

CHREV. 141

MECHANISM OF SOLUTE RETENTION IN LIQUID-SOLID CHROMATOGRAPHY AND THE ROLE OF THE MOBILE PHASE IN AFFECTING SEPARATION

COMPETITION *VERSUS* "SORPTION"

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1. INTRODUCTION

The use of liquid-solid chromatography (LSC) with polar adsorbents as stationary phase continues to find widespread application, despite the recent inroads of non-polar reversed-phase packings. These LSC* separations are largely controlled by the choice of mobile phase composition, with only occasional use of column packings other than silica. By varying mobile phase composition in LSC separation, it is usually possible to adjust both solvent strength (k' values) and selectivity (α values) for adequate resolution of the sample (*e.g.*, discussion of ref. 1). This procedure is often carried out empirically, but a better approach is suggested by some combination of past experience plus a theory of solute retention in LSC systems.

The development of an overall theory of LSC retention has been underway for several decades. In the 1960s one of us¹ developed a comprehensive and detailed model for LSC retention, including the role of the mobile phase in affecting separation. A somewhat different model of retention was presented a few years later by Soczewinski², but it was subsequently shown³ that the two models are essentially equivalent. While we refer to the latter as the Snyder-Soczewinski (S-S) model of LSC retention, it can also be described as the displacement model, from the assumption that an adsorbing molecule of solute displaces adsorbed solvent molecules during the retention process. We will describe the S-S model more fully in the next section.

In 1973 a third model of retention in LSC was presented by Scott and Kucera⁴. The Scott-Kucera (S-K) model differs almost diametrically from the S-S model, and is detailed in the following section. During the next 6 years the S-K model was further developed, and a considerable amount of experimental data was presented on its behalf⁵⁻¹¹. As this evolution of the S-K model proceeded, several qualifications were introduced, the generality of the model was then restricted to certain LSC systems, and certain earlier proposals were discarded. Throughout this series of papers⁴⁻¹² there has been only a limited effort at testing the S-K model against earlier experimental findings in the broad field of adsorption. Also, no attempt was made to test the ability of the S-S model to explain the newer data reported in refs. 4-12.

A critical review of these two models (S-S and S-K) of LSC retention seems, therefore, appropriate at the present time. The aims of the present communication include:

- (1) to review accurately the present status of these two theories of retention in LSC, with emphasis on points of difference;
- (2) to examine critically the points of difference with respect to previously published experimental evidence;
- (3) to draw conclusions concerning the relative validity of various assumptions and descriptions pertaining to LSC retention, so far as these can be known at the present time;

* Unless otherwise noted, we use LSC here only for polar adsorbents.

(4) to assess the practical impact of these final conclusions: in what cases do they apply (or not apply)? how do they affect our ability to predict separation and its dependence on mobile phase composition? etc.

If an informed consensus can be reached concerning the mechanism of retention on silica as stationary phase, it may be possible to extend these findings to related chromatographic systems. Earlier work showed that the S-S model provides an accurate basis for understanding retention in gas-solid chromatography¹³. More recently, De Ligny and co-workers¹⁴⁻¹⁸ have shown that the S-S model allows the satisfactory interpretation of retention in bonded-phase liquid chromatography, when these systems are run in normal (non-polar mobile phase) mode, as opposed to reversed-phase separation. One might also expect that a good understanding of retention in LSC on silica can prove useful in analyzing experimental data from reversed-phase separations on alkyl-bonded-phase columns. No agreement has yet been reached on the mechanism of retention in these reversed-phase systems (*e.g.*, ref. 19 vs. ref. 20), with the same basic questions still unresolved as are being argued in the case of LSC retention on silica. However, the question of retention mechanism on modified silicas will not be discussed here.

2. REVIEW OF SNYDER-SOCZEWINSKI AND SCOTT-KUCERA MODELS OF LSC RETENTION

In considering the mechanism of retention in LSC, it is important to begin with a rough classification of different systems; *e.g.*, according to differences in adsorbent, mobile phase, and/or solute. This allows us to anticipate the possibility of changes in retention mechanism as the latter variables are changed over wide limits. Such a classification is also essential in comparing, evaluating and extending the S-S and S-K models of LSC retention. Table 1 provides one such description of LSC adsorbents and mobile phases. In terms of the adsorbent, the present discussion will center on adsorbents of class I (polar inorganics), and specifically on silica, which is widely used today in high-performance liquid chromatography (HPLC). Other studies (*e.g.*, ref. 1) have shown that significant differences in the adsorption process can arise as the adsorbent is changed from a wide-pore silica (*i.e.*, of the type used in HPLC), to a fine-pore silica, or to alumina. However, these differences can be explained in terms of a continuum of effects comprised within the S-S model. Adsorbents of class II (*e.g.*, charcoal) have long been recognized as giving rise to quite different separations *versus* adsorbents of class I. Nevertheless, Guiochon and co-workers (*e.g.*, ref. 21) have interpreted retention on graphitized carbon in terms of the S-S model, while Robinson *et al.*²² have applied the S-S model to retention on XAD resin. In some respects, adsorbents of class III (polar bonded phases) bear a closer resemblance to silica and alumina than to charcoal; De Ligny and co-workers^{17,18} have shown the applicability of the S-S model in these systems for interpretation of retention data. Adsorbents of class IV (non-polar bonded phases) might be expected to be similar to those of class II, but no systematic comparison of retention in reversed-phase systems with these class II column packings has yet been made.

Returning to Table 1, three classes of mobile phase are considered. Class N comprises the less polar solvents with LSC solvent strength values ϵ^0 (for alumina, see ref. 1) which fall in the range 0.00 to about 0.40. This also corresponds to solvent

TABLE I
CLASSIFICATION OF LSC ADSORBENTS AND MOBILE PHASES

Classification	General class	Examples*
<i>Adsorbents</i>		
I	Polar inorganic	Silica, alumina
II	Non-polar inorganic	Graphite, charcoal
III	Polar bonded phase	Amino-propyl (C ₃ NH ₂), cyano-propyl(C ₃ CN), diol phase (-O-CH ₂ -CHOH-CH ₂ OH)
IV	Non-polar bonded phase	C ₈ , C ₁₈ bonded phase
<i>Mobile phases</i>		
N	Non-polar, moderately polar	Heptane (0.01), butyl chloride (0.26), benzene (0.32), chloroform (0.40)
P	Non-amphoteric polar	Methylethylketone (0.51), tetrahydrofuran (0.57), ethyl acetate (0.58), acetonitrile (0.71)
AB	Amphoteric polar	<i>n</i> -Propanol (0.82), methanol (0.95), water

* Values in parentheses refer to ϵ^0 values on alumina as adsorbent²⁴.

polarities P' (from Rohrschneider, see ref. 23) of roughly 0.0 to 4.0. Class P includes the more polar solvents, with ϵ^0 values of roughly 0.5–0.8 (and P' values of 4 to 7), which are not amphoteric. By "amphoteric" we mean capable of self-hydrogen-bonding in the pure solvent. The non-amphoteric solvents of class P thus exclude compounds with -OH or -NH groups. Class AB consists of so-called amphoteric polar solvents, and this group is largely restricted to such compounds as alcohols, carboxylic acids and phenols. The following review will be concerned mainly with mobile phases that are drawn from class N or P of Table I. A minor exception, which we will not pursue, should nevertheless be pointed out. For mobile phases of class N, the addition of small amounts of water to the LSC system results in so-called *deactivation* of the adsorbent surface. The latter refers to the partial blockage of a portion of the surface by adsorbed water. There is then no further effect of water in the mobile phase on the retention process.

To conclude, the remainder of this review will be concerned with LSC retention on silica, using mobile phases from classes N or P. A mixture of two solvents drawn from both class N and P (e.g., ethyl acetate–heptane binary) is considered to have the characteristics of a class P solvent; *i.e.*, the polar component (ethyl acetate) dominates the retention process.

2.1. The Snyder–Soczewinski model

This model has been reviewed in considerable detail (refs. 1 and 3 and references cited therein). The following discussion therefore emphasizes aspects of this model which are of specific interest in its comparison with the S–K model. The S–S model assumes that in LSC systems the entire adsorbent surface is covered by an adsorbate monolayer which consists variously of mobile phase or solute molecules. The adsorbent plus adsorbed monolayer effectively defines the stationary phase. The volume of the adsorbed monolayer (ml/m² of adsorbent surface) will be roughly constant, varying in minor degree with change in the mobile phase or solute, and in turn with the orientation of molecules within the monolayer. Under usual chromatographic conditions, the concentration of solute (sample) will be small, and the ad-

sorbed monolayer consists mainly of mobile phase molecules. Retention of a solute molecule then occurs by displacing a roughly equivalent volume of mobile phase molecules from the monolayer, so as to make the surface accessible to the adsorbed solute molecule. More precisely, if the area on the surface required by an adsorbed molecule X is covered by some number n of previously adsorbed mobile phase molecules M, the retention equilibrium is given by



Here, subscripts s and a refer to molecules in the mobile or adsorbed phase, respectively. It is assumed that the rate of equilibration in eqn. 1 is fast, even when the retention of M is more favorable than that of X (*i.e.*, for small k' values).

The net reaction free energy (actually dimensionless free energy; see ref. 1 and Glossary) corresponding to eqn. 1, which allows the prediction of relative retention and of k' as a function of conditions, is given as

$$\Delta E = E_{Xa} + nE_{Ms} - E_{Xs} - nE_{Ma} \quad (2)$$

i.e., the sum of energies for the species on the right of eqn. 1 minus the sum of energies for the species on the left (reactants). A further assumption of the S-S model is that various interactions between mobile phase and/or solute molecules in solution are normally cancelled by corresponding interactions in the adsorbed phase. This assumption should hold generally in LSC systems with class N mobile phases, since for such systems the solute-solvent interactions are primarily due to dispersion forces, and are of roughly equal magnitude for various compounds in condensed phases²⁵. For class P mobile phases, this assumption is less valid because of the increasing importance of specific (non-dispersion) interactions, but even in this case there can be rough cancellation of such effects. In either case, to a first approximation the mobile phase terms nE_{Ms} and E_{Xs} of eqn. 2 cancel, leaving

$$\Delta E \approx E_{Xa} - nE_{Ma} \quad (2a)$$

Eqn. 2a then leads to simple expressions for the dependence of solute k' values on mobile phase composition. The basic equation is¹

$$\log k' = \log (V_a W / V_m) + S^0 - \varepsilon^0 A_s + \Delta_{cas} \quad (3)$$

(i) (ii) (iii) (iv)

Here, k' refers to the capacity factor of the solute in a given LSC system, V_a is the (approximate) volume of the adsorbed monolayer per gram of adsorbent, W is the weight of adsorbent in the column, V_m is the column void volume, S^0 is a parameter which reflects the relative interaction energy of the solute molecule with the adsorbent surface (*i.e.*, E_{Xa}), ε^0 is the solvent strength parameter which reflects the relative interaction energy of mobile phase molecules with the adsorbent surface (*i.e.*, E_{Ma}), A_s is the relative area of the solute molecule when adsorbed (therefore proportional to n), and Δ_{cas} is a second order term which can correct for any imprecision in eqn. 2a, particularly for mobile phases of class P or AB. Eqn. 3 differs from its usual

form in ref. 1, by omitting an adsorbent activity term α . As we will see below, the silica surface is believed to be relatively homogeneous, so that adsorbent surface activity (α) does not vary with experimental conditions in HPLC systems based on wide-pore silica as adsorbent. Therefore, for the present discussion where numerical values of the various parameters are not relevant, we consider α to be included in S^0 , ϵ^0 and Δ_{cas} values (*i.e.*, α constant), which will simplify the following equations.

Considered in another way, terms (i-iv) of eqn. 3 can be defined as: (i) a phase ratio term, (ii) the energy of adsorption of a mole of solute from a non-polar (reference) mobile phase, (iii) the total energy of adsorption of n moles of mobile phase molecules M from the reference mobile phase and (iv) a second order term, due to effects not considered by the S-S model in its simplest form.

Eqn. 3 with Δ_{cas} equal zero has been shown¹ to provide a generally reliable description of experimental data for LSC systems based on pure solvents as mobile phase. Generally, however, binary-solvent mobile phases are used in HPLC separation. If it is further assumed for this case that the adsorption of the more polar mobile phase constituent B (in binaries A-B) follows a Langmuir isotherm (see below) and the molecular areas of solute (A_s) and B-solvent (n_B) are equal, then fairly simple expressions can be derived for the binary-solvent strength ϵ^0 in eqn. 3. A general expression for binary solvents, assuming α equal unity as before is

$$\epsilon_{AB} = \epsilon_A + \{\log[N_B 10^{n_B(\epsilon_B - \epsilon_A)} + 1 - N_B]\}/n_B \quad (4)$$

Eqn. 4 is also found to correlate experimental data well in cases where $n_B \neq A_s$. Here, ϵ_{AB} , ϵ_A and ϵ_B refer to ϵ^0 values for the binary A-B, pure A and pure B, respectively. N_B is the mole fraction of B in the binary solvent mixture, and n_B is the value of A_s for compound B (*i.e.*, its relative molecular area).

A derivation similar to that for eqn. 4 (same assumptions) leads to an equivalent expression for the dependence of k' on mobile phase composition as the mole fraction N_B of a binary solvent is varied²⁶ (for the case $n_B = A_s$):

$$1/k'_{AB} = 1/k'_A + (1/k'_B - 1/k'_A) N_B \quad (4a)$$

Here k'_{AB} is the k' value of a given solute with mobile phase of mole fraction N_B ; k'_A and k'_B refer to solute k' values for pure A or B, respectively, as mobile phase.

For the special case where $\epsilon_B \gg \epsilon_A$ and $N_B \gg 0$, still another relationship can be derived² from eqn. 4:

$$\log k' = \log k'_B - n \log N_B \quad (4b)$$

Here, n is equal to (A_s/n_B) . Eqns. 3-4b allow the prediction of k' as a function of mobile phase composition for a wide range of LSC conditions; their ability to provide accurate predictions of retention, or to precisely fit plots of experimental k' values vs. N_B has been repeatedly verified (*e.g.*, refs. 1-3).

The S-S model also treats the relative solvent strengths (ϵ^0 values) of pure solvents as a function of their molecular structure. The S-S model states that ϵ^0 values should be equal to the adsorption energy of the solvent molecule when the

latter is injected as a sample (S_M^0), divided by the molecular area (n_B) of the solvent molecule:

$$\epsilon^0 = S_M^0/n_B \quad (5)$$

Starting with experimental S^0 values for various pure solvents, eqn. 5 does in fact give a good prediction of solvent ϵ^0 values for a wide range of solvent structures (see Figs. 8–15 in ref. 1). However, the effects of solvent *localization* (see below) must be taken into account in such a calculation, or calculated ϵ^0 values can be seriously in error.

Since the value of S_M^0 (or E_{Ma}) reflects specific intermolecular interactions between the adsorbed solvent molecule and the adsorbent surface, it should also be possible to correlate values of ϵ^0 with these interactions. This is indeed the case, with the so-called partial or specific solubility parameters of Karger *et al.*²⁵ providing a good correlation²⁷. Thus, it is possible to predict accurately pure-solvent ϵ^0 values starting from different viewpoints, or beginning with different physical properties of the solvents of interest.

This foregoing model of retention in LSC systems is in generally good agreement with experimental data, particularly for less polar solute–solvent combinations; *i.e.* in LSC systems with class N solvents as mobile phase. That is, eqns. 3–5 apply with reasonable precision with the Δ_{cas} term taken as zero, and with values of n_B and A_s which are calculable from the molecular dimensions of the appropriate molecules. As the polarity of solute and/or solvent molecules increase, however, and especially for class P solvents as mobile phase, the above simple model of LSC retention becomes significantly more complex. This arises from two experimental effects, which we will discuss in turn: solute–solvent interactions and localization of solute and/or solvent during adsorption.

2.1.1. Solute–solvent interactions. Referring to eqns. 2 and 2a, deviations from the ensuing LSC model are likely to occur when the term $E_{Xs} - nE_{Ms}$ can no longer be neglected. This is the case for more polar mobile phases for various reasons: (i) the terms E_{Xs} and E_{Ms} each increase in absolute magnitude, so that exact cancellation becomes less likely; (ii) the latter terms are now determined to a great extent by polar interactions instead of dispersion forces; as these polar interactions are specific in nature, X and M can show differing behavior, so that values of E_{Xs} and E_{Ms} no longer cancel as the concentration of B in the mobile phase binary A–B is varied; (iii), special adsorbate-orientation effects in the adsorbed phases are possible (*e.g.* Figs. 8–11 in ref. 1).

It must be clear that for polar solvents and solutes a very precise description of LSC retention equilibria will require a rather complicated and detailed model involving many parameters. At the present stage of knowledge concerning bulk-liquid and adsorbed-phase interactions this cannot be expected for *any* model. Nevertheless, semi-quantitative estimates of the effects of such solute–solvent interactions appear possible in practice.

It has been pointed out³ that hydrogen bonding between solute and solvent is most likely to lead to important failures of eqn. 3 (*i.e.*, non-zero values of Δ_{cas}). This situation is more likely to arise with class P solvents (and appropriate solutes), which means that the polar solvent B of an A–B binary mobile phase will largely cover the adsorbent surface, and have a concentration in the adsorbed monolayer

much larger than in the bulk mobile phase. This means that the net effect of solute-solvent hydrogen bonding will be largely determined by interactions in the stationary rather than mobile phase. This has been observed in several LSC systems (ref. 1, pp. 218-225). Consequently it is predicted in most cases that solute retention will increase as hydrogen bonding between sample and solvent molecules becomes stronger.

2.1.2. Localization. For the use of class N solvents as mobile phase, the adsorbent surface can be regarded as effectively homogeneous and continuous, so far as adsorption of the solvent is concerned. That is, there is little preference for adsorption of a solvent molecule on any given part of the surface, nor is there any marked restraint on the positioning of the adsorbing molecule within the monolayer (no configurational requirements). Thus, there is little tendency for weakly retained molecules to localize on a given adsorbent site. This may appear surprising, since the active sites on the silica surface are widely believed to consist of free silanol groups which interact directly with adsorbing molecules. Furthermore, it is known that various silanol types (e.g., "free" vs. "bound" or "reactive" silanols) of differing retention activity are present in different silicas¹. However, there is normally a considerably greater number of silanols available on the surface than there are adsorbed molecules competing for these sites (see section 5.2.2). Furthermore, the silanol group can be oriented to sweep out a considerable area within which optimum adsorbate-adsorbent interactions are possible. Under these conditions, and when the solute and solvent molecules involved are not very polar, every adsorbed molecule can interact effectively with one or more adjacent silanol groups.

