

LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

III. FURTHER DELINEATION OF THE ELUENT
ROLE IN SEPARATIONS OVER ALUMINA

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INTRODUCTION

Part II in the present series¹ developed a preliminary theoretical model for the correlation and prediction of compound separability in linear elution adsorption chromatographic (LEAC) systems. Solute linear equivalent retention volumes \underline{R}° (ml of eluent per g of adsorbent) were related to adsorbent surface volume V_a and activity α , eluent strength or "polarity" ε° , and solute structure through the fundamental relationship:

$$\log \underline{R}^\circ = \log V_a + \alpha \left(\sum^i Q^\circ_i + \sum^j q^\circ_j - \varepsilon^\circ \sum^i \delta_i \right) \quad (1)$$

For each structural group i of the solute, Q°_i is a constant defined by the group. The summation is over all such groups in the solute. One or more q°_j terms may be required for certain specific solute geometries. $\sum^i \delta_i$ is approximately the molar volume of the solute, with exceptions in some cases. Part II presented a number of experimental \underline{R}° data for elution from alumina, where all of the terms of equation (1) were varied. These data were semi-quantitatively correlated through this relationship.

The application of equation (1) to the understanding and prediction of adsorption separation phenomena requires that each of the experimental parameters be evaluated for chromatographic systems of interest. Values of α and V_a were tabulated in Part II for samples of Alcoa F-20 activated alumina of varying water content. Values of the other parameters for elution from this adsorbent were presented for a few eluents and solute types. It is the purpose of the present paper to extend the application of equation (1) with respect to the effect of eluent on \underline{R}° ; this involves the calculation of the eluent term $\alpha \varepsilon^\circ \sum^i \delta_i$. ε° values for additional eluents have been measured, the use of binary eluents has been examined, and the calculation of $\sum^i \delta_i$ has been further tested. Part IV² in this series will round out the characterization of Alcoa F-20 alumina as an adsorbent by undertaking a corresponding study of the solute parameters Q°_i and q°_j .

EXPERIMENTAL

The acquisition of experimental LEAC \underline{R}° data has been discussed in detail in Part II. In the present investigation, \underline{R}° ratios in two eluent systems are frequently reported,

rather than individual \underline{R}° values. The individual retention volumes determining these ratios, when not presented in this paper, are given in Part IV. Linearity was not tested in the case of most of the individual solutes reported in this and the following paper, since this would have greatly increased the required work. Rather, it was found for a small number of widely differing solutes that the adsorbent linear capacity was very close to $2 \cdot 10^{-1}$ g/g for 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$. \underline{R} data for other solutes in this adsorbent system were then obtained at column loadings below this linear capacity (10^{-5} to $5 \cdot 10^{-5}$), and are believed linear well within the criterion previously advanced ($\underline{R}^\circ > \underline{R} > 0.9 \underline{R}^\circ$). A similar approach was employed for the data using other adsorbent activities. As a further aid in minimizing experimental work, each column of adsorbent was used for only one \underline{R}° measurement and then rejected. This eliminated the need to check the adsorbent activity changes with continued elution through the column (as in Part II).

The eluents used in the present study were reagent grade or 99 % pure commercial samples, further purified by percolation over a suitable calcined adsorbent: silica for saturate eluents, alumina for other eluents. The adsorbent, Alcoa F-20 alumina, had an average BET surface area of 190 ± 15 m²/g after calcining at 400° for 8-16 h. Water deactivated adsorbent was made up from calcined material and tested for relative activity by means of \underline{R}° for the elution of naphthalene by *n*-pentane (as in Part II). The individual solutes were commercial samples or our own synthetic products. Solute detection in the eluate was accomplished in most cases by adsorption measurements at a suitable wavelength in the ultraviolet. In special cases where solute absorptivity was too low, complex formation (e.g., with iodine in the elution of the alkyl sulfides) or chemical reaction (e.g., with anisaldehyde for the detection of acetone) to give strongly absorbing species was employed.

THE PREDICTION OF LEAC RETENTION VOLUME DATA

The present paper is concerned primarily with modifications and extensions of the preceding treatment of the eluent term of equation (1): $\alpha \varepsilon^\circ \sum_i \delta_i$. In Part II, δ_i for each solute atom *i*, exclusive of hydrogen, was assumed equal to one for elements in the first row of the periodic table, and three (or larger) for elements of higher atomic number. Saturated carbon atoms, where it was possible for them to lie in the solution phase, were assumed to do so for elution by eluents stronger than the saturates. Thus, δ_i for an alkyl group attached to an aromatic nucleus was assumed equal to one, since only one alkyl carbon is constrained to the adsorbed phase. In the case of the benzene elution of the aromatic hydrocarbons, an empirical adjustment of equation (1) was required: the eluent term was set equal to zero, and six aromatic carbons were not counted in the summation $\sum_i Q^\circ_i$.

Significant improvements in the old approximation to solute surface volume $\sum_i \delta_i$ have since been realized from the study of additional experimental data. In the resulting revised correlational procedure, the various atoms in aromatic rings, exclusive of substituents and hydrogen atoms, are first counted, and δ_i is assumed equal to one for the first six such atoms, and one-half for additional atoms. The naphthalene nucleus thus has a value of $\sum_i \delta_i$ equal to 8, the biphenyl nucleus 9, the benzothiophene nucleus $7\frac{1}{2}$, and so forth. Substituent groups *i* will have δ_i values

approximately equal to the sum of atoms exclusive of hydrogen; e.g., one for amino, four for carbomethoxy, etc. However, in some cases more precise values of δ_i for substituent groups have been experimentally evaluated. Table I summarizes some of these preferred values. The preferred values of Table I are all within one unit of the approximate rule (sum of non-hydrogen atoms) for estimating δ_i of substituents.

α,ω -Disubstituted alkanes may be anchored to the adsorbent surface at both

TABLE I
ATOM OR GROUP CONTRIBUTIONS δ_i TO SOLUTE SURFACE VOLUME $\sum_i \delta_i$

Group	δ_i	
	Preferred ^a	Calculated from solute molar volume
Hydrogen atom	0	
Aromatic atoms exclusive of hydrogen		
first six atoms in rings (type 1)	1 ^b	(1)
additional atoms in rings past first six (types 2 and 4)	1/2 ^b	0.5-0.6
Other atoms exclusive of hydrogen (type 3)	1 ^b	0.9
Nitro —NO ₂	2 1/2 ^c	0.9
Ester —CO ₂ R	3 ^c	2.5 ^d
Alkoxy —OR	2 ^c	1.3 ^d
Formyl —CHO	1 ^b	0.8
r-Thia-alkyl—SR	2 1/2 ^c	
Cyano —CN	2 ^c	0.9
Amino —NH ₂	1 1/2 ^c	0.2
Methylene ^e —CH ₂ —	1 ^c	
Keto —COR	2 ^c	
Fluoro —F		0.3
Chloro —Cl		0.8
Bromo —Br		1.0
Iodo —I		1.5
Alkyl —C _p H _{2p+1}	p ^e 1 ^f	

^a For use in equation (1) where data exist; otherwise, δ_i per non-hydrogen atom equal 1.

^b From density data of Table III.

^c Average of experimental \bar{R}° data using eqn. (1) and data of Table III.

^d For R equal methyl.

^e For alkyl chains constrained to adsorbed phase.

^f For alkyl groups constrained at only one end to the adsorbed phase.

ends of the paraffin chain by strongly adsorbing groups. The previous treatment did not consider the possibility that some of these alkyl carbons might lie in the solution phase through puckering of the alkyl chain in the middle. Data have since been acquired which indicate that, for anchored alkyl chains up to ten carbons in length, puckering is unimportant in the eluent systems studied; i.e., all such alkyl carbon atoms lie in the adsorbed phase.

A number of examples of the calculation of $\sum_i \delta_i$ by the new procedure are given in Table IV.

With the present revisions in the method of calculating $\sum_i \delta_i$, the empiricism is removed from the application of eqn. (1) to the elution of certain classes of solutes (such as the aromatic hydrocarbons) by special eluents (such as benzene); that is, these chromatographic systems need no longer be treated as special cases.

