

LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

IV. GROUP LOCALIZATION IN THE ADSORBATE.
EXTENSION OF THE ROLE OF SOLUTE STRUCTURE
IN SEPARATIONS OVER ALUMINA

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INTRODUCTION

Part II of this series¹ presented the derivation of equation (1)

$$\log \underline{R}^{\circ} = \log V_a + \alpha \left[\sum_i^k Q^{\circ}_i + \sum_j^l q^{\circ}_j - \varepsilon^{\circ} \sum_i^k \delta_i \right] \quad (1)$$

for the correlation of solute retention volume \underline{R}° in linear elution adsorption chromatographic (LEAC) systems. In Part II, values of the adsorbent surface volume V_a and activity α were also tabulated for Alcoa F-20 alumina of varying water content. Limited data on the other parameters of equation (1) were also given, particularly with respect to solute geometry terms q°_j . Part III of the present series² discussed the eluent term $\varepsilon^{\circ} \sum_i^k \delta_i$ of equation (1) in some detail, describing the accurate calculation of solute surface volume $\sum_i^k \delta_i$, listing values of eluent strength ε° for various solvents, and relating the strengths of solvent binaries to those of the pure constituents. The application of equation (1) to a variety of alumina based chromatographic systems requires comparable detail in the list of solute group adsorption parameters Q°_i .

With the extension of equation (1) to solutes showing a wide range in group adsorption energies, the applicability of equation (1) requires reappraisal. Thus, the derivation of equation (1) does not consider that any part of the solute molecule will ever be preferentially oriented on the adsorbent surface, or "localized" with respect to a particular adsorption site. Theoretically, however, as the adsorption energy of a particular solute group increases there will be an increasing tendency toward localization of that group, *i.e.*, shortening of the distance between the group and a specific site on the adsorbent. The data of Part II are largely limited to solutes with no strongly adsorbed groups. In the case of the aromatic hydrocarbons, the solute type studied most extensively in Part II, the average adsorption energy for each aromatic carbon is relatively small, and the localization of individual carbon atoms of high reactivity is not indicated. Thus, anthracene with 14 aromatic carbons, and very reactive 9 and 10 positions (LCAO free valence 0.520), is much less strongly adsorbed than triphenylene with 18 aromatic carbon atoms, and no carbons approach-

ing the reactivity of the 9 and 10 carbons of anthracene (maximum LCAO free valence in triphenylene is 0.439). In those cases where \underline{R}° data were previously available (Part II) for solutes with strongly adsorbed groups, the variation in solute structure was insufficient to prove the existence of localization. The interpretation of these initial data on solutes with strong groups was further complicated by additional factors which we shall discuss in the present paper. Prior to the present work, therefore, there has been no experimental basis for evaluating the importance of group localization in influencing solute adsorption on alumina. SPORER AND TRUEBLOOD's data³ for the adsorption of various solutes on silicic acid suggest that localization does not occur on this adsorbent.

The further tabulation of Q°_i values for various solute groups and the examination of the possibility of group localization in adsorption on alumina form the basis of the present investigation.

EXPERIMENTAL

The experimental techniques employed in the present work and the preparation and purification of the various materials used have been described in Parts II and III. In the present work, as previously, the adsorbent is Alcoa F-20 alumina whose activity has been controlled by chromatographic testing of material prepared through calcination and addition of water.

THE PREDICTION OF LEAC RETENTION VOLUME DATA

The present paper rounds out our correlation of simple LEAC systems using alumina as adsorbent. It is believed that most of the major factors which determine solute adsorption energy and retention volume are now understood and are capable of quantitative treatment, for all cases except those involving solutes or eluents with active hydrogens (alcohols, thiols, acids, etc.) Papers II through IV of the present series offer a reasonable basis for the prediction of retention volume data in systems within the scope of equation (2) below. Equally important, they permit the comparison of calculated values with experimental data in the elucidation of secondary contributions to solute adsorption energy.

The present work demonstrates that equation (1) is in some cases inaccurate because of the partial localization of strongly adsorbed solute groups on adsorbent sites. When this occurs, the remainder of the solute tends to delocalize, and the adsorption energy of the solute is decreased relative to that which would have been calculated from equation (1) which assumes no dependence of localization on solute structure. The effect of localization on \underline{R}° can be quantitatively treated by adding an additional term to eqn. (1) to give eqn. (2):

$$\log \underline{R}^\circ = \log V_a + \alpha \left[\sum_i Q^\circ_i - f(Q^\circ_k) \sum_{i \neq k} Q^\circ_i + \sum_j q^\circ_j - \epsilon^\circ \sum_i \delta_i \right] \quad (2)$$

The localization term, $f(Q^\circ_k) \sum_{i \neq k} Q^\circ_i$, represents a loss in solute adsorption energy due to the localization of the strongest solute substituent k . The procedure used in calculating \underline{R}° by means of eqn. (2) will be described below.

Values of the parameters V_a , α , ε° , δ_t , and q°_t have been presented in Parts II and III. The present paper summarizes the known values of Q°_t for various solute groups (Tables I and IV), tabulates values of the localization function $f(Q^\circ_k)$ (Table II), and provides additional q°_j values (Table III).

The localization term of eqn. (2) is calculated as follows. First, select the solute group with largest adsorption energy factor Q°_t ; denote it as the "anchoring"

TABLE I
GROUP ADSORPTION PARAMETERS FOR ALUMINA

<i>Aromatic substituents, (Ar)-X or (Ar)-X-(Ar)</i>			
<i>Group</i>	Q°_t	<i>Group</i>	Q°_t
Carbon, —CH= or > C=	0.31	Ester, —CO ₂ —	2.67
Nitrogen, —NH— or —N=	a	Amine, —NH ₂	4.41
Sulfur, —S—	0.76	Fluoro, —F	0.11
Aldehyde, —CHO	3.35	Chloro, —Cl	0.20
Nitrile, —CN	3.25	Bromo, —Br	0.33
Nitro, —NO ₂	2.75	Iodo, —I	0.51
<i>Mixed aromatic-aliphatic substituents, (Ar)-X-R</i>			
<i>Group</i>	Q°_t		
Ketone, —CO—R	3.74		
Ester of an aromatic acid, —CO ₂ —R	3.32		
Aromatic ester of an aliphatic acid, R—CO ₂ —	3.48		
Ether, —O—R	1.77		
Sulfide, —S—R	1.32		
Dialkyl substituted amine, —N—R ₂	2.48		
<i>Aliphatic substituents, R-X or R-X-R</i>			
<i>Group</i>	Q°_t	<i>Group</i>	Q°_t
Sulfide, —S—	2.65	Chloride, —Cl	1.8 ^b
Ether, —O—	3.5 ^b	Bromide, —Br	2.0 ^b
Ketone, >C=O	5.0	Iodide, —I	2.0 ^b
Ester, —CO ₂ —	5.0 ^b	Nitrile, —CN	5.0 ^b
Aliphatic carbon ^c	0.02		

^a See Table IV.

^b Extrapolated from data for disubstituted alkanes; see Table IX.

^c Any configuration or attachment.

group k . If k is a substituent on, or part of, an aromatic nucleus, $f(Q^\circ_k)$ is given in Table II for various values of Q°_k under the column " $x = 0$ ". $\sum_{i \neq k} Q^\circ_t$ is calculated as $\sum_i Q^\circ_t$ less Q°_t for the group k and six aromatic carbons ($\sum_i Q^\circ_t - Q^\circ_k - 1.86$). It is assumed that the group k does not delocalize, and the delocalization of the phenyl group to which k is attached is already accounted for in the value of Q°_k . The selection of k must be in accordance with the classification of Table I. Thus, a "phenyl" group cannot be considered as an anchoring group, although one atom

of an aromatic ring can. For solutes where the anchoring group k is attached to an alkyl chain which is in turn substituted by another strongly adsorbed group, the calculation of the localization term is similar but not identical to that outlined above. It is necessary in this case, furthermore, to determine what the adsorbate configuration is. Thus, in the elution of solutes of the type Y-R-Z by strong eluents, where Y is assumed to be the anchoring group, unless Z is also quite strongly adsorbed, the