With regard to the evidence for other silanol types on the silica surface, several studies (e.g., refs. 28 and 29) suggest that free silanols comprise almost all (>90%) of the available silanols in the case of wide-pore silicas. Deactivation of the silica surface by added water appears to remove selectively the non-free silanols and provide further increase in surface homogeneity for aromatic hydrocarbons as solutes¹. However, for the case of more polar solutes, this water-deactivation process has little effect on surface homogeneity (see Fig. 1 of ref. 30 and related discussion) suggesting that the non-free silanols do not play an important role in the adsorption of most polar compounds on silica. Therefore, this small concentration of non-free silanols does not contribute to surface inhomogeneity so far as the adsorption of polar solutes (and solvents) on silica.

With continuing increase in the polarity of adsorbing solute or mobile phase molecules, localization effects on the silica surface eventually arise. That is, there is an energetic advantage to aligning the most polar functional group in the molecule with a particular silanol group on the surface. Furthermore, the configurational requirements for optimum interaction become more pronounced. Such localization is essentially the result of an adsorption interaction which is sufficiently strong to overcome the normal thermal motion of the molecule within the monolayer. Carried to the extreme, localized adsorption becomes chemisorption.

Localized adsorption is well accepted in classical adsorption theory. Similarly, it is straightforward to describe how the tendency toward localization will vary with the adsorbate polarity or retention strength. Fig. 1a portrays the sites on the silica surface, and the random motion of an adsorbing molecules along the surface. Fig. 1b shows how the energy of adsorption will vary for the molecule in Fig. 1a as a function

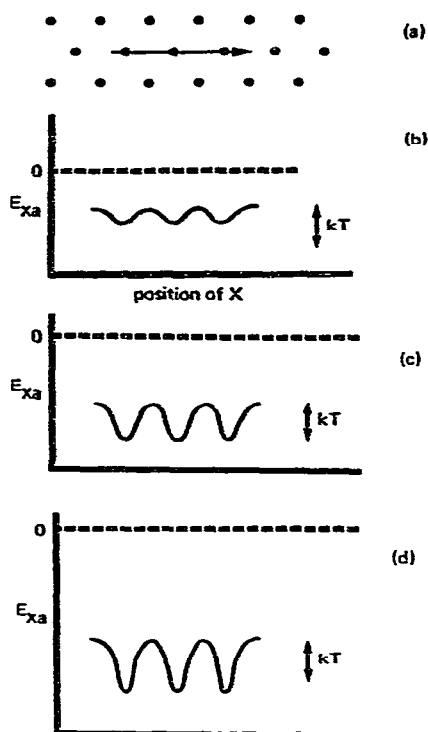


Fig. 1. Energy of adsorption of a molecule X as a function of polarity and position on adsorbent surface. (a) Position of X during movement across surface (—) in relationship to adsorption sites (shown as ●); (b) adsorption energy E_{Xa} vs. position of X from (a); less polar molecule X (delocalized adsorption); (c) same as (b), except moderately polar X; (d) same as (b), except strongly polar X (localized adsorption). (See also Fig. 10.3 in ref. 1 and its related discussion.)

of its position along the surface, for the case of a weakly-polar adsorbing molecule. There will be minor fluctuations in E_{Xa} for the molecule as a function of position, but these are insufficient to result in localization; there is simply not enough energy advantage to "freeze" the molecule at one position. As the polarity of the adsorbate molecule increases, as in Fig. 1c, localization becomes more attractive, because E_{Xa} varies more sharply with position. Nevertheless, even in Fig. 1c the adsorbed molecule has essentially the same E_{Xa} value over modest limits in position. This, combined with the rotational freedom of the silanol group plus the large concentration of such adsorption sites, means that true localization is still unfavorable. For sufficiently polar compounds, as in Fig. 1d, the situation shifts to favor localization. For combinations of solvent and solute molecules falling in this category, a number of interesting adsorption effects can be anticipated (for a fuller discussion of the effects of Fig. 1, see ref. 1, Ch. 10). We will pursue these as we proceed, but for other examples of localization, see ref. 1, Ch. 8, 10 and 11, and ref. 31. As discussed in the latter, a wide range of experimental "anomalies" can be understood quantitatively in terms of solute or solvent localization. Furthermore, this understanding has led to a number of semi-empirical modifications of eqn. 3 which allow accurate predictions of retention even when localization effects are important (ref. 1, pp. 202–205, 272–282 315–320, 324–329; also, ref. 31).

In the following discussion of the S-K model, the relative localization of the B-solvent is of major interest. It has been suggested previously³⁰ that strong solvents such as ethyl ether and ethyl acetate (class P solvents) are localized on silica, leading to an atypical dependence of k' values on % (v/v) B in the mobile phase mixture. Similarly, weaker solvents such as benzene and methylene chloride (class N) exhibit typical behaviour and were assumed^{1,30} to be non-localized. As we will see in a later section, localization of the B-solvent will play a marked role in affecting isotherm shape, such that the resulting isotherms for that B-solvent should differ markedly between class N and P solvents. Localization of polar solute molecules on silica also occurs.

These solvent and solute localization phenomena can be empirically handled in the S-S model simply by assigning larger values of A_s (eqn. 3) and n_B (eqn. 4) than are calculated from the dimensions of the solute and solvent molecules involved. The values of these empirically adjusted A_s and n_B values can be correlated with

TABLE 2
NOVEL FEATURES OF THE SCOTT-KUCERA MODEL OF LSC RETENTION*

<i>Postulate</i>	<i>Ref.</i>
1. A solvent interaction model (SIM) can be derived which is able to predict solute-solvent interactions in binary-solvent solutions. This in turn allows retention predictions in such systems, for both LSC and ion-exchange chromatography.	7, 8
2. Solute and solvent polarizability determine solvent-solute polar interactions and the retention of polar solutes in LSC; solvent density similarly determines dispersion interactions and retention of non-polar solutes in LSC.	7, 8
3. Dispersion interactions between adsorbed molecules and the silica surface are negligible or altogether absent.	7
4. The sorption (as opposed to competition) model of retention in LSC applies to almost all class P solvent systems. Solutes that are less polar than the B-solvent are not retained in the monolayer that is adjacent to the adsorbent surface; such solutes are sorbed onto the primary solvent monolayer, and may or may not displace adsorbed solvent molecules upon retention.	10, 11
5. Monolayer (and bilayer) adsorption of the B-solvent from binary mixtures of class P solvents (B) in a class N solvent (A) can be described by the simple Langmuir isotherm separately applied to each layer.	10, 11
6. The shape of the B-solvent isotherm for adsorbed B <i>versus</i> concentration of B in solution demonstrates bilayer adsorption for all class P solvents.	10, 11
7. The bilayer hypothesis is further confirmed by the finding that all solvents so far studied yield a constant number of adsorbed molecules in the first monolayer, when that monolayer is completed.	11
8. The infrared band at 3750 cm^{-1} in heated silicas is due to chemically bound water, not free silanol groups as believed earlier.	11
9. Silicas require heating to temperatures of 600°C or above before the surface becomes uniform; such silicas are ideal for LSC separation.	6
10. Referring to the S-S model (based on thermodynamic and extrathermodynamic postulates): "... the thermodynamic approach has severe limitations from the practical point of view... if there is more than one effect present, the individual interactions cannot easily be separated or identified..... there is a very limited amount of thermodynamic data available... such data are difficult... to obtain".	7

* Our conclusions with respect to each postulate are listed within the text (beginning section 3), in italics.

solute and solvent polarity, allowing their accurate estimation in given cases. For a detailed discussion, see ref. 1, Ch. 8.

2.2. The Scott-Kucera model

The S-K model comprises some features put forth by earlier workers, in combination with several distinct points of departure from previous theory. We will concentrate mainly on the novel proposals of this model, some of which are enumerated in Table 2 and specifically discussed later on (with conclusions in the text italicized). Most of the discussion and data in publications by Scott and Kucera relate to the use of binary-solvent systems. In this connection, considerable stress is placed on the coverage of the adsorbent surface by the stronger solvent component B (in the binary A-B) as the mobile phase concentration of B varies from 0 to 100%. Initially it was claimed that a monolayer of B is formed within the first few percent addition of B to the binary. Following completion of this monolayer, adsorbing solute molecules interact with the monolayer of B, rather than directly with the adsorbent surface; this retention mechanism is referred to as "sorption". As a consequence, there is then no displacement of adsorbed solvent molecules B upon retention of the solute within the stationary phase, and solution interactions between molecules of mobile phase and solute largely determine solute retention. As the concentration of B in the mobile phase increases, the mobile phase becomes more polar, the strength of solvent-solute interactions increases, and solute k' values decrease. In terms of eqn. 2 this model therefore states that E_{X_s} determines the dependence of k' on solvent composition; E_{X_a} is assumed to be constant (as in the basic S-S model), and E_{M_s} and E_{M_a} do not influence ΔE because displacement is assumed not to occur ($n = 0$).

It was also postulated in this first paper⁴ that solvent-solute dispersion interactions play an important role in retention, with solvent dispersion forces being proportional to solvent molecular weight. This latter hypothesis was criticized⁵ on the grounds of its incompatibility with well-established theory, and a later paper⁷ gave a modified description of dispersion interactions in LSC. It was conceded that such interactions are less important and the solvent dispersion forces were now claimed to be proportional to solvent density. The validity of the latter generalization was demonstrated by using weak solvents A from a series of homologous alkanes, and noting that the effects attributed to dispersion increased with increasing alkane density.

The next major thrust in the development of the S-K model^{7,8} was the derivation of an equation to predict the dependence of solute k' values on the concentration c_p of the strong solvent B in the mobile phase binary:

$$1/k' = A' + B'c_p \quad (6)$$

Here, A' and B' are constants for a particular solute and polar solvent B. In the derivation of eqn. 6, it was assumed that both polar and non-polar interactions of the solute in the stationary phase remain constant, as c_p varies (because the composition of the stationary phase is constant for c_p greater than a few percent)*. Section 3 examines this derivation in greater detail.

* An earlier derivation of eqn. 6 in ref. 7 was made on the basis of different assumptions. There it was assumed that these solute interactions in the stationary phase are exclusively polar (negligible non-polar interactions).

Eqn. 6 was compared with experimental data for several LSC systems, and it was noted that it provides a reasonable fit over a wide range in c_p values, particularly when the concentration of B exceeds 2–5% (v/v). The agreement between experiment and eqn. 6 was advanced as proof of the validity of both eqn. 6 and the S–K model. We note in passing that eqn. 6 is identical in form to eqn. 4a from the S–S model, so that experimental data of this type cannot be used to differentiate the two models.

The development of eqn. 6 was accompanied by a discussion of the physical basis of solvent strength and solute retention affinity^{7,8}. The coefficient B' of eqn. 6 can be used to measure either of these two solute–solvent properties, and it was claimed that B' is directly correlated with solvent or solute polarizability, which is in turn a function of dielectric constant. Experimental plots of B' versus polarizability gave linear correlation plots for a limited number of LSC systems. However, an empirical adjustment in polarizability values was required for the solvent plots, and the solute plots show considerable scatter^{7,8}. These deviations were rationalized in terms of special adsorption effects. In summary, solvent strength was claimed to be determined by solvent dielectric constant, a generalization which is not new (*e.g.* review of ref. 32).

In the two most recent papers^{10,11} of the S–K series, the “sorption” model is stated to hold only for mobile phases of class P, and solutes with polarities or retention affinity less than that of the polar solvent component B. On the basis of refs. 10–12 the following details of the model under these circumstances can be deduced. Solvents of class P are referred to as “hydrogen-bonding” solvents, which includes esters, ketones and ethers but not chloroform. The monolayer of the B-solvent, once formed, then acts as a “hydrogen-bonded phase”. Solute molecules are retained by interaction with this phase, presumably by hydrogen bonding. With the completion of monolayer formation by adsorbed B (\approx concentrations of B equal 1–3%, v/v), a second adsorbed layer (“second” layer as opposed to “first” monolayer) begins to form (bilayer formation). Depending upon the extent of formation of the second layer, solute molecules may or may not displace a solvent molecule from the second layer. However, once the first monolayer is formed, solute molecules do not displace solvent molecules

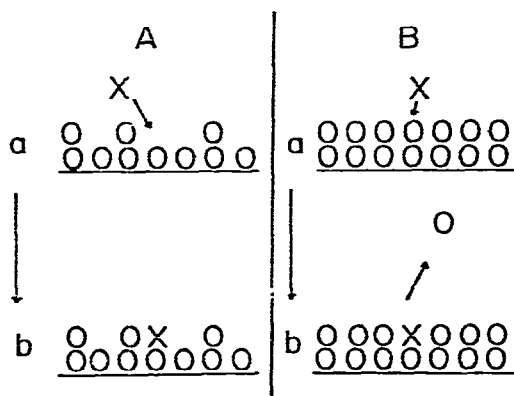


Fig. 2. The sorption process, from Scott and Kucera¹¹. —, silica surface; O, class P solvent molecules forming first or second adsorbed layers; X, less polar solute molecules; class N solvent molecules not shown. A, incomplete bilayer with non-displacement; B, complete bilayer with displacement.

from this layer unless the solute molecule is more polar than the solvent. Details of this process for less polar solute molecules X are illustrated in Fig. 2.

The hypothesis that solute molecules can be retained in LSC without displacement of adsorbed solvent molecules was tested by both equilibrium and chromatographic means¹⁰. It was found that solutes with k' values less than about 20 do not displace a full equivalent of the B-solvent, thus apparently confirming the concept of retention of solute — under certain conditions— in the second adsorbed solvent layer.

Bilayer adsorption of the B-solvent in the case of class P solvents was tested in terms of isotherm measurements on both class N and P solvent systems¹¹. It was found that a Langmuir isotherm accurately fits the uptake by adsorbent of the B-solvent in the case of class N solvents (e.g., chloroform), but not in the case of class P solvents (e.g., ethyl acetate). For the latter, a model based on bilayer adsorption (with Langmuir adsorption in each layer) was more successful. Further, extrapolation of the monolayer uptake for both class N and P solvents gave a constant number of molecules in the monolayer for all solvents studied. Since extrapolation of the second-layer adsorption gave a similar number of adsorbed molecules as in the adsorbed monolayer, this was taken as final proof of bilayer coverage in the case of class P solvents.

2.3. Scope of Snyder–Soczewinski versus Scott–Kucera models

Apart from basic differences in the physical models assumed by these two treatments of LSC retention, the S–S and S–K approaches differ further in other respects:

- (1) the range of LSC systems for which they are claimed to be applicable;
- (2) the level of detail provided on the relative retention of different compounds as separation conditions are varied;
- (3) the extent to which the models have been tested for different solutes and mobile-phase solvents.

With regard to the different kinds of LSC systems that can be treated by the S–S and S–K models, the latter is presently claimed to apply to a single case: silica as adsorbent and class P solvents as mobile phase. The S–S treatment, on the other hand, has been shown useful for a wider range of situations¹: class N and P mobile phases, several adsorbents (silica, alumina, Florisil, magnesia), bonded-phase materials with amino and cyano functionality^{16,17}, and even gas–solid chromatography¹³. Concerning the extent to which detailed predictions of relative retention can be made in LSC separations, the S–K model has been largely restricted to the prediction of retention as the concentration of polar solvent in heptane solutions is varied. However, it is known that relative retention (and separation) in LSC can be greatly altered as experimental conditions are further changed. The S–S model has resulted in general rules^{1,3,31} for (1) the effect of different polar solvents on separation selectivity or α values, (2) the separability of isomers under differing conditions, (3) the differing separations provided by different adsorbents and (4) the effect of temperature on separation.

Finally, the S–K model has been tested against a relatively small number of solute–solvent combinations: about a half dozen individual B-solvents, and a like number of solutes. The S–S model has been verified for a much larger number of solute–solvent–adsorbent combinations (e.g. refs. 1, 3 and 35).

3. SOLVENT-SOLUTE INTERACTIONS: THE SCOTT-KUCERA SOLUTION INTERACTION MODEL

The solution interaction model (SIM) as derived by Scott and Kucera plays an important role in their overall description of retention in LSC systems. Changes in solute retention when varying the percentage of the more polar solvent are attributed solely to changes in solvent-solute interactions in the mobile phase, and on this basis a final expression (eqn. 6) is derived for the dependence of k' values on the concentration (c_p) of the solvent B. Originally^{7,8} the SIM was used to correlate retention behavior for both class N and P solvents as mobile phase, although later¹⁰⁻¹² the competition model was accepted for class N solvents. The latter would suggest that the SIM is therefore meant to be restricted to class P solvent systems, although this point has not been clarified. Because the SIM deals with interactions in the mobile phase alone, it was further suggested^{7,8} that this model (SIM) should apply to both ion-exchange and gas chromatographic (GC) systems. Retention data are cited by the authors which purport to show the validity of eqn. 6 in ion-exchange and GC, and this is taken as further evidence of the correctness of the SIM. Since we are mainly concerned with what is going on in class P solvent systems in LSC, the following discussions will center on this area. At the end of this section we will return to the questions of class N solvents in LSC and retention in these other chromatographic systems (GC and ion-exchange chromatography).

The derivation of the SIM^{7,8} postulates that the "total force" exerted on a solute in a given phase (mobile or stationary) is the sum of individual "forces", the latter being broken down into "dispersive", "polar" or "ionic". Each of these individual forces is in turn supposed to be proportional to the amount of material associated with this force and present in the given phase. Thus, for the mobile phase, dispersion forces are held to be proportional to the density of the solvent, polar forces are proportional to the concentration of polar solvent B in solvent binaries A-B, and ionic forces are proportional to the concentration of ions of opposed charge.

A precise and straightforward discussion of the various relationships leading to the SIM is difficult, because no precise physical meaning or definition has been given to these "forces". However, the form of eqn. 6 combined with the assumptions of the SIM suggests that (see ref. 38 for details)

$$1/\gamma_{Xs} \bar{v}_s = A' + B'c_p \quad (7)$$

Here, γ_{Xs} is the activity coefficient of solute X in the mobile phase S, and \bar{v}_s is the (average) molar volume of phase S. The remaining terms of eqn. 7 are the same as in eqn. 6. This relationship (eqn. 7) is purportedly valid for solutes X dissolved in alkane-polar-moderator mixtures, as well as any other mixture (e.g., aqueous salt solutions in ion exchange). Eqn. 7 follows directly if molecules of solvent and solute form separate equilibrium complexes of a certain "force" type (e.g., X-A dispersion, X-B dispersion, X-B polar, etc.), with constant equilibrium constants for each of these interactions or complexes.

Several objections can be immediately raised to this simplified theory of solution thermodynamics. Thus present theory based on the pioneering work of London and Debye teaches that these interactions occur simultaneously, and do not normally

involve 1:1 complexes. Also, simple complex formation as an explanation for all solution activity coefficients has not been demonstrated in practice. More specifically we can focus on a number of shortcomings of eqn. 7 and the SIM. First, it can be noted that eqn. 7 is thermodynamically inconsistent, if it is applied to the two (or more) constituents of a phase system*. The resulting dependence of the γ_{x_s} values on the composition does not fulfill the Gibbs–Duhem equation:

$$N_1 \ln \gamma_1 + N_2 \ln \gamma_2 + \dots = 0 \quad (7a)$$

Here, N_i is the mole fraction of a component i in the system, and γ_i is its activity coefficient in the same system.

