LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

XI. SEPARABILITY OF AROMATIC ISOMERS ON ALUMINA. MECHANISMS OF ADSORPTION

L. R. SNYDER

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

(Received June 2nd, 1965)

INTRODUCTION

Previous papers in this series[1-6] and elsewhere[7-11] have provided a fairly detailed description of the major factors which influence the relative adsorption of different solutes on alumina under linear isotherm conditions (linear elution adsorption chromatography; LEAC): adsorbent activity[1,8,10], eluent type[2,5,10,11], solute molecular structure[1,3-10], and column temperature[10]. Those secondary factors which determine differences in the relative adsorption of solute isomers have also received considerable attention. The relative separation of *ortho versus* non-*ortho* aromatic isomers has been reported[1,3,6,8,9,12] and interpreted in terms of various physical effects, including restricted internal rotation, simultaneous interaction (chelation) of two strong solute groups with the same adsorbent site, intramolecular hydrogen bonding of *ortho* solute groups, interference of one solute group to the adsorption of another, etc. The separability of various planar aromatic hydrocarbon isomers has been studied and correlated with solute molecular dimensions[7]. The relative adsorption of different hydrocarbon and nitrogen compound stereoisomers has been discussed[6,8], and shown to depend upon the ease of attaining solute planarity, as well as other factors. The separability of various non-*ortho* substituted heteroaromatics has been examined[3,5,6,9], and differences in adsorption correlated with intramolecular electronic effects.

The present communication describes the further study of those factors which determine the relative separation of isomeric aromatic solutes. It began with a re-examination of certain anomalies in the adsorption on alumina of various isomers of the halogen substituted aromatic hydrocarbons; it had been observed earlier[1] that the *meta* dihalobenzenes, the trihalobenzenes, and 1-halonaphthalenes are all adsorbed less strongly than predicted. In the course of confirming and expanding the original, rather limited data on which these observations were based, it became apparent that these anomalies in the adsorption of the haloaromatics are fundamentally related to the differences in adsorption of fused aromatic hydrocarbon isomers[7,8]. This in turn led to a general examination of the factors which determine the separation of a large class of aromatic isomers on alumina. Also, the present investigation provided additional insight into the general mechanism of adsorption on alumina,

as well as further verification of earlier theories on the role of adsorbent activity in separations over alumina.

EXPERIMENTAL

Linear equivalent retention volumes $\underline{R}^\circ$ (ml/g) were determined as before[2]. Since we were concerned in several cases with the accurate measurement of small differences in the retention volumes of isomers, additional precautions were taken. Where possible the two isomers were run simultaneously on the same column. The linear capacity of the various adsorbents used ranged from 10^{-5} g/g (0.7 % H_2O–Al_2O_3) to 2.10^{-4} g/g (3.7 % H_2O–Al_2O_3). The maximum column loading never exceeded half the linear capacity and was generally lower. In separations of a group of isomers the sample/adsorbent weight ratio for each isomer was maintained constant, at a given adsorbent activity. The adsorbent activities (Alcoa F-20) reported here are based on the most recent standardization scale (Table I, ref. 5), *viz.* the elution of naphthalene with pentane: 0.7 % H_2O–Al_2O_3, 23.2 ml/g; 1.7 % H_2O–Al_2O_3, 11.2 ml/g; 2.7 % H_2O–Al_2O_3, 4.1 ml/g; 3.7 % H_2O–Al_2O_3, 1.8 ml/g. In using dilute binary solutions (0.5–5 %) of very strong eluents, the columns were first pre-equilibrated with the strong eluent by charging 0.2 ml/g of the pure strong eluent and washing it from the column with the binary eluent in question.

DISCUSSION

The purpose of this section is to provide a practical summary of the results of following sections, where the principal factors which influence the separation of various aromatic isomers on alumina are examined in detail, and where the effect of adsorbent activity on isomer and other separations is discussed. It has been found in the present study that several classes of aromatic isomers may be defined with respect to the preferential adsorption of a solute as a function of molecular structure, adsorbent activity, and eluent type. First (class I), there are the aromatic hydrocarbons, their non-*ortho* halogen-substituted derivatives, and certain related heteroaromatics such as the benzcarbazoles. These compounds all show preferential adsorption of the most "linear" molecule; *e.g.* anthracene more strongly adsorbed than phenanthrene, *p*-dichlorobenzene more strongly adsorbed than *m*-dichlorobenzene, 2-bromonaphthalene more strongly adsorbed than 1-bromonaphthalene, 4-iodobiphenyl more strongly adsorbed than 3-iodobiphenyl, 2,3-benzcarbazole more strongly adsorbed than 3,4-benzcarbazole. While the relative separation of all isomers (*i.e.* difference in their retention volumes) decreases somewhat as adsorbent activity is lowered, the relative separation of class I isomers is much more strongly dependent upon adsorbent activity. This is illustrated in Fig. 1, where several adsorbent functions ($\alpha, \alpha_i, \theta_{0.1}$) are plotted *versus* alumina–water content. The function α describes the normal dependence of solute adsorption energy on adsorbent activity or water content, and is seen to decrease by a factor of about $1/3$ as the alumina–water content increases from 0 to 4 %. The function α_i describes the dependence on alumina–water content of the adsorption energy *difference* between class I isomers. α_i is seen to decrease by over 90 % in going from 0 to 4 % H_2O–Al_2O_3. As a practical consequence, class I isomers are generally well separated on 1–2 % H_2O–Al_2O_3, but are separated only poorly (if at all) on

3.5–5 % H_2O–Al_2O_3. Varying the eluent in the separation of isomers normally has little effect upon their relative separation; that is, the ratios of isomer retention volumes are normally constant for all eluents. In the case of class I isomers, however, there is a strong dependence of their relative separation on eluent type. Thus, the weak eluents such as pentane and cyclohexane maximize differences in class I isomer
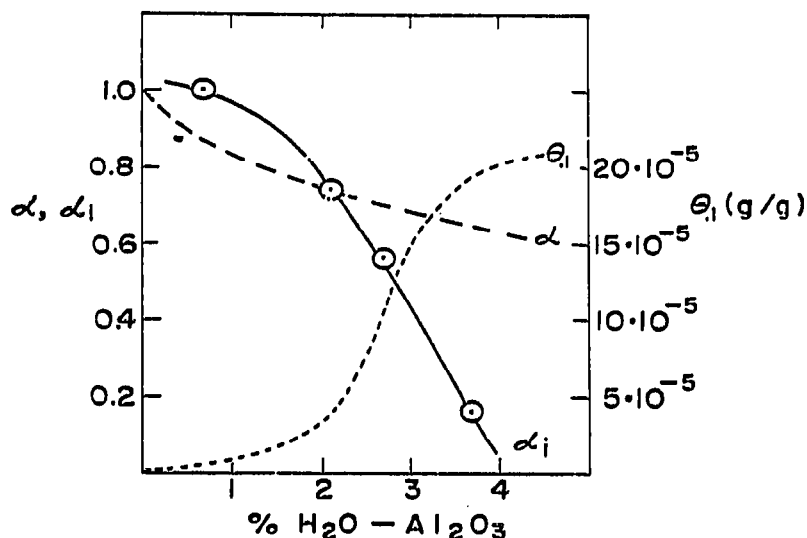

Fig. 1. Variation of adsorbent activity functions α and α_i and linear capacity $\theta_{.1}$ with % H_2O–Al_2O_3.

separations. Similarly, eluents of intermediate strength ($\varepsilon° < 0.5$), or their solutions with weak eluents, show intermediate separation of isomers, while strong eluents ($\varepsilon° > 0.5$) and their solutions with weaker eluents show little or no separation of isomers. For example, consider the relative separation of anthracene from phenanthrene under different chromatographic conditions. The relative separation may be defined as the ratio of retention volumes of anthracene to phenanthrene, χ. For elution of these two isomers from 0.7 % H_2O–Al_2O_3 by 10 % v CH_2Cl_2–pentane, χ is equal to 4.3, while for elution from 3.7 % H_2O–Al_2O_3 by the same eluent, χ is equal to 1.1. That is, separation is quite good in the former case, involving an active adsorbent, but very poor in the latter case. For elution of this same pair of isomers from 2.7 % H_2O–Al_2O_3 by the weak eluent cyclohexane, χ is equal to 2.8; for elution from the same adsorbent by the eluent CCl_4 (intermediate strength), χ is equal to 1.5; for elution from the same adsorbent by a 1 % v solution in pentane of the strong eluent pyridine, χ is equal to 1.05. That is, the relative separation of the two isomers varies from essentially complete to essentially nil, as the strength of the eluent (or of the strongest eluent) constituent varies from weak to strong.

Inasmuch as the separation of class I isomers is a marked function of adsorbent activity, the question arises as to what adsorbent activity is generally optimum in such separations. There are two factors of primary importance in this connection: the relative separation of the isomers, which is proportional to the adsorbent function α_i (Fig. 1), and the linear capacity $\theta_{.1}$ of the adsorbent (also plotted versus adsorbent water content in Fig. 1). For optimum separation under linear isotherm conditions, it is desirable to maximize both α_i and $\theta_{.1}$. Since α_i decreases and $\theta_{.1}$ increases with increasing adsorbent water content, some compromise is necessary in attempting to

maximize each of these quantities. From Fig. 1 it is seen that 2.5-3 % $H_2O-Al_2O_3$ gives reasonable values for both linear capacity (10^{-4} g/g, about half that of fully deactivated adsorbent) and α_t (0.5, about half the value for calcined adsorbent). Adsorbent of this intermediate activity therefore appears near optimum for the separation of isomers in general, and the class I compounds in particular.

The separation and analysis of mixtures of the aromatic hydrocarbons has been a subject of recurring interest (e.g. ref. 13) because of the physiological importance of this group of compounds. Attempts at their separation have been largely confined to adsorption chromatography on alumina, either in columns or plates. On the basis of the preceding discussion, the following general scheme should provide near-ultimate separation of the aromatic hydrocarbons on alumina: two-dimensional chromatography on plates containing 2.5-3 % $H_2O-Al_2O_3$, using a strong eluent solution (e.g. acetone–pentane) in the first development, and an intermediate strength eluent solution (e.g. CH_2Cl_2–pentane) in the second development. This procedure would provide separation according to the number of aromatic carbon atoms in the first development, and then separation of each resulting group of isomers according to shape (i.e. linearity) in the second development. In this way all of the separation potential of the adsorbent would be used without remixing any bands that have once been separated.

A second class of isomers (class II) discussed in following sections are the so-called "ortho" aromatics, i.e. aromatic hydrocarbons substituted by a strongly adsorbing group X with is ortho to some other solute group Y which sterically alters the adsorption of X. For non-adsorbing groups Y (class II a) such as the methyl group in o-nitrotoluene or the 8-hydrogen in 1-methoxynaphthalene, such sterically hindered, ortho isomers are less strongly adsorbed than non-ortho isomers. Thus, o-nitrotoluene is less strongly adsorbed than p-nitrotoluene, and 1-methoxynaphthalene is less strongly adsorbed than 2-methoxynaphthalene. The difference in adsorption of the two isomers, ortho versus non-ortho (that is, their separation), increases proportionately with the adsorption energy or $Q°_i$ value of the group X and with the size of group Y. The difference in adsorption between class II a isomers does not vary much with adsorbent activity or eluent type, in contrast to the behavior of class I isomers. One exception to the rule of decreasing adsorption in the sterically hindered isomer is found in mildly hindered, acidic solutes such as the pyrrole derivatives. Here, moderate hindrance of the group X by an adjacent group Y increases adsorption, as discussed earlier[9].

Among the ortho aromatics, those solutes where the ortho group Y is moderately strongly adsorbing (class II b) generally show a reversal of isomer separation, i.e. ortho isomers of this type are more strongly adsorbed than non-ortho isomers. Thus, o-dimethoxybenzene is more strongly adsorbed than m- or p-dimethoxybenzene, o-fluoroanisole is more strongly adsorbing than p-fluoroanisole, etc. In the polysubstituted halo benzenes, a combination of effects is found. Thus, as in other class I isomers (aromatic hydrocarbons, haloaromatics, etc.) the linear para dihalobenzenes are more strongly adsorbed than meta isomers. The ortho dihalobenzenes (class II a), on the other hand, are more strongly adsorbed than meta isomers, and are adsorbed about as strongly as the para isomers.

A third and final class of isomers (class III) considered in following sections are the non-ortho disubstituted benzenes, higher aromatics (e.g. naphthalene) and hetero-

aromatics (*e.g.* pyridine), which have at least one strongly adsorbing substituent X plus a second substituent Y capable of electronically activating X. In general it is found that class III isomers are most strongly adsorbed where Y confers a maximum negative charge on X (Y is strongly electron donating), or a minimum positive charge. Thus, a *para*-methoxyl group confers a negative charge upon a 1- substituent, and a *meta*-methoxyl a positive charge; consequently, *p*-methyloxynitrobenzene is more strongly held than its *meta* isomer. Similarly, a *para* bromo substituent creates a small positive charge upon a 1- substituent, and a *meta* bromo substituent a larger positive charge; as a result, *p*-bromoacetophenone is more strongly adsorbed than *m*-bromoacetophenone. These electron activation effects have been extensively studied in previous papers[1,3,6,9], and do not appear to be much affected by the type of eluent used or the activity of the adsorbent. For the polysubstituted aromatic hydrocarbon isomers of class III, these separation effects are generally small and in some cases subordinated to other effects.

Despite the different classification (*i.e.* classes I, IIa, IIb, III) of these various isomer separation effects (which reflect fundamentally different adsorption mechanisms, and different responses to changes in adsorbent activity and eluent type), some rough, overall generalizations can be recognized. Thus, *para* isomers are usually more strongly adsorbed than *meta* isomers, and 2-substituted naphthalenes are generally more strongly adsorbed than 1-substituted naphthalenes.

