S^\circ$  values are plotted *versus* the sum of solute group adsorption factors  $\sum_i Q_i^\circ$ . This provides a test for localization of the solute, as in the case of alumina<sup>3</sup>. As seen in Fig. 5, the experimental plot breaks rather definitely at  $S^\circ \approx 8$ , indicating the necessity of including the  $c_2 L_2 (Q_i^\circ) \sum_{i \neq k} Q_i^\circ$  term of eqn. (3) in calculations for Florisil.

Fig. 5, which should be compared to Fig. 9 and 10 of Part V<sup>4</sup> (and related discussion), confirms the importance of localization and its effect on  $S^\circ$  for Florisil as adsorbent. The  $c_2 L_2 (Q_i^\circ)$  term for Florisil is therefore non-zero. This Florisil term is well approximated by the relationship:

$$c_2 L_2 (Q_i^\circ) = 0.65 f (Q_i^\circ / 1.6) \quad (5)$$

where  $f(x)$  is the same functional relationship defined for alumina<sup>3</sup>. The differing form of the above relationship ( $c_2 \neq 1$ ,  $1/1.6$  factor), which should be compared with eqn. (4), is logical if we recall our above remarks on the larger  $Q_i^\circ$  values for Florisil relative to silica. Thus, the localization function should be related to the energy of adsorption sites, and should assume similar values when adsorbent surfaces of similar energies (*e.g.*, silica and alumina) are involved. Since 1% H<sub>2</sub>O-Florisil is comparable in this respect to calcined alumina and silica, the localization function  $f(x)$  should be defined relative to  $Q_i^\circ$  values defined for this Florisil activity (set  $\alpha$  equal 1.00 for 1.0% H<sub>2</sub>O-Florisil). This is equivalent to dividing the actual  $Q_i^\circ$  values (defined relative to calcined Florisil) by 1.6 as in eqn. (4) and (5). The  $c_2$  value of 0.65 for 1.0% H<sub>2</sub>O-Florisil appears consistent with the resemblance of Florisil to both alumina ( $c_2 = 1.00$ ) and silica ( $c_2 = 0.40$ ) in other respects, and hence is intermediate between the other two adsorbents.

The adequacy of the localization term of eqn. (5) is tested in Table XIII by comparing experimental and calculated  $S^\circ$  values. The latter are simply  $[\sum_i Q_i^\circ - f(Q_i^\circ / 1.6) \sum_{i \neq k} Q_i^\circ]$ . The average deviation is  $\pm 0.4$  units, which is reasonable when it is noted that the  $q_j$  terms involved in isomer  $S^\circ$  values have been ignored, and the experimental variation in isomer  $S^\circ$  values is  $\pm 0.3$  units.

#### COMPARISON OF FLORISIL, ALUMINA, AND SILICA AS CHROMATOGRAPHIC ADSORBENTS

With the completion of the present experimental study, it is appropriate to compare the separation capabilities of the three adsorbents so far investigated. This is conveniently done by reviewing the dependence upon adsorbent type of each of the terms in eqns. (1-3). The adsorbent parameters  $V_a$  and  $\alpha$  measure the effect of water content on the separation characteristics of the adsorbent. Since the separation sequence of a group of solutes is determined solely by the  $(S^\circ - \epsilon^\circ A_s)$  term of eqn. (1), it is apparent that changes in  $V_a$  or in  $\alpha$  cannot be relied on to separate solute pairs having the same  $R^\circ$  values at one adsorbent activity. The ex-



