LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

II. COMPOUND SEPARABILITY WITH ALUMINA AS ADSORBENT

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

L. R. SNYDER

(Received September 20th, 1960)

INTRODUCTION

The theoretical possibility of linear elution adsorption chromatography (LEAC) in the case of adsorbents which are energetically heterogeneous has been discussed, and experimental examples of the phenomenon have been cited for chromatographic systems featuring both activated alumina and silica as adsorbents[1]. In the related area of liquid–liquid and gas–liquid elution chromatography, PIEROTTI *et al.*[2] and REDLICH *et al.*[3] have used a molecular building block approach to relate solute structure to equilibrium solute activity coefficients at infinite dilution; these coefficients are in turn directly relatable to linear elution retention volumes in the corresponding chromatographic systems. Similarly, REICHL[4] has shown that R_M values in certain paper chromatographic systems may be accurately predicted as the sum of structural group parameters. SPORER AND TRUEBLOOD[5] have made use of the same model in the correlation of a number of compound separation factors for the chromatographic system benzene–silica. These latter authors have postulated a simple additive free energy relationship for the adsorption equilibrium involving a solute with multiple functional groups, while recognizing certain theoretical limitations in this model. A considerable number of other published studies[6-8] have treated the question of compound chromatographic separability as it relates to molecular structure; few such studies have been carried out for chromatographic systems known to be linear. The general desirability of limiting experimental data of this type to linear systems has been discussed previously[1,5], especially where the quantitative interpretation of adsorption phenomena is important.

The use of different eluents in these chromatographic studies, as well as adsorbents that have been water-deactivated to varying extents, further complicates even the qualitative comparison of the results of different workers. The need for a general theoretical model which is capable of interrelating solute chromatographic separability, solute molecular structure, adsorbent deactivation and eluent structure is apparent. Given such a correlational scheme, it should be possible to predict, at least semi-quantitatively, separation factors for a large number of experimental LEAC systems (and to estimate separation order in non-linear systems) on the basis of a

limited number of observations and a small number of theoretical concepts. Of equal importance, where the theoretical model is incomplete or inaccurate, comparison of calculated and experimental data can facilitate the recognition of defects in the existent science of adsorption chromatography.

<div align="center">EXPERIMENTAL</div>

All of the chromatographic data described in the present and previous[1] communications were obtained by the following general procedure. The glass and teflon apparatus of Fig. 1 was used, with the various ball and socket joints externally coated with a plastic paint in earlier runs. Later studies dispensed with this feature,
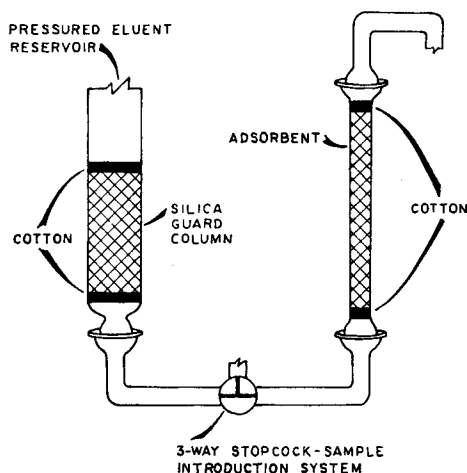

Fig. 1. Apparatus.

since it was found that leakage was invariably small and confined to joints between the eluent reservoir and the beginning of the chromatographic column; this had no effect on the data obtained. Columns (10 mm × 50–500 mm) were packed dry to maximum density by tamping and vibrating, the adsorbent weight determined by difference, the columns mounted, and then wetted with solvent prior to introduction of solute.

One example will demonstrate both the experimental steps used in determining solute retention volumes and the equivalence of linear retention volumes so obtained to corresponding equilibrium distribution $\underline{K}$ values. A 10 mm × 75 mm glass column was filled with 2.07 g of "nominal" 2.5 % H_2O–Al_2O_3. A known weight of a solute, azulene, was introduced into the column at the three-way stopcock, and this was eluted through the column with pentane. Eluent fractions of measured volume were collected. The concentration of azulene in these fractions was determined by ultraviolet spectroscopy in the 270 to 353 mμ region. From these data the cumulative weight percent solute removal from the column was plotted against the cumulative eluent volume. The retention volume R', defined as the eluent volume required to

elute 50 % of the solute, can be interpolated from the above plot, as shown in Fig. 2; this plot is on arithmetic probability graph paper. The Gaussian elution band predicted by theory should give a linear plot in the latter case; most experimental adsorption elution cases show band asymmetry (and non-linearity of the plot of
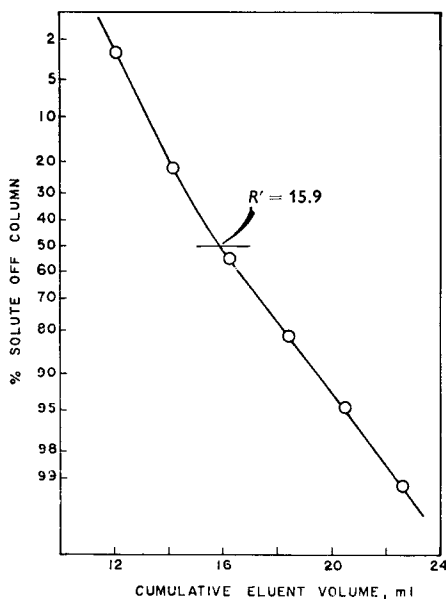

Fig. 2. Elution data plot to show interpolation of R'.

Fig. 2), however, persisting for column loadings *well below* those required for retention volume linearity. This suggests that the frequently reported practice of interpreting chromatographic linearity from band shape is ill advised. The column void volume V_0 is equal to the retention volume obtained when iso-octane is solute, using refractive index to follow elution. The corrected solute retention volume R was then obtained as $R' - V_0$. Finally, division of this quantity by the adsorbent weight gave the equivalent retention volume $\underline{R}$ for azulene. Using this technique with varying amounts of the solute azulene for the above column, a number of experimental values of $\underline{R}$ can be obtained which correspond to different solute to alumina ratios, W_s. In addition, the equilibrium measurement of solute distribution coefficients $\underline{K}$ for the same solute, eluent, and adsorbent system was also carried out, with the results shown in Table I. For the equilibrium data, an average value of the distribution coefficient $\underline{K}$ of 6.5 ml/g is found, in good agreement with the average of the chromatographic values (6.7 ml/g) in the linear region (for W_s values less than $120 \cdot 10^{-6}$). As previously defined[1], the values of $\underline{K}$ and $\underline{R}$ in the linear concentration region are referred to by superscript zeros, $\underline{K}^\circ$ and $\underline{R}^\circ$; unless otherwise specified, all retention volumes referred to in the present paper are linear equivalent retention volumes, $\underline{R}^\circ$. As a final commentary on the data of Table I, it has previously been shown[1] that the linear extrapolation of non-linear chromatographic data to zero solute concentration

provides correct linear retention volumes *only* under certain conditions. The previous test for these conditions specified that the two non-linear retention volumes extrapolated should differ by no more than 10 % and that the solute column loadings (W_s) for the two retention volume values should differ by at least a factor of 10. This may

TABLE I

EQUILIBRIUM SOLUTE DISTRIBUTION COEFFICIENTS AND CHROMATOGRAPHIC
EQUIVALENT RETENTION VOLUMES AS A FUNCTION OF SOLUTE CONCENTRATION
FOR THE SYSTEM AZULENE (SOLUTE)–n-PENTANE–2.3 % H_2O-Al_2O_3

Equilibrium data Solute concentrations			Chromatographic data	
Non-sorbed phase $\times$ 10^6 g/ml	Adsorbed phase $\times$ 10^6 g/g	$\underline{K}$ (ml/g)	W_s $\times$ 10^6 g/g	$\underline{R}$ (ml/g)
66.4	443	6.7	300	5.6
23.1	139.2	6.0	120	6.1
5.60	35.9	6.4	30	6.5
2.30	14.1	6.1	12	6.8
0.552	3.61	6.5	3.6	6.8
0.212	1.52	7.2	1.2	6.7
Average		6.5		6.7 $\pm$ 0.1*

* Average of last four values.

be rephrased as follows: The percent change in retention volume on going to a lower column loading, divided by the logarithm of the ratio of larger to smaller solute column loadings, should be less than 10. If we apply this test to the non-linear chromatographic values of Table I, we see that the two $\underline{R}$ values for W_s equal 300 · 10^{-6} and 120 · 10^{-6} do not meet this condition, since the percentage increase in retention volume (9 %) divided by the log of the ratio of W_s values (0.40) is greater than 10 % (22 %). The next pair of retention volumes, for W_s equal 120 · 10^{-6} and 30 · 10^{-6}, essentially meet the condition, the percentage increase in retention volume per logarithm W_s ratio equaling 11 %. In the latter case, the linear extrapolation of $\underline{R}$ to W_s equal zero gives a value of $\underline{R}^\circ$ equal to 6.6, which is quite close to the observed value in the linear region. For the former pair of $\underline{R}$ values, linear extrapolation gives a value of $\underline{R}^\circ$ equal to 6.4, which is significantly lower than the average of linear $\underline{R}$ values. Since neither of these pairs of values fails the extrapolation condition severely, the extrapolated value of $\underline{R}^\circ$ is close to the observed values in each case.

Counter gravity pressured flow was maintained in every case, as implied by the equipment diagram of Fig. 1. All experiments were carried out at room temperature (24 $\pm$ 1°).