Eqn. 7a allows the verification of the so-called thermodynamic consistency³⁶ of a proposed dependence of the activity coefficients γ_i on the composition parameters N_i . That is, if the “forces” equation possesses universal validity as claimed, it must apply also to the activity coefficients γ_A and γ_B of the mobile phase constituents themselves. However, there is no possibility of γ_A and γ_B obeying eqn. 7 while not violating eqn. 7a. Stated in another way, if we suppose γ_A to obey eqn. 7, eqn. 7a allows us to calculate the dependence of γ_B on the composition. Resulting values for γ_B do not obey eqn. 7. Thus, in a binary solvent, thermodynamics predicts that at least one solvent component will not follow eqn. 7 (see Appendix II for details). The fact that eqn. 7 violates a fundamental requirement of thermodynamics raises doubt concerning its ability to accurately describe the broad range of systems encompassed by the SIM.

A direct example of the invalidity of eqn. 7 in LSC systems based on class P solvents is provided by data of Slaats *et al.*³⁸ for the solutes studied by Scott and Kucera in the solvent systems ethyl acetate–heptane and 2-propanol–heptane. Slaats *et al.* measured the actual solute activity coefficients γ_{x_s} and plotted the quantity $1/\gamma_{x_s} \bar{v}_s$ of eqn. 7 versus the concentration of the B-solvent. The resulting plots, which are predicted to be linear by eqn. 7, are reproduced in Fig. 3a (B equal ethyl acetate) and Fig. 3b (B equal isopropanol). These plots show obvious curvature over the range 0–40% (v/v) of B, thus invalidating eqn. 7.

Another objection to the SIM model is the premise that the effect of polar “forces” can be represented by a single property of solvent and solute: polarizability. One-factor descriptions of the polar component of distribution constants or activity coefficients have been shown by numerous studies to be inaccurate. This arises from the well known fact (*e.g.*, ref 37) that dipole interactions and hydrogen bonding each contribute to solvent–solute interaction, so that the dipole moment, proton-donor strength, and proton-acceptor strength of solute molecules will each play a role in determining γ_{x_s} . As experimental examples of the failure of single-factor polarity models we can cite: (1) the Rohrschneider and McReynolds schemes for correlating solvent polarity in GC^{39,40}, where five or more parameters are required to describe accurately the combined effects of dispersion and polar interactions; (2) the similar study of Rohrschneider⁴¹ for various solvents used as mobile phases in liquid chromatography, where the polar interactions require three terms for even an approximate prediction of solvent–solute interactions²³; (3) many previous studies of solvent–solute

* According to the derivation of Scott and Kucera, there is no reason not to treat the solvent components A and B in the same fashion as the solute X.

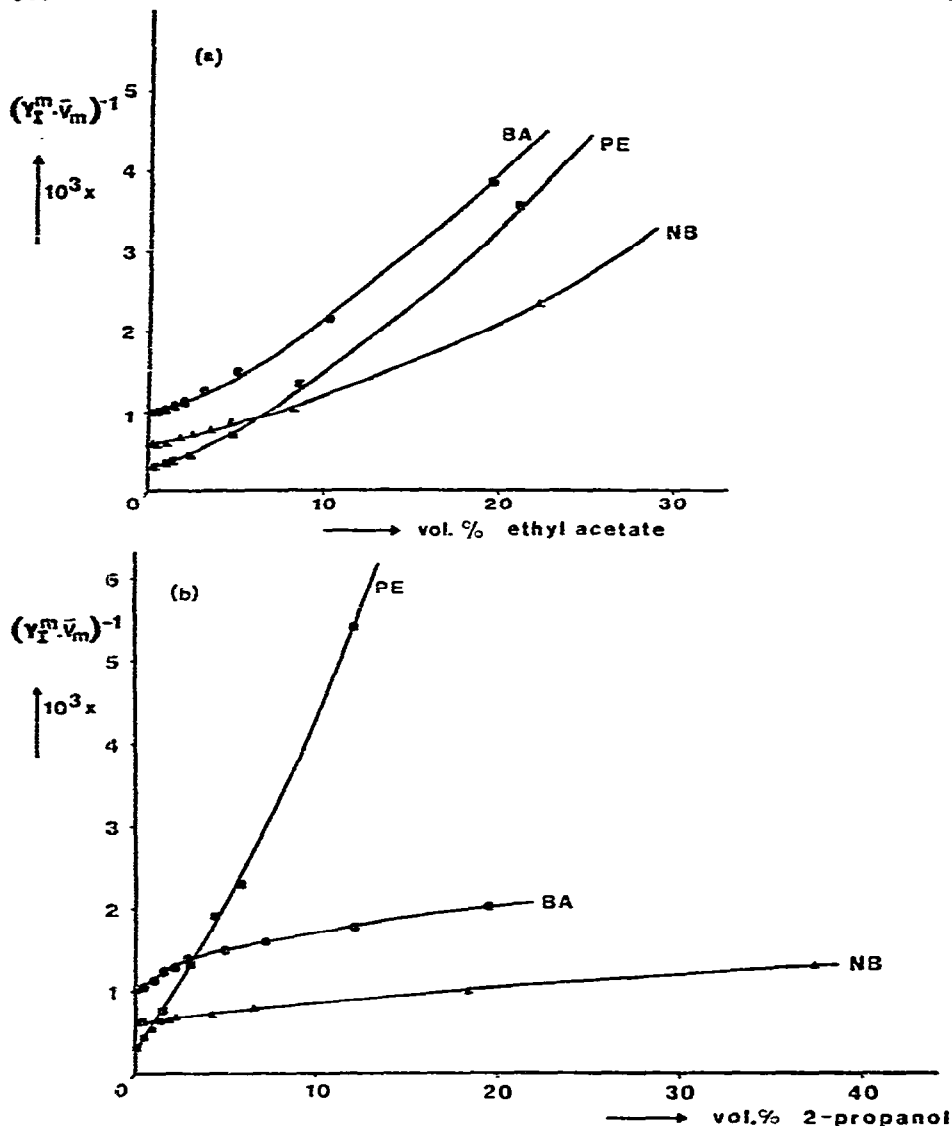


Fig. 3. Experimental activity coefficient data (from ref. 38). Systems described by Scott and Kucera in refs. 10 and 11; test of validity of eqn. 7. (a) Data for heptane-ethyl acetate binaries; (b) data for heptane-isopropanol binaries. BA = benzyl acetate; PE = phenyl ethanol; NB = nitrobenzene.

interactions in terms of multi-factor solubility parameters (see ref. 27 for a review and current evaluation); (4) in the LSC systems studied by Scott and Kucera, Slaats *et al.*³⁸ have shown that the solute activity coefficients indicate one order of relative polarity for 2-propanol as B-solvent (phenylethanol more polar than benzyl acetate) and another for ethyl acetate as B-solvent (phenylethanol equal in polarity to benzyl acetate); see Fig. 3. It should be noted for the latter cases^{23,27,37-41} that bulk solutions are involved in all cases, with none of the uncertainty in LSC associated with the (possibly changing) solute-solvent interactions in the adsorbed phase (with change in c_p).

While past work has shown that the polar component of solvent-solute inter-

actions requires more than one parameter to characterize its effects, there is general agreement that the dispersion component of such interactions can be described in simpler terms. Elementary theory (plus some reasonable approximations) and experiment suggest that the tendency of a solute or solvent molecule to interact by dispersion interactions can be related to its refractive index rather accurately³⁷. The S-K model, on the other hand, holds that these interactions are proportional to solvent density. Substantiation⁸ is based on the observation that in LSC (for certain solutes) the strength and density of *n*-alkane mobile phases each increase in going from *n*-pentane to *n*-decane. It might be pointed out that refractive index (and many other physical properties of hydrocarbons) likewise changes in regular fashion in this sequence. However, a better test of density *versus* refractive index in this respect is provided by the example of perfluoroalkanes as solvents. The latter have lower refractive indices and higher densities than the alkanes, and thus serve to distinguish these two hypotheses. In fact, the perfluoroalkanes are observed⁴² to be much weaker solvents in LSC than the alkanes, as predicted on the basis of their lower refractive index values. Thus, refractive index, not density, is a better predictor of these dispersion interactions.

Finally, there is no legitimate reason to restrict the use of the SIM model to class P solvent systems, since the same arguments should hold for its extension to moderately polar class N solvents. However, Scott and Kucera^{10,11} have argued that the Langmuir isotherm accurately describes the equilibrium between class N solvent pairs such as heptane and chloroform and the silica surface in an LSC system. One of the requirements for the applicability of the Langmuir isotherm (see section 5.1) is that solution interactions between molecules of solute and solvent (or two solvent molecules, in the present example) are either absent or cancel by virtue of their similarity (*i.e.*, $E_{xs} = nE_{Ms}$). Thus, there is a basic contradiction in the S-K conclusions concerning this situation; *i.e.*, the authors do not admit the possibility of cancellation of solution and adsorbed-phase interactions in LSC systems (rather they argue that solution interactions *determine* retention; the essence of the SIM model), yet at the same time they implicitly require such cancellation in the adsorption of chloroform from mixtures of heptane-chloroform (which is found to obey the Langmuir isotherm). A more reasonable explanation of the heptane-chloroform isotherm data is that the solution polar interactions are relatively minor and are largely cancelled by corresponding interactions of the mobile phase with the exposed monolayer of adsorbed chloroform.

Consider also the extension of the SIM to ion-exchange chromatography and GC^{7,8}. In the case of ion exchange, it has been long accepted that this is the classic and unequivocal example of a displacement process. The requirement for overall electrical neutrality in any chemical system requires that an ion exchanger hold an equivalent number of sample ions or counter-ions from the mobile phase. Retention of a sample ion then occurs via displacement of a previously held counter-ion. The primary effect of any change in counter-ion concentration in the mobile phase is to change retention via a simple mass-action effect, as described in any fundamental treatment of ion exchange (*e.g.*, ref. 43). According to the SIM treatment, on the other hand, this change in sample retention in ion-exchange systems is due instead to changing solvent-solute interactions in the mobile phase. Not only is this at odds with the basic concept of ion *exchange* in such systems, it completely ignores the classical

treatments beginning with Debye on the variation of ion activity coefficients in solution as ionic strength is varied.

In the case of GC it has been argued^{7,8} that eqn. 6 describes the dependence of experimental k' values in binary-solvent stationary phase systems, and from this they deduce another verification of their SIM treatment. If eqn. 6 holds in such systems, then the k' value of a solute in a given GC system with the binary-solvent stationary phase (A-B) should be

$$k' = k'_A \phi_A + k'_B \phi_B \quad (8)$$

Here, k'_A and k'_B are k' values for the same solute with pure solvents A and B as stationary phases, respectively. The quantities ϕ_A and ϕ_B refer to the volume fractions of A and B in the stationary phase A-B. Eqn. 8 is claimed by Purnell and co-workers⁴⁴⁻⁴⁶ to be broadly applicable for mixed stationary phase systems in GC.

There are several problems in extrapolating the findings of Purnell *et al.* to LSC systems. First, the assumptions made in the derivation of the SIM treatment (eqn. 6) and the Purnell equation (eqn. 8) are completely different. Purnell *et al.* assume "local immiscibility" or an actual demixing of binary solvent mixture into microscopic regions of pure A and pure B. Scott and Kucera, on the other hand, consider the different physical interactions (dispersive and polar) in the random mixture as mathematically separable, rather than the actual components of the binary mixture. Furthermore (see Appendix III), there is reason to doubt the generality and accuracy of eqn. 8 as applied to various GC systems. Finally, the extrapolation of eqn. 8 from typical GC systems to the low-molecular-weight solvent mixtures of class P (e.g., heptane-ethyl acetate) seems even more tenuous. Thus on both theoretical and experimental grounds, eqn. 8 does not provide significant support for the SIM treatment. A more detailed discussion of these latter points with respect to eqn. 8 is provided in Appendices II and III.

It is also interesting to note that eqn. 6 is claimed to be valid for virtually every type of chromatographic system except reversed-phase liquid chromatography (RP-LC). This omission is odd, since one might assume that the aqueous solutions used in ion exchange and the organic solvents used in LSC would bracket the mixed aqueous-organic solvents used in RP-LC. Furthermore, a much better case can be made for emphasizing interactions in the mobile phase, since these must be quite strong *versus* interactions among solvent and solute molecules in the stationary phase. In this connection it is well known that retention data in RP-LC follow a relationship different from eqn. 6, namely^{33,34}:

$$\log k' = A' + B' \phi_B \quad (8a)$$

where ϕ_B is the volume fraction of B in the binary mixture A-B, and A' and B' are constants.

Finally, we note in passing the claim⁷ that "...dispersive forces on silica gel, if present at all, do not have a significant effect on solute retention...". This argument was essential to the original derivation of eqn. 6 in ref. 7, but was dropped in a similar re-derivation in ref. 8. In ref. 8 it was argued that the composition of the stationary phase remains constant as the composition of the mobile phase changes (for a given

A-B binary), which removes the original necessity of assumptions concerning the relative importance of dispersion interactions with the silica surface. We are, therefore, uncertain as to whether the unimportance of these dispersion interactions is still maintained by the authors. In fact, it is quite clear that dispersion forces normally play a major role in determining the total energy of adsorption on silica and other adsorbents, as would be predicted by theory. We do not disagree with ref. 7 concerning the *net* effect of dispersion forces on LSC retention; this is in all probability small. However, the *presence* of these forces (as in any condensed phase) cannot be put into question, as may have been done in the above quotation. For a further discussion of this area, see ref. 27 and especially Fig. 3 (plus related text) of that reference.

Conclusion 1. The SIM does not provide an adequate description of the effects of solvent-solute interactions on solution activity coefficients or solute retention in LSC or ion-exchange systems. The apparent applicability of eqn. 6 in experimental LSC systems can be explained by assuming a displacement mechanism and approximate cancellation of solute-solvent interactions in mobile vs. stationary phases.*

Conclusion 2. The postulate that solute and solvent polarizability quantitatively predict polar interactions in solution is questionable. At best, a single-parameter description of such tendencies of a molecule toward polar interaction is only a rough approximation based on averaging the (at least) three parameters known to be involved in such interactions. Similarly, the postulate that dispersion interactions are proportional to solute and solvent density is not true. Refractive index is a much better parameter for correlating dispersion interactions or their effects.

Conclusion 3. The inference that dispersion interactions between the silica surface and adsorbing molecules are negligible or altogether absent is misleading. These interactions contribute very substantially to the total interaction energy between adsorbing molecules and the silica surface. However, their effect on LSC retention is largely cancelled, because the dispersive interactions of various organic molecules (i.e., solutes and solvents) with the silica surface are similar on a per-unit-volume basis, and because solute-solvent and solvent-solvent dispersive interactions in the mobile phase are also similar. In gas-solid chromatography, on the other hand, these same dispersion interactions play a primary role in determining solute retention (e.g., ref. 13). Here, there can be no cancellation of silica-solute interactions by corresponding interactions of displaced solvent molecules with the silica surface, because there are no mobile phase molecules to displace in a GC system.

4. DISPLACEMENT VERSUS SORPTION

The retention of a solute molecule by the stationary phase of an LSC system might in principle occur in any of several ways:

- (1) adsorption onto the adsorbent surface, so that the retained solute molecule forms part of the first monolayer (displacement model);
- (2) adsorption onto an adsorbed-solvent monolayer, so that the solute molecule forms part of the second monolayer of a bilayer solvent stationary phase; this mechanism is referred to as "sorption" by Scott and Kucera;

* These conclusions are keyed to the postulates of Table 2.

(3) partitioning into a multi-layer solvent phase held at the adsorbent surface or within fine pores of the adsorbent by capillary condensation.

It has been argued^{10,11} that case 2 above generally describes the retention of solutes in LSC systems with class P solvents as mobile phase. The latter retention mechanism is further defined in Fig. 2 (from ref. 11), for the retention of a solute molecule X. Solvent molecules (solvent B only) in the retained phase are shown as circles. In Fig. 2A, for 1–3% (v/v) B in the mobile phase, the first solvent monolayer is complete, and the second monolayer is partially formed. Retention of the solute molecule X in Fig. 2A-b occurs by adsorption onto the first monolayer, without displacement of a B-solvent molecule from the surface. In Fig. 2B, for 10–20% (v/v) B in the mobile phase, both the first and second solvent monolayers are complete, and retention of the solute molecule X in Fig. 2B-b occurs with displacement of a B-solvent molecule from the second layer. However, if the polarity (and retention strength) of solvent and solute molecules are similar, the retention mechanism with solvent of class P reverts to adsorption with displacement from the first solvent-monolayer. In this section we will first examine the physical conditions necessary for sorption to occur, which in turn defines when sorption is *possible* in an LSC system. We will then examine data from ref. 10 which purport to show sorption in certain LSC systems, and we will consider an alternative explanation. Finally, we will examine the two models (displacement vs. sorption) for solute retention in class P solvent systems in terms of certain physical-chemical considerations, which argues against the likelihood of sorption in such systems. A later section provides a separate discussion of the probability of bilayer solvent adsorption, which is crucial to the sorption model *ab initio*. That discussion casts further doubt on the sorption mechanism, by bringing into question the assumption of bilayer adsorption in class P solvent systems.

4.1. Experimental requirements for sorption

The S-K model^{10,11} for sorption as in Fig. 2 assumes that solute molecules can only compete for a place in the first monolayer when their polarity is roughly equal to or greater than that of the solvent component B. This assumption immediately provokes the question why solutes of lesser polarity, but with measurable retention, cannot compete with solvent B molecules for a place in the first monolayer: if solute polarity is great enough for displacing B molecules from the second layer to any measurable extent, it is not clear how this polarity at the same time can be small enough to avoid replacement of at least some B from the first layer. In a private communication¹² it was put forward that slow desorption kinetics may prevent any significant exchange of solute for solvent in the first layer. We note in passing that such an assumption would require that in the chromatography of mobile phase disturbances (e.g., injection of 0.3% ethyl acetate in a 0.2% ethyl acetate mobile phase) anomalous peak-shape effects should occur, and these effects have not been observed in experiments by one of us (H.P.), nor, reported in the previous literature.