In Table II, ϵ° values are given for a number of different eluents which cover a wide range in type and strength. The value of ϵ° for CCl_4 (0.18) is different than that given in Part II (0.13); this reflects the present improvements in the $\sum \delta_i$ calculation. A major eluent type not represented in Table II is the class of solvents possessing active hydrogens, such as alcohols, thiols, and organic acids. It is known that these eluent types are quite strong, but their fundamental mode of adsorption is probably different

TABLE II
ELUENT PROPERTIES

Eluent	Strength ϵ°	Relative band width ^a	Ultraviolet cut off $m\mu$	n_D
<i>n</i> -Pentane	(0.00)	(1.0)	< 210	5
Isooctane (2,2,4-trimethylpentane)	0.007	1.7	< 210	8
<i>n</i> -Hexane	0.015	1.5	< 210	6
<i>n</i> -Octane	0.013	—	< 210	8
Cyclohexane	0.036	1.7	< 210	6
<i>n</i> -Decane	0.039	1.9	< 210	10
Cyclopentane	0.053	1.4	< 210	5
Carbon tetrachloride	0.18	1.9	260	4 ^b
Carbon bisulfide	0.26 ^c	—	380	3
Isopropyl chloride	0.29 ^c	—	255	2
Toluene	0.29 ^c	—	285	7
<i>n</i> -Propyl chloride	0.30 ^c	1.4	225	2
Benzene	0.32	2.3	280	6
Di-isopropyl ether	0.36 ^c	—	240	3
Chloroform	0.40	—	245	4
Methylene chloride	0.42	—	235	3
Ethyl ether	0.46	—	210	3
Ethyl acetate	0.60	—	250	4
Dioxane	0.63	1.6	250	6
Pyridine	0.65 ^d	—	300	6

^a 400 mm columns of 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$; eluent flow rate equal 250 mm/min.

^b Does not include one Cl atom, since only three of the four can be accommodated in the adsorbed phase.

^c Averages for limited, unreported, data.

^d Extrapolated from polarities of pyridine-pentane solutions by means of eqn. (2).

than the eluents represented in Table II, and their inclusion in eqn. (1) is questionable. Thus it is possible that different adsorption sites are effective in the adsorption of hydroxylated molecules, or that only a fraction of the total adsorbate lies in the adsorbed phase³. In addition, the possibility of interaction with or replacement of adsorbent water of deactivation complicates their study. Their experimental and theoretical examination will be reserved for the future.

As is discussed in a following section, binary eluents are not comparable in all respects to single component eluents. At a particular adsorbent activity, a binary eluent has a unique value of ϵ° , but in general this value of ϵ° decreases with decreasing adsorbent activity. In contrast, the ϵ° values of single component eluents remain constant at all adsorbent activities, as required by eqn. (1). The product of the binary

eluent strength and the adsorbent activity, $\alpha\varepsilon^{\circ}_{AB}$, which is the effective eluent strength for a particular adsorbent activity, can be calculated from the strengths of the pure eluents composing the binary through eqn. (2):

$$\alpha\varepsilon^{\circ}_{AB} = \alpha\varepsilon^{\circ}_A + \frac{\log [X_B \cdot 10^{\alpha n_b (\varepsilon^{\circ}_B - \varepsilon^{\circ}_A)} + 1 - X_B]}{n_b} \quad (2)$$

The derivation and validity of eqn. (2) is discussed in a following section. Here, ε°_A and ε°_B refer to the strengths of the single eluents A and B which make up the binary, B being the stronger of the two. X_B is the mole fraction of B in the binary, and n_b is the stronger eluent's surface volume, $\sum \delta_i$. Values of n_b for the various eluents of Table II are listed there.

Application of the present "rules" and the data of Tables I and II in calculating the eluent term of eqn. (1) requires an expression for the effect of eluent variation on \underline{R}° . If \underline{R}°_A and \underline{R}°_B are the retention volumes of a given solute in the eluent systems A and B, the adsorbent activity remaining constant, it follows from eqn. (1) that

$$\log (\underline{R}^{\circ}_A / \underline{R}^{\circ}_B) = \alpha (\varepsilon^{\circ}_B - \varepsilon^{\circ}_A) \sum \delta_i \quad (3)$$

Calculated eluent terms, $\alpha\varepsilon^{\circ} \sum \delta_i$, can thus be compared with experimental values of $\log (\underline{R}^{\circ}_A / \underline{R}^{\circ}_B)$ through eqn. (3). Five examples follow.

First, consider the elution of the solute coronene, $C_{24}H_{12}$, from 3.7% $H_2O-Al_2O_3$ by the eluents CCl_4 (A) and benzene (B). All twenty-four aromatic carbons of the solute are in rings, so $\sum \delta_i = 6(1) + 18(1/2) = 15$. From Table II, ε°_A and ε°_B equal 0.18 and 0.32, respectively. α for 3.7% $H_2O-Al_2O_3$ is 0.65 (Part II), so

$$\begin{aligned} \log (\underline{R}^{\circ}_A / \underline{R}^{\circ}_B) &= 0.65 (0.32 - 0.18) (15) \\ &= 1.36. \end{aligned}$$

In this case, an experimental value of 1.35 was observed.

In a second example, the solute 6-methoxyquinoline is eluted from 3.7% $H_2O-Al_2O_3$ by the eluents benzene (A) and methylene chloride (B). Here, 10 aromatic atoms exclusive of hydrogen are in rings, thus contributing 8 units to $\sum \delta_i$. The methoxy group has a value of 2 (Table I) so $\sum \delta_i$ for the total solute equals 10. From Table II, ε°_A and ε°_B equal 0.32 and 0.42, respectively, and

$$\begin{aligned} \log (\underline{R}^{\circ}_A / \underline{R}^{\circ}_B) &= 0.65 (0.42 - 0.32) (10) \\ &= 0.65. \end{aligned}$$

An experimental value of 0.52 was found.

In a third example, consider the elution of the solute 1,12-diphenyl-1,12-dithia-dodecane ($C_6H_5-S-C_{10}H_{20}-S-C_6H_5$) from 3.7% $H_2O-Al_2O_3$ by *n*-pentane (A) and carbon tetrachloride (B). For doubly "anchored" alkyl chains of lengths as great as 10 carbons, we note that puckering of the alkyl chain does not occur, so if both ends of the solute are in the adsorbed phase, the two phenyl rings contribute 9 to $\sum \delta_i$, and the 10 methylene carbons and two sulfur atoms one each for a total $\sum \delta_i$ of 21. We shall

see additional evidence (Part IV²) to show that this solute is in fact constrained at both ends to the adsorbed phase. From Table II, ε°_A equals 0.00 and ε°_B equals 0.18, so that

$$\begin{aligned}\log (\underline{R}^{\circ}_A/\underline{R}^{\circ}_B) &= 0.65 [0.18 (21)] \\ &= 2.46\end{aligned}$$

An experimental value of 2.36 was observed, and this furnishes a check on the configuration of the adsorbed solute, since with only one end anchored to the adsorbent surface, $\sum \delta_i$ would have been equal to 8^{1/2} and $\log (\underline{R}^{\circ}_A/\underline{R}^{\circ}_B)$ would then have been only 1.00.

In a fourth example, let the solute phenanthrene be eluted from calcined alumina by the eluents 18.6 mole % benzene-pentane (A) and benzene (B). In this case, $\sum \delta_i$ for the solute is equal to 10, and $\alpha = 1.00$ (Part II). ε°_B is 0.32 from Table II and ε° for *n*-pentane is 0.00. $\alpha\varepsilon^{\circ}_A$ must be calculated from eqn. (2):

$$\begin{aligned}\alpha\varepsilon^{\circ}_A &= 0.00 + \frac{\log (0.186 \times 10^{(1.0)} (6) (0.32 - 0.00) + 1 - 0.186)}{6} \\ &= 0.203.\end{aligned}$$

Now,

$$\begin{aligned}\log (\underline{R}^{\circ}_A/\underline{R}^{\circ}_B) &= (\alpha\varepsilon^{\circ}_B - \alpha\varepsilon^{\circ}_A) (\sum \delta_i) \\ &= (1.0 \times 0.32 - 0.203) (10) \\ &= 1.17.\end{aligned}$$

The experimental value was 1.31.

