LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

I. CONDITIONS FOR EXISTENCE

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Of the three basic chromatographic techniques, elution chromatography has long been recognized as uniquely suited for the separation of multicomponent mixtures. The theory of elution chromatography is well developed[1,2] for linear isotherm systems, and considerable progress has been made in the quantitative correlation of solute separabilities with molecular structure in such cases[3]. With few exceptions, linear elution chromatographic (LEC) separations are experimentally noted only in systems with liquid stationary phases. Isotherm linearity, or the validity of Henry's law in stationary and moving phases, is generally recognized as the rule in these chromatographic cases, and the exception in those employing a solid adsorbent for the entire stationary phase. Data have been reported[4-6] (among others) as examples of LEC behavior for solid–liquid and solid–gas chromatographic systems, but the phenomenon has been obscured by the frequent use of deactivated solid stationary phases, where both solid and adsorbed liquid constitute the total stationary phase. SPORER AND TROMBLOOD[7] have presented the only extensive data for a non-deactivated adsorbent (silica gel) which exhibits isotherm linearity, using frontal analysis. The extent to which isotherm linearity exists in this system is not clear, however, since data are given both from observations on the linear region and extrapolations from non-linear data. Nothing is known about the possible generality of linear elution behavior at practical column loadings for chromatographic systems featuring a solid adsorbent, and this has discouraged systematic studies of the quantitative relationships between solute separability and structure.

Certain physical separations, particularly of petroleum[8,9] and other natural constituent compound classes, appear possible only by elution chromatography from a solid stationary phase. The experimental convenience of adsorption chromatography has also recommended its use where other separation procedures are applicable. The quantitative description of given multicomponent chromatographic separations is only conceivable should linearity in the distribution isotherm exist. Linear adsorption isotherm systems are also potentially of value in obtaining greater insight into the adsorption process, as by examining the variation of solute adsorption energy with systematic change in solute structure. Quantitative comparisons of this type depend on the existence of unique thermodynamic standard states for the adsorbed solutes

compared. The region of isotherm linearity affords such a standard state, comparable to the dilute solution state. Similarly, the adsorbed state can be used to gain information on the intramolecular forces, or configuration, pertinent to the non-adsorbed molecule by forcing it into a co-planar state upon adsorption. Chromatographic separation order has been used in this connection[10] to obtain qualitative interaction forces (or energies) for molecules with sterically hindered internal rotation. Again, use of linear systems would furnish data for quantitative interpretation. Finally, a knowledge of linear elution adsorption chromatographic (LEAC) solute separabilities leads to greater understanding of the more common non-linear chromatographic cases.

Before attempting a thorough investigation of LEAC compound separability, it is desirable to understand the factors which contribute to non-linear separation, to learn how linearity may be attained in practical adsorption systems, and to develop tests for linearity in cases where lack of experimental precision makes it uncertain that linearity exists. The following discussion begins with a theoretical analysis of linearity in the equilibrium adsorption isotherm, and is followed by an experimental study which relates it to linear elution separation.

EQUILIBRIUM ADSORPTION FROM SOLUTION

The Langmuir isotherm offers the simplest and most frequently used model for interpretation of the adsorption process. It is limited by its failure to consider adsorbent heterogeneity, that is, differences in the energy of adsorption sites, and its neglect of lateral interactions between adjacent adsorbed molecules. Furthermore, in most adsorption systems of chromatographic interest, polyatomic molecules are involved which presumably use more than one adsorption site per adsorbed molecule. FOWLER[11] has derived the theoretical isotherm expression for adsorption without lateral interaction of a monatomic gas on a heterogeneous surface. A re-derivation for the adsorption of a polyatomic solute X from solution in a solvent S will be made. With all adsorbent sites occupied, the adsorption equilibrium is