Nevertheless, accepting for the moment the proposal that a first layer can be distinguished, which does not take part in the retention process of less polar solutes, we can examine the consequences of this picture for practical LSC. Scott and Kucera measure relative solute polarity in terms of solute k' value in a particular LSC system^{10,11}, which seems a reasonable criterion. To quantitate the relative polarities of solute and solvent molecules in terms of k' , it is necessary to calculate the k' value of

the polar solvent component B in the mobile phase. This is easily done in terms of the definition of k' :

$$k' = \frac{\text{(amount B in stationary phase)}}{\text{(amount B in mobile phase)}}$$

For mobile phase concentrations of B larger than 0.3% (v/v), the equilibrium concentration of B in the stationary phase^{9,10} is 0.08–0.14 g/g in the case of B equal ethyl acetate, or an average value of 0.13 g/g. Similar values of the uptake of B by the adsorbent are found for other class P solvents (Table 3). The volume of mobile phase within the column of silica was found to be 1.5 ml/g of silica for a similar Partisil 20 (ref. 6). If the volume fraction of B in the mobile phase is \emptyset_B , the total quantity of B in the mobile phase per gram of silica is $1.5\emptyset_B$, and k' for B in the system (k'_B) is then

$$\begin{aligned} k'_B &= 0.13/1.5\emptyset_B \\ &= 0.09/\emptyset_B \end{aligned} \quad (9)$$

We can now compare the reasonableness of eqn. 9 in terms of data from ref. 10. There it was found with 0.35% (w/v) ethyl acetate–heptane that displacement of B from the stationary phase was not observed with solutes having $k' \leq 10.5$, but displacement was observed for $k' = 27$. The value of k'_B for this system (from eqn. 9) is 26, which is in good agreement with the onset of displacement at $k' = 27$. Similarly, with 13% (w/v) ethyl acetate as mobile phase, displacement was observed for solutes with k' greater than 4.3.* The value of k'_B for the latter system (eqn. 9) is 0.7, so that the data of ref. 10 are in agreement with eqn. 9.

To summarize, the data of ref. 10 are consistent with displacement of solvent from the primary monolayer by solutes of similar or greater polarity, and relative polarity can be measured by the k' value of the solvent or solute molecule. Eqn. 9 serves for estimating k' for the solvent. This is not to say that the data of ref. 10 prove the existence of sorption in cases where $k' < k'_B$. Let us pursue the significance of eqn. 9 further. For different values of \emptyset_B , at what solute k' value will displacement begin to compete with sorption as the primary retention mechanism? We can calculate

* It is actually argued in ref. 10 that displacement of B from the primary monolayer does *not* occur in the above example of 13% (w/w) ethyl acetate for $4.6 < k' < 9.5$ solutes. This is apparently at odds with the conclusion that displacement should take place, since $k' > k'_B$. However, Scott and Kucera observe that the solutes in question do displace ethyl acetate, but only half as much ethyl acetate is set free upon their injection onto the column, as for the case of injection of an equivalent volume of the much more strongly retained methanol as solute. Arguing that methanol displaces ethyl acetate from the primary layer, the authors then conclude that the solutes in question ($4.6 < k' < 9.5$) are retained by sorption rather than displacement (see Fig. 2b). There are several problems with this explanation, however. First, there is no reason to assume that displacement of solvent from the first layer requires simultaneous displacement of solvent from the second layer. If sorption of ethyl acetate onto an ethyl acetate surface is possible why not sorption of ethyl acetate onto a methanol surface. Second, the molar volume of methanol is less than half that of the other solutes. Thus if the polar functional group of these various solutes (including methanol) is localized onto a silanol group in the monolayer, then one *molecule* of solute will displace one molecule of ethyl acetate. In this case, lesser volumes of ethyl acetate will be displaced by unit volumes of the larger solute molecules *versus* the smaller methanol molecule (see also discussions of refs. 2 and 11).

TABLE 3

SATURATION UPTAKE OF DIFFERENT B-SOLVENTS ON SILICA. COMPARISON WITH VALUES CALCULATED FOR MONOLAYER ADSORPTION

<i>B-solvent</i>	<i>Saturation uptake (g/g)</i>				
	<i>Calculated for monolayer*</i>	<i>Experimental data of refs.</i>			
		<i>10 and 11</i>	<i>47</i>	<i>38</i>	<i>68</i>
Benzene	0.12	0.08			
Chloroform	0.17	0.12			
1-Chlorobutane	0.12-0.16**	0.10			
Ethyl acetate	0.13-0.14**	0.15		0.12	0.12
Tetrahydrofuran	0.13	0.11			
2-Propanol	0.11	0.12		0.12	0.12-0.16
1-Butanol	0.11-0.16**		0.07		
Toluene	0.12				0.14

* Based on 0.00035 ml/m² (as in ref. 1).

** Larger value assumes partial desorption of alkyl group (as in ref. 1).

values of k'_B as a function of \varnothing_B (eqn. 9, assuming total adsorbent uptake of B is constant):

\varnothing_B	k'_B
0.01	9
0.05	1.8
0.10	0.9

Values of k' are optimally held in the range of 2-5 for maximum resolution and minimum separation time, and this accords with usual laboratory practice. This implies that sorption (as opposed to displacement) will be restricted to class P solvents when the concentration of B is less than 5% (v/v). Thus sorption, if it occurs at all, is at best restricted to a small range of solvent concentrations for class P solvents alone.

4.2. Further analysis of the sorption model

The formation of the second layer in the S-K model (for class P solvents and less polar solutes) is assumed to be much less favorable energetically than for the primary monolayer. In the case of ethyl acetate as B-solvent, the isotherm studies of ref. 10 suggest that the equilibrium constant for formation of the monolayer is 100 times larger than for formation of the second layer. Presumably, a similar disparity in relative retention within the two monolayers exists for solutes of similar polarity. That is, a solute of polarity equal to that of ethyl acetate would be retained 100 times more strongly in the primary monolayer, *versus* the second monolayer. This creates a basic problem in rationalizing the non-displacement of B, using solute k' values according to eqn. 9. The problem can be stated in various ways; one way is as follows. If indeed the solute is retained only in the second layer, the primary monolayer can be ignored. The solute then competes with ethyl acetate for a place in the second layer. The isotherm for formation of the second ethyl acetate layer has been determined in ref. 10, and for the previous example of 0.35% (w/v) ethyl acetate

mobile phase, it is claimed that there is 0.0035 g/g ethyl acetate taken up in the second layer. The k' value for ethyl acetate with respect to the second layer is then calculable as in the derivation of eqn. 9, and is equal to $0.0035/1.5\phi_B$ or 0.7 (for c_p equal 0.35%). As expected, k' for ethyl acetate retained in the second layer is much less than the average k' value for the first plus second layers (k'_B equal 26). However, in view of the claim that solutes with $k' < 10.5$ are not retained in the first layer, the relative polarity of ethyl acetate and solute should be given by the corresponding k' values for the second layer alone (*i.e.* ignoring the ethyl acetate in the first layer); that is, k'_B is now equal to only 0.7 for ethyl acetate, but k' for the solute is equal to its *observed* k' value. Since solutes with $2.4 \leq k' \leq 10.5$ were observed to be adsorbed without displacement of ethyl acetate in ref. 10 (for 0.35%, v/v), there is a logical inconsistency in assuming *both* their lesser polarity than ethyl acetate (since their k' values > 0.7) *and* their exclusive retention in the second monolayer. One or the other of these two premises might be argued from the existing data, but not both simultaneously.

Stated in another way, retention in the second monolayer (*versus* retention in the primary monolayer) is postulated as being much weaker in the S-K model. In fact, this assumption is basic to the interpretation of isotherm data in support of bilayer adsorption of the solvent. If a solute is polar enough to be retained by such weak interaction with the primary layer ("sorption", or retention in the second layer) it follows that its interaction with and retention by the surface of the adsorbent (monolayer retention) would be such larger. But then a straightforward analysis of the data suggests that solute polarity *versus* that of ethyl acetate would be comparable for solutes with $k' \approx 0.7$, with 0.35% (w/v) ethyl acetate as mobile phase. If this argument is pursued, not only does it contradict the S-K interpretation of the displacement data of ref. 10, it would also suggest that sorption cannot occur whenever (a) the concentration of a class B solvent (*e.g.*, ethyl acetate) is greater than a few tenths of a percent and (b) k' for the solute exceeds a value of about 1; *i.e.*, even less often than suggested in the preceding section.

It might be argued that less polar solutes are in fact retained relatively more strongly in the second layer, *versus* polar solvents such as ethyl acetate. We believe this argument fails immediately, since then there is no longer any driving force for retention of the solute in the stationary phase. That is, if there is any tendency toward formation of a second monolayer in class P solvent systems, it is because of the polar interactions (however weak) between the primary monolayer and the second layer. These polar interactions will always be stronger, the more polar the molecule (solvent or solute) in the second layer. Note, also, that Scott and Kucera argue that a single molecular property (polarizability) determines polarity. This then requires that solute polarity as measured in either the first or second adsorbed layer be the same, relative to the polarity of the solvent (*e.g.*, ethyl acetate).

There are other ways of looking at the data of refs. 10 and 11 which cast similar doubt on the internal consistency of the sorption model. The data of Slaats *et al.*³⁸ allow correction for solution interactions *directly*, by taking into account the experimental activity coefficient of the solute in the mobile phase. When solute k' values corrected in this fashion are extrapolated to 100% B-solvent (see Fig. 5 of ref. 38), it is found that the resulting k' values show greater retention in the ethyl acetate stationary phase—by about 0.4 log units—*versus* isopropanol as stationary phase. That is, polar solutes appear to interact more strongly with the less polar ethyl acetate

as stationary phase (for sorption) *versus* the more polar isopropanol phase. This again is contrary to the assumption of the SIM model and to general experience, for sorption systems (LL), suggesting that something is wrong with the sorption model that leads to these conclusions. Similarly, this approach when applied to the S-K system of 0.35% ethyl acetate-heptane by Slaats *et al.*³⁸ supports *competition* rather than sorption as the retention mechanism. In section 4.3 we will explore some alternatives to sorption [for 0-5% (v/v) B mobile phases] that are better able to account for the experimental observations of ref. 10 which relate to sorption *versus* displacement.

4.3. An alternative to sorption

For the special case of mobile phases from class P and concentrations of the B-solvent equal to 0-5% (v/v), there is a simple, alternative explanation for the failure to observe displacement of molecules B from the stationary phase upon addition of solutes with k' less than k'_B as given by eqn. 9. As developed in the following section, there is reason to doubt the formation of adsorbed bilayers for class P solvents, or at least to question the data and logic thus far advanced in support of bilayer adsorption. Rather, it is believed that initial addition of B to the mobile phase (up to about 3%, v/v) results in the localization of molecules of B at preferred positions on the adsorbent surface. This is a consequence not of adsorbent inhomogeneity, but rather of the existence on the surface of discrete adsorption sites (silanol groups). In terms of the simplified picture of the silica surface shown in Fig. 1, completion of this localized monolayer after addition of about 1% (v/v) B to the mobile phase is as depicted in Fig. 4a. This can be contrasted with non-localized adsorption as in Fig. 4b. Since the adsorbed molecules of B do not totally cover the surface at this point (Fig. 4a), the remainder of the surface should be covered by adsorbed molecules of the weaker solvent component A; *i.e.* solvent A wets the silica surface. Now the energy diagrams of Fig. 1b-d show that as k' increases (for either solute or B), there is an increasing

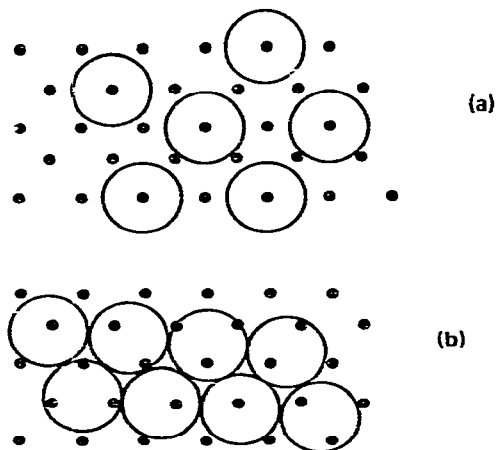


Fig. 4. Postulated coverage of adsorbent surface by solvent molecules B, shown as circles. (a) Class B solvent, for 1% (v/v) B in mobile phase and localized adsorption of B. The polar group in the molecule B is assumed to occupy the center of the circle. Spaces between B-molecules assumed to be filled by A-solvent (heptane). (b) Class A solvent, with closely packed (non-localized) monolayer, at higher concentration of B.

energy advantage to positioning the adsorbed molecule directly over an adsorption site or silanol group. Thus, as long as k' for the solute is less than k'_B , the solvent molecule B will have a marked preference for localized adsorption at specific positions on the surface. Under these circumstances, the adsorbing solute molecule will seek instead to displace a molecule of adsorbed A at a position on the surface that is unfavorable to localization. Thus, in the experiment of ref. 10 with 0.35% (w/v) ethyl acetate-heptane as mobile phase, it is believed that addition of solutes with $k' \leq 10.5$ leads to adsorption of the solute with (primarily) displacement of heptane (rather than ethyl acetate) from the primary monolayer. Unfortunately, there is no experimentally practical procedure for measuring the displacement of heptane when the mobile phase is largely composed of heptane (99.7% in this case).

Conclusion 4. The assumption that solutes less polar than the B-solvent cannot displace the latter from the adsorbed monolayer leads to certain additional requirements, for logical consistency. But these latter considerations when applied to the class P solvent systems of Scott and Kucera show that displacement (rather than sorption) is probably occurring. These contradictions can be fully resolved by assuming competition and also considering the probable effects of solvent localization in the monolayer.

5. MONOLAYER VERSUS BILAYER ADSORPTION

In the S-K model of retention in LSC, it is deduced that solvents of class P can form multiple, adsorbed layers, as illustrated in Fig. 2 for bilayer adsorption^{10,11}. It is further concluded that the bulk of adsorbed B-solvent is found in either a first or second layer (bilayer model), and the bilayer model in turn plays a key role in the sorption model discussed in the preceding section. The direct evidence for bilayer adsorption is provided by isotherm measurements for various A-B binaries, where B is variously a class N or P solvent. For class N solvents it is found that the isotherm can be fit accurately by the usual Langmuir equation*:

$$(B)_a = K(B)_s^0 N_B / (1 + KN_B). \quad (10)$$

Here, $(B)_a$ is the concentration of adsorbed B (g/g), $(B)_s^0$ is the saturation (monolayer) concentration when pure B is the mobile phase, K is an equilibrium constant at the isotherm temperature and N_B is the mole fraction of B in the mobile phase. In the case of class P solvents, eqn. 10 does not satisfactorily describe the experimental isotherm data. However, an equation based on the Langmuir model but allowing the formation of two successive layers (bilayer Langmuir) did give a close fit to experimental data^{10,11}. It was further shown that the monolayer concentration of B-solvent molecules was approximately constant for all class N and P solvents studied, and it was argued that the area per molecule for all these solvents is also approximately constant. Thus, both

* Scott and Kucera use a derivation of the Langmuir isotherm which is based on gas-phase adsorption. The main difference in the final expression for $(B)_a$ is to substitute the concentration $(B)_s$ in the mobile phase for the corresponding mole fraction N_B . We do not regard this difference as significant in the following discussion, particularly as values of $(B)_s$ are approximately proportional to values of N_B . However, it does lead to problems as $N_B \rightarrow 1$; e.g. predictions of incomplete filling of monolayers.

N- and P-solvents appear to form a monolayer of about the same area (equal to the adsorbent surface area)—as expected from theory. Finally the (extrapolated) uptake in the second layer similarly gives close to 100% of the monolayer uptake*, which is physically reasonable.

The argument as advanced above is superficially logical and seems to incorporate a number of separate checks on the overall hypothesis of bilayer adsorption. A more thorough examination of these data, however, appears to show otherwise. In the following discussion we will focus first on certain theoretical constraints for Langmuir adsorption that were not taken into account in refs. 10 and 11, and we will seek additional tests of internal consistency between the bilayer and SIM theories. Then we will consider the experimental data reported in refs. 10 and 11 more closely, as well as look at data from other laboratories for related LSC systems.

5.1. Requirements for Langmuir adsorption

Consider first the theoretical requirements for Langmuir adsorption:

(1) A defined adsorbent surface which accomodates some fixed quantity of a given adsorbate; in LSC systems, the monolayer (and subsequent layers) will each be filled at all times by either A or B molecules (if liquids A and B wet the adsorbent surface).

(2) Constant activity coefficients for the adsorbate molecule(s) in each phase, which in turn requires: (a) constant interactions between molecules A and B in the mobile phase, as the concentration of B is varied in the mobile phase; (b) constant interactions between molecules A and B within the adsorbed phase (first and second layers), as the concentration of B in the stationary phase varies; (c) constant interactions between molecules A and B with the adsorbent surface (or with the first-layer surface for the case of bilayer adsorption), as the concentration of B in the stationary phase varies.

Let us examine some consequences of the requirement for constant activity coefficients as the concentration of B in the mobile phase varies. The derivation of eqn. 10 (or its equivalent) in ref. 10 is kinetic rather than thermodynamic, so that the need for constant activity coefficients tends to be obscured. However, the principle of microscopic reversability firmly links the kinetic and equilibrium properties of a system, and it is the activities of species undergoing the adsorption-desorption process which are relevant in the equilibrium and thermodynamic expressions for Langmuir adsorption. Now the SIM model and eqn. 7 postulate a marked change in interactions among molecules of solute (or adsorbate) and solvent in the mobile phase, as the concentration of B varies. As a necessary consequence, the activity coefficient of the solute varies also, for solutes that are either of class N or P. On this basis there is no reason to expect a different result for molecules of the solvent B in the same LSC systems. Clearly their activity coefficients must also vary with change in the concentration of B, and this is experimentally observed^{38,47}. Thus the assumption of Langmuir adsorption of solvent molecules in either class N or P LSC systems, with its implicit requirement for constant B-solvent activity coefficients, contradicts the SIM model fundamentally and irreconcilably.

A similar difficulty holds for the activity coefficient of the B-solvent in the

* However, this result is a necessary consequence of the form of the S-K equation (Appendix I).

stationary phase (in *both* monolayer and second layer). Thus, at sufficiently low values of the solution concentration of B (c_p), the surface concentration of B will also be small. For this part of the isotherm, adsorbed molecules of B will be surrounded mainly by molecules of adsorbed A. For somewhat higher values of c_p , the monolayer will approach saturation, and an adsorbed molecule of B will see mainly other B-molecules. Thus, the adsorbed-phase interactions involving molecules of B will change drastically, just as for molecules of B in solution. Since the surface fills with B for rather small concentrations of B in solution, there will be little opportunity for cancellation of these effects (parallel change in the activity coefficients of B in each phase, as the concentration of B in solution is varied). This represents a second difficulty in accepting a simple Langmuir isotherm for these various LSC systems, at least for those involving B-solvents of class P, with their strong polar interactions between molecules of B and solute in either phase.