In a final example, consider the elution of the solute di-*n*-hexadecyl phthalate from 3.7 % H₂O-Al₂O₃ by the eluents 37.7 mole % methylene chloride-pentane (A) and benzene (B). In this case the alkyl groups are anchored at one end only so that δ_i for each ester group is given as 3 from Table I, and $\sum \delta_i$ for the entire solute is then 12. The value of $\alpha\varepsilon^{\circ}$ for the binary eluent 37.7 mole % methylene chloride-pentane in systems using 3.7 % H₂O-Al₂O₃ can be calculated in the above manner as 0.163, while ε° for benzene is 0.32. Thus,

$$\begin{aligned}\log (\underline{R}^{\circ}_A/\underline{R}^{\circ}_B) &= (0.65 \times 0.32 - 0.163) (12) \\ &= 0.54.\end{aligned}$$

An experimental value of 0.68 was found.

It will frequently be necessary to control the \underline{R}° value of a specific solute, either through changes in eluent strength or adsorbent activity. Thus, solutes which are required to be separated from less strongly adsorbed material *must* have \underline{R}° values greater than about one, while solutes which are to be separated from more strongly adsorbed material should have \underline{R}° values less than 25-100 for experimental convenience. The preceding discussion provides a basis for choosing a single or binary eluent on the basis of effective strength. In general, it may also be required that the eluent used be transparent at some wavelength in the visible or ultraviolet. Table II summarizes the ultraviolet cut off wavelengths for the solvents listed. Below the wavelength shown, solvent absorbance is greater than 90 % and in most cases is approaching 100 % very rapidly.

Little has been said in the present series of papers about column separation efficiency or solute band width, except to relate it to adsorbent linear capacity⁴. The relative importance of separation efficiency in determining compound and compound class separation has been discussed elsewhere⁵. LEAC separation efficiency is less important in compound class than, in compound separations, separation efficiency increases with decreasing eluent flow rate, and, in accordance with theory, solute band width divided by retention volume is approximately constant for all solutes under the same separation conditions and decreases with the square root of column length. In Table II, some relative band width data are tabulated for chromatographic systems which are comparable except for the eluent used. In general, it is found that separation is much better using eluents of low boiling point or low viscosity. Thus, those eluents in Table II with boiling points below 70° have relative band widths less than 1.6, and give reasonably sharp bands for convenient flow rates and column lengths. Higher boiling eluents have relative band widths greater than 1.6, and show sharp separation of individual solutes only when the flow rate is made inconveniently slow or the columns excessively long. In the case of binary eluents, band widths intermediate between the two constituent solvents are to be expected. The use of binary eluents therefore provides additional flexibility with respect to controlling separation efficiency.

SOLUTE SURFACE VOLUME, $\sum \delta_i$

The solute surface volume $\sum \delta_i$ is proportional to the surface area covered by the adsorbed solute. In general, it should approximate the solute molar volume *when* all solute groups are attached to the adsorbent surface. We have previously estimated the value of $\sum \delta_i$ for a solute by the sum of atom contributions, δ_i , the effective surface volume of each atom *i* of the solute. On the basis of covalent radii, it was assumed that δ_i equals zero for hydrogen, one for first row elements of the periodic table (carbon, nitrogen, etc.), and larger values for elements of higher atomic number. While this method of calculating δ_i gives semiquantitative correlation of most of the experimental R° data presented in the previous paper, an exception is noted in the case of aromatic hydrocarbons eluted by benzene. In this case it is empirically required that the eluent term— $\epsilon^\circ \sum \delta_i$ —of equation (1) be ignored, that the number of solute aromatic carbons used in calculating $\sum Q^\circ_i$ be reduced by six, and that the Q°_i value for aromatic carbon be reduced from 0.31 to 0.14.

As will be seen, a reconsideration of the basis for calculating $\sum \delta_i$ can resolve the above paradox in the case of the benzene elution of aromatic hydrocarbons, and improve the accuracy of calculating the eluent contribution to retention volume in other chromatographic systems. Consider the solutes of Table III. Each is a completely pi-bonded hydrocarbon for which densities in the liquid state are known or can be calculated at a common temperature, 100°. It is presumed that each of these compounds is planar in the adsorbed state. Since the same atom (carbon) in the same bonding state (sp^2) makes up the skeleton of each of these compounds, it may be assumed that the thickness of the space occupied by the adsorbed molecule will be constant for each. Molar volumes calculated from the densities of the pure liquids should therefore be proportional to adsorbate molar surface volume, since in solution the relative thickness of the space occupied by each of these molecules will also be

constant. The thicknesses of adsorbed and solution configurations need not be the same for this proportionality to hold, and probably are not. Four types of atoms (exclusive of hydrogen) can be defined in these and other aromatic systems: (1) those constituting the first unfused ring system, such as the six carbons of benzene, or the first six-membered ring of a condensed multi-ring molecule, such as six of the ten carbons in naphthalene; (2) those additional atoms in a fused polycyclic aromatic beyond the initial six, such as the remaining four of naphthalene; (3) acyclic atoms,

TABLE III
ATOM CONTRIBUTIONS TO MOLAR VOLUME IN THE LIQUID STATE

Compound	Molar volume of liquid at 100° (ml/mole)	Volume per mole-atom of aromatic carbon (ml/mole)			
		(1) First ring	(2) Additional fused rings	(3) Acyclic groups	(4) Additional non-fused rings
Benzene	98.6 ^a	16.4	—	—	—
Naphthalene	133.4 ^a	(16.4)	8.7	—	—
Phenanthrene	167.4 ^b	(16.4)	8.6	—	—
Styrene	127.0 ^a	(16.4)	—	14.2	—
Biphenyl	159.0 ^a	(16.4)	—	—	10.1

^a Calculated from extrapolated liquid density data at lower temperatures^d.

^b Calculated from the compound density at 100°^e.

such as the two side chain atoms of styrene; (4) atoms present in additional unfused rings, as in the second six aromatic carbons of biphenyl or diphenylmethane. Mole-atom volumes in the liquid state at 100°, proportional to atom contributions to solute molar surface volume, have been calculated for aromatic carbon in these four types as shown in Table III. The contributions of individual hydrogens are lumped in with the carbon contributions, in accordance with previous practice. In the case of type (1) carbons, the six of benzene all fall in this category, from which a value of the mole-atom volume can be calculated, equal to 16.4 ml/mole (98.6/6). Similarly, the mole-volume of a type (2) carbon can be calculated from the value for a type (1) atom and the molar volumes of naphthalene or phenanthrene. As seen in Table III, the values obtained for type (2) carbon are essentially identical for both compounds. Completing the calculation for types (3) and (4) carbon atoms, it is noted that the mole-volumes of types (1) and (3) atoms are essentially identical, while those of types (2) and (4) atoms are very close to one-half as great. Because of the anticipated proportionality between liquid and adsorbed solute volumes, δ_t for types (1) and (3) carbon atoms may be defined as unity, while for types (2) and (4) atoms it can be assumed equal to one-half.