$$X_{(n)} + mS_{(a)} \rightleftharpoons X_{(a)} + mS_{(n)} , \tag{1}$$
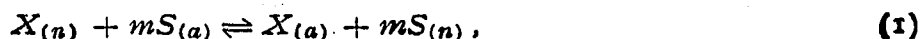
with the solute requiring m times the number of sites needed by solvent. The present discussion concerns the isotherm region of linearity or near linearity, the adsorbed solute concentration will be small, and therefore lateral interactions involving solute will be almost exclusively those between solute and solvent. These energy terms may be grouped with the site energy since they are independent of solute concentration. The isotherm expression for adsorption of X on a set of homogeneous sites i is then,

$$K_i = \frac{\theta_i}{(X)_n (1 - m\theta_i) m} , \tag{2}$$

the derivation being completely analogous to that for the Langmuir expression. K_i is a thermodynamic equilibrium constant for reaction (1) and sites i, θ_i is the frac-

tion of sites i which are covered by X, and $(X)_n$ is the solution concentration of X. Eqn. (2) reduces to the Langmuir isotherm for m equal one, and is essentially intractable for other cases. By proceeding with the assumption of m equal one we can anticipate a model which will illustrate the qualitative features of near linear adsorption, which is all that is desired at present.

θ, the fraction of the total adsorbent surface covered by X, is given by

$$\theta = \int_{-\infty}^{\infty} \theta_i N_i \, dF_i ; \qquad (3)$$

here N_i is the fraction of the total number of sites in set i, and F_i is the dimensionless free energy of sites of set i, defined as $-\log K_i$. The distribution coefficient K for solute partitioned between total adsorbed phase and non-sorbed phase is equal to $\theta/(X)_n$. It is desired to solve for K as a function of solute concentration in the case of specific site energy distributions which are illustrative of certain features of isotherm linearity. The combination of eqn. (2) with m equal one and eqn. (3), plus the definitions $K_i = e^{-F_i}$ and $K = \theta/(X)_n$, yields

$$K = \int_{-\infty}^{\infty} \frac{N_i \, dF_i}{e^{F_i} + \theta/K} \qquad (4)$$

The limiting value of K as θ approaches zero is the linear distribution coefficient K_0.

The ratio K/K_0 provides a test of isotherm linearity, $1 - K/K_0 \lesssim \varepsilon$, with ε arbitrarily small. Corresponding to adsorbent capacity V_a, the specific volume of the adsorbed phase for complete site coverage, there exists a *linear capacity*, θ_ε, at which fractional coverage $(1 - K/K_0)$ equals ε.

In Fig. 1, a hypothetical site energy distribution is shown. We may characterize such distribution functions by their shape or type (*e.g.*, rectangular, triangular, Gaussian), their width or energy spread p, and the average strength of the sites F_0. K/K_0 is thus specified through eqn. (4) by these three loosely defined site distribution
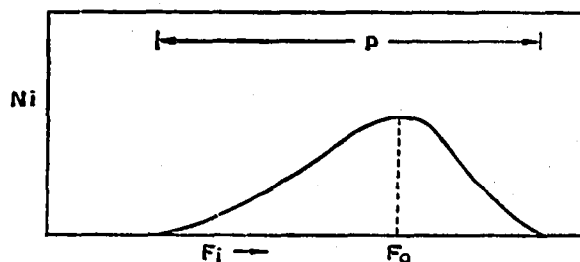

Fig. 1. General site energy distribution curve.

parameters, and by θ. It is interesting and simplifying to note, however, that the ratio of interest K/K_0 is independent of the average strength of the sites, F_0. It may be seen that if F_0 is increased by an amount E, corresponding to the increase of all site free energies by E, e^{F_i} in eqn. (4) is replaced by $[e^{F_i} e^E]$, N_i and dF_i remaining unchanged and F_i referring to the original distribution function. But this requires

that the new value of the distribution coefficient K' resulting from this change in F_0 be $K e^{-E}$, since substitution of these new values of the changed terms in eqn. (4) results in an identity. Similarly, the new value of the linear distribution coefficient K'_0 is $K_0 e^{-E}$, and the ratio K/K_0 is thus independent of changes in F_0. Thus, the question of linearity reduces to the value of θ_ε as a function of two site distribution parameters (curve type and energy spread).

