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THE ROLE OF DISPERSION INTERACTIONS IN ADSORPTION CHROMATOGRAPHY

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SUMMARY

Previous treatments of the theory of adsorption chromatography have emphasized the role of so-called "specific" or non-dispersion interactions in determining adsorption energies (and sample migration) in systems of practical interest. In many cases the corresponding contributions of dispersion interactions to adsorption energy cancel and can therefore be ignored. This is not true, however, for separations by gas-solid chromatography, separations on charcoal, or separations with very weak solvents such as the perfluoroalkanes. A general theory of the effects of dispersion interactions in separations by adsorption chromatography has been developed and applied to some pertinent data from the literature.

INTRODUCTION

The theory of separation in typical liquid-solid (*i.e.* adsorption) chromatography systems is now reasonably well developed (for a review, see ref. 1). Retention volumes and R_F values can be related to experimental separation conditions and the molecular structure of the sample by means of the relationships

$$\log \bar{R}^\circ = \log V_a + \alpha(S^\circ - A_s \epsilon^\circ) \quad (1)$$

and

$$R'_M = \log (V_a W/V^\circ) + \alpha(S^\circ - A_s \epsilon^\circ), \quad (1a)$$

Here \bar{R}° is the linear-isotherm equivalent retention volume of a given compound X (ml/gram, corrected for column void volume), and R'_M is equal to $\log[(1/\xi R_F) - 1]$, where ξ is a solvent concentration parameter which is normally equal to about 1.1 in thin-layer chromatography. V_a is the adsorbent surface volume (proportional to adsorbent surface area), α is the adsorbent surface activity function (proportional to the strength or activity of the adsorbent surface), S° is the adsorption energy of X in a standard chromatographic system, A_s is the area required by X when it is adsorbed on the adsorbent surface, ϵ° is the solvent strength parameter, W is the weight of adsorbent (g), and V° is the bed free-volume (ml). The parameter S° can be related to the molecular structure of X by means of other theoretical relationships. The derivation of eqn. 1 (see ref. 1) is based on two important approximations:

For specific interactions of a given kind (implying a single type of adsorption site and a single adsorption mechanism), it has been shown (see section 4-2A of ref. 1) that these energy terms $(E_{t,a})_{\text{spec}}$ are generally of the form

$$(E_{t,a})_{\text{spec}} = \alpha f(i), \quad (4c)$$

where α is some function of the adsorbent surface (the surface activity function of eqn. 1), and $f(i)$ is some function of the adsorbing molecule i (the specific interaction energy of i with an adsorbent surface of standard activity, $\alpha = 1$). We will define S° as the value of $f(i)$ for a sample molecule X, and E° as the value of $f(i)$ for a solvent molecule S. If the areas of molecules X and S are defined as A_s and A_e , respectively, the interaction energy per unit area of adsorbed solvent ϵ° (the solvent strength parameter) is equal to E°/A_e and the quantity m is equal to A_s/A_e . Substituting these various expressions into eqn. 4b gives

$$\begin{aligned} \Delta E &= (E_{x,a} - mE_{s,a})_{\text{disp}} + \alpha(S^\circ - mE^\circ) \\ &= (E_{x,a} - mE_{s,a})_{\text{disp}} + \alpha(S^\circ - A_s\epsilon^\circ), \end{aligned} \quad (5)$$

The dispersion interaction energy between two adjacent atoms 1 and 2 is given as

$$E_{12} = \frac{-3 \alpha_1 \alpha_2}{2 r_{12}^6} \left[\frac{I_1 I_2}{I_1 + I_2} \right]$$

where α_1 and α_2 refer to the polarizabilities of atoms 1 and 2, respectively, I_1 and I_2 are their ionization potentials, and r_{12} is the distance separating the two atoms. It has been shown² that the above expression may be recast into a good approximation which will prove more useful:

$$E_{12} \approx \frac{3\alpha_1\alpha_2 I_1 I_2}{4r_{11}^3 r_{22}^3 \sqrt{I_1 I_2}} \quad (6)$$

The quantities r_{11} and r_{22} refer to the distance of separation between two adjacent, nonbonded atoms of 1 or 2, respectively. The adsorption energy of an atom 1 (ΔE_1) on an adsorbent composed of atoms 2 is given by the summation of eqn. 6 over all atoms of 2 in the adsorbent:

$$\Delta E_1 = \left[-\frac{\alpha_1 \sqrt{I_1}}{r_{11}^3} \right] \sum \left[\frac{3\alpha_2 \sqrt{I_2}}{4r_{22}^3} \right], \quad (6a)$$

A similar expression for an adsorbed molecule i is obtained by summing eqn. 6a over the various atoms in the molecule. The dispersion interaction $(E_{t,a})_{\text{disp}}$ between an adsorbed molecule i and the adsorbent surface is now seen to be of the same form as eqn. 4c for specific interactions:

$$(E_{t,a})_{\text{disp}} = \alpha_a f_a(i), \quad (6b)$$

α_a is some property of the adsorbent (analogous to α), and $f_a(i)$ is some property of the adsorbate molecule i (analogous to $f(i)$). From eqn. 6b it can be seen that $f_a(i)$ is

related to the polarizability of i , and experimentally it is found³ that dispersion interaction energies (adsorption energies on graphite, see below) are proportional to adsorbate polarizability.

We can define the dispersion energy terms S_d and E_d , analogous to the selective energy terms S° and E° . S_d is the value of $f_d(i)$ for a sample molecule X, and E_d is the value of $f_d(i)$ for a solvent molecule S. The dispersion adsorption energy of the solvent per unit area ($\epsilon_d = E_d/A_e$) can be defined also; ϵ_d is analogous to the solvent strength parameter ϵ° . Eqn. 5 can now be rewritten as

$$\begin{aligned} \Delta E &= \alpha_d(S_d - mE_d) + \alpha(S^\circ - A_s\epsilon^\circ) \\ &= \alpha_d(S_d - A_s\epsilon_d) + \alpha(S^\circ - A_s\epsilon^\circ), \end{aligned} \quad (7)$$

Finally eqns. 3 and 7 can be combined to give a general expression for \underline{R}° :

$$\log \underline{R}^\circ = \log V_a + \alpha_d(S_d - A_s\epsilon_d) + \alpha(S^\circ - A_s\epsilon^\circ) \quad (8)$$

We will next examine the variation of the dispersion energy terms $\alpha_d S_d$ and $\alpha_d \epsilon_d$ with the nature of X and S. Then we will show how eqn. 8 can be applied to various chromatographic systems.

