LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

V. SILICA AS ADSORBENT. ADSORBENT STANDARDIZATION

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INTRODUCTION

Silica (virtually synonymous with silica gel, silicic acid[1,2]) has probably been used more frequently in liquid-adsorption chromatographic separation than any other single adsorbent. Its properties as an adsorbent and the mechanism whereby it functions in this capacity form the subject of an extensive literature[2]. As early as 1950 TRUEBLOOD AND MALMBERG[3] noted that many chromatographic systems employing silicic acid as adsorbent show linearity in the adsorption isotherm over a wide range of solute concentrations. Despite this observation and the general recognition[4,5] of the desirability of restricting systematic studies of the chromatographic process to linear isotherm systems, the only systematic study of linear adsorption on silica to date is that of SPORER AND TRUEBLOOD[4] for a silicic acid–celite mixture. This investigation was limited to the effect of solute molecular structure on separation, only one eluent (benzene) and one adsorbent activity being used.

Parts II–IV[6-8] in this series of papers have presented a physical model of linear elution adsorption chromatography (LEAC) on alumina, and have related adsorption affinity or solute linear retention volumes, $\underline{R}^\circ$, to solute molecular structure, eluent type, and adsorbent activity through the correlational eqn. (1):

$$\log \underline{R}^\circ = \log V_a + \alpha \, [\overset{i}{\Sigma} Q^\circ{}_i - f(Q^\circ{}_k) \overset{i \neq k}{\Sigma} Q^\circ{}_i + \overset{j}{\Sigma} q^\circ{}_j - \varepsilon^\circ \; \overset{i}{\Sigma} \delta_i] \qquad (1)$$

V_a and α are adsorbent parameters; V_a is proportional to the surface area of the adsorbent, and α is a measure of the average strength of adsorbent sites. ε° is an eluent parameter, increasing in value for more strongly adsorbing solvents. $\overset{i}{\Sigma}\, \delta_i$ is proportional to the size or area of the solute, $\overset{i}{\Sigma}\, Q^\circ{}_i$ is the sum of the adsorption energies $Q^\circ{}_i$ of individual solute groups i, $\overset{j}{\Sigma}\, q^\circ{}_j$ includes the effect of various solute geometries j which influence adsorption, and the term $f(Q^\circ{}_k) \overset{i \neq k}{\Sigma} Q^\circ{}_i$ arises from the localization of a strong solute group k on a particular adsorbent site.

The general chemical and physical similarity of the adsorbents alumina and silica, as well as the considerable practical interest and theoretical background associated with the latter adsorbent, make silica a logical choice for study in the context of our preceding work on alumina. The present communication represents a preliminary effort at the understanding of the factors which determine adsorption affinity on silica, with special emphasis on the similarities and differences in the adsorptive properties of it and alumina.

EXPERIMENTAL

The acquisition of experimental LEAC retention volume data ($\underline{R}°$ values in ml/g) was carried out as described in Part III[7] for alumina. Davison Code Number 12 and 62 silica gels were used as adsorbents. The manufacturer's product was first calcined at 400° for 16 h, following which adsorbent samples of varying activity were prepared by adding liquid water to the calcined material and permitting it to equilibrate for at least 24 h. KLEIN[9] has suggested that the addition of liquid water rather than water vapor may have an adverse effect upon the separation efficiency (*i.e.*, HETP) of deactivated silica. While this *may* be a consideration in the preparation of adsorbent for practical separations, KLEIN's data do not show any significant differences in adsorption affinity (*i.e.*, $\underline{R}°$ values) arising from the method of adsorbent preparation. In related studies on alumina, we find the adsorptive properties of deactivated aluminas to be independent of the method of adding water. The purification of solutes and eluents has been previously described in Part II[6].

Table I gives some of the physical properties of the two silica samples used in the present study. These figures include our values on calcined adsorbent and data for the original adsorbents from the manufacturer's specifications and from the study by KLEIN[10] of the same two adsorbents. The thermal processing of silica at temperatures above 300° has been shown[11] to reduce surface area (through sintering) and, eventually, to destroy adsorptive properties[12]. Little if any surface area appears to have been lost in the two calcined samples of Table I.

TABLE I

PHYSICAL PROPERTIES OF ADSORBENTS USED IN PRESENT STUDY

Adsorbent	*Surface area (BET) (m²/g)*	*Pore volume (ml/g)*	*Average pore diameter (Å)*
Davison Code No. 12			
calcined 400°	778	0.40	20
original manufacturer	830	0.45	22
Klein	805	0.41	20
Davison Code No. 62			
calcined 400°	287	1.28	178
original manufacturer	340	1.16	140
Klein	274	1.16	170

The equivalence of LEAC retention volume data and equilibrium distribution coefficients has been demonstrated for alumina as adsorbent[6]. A similar comparison of equilibrium and chromatographic data for Code 12 silica deactivated with 4.6 % added water is given in Table II. The linearity of both equilibrium and chromatographic systems is evident, but the chromatographic retention volumes are lower

TABLE II

EQUILIBRIUM SOLUTE DISTRIBUTION COEFFICIENTS AND CHROMATOGRAPHIC EQUIVALENT RETENTION VOLUMES AS A FUNCTION OF SOLUTE CONCENTRATIONS FOR THE SYSTEM NAPHTHALENE (SOLUTE)–*n*-PENTANE–CODE 12 4.6% H_2O–SiO_2

Equilibrium data			*Chromatographic data*	
Solute concentrations				
Non-sorbed phase (g/ml) $\times 10^6$	*Adsorbed phase (g/g)* $\times 10^6$	$\underline{K}$ *(ml/g)*	*Column loading (g/g)* $\times 10^6$	$\underline{R}$ *(ml/g)*
161	459	8.2	620	7.8
52.5	153	8.4	263	8.0
13.4	38.0	8.3	240	7.9
5.36	15.3	8.4	68	7.7
1.32	3.82	8.5	31	7.7
	Average	8.4	8	7.8
			Average	7.8

than the equilibrium coefficients by 7%. As seen in Table III for several other systems, this phenomenon is rather general. The magnitude of the discrepancy will not seriously affect the significance or the interpretation of the chromatographic data we will describe. It will be shown in a forthcoming publication that the differences in chromatographic and equilibrium $\underline{R}^\circ$ values for Code 12 silica result partially from the smaller equivalent theoretical plate numbers associated with columns of this adsorbent. Using silicic acid of unspecified pore diameter, SPORER AND TRUEBLOOD[4] observed equivalence of chromatographic and equilibrium data at flow rates of 0.1–0.2 ml/min. For columns of similar diameter, our flow rates were considerably larger, 2–5 ml/min for experimental convenience.

An additional experimental difference between adsorption on alumina and silica was noted in the present study. The elution of solutes containing basic nitrogen from silica results in incomplete recovery of sample from the column. The effect is most pronounced at small column loadings, and in some cases no sample elutes from a column from which elution occurs readily (but with incomplete recovery) at higher sample concentrations. Table IV presents some equilibrium isotherm data for the adsorption of aniline from benzene onto 16% H_2O–SiO_2 (Code 12). The equilibrium distribution coefficients $\underline{K}$ show a singular dependence upon solute concentration. Some of these adsorption data are plotted (adsorbed *versus* solution concentrations)

TABLE III

COMPARISON OF EQUILIBRIUM LINEAR DISTRIBUTION COEFFICIENTS WITH LINEAR EQUIVALENT RETENTION VOLUMES FOR SEVERAL ADSORPTION SYSTEMS; CODE 12 SILICA

Solute	*% H_2O on silica**	*Eluent*	$\underline{R}^\circ$	$\underline{K}^\circ$	$\underline{R}^\circ/\underline{K}^\circ$
Naphthalene	4.6	Pentane	7.8	8.4	0.93
Dibenzyl	4.6	Pentane	27.5	34.6	0.79
Phenanthrene	4.6	Pentane	16.2	17.6	0.92
Naphthalene	8.0	Pentane	4.8	5.3	0.91

* Chromatographic activity.

TABLE IV

EQUILIBRIUM SOLUTE DISTRIBUTION COEFFICIENTS AS A FUNCTION OF SOLUTE CONCENTRATION FOR THE SYSTEM ANILINE (SOLUTE)–BENZENE–CODE 12 16% H_2O–SiO_2

Solute concentrations		$\underline{K}$ (*ml/g*)	$\underline{K}'$ (*ml/g*)
Non-sorbed phase (g/ml) × 10^6	*Adsorbed phase (g/ml)* × 10^6		
0.0	29	290	—
0.5	73	146	—
4.5	220	49	—
22.9	536	23.4	8.8
37.5	694	18.5	9.2
222	2370	10.7	9.1
519	4830	9.3	8.6
1030	9510	9.2	8.9
2270	17200	7.6	7.4
2760	20000	7.3	7.1
4470	27700	6.2	6.1
9900	44500	4.5	4.5
16400	57800	3.5	3.5

in Fig. 1, and it is noted that the straight line through the values at high aniline concentrations intersects the vertical axis at a concentration corresponding to $350 \cdot 10^{-6}$ g aniline/g of adsorbent, rather than passing through the origin as in "normal" adsorption. It is believed that this behavior reflects the presence of a small number of sites on the silica surface (probably strong acid groups) upon which chemisorption (or very strong physical adsorption) can occur. If the extrapolated value of aniline uptake by the adsorbent at zero solution concentration is assumed to correspond to the concentration of these chemisorption sites in terms of their capacity for aniline, "normal" adsorption of this solute on silica can be calculated by subtracting $350 \cdot 10^{-6}$ g/g from the total adsorbed phase concentrations. Distribution coefficients $\underline{K}'$ corrected in this manner for chemisorption are listed in Table IV, and are seen to show a rather normal dependence upon adsorbent loading. For adsorbent loadings less than 0.01 g/g, values of $\underline{K}'$ are constant (linear) within experimental error, and for greater adsorbent loadings the values of $\underline{K}'$ decline as for other systems with a linear capacity[5] of about

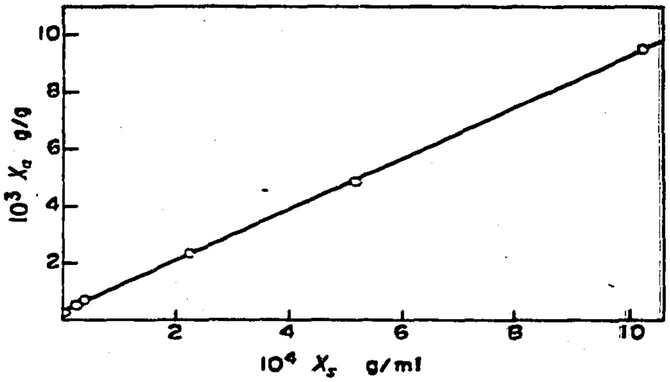

Fig. 1. Equilibrium adsorption data for aniline (solute), benzene (eluent), and 16% Code 12 H_2O–SiO_2.

0.01 g/g. The occurrence of chemisorption during a chromatographic elution should theoretically have little, if any, effect upon the "normal" adsorption and elution of the solute in excess of that chemisorbed. In confirmation of this expectation in the system of Table IV, $\underline{R}^\circ$ for aniline eluted by benzene from 16% H_2O–SiO_2 (Code 12) was found equal to 10.0 ml/g, within experimental error of the corrected linear distribution coefficient $\underline{K}'$ (8.9 ml/g).

Although the effects of chemisorption in chromatographic systems may be unimportant in theoretical studies such as the present, chemisorption seriously limits the usefulness of an adsorbent in practical separations of chemisorbed species. Chemisorbed substances will normally be smeared over the entire column, rather than concentrated in the usual narrow elution band. Under such circumstances, it is also possible for the same solute to give two apparently distinct and widely separated elution bands if after collection of the physically adsorbed solute (in a normal elution band) and several intermediate fractions, a new eluent sufficiently strong to displace the chemisorbed solute is used.