TABLE II
LOCALIZATION FACTORS AS A FUNCTION OF GROUP ADSORPTION ENERGY

Q°_k	$f(Q^{\circ}_k)$					
	$x = 0$	$x = 1$	$x = 2$	$x = 3$	$x = 5$	$x = 10$
0.00	0.00	0.29	0.13	0.00	0.00	0.00
0.20	0.00	0.31	0.16	0.02	0.00	0.00
0.40	0.00	0.35	0.19	0.08	0.00	0.00
0.60	0.00	0.36	0.22	0.12	0.05	0.00
0.80	0.00	0.37	0.25	0.16	0.09	0.00
1.00	0.00	0.39	0.27	0.19	0.11	0.01
1.20	0.01	0.40	0.29	0.21	0.14	0.04
1.40	0.04	0.41	0.31	0.23	0.17	0.07
1.60	0.09	0.42	0.33	0.25	0.19	0.09
1.80	0.13	0.43	0.35	0.27	0.21	0.11
2.00	0.17	0.43	0.36	0.28	0.22	0.13
2.5	0.26	0.46	0.40	0.32	0.26	0.17
3.0	0.34	0.48	0.41	0.34	0.28	0.20
3.5	0.42	0.51	0.44	0.37	0.32	0.23
4.0	0.45	0.53	0.46	0.39	0.34	0.25
5.0	0.45	0.57	0.52	0.44	0.39	0.31
6.0	0.45	0.62	0.57	0.49	0.45	0.36

preferred adsorbate configuration may involve desorption of the group Z and all but one carbon of the alkyl chain R. This uncertainty may be resolved by calculating \underline{R}° for both configurations, with the larger \underline{R}° determining the preferred configuration. Continuing with the calculation for the totally adsorbed molecule, the number of alkyl carbon atoms which separate the anchoring group k and the other substituent must first be determined. $f(Q^{\circ}_k)$ is then given in Table II in the appropriate column. The summation $\sum_{i \neq k}^i Q^{\circ}_i$ is taken over the entire second (weaker) substituent exclusive of k , i.e., $(\sum_i Q^{\circ}_i - Q^{\circ}_k)$.

In the most general case, where more than two substituents and a multi-substituted alkyl chain are involved, a combination of the above procedures is required. The following examples will clarify this and the previous remarks on the use of eqn. (2).

The present paper throws additional light on the nature and magnitude of the solute geometry factors, q°_j , which are required for the accurate calculation of \underline{R}° . In the case of poly-substituted aromatic hydrocarbons, these factors are normally small. Table III summarizes some q°_j values for the *ortho* disubstituted aromatics, as a function of the two groups which are adjacent. Other solute geometries (*m*, *p*, etc.) are believed less important. Where one of the solute functional groups forms an integral part of the ring system, as the nitrogen does in 6-methoxyquinoline, solute geometry can be important in determining \underline{R}° . The ring contained group may interact

either with another substituent, as with the methoxy group in the latter solute, or with the hydrogens or carbons of adjacent rings. Thus, in the aza-aromatics, the adsorption energy of the nitrogen is quite sensitive to solute configuration in the vicinity of the nitrogen. In Table IV a number of these geometry factors are shown for the aza-aromatics. In the case of interaction of nitrogen with the carbons and hydrogens in its vicinity, Table IV shows these q°_j values for each nitrogen type as a combined ($Q^{\circ}_i + q^{\circ}_j$) value. This convention is followed in this case because the only advantage in the separation of Q°_i and q°_j terms occurs when the latter are

TABLE III
GEOMETRY FACTORS q°_j FOR SUBSTITUTION OF GROUP A *ortho* TO GROUP B

A \ B	—NO ₂	—OR	—CO ₂ R	—NH ₂	—COR
—NO ₂	— ^a	+ 0.11	— ^a	— 0.23	— ^a
—OR	+ 0.11	— ^a	— 0.55	— ^a	+ 0.21
—CO ₂ R	— ^a	— 0.55	+ 0.48	— ^a	— ^a
—NH ₂	— 0.23	— ^a	— ^a	+ 0.42	— ^a
—COR	— ^a	+ 0.21	— ^a	— ^a	— ^a


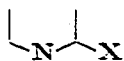
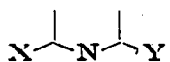
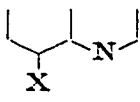
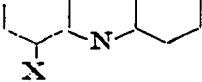
^a Not measured.

Geometry factor for 5, 6, and 7 substituted quinolines

$$q^{\circ}_j = + 0.90 \bar{\sigma}$$

$\bar{\sigma}$ is the average of HAMMETT *meta* and *para* sigma values⁴ for the group in question.

TABLE IV
GROUP ADSORPTION FACTORS FOR RING-CONTAINED NITROGEN IN VARIOUS CONFIGURATIONS

Configuration	$(Q^{\circ}_i + q^{\circ}_j)$			
	Basic nitrogen			Non-basic nitrogen $X, Y = -C=$
	$X = R$	$X = -C=$	$X = N-$	
I 	4.65	4.65	4.65	4.3
II 	4.11	4.09	4.0 ^c	4.1
III 	3.85 ^a 3.65 ^b	3.94 ^b	4.2 ^{b, c}	4.1
IV 	3.34	2.06	(2.62)	
V 		0.83		

^a Y equal R.

^b Y equal —C.

^c Includes one basic, one non-basic nitrogen.

additive (*e.g.*, as in the alkylbenzenes¹). This does not appear to be true of the nitrogen atom geometry factors; thus, q°_j for a nitrogen atom in the acridine configuration (relative to pyridine) is *not* equal to twice the value for an atom in the quinoline configuration.

Several examples of the calculation of $\log \underline{R}^{\circ}$ values by means of eqn. (2) will now be offered. First, consider the elution of 2,4-dinitroanisole from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by benzene. The anchoring group k in this case is one of the two nitro groups, and since Q°_i for an aromatic $-\text{NO}_2$ group is equal to 2.75 (Table I), $f(Q^{\circ}_k)$ is 0.30 (by interpolation in Table II). $\sum^{i \neq k} Q^{\circ}_i$ is (9.13 - 1.86 - 2.75) or 4.52. Since there is an *ortho* grouping which involves a nitro and an ether substituent, $\sum^j q^{\circ}_j$ is + 0.11 (Table III). Inserting the appropriate parameter values into eqn. (2), we have

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.80 + 0.65 (9.13 - 0.30 \times 4.52 + 0.11 - 0.32 \times 13) \\ &= 0.62\end{aligned}$$

An experimental value of 0.46 was observed.

Next, consider the elution of isoquinoline from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by carbon tetrachloride. The anchoring group k in this case is the aromatic nitrogen atom, with pyridine (Type I) geometry, and therefore Q°_i equals 4.65 (Table IV). $f(Q^{\circ}_k)$ is 0.45, and $\sum^{i \neq k} Q^{\circ}_i$ equals (7.44 - 4.58 - 1.86) or 0.93.

Thus,

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.80 + 0.65 (7.44 - 0.45 \times 0.93 + 0 - 0.18 \times 8) \\ &= 1.83\end{aligned}$$

The experimental value was 1.76.

A third example is the elution of the solute 6-nitroquinoline by methylene chloride from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$. Here, the anchoring group is an aromatic nitrogen with quinoline geometry, and Q°_i equals 4.09. $f(Q^{\circ}_k)$ is 0.45, and $\sum^{i \neq k} Q^{\circ}_i$ is 3.68. From Table III, a geometry factor q°_j is indicated for the 6-nitro substituent, equal to $0.90 \bar{\sigma}$, where $\bar{\sigma}$ is the average of HAMMETT sigma values⁴ for the *meta* and *para* positions, equal to 0.75 for $-\text{NO}_2$. So,

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.80 + 0.65 (9.63 - 0.45 \times 3.68 - 0.90 \times 0.75 - 0.42 \times 10 \frac{1}{2}) \\ &= 0.07\end{aligned}$$

An experimental value of 0.02 was observed.

A fourth example is the elution of the disulfide, 3,9-dithia-undecane from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by carbon tetrachloride. In this case, one of the sulfide groups is the anchoring group k with Q°_i equal to 2.65. Two adsorbate configurations are conceivable, one with the two sulfur atoms and seven alkyl carbons lying in the adsorbed phase, and the other with only one sulfur and two alkyl carbons adsorbed. That configuration which gives the greatest adsorption energy or calculated value of \underline{R}° will be favored. In the second, partially adsorbed, case, it can be calculated that

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.80 + 0.65 (2.69 - 0.18 \times 3 \frac{1}{2}) \\ &= -0.46\end{aligned}$$

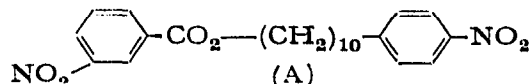
For the totally adsorbed configuration, there are five alkyl carbons separating the two strongly adsorbed sulfide groups, so x equals five, and from Table II $f(Q^{\circ}_k)$ equals

0.27. There are a total of five alkyl carbons confined to the adsorbed phase, in addition to those associated with the —SR groups. As before,

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.80 + 0.65 (5.44 - 0.27 \times 2.65 + 0 - 0.18 \times 10) \\ &= -0.10\end{aligned}$$

Thus, the preferred adsorbate configuration has both sulfur atoms (and the intermediate alkyl carbons) in the adsorbed phase. The value we calculate is therefore —0.10. The experimental value found was 0.04.