Consider, first, the rectangular distribution function, $N_i = 1/p$, for $-p \leqslant F_i \leqslant 0$, shown in Fig. 2. The normalization requirement

$$\int_{-\infty}^{\infty} N_i \, dF_i = 1$$

is observed. Eqn. (4) provides

$$K_0 = (1/p) \int_{-p}^{0} e^{-F_i} \, d F_i \tag{5a}$$

and

$$K = (1/p) \int_{-p}^{0} \frac{d F_i}{e^{F_i} + \theta/K} \cdot \tag{5b}$$

Combination of integrated eqns. (5a) and (5b) then yields

$$K/K_0 = \theta \, p \left[\frac{e^p}{(e^p - 1)(e^{p\theta} - 1)} - \frac{e^{p\theta}}{(e^p - 1)(e^{p\theta} - 1)} \right] \tag{6}$$

As p becomes large, eqn. (6) approaches the limit (7) for small values of θ (near the linear region):

$$K/K_0 = \frac{\theta p}{e^{\theta p} - 1} \tag{7}$$

Linear capacity θ_ε is defined by the value of K/K_0, and in eqn. (7) it is seen that for a given value of K/K_0, θ (and linear capacity) is inversely proportional to p. The wide rectangular distribution is illustrative of a general property of all site distributions, inear capacity decreases with increasing site energy spread p.
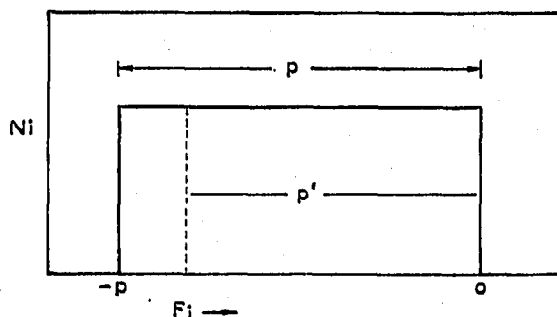

Fig. 2. Rectangular site energy distribution function.

In addition to illustrating one of the general properties of all wide site distributions, the rectangular function of Fig. 2 should prove a good approximation to

natural distributions which have been artificially truncated, as by water deactivation of the adsorbent.

It has been noted by CAHNMAN[12] that partial deactivation of silica by water improves its chromatographic characteristics, and this has proved to be a rather general phenomenon[13]. The effect has been attributed to removal of very strong sites which cause tailing of solute elution bands. The demonstration that K/K_0 is independent of F_0 suggests that strong sites as such do not contribute to non-linearity. It is of interest to consider the effect of adsorbent deactivation on adsorbent linear capacity.

If the rectangular distribution is partially deactivated by a selective adsorbate, so as to approach the truncation indicated in Fig. 2 by the dotted line, the integrations of eqns. (5a) and (5b) can be repeated, changing only the limits of integration to p' and θ, to give finally

$$K/K_0 = \frac{\theta p}{(e^{p'} - 1)} \frac{(e^{p'} - e^{p\theta})}{(e^{p\theta} - 1)} \tag{8}$$

where θ refers to adsorbent loading relative to the original distribution. For large values of p (and hence p'), eqn. (8) reduces exactly to eqn. (7), or *the moderate deactivation of a rectangular site distribution does not change linear capacity when the site energy spread p is large.* That this is so can be seen in terms of the demonstration that K/K_0 is dependent on θ but independent of F_0. When p is large and θ is small, only the sites at small values of F_i are appreciably covered, and the relative loading of these sites determines the relation between K/K_0 and θ. Truncating the distribution curve at the large F_i end does not affect either the latter relationship or any part of the adsorption process. But truncation at the large F_i end of the curve is equivalent, for the dependence of K/K_0 on θ, to truncation at the lower F_i end. The end result is merely a change in value of F_0. Hence, adsorbent deactivation does not change the dependence of K/K_0 on θ until p' becomes small enough for eqn. (8) to fail as an approximation to eqn. (7).