Dependence of $\alpha_d S_d$ on the structure of X

For adsorption onto charcoal or graphite it is generally agreed that only dispersion forces contribute to adsorption energy (*i.e.* $\alpha[S^\circ - A_s\epsilon^\circ]$ equals zero; see discussion of section 3-1B, ref. 1). Similarly for gas-solid systems in which the carrier gas does not adsorb, ϵ° and ϵ_d must also equal zero; *i.e.* an adsorbing sample molecule X does not displace any solvent molecules S from the adsorbent surface. Consequently eqn. 8 for gas-solid adsorption on graphite simplifies to

$$\log \underline{R}^\circ = \log V_a + C + \alpha_d S_d, \quad (9)$$

The constant term C in eqn. 9 recognizes certain differences in the entropy of adsorption for gas-solid *versus* liquid-solid systems (see later discussion). It is appropriate to define $\alpha_d S_d$ in such a way that it is equal to zero when dispersion interactions between adsorbed X and the adsorbent surface are absent; *i.e.* when the dispersion energy of adsorption (or the heat of adsorption) is zero. Some recent data of KISELEV *et al.*⁴ for gas-solid chromatography on a graphitized carbon black can now be used to evaluate the parameter $\alpha_d S_d$ for adsorption of several common organic compounds on this adsorbent. Retention volume values V_s are reported for nitrogen elution of the compounds of Table I at 100° and 200°, and these data can be extrapolated to give V_s values at room temperature (24°). For a compound with zero heat of adsorption (no dispersion interactions), these data show that $\log V_s = -2.84$ (V_s in units of ml/m²). Consequently we can calculate $\alpha_d S_d$ from these data and eqn. 8 by means of the relationship

$$\log V_s = -2.84 + \alpha_d S_d, \quad (9a)$$

It is convenient at this point to define α_d for the charcoal surface* equal to 1.00. With

* More specifically, α_d is defined equal to 1.00 for this particular charcoal⁴, at a separation temperature of 24°.

TABLE I

VALUES OF S_d FOR DIFFERENT COMPOUNDS FROM EQN. 9a AND THE DATA OF KISELEV *et al.*^a

Compound	S_d (<i>expt.</i>)	A_s^b	S_d/A_s	S°/A_s^b	S_d (<i>calc.</i>) ^c
Methanol	2.21	2.9	0.76	2.24	1.7
Nitromethane	3.23	3.8	0.85	1.42	3.2
Carbon tetrachloride	3.84	5.0	0.77		
Acetonitrile	3.05	3.1	0.98	1.61	3.0
Ethanol	2.86	3.7	0.77	1.76	2.5
Acetic acid	3.56	4.4	0.81		3.6
<i>n</i> -Propanol	3.34	4.4	0.76		3.4
Acetone	3.50	4.2	0.83	1.19	3.5
Ethyl ether	3.66	5.2	0.70	0.68	3.7
Ethyl acetate	4.17	5.5	0.76	0.91	4.2
<i>n</i> -Butanol	4.09	5.2	0.79		4.2
<i>n</i> -Pentane	3.88	5.9	0.66	0.00	4.0
<i>n</i> -Propanol	4.93	5.9	0.84	0.77	4.9
Pyridine	4.61	5.8	0.79		4.6
Cyclohexane	4.05	6.4	0.63	0.00	4.0
Benzene	4.46	6.0	0.74	0.31	4.7
<i>n</i> -Hexane	4.82	6.6	0.73		4.8
Phenol	5.93	6.4	0.93		5.7
Aniline	5.98	6.6	0.91	0.95	6.0
Nitrobenzene	6.55	7.3	0.90	0.63	7.3
Toluene	5.56	6.8	0.82	0.30	5.5
<i>n</i> -Heptane	5.71	7.4	0.77	0.01	5.7
Benzaldehyde	6.10	7.1	0.86	0.73	6.1
Anisole	6.25	7.1	0.88		6.0
Average			0.80 ± 0.08 (std. dev.)		

^a Calculated from Table 8-4 of ref. 1, except that α_t value for $-\text{CH}_2-$ is taken as 0.75 and A_s for *n*-alkanes is $2.1 + 0.75 n$, where n is number of carbon atoms in molecule (see comments of ref. 5).

^b Calculated from data of ref. 1.

^c Eqn. 9b and data of Table II.

these conventions, the data of KISELEV *et al.* yield the S_d values of Table I. Values of the effective molecular area A_s for the compounds of Table I are also tabulated, and the ratio S_d/A_s is shown in Table I. We see that these values of S_d/A_s are reasonably constant (0.80 ± 0.08 std. dev.), a fact which will prove important with respect to the role of dispersion forces in adsorption chromatographic systems. By way of contrast, the ratio S°/A_s is also calculated for several of the compounds of Table I. S°/A_s is seen to vary from 0.0 to 2.2 and exhibits no tendency toward constancy. That is, dispersion energies per unit area of adsorbate-adsorbent interface are approximately constant for different adsorbates, while selective interaction energies per unit area vary widely. The constancy of these dispersion interaction energies per unit area is also predicted on the basis of other observations (see discussion of section 3-1A, ref. 1).

Another consequence of the nature of dispersion forces is the approximate additivity of dispersion energies for different atoms or groups in the adsorbate

molecule (e.g. methyl, methylene, halogen, hydroxyl, amino). That is, to a first approximation S_a should be equal to the sum of adsorption energies $(Q_i)_a$ for individual groups i in the molecule X:

$$S_a = \sum (Q_i)_a \quad (9b)$$

This relationship can be tested for the compounds of Table I by deriving best values of the group adsorption energies (Table II) and using these to calculate values of S_a .

TABLE II
VALUES OF $(Q_i)_a$ FOR VARIOUS MOLECULAR GROUPS i

Group	$(Q_i)_a$	Group	$(Q_i)_a$
Methyl, $-\text{CH}_3$	0.71	Keto, $\text{C}=\text{O}$	2.08
Methylene, $-\text{CH}_2-$	0.85	Cyclohexane	4.05
Methyne, $-\text{CH}<$	0.87 ^a		
Ether, $-\text{O}-$	0.54	Formyl, $-\text{CHO}$	1.35
Hydroxy, $-\text{OH}$	0.96	Amino, $-\text{NH}_2$	1.23
Nitro, $-\text{NO}_2$	2.52	Benzene	4.75
Cyano, $-\text{C}\equiv\text{N}$	2.34	$-\text{COOCH}_3$	2.61
Carboxyl, $-\text{COOH}$	2.85	Pyridine	4.6

^a Data of ref. 10.

As seen in Table I, these calculated values of S_a agree with experimental values within ± 0.2 units (std. dev.).

Adsorption from normal solvents onto polar adsorbents

The quantities E_a and S_a for a given compound are equal, since both quantities refer to the dispersion adsorption energy for that compound. We have noted that $S_a \approx 0.8 A_s$, and therefore $E_a \approx 0.8 A_e$ (recalling that A_e is the area required by an adsorbed solvent molecule). The quantity ϵ_a is equal to E_a/A_e , and therefore $\epsilon_a \approx 0.8$. Inserting these approximate relationships into eqn. 8 then gives

$$\log R^\circ = \log V_a + \alpha_a(0.8 A_s - 0.8 A_s) + \alpha(S^\circ - A_s \epsilon^\circ),$$

which is seen to reduce to eqn. 1. That is, dispersion interactions normally cancel in liquid-solid chromatography. Eqn. 1 has been tested in numerous separations by liquid-solid chromatography on polar adsorbents, and it has been found to be generally reliable*. It should be pointed out that the cancellation of dispersion energy terms need not be exact for eqn. 1 to be obeyed. Small differences in S_a and $A_s \epsilon_a$ can be accommodated within the corresponding S° or ϵ° values. The applicability of eqn. 1 requires only that these net dispersion energies be small relative to S° and $A_s \epsilon^\circ$ values.