A third problem is involved with the assumption that all molecules of B within the monolayer experience the same interaction with the adsorbent surface. For class P solvents, localized adsorption of the B-solvent is expected for lower coverages of the surface, as in Fig. 4a (localized) *versus* Fig. 4b (non-localized). Eventually, however, the remaining surface in between localized molecules of the B-solvent must be filled. This space also belongs to the monolayer, although Scott and Kucera refer to it as a "mezzanine layer" (ref. 11; see section 7.1 and discussion there of Fig. 7). However, the final filling of the monolayer by the B-solvent under these circumstances (non-localization of B molecules during this stage) cannot be energetically as favorable as for initial adsorption of localized B-solvent. The energy diagrams of Fig. 1d imply a considerable advantage for localization in this respect, so that the energy of adsorption for filling in the "mezzanine layer" must be considerably less than that for initially adsorbed (localized) molecules of B. Thus, if we accept the possibility of adsorbate localization, still another objection to the simple Langmuir adsorption treatment of Scott and Kucera is raised*.

Thus far our discussion has been concerned with the interpretation of the shapes of isotherms measured in a static (batch) fashion by means of the impressively precise GC method. Similar experiments¹⁰ carried out in a dynamic (chromatographic) mode have, however, been misinterpreted. This problem is examined in detail in Appendix IV. We conclude that the S-K studies on the retention of the moderator¹⁰ do not furnish any new argument for the bilayer hypotheses; when properly handled, these data could have been of use only for reinforcing the experimental validity of the isotherm measurement.

Conclusion 5. The requirements of the Langmuir model are unlikely to be met in class P solvent systems. Therefore, the analysis of isotherm data to infer bilayer formation as in refs. 10 and 11 is suspect.

* Note also another consequence of Fig. 1. For modest differences in k' between solute and B-solvent molecules (solute less strongly retained), the solute can still effectively compete with the B-solvent for a specific adsorption site, as long as the B-solvent is not localized. However, when the B-solvent molecule is localized, the solute has a choice of non-localized adsorption with displacement of an A-solvent molecule, or competition with localized B-solvent. Under these conditions, there is a much larger advantage to displacement of the A-solvent rather than B-solvent, even for small decrease in polarity of the solute *vs.* that of the B-solvent.

Conclusion 5a. The requirements of the Langmuir model contradict all other postulates of the SIM; an attempt to prove these SIM postulates by interpretation in terms of Langmuir adsorption is therefore logically inconsistent.

5.2. Experimental isotherm data

Two aspects of the experimental isotherm data reported and discussed in refs. 10 and 11 will be examined here: (1) the form of the isotherm curves, and (2) the amount of B-solvent taken up in the monolayer. Consider first the shape of the $(B)_a$ versus c_p plot; i.e., the isotherm plot of B-solvent uptake versus B-solvent concentration in solution.

5.2.1. Isotherm shape. The arguments on behalf of bilayer formation^{10,11} focus strongly on the normal Langmuir behavior of class N systems as contrasted with abnormal isotherms for the class P solvents, suggesting some discontinuous event such as bilayer formation. This interpretation can be illustrated by rearranging eqn. 10 as follows:

$$\begin{aligned} N_B/(B)_a &= 1/K(B)_a^0 + N_B/(B)_a^0 \\ &= C + DN_B \end{aligned} \quad (10a)$$

Here, C and D are constants for a given isotherm. For small values of N_B (the usual situation for S-K isotherm data from refs. 10 and 11), N_B is proportional to c_p , and the expression on the left-hand-side of eqn. 10a is proportional to $1/k'$ for the B-solvent. Therefore, if isotherm data for the solvent system A-B are plotted as $1/k'$ (for B) versus c_p , a straight line should result. Furthermore, the extrapolated value of k' at c_p equal 0 should be proportional to the monolayer uptake of B at surface saturation. This is illustrated in Fig. 5a by such a plot from ref. 10 for the system heptane (A)-butyl chloride (B).

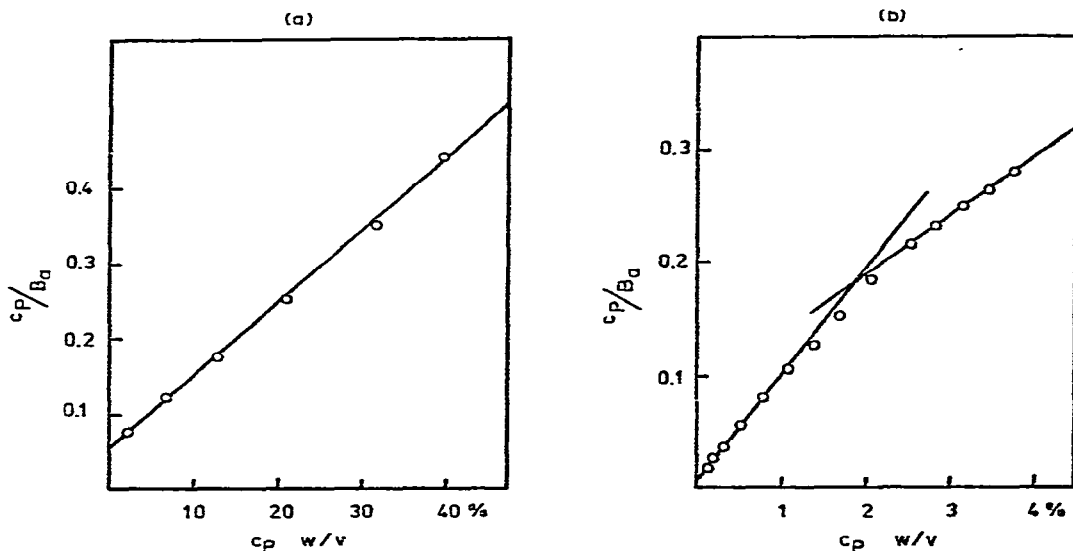


Fig. 5.

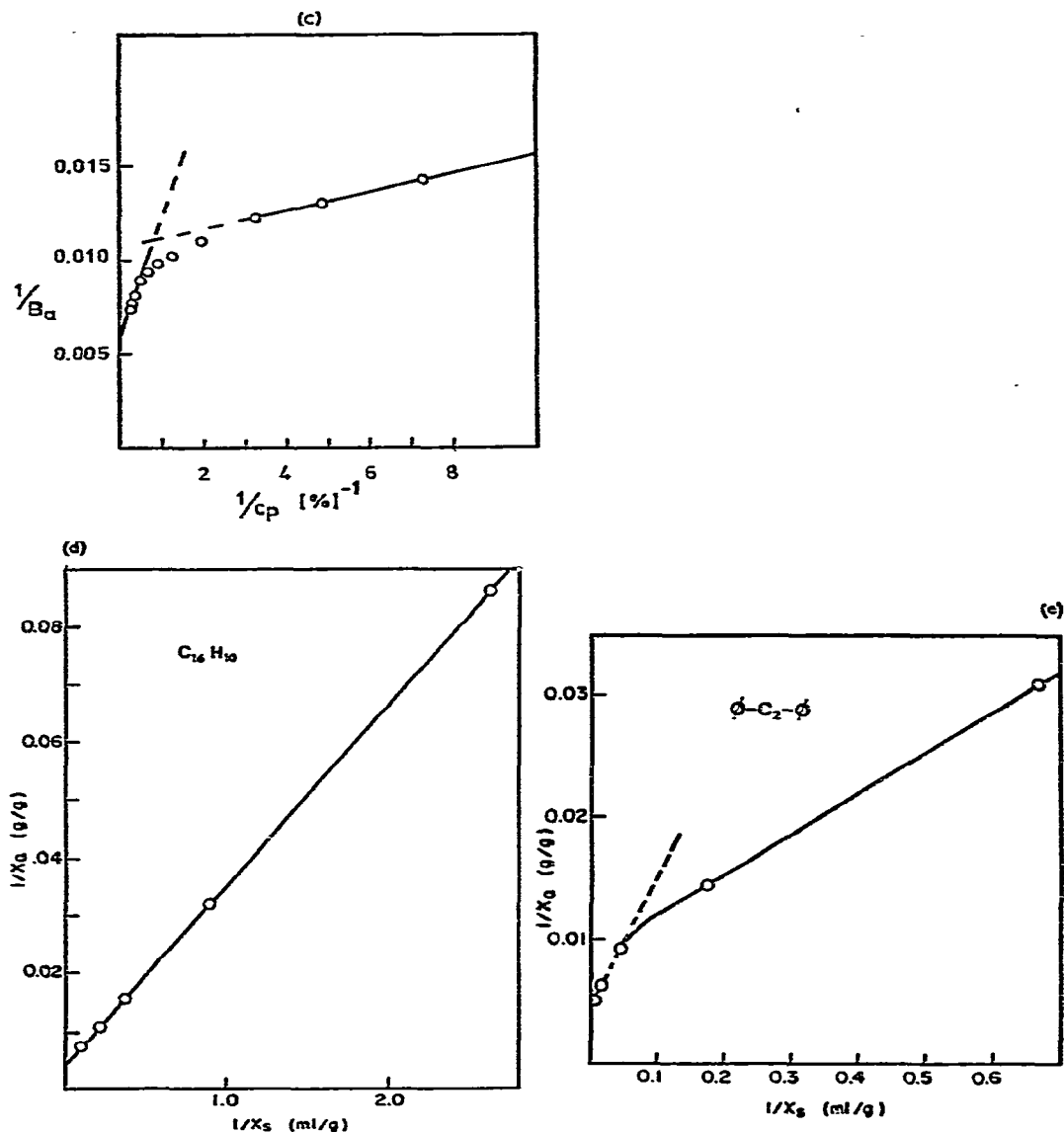


Fig. 5. Langmuir plot of A-B solvent isotherms for various LSC systems. (a) Data from ref. 10 for butylchloride in heptane on Partisil; (b) data from ref. 10 for ethyl acetate in heptane on Partisil; (c) same data as in (5b), plotted according to eqn. 10b; (d) fluoranthene-pentane on silica, from ref. 50 according to eqn. 10b; (e) same as (d), for dibenzyl-pentane.

The situation is more complex for isotherms of class P solvents, as illustrated in Fig. 5b (from ref. 10) for ethyl acetate as B-solvent. Here, a distinct break in the linear plot from 1-4% (w/v) ethyl acetate concentration in solution is observed at 2% ethyl acetate. As seen in this figure, the points below 1% ethyl acetate fall on a new straight line of different slope. These plots for ethyl acetate suggest some discontinuity in the adsorption of B from solution, and the interpretation in ref. 10 is that the

new straight line for concentrations larger than 2% ethyl acetate corresponds to the filling of the second adsorbed layer of the B-solvent.

The simple interpretation of plots such as those of Fig. 5b in terms of bilayer adsorption of the B-solvent is not at all straightforward. We have already noted in a preceding section that the conditions for Langmuir adsorption of class P solvents (*i.e.*, applicability of eqn. 10) are not met in practice for the systems of Scott and Kucera, and specifically for ethyl acetate-heptane. Eqn. 10 can be further rearranged to give another (equivalent) form*:

$$1/(B)_a = 1/K(B)_a^0 N_B + 1/(B)_a^0 \quad (10b)$$

This well-known relationship predicts linear plots for Langmuir-isotherm systems when the reciprocal concentrations of adsorbed and dissolved adsorbate are used. For the data for butylchloride we obtain again (eqn. 10b) a straight line (not shown). Fig. 5c also shows a break for the ethyl acetate data. Figs. 5d and e show two such plots from a class N system studied several years ago by one of us⁵⁰: the isotherms on silica for the aromatic hydrocarbons fluoranthene (5d) and dibenzyl (5e) in pentane as solvent. The Langmuir plot in Fig. 5d for fluoranthene is clearly linear, whereas that in Fig. 5e for dibenzyl is clearly not — much like the situation in Figs. 5b and c. However, we know that each of the systems of Figs. 5d and e are giving monolayer (only) adsorption of the B-component (aromatic hydrocarbon). First, these are class N mixtures, where Scott and Kucera concede bilayer formation is not expected. Second, it is possible to extrapolate each of these plots to $1/X_s$ (or $1/[B]_a$) equal zero, and calculate the amounts of aromatic hydrocarbon taken up at saturation; *i.e.*, the value of $(B)_a^0$. When this is done, it is found that the amount of aromatic hydrocarbon in the completed layer is equal for both fluoranthene and dibenzyl (within experimental error) and within 10% of the uptake calculated from the surface area of the silica and the molecular dimensions of these two compounds. Furthermore, there is no obvious driving force toward bilayer formation in these systems. Rather, the behavior of dibenzyl in Fig. 5e has been satisfactorily explained in terms of adsorbate localization** on the silica surface^{50,51}.

Thus we see that even in simple (non-polar adsorbate) LSC systems, it is possible to misinterpret the shape of the isotherm. Particularly in the case of Figs. 5d versus 5e, it would be tempting to note that the extrapolation of the two apparently linear portions of the isotherm (solid and dashed curves in Fig. 5e) yield saturation uptake values of X_a or $(B)_a^0$ that are about in two-to-one ratio. The simplistic conclusion at this point would be that Fig. 5e is providing an example of bilayer adsorption; *i.e.*, the solid curve corresponds to filling the first monolayer, while the dashed

* Note that a strict derivation for eqn. 10b (and eqn. 10) gives:

$$1/(B)_a = \left[\frac{(K-1)}{K(B)_a^0} \right] + \frac{1}{K(B)_a^0 N_B} \quad (10c)$$

The latter which reduces to eqn. 10b for the usual case of $K \gg 1$, recognizes that the monolayer must be completely filled by molecules of A or B; *i.e.*, $(B)_a = (B)_a^0$, when $N_B = 1$.

** Localization of non-polar dibenzyl molecules on silica may appear surprising. It is believed that phenyl groups are strongly adsorbed on non-free silanols, which constitute a small fraction of all silanols in wide-pore silicas or in water-deactivated silicas of any pore diameter. Thus, there is a strong tendency to localized adsorption of a molecule such as dibenzyl on silica.

curve indicates buildup of the second layer. The example of Figs. 5d and e suggests that extreme caution is in order in the interpretation of isotherm shape for all but the simplest LSC systems. Even in these cases, where other requirements for Langmuir behavior are reasonably fulfilled (as for the fluoranthene-dibenzyl data of Figs. 5d and e), wrong conclusions are easily drawn in such an approach.

We believe that discontinuity in plots such as that of Figs. 5b and c for class P solvent systems are mainly due to the localization of the B-solvent as discussed earlier (see Fig. 4 and related text), and/or changes in the activity coefficients of B^* . Following formation of a localized layer of B-solvent molecules, the monolayer is then completed via filling in with non-localized molecules of the B-solvent.

Conclusion 6. The interpretation of isotherm shape alone in the case of class P solvent systems cannot demonstrate whether one or two monolayers are built up during adsorption of the B-solvent. In fact, we believe discontinuity in the isotherm for monolayer uptake is expected for class P solvents, because they will generally exhibit localized adsorption.

5.2.2. Saturation uptake of B-solvents. The traditional approach to determining how much material is taken up in the adsorbed monolayer has involved either the BET scheme in the case of gas-solid adsorption systems, or simple Langmuir extrapolation (as in Figs. 5d and e, whether linear plots are found or not) in the case of liquid-solid systems. These studies have in turn yielded cross-sectional areas for various adsorbate molecules (*i.e.*, the area required by the molecule on the adsorbent surface). The latter values can be rationalized in terms of various calculations of molecular size, so that given any molecular structure, a cross-sectional area can be calculated for that molecule with reasonable precision. For a general discussion see refs. 13 and 52 and Ch. 8 plus pp. 63-64 of ref. 1. It is then possible to take the saturation uptake of an adsorbent for some compound (*e.g.*, a B-solvent), calculate the area required for that amount of material from the molecular cross-sectional area, and then compare the latter area with the surface area of the adsorbent. In this way it can be established how many monolayers of adsorbate are taken up at saturation. Alternatively, it is possible to calculate the quantity of material taken up in a monolayer (from the cross-sectional area), and compare this with the saturation uptake. In either case, we are able to estimate the maximum number of layers of B-solvent that can be adsorbed.

Either of the latter two schemes seems a more straightforward approach to the question of monolayer *versus* bilayer adsorption in the systems of refs. 10 and 11. No assumptions are required concerning the requirements for Langmuir adsorption and the validity of eqn. 10, and the method will work regardless of any localization of B-solvents in the first monolayer. Using data of Scott and Kucera¹⁰ and of Slaats *et al.*³⁸ we can determine saturation-uptake values for various B-solvents and compare these with values calculated for a monolayer (as above). These results are summarized in Table 3. There we see generally good agreement with the (approximate) calculated saturation-uptake values (for a monolayer) and the actual values for several different B-solvents in four studies. A few compounds give lower experimental uptake values

* Solute activity coefficients are also generally larger for small values of N_B ; for larger N_B , γ_{XS} values decrease to values approaching 1. Thus a sharp rise in the first part of the isotherm and a much smaller slope in a second part can be rationalized by this effect as well.

than expected, but that can be attributed to various effects: difficulty in accurately extrapolating the isotherm to saturation uptake, uncertainty in the molecular cross-sections used in the calculation, etc. More important, none of the class P solvents of Table 3 show a saturation-uptake value which is anywhere near that predicted for bilayer adsorption (0.24–0.32 g/g). The easiest conclusion to draw from these data of Table 3 is that they contradict the likelihood of bilayer adsorption in each LSC system.