Alcoa F-20 grade alumina was first calcined at 400° for 8 to 16 h, and adsorbent samples of various "nominal" activities prepared by the addition of known amounts of water to weighed samples of the dry adsorbent. The samples were kept in rubber-stoppered flasks and were permitted to equilibrate for at least 24 h prior to use. This procedure appeared to give samples of reproducible activity, when the alumina

was from the same batch. There is some indication, however, that adsorbent "activity", even after calcining, varies slightly with different batches. Because of this, we have defined adsorbent activity in terms of the $\underline{R}°$ value for a standard solute–eluent combination. Fig. 3 shows $\underline{R}°$ values for naphthalene as solute and n-pentane as eluent as a function of the percent water added to a calcined sample of alumina. For adsorbent with less than 1.0 % added water, linearity occurs for this particular solute only at very low column loadings, (W_s values). These $\underline{R}°$ values were themselves
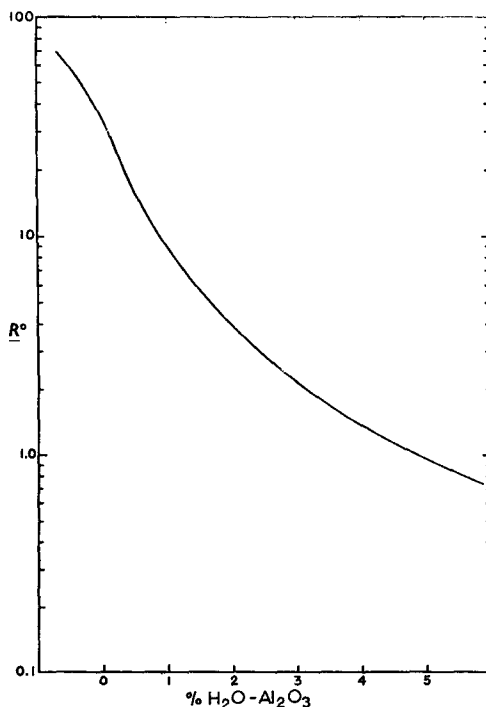

Fig. 3. $\underline{R}°$ for $C_{10}H_8$ as a function of adsorbent activity; n-pentane eluent.

determined at a constant column loading ($W_s = 5 \cdot 10^{-6}$) which represents a compromise between linearity and detection of the eluted solute. All of the data of the present paper report adsorbent activities in terms of percent water contained, this value being determined experimentally by this correlation. The extension of the adsorbent deactivation scale of Fig. 3 into negative values reflects the slight variation of activity in starting calcined adsorbent samples.

Continued elution of a chromatographic column can lead to changes in the average activity of the adsorbent, as measured by a standard $R°$ value. With calcined and lightly deactivated aluminas, adsorbent deactivation occurs rapidly unless the eluents used are scrupulously purified prior to use. In the present studies, reagent-grade or 99+ % eluents were first purified by passage over silica gel, and the apparatus of Fig. 1 is seen to contain a silica gel guard column for further purification of eluent

during use. As a further precaution, when the same column was used for several elution runs, the column activity was frequently checked by means of the measurement of $R°$ for a standard solute. For alumina samples containing more than 4 to 5 % water, use of strong eluents such as benzene leads to a very rapid increase in adsorbent activity (to that of 4–5 % H_2O–Al_2O_3), presumably due to the removal of non-chemically bound water. The same phenomenon occurs less rapidly in the case of saturate eluents. As a result, the use of aluminas containing more than 5 % water is excluded with eluents stronger than pentane, and is limited even for the saturate eluents.

It has been observed in isolated examples that when eluent flow rate is increased much above 150 ml/min, values of $R°$ begin to increase above the constant value observed at lower flow rates. Consequently, all $R°$ values reported in the present and previous papers were obtained for flow rates below this critical value. It is assumed that non-equilibrium conditions associated with the higher rates are responsible for this dependence of retention volume values on the higher flow rates.

The solutes used were either the best commercial samples available, or gifts from various individuals and institutions, and not further purified. Purity is of limited importance in the determination of $R°$ values, providing that the impurities are not present in major ($\sim$ 50 % wt.) amounts and do not have closely similar adsorption and ultraviolet absorption properties.

THE PREDICTION OF LEAC RETENTION VOLUMES

The following sections present the systematic development of a mathematical model for the correlation of solute retention volume data in LEAC systems with experimental conditions and solute structure. The model permits the quantitative prediction of $R°$ values for alumina as adsorbent when the values of certain experimental parameters are known. With certain modifications, the model should be applicable to other adsorbent systems, but this will provide the subject for future communications. Before considering the detailed mathematical development of the model under discussion, the final correlational equation will first be presented, following which some examples of its application will be given. Eqn. (1) relates the logarithm of a linear equivalent retention volume to adsorbent surface volume V_a, proportional to adsorbent surface area, an adsorbent activity function α, eluent polarity or eluting power $\varepsilon°$, solute size $\overset{i}{\Sigma} \delta_i$, solute structural groups $Q°_i$, and solute geometry terms $q°_j$.

$$\log \underline{R}° = \log V_a + \alpha \left[\overset{i}{\Sigma} Q°_i + \overset{j}{\Sigma} q°_j - \varepsilon° \overset{i}{\Sigma} \delta_i \right] \tag{1}$$

As will be shown, $\log \underline{R}°$ is proportional to an energy of adsorption, and is equivalent to the log retention volume of gas chromatography and R_M of paper chromatography. The adsorbent surface volume V_a can be easily measured by the BET technique in the case of calcined adsorbents, but the similar determination of V_a for partially deactivated adsorbents presents experimental difficulties and we have used an alternative

procedure in the present paper. Table II presents values of V_a for a typical Alcoa F-20 activated alumina as a function of water deactivation. a is an adsorbent activity parameter, ranging in the case of alumina from values of 1 for calcined material to smaller values for deactivated samples. Values of a as a function of percent water deactivation are shown in Table II, again for a particular Alcoa F-20 alumina. Alumina samples with surface areas comparable to this sample may be treated as equivalent by measuring the activity (% H_2O–Al_2O_3) in terms of the experimental $\underline{R}^\circ$ value for naphthalene eluted by pentane, as discussed in the experimental section. These standard $\underline{R}^\circ$ values for the adsorbent in question as a function of water deactivation are also listed in Table II. Each structural group i in the solute contributes a term

TABLE II

ALUMINA ACTIVITY FUNCTION AND ADSORBED VOLUME AS A FUNCTION
OF PERCENT WATER DEACTIVATION

% H_2O–Al_2O_3	Activity function α	Adsorbed volume V_a	Standard solute retention volume*
0.0	1.00	0.038	35
0.5	0.90	0.033	16
1.0	0.84	0.029	9.0
1.5	0.79	0.025	5.8
2.0	0.75	0.022	4.0
3.0	0.69	0.018	2.2
4.0	0.63	0.015	1.4
5.0	0.57	0.013	0.97

* Value of $\underline{R}^\circ$ for naphthalene solute, n-pentane eluent.

Q°_i to $\underline{R}^\circ$, as seen in the summation $\overset{i}{\sum} Q^\circ_i$ of eqn. (1). These structural groups are defined exclusive of hydrogen for simplicity. Some experimental values of Q°_i are listed in Table III for various groups i. Where the geometry of the molecule affects $\underline{R}^\circ$, a term q°_j must be introduced. Some examples of this effect, along with experimental values of q°_j are also provided in Table III.

The eluent polarity parameter ε° is defined as zero for n-pentane (and probably other saturate eluents as well), and increases for more polar eluents. As seen in Table III, eluent polarity increases in the order pentane, carbon tetrachloride, benzene. The molar volume of the solute $\overset{i}{\sum} \delta_i$ is determined by adding up the contributions shown in Table III, from individual solute atoms i. In calculating solute molar volume, only those groups or atoms which are confined to the adsorbed phase can be counted. Thus, for alkyl substituents on an aromatic nucleus, $\overset{i}{\sum} \delta_i$ equals one, since only the methylene group attached to the ring is confined to the plane of the aromatic ring and hence to the adsorbed phase.

An exception to eqn. (1) exists in the case of the elution of aromatic hydrocarbons by benzene. As eqn. (1) stands, $\underline{R}^\circ$ for aromatic hydrocarbon solutes would be $\log V_a$ in this case, since ε° for benzene (0.32) is essentially the same as Q°_i for aromatic carbon (0.31). Actually, experimental $\underline{R}^\circ$ values are small but measurably larger than log

TABLE III

SOLUTE GROUP SEPARATION FACTORS

Group i[a]	$Q°_i$
Aliphatic carbon (for saturate eluents only)	0.020
Aromatic carbon	0.31
Aromatic sulfur, as in thiophene ring	0.76
Aliphatic sulfur, as in alkyl sulfide	2.6
Aromatic carbonyl, as in benzaldehyde	3.3
Basic aromatic nitrogen (as in pyridine)	4.8
Non-basic aromatic nitrogen (as in pyrrole, carbazole, etc.)	4.2
Aromatic fluoro (as in fluorobenzene)	0.11
Aromatic chloro	0.20
Aromatic bromo	0.33
Aromatic iodo	0.51
Aliphatic chloro (as in benzyl chloride)	1.11
Aromatic ether, as in anisole	1.7
Aromatic ester, as methyl benzoate	2.4

Second order effects j	$q°_j$
Methyl substituent on aromatic or thiophene[b]	0.04
Alkyl substitution on thiophene ring	— 0.039
Alkyl substitution on N-containing ring of nitrogen aromatic compound	0.5[d]
Alkyl substitution *ortho* to N of aromatic nitrogen compound	— 0.7[d]
Alkyl substitution on ring adjacent to nitrogen-containing ring	0.3[d]
Alkyl iso branch	
Isolated from aromatic ring	— 0.045
Adjacent to ring	— 0.13
Ortho, ortho di-alkyl substitution in thiophenes[c]	— 0.09
Vicinal alkyl substitution on aromatic ring (for each substituent in excess of the first one)[c]	0.09
Naphthene ring closure	0.08
Halogen substituent in naphthalene	— 0.37
m-Halo substituents and *o,p*-substituents past the second one	ignore

Eluent parameters	$ε°$
n-Pentane	0.00
Carbon tetrachloride	0.13
Benzene	0.32

Atom	Values of $δ_i$
Hydrogen	0
First-row elements (C, N, O, F, etc.)	1
Second-row elements (P, S, Cl, etc.).	3

  [a] We have chosen to define the group i both with respect to its constituent atom(s), exclusive of hydrogen, and to its nearest neighbor atoms.
  [b] Does not include $Q°_i$ for one aliphatic carbon.
  [c] In addition to normal substituent effect.
  [d] Assumes $ε°$ for 50% benzene–iso-octane equal 0.20.

V_a. The reason for this discrepancy is discussed in the following text. Eqn. (1) must be modified for this particular case as follows. A value of $Q°_i$ for each aromatic carbon is assumed equal to 0.14, and the actual number of aromatic carbons n in the solute is decreased by six before adding the $Q°_i$ terms; $\sum\limits^{i} Q°_i$ is therefore 0.14 $(n$—6). In addition $\varepsilon°$ is set equal to zero.

A few examples of the application of eqn. (1) and the data of Tables II and III to the prediction of $\underline{R}°$ values for specific cases will be offered. First, assume it is desired to calculate $\underline{R}°$ for the solute chrysene, using n-pentane elution from 3.9 % H_2O–Al_2O_3. There are 18 aromatic carbons in this compound, so that $\sum\limits^{i} Q°_i$ equals 18 × 0.31 or 5.58. No second order (q_j) terms for the unsubstituted aromatic hydrocarbons are shown in Table III (although a later communication will show their existence and discuss their origin), so that $\sum\limits^{j} q°_j$ equals zero. For pentane as eluent, $\varepsilon°$ is equal to zero, so that the last term of eqn. (1) also vanishes. From Table II, values of α (0.634) and of V_a (0.0153) may be interpolated for 3.9 % H_2O–Al_2O_3. Substitution of these various terms into eqn. (1) then gives:

$$\log \underline{R}° = \log (0.0153) + 0.634\,(5.58 + 0 - 0)$$
$$= 1.71$$

In this case, an experimental value was found equal to 1.72.