In our final example, consider the elution of the solute A from 1.0% H₂O—Al₂O₃



by carbon bisulfide. In this case, the localizing group is the ester substituent with Q°_i equal 3.32. The localization term of eqn. (2) must be split into two parts for the solute A, since there are two delocalized groups involved which are separated by an alkyl chain. For the aromatic nucleus containing the ester group, $\sum^{i \neq k} Q^{\circ}_i = 2.75$, and for the nitrophenyl substituent at the other end of the alkyl linkage, $\sum^{i \neq k} Q^{\circ}_i = 4.61$. $f(Q^{\circ}_k)$ for the first group is 0.39, and for the second it is 0.22. Thus, for the totally adsorbed molecule,

$$\begin{aligned}\log \underline{R}^{\circ} &= -1.54 + 0.84 (12.75 - 2.75 \times 0.39 + 4.61 \times 0.22 + 0 - 0.26 \times 27) \\ &= 1.51\end{aligned}$$

In a similar calculation for the partially adsorbed molecule, where it is assumed that the nitrophenyl group with ester substituent would be adsorbed including only one —CH₂— group, it can be calculated that $\log \underline{R}^{\circ}$ is 1.41. Again, the totally adsorbed molecule is favored, but only narrowly. No experimental value is available in this case for comparison.

As will be discussed in the following section, it is anticipated that di-substituted alkanes such as the solutes of the preceding two examples will be correlated less accurately than other solute types.

GROUP LOCALIZATION AND THE ADDITIVITY OF GROUP Q°_i FACTORS

Experimental \underline{R}° data are shown in Table V for a number of monosubstituted benzenes eluted by various eluents from 3.7% H₂O—Al₂O₃. Use of these data and eqn. (1), with the known values of the adsorbent parameters α and V_a , the eluent polarities ϵ° , the solute surface volume $\sum^i \delta_i$, and the Q°_i factor of an aromatic carbon permits the calculation of Q°_i for the various substituents represented in Table V. All q°_j terms are lumped into the value of Q°_i thus obtained. With values of Q°_i for each substituent specified, the procedure can be reversed to furnish a calculated value of $\log \underline{R}^{\circ}$ in each eluent system. These values, which are shown in Table V, have an average deviation of ± 0.04 log units from the experimental data. This comparison constitutes a check on only the eluent term of eqn. (1), all other parameters having been used in the initial calculation of Q°_i for each substituent group.

The Q°_i values of the substituents in Table I are taken from Table V, along with other such data from Part II and the following sections. The order of relative adsorption affinities for these various groups is in reasonable agreement with those reported by BROCKMANN AND VOLPERS⁵ for the elution of substituted stilbenes from alumina by carbon tetrachloride. Their sequence of group adsorption affinities is shown below,

TABLE V

EXPERIMENTAL AND CALCULATED RETENTION VOLUME DATA FOR MONO-SUBSTITUTED BENZENES
3.7% H₂O-Al₂O₃

Solute	Group	Average ^a Q°_i	Log R°							
			n-Pentane		CCl ₄		Benzene		CH ₂ Cl ₂	
			Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
Nitrobenzene	—NO ₂	2.75	1.14	1.19	0.25	0.20				
Anisole	—OR	1.74	0.53	0.53						
Phenetole	—OR	1.80	0.57	0.57						
Benzaldehyde	—CHO	3.35	1.57	1.58	0.77	0.76				
Acetophenone	—COR	3.74	1.86	1.83	0.84	0.92				
Benzonitrile	—CN	3.25			0.58	0.57	—0.16	—0.15		
Phenyl ethyl sulfide	—SR	1.32	0.26	0.26						
Methyl benzoate	—CO ₂ R	3.32	1.51	1.56	0.57	0.51				
Aniline	—NH ₂	4.41			1.46	1.49	0.75	0.66	0.13	0.17
N,N-Dimethyl- aniline	—NR ₂	2.48	0.99	1.01	—0.02	—0.04				
Phenyl acetate	—OCOR	3.48 ^b								
Phenyl benzoate	—CO ₂ —	2.67 ^c			0.58	0.58				

^a Not corrected for localization of phenyl rings; refers to aromatic substituent in every case.

^b Extrapolated from 25% CH₂Cl₂-pentane.

^c Assumes one phenyl group delocalized.

along with our values of the *effective* group adsorption factors in this eluent system ($Q^{\circ}_i - 0.18 \delta_i$).

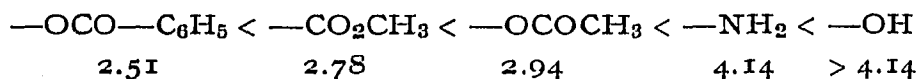
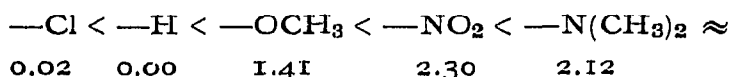


Table VI presents a number of data on the polysubstituted benzenes and substituted naphthalenes. Using the eluent terms of eqn. (1), it is possible to extrapolate all of these data to a common eluent basis for comparison. Values of log R°_p , the average of values extrapolated to a pentane basis, are shown in Table VI for each solute. Since Q°_i for each of the solute substituents in Table VI has been evaluated in Table V, it is possible to test the validity of eqn. (1) for the data of Table VI by comparing experimental and calculated values. As is seen in Table VI (second column of numbers), the latter are in general higher than the experimental values, and the discrepancy becomes large for solutes containing strongly adsorbing groups ($Q^{\circ}_i > 3$).

Resonance interaction between substituent groups and localization of strongly adsorbed groups on specific sites have both been invoked^{1,3} as explanations for non-additivity in group contributions to total solute adsorption energy. Resonance appears

TABLE VI

EXPERIMENTAL AND CALCULATED RETENTION VOLUME DATA FOR SUBSTITUTED NAPHTHALENES AND POLY-SUBSTITUTED BENZENES; 3.7% H₂O-Al₂O₃

Solute	Log R_p^o			Exptl. log R^o			
	Exptl. ^a	Calc. ^b	Calc. ^c	<i>n</i> -Pentane	CCl ₄	Benzene	CH ₂ Cl ₂
2-(1-Thia-propyl)-naphthalene	1.10	1.07	1.05	1.10	-0.13		
1-Methoxynaphthalene	1.02	1.37	1.27	0.92	-0.05		
2-Methoxynaphthalene	1.23	1.37	1.27	1.22	0.08		
<i>m</i> -Diethoxybenzene	1.88	1.71	1.56	1.88			
<i>p</i> -Diethoxybenzene	1.58	1.71	1.56	1.57	0.42		
Diphenyl phthalate	4.17	5.30	4.10			0.41	-0.72
1-Nitronaphthalene	1.61	2.00	1.76	1.55	0.45		
<i>p</i> -Nitroanisole	2.13	2.35	2.00	2.07	0.97		
<i>m</i> -Nitroanisole	1.79	2.35	2.00		0.56		
<i>o</i> -Nitroanisole	2.31	2.35	2.00		1.08		
<i>p</i> -Dinitrobenzene	2.27	2.98	2.44		0.98		
<i>m</i> -Dinitrobenzene	2.33	2.98	2.44	2.30	1.07		
1,4-Dimethoxy-2-nitrobenzene	2.94	3.50	2.89			0.34	
2,4-Dinitroanisole	3.16	4.13	3.25			0.46	
1-Cyanonaphthalene	1.79	2.33	2.02		0.62		
<i>p</i> -Nitrobenzonitrile	2.29	3.31	2.61			0.11	
Dimethyl phthalate	3.43	3.73	2.89			0.87	0.21
Dimethyl isophthalate	3.10	3.73	2.89			0.60	
Dimethyl terephthalate	3.04	3.73	2.89			0.54	
Methyl <i>p</i> -nitrobenzoate	2.52	3.35	2.65		1.17		
Methyl <i>m</i> -nitrobenzoate	2.53	3.35	2.65		1.18		
Methyl <i>o</i> -methoxybenzoate	1.91	2.72	2.27		0.62		
1-Methyl naphthoate	2.05	2.37	2.06		0.76		
2-Methyl naphthoate	2.02	2.37	2.06		0.73		
1,2,4-Tricarbomethoxybenzene	4.46	5.88	4.20			1.39	0.31
Methyl 3,5-dinitrobenzoate	3.23	5.14	3.74			0.32	
1-Naphthaldehyde	1.86	2.39	2.05			-0.01	
<i>p</i> -N,N-Dimethylamino-benzaldehyde	2.90	3.19	2.51			1.06	0.41
<i>p</i> -Methoxybenzaldehyde	2.41	2.74	2.26		1.36		
<i>m</i> -Nitrobenzaldehyde	2.74	3.37	2.62			0.76	
<i>p</i> -Nitrobenzaldehyde	2.64	3.37	2.62			0.66	
1-Acetonaphthone	2.31	2.64	2.28		1.15	0.23	
2-Acetonaphthone	2.43	2.64	2.28		1.20	0.42	
<i>m</i> -Nitroacetophenone	2.66	3.63	2.82			0.48	
<i>p</i> -Nitroacetophenone	2.71	3.63	2.82			0.53	
2,5-Dimethoxyacetophenone	3.24	4.14	3.10			0.74	
<i>p</i> -Nitroaniline	3.25	4.06	3.25				0.52
<i>m</i> -Nitroaniline	3.10	4.06	3.25				0.37
<i>o</i> -Nitroaniline	2.91	4.06	3.25				0.18
<i>p</i> -Diaminobenzene	3.90 ^d	5.14	3.85				
<i>m</i> -Diaminobenzene	3.93 ^d	5.14	3.85				
<i>o</i> -Diaminobenzene	4.19 ^d	5.14	3.85				
1,5-Diaminonaphthalene	4.46 ^d	5.94	4.30				
2,4-Dinitroaniline	4.20	5.85	4.24				