The experimental measurement of large retention volumes ($\underline{R}^\circ > 100$) is frequently tedious and time consuming, while the pronounced spreading of the elution band in such cases makes the detection of solute in the eluate impossible in some cases. If the retention volume ($\underline{R}^\circ_1$) is desired for eluent 1 and a particular adsorbent, and it is anticipated that $\underline{R}^\circ_1$ will be inconveniently large, the quantity may be obtained indirectly as follows. Assume the measurement of a retention volume of convenient size for the same solute and adsorbent, but using a stronger eluent 2. $\underline{R}^\circ_2$ should be larger than 5 ml/g. Finally, charge the solute to its column in the usual manner, and elute with some volume V_1 (ml/g) of eluent 1, where V_1 is less than $\underline{R}^\circ_1$. This will cause the movement of the solute a fractional distance ($V_1/\underline{R}^\circ_1$) up the column. Then change eluents from 1 to 2, cleaning eluent 1 out of the lines to the column, and elute with eluent 2 to determine a new retention volume $\underline{R}'_2$ for this eluent. $\underline{R}^\circ_1$ is now given as:

$$\underline{R}^\circ_1 = (V_1\underline{R}^\circ_2)/(\underline{R}^\circ_2 - \underline{R}'_2) \qquad (2)$$

Eqn. (2) and the related technique have been used to advantage on several occasions in the present study.

THE PREDICTION OF LEAC RETENTION VOLUME DATA

Relative to the adsorbent alumina, chromatographic separation over silica is characterized by both pronounced similarities and differences. It is shown in the following sections that eqn. (1) for alumina as adsorbent must be modified when silica is used, because of fundamental differences in the mode of adsorption on these two adsorbents. Eqn. (3) predicts LEAC solute retention volumes on silica:

$$\log \underline{R}^\circ = \log V_a + \alpha\{\sum^{i} Q^\circ_i - 0.113\,(n - 6\,r) + \sum^{j} q^\circ_j - \varepsilon^\circ \sum^{i} [\delta_i + 14.5\,f\,(Q^\circ_i)]\} \qquad (3)$$

Here, V_a and α have the same significance as in eqn. (1) for alumina. As illustrated by the data of Table I, commercial samples of silica come in a wide range of surface areas. This generally necessitates the consideration of *both* adsorbent surface volume V_a

and surface energy α in the standardization of adsorbent, as discussed in some detail in a following section. For a particular grade of adsorbent, where the surface area and hence V_a are reasonably constant, a single measurement of $\underline{R}^\circ$ for a standard solute (*e.g.*, naphthalene) eluted by a standard solvent (*e.g.*, pentane) suffices to determine both V_a and α. While both V_a and α are independently variable for alumina as well as silica, the latter procedure was used (Part II[6]) for the standardization of Alcoa F-20 alumina. Table V offers a similar tabulation of values of V_a, α, and the standard solute $\underline{R}^\circ$ value for samples of Davison Code 12 silica of varying water content. For this particular adsorbent, activity standardization and the determination of V_a and α values are carried out exactly as for Alcoa F-20 alumina in Part II.

TABLE V

CODE 12 SILICA GEL ACTIVITY FUNCTION AND ADSORBED VOLUME AS A FUNCTION OF PERCENT ADSORBED WATER

% H_2O-SiO_2	*Activity function* α	*Adsorbed volume*		*Standard solute retention volume**	
		V_a	$\log V_a$	$\underline{R}^\circ$ (ml/g)	$\underline{R}^\circ/V_a$
0.0	1.00	0.30	—0.52	32	107
1.0	0.94	0.29	—0.54	21	72
2.0	0.85	0.28	—0.55	14	50
4.0	0.75	0.26	—0.58	9.0	35
7.5	0.68	0.22	—0.65	5.1	23
10.0	0.64	0.20	—0.70	4.0	20
15.0	0.61	0.15	—0.82	2.6	17
20.0	0.58	0.10	—1.00	1.5	15

* Elution of naphthalene by pentane.

For other silica samples (generally of lower surface area than Davison Code 12), V_a is given by eqn. (4), which is theoretically justified in a latter section.

$$V_a = 0.00035 \text{ (surface area of calcined adsorbent in m}^2\text{/g)} - 0.01 \text{ (\% water added to calcined sample)} \tag{4}$$

The standard $\underline{R}^\circ$ value (for naphthalene, pentane) is obtained, and the ratio ($\underline{R}^\circ/V_a$) calculated. The adsorbent surface energy α may be interpolated from the second and fifth columns of Table V.

The term $\sum^{i} Q^\circ_i$ of eqn. (3) plays the same role as in eqn. (1), and in general has virtually the same value. Table VI lists some specific experimental Q°_i values for silica. For the adsorption of other solute groups i on silica, the alumina Q°_i values of Part IV[8] are believed interchangeable with an accuracy of ±20%. If the Q°_i values of Table VI are compared with previous values for alumina in the case of *aliphatic carbon* groups, it is seen that these latter values for silica include the q°_j terms for substitution on aromatic carbon, terms that were reported separately for alumina in Part II[6]. Similarly, a distinction is now made between methyl aliphatic carbon groups, and other saturated carbon atoms. These changes in classification are made for purposes of convenience and consistency.

The term 0.113 ($n - 6r$) of eqn. (3) is used only for solute's possessing aromatic ring systems. r refers to the number of such uncondensed ring systems (*e.g.*, one in benzene, naphthalene, two in dibenzyl), while n is the total number of unsaturated carbon atoms in the solute.

TABLE VI

SOLUTE GROUP ADSORPTION FACTORS Q°_i FOR SILICA AS ADSORBENT

Group	*Attachment*	
	Aromatic carbon	*Aliphatic carbon*
$-CH_2-$, $-CH$	+0.01	—0.05
$-CH_3$	+0.13	+0.07
$-CH=$	+0.25	+0.25
$-S-R$	+1.29	+2.94
$-O-R$	+1.83	
$-NO_2$	+2.77	
$-CO_2-R$	+3.45	
$-CHO$	(3.9)*	
$-CO-R$	+4.69	
$-OH$	(4.2)*	(5.6)*
$-NH_2$	+5.1	(7.8)*
$-NH-$ (carbazole)	+3.00	
$-COOH$	(6.1)*	

* Estimated values from data of SPORER AND TRUEBLOOD[4] (see following section).

The term $\sum^{i} q^\circ_j$ of eqn. (3) is equivalent to the same term in eqn. (1), and it is assumed that its value is in general comparable for both adsorbents.

The eluent term $\varepsilon^\circ \sum^{i} [\delta_i + 14.6 f(Q^\circ_i)]$ of eqn. (3) is quite similar to the term $\varepsilon^\circ \sum^{i} \delta_i$ for alumina (eqn. (1)). This is more readily seen if we equate the term $[\delta_i + 14.6 f(Q^\circ_i)]$ for each solute group i to an *effective* solute group area δ_i', comparable to δ_i. Values of the eluent strength parameter ε° have been measured for three pure solvents (in addition to pentane), and these values are given in Table VII. As shown, these values are in general slightly lower than the corresponding alumina ε° values, but it is not known if this effect is general. Values of ε° for several binary solvents were also measured, and it was found that the previous relationship for alumina (eqn. (2) of

TABLE VII

ELUENT PARAMETERS FOR ADSORPTION ON SILICA

Solvent	ε°	
	SiO_2	Al_2O_3
n-Pentane	0.000	0.000
Carbon tetrachloride	0.11*	0.18
Benzene	0.25	0.32
Methylene chloride	0.32	0.42

* Approximate value for limited data on CCl_4–pentane binaries and Code 12 silica; pure CCl_4 does not have a unique value of ε° for elution from Code 12 silica.

Part III[7]) between pure solvent ε° values and the ε° values of binaries holds for silica as well:

$$\varepsilon^\circ_{AB} = \varepsilon^\circ_A + \frac{\log\left[X_B\, 10^{\alpha\, n_b\, (\varepsilon^\circ_B - \varepsilon^\circ_A)} + 1 - X_B\right]}{n_b\, \alpha} \tag{5}$$

n_b refers to the value of $\sum^i \delta_i$ for the stronger solvent B. ε°_A and ε°_B are the eluent strengths of eluents A and B, respectively. ε°_{AB} is the corresponding value of the resulting binary eluent.

The values of δ_i in eqn. (3) are the same as previously tabulated values for alumina (Part III[7]). The increase in the effective size δ'_i of these groups on silica is due to a localization phenomenon, and the localization function $f(Q^\circ_i)$ for silica is the same as the corresponding function $f(Q^\circ_k)$ described in Part IV[8] for alumina.

As is the case for eqn. (1) and adsorption on alumina, the application of eqn. (3) has varying levels of accuracy according to what is calculated. For example, eqn. (3), or (1) for alumina, may be re-written to predict the effect of adsorbent activity change on retention volume:

$$\log \underline{R}^\circ = \log V_a + \alpha\, (\overline{S, E}) \tag{6}$$

The term $(\overline{S, E})$ is readily identified with the solute and eluent terms of eqns. (1) and (3), and is hence *constant* for a particular solute, eluent combination. Measurement of a solute retention volume using an adsorbent sample of defined activity (V_a and α known) permits the calculation of $(\overline{S, E})$ from eqn. (6), following which $\underline{R}^\circ$ for the same solute and eluent can be calculated for any other adsorbent whose values of V_a and α are specified. The accuracy of eqn. (6) is generally greater than for eqn. (3), as expected from its greater simplicity. It should also be noted that while eqn. (6) applies to elution from both alumina and silica, the value of the parameter $(\overline{S, E})$ will be different for the two adsorbents.

The effect on solute retention volume of changing both adsorbent activity and eluent type is given by eqn. (7):

$$\log \underline{R}^\circ = \log V_a + \alpha\, (S^\circ - \varepsilon^\circ \sum^i \delta_i') \tag{7}$$

where for alumina,

$$\delta_i' = \delta_i$$

and for silica,

$$\delta_i' = \delta_i + 14.5\, f(Q^\circ_i)$$

The solute parameter S° is measurable from a single value of $\underline{R}^\circ$ using any adsorbent–eluent combination. It is assumed that the adsorbent and eluent parameters have been evaluated for the combination in question. Values of $\underline{R}^\circ$ for the same solute and any other adsorbent–eluent combination can then be calculated from eqn. (7). The accuracy of eqn. (7) is intermediate between that of eqns. (3) and (6). The following paragraphs provide some examples of the applications of these correlational equations in predicting $\underline{R}^\circ$ values for silica as adsorbent, and through comparison with experimental data give some insight into the accuracy associated with each type of calculation.

The first example demonstrates the application of eqn. (6) to the prediction of $\underline{R}^\circ$ values for different adsorbent activities. Consider the elution of the hydrocarbon acenaphthylene by *n*-pentane from a variety of silica adsorbents. It is assumed that for the large surface area Davison Code 12 (D-12) silica samples an *effective* rather than "nominal" (% water actually added to calcined adsorbent) water content has been *chromatographically measured*, using the standard solute retention volume data of Table V (same procedure as for alumina in Parts II–IV[6–8]). Further assume that $\underline{R}^\circ$ has been measured for acenaphthylene eluted by pentane from D-12 4.6 % H_2O–SiO_2 (actual value of log $\underline{R}^\circ$ found equals 1.10). It is desired to predict log $\underline{R}^\circ$ for the pentane elution of acenaphthylene from three other adsorbent samples: (a) D-12 1.0 % H_2O–SiO_2, (b) D-12 8.0 % H_2O–SiO_2, and (c) Davison Code 62 (D-62) silica which has had 1 % water added to calcined adsorbent. It is necessary first to calculate the value of the parameter $(\overline{S,E})$ in eqn. (6) for the elution of acenaphthylene by pentane. From the experimental value of $\underline{R}^\circ$ for the D-12 4.6 % H_2O–SiO_2, we have:

$$1.10 = -0.59 + 0.74\,(\overline{S,E})$$

since log V_a and α are, respectively, —0.59 and 0.74 from Table V. From this, $(\overline{S,E})$ is calculated at 2.28. Similarly, values of log V_a and α for adsorbents (a) and (b) may also be obtained from Table V, and log $\underline{R}^\circ$ for the elution of acenaphthylene by pentane from these two adsorbents calculated from eqn. (6).

