SOLVENT SELECTIVITY IN ADSORPTION CHROMATOGRAPHY ON ALUMINA

NON-DONOR SOLVENTS AND SOLUTES

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SUMMARY

The ability of the solvent in adsorption chromatography to create differences in relative sample migration rate has been studied for forty-six solvent systems (involving twenty different strong solvent components) and thirty different solutes. Most of the experimental data were collected for columns of water-deactivated alumina, although supplementary data for alumina of varying water content and for silica were also obtained. With the exception of one solute (N-methylaniline), the various solvents and solutes were incapable of solvent/solute hydrogen bonding (non-donor compounds). The results of this study could be correlated quantitatively in terms of a single adsorption mechanism: competition of localizing solvents and solute groups for strong adsorption sites. The ability of different non-donor solvent systems to maximize the separation of non-donor solutes can therefore be predicted. The present study lays the foundation for a similar examination of solvent/solute systems which are capable of hydrogen bonding (donor solutes and/or donor solvents).

INTRODUCTION

The performance of the solvent in adsorption chromatography (thin-layer chromatography (TLC) or column chromatography (CC)) can be defined by two important general characteristics: strength and selectivity. Solvent strength determines the relative adsorption and migration of all sample types; strong solvents favor decreased adsorption and faster migration, and weak solvents provide slower migration. Solvent selectivity refers to the ability of the solvent to create differences in the relative migration of two sample components (solutes). A selective solvent gives greater migration differences and easier separation. Solvent strength can be regarded as more or less independent of sample type. Solvent selectivity is necessarily a function of the two (or more) solutes involved.

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The selection of the correct solvent strength for a given separation problem is of major importance. Sample resolution is greater, other considerations being equal, for intermediate sample migration rates. Fortunately the selection of the right solvent strength for a given separation usually presents little difficulty (see discussion in ref. 1).

Once a solvent of the correct strength has been selected, it sometimes happens that two (or more) solutes of interest are still unseparated, *i.e.* their migration rates are approximately equal. In this case it is advantageous to vary solvent selectivity while holding solvent strength constant. NEHER[2] has discussed this approach in terms of so-called equieluotropic series, groups of solvents of similar strength but varied composition. Having determined that a particular solvent is of the right strength, other solvents within the same group (same equieluotropic series) can then be substituted. The resulting change in solvent composition may (or may not) result in a sufficient change in solvent selectivity to provide the required separation. This approach to altering solvent selectivity is an empirical, trial-and-error process. Because of the large number of possible solvent systems, and our present inability to predict how solvent selectivity varies with sample and solvent composition in most cases (for a review, see ref. 1), the NEHER scheme can be tedious to apply. Sometimes no solvent can be found which provides the desired selectivity. This approach is severely limited by our present ignorance of the basis of solvent selectivity.

The ability to control solvent selectivity has other potential advantages in addition to simplifying the separation of two compounds of similar structure and retention. An increase in selectivity makes it possible to carry out repeated separations more rapidly. In the case of more easily separated solutes, further increase in their retention differences facilitates their preparative separation, since this means that higher column loadings are possible. Similarly, the separation of typical mixtures shows the resulting bands distributed unevenly across the chromatogram (*e.g.* Fig. 1a). With the right solvent, an approach to the equally spaced chromatogram of Fig. 1b is possible. The advantages of the latter are apparent: adequate resolution for every adjacent pair of bands, with minimum separation time.

This paper describes initial work aimed at understanding the basis of solvent selectivity in adsorption chromatography. Our ultimate goal is the discovery of general rules for controlling solvent selectivity in any separation problem, regardless of whether the structures of individual sample components are known or unknown.
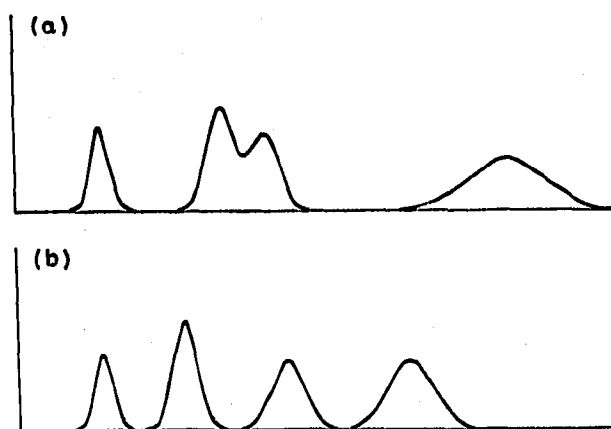

Fig. 1. Control of band spacing by separation selectivity.

Solvent selectivity depends upon the various interactions between sample, solvent and/or adsorbent. These interactions may be purely physical, they may involve chemical bonding (*e.g.* acid–base equilibria, complex formation, etc.), or they may be of intermediate character, as in hydrogen bonding. The potential importance of chemical bonding as a source of increased separation selectivity is widely appreciated, and predictions of selectivity in such cases are easily made. The present study will be concerned mainly with the role of physical interactions in affecting solvent selectivity in adsorption chromatography. Once this aspect of solvent selectivity is understood, the role of hydrogen bonding in determining solvent selectivity can then be examined.

For the most part, the systems described in the present paper involve solutes and solvents which cannot interact with each other by hydrogen bonding. That is, we will be dealing with compounds which cannot function as proton donors. Our main emphasis is on a single adsorbent, 4.3% H_2O on alumina, but some data are reported for drier and wetter aluminas, and for silica. The results of this study should prove equally applicable to TLC and CC since relative solute migration in each technique is determined by the same underlying factors. However, a detailed understanding of solvent selectivity requires accurate experimental data for precisely specified systems (solvent and adsorbent). As discussed elsewhere (ref. 1, pp. 355–357), this is easily achieved with CC, but not with TLC. Our experimental approach will therefore be based entirely on column systems, but some examples of corresponding TLC systems will be given.

A PRACTICAL SUMMARY OF THE PRESENT PAPER

The length and complexity of following sections make them occasionally difficult to follow. Similarly the practical conclusions of the present study tend to be obscured. For these reasons, the present section provides an initial overview of the total project with particular emphasis on its practical aspects.

The selectivity of a separation system can be expressed in terms of the separation factor α for two solutes, *viz.* $\alpha = k_1/k_2$, where k_1 and k_2 are the capacity factors, k', of solutes 1 and 2, respectively. α can be expressed as a function of various solvent, adsorbent and solute properties[1]:

$$\log \alpha = \log(k_1/k_2)_p + \alpha' \varepsilon^0 (A_2 - A_1) + \Delta_1 - \Delta_2 \qquad (1)$$

$$ \underset{a}{} \qquad \underset{b}{} \qquad \underset{c}{}$$

where $(k_1/k_2)_p$ is the ratio of k' values for solutes 1 and 2 with pentane as solvent, α' is an adsorbent activity parameter, ε^0 is the solvent strength parameter, A_1 and A_2 refer to the sizes (areas required on the adsorbent surface) of solute molecules 1 and 2, and Δ_1 and Δ_2 are so-called secondary adsorption terms. Eqn. 1 recognizes three general contributions to separation selectivity in adsorption chromatography: terms *a*, *b* and *c*. Term *a* reflects the primary effect of the adsorbent on separation (this term is independent of the solvent). Term *b* describes the primary effect of the solvent upon separation. If two solute molecules are of different size, a change in solvent strength, ε^0, will cause a corresponding change in α. The magnitude of this change is proportional to the adsorbent activity parameter (α'). Term *c* is the result of so-called secondary adsorption effects, and in general this term is a complex function of solvent,

adsorbent and solute. The variation of term c by a change in solvent composition is an attractive route to improved selectivity in adsorption chromatography (either in columns or on plates). Often we begin with a given column or adsorbent, and ε^0 must be maintained within narrow limits for optimum resolution (see following section). In the present study, we will focus attention on the role of the solvent in determining term c and separation selectivity.

For changes only in the solvent, we have found that term c is accurately given by the empirical expression

$$\Delta_1 - \Delta_2 = m(\Delta_1{}^0 - \Delta_2{}^0) \tag{2}$$

in the case of non-donor solvents and solutes. Here m is a function of solvent composition, and $\Delta_1{}^0$ and $\Delta_2{}^0$ are functions of solute structure. If two solutes of interest have equal values of Δ^0, no change in solvent will provide a change in α (looking only at eqn. 2). Assuming that $\Delta_1{}^0 \neq \Delta_2{}^0$, however, maximum selectivity will occur for that solvent which has either the largest or the smallest value of m (recall that maximum selectivity occurs for maximum α or maximum $1/\alpha$, $i.e.$ separation factors of $1/2$ and 2 are equivalent). This is illustrated in the representative data below for the two solutes 1,5-dinitronaphthalene (DNN) and 1-acetonaphthalene (AN) and the adsorbent 4.3% H_2O–Al_2O_3:

Solvent	m	k'		α
		DNN	AN	
50% (v/v) benzene/pentane	—0.25	2.5	5.1	0.5 ≡ 2.0
23% (v/v) dichloromethane/ pentane	0.25	5.8	5.5	0.95
4% (v/v) ethyl acetate/pentane	0.72	5.4	2.9	1.8
5% pyridine/pentane	1.14	5.4	2.3	2.4
0.05% (v/v) dimethyl sulfoxide/ 30% (v/v) carbon tetrachloride/ pentane	1.26	3.5	1.0	3.5

Simple changes in solvent composition, while maintaining k' in the optimum range of 1–5, are seen to result in a change of α by a factor of 7 for this system.

Since maximum α (or $1/\alpha$) occurs for large and small m values, the prediction of m as a function of solvent composition is of obvious practical importance. Fig. 2 shows the variation of m with ε^0 for a variety of binary solvent blends (pentane plus a stronger solvent). Forty-six solvent blends which involve twenty different strong solvent components are summarized in Fig. 2 (see Tables III and VI and Figs. 6 and 7 for details). These data fall into roughly seven classes, represented by curves I–VI of Fig. 2. The strong solvent component in the blend determines the dependence of m on ε^0, and these solvents are classified in Table I. Here it is seen that solvent components which are relatively weak ($0.18 \leqslant \varepsilon^0 \leqslant 0.35$) give small or negative values of m, while the largest values of m are given by blends of very strong solvent components ($0.56 \leqslant \varepsilon^0 \leqslant 0.75$). In general, Table I shows a remarkably consistent correlation of solvent class with the strength, ε^0, of the strong solvent component. This can also be seen in the above data for the separation of AN and DNN. Since ε^0 for the solvent
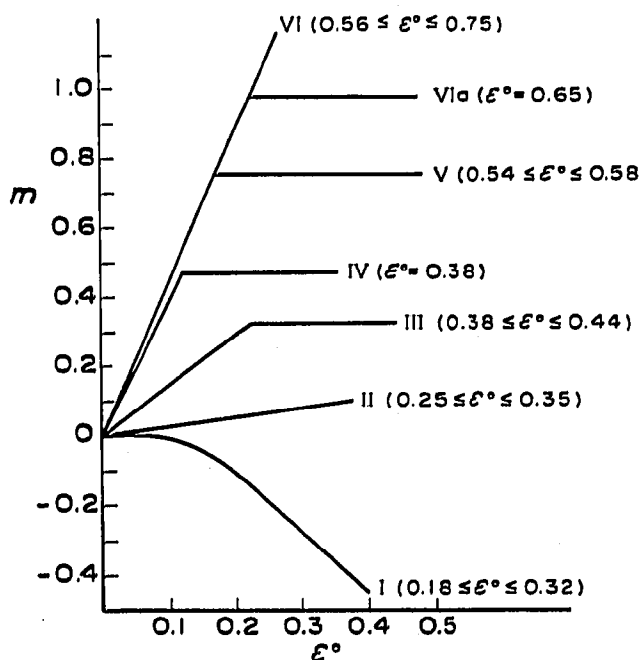
Fig. 2. Classification of solvent m values; see Figs. 6 and 7 for details. ε^0 (abscissa) refers to the solvent strength of the solvent mixture; ε^0 ranges ($e.g.$ $0.18 \leqslant \varepsilon^0 \leqslant 0.32$) refer to ε^0 values of the strong solvent component (pure compound) of the mixture.