TABLE XIII  
 SOLUTE  $S^\circ$  FACTORS FOR ELUTION FROM FLORISIL

Solute	System*	$\log R^\circ$	$S^\circ$		
			<i>Exptl.</i>	<i>Calc.**</i>	$\sum Q^\circ_i$
<i>p</i> -Diethoxybenzene	A	—	7.6	7.2	7.4
<i>o</i> -Diethoxybenzene	B	1.39	8.9	7.2	7.4
1-Methoxynaphthalene	C	0.34	5.5	5.6	5.7
2-Methoxynaphthalene	C	0.69	6.0	5.6	5.7
<i>m</i> -Dinitrobenzene	A	—	10.0	10.3	11.4
<i>p</i> -Dinitrobenzene	D	0.38	9.9	10.3	11.4
<i>p</i> -Nitroanisole	D	0.20	9.1	8.8	9.4
2,4-Dinitroanisole	D	1.00	12.6	12.6	14.4
2,4-Dimethoxynitrobenzene	D	0.58	11.0	11.0	12.3
1-Nitronaphthalene	C	0.67	6.5	7.4	7.7
Dimethyl terephthalate	D	1.17	10.7	11.2	12.6
Dimethyl phthalate	D	1.32	11.0	11.2	12.6
Methyl <i>m</i> -nitrobenzoate	D	0.94	10.7	10.8	12.0
Methyl 1-naphthoate	E	0.60	7.4	8.0	8.4
Methyl 2-naphthoate	E	1.03	8.2	8.0	8.4
1-Acetonaphthone	E	1.15	9.3	9.3	9.7
2-Acetonaphthone	E	1.45	9.9	9.3	9.7
2,5-Dimethoxyacetophenone	D	1.26	13.1	12.6	14.3
<i>m</i> -Nitroacetophenone	D	1.06	12.1	12.0	13.4
<i>p</i> -Nitroacetophenone	D	1.05	12.0	12.0	13.4

\* A: See Table VIII; B: 30% v methylene chloride-pentane; 3.5% H<sub>2</sub>O-Florisil (No. 2); C: 20% v methylene chloride-pentane; 3.5% H<sub>2</sub>O-Florisil (No. 2); D: Methylene chloride; 3.5% H<sub>2</sub>O-Florisil (No. 2); E: Benzene; 3.5% H<sub>2</sub>O-Florisil (No. 2).

$$** \sum Q^\circ_i = 0.65 f(Q^\circ_k/1.6) \sum Q^\circ_i.$$

ception in the case of 0-1% H<sub>2</sub>O-Florisil has already been noted. Assuming that the ( $S^\circ - \epsilon^\circ A_s$ ) terms for two solutes differ, however, both  $V_a$  and  $\alpha$  can play a role in the relative separability of the solute pair. In general, the larger is  $\alpha$  the larger will be the retention volume ratio for the two solutes, and the better the separation. This consideration must be weighed against possible reduced linear capacity in more active adsorbents<sup>5, 18</sup>, and inconveniently large cut point volumes in the separation. Both alumina and silica have comparable ranges in  $\alpha$  (1.0-0.6) achievable by varying water content, but the larger linear capacity of calcined large surface area silica samples<sup>5</sup> somewhat increases their *practical* range in  $\alpha$  values. Florisil, on the other hand, because of the necessity of deactivating with one or more percent of added water, has a very small range (0.63-0.50) in possible  $\alpha$  values.

Differences in adsorbent  $V_a$  values play a more important role in determining the potential separation of certain mixtures, notably those of weakly adsorbing solutes. In this case, the various ( $S^\circ - \epsilon^\circ A_s$ ) values may be sufficiently small, although differing appreciably in value, to make the resulting  $R^\circ$  values all less than or equal unity, even for the largest  $\alpha$  values. In general, solute mixtures where  $R \leq 1$  for all solutes cannot readily be separated. If the ( $S^\circ - \epsilon^\circ A_s$ ) terms for each solute in such a mixture are comparable between adsorbents, and if the maximum  $\alpha$  values possible for each adsorbent are similar, then the  $V_a$  terms will control the "goodness"

of separation, the larger  $V_a$  value giving the better separation (or the only separation). An example is provided by the separation of aliphatic mono-olefins from saturated hydrocarbons. Only large surface area adsorbents (with correspondingly large  $V_a$  values) are capable of this separation<sup>5</sup>. Among the three commercial adsorbent types so far studied, the maximum  $V_a$  values are: Davison Code 12 silica (calcined), 0.30; Florisil (1% water), 0.08; Alcoa F-20 alumina (calcined), 0.05. The code 12 silica is obviously the best of these adsorbents for the separation of very weakly adsorbing mixtures.