The situation with respect to adsorbent deactivation is different in the case of other site distributions. Where p is small, all site distributions approach the behavior of a homogeneous set, with deactivation causing a proportional *reduction* in linear capacity. As p goes to zero, adsorbent coverage is described by the Langmuir isotherm and

$$K/K_0 = 1 - \theta . \tag{9}$$

Here, θ refers to the coverage relative to the sites left after deactivation, so that decline in adsorbent capacity leads to a proportional decline in linear capacity.

Alternately, distributions where N_i declines with F_i, rather than holding constant to some value $-p$, and where p is moderately large show linear capacity *increasing* for moderate deactivation. This is shown for an isosceles triangular distribution in Fig. 3 where $\theta_{.1}$ is plotted *versus* percent truncation or deactivation for various values of p. The values shown in Fig. 3 were obtained by numerical integration of eqn. (4) for K/K_0. The behavior of the triangular distribution is representative of

other declining site energy functions such as exponential or Gaussian distributions. As deactivation proceeds towards 100 %, adsorbent linear capacity must eventually decline.

The experimental observations of CAHNMAN cited above can be attributed to a closer approach to isotherm linearity with increasing adsorbent deactivation. This results, however, not from the removal of strong adsorption sites as strong sites, but as sites on a distribution tail, as in the triangular distribution.
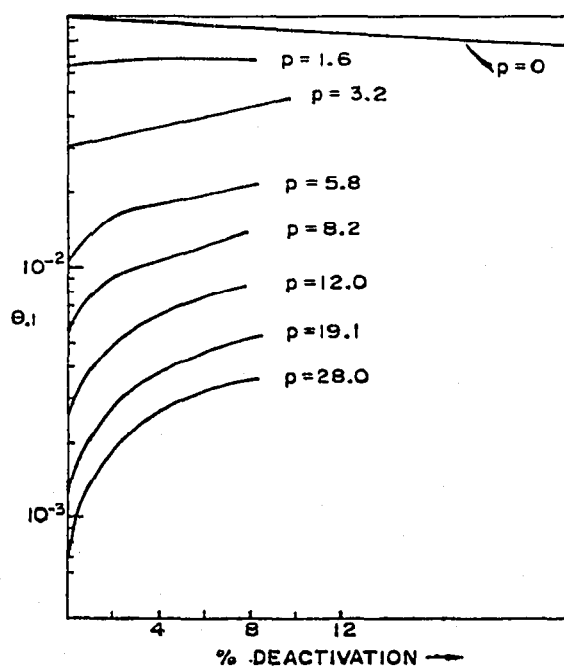

Fig. 3. Linear capacity as a function of site energy distribution width and truncation

Suitable tests for isotherm linearity and the related experimental evaluation of the linear coefficient K_0 for given systems are important. The experimental measurement of K as a function of adsorbent coverage (or solute concentration) over a range of values which includes a region of isotherm linearity (constancy of K) is the surest procedure, but this can be time-consuming. In some cases it is uncertain whether linearity has been achieved at the lowest coverages studied because of the larger experimental error associated with values of K measured at small values of θ. It is desirable to be able to use two values of K at different values of θ close to the region of linearity, and extrapolate to a value of K_0. The Langmuir expression has been used in this connection by SPORER AND TRUEBLOOD[7]. For the homogeneous (Langmuir) distribution

$$K = K_0 (1 - \theta),$$
(9a)

and a linear extrapolation of K as a function of θ to θ equal zero yields K_0. For the wide rectangular distribution with K as a function of θ given by eqn. (7),

$$K/K_0 = 1 - \tfrac{1}{2}\theta p$$
(10)