TABLE I

SOLVENT COMPONENTS USED IN THE PRESENT STUDY (SEE FIG. 2)

Group	Solvent	$\varepsilon^{0\,b}$
a	Pentane	0.00
I	Carbon tetrachloride	0.18
	Toluene	0.29
	Benzene	0.32
II	Perchloroethylene	0.25
	2-Chloropropane	0.29
	Chlorobenzene	0.30
	Ethyl bromide	0.35[c]
III	Ethyl sulfide	0.38
	Chloroform	0.40
	Dichloromethane	0.42
	Ethylene dichloride	0.44[c]
IV	Ethyl ether	0.38
V	Triethylamine	0.54[c]
	Tetrahydrofuran	0.57[c]
	Ethyl acetate	0.58
VIa	Acetonitrile	0.65
VI	Acetone	0.56
	Nitromethane	0.64
	Pyridine	0.71
	Dimethyl sulfoxide	~0.75[c]

[a] Weak solvent used to blend strong solvents into right ε^0 range.
[b] Values reported in ref. 1 unless noted otherwise.
[c] Values obtained from present study.

mixture is held roughly constant (for constant k'), a change in ε^0 for the strong solvent component must be balanced by a reduction in its concentration in the solvent blend. This leads to an inverse correlation of m with the concentration of the strong solvent component of the solvent blend (at constant ε^0). As a practical corollary, extremes of m (one of which should provide maximum α) will occur for solvent solutions in which the concentration of the strong solvent component is either very high (*e.g.* 50% (v/v) benzene) or very low (*e.g.* 0.05% (v/v) dimethyl sulfoxide). Solvent blends involving intermediate concentrations of the strong solvent component will generally yield intermediate values of m and poorer selectivity. Another practical conclusion which can be drawn from Fig. 2 is that maximum changes in solvent selectivity are only achievable for strong solvent systems (ε^0 large). For very weak solvents ($\varepsilon^0 \to 0$),
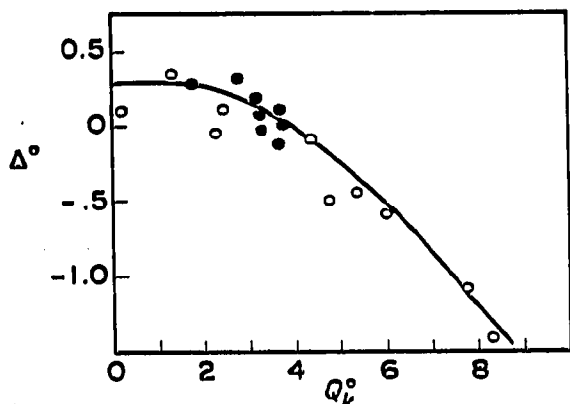

Fig. 3. Dependence of solute Δ^0 values on adsorption energy $Q^0{}_k$ of most strongly adsorbing group k in solute molecule.

m approaches zero for all solvent compositions. It should be emphasized that these conclusions apply only to the separation of two adjacent bands in systems which do not involve hydrogen bonding between solvent and solute (no proton donors involved).

Consider next the dependence of Δ^0 on the structure of the solute. Δ^0 has been found to correlate with the adsorption energy $Q^0{}_k$ of the most strongly adsorbing substituent k in the solute molecule, as shown in Fig. 3. Weakly adsorbing groups ($Q^0{}_k < 3$) such as methoxy and nitro give small positive values of Δ^0; strongly adsorbing solute groups ($Q^0{}_k > 7$) such as sulfoxy ($-SOCH_3$) and amido ($-CON(CH_3)_2$) give large negative values of Δ^0. In certain favorable cases, where two solutes differ markedly in the adsorption affinity of the strongest substituent k in the molecule, very large changes in selectivity can be achieved by a change in solvent. This is illustrated below for the solutes 1,3,5-trinitrobenzene (TNB) and N,N-dimethyl-1-naphthamide (DMNA), using two solvents of quite different m values:

Solvent	m	k'^a		α
		TNB	DMNA	
Benzene	—0.4	0.32	88	275
5% (v/v) acetonitrile/10% (v/v) benzene/pentane	0.8	5.9	7.1	1.2
$Q^0{}_k$		2.8	8.3	
Δ^0		0.56	—1.40	

ᵃ Adsorbent: 4.3% H_2O–Al_2O_3.

Here we have a change in α by a factor of 230, without the intervention of hydrogen bonding or chemical interaction effects. This is a spectacular result, but not very typical; furthermore, solutes with Δ^0 values as different as those of TNB and DMNA are generally sufficiently different in structure to allow their easy separation by any of a variety of different techniques. However, the possibility of changes in α of this magnitude implies the corresponding possibility of smaller, but still useful, changes in α for solute pairs which are more difficult to separate. In actual practice, a change in α by only 10% often means the difference between a relatively easy separation and one that is impossible; e.g. α values of 1.00 and 1.1.

As an example, consider the TLC separation of the isomers I and II[3]:
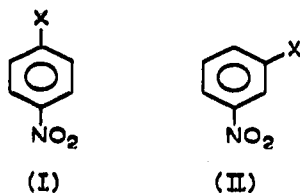
Here the group X can be either F, Cl or Br. On silica or magnesium silicate with hydrocarbon solvents (hexane, cyclohexane, $m \approx 0$), the *para* isomers are more strongly adsorbed than corresponding *meta* isomers. This is the result of electronic activation of the nitro group by the methyl group, with an increase in the adsorption energy $Q^0{}_k$ of the nitro group in the *para* isomer relative to that of the *meta* isomer[1]. Consequently, Δ^0 for the *para* isomers should be less than Δ^0 for the *meta* isomers. We therefore predict that a change in solvent to one of larger m will result in decreased adsorption of I relative to II (as in the examples above). This is in fact observed; hydrocarbon solutions of ether or esters as solvents (m large) result in a reversal of the separation order of these isomers (II adsorbed more strongly).

The origin of these solvent selectivity effects (Eqn. 2) can be explained as follows. Solute molecules with strongly adsorbing groups tend to localize on strong adsorption sites on the surface of the adsorbent[1]. There is a similar tendency for localization of strongly adsorbed solvent molecules on these same sites. When both of these processes occur simultaneously, the net adsorption energy of localized solute groups is thereby decreased because of competition between solute and solvent for the same strong sites. This loss in solute adsorption energy (and decreased solute adsorption) is proportional to the extent of solute localization (proportional to $Q^0{}_k$ or Δ^0) and the extent of solvent localization (proportional to ε^0 for the strong solvent component and its concentration in the solvent blend, or to m). Thus maximum adsorption and retention of solutes with strongly adsorbing groups is favored by solvents which do not tend to localize on strong adsorbent sites, and is opposed by solvents which localize strongly.

The same kind of solvent selectivity found in separations on alumina is also observed on silica. An example is provided in the TLC separations shown in Fig. 4. Here the separation of 1,7-dimethoxynaphthalene (DMN, $\Delta^0 = 0.16$) and 1-nitronaphthalene (NN, $\Delta^0 = 0.38$) on silica is shown. With a solvent of low m value (20% (v/v) benzene/pentane), NN migrates more rapidly than DMN (Fig. 4a). With a solvent of high m value (1.5% (v/v) acetonitrile/pentane), the separation order is
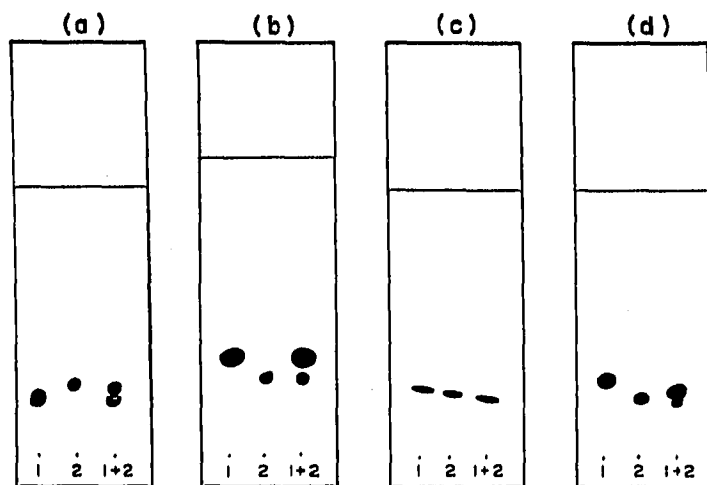
Fig. 4. TLC separations of 1,7-dimethoxynaphthalene (1) and 1-nitronaphthalene (2) on silica plates. (a) 20% (v/v) benzene/pentane solvent; (b) 1.5% acetonitrile/pentane solvent, pre-equilibration of plate in TLC chamber; (c) 1% acetonitrile/pentane solvent, no pre-equilibration; (d) 1% acetonitrile/pentane, equilibrated.

reversed (Fig. 4b). In TLC, a practical problem arises in the use of solvents of high m (*i.e.* dilute solutions of a strong solvent in a weak solvent), namely solvent demixing and front formation. This is illustrated in Fig. 4c for the same separation with 1% (v/v) acetonitrile/pentane. In this case, both solutes migrate at the boundary between pentane and acetonitrile/pentane. By first exposing the plate to the solvent vapors, however, adsorption of acetonitrile occurs and subsequent separation does not result in solvent demixing. This is illustrated in Fig. 4d. The same procedure was used in the separation of Fig. 4b.

EXPERIMENTAL

The adsorbent used for most of the following measurements was chromato-graphically standardized 4.3% H_2O–Al_2O_3*, prepared by addition of water to calcined (400°) Alcoa F-20 alumina[4]. In a few cases, measurements were made on alumina containing more or less water, in order to determine the effect of adsorbent activity on secondary solvent effects. Similarly, a few data were obtained for 10% H_2O–SiO_2 as adsorbent (Waters Associates Porasil A, preheated at 120°).

All solvents were prepared from reagent-grade materials. Several solvents were further purified over calcined alumina immediately before use: ethyl sulfide, 2-chloro-propane, ethyl acetate and chloroform. *n*-Pentane (Phillips Petroleum, 99% pure) was purified over activated silica before use. All solvent solutions were saturated with water, then blended with dry (*i.e.* water-free) solvent to give 25% water satura-tion for experiments with 4.3% H_2O–Al_2O_3. The thermodynamic activity of water in these solutions was approximately equal to the activity of water on the starting 4.3% H_2O–Al_2O_3 (see discussion ref. 5). Experiments with 2% H_2O–Al_2O_3 were run with dry solvents, while 100% water-saturated solvents were used in runs with 8% H_2O–Al_2O_3 and 10% H_2O–SiO_2. In the case of solvent blends containing water-

* Corrected retention volume (naphthalene solute, pentane solvent) equal to 1.05 ml/g.

miscible components, the amount of water used to saturate the solvent mixture was kept sufficiently small to avoid extracting significant amounts of water-miscible solvent (the final volume ratio of water to solvent phases was less than 1:500). No water was added to solutions of dimethyl sulfoxide.