For the elution of the same solute (chrysene) from the same adsorbent (3.9 % H_2O–Al_2O_3) by carbon tetrachloride, only the eluent term $\varepsilon° \sum\limits^{i} \delta_i$ changes. For this eluent, $\varepsilon° = 0.13$, and since there are 18 carbon atoms in the solute which must lie in the adsorbed phase, $\sum\limits^{i} \delta_i = 18$. Substituting this new value of $\varepsilon° \sum\limits^{i} \delta_i$ (2.34) into the above calculation based on eqn. (1) gives:

$$\log \underline{R}° = \log (0.0153) + 0.634\,(5.58 + 0 - 2.34)$$
$$= 0.23;$$

an experimental value equal to 0.38 was found. The elution of 3,4-benzpyrene by benzene from 1.6 % H_2O–Al_2O_3 represents an exception to the direct application of eqn. (1). As previously discussed, the structural groups counted are the 20 aromatic carbons of the solute, less the 6 of the eluent, or 14. A value of $Q°_i$ equal to 0.14 is assumed, and the eluent terms are ignored. Substitution of the appropriate terms into eqn. (1) now gives:

$$\log \underline{R}° = \log (0.0244) + 0.782\,(1.96 + 0)$$
$$= -0.08.$$

The experimental value found was — 0.10.

In the elution of 2,6-dimethylpyridine from 4.25 % H_2O–Al_2O_3 by benzene, the $Q°_i$ terms include two alkyl carbons (0.04), five aromatic carbons (1.55), and a basic nitrogen (4.8), for a total of 6.39. The q_j terms include two alkyl substituents on a nitrogen-containing ring (1.0), and two *ortho* alkyl substitutions to the N atom (— 1.4), for a total of — 0.4. There are eight first-row atoms in the solute, so $\sum\limits^{i} \delta_i$

equals 8, and ε° for benzene as eluent equals 0.32. Inserting these and the other appropriate terms (from Table II) into (1) gives:

$$\log \underline{R}^\circ = \log (0.0145) + 0.615 (6.39 - 0.4 - 2.56)$$
$$= 0.26.$$

The experimental value found was 0.34.

Consider finally the elution of the hypothetical solute 1-chloro-3-*n*-hexyl-5,6-dimethyl-naphthalene (I) from 3.2 % H_2O–Al_2O_3 by carbon tetrachloride.

(I)
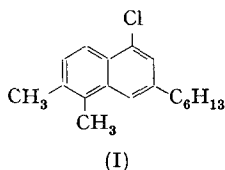
The Q°_i terms for the solute include 10 aromatic carbons (3.1), one aromatic chloro atom (0.20), and the three aliphatic carbon atoms (0.06) which are confined to the plane of the solute nucleus (it is assumed that for an eluent more polar than pentane, the five terminal carbons of the *n*-hexyl group will lie in the eluent phase). The first-order substituent terms total 3.36. The second-order q°_j terms include the correction for the chloro substitution in naphthalene relative to benzene (— 0.37), two aromatic methyls (0.08), and *two* vicinal alkyl groups (0.18) since the α-methyl group in naphthalene is considered *ortho* to the adjacent 8-hydrogen. The total of the q°_j terms is seen equal to + 0.15. There are 13 first-row atoms of the solute confined to the adsorbed phase, and one second-row atom for a total $\overset{i}{\sum} \delta_i$ of 16; $\varepsilon^\circ \overset{i}{\sum} \delta_i$ is therefore 2.08. Inserting the other parameter values of Tables II and III into eqn. (1) we have:

$$\log \underline{R}^\circ = \log (0.017) + 0.68 (3.36 + 0.15 - 2.08)$$
$$= - 0.79.$$

The limited group factor (Q°_i) data of Table III pose an obvious restriction on the range in solute types for which retention volume may presently be predicted. In addition, even for the solute types considered, some simplification in the q°_j terms has been effected in Table III. Thus, no notice is taken of the effect of size and structure of the alkyl substituent *ortho* to ring nitrogen or thiophene sulfur atoms. In both cases, the following data of Tables IX and X suggest that as the *ortho* groups get bulkier, the retention volumes will fall below those predicted by the parameters of Table III. These steric effects will no doubt be highly specific, and there may be some question of our ability to make quantitative correlations in this area.

The accuracy of eqn. (1) as a prediction tool is conditional, as indicated above, on the inclusion of all important q°_j terms. Beyond this, the relationship may be described as semi-quantitative. Tables IV and V show some examples of its reliability in the case of the aromatic hydrocarbons and two non-basic nitrogen compounds. Subsequent tables present a number of additional experimental $\underline{R}^\circ$ values, expressed as relative retention volumes $\underline{R}^*$ ($\underline{R}^\circ$ for substituted aromatic divided by that of

TABLE IV

EXPERIMENTAL AND CALCULATED R° VALUES
FOR AROMATIC HYDROCARBONS OVER A RANGE IN CONDITIONS

Number of aromatic carbons in solute	Log R°							
	n-Pentane 1.2% $H_2O–Al_2O_3$		n-Pentane 4.0% $H_2O–Al_2O_3$		CCl_4 4.0% $H_2O–Al_2O_3$		Benzene calcined alumina	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
6 (Benzene)	0.09	— 0.05	— 0.58	— 0.65				
10 (Naphthalene)	0.92	0.97	0.15	0.13	— 0.68	— 0.69	— 0.86	— 0.86
12 (Acenaphthylene)	1.43	1.47	0.54	0.52	— 0.51	— 0.46	— 0.52	— 0.58
14 (Phenanthrene,	2.05	1.98	0.91	0.91	— 0.21	— 0.23	— 0.29	— 0.30
anthracene)	2.12		0.95		— 0.20		— 0.10	
16 (Pyrene,	2.37	2.49	1.18	1.30	— 0.03	— 0.01	— 0.07	— 0.02
fluoranthene)	2.57		1.29		0.05	— 0.01	0.01	
18 (Triphenylene,	2.87	3.00	1.64	1.69	0.38	0.22	0.26	0.26
chrysene)	3.05		1.72		0.38		0.40	
20 (Benzpyrene)			2.20	2.08	0.58	0.44	0.57	0.54

TABLE V

EXPERIMENTAL AND CALCULATED LOG R° VALUES
FOR INDOLE AND CARBAZOLE OVER A RANGE IN CONDITIONS

Solute	% H_2O-Al_2O_3	Eluent	Log R°	
			Experimental	Calculated
Indole	1.6	Benzene	1.10	1.46
Indole	3.0	Benzene	0.84	0.95
Indole	5.0	Benzene	0.23	0.33
Indole	4.8	Pentane	2.18	2.01
Carbazole	1.6	Benzene	1.56	1.46
Carbazole	3.0	Benzene	0.98	0.95
Carbazole	4.0	Benzene	0.56	0.64
Carbazole	5.0	Benzene	0.15	0.33
Carbazole	4.8	Pentane	2.54	2.73

unsubstituted aromatic). When the parameter values of Tables II and III are used with eqn. (1) to calculate these data, the average difference or error between experimental and calculated values is as follows.

Substitution class	Average error (log units)	Range in experimental values (log units)	Number of solutes
Halo aromatics (Table VII)	0.04	1.02	18
Alkyl benzenes (Table VIII)	0.02	0.78	35
Alkyl thiophenes (Table IX)	0.02	0.38	25
Alkyl pyridines* (Table X)	0.07	0.83	12

* Excluding 3-methyl-4-ethyl-pyridine.

The extension of the present model to the interpretation of other adsorbent chromatographic systems appears justified in view of its relative success in the correlation of retention volume data for alumina.

Dependence of retention volume on solute structure and adsorbent activity

Consider a general solute molecule, *x-y-z-*, composed of structural elements or groups *x*, *y*, *z*, etc., which is present in small concentration in an eluent–adsorbent system. At equilibrium a competition will exist between the solute and the eluent E for a place in the adsorbed phase. This equilibrium can be written:

$$x\text{-}y\text{-}z\text{-}_{(n)} + rE_{(a)} \rightleftharpoons x\text{-}y\text{-}z\text{-}_{(a)} + rE_{(n)} . \tag{2}$$
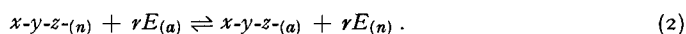
The subscripts (n) and (a) refer, respectively, to non-sorbed and adsorbed phases. Eqn. (2) implies an adsorbed phase of constant volume (monomolecular layer), with r given as the volume ratio of solute to eluent. This assumption is in agreement with the observation of BACHMAN[9] and others[10]. The equilibrium constant $K°$ for eqn. (2) will be determined by the partial molal free energies of molecules *x-y-z-* and E in the adsorbed and non-sorbed phases. For the transfer process eqn. (2),

$$F_t = (F_{xyz})_a + r\,(F_E)_n - (F_{xyz})_n - r\,(F_E)_a,$$

with F_t referring to the net transfer free energy divided by $2.3\,RT$ and $(F_i)_j$ referring to the partial molal free energy ($\div 2.3\,RT$) of component i in phase j; $K° = 10^{-F_t}$.

As a first approximation $(F_{xyz})_j$ will be expressible as a linear combination of structural group free energy terms, $(F_x)_j$, $(F_y)_j$, etc., so that:

$$(F_{xyz})_j = (F_x)_j + (F_y)_j + (F_z)_j \tag{3}$$

Two obvious limitations on eqn. (3) exist. First, the phase j must be strictly comparable or constant; each structural group i must "see" a constant molecular environment outside the solute molecule. For a given *linear* chromatographic system (same eluent and adsorbent) this limitation is unimportant since adsorbent coverage, θ, is small. Second, the structural group i must similarly "see" the same internal molecular surroundings. When the electronic and/or steric interaction of the remainder of the solute molecule with i is changed, $(F_i)_j$ must change accordingly.

Corresponding to the volume equivalence of r molecules of eluent to one molecule of solute, a similar equivalence of some fractional volume of an eluent molecule to a group i can be hypothesized. This permits the formulation of the group transfer equilibrium:

$$i_{(n)} + \delta_i\,E_{(a)} \rightleftharpoons i_{(a)} + \delta_i\,E_{(n)} ,$$
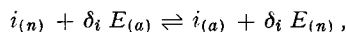
with net free energy ($\div 2.3\,RT$) F_{iE} equal to:

$$F_{iE} = (F_i)_a + \delta_i\,(F_E)_n - (F_i)_n - \delta_i\,(F_E)_a . \tag{4}$$

For the solute *x-y-z-*, F_t is equal to $\overset{i}{\sum} F_{iE}$.