SEPARABILITY OF ISOMERS OF THE UNSUBSTITUTED AND HALOGEN SUBSTITUTED AROMATIC HYDROCARBONS (CLASS I): CORRELATION WITH ADSORBENT ACTIVITY, ELUENT TYPE, AND SOLUTE STRUCTURE

Previous studies (*e.g.* ref. 10) of LEAC separation on alumina have resulted in a general correlational equation for the dependence of solute retention volume $\underline{R}^\circ$ (ml/g) on adsorbent activity, eluent type, and solute molecular structure:

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

V_a and α are the adsorbent surface volume and activity function, respectively, αS° is approximately the dimensionless net adsorption energy of the solute from pentane onto 4.0 % H_2O–Al_2O_3, ε° is the eluent strength parameter, and A_s is the relative area required by the solute upon adsorption. The term $\Sigma \Delta_{eas}$ represents the sum of second order solute–eluent–adsorbent interaction effects, similar to the term $\alpha \Delta_{eas}$ defined in part IX (5). The $\alpha \Delta_{es}$ term was previously included with the solute geometry term Σq°_j defined in Eqn. (2) below; however, with the discovery of important additional second order terms, we have now decided to distinguish between those terms which are functions only of the solute (q°_j) and those which are functions of eluent and/or adsorbent as well ($\alpha \Delta_{es}$, Δ_{eas}). The solute adsorption energy S°, the extrapolated value of αS° for adsorption on calcined alumina ($\alpha = 1.00$), is in turn given by:

$$S^\circ = \overset{i}{\Sigma} Q^\circ_i + \overset{j}{\Sigma} q^\circ_j - f(Q^\circ_k) \overset{i \neq k}{\Sigma} Q^\circ_i \tag{2}$$

Here, Q°_i refers to the adsorption energy per solute group i, q°_j refers to an effect of solute geometry on adsorption, and $f(Q^\circ_k)$ is the localization function of the

strongest adsorbing solute group k. The present study, which is concerned with the variation of isomer separation, is seen to involve adsorption phenomena which are described by the solute geometry term $\overset{j}{\Sigma} q°_j$ and by $\Sigma \Delta_{eas}$. As in previous studies, we can measure these isomer or solute geometry factors by first calculating $\underline{R}°$ from Eqn. (1) and (2) without taking the solute geometry term into account (assume $\overset{i}{\Sigma} q°_j + \Sigma \Delta_{eas}$ equals zero), and then comparing calculated and experimental $\underline{R}°$ values. The combined solute geometry and $\Sigma \Delta_{eas}$ term Δ_i is then given as:

$$\Delta_i = \alpha \overset{j}{\Sigma} q°_j + \Sigma \Delta_{eas} = (\log \underline{R}°)_{\text{exptl.}} - (\log \underline{R}°)_{\text{calc.}} \tag{3}$$

The difference in isomer geometry factors Δ_{12}, equal $[(\Delta_i)_1 - (\Delta_i)_2]$, can be calculated directly from the $\underline{R}°$ values of the two isomers 1 and 2 (R_1 and R_2, respectively) without recourse to Eqns. (1) and (2):

$$\Delta_{12} = \log R_1 - \log R_2 \tag{4}$$

In the present study values of Δ_i were calculated from Eqn. (3) where it was convenient or necessary; otherwise values of Δ_{12} were employed in the interpretation of isomer effects. The calculation of Δ_i values for the substituted aromatics, as in the present study, is most accurate if the $\underline{R}°$ value of the unsubstituted aromatic is also measured under identical experimental conditions (same adsorbent activity, same eluent), and used to evaluate $S°$ in Eqn. (1). This is equivalent to the use of relative retention volumes as discussed previously [1], and was used exclusively in the present calculations of Δ_i values.

Tables I and II summarize retention volume data for a total of 42 halogen substituted benzenes and 23 halogen substituted higher aromatics. $\underline{R}°$ values for 18 of these compounds have been reported previously[1] for a slightly less active alumina (1.1 % H_2O-Al_2O_3, equivalent to 0.5 % H_2O-Al_2O_3 on old adsorbent activity scale; see refs. 5 and 10). Adjusting for the difference in adsorbent activity between the data of Tables I and II and ref. (1) by means of Eqn. (1), the present and previously reported log $\underline{R}°$ values for the halogen substituted aromatics agree within ± 0.04 log units (standard deviation), with the exception of the value previously reported for p-dibromobenzene (which now appears to have been erroneously low). It is seen, as observed previously[1], that many of these haloaromatics have anomalously low $\underline{R}°$ values; that is, the calculated values of Δ_i are negative rather than zero. The various Δ_i values appear to correlate quite closely with the substitution pattern on the aromatic hydrocarbon nucleus, as noted earlier[1]: for the disubstituted benzenes of Table I the average values of Δ_i with their standard deviations (S.D.) are, respectively:

ortho   0.00 $\pm$ 0.04 (S.D.)
meta   —0.21 $\pm$ 0.04 (S.D.)
para   —0.01 $\pm$ 0.03 (S.D.)

Similarly, for the polysubstituted benzenes and monosubstituted naphthalenes

TABLE I

RETENTION VOLUMES OF HALOGEN SUBSTITUTED BENZENES
Eluent: n-pentane; adsorbent: 0.7 % H_2O–Al_2O_3.

Solute	Log R_p*		Δ_i
	Exptl.	Calc.**	
Benzene	0.16	—	—
Fluorobenzene	0.28	—	—
Chlorobenzene	0.35	—	—
Bromobenzene	0.51	—	—
Iodobenzene	0.70	—	—
o-Difluorobenzene	0.33	0.40	—0.07
m-Difluorobenzene	0.20	0.40	—0.20
p-Difluorobenzene	0.37	0.40	—0.03
o-Fluorochlorobenzene	0.42	0.47	—0.05
m-Fluorochlorobenzene	0.30	0.47	—0.17
p-Fluorochlorobenzene	0.48	0.47	0.01
o-Fluorobromobenzene	0.56	0.63	—0.07
m-Fluorobromobenzene	0.42	0.63	—0.21
p-Fluorobromobenzene	0.50	0.63	—0.13
o-Fluoroiodobenzene	0.85	0.82	0.03
m-Fluoroiodobenzene	0.66	0.82	—0.16
p-Fluoroiodobenzene	0.78	0.82	—0.04
o-Dichlorobenzene	0.54	0.54	0.00
m-Dichlorobenzene	0.37	0.54	—0.17
p-Dichlorobenzene	0.52	0.54	—0.02
o-Chlorobromobenzene	0.66	0.70	—0.04
m-Chlorobromobenzene	0.47	0.70	—0.23
p-Chlorobromobenzene	0.65	0.70	—0.05
o-Chloroiodobenzene	0.91	0.89	0.02
m-Chloroiodobenzene	0.69	0.89	—0.20
p-Chloroiodobenzene	0.90	0.89	0.01
o-Dibromobenzene	0.79	0.86	—0.07
m-Dibromobenzene	0.58	0.86	—0.28
p-Dibromobenzene	0.84	0.86	—0.02
o-Bromoiodobenzene	1.07	1.05	0.02
m-Bromoiodobenzene	0.81	1.05	—0.24
p-Bromoiodobenzene	1.05	1.05	0.00
o-Diiodobenzene	1.26	1.24	0.02
m-Diiodobenzene	0.97	1.24	—0.27
p-Diiodobenzene	1.30	1.24	0.06
1,2,3-Trichlorobenzene	0.53	0.73	—0.20
1,2,4-Trichlorobenzene	0.43	0.73	—0.30
1,2,4,5-Tetrachlorobenzene	0.28	0.92	—0.64
Hexachlorobenzene	0.37	1.30	—0.93
1,2-Dichloro-4-bromobenzene	0.57	0.89	—0.32
1,2-Dichloro-4-iodobenzene	0.83	1.08	—0.25
1,3,5-Tribromobenzene	0.36	1.21	—0.85
1,2,4,5-Tetrabromobenzene	0.86	1.56	—0.69

* Value of R° for pentane eluent.
** Eqns. (1–2).

TABLE II

RETENTION VOLUMES OF HALOGEN SUBSTITUTED POLYAROMATIC HYDROCARBONS; 0.7 % $H_2O-Al_2O_3$

Solute	Log $\underline{R}°$			Log $\underline{R}_p$		(Δ_t)	A_s
	P[a]	5%[b] M–P	10%[c] M–P	Exptl.	Calc.[d]		
Naphthalene	1.39			—	—		
1-Fluoronaphthalene	1.13			1.51	—0.38[e]		
2-Fluoronaphthalene	1.50			1.51	—0.01[c]		
1-Chloronaphthalene	1.25			1.58	—0.33[c]		
2-Chloronaphthalene	1.72	0.49	0.16	1.58	0.14[c]		
1-Bromonaphthalene	1.40	0.23	0.02	1.74	—0.34[c]		
2-Bromonaphthalene	1.83			1.74	0.09[c]		
1-Iodonaphthalene	1.56			1.93	—0.39[e]		
1,4-Dibromonaphthalene	1.31			2.09	—0.78[c]		
Biphenyl			0.15	1.71	—	—	9.6
4-Fluorobiphenyl			0.21	1.81	1.83	—0.02[f]	9.8
3-Chlorobiphenyl			0.10	1.80	1.90	—0.10[f]	10.4
4-Chlorobiphenyl			0.42	2.12	1.90	0.22[f]	10.4
3-Bromobiphenyl			0.05	1.79	2.06	—0.27[f]	10.7
4-Bromobiphenyl			0.58	2.32	2.06	0.26[f]	10.7
4-Iodobiphenyl			0.76	2.52	2.25	0.27[f]	10.8
3,3'-Difluorobiphenyl			0.07	1.70	1.95	—0.25[f]	10.0
4,4'-Difluorobiphenyl			0.22	1.85	1.95	—0.10[f]	10.0
3,3'-Dichlorobiphenyl			—0.08	1.75	2.09	—0.34[f]	11.2
4,4'-Dichlorobiphenyl			0.74	2.57	2.09	0.48[f]	11.2
4,4'-Dibromobiphenyl			1.11	3.03	2.41	0.62[f]	11.8
4,4'-Diiodobiphenyl			1.56	3.52	2.79	0.73[f]	12.0
Phenanthrene			0.88	2.51	—	—	
9-Bromophenanthrene	1.28		0.78	2.65	2.86	—0.21[f]	
Anthracene			1.54	3.17	—	—	
9-Bromoanthracene	0.80		0.37	2.20	3.52	—1.32[f]	
9,10-Dichloroanthracene	0.60		0.16	2.07	3.55	—1.48[f]	
9-Methylanthracene			1.29	3.12	3.21		

[a] Pentane eluent.
[b] 5% v methylene chloride–pentane eluent ($\alpha\varepsilon° = 0.133$).
[c] 10% v methylene chloride–pentane eluent ($\alpha\varepsilon° = 0.163$).
[d] Eqn. (1), relative to unsubstituted hydrocarbon.
[e] Calculated from pentane data only.
[f] Values are for CH_2Cl_2 strong eluent.

of similar substitution pattern the average values of Δ_t and their standard deviations are, respectively:

1,2,4-(benzenes)   —0.29 ± 0.04 (S.D.)
1,2,4,5-(benzenes)   —0.66 ± 0.04 (S.D.)
1-(naphthalenes)   —0.36 ± 0.04 (S.D.)
2-(naphthalenes)   0.07 ± 0.08 (S.D.)

In the course of acquiring and interpreting the data of Tables I and II it became clear that certain similarities exist between the Δ_t and Δ_{12} values on alumina of the haloaromatics and of the unsubstituted aromatic hydrocarbons. Thus, with the exception of the *ortho* disubstituted benzenes (class II a), which are unique in permitting

steric interaction of the two halogens and which will be discussed in another section, there is invariably a tendency among these isomers for the preferential adsorption of the longer and narrower compound. This is evidenced in the stronger adsorption of the *para versus meta* dihalobenzenes, of 2- *versus* 1-halonaphthalenes, and of the 4- *versus* 3-halobiphenyls. Similarly, it has previously been shown[7] that there is a statistically significant correlation of aromatic hydrocarbon adsorption energy (on alumina) on the length and/or width of the molecule; long, narrow isomers (*e.g.* anthracene) are generally adsorbed more strongly than shorter, wider isomers (*e.g.* phenanthrene). As we shall shortly see, the similarity of isomer effects in these two series of compounds, the haloaromatics and the unsubstituted aromatics, is reaffirmed in a number of other "peculiarities" associated with these various Δ_i and Δ_{12} values.

