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IDENTIFICATION AND EVALUATION OF RETENTION MECHANISMS IN GAS–LIQUID CHROMATOGRAPHIC SYSTEMS*

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SUMMARY

A procedure for identification of the retention mechanisms in gas–liquid chromatographic systems is proposed. It is based on the introduction of a sorption model for these systems, in which the presence of two layers of liquid stationary phase on the support is assumed. First a multimolecular layer of highly oriented molecules adjacent to the solid surface is formed, followed by a second bulk layer. The partition properties of both layers were expected to be different due to their structural peculiarities. An appropriate retention equation assuming all probable sorption retention mechanisms is derived. Problems attendant upon the application of this equation for identification purposes are discussed. The knowledge of some experimental parameters and the employment of a suitable computer program lead to unequivocal identification of solute retention mechanisms as well as to determination of partial partition coefficients. The reliability of the identification procedure was verified with published and new experimental data. Calculated partition coefficients allowed to the evaluation of the relative contributions of the identified mechanisms to the solute retention. The results obtained are in good agreement with the requirements of the introduced sorption model.

INTRODUCTION

A previously derived retention equation

$$E = \sum_i K_i S_i \tag{1}$$

was found to be applicable for all column chromatographic systems[1]. Here E is the so-called integral retention effect, representing the net retention volume per gram of packing; K_i are the appropriate partial partition coefficients and S_i the corresponding

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specific phase characteristics of the packing. Hence eqn. 1 accounts in a most general form for the mixed retention mechanisms in a chromatographic system.

In gas–liquid chromatography (GLC) a commonly accepted approach is to consider the mixed retention mechanisms as a result of interfacial adsorption effects in addition to the dissolution in the liquid stationary phase (LSP)[2–13]. Then, the contributions of all sorption phenomena to the solute retention are generally expressed in a three-term equation

$$E = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \tag{2}$$

where V_L is the volume of LSP while A_{GL} and A_{LS} are the gas–liquid and liquid–solid interfacial areas, respectively. Usually, all these quantities are expressed per gram of packing. The partition coefficients K_L, K_{GL} and K_{GLS} correspond to dissolution in the LSP and to adsorption at the gas–liquid and liquid–solid interfaces. For some GLC systems the reduced forms of eqn. 2

$$E = V_L K_L + A_{GL} K_{GL} \tag{3}$$

or

$$E = V_L K_L + A_{LS} K_{GLS} \tag{4}$$

are also employed with the assumption that only two mechanisms contribute to the retention[2–4,6].

An important problem concerning the application of retention equations is the correct determination of their terms, *i.e.*, the exact identification of retention mechanisms acting in the GLC system investigated. This originates in the necessity to find a solution of the so-called inverse retention problem[14], which means determining the partition coefficients if the integral retention effect and the specific phase characteristics are known. A particular case of the inverse retention problem is related to thermodynamic measurements by GLC when an accurate value of K_L must be obtained from a system with mixed retention mechanisms[11,15].

Usually, the dimensionality of retention equations is intuitively determined without guarantee of their correct presentation. Hence, the development of new approaches for this purpose is of pronounced interest. It is of note that Weiner *et al.*[16] considered factor analysis to be potentially able to solve the problem. Unfortunately, the example chosen was not complex enough to demonstrate the power of the method.

In the present paper a procedure for identification of the retention mechanisms in GLC systems is proposed. It is based on the introduction of a sorption model specific to these systems. The application of the procedure requires knowledge of some experimental parameters as well as employment of an appropriate computer program.

THEORETICAL

State of liquid stationary phase on the support

The loading of solid support with a film of LSP leads to a perceptible modification of the film properties in comparison with the bulk phase[17–23]. The cause for this phenomenon appears to be the specific orientation of molecules in the multimolecular structurally modified liquid layer. Principally, the orientation of molecules can take place up to a considerable thickness of LSP film, gradually falling off with the distance from the support surface. Beyond the effective thickness of this modified liquid layer, the loaded LSP retains the properties of bulk phase.

The existence of a highly oriented liquid layer in the vicinity of the solid surface is a manifestation of the so-called "long-range" interaction forces[24,25] which arise at interfaces and sometimes cause inexplicable behaviour of molecules. Briefly, two different layers could be distinguished at sufficient LSP amount on the support:

(i) a multimolecular layer of highly oriented LSP molecules, adjacent to the solid surface and denoted here as the *structured* layer

(ii) a *bulk* LSP layer covering the structured one

If the solute molecules show propensity towards adsorption at the liquid–solid interface they could displace the adsorbed phase molecules because of a larger affinity to the solid surface. Following a two-dimensional adsorption model, the adsorbed solute molecules will be considered to have direct contact with the support. On the other hand, those dispersed in the structured LSP layer will be treated as dissolved molecules similarly to these in the bulk phase. However, a noticeable difference in the partition properties of both layers could be expected due to their structural peculiarities.

Sorption model of GLC systems

Let us consider a section of a GLC packed column. It is supposed that the packing consists of a usual wide-pore non-silanized solid support loaded with a LSP. The phase amount is adequate to guarantee complete coverage of solid surface with a multimolecular liquid film. The amount of packing in the section is considered to be 1 g, so that the specific phase characteristics listed below are expressed per gram of packing. V_G, V_L, V_S and V_B are the volumes of the gas phase, total LSP, structured and bulk LSP layers respectively, and A_{GL} and A_{LS} are the corresponding gas–liquid and liquid–solid interfacial areas. Then, the general retention equation assuming all probable sorption mechanisms can be presented in the form

$$E = V_S K_S + V_B K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \qquad (5)$$

where K_S and K_L could be interpreted as "structured" and "bulk" partition coefficients, respectively.

Eqn. 5 is valid under conditions of infinite dilution whereas K_i are constants at a given temperature. Thorough examination shows the complex nature of K_S and K_{GLS}, with respect to the solute distribution between phases having no immediate contact. In fact

$$K_S = K_{BS} K_L \qquad (6)$$

$$K_{GLS} = K_{SA} K_S \qquad (7)$$

where K_{BS} is the partition coefficient between structured and bulk LSP layers and K_{SA} is that between liquid–solid interface and structured layer. A combination of eqns. 6 and 7

$$K_{GLS} = K_{SA} K_{BS} K_L \qquad (8)$$

enables the rigorous evaluation of the liquid–solid adsorption by means of K_{SA}.