The relationship between the thermodynamic equilibrium constant $K°$ and the distribution coefficient $\underline{K}°$ previously defined is:

$$\underline{K}° = V_a\,K° , \tag{5}$$

from which:
$$\underline{R}^\circ = V_a K^\circ \tag{5a}$$

The quantity V_a refers to the adsorbent capacity, or volume of the adsorbed phase per unit weight of adsorbent; it is required to make the concentration units in the adsorbed and non-sorbed phases comparable. If the dimensionless parameter $Q_i = - F_{iE}$ is defined, then the relationship between chromatographic separability and molecular structure is given by:

$$\log \underline{R}^\circ = \log V_a + \overset{i}{\Sigma} Q_i \tag{6}$$

and for the special case where the solute xyz- is composed of n equivalent groups, k,

$$\log \underline{R}^\circ = \log V_a + n Q_k \tag{7}$$

In Fig. 4, the applicability of eqn. (7) is illustrated for calcined alumina as adsorbent, unsubstituted aromatic hydrocarbons (or olefins) as solutes and three different eluents. In each case the unsaturated carbon atoms are taken as structural groups k.
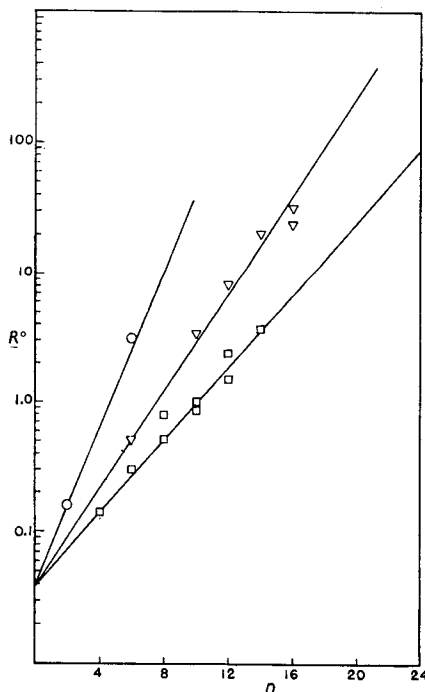

Fig. 4. R° *versus* carbon number for aromatic hydrocarbons and calcined alumina. Eluent: O n-pentane; ∇ carbon tetrachloride; $\square$ benzene.

For pentane and CCl_4 as eluents, the value of n for eqn. (7) is set equal to the total number of these unsaturated carbon atoms in the molecule, while for benzene as eluent, the value of n taken is the total number of aromatic carbons less 6, since in this case the eluent (for which $\underline{R}^\circ$ must equal V_a) is a member of the solute series

with $n = 6$ (this latter adjustment of n will be considered in greater detail in another part of this paper). It is seen that the data for each eluent are linear in n, within a certain scatter, and that the various curves intersect at a common point on the n equal zero axis, as required by eqn. (7). A value of 0.04 ml/g for V_a can be inferred from the data of Fig. 4. This value is in good agreement with the previous value[10] of 0.05 ml/g obtained from the equilibrium uptake of 1,2,3,5-tetramethylbenzene by calcined alumina. Measurement of the same quantity by the BET technique (uptake of nitrogen at $-195°$) gives a value of 0.054 ml/g (equivalent to a surface area of 156 m²/g), also in agreement with the value obtained from Fig. 4. Fig. 5 shows a plot of experimental values of V_a for alumina (obtained by the extrapolation procedure of Fig. 4) *versus* the extent of water deactivation.
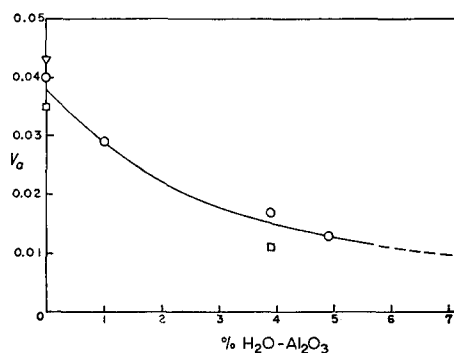

Fig. 5. Variation of V_a with adsorbent activity. Eluent: ○ pentane; ▽ carbon tetrachloride; □ benzene.

Eqn. (7) should also describe the retention volume data for an eluent molecule substituted by n equivalent groups; *e.g.*, for the elution of substituted benzenes by benzene. SPORER AND TRUEBLOOD[5] have reported retention volume data for a number of substituted benzenes, using silicic acid as adsorbent and benzene as eluent. Their calculated values of K_{ph} (the equivalent of our value of 10^{Q_i} for the benzene ring) are therefore equivalent to V_a. These values of K_{ph}, excluding anomalous data for the methoxy and biphenyl derivatives, give an average value of 0.3 ± 0.1. Comparison with the value of 0.05 for alumina shows an adsorbed phase volume V_a substantially larger for silicic acid than for alumina; this is in agreement with surface area measurements for "average" samples of these two adsorbents (*e.g.*, Davison chromatographic-grade silica shows V_a equal to 0.29 ml/g by BET). These authors' assumption that $\underline{R}°$ for the biphenyl solutes should be equal to K_{ph} times $\underline{R}°$ for the corresponding benzene derivative is in error, because of the equality of K_{ph} and V_a for benzene as eluent. The observed small reduction in $\underline{R}°$ for the substituted biphenyls relative to the benzenes is primarily the result of the strain energy arising from forcing the biphenyl ring system into planarity upon adsorption, rather than a Q_i term for the phenyl ring, which is theoretically zero. Because this reduction in $\underline{R}°$ is less than V_a, values of K_{ph} calculated from the biphenyl solutes are uniformly high, as can be seen in Table 4 of their paper[5].

The structural group retention factors Q_i decrease regularly with increasing water deactivation of the adsorbent, and an approximate linear free energy relationship appears to exist between Q_i and a function α of the percent water deactivation:

$$Q_i = \alpha \, Q^\circ_i \tag{8}$$

Q°_i is equal to Q_i for the calcined adsorbent, and hence α must be set equal to 1 for 0.0 % H_2O–Al_2O_3. The adsorbent activity function α is shown in Fig. 6 as a function
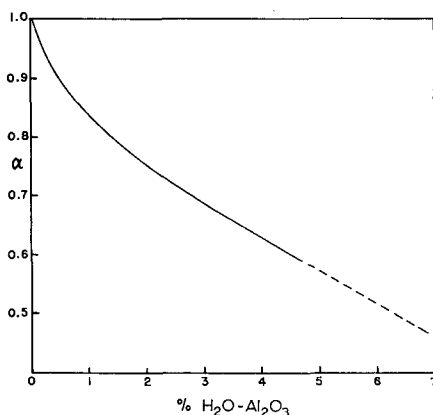

Fig. 6. α *versus* adsorbent water deactivation.

of percent added water. Within the accuracy of eqn. (8) as a correlational equation, a composite relationship may be set down relating solute separability to structure and adsorbent activity:

$$\log \underline{R}^\circ = \log V_a + \alpha \sum^i Q^\circ_i \tag{9}$$

Fig. 7 shows the family of curves relating retention volume $\underline{R}^\circ$ to adsorbent activity for various values of $\sum^i Q^\circ_i$. Within the accuracy of eqns. (6) and (8), retention volume data for a single solute and eluent should fall on one of these curves for alumina as adsorbent. Fig. 7 also shows some typical data in this respect, thus verifying the usefulness of eqn. (9) as a correlational relationship, and the validity of eqn. (8).

To the extent that eqn. (8) is valid, it is seen that for a given eluent, relative solute separability must remain unchanged as adsorbent activity is varied. This might be termed a "constant eluent non-crossing rule". This preservation of separation order is consistent with the removal of the more active sites *without* producing a new phase (water) or a new set of sites of fundamentally different adsorption properties. The regular decrease in the volume of the adsorbed phase (V_a) with increasing adsorbent water content bears this conclusion out, as does the decline with deactivation of α, which is proportional to the average energy (of interaction with solute) of the remaining adsorbent sites. As discussed in the experimental section, when water content exceeds 5 %, the excess water is readily eluted by the stronger eluents such as benzene, and more slowly by saturate eluents. This constitutes a further

check on the experimental value of V_a (0.04–0.05) for alumina, and also rules out the importance of a water *phase* for adsorbent samples containing less than 5 % water.

Previous investigators have emphasized the importance of restricting chromatographic studies such as the present to fully activated adsorbents, in order to ensure systems free of partition effects. The above discussion suggests, at least for alumina as
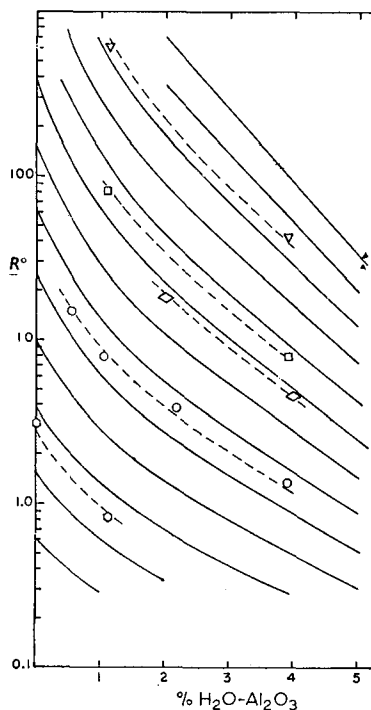

Fig. 7. Theoretical retention volume–adsorbent activity curves.

Solute	Eluent
△ Triphenylene	n-Pentane
□ Phenanthrene	n-Pentane
◇ 2,6-Dimethylpyridine	Carbon tetrachloride
○ Naphthalene	n-Pentane
⬡ Benzene	n-Pentane.

adsorbent, that (a) partition as a phenomenon is unimportant for 0–5 % H_2O–Al_2O_3, and (b) measurements made on adsorbent within this compositional range can be quantitatively compared. Experimentally, the study of deactivated adsorbents is frequently preferable to corresponding investigations of fully activated samples for at least two reasons: first, adsorbent *linear* capacity, θ_1, increases markedly with adsorbent deactivation in the case of alumina[1], and probably other adsorbents as well; and second, the measurement of large $\underline{R}^\circ$ values by elution techniques is experimentally inconvenient; use of less active adsorbents can reduce retention volumes to a more desirable range. Of equal importance, as will be seen, the measurement of $\underline{R}^\circ$ values as a function of adsorbent activity (a) offers certain possibilities in the theoretical interpretation of the nature of the adsorbed state.