* This is particularly true for weak and moderately strong solvent systems (i.e. $\epsilon^\circ < 0.5$), where solution interactions (which tend to cause deviations from eqn. 1) are generally unimportant, and dispersion energy contributions are relatively large compared to specific interaction energy contributions. This further emphasizes the effective cancellation of the dispersion energy term $\alpha_a(S_a - A_s \epsilon_a)$ of eqn. 8 for most liquid-solid separations on polar adsorbents.

Adsorption from perfluoroalkane solvents onto polar adsorbents

Solvents such as the saturated hydrocarbons and perfluoroalkanes are commonly assumed to be incapable of specific interaction with the surfaces of polar adsorbents. (See following section on gas-solid separations.) Consequently the ϵ° values of these very weak solvents should be equal to zero. We can therefore write for these chromatographic systems

$$\log R^\circ = \log V_a + \alpha S^\circ + \alpha_a(S_a - A_s \epsilon_a) . \quad (10)$$

In the case of the saturated hydrocarbons (and other "normal" solvents) we have seen that the term $\alpha_a(S_a - A_s \epsilon_a)$ normally cancels (approximately). This is equivalent to saying that ϵ_a values for the saturated hydrocarbon solvents (and other "normal" solvents) are approximately constant. In the case of the perfluoroalkanes, however, it is known (*e.g.* ref. 2) that their dispersion interactions with other substances (*e.g.* the adsorbent surface) are abnormally weak. As a result we would expect that ϵ_a values for the perfluoroalkanes will be significantly less than ϵ_a values for the saturated hydrocarbons. In agreement with theory, ATTAWAY and coworkers^{6,7} have found that the perfluoroalkanes are significantly weaker solvents than the saturated hydrocarbons.

The retention volumes for a given compound X in two different solvent systems 1 and 2, each of which solvents adsorb by dispersion interactions only, can be related through eqn. 10. For solvent 1 we can write

$$\log R_1 = \log V_a + \alpha S^\circ + \alpha_a(S_a - A_s \epsilon_1') ,$$

and for solvent 2,

$$\log R_2 = \log V_a + \alpha S^\circ + \alpha_a(S_a - A_s \epsilon_2') .$$

Here R_1 and R_2 are the R° values in solvents 1 and 2, respectively, and ϵ_1' and ϵ_2' are the ϵ_a values of solvents 1 and 2. Subtracting the second equation from the first, we have

$$\log (R_1/R_2) = \alpha_a A_s (\epsilon_2' - \epsilon_1') . \quad (11)$$

Eqn. 11 permits us to calculate values of ϵ_a when we have retention volume values in two solvents, one of known ϵ_a value. Table III summarizes ϵ_a values for several solvents of the type under discussion (*i.e.* for which ϵ° is zero) on either silica or alumina. These data were obtained by application of eqn. 11, with ϵ_a values for pentane obtained by other means (see following discussion on gas-solid chromatography). Values of ϵ_a should be approximately independent of adsorbent type, since the effect of the adsorbent on ϵ_a is taken care of by the adsorbent parameter α_a . We see in Table III that ϵ_a values for a given solvent on both alumina and silica are in fact quite similar. We also see in Table III that both the perfluoroalkanes and the perfluorocyclic ethers are much weaker solvents than the saturated hydrocarbons. Introduction of chloro groups into a perfluoroalkane increases ϵ_a for these solvents to the point where their solvent strengths are comparable to those of the saturated hydrocarbons. Perfluoroaromatics (*e.g.* hexafluorobenzene) have solvent strengths

TABLE III

VALUES OF α_d AND ϵ_d FOR VARIOUS ADSORBENTS

	Charcoal	Alumina	Silica
α_d	(1.0)	0.80 ^a	0.59 ^b
ϵ_d			
He, N ₂ (gas-solid)	0.00	0.00	0.00
FC-75 ^c		0.92	0.98
FC-78 ^c		0.94	1.01
Perfluoroalkane ^d			1.03
Pentane		1.16	1.22
Isooctane ^e		1.17	
<i>n</i> -Hexane ^e		1.17	
<i>n</i> -Octane ^e		1.17	
2,3-Dichlorooctafluorobutane ^f			1.23
<i>n</i> -Decane ^e		1.19	
Cyclohexane ^e		1.19	
Cyclopentane ^e		1.20	
1,2-Dichlorohexafluoropentene-1 ^f			1.27
Hexafluorobenzene ^f			1.27
Benzene ^g	1.05		
Ethanol ^g	0.98		

^a Data of SCOTT⁹; see discussion of text.

^b Data of BELLAR AND SIGSBY¹⁰; see discussion of text.

^c Perfluorocyclic ethers⁵.

^d Estimated from data of ref. 6.

^e Calculated from data of ref. 11.

^f Estimated from data of ref. 7.

^g See text.

greater than those of the saturated hydrocarbons. The very low ϵ_d values of the perfluoroalkanes and perfluorocyclic ethers permit a number of unique separations (see ref. 6-8).

The form of eqn. 11 is essentially similar to the relationship between retention volumes in normal solvent systems (derivable from eqn. 1):

$$\log (R_1/R_2) = \alpha A_s(\epsilon_2 - \epsilon_1) \quad (11a)$$

Here ϵ_2 and ϵ_1 refer to the ϵ° values of the two solvents 1 and 2. Change in $\log R^\circ$ with change in solvent strength (ϵ° or ϵ_d) is predicted to be proportional to the value of A_s for the sample molecule in both "normal" and "abnormal" (as in Table III) solvents. This has already been verified for normal solvents (eqn. 11a; see section 8-1 of ref. 1), and a following paper⁵ provides a similar verification of eqn. 11 for the perfluorocyclic ethers and pentane as solvents. The only real difference between eqns. 11 and 11a is in the effect of adsorbent activity (α or α_d) on the difference in $\log R^\circ$ values in two different solvents. α_d is often constant for an adsorbent of given type, regardless of adsorbent water content (see a following section). Consequently $\log (R_1/R_2)$ in eqn. 11 does not vary much as adsorbent water content is changed (as by adding water or by thermally activating the adsorbent). The adsorbent parameter α , on the other hand, varies markedly with changes in adsorbent water content (see Chapter 7 of ref. 1). Consequently $\log (R_1/R_2)$ for normal solvents varies correspondingly with changes in adsorbent water content.

Eqn. 8 is a more general, and potentially a more accurate, relationship than either eqns. 1 or 10 for separations on polar adsorbents. However in most cases it is much simpler and equally accurate to use either eqn. 1 or eqn. 10, depending upon solvent type. We will arbitrarily accept eqn. 1 as a limiting form of eqn. 8 for solvents stronger than pentane ($\epsilon^\circ > 0.00$), and eqn. 10 will be taken as a limiting form of eqn. 8 for weaker solvents (*e.g.* the perfluoroalkanes, perfluorocyclic ethers). Either eqn. 1 or 10 can be used for pentane as solvent.