The separation of two or more solutes or solute types ultimately requires significant differences in either their  $S^\circ$  (adsorption energy) or  $A_s$  (effective area) values. In comparing the three adsorbent types with respect to selected separations, it is useful to classify the compound types so far studied as follows: (I) unsubstituted and alkyl-substituted aromatic hydrocarbons; (II) other substituted aromatic hydrocarbons; (III) substituted aliphatics; (IV) pyrrole derivatives; (V) basic nitrogen compounds. Separations of these various compound types, both within and between various classes, may be further subdivided according to whether separation by compound type (groups of similar compounds) or separation between individual compounds is desired.

Separation of the unsubstituted and alkyl-substituted aromatic hydrocarbons (I) by type (e.g., alkylbenzenes, alkylnaphthalenes) is best done using alumina, primarily because the alkyl substitution parameters ( $Q_i^\circ$ ,  $q_j^\circ$ ) for alumina are so much smaller than for silica or Florisil (see Table XI). Additionally, the  $c_3$  ( $n - 6r$ ) term for silica (eqn. 3) leads to decreased differences between the  $S^\circ$  values of the unsubstituted aromatic hydrocarbons, with further worsening of the separation of aromatic types using silica. Conversely, the separation of individual alkyl aromatics should be best accomplished with Florisil, because the alkyl substitution parameters (Table XI) are by far the largest. The separation of individual unsubstituted aromatic hydrocarbons, and particularly isomers, has not been extensively investigated, except in the case of alumina<sup>15, 16</sup>. It appears, however, that alumina is the preferred adsorbent in this capacity, and many successful separations of this type by alumina have been reported.

Aromatic hydrocarbons substituted by groups other than alkyl (II) constitute the most extensively studied group of solutes in the present series of papers. Table XIV has been prepared to focus attention on the many differences in separation order which arise among the three adsorbent types. Values of the solute parameters  $S^\circ$  and  $A_s$  were calculated for each of the solutes of Table XIV, and these were used to calculate the term ( $S^\circ - \varepsilon^\circ A_s$ ) for eluent strengths ( $\varepsilon^\circ$ ) of 0.00 and 0.30. Differences in the ( $S^\circ - \varepsilon^\circ A_s$ ) term between two solutes in the same chromatographic system (same adsorbent, eluent) are a good index of the separability of that solute pair. The term ( $S^\circ - \varepsilon^\circ A_s$ ) for Florisil was multiplied by the  $\alpha$  value for 1% H<sub>2</sub>O-Florisil (0.63), since this is the highest adsorbent activity for which these data are applicable.

As previously pointed out, the solute group  $Q_i^\circ$  values for the three adsorbents are all quite comparable, at least when the values of  $Q_i^\circ$  for Florisil are expressed, as in Table XIV, on a 1% water-adsorbent basis. Consequently, the major differences in separation order of a series of solutes of the type C<sub>3</sub>H<sub>5</sub>-X, C<sub>6</sub>H<sub>4</sub>-X<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>-X<sub>3</sub> are determined by the localization of strong solute groups, for elution by pentane or other weak eluents. In such cases, silica is better than Florisil which is better than alumina.

