# MIXED RETENTION MECHANISMS IN GAS-LIQUID CHROMATO-GRAPHY

## I. THE RELATION BETWEEN RETENTION VOLUME AND SAMPLE SIZE: DETERMINATION OF BULK LIQUID CONTRIBUTION

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SUMMARY

An equation is proposed in which the retention volume in gas chromatography is expressed as a function of sample size when both bulk partition and surface adsorption contribute to the retention. The adsorption is assumed to vary with sample size, and the partition coefficient is assumed to be constant. The equation was fitted to experimental data for ethyl methyl ketone and diisopropyl ether on *n*-octadecane columns of various loadings. With this method, the contributions to the retention volume from bulk solution and adsorption could be separately determined, using data from only one column.

INTRODUCTION

It has been known for some years that adsorption on the various surfaces in a gas–liquid chromatographic (GLC) column often plays an important role in the retention of a solute. Martin[1] initiated the research in this field.

When surface adsorption is appreciable, whether on the surface of the solid support or on the surface of the liquid phase, the retention volume usually varies with sample size. Accurate measurements of retention data thus require the retention volume to be corrected for adsorption. For most physico-chemical investigations the gas–liquid distribution coefficient ($K_d$) is needed. Various methods have been proposed[2-6] for determining $K_d$ from gas chromatographic (GC) data in the case of mixed retention mechanisms.

With appropriate assumptions about the nature of the non-linear adsorption isotherms, it is possible to derive equations for the dependence of the retention volume on sample size which can then be fitted to experimental data. Berezkin and Pakhomov[7] assumed a Freundlich isotherm and developed an equation which fitted well the experimental data. No attempts were made to use this approach to determine $K_d$. Recently, Suprynowicz *et al.*[8] have developed an equation valid only for gas–solid chromatography (GSC) based on the Jovanović isotherm. In addition,

several workers[9-11] have published plots of experimental results and discussed the relationship between sample size and retention volume.

We consider the problems of determining $K_d$ and the relation between sample size and retention volume to be closely related. In this paper we propose a method of dealing with both which only requires conventional measurements of peak area and retention volume at the peak maximum.

## THEORETICAL

A list of symbols is given at the end of the paper.

To express the relation of retention volume to the sample size in GLC, the following assumptions are made:

(1) The retention of the solute is caused partly by dissolution of the sample in the liquid phase, partly by adsorption at one or more surfaces.

(2) The solution is assumed to be ideal, so that its contribution to $V_N$ is constant and equal to $K_d \cdot V_1$ over the range of sample sizes studied.

(3) The adsorption follows a Langmuir-type relation so that its contribution to $V_N$ decreases asymptotically to zero as the sample concentration increases and has a finite value at zero concentration.

(4) The total retention volume of the solute can be regarded as the sum of the contributions from solution and adsorption.

We suggest the equation

$$V_N = A + \frac{C}{\left[1 + B \left(\dfrac{n_t}{V_N + V_M}\right)^D\right]^2} \tag{1}$$

which is consistent with the assumptions above and which fits well the experimental data.

The retention volume at infinite dilution can be written[12]:

$$V_N = K_d \cdot V_1 + K_s \cdot A_s \tag{2}$$

The term $A$ in eqn. 1 is $K_d \cdot V_1$, the solution contribution, and $C = K_s \cdot A_s$ is the adsorption contribution at infinite dilution ($n_t = 0$). The second term of eqn. 1 expresses the decrease in adsorption with increasing sample size. The constants $B$ and $D$ control the shape of this decrease and should be regarded as empirical constants. The fitting of eqn. 1 to experimental data gives the possibility of obtaining both the adsorption and solution contributions to $V_N$.

## EXPERIMENTAL

Eqn. 1 was tested on data from different columns, one containing only Supasorb AW DMS (40–60 mesh), acid-washed and treated with hexamethyl-disilazane (BDH, Poole, Great Britain). The other columns contained various loadings of $n$-octadecane on the same support. The column temperature was 333.2 °K in all the experiments.

The volume of the stationary phase was varied between 0 and 1.2 ml. The total amount of packing was 3–4 g. Glass columns (V-shapes, 1000 × 4 mm I.D.) were used. Hydrogen was used as carrier gas and methane for the determination of the void volume. The carrier gas flow-rate was *ca.* 50 ml/min. The retention volume for diisopropyl ether and ethyl methyl ketone was measured over a wide range of injected amount ($5 \cdot 10^{-10}$–$5 \cdot 10^{-5}$ mole) for each column. For these measurements, the precision gas chromatograph described earlier[13–15] was used.