Generalizing from these data, comparable values of δ_t might be assigned to atoms other than aromatic carbon in these various type classifications. The use of solute density and derived molar volume data as in Table III can be extended to other types of atoms or groups in order to calculate relative δ_t values, but the factors which have been cited in defense of such a procedure for the compounds of Table III no longer apply to compounds composed of other atoms or bonding states. Thus, the covalent thickness of such atoms can no longer be assumed constant, since atomic radius varies with both atomic number and bonding state, while the solution thickness of particular

TABLE IV

 EXPERIMENTAL AND CALCULATED RETENTION VOLUME RATIOS FOR VARIOUS ELUENT PAIRS
 3.7% H₂O-Al₂O₃

Solute	$\sum \delta_i$	Log (R°_A/R°_B)					
		Pentane-CCl ₄		CCl ₄ -benzene		Benzene-CH ₂ Cl ₂	
		Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
Benzaldehyde ^a	7	0.80	0.82				
3,6-Dithiaoctane	7	1.10	0.82				
Aniline	7 ^{1/2}			0.71	0.68	0.62	0.49
Naphthalene ^a	8	0.85	0.94				
Acetophenone	8	1.02	0.94	0.66	0.73		
Benzonitrile	8			0.74	0.73		
Quinoline	8			0.60	0.73	0.40	0.52
Isoquinoline	8			0.49	0.73		
3,7-Dithia-nonane	8	1.08	0.94				
Nitrobenzene	8 ^{1/2}	0.89	0.94				
Acenaphthylene ^a	9	1.05	1.05				
Methyl benzoate	9	0.94	1.05				
<i>p</i> -Dimethylamino-benzaldehyde	9 ^b					0.65	0.59
1-Methoxynaphthalene	10	0.97	1.17				
2-Methoxynaphthalene	10	1.14	1.17				
6-Methoxyquinoline	10					0.52	0.65
Phenanthrene ^a	10	1.15	1.17				
Anthracene ^a	10	1.19	1.17				
1-Acetonaphthone	10			0.92	0.91		
2-Acetonaphthone	10			0.78	0.91		
<i>o</i> -Nitroanisole	10			1.00	0.91		
<i>p</i> -Nitroanisole	10	1.10	1.17				
<i>p</i> -Diethoxybenzene	10	1.15	1.17				
Phenylacetic acid, methyl ester	10	1.08	1.17				
Phenanthridine	10			0.67	0.91		
Acridine	10			0.59	0.91		
Benzophenone	10	1.17	1.17				
3,9-Dithia-undecane	10	1.19	1.17				
1-Nitronaphthalene	10 ^{1/2}	1.10	1.23				
2-(1- <i>n</i> -Thiapropryl)-naphthalene	10 ^{1/2}	1.23	1.23				
6-Nitroquinoline	10 ^{1/2}			1.07	0.96	0.70	0.69
<i>p</i> -Nitrobenzonitrile	10 ^{1/2}					0.68	0.69
Fluoranthene ^a	11	1.25	1.29				
Methyl 1-naphthoate	11			1.06	1.00		
Pyrene	11	1.25	1.29				
<i>m</i> -Dinitrobenzene	11	1.13	1.29	1.18	1.00		
1-Azapyrene	11			0.92	1.00		
Methyl <i>p</i> -nitrobenzoate	11 ^{1/2}	1.05	1.35				
Triphenylene ^a	12	1.30	1.36				
Chrysene ^a	12	1.38	1.36				
Dimethyl phthalate	12					0.66	0.78
3,4-Benzacridine	12			1.02	1.09		
3,4-Benzopyrene	13	1.67	1.52	1.14	1.18		
Picene	14			1.48	1.27		
1,5-Diphenyl-1,5-dithia-pentane	14	1.73	1.64				
3,14-Dithia-hexadecane	15	1.67	1.75				
Coronene	15			1.35	1.37		
1,2,4-Tricarbomethoxy-benzene	15					1.08	0.98
1,7-Diphenyl-1,7-dithia-heptane	16	1.69	1.87				
Benzocoronene	17			1.46	1.54		
Diphenyl phthalate	18					1.13	1.17
1,12-Diphenyl-1,12-dithia-dodecane	21	2.36	2.46				

^a Extrapolated from previous data¹ for 4.0% H₂O-Al₂O₃.

^b Assumes *p* bonding and therefore only one methyl in adsorbed phase.

groups is a function of the varying forces of intermolecular attraction between solute molecules in the pure liquids. We will, however, assume for the present that all non-hydrogen atoms in aromatic ring systems have δ_i values equal to those of the corresponding carbon atoms of Table III.

The differences in molar volumes of the various aromatic carbon types of Table III can be rationalized in terms of two effects. First, types (1) and (4) carbons have more associated hydrogen atoms in general, and these hydrogen atoms although small must make some contribution to molecular volume. Second, as the size of a fused aromatic system increases, as in the series benzene, naphthalene, phenanthrene, peripheral effects come into play. Thus, interatomic distances are covalent within the molecule and Van der Waals (greater) without. The effective volume of edge carbons is therefore greater than internal carbons, and the *average* volume per carbon must decrease with increasing size of the fused ring system, *exclusive* of the volumes of attached hydrogens.

Using eqn. (3) and the values of δ_i in Table I for various aromatic carbon types, it is possible to experimentally evaluate eluent strength values from R^o data for the elution of aromatic hydrocarbons by pentane and by the eluent in question. Having obtained values of ϵ^o for certain eluents, benzene, carbon tetrachloride, and methylene chloride in the present case, it is possible through eqn. (3) to measure $\sum \delta_i$ for *substituted* aromatics and to infer values of δ_i for specific substituents, after subtracting out the known contributions of the aromatic carbons to solute surface volume. Table II gives values of ϵ^o measured in this way for the above eluents, and Table I shows values of δ_i for various groups other than aromatic carbon. The experimental data from which these calculated values are derived are shown in Table IV.

In addition to the experimental values of δ_i derived as above, Table I contains substituent δ_i factors calculated from the densities of the pure liquids, as in Table III. The agreement is in general poor. This is not surprising for the reasons previously

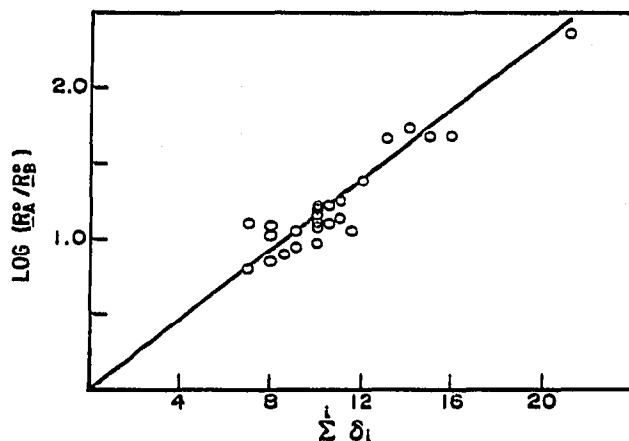


Fig. 1. Retention volume ratios *versus* solute surface volume; *n*-Pentane (A), CCl_4 (B) as eluents; 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

cited. Most of the preferred δ_i values are for groups composed of elements in the first row of the periodic table, and it can be seen that these group δ_i values are within one unit of the simple sum of the first row atoms: *e.g.*, three for nitro, one for amino, two for alkoxy, recalling that one aliphatic carbon of alkyl chains is required to remain in the adsorbed phase. In the case of higher row elements, there are indications

that their atomic surface volumes are slightly greater than 1, but it is not presently believed that this approximation to group δ_i values (the sum of non-hydrogen atoms) will prove to be significantly in error, since the precision of the preferred values of Table I is not greater than ± 1 .

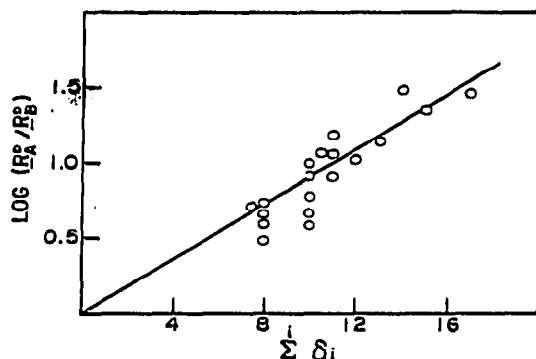


Fig. 2. Retention volume ratios *versus* solute surface volume; CCl_4 (A), Benzene (B) as eluents; 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

In Table IV, experimental and calculated retention volume ratios are compared for fifty solutes and four eluents. The parameters of Tables I and II were used in eqns. (3) or (4) to obtain the calculated values. The average deviation of the experimental and calculated values of Table IV is just less than ± 0.1 . A wide range in solute types is represented, so that the essential validity of the present treatment of eluent effects is confirmed. The prediction of eluent effects for these eluents shown in Table IV and other solutes and/or adsorbent activities should be of comparable ac-

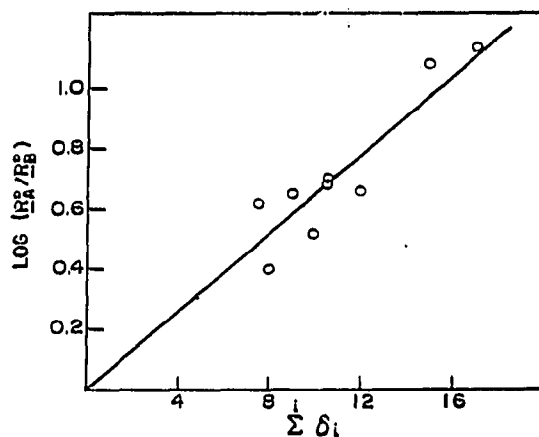


Fig. 3. Retention volume ratios *versus* solute surface volume; benzene (A), CH_2Cl_2 (B) as eluents; 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

curacy. The data of Table IV are also plotted in Figs. 1, 2 and 3 as $\log (R_A^\circ/R_B^\circ)$ *versus* $\sum \delta_i$. The dependence of the eluent term on solute size is apparent in these graphs.