The non-equal possibilities of obtaining data for all phase characteristics makes eqn. 5 inapplicable in practice. Thus, A_{GL} and A_{LS} can be determined experimentally, while V_S and V_B cannot. However,

$$V_S + V_B = V_L \tag{9}$$

where V_L is usually known. Combining eqns. 5 and 9 we obtain

$$E = V_S(K_S - K_L) + V_L K_L + A_{GL}K_{GL} + A_{LS}K_{GLS} \tag{10}$$

where only V_S cannot be determined by an appropriate experimental technique.

In fact V_S is a function of V_L and LSP film thickness, d. With increase of V_L, starting from zero, d increases gradually to the utmost effective thickness, d_S, of the structured layer. Consequently, d_S is considered here as a measure of the mean distance to which the long-range forces affect the LSP bulk properties and then:

$$V_S = V_L, \text{ whereas } d < d_S \tag{11}$$

With further increase of V_L formation of the LSP bulk layer starts. Then, d_S remains constant while d increases and a satisfactory evaluation of V_S could be obtained from:

$$V_S = A_{LS}d_S, \text{ when } d \geqslant d_S \tag{12}$$

Taking into account eqns. 11 and 12, eqn. 10 can be presented in the form

$$E = V_L K_L + \delta V_L(K_S - K_L) + (1 - \delta)\, A_{LS}\, [d_S(K_S - K_L)] + A_{GL}K_{GL} + A_{LS}K_{GLS} \tag{13}$$

where:

$$\delta = 1, \text{ when } d < d_S \tag{13a}$$

or

$$\delta = 0, \text{ when } d \geqslant d_S \tag{13b}$$

Similarly, for K_L, K_{GL} and K_{GLS} the quantities

$$K_S - K_L = K_{SL} \tag{13c}$$

and

$$d_S(K_S - K_L) = K_{DSL} \tag{13d}$$

are to be considered as constant terms under infinite dilution and at a given temperature. They are independent of the variations of phase characteristics in a certain GLC system. Introducing the new eqns. 13c and 13d into eqn. 13, we obtain the final form:

$$E = V_L K_L + \delta V_L K_{SL} + (1 - \delta)\, A_{LS}K_{DSL} + A_{GL}K_{GL} + A_{LS}K_{GLS} \tag{14}$$

Eqn. 14 involves all probable retention mechanisms in accordance with the introduced sorption model of GLC systems. It can be interpreted as a general retention equation that permits the development of a procedure for identification of the retention mechanisms.

Problems of identification

The use of eqn. 14 gives rise to some experimental and mathematical problems. Prior to proceeding to the identification of the retention mechanisms, it will be shown how these problems can be overcome.

Experimental problems. Eqn. 14 is linear with five unknowns (K_L, K_{SL}, K_{DSL}, K_{GL} and K_{GLS}) which can be determined only by solution of a system of minimum five linear equations. This requires knowledge of the phase characteristics (V_L, A_{GL} and A_{LS}) for a minimum of five column packings prepared from identical LSP and solid support at different liquid loadings[14]. Each solute must be chromatographed on each packing at the required constant temperature, thus obtaining a set of integral retention effects, E. Hence, it is necessary to arrange a large number of precise chromatographic experiments, the basic problems being:

determination of minimal amount of LSP providing eqn. 14 is still valid and

exact determination of V_L, A_{GL} and A_{LS}

Experience with wide-pore supports with specific surface area 1–4 m^2 g^{-1} indicates that approximately 1% LSP is adequate to cover the surface with a layer thicker than one molecular diameter[26]. Obviously, such a packing could be the first in a series of packings with increased liquid loadings. For determination of V_L the so-called evaporation method[27,28] is recommended, since this requires minimal time and yields satisfactory accuracy. Usually, the BET technique or the continuous flow method is applicable for determining both A_{GL} and A_{LS}, the latter being considered here as the specific surface area of the support.

To avoid difficulties with area measurements some workers do not use such experimental data, especially when their interest is focused on the calculation of K_L only[6,11,29]. However, to identify the retention mechanisms in a GLC system it is obligatory to employ A_{GL} and A_{LS}. In this case, a modified BET technique offering considerable accuracy with small surface areas can be recommended[30], and has successfully been applied[26,31].

Mathematical problems. It is well known that solute retention in GLC systems is not always a result of mixed mechanisms. For some solutes there exist the so-called "pure" systems in which dissolution in the LSP is the unique mechanism of retention. Then, the retention equation takes the forms

$$E = V_L K_L \tag{15}$$

or

$$E = V_S K_S + V_B K_L \tag{16}$$

Since the application of eqn. 14 is meaningless in such cases, the first mathematical problem is to establish when it can be applied. In other words, it is necessary to examine whether solute retention results from mixed mechanisms or not.

Let us represent eqn. 5 in the form:

$$E = V_L \bar{K}_L + I_A \tag{17}$$

where

$$I_A = A_{GL} K_{GL} + A_{LS} K_{GLS}$$

Here $\bar{K}_L$ is considered as a mean value between K_S and K_L, so that $V_L \bar{K}_L = V_S K_S + V_B K_L$. It will be shown later that such an approximation is quite acceptable because $K_S \approx K_L$.

If adsorption effects contribute to the solute retention, *i.e.*, if $I_A > 0$ an E *vs.* V_L plot would give a curve convex to the abscissa for small V_L values. Then, applying regression analysis to eqn. 17 the latter can be tested for linear correlation between E and V_L. If precise experimental data are used the obtained straight line with slope $\bar{K}_L$, intercept I_A and correlation coefficient R will be the first step in estimating the presence or absence of mixed mechanisms. Obviously, if $\bar{K}_L > 0$, $R \approx 1$ and the absolute value of I_A does not exceed the standard error of estimation (S.E.E.) for E (*i.e.*, $|I_A| \leqslant$ S.E.E. > 0), it means $I_A = 0$. Consequently, the solute retention is due to the solution only (absorption mechanisms) and eqn. 17 has to be reduced to eqns. 15 or 16. If $\bar{K}_L > 0$, $R << 1$ and $I_A >$ S.E.E. > 0, it is to be accepted that retention results from mixed mechanisms. Then, the application of eqn. 14 is reasonable.

It could happen that $\bar{K}_L \leqslant 0$, $|R| < 1$ and $I_A >>$ S.E.E. > 0. The fact that I_A is too large indicates the action of at least one adsorption mechanism while the negative $\bar{K}_L$ means that absorption may not be absent. It is clear that a linear correlation on the basis of the non-linear eqn. 17 leads principally to a decreased slope, $\bar{K}_L$. Hence, if $\bar{K}_L$ is *a priori* small and I_A extremely large, an incorrect evaluation of $\bar{K}_L$ by regression analysis is quite possible. A recommended approach in such cases is to apply directly eqn. 14 that can give an unequivocal answer.