Values for the retention volume (measured both to the maximum of the peak and to the median) and the corresponding sample amount (measured from the area of the peak) were collected on floppy discs and processed using the BASIC language.

To fit eqn. 1, initial values of $B$ and $D$ were guessed, whereafter quantities $x = 1/\{1 + B[n_t/(V_N + V_M)]^D\}^2$ were calculated for every $V_N$–$n_t$ pair. Then, by using the method of least squares, the constants $A$ and $C$ in the linear equation $V_N = A + C \cdot x$ were computed. By systematic variation of $B$ and $D$ to minimize the sum of the squares of the deviations from the line, the best fit of the eqation to the data can be obtained. The systematic variation of $B$ and $D$ was accomplished using the "Simplex" method[16].

## RESULTS AND DISCUSSION

Fits of eqn. 1 to several systems were performed in the manner described above. The best fit was normally obtained with $D$ in the range 0.4–0.6. In this range, however, the goodness of fit was nearly independent of the value of $D$. To simplify the calculation, $D$ could be given a fixed value. In ref. 17 $D$ was set to 0.5 and for the fits shown in Fig. 1 and Table I, $D$ was set to 0.4 which is slightly better. To obtain valid results, it is desirable that the range of sample sizes is so wide that the characteristic S-shaped curve appears. For very skewed peaks, it can be difficult to get data for the smallest sample sizes. In such cases, unreliable fits are obtained unless $D$ is given a fixed value.

To check the validity of the approach in eqn. 1 we first consider the experimentally obtained values of $A$. For the GSC column C1 in Table I, $A$ is negligible, which supports the interpretation of $A$ as $K_d \cdot V_1$.

In Fig. 2 values of $A$ for diisopropyl ether and ethyl methyl ketone on eleven columns are plotted against the volume of the stationary phase $V_1$ on each column. A closely linear relationship is obtained. The slope of the regression line for diisopropyl ether is $101.4 \pm 3.9$ and the intercept is $-1.4 \pm 2.1$ ml (95% confidence intervals), and for ethyl methyl ketone the slope is $58.8 \pm 3.5$ and the intercept $1.0 \pm 1.9$ ml. Furthermore, determinations of the partition coefficient for diisopropyl ether and ethyl methyl ketone on *n*-octadecane at 333.2 °K by a static method[18] have given the $K_d$ values $99.4 \pm 0.3$ and $59.2 \pm 0.6$, respectively. We can therefore conclude that the interpretation of $A$ as the solution contribution is in good agreement with our experimental results. Thus, the second term in eqn. 1 describes the adsorption, and here $C$ is the adsorption contribution to $V_N$ at infinite sample dilution.

The retention volume for a skewed peak can be defined in several ways, which give different values. In this work we used the maximum of the peak, $V_N^{max}$, since this is the simplest point to evaluate and it is also the quantity which is
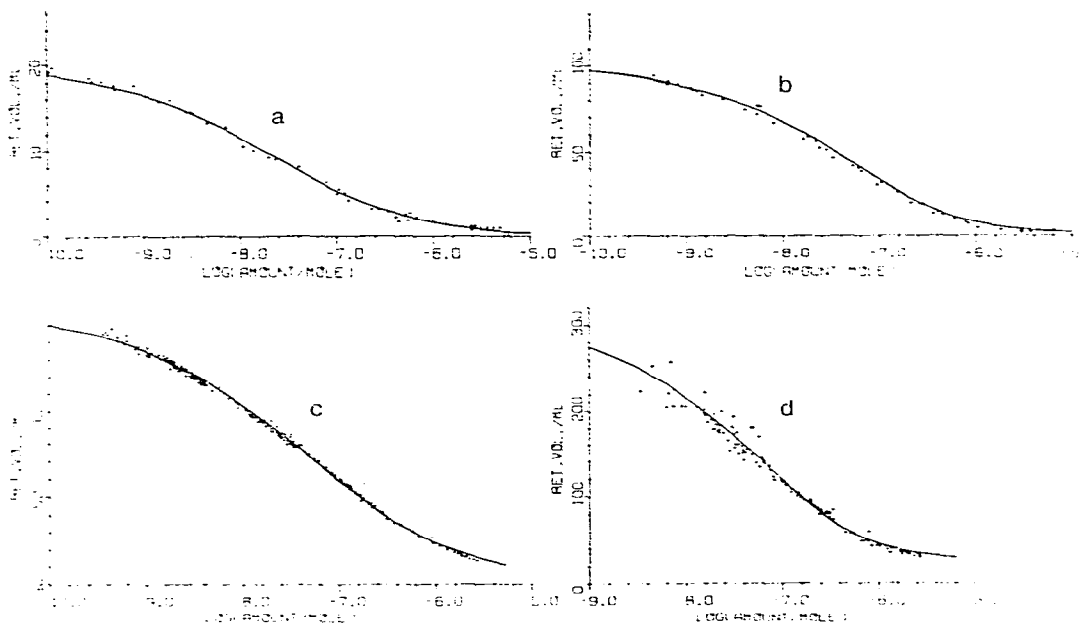
Fig. 1. Fits of eqn. 1 with $D = 0.4$ to experimental points. Systems: a = diisopropyl ether on Supasorb AW DMS column; b = ethyl methyl ketone on Supasorb AW DMS column; c = diisopropyl ether on 10% octadecane column; d = ethyl methyl ketone on 10% octadecane column.