Adsorption on charcoal

We have already noted that specific adsorption interactions are essentially absent in adsorption on charcoal (except for the special case of "oxidized" charcoals¹). Therefore eqn. 10 should describe the relative adsorption of different sample molecules X onto charcoal, as a function of separation conditions. Since S_a does not vary much among different compound types, there should be little tendency toward separation of samples on charcoal according to compound type (*e.g.* hydrocarbons, ethers, esters, alcohols, etc.). In this respect charcoal differs markedly from polar adsorbents such as silica and alumina. The data of Tables I and II do predict that R° values on charcoal should increase regularly with increasing sample molecular weight, at least for most solvents. This can be seen by considering the S_a value of a member of a homologous series $X-(CH_2)_n-CH_3$. If $(S_a)_0$ refers to the S_a value for the compound $X-CH_3$, and if $(A_s)_0$ is its A_s value, then from eqn. (9b) and Table II we have for a member of the homologous series

$$S_a = (S_a)_0 + 0.85 n,$$

and similarly (see Table I, footnote a),

$$A_s = (A_s)_0 + 0.75 n.$$

The difference in R° values for a homolog (R_n) and the parent compound $X-CH_3$ (R_0) is then given as

$$\log R_n - \log R_0 = n\alpha_a(0.85 - 0.75 n\epsilon_a).$$

Recalling that for the average solvent, $\epsilon_a \approx 0.8$, we have

$$\log R_n - \log R_0 = 0.25 n.$$

The preferential adsorption of higher molecular weight samples on charcoal from most solvents is now well established (see review of ref. 1). This fact is not based upon an especially strong adsorption of the $-CH_2-$ group, since the preferential adsorption of higher molecular weight samples on charcoal is not limited to homologous series. Rather, there is a general trend to higher molecular polarizabilities per unit area (per unit of A_s) for all samples as molecular weight increases.

Let us next examine the applicability of eqn. 10 for adsorption on charcoal, in terms of some literature data. SMITH AND LERSEN¹² have reported R_F values for several ketones in column development on charcoal, using benzene as solvent. These data are summarized in Table IV, along with calculated values of $\alpha_a S_a$ and A_s . The

TABLE IV

SEPARATION OF VARIOUS KETONES ON CHARCOAL (BENZENE DEVELOPMENT); CORRELATION WITH EQN. 10

Compound	R_F (<i>expt.</i>) ^a	S_d ^b	A_s ^c	R_F (<i>calc.</i>) ^d
Acetone	0.79	3.50	4.2	0.74
Methyl ethyl ketone	0.79	4.35	4.9	0.69
Methyl propyl ketone	0.78	5.20	5.7	0.64
Methyl iso-propyl ketone	0.89	5.08	5.7	0.70
Diethyl ketone	0.79	5.20	5.7	0.64
Methyl butyl ketone	0.73	6.05	6.4	0.63
Methyl iso-butyl ketone	0.86	5.93	6.4	0.69
Cyclohexanone	0.80	5.28	6.5	0.93
Methyl pentyl ketone	0.69	6.90	7.2	0.57
Methyl hexyl ketone	0.63	7.75	7.9	0.56
Methyl phenyl ketone	0.34	7.54	7.5	0.43
Methyl heptyl ketone	0.60	8.60	8.7	0.50
Methyl phenyl ketone	0.29	8.39	8.3	0.43
Methyl octyl ketone	0.51	9.45	9.4	0.48
Methyl nonyl ketone	0.52	10.35	10.2	0.47
Methyl decyl ketone	0.43	11.15	10.9	0.41
Methyl undecyl ketone	0.41	12.00	11.7	0.41
Methyl dodecyl ketone	0.44	12.85	12.4	0.35
Methyl tridecyl ketone	0.36	13.70	13.2	0.34
Dibenzyl ketone	0.31	13.28	12.6	0.43
Methyl tetradecyl ketone	0.32	14.55	13.9	0.29
Methyl pentadecyl ketone	0.30	15.40	14.7	0.28
Methyl hexadecyl ketone	0.28	16.25	15.4	0.23
Methyl heptadecyl ketone	0.29	17.10	16.2	0.23

^a Experimental data of ref 12; ξ assumed equal 1.0 in calculation of R'_M values.^b Calculated from $(Q_t)_d$ values of Table II and eqn. 8b.^c Calculated as in Table I.^d Calculated as described in text, with $(S_d - R'_M) = 1.05 A_s - 0.45$.

R'_M value, defined as $\log [(1/\xi R_F) - 1]$, can be shown to be equal to $\log \frac{R^\circ}{W/V^\circ} + \log (W/V^\circ)$, where W refers to the weight of adsorbent in the column and V° is the column void-volume. Combining this expression for R'_M with eqn. 10 then gives

$$R'_M = \log (V_a W / V^\circ) + \alpha_d (S_d - A_s \epsilon_d), \quad (12)$$

OR

$$\alpha_d S_d - R'_M = -\log (V_a W / V^\circ) + \alpha_d \epsilon_d A_s.$$

The latter expression is tested in Fig. 1, using the data of Table IV, as a plot of $(\alpha_d S_d - R'_M)$ versus A_s . The linear plot predicted by eqn. 12 is obtained, and the slope of this plot (value of $\alpha_d \epsilon_d$) is equal to 1.05. The deviation of individual points from the curve of Fig. 1 is only ± 0.2 units, which corresponds to an error in A_s of 0.2 units. The calculated values of A_s shown in Table IV are certainly no more accurate than this, so eqn. 9 is obeyed as closely as could have been expected. The R_F values

of the various compounds of Table IV can now be calculated, using the values of $\log(V_a W/V^0)$ and $\alpha_a \epsilon_a$ derivable from the plot of Fig. 1 (0.45 and 1.05, respectively). These calculated R_F values are shown in Table IV. The preferential adsorption of aromatic ketones relative to aliphatic ketones of similar molecular weight is correctly predicted by eqn. 12, as is the preferential adsorption of *n*-alkyl ketones relative to

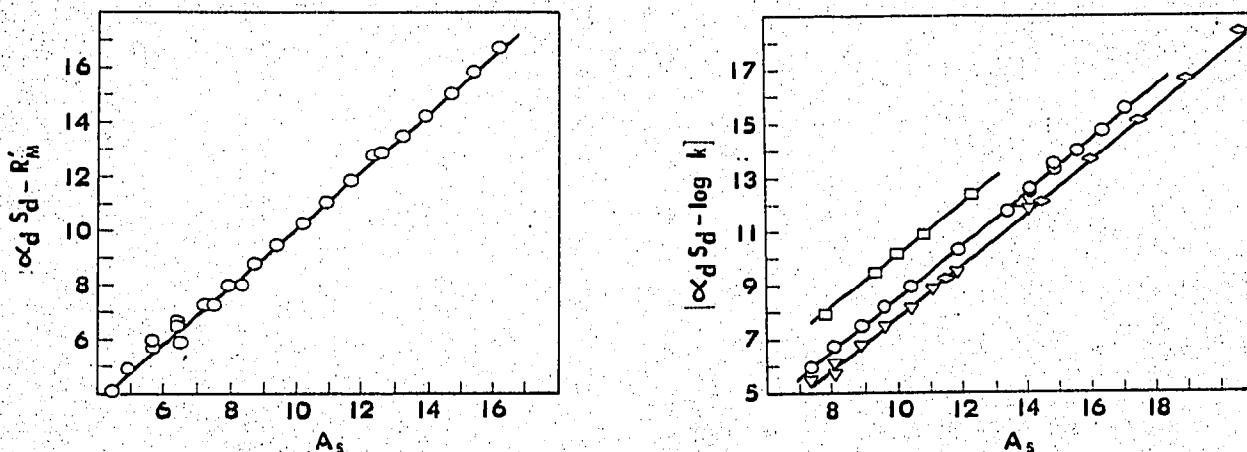


Fig. 1. Correlation of data of Table IV with eqn. 10.