Tables III–V summarize $\underline{R}°$ values for the isomer pairs anthracene/phenanthrene, chrysene/triphenylene, and picene/1,2,3,4-dibenzanthracene, using several

TABLE III

RELATIVE SEPARATION OF PHENANTHRENE FROM ANTHRACENE ON ALUMINA; VARIATION WITH ADSORBENT ACTIVITY AND ELUENT

Eluent	*Log $\underline{R}°$*		Δ_{12}		
	Anthracene (1)	*Phenanthrene (2)*	*Exptl.*	*Exptl. av.*	*Calc.**
0.7% H_2O–Al_2O_3					
25 % v benzene–pentane	0.87	0.60	0.27		
50% v benzene–pentane	0.37	0.15	0.22	0.24	0.34
Benzene	—0.29	—0.51	0.23		
CCl₄	1.40	1.11	0.29	0.29	0.48
10% v CH₂Cl₂–pentane	1.44	0.81	0.63		
25% v CH₂Cl₂–pentane	0.71	0.20	0.51	0.56	0.58
50% v CH₂Cl₂–pentane	0.01	—0.46	0.55		
50% v isopropyl chloride–pentane	1.50	0.79	0.71		
Isopropyl chloride	0.90	0.25	0.65	0.68	0.55
25% v ethyl ether–pentane	1.22	0.35	0.87		
50% v ethyl ether–pentane	0.72	0.09	0.63	0.70	0.53
Ethyl ether	0.17	—0.43	0.60		
2.7% H_2O–Al_2O_3					
1% v pyridine–pentane	0.25	0.23	0.02		—0.03
1% v acetone–pentane	0.32	0.19	0.13		0.10
10% v benzene–pentane	0.85	0.71	0.14		0.18
CCl₄	0.51	0.32	0.19		0.26
5% v phenetole–pentane	0.50	0.29	0.21		0.16
10% v CH₂Cl₂–pentane	0.62	0.38	0.24		0.31
25% v isopropyl chloride–pentane	0.96	0.59	0.37		0.29
Pentane	2.07	1.70	0.37		0.41
10% v ethyl ether–pentane	0.83	0.40	0.43		0.28
Cyclohexane	1.82	1.37	0.45		
3.7% H_2O–Al_2O_3					
25% v benzene–pentane	0.02	—0.04	0.06		0.06
CCl₄	—0.11	—0.13	0.02		0.08
10 % v CH₂Cl₂–pentane	0.16	0.11	0.05		0.10
10 % v isopropyl chloride–pentane	0.66	0.59	0.07		0.09
Pentane	1.18	1.11	0.07		0.13

* Eqn. (5).

TABLE IV

RELATIVE SEPARATION OF TRIPHENYLENE FROM CHRYSENE ON ALUMINA; VARIATION WITH ADSORBENT ACTIVITY AND ELUENT

Eluent	Log R°		Δ_{12}	
	Chrysene (1)	Triphenyl-ene (2)	Exptl.	Calc.*
0.7 % $H_2O-Al_2O_3$				
50 % v benzene–pentane	0.93	0.77	0.16	0.23
Ethyl ether	0.34	0.03	0.31	0.36
50 % v CH_2Cl_2–pentane	0.37	0.05	0.32	0.40
2.7 % $H_2O-Al_2O_3$				
25 % v benzene–pentane	1.17	1.08	0.09	0.13
CCl_4	1.04	0.92	0.12	0.18
25 % v ethyl ether–pentane	0.69	0.51	0.18	0.20
25 % v CH_2Cl_2–pentane	0.48	0.29	0.19	0.22
50 % v isopropyl chloride–pentane	0.90	0.71	0.19	0.20
3.7 % $H_2O-Al_2O_3$				
25 % v benzene–pentane	0.64	0.61	0.03	0.04
CCl_4	0.60	0.54	0.06	0.06
10 % v ethyl ether–pentane	0.64	0.58	0.06	0.06
10 % v CH_2Cl_2–pentane	0.79	0.71	0.08	0.07

* Eqn. (5).

TABLE V

RELATIVE SEPARATION OF PICENE FROM 1,2,3,4-DIBENZANTHRACENE ON ALUMINA; VARIATION WITH ADSORBENT ACTIVITY AND ELUENT

Eluent	Log R°		Δ_{12}	
	Picene (1)	1,2,3,4-dibenzanthra-cene (2)	Exptl.	Calc.*
0.7 % $H_2O-Al_2O_3$				
Benzene	1.34	0.44	0.90	0.80
Ethyl ether	1.51	0.50	1.11	1.23
CH_2Cl_2	1.08	—0.24	1.32	1.37
2.7 % $H_2O-Al_2O_3$				
5 % v pyridine–pentane	0.63	0.59	0.04	—0.07
10 % v acetone–pentane	0.19	0.01	0.18	0.23
25 % v phenetole–pentane	0.85	0.50	0.35	0.38
Benzene	0.40	—0.13	0.53	0.43
Isopropyl chloride	1.19	0.58	0.61	0.69
50 % v ethyl ether–pentane	1.05	0.42	0.63	0.66
25 % v CH_2Cl_2–pentane	1.53	0.82	0.71	0.74
3.7 % $H_2O-Al_2O_3$				
50 % v benzene–pentane	0.70	0.54	0.16	0.14
CCl_4	1.37	1.16	0.21	0.19
10 % v ethyl ether–pentane	0.77	0.54	0.23	0.21
25 % v CH_2Cl_2–pentane	0.62	0.35	0.27	0.23

* Eqn. (5).

different eluents and adsorbent activities. In all cases the longer of the two isomers is preferentially adsorbed, as previously noted[7]. A most interesting (and previously unreported) dependence of these hydrocarbon Δ_{12} values on eluent type can be observed in Tables III–V. In the adsorption of anthracene and phenanthrene on 0.7 % H_2O–Al_2O_3, for example, the Δ_{12} values vary by a factor of about three in going from eluents containing benzene to those containing ethyl ether. This effect is unrelated to the *strength* $\alpha\varepsilon°$ of the eluent mixture, as may be seen from the complete lack of dependence of Δ_{12} on $R°$ for either solute ($R°$ decreases with increasing $\alpha\varepsilon°$; see Eqn. 1). Rather, the dependence of Δ_{12} on eluent type appears to be associated with the nature of the strong eluent in the particular binary (or pure solvent) used. Thus, for concentrations of the strong eluent ranging from 10 to 100 % in a given eluent linary, the value of Δ_{12} (at a particular adsorbent activity) is relatively constant for a particular isomer pair. The weak eluent in the binary appears to play no part in determining Δ_{12}, as is further suggested by the data of Table III for 2.7 % H_2O–Al_2O_3: here, pentane as eluent gives one of the largest Δ_{12} values, while addition of only 1 % pyridine to the eluent reduces Δ_{12} to almost zero. This dependence of Δ_{12} on eluent composition parallels other eluent anomalies examined in a previous paper[5], where it was also found that eluent-related Δ_{12} values (*i.e.* $\alpha\Delta_{es}$ values) were determined largely by the nature of the strong eluent in a binary, rather than by its concentration in the binary. This behavior was previously rationalized in terms of adsorbed phase interactions of eluent and/or solute with the adsorbent; the coverage of the surface by strong eluent is nearly complete from solutions such as those of Tables III–V, so that regardless of the concentration of the strong eluent component in the eluent phase, its concentration in the adsorbed phase is relatively constant (equal $\sim$ 100 %).

Whereas the total adsorption energy of the solute shows a gradual decline with increasing water content (see dashed curve for α in Fig. 1), it has previously been noted[8] that Δ_{12} for the aromatic hydrocarbon isomers shows a more drastic reduction with decreasing adsorbent water content. This behavior is adequately confirmed in the data of Tables I–III. If the Δ_{12} values for a particular strong eluent component/ isomer pair combination are compared relative to the value at 0.7 % H_2O–Al_2O_3, it is found that the relative values of Δ_{12} at 0.7, 2.7, and 3.7 % H_2O–Al_2O_3 are in the ratios 1.00:0.54 ($\pm$0.06 S.D.):0.17 ($\pm$0.07 S.D.). These ratios are plotted as α_t *versus* adsorbent water content in Fig. 1 (solid curve, open circles). A value for 2.1 % H_2O–Al_2O_3 from a previous study[7] is also included, using Δ_{12} values for the isomer pairs anthracene/phenanthrene (ether, CCl_4) and picene/1,2,3,4-dibenzanthracene (benzene)*

The difference in the dependence of total solute adsorption energy (proportional to α) and of Δ_{12} (proportional to α_t) on adsorbent water content is quite apparent in Fig. 1. α decreases sharply at first, and levels off at a value of about 0.6 (relative to 0 % H_2O–Al_2O_3) past 4 % H_2O–Al_2O_3. α_t on the other hand shows its steepest decline between 1.5 and 4 % H_2O–Al_2O_3, and appears to approach zero beyond 4 % H_2O–Al_2O_3. Clearly the two adsorbent activity functions α and α_t are different, presumably reflecting different processes on the adsorbent surface.

---

* Values of Δ_{12} for the isomer pair chrysene/triphenylene from this same study[7] appear somewhat out of line, probably because of the difficulty in measuring large $R°$ values for these two solutes in systems with particularly low linear capacities, as well as the absence in that study of special precautions (see Experimental).

We will next show that this peculiar dependence of the hydrocarbon Δ_{12} values on adsorbent activity and eluent type also extends to the halogen substituted aromatics of Tables I and II. The variation of haloaromatic Δ_{12} values with adsorbent water content and eluent type is summarized in Table VI (compare with Tables I and II). Consider first the variation of Δ_{12} with adsorbent water content. Values of Δ_{12} at one adsorbent activity can be calculated from a Δ_{12} value at another activity (same strong eluent), simply by multiplying by the ratios of α_i or α values (whichever function might prove applicable). The results of treatment of the data of Tables I, II and VI in this fashion are given in Table VI a. Clearly the above correlation of the halo-aromatic Δ_{12} values with α_i is satisfactory, while the correlation with α is poor, just as in the case of the hydrocarbon isomers.

Comparison of the effect of the strong eluent on the Δ_{12} values for both aromatic hydrocarbons and haloaromatics shows some obvious similarities. Pentane gives generally large values of Δ_{12} for both the hydrocarbons (Tables III, IV) and halobiphenyls (Table VI); pyridine and acetone give small values (Tables III, V, VI). The correlation can be made quantitative by noting that Δ_{12} can be expressed by the following theoretically reasonable relationship:

$$\Delta_{12} = \alpha_i \varepsilon_i S_{12}, \tag{5}$$

where ε_i represents an eluent–isomer function, and S_{12} is a property only of the two solutes 1 and 2. Best values of the eluent–isomer function ε_i were derived from the data of Tables III–VI and are summarized in Table VII. Fig. 2 demonstrates the validity of Eqn. (5) with respect to the eluent term ε_i, as well as the identical dependence of the hydrocarbon and haloaromatic Δ_{12} values on the type of strong eluent used. Here the average Δ_{12} values (same strong eluent, one to three different adsorbent activities; ($\overline{\Delta_i/\alpha} = \Sigma \Delta_{12}/\Sigma \alpha_i$) for each of the four isomer pairs shown are plotted versus the best values of ε_i. The validity of Eqn. (5) is further shown by comparison of experimental Δ_{12} values in Tables III–VI with values calculated from Eqn. (5) and
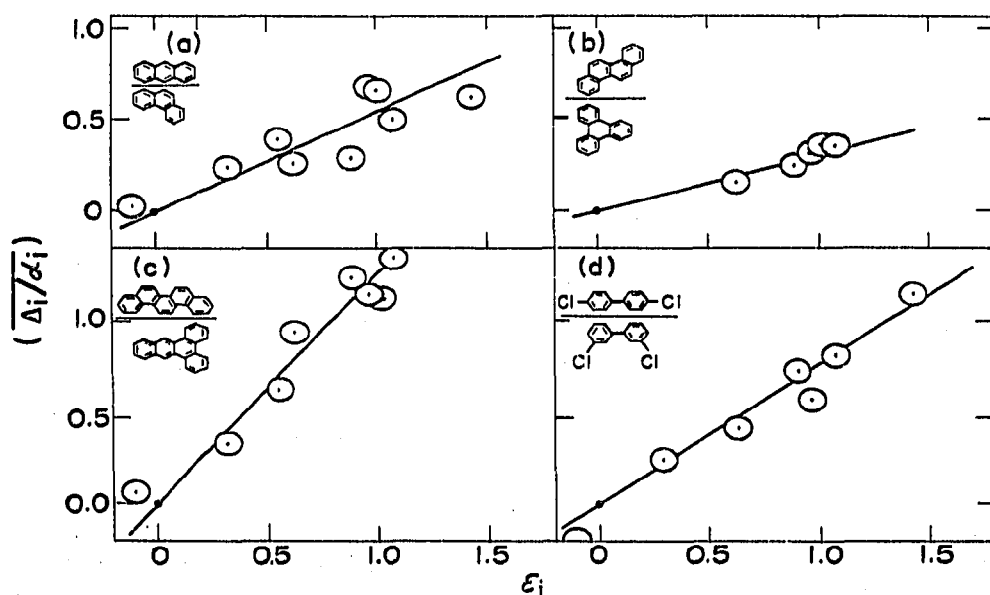

Fig. 2. Dependence of weak localization isomer effects on eluent type. Test of Eqn. (5).

TABLE VI

RELATIVE SEPARATION OF HALOGEN SUBSTITUTED AROMATIC ISOMERS; VARIATION WITH ADSORBENT ACTIVITY AND ELUENT

Solute	Eluent	Log $R^°$		Δ_i	Δ_{12}	
		Exptl.	Calc.[*]		Exptl.	Calc.[*]
2.7 % H_2O–Al_2O_3						
4,4'-Dichlorobiphenyl (1)	$^1/_2$ % v pyridine–pentane	0.03			—0.14	—0.04
3,3'-Dichlorobiphenyl (2)	$^1/_2$ % v pyridine–pentane	0.17				
4,4'-Dichlorobiphenyl (1)	$^1/_2$ % v acetone–pentane	0.26				
3,3'-Dichlorobiphenyl (2)	$^1/_2$ % v acetone–pentane	0.13			0.13	0.14
4,4'-Dichlorobiphenyl (1)	10 % v benzene–pentane	0.37			0.22	0.26
3,3'-Dichlorobiphenyl (2)	10 % v benzene–pentane	0.15				
4,4'-Dichlorobiphenyl (1)	5 % v ethyl ether–pentane	0.49			0.31	0.40
3,3'-Dichlorobiphenyl (2)	5 % v ethyl ether–pentane	0.18				
4,4'-Dichlorobiphenyl (1)	50 % v CCl_4–pentane	0.31			0.39	0.37
3,3'-Dichlorobiphenyl (2)	50 % v CCl_4–pentane	—0.08				
4,4'-Dichlorobiphenyl (2)	5 % CH_2Cl_2–pentane	0.44			0.42	0.45
3,3'-Dichlorobiphenyl (1)	5 % CH_2Cl_2–pentane	0.02				
4,4'-Dichlorobiphenyl (1)	pentane	1.36			0.55	0.59
3,3'-Dichlorobiphenyl (2)	pentane	0.81				
3.7 % H_2O–Al_2O_3						
4,4'-Dichlorobiphenyl (1)	pentane	0.63			0.27	0.19
3,3'-Dichlorobiphenyl (2)	pentane	0.36				
Benzene	pentane	—0.53				
o-Iodochlorobenzene	pentane	0.01	0.14	—0.13		
m-Iodochlorobenzene (2)	pentane	—0.11	0.14	—0.25	0.03	0.04
p-Iodochlorobenzene (1)	pentane	—0.08	0.14	—0.22		
o-Diiodobenzene	pentane	0.21	0.29	—0.08		
m-Diiodobenzene (2)	pentane	0.01	0.29	—0.28	0.08	0.06
p-Diiodobenzene (1)	pentane	0.09	0.29	—0.20		
Naphthalene	pentane	0.23				
1-Chloronaphthalene (2)	pentane	0.24	0.37	—0.13	0.03	0.07
2-Chloronaphthalene (1)	pentane	0.27	0.37	—0.10		

[*] Eqn. (5).