The chromatographic unit consisted of a stainless steel solvent reservoir pressured by nitrogen, followed by a guard column (100 × 0.28 cm) containing the same adsorbent used in the chromatographic column. Solvent from the guard column entered a sample introduction valve (25 μl loop) connected to the chromatographic column (25 × 0.28 cm), and then a UV detector. The columns, sample valve and connecting tubing (Teflon/glass construction) were from Chromatronix Inc. (Berkeley, Calif., U.S.A.). The detector was a modified Hitachi-Colman 124 spectrophotometer with a Zeiss flow cell (Ultramicro MR1D, 1.0 cm path-length). The columns were packed dry and settled by tapping. Before measurements were made on a given column, sufficient solvent was passed through the system to give complete equilibration of adsorbent with initial solvent, as checked by constancy of solute retention times for repeated injection of the same sample. Both guard and chromatographic columns were changed for each new solvent mixture. Retention times were measured for each compound (introduced individually as 0.1% solutions in isooctane) from the time of injection, and for the non-retained solvent peak (isooctane). Capacity factors, k', were calculated from the retention times of solute (t_R) and solvent (t_0): $k' = (t_R — t_0)/t_0$.

Retention times for a standard compound (1,7-dimethoxynaphthalene or picene) were usually constant within ±2% throughout a series of runs with a given solvent (same column). For the sample size (8 × 10^{-6} g/g) used in the present study, retention time was not a function of sample concentration. When variations in retention time for the standard compound exceeded 2% from beginning to end of a given series, individual retention time measurements were corrected by assuming a constant proportionality between all solute retention times at a given time. Comparisons of corrected retention times in repeat experiments (new columns, same solutes and solvent) suggest a relative repeatability of about ±4% (standard deviation), as illustrated in Table II for 23% (v/v) dichloromethane/pentane as solvent and 4.3% H_2O–Al_2O_3 as adsorbent. This variability was somewhat greater for different batches of adsorbent, and in one case was as high as ±20% for a very strong solvent system. Only a few data were collected for such systems, but this problem should be kept in mind during future work with strong solvents ($\varepsilon^0 > 0.3$).

GENERAL THEORY

The problem of immediate interest is that of the separation or resolution of adjacent bands in liquid–solid chromatography, either as they elute from a column or are found on a TLC plate. Resolution, R_s, is normally defined as the distance between band centers (at the end of separation), divided by average band width. For either columns or plates this leads to a well known relationship (e.g. ref. 6):

$$R_s = (1/4)(\alpha — 1)\sqrt{N}[k'/(k' + 1)] \tag{3}$$

Here α is the separation factor defined earlier (the ratio of capacity factors k_1/k_2 for the two bands), N is the number of theoretical plates in the adsorbent bed through

TABLE II

REPEAT DETERMINATION OF k' VALUES ON 4.3% H_2O–Al_2O_3 WITH 23% (v/v) DICHLOROMETHANE/PENTANE AS SOLVENT. EXPERIMENTAL PRECISION

(I) 2-Methoxynaphthalene; (II) 1,7-dimethoxynaphthalene; (III) 1-nitronaphthalene; (IV) 1,5-dinitronaphthalene; (V) 1-methylnaphthoate; (VI) 1-cyanonaphthalene; (VII) 1-naphthaldehyde; (VIII) 1-acetonaphthalene; (IX) 2-chloroquinoline; (X) N-methylaniline; (XI) picene ($C_{22}H_{14}$).

Run No.[a]	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
k'											
1	0.62	1.38	1.85	6.06	2.08	2.70	3.23	5.50	2.35	2.25	1.42
2	0.72	1.52	2.09	7.08	2.42	3.23	3.85	6.79	2.59	2.55	1.60
3	0.65	1.32	1.82	5.91	2.14	2.58	3.30	5.17	2.17	2.37	1.28
4	0.64	1.24	1.93	5.80	2.15	2.74	3.37	5.52	2.43	2.33	1.49
Average	0.66	1.36	1.92	6.21	2.20	2.91	3.43	5.75	2.38	2.37	1.45
$k'/[k'$ for II]											
1	0.45	1.00	1.34	4.39	1.51	1.96	2.35	4.00	1.71	1.64	1.03
2	0.47	1.00	1.38	4.66	1.59	2.13	2.53	4.47	1.70	1.68	1.05
3	0.49	1.00	1.38	4.48	1.62	1.96	2.50	3.92	1.64	1.80	0.97
4	0.49	1.00	1.41	4.56	1.62	2.14	2.52	4.23	1.75	1.74	1.07
Average	0.47	1.00	1.38	4.52	1.59	2.05	2.47	4.15	1.70	1.71	1.03
S.D. of average[b]	±0.02		±0.03	±0.10	±0.05	±0.10	±0.08	±0.21	±0.04	±0.07	±0.05
S.D. as % relative[b]	+3%		2.2%	2.2%	3.1%	4.9%	3.2%	5.1%	2.4%	±1%	+9%

±3.8% overall

[a] Different column used for each run.
[b] Precision of relative k' values.

which the two bands have passed, and k' is the average of k_1 and k_2 (the capacity factor, k', is the equilibrium ratio of total solute in the stationary phase to total solute in the moving phase). Resolution is seen to be determined by three different factors: α, N and k'. N is largely a function of the particular adsorbent bed (column or plate). k' reflects the average migration speed of the two bands and is determined by solvent strength ε^0. k' and ε^0 must be held within narrow limits for optimum resolution, e.g. $1 < k' < 5$. For resolution to be possible, α must be different from unity. α is determined by the adsorbent and the composition of the solvent. In the present study, we will be concerned mainly with the variation of α with solvent composition.

Values of k' can be related to certain properties of the adsorbent, solvent and solute[1]:

$$\log k' = \log k_p - \alpha' \varepsilon^0 A_s + \Delta \qquad (4)$$

where k_p is the value of k' for pentane as solvent, α' (unrelated to the separation factor, α) is a function of adsorbent activity*, ε^0 is a solvent strength parameter, A_s is proportional to the area of the adsorbed solute molecule, and Δ is a so-called secondary solvent effect* which can be a function of adsorbent, solvent and/or solute. Substitution of Eqn. 4 into $\alpha = k_1/k_2$ gives Eqn. 1. The so-called primary effect of the solvent on selectivity (term b of Eqn. 1) is usually of limited value in changing α. Thus the sizes of the two solutes must be appreciably different, and this is often not the case for difficultly separable compounds. Also, a change in selectivity is achieved only by relatively large changes in ε^0 and k', which works against optimum resolution (for which $1 < k' < 5$). Secondary solvent effects, term c of Eqn. 1, offer the greatest promise for useful changes in separation selectivity. To understand the basis of this solvent selectivity term, we must study the variation of Δ values with solvent composition and solute structure.

Δ VALUES AS A FUNCTION OF SOLUTE AND SOLVENT

Table III summarizes 424 experimental k' values for 11 solutes and 41 different solvent systems. Solutes I through VIII are substituted naphthalenes which carry a variety of different substituent groups ($-OCH_3$, $-NO_2$, $-COOCH_3$, $-CN$, $-CHO$, $-COCH_3$), solute IX is 2-chloroquinoline, X is N-methylaniline, and XI is the aromatic hydrocarbon picene ($C_{23}H_{14}$). Solutes I through IX are intended to test the effect of solvent composition on relative adsorption of solute functional groups, where hydrogen bonding is not involved (none of these solutes are proton donors). Solute XI (picene) has no such functional group substituents, and is included to provide a measurement of ε^0 for each solvent (from Eqn. 4, assuming $\Delta = 0$). Solute X (N-methylaniline) is a weak donor which is included for preliminary exploration of the effect on solvent selectivity of hydrogen bonding between solute and solvent. These particular solutes were selected because their retention times and k' values fall in a convenient range for measurement, and their UV absorptivities are suitable for UV detection during elution from the column by solvents of interest (some of these solvents do not transmit light below 310 nm).

The 41 solvents of Table I are solutions of strong, non-donor solvents in

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* In ref. 1, α' and Δ are referred to as α and Δ_{eas}, respectively.

TABLE III

k' VALUES FOR STANDARD SOLUTES AND FORTY-ONE SOLVENTS OF INTERMEDIATE STRENGTH; 4.3% $H_2O-Al_2O_3$

Values of Δ in parentheses. (I) 2-Methoxynaphthalene; (II) 1,7-dimethoxynaphthalene; (III) 1-nitronaphthalene; (IV) 1,5-dinitronaphthalene; (V) 1-methylnaphthoate; (VI) 1-cyanonaphthalene; (VII) 1-naphthaldehyde; (VIII) 1-acetonaphthalene; (IX) 2-chloroquinoline; (X) N-methylaniline; (XI) picene.

Solvent[a]	k'					
	I	II	III	IV	V	VI
15% (v/v) benzene	2.28 (0.02)	6.47 (0.05)	6.75 (0.03)	—	10.6 (0.01)	12.2 (0.08)
28% (v/v) benzene	1.08 (0.04)	2.34 (0.01)	2.80 (0.01)	9.20 (0.00)	4.27 (0.01)	4.86 (0.01)
50% (v/v) benzene	0.39 (0.00)	0.98 (0.06)	1.08 (0.00)	2.52 (—0.12)	1.71 (0.05)	1.99 (0.00)
80% (v/v) benzene	—	0.39 (0.21)	0.38 (0.05)	0.97 (0.04)	0.76 (0.26)	0.95 (0.15)
50% (v/v) carbon tetrachloride	0.80 (—0.01)	1.86 (—0.01)	2.19 (—0.02)	6.83 (—0.06)	3.40 (0.00)	3.61 (0.04)
30% (v/v) toluene	0.86 (0.00)	2.37 (0.06)	2.51 (0.02)	8.83 (0.02)	4.32 (0.08)	4.52 (0.04)
35% (v/v) 2-chloropropane	0.86 (—0.06)	2.13 (—0.05)	1.91 (—0.16)	7.47 (—0.12)	3.43 (—0.09)	3.10 (—0.18)
60% (v/v) 2-chloropropane	0.45 (0.04)	0.83 (—0.03)	0.79 (—0.15)	2.29 (—0.18)	1.37 (—0.05)	1.19 (—0.23)
Perchloroethylene	0.80 (0.25)	1.79 (0.25)	2.09 (0.03)	8.35 (0.32)	3.26 (0.27)	4.07 (0.25)
40% (v/v) ethyl bromide	0.57 (0.05)	1.16 (0.01)	1.17 (—0.08)	4.27 (—0.02)	1.90 (—0.02)	1.97 (—0.10)
30% (v/v) chlorobenzene	0.83 (0.01)	1.83 (—0.01)	2.41 (0.03)	8.02 (0.02)	3.51 (0.02)	4.09 (0.02)
8% (v/v) ethyl sulfide	2.10 (—0.05)	5.59 (—0.05)	5.82 (—0.04)	30.1 (0.02)	8.62 (—0.08)	9.64 (—0.06)
15% (v/v) ethyl sulfide	1.15 (0.00)	2.40 (—0.07)	2.90 (—0.06)	12.2 (0.05)	4.11 (—0.12)	4.66 (—0.05)
13% (v/v) dichloromethane	1.26 (0.13)	3.06 (0.12)	3.95 (0.17)	16.4 (0.29)	5.10 (0.10)	6.19 (0.13)
23% (v/v) dichloromethane	0.62 (0.19)	1.38 (0.18)	1.85 (0.23)	6.06 (0.24)	2.08 (0.14)	2.70 (0.14)
15% (v/v) chloroform	1.58 (0.10)	4.09 (0.12)	5.07 (0.15)	20.6 (0.20)	6.44 (0.06)	7.34 (0.09)
30% (v/v) chloroform	0.84 (0.28)	1.72 (0.26)	2.11 (0.25)	—	2.37 (0.15)	2.79 (0.11)
15% (v/v) ethylene chloride	0.90 (0.23)	1.72 (0.17)	2.61 (0.26)	10.5 (0.35)	2.88 (0.20)	4.13 (0.20)
2% (v/v) ethyl ether	3.24 (—0.02)	6.97 (—0.13)	7.00 (—0.15)	—	(10.4 —0.22)	11.5 (—0.12)
5% (v/v) ethyl ether	1.42 (—0.08)	3.15 (—0.14)	4.05 (—0.08)	20.0 (0.04)	4.84 (—0.21)	5.90 (—0.13)
9% (v/v) ethyl ether	0.97 (—0.03)	1.95 (—0.11)	2.81 (—0.01)	10.9 (0.02)	2.86 (—0.19)	3.71 (—0.11)
23% (v/v) ethyl ether	0.49 (0.08)	0.85 (—0.01)	1.22 (0.04)	2.94 (—0.07)	1.12 (—0.14)	1.44 (—0.15)
1% (v/v) ethyl acetate	1.41 (0.09)	2.76 (—0.01)	4.16 (0.11)	21.9 (0.27)	4.18 (—0.08)	5.99 (0.04)
4% (v/v) ethyl acetate	0.62 (0.16)	1.00 (0.03)	1.80 (0.18)	5.38 (0.16)	1.34 (—0.09)	2.13 (0.00)
2% (v/v) tetrahydrofuran	1.12 (0.13)	1.94 (—0.01)	3.33 (0.16)	13.2 (0.22)	2.66 (—0.12)	4.05 (0.00)
5% (v/v) tetrahydrofuran	0.71 (0.12)	1.07 (—0.06)	2.14 (0.16)	5.30 (0.04)	1.37 (—0.19)	2.17 (—0.09)