Limited experimental data, some of it reported in Part II, are compared with calculated values in Table V for elution from *calcined* alumina. These illustrate that the eluent strengths of Table II are independent of adsorbent activity as required by

eqn. (1). The agreement of the experimental and calculated values of Table V is satisfactory (average deviation = 0.12), particularly when the extremely low linear capacity of calcined alumina, with resulting difficulty in acquiring reliable linear data, is considered. It is noted that the data of Tables IV and V include numerous values

TABLE V
RETENTION VOLUME DATA FOR ELUTION OF AROMATIC HYDROCARBONS
FROM 0.0% $H_2O-Al_2O_3$

Solute	$\text{Log } R^{\circ}$					
	Eluent <i>n</i> -pentane		Eluent CCl_4		Eluent benzene	
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
Benzene	0.47	0.46				
Naphthalene	1.61	1.70	0.53	0.26	-0.82	-0.86
Acenaphthylene			0.91	0.70	-0.52	-0.56
Phenanthrene			1.30	1.14	-0.30	-0.26
Pyrene			1.38	1.58	-0.15	0.04
Fluoranthene			1.51	1.58		
Triphenylene					0.08	0.34
Chrysene					0.36	0.34
3.4-Benzopyrene					0.53	0.64

for the elution of aromatic hydrocarbons by benzene. These data are in good agreement with calculated values based on the *strict* application of eqn. (1), so that no ambiguity for this chromatographic case now exists.

THE TREATMENT OF BINARY ELUENT SYSTEMS

It may be required that an eluent possess simultaneously a particular strength and one or more physical properties such as transparency at some wavelength in the ultraviolet, low viscosity (for maximum separation efficiency), or solvency for a particular sample type. While it will frequently happen that no single solvent sufficiently approximates the desired characteristics, a blend of two solvents having strengths greater and less than that required may be satisfactory. It is therefore worthwhile to consider the application of eqn. (1) to mixed eluent systems, and to relate the strength of a binary eluent to the strengths of the constituent solvents.

First, consider the data of Tables VI and VII for certain mixed eluent systems. Average values of $\alpha\epsilon^{\circ}_{AB}$, the binary eluent effective strength, were calculated for each eluent by application of eqn. (3). For the data of Table VI, the values of $\log R^{\circ}_A$ (A equal pentane) required in eqn. (3) were calculated from eqn. (1) and the parameter values given in Part II for the aromatic hydrocarbons and this chromatographic system. For the solutes of Table VII, $\log R^{\circ}_A$ (A equal pentane) was obtainable from average values of $\log R^{\circ}$ in pure eluent systems for which we have measured eluent strength (pentane, CCl_4 , benzene, and CH_2Cl_2). The conversion to a pentane basis was accomplished through eqn. (3). The experimental data on which these values are based is given in the next paper in this series². Since values of $\sum \delta_i$ are also calculable for each of the solutes of Tables VI and VII (see Table IV), each value of $\log R^{\circ}$ in these binary

TABLE VI
RETENTION VOLUME DATA FOR ELUTION OF AROMATIC HYDROCARBONS FROM 0.0% H₂O-Al₂O₃
BY BENZENE-PENTANE MIXTURES

Eluent, % ^v benzene	α ^o AB	Log R ^o															
		Naphthalene		Acenaphthylene		Phenanthrene		Pyrene		Triphenylene		Chrysene		3,4-Benzopyrene			
		Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.		
1.5	0.095	0.95	0.94	1.45	1.46												
5.0	0.141	0.57	0.57	1.05	1.05												
15	0.194	0.15	0.15	0.56	0.57	1.01	1.00										
30	0.235	-0.30	-0.12	0.18	0.20	0.59	0.59	0.91	0.98	1.13	1.36	1.58	1.36				
70	0.293					-0.10	0.01	0.26	0.34	0.59	0.66	0.84	0.66	1.05	0.99		

eluent systems can furnish a value of $\alpha\epsilon^{\circ}_{AB}$ for the eluent in question. The values shown in each case are weighted averages. With the insertion of the resulting average values of each binary eluent strength into eqn. (3), values of $\log R^{\circ}$ can be calculated for comparison with experimental data. In each case, the average deviation is about ± 0.06 , which, although representing a smaller number of data, is comparable to the precision of calculated values in Table IV (± 0.1). A similar result is encountered in

TABLE VII

RETENTION VOLUME DATA FOR CERTAIN SOLUTES ELUTED FROM 3.7% H₂O-Al₂O₃ BY THE BINARY ELUENTS CH₂Cl₂-PENTANE AND CCl₄-PENTANE

Eluent	$\alpha\epsilon^{\circ}_{AB}$	Log R°							
		1-Methoxynaphthalene		1-Nitronaphthalene		Acetophenone		Dimethyl phthalate	
		Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
<i>n</i> -Pentane			0.98		1.61		1.83		3.33
5 % v CH ₂ Cl ₂	0.052			1.04	1.06	1.43	1.41		
10 % v CH ₂ Cl ₂	0.084			0.80	0.73	1.17	1.16	2.25	2.33
25 % v CH ₂ Cl ₂	0.146			0.22	0.08	0.61	0.66	1.48	1.58
50 % v CH ₂ Cl ₂	0.206			-0.25	-0.53	0.09	0.20	0.65	0.78
70 % v CH ₂ Cl ₂	0.248					-0.13	-0.15	0.32	0.35
10 % v CCl ₄	0.028	0.68	0.70	1.34	1.32				
25 % v CCl ₄	0.044	0.51	0.54	1.18	1.15				
50 % v CCl ₄	0.072	0.30	0.26	0.84	0.86				

the next section for binary eluent mixtures consisting of pentane and dioxane. It may therefore be concluded that eqns. (1) and (3) apply equally well to binary or single eluents, providing a value of ϵ°_{AB} is specified for the adsorbent activity in question. As will be seen, however, ϵ°_{AB} is *not* independent of adsorbent activity, as is the case for pure eluents.

