# CHANGES OCCURRING WITH THE IMMOBILE LIQUID PHASE IN GAS–LIQUID CHROMATOGRAPHY

## II. THE EFFECT ON RETENTION VOLUMES

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KELLER, BATE, COSTA AND FORMAN[1] reviewed the literature dealing with transformations which occur with the immobile liquid phase during gas–liquid chromatography and experimentally examined changes in retention volumes as columns were used either for prolonged periods of time or at conditions outside of those recommended for the partitioning liquids concerned. The actual distribution of liquid was determined by cutting the column into short sections and extracting the partitioner in each section. Rates of loss of partitioner from the support were determined by heating in air. Two kinds of discontinuities in the column were recognized. One was a discontinuity of the nature of the partitioner which could arise from complete evaporation of the immobile liquid leaving exposed support at the inlet of the column. Solutes might experience adsorption on the support in this region followed by solution in the liquid partitioner farther along the column. With the alcohols, two peaks could be produced from a single species if the solute had been preceded by another alcohol. This was explained by adsorption of the first alcohol followed by its displacement by the second alcohol. The second discontinuity was one of concentration of the immobile phase on the support. This was explained by assuming that the partitioner partially evaporated from the support at the inlet end on encountering unsaturated carrier. As soon as the carrier became saturated and evaporation ceased the concentration of the immobile phase rose from a low value to that of the original packing employed. There was no change in the mechanism by which solutes were retained but instead there was a very sharp change in partitioner concentration. Experimentally it was found that the semi-logarithmic plots of retention volumes *vs.* the number of carbon atoms for the homologous series of primary alkyl alcohols, as determined on a column subjected to periods of heating at elevated temperature between chromatograms, showed a change in the intercept of the line but no change in slope when tested at the 5 % significance level. It is the purpose of this communication to investigate this result more fully from a theoretical point of view. The problem is relevant to column conditioning prior to use, *e.g.*, heating while carrier is passed through the column, which seems to improve its performance, and the lifetime of a column where it seems that the performance deteriorates. Presumably some changes within the column are completed in a short period of time while others occur continuously.

Direct observation of such changes is destructive, *e.g.*, cutting the column into sections and examining the packing in each section. Hence indirect observations, *e.g.*, changes in chromatographic behavior or column bleeding, are preferred if the column is to be preserved. Here we examine the kinds of changes which may occur and attempt to relate these to changes in chromatographic behavior through an appeal to theory. We also raise the question as to whether it is meaningful to describe the packing material in terms of percentage liquid placed on the support if during the conditioning process or use of the column both of these change to something new and unknown.

## CLASSIFICATION OF CHANGES

Changes occurring with the immobile phase can be physical or chemical. Physical changes may be classified as: (1) Microscopic. There is a redistribution of the liquid among the capillary spaces of the support and at the contact points of the particles which minimizes the surface free energy and eventually gives a uniform free energy over the entire liquid surface. This is probably the primary process which takes place during column conditioning and can only be achieved with the column packed. This initial microscopic equilibration necessitates a preconditioning period. Once accomplished, it is complete unless the packing is physically disturbed. (2) Macroscopic. Unless the carrier gas is presaturated with partitioner before entering the column, partitioner will evaporate from the packing to alter the total quantity of liquid present and its distribution on the column. Experimentally this loss and redistribution occurs in the early sections of the column[1]. Such changes will depend upon the nature of the partitioner, its homogeneity, the operating temperature, and the volume and flowrate of the carrier passed through the column. If the liquid is heterogeneous, the rate of loss of each component will depend upon the temperature and the ideality of the solution. If the column is operated at several temperatures several discontinuities may be introduced into the column as has been shown with polyethylene glycol[1].