Adsorbent	*log V_a*	*α*	*Calc. log $\underline{R}^\circ$*
(a) 1.0 % D-12	—0.54	0.94	1.60
(b) 8.0 % D-12	—0.66	0.67	0.87

The experimental values found were (a) 1.56 and (b) 0.88. For the D-62 1 % H_2O–SiO_2, the surface area of the calcined adsorbent is 287 m^2/g, and V_a is calculated as 0.090 from eqn. (4). $\underline{R}^\circ$ for the standard solute (naphthalene–pentane) elution was found equal to 2.6, so that $(\underline{R}^\circ/V_a)$ is 29. α is interpolated as 0.715 in Table V. Finally, from eqn. (6) for this adsorbent,

$$\log \underline{R}^\circ = -1.05 + 0.715\,(2.28) = 0.58$$

An experimental value of 0.56 was found.

In a second application of eqn. (6), consider the elution of the solute phenetole (ethoxybenzene) by *n*-pentane from a number of different silica samples. Assume that an experimental value of $\underline{R}^\circ$ is available for the elution of phenetole by pentane from D-12 6.9 % H_2O–SiO_2 (log $\underline{R}^\circ$ equal 1.66), and that values of $\underline{R}^\circ$ are desired for the adsorbents (a) D-12 4.6 % H_2O–SiO_2, (b) D-12 16.0 % H_2O–SiO_2, and (c) D-62 1 %

Adsorbent	*log V_a*	*α*	*Calc. log $\underline{R}^\circ$*
D-12 6.9 % H_2O–SiO_2	—0.64	0.69	$(\overline{S,E})$ equal 3.33
(a) D-12 4.6 %	—0.53	0.74	1.93
(b) D-12 16 %	—0.86	0.60	1.14
(c) D-62 1 %	—1.05	0.715	1.33

H_2O–SiO_2 (the adsorbent used in the preceding example). Values of log V_a and α for these four adsorbents may again be obtained as in the preceding example, a value of $(\overline{S, E})$ calculated, and values of log $\underline{R}^\circ$ predicted for the latter three adsorbents. The experimental values of log $\underline{R}^\circ$ observed for adsorbents (a–c) were, respectively, 1.92, 1.13 and 1.46.

A third example illustrates the application of eqn. (7) in predicting the effect of both eluent and adsorbent activity change on $\underline{R}^\circ$. Consider the elution of the solute methyl benzoate by a variety of eluents from three adsorbents: (a) D-12 1.6 % H_2O–SiO_2, (b) D-12 16 % H_2O–SiO_2, and (c) the same D-62 1 % H_2O–SiO_2 of preceding examples. Assume that an experimental $\underline{R}^\circ$ value for methyl benzoate has been measured for the elution by pentane from D-12 16 % H_2O–SiO_2 (log $\underline{R}^\circ$ equal 2.24). It is desired to calculate $\underline{R}^\circ$ in the following chromatographic systems (I–V).

System	*Adsorbent*	*Eluent*	*log V_a*	*α*	*ε°*
—	(b) D-12 16 %	*n*-Pentane	—0.86	0.60	0.00
I	(a) D-12 1.6 %	50 % v Benzene–pentane	—0.55	0.89	0.207
II	(b) D-12 16 %	10 % v Benzene–pentane	—0.86	0.60	0.077
III	(b) D-12 16 %	25 % v Benzene–pentane	—0.86	0.60	0.137
IV	(b) D-12 16 %	Benzene	—0.86	0.60	0.250
V	(c) D-62 1 %	*n*-Pentane	—1.05	0.715	0.000

Values of log V_a and α for each chromatographic system are listed, as previously. The ε° values for the pure eluents are those of Table VII. For the binary eluents, eqn. (5) was used to evaluate ε°. It is first necessary to calculate $\overset{i}{\Sigma}\ \delta_i'$ for methyl benzoate. The value of δ_i for each aromatic carbon atom in this solute is 1.0, and for the $-CO_2CH_3$ group, 3.0, from Part III[7]. $f(Q^\circ_i)$ from Part IV[8] is 0.00 for the aromatic carbon atoms (Q°_i equal 0.25 from Table VI). Similarly, $f(Q^\circ_i)$ is 0.43 for the ester group (Q°_i equal 3.45). δ_i' is therefore 1.0 for each aromatic carbon atom in methyl benzoate, and (3 + 14.5 × 0.41) or 8.9 for the ester group. The sum of these contributions to $\overset{i}{\Sigma}\ \delta_i'$ equals 14.9. The solute parameter S° is calculated for methyl benzoate from the experimental $\underline{R}^\circ$ value for this solute, using eqn. (7):

$$2.24 = -0.86 + 0.60\,[S^\circ - (0.00 \times 14.9)]$$

or S° equals 5.17. Values of $\underline{R}^\circ$ can be calculated for each of the above chromatographic systems I–V.

$$\text{(I)}\ \log \underline{R}^\circ = -0.55 + 0.89\,[5.17 - (0.207 \times 14.9)]$$
$$= 1.31$$

The experimental value was 1.33.

$$\text{(II)}\ \log \underline{R}^\circ = -0.86 + 0.60\,[5.17 - (0.077 \times 14.9)]$$
$$= 1.55$$

$\underline{R}^\circ$ vexperimental value was 1.52.

$$\text{(III)}\ \log \underline{R}^\circ = -0.86 + 0.60\,[5.17 - (0.137 \times 14.9)] = 1.02$$

The experimental value was 1.04.

$$\text{(IV)}\ \log \underline{R}^\circ = -0.86 + 0.60\,[5.17 - (0.25 \times 14.9)] = 0.00$$

The experimental value was —0.08.

$$\text{(V)}\ \log \underline{R}^\circ = -1.05 + 0.715\,[5.17 - (0.00 \times 14.9)] = 2.65$$

The experimental value was 2.34.

The following five examples will illustrate the calculation of $\underline{R}^\circ$ values from eqn. (3). First, consider the elution of n-butylbenzene by pentane from D-12 1.0 % H_2O–SiO_2. Log V_a and α are —0.54 and 0.94, respectively. $\sum\limits_i Q^\circ_i$ is the sum of contributions from six aromatic carbon atoms (6 × 0.25), one methylene carbon attached to an aromatic ring (1 × 0.01), two methylene groups attached to aliphatic carbon [2 × (—0.05)], and one methyl group attached to aliphatic carbon (0.07) for a total of 1.48. The number of aromatic carbon atoms (n) is six, and the number of aromatic rings (r) equals one. No specific geometry terms are known for this solute, so $\sum\limits_j q^\circ_j$ equals zero. Finally, the eluent strength ε° for pentane equals zero and

$$\log \underline{R}^\circ = -0.54 + 0.94\,[1.48 - 0.113\,(6 - 6) + 0 - 0] = 0.85$$

The experimental value was 0.86.

Second, consider the elution of phenanthrene by pentane from D-62 1 % H_2O–SiO_2. Log V_a and α for this adsorbent (which is the same as in previous examples) are —1.05 and 0.715, respectively. Fourteen aromatic carbon atoms make a total contribution to $\sum\limits_i Q^\circ_i$ of 3.50, and n equals 14. There is only one uncondensed ring system (r equal 1). There are no geometry terms q°_j, and the eluent parameter is again zero. Therefore,

$$\log \underline{R}^\circ = -1.05 + 0.715\,[3.50 - 0.113\,(14 - 6) + 0 - 0] = 0.81$$

The experimental value was 0.70.

Third, to calculate $\underline{R}^\circ$ for the elution of 1,2-diphenylethane (dibenzyl) from D-12 8.0 % H_2O–SiO_2 by pentane. The values of log V_a and α are —0.66 and 0.67, respectively. $\sum\limits_i Q^\circ_i$ is the sum of contributions from 12 aromatic carbon atoms (12 × 0.25) and two methylene groups attached to aromatic rings (2 × 0.01), for a total of 3.02. The values of n and r are 12 and 2, respectively. $\sum\limits_i q^\circ_j$ and ε° are zero, so

$$\begin{aligned}\log \underline{R}^{\circ} &= -0.66 + 0.67\ [3.02 - 0.113\,(12 - 12) + 0 - 0]\\ &= 1.36\end{aligned}$$

The experimental value was 1.30.

Fourth, consider the elution of 1,2,4-tricarbomethoxybenzene from D-12 16% H_2O–SiO_2 by methylene chloride. The values of log V_a and α are —0.86 and 0.60, respectively. The contributions to $\sum^{i} Q^{\circ}_{i}$ include 6 aromatic carbon atoms (6×0.25) and three aromatic ester groups (3×3.45) for a total of 11.85. n and r are 6 and 1, respectively. An *ortho* ester grouping contributes a q°_{j} value of 0.48 (Table III, Part IV[8]), and ε° is equal to 0.32 (Table VII). The δ_i values of aromatic carbon and $-CO_2CH_3$ groups are 1.0 and 3.0, as before. The localization functions $f(Q^{\circ}_{i})$ for these two groups are 0.00 and 0.41, respectively. Therefore,

$$\begin{aligned}\log \underline{R}^{\circ} &= -0.86 + 0.60\,\{11.85 - 0.113\,(6 - 6) + 0.48 - 0.32\,[6 + 3\,(3 + 14.5 \times 0.41)]\}\\ &= 0.24\end{aligned}$$

The experimental value was 0.30.

In a final example of the application of eqn. (3), consider the elution of carbazole by 15% v methylene chloride–pentane from D-12 16% H_2O–SiO_2. Log V_a and α are given in the preceding example, $\sum^{i} Q^{\circ}_{i}$ equals ($12 \times 0.25 + 3.00$), or 6.00, and n and r are 12 and 1, respectively. $\sum^{j} q^{\circ}_{j}$ is zero, and ε° can be calculated from eqn. (5) as 0.123. δ_i for each of the first six carbon atoms is 1.0, and for the second six and the nitrogen atom, 0.5. $f(Q^{\circ}_{i})$ is 0.00 for aromatic carbons and 0.32 for the nitrogen group (Q°_{i} equal 3.00). Therefore,

$$\begin{aligned}\log \underline{R}^{\circ} &= -0.86 + 0.60\ [6.00 - 0.113\,(12 - 6) + 0 - 1.23\,(9.5 + 14.5 \times 32)]\\ &= 1.29\end{aligned}$$

The experimental value was 1.04.

EFFECT OF ADSORBENT ACTIVITY IN SEPARATIONS ON SILICA

The derivation of the parameters V_a and α for alumina as adsorbent has been discussed in Part II[6]. As will be evident from the discussion in the latter part of this communication, the same procedure is inapplicable for the measurement of silica V_a values. Eqn. (4) provides a satisfactory alternative to the problem of deriving V_a for silica of varying water content. The adsorbent parameters for Code 12 silica as a function of added water are listed in Table V; these values were obtained from eqns. (4) and (6), and a number of chromatographic measurements. Fig. 2 compares the adsorbent activity functions of Alcoa F-20 alumina and D-12 silica for various fractional coverages by added water (ml added water/ml water for monolayer coverage). Both adsorbent activity functions decline with increasing water coverage, as expected, with the effect more pronounced for silica as adsorbent.

The validity of eqn. (6) permits the construction for any adsorbent of a family of "master curves" as in Part II for alumina. Fig. 3 shows such a plot for D-12 silica.

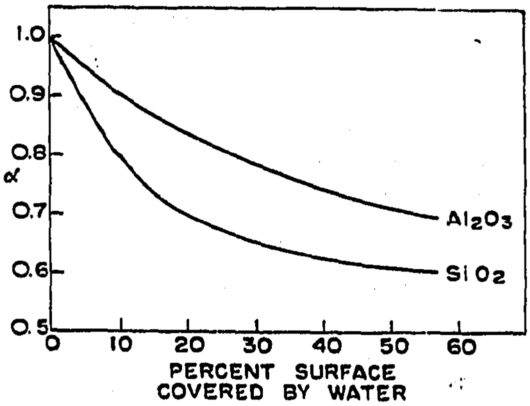

Fig. 2. Adsorbent activity function for silica and alumina *versus* water deactivation.