Briefly, to identify mixed retention mechanisms in a GLC system the application of eqn. 14 is required. It is necessary to compose a "suitable" system of linear equations. That is the second important mathematical problem.

Whether the system of equations will be a "suitable" one or not will depend on the selection of δ values in the particular equations. Expressions 13a and 13b show the dependence of δ on the relation between LSP film thickness, d, and structured layer effective thickness, d_S. Usually, d is given by the approximation

$$d = V_L / A_{LS} \tag{18}$$

while d_S is unknown. This makes impossible a direct compilation of the "suitable" system, but does not exclude the possibility of "finding" it among the set of several similar systems based on eqn. 14.

To that purpose, the first equation must be related to the serial packing containing minimal amount of LSP. Each successive equation will correspond to a more heavily loaded packing than the previous one and the last equation will correspond to the packing with greatest loading. Supposing d_S to be within the interval of d values for two "neighbouring" packings, the unequivocal selection of δ values in all equations will be facilitated. Since d_S could lie between the d values of any pair of "neighbouring" serial packings, a set of similar systems of equations can be obtained.

For example, with a series of p column packings where $p \geqslant 5$, following eqn. 18 we obtain for each packing:

$$d^i = V_L^i / A_{LS}^i \ (i = 1, 2, \ldots, m, n, \ldots, p) \tag{18a}$$

Supposing $d^m < d_S \leqslant d^n$ (where $n = m + 1$) and taking into account eqns. 13a, 13b and 14, the general form for similar systems can be written as follows:

$$\begin{array}{lllllll}
V_L^1 K_L + & V_L^1 K_{SL} + & 0 & + A_{GL}^1 K_{GL} & + A_{LS}^1 K_{GLS} & = E^1 \\
\vdots & & & & & \\
V_L^m K_L + & V_L^m K_{SL} + & 0 & + A_{GL}^m K_{GL} & + A_{LS}^m K_{GLS} & = E^m \\
V_L^n K_L + & 0 & + A_{LS}^n K_{DSL} & + A_{GL}^n K_{GL} & + A_{LS}^n K_{GLS} & = E^n \\
\vdots & & & & & \\
V_L^p K_L + & 0 & + A_{LS}^p K_{DSL} & + A_{GL}^p K_{GL} & + A_{LS}^p K_{GLS} & = E^p
\end{array} \tag{19}$$

Principally, the maximum number of these systems can be $p - 1$. However, in the case when d_S is supposed to fall into intervals $(d^1, d^2]$ or $(d^{p-1}, d^p]$ the corresponding systems contain linear dependent equations and cannot be solved. Hence, the real number of similar systems is limited to $p - 3$, among which one is the so-called "suitable" system. Its solution enables further identification of the retention mechanisms and the problem here reduces to discovery of this system. To do this, the solutions of all $p - 3$ systems must be obtained. Then, an appropriate test for K_i and d_S values in conformity with a logical system of criteria permits the unequivocal determination of the "suitable" system of equations.

Prior to considering the principles of the system of criteria, a note concerning the mathematical approach to solution of the similar systems is needed. Since the systems are approximate (because of the presence of experimentally determined quantities) their solutions are strongly influenced by the computational method employed. It was shown elsewhere[14] that methods of matrix algebra give the best results, the latter being least-squares averaged. Such an approach leads to possibly the best approximate solution.

System of criteria. In order to discover the "suitable" system of equations it is necessary to define the fundamental physical relationships which as criteria are to be obeyed by the unknowns in system 19. Failure to satisfy any one of these criteria is an indication of perturbation in the system of equations. Such a perturbation could be caused either by an incorrect assumption in the location of d_S within a certain interval $(d^m, d^n]$ or by the absence of some mechanism whose contribution to the solute retention is take into account through the corresponding term.

The fundamental criterion for testing the solution of system 19 is the inequality

$$K_L > 0 \tag{20}$$

whose physical sense is obvious. Further, a reliable K_L value must obey all equations of the system. Since the adsorption contributions to retention are smallest in case of the most heavily loaded, *i.e.*, p-th packing, it is clear that fulfilment of the additional criterion

$$K_L \leqslant E^p / V_L^p \tag{21}$$

will enable a reasonable K_L value to be obtained.

In the case of criteria 20 and 21, the relation

$$K_S > 0 \tag{22}$$

is relevant. The coefficient K_S is analogous to K_L and characterizes the partition properties of the structured LSP layer. Moreover, K_S and K_L appear to be approximately equal, thus the satisfaction of inequality 22 will be obligatory in case of a "suitable" system.

Significant for the correct evaluation of d_S are the criteria:

$$d_S > 0 \tag{23}$$

and

$$d^m < d_S \leqslant d^n \; (m = 2, 3, \ldots, p - 2; n = m + 1) \tag{24}$$

While inequality 23 reflects a clear physical requirement for d_S, the fulfilment of criterion 24 denotes a correct location of d_S within the interval considered. Hence, from a mathematical point of view this is a reliable indication for final discovery of the "suitable" system.

To continue with the identification procedure, the values of K_{GL} and K_{GLS} have to be examined. If they satisfy the inequalities

$$K_{GL} > 0 \tag{25}$$

and

$$K_{GLS} > 0 \tag{26}$$

the solute is retained by all possible sorption mechanisms and the corresponding K_i values obtained represent the solution of the so-called inverse retention problem.

If $K_{GL} < 0$ and/or $K_{GLS} < 0$, the system of equations is perturbed and the calculated K_S, K_L and d_S are non-reliable. Their correct values can be determined by solving the systems of equations based on properly reduced variants of eqn. 14. For example, if $K_{GL} > 0$ and $K_{GLS} < 0$, the appropriate equation will be

$$E = V_L K_L + \delta V_L K_{SL} + (1 - \delta) A_{LS} K_{DSL} + A_{GL} K_{GL} \tag{27}$$

while when $K_{GL} < 0$ and $K_{GLS} > 0$, it will be:

$$E = V_L K_L + \delta V_L K_{SL} + (1 - \delta) A_{LS} K_{DSL} + A_{LS} K_{GLS} \tag{28}$$

To compose the set of similar systems corresponding to any one of the above equations, the same procedure as for the system 19 must be followed. The fulfilment of criteria 20–24 is required in order to discover the "suitable" system of equations and if criterion 25 or 26 is also obeyed the identification procedure is completed.

In case of $K_S \leqslant 0$ for all similar systems of equations, the observed perturbation could be due to identical or nearly equal partition properties of both the structured and the bulk LSP layers with respect to the solute. This means that all the similar systems are inexpedient and others, based on the alternatively valid eqns. 2, 3 or 4, must be composed and solved.