We classify as chemical changes any transformation which alters the specific interactions of the solutes with the immobile liquid or partitioner–support combination by virtue of a change in properties of the liquid or its distribution. Such changes may be classified as: (1) Evaporation of the partitioner to expose the support or to enhance its participation in retention. (2) Changes due to the heterogeneity of the liquid applied to the support. A loss of a component or a contaminant of the liquid may leave behind a partitioner of properties different from the original liquid. (3) Chemical reaction with contaminants present in the liquid and/or carrier gas, *e.g.*, oxidation, catalyzed decomposition, esterification, etc. (4) Chemical changes inherent with the liquid, *e.g.*, polymerization, pyrolysis, dehydration, etc.

It is conceivable that a chemical change might not appreciably affect solute–partitioner interactions but so change the physical properties of the immobile liquid as to seriously alter the kinetic steps involved and change the range of carrier velocities in which the near-equilibrium approximation is valid. An example would be an increase in viscosity of the liquid phase. If, indeed, diffusion through the partitioning liquid is the rate controlling step, then this change is particularly important with regard to column efficiency.

## THEORY

As our model, we assume that the chromatographic tube is packed with an impermeable solid which is coated with a liquid of cross-sectional area $A_L$. The solute molecules partition themselves between this immobile liquid and the flowing gas phase of cross-sectional area $A_M$. There is no adsorption of solute by the support nor at the gas–liquid interface, the chemical properties of the immobile liquid are independent of the amount applied, and the surface free energy of the liquid has reached its equilibrium value and is uniform over the entire liquid surface. This model is most closely approximated by columns packed with spherical glass beads covered with a thin liquid film. The definition of $R$ as the fraction of solute molecules in the mobile phase leads to the expression:

$$R = \frac{1}{1 + \alpha(A_L/A_M)} \tag{1}$$

where $\alpha$ is the ratio of the concentration of solute in the stationary phase to that in the mobile phase, *i.e.*, the distribution coefficient. $R$ is also the distance moved by the point of maximum concentration of a particular solute relative to that of the front of the mobile fluid phase ($R_F$) subject to the limitations discussed by GIDDINGS AND KELLER[2]. Physical changes would bring about a change in $(A_L/A_M)$ leaving $\alpha$ constant while strictly chemical changes not involving column bleeding would bring about a change in $\alpha$ leaving $(A_L/A_M)$ constant.

The retention time of a solute in a column[3] is:

$$t = \int_0^L \mathrm{d}x/u \tag{2}$$

where $L$ is the length of the column, $\mathrm{d}x$ the element of length, and $u$ the average velocity of the vapor. Since $u = Rv$ where $v$ is the average velocity of the mobile carrier gas, then:

$$t_i = \int_0^L \mathrm{d}x/R_i v \tag{3}$$

where the subscript refers to the $i$th component of the mixture being chromatographed. This expression neglects extra-column contributions to $t_i$, *e.g.*, sample injector and detector designs, etc. Here we assume $R_i$ to be independent of the column length and flowrate. This is not generally true since changes in composition of the liquid, non-linearity in the retention isotherm, and a non-equilibrium situation associated with high flow velocities may cause $R_i$ to depend strongly on the distance of the solute along the column. It is expedient to make this assumption which is in part justified by the fact that the data reported in the carlier publication were collected at moderate operating conditions. Then, using the flowrate to convert to retention volumes:

$$V_i = \frac{2A_M L}{3R_i} \frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \tag{4}$$

where $P_o$ is the pressure of the carrier gas at the column outlet and $P_i$ is the pressure at the inlet. Substituting for $R_i$ and letting:

$$K_p = \frac{2}{3}\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1}$$

$$V_i = LK_pA_M + \alpha_i LK_pA_L \tag{5}$$

The partition coefficient, $\alpha$, is zero for an unretained solute. Assuming this to be true of air, the first term is the retention volume of the air peak. Two practices are common to the literature. Eqn. (5) is valid where retention times are measured from the instant of sample introduction into the column. If one measures retention times from the air peak, then:

$$V_i^a = \alpha_i LK_pA_L \tag{6}$$

as was done by KELLER and coworkers[1]. These volumes may be further reduced to standard temperature and pressure.