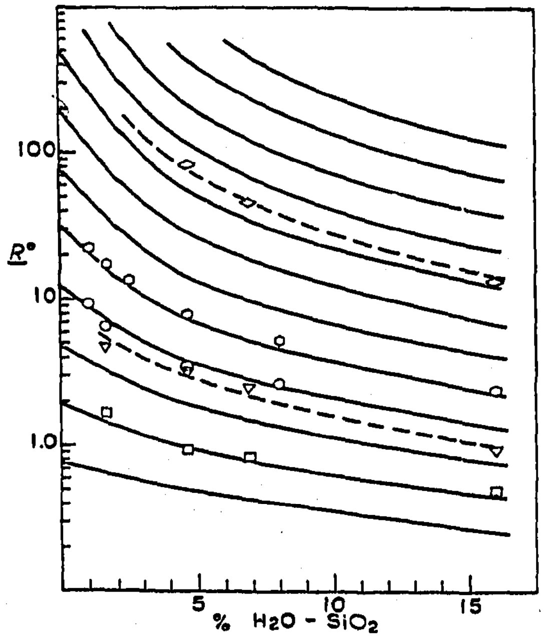

Fig. 3. Dependence of retention volume on adsorbent activity; Code 12 silica gel. ○ isopropylbenzene, pentane; □ nitrobenzene, benzene; ▽ 2-acetonaphthone, benzene; ◇ phenetole, pentane; ⬡ naphthalene, pentane; ······ theoretical curves.

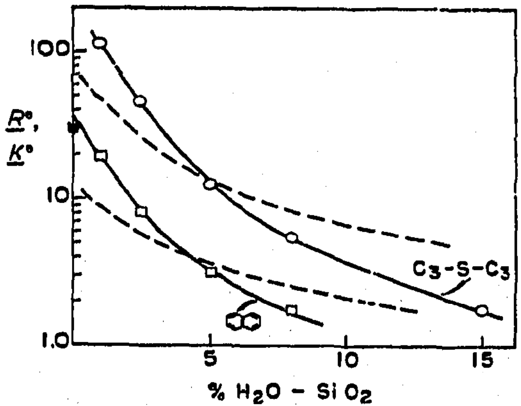

Fig. 4. Equilibrium and chromatographic data for naphthalene and propyl sulfide (solutes), carbon tetrachloride (eluent), and Code 12 silica of varying activity. □ $\underline{K}^\circ$, naphthalene; ■ $\underline{R}^\circ$, naphthalene; ○ $\underline{K}^\circ$, propyl sulfide; – – – eqn. (6).

The applicability of eqn. (6) requires that a series of $\underline{R}^\circ$ values for the same solute and eluent (changing adsorbent activity) fall on a single master curve. Several experimental tests of this requirement are shown in Fig. 3, with the adherence of data to the master plots, and to eqn. (6), being demonstrated. Additional tests of eqn. (6) and of the D-12 adsorbent parameters of Table V are offered in Tables VIII and IX. In all cases, the retention volumes calculated from average $(\overline{S, E})$ values are in reasonable agreement (± 0.02 log units in Table VIII, ± 0.05 log units in Table IX) with values predicted from eqn. (6).

TABLE VIII

TEST OF EQUATION (6) IN CORRELATION OF SOLUTE RETENTION VOLUMES WITH ADSORBENT ACTIVITY; PENTANE ELUTION OF HYDROCARBONS

Solute	*log $\underline{R}^\circ$ for various adsorbent water contents*						*Av. dev.*	$\overline{S, E}$
	1.0%	*1.6%*	*2.5%*	*4.6%*	*8.0%*	*16.0%*		
Isopropylbenzene								
(Exptl.)	0.97	0.81		0.54	0.42		±0.03	1.61
(Calc.)	0.97	0.76		0.60	0.42			
Naphthalene								
(Exptl.)	1.33	1.22	1.13	0.90	0.72	0.38	±0.02	2.02
(Calc.)	1.36	1.25	1.10	0.90	0.69	0.35		
Acenaphthylene								
(Exptl.)	1.56			1.10	0.88		±0.02	2.28
(Calc.)	1.60			1.10	0.87			
Dibenzyl								
(Exptl.)		2.08			1.30	0.87	±0.02	2.92
(Calc.)		2.05			1.30	0.89		
Perylene								
(Exptl.)				1.76	1.52	1.10	±0.03	3.23
(Calc.)				1.80	1.50	1.08		

One exception to the applicability of eqn. (6) to Code 12 silica has been noted. Elution with CCl_4, which is "regular" in the case of alumina, does not give the predicted dependence of $\underline{R}^\circ$ values on adsorbent activity (as in Fig. 3). This is illustrated in Fig. 4 for the elution of both naphthalene and propyl sulfide from D-12 silica of varying activity. The dashed lines superimposed on the experimental plots are the theoretical curves predicted by eqn. (6) and Fig. 3. This "irregularity" of the eluent CCl_4 for the present adsorbent is believed to arise from the combination of a small average pore diameter in Code 12 silica with a large eluent diameter. As an immediate result, it is assumed that certain of the smaller adsorbent pores in Code 12 silica are inaccessible to CCl_4 and other eluents of comparable cross section. In the case of calcined adsorbent, there is no possibility of the redistribution of adsorbed water to cover these "bare" pores, so that there will exist adsorption regions uncovered by any adsorbed species. Solute adsorption energies in these uncovered regions will be very much larger than for "normal" adsorption on covered regions, and this will increase the *average* adsorption energy of solute in all regions and, in turn $\underline{R}^\circ$. This is observed, CCl_4 being a strong eluent relative to pentane for alumina as adsorbent ("normal" behavior), but *apparently* weaker than pentane in the elution of naphthalene from calcined Code 12 silica ($\underline{R}^\circ$ is 27.5 and 30.0 ml/g, respectively, for elution of naphtha-

TABLE IX

TEST OF EQUATION (6) IN CORRELATION OF SOLUTE RETENTION VOLUMES WITH ADSORBENT ACTIVITY; ELUTION OF NON-HYDROCARBONS FROM CODE 12 SILICA

Solute	*Eluent*	*log $\underline{R}^\circ$ for various water contents*				*Av. dev.*	$\overline{S,E}$
		1.6%	*4.6%*	*6.9%*	*16.0%*		
Propyl sulfide	Pentane						
(Exptl.)		2.07	1.45	1.39	0.88	±0.01	2.94
(Calc.)		2.06	1.44	1.39	0.90		
Nitrobenzene	Benzene						
(Exptl.)		0.22	—0.03	—0.08	—0.30	±0.04	0.84
(Calc.)		0.20	0.03	—0.10	—0.36		
p-Nitroanisole	Benzene						
(Exptl.)		0.67	0.52	0.40	—0.04	±0.05	1.44
(Calc.)		0.73	0.47	0.35	0.00		
2-Acetonaphthalene	Benzene						
(Exptl.)		1.18	0.88	0.86	0.55	±0.11	2.12
(Calc.)		1.34	0.98	0.82	0.41		
Dimethyl isophthalate	CH_2Cl_2						
(Exptl.)		1.43		0.87	0.34	±0.08	2.17
(Calc.)		1.38		0.79	0.44		
Phenyl ethyl sulfide	Pentane						
(Exptl.)			1.53	1.27	0.81	±0.03	2.80
(Calc.)			1.48	1.29	0.82		
Phenetole	Pentane						
(Exptl.)			1.92	1.66	1.13	±0.02	3.35
(Calc.)			1.89	1.67	1.15		

lene from Code 12 silica by pentane and CCl_4). If this explanation of these latter data is true, then a plot of eluent strength ε° *versus* percentage CCl_4 for pentane–CCl_4 binary eluents should go through a maximum, and $\underline{R}^\circ$ for naphthalene should pass through a minimum, because of the ability of pentane to cover adsorbent surfaces inaccessible to CCl_4, and the greater adsorption affinity of CCl_4 on remaining adsorption regions. This is in fact observed; $\underline{R}^\circ$ for naphthalene eluted by 25 % v CCl_4–pentane from the same calcined Code 12 silica was found equal to 15.5 ml/g. It is assumed that elution by CCl_4 from water deactivated adsorbent permits the redistribution of adsorbed water into "bare" pores, with resulting cancellation of the efficiency of these regions for adsorption of solute. The overall effect is to produce the "irregular" dependence of $\underline{R}^\circ$ on adsorbent activity which is shown in Fig. 4.

While only three eluents are represented in the data of Tables VI and VII, there is no reason to doubt the validity of eqn. (5) in the case of other eluents, except where small pore diameter adsorbents and eluents of large cross section are combined in a single chromatographic system.

EFFECT OF ELUENT TYPE IN SEPARATION OVER SILICA

The effect of eluent type on solute retention volume can be obtained from eqn. (1) for alumina or eqn. (3) for silica by combining certain of the solute terms into a solute adsorption energy factor S° as in eqn. (7). For alumina, S° in eqn. (7) is defined by:

$$S^\circ = \sum^{i} Q^\circ_i - f(Q^\circ_k) \sum^{i \neq k} Q^\circ_i + \sum^{j} q^\circ_j$$

The area of the solute $\sum^{i} \delta_i$ is assumed to determine the number of eluent molecules displaced from the adsorbent surface by a solute molecule, and this in combination with the relative adsorption energy of the eluent ε° determines the effect of eluent on $\underline{R}^\circ$. In Part III[7], eqn. (7) was tested for a broad range of solute and eluent types in adsorption on alumina. The verification of its validity for alumina was accomplished largely with pure eluents as opposed to binaries. The similar test of eqn. (7) for silica as adsorbent using pure eluents is unreasonable for several reasons[*].

TABLE X

EFFECT OF ELUENT IN ELUTION OF HYDROCARBONS FROM CODE 12 SILICA

Solute	$\sum^{i} \delta_i$		*log $\underline{R}^\circ$*						*Av. dev.*	S°
		*Adsorbent**	*1.6%*		*16%*					
		*Eluent***	*10% B-P*	*50% B-P*	*10% B-P*	*25% B-P*	*5% M-P*	*15% M-P*		
		$\alpha\varepsilon^\circ$*****	*0.099*	*0.195*	*0.042*	*0.076*	*0.0333*	*0.075*		
Naphthalene	8									
(Exptl.)			0.38						±0.07	2.02
(Calc.)			0.45							
Phenanthrene	10									
(Exptl.)			0.76	—0.21	0.20		0.35		±0.03	2.55
(Calc.)			0.73	—0.23	0.25		0.34			
Chrysene	12									
(Exptl.)			1.05	—0.17	0.51		0.52	0.04	±0.04	3.09
(Calc.)			1.01	—0.14	0.49		0.59	0.09		
Perylene	13									
(Exptl.)			1.05		0.49	0.12	0.69	0.16	±0.03	3.23
(Calc.)			1.04		0.53	0.09	0.65	0.11		
Picene	14									
(Exptl.)					0.84	0.26	0.90	0.28	±0.04	3.67
(Calc.)					0.75	0.28	0.88	0.29		

[*] % Water (chromatographic) on Code 12 silica.

[**] Symbols defined as following: P, pentane; B, benzene; M, methylene chloride; % refers to volume percent.

[***] Measured from above data (best fit).