Fig. 2. Correlation of data of Table V with eqn. 10. \circ = mono-acids; \square = di-acids; \triangle = alcohols; \diamond = ethyl esters.

isomeric *iso*-alkyl ketones. The preferential adsorption of aromatics on charcoal is a general phenomenon, as has been observed for a wide variety of sample types (see ref. 1).

CLAESSON¹³ has reported data for the equilibrium adsorption of several alcohols, esters and carboxylic acids on charcoal from ethanol. The Langmuir coefficient k , derivable from these data, can be shown to be proportional to R^0 . Consequently we have from eqn. 10

$$\log k = C + \alpha_a(S_a - A_s \epsilon_a),$$

with C constant. As in Fig. 1 for the data of Table IV, a plot of $(\alpha_a S_a - \log k)$ versus A_s should be linear, with the slope of the plot equal to $\alpha_a \epsilon_a$. Table V summarizes values of $\log k$ from ref. 13, along with calculated values of S_a and A_s . Fig. 2 tests the applicability of eqn. 10 for the data of CLAESSON. It is seen that a single linear plot is obtained for the alcohols and esters, but the corresponding plots for the acids and di-acids are displaced upward by 0.7 and 2.3 log units, respectively. This means that acids are adsorbed less strongly than predicted on the basis of eqn. 10 along, and this deviation is much greater than is expected on the basis of uncertainties in calculated values of S_a and A_s . We believe that solution interactions between sample and solvent molecules (which were ignored in the derivation of eqn. 10) are largely responsible for the deviations of Fig. 2. Thus the hydrogen bonding of ethanol molecules (solvent) with the various functional groups of these sample molecules ($-\text{OH}$, $-\text{COOC}_2\text{H}_5$, or $-\text{COOH}$) will increase the solution energy of the sample molecule ($E_{x,s}$ of eqn. 4) and thereby decrease k . If we assume equal interactions between solvent molecules

TABLE V

EQUILIBRIUM ADSORPTION OF VARIOUS COMPOUNDS ON CHARCOAL FROM ETHANOL

Compound	$\log k^a$	S_d^b	A_s^c
Carboxylic acids			
$C_nH_{2n+1}COOH$			
C ₅	1.00	6.96	7.4
C ₆	1.10	7.81	8.1
C ₇	1.23	8.66	8.9
C ₈	1.32	9.51	9.6
C ₉	1.43	10.36	10.4
C ₁₁	1.74	12.06	11.9
C ₁₃	1.99	13.76	13.4
C ₁₄	2.08	14.61	14.1
2-Methyl, C ₁₃	1.90	14.49	14.1
C ₁₅	2.22	15.46	14.9
2-Heptyl, C ₈	1.83	15.34	14.9
C ₁₆	2.33	16.31	15.6
C ₁₇	2.44	17.16	16.4
C ₁₈	2.48	18.01	17.1
Dicarboxylic acids			
$HOOC-C_nH_{2n}-COOH$			
C ₄	1.13	9.10	7.8
C ₆	1.34	10.80	9.3
C ₇	1.46	11.65	10.0
C ₈	1.59	12.50	10.8
C ₁₀	1.83	14.20	12.3
Alcohols			
$C_nH_{2n+1}OH$			
C ₇	1.34	6.77	7.4
C ₈	1.52	7.62	8.1
sec-C ₈	1.47	7.2	8.1
C ₉	1.68	8.47	8.9
C ₁₀	1.87	9.32	9.6
C ₁₁	2.01	10.17	10.4
C ₁₂	2.20	11.02	11.1
C ₁₃	2.37	11.87	11.9
C ₁₆	2.54	14.42	14.1
Ethyl esters			
$C_nH_{2n+1}COOC_2H_5$			
C ₉	1.74	10.97	11.5
C ₁₃	2.08	12.67	14.5
C ₁₅	2.27	14.37	16.0
C ₁₇	2.43	16.07	17.5
C ₁₉	2.65	17.77	19.0
C ₂₁	2.80	19.47	20.5

^a Experimental data of ref. 13.

^b Calculated from $(Q_1)_d$ values of Table II and eqn. 8b.

^c Calculated as in Table I.

and each of the two carboxyl groups of the various di-acids, we can estimate that hydrogen bonding between sample and solvent decreases $\log k$ (relative to noninteracting samples such as the hydrocarbons) by the following amounts:

ethyl esters R-COOC ₂ H ₅	0.9 log units
alcohols R-OH	0.9
acids R-COOH	1.6
di-acids R(COOH) ₂	3.2.

This order of increasing solution interaction energies is about what we would have expected on the basis of the strengths of the hydrogen bonds involved. These data of CLAESSON emphasize the general importance of solution interaction effects in adsorption on charcoal from polar solvents. Consequently eqn. 10 is expected to be only approximately valid for adsorption from polar solvents onto charcoal. Those systems where strong hydrogen bonding between solvent and sample molecules occur should give generally lower \bar{R}° values than predicted by eqn. 10, and the relative lowering of \bar{R}° values should be in proportion to the strengths of the hydrogen bonds formed.

If we assume that α_a for all charcoals is ~ 1.00 , then the above data suggest ϵ_a values of 1.05 for benzene and 0.98 for ethanol. These values (as well as other ϵ_a values Table III) are slightly higher than the S_a/A_s values of Table I (which should be equal to ϵ_a for these compounds). This discrepancy is probably the result of experimental uncertainties in the S_a and A_s values of Table I, as well as the approximate nature of our present general theory of the role of dispersion forces in adsorption.

DISPERSION INTERACTIONS IN GAS-SOLID CHROMATOGRAPHY

A previous derivation⁵ for retention volumes in gas-solid chromatography (GSC) has yielded the relationship

$$\log U'_g = \log V_a - 0.65 + \alpha(S^\circ - A_s \epsilon^\circ_g) . \quad (13)$$

Here U'_g is essentially equivalent to a retention volume \bar{R}° (corrected for differences in ambient versus column temperatures and pressures), and ϵ°_g has a constant value for any nonadsorbing carrier gas. The derivation of eqn. 13 does not recognize that the adsorption energy of pentane (*i.e.* its $\alpha_a S_a$ value) varies with α_a rather than with α . Furthermore, the constant term -0.65 of eqn. 13 represents an error in the theoretical derivation of eqn. 13. Eqn. 13 is therefore incorrect as it stands. We can re-derive a correct expression for U'_g in GSC by beginning with eqn. (8). For a nonadsorbing carrier gas we see that $E_{s,a}$ (and therefore ϵ° and ϵ_a) are zero. That is, the adsorption energy of the solvent need not be considered in GSC. Furthermore, there is a difference in the translational entropies of adsorbed and nonadsorbed sample molecules. This effectively adds a constant term C to the adsorption energy of the sample (ΔE); C apparently varies with the temperature of separation and the nature of the adsorbent. Combining these modifications of eqn. 8 we have

$$\log U'_g = \log V_a + C + \alpha_a S_a + \alpha S^\circ . \quad (13a)$$

In the case of GSC on charcoal, the term αS° equals zero, and eqn. 13a reduces to

$$\log U'_g = \log V_a + C + \alpha_a S_a (\text{charcoal}) . \quad (13b)$$

Comparison of eqn. 13b with the data of KISELEV *et al.*⁴ suggests that C varies from 0.6 (100°) to 0.8 (200°) for adsorption on graphite. Earlier data for adsorption on alumina⁵ indicate a value of C equal to -0.65 (83°).