An appropriate computer program incorporating the system of criteria was written to facilitate the identification procedure. Experimental data of Pecsok *et al.*[3] were used to test the program. Their experiments concerned nineteen solutes with different functional groups chromatographed at 25°C in the system β,β'-thiodipropionitrile (TDPN)–firebrick (42–60 mesh). Unfortunately, data for V_L, A_{GL} and A_{LS} were recalculated from the amount of LSP and those for A_{GL} were interpolated from a plot of A_{GL} *vs.* LSP percentage. Results of the program verification are shown in Table I. They will be discussed later together with the results of the present experiments.

EXPERIMENTAL

Materials

Celite 545 (BDH, Poole, Great Britain), 60–80 mesh, with specific surface area 1.92 $m^2\ g^{-1}$ was used as solid support. Non-polar Apiezon M and moderately polar Carbowax 4000 (both from Carlo Erba, Milan, Italy) were the liquid stationary phases.

Twelve individual solutes, *n*-octane, cyclohexane, benzene, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanone, 4-methyl-2-pentanone, chlorobenzene and thiophene, were selected for the chromatographic experiments. Except for cyclohexane, chlorobenzene and thiophene (E. Merck, Darmstadt, G.F.R.), all of 99% purity, the other solutes (Poly Science Corporation, Niles, IL, U.S.A.) were of minimum 99.5% purity. Pure hydrogen (99,95%) dried with molecular sieve 5A was used as carrier gas.

Apparatus

A Fractovap Model B gas chromatograph (Carlo Erba, Milan, Italy) with thermistor detector was employed. The instrument was home-modified to ensure constant column and detector temperatures within ±0.02°C. Stainless-steel columns were 2 m × 3 mm I.D. A 1-mV Model 194 electronic recorder (Honeywell, Newhouse, Great Britain) was used for registration of chromatographic peaks.

Procedures

Initially, a series of six packings containing different LSP amounts within 1–18% was prepared for both Apiezon M and Carbowax 4000. In addition, a new series of four packings with Carbowax 4000 whose amount varied within 1–5% was examined in order to verify the GLC sorption model. To prepare each packing a certain amount of support was thoroughly dried at 150°C under vacuum at 2 × 10^{-4} Torr for 4 h. The LSP deposition was accomplished from dilute solution in analytical grade solvents using a rotating vacuum-evaporator. Conditioning at 150°C for 16 h was carried out for each column.

The LSP amount in the packings was determined after completion of the chromatographic experiments. An accuracy of ±0.05–±0.1% was achieved by means of the evaporation method[28]. Using the method of Bliznakov *et al.*[30], LSP specific surface areas were measured with a reproducibility in three determinations within ±1.5%.

All chromatographic experiments were carried out at 70°C. On-column injections of solutes were made with a 1-μl Hamilton microsyringe. For each solute, three to five samples of different amounts were chromatographed on all serial packings.

In order to ensure exact retention time determinations the recorder a.c. supply was additionally stabilized and the chart speed was suitably chosen for each solute. The reproducibility achieved was within ±0.06%, allowing accurate determination of integral retention effects within ±0.2%.

RESULTS AND DISCUSSION

Partial partition coefficients of nineteen solutes in the system TDPN–firebrick calculated at 25°C are presented in Table I. This system was chosen for verification of

TABLE I

CALCULATED PARTIAL PARTITION COEFFICIENTS FOR IDENTIFIED RETENTION MECHANISMS ON β,β'-THIODIPROPIONITRILE–FIREBRICK AT 25°C ACCORDING TO EXPERIMENTAL DATA[3]

Solute	K_S	K_L	K_{GL}	K_{GLS}	K_{SA}	D^*_{SL}	d_S
	—	—	*(10^{-6} cm)*	*(10^{-6} cm)*	*(10^{-6} cm)*	*(%)*	*(10^{-6} cm)*
n-Hexane	9.3	9.2	64.4			(0.8)	
2-Methylpentane	6.7	6.7	53.0			(−0.9)	
3-Methylpentane	8.7	8.7	52.8			(−0.7)	
2,3-Dimethylbutane	7.4	7.4	48.2			(−0.7)	
n-Heptane	20.7	20.6	188			0.5	
2,2,4-Trimethylpentane	17.2	17.3	233			−0.6	
Cyclopentane	16.2	16.1	21.0			0.6	
Cyclohexane	32.5	32.3	58.3			0.6	
Methylcyclopentane	21.2	21.3	53.0			(−0.9)	
Hexene-1	20.2	14.5	73.6			39.3	1.9
Cyclohexene	94.2	85.8	72.9			9.8	2.0
Benzene	441	421	116			4.8	2.4
Diethyl ether	26.9	31.9	56.4			−15.7	2.0
n-Butyl ethyl ether	99.9	56.0	386			78.4	2.8
Propionaldehyde	299	246	109			21.4	2.3
Isobutyraldehyde	270	317	91.4	137	0.51	−14.7	2.1
Ethyl acetate	465	442	481			5.2	1.9
Acetone	427	447	247			− 4.3	2.0
Methyl ethyl ketone	769	808	526			− 4.9	1.9

* $D_{SL} = 10^2(K_S - K_L)/K_L$. All values in parentheses were obtained from unrounded K_S and K_L respectively, while the others were from those values listed in the table.

the computer program, *i.e.*, of the identification procedure described. In agreement with the observations of Pecsok *et al.*[3] it was found that paraffins and cycloparaffins are retained by both dissolution in LSP and adsorption at the gas–liquid interface. For these solutes the absolute values, $|D_{SL}|$, of the deviations of K_S from K_L were less than 1%. Simultaneously, the d_S values obtained were always greater than the LSP film thickness in the most heavily loaded packing, failing to satisfy criterion 24. In accordance with the accuracy of the published data, it was decided to neglect D_{SL} values within ±1% and to consider $K_S = K_L$. Nevertheless, both coefficients are presented in Table I, while the incorrect d_S values are omitted in order to indicate the perturbation. Hence, both the structured and the bulk LSP layers have equal partition properties towards the hydrocarbons considered.

On the contrary, hexene-1, cyclohexene and benzene are retained by means of two absorption and one adsorption mechanisms. Their $|D_{SL}|$ values are large, varying within 5–39%. Without exception $K_S > K_L$, thus indicating the more intensive interactions in the structured layer. The third retention mechanism is connected with gas–liquid interfacial adsorption of the solutes, their K_{GL} values being nearly equal to those obtained by Pecsok *et al.*[3].