^a Average of extrapolated experimental values using various eluents.^b Calculated from eqn. (1); no geometry factors.^c Calculated from eqn. (2); no geometry factors.^d Extrapolated from values for elution by 50% v dioxane-pentane.

of secondary importance in determining the present \underline{R}° data, since the discrepancies between calculated and experimental \underline{R}° values are relatively independent of isomeric type in disubstituted benzenes where resonance can occur in some of the isomers. For example, the calculated value of $\log \underline{R}^\circ_p$ for each of the nitroanilines is 4.06, using eqn. (1) and the parameter values of Table V. The experimental values for the *meta* and *para* isomers are 3.10 and 3.25, respectively. If resonance were primarily responsible for this discrepancy between calculated and experimental values, the effect should be largest in the case of the *para* derivative, while the reverse is actually observed. More significant, however, is the observation that the experimental values are much closer to each other than to the calculated value. A further indication of the relative unimportance of resonance effects is shown by the discrepancy between calculated and experimental $\log \underline{R}^\circ$ values for the three diaminobenzenes. Here, where resonance should be less important than in the case of the nitroanilines, the discrepancy is actually larger. A final example of the relative unimportance of resonance in polysubstituted aromatic hydrocarbons is offered by *ortho*- and *para*-nitroanisole. Resonance between substituent groups in the case of these two solutes should be much greater than for any of the diaminobenzenes. The discrepancy between calculated and experimental $\log \underline{R}^\circ$ values is, however, fairly small.

Having disposed of resonance between substituent groups as a major contributor to the shortcomings of eqn. (1), it will now be shown that localization is largely responsible for the difference between experimental values and those calculated by means of this equation. First, consider the interaction between a planar aromatic nucleus composed of relatively weak adsorbing groups (aromatic carbon, aromatic sulfur, the halogens, etc.) and an adsorbent surface covered with discrete sites. In general, no configuration of the adsorbate will permit optimum overlap of every solute atom or group with a nearest adsorbent site, so that one of two cases must follow. Either a few of the total solute atoms will be localized, *i.e.*, lie in an optimum position with respect to adsorbent sites, with the remaining solute groups being effectively delocalized, or else all of the solute atoms will be semi-optimized with respect to site

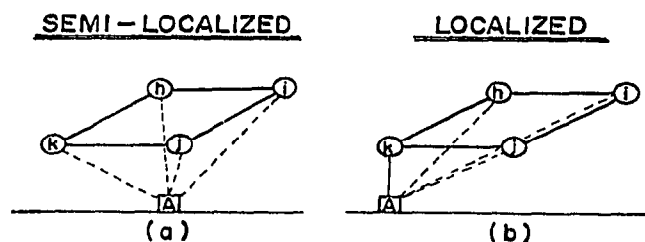


Fig. 1. Hypothetical representation of group localization.

overlap. That is, in the latter case, each solute atom will be "semi-localized". As discussed in the introduction, the retention volume data for the aromatic hydrocarbons do not fit the case of specific atom localization, so that these solutes and others composed of moderately weak adsorbing groups must be considered as semi-localized. If we start with a semi-localized poly-atomic adsorbate, *h-i-j-k*, as visualized in Fig. 1 (a), and if the strength or value of Q°_k of a particular group *k* is now continuously increased, it is seen that eventually the minimization of the free energy of adsorption with respect to adsorbate configuration may require increasing localization

of group k and decreasing localization of the remaining solute groups, as in Fig. 1 (b). Qualitatively, we would expect the delocalization of the remaining groups to increase with the strength of the anchoring group k . The energy of adsorption of each of the remaining solute groups should decrease with increasing delocalization, *i.e.*, the loss in total adsorption energy of the remaining groups should be proportional to the total semi-localized adsorption energy of the delocalizing groups $\alpha \sum_{i \neq k} Q^{\circ}_i$, and to some function of the strength of the anchoring group k , $f(Q^{\circ}_k)$,

$$\Delta \log \underline{R}^{\circ} = \alpha \sum_{i \neq k} Q^{\circ}_i f(Q^{\circ}_k)$$

which rearranges to

$$\text{Fractional delocalization} = \frac{\Delta \log \underline{R}^{\circ}}{\alpha \sum_{i \neq k} Q^{\circ}_i} = f(Q^{\circ}_k). \quad (3)$$

Here, $\Delta \log \underline{R}^{\circ}$ represents the loss in dimensionless free energy of adsorption of the remaining unanchored solute groups as a result of delocalization. It is equal to the difference between experimental values of $\log \underline{R}^{\circ}$ and those calculated by means of eqn. (1), which assumes no localization, and the parameters of Table V. The summation $\sum_{i \neq k} Q^{\circ}_i$ is over the constituent groups i of the solute exclusive of both the anchoring group k and the phenyl ring to which k is attached (since the delocalization of this ring has already been taken into account in the evaluation of Q°_k). It is seen that fractional delocalization is defined as the fractional loss in adsorption energy of the groups i with respect to their semi-localized (*i.e.*, normal) value, using the standard eluent pentane as reference state (as implied in the definition of Q°_i). The derivation of eqn. (3) is qualitative rather than rigorous, and "fractional delocalization" has no obvious relation to any one configuration of the adsorbate. In this respect, Fig. 1 also represents a simplification of the actual localization process.

The data of Table VI have been arranged with respect to increasing strength of the strongest (anchoring) substituent involved. Qualitatively, it can be seen that the discrepancy between the first two columns of numbers increases with increasing strength of the anchoring group, in accordance with eqn. (3). The quantitative evaluation of $f(Q^{\circ}_i)$ from the data of Table VI is complicated by the existence of factors other than localization, which while less important still contribute to $\Delta \log \underline{R}^{\circ}$. Where $\sum_{i \neq k} Q^{\circ}_i$ is small, these factors tend to essentially obscure the localization effect. Assuming that these undefined secondary factors which contribute to $\Delta \log \underline{R}^{\circ}$ vary randomly with the structures contained in Table VI, they should tend to be canceled out if the sum of $\Delta \log \underline{R}^{\circ}$, $\sum \Delta \log \underline{R}^{\circ}$, is divided by the sum of $\alpha \sum_{i \neq k} Q^{\circ}_i$, $\sum \alpha \sum_{i \neq k} Q^{\circ}_i$, for each set of solutes with a *common* anchoring group k , to give $f(Q^{\circ}_k)$. In addition to the statistical averaging of secondary adsorption factors, this treatment for the calculation of $f(Q^{\circ}_k)$ is weighted against the disproportionate effect of those solutes with small values of $\sum_{i \neq k} Q^{\circ}_i$. Table VII summarizes these calculations for each of the anchoring groups represented in Table VI. In Fig. 2 the $f(Q^{\circ}_k)$ values of Table VII are plotted against Q°_k . $f(Q^{\circ}_k)$ is seen to approximate zero for values of Q°_k less than 1.0, increases with Q°_k over the range $1.00 < Q^{\circ}_k < 3.7$, and levels off at a constant value of 0.45 for values of Q°_k greater than 3.7. With the exception of the data for —SR and —CN, the points of Fig. 2

fall reasonably close to a common curve, as required by eqn. (3). The deviation of the latter two substituents from the relationship of Fig. 2 is attractively ascribed to the small number of solutes used in the evaluation $f(Q_k^\circ)$ for each (one for —SR and two for —CN). The representation of the data of Table VI in Fig. 2 is consistent with the following argument for localization as an explanation of the deviations between