The role of the eluent

The role of the eluent in determining solute retention volumes can be described in terms of eqn. (4), the expression for the group free-energy factors F_{iE}. The solute terms, $(F_i)_j$, can be separated into those energies resulting from solvation forces acting on the group i by eluent, and those resulting from interaction of i with the adsorbent. Since only one side of the molecule is shielded from the non-sorbed phase during adsorption, only a fraction of the solvation energy of the group i will be lost on adsorption. Because the adsorption energy will, in addition, normally be substantially larger than the eluent solvation energy of the group i, the latter energy terms may, to a first approximation, be ignored. From a similar argument for the eluent free energy terms, $- \delta_i [(F_E)_a - (F_E)_n]$

$$F_{iE} \approx F_i - \delta_i F_E,\qquad (10)$$

where F_i and F_E refer simply to the energy associated with the formation of adsorbent bonds to group i and eluent E, respectively.

Eqn. (10) can be seen to be a condition for the validity of eqn. (8); when the adsorption energy terms F_i and F_E become small relative to the corresponding eluent solvation terms, differences in the latter energies will begin to determine solute separability, and the constant eluent non-crossing rule would be expected to fail. This further suggests that relationships such as eqn. (8) will be least applicable for the most highly deactivated adsorbents. Where the solute structural group i is the same as those of an eluent i_m, containing m identical groups i, eqn. (10) requires that $Q_i = 0$. Fig. 8 shows some relative retention volume data $\underline{R}^*$ (equal to $\underline{R}^\circ$ for solute divided by that of the unsubstituted aromatic) for the n-alkyl-benzenes $C_6H_5\text{-}(CH_2)_{n-1}CH_3$, with n-pentane as eluent and 0.5 % wt. H_2O–Al_2O_3 as adsorbent. No change in $\underline{R}^*$ with variation in n would be predicted. Actually, a modest increase
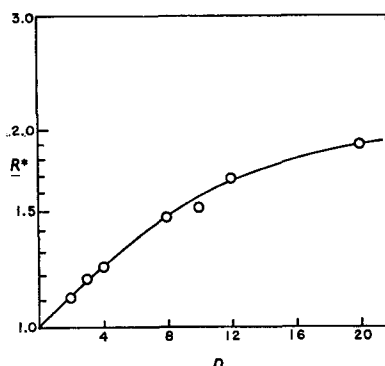

Fig. 8. $\underline{R}^*$ *versus* alkyl carbon number for n-alkyl-benzenes; n-pentane, 0.5 % H_2O–Al_2O_3.

of $\underline{R}^*$ with n is noted (average value of Q°_i for methylene group $\approx$ 0.020, compared to 0.31 for aromatic carbon), as seen in Fig. 8. Further improvement of the present model would be anticipated by recognition and application of two second-order effects. First, as solute size increases, thus requiring that a larger number of eluent

molecules be displaced into the non-sorbed phase, $\underline{R}°$ should increase, all else equal, because of the increase of translational entropy attendant on the substitution of one solute molecule for a larger number of eluent molecules in the adsorbed phase. Second, since the methyl groups of the n-pentane eluent are not exactly equivalent to the methylene groups of the solute side chain, there may be a small difference in adsorption energy. If the latter effect predominates (differing adsorption energies between solute side chain methylene groups and eluent methyl plus methylene groups), then the retention volume ratio for the two solutes of differing side chain lengths should vary with adsorbent activity in the same manner as the group i retention factors. From eqn. (8) and noting the relationship between $\underline{R}°$ and Q_i of eqn. (9) we obtain:

$$\log (\underline{R}°_1/\underline{R}°_2) = \alpha \log (\underline{R}°_1/\underline{R}°_2)_{\alpha = 1}$$

If the entropy effect is controlling, then this ratio should be independent of adsorbent activity. For a particular pair of n-alkyl solutes (2-ethyl and 2-n-decyl-thiophene) with n-pentane as eluent, the ratio of $\underline{R}°$ values was found to be 1.59 for 0.5% H_2O-Al_2O_3, and 1.18 for 4.0% H_2O-Al_2O_3. Using the experimental value at 0.5% as reference, the calculated ratio at 4.0% would be 1.59 for the size entropy effect and 1.39 for the adsorption energy effect. The latter appears to predominate, although the calculated magnitude of the change differs from the experimentally observed ratio.

In the correlation of Fig. 4, the structural groups i for the aromatic hydrocarbons were defined as aromatic carbons, with the attendant hydrogen atoms being ignored. The application of eqn. (10) to this case would lead us to predict that Q_i equals zero for the eluent benzene and aromatic carbons as groups i, an observation contrary to fact since the aromatics with carbon number greater than benzene have $\underline{R}°$ larger than V_a. Use of the theoretical model here without qualification probably fails because of the omission of the second-order role of the aromatic hydrogen atoms in determining adsorption energy. Strictly speaking, the structural group of a hydrocarbon should be represented by (CH_x); i.e., the hydrocarbon should be representable as $(CH_x)_n$, not merely by the number of carbon atoms. Under these conditions eqn. (7) will hold for the group (CH_x) regardless of differences between the adsorption energy per volume of aromatic carbons atoms and that for "aromatic" hydrogen atoms. Expressing the higher aromatics as derivatives of benzene, it is seen that each of the benz-derivatives ($C_{10}H_8$, $C_{14}H_{10}$, $C_{18}H_{12}$, etc.) can be rewritten as C_6H_6-$(CH_{0.5})_n$, and this is approximately true of the other higher aromatics as well (e.g., pyrene is C_6H_6-$(CH_{0.4})_{10}$). Now if the adsorption energy per volume of aromatic carbon and hydrogen atoms are different, the displacement of the (hypothetical average) $CH_{0.5}$ group from the adsorbent by some fraction of a CH (benzene) group will be accompanied by a net energy change and Q_i for the $CH_{0.5}$ group will be non-zero. The observation that this value is positive ($Q°_i = 0.14$) requires only that the carbon atom have higher adsorption energy per unit volume than the hydrogen atom, a not too surprising discovery. Finally, the retention volumes of the higher aromatics for benzene elution will be determined by the net number of $CH_{0.5}$ groups, which is seen

equal to the total number of aromatic carbons less the 6 which make up the benzene "nucleus" of the above formula; thus the correlation of experimental $R°$ values in Fig. 4 is not unanticipated. The fact that benzene as a solute also falls on the pentane and carbon tetrachloride curves of Fig. 4 probably arises from the fact that the polarity of aromatic hydrogens is intermediate between the eluents n-pentane and carbon tetrachloride and hence Q_i for hydrogen is approximately zero with these two eluents. The latter possibility is theoretically reasonable. The need to subtract 6 from the values of n for the benzene eluent data is apparent, since $R°$ for the eluent is theoretically equal to V_a.

Returning to eqn. (10), the first order effect on values of $R°$ produced by change in eluent may be obtained by taking the difference between values of F_{iE} for the two eluents 1 and 2:

$$(F_{iE})_2 - (F_{iE})_1 = \delta_i [(F_E)_1 - (F_E)_2]$$
$$= \delta_i \, \varepsilon_{12}$$

(11)

The quantity ε_{12} is proportional to the difference in adsorption energies per volume of the eluents 1 and 2; δ_i is determined by the volume of the group i. To a first approximation, the volumes of first-row elements (inferred from their covalent radii[11]) are constant, and those of second-row elements are about three times those of the first row of the periodic table. In addition, the volume of hydrogen is small compared to that of subsequent elements. Relative values of δ_i may thus be set forth as follows:

Atom	δ_i (tentative)
H	0
First-row element (C, N, O, etc.)	1
Second-row element (Si, P, S, etc.)	3

The relative retention volume of a solute in the same adsorbent system using eluents 1 and 2 is given as:

$$\log (R°_1/R°_2) = \varepsilon_{12} \sum^{i} \delta_i$$

(12)

Table VI contains retention volume data for a number of solutes, using pentane and benzene as eluents; eluent 1 refers to pentane. Adsorbent activity varied between 3.9 and 4.8% H_2O-Al_2O_3, and retention volume ratios for the two eluents $(R°_1/R°_2)$ have been calculated for a single adsorbent activity (3.9%) by extrapolation of $R°$ values by means of the master curves of Fig. 7. In Fig. 9, the logarithm of the ratio of these retention volumes is plotted *versus* $\sum^{i} \delta_i$. This plot clearly shows the dependence of the eluent-induced shift in retention volume on solute size or $\sum^{i} \delta_i$. The linear relationship predicted by eqn. (12) is also approximately confirmed. A value ε_{12} for this eluent pair is found from the slope of Fig. 9, equal to 0.20. Similar data for 3.9 % H_2O-Al_2O_3 and the eluent pair pentane (1)-carbon tetrachloride (2) are plotted

in Fig. 10, showing a value of ε_{12} equal to 0.08; carbon tetrachloride is thus inter-mediate between pentane and benzene as regards its adsorption energy per unit volume adsorbed, and eluting "power". In view of the range in molecular structure represented in the solutes of Fig. 9 and Fig. 10, and the anticipated corresponding differences in relative solubility or solvation of these solutes in the two eluents, the

TABLE VI

RETENTION VOLUME DATA FOR VARIOUS SOLUTES
USING BOTH n-PENTANE AND BENZENE AS ELUENTS

Solute	$\underline{R}^{\circ}$		$\sum_{i}^{i} \delta_i$	$\underline{R}^{\circ}{}_1/\underline{R}^{\circ}{}_2$[a]
	n-Pentane	Benzene		
Benzpyrene	159[a]	0.24[a]	20	660
Methyl ethyl sulfide	1.02[a]	0.10[a]	5[b]	10
Anisole	3.6[a]	0.12[a]	8	30
Benzaldehyde	30[a]	0.85[a]	8[a]	35
Benzene	0.26[a]	0.015[c]	6	17
2,6-Dimethylpyridine	46[d]	2.2[d]	8	23
Indole	153[e]	1.7[e]	9	129
Carbazole	346[e]	1.4[e]	13	393

[a] 3.9 % activity.
[b] Assumes two aliphatic carbons in adsorbed phase (see latter part of present section).
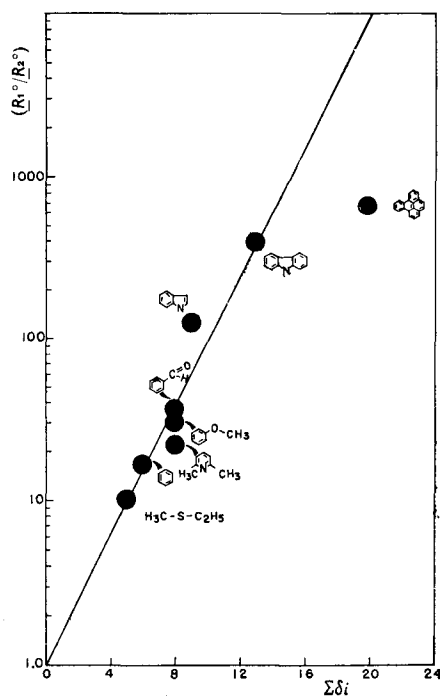[c] Value of V_a.
[d] 4.2 % activity.
[e] 4.8 % activity.