It is of particular interest to consider the behaviour of the polar oxygen-containing compounds. Except for isobutyraldehyde, all solutes are retained by means of dissolution in both layers as well as by adsorption at the gas–liquid interface. Liquid–solid adsorption is observed only with isobutyraldehyde and could be explained in terms of eventual hydrogen bonding of the α-H atom, due to the so-called hyperconjugation effect. In all cases K_S clearly deviates from K_L, while K_{GL} values remain approximately the same as reported by Pecsok *et al.*[3].

A noticeable difference is observed in K_S to K_L ratio for the pairs propionaldehyde–isobutyraldehyde and diethyl ether–*n*-butyl ethyl ether. The explanation can be found in the difference between both the steric factors (for the first pair) and the molecular polarizabilities (for the second), which affect the solute interactions with the LSP.

Further, calculated d_S values are presented in Table I for those solutes retained (among others) by two absorption mechanisms. Principally, the effective thickness of the structured layer does not depend on the solute nature. As shown the d_S values are of similar magnitude, the mean value together with the standard deviation being $(2.1 \pm 0.3) \times 10^{-6}$ cm. The observed range is due to the absence of original experimental data for V_L, A_{GL} and A_{LS}, as mentioned above. Nevertheless, these results allow a positive estimation of both the identification procedure and the corresponding computer program.

To demonstrate the ability of the proposed procedure to solve problems of mixed retention mechanisms under complicated conditions, the following experiments were carried out. Two conventional GLC systems were chosen under conditions of reduced adsorption contributions to the retention. Small specific surface area of the support and relatively high temperature were employed, thus complications with the identification were expected.

Plots of A_{LS} and A_{GL} *vs.* V_L for both Apiezon–Celite and Carbowax–Celite systems are shown in Fig. 1a and 1b, respectively. No significant dependence of A_{GL} on the nature of the LSP is observed, while A_{LS} varies because of difference in the LSP density. The final results of application of the identification procedure will be considered in detail separately for each system.

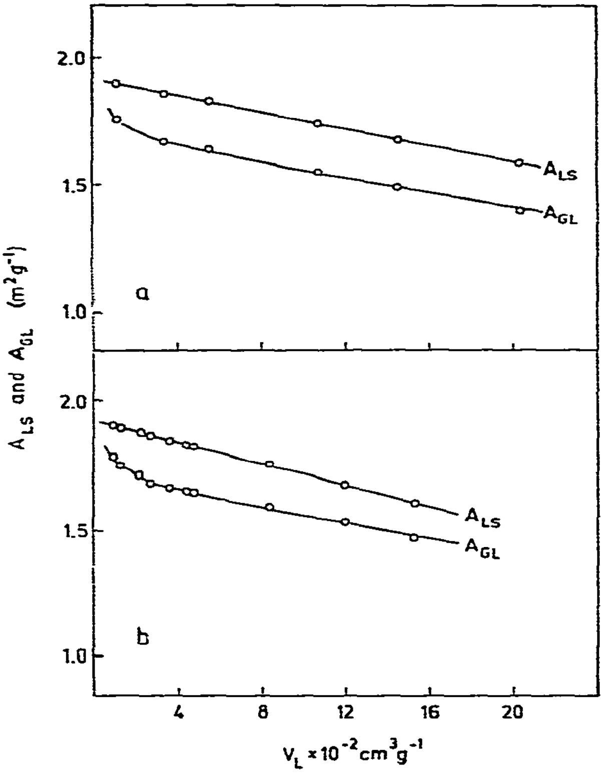

Fig. 1. Dependence of liquid–solid and gas–liquid interfacial specific surface areas on liquid stationary phase volume per gram of packing: a, Apiezon M–Celite 545; b, Carbowax 4000–Celite 545 (systems A and B).

System Apiezon M–Celite 545

As reported in Table II, *n*-octane, cyclohexane, benzene, chlorobenzene and thiophene are retained only by dissolution in the LSP. These solutes have large K_L values and show no tendency to adsorb at the gas–liquid or liquid–solid interfaces. In the case of benzene this behaviour is contradictory to the results of Komaita *et al.*[32], who found adsorption at a squalane–alumina interface. However, the present result can be explained in terms of the substantial difference in the supports (Celite *vs.* alumina) as well as in the liquid phases employed (Apiezone *vs.* squalane). Also it is known that the non-polar Apiezon M contains a definite amount of polymeric methyl phenyl ethers[33], which adsorb preferably on the support surface, thus invalidating the competition of solutes such as benzene, chlorobenzene and thiophene.

On the contrary, alcohols and ketones show relatively poor solubility in the LSP and a definite propensity towards liquid–solid adsorption. This behaviour is in agreement with some previous observations[5,34], but contradicts others, according to which alcohols and ketones adsorb also at the gas–liquid interface when saturated hydrocarbons are used as liquid phases[10,11]. In the present investigation no gas–liquid adsorption was observed. As pointed out by Conder[13], this could indicate absence of infite dilution for the solutes chromatographed. However, it seems more

TABLE II

CALCULATED PARTIAL PARTITION COEFFICIENTS FOR IDENTIFIED RETENTION MECHANISMS ON SYSTEM APIEZON M-CELITE [illegible] AT 70°C

Solute	K_L	K_{GLS} $(\cdot 10^{-6}\ cm)$	K_{SA} $(\cdot 10^{-6}\ cm)$
n-Octane	356.7		
Cyclohexane	117.5		
Benzene	107.5		
1-Propanol	24.18	78.5	3.25
2-Propanol	10.97	24.0	2.19
1-Butanol	57.47	245	4.26
2-Butanol	33.26	88.2	2.65
2-Methyl-1-propanol	45.92	145	3.16
2-Butanone	34.50	19.5	0.57
4-Methyl-2-pentanone	131.6	118	0.90
Chlorobenzene	541.9		
Thiophene	116.0		

reasonable that gas–liquid adsorption does not contribute to the retention of alcohols and ketones because of the higher temperature of the present experiments (70 *vs.* 30 or 40°C for investigations discussed by Conder).

K_S values are not presented in Table II because it was found $K_S < 0$ for all solutes. This fact, as already discussed, demonstrates the approximately equal partition properties of both structured and bulk LSP layers, so that K_S and K_L cannot be distinguished. A cursory inspection of the K_{SA} values indicates that alcohols adsorb more strongly than ketones. This parallels the hydrogen-bonding tendency of the solutes considered, and is responsible for their adsorption on the support surface. The more pronounced adsorption of primary alcohols in comparison with secondary ones is due to the well known steric factors.