TABLE VII
LOCALIZATION ENERGY LOSS *versus* STRENGTH OF ANCHORING GROUP

Group	Q_k°	Number of solutes	$\Sigma \Delta \log R^\circ$	$\Sigma \alpha^i \sum^k Q_i^\circ$	$f(Q_k^\circ)$
(Ar)-SR	1.32	1	+ 0.03	0.80	+ 0.04
(Ar)-OR	1.77	4	— 0.45	3.88	— 0.12
(Ar)-CO ₂ -(Ar)	2.70	1	— 1.13	4.15	— 0.27
(Ar)-NO ₂	2.75	8	— 4.10	13.1	— 0.31
(Ar)-CN	3.25	2	— 1.56	2.59	— 0.60
(Ar)-CO ₂ R	3.32	10	— 8.08	20.7	— 0.39
(Ar)-CHO	3.35	5	— 2.51	7.14	— 0.35
(Ar)-COR	3.74	5	— 3.38	7.49	— 0.44
(Ar)-NH ₂	4.41	8	— 9.46	21.2	— 0.45

experimental values and those calculated by means of eqn. (1). It appears that groups with Q_i° values less than 1.0 are not sufficiently strongly adsorbed to disturb the semi-localized status of the remainder of the solute molecule, while groups with Q_i° greater than 3.7 are completely localized, or at least are not capable of further localization. Where more than one group capable of localization is represented in a

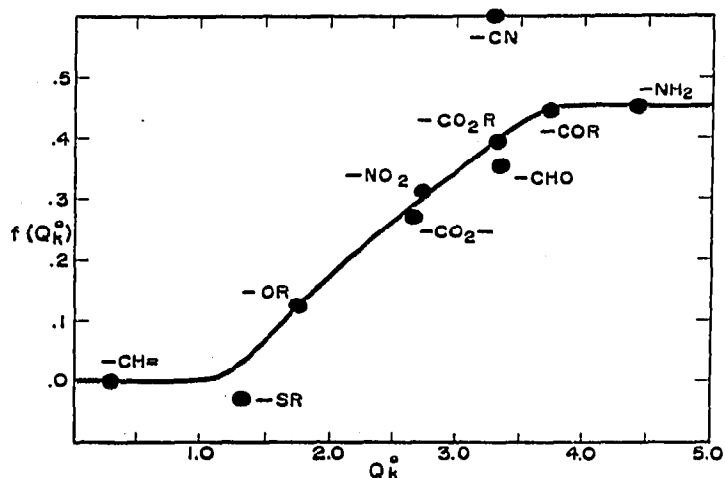


Fig. 2. Localization function for ring substituted aromatics *versus* anchoring group adsorption energy.

solute, the correlation of Fig. 2 suggests that only the strongest is effective in localization, all the remaining weak *and* strong groups then suffering partial or complete delocalization. However, while this mechanism is implicit in eqn. (3), and will be assumed in the following treatment of localization, it appears equally likely that in such solutes as dinitrobenzene, or diaminobenzene, each of the strong groups tends

to localize but is prevented by the other from assuming its normal degree of localization. When eqn. (3) is incorporated into eqn. (1) to include the effect of localization, eqn. (2) results. The values of $f(Q^\circ_k)$ required for the use of eqn. (2) are provided by Fig. 2 and are listed in Table II, under $x = 0$. Table VI includes values of $\log \underline{R}^\circ$ calculated by means of eqn. (2). For the values of $\log \underline{R}^\circ_p$, where the errors due to shortcomings in the eluent terms of eqns. (1) and (2) tend to average out, the average deviation between experimental values and those calculated by means of eqn. (2) is ± 0.17 , while the maximum deviation is 0.54. It is apparent that additional improvements in the present calculation are possible, although this represents a reasonable correlation in view of the range in structural types represented in the data of Tables V and VI.

In Part II we noted that geometry factors are associated with *ortho* alkyl substituted aromatics and 1-alkyl substituted naphthalenes; these effects were interpreted in terms of hindered internal rotation. A similar difference between *ortho* and non-*ortho* derivatives exists in the solutes of Table VI, as shown by the greater average deviation of the calculated and experimental values in the case of the *ortho* substituted benzenes (± 0.24) relative to the non-*ortho* substituted benzenes (± 0.16). In the case of *ortho* groupings which do not involve alkyl substituents, both steric and electronic interaction of the neighboring groups can occur. Consequently, both positive and negative deviations of experimental values from calculated ones are possible. Table III summarizes a number of q°_j values for various combinations of *ortho* substituents. When these factors are included in eqn. (2), the averaged deviation of the experimental data from calculated values drops to ± 0.14 , and only one of the forty-four solutes of Table VI (methyl 3,5-dinitrobenzoate) shows an experimental value of \underline{R}° which misses the calculated value by a factor of more than 2.5.

In the case of the substituted naphthalenes, the data of Table VI do not show any consistent deviations between experimental and calculated values which may be ascribed to decreased rotational freedom of 1-substituents. We have already seen that additional secondary effects are operative in the substituted naphthalenes, the 1-halo derivatives for example showing a constant lowering of solute adsorption energy relative to the calculated value¹. Resonance interaction between substituents on a fused ring system, while not of major importance, probably leads to minor alteration of solute adsorption energy. It is probable that a combination of effects such as these are responsible for the residual differences between calculated and observed retention volumes in Table VI.

The deviations between the experimental data of Table VI and values calculated by eqn. (1) are reminiscent of a similar situation¹ for the polyhalobenzenes. There, it was observed that additivity of group Q°_i parameters holds for all substituents which are not *meta* to one another, while *meta* groups actually lessen \underline{R}° slightly relative to the unsubstituted compound. Thus, for elution by pentane from 0.5% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$, 1,3-dichlorobenzene has a value of \underline{R}° 1.48 just less than that of chlorobenzene (1.52), while 1,2,4-trichlorobenzene, where the 2- and 4-chloro groups are *meta*, has a value of \underline{R}° (1.70) slightly less than that of 1,2- (2.13) or 1,4-dichlorobenzene (2.18). Group localization should be unimportant in the case of the halobenzenes, because the Q°_i values of all the halo substituents on aromatic rings are much less (0.1-0.5) than the threshold value for localization (1.00). The other major factor, resonance interaction between substituents, has already been discussed

for the solutes of Table VI, and in the light of those data does not appear a likely factor in the anomalous retention volumes of the halobenzenes. In Table VIII, the retention volumes of four multi-substituted benzenes which include one or more bromo groups are shown. Application of eqn. (2) to these compounds does not furnish a good calculated value for 2,4,6-tribromoanisole, while sufficing for the three monobromo derivatives. If the previous convention of omitting all halo groups which are *meta* to previously counted ones is used, however, all four solutes are correlated reasonably well by eqn. (2).

TABLE VIII
CORRELATION OF HALOBENZENE SOLUTES

Solute	Log $\bar{R}^{\circ} p$		
	Exptl.	Calc., eqn. 2	Calc., eqn. 2 ignoring <i>m</i> -halo groups
<i>p</i> -Nitrobromobenzene	1.35	1.33	1.33
<i>m</i> -Nitrobromobenzene	1.40	1.33	1.33
<i>p</i> -Bromoacetophenone	1.85	1.95	1.95
2,4,6-Tribromoanisole	0.50	1.16	0.74

As noted above, the present theoretical treatment of localization does not furnish a good explanation of the adsorption behavior of the polyhalobenzenes, although the actual differences in calculated and measured values of $\log \bar{R}^{\circ}$ are in most cases small. This difficulty can be rationalized in terms of certain simplifications which have been effected in our localization model. First, it is tacitly assumed in the development of eqn. (3) and the plot in Fig. 2 that the total adsorption energy of a group k can be concentrated at a single site. This is reasonable in the case of groups with one strongly adsorbing atom (*e.g.*, amino, alkoxy, etc.), but becomes less tenable for such polyatomic species as carbomethoxy and nitro. Thus, the localization function $f(Q^{\circ}_k)$ should be smaller for substituents of the latter type than for monatomic substituents of comparable Q°_k . Second, the total effect of substitution on solute adsorption energy is assumed to be centered in the adsorption energy of group i , whereas concomitant changes in the adsorption energy of the aromatic nucleus must also occur. Thus, if i activates the nucleus (*i.e.*, increases the energy of bonds between the nucleus and the adsorbent), the total effect Q°_i of i on solute adsorption can be broken down into separate contributions from the intrinsic adsorption energy of i \underline{Q}°_i and the increase in adsorption energy of the nucleus q°_a as a result of activation:

$$Q^{\circ}_i = \underline{Q}^{\circ}_i + q^{\circ}_a .$$

When q°_a is positive, $f(Q^{\circ}_k)$ will be smaller for a particular value of Q°_k , since the "true" adsorption strength of the group k \underline{Q}°_k is really less than the value Q°_k indicates. These two secondary factors, the size of the substituent group and its activation of the aromatic nucleus, are such as to oppose one another in all the substituents of Fig. 2. Thus, electron donating groups (amino, α -thia-alkyl, alkoxy) should have a positive value of q°_a (see next section for a more detailed discussion of this point), and all of

these substituents in Fig. 2 are monatomic (exclusive of hydrogens). Electron attracting groups (ester, carbonyl, nitro, nitrile), on the other hand, should have negative values of q°_a , and all of these groups in Fig. 2 are polyatomic. The halo-substituents do not fit into this pattern, since they are both electron attracting and monatomic, both of which factors work to increase $f(Q^{\circ}_k)$ over that predicted from Fig. 2. Qualitatively, this accords with our observations on the anomalies in the poly-halo aromatics, since the calculated retention volumes are in many cases too large. Inasmuch as the total discrepancies are relatively small, however, it is not profitable to carry out a more detailed analysis than the present qualitative discussion.