TABLE VIa

DEPENDENCE ON α_i OF Δ_{12} VALUES FOR HALOGEN SUBSTITUTED AROMATICS

Solute pair	Strong eluent component	Adsorbent activity (% H_2O–Al_2O_3)		Δ_{12} (b)		
		a	b	Exptl.	Calc. (α)	Calc. (α_i)
3,3'-, 4,4'-Dichlorobiphenyl	CH_2Cl_2	0.7	2.7	0.42	0.66	0.44
3,3'-, 4,4'-Dichlorobiphenyl	pentane	2.7	3.7	0.27	0.51	0.17
m-, p-Chloroiodobenzene	pentane	0.7	3.7	0.03	0.16	0.04
m, p-Diiodobenzene	pentane	0.7	3.7	0.08	0.24	0.06
1-, 2-Chloronaphthalene	pentane	0.7	3.7	0.03	0.30	0.07
Standard deviation					±0.24	±0.06

TABLE VII

SUMMARY OF ISOMER PARAMETERS USED IN CALCULATIONS OF TABLES III–VI

% H_2O–Al_2O_3	α_t		Solute pair	S_{12}
0.7	1.00		Anthracene Phenanthrene	0.54
2.7	0.54		Chrysene Triphenylene	0.37
3.7	0.17		Picene 1,2,3,5-Dibenzanthracene	1.27
			4,4'-Dichlorobiphenyl 3,3'-Dichlorobiphenyl	0.77

Strong eluent component	ε_t	ε°
Cyclohexane	1.48	0.04
Pentane	1.43	0.00
CH_2Cl_2	1.08	0.42
Isopropyl chloride	1.01	0.29
Ethyl ether	0.97	0.38
CCl_4	0.89	0.18
Benzene	0.63	0.32
Phenetole	0.56	0.40
Acetone	0.33	0.56
Pyridine	—0.10	0.71

the functions α_t, ε_t, and the best values of S_{12} for the various isomer pairs involved. These values of S_{12} are given in Table VII. The standard deviation between the various experimental Δ_{12} values of Tables III–VI and those calculated from Eqn. (5) is ± 0.07 log units, which appears to constitute good agreement, considering the range of values of Δ_{12} (—0.14 to 1.32) and the slight variability of Δ_t with the percent of a given strong eluent in an eluent binary (S.D. ± 0.07 from data of Table III).

SEPARABILITY OF ISOMERS OF SOME ADDITIONAL AROMATIC TYPES (CLASS II AND III)

Tables VIII and IX provide some additional data on the relative separation of aromatic isomers over alumina. For the halotoluenes, anisoles, methyl benzoates, acetophenones, and anilines, it is seen that on 0.7 % H_2O–Al_2O_3 the *para* isomer is more strongly adsorbed than the *meta* isomer, just as in the case of the dihalobenzenes. The halonitrobenzenes appear to be an exception to this rule, however. Similarly, the dimethoxybenzenes follow the same rule, the *para* isomer being more strongly adsorbed than the *meta*. As in the case of the 1- and 2-halonaphthalenes, 2-methoxynaphthalene and 2-acetonaphthalene are more strongly held than the 1-isomers. The dinitrobenzene isomers show little difference in retention volumes, and the *meta* isomer is actually preferentially retained with benzene as strong solvent. The methoxynitrobenzene isomers appear to follow the general rule of preferential adsorption of the *para* derivative. The non-*ortho* (2,3-, 3,4-) benzcarbazoles follow the rule of preferential adsorption of the longest isomer at higher adsorbent activities

TABLE VIII

RELATIVE SEPARATION OF SOME OTHER ISOMER TYPES ON ALUMINA

Solute	Eluent*	$\%H_2O$ $-Al_2O_3$	$\log \underline{R}^°$	Δ_i Exptl.	Calc.**	Δ_{12} Exptl.	Calc.**
Toluene	pentane	0.7	0.22				
m-Chlorotoluene (2)	pentane	0.7	0.33	—0.08		0.06	
p-Chlorotoluene (1)	pentane	0.7	0.39	—0.02			
o-Bromotoluene	pentane	0.7	0.47	—0.10			
m-Bromotoluene (2)	pentane	0.7	0.45	—0.12		0.11	
p-Bromotoluene (1)	pentane	0.7	0.56	—0.01			
Anisole	10 % v M–P	0.7	0.45				
o-Fluoroanisole	10 % v M–P	0.7	0.63	0.11			
m-Fluoroanisole (2)	10 % v M–P	0.7	0.23	—0.29	—0.31	0.20	
p-Fluoroanisole (1)	10 % v M–P	0.7	0.43	—0.09	—0.06		
p-Chloroanisole	10 % v M–P	0.7	0.42	—0.07	—0.21		
m-Iodoanisole (2)	10 % v M–P	0.7	0.34	—0.53	—0.32	0.27	
p-Iodoanisole (1)	10 % v M–P	0.7	0.61	—0.26	—0.26		
2,4-Dichloroanisole	10 % v M–P	0.7	0.32	—0.21			
2,4,6-Tribromoanisole	10 % v M–P	0.7	0.44	—0.82			
o-Dimethoxybenzene	50 % v M–P	0.7	0.71	0.51			
m-Dimethoxybenzene (2)	50 % v M–P	0.7	0.10	—0.10	—0.11	0.28	
p-Dimethoxybenzene (1)	50 % v M–P	0.7	0.38	0.18	0.25		
o-Dimethoxybenzene	10 % v M–P	3.7	0.49				
m-Dimethoxybenzene (2)	10 % v M–P	3.7	0.05			0.16	
p-Dimethoxybenzene (1)	10 % v M–P	3.7	0.21				
1-Methoxynaphthalene (2)	10 % v M–P	0.7	0.66			0.45	
2-Methoxynaphthalene (1)	10 % v M–P	0.7	1.11				
m-Nitrobromobenzene (2)	25 % v M–P	0.7	0.52			0.00	0.23
p-Nitrobromobenzene (1)	25 % v M–P	0.7	0.52				
m-Dinitrobenzene (2)	50 % v B–P	2.7	0.90			—0.06	—0.10
p-Dinitrobenzene (1)	50 % v B–P	2.7	0.84				
m-Dinitrobenzene (2)	25 % v M–P	2.7	0.91			—0.05	—0.10
p-Dinitrobenzene (1)	25 % v M–P	2.7	0.86				
m-Methoxynitrobenzene (2)	50 % v B–P	2.7	0.52			0.35	0.55
p-Methoxynitrobenzene (1)	50 % v B–P	2.7	0.87				
m-Methoxynitrobenzene (2)	25 % v M–P	2.7	0.53			0.30	0.55
p-Methoxynitrobenzene (1)	25 % v M–P	2.7	0.83				
m-Bromo methylbenzoate (2)	50 % v M–P	0.7	0.19			0.09	0.27
p-Bromo methylbenzoate (1)	50 % v M–P	0.7	0.28				
m-Bromoacetophenone (2)	50 % v M–P	0.7	0.72			0.14	0.32
p-Bromoacetophenone (2)	50 % v M–P	0.7	0.86				
m-Bromoacetophenone (2)	10 % v M–P	3.7	0.45			0.09	
p-Bromoacetophenone (1)	10 % v M–P	3.7	0.54				
1-Acetonaphthalene (2)	M	0.7	0.53			0.16	
2-Acetonaphthalene (1)	M	0.7	0.69				

TABLE VIII (continued)

Solute	Eluent*	% H₂O –Al₂O₃	log R°	Δt Exptl.	Calc.**	Δ₁₂ Exptl.	Calc.**
m-Chloroaniline (2)	M	1.7	0.95			0.13	
p-Chloroaniline (1)	M	1.7	1.08				
m-Chloroaniline (2)	M	2.7	0.37			0.07	
p-Chloroaniline (1)	M	2.7	0.44				
m-Chloroaniline (2)	50% v M–P	3.7	0.53			0.04	
p-Chloroaniline (1)	50% v M–P	3.7	0.57				
1,2-Benzcarbazole	M	2.7	0.84				
2,3-Benzcarbazole (1)	M	2.7	1.06			0.33	
3,4-Benzcarbazole (2)	M	2.7	0.73				
1,2-Benzcarbazole	M	3.7	0.28				
2,3-Benzcarbazole (1)	M	3.7	0.07			—0.03	
3,4-Benzcarbazole (2)	M	3.7	0.10				

* M–P = CH₂Cl₂–pentane; B–P = benzene–pentane; M = CH₂Cl₂.
** Eqn. (5); see text.

TABLE IX

STERIC AND ELECTRONIC EFFECTS IN THE SUBSTITUTED BENZENES; 3.7% H₂O–Al₂O₃

Solute	Eluent*	Log R°	Δ_e**	Δ_s***	α Q°_t	σ
Anisole	pentane	0.57	0.11	—0.20	1.13	—0.17
p-Methyl anisole	pentane	0.72				
o-Methyl anisole	pentane	0.52				
Nitrobenzene	10% v M–P	0.57	0.20		1.77	—0.17
p-Nitrotoluene	10% v M–P	0.71				
Benzonitrile	25% v M–P	0.31	0.23	—0.15	2.08	—0.17
p-Methyl benzonitrile	25% v M–P	0.42				
o-Methyl benzonitrile	25% v M–P	0.27				
Methyl benzoate	25% v M–P	0.27	0.20	—0.29	2.12	—0.17
p-Methyl methylbenzoate	25% v M–P	0.35				
o-Methyl	25% v M–P	0.06				
Acetophenone	25% v M–P	0.65	0.24		2.39	—0.17
p-Methyl acetophenone	25% v M–P	0.77				
Aniline	25, 50% v M–P	ref. (9)	0.27	—0.36	2.82	—0.17
p-Methyl aniline						
o-Methyl aniline						
Pyridine	50% v B–I	ref. (9)	0.31	—0.43	3.07	—0.17
α-Picoline						
γ-Picoline						
Bromobenzene ****	pentane	0.51	—0.01	—0.09	0.35	—0.17
p-Bromotoluene	pentane	0.56				
o-Bromotoluene	pentane	0.47				

* M–P = CH₂Cl₂–pentane (10% v: αε° = 0.101; 25% v: αε° = 0.163); B–I = benzene-isooctane.
** Calculated from p-methyl derivative, relative to toluene and parent compound.
*** Calculated as (log R°)_ortho — (log R°)_para.
**** Data for 0.7% H₂O–Al₂O₃.

(class I), with the 2,3-isomer being more strongly held than the 3,4-isomer on 2.7 %
H_2O–Al_2O_3. The dependence of these Δ_{12} values of Table VIII on adsorbent activity
and eluent type shows certain differences, however, relative to the hydrocarbon
and haloaromatic isomer Δ_{12} values. In some cases the decrease in Δ_{12} with increasing
adsorbent water content is less than predicted by α_t, and closer to that predicted by α.
Table X summarizes these results as previously for the haloaromatics. In the case of
the chloroanilines and the benzcarbazoles, Δ_{12} appears to correlate reasonably well
with α_t, but in the other four examples of Table X this is clearly not the case. Similarly,
in the case of the methoxynitrobenzenes of Table VIII, and the acetonaphthalenes
from ref. (3), the expected dependence of Δ_{12} on the strong eluent ε_t value (Eqn. 5) is
not observed. These observations, in conjunction with the absence of an isomer effect
in the nitrobromobenzenes and a small reverse effect in the dinitrobenzenes, strongly
suggest that for most of the *meta* and *para* disubstituted benzenes, and 1- and 2-
substituted naph⁺halenes of Table VIII, fundamentally different factors determine
isomer adsorption in these solutes relative to isomers of the aromatic hydrocarbons
and haloaromatics (class I).

TABLE X

DEPENDENCE OF Δ_{12} ON ADSORBENT WATER CONTENT FOR ISOMER PAIRS OF TABLE VIII;
METHYLENE CHLORIDE STRONG ELUENT

Isomer pair	Adsorbent activituy (% H_2O–Al_2O_3)		Δ_{12} values (adsorbent 2)		
	I	2	Exptl.	Calc. (α_t)	Calc. (α)
m-, *p*-Dimethoxybenzene	0.7	3.7	0.16	0.05	0.21
1,2-Methoxynaphthalene	0.7	3.7[a]	0.20[b]	0.08	0.34
m-,*p*-Methoxynitrobenzene	0.7	3.7[a]	0.49[b]	0.05	0.22
1-, 2-Acetonaphthalene	0.7	3.7[a]	0.19[b]	0.03	0.12
m-, *p*-Chloroaniline	0.7	3.7[c]	0.04	0.02	0.10
2-, 3-, 3,4-Benzcarbazole	2.7	3.7	—0.03	0.11	0.31

[a] Data of ref. (3).
[b] Corrected for different strong eluents, according to Eqn. (5).
[c] Data of ref. (9).