at low values of θ. This may be seen by expansion of eqn. (7) with retention of first order terms. It is observed that linear extrapolation of K *versus* θ for K_0 is again valid. For site distributions characterized by declining values of N_t as site adsorption strength increases, linear extrapolation begins to fail at large values of p, although it is adequate as an empirical relationship for all but the widest distributions. In general, if two K values are measured for solute concentrations (or coverages) differing by at least a factor of 10, and if the difference between these K values is less than 10 %, then the linear extrapolation of K to zero coverage gives K_0 accurate within 5 %. As an extreme example, the test was applied to a very wide exponential distribution, where p was 20 % less than that value sufficient to make K_0 indeterminate and linearity impossible at any value of θ. The extrapolation procedure (within the above conditions) produced a value of K_0 always within 6 % of the theoretical value. The simple condition that K change by no more than 10 % over a 10-fold range in θ requires that even where non-linearity exists, the Freundlich exponent must be equal to or greater than 0.96. Other workers[6] have equated cases this close to linearity with linear systems.

LINEAR ELUTION ADSORPTION CHROMATOGRAPHY (LEAC) AND THE ADSORPTION ISOTHERM

When isotherm linearity exists throughout the elution of a solute from an adsorbent chromatographic column, the equivalent plate treatment of MARTIN AND SYNGE[2] gives solute retention volume R' (eluent volume to elute 50 % of solute from column) as

$$R' = (V_a/V_n) K_0 V_0 + V_0 . \tag{11}$$

(V_a/V_n) is the ratio of adsorbed to non-sorbed phases, and V_0 is the total volume of non-sorbed phase within the column. The corrected retention volume, R equal $R' - V_0$, can be defined, as can the equivalent retention volume, $\underline{R}^0$ equal R/W. W is the total adsorbent weight. If V_a is the adsorbent capacity, V_0 equals $V_n W$, and

$$\underline{R}^0 = V_a K_0 . \tag{12}$$

If K_0 is calculated from adsorbed phase concentrations in weight of solute per weight of adsorbent, rather than per volume of adsorbed phase, $\underline{R}^0 = K_0$. For experimental cases involving a non-linear isotherm, the non-linear equivalent retention volumes R define an "average" K for the entire elution.

Given the number of equivalent stages for an experimental elution case, and knowing $K/K_0 = f(\theta)$, it is straightforward to formulate the calculation of values of R (and $\underline{R}/\underline{R}^0$) for specified values of the column loading W_s. The actual calculation for most cases of interest strains the capabilities of an intermediate speed computer, however, and is impossible of manual solution. Qualitatively, it is noted that only a fraction of the total adsorbent is accessible to the solute band at any time during elution, and this fraction is proportional to solute elution band width w/R'. The

adsorbent coverage is proportional to the fraction of the total solute which is adsorbed, $V_a K/(V_a K + V_n)$. If an intermediate value of w/R' is chosen as a standard of comparison (0.3), then a factor α equal to the fraction of the column "used" by the solute band can be defined, and values of W_s and θ can be associated with equal values of $\underline{R}$ and K, relative to the standard w/R' case:

$$\theta = \frac{0.3 W_s R/(R + V_n)}{W_a \alpha \, (w/R')} \tag{13}$$

W_a refers to the weight of adsorbed phase per gram of adsorbent.