For GSC on the polar adsorbents, measured values of S° are derived from \bar{R}° values in liquid-solid chromatography (with pentane as solvent). As we have seen, any net contribution of dispersion interactions to \bar{R}° (*i.e.* $\alpha_a[S_a - A_{s\epsilon_a}]$) are lumped into αS° (since S_a is assumed equal to $A_{s\epsilon_a}$). Let us assume that this cancellation of dispersion terms is in fact incomplete, so that $\alpha_a(S_a - A_{s\epsilon_a})$ is not zero. From eqn. 8 we see that a value of αS° derived from an experimental \bar{R}° value in pentane (assuming dispersion interactions cancel) will be related to a "true" value of αS° as

$$(\alpha S^\circ)_{\text{expt}} = (\alpha S^\circ)_{\text{true}} + \alpha_a(S_a - A_{s\epsilon_a}).$$

If eqn. 13a is used with experimental values of S° (as it must), then substituting the above expression for $(\alpha S^\circ)_{\text{expt}}$ into eqn. 13a gives

$$U'_g = \log V_a - 0.65 + \alpha S^\circ + \alpha_a A_{s\epsilon_p} \text{ (polar adsorbents)} \quad (13c)$$

Here ϵ_p refers to the ϵ_a value for pentane on the adsorbent in question (see Table III). As we will see, eqn. 13c is a reliable and useful expression for predicting retention volumes in GSC on the polar adsorbents. Before examining the experimental reliability of eqn. 13c, however, we will first look at the variation of α_a with the water content of the adsorbent (*i.e.* α_a as a function of adsorbent activation temperature or amount of added water) and separation temperature.

The variation of α_a with the water content of polar adsorbents

The value of α_a for a given adsorbent sample can be determined from the U'_g values of two or more n -alkanes. S° is approximately zero for these compounds (no specific interactions), and $S_a = 1.42 + 0.85 \alpha_a n$ for an n -alkane $\text{CH}_3(\text{CH}_2)_n\text{-CH}_3$ (Table II and eqn. 9b). For any two adjacent n -alkanes, $\text{CH}_3\text{-(CH}_2)_n\text{-CH}_3$ and $\text{CH}_3\text{-(CH}_2)_{n+1}\text{-CH}_3$, eqn. 13a then gives

$$\log(U_{n+1}/U_n) = 0.85 \alpha_a. \quad (14)$$

Here U_n and U_{n+1} refer to U'_g or retention volume values for the two n -alkanes. SCOTT has reported GSC retention volume values for ethane and propane at 15° on aluminas treated in various ways⁹. For aluminas preactivated at 100° intervals between 100° and 1000°, it can be calculated from SCOTT's data that $\alpha_a = 0.84 \pm 0.02$ (15°). That is, α_a does not vary with the activation temperature of the alumina. By contrast, the adsorbent parameter α (for specific interactions) varies from 0.7 for alumina preactivated at 100° to 2.1 for alumina preactivated at 1000°¹. For water deactivation of aluminas, α_a appears eventually to decrease with addition of large amounts of water. For a highly water-deactivated alumina studied by SCOTT, α_a can be calculated equal to 0.54 (versus above value of 0.84). Similarly for GSC separation at 83°⁶, α_a appears to vary from 0.60 for 1.5% $\text{H}_2\text{O-Al}_2\text{O}_3$ to 0.50 for 2.7% $\text{H}_2\text{O-Al}_2\text{O}_3$. However studies by liquid-solid chromatography⁸, suggests that α_a remains constant for 0 to 4% $\text{H}_2\text{O-Al}_2\text{O}_3$. With the exception of heavily water deactivated aluminas, we will assume that α_a is independent of adsorbent activation temperature and water content.

In the case of silica, KISELEV¹⁴ has noted that the relative (gas phase) adsorption of hexane on silica (per unit area) is independent of adsorbent activation temperature. This implies a constant value of α_d for silica, regardless of activation temperature. BELLAR AND SIGSBY¹⁰ have reported GSC data for separation of several hydrocarbons on a silica of varying water content (300 m²/g surface area, 150 Å pore diameter). For water contents which we estimate at 0 to 7% (no water deactivation, or water diffusion cell temperatures of 23° and 51°), α_d can be calculated (eqn. 14) equal to 0.59 ± 0.02 (elution at 22°). For higher adsorbent water contents (water diffusion cell temperature of 85°), α_d appears to drop slightly; however this may reflect some sample adsorption on a water phase on the adsorbent. Data of BELLAR AND SIGSBY for three other silicas of higher surface area (340–600 m²/g, pore diameters of 48–150 Å) yield α_d values of 0.60 ± 0.02 (22°). Data of KISELEV *et al.*¹⁵ suggest that silicas with surface areas higher than 300 m²/g (pore diameters less than 100 Å) give higher values of α_d than do silicas of lower surface area. The latter authors attribute this to increased dispersion interactions in very small pores of the adsorbent*. With the exception of high surface area, fine pore silicas, or of silicas with large water contents, we will assume that α_d is reasonably constant for different silica samples (just as in the case of alumina).

The temperature variation of α_d

A previous treatment (Chapter 12 of ref. 1) has shown that the effect of temperature changes on \bar{R}° can be expressed as an equivalent variation of α with temperature:

$$\alpha_T = a \left[1 - \frac{1 - 297/T}{1 - 297/a} \right]. \quad (15)$$

Here α_T is the value of α at some temperature T (°K), and α refers to the value at 24° (the standard reference temperature). The constant a was found to be equal to 2280 for separation on alumina (liquid–solid chromatography). Eqn. 15 predicts that α and \bar{R}° values will decrease with increasing separation temperature. Eqn. 15 is based on the empirical relationship

$$\Delta H_a^\circ = a \Delta S_a^\circ, \quad (15a)$$

which appears to hold for many adsorption systems. ΔH_a° refers to the heat of adsorption of a sample compound X, a is a constant, and ΔS_a° is the entropy of adsorption of X. Since eqn. 15a seems to hold for gas–solid adsorption on charcoal⁴, it is reasonable to postulate an expression for α_d which is analogous to that of eqn. 15 for α_d :

$$(\alpha_d)_T = \alpha_d \left[1 - \frac{1 - 297/T}{1 - 297/a} \right]. \quad (15b)$$

The constant a in eqn. 15b is found to be generally smaller than the value of a observed in eqn. 15 (2280). Thus for adsorption on charcoal, data of KISELEV *et al.*⁴ show a equal to 770. Similarly for adsorption of *n*-alkanes onto silica, data of KISELEV *et al.*¹⁵