Having demonstrated that localization occurs in the case of strongly adsorbed exocyclic substituents on aromatic rings, it will now be shown that strongly adsorbing groups which form part of the aromatic ring itself also localize and are governed by eqn. (2). Table X presents data for several unsubstituted aza-aromatics. As is discussed in the next section, the Q°_i value of a nitrogen atom which forms part of an aromatic ring varies with the nature of the *ortho* substituents on the nitrogen-containing ring. The compounds pyridine and isoquinoline thus form one class of aza-aromatics with constant value of Q°_i for the nitrogen in each compound, while the solutes quinoline, phenanthridine, β -naphthoquinoline, and 1-azapyrene form another such class. In each of these two cases, Q°_i for the nitrogen is in excess of 4.0, so localization is complete and $f(Q^{\circ}_k)$ equals 0.45. If eqn. (2) is now applied to the $\log \underline{R}^{\circ}$ values for elution of the above aza-aromatics by CCl_4 from 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$, it can be calculated that the addition of one aromatic carbon to an aza-aromatic, all else remaining unchanged, should result in an increase in $\log \underline{R}^{\circ}$ of 0.052. In Fig. 3, these experimental values of $\log \underline{R}^{\circ}$ are plotted *versus* the number of aromatic carbon atoms in the nucleus.

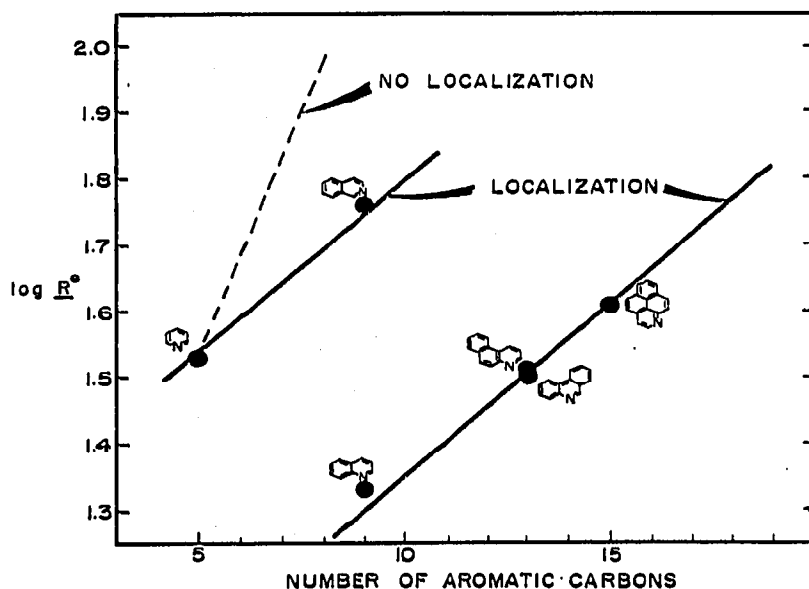


Fig. 3. Delocalization in the aza-aromatics; data for elution from 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by CCl_4 .

A solid line of slope 0.052 is drawn through the data of each class of aza-aromatics. The experimental data are seen to closely follow the calculated curves, while the dashed curve of slope 0.143 corresponding to no localization diverges widely from the ex-

perimental points. It may be concluded that strongly adsorbing groups which are part of the aromatic ring system are equivalent to other strong groups as regards localization. The data of Fig. 3 further strengthen the concept of group localization as a factor in solute adsorption.

A final example of group localization is provided by the α, ω -disubstituted alkanes, $Y-(CH_2)_x-Z$, of Table IX. If one of the terminal groups Y in such solutes is strong enough to localize, some delocalization of Z would be expected, particularly where x is small. As x becomes large, the effect of the localization of Y on the adsorption of

TABLE IX
RETENTION VOLUME DATA FOR TERMINALLY SUBSTITUTED ALKANES;
3.7% $H_2O-Al_2O_3$

Solute	x	$\text{Log } R^{\circ}_p$			$\text{Log } R^{\circ}$	
		Exptl. ^a	Calc. ^b	$f(Q^{\circ}_k)$	Pentane	CCl_4
Benzyl chloride	1	0.18			0.18	
1-Phenyl-2-chloroethane	2	0.24			0.24	
1-Phenyl-3-chloropropane	3	0.25			0.25	
Benzyl bromide	1	0.21			0.21	
1-Phenyl-2-bromoethane	2	0.29			0.29	
1-Phenyl-2-iodoethane	2	0.28			0.28	
Benzyl methyl ether	1	1.16			1.16	
1-Phenyl-2-thia-butane	1	0.60	1.12	0.43	0.60	
1-Phenyl-3-thia-pentane	2	0.76	1.13	0.31		
1-Phenyl-4-thia-hexane	3	0.76	1.15	0.33		
3,5-Dithia-heptane	1	0.76	1.63	0.50		
3,6-Dithia-octane	2	0.87	1.64	0.45	1.02	—0.08
3,7-Dithia-nonane	3	1.13	1.65	0.30	1.13	
3,9-Dithia-undecane	5	1.24	1.68	0.26	1.26	0.04
3,14-Dithia-hexadecane	10	1.43	1.74	0.18	1.43	
1,3-Diphenyl-1,3-dithia-propane	1	1.37	2.31	0.46	1.37	
1,5-Diphenyl-1,5-dithia-pentane	3	1.77	2.33	0.27	1.81	0.08
1,7-Diphenyl-1,7-dithia-heptane	5	1.94	2.36	0.20	1.85	0.16
1,12-Diphenyl-1,12-dithia-dodecane	10	2.31	2.42	0.05	2.26	—0.10
1-Phenylacetonitrile	1	1.97 ^f				
1-Phenyl methyl acetate	1	1.95			1.91	0.83
Diphenylmethane	1	0.29 ^d	(0.62) ^e	0.28		
1,2-Diphenylethane	2	0.45 ^d	(0.64) ^e	0.16		
Benzyl methyl ketone	1	2.14	2.85	0.59	2.14	
Benzylacetone	2	2.23	2.86	0.53	2.23	
Acetone	—	1.65			1.65	
Methyl ethyl sulfide	—	—0.08 ^c				

^a Average of extrapolated values.

^b Assuming no localization.

^c Extrapolated from value for 1.0% $H_2O-Al_2O_3$.

^d Extrapolated from data for 4.0% $H_2O-Al_2O_3$.

^e Assumes Q°_t equal 0.31 for aromatic carbon, and $q^{\circ}_f = 0$.

^f Extrapolated from value in CH_2Cl_2 .

STERIC AND ELECTRONIC EFFECTS IN HETERO-AROMATIC SOLUTES

In the preceding section it has been observed that resonance interaction between substituents on an aromatic hydrocarbon does not lead to significant alteration of solute adsorption energy. In the *ortho* substituted aromatics, steric and/or electronic interaction of neighboring groups appears to cause relatively small changes in \bar{R}° , in either direction depending upon the substituents involved. In the case of the substituted hetero-aromatics, where an atom or group other than aromatic carbon forms part of the aromatic ring, we shall see that the preceding two effects can each significantly effect solute adsorption energy.

Consider first the classification scheme of Table IV. Here, a nitrogen atom which is part of an aromatic ring is shown in increasingly crowded configurations. Hydrogen atoms, which contribute substantially less than heavier elements to intramolecular crowding, are not considered in the structures of Table IV. In Part II data were presented which show that the introduction of alkyl groups in the *ortho* positions of a nitrogen bearing ring results in a substantial reduction in solute adsorption energy, particularly when the "normal" effect of alkyl (*meta* and *para* substituents increase \bar{R}°) is considered. The two curves of Fig. 3 demonstrate that a constant Q°_i may be

TABLE X

EXPERIMENTAL AND CALCULATED RETENTION VOLUME DATA FOR VARIOUS AZA-AROMATICS
3.7% $H_2O-Al_2O_3$

Aza-aromatic	Log \bar{R}°									
	CCl_4		Benzene		CH_2Cl_2		Ethyl acetate		Dioxane	
	Exptl.	Calc. ^a	Exptl.	Calc. ^a	Exptl.	Calc. ^a	Exptl.	Calc. ^a	Exptl.	Calc. ^a
Pyridine	1.53	1.59			0.65	0.65	0.01	—0.06		
Quinoline	1.33	1.36	0.73	0.64	0.33	0.11	—0.6	—0.8		
Isoquinoline	1.76	1.94	1.27	1.23						
Phenanthridine	1.50	1.67	0.83	0.76						
β -Naphthoquinoline	1.51	1.67								
Acridine	1.37	1.53	0.78	0.62						
7,8-Benzoquinoline	0.72	0.72								
1-Azapyrene	1.61	1.77	0.69	0.77						
3,4-Benzacridine	0.72	0.77	—0.30	—0.33						
Pyrrole	1.41 ^b	1.41								
Indole	1.61	1.42								
Carbazole			0.57	0.76						
α,α -Dipyridyl					0.46	0.46				
7-Azaindole									0.52	0.52
1-Azacarbazole									0.30	0.30
2-Aminopyridine									0.45	0.57
6-Bromoquinoline			0.42	0.47						
6-Chloroquinoline			0.45	0.40						
6-Methoxyquinoline			0.96	1.00	0.44	0.35				
6-Nitroquinoline	1.79	1.71	0.72	0.76	0.02	0.07				
7-Methylquinoline			0.74	0.53						

^a Equation (2) and Q°_i values of Table IV.