In Fig. 4, experimental equilibrium (K) and chromatographic $(\underline{R})$ data are plotted against θ for elution of 1,2,3,5-tetramethylbenzene from calcined alumina by pentane. Eqn. (13) was used to calculate values of θ for the chromatographic data from values of W_s. The best superposition of the chromatographic and equilibrium data required a value of α equal to 0.05. This means that 5 % of the chromatographic
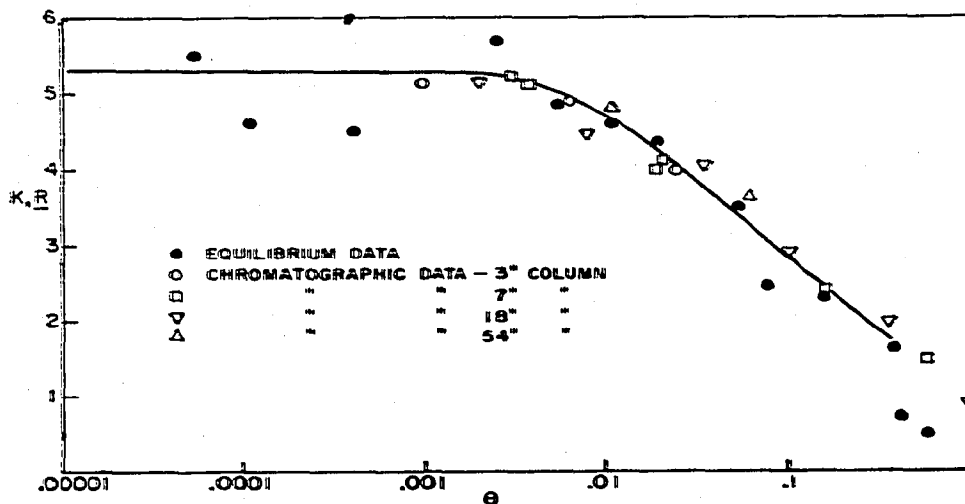

Fig. 4. Superposition of equilibrium and elution K values to show fraction of total column effective in adsorption.

column is effective in containing the solute, or that this fraction of the column, used as an equilibrium system, would have a value of K associated with it equal to $\underline{R}$ for the total column. While the particular value of α must be a function of the shape of the isotherm for each chromatographic system, it will be considered constant for purposes of relating values of W_s and θ in the next section. Returning to the data of Fig. 4, it is noted that the various chromatographic data all fall close to the same curve, even though a wide range in chromatographic conditions are represented (e.g., column lengths from 3 to 54 inches). This means that eqn. (13) is capable of accurately reducing various chromatographic systems to a comparable basis. In addition, the agreement between equilibrium and superimposed chromatographic data is suggestive of a correspondence between $\underline{R}$ and K values.

The maximum column loading permissible for LEAC (linear capacity) with

alumina as adsorbent can be calculated, assuming the most favorable case (a homogeneous site distribution). W_a is equal to about 0.05 for calcined alumina, $\theta._1$ equals 0.1 for a homogeneous site distribution, and taking a value of α equal to 0.05, a maximum value of W_s equal to $2.5 \cdot 10^{-4}$ is calculated for $\underline{R}/R^0 \geqslant 0.9$. Since site heterogeneity is not unexpected in the various metal oxide adsorbents (compare next section), it could have been anticipated that LEAC would have been confined to column loadings of the order of 10^{-4} or less for elution from alumina.

EXPERIMENTAL OBSERVATIONS ON SOME ELUTION ADSORPTION CHROMATOGRAPHIC SYSTEMS

Equivalent retention volumes $\underline{R}$ have been measured for a number of chromatographic systems. Fig. 5 shows data for calcined alumina and silica as adsorbents, with a linear isotherm region observable in each case. Since linearity has already been observed by SPORER AND TRUEBLOOD[7] in systems featuring calcined silica, the latter observation is unsurprising. Fig. 6 shows the dependence of adsorbent linear capacity $(\theta._1)$ on the water deactivation of alumina, for the elution of naphthalene as solute by carbon tetrachloride as eluent. With from 0 to 2% water on alumina, $\theta._1$ continues to increase with added water. From this it may be inferred that the effective site distribution is of the "declining" rather than rectangular type for this adsorbent.
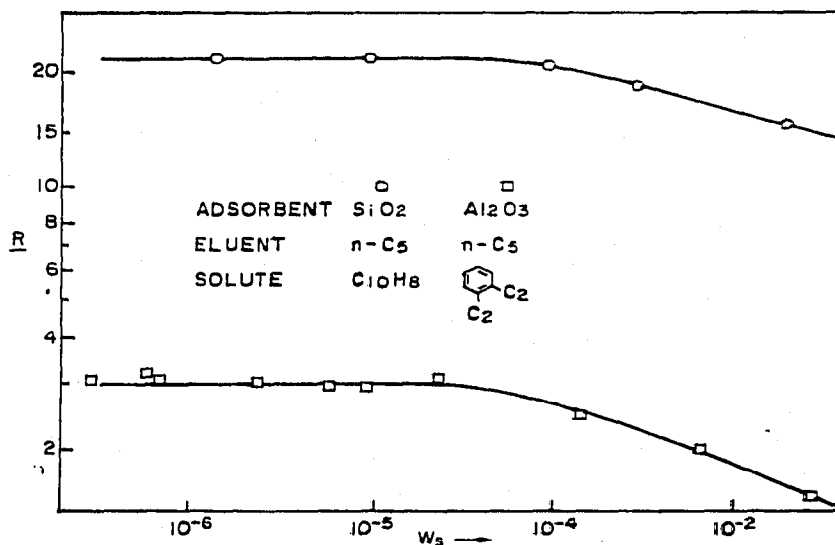