We shall now derive the relationship between $\alpha\epsilon^{\circ}_{AB}$ and the corresponding single eluent strengths ϵ°_A and ϵ°_B . Consider the equilibrium which exists between a binary composed of solvents A and B, and an adsorbent with a complete monolayer of total adsorbate. As in Part II, a competition is postulated between molecules in solution for a place on the adsorbent surface, so that the equilibrium (4) exists:



Here, *a* and *n* refer to adsorbed and solution phases, respectively. It is assumed in (4) that the mole volumes and mole surface volumes of A and B are identical, although this qualification can be shown not to affect the generality of our development. It will be assumed that B is the stronger eluent, so that $\epsilon^{\circ}_B > \epsilon^{\circ}_A$. Let the molar surface volume of solvent B be n_b . We assume that n_b is calculable by the same rule that determines $\sum \delta_i$ for solute molecules. The dimensionless free energy ($\Delta F/2.3 RT$)

for reaction (4) is given as $-\alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A)$, and a proper definition of standard states in phases A and B, along with the assumption of constant activity coefficients, gives:

$$\frac{S_B (1 - X_B)}{X_B (1 - S_B)} = 10^{\alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A)} \quad (5)$$

S_B is the fraction of the adsorbent surface covered by B, and X_B is the mole fraction of B in the original binary eluent. Solving for S_B gives eqn. (6).

$$S_B = \frac{X_{B10} \alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A)}{X_{B10} \alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A) + 1 - X_B} \quad (6)$$

Now consider the equilibrium distribution of solute Z between adsorbed and non-sorbed phases, with the distribution coefficient K_i defined as $(Z)_a/(Z)_n$ in the eluent system i . $(Z)_a$ and $(Z)_n$ refer to the mole fraction of solute in adsorbed and solution phases, respectively. Let $\sum_i \delta_i$ of Z be equal to that of eluent B: n_b . From eqn. (1)

$$K_B = K_A 10^{-\alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A)} \quad (7)$$

It is desired to solve for K_{ab} , the distribution coefficient in the binary eluent system. First, hypothecate the compartmentalization of the adsorbent surface into a region covered exclusively by A, of fractional area $(1 - S_B)$, and a residual region covered exclusively by B, of fractional area S_B . While the solution over each such region would be different than pure A or pure B, as is the case in the comparable single eluent systems, the activities of A in adsorbed and solution phases are identical because the system is at equilibrium. The same applies to the activities of B in each phase. Consequently, the values of K_i appropriate to each compartmentalized region will be K_A and K_B , respectively. K_{AB} can now be calculated from the ratio of total concentration of Z in the adsorbed phase to $(Z)_s$:

$$K_{AB} = (1 - S_B) K_A + S_B K_B \quad (8)$$

Combination of eqns. (6) through (8) yields

$$K_{AB} = K_A / (X_B 10^{\alpha n_b (\varepsilon^\circ_B - \varepsilon^\circ_A)} + 1 - X_B) \quad (9)$$

In terms of eqn. (1), the eluent polarity ε°_{AB} appropriate to the binary mixture of A and B is given through

$$\log (K_A/K_{AB}) = \alpha n_b (\varepsilon^\circ_{AB} - \varepsilon^\circ_A),$$

from which eqn. (2) follows.

Eqn. (2) is the fundamental relationship describing the elution properties of a binary eluent in terms of the strengths of the constituent eluents and the mole fraction X_B of the stronger eluent. While the derivation of eqn. (2) is in terms of a

particular size solute, the experimental applicability of eqn. (1) in binary eluent systems featuring an adsorbent of given activity (Tables VI and VII) shows that the equation holds for any size solute. Table VIII compares the experimentally measured strengths of the binary eluents in Tables VI, VII and X with values calculated from eqn. (2) using the pure eluent strengths of Table II and values of n_b calculated as

TABLE VIII

COMPARISON OF EXPERIMENTAL AND CALCULATED ELUENT STRENGTH VALUES FOR BINARY ELUENT SYSTEMS

Eluent composition %v strong eluent	$ae^{\circ} AB$							
	Benzene-pentane 0.0% $H_2O-Al_2O_3$		Dioxane-pentane 3.7% $H_2O-Al_2O_3$		CCl_4 -pentane 3.7% $H_2O-Al_2O_3$		Methylene chloride-pentane 3.7% $H_2O-Al_2O_3$	
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
1.5	0.095	0.070						
5.0	0.141	0.135					0.052	0.058
10.0			0.242	0.259	0.028	0.023	0.084	0.098
15.0	0.194	0.203						
25.0			0.307	0.322	0.044	0.048	0.146	0.163
30.0	0.235	0.248						
50.0			0.357	0.367	0.072	0.079	0.206	0.222
70.0	0.293	0.300					0.248	0.248
100.0	0.32		0.407		0.117		0.273	
Average deviation		± 0.012		± 0.014		± 0.005		± 0.011

previously; 6 for benzene and dioxane, 4 for CCl_4 (since one chlorine must lie out of the adsorbed phase), and 3 for methylene chloride. When the approximations contained in the derivation of eqn. (2) are considered, the observed agreement is satisfactory. The average deviation between the two sets of values is about ± 0.01 , so that for a solute with $\sum \delta_i$ equal 10, the average error in the application of eqn. (2) to the prediction of $\log R^{\circ}$ values would be 0.1. Fig. 4 shows plots of strength *versus* composition for the binary eluent systems of Table VIII. The experimental points closely follow the calculated curves (solid lines).

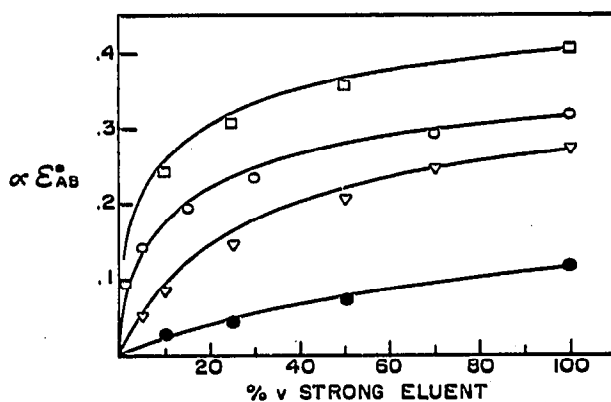


Fig. 4. Comparison of calculated and experimental eluent strengths for binary mixtures. \square Dioxane-pentane; 3.7% $H_2O-Al_2O_3$. \circ Benzene-pentane; 0.0% $H_2O-Al_2O_3$. ∇ CH_2Cl_2 -pentane; 3.7% $H_2O-Al_2O_3$. \bullet CCl_4 -pentane; 3.7% $H_2O-Al_2O_3$. — Calculated.

The generality of eqn. (1) in its application to binary eluent systems can be examined in terms of eqn. (2). Consider the model chromatographic system, 5 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ with benzene as eluent. With α equal to 0.57 and ϵ° for benzene given in Table II, $\alpha\epsilon^\circ$ is calculable as 0.182. Eqn. (2) then gives ϵ°_{AB} for 15 mole % benzene-pentane for the same adsorbent as 0.072. In a similar calculation of 0.0 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$, ϵ°_{AB} for the same binary is calculable as 0.194. If ϵ°_{AB} for this binary were constant at all adsorbent activities, the value for 5.0 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ should be equal to $\alpha\epsilon^\circ_{AB}$ or 0.111, but the actual value is 0.072. This is equivalent to a decrease in ϵ°_{AB} of the binary with decreasing adsorbent activity, or *equation (1) fails to apply to binary eluent systems as adsorbent activity is varied*. The example chosen is general for all binary systems, and the application of eqn. (1) to eluent binaries requires that the value of $\alpha\epsilon^\circ$ used be calculated or measured for a specific adsorbent activity.

THE STRENGTHS OF SOME PURE ELUENTS

The derivation of the eluent strengths in Table II for pentane, CCl_4 , benzene, and CH_2Cl_2 has been previously discussed. The measurement of the strengths of the other saturate eluents of Table II results from the application of eqn. (3) to the data in Table IX for the elution of phenanthrene from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$. Several generalizations on the strengths of saturate eluents may be drawn. They are all rather weak;

TABLE IX
STRENGTHS OF SOME SATURATE ELUENTS

Eluent	$\text{Log } R^{a,b}$	$\alpha \epsilon^\circ$	ϵ°
<i>n</i> -Pentane	1.164	—	0.000
Isooctane (2,2,4-trimethylpentane)	1.121	0.0043	0.007
<i>n</i> -Octane	1.076	0.0088	0.013
<i>n</i> -Hexane	1.068	0.0096	0.015
Cyclohexane	0.929	0.0235	0.036
<i>n</i> -Decane	0.909	0.0255	0.039
Cyclopentane	0.814	0.0350	0.054

^a For elution of phenanthrene from 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

^b For 3.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

strength increases with molecular weight in the normal paraffins and is less for branched than for straight chain isomers of similar molecular weight. Cycloalkanes are stronger eluents than are acyclic saturates of comparable molecular weight.