It will become increasingly more apparent that eqn. (4) and all subsequent expressions involve average values. This is permissible only in the absence of large velocity gradients and is particularly important here where the column is non-uniform with regard to the distribution of partitioner. For example, with a large velocity gradient each solute would spend a far longer period of time at the inlet end of the column in contact with the partitioner distribution particular to this region than at the outlet end, where the flow velocity is great. The solutes would encounter a partitioner distribution in time which differs from the measurable distribution in distance along the column. Average values based on the spatial distribution would be inappropriate with large $P_i/P_o$ ratios. As Table I shows, $K_p$ values did not differ greatly from unity and the velocity gradient should not have been very large.

The partition coefficient, $\alpha$, is an equilibrium constant related thermodynamically to the difference in chemical potential, $\Delta\mu^\circ$, of solute in the stationary phase and solute in the mobile phase, both at some standard concentration[2]. For ideal behavior:

$$\alpha = e^{-\Delta\mu^\circ/RT} \tag{7}$$

Substituting in eqn. (6) and expressing the result in logarithmic form:

$$\ln V_i^a = \ln A_L K_p L - \frac{\Delta\mu^\circ}{RT} \tag{8}$$

The difference in chemical potential can be expressed as a linear combination of terms descriptive of the groups present in the molecule. For a homologous series:

$$\Delta\mu^\circ = n_{CH_2}\Delta\mu^\circ_{CH_2} + \sum\Delta\mu_j^\circ \tag{9}$$

where $\Delta\mu^\circ_{CH_2}$ is characteristic of the methylene group while $\Delta\mu_j^\circ$ refers to other kinds of groups (methyl, hydroxyl, etc.). Eqn. (8) becomes:

$$\ln V_i^a = \ln A_L K_p L - \frac{\sum\Delta\mu_j^\circ}{RT} - n_{CH_2}\frac{\Delta\mu^\circ_{CH_2}}{RT} \tag{10}$$

On the basis of the simple picture presented here, if there is only a change in the cross-sectional area of the partitioning liquid, $A_L$, due to a loss or redistribution, then the

intercept of the semi-logarithmic plot of the retention volume *vs.* the number of carbon atoms will change but not the slope. If the column loses material to the flowing gas equally throughout its entire length then $A_L$ represents the real cross-sectional area of the liquid. This is not the case. Since material is lost predominantly from the inlet end, $A_L$ is an effective value which does not represent the actual distribution of partitioner. If the difference in chemical potential changes by virtue of an alteration of the chemical nature of the partitioner, then the slope of the plot will be altered, if such chemical change affects $\Delta\mu^\circ_{CH_2}$ for the methylene groups. We, however, envision that retention of polar compounds, *e.g.*, alcohols, on a polar partitioner, *e.g.*, glycol, is primarily due to the interaction of the polar groups of the materials which is largely independent of the methylene groups, *i.e.*, the interaction is described by a term in $\Sigma\Delta\mu_j^\circ$ which in turn affects the intercept. Since interaction of this kind is probably the predominant one in most chromatographic separations and since it cannot be separated from $A_L$ without some independent means of determining this latter quantity, it is not likely that one can deduce the kind of change which occurs in the column from an examination of chromatographic behavior alone. Eqn. (10) is valid only when retention volumes are measured relative to the air peak. Eqn. (5) is not amendable to as simple a separation of physical and chemical effects. Rearrangement and expansion in an infinite series gives:

$$\ln V_i = \ln \frac{K_p L}{A_M} + \frac{\alpha A_L}{A_M} - \frac{1}{2}\alpha^2 \left(\frac{A_L}{A_M}\right)^2 + \frac{1}{3}\alpha^3 \left(\frac{A_L}{A_M}\right)^3 + \ldots \tag{11}$$

which is valid for $-1 < \alpha A_L/A_M < 1$. If one neglects higher ordered terms and expands the exponential form of $\alpha$, then, again neglecting higher ordered terms:

$$\ln V_i = \ln \frac{K_p L}{A_M} + \frac{A_L}{A_M}\left[1 - \frac{\Delta\mu^\circ}{RT} + \frac{1}{2!}\left(\frac{\Delta\mu^\circ}{RT}\right)^2 - \ldots\right] \tag{12}$$

$$= \ln \frac{K_p L}{A_M} + \frac{A_L}{A_M} - \frac{A_L}{A_M}\frac{\Delta\mu^\circ}{RT} \tag{13}$$