Fig. 9. Dependence of retention volume on eluent as a function of solute size; 3.9 % H_2O–Al_2O_3, n-pentane–benzene eluents.

linear nature of the latter plot tends to confirm the *relative* unimportance of solubility effects in the determination of solute retention volume (as previously predicated). This conclusion is strengthened by the fact that the adsorbent activity in this case is quite low, and solubility effects should be most important at the lower adsorbent activities.
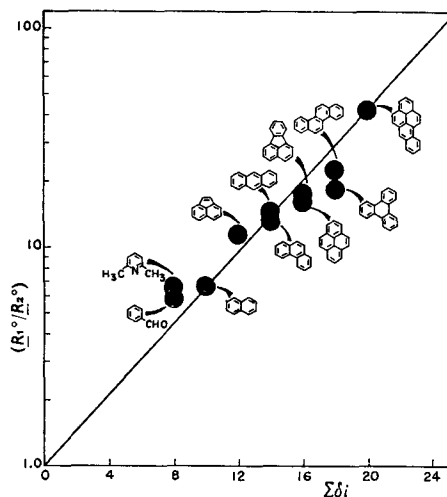

Fig. 10. Dependence of retention volume on eluent as a function of solute size; 3.9 % H_2O–Al_2O_3, n-pentane–carbon tetrachloride eluents.

Since the adsorption energy of the eluent is expected to change with adsorbent activity in the same manner as that of the solute, ε_{12} should vary with α as does Q_i. Thus, ε_{12} should be related to its value ε°_{12} for calcined adsorbent as:

$$\varepsilon_{12} = \varepsilon^\circ_{12}\,\alpha \tag{13}$$

Throughout the preceding discussion, it has been implicitly assumed that the total solute molecule is confined to the surface of the adsorbent. For planar aromatics this is necessarily so, *if* the adsorption region approximates planarity. That the total aromatic molecule *is* involved in the adsorption process may be concluded from the data of Fig. 4. These data show a linear $\underline{R}^\circ$–n plot, thus implying that every additional aromatic carbon atom participates in adsorption. The possibility that only a few of the many aromatic carbons form adsorption bonds is ruled out by the observation that molecules with "reactive" carbons (those possessing a high free valence, and low localization energies) such as anthracene are much less strongly adsorbed than are molecules with more, but less reactive, carbon atoms such as triphenylene (see Table IV). When a portion of the solute molecule is free to lie either in or out of the adsorbed phase, the relative value of $\Sigma\,Q_i$ for the part in question should determine its location. Thus, for the n-alkyl benzenes and thiophenes, a positive value of Q_i for the methylene group is observed, and this suggests that a considerable portion of such alkyl groups will be confined to the adsorbed phase. That less than all of the very long alkyl groups will remain in the adsorbed phase is indicated by two ob-

servations. First, the plot. of experimental log $\underline{R}^\circ$ values *versus* n for the alkylbenzenes (Fig. 8) declines from the initial linear plot at large values of n, whereas a constant value of Q_i for the methylene group *and* the restriction of the total alkyl group to the adsorbed phase would require linearity over the entire range of this plot (log $\underline{R}^\circ$ = constant + nQ_i). Secondly, it has been noted that the ratio of $\underline{R}^\circ$ values for 2-*n*-decyl-thiophene relative to 2-ethyl-thiophene declines from 1.58 at 0.5% H_2O–Al_2O_3 to 1.18 at 4.5% H_2O–Al_2O_3, whereas the extrapolated value from the former to the latter value by means of eqn. (8) is 1.38. The extrapolation assumes that for each solute the same number of methylene groups will occupy the adsorbed phase for both adsorbent activities. The experimental value of the retention volume ratio at the lower adsorbent activity implies that for decylthiophene only about one-half of the number of methylene groups held in the adsorbed phase at the higher adsorbent activity are so held in the case of the less active adsorbent. This is consistent with the expectation that as Q_i decreases (with decreasing adsorbent activity), for the methylene group, an increasing portion of the terminal carbons in an alkyl chain (particularly for long chains) will be statistically favored to occupy the non-sorbed phase.

In the case of stronger eluents than pentane, Q_i for the methylene group should be negative, the alkyl group of aromatics should lie (except for the ring-attached carbon) in the non-sorbed phase, and the retention volumes of a series of alkyl aromatics should be constant. This does not mean that substituted aromatics should have the same $\underline{R}^\circ$ values as unsubstituted ones, since the effect of substitution *per se* on the aromatic may be considerable. Experimental data for the 4-*n*-alkyl-pyridines, using 50% benzene–iso-octane as eluent and 5.0% H_2O–Al_2O_3, tentatively bear this out. The $\underline{R}^\circ$ values of the methyl, ethyl, and amyl derivatives stand in the ratio 1.0:1.1:1.0. Although this is not a sensitive test of the previous assertion, because of the low adsorbent activity and small range in n, it is suggestive of its validity.

Additivity in the adsorption free energy of substituted aromatics

For a substituted aromatic, if the relative retention volume R^* is as previously defined ($\underline{R}^\circ$ for the substituted compound divided by R° for the unsubstituted compound), eqn. (6) requires:

$$\log \underline{R}^* = \overset{i}{\Sigma} Q_i \tag{14}$$

where the summation is over all *substituents i*. SPORER AND TRUEBLOOD[5] have analyzed a number of retention volume data for substituted benzenes eluted from silicic acid by benzene in terms of an expression equivalent to eqn. (14). Table VII presents some relative retention volume data for the halogen-substituted benzenes and naphthalenes, using *n*-pentane as eluent and 0.5% H_2O–Al_2O_3 as adsorbent. It is seen first that Q_i for the halogens as substituents increases with atomic number, or parallels the polarizability of the atom i. Deriving values of Q_i from the mono-substituted benzenes (see Table III), it is possible to calculate relative retention volumes for the poly-substituted aromatics. For the *ortho* and *para* substituted di-halobenzenes it is seen

that reasonably good agreement between calculated and experimental values exists; the average deviation is only ± 12%. For the one *meta* substituted compound (*m*-dichlorobenzene), the calculated value is substantially too high, and the experimental value is actually less than for the monosubstituted compound. The deviation between calculated and experimental values increases still more in the case of the *ortho-para* substituted tri-halobenzenes, and finally reaches a maximum in the case of the one all *meta tri-halobenzene*, 1,3,5-tribromobenzene. For the 1-halo-naphthalenes, the calculated values are uniformly high by 120 ± 4%. Two second-order effects which affect the validity of eqn. (14) must be recognized. First, resonance interaction of the various substituent groups can result in values of Q_i which vary with substitutional position. Second, only certain substituted isomers (*o,m,p*) may overlap the adsorption sites in an optimum manner. Both of these phenomena have been discussed by SPORER AND TRUEBLOOD[5]. It is difficult to separate the relative impor-

TABLE VII

RELATIVE RETENTION VOLUME DATA FOR SUBSTITUTED
AROMATIC SOLUTES: *n*-PENTANE ELUENT, 0.5 % H_2O–Al_2O_3 ADSORBENT

Solute	$R°$		Deviation, %
	Experimental	Calculated	
Benzene	(1.00)	(1.00)	—
Fluorobenzene	1.25	(1.25)	—
Chlorobenzene	1.52	(1.52)	—
Bromobenzene	1.97	(1.97)	—
Iodobenzene	2.88	(2.88)	—
1,2-Dichlorobenzene	2.13	2.31	7
1,4-Dichlorobenzene	2.18	2.31	6
1,2-Dibromobenzene	3.75	3.88	4
1,4-Dibromobenzene	2.80	3.88	39
1,4-Diiodobenzene	10.4	8.3	—20
1,2-Iodobromobenzene	5.9	5.7	—3
1,4-Chlorobromobenzene	2.73	2.99	9
1,3-Dichlorobenzene	1.48	2.31	55
1,2,4-Trichlorobenzene	1.70	3.51	106
1,2-Dichloro-4-bromobenzene	2.24	4.55	103
1,3,5-Tribromobenzene	1.50	7.6	407
2-Chloroethylbenzene	10.3		
Naphthalene	(1.00)	(1.00)	—
1-Chloronaphthalene	0.69	1.52	120
1-Bromonaphthalene	0.92	1.97	114
1-Iodonaphthalene	1.27	2.88	127

tance of these possibilities. Group–ring resonance interaction must be significant, since 1,3,5-tribromobenzene is less strongly adsorbed than is bromobenzene. This implies some deactivation of the nucleus by the second and third bromine groups, without sufficient interaction of these groups with the adsorbent to overcome the effect. Similarly, the 1-halo-naphthalenes are less strongly adsorbed than predicted by a constant adsorption energy increment ($q_j = -0.35 \pm 0.01$). This suggests that the greater number of aromatic carbons in the naphthalene nucleus permit a greater

deactivation of the ring by a halo substituent, and a corresponding reduction in Q_i for the ring. That the lowering of the naphthalene ring adsorption energy is constant for each substituent is reasonable from the similar values for the HAMMETT σ function[12] for these three halogen substituents. Conversely, the differing atomic radii of chlorine, bromine, and iodine (0.99–1.33) would be expected to result in differences in the deviation of calculated and experimental $\underline{R}^\circ$ values for the 1-halo-naphthalenes if optimum site overlap were the important consideration. SPORER AND TRUEBLOOD[5] have interpreted differences in $\underline{R}^\circ$ values for *meta* and *para* disubstituted benzenes in terms of the optimum coverage of adsorbent sites, and some justification for the importance of this effect can be inferred from the data of Table III. Thus, the all *meta* derivatives in each case have a value of $\underline{R}^\circ$ close to that of the corresponding monosubstituted benzene, suggesting perhaps that only one *meta* substituent can overlap an adsorbent site while the ring is adsorbed. Similarly, all *ortho-para* trisubstituted benzenes have retention volumes approximating those of the corresponding disubstituted benzene, again suggesting that a maximum number of substituent groups can be brought into an optimum overlapping position with respect to the adsorbent sites (in this example, two).