The measurement of the strengths of very strong eluents ($\epsilon^\circ > 0.4$) is experimentally difficult. Most serious is the limited availability of strongly adsorbed solutes whose retention volumes fall in a retention volume range convenient to their measurement in a particular strong eluent system. Varying adsorbent activity can partially solve this problem, but was not used in the present study. Table X presents a limited number of retention volume data for some strong eluent systems. In addition to the pure eluents CHCl_3 , diethyl ether, ethyl acetate, and dioxane, several dioxane-pentane binaries are represented. The strengths of each eluent system were calculated from the average values resulting from the application of eqn. (3) to the data for each

eluent. The values of \underline{R}°_p (R° for pentane as eluent) required in this procedure were obtained from the average of values extrapolated from data using CCl_4 , benzene, or CH_2Cl_2 as eluents in the case of the less strongly adsorbed solutes (a). Using these values of \underline{R}°_p , $\alpha\varepsilon^{\circ}$ for the eluent 25 vol. % dioxane-pentane was calculated from eqn. (3). Finally, values of \underline{R}°_p for the strongly adsorbed solutes (b) were extrapolated from the retention volume data in the latter binary eluent.

The average deviation between the data of Table X and those calculated from eqn. (3) (as in Tables V, VI, and VII) is about ± 0.13 , which represents somewhat

TABLE X

RETENTION VOLUMES IN SOME STRONG ELUENT SYSTEMS AND DERIVED ELUENT STRENGTHS

Solute	Log \underline{R}°							
	<i>n</i> -Pentane	10%v Dioxane- pentane	CHCl_3	Ethyl ether	25%v Dioxane- pentane	50%v Dioxane- pentane	Ethyl acetate	Dioxane
Aniline	2.25 ^a	0.67	0.35		0.10			
Pyridine	2.26 ^a		0.72	0.15	-0.10		0.01	
Quinoline	2.39 ^a			-0.06			-0.6	
6-Methoxyquinoline	2.99 ^a		0.38	0.12				
1,2,4-Tricarbomethoxy- benzene	4.31 ^a	0.67		0.24	0.01			
1,5-Diaminonaphthalene	4.42 ^b				1.02 ^c	0.46	-0.08	
2-Aminoanthraquinone	5.01 ^b				1.15 ^c	0.39	0.10	
2-Aminopyridine	3.58 ^b	1.91			1.26 ^c	0.81		0.45
7-Azaindole	3.63 ^b				1.31 ^c	0.84		0.52
1-Azacarbazole	4.06 ^b				1.12 ^c	0.59		0.30
Strength, $\alpha\varepsilon^{\circ}$		0.230	0.263	0.299	0.309	0.367	0.392	0.407

^a Average of values for elution by CCl_4 , benzene, and CH_2Cl_2 ; extrapolated to pentane basis.

^b Extrapolated from values for elution by 25 %v dioxane-pentane.

^c These values define the standard pentane values, so are not included in determining $\alpha\varepsilon^{\circ}$.

poorer agreement than appears to exist in weaker eluent systems. It is probable that the eluent term of eqn. (1) is subject to some average fractional uncertainty, and that this in turn means that the accuracy of eqns. (1) and (3) is poorer in strong eluent systems than in weak.

The order of ε° values in Table II is comparable to that established in other chromatographic systems⁸. As a first approximation, the strength of a given eluent should be given by eqn. (10), which fulfills the conditions that \underline{R}° for the eluent be equal to V_a (see Part II).

$$\varepsilon^{\circ} = \frac{\sum_i Q^{\circ}_i + \sum_j q^{\circ}_j}{\sum_i \delta_i} \quad (10)$$

Here, the summation $\sum_i Q^{\circ}_i + \sum_j q^{\circ}_j$ is taken over all eluent groups i confined to the adsorbent phase. Since $\sum_i Q^{\circ}_i$ for n -pentane must equal zero, and since the value of Q°_i assumed for a methylene group is 0.02¹, if the term $\sum_j q^{\circ}_j$ is ignored; Q°_i for a methyl group is required to be -0.03. Equation (10) and these values of Q°_i provide

a satisfactory theoretical basis for the previous generalizations on the relative strength of the saturate eluents. The actual values calculated by eqn. (10) are in fair agreement with experimental polarities.

Values have been calculated by means of eqn. (10) for those strong eluents where the necessary values of Q°_i and q°_j are known². These calculated values are plotted *versus* experimental ones in Fig. 5.

As discussed in Part IV², solutes with groups which have adsorption energies in excess of a certain amount ($Q^{\circ}_i > 1.3$) tend to localize at specific sites on the ad-

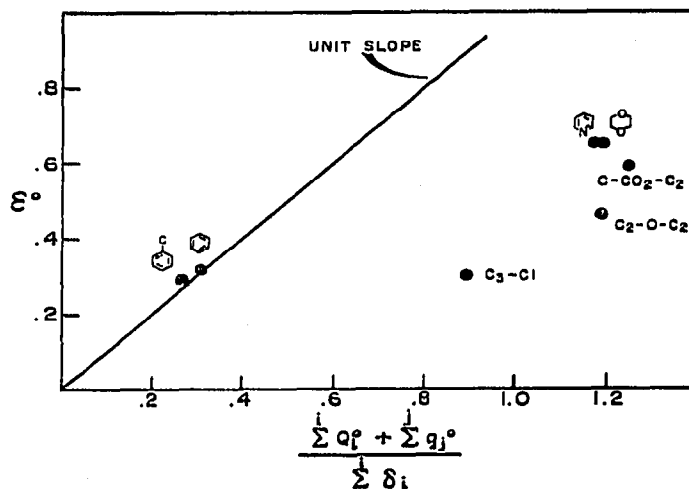


Fig. 5. Comparison of experimental and calculated eluent strengths.

sorbent surface, while those with weaker groups are "semilocalized". By analogy, it is assumed that localization also occurs in eluents made up of sufficiently strong groups. Equation (10) should therefore be inapplicable to eluents which have a tendency to localize, because the degree of localization possible will be different for the localized *solute* on the one hand (from which the necessary values of Q°_i and q°_j must be calculated), and the same solute as *eluent* on the other. This results from the greater competition for adsorbent sites in the latter case. As is observed in Fig. 5, this is in fact experimentally observed, the semilocalized eluents benzene and toluene falling on the calculated curve, while the other *localized* eluents with strongly adsorbing groups show less than calculated strengths.

THE DETERMINATION OF ADSORBATE CONFIGURATION BY ELUENT VARIATION

Equation (3) permits the prediction of the effect of eluent variation on solute retention volume. If, on the other hand, the ratio $\log (R^{\circ}_A/R^{\circ}_B)$ is measured for a given solute, it is seen that eqn. (3) can furnish an experimental value of $\sum \delta_i$, the solute surface volume. In the eluent systems of Table IV, the average deviation between experimental and calculated retention volume ratios suggests that $\sum \delta_i$ is thus measurable with a precision of 1-2 units. This procedure underlies the calculation of the preferred values of group δ_i values shown in Table I, and their agreement with those inferred from the data of Table III further attests to the potential accuracy of

the procedure. With values of δ_i for every group or atom of a solute either known or calculable, and $\sum^i \delta_i$ measurable through eqn. (3), it is possible to compare experimental values of $\sum^i \delta_i$ with those calculated for various configurations of the adsorbate. In this way it may be possible to determine the actual adsorbate configuration in cases where more than one is conceivable.

In Table XI, data for a number of solutes eluted by various eluent pairs (A,B)

TABLE XI
ADSORBATE CONFIGURATION VIA ELUENT VARIATION FOR ADSORPTION ON
3.7% $H_2O-Al_2O_3$

Solute	$\sum^i \delta_i$					
	Eluent A: 25%v CH_2Cl_2 -pentane		Benzene		Pentane	
	Eluent B: Benzene		70%v CH_2Cl_2 - pentane		CCl_4	
	Exptl.	Calc. ^a	Exptl.	Calc. ^a	Exptl.	Calc. ^b
Dimethyl phthalate	10.2	12	13.2	12		
Di- <i>n</i> -butyl phthalate	11.1	12	11.5	12		
Di- <i>n</i> -hexadecyl phthalate	11.1	12				
1,5-Diphenyl-1,5-dithia-pentane					14.8	14
1,7-Diphenyl-1,7-dithia-heptane					14.4	16
1,12-Diphenyl-1,12-dithia-dodecane					20.2	21
3,6-Dithia-octane					9.4	7
3,7-Dithia-nonane					9.2	8
3,9-Dithia-undecane					10.2	10
3,14-Dithia-hexadecane					14.3	15

^a Assumes that only one alkyl carbon of each alkyl group is in adsorbed phase.