Experimental retention volume data are presented in Table X for the elution of several hydrocarbons from Code 12 silica of two activities by several *binary* eluents. Values of S° for these various solutes had been previously obtained from eqn. (7) and retention volume data for pentane elution (see Table XV). Given the values of

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[*] First, as noted in the previous section, eqn. (6) does not apply to Code 12 silica and the eluent CCl_4, and, for the same reasons, neither does eqn. (7). The testing of eqn. (7) is most accurately and conveniently done with eluent pairs whose strengths are not widely different. With the exception of CCl_4, there are no pure eluents with ε° values intermediate between the saturate solvents and solvents as strong or stronger than benzene. Consequently, if CCl_4 cannot be used, those solutes which are readily eluted by the saturates cannot be tested for Code 12 silica in eqn. (7). Second, as will be seen, the retention volumes of the aromatic hydrocarbons are essentially zero for elution by benzene and stronger solvents. These hydrocarbon solutes were used as standards in Part III for the evaluation of alumina ε° values, but cannot be similarly used for elution from Code 12 silica by pure solvents. Finally, as will also be seen the variation of solute retention volume with eluent strength is much more pronounced for the elution of non-hydrocarbons from any silica relative to alumina. This greatly increases the necessity of the similarity of ε° values in the eluents used to test eqn. (7) and to evaluate $\sum^{i} \delta_i'$ for these solutes. These various considerations make it mandatory to use binary eluents in testing the applicability of eqn. (7) for silica as adsorbent.

V_a and α for these two adsorbents (Table V), it is possible to calculate best values of the effective eluent strength $\alpha\varepsilon^\circ$ for each binary by means of eqn. (7), if the $\sum_i \delta_i'$ values for each solute are assumed the same ($\sum_i \delta_i$) as for alumina. These values of $\alpha\varepsilon^\circ$ are summarized at the top of Table X. Finally, the adequacy of eqn. (7) in correlating the eluent effects of Table X is shown in the comparison of experimental values with those calculated by means of eqn. (7) and the various associated parameters. Agreement is good (average deviation ± 0.04 log units). The fit of these hydrocarbon elution data to eqn. (7) is further illustrated in Fig. 5, where log $\underline{R}^\circ$ values for the hydrocarbon picene and the adsorbent D-12 16% H_2O–SiO_2 are plotted *versus* $\alpha\varepsilon^\circ$. The slope of the straight line through these points is the calculated value of $\sum_i \delta_i$ for picene (14).

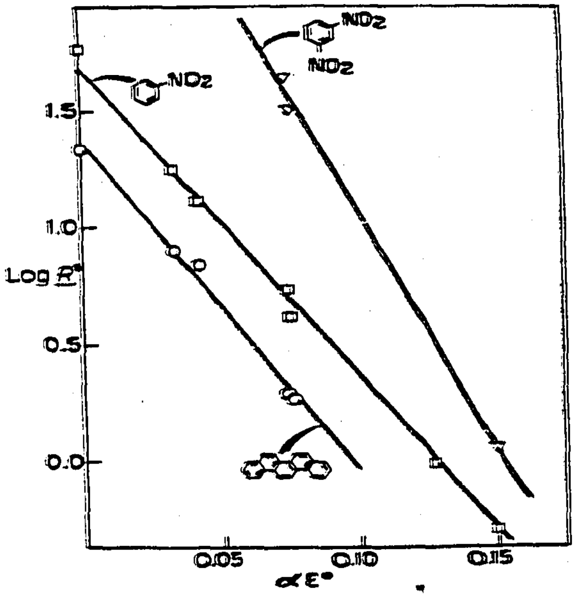

Fig. 5 Dependence of solute retention volume on eluent strength; elution from Code 12 16% H_2O–SiO_2.

Experimental data for the elution of several non-hydrocarbons from the same two adsorbents of Table X are presented in Table XI. The values of $\alpha\varepsilon^\circ$ shown for each binary at the top of Table XI are either the values previously calculated from the data of Table X for the hydrocarbons, or are extrapolated values from eqn. (7) and the data of Table XI. Data for two of the solutes of Table XI, nitrobenzene (NB) and dinitrobenzene (DNB), eluted from 16% H_2O–SiO_2 are plotted in Fig. 5. The predicted linear relationship between log $\underline{R}^\circ$ and $\alpha\varepsilon^\circ$ is again observed (as for picene), but the slopes of the plots for NB and DNB ($\sum_i \delta_i'$) are much larger than predicted from the δ_i values measured for elution from alumina (Part III[7]); *observed* $\sum \delta_i'$, NB, 13.4; DNB, 20.4; *predicted* $\sum \delta_i$, NB, 8.5; DNB, 11.0. The excellent correlation of the data of Table X suggests that δ_i' for the aromatic carbon atom is the same for both silica and alumina, as required by the equivalence of this quantity with the *area* of the aromatic carbon group (a quantity independent of adsorbent). For the adsorption of the nitro group on silica, however, δ_i' for this group is much larger than for ad-

TABLE XI

EFFECT OF ELUENT ON ELUTION OF NON-HYDROCARBONS FROM CODE 12 SILICA

Solute	$\sum^{i} \delta_i'$		*log R°*									*Av. dev.*	*S°*
		*Adsorbent**	*1.6%*	*16%*									
		*Eluent***	*50% B-P*	*P*	*10% B-P*	*25% B-P*	*B*	*5% M-P*	*15% M-P*	*40% M-P*	*M*		
		*αε°****	*0.195*	*0.000*	*0.042*	*0.076*	*0.150*	*0.033*	*0.075*	*0.127*	*0.192*		
Phenyl ethyl sulfide													
(Exptl.)	9.4		0.06	0.81	0.35			0.46				±0.02	2.75
(Calc.)	9.6		0.03	0.79	0.39			0.47					
Phenetole													
(Exptl.)	10.4		0.38	1.13	0.66	0.27		0.74				±0.03	3.29
(Calc.)	10.6		0.31	1.11	0.66	0.30		0.76					
Nitrobenzene													
(Exptl.)	13.4		0.72	1.76	1.11	0.61	—0.30	1.25	0.73	—0.01		±0.04	4.25
(Calc.)	13.2		0.66	1.69	1.14	0.69	—0.29	1.25	0.70	0.01			
Methyl benzoate													
(Exptl.)	14.1		1.33	2.13	1.52	1.04	—0.08	1.69	1.14			±0.06	4.93
(Calc.)	13.5		1.21	2.10	1.53	1.07	0.07	1.65	1.09				
2-(1-Thiapropyl)-naphthalene													
(Exptl.)	11.8		0.03	1.07	0.54	0.05						±0.05	3.13
(Calc.)	11.6		—0.02	1.02	0.53	0.14							

2-Methoxynaphthalene												
(Exptl.)	11.2	0.57	1.35	0.89	0.42						±0.06	3.77
(Calc.)	12.2	0.43	1.40	0.89	0.47							
2-Acetonaphthone												
(Exptl.)	17.2					0.55	2.61	1.78	0.94	—0.11	±0.06	6.58
(Calc.)	17.2					0.51	2.52	1.80	0.91	—0.21		
p-Diethoxybenzene												
(Exptl.)	16.5				1.46	0.09	1.96	1.20	0.36		±0.10	5.46
(Calc.)	15.2				1.26	0.14	1.92	1.28	0.49			
m-Dinitrobenzene												
(Exptl.)	20.0				1.50	0.08		1.64			±0.05	6.64
(Calc.)	20.2				1.57	0.06		1.59				
m-Nitroanisole												
(Exptl.)	17.1			1.49	1.03	—0.31		1.08			±0.05	5.30
(Calc.)	17.4			1.59	1.00	—0.29		1.01				
Carbazole												
(Exptl.)	17.9			1.47	0.88	—0.53	1.71	1.04	0.17		±0.08	5.25
(Calc.)	17.9			1.54	0.89	—0.40	1.70	0.95	0.02			
Dimethyl isophthalate												
(Exptl.)	(14.2)					0.91			1.26	0.34	±0.17	8.30
(Calc.)	21.0					0.97			1.46	0.09		

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* % Water (chromatographic) on Code 12 silica.

** Symbols defined as follows: P, pentane; B, benzene; M, methylene chloride; % refers to volume percent.

*** Experimental value from hydrocarbon $\underline{R}°$ values.

TABLE XII

SUMMARY OF SOLUTE PARAMETERS FOR SILICA AS ADSORBENT (EXPERIMENTAL DATA FOR CODE 12)

Group	δ_i'	$(\delta_i' - \delta_i)$		Q°_i		
				SiO_2		Al_2O_3 Ref.[8]
		Exptl.	*Calc.**	*This study*	*Ref.*[4]	
–CH=	0.5–1	0.0	0.0	0.25	—	0.31
Ar–S–R	3.6	1.1	0.4	1.29	—	1.32
Ar–O–R	4.6	2.6	1.9	1.83	2.3	1.77
Ar–NO_2	7.2	4.7	4.4	2.77	2.5	2.75
Ar–CO_2–R	7.5	4.5	5.9	3.45	—	3.32
Ar–CO–R	9.2	7.2	6.5	4.69	4.9	3.74
Ar–NH_2			6.5	5.1**	4.7	4.41
=NH (carbazole)	8.9	8.4	4.6	3.00	—	4.1
R–S–R				2.94	—	2.65

* $14.5\, f(Q^\circ_k)$.

** Assumed δ_i' for $-NH_2$ equal $14.5\, f(Q^\circ_k) + \delta_i$.

sorption on alumina: 2.5 on alumina, 7.2–7.4 on silica (from plots of Fig. 5). This increase in the *apparent area* δ_i' of non-hydrocarbon adsorbing groups on silica relative to alumina is rather general, as shown by the experimental (least squares) $\overset{i}{\Sigma}\, \delta_i'$ values of the solutes in Table XI, and the summary of best δ_i' values in Table XII. These latter values were derived from the data of Table XI, just as the δ_i' value of a nitro group can be derived from Fig. 5. Using these δ_i' values of Table XII in eqn. (7), the experimental data of Table XI can be calculated with satisfactory accuracy (average deviation ± 0.06 log units). The S° values used are the average values calculated from the data of Table XI by means of eqn. (7).

For elution from alumina, the δ_i' (or δ_i) values of various groups *i* closely approximate the relative area of *i*. In the case of elution from silica, it is apparent that this is no longer true, a group such as aceto (δ_i' equal 9.2) appearing larger than an entire naphthalene molecule ($\overset{i}{\Sigma}\, \delta_i'$ equal 8.0), in regard to the number of eluent molecules that appear to be displaced by the aceto group. If the nominal area δ_i (from adsorption on alumina) is subtracted from δ_i' for each group *i*, the difference may be taken as the excess area required by *i* in adsorption on silica. Interestingly, this excess area appears to correlate with the localization function $f(Q^\circ_k)$ described in Part IV[8]

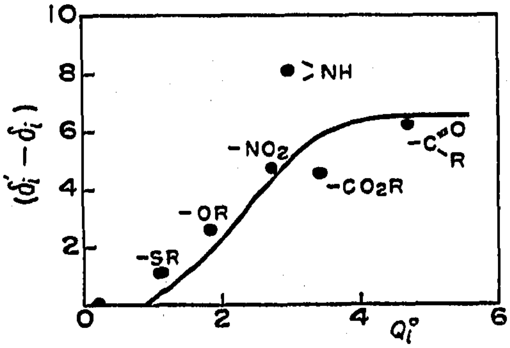

Fig. 6. Dependence of solute group excess area on adsorption strength of group (Code 12 silica).

for alumina. This is demonstrated in Fig. 6, where $(\delta_i'-\delta_i)$ is plotted *versus* $Q°_i$, the relative adsorption energy of the group *i* in silica (see next section for derivation of these latter values). Superimposed on this plot is the curve $14.5\ f(Q°_i)$. This correlation of $(\delta_i'-\delta_i)$ and $f(Q°_i)$ is also shown by the comparison of experimental and calculated values of $(\delta_i' - \delta_i)$ in Table XII, an average deviation of only ± 0.7 units being observed for the *exocyclic* substituents. The excess area of the nitrogen group which forms part of the carbazole nucleus is somewhat larger than predicted by the expression $14.5\,f(Q°_i)$, and this may be a general property of strongly adsorbed groups forming part of an aromatic nucleus.

Eqn. (7) may be made specific for adsorption upon silica by substituting the expression: $[\delta_i + 14.5\ f(Q°_i)]$ for δ_i':

$$\log R° = \log V_a + \alpha \{ S° - \varepsilon° \sum^{i} [\delta_i + 14.5\ f(Q°_i)]\} \tag{8}$$

The correlation of Fig. 6 suggests that the large *apparent* areas δ_i' of strongly adsorbing groups arises from a localization phenomenon similar to that observed in adsorption on alumina, but which takes a different manifestation in adsorption on silica. This possibility will be further explored in a forthcoming publication.