Table IX summarizes the effect of *para* and *ortho* methyl substituents on the
retention volumes of various substituted benzenes, primarily to evaluate the effects of
electronic activation, and steric interference to adsorption by an *ortho* methyl. These
data are discussed in greater detail in the next section.

ORIGIN OF ISOMER EFFECTS IN THE PRESENT SOLUTES: MECHANISMS OF ADSORPTION

The previously discussed data of Tables I–VI, VIII, and IX permit a number of
intriguing generalizations on the factors which determine isomer separation on alumina.
These generalizations and the data upon which they are based deserve further exam-
ination from a fundamental viewpoint, so as to determine the ultimate scope of their
application and to gain insight into the basic molecular processes which occur in the
adsorption of these and other solutes on alumina. During this examination it is
important to keep in mind the differences between *ortho* isomer types (class II, e.g.

o-dichlorobenzene, 1-chloronaphthalene, 9-chloroanthracene, 1-2-benzcarbazole, etc.) and non-*ortho* isomers (*e.g. meta* and *para* isomers, 2-substituted naphthalenes, 2,3- and 3,4-benzcarbazoles, etc.). The various factors which can lead to special effects in the adsorption of *ortho* isomers have been briefly reviewed in the Introduction. Factors leading to differences in the adsorption of non-*ortho* isomers include electronic activation of one group by another[3,5,6,9], the relative orientation of solute adsorbing groups *vis a vis* adsorbent sites[3,7,14,15], and the ability of an adsorption region on the adsorbent surface to accommodate (*i.e.* fit) the adsorbing solute[7].

Among the simplest and most easily evaluated factors are electronic activation of one group by another (class III), and the steric hindrance of a strongly adsorbing group by a more weakly adsorbing group (class II a). Two preceding papers[6,9] have discussed these effects in considerable detail for several classes of heteroaromatic solutes. The data of Table IX permit the further examination of these factors. In the case of the *p*-methyl derivatives (class III), steric effects are absent and any Δ_i values for these solutes (relative to toluene and the non-methyl substituted benzene derivative) may be attributed to electronic activation of the other substituent by the methyl group. Since the methyl group itself is very weakly adsorbing, activation of the methyl group by the other substituent cannot appreciably affect solute adsorption energy. Values of Δ_i for the *p*-methyl derivatives of Table IX are listed as values of Δ_e, referring to the electronic activation of a group (X) by a second group (Y). Previously[6] it has been found for a single group X that Δ_e is proportional to the adsorption energy of X (which may change with steric crowding of X by other groups), *i.e.* αQ°_x, and to the HAMMETT σ function[16] of the group Y (*e.g.* see Fig. 4, ref. 6) σ_y.
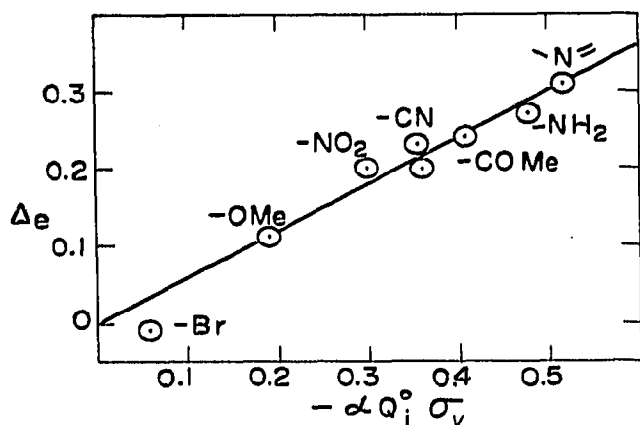

Fig. 3. Solute geometry effects in the *para* substituted toluenes. Variation of Δ_e with group adsorption energy αQ°_i ($\sigma_y = -0.17$). Verification of Eqn. (6).
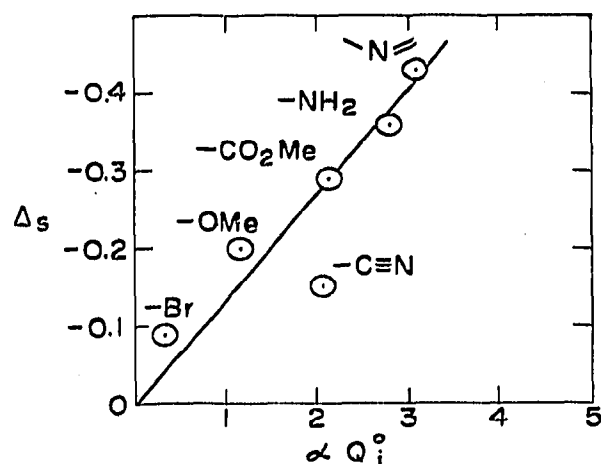
Fig. 4. Solute geometry effects in the *ortho* substituted toluenes. Variation of Δ_s with group adsorption energy αQ°_i. Verification of Eqn. (7).

This also appears to be true of the Δ_e values for the various substituted benzenes of Table IX, as may be seen by plotting them *versus* $\alpha Q^\circ_i \sigma_y$ in Fig. 3. From this plot we can calculate the electronic activation of other groups X by any group Y:

$$\Delta_e = -0.6 \, \alpha \, Q^\circ_x \, \sigma_y \tag{6}$$

It is noted in Fig. 3 that the relationship appears to hold for all solute groups with the possible exception of bromo, whose adsorption energy is too small to determine whether Δ_e is really zero or $+0.03$ as predicted by Eqn. (6). Besides permitting us to calculate Δ_e in other solutes, and to evaluate electronic contributions to isomer separation, the applicability of Eqn. (6) to the data of Fig. 3 has added significance. All of the solute groups represented in Fig. 3 show an increase in adsorption energy with substitution of the electron donating methyl group, implying that they adsorb with electron donation to an adsorbent site. The fact that Δ_e is proportional to $\alpha Q°_x$ for the various solute groups represented here further suggests a basically similar adsorption mechanism, one where the energy of adsorption of x is simply proportional to the net negative charge localized on X. This suggests simple coulombic attraction between a negative group X and a positive adsorbent site. The aromatic keto group discussed earlier[6] does not appear to fit the correlation of Fig. 3, implying a different adsorption mechanism. However, this does not seem reasonable in view of the correlation of Δ_e for the acetyl group in Fig. 3, since both the acetyl and keto groups would be assumed to adsorb by the same mechanism. Possibly the approximate method of estimating σ_y values in the preceding treatment[6] of the aromatic keto groups was in error by an amount sufficient to explain this discrepancy.

The effect of an *ortho* methyl in the solutes of Table IX is twofold: the methyl in the *ortho* position provides approximately the same electronic activation of X as a *para* methyl (see discussion in ref. 9), and an *ortho* methyl may sterically interfere with the optimum interaction of X with an adsorbent site. The purely steric effect (class II a) in the *ortho* substituted solutes of Table IX Δ_s is therefore given by (log $\underline{R}°$) *para*–(*log $\underline{R}°$*) *ortho* for these methyl substituted compounds, since in other respects the adsorption of *ortho* and *para* isomers should be identical. As shown in Fig. 4, values of Δ_s are also porportional to $\alpha Q°_x$, just as were values of Δ_e. This correlation tends to support a coulombic interaction adsorption of X as suggested by Fig. 3, since if the effect of the *ortho* methyl is to increase the distance between X and the adsorption site (by crowding) by a fixed amount, the loss in adsorption energy of X would be proportional to the original adsorption energy $\alpha Q°_x$ (see discussion of ref. 8). This analysis also suggests that Δ_s should be given as the product of $\alpha Q°_x$ and a steric factor s_y for the group Y (s_y proportional to the size of Y).

$$\Delta_s = s_y \, \alpha Q°_x \tag{7}$$

Values of s_y can then be estimated from the size of Y and previous values of Δ_s as a function of the group Y (see ref. 9). Eqn. (7) is expected to be only approximately valid because of the complexity of steric interactions, but should be fairly accurate in comparing effects for groups Y of comparable size. For example, on the basis of bond length and Van der Waals radius data[17] it can be estimated that the same steric hindrance (same value of s_y) to the adsorption of the chloro group would be involved in the three compounds, 1,2-dichlorobenzene, *o*-chlorotoluene, and 1-chloronaphthalene.

Class I isomers

Returning to the non-*ortho* disubstituted halobenzenes of Table I (class I), we will attempt next to evaluate the relative importance of various factors which might

be determining these $\underline{R}°$ and Δ_i values. Electronic activation of one halogen group by another is an apparently plausible explanation for the preferential adsorption of *para versus meta* isomers, since the halogen group in the *meta* position is more strongly electron withdrawing (larger value of σ_y, and therefore larger value of Δ_e). However, the *para* halogen substituent is also deactivating, so that if this explanation possessed any merit, negative values of Δ_i for the *para* disubstituted benzenes should also be observed (equal to approximately half the *meta* Δ_i values). This is not observed, the *para* Δ_i values being equal to zero within experimental error. This conclusion concerning the unimportance of electronic effects is further strengthened by calculations of the magnitude of Δ_i for the *meta* and *para* dihalobenzenes. By comparison with p-bromotoluene, electronic effects are predicted to be zero; using Eqn. (6), on the other hand, we calculate* values of Δ_i ranging from —0.11 to —0.32 for the *meta* derivatives, and —0.02 to 0.26— for the *para* derivatives*. In neither case do these calculated Δ_i values bear much resemblance to the experimental values, and we conclude that electronic interaction of the two halogen atoms cannot explain the anomalous adsorption of the dihalogen substituted benzenes. The similarity of the haloaromatic and hydrocarbon isomer effects also supports this conclusion since electronic effects cannot be involved[17] in most unsubstituted hydrocarbon isomers (*i.e.* alternant hydrocarbons).

Another possible effect in the adsorption of the *meta* and *para* dihalobenzenes is the relative ease of accommodating the adsorbing solute molecule in the region surrounding an adsorption site. Thus, due to the geometry of the adsorbent surface, molecules of certain shapes might not easily "fit" onto an adsorption site. Some evidence for the preferential exclusion of very wide molecules (*e.g.* decacyclene) from the alumina surface has been reported in the case of the aromatic hydrocarbons[6]. Calculation of Δ_i values for the corresponding alkyl benzenes should resolve this point, since the geometries of toluene and of the halobenzenes are generally similar[18]. Previous data[1] for 1.1 % H_2O–Al_2O_3 show Δ_i values of the xylenes equal to —0.03 for *para* and —0.04 for *meta*, while average values for various *meta* and *para* dialkyl benzenes** are —0.04 (*para*) and —0.01 (*meta*). The geometrical shape of the substituted benzenes seems therefore to play no significant role in determining Δ_i; there is clearly no correspondence between Δ_i values for the isomeric alkyl and halo benzenes of similar shape.

Another possible explanation of the differences in adsorption of the *meta* and *para* dihalobenzenes, and the one we believe to be correct, is that the adsorbing groups in these solute molecules (two halogens, one phenyl) prefer to overlap strong adsorbent sites or active adsorption regions on the adsorbent surface. Previously we have shown[3] that where very strongly adsorbing solute groups are involved, only one such group can adsorb on a strong adsorbent site, and the adsorption energies of other solute groups on the same molecule are reduced in proportion to the "tightness" with which the one strongly adsorbing group is held to the strong site. Clearly no such effect is involved in the halobenzenes, since the adsorption energies $Q°_i$ of the various halogen atoms are too small for "strong" localization of this type; further-

---

* Calculation from Eqn. (6) assumes electronic activation of each halogen group by the other, and assumes Δ_e is proportional to the *intrinsic* adsorption energy of $x,Q°_x$ (see subsequent discussion and ref. 3) rather than to $Q°_x$.
** Alkyl group is methyl or ethyl.

more, strong localization does not appear to lead to pronounced differences in the adsorption of *meta versus para* isomers. Rather, the delocalization or energy loss of other strongly adsorbing solute groups is reduced as the distance between them and the localizing solute group increases[3,9]. If we distinguish between strong localization of one solute group on an adsorbent site (as previously[3]), and "weak" localization of certain weakly adsorbing solute groups (class I solutes) on some *group* of adsorbent sites (these may or may not be the same as are involved in strong localization), it appears that the sites involved in weak localization lie on straight lines on the adsorbent surface, and involve "regions" of strong adsorption interaction rather than discrete, separated points. Thus, in the monohalo- and *para*-dihalobenzenes, the centers of these various groups (halogen or phenyl) may lie on a straight line, but cannot always overlap a set of discrete point-sites since the distance between the different group centers is variable (because of the differing halogen–carbon bond lengths). In the case of the *meta* dihalobenzenes, accommodation of all the adsorbing groups over the linear group of active sites is not possible; this is illustrated in the diagrams of Fig. 5 (top line), with the active site region indicated by the faint straight line.
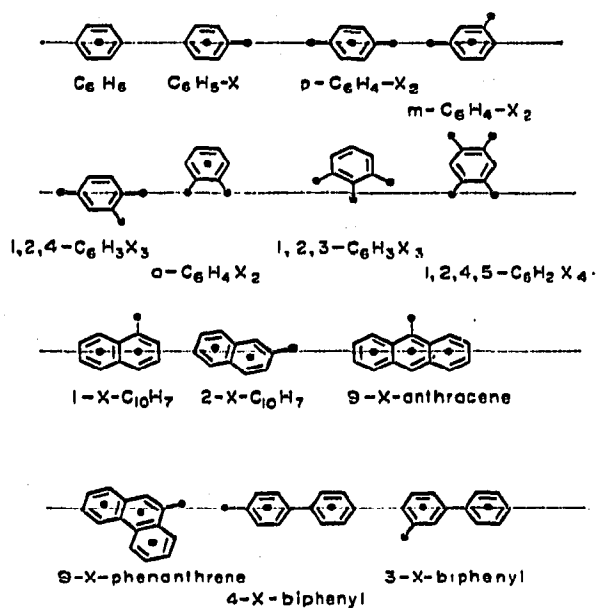

Fig. 5. Hypothetical configuration of various solutes for weak localization on alumina line-of-sites.