Fig. 5. Examples of linear elution adsorption chromatography.

Since $\theta._1$ is defined in terms of the *original* adsorbent capacity W_a in Fig. 6, the site distribution appears to have become almost homogeneous with the addition of 2% water. The W_s scale on the right of Fig. 6 gives the maximum column leadings for the maintenance of linear behavior, assuming the standard band width case but not taking into account the fact that the fraction of solute in the adsorbed phase varies. They are useful indications of the relative oil to gel ratios required for linearity in a typical elution system.

A number of R versus θ (or, what is equivalent at values of R close to R^0, of R versus W_s) plots have been obtained for different chromatographic systems featuring alumina or silica as adsorbent. Applying the previous criterion for the linear extrapola-
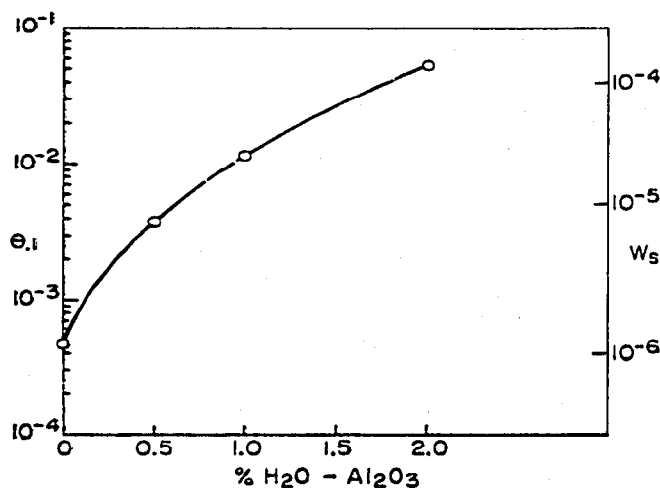

Fig. 6. Linear capacity as a function of adsorbent deactivation; elution of naphthalene by carbon tetrachloride from alumina.

tion of these plots to give values of R^0, extrapolated values are compared in Table I with those observed in the linear region. This extrapolative procedure is designed to permit extrapolation only of R data lying between $0.9\ R^0$ and R^0. For more "extreme" extrapolation, where a ten-fold change in oil to gel ratio causes more than a 10 % change in R, the linear extrapolation fails. This is also shown in Table I, where the results of extrapolating from R equals $0.5\ R$ (with the second oil to gel value being 0.1 times the latter) are shown.

TABLE I

THE USE OF LINEAR EXTRAPOLATION FOR VALUES OF R^0

Adsorbent	Eluent	Solute	R^{0*}	Extrapolated values of R^0	
				10 %**	50 %**
1.0 % H_2O–Al_2O_3	n-Pentane	Naphthalene	8.4	8.5	6.2
3.9 % H_2O–Al_2O_3	n-Pentane	Naphthalene	1.385	1.385	1.27
SiO_2 (calcined)	n-Pentane	Naphthalene	22.0	22.5	17.0
1.0 % H_2O–Al_2O_3	CCl_4	Naphthalene	2.33	2.35	
2.0 % H_2O–Al_2O_3	CCl_4	Naphthalene	0.68	0.675	
0.5 % H_2O–Al_2O_3	CCl_4	Methyl ethyl sulfide	6.8	6.75	

* Average value measured in linear region.
** Change in R produced by ten-fold change in W_s.