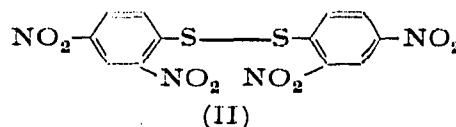
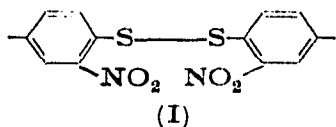
^b Assumes that all alkyl carbons joining two end substituents are in adsorbed phase.

from 3.7% $H_2O-Al_2O_3$ have been treated as above to give experimental values of $\sum^i \delta_i$ for each solute. Consider, first, the di-alkyl phthalates. With all atoms in the adsorbed phase, dimethyl phthalate has a calculated value of $\sum^i \delta_i$ equal to 12, and the average of the experimental values (11.7) is within experimental deviation of this figure. Di-*n*-butyl and di-*n*-hexadecyl phthalate have several potential configurations, ranging from that for the totally adsorbed molecule to that with all but one of the alkyl group carbons unadsorbed. The experimental values of $\sum^i \delta_i$ for di-*n*-butyl and di-*n*-hexadecyl phthalate are 11.3 and 11.1, respectively, within experimental error of the theoretical value of 12 for the configuration with all but one alkyl carbon lying in solution. This configuration of "free" alkyl groups in strong eluent systems has already been observed in Part II for limited data of another type on the alkyl pyridines. Certainly, it is not surprising that the alkyl groups seek the solution phase inasmuch as the calculated energy of adsorption is very favorable for this configuration.

Next, consider the α,ω -disubstituted alkanes of Table XI. These solutes could conceivably adopt one of several different configurations on adsorption. The preceding data for the di-*n*-alkyl phthalates make it reasonably certain that only one of the two alkyl carbons in each α -thia-propyl group is adsorbed in the case of the alkyl disulfides

of Table XI. Aside from this consideration, each of the disubstituted alkanes of Table XI can either lie entirely in the adsorbed phase, or have only one substituent and its attached alkyl carbon in the adsorbed phase. In the case of the solutes with large linking alkyl groups, the further possibility exists that the two terminal substituents lie in the adsorbed phase, and some fraction of the alkyl carbons linking them lies in the solution phase through puckering of the alkyl chain. In each of these various cases, a unique value of $\sum^i \delta_i$ for the solute is determined. The values calculated for these solutes in Table XI assume that all internal alkyl carbons are adsorbed—no puckering—and are seen to agree within experimental error with the observed values. It thus appears that in the eluent systems (pentane, CCl_4) studied, puckering of alkyl chains of up to ten carbons in length occurs to a limited extent, if at all. In this case, as in other examples of the present technique, the final conclusion is obscured by possible error in the calculation of $\sum^i \delta_i$ for each adsorbate configuration. Thus, in the case of the diphenyl-dithia-alkanes, it is assumed that one of the two phenyl groups contributes only three units to the total solute surface volume. However, it is likely that by the time the length of the alkyl chain has increased to ten carbons that δ_i for each carbon in the second phenyl group is closer to one than it is to the value of $1/2$ for biphenyl.

As a final example of the application of eluent variation to the study of adsorbate configuration, consider the two solutes, di-(2-nitrophenyl) disulfide (I) and di-(2,4-dinitrophenyl) disulfide (II). It was initially anticipated that these two solutes



would lie totally in the adsorbed phase, and would have $\sum^i \delta_i$ values of 16 for (I) and 21 for (II). Experimental retention volume data were acquired for elution of each solute from 3.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ by several eluents whose effective strengths $\alpha\epsilon^\circ$ ranged from 0.05 to 0.27. These included both pure and binary eluents. It was found that the experimental values of $\sum^i \delta_i$ thus obtained for (I) and (II) were in every case lower than predicted. In the case of (I), $\sum^i \delta_i$ appears to vary with eluent strength, equalling about 10.6 for strengths in the region of 0.24, and 13.1 for strengths around 0.14. More limited data on (II) show a value of $\sum^i \delta_i$ equal to 13.7 at a strength of 0.24. At the higher strengths (0.24), $\sum^i \delta_i$ for each of these solutes is close to that predicted for the adsorption of just one-half of the molecule, $9^{1/2}$ for (I) and 12 for (II). This suggests that these solutes either find difficulty in attaining a planar configuration, or else the planar solute cannot be easily accommodated on the adsorbent surface, possibly because the solute is too large. The latter explanation does not appear reasonable in view of the great varieties of solute sizes represented in the data of Table IV, all of which appear "regular" in their adsorption characteristics. If the planar configuration is difficult for the diphenyl disulfides to attain, it suggests that the carbon-sulfur-sulfur bonding angle is such as to result in steric interaction between the sulfur of one ring and the *ortho* hydrogens of the other. This requires a value of this angle close to 90° , which may not be unreasonable in view of the similar angle in such

species as hydrogen sulfide⁹. As the eluent becomes weaker ($\alpha\epsilon^\circ < 0.24$), the fraction of (I) in the adsorbed phase appears to increase. This could arise from a partial "return" of the unadsorbed half of the molecule, with perhaps only the nitro group and some of the ring carbons bonded to the adsorbent surface.

KLEMM¹⁰ has suggested that a number of the aza-aromatics adsorb as the n -complex, wherein the adsorbate has an edgewise or tilted configuration. The present study of the effect of eluent variation on the retention volumes of certain of the aza-aromatics does not support the concept of edgewise adsorption. Eluent variation in our system, however, is not sufficiently sensitive to rule out tilted adsorption where the angle between the planes of the adsorbate and of the adsorbent surface is small. The following paper in this series² will discuss the question of adsorption mechanism and configuration in somewhat greater detail.

It must be emphasized that the present method for evaluating adsorbate surface volume assumes that $\sum^i \delta_i$ remains *constant* while the eluent is varied. When this is not true, as may be the case for solutes I and II in weak eluent systems, the values of $\sum^i \delta_i$ obtained can be quite inaccurate. Not only is $\sum^i \delta_i$ not constant, as assumed in the development of eqn. (3), but, even more important, $\sum^i Q^\circ_i$ is not.

GLOSSARY OF TERMS

a, n	Subscripts refer to adsorbed and non-sorbed phases
n_b	Eluent surface volume
$\underline{R}^\circ, \underline{R}^\circ_A, \underline{R}^\circ_B$	Linear equivalent retention volumes; volume of eluent per weight of adsorbent (ml/g) required to elute 50 % of a given solute
\underline{R}	Non-linear equivalent retention volume.
S_B	Fraction of adsorbent surface covered by strong eluent, B
V_a	Adsorbent surface volume per unit weight; ml/g
X_B	Mole fraction of stronger constituent of a binary eluent
α	Adsorbent activity function
δ_i	Contribution of atom or group i to solute surface volume
$\epsilon^\circ, \epsilon^\circ_A, \epsilon^\circ_B$	Eluent strength function; value for elution from calcined adsorbent
$\sum^i \delta_i$	Solute surface volume
$\sum^j q^\circ_j$	Solute geometry function; contribution of solute structure to $\log \underline{R}^\circ$
$\sum^i Q^\circ_i$	Total contribution of solute groups i to adsorption energy
K_i, K_A, K_B	$(Z)_a/(Z)_n$ in eluent systems i, A, B , respectively
$(Z)_i$	concentration of Z in phase i .

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SUMMARY

The previous treatment of the effect of eluent on solute retention volume in linear elution adsorption chromatographic systems has been advanced by improving the accuracy of solute surface volume calculations and by measuring experimental eluent

strength values ϵ° for several new eluents. A quantitative theory for the calculation of binary eluent strengths from the ϵ° values of constituent eluents has been developed. A new technique for determining the fraction of an adsorbed solute in the adsorbed phase is proposed.

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