One test of this localization theory of the halobenzene Δ_i values is afforded by the magnitude of the energy loss Δ_i. In the case of the *para* derivatives the theory predicts that Δ_i equal 0.00, and this is within experimental error of the observed values (av. —0.01 ± 0.03). For the *meta* derivatives, the theory would predict that Δ_i is equal to some fraction of αQ°_i, where i refers to the "delocalized" halogen atom. Actually, as seen in Table I, for some solutes (*e.g. m*-difluorobenzene) the observed energy loss appears to exceed αQ°_i (*i.e. m*-difluorobenzene is less strongly adsorbed than fluorobenzene), implying more than 100 % loss of the adsorption energy of X upon delocalization. This apparent paradox results from a failure to distinguish between the nominal adsorption energy of X, αQ°_x, and its "intrinsic" adsorption

energy $\alpha Q°_x{}^3$. The nominal adsorption energy $\alpha Q°_i$ is actually the sum of the intrinsic (actual) adsorption energy of X plus the effect of the substituent X on the adsorption energy of the benzene ring. As seen in Fig. 3, an electron donating substituent generally increases the adsorption energies of other groups in the same solute, and the same is true of the phenyl group, where introduction of a methyl group increases the adsorption energy of the ring on calcined alumina by $+$ 0.09 units[10]. From this observation and the ratio of average (*meta* and *para*) σ values for the methyl and various halo substituents we can estimate that the introduction of the various halogen substituents into a benzene ring causes the following respective changes in the adsorption energy $\alpha S°$ of the benzene ring (on adsorbent of Table I): fluoro, —0.15; chloro, —0.22; bromo, —0.23; iodo, —0.23. The intrinsic adsorption energies $Q°_i$ of the aromatic halogen groups on 0.7 % H_2O–Al_2O_3 are then calculated as 0.27 (fluoro), 0.41 (chloro), 0.58 (bromo), and 0.77 (iodo). Assuming these latter values of $\alpha Q°_i$, all of the *meta* derivatives of Table I now show less than 100 % loss of adsorption energy for the second halo group, as theoretically required.

In the localization of the *meta* dihalobenzenes as in Fig. 5, it is apparent that there should be a tendency for the more strongly adsorbing halogen atom to localize, and therefore Δ_i should be proportional to the $\alpha Q°_i$ value of the delocalized halogen. For the four *meta* derivatives of Table I containing a fluoro substituent, we would predict that this atom is delocalized (it is the most weakly adsorbing halogen); it is found that the average value of Δ_i is —0.19 $\pm$ 0.02. Similarly, for the three *meta* derivatives containing a chloro (but no fluoro), the average value of Δ_i is —0.20 $\pm$ 0.03; for the two *meta* derivatives containing bromo (but no fluoro or chloro), the average Δ_i value is 0.26 $\pm$ 0.03; for *meta* diiodobenzene, Δ_i equals —0.27. Thus, in support of our theory the average value of Δ_i increases with the adsorption energy of the delocalized halogen.

The relative orientation of the *ortho* dihalobenzenes along the linear active site region is somewhat obscure. The orientation shown in Fig. 5 (second line) is one possibility, although the phenyl ring now appears to be delocalized, which should lead to a negative value of Δ_i. However, we have previously shown[6] that two *ortho* groups can form an especially strong bond to a single adsorption site by chelation, and it is possible that in the case of the *ortho* dihalobenzenes the advantage of this bonding situation overcomes the disadvantage of delocalizing the benzene ring. If the orientation of the *ortho* dihalobenzenes is conceived of as straddling the line of active sites, with the center of the ring on the line and the two halogens each slightly displaced from the line (line bisecting the angle between the two halogens), the 1,2,4-trihalobenzenes would appear to suffer little if any energy loss (the 4-halo group is fairly close to the line of sites in this case), while in the 1,2,3-trihalobenzenes, the 3-halo group should be completely delocalized. Actually, the 1,2,3-trihalobenzenes have smaller Δ_i values (—0.20) than the 1,2,4-isomers (—0.29), suggesting the alternative configurations of Fig. 5 (line two) for these isomers. The Δ_i values for the remaining polyhalobenzenes of Table I can now be estimated in terms of the preceding analysis. For 1,2,4,5-tetrachloro- and tetrabromobenzenes, the configuration of Fig. 5 (line two) with two delocalized halogens should apply, so that Δ_i should be equal to —0.40 and —0.52, respectively. Values of —0.64 and —0.69 were actually observed. For 1,3,5-tribromobenzene, the configuration would be the same as for the *meta* dihalobenzene of Fig. 5 (line one) with two delocalized bromo groups and Δ_i cal-

culated equal to —0.52 *versus* —0.85 experimental. Similarly, for hexachlorobenzene, we have the same configuration as for 1,2,3-dichlorobenzene (Fig. 5, line two) with three additional delocalized chlorines; a total Δ_i of —0.20 (for the partial localization of 1,2,3-trichlorobenzene) plus —0.60 (three delocalized chloro groups) or —0.80 is predicted *versus* the experimental value of —0.93. Considering the complexity of the present phenomenon, the weak localization theory appears to give a reasonable explanation of the Δ_i values of the polyhalobenzenes.

Similarly, as shown in Fig. 5, line 3, the present theory predicts the preferential adsorption of the 2-halonaphthalenes relative to the 1-halonaphthalenes. The 1-position is also sterically hindered by the 8-hydrogen*, so that the average Δ_i value (pentane eluent) for the 1-halonaphthalenes (equal —0.36) is quite reasonable (estimated —0.21 for delocalization plus —0.09 for Δ_s). Similarly, the diagrams for 9-haloanthracene and phenanthrene in Fig. 5 (lines 3, 4) suggest a larger negative value of Δ_i for the anthracene derivatives, relative to the unsubstituted hydrocarbon, as is experimentally observed. The calculated value of Δ_i for 9-bromophenanthrene relative to phenanthrene should be the sum of delocalization and steric hindrance effects: zero for delocalization plus —0.09 for steric hindrance, equal a total of —0.09 *versus* —0.21 experimental. The calculated value of Δ_i for 9-bromoanthracene and 9,10-dichloroanthracene would be about —0.2 for each delocalized halogen plus an unknown amount for the crowding of each halogen in the 9-position of anthracene. The actual values of Δ_i for these two compounds —1.32 and —1.48 appear too large. An average value of Δ_s equal to —0.7 is implied by these Δ_i values, and this is certainly too large (the maximum value of Δ_s for a group X must be less than the inherent adsorption energy of X *after* delocalization; 0.2–0.4 in this case). Possibly other, normally minor, factors are involved in the case of the 9-haloanthracenes, such as electronic activation of all three anthracene rings by the 9-halo group, rather than just the ring attached to the halogen, with greater than normal reduction in the adsorption energy of the hydrocarbon nucleus. Also the increase in solute width which occurs when a 9-substituent is introduced into the anthracene nucleus may be important. The $\underline{R}°$ value for 9-methyl anthracene in Table II, relative to anthracene and the increase in energy in going from benzene to toluene, suggests a contribution to Δ_i for a 9-haloanthracene from this width effect of about 0.1 units.

The 3-halobiphenyls of Table II show Δ_i values close to what we would predict from the present theory. As shown in Fig. 5 (line 4) the 3-halo substituent will be completely delocalized, as in the case of one of the substituents in the *meta* dihalobenzenes. We would therefore predict the following Δ_i values for the various *meta* halobiphenyls of Table II (corrected to CH_2Cl_2 eluent; Eqn. 5):

3-Chlorobiphenyl	—0.15 (—0.10 exptl.)
3-Bromobiphenyl	—0.20 (—0.27 exptl.)
3,3'-Difluorobiphenyl	—0.29 (—0.25 exptl.)
3,3'-Dichlorobiphenyl	—0.30 (—0.34 exptl.)

Agreement between calculated and experimental values is satisfactory. As expected the 4-halobiphenyls are all more strongly adsorbed than the 3-halo isomers, but in most cases the Δ_i values of these solutes are significantly *positive*, rather than

---

* Δ_s for this hindrance should be about equal to Δ_s for an *ortho* methyl, as previously discussed.

close to zero as predicted by our simple theory. We will comment on this fact shortly.

The preferential adsorption of long aromatic hydrocarbons relative to shorter isomers (*e.g.* anthracene *versus* phenanthrene) is also easily explained by the present theory, as illustrated by the figures of Fig. 5 for the substituted anthracene and phenanthrene isomers. That is, a larger fraction of the anthracene molecule can lie on top of the line of active sites than in the case of phenanthrene. The same would be true of chrysene relative to triphenylene, and of picene relative to 1,2,3,4-dibenzanthracene (Tables III–V), as well as other aromatic isomers (*e.g.* ref. 7).

The peculiar dependence of Δ_{12} for the haloaromatic and aromatic hydrocarbon isomers on adsorbent water content (*e.g.* α_t function in Fig. 1) tends to support the present theory since the localization of molecules on lines of sites would be expected to be a marked function of the coverage of these sites by adsorbed water. Presumably initial water either adds to a different class of sites, or else adds to the line of sites unselectively. This would agree with the "weak" nature of the present localization effect. Ultimately, between addition of 2 and 4 % water to the adsorbent, the lines of sites become largely covered, or else are disrupted by intermittent adsorption of water along the line. Either process would explain the decline of these Δ_{12} values to zero for adsorbent water contents greater than 4 %.

The peculiar effect of the eluent on these Δ_{12} values of the aromatic hydrocarbons and their halo derivatives also appears understandable in terms of the present theory. If the strong eluent itself shows any preference for adsorption on the weak linear sites, relative to other parts of the adsorbent surface, the value of ε_t should tend to decrease with increasing adsorption energy of the strong eluent molecule, which is roughly proportional to ε° for the strong eluent. As noted in Fig. 6 there is a definite correlation between ε_t and ε° of the type expected. The variability of ε_t values for the same strong eluent between different isomer pairs appears about as great as the scatter of the data in Fig. 6.
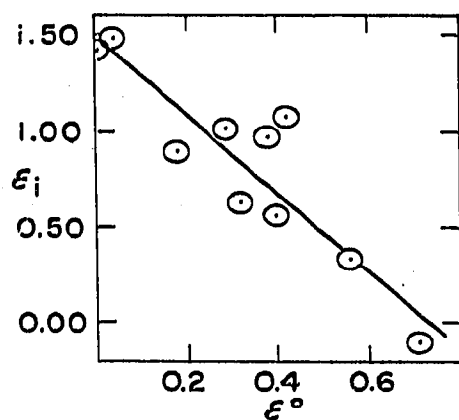

Fig. 6. Dependence of eluent–isomer parameter on strength of strong eluent component.

The nature of the linear sites which give rise to these weak localization effects in the adsorption of the aromatic hydrocarbons and haloaromatics on alumina is of considerable interest. Fig. 3 suggests that the adsorption of most solute groups on alumina involves coulombic interaction with a positive field associated with an adsorbent site. This positive field might be associated either with surface aluminum

atoms or hydroxyl groups (*i.e.* hydrogen bonding). These aluminum atoms or attached hydroxyl groups are presumed to be distributed in a regular, crystalline array on the adsorbent surface, at least over small regions which are part of a single crystallite. Fig. 7 shows such a hypothetical distribution of surface aluminum atoms. As in every crystalline array, lines may be drawn through various sets of aluminum atoms; these linear regions then constitute areas of net positive fields, on which the preferential adsorption of linearly arranged electron donating groups is easy to visualize. Alternatively, these lines of sites might correspond to linear lattice defects or crystallite edges.
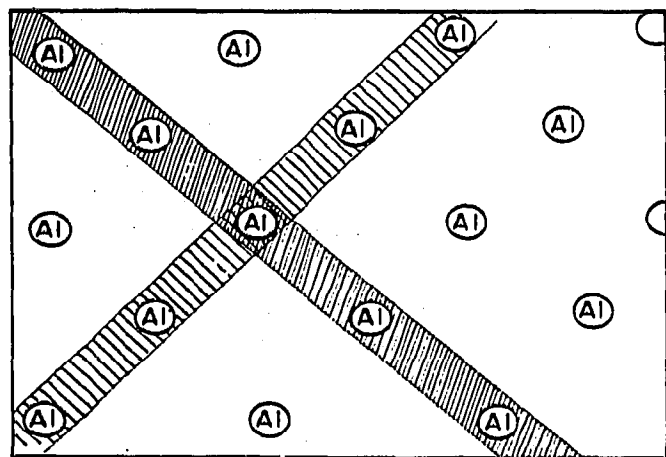
Fig. 7. Hypothetical view of alumina surface showing regular array of exposed aluminum atoms and resulting line-of-sites.