Substituting eqn. (9) for $\Delta\mu^\circ$:

$$\ln V_i = \ln \frac{K_p L}{A_M} + \frac{A_L}{A_M} - \frac{\Sigma\Delta\mu_j^\circ}{RT}\frac{A_L}{A_M} - n_{CH_2}\frac{\Delta\mu^\circ_{CH_2}}{RT}\frac{A_L}{A_M} \tag{14}$$

The effect of physical changes with the partitioner cannot be separated from chemical changes. For diagnostic purposes, retention volumes relative to the air peak are to be preferred.

HETP has been reported to vary directly with the effective thickness squared of the liquid layer[4]. This thickness behaves like $A_L$ on redistribution and its effective value will decrease with the kind of redistribution reported by KELLER *et al.*

If one has two columns, (1) and (2), which differ only in the amount of liquid phase present, the difference of the intercepts is given by:

$$\ln V_i^a(1) - \ln V_i^a(2) = \ln \frac{A_L(1)}{A_L(2)} + \ln \frac{K_p(1)L(1)}{K_p(2)L(2)} \tag{15}$$

The volume of liquid adhering to each particle is the volume of the coated particle of radius $r_2$ minus the volume of the support particle of radius $r_1$ or:

$$\frac{4}{3}\pi(r_2^3 - r_1^3) = W_L/n\rho_L \tag{16}$$

where $W_L$ is the total weight of liquid on the column, $\rho_L$ its density, and $n$ the number of particles in the column. In a similar fashion, the cross-sectional area of the liquid phase is the cross-section of the coated particle minus the cross-section of the support or:

$$A_L = \pi(r_2^2 - r_1^2) \tag{17}$$

If $(r_2 - r_1)$ is factored from each polynomial, its value from eqn. (16) substituted in eqn. (17), and the result simplified by completion of the square, then:

$$A_L = \frac{3\pi W_L}{4n\rho_L\left[r_2 + r_1 - \dfrac{r_2 r_1}{r_2 + r_1}\right]} \tag{18}$$

Assuming that $r_1 = r_2 = r$ or that the thickness of the liquid is negligible compared to the radius of the particle:

$$A_L = \frac{\pi W_L}{2n\rho_L r} \tag{19}$$

We may write:

$$\frac{A_L(1)}{A_L(2)} = \frac{W_L(1)n(2)}{W_L(2)n(1)} \tag{20}$$

since $\rho_L$ and $r$ are the same for both columns. Also:

$$n = W_S d_S \tag{21}$$

where $W_S$ is the weight of the bare support material in the column and $d_S$ is the number of support particles per gram. Using this, eqn. (15)

$$\ln V_i^a(1) - \ln V_i^a(2) = \ln \frac{W_L(1)W_S(2)}{W_L(2)W_S(1)} + \ln \frac{K_p(1)L(1)}{K_p(2)L(2)} \tag{22}$$

If there is more than one immobile phase involved in the retention of the solute, *e.g.*, adsorption by the solid support or retention at the liquid–gas interface as suggested by MARTIN[5] such that $\alpha$ as measured chromatographically by a treatment based on eqn. (1) does not compare with values found by other independent means, then we may attempt to separate these effects by defining as many arbitrary partition coefficients, $\alpha$, $\beta$, $\gamma$,... as necessary to describe these other active interfaces. For example, let $\beta$ equal the concentration of solute at the support–liquid interface (moles/unit surface)/concentration of solute in the mobile gas phase. Following the development of GIDDINGS AND KELLER[2], then for two active immobile phases:

$$R = \frac{1}{1 + \alpha(A_L/A_M) + \beta(A_S/A_M)} \tag{23}$$

Here one may try to assign values to the cross-sectional area of the solid support from measurements performed on the support particles. If $\beta$ can be obtained from non-chromatographic results, $R$ may be calculated. Otherwise $\beta$ must be determined from $R$ for appropriate values of $\alpha$, $A_L$, $A_S$, and $A_M$. Extension of eqn. (23) to other active sites such as the liquid–gas interface or an attempt to distinguish between the partitioning in the adsorbed partitioner and the liquid held in capillary puddles assuming the $\Delta\mu^\circ$ of the solute to be different in these two regions, leads to speculation as to the values of both the partition coefficient and the effective cross-section. We make further remarks about this distribution of liquid regions later.

For a liquid phase held on a support which contributes to retention, eqn. (6) becomes:

$$V_i^a = \alpha_i L K_p A_L + \beta_i L K_p A_S \tag{24}$$

We presume that some sort of functional relationship exists between $A_L$ and $A_S$ such that $A_S = f(A_L)$, *i.e.*, the participation of the support in retention depends upon the quantity and perhaps the distribution of the liquid in the column. In order to characterize the variation of $\ln V_i^a$ with the number of methylene groups in a homologous series when both liquid partition and solid adsorption occur, we take the total derivative of the logarithmic form of eqn. (24) with respect to $\alpha_i$ and $\beta_i$ to obtain:

$$d(\ln V_i^a) = \frac{A_L d\alpha_i + f(A_L) d\beta_i}{\alpha_i A_L + \beta_i f(A_L)} \tag{25}$$

Substitution of eqn. (9) in (7) and differentiation with respect to $n_{CH_2}$ yields:

$$\frac{d\alpha_i}{dn_{CH_2}} = -\frac{\alpha_i}{RT} \Delta\mu^\circ_{CH_2(L)} \tag{26}$$

and an analogous expression for $d\beta_i/dn_{CH_2}$. Here $\Delta\mu^\circ_{CH_2(L)}$ is the difference in chemical potential for distribution of methylene groups between the liquid partitioner and the vapor state while $\Delta\mu^\circ_{CH_2(S)}$ pertains to solute distributed between the active solid and the vapor. With these substitutions, eqn. (25) becomes:

$$\frac{d(\ln V_i^a)}{dn_{CH_2}} = -\frac{\alpha_i A_L \Delta\mu^\circ_{CH_2(L)} + \beta_i f(A_L) \Delta\mu^\circ_{CH_2(S)}}{RT[\alpha_i A_L + \beta_i f(A_L)]} \tag{27}$$

If we assume that the nature of the chemical interaction between the liquid and the solid as it affects the solute activity is independent of the quantity of partitioner or its distribution then $\Delta\mu^\circ_{CH(L)}$ and $\Delta\mu^\circ_{CH_2(S)}$ are constants. Deviation of this plot from linearity suggests that the solid support participates in retention through the non-linearity of $f(A_L)$. MARTIN[5] suggested that for his particular case the solid surface area is proportional to the bulk liquid above a 3 % liquid load. With linearity of $A_S$ in $A_L$, eqn. (27) becomes:

$$\frac{d(\ln V_i^a)}{dn_{CH_2}} = -\frac{k_1\alpha_i + k_2\beta_i}{\alpha_i + k_3\beta_i} \tag{28}$$

That eqn. (28) equals a constant requires that $\alpha_i/\beta_i = k$ which implies that:

$$\Delta\mu^\circ_{CH_2(L)} = K + \Delta\mu^\circ_{CH_2(S)} \tag{29}$$

where $K$ is a constant. This is always true if, as we have supposed, both chemical potentials are constant.

The opportunity to write:

$$A_S = kA_L \tag{30}$$

represents a considerable algebraic simplification since eqn. (24) then becomes:

$$V_i^a = (\alpha_i + k\beta_i)LK_pA_L \tag{31}$$

and the remainder of the equations follow as before with $\alpha_i = \alpha_i'$ and $\Delta\mu_i^\circ = \Delta\mu_i^{\circ\prime}$ where $\alpha_i'$ and $\Delta\mu_i'$ are measures of the combined influence of the partitioning liquid and active solid support in retention. Thus participation of the solid support is equivalent in effect to chemical change of the partitioner under the assumptions made here and there is no non-linearity introduced into $\ln V_i^a$ *vs.* $n_{CH_2}$.