^b Extrapolated from pentane.

ascribed to nitrogen in a given configuration as defined in Table IV, but that Q°_i (when this includes a geometry factor q°_j) varies with configuration. In Table X, a number of retention volume data are presented for the aza-aromatics. Application of eqn. (2) to the data for the unsubstituted aza-aromatics permits the derivation of Q°_i factors for each nitrogen configuration. As in Part II we differentiate here between basic and non-basic nitrogen atoms. These derived Q°_i values ($Q^{\circ}_i + q^{\circ}_j$) are listed in Table IV under the columns "X = CH =". The non-basic nitrogen values are based on the more extensive data of Part II (Table V), as well as the values of Table X. Table IV also includes Q°_i values for the *ortho* alkyl substituted aza-aromatics, derived from the experimental data of Part II. These latter values assume that all alkyl substituents on a nitrogen bearing ring increase solute adsorption energy through interaction through the ring by a constant amount (q°_j equal + 0.5). Thus, a methyl substituent in either the 3 or 4 position of pyridine increases \underline{R}° by an amount $q^{\circ}_j = +0.5$. CHARTON⁶ has shown that the purely electronic effect of a substituent on a benzene ring is comparable at the *ortho* and *para* positions. By analogy, the non-steric effect of *ortho*- and *para*-alkylpyridine on the nitrogen adsorption energy should be comparable. Finally, Table IV includes data for the aza-aromatics where one of the atoms X is another nitrogen. In this connection, it is assumed that the compound α,α -dipyridyl assumes the configuration indicated in Table IV on adsorption; we shall comment on this further in the following section.

The Q°_i values of Table IV fall in distinct ranges for all nitrogen atoms in a similar configuration, while the average values for each configuration steadily decrease with increasing crowding of the nitrogen atom. When eqn. (2) and the Q°_i values of Table IV are used to calculate $\log \underline{R}^{\circ}$ values for the data of Table X and those reported in Part II (Table V) for the unsubstituted aza-aromatics, reasonable agreement with experimental values is found (average deviation ± 0.14).

The combined effect of the electronic and steric interaction of an alkyl group with the nitrogen atom in the substituted quinolines and pyridines is such as to produce the following separation order in the mono-alkyl derivatives:



It is interesting to note that the same sequence holds in the gas-liquid chromatographic separation of isomeric alkyl pyridines and quinolines^{7,8}. Similarly, isoquinoline is more strongly held in the stationary phase than is quinoline⁸. Presumably the same factors that determine the energy of adsorption of a basic nitrogen atom also control its interaction with other molecules in the solution phase.

Retention volume data are given in Table X for quinolines substituted in the non-nitrogen ring. The values of $\log \underline{R}^{\circ}$ for these solutes can be calculated by means of eqn. (2), assuming a Type II configuration for these solutes. Comparison of these values with experimental ones permits the derivation of corresponding $\Delta \log \underline{R}^{\circ}$ values as previously. It is found that $\Delta \log \underline{R}^{\circ}$ parallels the HAMMETT sigma values⁴ of the substituents involved. In this particular case any resonance interaction between the nitrogen and a substituent on the other ring should have its greatest effect on the adsorption energy of the nitrogen, since Q°_i for nitrogen is considerably larger than for the substituents represented in Table X. The resulting gain or loss in solute adsorption energy would be expected to follow the HAMMETT relationship, if correct

values of the substituent constant σ are ascribed to the various substituents. In the absence of values for the 5, 6, or 7 positions of adsorbed quinoline, we assume the simple *average* of values for *meta* and *para* substituents $\bar{\sigma}$. The HAMMETT relationship in the present instance then takes the form

$$\Delta \log \underline{R}^{\circ} = \rho \bar{\sigma}. \quad (4)$$

Equation (4) is tested in Fig. 5, and it is seen to account reasonably well for the observed discrepancies. The observed value of ρ in eqn. (4) is $+0.59$, and therefore ρ°_j equals $+0.90 \bar{\sigma}$. The positive sign of ρ indicates that electron donating groups increase

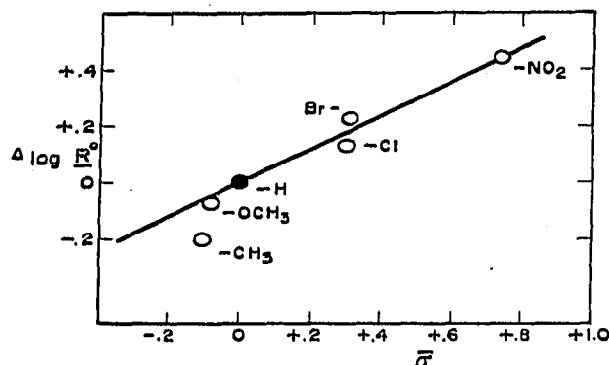


Fig. 5. $\Delta \log \underline{R}^{\circ}$ in 6- and 7-substituted quinolines *versus* HAMMETT "average" sigma function, $\bar{\sigma}$.

the adsorption energy of the nitrogen atom, and since values of Q°_t parallel the electron density of various substituents, this is theoretically reasonable. The use of eqns. (2) and (4) for the substituted quinolines of Table X furnishes calculated values which are in close agreement with those observed (average deviation ± 0.07).

THE FUNDAMENTAL LEAC EQUATION AND OBSERVATIONS ON THE ADSORBED STATE

Almost four hundred individual values of $\log \underline{R}^{\circ}$ have been reported in the present and preceding papers. These include data on the elution of over two hundred separate solutes, by thirty-five different pure or binary eluents, from alumina ranging in activity from calcined material to that which has had 5% water added to it. Equation (2) is capable of calculating all of these data with an average deviation of about ± 0.1 , when all of the various parameters are included. The accuracy on the 95% confidence level is about ± 0.3 , or in general it can be expected that \underline{R}° will be calculable within a factor of two in those cases where all the parameter values of eqn. (2) are known.

In Part III it was shown that certain information on the configuration of the adsorbed solute can be inferred from the study of the variation of solute retention volume with eluent strength. Specifically, it is possible to specify what fraction of the total solute is adsorbed in those cases where this is not known *a priori*. It will now be shown that a similar analysis of adsorbate configuration is possible by application of eqn. (2) to a single retention volume value. The proposed technique assumes that eqn. (2) can furnish accurate values of \underline{R}° for various potential adsorbate configurations. Comparison of these values with that experimentally observed then permits the selection of the actual configuration of the adsorbate. The following examples suggest the potential usefulness of the method.

First, consider the question of the size of a region on the adsorbent surface where adsorption may occur. As long as eqn. (2) correctly calculates $\log \bar{R}^\circ$ for a solute, no matter how large, it may be inferred that all of the solute is accommodated on the adsorbent surface. In Table XI data are presented on the elution of some large aromatic hydrocarbons from 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by two different eluents. The calculated values are seen to be in good agreement with those observed (average deviation ± 0.08), particularly when it is recalled that no geometry factors are invoked. It may be concluded that solutes at least as large as benzocoronene (diameter $\sim 10 \text{ \AA}$) "fit" onto the adsorbent surface, and that the average adsorption region is at least this large. It is worth noting in this connection that the presence of smaller adsorption regions

TABLE XI
RETENTION VOLUMES OF LARGE AROMATIC HYDROCARBONS

Solute	$\log \bar{R}^\circ$			
	CCl_4		Benzene	
	Exptl.	Calc. ^a	Exptl.	Calc. ^a
3,4-Benzopyrene	0.62	0.71	-0.52	-0.47
Picene	1.18	1.00	-0.30	-0.28
Coronene	1.22	1.28	-0.13	-0.08
1,2-Benzocoronene	1.73	1.85	0.24	0.31

^a Equation (2).

than suffice for the total adsorption of molecules of a certain size would produce effects similar to those we have ascribed to localization. However, the data of Table XI in conjunction with the lack of dependence of \bar{R}° on substitution position in poly-substituted benzenes appear to exclude this explanation of the deviations of experimental data from eqn. (1).