As a final commentary on the nature of the alumina sites responsible for the weak class I localization of the aromatic hydrocarbons and their halo derivatives (as in Fig. 5), it is interesting to compare the adsorption of these two groups of solutes on alumina *versus* silica. The aromatic hydrocarbons are believed[14] to localize on surface silanol groups in the case of adsorption on silica, and the resulting relationship between solute adsorption energy and solute molecular structure is markedly different for silica relative to alumina. Similarly, the adsorption of the haloaromatics on silica does not at all resemble their adsorption on alumina, as may be seen from the data of Table XI. Here, log $\underline{R}^{\circ}$ values for the halobenzenes on 2.5 % $H_2O-Al_2O_3$ are given, and the intrinsic adsorption energy Q°_i of the various aromatic halo groups calculated as previously for alumina. Whereas Q°_i for the adsorption of these halo

TABLE XI

ELUTION OF THE HALOBENZENES FROM 2.5% H_2O-SiO_2 (DAVISON CODE 12) BY PENTANE

Solute	Log $\underline{R}^{\circ}$	α $\underline{Q}^{\circ}_i$
Benzene	0.79	
Fluorobenzene	0.64	—0.06
Chlorobenzene	0.59	—0.06
Bromobenzene	0.62	—0.03
Iodobenzene	0.64	—0.01

groups on alumina ranges from 0.27 to 0.77, on silica the average value of $Q°_i$ is zero within experimental error (—0.04 ± 0.02). That is, these aromatic halo groups show no tendency to adsorb on the silica surface from pentane. From these two observations we conclude that the alumina sites responsible for weak localization effects appear quite different from the sites responsible for normal adsorption on silica; these alumina sites are therefore probably surface or second row aluminum atoms rather than hydroxyl groups.

The existence of large, positive Δ_i values for the 4-halobiphenyls remains an anomaly in terms of the preceding theory, which is concerned only with how solutes suffer adsorption energy losses (minus Δ_i values) through delocalization of adsorbing solute groups. Nevertheless, these positive Δ_i values for the 4-halobiphenyls appear to be related to the Δ_i and S_{12} values of the remaining haloaromatics and aromatic hydrocarbons in Tables I–VI, since the effect of strong eluent type and adsorbent activity on all of these various Δ_i and S_{12} values is quite similar (*i.e.* Eqn. (5) holds). These positive Δ_i values for the 4-halobiphenyls are reminiscent of the adsorption behavior of the *p*-polyphenyls[8], which also show larger than predicted $R°$ values, as well as eluent and adsorbent activity effects of the type governed by Eqn. (5).

Values of S_i may be defined for a *solute*, analogous to S_{12} for a *solute pair*, and calculated from Eqn. (5) with Δ_i replacing Δ_{12} and S_i replacing S_{12}.

In Fig. 8 we have plotted S_i values for the *p*-polyphenyls (circles) relative to biphenyl, *versus* solute length*. S_i is seen to be a marked function of solute length,
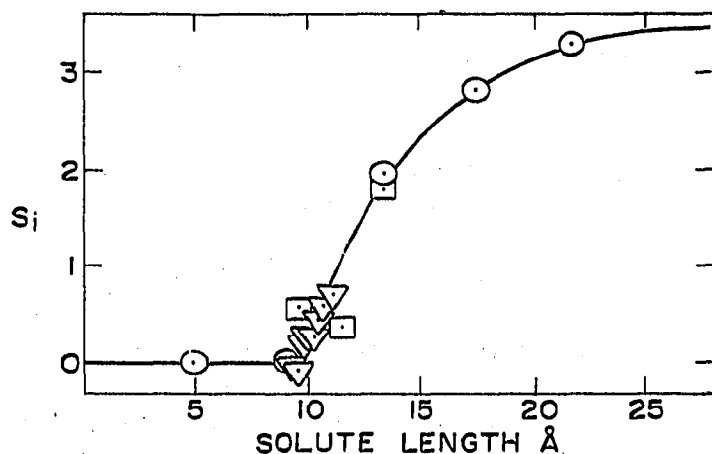

Fig. 8. Dependence of solute S_i values on solute length. $\square$ = fused hydrocarbons; $\odot$ = *p*-polyphenyls; $\triangledown$ = *p*-halobiphenyls.

rising sharply for lengths greater than 10 Å, and eventually leveling off for lengths beyond 22 Å. If we assume that S_i for these and other solutes is in fact governed by solute length, then we can calculate S_i for the solutes anthracene, triphenylene, and picene for inclusion in Fig. 8. Phenanthrene and triphenylene have the same lengths as

---

* This calculation was performed as follows: values of $R°$ for the *p*-polyphenyls from benzene through *p*-quinquephenyl were available from a previous study[8]; Δ_i was assumed zero for benzene and biphenyl, and Eqns. (1) and (2) then predict that $R°$ for a *p*-polyphenyl with n phenyl rings is given as $R_b \, r^{n-1}$ where R_b is the $R°$ value for benzene (solute) and r is the ratio of $R°$ values for biphenyl to benzene; Δ_i was then calculated as in Eqn. (3), and S_i calculated as $\Delta_i/\alpha_i \varepsilon_i$, as in Eqn. (5) for S_{12}.

biphenyl, so the S_i values of anthracene and chrysene relative to biphenyl are simply the S_{12} values of the two solute pairs anthracene/phenanthrene and chrysene/triphenylene. 1,2,3,4-Dibenzanthracene has approximately the same length as anthracene, so S_{12} for picene is approximately the sum of S_{12} values for the two solute pairs picene/1,2,3,4-dibenzanthracene and anthracene/phenanthrene. The resulting S_i values for the hydrocarbons anthracene, chrysene, and picene (relative to biphenyl) are also plotted *versus* solute length in Fig. 8 (squares). Finally, the S_i values of the various 4-halobiphenyls (defined relative to biphenyl) are also included in Fig. 8 (triangles). A single smooth curve is seen to fall on top of all of these data, suggesting that a common adsorption mechanism is determining the large, positive values of Δ_i in each of these three classes of solutes. Previously this effect has been attributed[7] to the localization of aromatic hydrocarbons on strong adsorption sites, where longer solute molecules have a greater chance for simultaneously overlapping two such strong sites; in terms of this explanation, the plot of Fig. 8 would suggest an average spacing of about 13 Å between strong sites. However, the size of the limiting value of S_i, which corresponds to the adsorption energy of about 10 aromatic carbons, makes this explanation completely untenable in terms of a preceding analysis[14] of adsorption on heterogeneous surfaces. Thus, the adsorption energies or $S°$ values of benzene and naphthalene (whose lengths are well under 10 Å, the threshold length in Fig. 8) are in close proportion to the number of aromatic carbon atoms in each solute molecule. The separated strong site hypothesis (13 Å spacing of sites) would predict that benzene is localized on a strong site, with its adsorption energy or $S°$ value some 3.2 units higher than for non-localized adsorption, and that the second four carbons of naphthalene are not localized with the increase in adsorption energy proportionately smaller (see discussion of adsorption of fused aromatic hydrocarbons on silica, ref. 14); this is clearly not the case. Moreover, the advantage of initial adsorption of an aromatic solute on a strong site, $\Delta S°$ equal 3.2 units, is actually much larger than the observed $S°$ value for benzene (1.86 units). These various considerations suggest that the adsorption of solutes less than 10 Å long do not experience strong localization, while for longer solutes some new adsorption phenomenon is becoming available for stabilizing the solute in the adsorbed phase. One possibility, for which there is no supporting physical evidence, is a concerted adsorption mechanism at two widely separated, *potentially* strong sites, where the adsorbing molecule actually serves as a bridge for interaction of the two sites. For example, an electron might be added to one end of the adsorbing solute, and removed from the other; or a positively and negatively charged site pair might be neutralized by interaction with the same adsorbed solute. Until additional information is uncovered about the fundamental aspects of this phenomenon, however, further speculation does not appear warranted.

Because the various Δ_i values in class I isomers are "unique" functions of eluent and adsorbent activity (Eqn. 5), these effects are grouped in the $\Sigma\Delta_{eas}$ term of Eqn. (2); that is, $\Delta_i = \Delta_{eas}$.

Class II and III isomers

It has already been noted that the Δ_{12} values of the solutes of Table VIII follow the same trends with isomer structure as in the haloaromatics and hydrocarbons of Tables I–VI: preferential adsorption of *ortho* and *para* disubstituted benzenes and 2-substituted naphthalenes. Several of the solutes of Table VIII, however,

do not obey Eqn. (5) with respect to the effect of adsorbent activity and eluent type upon relative isomer separation or Δ_{12} value. This suggests that for some of the solutes of Table VIII weak localization (as in the case of the haloaromatics and aromatic hydrocarbons) is not responsible for these differences in isomer adsorption. Previous studies[3] have established that solutes with one or more strongly adsorbing solute groups (e.g. methoxy, nitro, acetyl, etc.) tend to localize on strong adsorbent sites, with resultant delocalization of the remainder of the solute molecule. Thus, in a solute such as p-dimethoxy benzene, one methoxyl group tends to become attached to a strong site, with the remaining methoxyl group then delocalized. Strong localization effects of this sort should logically preclude weak localization as in the various solutes of Tables I–VI (e.g. as in Fig. 5). In the ortho disubstituted benzenes where one or both groups are strongly adsorbing, previous studies[6] have shown that an ortho arrangement of two adsorbing solute groups (class IIb) strongly increases solute adsorption energy by permitting simultaneous interaction of the two groups with a single site; the pronounced preferential adsorption of the ortho isomers of Table VIII suggests that the same phenomenon is involved with these solutes as well. The difference in adsorption between the meta and para isomers of Table VIII can reasonably be ascribed to electronic effects (class III) of the kind embodied in Fig. 3 and Eqn. (6), as may be seen from the calculated Δ_i and Δ_{12} values of Table VIII for these solutes, which assume electronic activation of the strongest adsorbing (localized) solute group by a meta or para substituent. The standard deviation of these calculated and experimental values is ± 0.14 units, and the experimental Δ_i and Δ_{12} values are plotted versus calculated values in Fig. 9. It seems clear from the latter plot that the major differences in the adsorption of these meta and para isomers are explained by simple electronic activation of the localized solute group. Similarly, it is possible to explain the weaker adsorption of the 1-substituted naphthalene derivatives of Table VIII by steric hindrance of the 8-hydrogen (class IIa), just as in the ortho methyl benzene derivatives of Fig. 4. The data of Fig. 9 do not include the chloro-
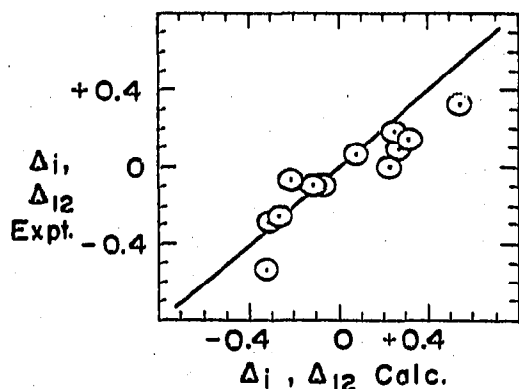

Fig. 9. Calculation of isomer electronic effects for solutes of Table VIII by Eqn. (6).

anilines of Table VIII, because these solutes are believed to adsorb by a dual acid-base mechanism[6], and the simple treatment implied in Eqn. (6) does not apply without elaboration. In the case of the benzcarbazole isomers, the preferential adsorption of the 1,2-isomer at lower adsorbent activities has previously been ascribed[9] to the fact that the pyrrole derivatives adsorb by proton transfer, and crowding the nitrogen

proton by *ortho* substitution as in 1,2-benzcarbazole increases the proton acidity and adsorption energy of the N–H group. The preferential adsorption of the 2,3-isomer at higher adsorbent activities appears to be the same sort of effect as noted in the *p*-polyphenyls and other solutes of Fig. 8; by comparison of the 2,3- and 3,4-isomers (where steric effects are absent) in terms of Fig. 8, with correction for the adsorbent activity and eluent type, we would calculate for 2.7 % $H_2O-Al_2O_3$ and methylene chloride eluent, Δ_{12} equal 0.49 (*versus* 0.33 experimental).

Since class II and III isomers appear to be free of "unique" eluent and adsorbent activity effects, their Δ_t and Δ_{12} values are grouped in the $\Sigma \, q°_j$ of Eqn. (2); *i.e.* $\Delta_t = \alpha \, q°_j$.

FURTHER VERIFICATION OF EQN. (1) FOR VARYING ADSORBENT ACTIVITY

For a given eluent and solute, the effect of varying adsorbent activity on solute retention volume is easily predicted from Eqn. (1). Given a value of $\underline{R}°$ at one adsorbent activity, the quantity $(S° - \varepsilon_t A_s)$ can be calculated (assuming $\Sigma \Delta_{eas} = 0$), and values of $\underline{R}°$ at other adsorbent activities estimated, using previously tabulated[5,10] values of the adsorbent parameters V_a and α. Previous tests of Eqn. (1) in this connection, however, have been largely limited to the aromatic hydrocarbons as solutes and only a few eluents (*e.g.* pentane, CCl_4, benzene) of weak to moderate strength. In view of the peculiar dependence of the hydrocarbon and haloaromatic Δ_{12} values on adsorbent activity (*i.e.* correlating with α_t rather than with α), it seems worthwhile to further evaluate the general accuracy of Eqn. (1) as regards dependence of $\underline{R}°$ on adsorbent activity. Table XII presents experimental $\underline{R}°$ data for 11 different solute/ eluent combinations at 3 or 4 different adsorbent activities. The solute and eluent types represented in Table XII cover a wide range of molecular structures and adsorption affinities. Values of $(S° - \varepsilon°A_s)$ for each solute/eluent combination were calculated from the $\underline{R}°$ values for 3.7 % $H_2O-Al_2O_3$, and are listed in Table XII. $\underline{R}°$ values for the remaining adsorbent activities were then calculated from Eqn. (1). These calculated $\underline{R}°$ values are included in Table XII, and the average standard deviations at each adsorbent activity between experimental and calculated $\underline{R}°$ values are shown at the bottom of Table XII. The uncertainty of the calculated $\underline{R}°$ values is seen to increase with decreasing adsorbent activity, as expected from the correspondingly greater extrapolation of Eqn. (1) involved. Deviations of calculated from experimental $\underline{R}°$ values appear randomly distributed, showing no trends with eluent type or $S°$ value of the solute; this suggests that Eqn. (1) is basically correct as regards the dependence of $\underline{R}°$ on adsorbent activity. Most previously reported data for LEAC separation have been determined for 3.7–4.0 % $H_2O-Al_2O_3$; the extrapolation of these $\underline{R}°$ values to higher adsorbent activities is seen from Table XII to involve an uncertainty of 0.1 to 0.2 log units. The system N-methyl-2-quinolone/ dioxane in Table XII, which is not included in the standard deviations at the bottom of Table XII, fits Eqn. (1) only poorly; the standard deviation for this system is over three times the average standard deviation for the remaining 10 solute/eluent systems of Table XII. Dioxane ($\varepsilon° = 0.56^*$) is considerably stronger than the remaining

---

*The value for dioxane has previously been reported[5] as somewhat higher (0.63). The present value (0.56) is believed to reflect greater purity of the dioxane used in acquiring the data of Table XII. This change in $\varepsilon°$ for dioxane has no effect on the calculations based on this eluent in preceding papers.