It is to be clearly understood that eqn. (30) states that the average value of $A_S$ is a linear function of the average value of $A_L$. The effect of particular distributions as a function of the distance along the column has not been explored experimentally.

## EXPERIMENTAL

KELLER *et al.*[1] prepared two 1.5 m columns with packings of polyethylene glycol on firebrick. Column 4 contained 16.45 g of packing holding 31.6 % liquid phase. From this $W_S(1) = 11.25$ g. Column 5 contained 11.80 g of packing holding 2.80 % liquid which gives $W_S(2) = 11.47$ g and $W_L = 0.33$ g. These columns were conditioned, a series of chromatograms performed, the column heated at a higher temperature, another series run, and this procedure repeated once again. After the third series of chromatograms the columns were cut into sections and the immobile phase determined in each. Column 4 lost a great deal of volatile material during conditioning so that the liquid load for the first or *a*-series chromatograms was doubtful. Column 5 was

TABLE I

LIQUID LOAD CALCULATED FROM CHROMATOGRAPHIC RESULTS

| *Column* | *Series* | *Intercept* | $K_p$ *(av.)* | $W_S$ *(g)* | *Calculated amount of liquid* | |
|---|---|---|---|---|---|---|
| | | | | | $W_L$ | % |
| 4 | *a* | 1.916 | 0.9025 | 11.25 | 3.01 | 21.0 |
| | *b* | 1.756 | 0.9119 | 11.25 | 2.06 | 15.4 |
| | *c* | 1.624 | 0.9231 | 11.25 | 1.54 | 12.0 |
| 5 | *d** | 0.964 | 0.9378 | 11.47 | — | — |
| | *e* | 0.564 | 0.9387 | 11.47 | 0.131 | 1.13 |
| | *f* | 0.446 | 0.9495 | 11.47 | 0.097 | 0.84 |

* Standard for comparison with $W_L = 0.33$ g and per cent loading of 2.80.

prepared from packing which had been heated in a drying oven prior to preparation of the column. As evidenced by negligible column bleeding, it lost its volatiles during this process and we have confidence that its liquid load did not change during conditioning. This justifies its use as a standard for the comparison of the series. Table I

lists the observed intercepts and the average value of $K_p$ for the columns. From these data we can calculate the weight of liquid on each column. Polyethylene glycol is a poor substance to use because of the pronounced bleeding during conditioning and the redistribution on the support. It is not surprising, therefore, that the calculated per cent liquid load (21.0%) for the *a*-series is much lower than the amount found on the original packing (31.6%). After the *c*-series, the column was cut and the liquid distribution determined. This is shown in Fig. 9 of the earlier communication[1]. The maximum liquid in any one section was 14%. The average per cent liquid in each section as computed from the actual distribution was 12.5 which is remarkably close to the 12.0 % reported in Table I. The same thing was done for column 5 after the *f*-series to give an average liquid load of 1.23 % whereas the table shows 0.84%, a difference of 0.4%. These results are probably within experimental error.

## DISCUSSION

With regard to retention volumes only, we conclude that if the immobile liquid phase undergoes a macroscopic redistribution of partitioner without chemical change, the column behaves as if it were uniformly coated with the liquid remaining. It also appears that the change in intercept but constancy of slope reported in the earlier paper can be explained satisfactorily by physical macroscopic redistribution alone. These conclusions are only valid in the region of small velocity gradients within the column and where the amount of retention at other interfaces is proportional to the liquid load. The problem of the effect of redistribution on peak shapes and plate height may well require a different approach. This will be the subject of a subsequent paper.