TABLE XIV  
SOLUTE/ELUENT PARAMETERS FOR SUBSTITUTED AROMATICS

Substituents		Nucleus*	$(S^\circ - e^\circ A_g)$					
1	2		$e^\circ = 0.0$			$e^\circ = 0.3$		
			Alum.	Sil.	Flor.**	Alum.	Sil.	Flor.**
-H	-H	B	1.9	1.5	1.1	0.1	0.3	-0.1
		N	3.1	2.0	1.8	0.7	-0.3	0.3
-SR	-H	B	3.1	2.8	2.4	0.6	-0.1	0.8
		N	4.4	3.3	3.1	1.2	-0.1	1.1
-SR	-SR	B	4.5	4.1	3.7	1.2	0.1	1.6
		N	5.7	4.6	4.3	1.8	0.0	1.9
-OR	-H	B	3.6	3.3	2.9	1.2	0.2	0.9
		N	4.7	3.9	3.5	1.7	0.1	1.2
-OR	-OR	B	5.2	5.1	4.5	2.2	0.5	1.7
		N	6.4	5.6	5.2	2.8	0.4	2.1
-OR	-SR	B	4.8	4.6	4.1	1.6	0.3	2.3
		N	5.9	5.1	4.7	2.1	0.2	2.0
-NO <sub>2</sub>	-H	B	4.6	4.3	4.2	2.1	0.3	1.9
		N	5.5	4.8	4.7	2.3	0.2	2.0
-NO <sub>2</sub>	-NO <sub>2</sub>	B	6.5	6.7	6.5	3.2	0.6	3.1
		N	7.4	7.2	7.1	3.5	0.5	3.3
-NO <sub>2</sub>	-OR	B	5.9	5.9	5.6	2.7	0.6	2.5
		N	6.7	6.4	6.0	3.0	0.4	2.6
-NO <sub>2</sub>	-SR	B	5.5	5.4	5.2	2.2	0.4	2.4
		N	6.4	5.9	5.7	2.5	0.3	2.6
-CO <sub>2</sub> R	-H	B	5.2	5.0	4.5	2.5	0.9	2.5
		N	5.9	5.4	5.0	2.6	0.8	2.6
-CO <sub>2</sub> R	-CO <sub>2</sub> R	B	7.2	7.9	7.0	3.6	1.6	4.0
		N	7.9	8.3	7.6	3.7	1.4	4.2
-CO <sub>2</sub> R	-NO <sub>2</sub>	B	6.8	7.3	6.7	3.4	1.1	3.5
		N	7.6	7.7	7.2	3.5	0.9	3.7
-CO <sub>2</sub> R	-OR	B	6.2	6.5	5.9	2.9	1.0	3.0
		N	7.0	7.0	6.5	3.1	0.8	3.2
-CO <sub>2</sub> R	-SR	B	6.0	6.0	5.5	2.5	0.9	2.9
		N	6.7	6.5	6.0	2.7	0.8	3.0
-CHO	-H	B	5.2	5.4	5.0	3.1	1.4	2.5
		N	6.0	5.9	5.5	3.3	1.2	2.6
-CHO	-CHO	B	7.2	8.6	7.8	4.8	2.3	3.8
		N	8.0	9.1	8.3	5.0	2.2	4.0
-CHO	-CO <sub>2</sub> R	B	7.2	8.2	7.4	4.2	1.9	4.0
		N	8.0	8.7	7.9	4.4	1.8	4.1
-CHO	-NO <sub>2</sub>	B	6.9	7.7	7.2	4.0	1.5	3.5
		N	7.6	8.1	7.7	4.2	1.3	3.6
-CHO	-OR	B	6.3	6.9	6.3	3.6	1.5	2.9
		N	7.0	7.4	6.8	3.7	1.3	3.0
-CHO	-SR	B	6.0	6.5	6.2	3.2	1.3	3.0
		N	6.8	6.9	5.4	3.3	1.2	3.2

(continued on p. 507)

TABLE XIV (continued)

Substituents		Nucleus*	$(S^\circ = \epsilon^\circ A_s)$					
1	2		$\epsilon^\circ = 0.0$			$\epsilon^\circ = 0.3$		
			Alum.	Sil.	Flor.**	Alum.	Sil.	Flor.**
-COR	-H	B	5.6	6.2	5.4	3.2	1.6	2.7
		N	6.3	6.6	5.9	3.3	1.5	2.8
-COR	-COR	B	7.7	10.0	8.4	4.7	2.7	4.2
		N	8.4	10.5	8.9	4.8	2.6	4.3
-COR	-CHO	B	7.5	9.4	8.2	4.8	2.6	4.1
		N	8.2	9.8	8.7	4.9	2.4	4.2
-COR	-CO <sub>2</sub> R	B	7.5	9.0	7.8	4.2	2.2	4.2
		N	8.2	9.5	8.3	4.3	2.1	4.3
-COR	-OR	B	6.6	7.7	6.7	3.6	1.7	3.2
		N	7.3	8.1	7.2	3.7	1.6	3.3
-COR	-SR	B	6.3	7.2	6.3	3.2	1.6	3.1
		N	7.0	7.7	6.8	3.3	1.5	3.3

\* B, benzene derivatives; N, naphthalene derivative.