How then do Scott and Kucera draw an essentially opposite conclusion from the same data of Table 3? The latter authors have already questioned our data of Table 3 (ref. 12) on the basis that the molecular cross-sectional areas required in the calculations of Table 3 are for various reasons uncertain. Nevertheless, in ref. 11 they argue that these molecular areas for the compounds of Table 3 are essentially constant, on the basis of somewhat crude methods for estimating the latter. They then proceed to show that their analysis of the isotherm curves in terms of the bilayer model gives roughly the same number of molecules of each solvent in the saturated monolayer. One is left with the impression that a constant number of molecules in

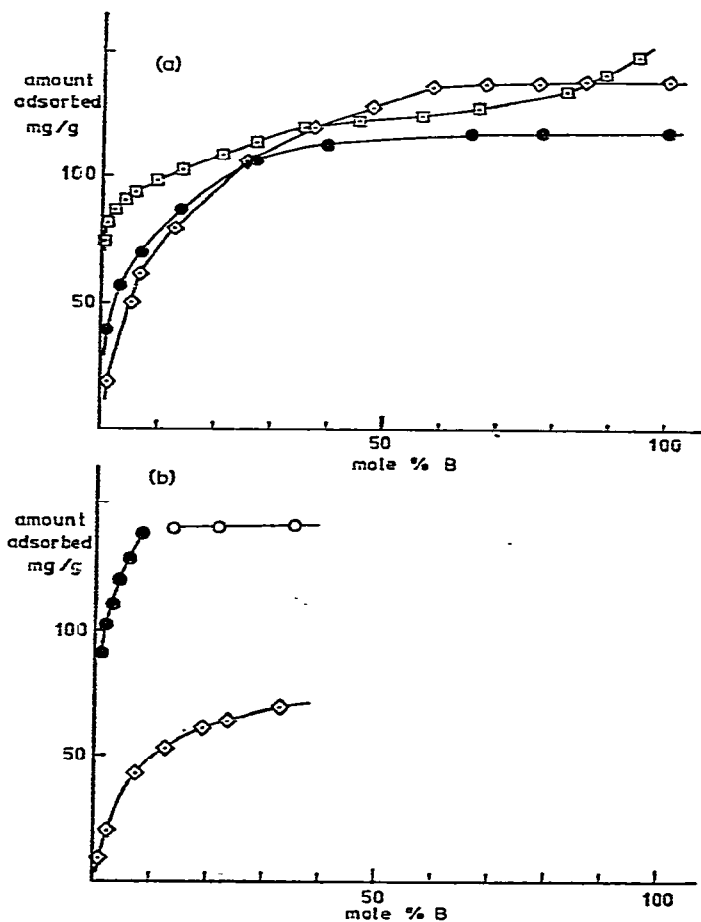


Fig. 6. (a) Adsorption isotherms⁴⁷ on Partisil 10 for toluene (◇), ethyl acetate (●) and 2-propanol (□) in *n*-heptane. Experimental method and data handling (zero volume!) as in ref. 38. (b) Adsorption isotherms on same adsorbent for ethyl acetate (○, ●) and benzene (◇), replotted from data from refs. 9 and 10.

the monolayer is somehow fundamentally reasonable, whereas this is not the case*.

Actually, whether one uses the molecular cross-sectional areas as determined by us for Table 3, or the values estimated by Scott and Kucera in ref. 11, the number of molecules calculated for a single monolayer differ by at most 30%. The real difference in values reported in ref. 11 and in Table 3 arises from how the extrapolation of the isotherm data to c_p equal 100% is carried out. We should note that the extrapolation of monolayer uptake as in Figs. 5d and e is subject to significant experimental error. In the case of extrapolating the "bilayer uptake" as described in ref. 11, there is also the further uncertainty introduced by the apparently incorrect assumptions concerning the applicability of eqn. 10 for class P solvents.

Other minor discrepancies emerge from the approach taken in refs. 10 and 11 for extrapolating the isotherm to 100% (v/v) B-solvent. Thus it is concluded that only 95% of the first monolayer is completed in the case of chloroform and 1-chlorobutane. Similarly, only 91% of the second ethyl acetate layer is filled in the presence of pure ethyl acetate as mobile phase. It is unclear what is meant in these instances, since the entire surface (of either the adsorbent or first monolayer) must be covered by either A or B molecules, in the presence of a surface-wetting liquid phase**.

In ref. 11 the first-monolayer saturation-uptake is given as 0.097 g/g for ethyl acetate as B-solvent. Therefore, one can extrapolate to a total uptake in bilayer adsorption of 0.19 g/g for pure ethyl acetate (0.18 g/g if we assume 91% filling of the second layer as above). Yet in ref. 9 a more complete isotherm for the ethyl acetate-heptane system is published (to 30%, v/v, ethyl acetate), and it is clear that this isotherm is flat from about 10% (v/v) ethyl acetate and higher; the (more accurate) saturation-uptake value for this isotherm⁹ is only 0.14 g/g, which is exactly the value calculated for a single monolayer in Table 3. This independent check on the S-K isotherm extrapolations agrees with other data, as shown in Fig. 6a. Here a set of data obtained over a much larger concentration range for the polar solvents toluene, ethyl acetate and isopropanol are shown. Note especially that the saturation uptake of toluene (class N) exceeds that of ethyl acetate (class P); if a single monolayer is assumed for toluene no more than one monolayer is possible for ethyl acetate.

The problems encountered when measuring isotherms in more concentrated

* At first glance the monolayer uptake of a constant number of molecules for all B-solvents studied in ref. 11 seems to fit some fundamental law based on simple stoichiometry. However, this is not the case. Thus, the extent of the adsorbent surface restricts the maximum number of molecules that can adsorb into the monolayer, and this number *must* always decrease for larger adsorbate molecules. Scott and Kucera attempt to circumvent this by suggesting that the molecules studied are all of the same size. Second, any true stoichiometric relationship requires a 1:1 ratio between the number of adsorbent centers (surface silanols) and the number of adsorbing molecules. However, while the number of molecules in the monolayer (per gram of silica) is estimated at $6-7 \cdot 10^{20}$ in ref. 11, the number of surface silanols can be estimated from ref. 6 at about 3 times this value ($2 \cdot 10^{21}$). Finally, if a 1:1 relationship was postulated between surface silanols and the molecules in the first monolayer, what interactions between the first and second monolayers would serve to preserve the same 1:1 relationship required by the claim that the two monolayers contain the same number of molecules?

** These discrepancies reflect the use of c_p rather than (correctly) N_B as in eqn. 10, as well as not using the correct eqn. 10c; see discussion of eqn. 10b (footnote). More vexing, however, is the problem of reconciling apparently 100% filling of the second monolayer with ethyl acetate as B-solvent for $c_p > 20\%$ (see Fig. 2B and related discussion), *versus* the observation above that at 100% ethyl acetate the filling of the second monolayer is only 91% complete.

solutions, and their interpretation, require further discussion which will be presented elsewhere. However, for the present discussion it suffices to state that Fig. 6 shows that any extrapolation to 100% B (mole fractions) from data points in the 0–10% region is unreliable, especially for more polar moderators.

Conclusion 7. The roughly constant number of molecules in the monolayer found by Scott and Kucera for various B-solvents has no fundamental significance. Extrapolation of saturation-uptake values based on the bilayer isotherm model seems less reliable than simple extrapolation of the experimental plot by conventional means (e.g., using the standard Langmuir plot as in Figs. 5d and e). Using the latter procedure, saturation-uptake values for the B-solvent agree with calculated monolayer values (Table 3), confirming an absence of bilayer formation in the LSC systems of refs. 10 and 11.

6. OTHER QUESTIONS

The foregoing discussion has for the most part covered the major new proposals by Scott and Kucera. A few remaining claims that do not fit into these prior areas remain for comment.

6.1. Silica surface structure

Previous workers (see refs. 53 and 55 for a review) have concluded that strongly heated silicas are covered with so-called "free silanols", as opposed to adsorbed molecular water or silanols which hydrogen bond with each other. The infrared spectra of such silicas show a narrow band in the vicinity of 3750 cm^{-1} which has been attributed to the stretching vibration of free or isolated hydroxyl groups that do not interact with each other. This band persists for silicas that have been heated to at least 700°C . Confirmation that the 3750 cm^{-1} band is associated with free silanols has been achieved in several different ways, all of which are consistent with each other; e.g., calculation of the band frequency from first principles, shift of the band to 2700 cm^{-1} upon reaction of the sample with $^2\text{H}_2\text{O}$ (deuterium exchange with the Si-OH group), etc.

In ref. 11 it is claimed that this band at 3750 cm^{-1} ("... absorption between 3000 and 4000 wave numbers . . .", ref. 11) is instead due to "... the hydroxyl groups of the chemically bound water." The evidence consists of the apparent disappearance of this band from silica samples heated to over 600°C . Examination of the actual spectra in ref. 11 shows that these are of poor quality when compared with previous studies (e.g., refs. 28 and 53). The reason for this may be due to the different experimental technique employed by Scott and Kucera in obtaining their spectra. These workers used discs of silica pressed with KBr, then manually transferred their silica samples to the infrared spectrometer after heating. All previous workers (probably over a hundred citations in the 1950s and 1960s) use *in situ* heating and measurement of the pressed silica (no KBr). See also Appendix V.

Conclusion 8. The narrow infrared⁴ absorption band at 3750 cm^{-1} for heated silica samples arises from free silanol groups, not chemically bound water.

6.2. Silica surface uniformity

In ref. 6 it is claimed that the silica surface becomes homogeneous or "ideal" only after heating to temperatures of 600°C and higher. In ref. 11 it is pointed out that the bilayer model applies equally well for silicas heated at 200°C and higher, and therefore the silica surface is homogeneous when activated at 200°C or higher.

Conclusion 9. Silica does not require heating to 600°C or higher to become homogeneous, and there is no practical advantage in using silicas that have been activated at temperatures greater than 200°C.

6.3. Thermodynamic approach to LSC retention

Scott and Kucera have criticized the S-S model on the basis that it is thermodynamically based (see comment No. 11 of Table 2). This criticism represents a misconception of the relationship of thermodynamics to retention in LSC, and it shows some misunderstanding of what the S-S model actually is and how it can be used in practice. First, concerning the role of thermodynamics and equilibrium (which retention is based on), we feel it is unnecessary to prove that *any* practical theory of chromatographic retention must conform to the laws of thermodynamics. Second, the S-S model and most other simple models of retention and equilibrium in chromatography involve not only thermodynamic but also *extra-thermodynamic** relationships. The latter in turn often lead to simple expressions which require only a limited number of experimental data, but which permit the prediction of a large number of other k' values. Those experimental data are in turn derived from the chromatographic system itself, not from more fundamental tables of thermodynamic properties from the literature. For examples of this, see Appendices I and V of ref. 1, as well as refs. 35 and 56.

It should be noted in this context that any description of phase systems that correlates phase and solute molecular structure to retention is *necessarily* extra-thermodynamic (including the S-K SIM formulation). Relations derived from thermodynamics must generally be supplemented by other assumptions before a correlative or predictive tool for distribution constants can be developed. Thermodynamics, rather than being a non-rewarding alternative to other methods for prediction and correlation, is able to relate one phenomenon to another with the help of basic rules of physical reality. The language of thermodynamics implicitly allows such relationships to be developed. Therefore, this language is most useful to chromatographers in order to formulate hypotheses (models) in a precise, unambiguous form, so that these hypotheses can then be tested against results from chromatography and other fields.

Conclusion 10. A thermodynamic approach to retention in chromatography is an essential beginning to any constructive attempt at understanding and predicting retention. The S-S model is also based on extra-thermodynamic relationships which reduce the amount of data required for practical predictions of retention.

* E.g. additivity of functional-group free-energy-increments for ΔE , linear-free-energy relationships, etc.

7. DISCUSSION

We have attempted to analyze each of the major points put forth in refs. 4–11 (*cf.* Table 2), and to come to conclusions concerning the validity of these various claims. As a result, we are left with the almost total reputation of the “sorption, SIM, bilayer” model. It is possible to explain most of the data of refs. 6–11 in terms of previously held concepts, without encountering the external contradictions and internal inconsistencies which plague the S–K treatment. That is not to say, however, that we have a uniformly clear picture of the retention mechanism in LSC for all possible systems. Nor is it likely that a “pure competition” model holds for every experimental system. In this respect we are indebted to Scott and Kucera for stimulating a reexamination of previously held concepts.

In this section we will look further at some of these complications and the limits of our present knowledge concerning retention in LSC. We will also consider what kinds of experiments are likely to lead to deeper insights in this area.

7.1. “Hard” versus “soft” monolayers and multilayers adsorption

The isotherm data of refs. 10, 11 and 47 agree in showing a steep initial uptake of ethyl acetate from heptane solutions, followed by a shallower uptake as the ethyl acetate concentration is increased beyond 1% (v/v). We will refer to the quantity of ethyl acetate taken up initially as constituting a “hard” monolayer, with subsequently adsorbed ethyl acetate forming a “soft” monolayer. We have argued previously that the “hard” and “soft” layers together form a single monolayer that is directly in contact with the silica surface, and that “hard” and “soft” layers are differentiated by the localized adsorption of the “hard” layer. Scott and Kucera¹¹ have referred to this hypothesis as a “mezzanine” layer, implying that the “soft” layer is somewhat more distant from the surface than is the “hard” layer (see Fig. 7).

MEZZANINE LAYER THEORY

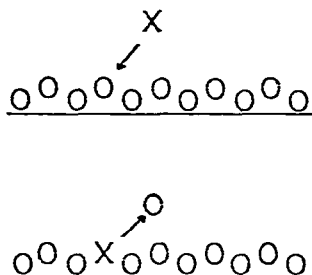


Fig. 7. Mezzanine structure for adsorbed monolayer according to ref. 11.

We have no quarrel with a “mezzanine” structure as an explanation of the “hard” and “soft” layers found in the ethyl acetate–heptane system. However, any attempt at defining the exact positions of adsorbed ethyl acetate molecules within the “hard” and “soft” layers seems both unlikely to succeed and completely divorced from any practical application in chromatography. One might extend this argument by observing that at some point the “mezzanine” model passes over to bilayer adsorption—when the separation of the “soft” layer from the surface is sufficiently great.

We accept this possibility, so long as molecules in the "soft" layer are still contiguous to the silica surface; *i.e.*, no molecules of the "hard" layer lie directly between the silica surface and molecules of the "soft" layer.

Why are we reluctant to accept bilayer adsorption, while recognizing the possibility of a "mezzanine" layer that is scarcely distinguishable from a bilayer as pictured in Fig. 2? Apart from the faults of the Scott-Kucera logic in this respect, and the arguments related to space-filling ("wetting-liquids") that were detailed in earlier sections, there is a basic problem in seeing any physical reason for bilayer formation. Scott and Kucera refer to bilayer formation as being associated with "hydrogen bonding" solvents such as ethyl acetate and tetrahydrofuran⁹, but these solvents do not self-hydrogen-bond; they are proton-acceptors, but not proton-donors. That is, the second ethyl acetate monolayer cannot hydrogen-bond to the first ethyl acetate monolayer. One might reasonably argue that the strong polar interactions among these solvent molecules arising from dipole orientation are the reason for the attraction of first and second (or "hard" and "soft") layers in the adsorbed phase. However, that leads to another fundamental difficulty. Why should the build-up of multilayers stop with the second layer? In the BET treatment, which has been successfully applied to a wide range of gas-solid adsorption systems, it is assumed that there is a distinct difference between the first layer and all subsequent layers, that the subsequent layers are held by equivalent adsorption energies, and that past the first layer subsequent layers do not form one-by-one but continuously. Clearly, there is a need for deeper theoretical examination of the whole question of multilayer adsorption in LSC systems.

For the case of class AB solvents as alcohols and water, the possibilities for multilayer adsorption and a non-displacement retention mechanism become more plausible; *e.g.*, case 3 of section 4. We would not expect to see clear-cut bilayer adsorption in these systems, but multilayer build-up would be facilitated by the possibility of strong hydrogen bonding between adsorbed layers. Attachment of solute molecules to such a multilayer phase could also be accommodated without any need for displacement. Limited data for the solvent system butanol-water-isooctane⁴⁷ suggest that some such process occurs in this system. However, such LSC systems must be extremely complex and difficult to describe with any sort of simple physical picture. While we must confess our ignorance in this area, it seems unlikely that useful models or predictive relationships will soon emerge for all class AB solvent systems.

Finally, returning to our model of "hard" and "soft" layers of adsorbed class P solvents as shown in Fig. 6a, it is interesting to note that in terms of this model most of the objections raised in section 5.1 against Langmuir adsorption now disappear, at least for small concentrations of ethyl acetate in solution. Similarly, the fit of actual P solvent isotherm data to the bilayer model as in refs. 10 and 11, becomes less surprising. First, the activity coefficient of the P solvent in the stationary phase is expected to be approximately constant during the filling of the "hard" layer. Thus, each adsorbing B molecule will be surrounded mainly by molecules of A, as indicated in Fig. 4a. Furthermore the localization of B molecules in the "hard" layer will impose a certain orientation on these B molecules, one which will prevent their simultaneous orientation within the monolayer for optimum interaction (dipole or hydrogen bonding) with adjacent B molecules. Second, the activity coefficient of the B solvent in the

"soft" layer should similarly remain constant during filling of this layer. Thus, the "soft" layer will be formed only after substantial filling of the "hard" layer, so that molecules of B in the "soft" layer will see mainly molecules of pre-adsorbed B (see Fig. 4a). Third, the interactions of B with the surface will be constant for the "hard" layer (localized B molecules), and constant (but different) for the "soft" layer. Fourth, for small concentrations of the P solvent, activity coefficients will not change much in the solution phase as the concentration of B is varied (*cf.* experimental data of Scott for 0–3% B⁶⁵).

However, solution interactions and change in solution activity coefficients become significant at higher concentrations of the B solvent in solution³⁸. While the forced fit (Appendix I) of the S–K bilayer model to isotherm data might be expected to give reasonable correlation of model and experimental data for a small range of B solvent concentrations (*e.g.*, 0–10%), it is unreasonable to expect that extrapolated values of total uptake of the adsorbent by B solvent at $N_B = 1$ can be accurate.

7.2. Activity coefficient effects

We have noted repeatedly the large activity coefficient changes for both solute and B-solvent in class P solvent systems. These are handled in the S–S model by assuming that the γ value for a particular species (solute or solvent) is roughly the same in both the mobile and stationary phases. If this is the case, activity coefficient effects cancel exactly, and the simple S–S treatment follows directly. However, the question of how much cancellation of γ values should be expected is by no means clearcut. The simple argument in favor of some cancellation is that with monolayer adsorption, the adsorbed molecule "sees" a similar environment on the side away from the adsorbent surface, as it "saw" in the mobile phase. And the molecular environment surrounding a molecule in a given phase determines the γ value of that molecule. If this possibility for γ value cancellation is not accepted, and it is assumed that γ values in the adsorbed phase are constant after approximate filling of the B-solvent monolayer, then one can test the sorption *versus* displacement mechanism by correcting for the experimentally measureable mobile phase γ values of solute and B-solvent. This has in fact been reported for the S–K system (ethyl acetate–heptane, same solutes) by Slaats *et al.*³⁸. Their results show that in fact the decrease in retention which occurs upon increasing ethyl acetate concentration in the range 30–40% is due for the most part to changes in the strength of the solute–solvent interactions; *i.e.*, to changes in γ_{X_s} for the solute. That is, for this range of ethyl acetate concentrations, solvent interactions and some sort of non-displacement (*e.g.*, "sorption") retention process could explain the experimental data.

We can summarize the above discussion as follows. There is still controversy and uncertainty over the possibility and extent of γ value cancellation in these class P solvent systems. One study³⁸ suggests for the higher range of ethyl acetate concentrations in the system of ref. 10 that displacement does not occur when solute molecules are retained in the adsorbed phase, providing that γ value cancellation does not occur. However, this same study (with its assumptions concerning non-cancellation of γ values) suggests that displacement occurs at lower ethyl acetate concentrations, specifically in the region (0.35% ethyl acetate) which is the principal focus of Scott and Kucera. Interestingly, the experimental studies of Slaats *et al.*³⁸ suggest that

sorption occurs at higher (but not lower) concentrations of ethyl acetate, while our present analysis of the S-K model in section 4.1 suggests that sorption should only occur at lower ethyl acetate concentrations (and for solute k' values < 1). Clearly more work is needed, both theoretically and experimentally, to resolve the question of γ value effects in class P solvent systems with higher concentrations of the B-solvent.