TABLE XII

TEST OF EQN. (1) FOR VARYING ADSORBENT ACTIVITY

Solute	Eluent	Log $\underline{R}^{\circ}$				$S^{\circ}-A_{s}\varepsilon^{\circ}$
		0.7% H_2O– Al_2O_3	1.7% H_2O– Al_2O_3	2.7% H_2O– Al_2O_3	3.7% H_2O– Al_2O_3	
Benzene (exptl.)	pentane	0.16	—0.05	—0.27	—0.53	1.92
(calc.)*		0.34	0.05	—0.23	—	
Naphthalene (exptl.)	pentane	1.36	1.05	0.61	0.24	3.09
(calc.)*		1.36	0.95	0.59	—	
Anisole (exptl.)	pentane	1.71	1.28	0.93	0.52	3.54
(calc.)*		1.73	1.28	0.89	—	
Phenanthrene (exptl.)	pentane	2.76	2.27	1.70	1.11	4.45
(calc.)*		2.54	2.00	1.55	—	
Phenanthrene (exptl.)	CCl$_4$	1.11	0.66	0.32	—0.13	2.54
(calc.)*		0.88	0.53	0.21	—	
6-Chloroquinoline (exptl.)	benzene		1.24	0.75	0.45	3.43
(calc.)*			1.21	0.83	—	
Quinoline (exptl.)	ethyl ether	0.72	0.48	0.22	—0.05	2.66
(calc.)*		0.98	0.62	0.29	—	
Dimethylphthalate (exptl.)	CH$_2$Cl$_2$		0.51	0.19	—0.08	2.62
(calc.)*			0.59	0.26	—	
p-Nitroaniline (exptl.)	CH$_2$Cl$_2$	1.94	1.35	0.99	0.46	3.45
(calc.)*		1.67	1.23	0.85	—	
Carbazole (exptl.)	benzene	1.85	1.48	1.13	0.51	3.52
(calc.)*		1.73	1.28	0.89	—	
N-Methyl-2-quinolone (exptl.)	dioxane	0.47	0.13		—0.04	2.68
(calc.)*		1.00	0.63		—	
Standard deviation between calculated and experimental values**		±0.20	±0.15	±0.12		

* Using Eqn. (1) and value of $(S^{\circ}-A_{s}\varepsilon^{\circ})$ calculated from $\underline{R}^{\circ}$ for 3.7% H_2O–Al_2O_3.

** Ignores values for N-methyl-2-quinolone eluted by dioxane.

eluents of Table XII ($\varepsilon^{\circ} \leqslant 0.42$), suggesting that Eqn. (1) may become less accurate for extrapolation of $\underline{R}^{\circ}$ values to higher adsorbent activity when eluent strength exceeds some intermediate value ($\varepsilon^{\circ} \sim 0.5$).

It is theoretically reasonable that the actual change in $\underline{R}^{\circ}$ for dioxane as eluent is less than predicted, since as the strength of the eluent continues to increase it must eventually begin to compete with water for the strongest adsorption sites. Ultimately, in the case of eluents as strong as water, water deactivation of the adorbent would have *no* effect on activity or $\underline{R}^{\circ}$.

An additional test of Eqn. (1) with respect to varying adsorbent activity is provided by values of $\alpha\varepsilon^{\circ}$ calculated from the data of Tables III–V for the weaker adsorbing hydrocarbon isomers (phenanthrene, triphenylene, and 1,2,3,4-dibenzanthracene, where Δ_{12} does not form part of the calculation of $\underline{R}^{\circ}$). These experimental $\alpha\varepsilon^{\circ}$ values can be compared with values calculated from ε° values for the pure eluents, or from Eqn. (8) (see ref. 2) for binary eluents:

$$\alpha\varepsilon^{\circ}_{AB} = \alpha\varepsilon^{\circ}_{A} + \frac{\log X_B 10^{\alpha n_b(\varepsilon^{\circ}_B - \varepsilon^{\circ}_A)} + 1 - X_B}{n_b} \qquad (8)$$

X_B refers to the mole fraction of the stronger eluent component in the binary, n_b is

the A_s value of the strong eluent component, and $\varepsilon°_{AB}$, $\varepsilon°_A$, and $\varepsilon°_B$ refer, respectively, to the $\varepsilon°$ values of the binary, of the weak eluent, and of the strong eluent. Eqn. (8) accurately describes the $\alpha\varepsilon°$ values of binary eluents for adsorption on 3.5–4.0 % H_2O–Al_2O_3 (*e.g.* 2.5). Experimental and calculated values of $\alpha\varepsilon°$ from Tables III–V for 0.7 and 2.7 % H_2O–Al_2O_3 are compared in Fig. 10. With the exception of data for the acetone–pentane and pyridine–pentane mixtures (crosses), reasonable agreement is observed between experimental and calculated $\alpha\varepsilon°$ values. The average error
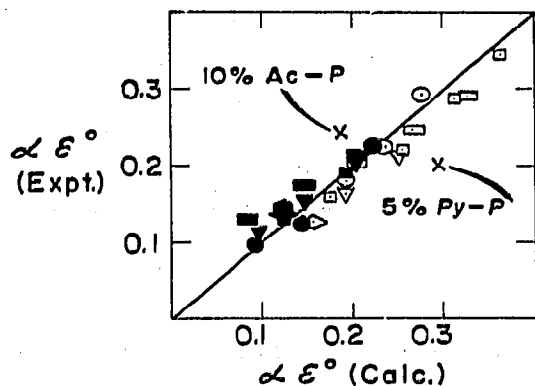

Fig. 10. Calculation of eluent strength for various eluents of Tables III–V. 0.7% H_2O–Al_2O_3: ⊙ = benzene–pentane binaries; ◇ = CCl_4–pentane binaries; ☐ = CH_2Cl_2–pentane binaries; ▽ = isopropyl chloride–pentane binaries; ▭ = ethyl ether–pentane binaries. 2.7% H_2O–Al_2O_3: ● = benzene–pentane binaries; ◆ = CCl_4–pentane binaries; ■ = CH_2Cl_2–pentane binaries; ▼ = isopropyl chloride–pentane binaries; ▰ = ethyl ether–pentane binaries; ◕ = phenetole–pentane binaries; × = acetone–pentane and pyridine–pentane binaries.

in the calculated values is 0.022 units, corresponding to an uncertainty in log $R°$ for the average solute of about 0.2 units. This compares closely to the uncertainty in calculated values of Table XII for adsorption on 0.7–2.7 % H_2O–Al_2O_3. No trends in the error of calculated values with eluent strength or adsorbent activity can be distinguished in Fig. 10. In the case of the binaries containing the very strong eluents pyridine ($\varepsilon° = 0.71$) and acetone ($\varepsilon° = 0.56$), the calculated $\alpha\varepsilon_i$ values are less accurate again suggesting the inapplicability of Eqn. (1) in predicting changes in $R°$ for changing adsorbent activity, when very strong eluents ($\varepsilon° > 0.5$) are involved.

ACKNOWLEDGEMENTS

GLOSSARY OF TERMS

A_s	= Solute surface volume, approximately proportional to area required by solute upon adsorption.
$f(Q°_k)$	= Localization function for solute strong adsorbing group k.
n_b	= Value of A_s for the strong eluent in a binary eluent solution.
$q°_j$	= Solute geometry factor.

Q°_i, Q°_x = Adsorption energy of solute groups i and x from pentane onto calcined adsorbent.

$\underline{Q}^\circ_i$ = Intrinsic adsorption energy of group i, equal Q°_i corrected for activation of benzene ring attached to i.

$\underline{r}$ = Ratio of retention volumes for two isomers, $\underline{r} = R_1/R_2$.

$\underline{R}^\circ$ = Solute linear equivalent retention volume (ml/g).

R_p = Value of $\underline{R}^\circ$ for pentane eluent.

R_1, R_2 = Values of $\underline{R}^\circ$ for isomers 1 and 2.

s_y = Steric factor proportional to size of group Y; see Eqn. (7).

S° = Solute adsorption energy from pentane onto calcined adsorbent.

S_i = Solute geometry factor for weak localization; $\alpha\Delta_i = \alpha\varepsilon_i S_i$, analogous to Eqn. (5).

S_{12} = Difference in S_i values for isomers 1 and 2; see Eqn. (5).

X_B = Mole fraction of strong eluent B in binary eluent mixture.

X, Y = Solute groups.

V_a = Adsorbent surface volume (ml/g).

α = Adsorbent activity function.

α_i = Adsorbent activity function for isomer effects arising from weak localization; see Eqn. (5).

Δ_i = Solute geometry factor, equal $\alpha \overset{j}{\Sigma} q^\circ_j + \Sigma \Delta_{cas}$; defined in Eqn. (3).

$(\Delta_i)_1, (\Delta_i)_2$ = Values of Δ_i for isomers 1 and 2.

Δ_{12} = $(\Delta_i)_1 - (\Delta_i)_2$; see Eqn. (4).

Δ_c = Value of q°_j arising from electronic interaction of two solute groups X and Y; see Eqn. (6); called $\Delta_{x,y}$ in part X.

Δ_s = Value of q°_j arising from steric interaction of two solute groups X and Y; see Eqn. (7).

ε° = Eluent strength parameter.

ε°_{AB} = Eluent strength of binary solution (A–B).

$\varepsilon^\circ_A, \varepsilon^\circ_B$ = Eluent strengths of solvents A and B.

ε_i = Eluent–isomer parameter for relating weak localization effects to eluent type; see Eqn. (5).

$\theta_{0.1}$ = Adsorbent linear capacity (ml/g).

σ = HAMMETT function[16].

σ_y = Value of σ for solute group Y which is electronically activating group X.

$\overline{\Delta_i/\alpha_i}$ = Average value of Δ_{12}/α_i for one isomer pair–eluent type combination; equal $\Sigma \Delta_{12}/\Sigma \alpha_i$.

SUMMARY

The separation on alumina of a number of isomeric aromatic hydrocarbons and their substituted derivatives has been investigated. Several factors which affect the relative separation of such isomers have been established. For solutes without strongly adsorbing groups ($Q^\circ_i > 1$), there is a marked tendency for the adsorption of the longest isomer, and the relative separation of such isomers is strongly dependent upon both the eluent type and adsorbent activity used. Solutes with strongly adsorbing groups show a general preference for the adsorption of that isomer in which electron donation to the strongest adsorbing group by other solute groups is greatest.

Ortho isomers (where adsorbing solute groups sterically interact) may be more or less strongly adsorbed than other isomers: where two adsorbing groups are *ortho* to one another (*e.g. o*-dichlorobenzene), adsorption of the isomer is generally increased.; where one of the *ortho* groups is non-adsorbing (*e.g. o*-chlorotoluene), adsorption of the isomer is generally decreased. Alumina containing 2.5–3 % water appears optimum for the separation of aromatic isomers. The separation of polynuclear aromatic hydrocarbons on alumina is discussed. The effect of adsorbent activity on other separations over alumina has been re-examined, and earlier conclusions have been largely confirmed. An effort has been made to further elucidate the various mechanisms of adsorption on alumina.

REFERENCES

1 L. R. SNYDER, *J. Chromatog.*, 6 (1961) 22.
2 L. R. SNYDER, *J. Chromatog.*, 8 (1962) 178.
3 L. R. SNYDER, *J. Chromatog.*, 8 (1962) 319.
4 L. R. SNYDER, *J. Chromatog.*, 15 (1964) 344.
5 L. R. SNYDER, *J. Chromatog.*, 16 (1964) 55.
6 L. R. SNYDER, *J. Chromatog.*, 17 (1964) 73.
7 L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 234.
8 L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 240.
9 L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 2344.
10 L. R. SNYDER, *Adv. Anal. Chem. Instr.*, 3 (1964) 251.
11 L. R. SNYDER AND E. R. FETT, *J. Chromatog.*, 18 (1965) 461.
12 H. HOYER, *Chem. Ber.*, 86 (1953) 1016.
13 E. SAWICKI, *Chem. Anal.*, 53 (1964) 24; *ibid.*, 56; *ibid.*, 88.
14 L. R. SNYDER, *J. Phys. Chem.*, 67 (1963) 2622.
15 A. H. SPORER AND K. N. TRUEBLOOD, *J. Chromatog.*, 2 (1959) 499.
16 L. P. HAMMETT, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, p. 186.
17 A. STREITWIESER, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961, p. 54.
18 L. PAULING, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1940, Chap. V.
19 L. R. SNYDER, *J. Chromatog.*, 11 (1963) 195.