\*\*  $\times 0.63$ .

The elution of most samples of the above type will require eluents stronger than pentane, however, and for eluent strengths as large as 0.30 (as seen in Table XIV), alumina becomes a *better* adsorbent than silica or Florisil, because of the larger solute  $A_s$  values in the latter two adsorbents. Alternately, for separations of a substituted benzene from a similarly substituted naphthalene or higher aromatic, alumina is *always* preferable to silica, and comparable to Florisil, by virtue of the  $c_3 (n - 6r)$  term of eqn. (3) for silica. Little difference in the separability of aromatic isomers on these three adsorbents appears indicated, since the few experimental  $q^\circ_j$  values that have been obtained appear generally similar for each adsorbent.

The form of eqn. (3) is such that values of  $(S^\circ - \epsilon^\circ A_s)$  for additional solutes can be readily obtained from the data of Table XIV, using simple extrapolation. For example,  $(S^\circ - \epsilon^\circ A_s)$  for dinitro-methoxybenzene is simply the value for dinitrobenzene plus the difference between nitrobenzene and methoxy-nitrobenzene (e.g., 7.8 for alumina with  $\epsilon^\circ$  equal 0.00). Such extrapolations must be carried out within the same group of solutes (grouped by lines in Table XIV). Similarly, the  $(S^\circ - \epsilon^\circ A_s)$  values for eluent strengths other than 0.00 and 0.30 can be obtained by simple interpolation or extrapolation between or beyond these latter  $\epsilon^\circ$  values.

With respect to the separation of the substituted aliphatics (III), these solute types tend to elute just before the corresponding substituted benzene on alumina (e.g.,  $S^\circ$  values: alkyl ketones, 5.0, alkyl phenyl ketones; 5.6; alkyl sulfides, 2.7; phenyl alkyl sulfides 3.2)<sup>9</sup>. On silica, limited experimental data show the substituted aliphatics eluting with the substituted benzenes, but the differences in these two adsorbents in this respect are not very pronounced. Nothing is known about the relative separation of substituted aliphatics on Florisil, and it would be expected that silica and Florisil would be similar in this regard.

The separation of pyrrole derivatives (IV) such as indole and carbazole on these three adsorbents show some important differences. Relative to other sample types, the pyrroles are preferentially held on alumina, and tend to be eluted more readily from silica and Florisil. Previously summarized data suggest that this results from a

larger  $Q^{\circ}_i$  value for the pyrrole nitrogen group on alumina, and a smaller contribution to the effective area  $A_s$  of the solute. It has been suggested<sup>6</sup> that this difference between silica and alumina can be utilized in the separation of complex mixtures such as petroleum, where a preliminary segregation of the sample components is made over alumina, followed by re-separation of the alumina fractions over silica.

With respect to the separation of basic nitrogen types (V), chemisorption has been reported for these species on both silica and Florisil. Removal of free acid from the adsorbent *may* eliminate this effect in the case of silica, as discussed in the experimental section. As long as chemisorption exists, however, separations *within* the basic nitrogen class are not profitable, and the separation of the *total* basic nitrogen compounds from other sample components is facilitated. With the advent of ion-exchange techniques for the segregation of basic nitrogen compounds as a group from most samples of interest<sup>6,10</sup>, the use of adsorption chromatography in this connection does not appear particularly desirable.

#### ACKNOWLEDGEMENTS

The editing and criticism by Dr. J. K. FOGO of the original manuscript and the experimental assistance of Mr. F. O. WOOD are gratefully acknowledged.