The majority of support materials used in gas chromatographic columns are not impermeable but are porous and permeated by capillary cavities which may be interconnecting. Capillary columns do not have smooth bores nor are they perfectly circular in cross section. These non-uniformities lead to non-uniform distributions of liquid. Even glass beads may deviate severely from the model because the bulk of the liquid is located at the contact points between the beads. Thus $A_L$ or the thickness of the liquid film is an effective value or a kind of average value which is not likely to describe reality at any location in the column. The problem is to calculate this effective value. This is not unique to gas chromatography nor is it particularly new to chromatographic literature[2]. GIDDINGS[6] has been much concerned with the effective thickness of this film since HETP is intimately dependent upon it. Using a model of adjacent conical cavities ("saw-tooth" profile) in a solid he has derived theoretical results important to further extension of our knowledge. If the liquid wets the solid then adsorption forces and capillary forces compete for the liquid. For a loading of 15 % liquid on a granular porous support, GIDDINGS calculates 2 to 4 % to be adsorbed liquid and 12 to 13 % to be in the capillary cavities. This conclusion has implications for those using columns of low liquid loading in an effort to realize greater column efficiency. If the chemical potential of a solute is different for surface adsorption on the support, solution in the capillary liquid, and solution in the adsorbed liquid then chromatographic behavior will be strongly dependent on column bleeding and partitioner redistribution because the extent of participation of these three sites depends on the liquid load. At low loads even a small loss is likely to alter their relative involvement. We predict that if the extent of participation of each kind of site can be

represented by an average cross-sectional area and if these are in turn linear functions of the cross-sectional area of the liquid partitioner then ln $V_i^a$ *vs.* $n_{CH_2}$ is linear and chromatographic behavior can be described by an effective partition coefficient characteristic of all three mechanisms. Any change in value of this coefficient is reflected by a change in slope of the plot. If these average cross-sections are related non-linearly then the plot is non-linear. Adsorption at the gas–liquid interface may also be included in this treatment. Attempts to separate these individual contributions involve the assessment of a partition coefficient and an effective cross-section for each active phase. For some of these phases, the concept of a cross-section is very unrealistic and it is unlikely that such values can be assigned from other than chromatographic data.

Although the chemical potential of the partitioning liquid held by adsorption is assumed to be the same as that held in capillary puddles, it is not necessarily true that the chemical potential of a solute dissolved in these two regions will be the same. For an inactive support holding a non-polar partitioner we do not expect much organization of the molecules of the partitioner in the adsorbed regions and there should be little difference between the liquid in the two regions and there should be equivalent solute behavior in each. However, for an active support holding a polar partitioner we might well expect such a difference. This distinction is probably only important at a few tenths of a per cent liquid load. Users of low load columns can expect that chromatographic sequences will be altered in an unpredictable manner as they reduce the loading and that ln $V_i^a$ *vs.* $n_{CH_2}$ plots may be non-linear.

For normal loadings we expect support participation to be minimal and that partitioning will predominantly occur in the liquid held by capillaries. The problem is merely the calculation of the effective $A_L$ by an averaging process. Here we conclude that a change in the intercept of the semi-logarithmic plot indicates a change in $A_L$ and/or $\Sigma \Delta\mu_j^\circ/RT$. Our work indicates that one may determine which of these may bring about this variation if one knows the weight of the liquid remaining on the column since $A_L$ as a function of $W_L$ is independent of both the microscopic and macroscopic distribution. Moreover, it is meaningful to report specific retention volumes even if there has been a macroscopic redistribution if the actual weight, not the preconditioning weight, of the partitioner on the column is used. Direct weighing of the column would furnish $W_L$ and not involve its destruction.

An additional remark is that if the liquid is deposited on the support in such a manner that the surface free energy is not uniform over the entire surface of liquid, microscopic redistribution can occur either by fluid flow over the surface or by vaporization and recondensation. GIDDINGS[6], on the basis of some assumed parameters, concludes that the two mechanisms are about equally involved, that the time required to reach an equilibrium distribution depends upon the average pore volume of the support, and that for a diatomaceous earth it is about thirty minutes. In general, this adjustment is apparently a small fraction of the lifetime of the column.