Systems Carbowax 4000–Celite 545

As pointed out above, a series of six packings loaded within 1–18% was prepared (system A). The results obtained by application of the identification procedure are presented in Table III. *n*-Octane and cyclohexane were retained by means of both dissolution in LSP and adsorption at the gas–liquid interface. In fact K_S and K_L were identical, their deviations, $|D_{SL}|$, being smaller than 0.5%. Calculated d_S values were greater than the LSP thickness in the most heavily loaded packing of the series. In other words the behaviour of these hydrocarbons was the same as that on TDPN–firebrick.

All other solutes were retained by means of two absorption and one adsorption mechanisms (at the gas–liquid interface). No liquid–solid adsorption was identified. A relatively small but clear difference between K_S and K_L was observed for each of these solutes. The corresponding $|D_{SL}|$ values were not so large as in the system TDPN–firebrick, but they were essentially greater than 0.5%. In accordance with the accuracy of the present experimental data, it was accepted that there was a difference between K_S and K_L only if $|D_{SL}| > 0.5\%$. It is seen in the table that $|D_{SL}| < 2\%$, thus indicating the small difference in the partition properties of both LSP layers at 70°C.

TABLE III

CALCULATED PARTIAL PARTITION COEFFICIENTS FOR IDENTIFIED RETENTION MECHANISMS IN SYSTEM A AND ESTIMATED DEVIATIONS OF K_S AND K_{GL} IN COMPARISON WITH SYSTEM B

All experiments at 70°C. Both A and B contain Carbowax 4000–Celite 545 packings in different loadings: A within 1–18% and B within 1–5%.

Solute	*System A*				*Comparison with system B*		
	K_S	K_L	K_{GL} ($\cdot 10^{-6}$ *cm*)	d_S ($\cdot 10^{-6}$ *cm*)	D_{SL} (%)	D_S (%)	D_{GL} (%)
n-Octane	46.03	45.88	16.8		0.33	0.57	−1.2
Cyclohexane	28.81	28.69	4.21		0.42	0.81	−1.8
Benzene	138.5	137.2	8.50	2.7	0.95	−0.52	1.5
1-Propanol	246.1	242.7	31.7	2.9	1.40	0.34	0.97
2-Propanol	114.3	116.2	19.4	2.8	−1.64	−0.44	1.3
1-Butanol	512.8	505.5	45.0	2.9	1.44	0.31	−0.74
2-Butanol	220.6	224.6	26.1	2.7	−1.78	−0.29	1.1
2-Methyl-1-propanol	353.6	350.7	38.6	2.8	0.83	0.18	−1.0
2-Butanone	103.4	101.9	11.9	2.9	1.47	−0.37	1.7
4-Methyl-2-pentanone	206.1	210.1	20.5	2.8	−1.90	−0.33	1.4
Chlorobenzene	830.7	825.6	16.2	3.0	0.62	0.31	−1.4
Thiophene	221.6	220.0	7.28	2.9	0.73	−0.26	−1.9

Because of the high temperature at which the solutes were chromatographed, their gas–liquid interfacial adsorption was weak, reflected in the relatively small K_{GL} values. Nevertheless, this adsorption mechanism was clearly identified without any complications.

In contrast to the system TDPN–firebrick, calculated d_S values for system A show a noticeable constancy with small standard deviation: $(2.8 \pm 0.1) \times 10^{-6}$ cm. This fact could be considered as evidence for a properly developed GLC sorption model. However, for final verification, an additional Carbowax–Celite system (system B) was examined under the same chromatographic conditions.

Four packings loaded within 1–5% were prepared in order to obtain only a structured layer coating on the support. This means that the LSP film thickness in the most heavily loaded packing should not exceed the calculated d_S middle value. If the sorption model is adequate the integral retention of solutes should be controlled by the equation

$$E = V_S K_S + A_{GL} K_{GL}$$

where V_S is now equal to the total LSP volume per gram of packing. A solution of the corresponding system of four linear equations should give K_S and K_{GL} values nearly equal to those obtained for system A.

In Table III the D_S and D_{GL} deviations are calculated as follows:

$$D_i = 10^2(K_i^A - K_i^B)/0.5(K_i^A + K_i^B)$$

where the superscripts A and B refer to the corresponding chromatographic systems, while i indicates S or GL respectively. Except for *n*-octane, cyclohexane and benzene, $|D_S|$ is less than 0.5%, thus being also smaller than the respective $|D_{SL}|$. In fact the K_S^B values are identical with K_S^A, while the differences between K_S^A and K_L^A are obviously greater. Coincidence of K_{GL} values for the solutes in both systems is also observed, so that $|D_{GL}| < 2\%$. These observations agree well with the sorption model, and confirm its reliability as a basis of the identification procedure developed. The latter appears to be an useful tool allowing one to solve problems of mixed retention mechanisms in GLC systems even under complex conditions.

As mentioned above, a correct identification of the retention mechanisms leads immediately to solution of the inverse retention problem. The partial partition coefficients obtained permit evaluation of the contributions of these mechanisms to the integral solute retention. Results for the systems Apiezon–Celite and Carbowax–Celite (system A) are presented in Table IV. For each solute the partial retention effects (PRE) are indicated in accordance with the corresponding retention mechanisms identified on the packings of both systems. All calculated values are percentages, thus allowing comparison of relative contributions to solute retention.

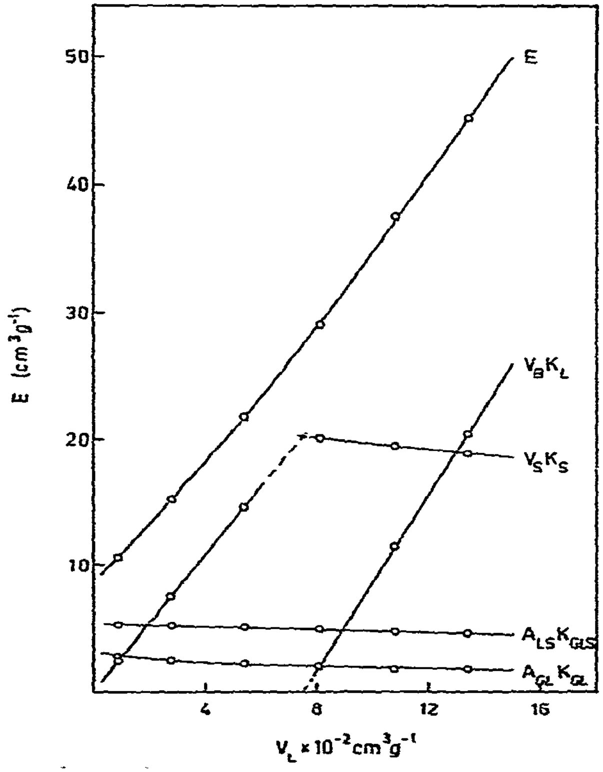

Fig. 2. Variation of partial retention effects and integral retention with liquid stationary phase volume per gram of packing for isobutyraldehyde on β,β'-thiodipropionitrile–firebrick at 25°C.