7.3. Other tests of retention mechanism

In the case of such physically different processes as "sorption" and "displacement", one would hope that some direct measurement of the system might result in an unambiguous assignment of retention mechanism. Alternatively, one would like to mathematically model each process, then compare carefully obtained experimental data with each model, so as to show that one model provides a better fit of the data than the other. These essentially have been the approaches taken by Scott and Kucera and Paanakker *et al.*⁴⁷. Unfortunately, as we have seen, the experimental data allow for more than one interpretation in terms of retention mechanism. On the basis of considerable thought and discussion among the authors and Scott and Kucera¹², it seems to us that further experimental testing of this type is unlikely to add greatly to our knowledge.

An alternative approach is one based on extra-thermodynamic considerations. Here we might hope to test seemingly different retention mechanisms by examining how retention varies with the molecular structure of solvent and solute. In fact this is the approach followed in the original Snyder treatment^{1,31}. At the present time one can state that this approach shows internal consistency for all the data so far reported, over a very wide range in both experimental conditions and the structural variation in solvents and solutes. However, the development of this model to date has not really been directed to a proof of displacement versus sorption. In fact, the few attempts to do so^{4,57} can now be said to be unconvincing, for various reasons we need not elaborate on here*. One can argue, however, that an essential difference between the displacement and sorption mechanisms is the possibility of solute and solvent localization in the former. If this distinction is accepted, then studies such as ref. 31 are difficult to explain in terms of any mechanism other than displacement. In ref. 31 for LSC systems free from the complication of solute-solvent hydrogen bonding, a number of apparent retention anomalies (in values of k') can be explained precisely ($\pm 4\%$) in terms of solute-solvent localization effects on the adsorbent surface. Finally the well-known tendency of LSC to provide large retention selectivity for positional isomers has been repeatedly noted in the literature, and explained in terms of the matching of solute functional groups to a rigid surface containing fixed adsorption sites (*e.g.*, ref. 24, pp. 356-361). Adsorption of the solute onto a non-rigid layer of adsorbed solvent molecules (as in Fig. 2) seems much less likely to afford such isomer differentiation.

* Briefly, the studies of refs. 3 and 5 deal with the comparison of experimental data with eqn. 4b vs. 6, which we have seen are really equivalent expressions. Also, γ value effects were ignored.

8. CONCLUSIONS

For the patient reader who has accompanied us to this point, what is there left to say by way of overview and summation? First, we must confess our disappointment at having to make our case so briefly. The large number of points that required consideration in this review has forced us to deal in cursory fashion with many background issues and specific situations, without providing the reader with all the facts needed for an on-the-spot conclusion. This has forced us to refer to previous articles in some cases. We have also assumed that the reader comes equipped with a good background in physical chemistry. Thus, if one hesitates to accept the reasoning offered here, he (or she) is in for a bit of hard work in chasing the various arguments to their origin. Unfortunately, no alternatives seemed available to us, with the possible exception of writing a book.

Specific conclusions have been drawn along the way with respect to the S-K model, and these make it clear that the latter treatment is largely discredited by internal contradiction and by comparison to current theory concerning solution and adsorption thermodynamics. The approach taken by these workers was perhaps intended to be deliberately provocative, and their work has certainly led to a thorough reexamination of previous theories of adsorption and retention in LSC systems.

The experimental studies of Scott and Kucera and of others on isotherms for class P solvent systems raise intriguing questions that have yet to be resolved to the satisfaction of the present authors. Does the saturation uptake of B-solvent in these systems correspond to a simple, "2-phase" monolayer, or is there some "mezzanine" character to the adsorbed phase? To what extent are activity coefficients in the two phases cancelled, in terms of eqn. 2? Does "sorption" or something other than simple displacement *ever* occur in these class P solvent systems? On the latter points there is some disagreement among the present authors, but agreement on the need for further experiments and additional theory to describe these effects. For the main part, however, the S-S model appears to give an adequate, practical description of LSC systems involving class P and (especially) class N solvents.

9. GLOSSARY OF TERMS

a	Subscript refers to "adsorbed phase"
A, B	Generally refers to two solvents of a mobile phase binary A-B; A, non-polar; B, polar
A', B'	Constants in eqns. 6, 7 or 8a
AB	Solvent or solute type in Table I (polar amphoteric)
A-B	Refers to binary solvent mixture composed of A and B
A _s	Relative molecular cross-sectional area of solute molecule, equal to area on surface covered by adsorbed molecule
B _s	Concentration (g/g) of adsorbed B (Fig. 5a-c); same as (B) _s
BA	Benzyl acetate (Fig. 3)
A, B, C, D, E, F	Constants in equations in Appendices I, II and IV (different from previous meaning)
(B) _s , (B) _s ⁰	Value of B _s for some point on isotherm, and value for monolayer saturation (100% B in mobile phase)

$(B)_s$	Concentration (g/ml) of solvent B in the mobile phase
C, D	Constants in eqn. 10a
c_p	Concentration (% w/v) of polar solvent B in binary A-B
$E_{Ma}, E_{Ms}, E_{Xa}, E_{Xs}$	Dimensionless partial molar free energies of various species (M, mobile phase molecule; X, solute molecule) in adsorbed (a) or solution (s) phases; eqn. 2; $\Delta E = \Delta G^\circ/RT$; E_{Ma} , etc. are partial molar free energies, divided by RT
k	Boltzmann constant (Fig. 1)
k'	Capacity factor of solute or B-solvent
k'_A, k'_B, k'_{AB}	k' values of solute in (A) A-solvent, (B) B-solvent or (AB) mobile phase A-B
K	Equilibrium constant for eqn. 1, with $n = 1$; see eqns. 10-10c
LSC	Liquid-solid chromatography; generally refers to silica as adsorbent
M	Mobile phase molecule (polar solvent)
n	See eqns. 1 and 2; one solute molecule displaces n molecules of mobile phase from adsorbent surface upon adsorption
n_B	Relative cross-sectional area of molecule of B-solvent (eqn. 4)
N	Solute or solvent type in Table 1 (non-polar)
N_B	Mole fraction of B in solvent binary A-B (eqn 4)
N_1, N_2, N_i	Mole fractions of components 1, 2, i of a homogeneous mixture (Gibbs-Duhem relationship); e.g., components A and B in solution A-B.
NB	Nitrobenzene (Fig. 3)
P	Solute or solvent type in Table 1 (polar)
P'	A measure of solvent polarity ²³
PE	Phenylethanol
q	Phase ratio
R	The gas constant
s	Superscript denotes "solution phase"
S^0	Dimensionless free energy of adsorption of a solute from a reference mobile phase (eqn. 3)
S_M^0	Value of S^0 for a solvent M
S-K	Scott-Kucera
S-S	Snyder-Soczewinski
SIM	Solution interaction model of S-K
T	Temperature ($^\circ\text{K}$)
\bar{v}_s	Molar volume of solvent molecule S
V_s	Volume (approximate) of an adsorbed monolayer (ml/g); see eqn. 3
V_m	Volume of mobile phase within column (ml)
W	Weight of adsorbent within column (g)
X	Solute molecule
X_s	Concentration of adsorbed solute (g/g)
X_s	Concentration of solute in solution (g/ml)
α	Adsorbent activity function; also separation factor for two adjacent bands

γ	Activity coefficient of solute or solvent in a given solution
$\gamma_1, \gamma_2, \gamma_i, \gamma_{xs}, \gamma_I^M$	Values of γ for components (1, 2, i), mobile phase components (A, B) or solute ($\gamma_{xs} = \gamma_I^M$) in mobile phase solution
Δ_{cas}	Correction factor in eqn. 3 to account for complications not considered in simple S-S model; values of Δ_{cas} can be correlated with various phenomena, leading to accurate prediction of Δ_{cas} values and correction of eqn. 3
$\varepsilon_A^0, \varepsilon_B^0, \varepsilon_{AB}^0$	Values of ε^0 for solvent A, solvent B and binary A-B, respectively
$\varnothing_A, \varnothing_B$	Volume fractions of solvents A and B in binary A-B

10. APPENDIX I

Forced equality of first and second layer uptake in the Scott-Kucera bilayer isotherm equation

The fit with a bilayer Langmuir formula used by Scott and Kucera does not yield the equality of the saturation values of the two layers as a result; this equality is already in the mathematical model. Thus,

$$(B)_s = \frac{\left(\frac{Bc}{A^2}\right) + Dc^2}{1 + Bc + Dc^2} \quad (\text{i-1})$$

is equivalent to their formula; that is, one layer corresponds to

$$A \frac{Bc}{Fc} = A/2 \quad (\text{i-2})$$

two layers to

$$A \frac{Dc^2}{Dc^2} = A \quad (\text{i-3})$$

While this is logical, for an *independent* two-layer model we would require *four* adjustable parameters. The lettering up to D obscures the fact that there are actually only three parameters in the model. Thus the equality of the two saturation values is built into the model from the outset.

11. APPENDIX II

Test of the solution interaction model and the Purnell equation against the Gibbs-Duhem equation (thermodynamic consistency)

As we already made clear in the text, both models are equivalent to a dependence of the activity coefficient γ_x of a solute in a binary mixture A-B, on the volume fraction \varnothing_B :

$$[\gamma_{xs}]^{-1} = A + B\varnothing_B \quad (\text{ii-1})$$

In the SIM the left-hand-side of the equation is the inverse of the capacity factor $1/k'$. In Purnell's equation it is K , the partition coefficient. In both cases we can substitute $\gamma_{X_s}^{-1}$ for $1/k'$ or K , when appropriate changes in the constants A and B are made and when the solute X and other conditions are unchanged.

We shall discuss the (mathematically) simplest case in which the binary-phase system shows no contraction and molar volumes of both constituents are the same. In that case the volume fractions \mathcal{O} equal the mole fractions N and we have

$$[\gamma_X]^{-1} = C + DN_B \quad \text{or}$$

$$\gamma_X = \frac{1}{C + DN_B} \quad (\text{ii-2})$$

The derivation of the Purnell equation limits the validity to a solute at infinite dilution; in the SIM derivation such a limitation is not made. However, it is easily shown that the equations cannot be valid for non-infinite dilution. Should this be the case, the theory would be able similarly to predict how the activity coefficients of the solvent constituents themselves depend on the solvent composition. The result would be

$$\gamma_A = \frac{1}{C + DN_B} \quad (\text{ii-3})$$

$$\gamma_B = \frac{1}{E + FN_B} \quad (\text{ii-4})$$

Taking the pure solvents A and B as the reference state, we have $\gamma_A = 1$ for $N_B = 0$ and $\gamma_B = 1$ for $N_A = 0$. If this is done the equations can be written as

$$\gamma_A = \frac{1}{1 + DN_B} \quad (\text{ii-5})$$

$$\gamma_B = \frac{1}{1 + EN_A} \quad (\text{ii-6})$$

The Gibbs-Duhem equation can be written as

$$N_A \frac{d \ln \gamma_A}{d N_B} - N_B \frac{d \ln \gamma_B}{d N_A} = 0 \quad (\text{ii-7})$$

This cannot be zero for every value of N_A ($= 1 - N_B$), as is required, and especially it is non-zero for the extreme points $N_A = 0$ and $N_B = 0$.

This violation of the Gibbs-Duhem equation, as applied to the activity coefficients of the phase constituents themselves, shows that the equation as proposed in the SIM and by Purnell *et al.* cannot have general significance. That is not to say that in specific situations such an equation might not be able to correlate experimental data well. Especially for the Purnell case this is not too surprising, as solvents and solutes in GC differ widely in molecular weight; the correlation might be useful for solutes, but it cannot be valid for the stationary phase (solvent). We have pointed out (Appendix III) the reasons why this description might be successful for a number of specific GC liquid phase mixtures.

However, in the case of the SIM as applied to LSC systems, solvent and solute molecules are very similar. It is, therefore, not possible to indicate any reason why the equations should not be equally applicable to the phase constituents themselves, especially also because in the papers on the SIM no indication about the range of validity of the model is given.

Finally, it should be noted that the Gibbs–Duhem equation, is applied to activity coefficients in binary mixture, allows the calculation of γ_B if the dependence of γ_A on the composition is known. This is a straight-forward and often applied method in physical chemistry (ref. 36, p. 202) when volatility data are only accessible for one compound. Likewise, a postulated dependence of γ_A on the composition allows us to calculate the corresponding dependence of γ_B on the composition. If this is applied to the SIM postulate, a problem occurs:

From

$$\gamma_A = \frac{1}{1 + DN_B} \quad (\text{ii-8})$$

it follows that $d\gamma_A/dN_B$ is non-zero for $N_B = 0$. The Gibbs–Duhem equation then yields an infinite value for $d\gamma_B/dN_B$ at this point. As a result the calculation of γ_B is not possible, as the required integration cannot be performed at $N_B = 1$. The non-zero value of $\ln \gamma_A/dN_B$ for $N_B = 0$, *i.e.* for $N_A = 1$, is at variance with all descriptions of binary mixtures on which, *e.g.*, methods such as boiling point evaluation are based.

The above analysis has no significance for the competition model and eqn. 4, since the latter relationship is not based on solution-interaction phenomena, but assumes the effects of such interactions cancel in the overall adsorption equilibrium.

12. APPENDIX III

The Purnell equation (eqn. 8) and its extrapolation to LSC systems

It is not our intent here to examine in full the validity of the Purnell equation and its underlying assumption of “microscopic partitioning” or “local immiscibility”. Instead we will try to focus on the possible reasons why eqn. 8 works for some GC systems, and then apply what we have learned to the case of LSC solvent systems and the SIM treatment.

It is appropriate to note at the beginning that the Purnell model is nominally a revolutionary concept that differs strikingly from other theories of solution thermodynamics. However, there are special situations where either the validity of eqn. 8 or the actual local demixing postulated by these workers might in fact be expected. Concerning the possibility of local demixing of the two solvents A and B in the binary A–B, one might look for such effects in either of two cases. First, for a solvent pair that is immiscible over some intermediate range in \mathcal{O}_A , one might expect some ordering of the binary solvent structure outside the range of immiscibility. That is, local demixing into A and B might persist when the binary is barely stable as a single phase. Consequently, the validity of eqn. 8 for such immiscible binaries as tributyl phosphate and ethylene glycol (ref. 45, pp. 209–220), which at first glance appears surprising, is perhaps not really unexpected. Furthermore, eqn. 8 is expected to apply over the range in A–B compositions where immiscibility is observed.

A second impetus to local demixing would be provided by solvents such as liquid crystals which possess a high degree of ordering in the liquid phase. It is not unreasonable that microscopic ordering and demixing can persist when such solvents are diluted with some "normal" solvent. In fact, evidence for such microscopic ordering in near-immiscible mixtures ("cybotaxis") has been obtained from spectroscopic studies⁵⁸, and further confirmed by chromatographic selectivity studies⁵⁹.

Another binary solvent system where the applicability of eqn. 8 is predicted by conventional theory has been pointed out by Martire⁶¹. Where the solvent B forms a 1:1 complex with the solute, and where other solution interactions (*e.g.*, dispersion forces) are comparable for the two solvents A and B, eqn. 8 can be derived in terms of the simple equilibrium



Thus, binary solvent systems of this type do not require the supposition of "local miscibility".

Many polar GC phases consist of large, essentially aliphatic molecules with a single polar-functional group X: R-X, R-X-R, etc. When such solvents (B) are mixed with a non-polar solvent A, the interaction of a polar solute with that binary solvent is similar to the case of 1:1 complexation, as in eqn. iii-1. In some cases, an actual complex between the solute and the functional group X may result. In other cases, the interaction may be weaker, and it may be questionable whether one can speak of a discrete complex. However, the concentration of the group X in the solvent binary will in any case be small, so that solute molecules never see more than one X-group at any given time. The relative immobility of the larger solvent molecules used in GC may further augment this tendency to 1:1 polar interactions or complexes in GC stationary phases. The net result in all cases is a situation which more or less resembles that of eqn. iii-1, and which should therefore be approximately described by eqn. 8 *i.e.*, (via classical theory). Laub and Wellington⁴⁵ have summarized data for the GC system di-*n*-octyl ether-*n*-heptadecane wherein eqn. 8 is obeyed quite nicely. This system (and others cited in ref. 45) illustrates the effects discussed immediately above, and the fit observed by Laub and Wellington is, therefore, unsurprising.

Finally, so far as GC systems are concerned, it is not at all clear that eqn. 8 is a generally valid relationship. Martire⁶¹ has pointed out that "... the remarkable agreement cited (by Purnell) is merely an artifact of the insensitive method of data testing used. ..." Thus when values of k'_A and k'_B (for the pure solvents A and B) do not differ greatly, one does not expect large percentage deviations from eqn. 8 on the basis of classical theory. In these cases, one can obtain an apparently high degree of correlation of experimental data with eqn. 8 despite obvious failure of the latter. Tiley⁶⁴ has also pointed out a variety of effects which allow classical theory to predict linear relationships of the form of eqn. 8. Other workers^{62-65,73} have cited numerous data on apparently "typical" binary-solvent GC systems which show poor agreement with eqn. 8, and better agreement with classical theory.

It thus appears that the Purnell equation is at best true for a restricted range of GC phases. The conditions which favor its applicability in a given case where k' values differ significantly include either a strong degree of solvent-ordering in the

binary A-B, or the restriction of polar solvent-solute interactions to 1:1 pairs as in eqn. iii-1. The latter condition will be found frequently in GC systems, but seldom in LSC binaries. In the case of LSC solvents, we generally deal with low-molecular-weight polar solvents B, where multiple interactions of a solute molecule with several surrounding solvent molecules (as well as solvent-solvent interactions) are probable. This is just the situation where eqn. iii-1 (and eqn. 8) should not apply. To be sure, Waksmundski and Suprynowicz⁶⁶, and Laub and Purnell⁶⁷ have pointed out a GC system which seems to refute this logic: the solvent system diethyl maleate-quinoline, which involves small molecules A and B. For the latter as GC stationary phase, it was pointed out that eqn. 8 was obeyed quite satisfactorily. However, for the latter system the solute k' values in the pure solvents A and B are quite similar. In this case eqn. 8 provides no meaningful test of the validity of the Purnell model, since classical theory similarly allows for roughly constant k' values as ϕ_A is varied (and linear plots of k' vs. ϕ_A , as predicted by eqn. 8).