II	VIII	IX	X	XI	$a'\varepsilon^0$	m	a	S.D.f	$\Delta\Delta X$
13.8 (0.03)	32.8 (0.09)	8.69 (0.01)	10.3	20.0	0.079	−0.04	0.05	±0.03	0.03
5.85 (0.02)	12.4 (0.04)	4.02 (0.00)	4.72	5.60	0.114	−0.02	0.02	±0.01	−0.01
2.61 (0.05)	5.06 (0.06)	1.83 (0.03)	2.14	1.35	0.160	−0.25	0.06	±0.03	−0.05
1.18 (0.20)	2.12 (0.20)	0.84 (0.15)	1.00 (0.04)	0.23	0.214	−0.29	0.21	±0.04	−0.13
4.42 (−0.04)	10.3 (0.04)	2.99 (−0.06)	4.10	3.35	0.126	−0.08	0.00	±0.03	0.03
5.78 (0.05)	12.7 (0.10)	3.98 (0.05)	4.59	4.65	0.123	−0.15	0.07	±0.02	0.00
4.32 (−0.13)	8.58 (−0.13)	2.72 (−0.17)	4.04	5.72	0.117	0.02	−0.12	±0.05	0.06
1.83 (−0.12)	3.13 (−0.16)	1.19 (−0.17)	1.81	1.42	0.159	0.02	−0.11	±0.09	0.01
4.64 (0.24)	10.1 (0.30)	3.03 (0.19)	4.94	1.70	0.153	0.03	0.24	±0.04	0.06
2.75 (−0.03)	5.07 (−0.05)	1.60 (−0.13)	2.98	2.00	0.149	0.08	−0.05	±0.05	−0.14
4.95 (0.02)	7.42 (−0.09)	3.35 (0.00)	3.35	4.11	0.127	0.12	−0.02	±0.03	−0.03
11.3 (−0.06)	22.1 (−0.11)	—	—	22.2	0.076	0.18	−0.09	±0.02	—
5.96 (−0.09)	10.3 (−0.11)	—	—	7.13	0.110	0.27	−0.11	±0.03	—
7.14 (0.10)	13.9 (0.07)	5.95 (0.18)	4.81	5.38	0.115	0.26	0.10	±0.03	−0.10
3.23 (0.15)	5.50 (0.10)	2.35 (0.13)	2.25	1.42	0.157	0.25	0.12	±0.01	−0.15
8.55 (0.06)	17.8 (0.08)·	5.53 (0.04)	5.84	8.38	0.105	0.23	0.06	±0.02	−0.08
3.62 (0.15)	5.65 (0.06)	2.56 (0.14)	1.98	1.58	0.156	0.41	0.12	±0.05	−0.32
4.78 (0.19)	8.18 (0.14)	2.92 (0.12)	3.22	2.12	0.147	0.33	0.14	±0.03	−0.12
13.0 (−0.19)	26.5 (−0.20)	7.40 (−0.24)	11.7	39.5	0.059	0.32	−0.20	±0.05	0.14
6.82 (−0.17)	11.9 (−0.24)	3.97 (−0.24)	6.46	14.0	0.090	0.55	−0.24	±0.03	0.12
4.52 (−0.14)	6.95 (−0.23)	—	—	6.12	0.115	0.47	−0.19	±0.01	—
1.93 (−0.09)	2.46 (−0.26)	—	—	1.42	0.159	0.43	−0.16	±0.08	—
6.40 (−0.03)	10.2 (−0.12)	3.79 (−0.09)	6.22	7.30	0.109	0.65	−0.09	±0.03	0.11
2.38 (−0.03)	2.92 (−0.21)	1.47 (−0.10)	2.29	1.54	0.156	0.72	−0.11	±0.03	0.01
4.51 (−0.04)	6.30 (−0.18)	2.94 (−0.07)	4.45	4.38	0.125	0.73	−0.11	±0.02	0.06
2.36 (−0.13)	2.90 (−0.32)	1.68 (−0.14)	2.35	2.23	0.145	0.77	−0.19	±0.06	0.02

TABLE III *(continued)*

Solvent	k'					
	I	II	III	IV	V	VI
5% (v/v) triethylamine	0.81	1.43	2.47	10.8	1.96	3.71
	(−0.01)	(−0.13)	(0.03)	(0.13)	(−0.25)	(−0.15)
0.2% (v/v) acetone	2.01	5.02	6.42	—	7.24	9.64
	(0.00)	(−0.03)	(0.05)		(−0.12)	(0.02)
0.4% (v/v) acetone	1.58	3.16	5.00	23.5	4.47	6.13
	(0.10)	(0.00)	(0.15)	(0.26)	(−0.09)	(0.01)
0.6% (v/v) acetone	1.17	2.42	4.00	—	3.24	5.23
	(0.04)	(−0.02)	(0.13)		(−0.15)	(0.02)
0.8% (v/v) acetone	1.14	2.20	4.03	16.4	3.00	4.62
	(0.15)	(0.06)	(0.25)	(0.33)	(−0.05)	(0.07)
2% (v/v) pyridine	0.96	1.77	3.91	11.5	1.73	3.28
	(0.11)	(0.01)	(0.28)	(0.22)	(−0.24)	(−0.04)
5% (v/v) pyridine	0.72	1.21	2.40	5.44	1.10	2.04
	(0.11)	(−0.02)	(0.19)	(0.03)	(−0.31)	(−0.13)
0.1% (v/v) acetonitrile	2.80	7.28	8.39	—	11.1	14.0
	(0.05)	(0.03)	(0.07)		(−0.04)	(0.09)
0.14% (v/v) acetonitrile	2.30	4.97	7.18	—	7.57	11.3
	(0.10)	(0.02)	(0.14)		(−0.05)	(0.13)
0.3% (v/v) acetonitrile	1.42	2.76	4.58	25.0	4.07	6.84
	(0.25)	(0.13)	(0.30)	(0.50)	(0.05)	(0.21)
0.4% (v/v) acetonitrile	1.09	1.83	3.62	17.0	2.51	4.11
	(0.26)	(0.13)	(0.34)	(0.50)	(0.03)	(0.15)
0.6% (v/v) acetonitrile	0.95	1.55	3.12	14.3	2.20	3.59
	(0.31)	(0.18)	(0.39)	(0.54)	(0.09)	(0.19)
0.7% (v/v) acetonitrile	0.77	1.36	2.65	11.9	1.62	2.89
	(0.27)	(0.18)	(0.37)	(0.53)	(0.01)	(0.15)
1% (v/v) nitromethane[b]	0.81	1.30	2.67	13.2	1.88	3.27
	(0.25)	(0.11)	(0.43)	(0.52)	(0.03)	(0.16)
0.05% (v/v) dimethyl sulfoxide[c]	0.27	0.35	1.06	3.54	0.37	0.92
	(0.01)	(−0.19)	(0.17)	(0.22)	(−0.41)	(−0.17)
$\log k_p$	1.07	1.58	1.54	2.24	1.84	1.69
Δ[a][d]	0.31	0.16	0.38	0.46	0.02	0.18
	±0.06	±0.04	±0.05	±0.07	±0.03	±0.04
A_s	9.2	10.3	9.4	10.7	10.4	8.7

[a] Mixture with *n*-pentane, except where indicated otherwise.
[b] 5% benzene added to pentane for miscibility.
[c] 30% (v/v) carbon tetrachloride added to pentane for miscibility.
[d] Average values derived from data for solvents with $m > 0.5$.
[e] Average value for 0.3–0.7% (v/v) acetonitrile solutions.
[f] Experimental Δ values *vs.* values calculated by Eqn. 5a.

pentane. The last two solvents of Table III required the addition of benzene or carbon tetrachloride to maintain miscibility of the mixture. The concentrations of these various solvent solutions are such that $0.1 < \varepsilon^0 < 0.3$, which again provides convenient k' values for the above solutes.