* A similar increase in α_d would be predicted for very fine pore charcoals. This probably accounts for the greater activity of some charcoals, and the reduction of this activity upon addition of "saturators" to the charcoal (see ref. 1). Presumably the added "saturator" fills the smallest adsorbent pores.

suggest a value of a equal to 620. Taking an average value of these values of a in eqn. 15b (700), we can calculate the variation of α_a with temperature as shown in Table VI. The corresponding variation of α with temperature is also shown in Table VI, and we see that α_a varies with temperature to a greater extent than does α . The α_a

TABLE VI

VARIATION OF α_a AND α WITH SEPARATION TEMPERATURE

T ($^{\circ}\text{C}$)	$(\alpha_a/\alpha_{a,24})^a$	$(\alpha/\alpha_{24})^b$
-100	2.23	1.82
- 50	1.57	1.38
0	1.15	1.10
20	1.02	1.01
40	0.91	0.94
60	0.81	0.88
80	0.73	0.82
100	0.65	0.76
150	0.51	0.66
200	0.36	0.57

^a Eqn. 15b; GSC.

^b Eqn. 15; liquid-solid chromatography.

values of Table III for charcoal, silica and alumina have been corrected for any temperature effects by means of eqn. 12b. The preceding α_a values for alumina as a function of adsorbent pretreatment can be adjusted to a 24° basis as follows:

Al_2O_3 (100°–1000° activation) ⁹	0.80
1.5 % H_2O - Al_2O_3 ⁵	0.81
2.7 % H_2O - Al_2O_3 ⁵	0.69
"water deactivated alumina" ¹⁰	0.51.

These values from two independent studies at different temperatures (15° versus 83°) are in reasonable agreement, confirming the accuracy of eqn. 15b (with a equal ~ 700) for this adsorbent as well. It should be noted at this point that the values of a which have been derived for eqns. 15 and 15b involve liquid-solid systems for eqn. 15 and gas-solid systems for 15b. Thus it is possible that these differences in a may reflect the difference between liquid and gas chromatographic systems, rather than the difference between dispersion and specific interactions (α and α_a). Further work will be required to clarify this point.

Values of ϵ_a for pentane (*i.e.* ϵ_a) at 24° can now be calculated from the above GSC data^{9,10}, using eqn. 13c. These values are summarized in Table III.

It has been claimed by KING AND BENSON¹⁶ that the adsorption energy of non-polar, saturated compounds on polar adsorbents such as alumina is contributed to by electrostatic induction forces. That is, the adsorption energy of a compound such as methane is in part the result of a polarization of the methane molecule by a strong electrostatic field associated with the adsorbent surface. The induced dipole thus formed then interacts with the surface field, and a net attraction between the methane molecule and the adsorbent surface results. The preceding data on the dependence of α and α_a for alumina as a function of adsorbent activation temperature do not agree with this view of KING AND BENSON. Thus the sharp increase of α with increasing

TABLE VII

GSC SEPARATION OF VARIOUS HYDROCARBONS ON DIFFERENT SILICA SAMPLES; EXPERIMENTAL DATA OF BELLAR AND SIGSBY¹⁰

Compound	Log <i>t_r</i> ^a		Grade 62		Grade 113		Grade 81	
	Grade 58		0% H ₂ O-SiO ₂ ^b		0% H ₂ O-SiO ₂ ^b		0% H ₂ O-SiO ₂ ^b	
	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
Ethane	-0.15	-0.14	-0.52	-0.44	-0.70	-0.57	-0.10	-0.07
Ethylene	0.15	0.22	-0.30	-0.09	-0.30	-0.20	0.18	0.26
Acetylene	0.61	0.61	0.26	0.28	0.08	0.20	0.60	0.57
Propane	0.30	0.33	0.05	0.03	-0.15	-0.11	0.38	0.40
Propylene	0.92	0.88	0.58	0.57	0.42	0.46	0.89	0.90
<i>iso</i> -Butane	0.76	0.79	0.43	0.50	0.32	0.35	0.80	0.88
<i>n</i> -Butane	0.83	0.86	0.52	0.56	0.42	0.42	0.87	0.95
<i>i</i> -Butene			1.15	1.10	0.96	0.98		
<i>iso</i> -Pentane	1.28	1.26	0.98	0.97	0.87	0.83	1.30	1.36
<i>n</i> -Pentane	1.35	1.33	1.05	1.04	0.91	0.98	1.37	1.43
α^p			0.82	0.80		0.84		0.74
log <i>V_a</i>			-0.98 ^f	-1.29 ^g		-1.43 ^g		-0.92 ^f
Surface area, m ² /gram		300						
Bulk density ^d (lbs./ft ³)		24		24		24		340
								25
								31
								550
								600
								36

^a *t_r* refers to retention time (min), corrected for column void volume; calculated values are from eqn. 16.^b No water deactivation.^c Water diffusion cell temperature 23°^d Water diffusion cell temperature 51°.^e Relative to value of 0.70 for 4% H₂O-SiO₂ (Davison grade 62) in liquid-solid chromatography.^f Calculated from adsorbent surface area (*V_a* = 0.0035 surface area).^g Best value from eqn. 16 plus experimental data; these values of *V_a* in turn permit estimates of the adsorbent water content.

temperature of activation implies a corresponding increase in the strength of the electrical field over the alumina surface. At the same time, however, the quantity α_d remains constant. Since the latter is proportional to the adsorption energy of non-polar, saturated molecules such as methane, ethane, etc., it is apparent that the adsorption energies of these latter compounds are independent of the field strength over the alumina surface.

Experimental validity of eqn. 13c for GSC on polar adsorbents

A previous study⁵ has shown that eqn. 13 can accurately predict R° values for a variety of common organic compounds in GSC on alumina, using experimental parameters (α , V_a , S° , A_s) obtained from corresponding liquid-chromatographic systems. Since eqn. 13c is of the same form as eqn. 13 (the constant term $-\alpha A_s \varepsilon^\circ_\theta$ in eqn. 13 is replaced by the constant term $\alpha_d A_s \varepsilon_p$ of eqn. 13c), it may easily be shown that eqn. 13c gives an equally good correlation of sample retention volumes in the study of ref. 5. The data of BELLAR AND SIGSBY¹⁰ for the GSC separation of various hydrocarbons on different Davison silica samples can also be predicted by means of eqn. 13c, using S° values from a following liquid-chromatographic study⁸. The GSC data of ref. 10 are in the form of experimental chromatographs, from which retention times t_r (min) can be estimated. These retention time values, corrected for column void volume, are summarized in Table VII. Each of these chromatographic systems of Table VII uses a column of identical size, so that adsorbent weight is proportional to the bulk density d of the adsorbent (values of d given in Table VII). Retention volumes, proportional to retention times t_r , are proportional to adsorbent weight. Eqn. 15c under these circumstances can be expressed as

$$\log t_r = \log V_a + C' + \log d + \alpha S^\circ + \alpha_d A_s \varepsilon_p. \quad (16)$$