Second, consider the two solutes di-(2-nitrophenyl) disulfide (B) and di-(2,4-dinitrophenyl) disulfide (C) previously discussed in Part III. On the basis of eluent variation studies, it was concluded that these two solutes are only half adsorbed in eluents as strong as methylene chloride. That is, one-half of the molecule lies in the adsorbed phase and the other half in solution. The experimental values of $\log \bar{R}^\circ$ for B and C are -0.64 and -0.24, respectively, for elution from 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by methylene chloride. It is assumed that the sulfur atoms in these disulfides have values Q°_i equal to that of the group (Ar)-SR, and if it is further assumed that the two sulfur atoms between the two rings of each solute are similar to an alkyl bridge ($x = 2$), then values of $\log \bar{R}^\circ$ can be calculated by means of eqn. (2) for the adsorbed and half adsorbed configurations of each molecule. These are found to be -0.80 and -0.23, respectively, for B and C half adsorbed, and +0.29 and +0.22 for the completely adsorbed solutes. The half adsorbed configuration predicted by eluent variation studies is thus supported by the use of eqn. (2). The severity of the two approximations which enter into this calculation largely destroy the rigor of the demonstration, but the logic of the argument furnishes a useful example of the possibilities in this direction.

Third, consider the adsorption of the solute α,α -dipyridyl. Two configurations of the adsorbed molecule are possible, one in which the planar molecule has the two

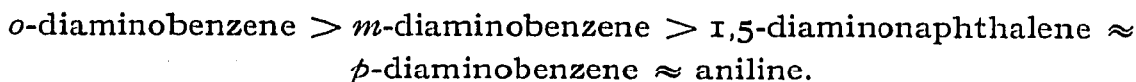
nitrogen atoms on the same side of the longitudinal axis of symmetry, and the other where the nitrogens do not oppose each other. In either case, both nitrogen atoms have identical configurations and a value of Q°_i for each nitrogen in dipyriddy can be calculated, equal to 2.62; this is accomplished by a trial and error procedure, and includes the effect of localization. The nitrogen atom in 7,8-benzoquinoline has a configuration identical to that of each nitrogen in adsorbed dipyriddy with nitrogen atoms lying on opposite sides of the long axis. Q°_i for the nitrogen in 7,8-benzoquinoline is equal to 2.06, which is substantially different than that observed for dipyriddy. A tentative conclusion on the configuration of adsorbed dipyriddy is therefore that the nitrogens are opposed. This tentative conclusion is strengthened by the expectation that Q°_i for opposed nitrogens would be larger than for those opposite a $-\text{CH}=\text{group}$, since the hydrogen atom in the latter configuration should provide increased steric interference to adsorption of the nitrogen atom. A final judgment on this point, however, would require the measurement of Q°_i for each nitrogen in a solute such as 9,10-phenanthroline, where nitrogens are identical in configurations to those of dipyriddy with nitrogens opposed. If Q°_i for each nitrogen in 9,10-phenanthroline was found to be significantly closer to 2.62 than is 2.06, the above observation on the adsorbed configuration of dipyriddy would be strengthened.

In a final commentary upon the usefulness of eqn. (2) in providing insight into the nature of the adsorbed state, we note that GILES AND MCKAY⁹ have studied the equilibrium uptake of condensed aromatic hydrocarbons by alumina from various solvents. On the basis of the experimental S-shaped isotherms obtained, these authors conclude that the condensed aromatics are adsorbed in clusters, with their edges adjacent to the adsorbent surface. The authors further suggest that this supports BASU'S¹⁰ molecular complex mechanism for the adsorption of aromatics on alumina. The totality of our data clearly contradict this postulate *in the chromatographic systems investigated by us*. The ability of eqn. (2) to correlate a wide range of solute R° values supports our original assumption that the total molecule is involved in formation of adsorbate-adsorbent bonds. Rather than simple charge transfer as implied in the molecular complex mechanism, bonds of comparable strength appear to exist between every adsorbate group and the adsorbent surface.

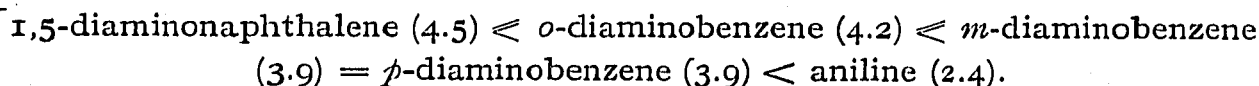
In the experimental systems studied by GILES AND MCKAY, more highly calcined adsorbent samples were used, and essentially all of the measured isotherm region is assumed to be outside of the linear region where our measurements are made. It therefore seems likely that the two chromatographic systems, theirs and ours, may not be comparable. Some support is given to this possibility by our previous observations¹¹ on the adsorption of tetramethylbenzene by calcined alumina from *n*-pentane. In this case, the isotherm observed is *not* S-shaped. Also of significance in the comparison of the two studies is the fact that close to the theoretical monolayer of tetramethylbenzene is taken up at saturation by our adsorbent, while GILES AND MCKAY note that under similar circumstances only a small fraction of the available surface of their adsorbent is covered by aromatic solutes.

Similarly, KLEMM¹² has suggested that a number of the aza-aromatics are adsorbed as the "*n*-complex", with an edgewise or tilted configuration of the adsorbate. As discussed in the preceding paper of this series², eluent variation studies appear to rule out an edgewise adsorption mechanism, but cannot test the *moderate* tilting of the adsorbate. At first glance, it might appear that a slightly tilted *n*-complex involving

a strongly adsorbing group k is capable of providing a rationalization of the adsorption effects we have ascribed to localization. Indeed, our data do not rule out a very modest tilting or similar adaptation of the adsorbate configuration so as to permit localization of a group k . However, the tilting of such molecules cannot be used *per se* to predict most of the adsorption effects which *are* explained by the localization hypothesis. Thus, in the aminobenzenes, significant tilting of the adsorbate so as to direct the amino group(s) toward a particular adsorbent site(s) — n -complex formation — would lead to the following adsorption order:



The actual adsorption sequence, which is accurately predicted by the assumption of localization, is as follows (values of $\log \bar{R}^{\circ}_p$ in parentheses):



Other examples of this sort are readily apparent from an examination of our localization correlation of experimental data presented in the present and preceding papers.

A forthcoming communication from this laboratory will offer a more detailed description of the nature of the adsorbed state in our chromatographic system. It will be shown that LEAC measurements are capable of evaluating the suggestion of KLEMM that the aza-aromatics are adsorbed as the n -complex, as well as that of KLEMM and other workers that the aromatic hydrocarbons are adsorbed as the π -complex.

GLOSSARY OF TERMS

$f(Q^{\circ}_k)$	localization function for anchoring group k
q°_a	fraction of Q°_i due to activation of nucleus; $q^{\circ}_a = Q^{\circ}_i - \underline{Q}^{\circ}_i$.
q°_j	solite geometry parameter
Q°_i	solite substituent adsorption parameter
\underline{Q}°_i	fraction of Q°_i due to adsorption energy of group i
\bar{R}°	linear equivalent retention volume; ml/g
\bar{R}°_p	\bar{R}° for n -pentane eluent
V_a	volume of adsorbent monolayer; ml/g
x	number of methylene groups separating the terminal substituents of a disubstituted alkane
X, Y, Z	substituent groups of various types
α	adsorbent activity function
δ_i	substituent surface volume
$\Delta \log \bar{R}^{\circ}$	difference in calculated and experimental values of $\log \bar{R}^{\circ}$
ε°	eluent strength parameter
$\sum_{i \neq k} Q^{\circ}_i$	summation of Q°_i values for all solite substituents except k , and in the case of ring substituted aromatics, six aromatic carbon atoms
$\bar{\sigma}$	average of HAMMETT sigma values for <i>meta</i> and <i>para</i> benzene substituents

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SUMMARY

Strongly adsorbed solute groups tend to localize, or attach to specific sites on the surface of alumina. When this occurs, the adsorption energies of other solute groups are decreased in proportion to the adsorption energy of the localizing group. The preceding treatment of the role of solute structure in determining retention volume has been amplified to correct for this effect. In addition to localization, steric or electronic interaction between substituents on fused ring systems and strongly adsorbed atoms which are part of that ring system can significantly affect solute adsorption energy and retention volume. The interaction of two substituents on an aromatic ring is less important in affecting solute R^o values. A number of group adsorption factors have been measured, and retention volumes can now be calculated for many solutes in most chromatographic systems which use alumina. The configuration of solutes adsorbed on alumina has been briefly discussed in terms of the present treatment.

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