Values of A_s for each solute in Table III were calculated as described in ref. 1 (Tables 8–4). Log k_p for picene could also be calculated[1], which permitted $a'\varepsilon^0$ for each solvent system to be measured from Eqn. 4 and a value of k' for picene (assuming $\Delta = 0$). Given values of $a'\varepsilon^0$ and A_s, from Eqn. 4 and an experimental value of k' we can calculate log $k_p + \Delta$ for each solute/solvent combination. Δ was initially defined as equal to zero for a group of less polar solvents (solutions of benzene,

II	VIII	IX	X	XI	$a'\varepsilon^0$	m	a	S.D.	$\frac{\Delta\Delta}{X}$
3.45	4.80	2.00	4.35	4.35	0.125	0.77	−0.24	±0.03	0.17
−0.30)	(−0.30)	(−0.23)							
9.99	17.6	6.24	8.63	17.5	0.083	0.42	−0.11	±0.02	0.07
−0.08)	(−0.14)	(−0.10)							
6.56	9.08	—	—	8.35	0.105	0.79	−0.13	±0.02	—
−0.05)	(−0.21)								
5.23	7.07	3.16	5.13	6.38	0.114	0.77	−0.16	±0.03	0.08
−0.08)	(−0.26)	(−0.13)							
4.84	5.74	—	—	4.16	0.126	0.91	−0.13	±0.02	—
(0.01)	(−0.21)								
2.95	3.63	2.03	2.91	3.62	0.130	1.16	−0.24	±0.05	0.01
−0.17)	(−0.37)	(−0.18)							
1.95	2.29	1.15	1.77	2.37	0.143	1.14	−0.31	±0.09	−0.05
−0.23)	(−0.44)	(−0.32)							
13.8	—	7.76	12.0	24.4	0.073	0.39	−0.05	±0.04	0.10
−0.03)		(−0.09)							
10.9	18.9	—	—	15.0	0.088	0.46	−0.03	±0.04	—
(0.00)	(−0.06)								
6.31	9.77	3.49	5.64	4.3	0.125	0.87	0.02	±0.05	0.02
(0.09)	(0.00)	(0.01)							
4.2	5.75	—	—	2.56	0.141	0.95	0.00	±0.03	—
(0.11)	(−0.07)								
3.59	4.92	2.02	3.17	1.75	0.152	0.98	0.03	±0.03	−0.06
(0.12)	(−0.02)	(0.11)							
2.81	3.56	—	—	1.45	0.158	1.09	−0.03	±0.03	—
(0.06)	(−0.11)								
3.42	4.11	1.83	2.02	1.7	0.153	1.09	−0.01	±0.04	−0.21
(0.11)	(−0.09)	(−0.03)							
0.86	1.03	0.63	1.84	0.73	0.179	1.26	−0.37	±0.04	0.27
−0.26)	(−0.45)	(−0.27)							
1.84	2.18	1.61	1.52	2.44					
0.09	−0.09	0.02	0.12ᵉ	0.12					
±0.05	±0.05	±0.03		±0.12					
9.2	9.6	8.6	7.3	14.4					

toluene, carbon tetrachloride, chlorobenzene and ethyl sulfide in Table III), so that log k_p could be calculated for each solute and these solvents. The resulting values of log k_p for each solute were averaged, and the values are shown in Table III. These log k_p values were constant (±0.05 units standard deviation) for each solute. Given these values of log k_p, Eqn. 4 then allows calculation of Δ values for every solute/ solvent combination. These values are shown in parentheses in Table III. Δ values for the less polar solvents used to measure k_p are generally small, confirming that minimal secondary solvent effects are involved with these solvents.

It was noted that a series of Δ values for one solvent a could be related to corresponding values (same solutes) for a second solvent b through the relationship

$$\Delta_a = a' + m' \Delta_b \tag{5}$$

Here Δ_a and Δ_b are Δ values for the same solute eluted by solvents a and b, respec-
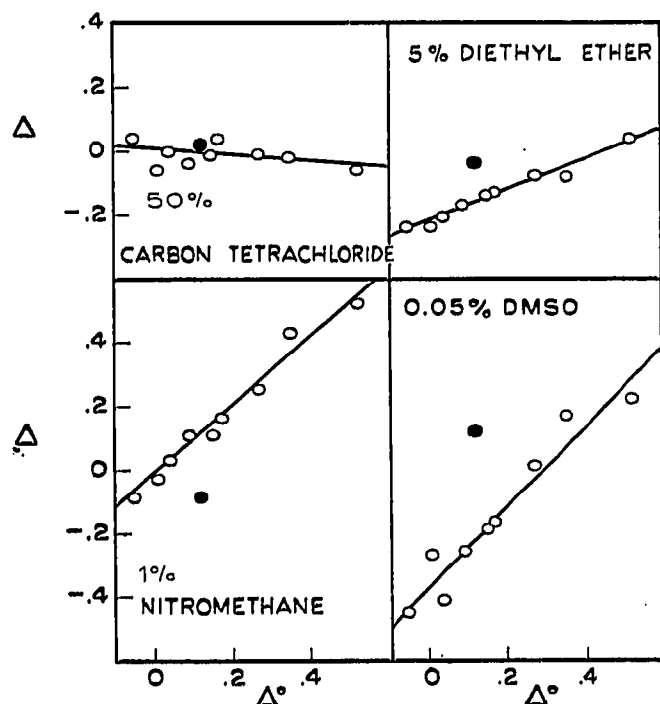
Fig. 5. Values of Δ for indicated solvents *versus* average Δ values for acetonitrile solutions as solvents. ●, data for N-methylaniline.

tively. a' and m' are constants characteristic of the solvent pair a and b. Thus if Δ values for a given series of solutes and a particular solvent are plotted *versus* corresponding values for a second solvent, a linear relationship is obtained. This is illustrated in Fig. 5, where data for some representative solvents are plotted against average Δ values for the solvents 0.3–0.7% (v/v) acetonitrile/pentane. In each case, a straight line plot is observed, with slight scatter of the data about this line. Only the points for the donor solute X (dark circles) deviate markedly from these plots, an effect which we will later relate to hydrogen bonding between solvent and solute.

Eqn. 5 implies that individual Δ values follow a relationship of the form

$$\Delta = a + m\,\Delta^0 \tag{5a}$$

where a and m are constants for a given solvent, and Δ^0 is a constant for a given solute. Using 0.3–0.7% (v/v) acetonitrile/pentane solutions as reference solvent (for which $\Delta = \Delta^0$), values of a and m were calculated for the remaining solvents of Table III from Eqn. 5a. Using these values of a and m, values of Δ^0 could be recalculated from Eqn. 5a for each solute and solvent. These Δ^0 values were averaged for each solute (excluding less accurate values for solvents where $m < 0.5$), resulting in slightly revised Δ^0 values relative to values derived initially from the 0.3–0.7% (v/v) acetonitrile/pentane data. Final (average) values of Δ^0 are shown for each solute in Table III, along with their standard deviation (for $m < 0.5$). Finally, values of a and m for each solvent were recalculated, using Eqn. 5a and the best values of Δ^0 for each solute shown in Table III. These final values of a and m for each solvent differed only slightly from the initial values, and use of these final a and m values to recalculate Δ^0 resulted in no further change in Δ^0. The a, m and Δ^0 values of Table III therefore

represent a best fit of Eqn. 5a to these Δ values, excluding data for the donor solute N-methylaniline.

The fit of the Δ values of Table III to Eqn. 5a and the parameters summarized in Table III is given by an overall standard deviation of ± 0.04 units. This compares with an experimental repeatability of $\pm 4\%$ relative, or ± 0.02 units. Only five Δ values in Table III deviate from calculated values by more than two standard deviation units, and there is no pattern to these deviations (which would suggest some additional effect not recognized by Eqn. 5a). Consequently it appears that Eqn. 3a accounts for all but a very minor part of the Δ values of Table III (which range in value from -0.45 to 0.52). The significance of this correlation (Eqn. 5a) will be examined after considering the dependence of the parameters a, m and Δ^0 on the solvent and solute.

DEPENDENCE OF m AND a ON SOLVENT COMPOSITION

The solvent parameter m is of direct interest with respect to solvent selectivity. For a given adsorbent, solvent strength, ε^0 (for optimum k'), and pair of solutes (1 and 2), terms a plus b of Eqn. 1 are seen to be a constant, C. Combination of Eqns. 1 and 2 then yields

$$\log \alpha = C + m(\Delta_1^0 - \Delta_2^0) \tag{6}$$

i.e. solvent selectivity for a given pair of solutes under these conditions is determined solely by m.

The variation of m with solvent composition is best shown in plots of m vs. $\alpha' \varepsilon^0$ for different concentrations of the same strong solvent (e.g. 15, 28, 50, 80 and 100%
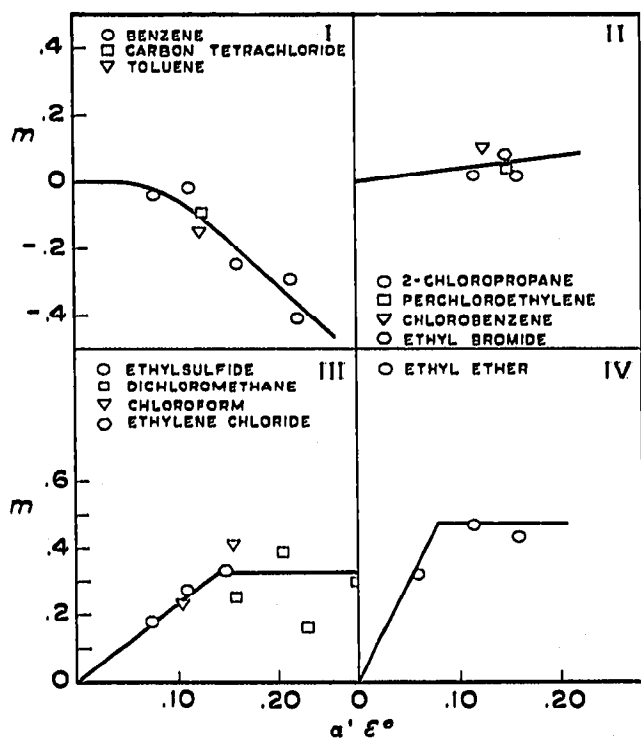

Fig. 6. Classification of solvent m values. Adsorbent: 4.3% $H_2O-Al_2O_3$.
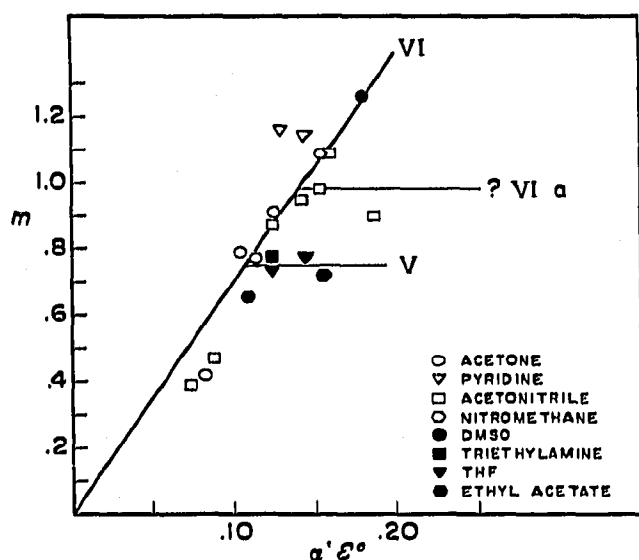
Fig. 7. Classification of solvent m values. Adsorbent: 4.3% H_2O–Al_2O_3.

(v/v) benzene/pentane in Fig. 6-I. As seen in Figs. 6 and 7, the 20 strong solvent components of Table III fall into roughly seven classes (Table I), each of which follows a characteristic curve of m vs. $a'\varepsilon^0$. These characteristic curves are replotted without points in Fig. 2. The relatively non-polar solvents of classes I and II show values of m which are negative or close to zero. The more polar solvents of classes III–VI show m increasing initially with increasing concentration of the strong solvent; eventually, m levels off and remains constant for further increases in $a'\varepsilon^0$ and the concentration of the strong solvent components. Plots of m versus $a'\varepsilon^0$ as in Figs. 6 and 7 are useful in showing the maximum range in m for solvents of given strength (as required for optimum k' values in a given separation problem).

The solvent parameter a is related to the value of Δ^0 for the reference solute picene (Δ_p). Since Δ is defined equal to zero for hydrocarbon solutes such as picene, we have, from Eqn. 5a,

$$a = -m\,\Delta_p \tag{7}$$

The a and m values of Table III yield a best value of Δ^0 for picene $\Delta_p = 0.12$. The standard deviation of experimental a values from values calculated by Eqn. 7 is ± 0.12 units. This is higher than the standard deviation for correlation of the data of Table III with Eqn. 5a (± 0.04 units), because the standard deviation for Eqn. 7 is determined by the absolute error of k', while that of Eqn. 5a is related to the relative error of k' (see Table II). In any event, the correlation of a with m appears reasonable in terms of the known repeatability of the experimental data.