TABLE I

RESULTS FROM FITTING OF EQN. 1 WITH $D = 0.4$ TO EXPERIMENTAL DATA

Samples: S1 = diisopropyl ether; S2 = ethyl methyl ketone. Columns: C1 = Supasorb AW DMS; C2 = 10% octadecane on Supasorb AW DMS.

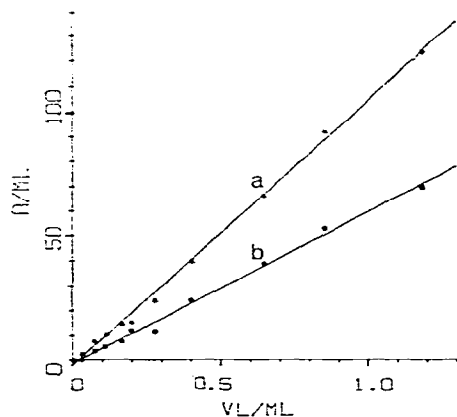| Sample | Column | A | C | Plot (Fig. 1) |
|--------|--------|------|-------|---------------|
| S1 | C1 | 0.01 | 20.8 | a |
| S2 | C1 | 0.2 | 103.3 | b |
| S1 | C2 | 40.7 | 31.6 | c |
| S2 | C2 | 23.9 | 296.4 | d |



Fig. 2. Parameter $A$ of eqn. 1 plotted against liquid phase volume $V_1$. Solutes: a = diisopropyl ether; b = ethyl methyl ketone. Column: $n$-octadecane on Supasorb AW DMS.

obtained by electronic integrators. Other choices could be the centre of gravity, $V_N^{cg}$, or the median, $V_N^{med}$. However, both for large samples, when ideal solution dominates, and for very small samples, where the adsorption isotherm is linear, the conditions will approach those of linear chromatography, so the peaks will be nearly symmetric. Therefore, the values of $A$ and $C$ should be independent of the choice of $V_N$ measure, although, for example, $V_N^{med}$ is always greater than $V_N^{max}$ for peaks in the sample range where they are substantially skewed. Some calculations were made using $V_N^{med}$ instead of $V_N^{max}$. As expected, eqn. 1 fitted the data equally well in each case and the values of $A$ and $C$ were only slightly influenced.

To derive a corresponding theoretically equation to the empirical eqn. 1, it is necessary to find a relation between the retention volume, at some point at the peak tail, to the gas phase concentration, properly corrected for diffusion. This may be possible by using the general retention equation[2]. However, with such an approach, although theoretically attractive, it would not be possible to use the parameters $V_N^{max}$ and the peak area which are those which are normally given by all electronic integrators and other evaluating devices. Another method for the evaluation of chromatograms would be required.

To determine $K_d$ by our method it is only necessary to use one column. This is in contrast to most other methods[3-6]. However, Martire and Riedl[3] have proposed a method of determining $K_d$ on one column. Large sample amounts were used so that the contribution from adsorption to the retention volume was negligible. Further, the partition coefficient was assumed to be linearly related to sample size for these large samples. However, in our opinion, it is important to utilize the entire curve form and therefore we believe that our approach is more accurate.

ACKNOWLEDGEMENT

LIST OF SYMBOLS

$A–D$   Constants
$A_s$     Area of the surface at which adsorption takes place
$C_g$, $C_l$ Concentration of solute in the gas phase and the liquid phase, respectively
$K_d$     Distribution coefficient ($= C_l/C_g$)
$K_s$     Adsorption coefficient
$n_t$     Total number of injected molecules
$V_M$    Volume of the gas phase in the column (void volume)
$V_l$     Volume of the liquid stationary phase
$V_N$    Retention volume, corrected for void volume measured at column temperature, and pressure[13]

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