Values of W_s rather than θ are experimentally more accessible, and the two quantities are essentially interchangeable in the extrapolation procedure when values

$\underline{R}$ are greater than 1, and V_n for the adsorbent is less than 1. Since θ is proportional to $R/(R + V_n)W_s$, the latter quantity may be substituted exactly for the former in linear extrapolations.

Experimental

The eluents were 99.0 % or reagent-grade commercial chemicals, and were purified prior to use by passage over silica gel for the removal of trace polar constituents. The solutes were American Petroleum Institute standard samples, of higher than 99 ½ % purity. The adsorbents, Alcoa F-20 grade alumina and Davison 28 mesh silica, were first calcined at 400° for 16 h, following which deactivated samples were made up by addition of water. The percentages of water refer to the grams added per 100 grams of adsorbent. Both equilibrium and chromatographic data were measured at room temperature, 24°. To obtain the equilibrium K data of Fig. 6, the concentration of solute in solution was measured by ultraviolet absorption, and a difference procedure was used to calculate the concentration of solute in the adsorbed phase. The volume of the adsorbed phase, which is required in the calculation of K, was 0.05 ml/g of adsorbent (from the extrapolation of the solute uptake data to infinite solution concentration — Langmuir plot).

DEFINITIONS OF SYMBOLS

a subscript refers to "in adsorbed phase"

F_i dimensionless site free energy, — log K_i

F_0 value of F_i for some particular point (*e.g.*, the maximum of a Gaussian) on a site energy distribution curve

K equilibrium constant defined for total adsorbent–solvent system; $K = \theta/(X)_n$; for the experimental data of Fig. 5 and related discussion, K is defined in terms of concentration of solute per unit weight of total adsorbent rather than volume of adsorbed phase

K_i Langmuir coefficient; (see eqn. (2)); e^{F_i}

K_0 value of K in the limit as solute concentration approaches zero; the linear distribution coefficient

m ratio of solute to solvent molar volumes; see eqn. (1)

n subscript refers to "in non-sorbed phase"

N_i fraction of total adsorbent sites possessing free energy of homogeneous set i

p width of site energy distribution curve in units of F_i; difference in F_i values between two arbitrary points on distribution curve

R' uncorrected retention volume

R retention volume corrected for column dead volume; $R = R' - V_0$

$\underline{R}$ equivalent corrected retention volume; R'/W

$\underline{R}^0$ linear equivalent corrected retention volume; R/W

$S_{(k)}$ solvent or eluent in phase k

V_0 column dead volume; equal to volume of moving phase plus adsorbed phase

V_a volume of adsorbed phase (monolayer) in ml per gram of adsorbent

V_n volume of non-sorbed phase per gram of adsorbent

w band width

W total weight of adsorbent in chromatographic column

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

W_a weight of adsorbed phase per gram of adsorbent

$X_{(k)}$ solute in phase k

$(X)_k$ solute concentration in phase k

α fraction of a chromatographic column which, when used as an equilibrium adsorption system would give a value of K equal to R for the column

θ fraction of adsorbent sites covered by solute

θ_ε linear adsorbent capacity; value of θ at which K/K_0 declines from 1 by amount ε.

SUMMARY

Adsorbent linear capacity has been shown to be independent of the average strength of adsorption sites, but inversely proportional to site energy distribution width. Water deactivation of an adsorbent normally leads to an increase in adsorbent linear capacity because the site distribution tails toward the strong site end. Linear extrapolation of experimental distribution coefficient values leads to correct linear coefficients if certain precautions are taken.

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