DEPENDENCE OF Δ^0 ON SOLUTE STRUCTURE

Values of Δ^0 for the solutes in Table III are summarized in Table IV. k' for additional solutes and other solvent systems are summarized in Tables V (weaker solvents) and VI (stronger solvents). Because a different batch of adsorbent was used in these studies, and (for Table VI) stronger solvent systems were necessary for

TABLE IV

SECONDARY SOLVENT PARAMETERS FOR DIFFERENT SOLUTES

Localized solute group k	Solute	Δ^0		$Q^0{}_k$ (ref. 1)
None	Picene	0.12		0.3
−SCH₃	Phenyl methyl sulfide	0.34	± 0.6	1.3
	2-Naphthyl methyl sulfide	0.36	± 0.2	
−OCH₃	Anisole	0.28	± 0.5	1.8
	2-Methoxynaphthalene	0.31	± 0.06	
	1,7-Dimethoxynaphthalene	0.16	± 0.04	
−N =	7,8-Benzoquinoline	−0.05	± 0.2	2.3
−N(CH₃)₂	N,N-Dimethylaniline	0.11	± 0.1	2.5
−NO₂	Nitrobenzene	0.28	± 0.1	2.8
	1-Nitronaphthalene	0.38	± 0.05	
	1,3-Dinitrobenzene	0.45	± 0.16	
	1,5-Dinitronaphthalene	0.46	± 0.07	
	1,3,5-Trinitrobenzene	0.56	± 0.23	
−CN	1-Cyanonaphthalene	0.18	± 0.04	3.2
−COOCH₃	Methyl benzoate	−0.06	± 0.2	3.3
	1-Methylnaphthoate	0.02	± 0.03	
−CHO	1-Naphthaldehyde	0.09	± 0.05	3.3
−COCH₃	Acetophenone	−0.15		3.7
	1-Acetonaphthalene	−0.09	± 0.05	
	1,4-Diacetylbenzene	−0.11	± 0.34	
	3-Nitroacetophenone	0.06	± 0.10	
−NHCH₃	N-Methylaniline	0.12		3.7
−N =	2-Chloroquinoline	0.02	± 0.03	3.8
−NH₂	Aniline	−0.05	± 0.17	4.4
	1-Aminonaphthalene	−0.11	± 0.10	
−N =	Isoquinoline	−0.5	± 0.4	4.8
−CO−CO−	9,10-Phenanthrenequinone	−0.44		5.4[a]
−SO₂CH₃	Naphthalene-2-methylsulfone	−0.58	± 0.13	6.0[a]
−SOCH₃	Naphthalene-2-methylsulfoxide	−1.08	± 0.10	7.8[a]
−CON(CH₃)₂	N,N-Dimethyl-1-naphthamide	−1.40	± 0.14	8.3[a]

[a] Benzene solvent, present study.

convenient k' values, the resulting k' values are somewhat less reliable than those of Table III (see EXPERIMENTAL section). The lesser accuracy of k' values is further compounded by the smaller number of data obtained, resulting in larger standard deviations for correlations with Eqn. 5a and in derived Δ^0 values (see Table IV)*. Thus Δ^0 values for the solutes of Table III show individual variations (standard deviation) of ±0.03–0.07 units, versus variations of ±0.1–0.6 units for the additional solutes in Tables V and VI.

It can be seen in Table IV that Δ^0 values for solutes which contain the same substituent groups (e.g. −OCH₃, −NO₂, −COOCH₃, −COCH₃, etc.) tend to be similar, particularly when the same number of groups is present in the molecule. This suggests that the substituent group(s), rather than the total molecule, determines the value of Δ^0. Previous studies (see review of ref. 1) have shown the general importance of group localization in adsorption chromatography, wherein strongly adsorbed groups are held more or less strongly on strong adsorption sites. The effect of group localiza-

* The treatment of these data is discussed in the APPENDIX.

TABLE V

k' VALUES FOR ADDITIONAL SOLUTES AND WEAKER SOLVENTS

Solute	k'				A_s
	20% (v/v) benzene	30% (v/v) CCl_4[b]	5% (v/v) ether[b]	0.5% (v/v) ethyl acetate	
2-Methoxynaphthalene	1.71	3.71	2.04	2.12	9.2
1,7-Dimethoxynaphthalene	4.22	13.6	4.91	4.77	10.3
1-Nitronaphthalene	4.58	9.83	5.13	5.99	9.4
Methyl-1-naphthoate	7.08	19.1	6.71	7.21	10.4
1-Cyanonaphthalene	8.0	—	—	9.10	8.7
1-Naphthaldehyde	7.9	—	—	8.49	9.2
2-Chloroquinoline	4.72	10.6	4.74	4.97	8.6
Phenanthrene	1.10	2.26	1.59	1.39	10.2
Phenyl methyl sulfide	0.81	0.96	0.87	0.76	7.7
2-Naphthyl methyl sulfide	1.53	3.17	1.97	1.51	9.8
Anisole	1.15	1.29	0.97	1.08	7.1
N,N-Dimethylaniline	1.60	3.22	1.54	1.55	8.3
Nitrobenzene	3.08	5.26	2.98	3.46	7.3
7,8-Benzoquinoline	10.4	24.5	9.45	9.04	10.0
Methyl benzoate		10.6	4.08		8.3
$a'\varepsilon^0$[a]	0.077	0.046	0.061	0.067	

[a] Determined from k' for phenanthrene.
[b] Different batch of adsorbent.

tion generally correlates with the adsorption energy Q^0_k of the most strongly adsorbing group k in the molecule. In Fig. 3 values of Δ^0 vs. Q^0_k are plotted. A reasonable correlation is observed, permitting the prediction of Δ^0 values for other solutes, and suggesting that group localization is responsible for the secondary solvent effects which give rise to the Δ^0 values of Eqn. 4. The dark circles of Fig. 3 refer to Δ^0 values for the solutes of Table III (more reliable), while the open circles refer to values for the solutes of Tables V and VI.

Variations in Δ^0 for solutes containing the same most strongly adsorbed group k also support the importance of group localization, since these differences in Δ^0 appear to correlate with expected changes in Q^0_k as a result of the substitution of other groups into the solute molecule. Thus introduction of electron donating groups (e.g. $-OCH_3$) increases Q^0_k, while electron withdrawing groups (e.g. $-NO_2$, $-COCH_3$) decrease Q^0_k. From the form of Fig. 3 (Δ^0 increasing with decreasing Q^0_k), we expect dimethoxynaphthalene to have a smaller value of Δ^0 than methoxynaphthalene or anisole, which is the case (0.16 vs. 0.31, 0.28). Similarly, Δ^0 should increase in going from mononitro to dinitro to trinitro compounds, as observed: mono-, 0.28, 0.38; di-, 0.45, 0.46; tri-, 0.56. Similarly, 3-nitroacetophenone should have a value of Δ^0 slightly greater than that of acetophenone or 1-acetonaphthalene, since the $-COCH_3$ group is localized in this solute. This is the case, 0.06 vs. values of -0.09 and -0.15. The only exception to the predicted change in Δ^0 with additional substitution on the molecule occurs for 1,4-diacetylbenzene, the experimental reliability of which (± 0.34 units) is so poor as to overshadow the anticipated increase in Δ^0 (by 0.1–0.2 units),

TABLE VI

k' VALUES FOR ADDITIONAL SOLUTES AND STRONGER SOLVENTS

Solute	Solvent[a]						A_s
	80% (v/v) benzene	Benzene	35% dichloromethane	60% (v/v) dichloromethane	Dichloromethane	5% (v/v) acetonitrile[b]	
1-Acetonaphthalene	2.04	0.53	2.41	1.06	—	2.72[d]	9.6
1-Naphthaldehyde	1.12	0.35	1.71	0.68	—	2.57[d]	9.2
1-Cyanonaphthalene	1.11	—	1.60	0.64	—	—	8.7
Methyl-1-naphthoate	0.91	0.33	1.20	—	—	0.74	10.4
1,5-Dinitronaphthalene	0.95	0.30	2.47	0.73	—	3.12	10.7
2-Chloroquinoline	0.97	0.33	1.43	0.63	—	0.76	8.6
N-Methylaniline	1.36	0.51	1.55	0.75	—	1.17	7.3
1,2,4,5,8,9-Tribenzopyrene	1.08	—	1.41	0.52	—	2.60	17.0
Methyl benzoate	1.13	—	1.31	0.76	—	0.80	8.3
3-Dinitrobenzene	1.19	0.26	2.47	0.86	—	3.53	8.6
Acetophenone	—	0.82	—	1.13	—	—	7.5
3-Nitroacetophenone	3.54	1.05	5.52	1.62	0.58	3.68	8.8
1-Naphthylamine	7.28	—	8.42	2.73	0.76	4.57	8.7
Aniline	5.99	2.38	6.35	2.57	0.81	4.57	6.6
1,4-Diacetylbenzene	6.48	4.30	15.6[d]	4.02	1.05	4.40	9.0
1,3,5-Trinitrobenzene	1.70	0.32	7.09[d]	1.78	0.32	5.86	9.9
N,N-Dimethyl-1-naphthylamide	—	88	59	27.5	5.3	7.13	12.0
Isoquinoline[d]	—	6.41	16.7	7.98	2.64	3.39	7.9
Naphthalene-2-methyl sulfone	—	14.4	—	9.8	1.70	11.2	10.4
Naphthalene-2-methyl sulfoxide	—	120	—	41	7.2	21.1	10.1
9,10-Phenanthrenequinone	—	—	—	13.3	2.3	12.8	10.4
$a'\epsilon°$e	0.211	0.220	0.204	0.230	0.280	0.188	
m	-0.29	-0.41	0.33	0.22	0.30	0.88	

a Solutions with pentane.
b Acetonitrile–benzene–pentane (5:10:85).
c Calculated from k' for tribenzopyrene as solute.
d Values correlate poorly with Eqn. 5a, suggesting experimental error.

TABLE VII

COMPARISON OF CALCULATED (EQN. 5A) AND EXPERIMENTAL Δ VALUES FOR SOLVENTS AND SOLUTES BEARING SIMILAR FUNCTIONAL GROUPS

Solute	Solvent	Δ		Difference[a]		S.D. for all solutes[b]
		Exptl.	Equ. 5a	Individual	Average	
2-Chloroquinoline[c]	2% (v/v) pyridine/pentane	−0.18	−0.22	0.04		±0.05
	5% (v/v) pyridine/pentane	−0.32	−0.29	−0.03		±0.09
					0.00	±0.07
2-Methoxynaphthalene, 1,7-dimethoxynaphthalene	2, 5, 9, 23% (v/v) ethyl ether, 2, 5% (v/v) tetrahydrofuran				0.03	±0.05
1-Nitronaphthalene, 1,5-dinitronaphthalene	1% nitromethane				0.00	±0.04
Methyl-1-naphthoate	1, 4% (v/v) ethyl acetate				0.00	±0.03
1-Cyanonaphthalene	0.1, 0.14, 0.3, 0.4, 0.6, 0.7% (v/v) acetonitrile				0.02	±0.04
1-Acetonaphthalene	0.2, 0.4, 0.6, 0.8% (v/v) acetone				−0.01	±0.02

a Experimental Δ minus calculated Δ.
b For indicated solvent(s).
c Detailed data reported as an example.

relative to acetophenone and 1-acetonaphthalene. The solvent selectivity noted earlier in the separation of the isomeric halogen-substituted nitrobenzenes (I and II) represents another example of the dependence of Δ^0 on $Q^0{}_k$, and illustrates how estimation of Δ^0 for related solutes can lead to predictions for change in solvent selectivity and (if necessary) improvement in resolution through change in solvent composition.