Here C' is a constant (best value equal -3.32) for the separations of Table VII. We can calculate V_a for the various dry adsorbents (0% H_2O-SiO_2) of Table VII from their surface areas ($V_a = 0.00035$ surface area)¹, and we can derive best value of V_a for the water wet silicas by application of eqn. 16 to t_r values for each adsorbent. Similarly we can derive best values of α for each of these adsorbents from the data of Table VII. We can also derive a value of the parameter $\alpha_d \varepsilon_p$, equal to 0.72. Finally, we can calculate values of S° and A_s for adsorption of the light hydrocarbons on silica; these values are summarized in Table VIII. The S° values are calculated on the basis that S° for pentane equals zero (pentane is the standard solvent in liquid-solid chromatography), and a methylene group itself contributes -0.05 units to S° (see ref. 17). The data of Table VII show that an *iso*-alkane has an S° value which is 0.10 units less than the corresponding *n*-alkane*. Finally, the S° values of the unsaturated hydrocarbons are derivable from a following study⁸ of liquid-solid chromatographic separation. By means of the various parameters summarized in Tables VII and VIII, or cited above, we can now calculate values of t_r in Table VII. Comparison of experimental and calculated values of t_r in Table VII shows agreement within ± 0.07 log units (std. dev.), which is close as could have been expected. In almost every case the

* The effect of chain branching on the adsorption energy of an alkane is probably better represented as a change in S_d , rather than in S° . Since it makes little difference in the present calculations, we have not made this distinction.

TABLE VIII

SAMPLE PARAMETERS FOR ADSORPTION OF LIGHT HYDROCARBONS ON SILICA^a

Compound	A_s	S°
Methane	2.9	0.20
Ethane	3.7	0.15
Ethylene	3.7	0.59
Acetylene	3.2	1.50
Propane	4.4	0.10
Propylene	4.4	0.77
<i>iso</i> -Butane	5.2	-0.04
<i>n</i> -Butane	5.2	0.05
Butene-1	5.2	0.72
<i>cis</i> -Butene-2	5.2	0.91
<i>trans</i> -Butene-2	5.2	0.91
<i>iso</i> -Butylene	5.2	0.91
<i>iso</i> -Pentane	5.9	-0.09
<i>n</i> -Pentane	5.9	0.00
Pentene-1	5.9	0.67
<i>cis</i> -Pentene-2	5.9	0.86
<i>trans</i> -pentene-2	5.9	0.86
2-Methyl-butene-1	5.9	0.86
2-Methyl-butene-2	5.9	1.00
3-Methyl-butene-1	5.9	0.67

^a Calculated from liquid-solid chromatographic data of ref. 8; Davison grade 62 silica (4% H_2O-SiO_2), α equal 0.70.

correct elution order of these compounds is given by eqn. 16. The correlations of Table VII involve a total of 52 separate t_r values and 10 adjustable parameters (C , 2 values of V_a , 6 values of α , and $\alpha_{d\epsilon p}$). In addition to providing a further verification of eqn. 13c for GSC separation on polar adsorbents, the correlations of Table VII show that the separation of the lower hydrocarbons on a given sample of silica (of given water content) is determined by the V_a value of that silica (which is determined by its surface area) and its α value.

The variation of α among the silica samples of Table VII is of fundamental interest. For adsorption of aromatic compounds on different silicas, it has been shown¹⁸ that α generally decreases with increasing silica water content and increases with increasing adsorbent surface area or decreasing pore diameter. In the case of monofunctional adsorbates, other data¹⁹ suggest that α remains relatively constant for variations in either silica water content or surface area. The α values of Table VII remain essentially constant for increasing adsorbent water content, and, if anything, tend to decrease with increasing silica surface area. This fits the same general pattern noted previously¹⁹. It reflects the greater importance of so-called free hydroxyls on the silica surface as adsorption sites for monofunctional adsorbates (*e.g.* the unsaturates of Table VII), and the greater importance of so-called reactive hydroxyls on the silica surface as adsorption sites for polyfunctional adsorbates (*e.g.* aromatic compounds) (see discussion of refs. 1, 18 and 19).

On the basis of the above correlations of GSC data on alumina and silica in

terms of eqn. 13c, we conclude that the latter relationship is reliable for all GSC separations on the polar adsorbents.

It has been noted previously (see section 8.1C of ref. 1) that the A_s values of certain polar compounds are abnormally large on silica, due to the phenomenon of solvent localization. Since the localization of strongly adsorbing sample groups on silica should not be related to the dispersion interactions of these groups, the quantity A_s in eqn. 13c should have the same value for adsorption of a given compound on either alumina or silica (*i.e.* the "normal" value calculated from the molecular dimensions of the compound).

RELATIVE ADSORPTION AFFINITY OF A METHYLENE GROUP IN LIQUID-SOLID CHROMATOGRAPHY

For liquid-solid chromatographic systems where specific interactions between solvent and adsorbent are absent, the preceding discussion suggests that the higher homologs of a given homologous series should be adsorbed more strongly than corresponding lower homologs. Such systems would include charcoal and any solvent, or the polar adsorbents with a saturated hydrocarbon or perfluoroalkane solvent. We further expect that the adsorption affinity of a methylene group in these systems (*i.e.* its ΔR_M value) will increase for higher adsorbent α_d values. In Table IX we have

TABLE IX

RELATIVE ADSORPTION OF A METHYLENE GROUP IN SOME LIQUID-SOLID SYSTEMS

Adsorbent	Solvent	Sample homologs	ΔR_M of -CH ₂ -group	α_d
Charcoal (13)	ethanol	see Table V	0.11	1.00
Charcoal (12)	benzene	methyl ketones	0.06	1.00
0.5 % H ₂ O-Al ₂ O ₃ (20)	pentane	alkyl benzenes	0.02	0.80
4.5 % H ₂ O-Al ₂ O ₃ (20)	pentane	alkyl thiophenes	0.01	0.7
Deactivated alumina (21)	cyclohexane	alkyl anthracenes, phenanthrenes	-0.01	0.5-0.8 (?)
Deactivated alumina (22)	cyclohexane	alkyl naphthalenes	-0.02	0.5-0.8 (?)
1 % H ₂ O-SiO ₂ (23)	pentane	alkyl benzenes	-0.02	0.59

summarized approximate ΔR_M values for a methylene group in several liquid-solid systems of this type. The data of refs. 21 and 22 are from thin-layer studies, using alumina of unspecified activity. It can be assumed that these latter adsorbents have higher water contents and lower α_d values. Comparison of the ΔR_M values (methylene group) for these various adsorbents with the corresponding α_d values shows the expected trend to lower ΔR_M values as α_d decreases. The negative values of ΔR_M for the adsorbents of low α_d may seem surprising. One explanation is that the flexible nature of an alkyl group permits a variety of configurations in an adsorbed sample molecule. The alkyl group might be totally adsorbed, totally desorbed, or something in between. The partially or totally desorbed states are favored on entropy considerations, because the alkyl group is less constrained. The interplay of interaction energy and entropy effects could then yield negative ΔR_M values when the inter-

actions energies (and α_a) are small. It should also be noted, in the case of cyclohexane as solvent (examples of Table IX), that this solvent is more strongly adsorbed than is pentane (larger ϵ_a value).

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