TABLE IV

RELATIVE CONTRIBUTIONS OF PARTIAL RETENTION EFFECTS (PRE) TO INTEGRAL RETENTION IN VARIOUS PACKINGS OF SYSTEMS APIEZON M–CELITE 545 AND CARBOWAX 4000–CELITE 545 (SYSTEM A), BOTH AT 70°C

Solute	*Apiezon M–Celite 545*							*Carbowax 4000–Celite 545 (system A)*						
	PRE	*% LSP*						*PRE*	*% LSP*					
		0.9899	*2.880*	*4.729*	*9.119*	*12.30*	*17.27*		*1.000*	*2.921*	*4.771*	*9.090*	*13.05*	*16.67*
n-Octane	$V_{\rm L}K_{\rm L}$	100.0	100.0	100.0	100.0	100.0	100.0	$V_{\rm L}K_{\rm L}$	58.3	81.5	87.8	93.4	95.5	96.6
								$A_{\rm GL}K_{\rm GL}$	41.7	18.5	12.2	6.6	4.5	3.4
Cyclohexane	$V_{\rm L}K_{\rm L}$	100.0	100.0	100.0	100.0	100.0	100.0	$V_{\rm L}K_{\rm L}$	76.5	91.7	94.7	97.2	98.3	98.7
								$A_{\rm GL}K_{\rm GL}$	23.5	8.3	5.3	2.8	1.7	1.3
Benzene	$V_{\rm L}K_{\rm L}$	100.0	100.0	100.0	100.0	100.0	100.0	$V_{\rm S}K_{\rm S}$	89.4	96.4	97.7	56.2	37.5	28.2
								$V_{\rm u}K_{\rm L}$				42.7	61.7	71.3
								$A_{\rm GL}K_{\rm GL}$	10.6	3.6	2.3	1.1	0.8	0.5
1-Propanol	$V_{\rm L}K_{\rm L}$	15.8	36.0	48.4	65.5	72.6	79.7	$V_{\rm S}K_{\rm S}$	80.1	92.6	95.4	59.7	40.1	30.2
	$A_{\rm LS}K_{\rm GLS}$	84.2	64.0	51.6	34.5	27.4	20.3	$V_{\rm u}K_{\rm L}$				37.9	58.2	68.5
								$A_{\rm GL}K_{\rm GL}$	19.9	7.4	4.6	2.4	1.7	1.3
2-Propanol	$V_{\rm L}K_{\rm L}$	22.0	45.1	58.1	73.8	79.9	85.5	$V_{\rm S}K_{\rm S}$	75.0	90.3	94.0	56.5	37.8	28.5
	$A_{\rm LS}K_{\rm GLS}$	78.0	54.9	41.9	26.2	20.1	14.5	$V_{\rm u}K_{\rm L}$				40.4	60.1	69.9
								$A_{\rm GL}K_{\rm GL}$	25.0	9.7	6.0	3.1	2.1	1.6

1-Butanol	$V_{\mathrm{L}}K_{\mathrm{L}}$	12.6	30.0	41.7	59.1	66.9	75.0	$V_{\mathrm{S}}K_{\mathrm{S}}$	85.5	94.8	96.8	60.2	40.4	30.4
	$A_{\mathrm{LS}}K_{\mathrm{GLS}}$	87.4	70.0	58.3	40.9	33.1	25.0	$V_{\mathrm{B}}K_{\mathrm{L}}$				38.2	58.5	68.8
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	14.5	5.2	3.2	1.6	1.1	0.8
2-Butanol	$V_{\mathrm{L}}K_{\mathrm{L}}$	18.8	40.8	53.5	70.0	76.5	82.9	$V_{\mathrm{S}}K_{\mathrm{S}}$	81.5	93.1	95.7	55.0	36.7	27.6
	$A_{\mathrm{LS}}K_{\mathrm{GLS}}$	81.2	59.2	46.5	30.0	23.5	17.1	$V_{\mathrm{B}}K_{\mathrm{L}}$				42.8	61.8	71.3
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	18.5	6.9	4.3	2.2	1.5	1.1
2-Methyl-1-propanol	$V_{\mathrm{L}}K_{\mathrm{L}}$	16.1	36.6	48.9	66.1	73.1	80.2	$V_{\mathrm{S}}K_{\mathrm{S}}$	82.2	93.5	96.0	57.6	38.6	29.0
	$A_{\mathrm{LS}}K_{\mathrm{GLS}}$	83.9	63.4	51.1	33.9	26.9	19.8	$V_{\mathrm{B}}K_{\mathrm{L}}$				40.4	60.0	69.9
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	17.8	6.5	4.0	2.0	1.4	1.1
2-Butanone	$V_{\mathrm{L}}K_{\mathrm{L}}$	51.9	76.5	84.2	91.6	93.8	95.8	$V_{\mathrm{S}}K_{\mathrm{S}}$	81.9	93.3	95.8	59.9	40.2	30.3
	$A_{\mathrm{LS}}K_{\mathrm{GLS}}$	48.1	23.5	15.8	8.4	6.2	4.2	$V_{\mathrm{B}}K_{\mathrm{L}}$				38.0	58.3	68.6
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	18.1	6.7	4.2	2.1	1.5	1.1
4-Methyl-2-pentanone	$V_{\mathrm{L}}K_{\mathrm{L}}$	40.7	67.1	77.3	87.4	90.6	93.5	$V_{\mathrm{S}}K_{\mathrm{S}}$	84.0	94.2	96.4	57.2	38.1	28.6
	$A_{\mathrm{LS}}K_{\mathrm{GLS}}$	59.3	32.9	22.7	12.6	9.4	6.5	$V_{\mathrm{B}}K_{\mathrm{L}}$				40.9	60.6	70.5
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	16.0	5.8	3.6	1.9	1.3	0.9
Chloro-benzene	$V_{\mathrm{L}}K_{\mathrm{L}}$	100.0	100.0	100.0	100.0	100.0	100.0	$V_{\mathrm{S}}K_{\mathrm{S}}$	96.3	98.8	99.3	62.8	41.8	31.4
								$V_{\mathrm{B}}K_{\mathrm{L}}$				36.8	57.9	68.4
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	3.7	1.2	0.7	0.4	0.3	0.2
Thiophene	$V_{\mathrm{L}}K_{\mathrm{L}}$	100.0	100.0	100.0	100.0	100.0	100.0	$V_{\mathrm{S}}K_{\mathrm{S}}$	94.0	98.0	98.8	60.6	40.5	30.4
								$V_{\mathrm{B}}K_{\mathrm{L}}$				38.7	59.1	69.3
								$A_{\mathrm{GL}}K_{\mathrm{GL}}$	6.0	2.0	1.2	0.7	0.4	0.3