The eluent strength parameters for benzene and methylene chloride which were evaluated from the data of Tables X and XI are summarized in Table VII. Table XIII compares experimental values of $\alpha\varepsilon°_{AB}$ for the various binaries of Tables X and XI with values calculated from eqn. (5) and the eluent parameters of Table VII. The agreement is good (average deviation ± 0.005).

TABLE XIII

COMPARISON OF EXPERIMENTAL AND CALCULATED $\alpha\varepsilon°$ VALUES FOR BINARY ELUENTS AND CODE 12 SILICA

Eluent	*Adsorbent activity (% H_2O - SiO_2)*	$\alpha\varepsilon°_{AB}$	
		Exptl.	*Calc.**
10 % v Benzene–pentane	1.6	0.099	0.093
50 % v Benzene–pentane	1.6	0.195	0.184
10 % v Benzene–pentane	16.0	0.042	0.046
25 % v Benzene–pentane	16.0	0.076	0.082
5 % v Methylene chloride–pentane	16.0	0.033	0.032
15 % v Methylene chloride–pentane	16.0	0.075	0.074
40 % v Methylene chloride–pentane	16.0	0.127	0.134

* From eqn. (5).

EFFECT OF SOLUTE STRUCTURE IN ADSORPTION ON SILICA

The effect of solute structure on adsorption affinity is included in the solute parameter $S°$, previously defined for adsorption on alumina, and experimentally measurable for adsorption on silica through eqn. (7). Elution of a large number of solutes from silica in the present study has provided experimental $S°$ values for a wide range in solute structures. Some of these S° values have already been presented in Tables X and XI. The following discussion of these S° values in terms of our previous correlations for alumina has been broken down into two parts, hydrocarbons and non-hydrocarbons.

Hydrocarbons

Values of $\underline{R}^\circ$ for the elution of a number of alkyl substituted hydrocarbons from Code 12 silica by pentane are summarized in Table XIV. These data permit the derivation of S° values for each compound (listed as "experimental" S° values) from eqn. (7). The assumption that the localization term $f(Q^\circ_k) \sum^{i \neq k} Q^\circ_i$ does not contribute to S° for the hydrocarbons (because of their small group adsorption energies) permits the reduction of these S° values into values of Q°_i and q°_j corresponding to each different structural group and those specific solute geometries which affect adsorption. The solute parameters for silica are summarized in Table XV, along with corresponding values for alumina from Part II for comparison. In some cases the alumina Q°_i values appear slightly different from those reported in Part II[6], since no distinction between methyl and methylene carbon types was made in Part II. The parameters of Table IV include this distinction, their derivation using the value of ε° for pentane (see Part III[7]). The most pronounced difference in these solute parameters of Table XV between the two adsorbents is in the preference for adsorption of methyl relative to methylene carbon groups on silica, and the reverse on alumina. The other parameters

TABLE XIV

RETENTION VOLUMES FOR THE ALKYL-SUBSTITUTED OLEFINS AND BENZENES; PENTANE ELUTION FROM CODE 12 1.0% H_2O–SiO_2

Solute	$\underline{R}^\circ$ *(ml/g)*	S°	
		Exptl.	*Calc.*
cis-Pentene-2	1.34	0.71	0.74
2-Methylbutene-2	2.11	0.91	0.91
2,3-Dimethylbutene-2	2.50	1.00	1.11
Pentadiene-1,3	3.50	1.15	1.11
Benzene	7.5	1.51	1.48
Toluene	9.8	1.63	1.61
o-Xylene	14.5	1.81	1.81
p-Xylene	13.2	1.77	1.77
1,2,3-Trimethylbenzene	20.3	1.97	1.97
1,3,5-Trimethylbenzene	17.4	1.89	1.89
Pentamethylbenzene	23.8	2.04	2.31
Hexamethylbenzene	24.5	2.05	2.52
n-Butylbenzene	7.2	1.49	1.46
n-Octylbenzene	4.9	1.31	1.37
n-Decylbenzene	3.6	1.17	1.17
n-Eicosylbenzene	1.84	0.85	0.68
Isopropylbenzene	9.0	1.60	1.66
tert.-Butylbenzene	8.8	1.59	1.73

TABLE XV

COMPARISON OF HYDROCARBON SOLUTE PARAMETERS FOR ALUMINA AND SILICA

Group or geometry	Q°_i		q°_j	
	SiO_2	*Al_2O_3*	*SiO_2*	*Al_2O_3*
$-CH_2-$, $-CH<$	—0.049	+0.02		
$-CH_3$	+0.074	—0.03		
$-CH=$	+0.247	+0.31		
Methyl substitution on aromatic carbon			+0.055	+0.09
Alkyl substitution on aromatic carbon			+0.055	+0.05
Vicinal alkyl substitution			+0.039	+0.09

of Table XV all show similar contributions to S° from different solute groups and geometries. The silica values tend to be lower than the alumina values, probably reflecting generally weaker bonding of the hydrocarbons to the former adsorbent. The only S° values of Table XIV which are not well correlated by the parameters of Table XIV are for pentamethyl- and hexamethylbenzene.

Table XVI summarizes S° values for a number of *unsubstituted* olefins and aromatic hydrocarbons. The S° values of ethylene and butadiene could not be conveniently

TABLE XVI

SOLUTE ADSORPTION FACTORS S° FOR THE UNSUBSTITUTED OLEFINS AND AROMATIC HYDROCARBONS; PENTANE ELUTION FROM CODE 12 SILICA

Solute	*S°*	*No. of S° values*	*Av. dev.**	*Adsorbent activities***
Ethylene	0.44***	3	±0.04	1.0
Butadiene	1.02***	1	—	1.0
Benzene	1.48	2	0.00	1.0 ,8.0
Styrene	1.71	1	—	1.6
Naphthalene	2.02	6	0.03	See Table IV
Azulene	2.35	2	0.06	1.0, 8.0
Acenaphthylene	2.28	3	0.03	See Table IV
Phenanthrene	2.55	2	0.02	4.6, 8.0
Anthracene	2.60	1	—	8.0
Fluoranthene	2.79	1	—	8.0
Pyrene	2.57	2	0.02	4.6, 8.0
Triphenylene	3.15	2	0.03	4.6, 8.0
Chrysene	3.09	2	0.01	8.0, 16.0
1,2-Benzanthracene	3.09	1	—	8.0
Perylene	3.23	3	0.03	4.6, 8.0, 16.0
1,2-Benzpyrene	3.28	1	—	16.0
Picene	3.67	1	—	16.0
3,4-Benztetraphene	3.68	1	—	16.0
Dibenzyl	2.92	3	0.03	1.6, 6.9, 16.0

* Between experimental S° values for same solute.
** Defined by silica water content (%).
*** Substituted olefin values corrected for effect of substituents.

measured for the compounds themselves, so the values for methyl-substituted olefins (Table XIV) were corrected to zero substituents using the parameters of Table XV. The $S°$ values of Table XVI are plotted *versus* the number of aromatic plus olefinic carbon atoms n in Fig. 7. $S°$ equals 0.246 n for $n \leqslant 6$, and $(0.246 \times 6) +$ 0.133 $(n - 6)$ for n larger than 6. In the case of the solute dibenzyl, where the two phenyl groups are not fused together, and where the effect of alkyl substitution on the two aromatic rings (2×0.055) is just canceled by the adsorption of the two methylene carbons $[2 \times (-0.049)]$, $S°$ is given by virtually the same expression (0.243 n) as for the solutes no larger than benzene ($n \leqslant 6$). It thus appears that the contribution to $S°$ from each group of fused aromatic or unsaturated carbon atoms is given as 0.246 n for the first six carbon atoms, and 0.133 n for additional carbon atoms in the fused cluster. The physical interpretation of this relationship will be discussed in the final section of this paper.

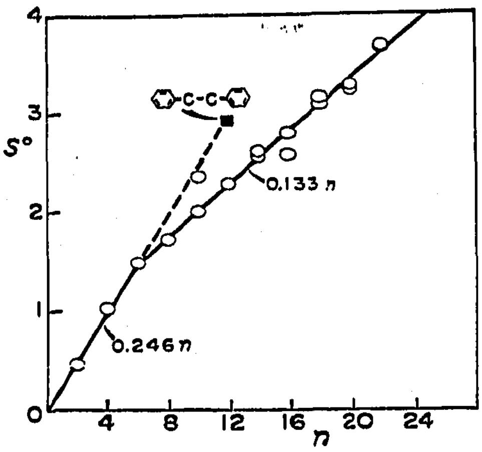

Fig. 7. Plot of $S°$ for unsubstituted aromatics *versus* aromatic carbon number n; Code 12 silica gel.

Non-hydrocarbons

Table XVII summarizes $S°$ values for 21 non-hydrocarbons. The monofunctional benzene derivatives were used to derive values of $Q°_i$ for each functional group represented, assuming that $Q°_i$ equals $S°$ for a group i substituted benzene, minus $S°$ for benzene (1.48). These values of $Q°_i$ are listed in Table XII, along with corresponding alumina values for comparison. Values of $Q°_i$ for aliphatic sulfur and carbazole nitrogen, which were derived in a somewhat different but consistent fashion, are also included. The solute group adsorption parameters $Q°_i$ for both adsorbents are quite similar, as shown in the plot of these values for silica *versus* those for alumina in Fig. 8. The values of $S°$ for the polysubstituted benzenes and substituted naphthalenes of Table XVII appear equal to $S°$ for the unsubstituted hydrocarbon plus the sum of $Q°_i$ values for all substituents. This relationship can be stated:

$$S° = \sum^{i} Q°_i - 0.113\,(n - 6r) + \sum^{i} q°_j \qquad (9)$$

The term 0.113 $(n - 6r)$ corrects for the lower adsorption energy of carbon atoms past the first six in each of r unfused ring systems comprising the solute. The compar-

TABLE XVII

SOLUTE ADSORPTION FACTORS S° FOR NON-HYDROCARBONS ELUTED FROM CODE 12 SILICA

Solute	S°		*No. of S° values*	*Av. dev.***	*Chromatographic system****
	Exptl.	*Calc.**			
Phenyl ethyl sulfide	2.77	—	6	±0.06	4.6%, pentane; 6.9%, pentane; see Table XI
Phenetole	3.31	—	7	0.04	Same as above
Nitrobenzene	4.25	—	8	0.06	See Table XI
Methyl benzoate	4.93	—	7	0.09	See Table XI
Acetophenone	6.17	—	1	—	16.0%, benzene
Aniline	6.6§	—	1	—	16.0%, benzene
2-(1-Thiapropyl)-naphthalene	3.13	3.31	4	0.07	See Table XI
1-Methoxynaphthalene	3.12	3.85	1	—	16.0%, pentane
2-Methoxynaphthalene	3.77	3.85	4	0.09	See Table XI
Methyl 2-naphthoate	5.32	5.47	1	—	16.0%, benzene
2-Acetonaphthone	6.58	6.71	5	0.16	See Table XI
o-Diethoxybenzene	5.75	5.14	1	—	16.0%, benzene
p-Diethoxybenzene	5.46	5.14	5	0.17	See Table XI
m-Nitroanisole	5.30	6.08	4	0.09	See Table XI
p-Nitroanisole	5.80	6.08	1	—	16.0%, benzene
m-Dinitrobenzene	6.64	7.02	3	0.08	See Table XI
Dimethyl isophthalate	8.55	8.38	4	0.37	See Tables IX, XI
2-Nitroaniline	8.1§	9.35	1	—	16.0%, methylene chloride
1,2,4-Tricarbomethoxybenzene	11.1	11.83	1	—	16.0%, methylene chloride
2,4-Dinitroaniline	11.3§	12.12	1	—	16.0%, methylene chloride
Carbazole	5.25	—	7	0.11	See Table XI

* From eqn. (9).