The most difficult problem in arguing the applicability of eqn. 8 (and therefore eqn. 7) for typical binary LSC solvents, is that the same logic should also be applicable to the activity coefficients of the solvents A and B (see similar logic of Appendix II). But in fact if there is true "micro-partitioning" of the two solvents, the mixture should exhibit the properties predicted for the simple sum of the two pure solvents. That is, one would expect the partial pressures of A and B over the mixture A-B to be equal to the partial pressures of pure A and B, respectively, regardless of the value of ϕ_B ; i.e. as for the case of mixtures of two immiscible solvents A and B. This unusual behavior is not observed experimentally, except where A and B are actually immiscible.

A direct test of eqn. 8 in binary LSC solvents is provided by experimental data on solute activity coefficients in binary solvent systems. While such data are limited in number, Paanakker *et al.*⁴⁷ have measured solute activity coefficient values for one of the systems of Scott and Kucera: 0-20% (v/v) ethyl acetate-heptane, for nitrobenzene, benzyl alcohol and phenylethanol as solutes. Even over this limited range in solvent composition, marked curvature of plots of $1/\gamma$ versus c_p is observed (Fig. 3).

Our conclusion is that the Purnell equation is a useful fitting function for some GC systems. The basic reasons for its success are not necessarily related to the limited-miscibility model, but rather to certain consequences of eqn. iii-1. If this is the case, it can be predicted that the Purnell model and eqn. 8 will not apply to typical LSC binary-solvent systems. Available experimental evidence apparently substantiates this failure.

13. APPENDIX IV

Isotherm studies carried out by Scott and Kucera

Consider the observed k' value for a peak generated by the injection of the solvent binary itself with a (slightly) changed composition. A disturbance of negligible small amplitude elutes from the column after a time (see for instance ref. 48)

$$t_{Rd} = t_{R0} \left[1 + q \frac{dc_{ts}}{dc_{lm}} \right] \quad (\text{iv-1})$$

where q is the phase ratio and c_{is} , c_{im} are the concentrations of i (the disturbed concentration) in the stationary and mobile phase. For the present case this would translate into

$$t_{RB} = t_{R0} \left(1 + \frac{W}{V_m} \frac{dB_s}{dc_B} \right) \quad (\text{iv-2})$$

which equation predicts the same as the usual expression $t_{R0} (1 + k')$ when the isotherm is linear, but yields quite different results when applied to non-linear isotherms. For instance, in the case of a saturated layer the equation predicts that a disturbance of c_B within the range of saturation elutes exactly after t_{R0} (a result which can also be derived from the basic consideration that no mass exchange with the layer occurs), irrespective of the static adsorbed amount of B which can be significant. In fact, this experiment is one of the experimental ways to measure isotherms^{48,49} and yields the derivative of the isotherm.

Scott and Kucera (see Figs. 7 and 8 of ref. 10) used this experiment to give further evidence for the two-layer adsorption of P-type moderators on silica. However, instead of using eqns. iv-1 or iv-2, they handled their data with an expression

$$t_{RB} = t_{R0} \left(1 + \frac{A}{1 + Bc_B} \right) \quad (\text{iv-3})$$

where A and B are the constants from the Langmuir expression. This expression was derived by assuming that only the empty (*i.e.* heptane covered) part of the surface contributes to the retention of the disturbance, an assumption already shown to be incorrect.

Rearranging the correct expression (eqn. iv-2) into a dependence of $1/k'$ on c_B , one obtains for the Langmuir isotherm

$$1/k' = \frac{(1 + Bc_B)^2}{A} \quad (\text{iv-4})$$

instead of the linear dependence of $1/k'$ on c_B derived in ref. 10.

Given a set of A , B values, measured statistically, eqn. iv-4 predicts a much faster decrease of k' with increasing c_B than eqn. iv-3, and that is indeed the experimental result found by Scott and Kucera. They themselves did not check the result of their column experiments against the experimental isotherms from batch studies, although for butyl chloride this check is possible. In Fig. 4 of ref. 10 it can be seen that the adsorbent is 50% covered for 5.9% butyl chloride in heptane. That is, for this concentration eqn. iv-4 predicts a four-fold increase in $1/k'$ for this point (5.9%) compared to the 0% value, while eqn. iv-3 predicts only a two-fold increase. Fig. 7 of the same paper shows indeed a four-fold increase; the two-fold increase in $1/k'$ is already reached at 1.6% (v/v) B.

14. APPENDIX V

The nature of the silica surface

At the time final proof for this review was being processed, another article by Scott appeared⁶⁹ which includes new hypotheses on the chemical structure of the silica surface. Previous workers have believed (1) the adsorption sites on the silica surface

consist of silanol groups, and (2) the surface concentration of these groups in a silica thermally activated at 150–200° (*i.e.* normal chromatographic silica) is constant at about 8 $\mu\text{moles}/\text{m}^2$. Scott now proposes that the actual concentration of these surface silanols is only 2.5 $\mu\text{moles}/\text{m}^2$, and that a molecule of water is adsorbed onto each silanol. This monomolecular layer of adsorbed water then constitutes the surface onto which solute or solvent molecules adsorb (or “sorb”) from solution.

The above proposals⁶⁹ differ radically from the picture previously assumed by most chromatographers and surface chemists; these proposals therefore deserve a critical evaluation in terms of previously reported data and (if needed) additional experimental work. It is not possible in this review to provide more than a preliminary discussion of the implications of previous work as regards Scott's latest proposals. On the one hand, these new hypotheses make it easier to disregard some of the criticism of the S–K model presented in this review. On the other hand, these new proposals appear even more difficult to rationalize with previous thinking and work in this area. Many hundreds of papers have already been published on the nature of the silica surface; for a partial listing of this literature, see references cited in refs. 28 and 53–55, as well as secondary references. Scott has repeated some of these studies on the silica he had worked with earlier (Partisil), has obtained results similar to those reported previously—with some exceptions that seem due to experimental methodology—but has ignored other relevant data.

A few major points are worth making at this time:

(1) It is assumed by Scott that dimethyloctylchlorosilane (DMOCS) is capable of reacting with all of the surface silanols present in a given silica, regardless of activation temperature. From this assumption he purports to measure directly the number of surface silanols, based on a simple 1:1 reaction stoichiometry. However, it is well known (*e.g.*, refs. 28 and 70) that the maximum number of silane molecules that can react with the silica surface is limited by steric considerations (space-filling). Small silanes such as trimethylchlorosilane can fill the silica surface to a maximum extent of about 4 $\mu\text{moles}/\text{m}^2$. Larger silanes such as DMOCS give even smaller reaction yields ($\approx 3 \mu\text{moles}/\text{m}^2$) for the same silica. Finally, residual (unreacted) silanols can be detected by infrared absorption after the complete silanization of a silica which is pre-activated at 150–200°. Therefore, the measurement of surface silanol concentrations by silanization is simply not possible.

(2) The maximum surface concentration of silica silanols can be inferred from various crystal structures for natural, crystalline silicas. Depending on the starting structure and the cleavage plane used to define the surface, predicted silanol concentrations range from 8 to 16 $\mu\text{moles}/\text{m}^2$. No structure has been put forth by Scott that can justify the lower silanol concentrations proposed; *i.e.*, the figure of 2.5 $\mu\text{moles}/\text{m}^2$ implies a large number of unsatisfied valences.

(3) Similarly, the 7 $\mu\text{moles}/\text{m}^2$ of water which Scott postulates in a 50% humidity silica on top of the hydrated silanols should be compared with the 19 $\mu\text{moles}/\text{m}^2$ that can be calculated from space-filling models. For the multi-layer model he assumes in the case of silicas activated at lower temperatures (up to 3 layers of water), one would infer a density of this adsorbed water equal to about 0.3 g/cm³. This is not physically reasonable.

(4) The presence of molecular water or silanols on the silica surface gives rise to infrared absorption in the region of 3400–3750 cm⁻¹. Detailed theoretical analysis

suggests that surface silanols are also a probable source of absorption in this region. Similarly, the absorption coefficients for free and hydrogen-bonded silanols are known to be different, which brings into question Scott's use of the integrated 3400–3750 absorbance band as a quantitative measure proportional to the amount of adsorbed water for silicas activated at different temperatures.

(5) In the interpretation of differential thermal analysis curves for silica, Scott observes three distinct dehydration steps. From this he infers three kinds of hydroxyls: surface silanols, water in a first layer, and water in additional layers. This simple analysis ignores two other kinds of hydroxyls whose concentration has been claimed to vary with silica activation temperature: water bound within the silica matrix (not on the surface), and two kinds of silanols: free vs. hydrogen-bonded.

(6) A large number of different reactions involving surface silanols have been reported in the literature. These include reactants that selectively react with silanols as opposed to water (*e.g.*, metal ions), as well as reactants that can combine with a dehydrated silica surface to yield a product equivalent to the reaction with a silanol group. All of these reported studies appear to show a similar concentration of surface silanols: $8 \mu\text{moles}/\text{m}^2$ for 150–200° silica.

It is true that some of these reactions would be predicted to give the same reactant uptake for either the classical or Scott's model of the silica surface. However, it is interesting to note that there has been little interest in this point for the past 15 years; *i.e.*, almost all recent workers have discarded the possibility of significant concentrations of adsorbed molecular water in silicas heated above 150°.

(7) Finally, the question of the activity coefficients of the B-solvent has been addressed by Scott⁶⁹. It is argued that solvents like ethyl acetate and methyl ethyl ketone behave "ideally" (Henry's law, constant activity coefficients) in mixtures with heptane up to 3% (w/v), because it is observed that the partition of such compounds between water and heptane phases shows a linear isotherm. Although this may seem reasonable at first glance, available experimental evidence shows that this conclusion is not justified. The activity coefficient of ethyl acetate (*B*), *e.g.*, in water, has been measured by numerous workers (*e.g.*, refs. 71 and 72 be it that these measurements were taken at constant pressure). The results show that the activity coefficient of ethyl acetate decreases by about 15% relative/% change in the ethyl acetate concentration in the region of interest. Thus the observed linearity in the distribution between water and heptane must be attributed to the cancellation of the γ dependence on concentration in both phases. This is not too surprising, as in both phases γ_B is much larger than 1 at $N_B = 0$, but necessarily has to go to 1 when N_B approaches 100%.

We conclude that the objections raised by us in section 5.2.1 against Scott's interpretation of adsorption isotherms for moderators, which considered the possible effect of a dependence of solution activity coefficients on concentration, remain valid.

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16. SUMMARY

In the present paper we have reviewed the experimental and theoretical evidence which relates to the mechanism of solute retention in LSC systems. It appears that the sorption mechanism proposed by Scott and Kucera contains internal inconsistencies and is further contradicted by other evidence. The displacement model of Snyder and Soczewinski, on the other hand, does a reasonable job of explaining available data on LSC retention, and is not contradicted by external evidence or the presently accepted laws of physical chemistry. The bilayer adsorption model proposed by Scott and Kucera seems also deficient, and it is likely that monolayer adsorption is the rule in the systems studied by these authors. The details of the retention mechanism for very polar mobile-phase systems (e.g., solutions of alcohols and water, and concentrated solutions of ethyl acetate) are less well understood, and further work is needed to clarify this area. The "microscopic partitioning" model of Purnell *et al.* is believed inapplicable to typical LSC solvent systems.

Finally, the scope of the S-S model is much broader than that of the S-K model. It is not restricted according to solvent class or adsorbent, it has been applied in polar-bonded-phase liquid chromatography and to gas-solid chromatography, and it is capable of predictions for the separation of different solutes by various solvents, especially as regards solvent selectivity effects. The S-S model has been experimentally validated in terms of thousands of k' measurements, for hundreds of different solutes and solvents.

REFERENCES

- 1 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
- 2 E. Soczewinski, *Anal. Chem.*, 41 (1969) 179.
- 3 L. R. Snyder, *Anal. Chem.*, 46 (1974) 1384.
- 4 R. P. W. Scott and P. Kucera, *Anal. Chem.*, 45 (1973) 749.
- 5 R. P. W. Scott and P. Kucera, *J. Chromatogr. Sci.*, 12 (1974) 473.
- 6 R. P. W. Scott and P. Kucera, *J. Chromatogr. Sci.*, 13 (1975) 337.
- 7 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 112 (1975) 425.
- 8 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 122 (1976) 35.
- 9 R. P. W. Scott, *Analyst (London)*, 103 (1978) 37.
- 10 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 149 (1978) 93.
- 11 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 171 (1979) 37.
- 12 R. P. W. Scott, personal communication.
- 13 L. R. Snyder and E. R. Fett, *J. Chromatogr.*, 18 (1965) 461.
- 14 W. E. Hammers, R. H. A. M. Janssen and C. L. de Ligny, *J. Chromatogr.*, 166 (1978) 9.
- 15 W. E. Hammers, R. H. A. M. Janssen, A. G. Baars and C. L. de Ligny, *J. Chromatogr.*, 167 (1978) 273.
- 16 W. E. Hammers, C. H. Kos, W. K. Brederode and C. L. de Ligny, *J. Chromatogr.*, 168 (1978) 9.
- 17 W. E. Hammers, M. C. Spanjer and C. L. de Ligny, *J. Chromatogr.*, 174 (1979) 291.
- 18 C. L. de Ligny, personal communication.
- 19 B. L. Karger and R. W. Giese, *Anal. Chem.*, 50 (1978) 1049.
- 20 P. Kucera, in preparation.
- 21 H. Colin, C. Eon and G. Guiochon, *J. Chromatogr.*, 122 (1976) 223.
- 22 J. L. Robinson, W. J. Robinson, M. A. Marshall, A. D. Barnes, K. J. Johnson and D. S. Salas, *J. Chromatogr.*, 189 (1980) 145.
- 23 L. R. Snyder, *J. Chromatogr.*, 92 (1974) 223; *J. Chromatogr. Sci.*, 16 (1978) 223.
- 24 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley-Interscience, New York, 2nd ed., 1979, pp. 248-250.

- 25 B. L. Karger, L. R. Snyder and C. Eon, *J. Chromatogr.*, 125 (1976) 71.
- 26 J. Narkiewicz, M. Jaroniec, M. Borówko and A. Patrykiewicz, *J. Chromatogr.*, 157 (1978) 1.
- 27 B. L. Karger, L. R. Snyder and C. Eon, *Anal. Chem.*, 52 (1978) 2126.
- 28 L. R. Snyder and J. W. Ward, *J. Phys. Chem.*, 70 (1966) 3941.
- 29 L. R. Snyder, *Separation Sci.*, 1 (1966) 191.
- 30 L. R. Snyder, *J. Chromatogr.*, 25 (1966) 274.
- 31 L. R. Snyder, *J. Chromatogr.*, 63 (1971) 15.
- 32 M. J. Sabacky, L. B. Jones, H. D. Frame, Jr. and H. H. Strain, *Anal. Chem.*, 34 (1962) 306.
- 33 L. R. Snyder, J. W. Dolan and J. R. Gant, *J. Chromatogr.*, 165 (1979) 3.
- 34 J. W. Dolan, J. R. Gant and L. R. Snyder, *J. Chromatogr.*, 165 (1979) 31.
- 35 L. R. Snyder, *Advan. Chromatogr.*, 4 (1967) 3.
- 36 Y. M. Prausnitz, *Molecular Thermodynamic of Fluid Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 1969, p. 212.
- 37 R. A. Keller, B. L. Karger and L. R. Snyder, in R. Stock (Editor), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 125.
- 38 E. H. Slaats, J. C. Kraak, W. J. T. Brugman and H. Poppe, *J. Chromatogr.*, 149 (1978) 255.
- 39 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
- 40 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 41 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
- 42 L. R. Snyder, *J. Chromatogr.*, 36 (1968) 476.
- 43 F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1972.
- 44 J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 97 (1975) 3585.
- 45 R. J. Laub and C. A. Wellington, in R. Foster (Editor), *Molecular Association*, Vol. 2, Academic Press, London, 1979, Ch. 3.
- 46 R. J. Laub and R. L. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley-Interscience, New York, 1978 pp. 169-205.
- 47 J. E. Paanakker, J. C. Kraak and H. Poppe, *J. Chromatogr.*, 149 (1978) 111.
- 48 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 58 (1971) 137.
- 49 A. W. J. de Jong, J. C. Kraak, H. Poppe and F. Nooitgedacht, *J. Chromatogr.*, 193 (1980) 181.
- 50 L. R. Snyder, *J. Phys. Chem.*, 67 (1963) 2622.
- 51 L. R. Snyder, in C. N. Reilley (Editor), *Advances in Analytical Chemistry and Instrumentation*, Vol. 3, Wiley-Interscience, New York, 1964, pp. 281-283.
- 52 A. L. McClellan and H. F. Harnsberger, *J. Colloid Interface Sci.*, 23 (1967) 577.
- 53 K. K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979, pp. 68-69.
- 54 R. K. Iler, *The Chemistry of Silica*, Wiley-Interscience, New York, 1979, pp. 624-654.
- 55 A. V. Kiselev and V. I. Lyggin, *Infrared Spectra of Surface Compounds*, Wiley, New York, 1975.
- 56 L. R. Snyder, *J. Chromatogr.*, 28 (1967) 432.
- 57 E. Soczewiński, *J. Chromatogr.*, 130 (1977) 23.
- 58 J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 97 (1975) 230.
- 59 A. Bjorseth, *4th Int. Symp. Anal. of Polynuclear Aromatic Hydrocarbons*, Battelle, 1980.
- 60 R. J. Laub and W. L. Roberts, *5th Int. Symp. Anal. of Polynuclear Aromatic Hydrocarbons*, Battelle, 1980.
- 61 D. E. Martire, *Anal. Chem.*, 48 (1976) 398.
- 62 M. W. P. Harbison, R. J. Laub, D. E. Martire, J. H. Purnell and P. S. Williams, *J. Phys. Chem.*, 83 (1979) 1262.
- 63 A. J. Ashworth and D. M. Hooker, *J. Chromatogr.*, 174 (1979) 307.
- 64 P. F. Tiley, *J. Chromatogr.*, 179 (1979) 247.
- 65 R. J. Laub and C. A. Wellington, in R. Foster (Editor), *Molecular Association*, Vol. 2, Academic Press, London, 1979, pp. 200-205.
- 66 A. Waksmundzki and Z. Suprynowicz, *J. Chromatogr.*, 18 (1965) 232.
- 67 R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 98 (1976) 30.
- 68 E. H. Slaats and J. Fekete, personal communication.
- 69 R. P. W. Scott, *J. Chromatogr. Sci.*, 18 (1980) 297.
- 70 G. E. Berendsen and L. de Galan, *J. Liquid Chromatogr.*, 1 (1978) 403.
- 71 S. R. M. Ellis and R. R. Garbett, *Ind. Eng. Chem.*, 52 (1960) 385.
- 72 J. Griswold, P. L. Chu and W. O. Winsauer, *Ind. Eng. Chem.*, 41 (1949) 2352.
- 73 J. F. K. Huber, E. Kenndler and H. Markens, *J. Chromatogr.*, 167 (1978) 291.