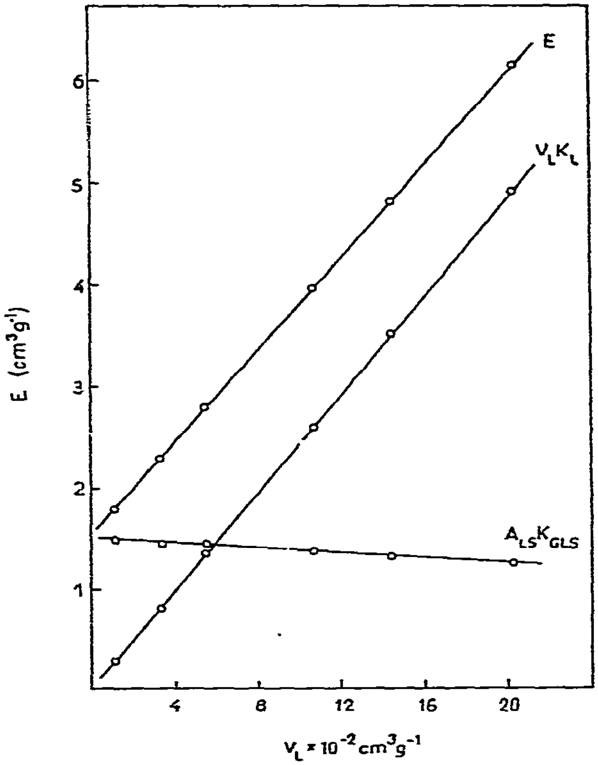

Fig. 3. Variation of partial retention effects and integral retention with liquid stationary phase volume per gram of packing for 1-propanol on Apiezon M–Celite 545 at 70°C.

It follows from Table IV that liquid–solid adsorption of polar solutes contributes to their integral retention in the Apiezon–Celite system. Even in the case of the most heavily loaded packing the adsorption contributions vary between 4 and 25%. On the contrary, in the Carbowax–Celite system the gas–liquid adsorption contributes moderately to the retention of all solutes, decreasing rapidly with increasing LSP loading. Considerable contributions varying between 3 and 42% are observed only in the packing with smallest amount of LSP. The most pronounced retention effect is due to dissolution in both the structured and/or the bulk LSP layers.

To demonstrate the variation of integral retention, E, and that of PRE with V_L, plots are presented in Figs. 2–4 for selected solutes. Fig. 2 shows absolute contributions of all mechanisms to the integral retention of isobutyraldehyde in the system TDPN–firebrick. As expected, with increasing V_L the V_SK_S contribution increases until the structured layer achieves its maximum thickness, d_S. After the appearance of the bulk LSP layer, V_SK_S decreases slowly since $V_S = A_{LS}d_S$, where A_{LS} decreases with increasing V_L and d_S remains constant. Apparently, the dependence of V_SK_S on V_L can be represented by means of two straight lines, illustrating the variation of this contribution before and after completion of the structured layer respectively. The intersection of both lines corresponds to that V_L value at which formation of the bulk

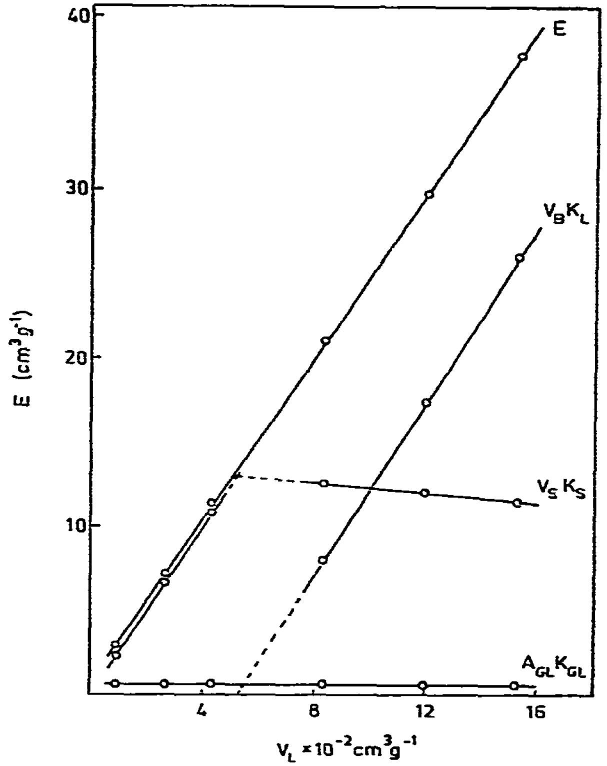

Fig. 4. Variation of partial retention effects and integral retention with liquid stationary phase volume per gram of packing for 1-propanol on Carbowax 4000–Celite 545 (system A) at 70°C.

layer starts, *i.e.*, this point is the origin of the V_BK_L retention contribution. Simultaneously, the contributions $A_{GL}K_{GL}$ and $A_{LS}K_{GLS}$ parallel the corresponding dependences of A_{GL} and A_{LS} on V_L. Regardless of the small K_{SA} for isobutyraldehyde, its liquid–solid adsorption contributes more to the integral retention than the adsorption at the gas–liquid interface.

Figs. 3 and 4 show the behaviour of PRE for 1-propanol on Apiezon–Celite and Carbowax–Celite respectively. Since in the former system $K_S = K_L$ the contribution of the unique absorption mechanism is indicated in Fig. 3 as V_LK_L. As discussed above, the $A_{LS}K_{GLS}$ contribution decreases with increasing V_L, remaining as a considerable part of the integral retention. On the other hand, the situation on Carbowax–Celite (system A) is quite different resulting in two absorption mechanisms. Fig. 4 shows that for 1-propanol V_SK_S and V_BK_L follow similar dependences on V_L to those in Fig. 2. Moreover, the contribution of $A_{GL}K_{GLS}$ is essentially small, while that of $A_{LS}K_{GLS}$ is completely absent.

In conclusion, the introduced GLC sorption model has allowed a reliable procedure to be developed which needs no investigator's intuition for identification of the retention mechanisms. The application of this procedure leads immediately to solution of the inverse retention problem, resulting in a set of precisely calculated partition coefficients. The latter permits one to evaluate absolute and/or relative contributions of identified mechanisms to the integral solute retention.

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