In the case of chloroethylbenzene, Q_i for the chloro substituent (1.01) is much higher than in the case of chlorobenzene (0.20). The same effect has been noted by SPORER AND TRUEBLOOD[5] in the adsorption on silica of amino and hydroxyl groups, where the adsorption affinity of the aliphatic substituent is much higher than that of the aromatic substituent. Converting their K_i values for these groups to the present Q_i factors ($K_i = 10^{Q_i}$), we have (for SiO_2 as adsorbent)

	Q_i (aliphatic)	Q_i (aromatic)
-NH$_2$	3.8	1.9
-OH	2.4	1.4

It is seen that these aliphatic substituents contribute about twice as much as the aromatic substituent to the adsorption energy of a solute. Still another example of this general phenomenon can be seen in the comparison of Q_i values for the sulfur atom in dialkyl sulfides and thiophenes. For alumina as adsorbent, and *n*-pentane as eluent, Q°_i is 2.7 in the sulfides and 0.76 in the thiophenes. This effect is attributed to differing resonance interaction of the group in question with the remainder of the solute molecule, similar to the progressive weakening by resonance of the basicity of the nitrogen in the series ammonia, pyridine, pyrrole. While this mechanism for the explanation of these differences in aromatic and aliphatic Q_i values must be important, it is worth noting that site overlap may also contribute, since the aliphatic substituents have greater freedom to adapt to the surface of the adsorbent after the ring is adsorbed.

Steric and other second-order effects in the retention volumes of alkyl-substituted aromatics

Tables VIII, IX, and X present a number of relative retention volume data for alkyl-

substituted benzenes, naphthalenes, thiophenes, pyridines and quinolines. A number of second order corrections or interaction effects (similar to those for the *meta* halobenzenes, tri-halo-benzenes, etc.) can be seen in these examples. Table XI summarizes some of the second-order q_j factors applying to special arrangements of alkyl and aromatic carbon atoms, for specified eluent–adsorbent systems. These q_j values must be added to $\sum^i Q_i$ for each solute in the calculation of eqn. (6) and following equations. For the relative retention volume data of Tables IV–VI, only the alkyl Q_i terms must

TABLE VIII

RELATIVE RETENTION VOLUMES OF ALKYL-SUBSTITUTED BENZENES
AND NAPHTHALENES FOR 0.5 % H_2O–Al_2O_3; n-PENTANE ELUENT

Solute	R*		Deviation, %
	Experimental	Calculated	
Benzene	(1.00)	(1.00)	—
Toluene	1.20	1.14	—5
Ethylbenzene	1.11	1.11	0
o-Xylene	1.75	1.57	—10
m-Xylene	1.32	1.30	—2
p-Xylene	1.34	1.30	—4
n-Propylbenzene	1.18	1.17	—1
Isopropylbenzene	0.96	0.88	—8
o-Methyl-ethyl-benzene	1.66	1.53	—8
m-Methyl-ethyl-benzene	1.27	1.26	—1
p-Methyl-ethyl-benzene	1.16	1.26	9
1,2,3-Trimethylbenzene	2.52	2.17	—16
1,2,4-Trimethylbenzene	1.84	1.79	—3
1,3,5-Trimethylbenzene	1.41	1.48	5
n-Butylbenzene	1.24	1.24	0
Isobutylbenzene	1.13	1.24	10
sec.-Butylbenzene	0.93	0.92	—1
tert.-Butylbenzene	1.01	0.92	—9
o-Diethylbenzene	1.47	1.49	2
m-Diethylbenzene	1.20	1.23	3
p-Diethylbenzene	1.15	1.23	7
1,3-Dimethyl-5-ethyl-benzene	1.23	1.44	17
m-Methyl-isopropyl-benzene	1.01	1.01	0
p-Methyl-isopropyl-benzene	0.91	1.01	11
1,2,3,5-Tetramethylbenzene	2.47	2.48	0
1,2,4,5-Tetramethylbenzene	2.49	2.48	0
Pentamethylbenzene	4.25	4.14	—3
Hexamethylbenzene	6.0	5.7	—5
n-Octylbenzene	1.46	1.47	1
n-Decylbenzene	1.52	1.57	3
n-Dodecylbenzene	1.69	1.65	—3
n-Eicosylbenzene	1.90	1.90	0
Indane	1.76	1.77	1
Tetralin	2.10	1.95	—7
Cyclohexylbenzene	1.67	1.60	—4
Benzylbenzene	1.52	1.67	10
Naphthalene	(1.00)	(1.00)	—
1-Methylnaphthalene	1.41	1.38	—2
2-Methylnaphthalene	1.22	1.14	—5
1-n-Hexylnaphthalene	1.82	1.65	—9
1-n-Butylnaphthalene	1.69	1.50	—11
Acenaphthene	2.18	1.93	—11

be taken into account, since the aromatic terms cancel out for the retention volumes of substituted aromatics relative to the unsubstituted ones. $\sum_{}^{i} Q_i$ for the alkyl terms is calculated from the data of Fig. 8 for the solutes of Tables VIII and IX, and assumed zero for the data of Table X (see later discussion).

The relative retention volumes $\underline{R}^*$ of the alkyl benzenes are the most easily interpreted. It is found that branching adjacent to the ring (as in isopropylbenzene) causes a reduction in $\underline{R}^\circ$ ($q_j = -$ 0.122), and that shifting of the branching by one or more carbon atoms from the ring (as in isobutylbenzene) reduces this contribution by about two thirds ($q_j = -$ 0.041). Methyl substitution directly on the ring has a larger effect ($Q_i = 0.057$) than would be expected from the extrapolation of the contribution of larger alkyl groups (in Fig. 9) to n equal 1 ($Q_i = 0.023$). These effects suggest that the α hydrogens are increasing the basicity and adsorption energy of the nucleus, and that alkyl substitution *per se* is reducing nucleus-adsorption energy, probably by forcing the adsorbed solute slightly out of the plane of the adsorbent surface.

It is further observed that *o*-alkyl aromatics invariably have larger $\underline{R}^\circ$ values than the corresponding non-vicinal isomers. An attractive interpretation of this effect (which recalls the higher boiling points of *o*-isomers) is offered by considering the

TABLE IX

RELATIVE RETENTION VOLUMES OF ALKYL-SUBSTITUTED THIOPHENES
FOR 0.5 % $H_2O-Al_2O_3$; *n*-PENTANE ELUENT

Solute	R^*		*Deviation, %*
	Experimental	*Calculated*	
Thiophene	(1.00)	(1.00)	—
3-Methylthiophene	1.03	1.05	2
2-Ethylthiophene	1.01	1.02	1
2-*n*-Propylthiophene	1.03	1.08	5
2-*n*-Butylthiophene	1.12	1.14	2
2-*n*-Hexylthiophene	1.29	1.26	—3
2-*n*-Heptylthiophene	1.28	1.31	3
2-*n*-Octylthiophene	1.37	1.35	—2
2-*n*-Decylthiophene	1.60	1.44	—10
2-Isobutylthiophene	0.96	1.03	7
2-Isopentylthiophene	1.12	1.09	—3
2-(2-Ethyl-1-butyl)-thiophene	1.11	1.15	4
2,5-Di-isopentyl-thiophene	0.95	1.19	20
2,5-Ethyl-isopentyl-thiophene	0.91	1.10	18
2,5-*n*-Propyl-isopentyl-thiophene	0.90	1.16	22
2,5-Diethylthiophene	0.83	1.04	20
2,5-Ethyl-*n*-propyl-thiophene	0.82	1.10	25
2,5-Ethyl-*n*-butyl-thiophene	0.92	1.16	21
2,5-Ethyl-*n*-hexyl-thiophene	1.12	1.28	13
2,5-Ethyl-*n*-octyl-thiophene	1.25	1.38	10
2,5-Di-*n*-propyl-thiophene	0.87	1.15	24
2,5-*n*-Propyl-*n*-pentyl-thiophene	1.02	1.29	21
2,5-Di-*n*-butyl-thiophene	0.93	1.29	28
2,5-Ethyl-isobutyl-thiophene	0.76	1.06	28
2,5-*n*-Butyl-isobutyl-thiophene	0.83	1.18	30
2,5-Di-isobutyl-thiophene	0.66	1.07	38

rotation around the aromatic carbon–aliphatic carbon bond. Because of steric hindrance, this rotation will be restricted in the gas phase for vicinal substituents relative to non-vicinal substituents. As a consequence, this rotational heat capacity contribution to the total molecular free energy will be such as to increase the free energy of non-*ortho* isomers. It is reasonable to expect that much of this rotational free energy contribution will be lost upon adsorption, and as a result the free energy of adsorption of *ortho* relative to non-*ortho* isomers will be decreased, and $\underline{R}°$ increased.

TABLE X

RETENTION VOLUMES OF THE ALKYL-SUBSTITUTED PYRIDINES AND QUINOLINES
FOR 5.0 % $H_2O-Al_2O_3$; 50 % BENZENE–ISO-OCTANE ELUENT

Compound	$R°$		Deviation, %
	Experimental	Calculated	
Pyridine	14.6	(14.6)	—
3-Methylpyridine	21.2	23.7	12
4-Methylpyridine	23	23.7	3
4-Ethylpyridine	26	23.7	—9
3,4-Dimethylpyridine	41	46	12
3-Methyl-4-ethyl-pyridine	6.2	46	641
4-Amylpyridine	23	23.7	3
Quinoline	11.5	(11.5)	—
4-Methylquinoline	18.8	18.6	—1
6-Methylquinoline	13.7	13.2	—4
7-Methylquinoline	12.4	13.2	6
2-Methylpyridine	9.6	23.7	147
2,3-Dimethylpyridine	13.3	46	245
2,4-Dimethylpyridine	7.5	38	406
2,5-Dimethylpyridine	10.6	38	258
2-Methylquinoline	8.1	18.6	130
2,6-Dimethylquinoline	9.3	31	233
2-Ethylpyridine	6.1	23.7	289
8-Methylquinoline	2.4	13.2	450
2,6-Dimethylpyridine	6.3	38	503
2,4,6-Trimethylpyridine	9.5	62	552

TABLE XI

SECOND ORDER FACTORS q_i

Group	Aromatic hydrocarbons*	Thiophenes*	Pyridines, quinolines**
Substitution on ring, Ar-R,	0.00	—0.036	0.21 (N ring)
Methyl on ring, Ar-CH$_3$	0.037	0.037	0.21 (N ring)
			0.06 (other)
Iso branch on ring, Ar-CHR$_2$	—0.122		
o-Alkyl substitution on ring	0.083	(0.083)	
Naphthene ring closure	0.072	(0.073)	
Iso branch not on ring, Ar-R-CH-R$_2$	—0.041	—0.041	

* 0.5 % $H_2O-Al_2O_3$; n-pentane eluent.
** 5.0 % $H_2O-Al_2O_3$; 50 % benzene-iso-octane eluent.