The origin of these secondary solvent effects is now fairly clear. Strongly adsorbing (localizing) solutes and solvents compete for the same strong adsorption sites. The adsorption of other compounds occurs mainly on the remainder of the adsorbent surface, and is described by Eqn. 4 with $\Delta = 0$. Thus localizing solvents (or solvent components) selectively reduce the adsorption of localizing solutes relative to non-localizing solutes and/or non-localizing solvents. The magnitude of the effect (Δ) increases with the adsorption energies of the localizing solute group ($Q^0{}_k$) and of the localizing solvent component (ε^0). Once the coverage of the adsorbent surface by a strong solvent component is complete (at high enough concentrations of that component in the original solvent mixture), further increase in concentration of the strong solvent component will have little effect on m. This is observed in Fig. 2 and has been discussed in detail elsewhere[7].

An example of the secondary solvent effects summarized by Eqn. 5a has been noted previously[7], the so-called "ether anomaly". The present study shows that ethers as solvents are merely one of many solvents which give rise to this effect. A following section shows that Eqn. 5a is also applicable to secondary solvent effects on silica, and the above example of the substituted nitrobenzenes was taken from adsorption on still another adsorbent—magnesium silicate. Thus, secondary solvent effects of this type appear to be general for most polar adsorbents. Since group localization likewise occurs on all polar adsorbents[1], this generalization is expected.

At the beginning of the present study, it was anticipated that selectivity in adsorption chromatography might arise from adsorption sites of differing character, each of which could interact in some characteristic way with different adsorbed solute molecules. Thus some sites might be highly polar (electrostatic interaction), others might emphasize acid–base interaction (hydrogen donors or Lewis acids, hydrogen acceptors, etc.), and other sites might utilize still other types of interaction. The results of the present study suggest that this is not the case, rather all sites appear to be of similar character (but differing adsorption strength). The reason for this conclusion is the excellent correlation of Δ values with Eqn. 5a for all solvents and solutes. If preferential adsorption of basic solutes (e.g. 2-chloroquinoline) on acidic sites were occurring, basic solvents (e.g. triethylamine, pyridine) should be particularly effective in competing with the adsorption of these solutes (giving lower Δ values than predicted by Eqn. 5a). Similarly, solvents with the same functional groups as the solute should also be more effective in lowering Δ than predicted by Eqn. 5a, e.g. ether or tetrahydrofuran solutions and the methoxynaphthalene solutes should give lower Δ values than predicted. Systems of this type from Table III are summarized in Table VII, and it is seen that there is no trend to lower experimental Δ values (relative to values calculated from Eqn. 5a).

Solvent selectivity might also be expected to arise from the preferential adsorption of the strong solvent component (e.g. acetonitrile from 0.7% acetonitrile/pentane), yielding an adsorbed solvent phase of different composition. This should lead

to different solute–solvent interactions in the adsorbed phase, and Δ values different from those predicted by Eqn. 5a (e.g. polar solvents and solutes such as acetonitrile and nitronaphthalene would interact preferentially in the adsorbed phase, giving larger Δ values than predicted). Again this is not observed. The dominant consideration in liquid–solid chromatographic systems is the competition of solutes and solvents for adsorbent sites, with minimal contributions (in moderately polar, non-donor systems) from solute–solvent interactions in either the adsorbed or solution phase.

Solvent selectivity as defined by Eqn. 5a bears some resemblance to the phenomenon of "weak localization"[1,8]. Weak localization refers to the preferential adsorption of linear or near-linear solute molecules on certain parts of the alumina surface, leading to the easy separation of a large class of such isomers (e.g. poly-aromatic hydrocarbons, halogen-substituted aromatics, etc.). The effect of the solvent on weak localization is quite similar to its effect as measured by Eqn. 5a; solutions of strong solvents suppress preferential adsorption of linear solutes, and solutions of weaker solvents enhance adsorption. However, there are some major differences which suggest that weak localization and Eqn. 5a are in fact unrelated. Thus in weak localization a change in alumina–water content from 2% to 4% drastically inhibits separation selectivity, reducing Δ values by a factor of 5. The corresponding effect of adsorbent–water content on Eqn. 5a is much more modest (see the following section), amounting to only a factor of 1.3 reduction in Δ. Weak localization occurs for alumina but not silica, whereas Eqn. 5a applies to both adsorbents. Finally, Eqn. 5a is determined by individual solute substituents, whereas weak localization is determined by overall solute shape. The only connection between these two adsorption phenomena is that both appear to involve a type of solute localization on the adsorbent surface which competes with corresponding localization of the solvent. Different adsorbent sites appear to be involved in the two cases, leading to grossly different kinds of potential selectivity.

SOLVENT SELECTIVITY ON SILICA

Table VIII summarizes limited data on the effect of solvent on separation selectivity for silica as adsorbent. The solutes studied are those in Table III, for which

TABLE VIII

SECONDARY SOLVENT EFFECTS FOR SILICA (10% WATER–PORASIL A) AS ADSORBENT

For solutes, see Table III.

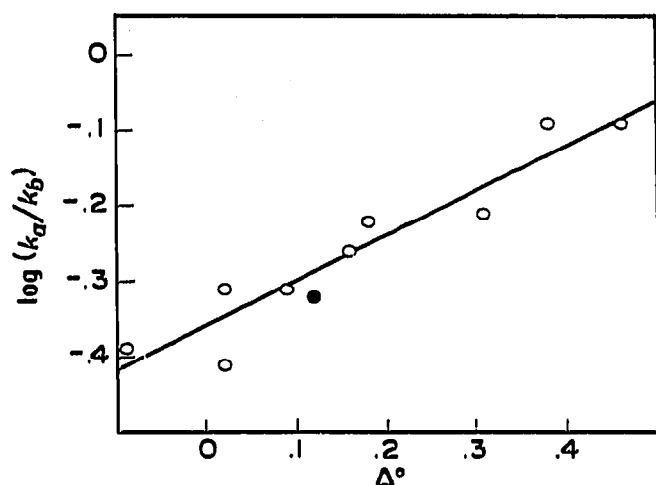| Solvent	k'										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
15% (v/v) benzene/ pentane (b)	1.40	3.05	3.01	12.3	6.06	7.25	8.43	19.6	19.4	10.9	1.11
0.2% (v/v) acetonitrile/ pentane (a)	0.86	1.67	2.43	10.1	2.94	4.42	4.13	8.05	7.48	5.2	1.11

Fig. 8. Solvent selectivity on silica.

accurate Δ^0 values are available. The solvent strengths ε^0 for the two solvents in Table VIII are noted to be identical (k' for picene is the same for each solvent). If we take the ratio of k' values for the same solute in these two solvents a and b (k_a/k_b), we see that the first two terms of Eqn. 4 cancel, giving

$$\log (k_a/k_b) = \Delta_a - \Delta_b$$

and upon substituting Eqn. 5a into this relationship we obtain

$$\log (k_a/k_b) = (m_a - m_b) \Delta^0 + (a_a - a_b)$$
$$= (m_a - m_b) \Delta^0 + c \tag{8}$$

Thus if Eqn. 5a is applicable for silica as adsorbent, a plot of $\log (k_a/k_b)$ vs. Δ^0 should be linear. This relationship is tested in Fig. 8. The resulting correlation is as satis-

TABLE IX

ADSORBENT SELECTIVITY EFFECTS: ALUMINA vs. SILICA

Solute	Silica[a] (15% benzene)	Alumina[b] (25% benzene)	k' (silica)/k' (alumina)
2-Methoxynaphthalene	1.40	1.37	1.02
1,7-Dimethoxynaphthalene	3.05	3.05	1.00
1-Nitronaphthalene	3.01	3.55	0.85
1,5-Dinitronaphthalene	12.3	12.1	1.02
Methyl-1-naphthoate	6.06	5.50	1.10
1-Cyanonaphthalene	7.25	6.00	1.21
1-Naphthaldehyde	8.43	7.40	1.14
1-Acetonaphthalene	19.6	16.1	1.22
2-Chloroquinoline	19.4	4.96	3.91
N-Methylaniline	10.9	5.85	1.86
Picene	1.11	7.9	0.14

[a] Values of Table VIII.
[b] Interpolated from data of Table III.

TABLE X

ADSORBENT ACTIVITY EFFECTS

For solutes, see Table III.

Adsorbent, solvent[a]	k'[b]										XI[c]	$a'\varepsilon^0$
	I	II	III	IV	V	VI	VII	VIII	IX	X		
2% H₂O–Al₂O₃ 65% (v/v) benzene	0.57 (1.84)	1.26 (2.24)	1.42 (2.29)	3.24 (2.94)	2.42 (2.75)	2.40 (2.36)	4.25 (2.71)	7.58 (3.06)	1.90 (2.46)	7.3 (2.52)	0.29	0.227
2% H₂O–Al₂O₃ 2% (v/v) acetonitrile	0.59 (1.80)	0.78 (2.17)	1.72 (2.31)	7.53 (3.24)	0.86 (2.23)	1.68 (2.14)	1.76 (2.28)	1.92 (2.40)	0.88 (1.85)	2.06 (1.93)	0.34	0.221
8% H₂O–Al₂O₃ 5% (v/v) benzene	1.08 (0.53)	2.51 (0.96)	3.49 (1.05)	14.6 (1.74)	5.31 (1.29)	6.58 (1.29)	5.09 (1.20)	13.5 (1.65)	5.01 (1.17)	3.22 (0.90)	0.51	0.054
$\Delta \log k_p$[d]	1.31	1.28	1.24	1.20	1.46	1.07	1.51	1.41	1.29	1.62		

a Pentane solutions.
b Values of $(\log k' + a'\varepsilon^0 A_s)$ in parentheses.
c Phenanthrene.
d Benzene solvents, $\Delta \log k_p \equiv [\log k_p + \Delta]_{2\%} - [\log k_p + \Delta]_{8\%} \equiv \Delta_{2\%} - \Delta_{8\%}$.

factory as those obtained on alumina (standard deviation $= \pm 0.04$ units), thus establishing that secondary solvent effects for non-donor solvents and solutes are essentially similar on both silica and alumina. On 4.3% $H_2O-Al_2O_3$, m_a (0.2% (v/v) acetonitrile) is equal to 0.61 (interpolated) and m_b (15% (v/v) benzene) is -0.04, so $(m_a - m_b)$ equals 0.65. This value compares well with the slope of the plot of Fig. 8 (equal to $m_a - m_b$), which is 0.60. Thus the magnitude of these secondary solvent effects on alumina and silica is quite similar.

The adsorbent selectivity of silica $vs.$ alumina is compared in Table IX for benzene/pentane solutions as solvent. Solvents were selected to give equal k' values for the solute 1,7-dimethoxynaphthalene (alumina k' values are interpolated from data in Table III). The ratio of k' values for each solute then measures the difference in adsorbent selectivity. Large aromatic hydrocarbons such as picene are preferentially eluted from silica, and basic compounds such as 2-chloroquinoline and N-methylaniline are preferentially retained. These differences in silica $vs.$ alumina have been noted previously[1]. Only minor differences in adsorbent selectivity (± 0.06 log units S.D.) are indicated for the other solutes of Table IX.