** Between experimental S° values for same solute.

*** Defined by silica water content and eluent.

§ Assumes δ_i' for $-NH_2$ equal 14.5 $f(Q^\circ_i)$.

ison of experimental and calculated S° values in Table XVII shows an average deviation of ± 0.3 log units, corresponding to an average deviation between calculated and experimental $\underline{R}^\circ$ values of about ± 0.2 log units. Eqn. (9) is seen not to include the localization term which is part of S° for adsorption on alumina. The localization term in alumina S° values results in a lowering of experimental S° values, with the effect being largest at large values of S°. The experimental S° values for the "poly-

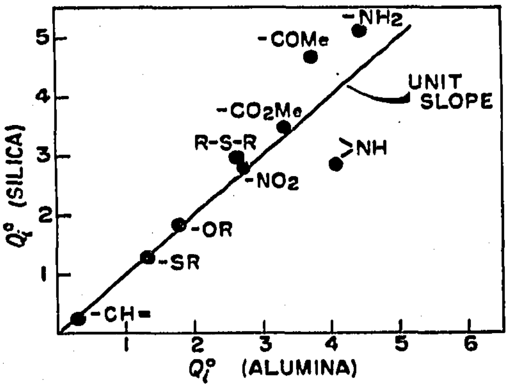

Fig. 8. Group adsorption factors Q°_i; Code 12 silica *versus* Alcoa F-20 alumina.

TABLE XVIII

SOLUTE RETENTION VOLUMES FOR CODE 62 1 % H_2O-SiO_2; PENTANE ELUTION

Solute	*log R°*	
	Exptl.	*Calc.**
Benzene	0.16	0.01
Naphthalene	0.42	0.39
Azulene	0.66	0.63
Acenaphthylene	0.56	0.58
Phenanthrene	0.70	0.77
Anthracene	0.70	0.81
Fluoranthene	0.78	0.94
Pyrene	0.66	0.79
Triphenylene	0.95	1.20
Chrysene	0.96	1.16
1,2-Benzanthracene	0.97	1.16
Perylene	0.98	1.26
1,2-Benzpyrene	0.96	1.30
Dibenzyl	1.10	1.04
Phenyl ethyl sulfide	1.07	0.93
Phenetole	1.46	1.33
Nitrobenzene	1.61	1.99
2-(1-Thiapropyl)-naphthalene	1.30	1.19
Methyl benzoate	2.34	2.47

* From eqn. (7), assumes V_a equal 0.09 and α equal 0.715; $S°$ data of Tables XVI and XVII.

functional" solutes of Table XVIII (substituted naphthalenes and polysubstituted benzenes) are plotted *versus* calculated values $\overset{i}{\Sigma}\, Q°_i$ from eqn. (9) in Fig. 9, while a similar plot for elution of these same solutes from alumina is offered for comparison in Fig. 10 (data of Part IV[8]). It appears that localization of the type exhibited in adsorption on alumina (Fig. 10) is absent for adsorption on silica (Fig. 9). This conclusion

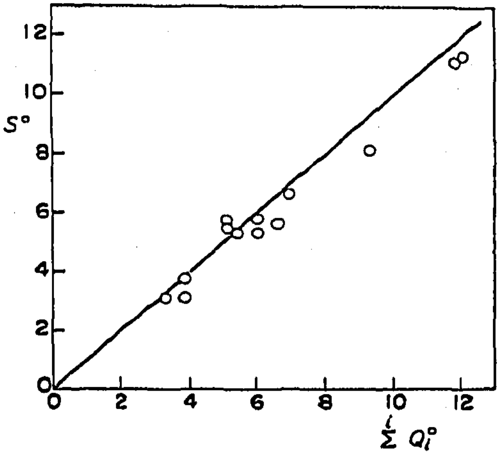

Fig. 9. Experimental *versus* calculated $S°$ values for polyfunctional non-hydrocarbons; Code 12 silica.

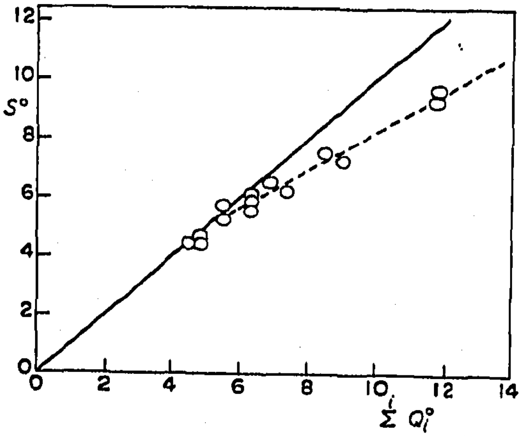

Fig. 10. Experimental *versus* calculated $S°$ values for polyfunctional non-hydrocarbons; Alcoa F-20 alumina.

is confirmed by the observations of SPORER AND TRUEBLOOD[4] on adsorption from benzene onto a silicic acid–celite mixture; these authors found that the adsorption energy ($S°$) of polysubstituted benzenes was given as the sum of group adsorption energy values.

ADSORBENT STANDARDIZATION

Adsorbent standardization can refer either to the characterization of the adsorptive properties of a solid, or to the selection and/or modification of such a solid so as to obtain an adsorbent which exactly duplicates some standard. The well-known procedure of BROCKMANN[14] for the classification of the adsorbent activity of water-deactivated aluminas was the first attempt at adsorbent standardization by means of a chromatographic test, and is still in use. A similar classification for water-deactivated silica has been proposed recently[15]. The activity grades reported by either procedure[14,15] represent ranges in adsorbent acitivities, and are intended to be qualitative rather than quantitative designations. Since these activity tests do not distinguish between the separate contributions of surface area and surface energy to adsorbent properties, it is likely that they will fail when applied to solids of widely varying surface area. It has been postulated (Part II[6]) that an adsorbent such as alumina can be completely characterized by its surface area (or V_a) and average surface energy (or α). The present section will be devoted to the further testing of this postulate in the case of silica, and the examination of some of its chromatographic consequences.

The experimental measurement of V_a and α for the adsorbent Alcoa F-20 alumina of varying water content was described in Part II. Eqn. (1) was used in conjunction with the elution of the unsubstituted aromatic hydrocarbons by pentane. For these solutes and this eluent, eqn. (1) simplifies to:

$$\log \underline{R}° = \log V_a + 0.31\, \alpha n \qquad (10)$$

where n is the number of carbon atoms. Extrapolation of the linear plot of $\log \underline{R}°$ *versus* n for a particular adsorbent sample to n equal zero gives V_a, while the slope of the plot divided by 0.31 gives α. This procedure is somewhat less suited for application to silica because of the non-linear form of such an experimental plot (as in Fig. 7). It was also shown in Part II for alumina that the value of V_a for calcined alumina is close to that predicted by the saturation uptake of tetramethylbenzene and by the BET surface area (nitrogen adsorption). Furthermore, the facile elution of adsorbed water from deactivated alumina which contains more than V_a ml/g of adsorbed water suggests that the volumes of a monolayer of water, nitrogen, and tetramethylbenzene are all approximately equal. This suggests that the adsorbent surface volume is calculable from the value corresponding to calcined adsorbent, minus the volume (ml/g) of added water. With V_a for calcined adsorbent calculable from the surface area, eqn. (4) follows. This relationship is tested below for the previously reported (Part II) data for V_a as a function of Alcoa F-20 alumina water content (Table XIX).

For all except possibly the 4.9 % H_2O–Al_2O_3 sample, the two columns of V_a values in Table XIX agree within the experimental uncertainty of the first column. This suggests, as is theoretically reasonable in the light of our preceding remarks, that eqn. (4) will apply to other adsorbents as long as the amount of adsorbed water does not approach monolayer coverage.

TABLE XIX

SURFACE VOLUME OF WATER-DEACTIVATED ALUMINAS (ALCOA F-20)

Added water (%)	V_a	
	Exptl., eqn. (10)	*Calc., eqn. (4)*
0.0	0.040, 0.034*	0.054
1.0	0.029	0.044
4.0	0.015	0.014
4.9	0.011	0.005

* Benzene eluent.

Assuming the measurement of V_a by means of eqn. (4), the value of α can be obtained from a single standard solute elution by means of eqn. (6), or

$$\alpha = \log(\underline{R}°/V_a)/(\overline{S, E})$$

We have defined α as 1.00 for calcined adsorbent in Part II[6] and the present paper. The value of $(\overline{S, E})$ can thus be evaluated from the standard solute $\underline{R}°$ value for calcined adsorbent, following which α for any other adsorbent activity can be calculated from a standard solute retention volume through the above relationship. This procedure provides the basis of the tabulation and use of the values of α and $(\underline{R}°/V_a)$ given in Table V.

Table XVIII presents some experimental data for the elution of several solutes from Code 62 1 % H_2O–SiO_2 by pentane. As in the first example of the preceding section on "The Prediction ..... etc.," V_a and α for this adsorbent were calculated as 0.090 and 0.715, respectively. With the adsorbent of Table XVIII thus characterized, the $\underline{R}°$ values in Table XVIII can be calculated by means of eqn. (7) and the $S°$ values of Tables XVI and XVII. The average deviation between these experimental and calculated values in Table XVIII is ± 0.15 log units, which is somewhat higher than expected for a Code 12 silica. The correlation for Code 62 silica would be improved moderately by assuming that the coefficient 0.113 in eqn. (3) is really 0.14 for Code 62 silica.

It is interesting to note that the adsorbent activity function α for a D-62 4 % H_2O–SiO_2 was measured as 0.70, relative to 0.71 for the same adsorbent with only 1 % added water. This implies that the surface energy of D-62 1 % H_2O–SiO_2 is reasonably constant, since further water deactivation gives insignificant reduction in average surface energy. For D-62 silica, 1 % and 4 % added water corresponds to 10 % and 40 % surface coverage by adsorbed water. By contrast, α for a D-12 silica deactivated with 10 % of a monolayer of adsorbed water (3 % adsorbed water) is 0.80, which declines to a value of 0.68 for deactivation by 40 % of a monolayer of adsorbed water (12 % H_2O).

SPORER AND TRUEBLOOD[11] have reported data for still another silica, a "silicic acid–celite" mixture. Their frontal analysis study of this adsorbent can be reduced to an equivalent LEAC basis by setting their values of K equal to $\underline{R}°$. Only the substituted benzenes eluted by benzene were studied by SPORER AND TRUEBLOOD. Because

ε° for benzene (0.25) is equal to Q°_i for each of the aromatic carbons of the benzene ring, eqn. (3) takes the following form for these data:

$$\log \underline{R}^\circ = \log V_a + \alpha\,[\sum^{i} (Q^\circ_i - 0.25\,\delta_i')]$$

where the summation is over the substituents i on the benzene ring, exclusive of ring carbon atoms. SPORER AND TRUEBLOOD have fitted their experimental data to a mathematical expression which can be related to the above equation. From their value K_{ph}, we have V_a equal to 0.3 ± 0.1. Similarly, their values of K_i for each of the substituents i reported by them are equal to $10^{\alpha(Q^\circ_i - 0.25\,\delta_i')}$. For those substituents studied by both us and the latter authors, we have plotted values of log K_i *versus* $(Q^\circ_i - 0.25\,\delta_i')$ in Fig. 11. The slope (0.71) of this plot is equal to α for their adsorbent. The plot of Fig. 11 shows reasonable agreement between these two independent studies, particularly when it is realized that the use of benzene as eluent by SPORER AND TRUEBLOOD has substracted a large term ($\varepsilon^\circ\delta_i'$) from each Q°_i value. Table XII lists values of Q°_i calculated from the data of SPORER AND TRUEBLOOD with the assumption α equal 0.71 for their adsorbent. The average deviation of their Q°_i values from those reported in the present study is only ± 11 %, or 0.4 units out of values of Q°_i ranging from 1.8 to 5.4. SPORER AND TRUEBLOOD's values of K_i for substituents not included in the present study have been used in Table VI to extend our list of Q°_i values for silica. The values of V_a and α for their adsorbent (0.3, 0.71) suggest that it is comparable to a D-12 6% H_2O–SiO_2 (V_a equal 0.24 and α equal 0.71).