## SYMBOLS

| | |
|---|---|
| $A_L$ | cross-sectional area of the immobile liquid phase. |
| $A_M$ | cross-sectional area of the mobile phase. |
| $A_S$ | cross-sectional area of the immobile support. |

| | |
|---|---|
| $\alpha_i$ | distribution coefficient of the $i$th solute for liquid partition. |
| $\alpha_i'$ | effective distribution coefficient of the $i$th solute where retention is at several active interfaces. |
| $\beta_i$ | distribution coefficient for retention of the $i$th solute on a solid surface. |
| $\gamma_i$, $\delta_i$... | distribution coefficients for retention of the $i$th solute at active interfaces. |
| $d_S$ | number of particles of support per gram. |
| $k$, $k_1$ $k_2$, $k_3$, $K$ | numerical constants. |
| $K_p$ | $\frac{2}{3}\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1}$. |
| $L$ | column length. |
| $\Delta\mu^\circ$ | difference in chemical potential of a solute in the stationary phase and solute in the mobile phase, both at some standard concentration. |
| $\Delta\mu^\circ_{CH_2}$ | $\Delta\mu^\circ$ for the methylene group. |
| $\Delta\mu^\circ_j$ | $\Delta\mu^\circ$ for functional groups other than methylene. |
| $\Delta\mu^\circ_{CH_2(L)}$ | $\Delta\mu^\circ_{CH_2}$ for distribution between immobile liquid and vapor. |
| $\Delta\mu^\circ_{CH_2(S)}$ | $\Delta\mu^\circ_{CH_2}$ for distribution between immobile solid and vapor. |
| $\Delta\mu_i^{\circ\prime}$ | effective $\Delta\mu_i^\circ$ of the $i$th solute where retention is at several active interfaces. |
| $n$ | number of particles in the column. |
| $n_{CH_2}$ | number of methylene groups in a molecule. |
| $P_i$ | pressure at the column inlet. |
| $P_o$ | pressure at the column outlet. |
| $R_i$ | fraction of the $i$th solute molecules in the mobile phase. |
| $R$ | universal gas constant. |
| $r_1$ | radius of the support particle. |
| $r_2$ | radius of the liquid coated particle. |
| $\rho_L$ | density of the partitioning liquid. |
| $t_i$ | retention time of the $i$th solute. |
| $T$ | absolute temperature. |
| $u$ | average velocity of solute vapor. |
| $v$ | average velocity of carrier gas. |
| $V_i$ | retention volume of the $i$th solute measured from the instant of sample entrance into the column. |
| $V_i^a$ | retention volume of the $i$th solute measured from the air peak. |
| $W_L$ | total weight of liquid on the column. |
| $W_S$ | total weight of uncoated support in the column. |
| $dx$ | element of column length. |

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SUMMARY

The immobile liquid phase of a gas chromatographic column may undergo physical and chemical changes during conditioning and use. Chemical changes are those which affect the difference in chemical potential of a solute between the solution in the partitioning liquid and the vapor state. Macroscopic physical changes are those which change the total amount of liquid and/or its distribution on the support. Microscopic physical redistribution of partitioner occurs until the surface free energy of the liquid is minimal and uniform over the entire liquid surface. This latter redistribution is probably complete within a small fraction of the lifetime of the column. The assumption that the packing consists of impermeable solid particles coated with a uniform liquid film leads to the conclusion that a chemical change which affects $\Delta\mu^\circ$ for the methylene groups of a homologous series changes the slope of the semi-logarithmic plot of retention volume *vs.* the number of carbon atoms in the molecule whereas the intercept is altered by either a change in $\Delta\mu^\circ$ for the functional groups of the molecule or by a change in the effective cross-sectional area of the partitioner. Evidence is given that the change due to the latter can be calculated by finding the average amount of liquid on the column irrespective of its distribution. The effect of retention by more than one kind of immobile phase is discussed.

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