THE EFFECT OF ADSORBENT ACTIVITY ON SOLVENT SELECTIVITY

k' values for adsorption on aluminas of higher and lower water content are shown in Table X for a few solvents and the solutes of Table III. Values of (log $k' + \alpha' \varepsilon^0 A_s$) are shown in parentheses, equal to (log $k_p + \Delta$). The difference in these values for a given solute and the two solvents used with 2% $H_2O-Al_2O_3$ (2% (v/v) acetonitrile, a; 65% (v/v) benzene, b) is then equal to $\Delta_a - \Delta_b$. This latter quantity is in turn equal to $(m_a - m_b) \Delta^0$, if Eqn. 5a applies. This relationship is tested in Fig. 9. A reasonable correlation is noted* (S.D. $= \pm 0.10$), verifying that solvent selectivity effects are similar on 2% and 4.3% $H_2O-Al_2O_3$. The somewhat greater
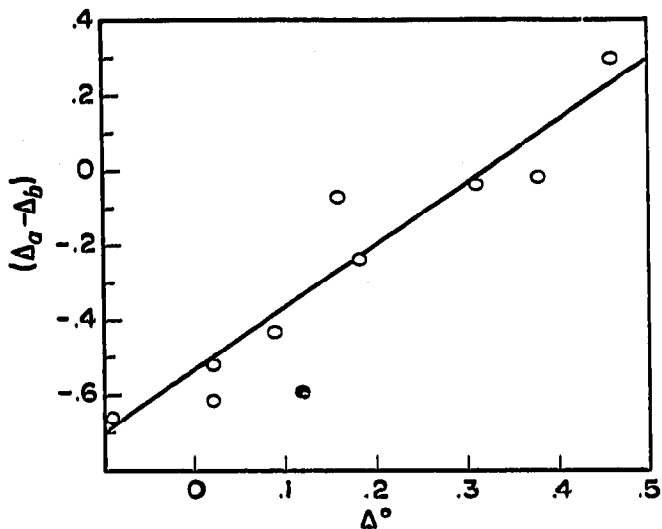

Fig. 9. Solvent selectivity on 2% $H_2O-Al_2O_3$.

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* The data of Fig. 9 do not pass through the origin as predicted. This is not of practical significance, and is probably the result of small variations in α' for different solutes in changing adsorbent activity.

scatter of the data of Fig. 9 can be attributed to lowered accuracy in the measured k' values, which is in turn related to the lower linear capacity of this more active adsorbent. For 4.3% $H_2O-Al_2O_3$ the slope of the plot of Fig. 9 $(m_a - m_b)$ is predicted to be about 1.3. The actual slope for 2% $H_2O-Al_2O_3$ is 1.69, indicating that solvent selectivity increases with adsorbent activity. This is expected from the basis of these solvent selectivity effects, since the strong adsorbent sites involved are selectively covered by adsorbed water.

Table X also summarizes differences in selectivity for 2% $vs.$ 8% $H_2O-Al_2O_3$ (benzene/pentane solvents), in terms of differences in $\log k_p + \Delta$ for these two adsorbents $\equiv \Delta \log k_p$. These differences in adsorbent water content are accompanied by corresponding differences in water content of the solvent at equilibrium (approaching 100% saturation for 8% $H_2O-Al_2O_3$ and 0% saturation for 2% $H_2O-Al_2O_3$ (ref. 5). Since water is quite strongly adsorbed, is a component of the solvent system, and is present in the solvent in quite different concentrations, it might be anticipated that
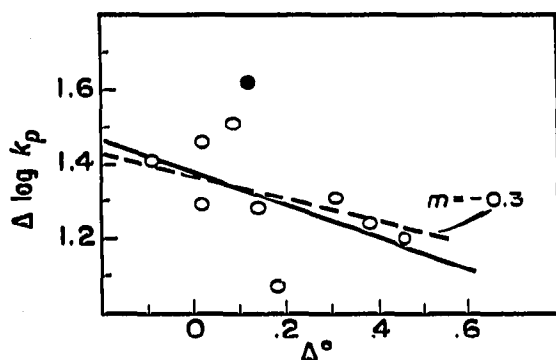

Fig. 10. Adsorbent selectivity (benzene/pentane solutions as solvent) for 2% $H_2O-Al_2O_3$ $vs.$ 8% $H_2O-Al_2O_3$.

$\Delta \log k_p$ will be of the same form as $\Delta_a - \Delta_b$ for two different solvents a and b, $i.c.$ proportional to Δ^0. This possibility is tested in Fig. 10. The scatter of the resulting correlation (S.D. ± 0.11) is little worse than that of Fig. 9, and the slope (-0.44) is of the right sign ($i.e.$ the value of m for the solvent of lower water content—2% $H_2O-Al_2O_3$—is lower than that for solvent of higher water content). However, the simple difference in benzene concentrations for the two cases (65% $vs.$ 5%) should yield an m value difference of about -0.3 (dashed curve in Fig. 10), which accounts for most of the observed dependence of $\Delta \log k_p$ on Δ^0. The solvent component water thus appears to contribute little to the selectivity differences for these two adsorbents, at least at the low water concentrations present in the solvent (probably about 100 p.p.m.).

HYDROGEN BONDING EFFECTS AS ILLUSTRATED BY N-METHYLANILINE

Table III lists differences between experimental Δ values for N-methylaniline and corresponding values calculated from Eqn. 5a ($\Delta\Delta$ in the last column of Table III). The average of these $\Delta\Delta$ values is ± 0.12 units, which is three times the standard deviation of other solutes in Table III from Eqn. 5a. The greater deviation of Δ values

for N-methylaniline is also apparent in the plots of Fig. 5. We will not attempt a detailed analysis of these $\Delta\Delta$ values here, since a wide variety of solvent/solute systems involving hydrogen bonding must be examined to achieve an unequivocal understanding of these effects. It is interesting to note, however, that those solvents (strong component) which give an average value of $\Delta\Delta$ less than -0.1 (ethyl bromide, dichloromethane, chloroform, nitromethane) are each weak proton acceptors, while those with an average value of $\Delta\Delta$ greater than 0.1 (ethyl ether, triethylamine, dimethyl sulfoxide) are all strong proton acceptors. This recalls the "basic eluent anomaly" discussed earlier[7], in which basic solvents (diethylamine, pyridine) were found to preferentially retain proton donor solutes such as carbazole, phenol and various aniline derivatives via solute/solvent hydrogen bonding in the adsorbent phase. N-Methylaniline appears to behave similarly, although the $\Delta\Delta$ values encountered are smaller than those for these latter solutes.

RE-EVALUATION OF PREVIOUSLY REPORTED ADSORPTION PARAMETERS

Values of ε^0 and log k_p (and related Q^0_i values) reported previously (for a summary, see ref. 1) generally ignore the complication of solvent selectivity arising from solute/solvent localization (Eqn. 5a). For the most part, this has had little effect on derived values of the solute parameters k_p and Q^0_i, because of the customary reliance on solvents of low m (e.g. solutions of carbon tetrachloride, benzene, dichloromethane). In a few cases, the use of solvents of large m has resulted in reported values of k_p and/or Q^0_i which are now realized to be low.

When strongly adsorbed solutes are used to measure values of ε^0 for mixtures of strong solvents (i.e. large m), and Δ is assumed to equal zero, however, the derived values of ε^0 will be larger than their true values (because Δ is actually negative). From a practical standpoint this is unimportant, because the use of strong solvents and solutes generally coincides in practical chromatographic systems, and errors which result from the use of incorrect ε^0 values are roughly cancelled by opposite errors associated with the assumption $\Delta = 0$.

REFERENCES

1 L. R. SNYDER, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2 R. NEHER, in G. B. MARINI-BETTÒLO (Editor), *Thin-Layer Chromatography*, Elsevier, Amsterdam, 1964, pp. 75–86.
3 K. BEREI AND L. VASÁROS, *J. Chromatogr.*, 26 (1967) 301.
4 L. R. SNYDER, *J. Chromatogr.*, 16 (1964) 55.
5 L. R. SNYDER, *J. Chromatogr. Sci.*, 7 (1969) 595.
6 L. R. SNYDER, *J. Chromatogr. Sci.*, 7 (1969) 352.
7 L. R. SNYDER, *J. Chromatogr.*, 16 (1964) 55.
8 L. R. SNYDER, *J. Chromatogr.*, 20 (1965) 463.

APPENDIX

The data in Table V were analyzed in terms of Eqn. 7. Values of log $k' + \alpha'\varepsilon^0 A_s$ were calculated for each solute and solvent, equal to log $k_p + \Delta$. Differences in this quantity for the same solute and two different solvents are equal to $\Delta_a - \Delta_b$, which is given by Eqn. 7. Values of $\Delta_a - \Delta_b$ for the two solvent pairs 5% ether/30% carbon

tetrachloride and 0.5% ethyl acetate/20% benzene were then plotted against Δ^0 values for the solutes which had been studied previously in Table III. The resulting linear curve permitted Δ^0 values for the remaining solutes of Table V to be determined from their $\Delta_a - \Delta_b$ values.

A similar approach to analyzing the data in Table VI was unsuccessful, as was the treatment of these data in the same fashion as those of Table III. The major problem is that these solutes show a much wider range in Δ^0 values than previously studied solutes, no solvents were studied for which it was expected that Δ would be zero, and the correction of k' values to give k_p involved a very large $\alpha'\varepsilon^0 A_s$ term (slight uncertainties in either $\alpha'\varepsilon^0$ or A_s are then greatly magnified). These problems were further compounded by the lesser reliability of these k' values, relative to the data in Tables III and V, and the smaller number of data collected. The approach eventually used was as follows. Data for pairs of solvents a and b of similar strength were selected. The log k' values for solvent b were then adjusted to give values for solvent of the same strength as a (by addition of the small term $\alpha'A_s[\varepsilon_b - \varepsilon_a]$). The resulting data could now be correlated in terms of Eqn. 7, as previously for the silica data of Table VIII. Values of log (k_a/k_b) were plotted against Δ^0 for those solutes of known Δ^0 (from Table III). These plots showed considerable scatter, and it was necessary to extrapolate the curves through a small range in Δ^0 values to cover a wide range in Δ^0. Simple least-squares correlation of such data was unsatisfactory. Instead, estimates of $(m_a - m_b)$ were made for solvents of composition similar to those studied in Table III, and curves with these slopes were drawn through data for solutes of known Δ^0. This then permitted approximate values of Δ^0 to be determined for the other solutes of Table VI. These Δ^0 values were averaged between different pairs of solvents a and b and the data replotted against Δ^0 values for all solutes. In the process, it became apparent that certain of the k' values deviated rather widely, and these points were ignored for purposes of drawing the best curves through the various sets of data. Finally, least-squares correlations were made and the variability of Δ^0 values for the various solutes obtained, as reported in Table IV. The resulting values of $(m_a - m_b)$ for the various solvent pairs correlated are summarized below, along with standard deviations for each set of data:

Solvent pairs from Table VI	$(m_a - m_b)$		$(a_a - a_b)$	$S.D.$ $(\Delta_a-\Delta_b)$[b]
	Exptl.	Calc.[a]		
5% acetonitrile/80% benzene	1.12	1.19	−0.28	±0.06
5% acetonitrile/60% dichloromethane	0.61	0.60	−0.13	±0.10
Dichloromethane/benzene	0.71	0.71	+0.09	±0.08
35% dichloromethane/80% benzene	0.67	0.57	0.05	±0.07
60% dichloromethane/80% benzene	0.39	0.59	−0.11	±0.08
5% acetonitrile/35% dichloromethane	0.54	0.62	−0.38	±0.09
60% dichloromethane/benzene	0.57	0.71	0.22	±0.12

[a] From values of m_a and m_b listed in Table VI.
[b] Experimental vs. calculated values.

k' values omitted from the above least-squares correlations include those indicated by [d] in Table VI.