#### GLOSSARY OF TERMS

$A_s$	solute surface volume, proportional to area required by solute on adsorbent surface
$c_1, c_2, c_3$	constants for particular adsorbents
$f(Q^{\circ}_k)$ ,	localization functions as defined in ref. 3 and Table III of this
$L_1(Q^{\circ}_i), L_2(Q^{\circ}_k)$	paper
$n$	number of aromatic carbon atoms in solute
$Q^{\circ}_j$	solute group adsorption energy factor
$q^{\circ}_j$	solute geometry factor
$r$	number of separate ring systems in solute ( <i>e.g.</i> , one in naphthalene, two in dibenzyl)
$S^{\circ}$	solute adsorption energy, pentane eluent
$\underline{R}^{\circ}$	solute equivalent linear retention volume (ml/g)
$V_a$	adsorbent specific surface volume (ml/g), proportional to adsorbent surface area
$\alpha$	adsorbent activity function
$\delta_i$	contribution of solute group $i$ to $A_s$ , exclusive of localization effects
$\varepsilon^{\circ}$	eluent strength function, proportional to eluent adsorption energy per unit area of adsorbent surface.

#### SUMMARY

The linear elution of several solutes by a number of eluents from Florisil samples of varying water content has been used to study this adsorbent in the context of preceding investigations on alumina and silica. Florisil exhibits certain unique

properties as an adsorbent. Many compounds tend to chemisorb on Florisil, and this restricts its usefulness in adsorption chromatographic separation. Relative to alumina and silica, the dependence of solute retention volume on Florisil water content is irregular when added water is less than 1%. Both of these phenomena appear related to the presence of strong acid sites on the Florisil surface. In other respects, the adsorptive properties of  $\geq 1\%$  H<sub>2</sub>O-Florisil appear intermediate between those of silica and alumina. A general correlational equation for the prediction of retention volume in the chromatographic systems so far studied is given, along with a summary of specific references to the necessary experimental parameters for easy calculation. The unique separation capabilities of Florisil, alumina, and silica for the class of compounds so far studied are summarized and contrasted.

## REFERENCES

- <sup>1</sup> L. R. SNYDER, *J. Chromatog.*, 6 (1961) 22.
- <sup>2</sup> L. R. SNYDER, *J. Chromatog.*, 8 (1962) 178.
- <sup>3</sup> L. R. SNYDER, *J. Chromatog.*, 8 (1962) 319.
- <sup>4</sup> L. R. SNYDER, *J. Chromatog.*, 11 (1963) 195.
- <sup>5</sup> L. R. SNYDER, *Anal. Chem.*, 33 (1961) 1527.
- <sup>6</sup> L. R. SNYDER AND B. E. BUELL, *Separation of Nitrogen, Sulfur, and Oxygen Compounds on Solid Adsorbents and Ion Exchange Resins*, presented at the *Symposium on Chemistry and Properties of the Petroleum-Type Sulfur and Nitrogen Compounds*, Univ. of Wyoming Science Camp, July 17-21, 1962.
- <sup>7</sup> J. R. SMITH, C. R. SMITH AND G. U. DINEEN, *Anal. Chem.*, 22 (1950) 867.
- <sup>8</sup> G. U. DINEEN, J. R. SMITH, R. A. VAN METER, C. S. ALLBRIGHT AND W. R. ANTHONY, *Anal. Chem.*, 27 (1955) 185.
- <sup>9</sup> H. J. CAHNMANN, *Anal. Chem.*, 27 (1955) 1235.
- <sup>10</sup> A. ASATOOR AND C. E. DALGLIESCH, *J. Chem. Soc.*, (1958) 1717.
- <sup>11</sup> Floridin Co., *Floridin Technical Data and Product Specifications*, Tallahassee, Fla., includes a detailed listing of other references to the use of Florisil in adsorption chromatography.
- <sup>12</sup> C. WALLING, *J. Am. Chem. Soc.*, 72 (1950) 1164.
- <sup>13</sup> J. S. BALL, private communication.
- <sup>14</sup> L. R. SNYDER, *Anal. Chem.*, 33 (1961) 1535.
- <sup>15</sup> L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 234.
- <sup>16</sup> L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 240.
- <sup>17</sup> L. R. SNYDER, *J. Phys. Chem.*, in press.
- <sup>18</sup> L. R. SNYDER, *J. Chromatog.*, 5 (1961) 468.
- <sup>19</sup> W. MUNDAY AND A. EAVES, *Proc. 5th World Petrol. Congr.*, New York, 1959, Paper 9, Section V.