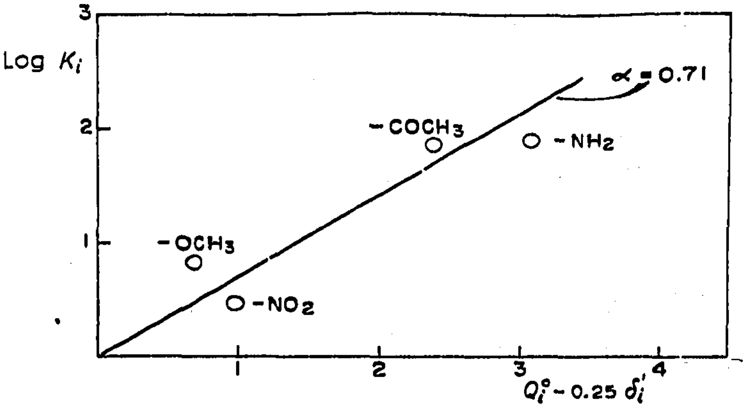

Fig. 11. Comparison of SPORER AND TRUEBLOOD solute group parameters with those of present study.

A final point of interest relative to adsorbent standardization is the exact duplication of adsorbent columns for routine separation and analysis. The problem has been briefly discussed elsewhere[16]. There are three separate aspects of the adsorbent which require standardization in the general case: V_a, α, and the effect of adsorbent on separation efficiency (HETP or solute band width). The last variable has been treated at length elsewhere[9,12,13,16], and a further discussion will not be attempted at this time. If the surface area of starting calcined adsorbent is reasonably constant from one batch of adsorbent to another, then addition of a given quantity of water to the adsorbent will always give the same values of V_a and α as for the standard adsorbent containing the same amount of adsorbed water. Slight differences in starting surface energies and areas may be compensated by corresponding changes in the amounts of water added. In any case, the final adsorbent is standardized by adjusting the total added water so that the final adsorbent has the same $\underline{R}^\circ$ value for a standard solute and eluent as does the original standard adsorbent. This procedure has been followed for Alcoa F-20 alumina in Part II[6] and in several recently reported analytical procedures which use this adsorbent[17-19]. STRAUCH[20] has reported an essentially equivalent adsorbent standardization technique, using the measurement of equilibrium values of K rather than $\underline{R}$. Where control of the adsorbent starting surface area within narrow limits is impossible (a phenomenon difficult to imagine), it is possible to standardize the adsorbent with respect to α, and then to compensate variation in V_a by reciprocally varying the weight of adsorbent used in the column.

KLEIN[10] and others[20,21] have reported that adsorbent pore diameter also plays a role in determining adsorbent properties. Where this effect is important, the adsorbent must be similarly matched to a standard in terms of pore diameter. We have been unable to verify the major importance of this variable *per se* in the present studies, other than to confirm that separation efficiency increases with pore diameter as claimed by KLEIN[10]. The next section provides additional comment on this subject.

THE MECHANISM OF ADSORPTION ON SILICA

Some differences (as well as similarities) may be noted in the adsorption of various solutes on silica relative to alumina. These differences are empirically summarized in the differing forms of the correlational equations for alumina, eqn. (1) and for silica, eqn. (3). It remains to comment briefly on the fundamental basis of these differences, a more detailed interpretation being reserved to a latter communication.

The surface structure of silica and its role in the adsorption process have been discussed extensively. It has been claimed that the topography and particularly the pore diameter[10,21,22] of silica samples are important factors in determining the relative adsorption of a solute. This postulate assumes either that the access of a solute to certain parts of the adsorbent surface is limited, or that the effective surface energy of some adsorption regions is reduced by virtue of certain solute geometries. In this connection, consider the 0.113 (n — 6) term of eqn. (3) and the related experimental dependence of S° on n in Fig. 7. For solutes no larger than benzene, the dependence of S° on n is "normal" relative to adsorption on alumina in two respects. First, S° increases linearly with n, implying that each additional aromatic carbon atom contributes an equal increment to the adsorption energy of the solute. Second, the value of this energy increment for silica (Q°_i equal 0.25) is comparable to that for alumina (Q°_i equal 0.31) as expected from the similarity of Q°_i for other solute groups i on the two adsorbents (see Fig. 8). For larger solutes, S° is smaller than expected by analogy with adsorption on alumina, and a previous communication[13] has attributed this phenomenon to the presence of pores of diameter small enough to exclude solutes larger than benzene. This explanation appears ruled out, however, by the behavior of Code 62 silica toward the larger aromatic hydrocarbons. The average pore diameter of this latter adsorbent (170 Å) is larger than that of either the Code 12 silica (22 Å) or the previously studied Alcoa F-20 alumina (79 Å), yet the curvature of the S° *versus* n plot for Code 62 silica is if anything *more* severe than for Code 12; this is shown by the deviation of the experimental data (for Code 62 silica) in Fig. 12 from the calculated curve (for Code 12 silica). It is now believed that the anomalous adsorption energies of the larger aromatic hydrocarbons on silica are related to a localization effect such as occurs in the adsorption of certain solutes on alumina[8]. Because of some as yet unexplained differences, however, in the two adsorbents, localization affects the S° values of the larger aromatics on silica, and the S° values of solutes with strongly adsorbing groups (large Q°_i values) on alumina. Consequently, the $f(Q^\circ_k) \sum^{i \neq k} Q^\circ_i$ term in the correlation equation for alumina is absent from that for silica.

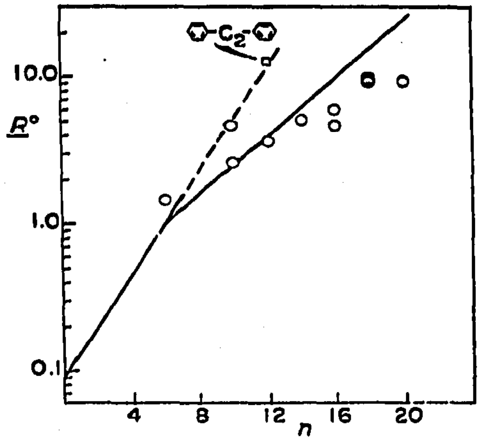

Fig. 12. Retention volumes of aromatic hydrocarbons as a function of carbon number; pentane, eluent; Code 62 1.0% H_2O–SiO_2.

Similarly, it has already been suggested that the large apparent areas δ' of strongly adsorbing groups when adsorbed on silica is related to the localization of these groups (see Fig. 6 and related discussion). This again suggests fundamental differences in the character of the adsorption sites on alumina and on silica. The further analysis of these differences is in progress.

GLOSSARY OF TERMS

D-12, D-62 = Refers to Davison Code Numbers 12 and 62.
$f(Q^\circ_i)$, $f(Q^\circ_k)$ = Localization function for adsorbing group i and k.
$\underline{K}$ = Solute distribution coefficient between adsorbed and non-sorbed phases; $\underline{K} = X_a/X_s$.
$\underline{K}^\circ$ = Value of $\underline{K}$ in linear isotherm region (low coverage).
$\underline{K}'$ = Value of $\underline{K}$ corrected for chemisorbed solute; see Table IV and related discussion.
K_i = Group adsorption factor as defined by SPORER AND TRUEBLOOD[4].
K_{ph} = Value of K_i for benzene ring.
n = Number of aromatic and unsaturated carbon atoms in a solute.
n_b = Value of $\sum^{i} \delta_i$ for an eluent B.
Q°_i = Solute substituent adsorption parameter.
q°_j = Solute geometry parameter.
r = The number of aromatic ring systems separated by alkyl groups in a solute.

$\underline{R}^\circ$ = Linear equivalent retention volume; ml/g.
$\underline{R}^\circ_1$, $\underline{R}^\circ_2$ = Values of $\underline{R}^\circ$ for a solute using eluents 1 and 2.
$\underline{R}'_2$ = Corrected equivalent retention volume after initial elution by a second eluent, 1; equal to total retention volume measured from point at which eluent 2 is used, minus column volume, divided by adsorbent weight (see experimental section).
S° = Total solute adsorption parameter.
SA = Surface area.
$(\overline{S, E})$ = Solute–eluent combined adsorption parameter.
V_a = Volume of adsorbent monolayer; ml/g.
X_s = Concentration of solute in solution phase; g/ml.
X_B = Mole fraction of stronger solvent B in eluent binary A–B.
α = Adsorbent activity function; adsorbent average surface energy.
δ_i = Substituent surface volume, proportional to surface area.
δ_i' = Apparent substituent surface volume; $\delta_i' = \delta_i$ for alumina; $\delta_i' = \delta_i + 14.6 f(Q^\circ_i)$ for silica.
ε° = Eluent strength parameter.
ε°_A, ε°_B, ε°_{AB} = Values of ε° for solvent A, solvent B and eluent binary A–B.

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SUMMARY

Linear retention volume data have been obtained for several solutes of widely varied molecular structure, eluted by a number of different eluents, from both high and low surface area silica samples of varying water content. All of these data can be quantitatively correlated with a fundamental equation similar, but not identical, to that previously developed for adsorption on alumina. The major differences which exist between adsorption on alumina and silica appear to arise from fundamental differences in the way solutes *localize* (or orient) around adsorption sites. Adsorbent pore diameter appears relatively unimportant in affecting adsorption affinity and solute retention volume, apart from the general dependence of adsorbent surface area on pore diameter, and with the exception of the combination of large eluents (such as carbon tetrachloride) and small pore diameters. The standardization of adsorbents for routine separation purposes has been discussed in detail.

REFERENCES

[1] E. LEDERER AND M. LEDERER, *Chromatography*, 2nd Ed., Elsevier, Amsterdam, 1957.
[2] J. J. WREN, *Chromatographic Reviews*, Vol. 3, Elsevier, Amsterdam, 1961, p. 111.
[3] K. N. TRUEBLOOD AND E. W. MALMBERG, *J. Am. Chem. Soc.*, 72 (1950) 4112.
[4] A. H. SPORER AND K. N. TRUEBLOOD, *J. Chromatog.*, 2 (1959) 499.
[5] L. R. SNYDER, *J. Chromatog.*, 5 (1961) 430.
[6] L. R. SNYDER, *J. Chromatog.*, 6 (1961) 22.
[7] L. R. SNYDER, *J. Chromatog.*, 8 (1962) 178.

[8] L. R. SNYDER, *J. Chromatog.*, 8 (1962) 319.
[9] P. D. KLEIN, *Anal. Chem.*, 34 (1962) 733.
[10] P. D. KLEIN, *Anal. Chem.*, 33 (1961) 1737.
[11] I. SHAPIRO AND I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 72 (1950) 776.
[12] K. N. TRUEBLOOD AND E. W. MALMBERG, *Anal. Chem.*, 21 (1949) 1055.
[13] L. R. SNYDER, *Anal. Chem.*, 33 (1961) 1527.
[14] (a) H. BROCKMANN AND H. SCHODDER, *Ber.*, 74 (1941) 73;
(b) P. B. MUELLER, *Helv. Chim. Acta*, 26 (1943) 1945.
[15] R. HERNANDEZ, R. HERNANDEZ, JR. AND L. R. AXELROD, *Anal. Chem.*, 33 (1961) 370.
[16] H. M. TENNEY AND F. R. STURGIS, *Anal. Chem.*, 26 (1954) 946.
[17] L. R. SNYDER, *Anal. Chem.*, 33 (1961) 1535.
[18] L. R. SNYDER, *Anal. Chem.*, 33 (1961) 1538.
[19] L. R. SNYDER, *Anal. Chem.*, 34 (1962) 771.
[20] L. STRAUCH, *Vestn. Sloven. Kem. Drustva*, 2 (1955) 71; *C.A.*, 51 (1957) 12382.
[21] A. WAKSMUNDZKI, J. OSCIK, J. MATUSEWICZ, R. NASUTO AND J. ROZYLO, *Przemysl Chem.*, 40 (1961) 387.
[22] I. E. NEĬMARK, I. B. SLINYAKOVA AND F. I. KHATSET, *C.A.*, 48 (1954) 2442.