In Fig. 11, the relative retention volumes $\underline{R}^*$ are logarithmically plotted *versus* the number of methyl groups for the series of vicinal compounds beginning with toluene and ending with hexamethylbenzene. A linear relationship is observed, permitting a value of q_j per *ortho* attachment of 0.087 to be calculated (after subtraction of the contribution per ring-attached methyl: 0.057). This constant contribution per *ortho* attachment (counted as $n - 1$ for each cluster of n vicinal substituents) suggests that vicinal alkyl groups through intermeshing of hydrogens may possess
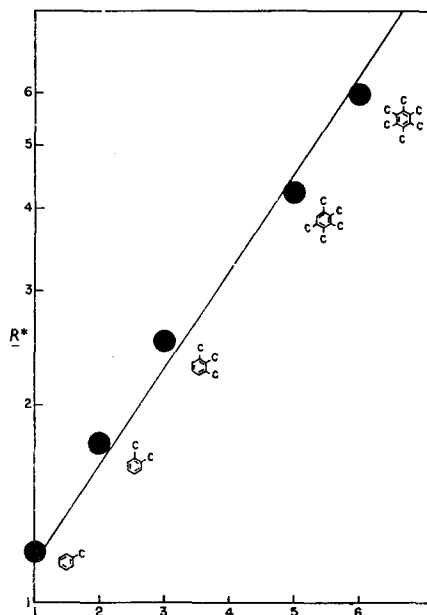

Fig. 11. $\underline{R}^*$ *versus* number of vicinal methyls for substituted benzene; n-pentane and 0.5 % $H_2O-Al_2O_3$.

(in the gas phase) only the rotational heat capacity of one non-vicinal group. The higher $\underline{R}^\circ$ value of 1- as opposed to 2-methyl-naphthalene suggests that substituents in the 1-position of naphthalene (and presumably 1-position of other polyaromatics) behave as *ortho* substituents; the ratio of $\underline{R}^\circ$ values for the methylnaphthalenes is observed to be 1.16, while that calculated on the basis of an *ortho* linkage would be 1.21.

The data of Table VIII further suggest that a naphthene ring has a value of q_j equal to 0.073, apart from the additional contribution of the *ortho* linkage in condensed cycloalkyl aromatics such as tetralin. When the various second-order *and* first-order *alkyl* contributions or values of Q_i and q_j are summed for each solute of Table IV, the *relative* retention volumes can be calculated. These calculated values show an average agreement with experimental of $\pm$ 5 %; furthermore, those few values which deviate by more than 10 % are not suggestive of special effects requiring the postulation of additional second-order terms or q_j values. Consequently it appears reasonable to claim at this point a practical understanding of the effects determining retention volume in the alkyl-substituted aromatic hydrocarbons.

Table IX lists the relative retention volumes for a number of alkylthiophenes. Calculated and experimental $\underline{R}°$ values for the monoalkylthiophenes show good agreement (average deviation $\pm$ 5 %), assuming a value of q_j for any alkyl substitution on the thiophene ring of — 0.036 (*versus* 0.00 for similar substitution on aromatic hydrocarbons). Significant discrepancies arise in the case of the di-substituted compounds, however. The calculated $\underline{R}°$ values for the 2,5-dialkylthiophenes, excluding the iso-butyl derivatives, are consistently high by 20 $\pm$ 4 %. When one of the substituents is iso-butyl, the deviation rises to 29 $\pm$ 1 %, and when both substituents are iso-butyl, the discrepancy is 38 %. These differences between experimental and calculated values obviously parallel the crowding of alkyl groups around the thiophene sulfur, and it is reasonable to postulate that the effect is a result of some sort of interference between the sulfur-adsorbent bond. The value of q_j for alkyl substitution may also reflect this effect. Because the deviations of calculated from experimental values are reasonably constant, it would be possible to derive additional second-order q_j values for specific bonding situations; however, insufficient substitution types are represented in Table IX to generalize on the quantitative dependence of such effects on molecular geometry.

In Table X, the retention volumes of a number of alkyl pyridines and quinolines are presented, for a necessarily less active adsorbent and more polar eluent. For the pyridines which do not possess a 2- or a 6-substituent, and the quinolines not substituted in position 2 or 8, $\underline{R}°$ values can be calculated with rather good overall agreement with experimental data, assuming the q_j values of Table XI for methyl and alkyl substitution on the pyridine and quinoline rings. The one case where the correlation fails is in the case of 3-methyl-4-ethyl-pyridine, and here the disagreement is so large as to cast doubt on the true identity of this commercial sample; there is no reason to invoke a specific second order effect to explain this anomaly. The large value (relative to the hydrocarbons and thiophenes) of q_j for methyl substitution in the nitrogen containing ring (q_j = 0.21) is not unexpected because of the greater basicity of the nitrogen atom, and its related greater sensitivity to electron-donating substituents; this difference should in fact be even larger for more active adsorbents. The reduction of q_j for methyl substitution in the non nitrogen-containing ring of quinoline (q_j = 0.06, relative to the value of 0.21) also emphasizes the greater sensitivity of the nitrogen-containing ring to alkyl substitution. The apparent agreement of this latter quantity with the methyl Q_i of the hydrocarbons is coincidental, since the adsorbent activities are not comparable.

Where one methyl substituent is present in the 2- or 6-position of pyridine, or the 2-position of quinoline, the values calculated using the parameters of Table VI are high by an average of 236 $\pm$ 66 %. This suggests a q_j value of — 0.56 for the calculation of *ortho versus* non-*ortho* methyl pyridines and quinolines. For two such *ortho* methyl groups, the calculated $\underline{R}°$ values are an average of 527 % high, from which a corresponding q_j contribution of — 0.80 can be calculated. These factors emphasize the sensitivity of the nitrogen atom adsorption bond to steric crowding around it. A similar effect has been noted in the case of the *ortho* alkylthiophenes, but there the

effect is much smaller, probably due to the smaller energy associated with the sulfur-adsorbent bond. The experimental $\underline{R}°$ value of 8-methylquinoline is substantially smaller than 2-methylquinoline, and this probably reflects more efficient steric interference of a substituent at the 8- as opposed to an *ortho* position.

GLOSSARY OF TERMS

a subscript refers to adsorbed phase

E refers to eluent molecule

F_t free energy per mole of transferring solute from non-sorbed to adsorbed phase (divided by 2.30 RT)

$(F_i)_j$ partial molar free energy of species or group i in phase j (divided by 2.30 RT)

F_{iE} free energy for transfer of group i from eluent E phase to adsorbed phase (divided by 2.30 RT)

$\underline{K}$ distribution coefficient or equilibrium constant for solute between adsorbed and non-sorbed phases; (g solute per g adsorbent)/(g solute per ml eluent)

$\underline{K}°$ value of K in linear region (concentration-independent value)

$K°$ thermodynamic equilibrium constant corresponding to $\underline{K}°$; see eqn. (5)

K_{ph} phenyl group contribution to solute $K°$ value (SPORER AND TRUEBLOOD[5])

n subscript refers to non-sorbed phase; also, number of equivalent structural groups; also, number of carbon atoms in alkyl group

Q_i group i retention volume factor

$Q°_i$ value of Q_i for calcined alumina

q_j second-order retention volume factor for geometric arrangement j

$q°_j$ value of q_j for calcined alumina

r molal volume ratio of solute to eluent

R' retention volume; eluent volume required to remove 50 % of solute from column

R corrected retention volume; R' minus V_0 the column void volume

$\underline{R}$ equivalent retention volume, R/W

$\underline{R}°$ equivalent retention volume, R/W, in linear region

$\underline{R}*$ relative equivalent retention volume, $\underline{R}°$ for substituted aromatic divided by that of unsubstituted compound

V_a volume of adsorbed phase per gram of adsorbent

V_0 column dead volume in ml

W_s solute oil to gel ratio; weight of sample divided by weight of adsorbent

x, y, z, i structural groups which constitute a solute

α adsorbent activity function

δ_i relative volume of group i; fraction of eluent molecule displaced from adsorbed phase by i, and varying with eluent

θ fractional adsorbent loading by solute

θ_i value of θ for linear elution

ε_{12} eluent polarity factor, proportional to eluent adsorption energy per unit volume, relative to n-pentane

ε°_{12} value of ε_{12} for calcined alumina

ε° ε°_{12} with pentane as eluent 1

SUMMARY

Linear elution retention volume data have been acquired for alumina as adsorbent. Solute structure, eluent type, and alumina water deactivation have been varied over wide ranges, and the results semiquantitatively correlated in terms of a physical model. Adsorbent deactivation by water is shown to cause progressive reduction in the number of adsorption sites, with the remaining sites being weaker, but partition effects appear unimportant for 0–5 % H_2O–Al_2O_3. Solute adsorption free energy has been found to be a linear function of adsorbent activity. A corollary of this observation is the "constant eluent non-crossing rule": for a given eluent, solute separation order is unchanged as adsorbent activity is varied. For certain chromatographic system and solutes, retention volumes can be quantitatively predicted.

REFERENCES

1 L. R. SNYDER, *J. Chromatog*, 5 (1961) 430.
2 G. J. PIEROTTI, C. H. DEAL, E. L. DERR AND P. E. PORTER, *J. Am. Chem. Soc.*, 78 (1956) 2989.
3 O. REDLICH, E. L. DERR AND G. J. PIEROTTI, *J. Am. Chem. Soc.*, 81 (1959) 2283.
4 E. R. REICHL, *Monatsh. Chem.*, 86 (1955) 69.
5 A. H. SPORER AND K. H. TRUEBLOOD, *J. Chromatog.*, 2 (1959) 499.
6 H. BROCKMAN AND F. VOLPERS, *Chem. Ber.*, 82 (1949) 95.
7 L. H. KLEMM, D. REED, L. A. MILLER AND B. T. HO, *J. Org. Chem.*, 24 (1959) 1468.
8 A. WINTERSTEIN AND K. SCHON, *Z. physiol. Chem.*, 230 (1934) 146.
9 W. BACHMAN, *Z. anorg. Chem.*, 79 (1913) 202.
10 C. N. ROWE, *Doctoral Thesis*, Pennsylvania State University, 1955, p. 5.
11 G. E. K. BRANCH AND M. CALVIN, *The Theory of Organic Chemistry*, Prentice-Hall, Inc., New York, 1941, p. 112.
12 L. P. HAMMETT, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, p. 188.