A NEW MODEL OF GAS LIQUID CHROMATOGRAPHY APPLYING THE KINETICS OF GASEOUS ADSORPTION AT SURFACES.

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ABSTRACT: The dependence of the adjusted retention volume, V_R^1 , in gas liquid chromatograph on carrier gas flow rate, u , was studied for several solutes using 5% squalane stationary phase and 40-60 mesh fluoropak 8 as support. In all cases V_R^1 increases in a stepwise fashion as u increases. In each step the rate of increase of V_R^1 is initially high, but gradually decreases until V_R^1 levels off. V_R^1 is further shown to be directly proportional to n , the number of adsorbant sites in the stationary phase recognised by a single analyte molecule during its passage through the column and, based on this relationship between V_R^1 and n , a new model of gas chromatography applying the kinetics of gaseous adsorption at surfaces, and whose predictions are consistent with the experimental data above, is presented.

Key words gas liquid chromatography, retention volume, carrier gas flow rate, gas adsorption kinetics

In gas liquid chromatography (GLC) the volume of carrier gas required to elute a given solute is a measure of the work required to elute the substance. This volume of carrier gas, V_R^1 , is given by

$$V_R^1 = t_R^1 u \quad (1)$$

Where t_R^1 is the adjusted retention time for the specific solute and u is the average flow rate of the carrier gas through the column. V_R^1 is a measure of the interaction energy between solute molecules and adsorbant sites on the column. It is well known in chromatography that t_R^1 is independent of sample size provided the column is not overloaded. This suggests that it is not the total interaction energy for all solute molecules adsorbed, but the average interaction energy experienced by each molecule as it traverses the column that determines V_R^1 . V_R^1 can therefore be assumed to depend on the nature and magnitude of the interaction energy and the density of adsorbant sites on the column. In this paper we discuss the relationship between V_R^1 and the number density, n , of adsorbant sites on the column.

THEORETICAL:

In GLC the specific volume, V_g , is given by $V_g = \frac{V_n \cdot 273}{W_s \cdot T_c}$ (2)

Where W_s is the mass of liquid stationary phase in the column, T_c is the absolute column temperature and V_n is the nett retention volume. The nett retention volume takes into consideration the compressibility of the carrier gas and is given by

$$V_n = t_R^1 \bar{F} = j F_c t_R^1 \quad (3)$$

Where $\bar{F}$ is the average flow rate corrected for compressibility, F_c is the measured flow rate corrected for temperature and for the partial pressure of water vapour, and j is the compressibility factor.

$$\text{Let } V_{\frac{n \cdot 273}{T_c}} = V_n^0 = j F_c^0 t_R^1$$

Where V° and F°_C are the nett retention volume and corrected carrier gas flow rate at 273 K respectively, then

$$V_g = \frac{j F^{\circ}_C t^1_R}{W_s} \quad (4)$$

It can be shown that for ideal behaviour, V_g at 273 K is also given by (1):

$$V_g = \frac{273 R}{F^{\circ}_C \gamma P^{\circ} (MW)_s} \quad (5)$$

Where R is the ideal gas constant, γ is the activity coefficient of the solute (or analyte) in the liquid stationary phase at infinite dilution, P° is the saturation vapour pressure of the pure solute at a given temperature, and $(MW)_s$ is the relative molecular mass of the stationary phase. Combining equations 4 and 5 and rearranging we have.

$$t^1_R = \frac{273 \cdot R \cdot W_s}{j \cdot F^{\circ}_C \cdot \gamma P^{\circ} \cdot (MW)_s} \quad (6)$$

Let $W_s = W^{\circ} \times L$, where W_s is the mass of stationary phase per unit length of column, and L is the column length.

Substituting into eqn 6:

$$t^1_R = \frac{273 \cdot r \cdot l}{j \cdot F^{\circ}_C \gamma P^{\circ}} \frac{W_s}{(MW)_s} = \frac{273 \cdot R \cdot L}{j \cdot F^{\circ}_C \gamma P^{\circ}} m \quad (7)$$

Where $m = W_s / (MW)_s$

= number of molecules of stationary per unit length of column.

Equation 7 gives the adjusted retention time in terms of the number of molecules of stationary phase per unit length of column and the fundamental properties of the solute (q and P°), the column length (L), and operational parameters j and F°_C . Since most stationary phases are polymeric, the important parameter in practice is not the number of molecules of stationary phase per unit length, but rather the number of active site per unit length. If the mass of stationary phase associated with a single active site is $(MW)_{as}$ then the number of active sites per unit length of column, n , is given by

$$n = W_s / (MW)_{as}$$

and equation 7 becomes

$$\begin{aligned} t^1_R &= \frac{273 \cdot R \cdot n \cdot L}{j \cdot F^{\circ}_C \gamma P^{\circ}} \\ &= \frac{K_C \cdot L}{j \cdot F^{\circ}_C \gamma P^{\circ}} \end{aligned} \quad (8)$$

Where $K_C = 273nR$, a column constant. Finally

$$\begin{aligned} V^1_R &= t^1_R U = \frac{273 \cdot R \cdot n \cdot L U}{j F^{\circ}_C \gamma P^{\circ}} \\ U &= \frac{T_c}{273} (j F^{\circ}_C) \end{aligned}$$

$$\text{Therefore } V^1_R = \frac{R \cdot n \cdot L \cdot T_c}{\gamma P^{\circ}} \quad (9)$$

i.e at constant column temperature V^1_R is independent of flow rate provided n is constant.

We studied the dependence of V^1_R on flow rate for benzene, n-pentane and acetonitrile. In this paper we present the results of these experiments and discuss a possible kinetic model to account for the observed results.

EXPERIMENTALMaterials:

Reagent grade benzene, n-pentane, and acetonitrile were double distilled prior to use to ensure purity.

Gas Chromatography

Gas liquid chromatographic determinations were made using a micro processor controlled Perkin Elmer 8700 GC equipped with a flame ionization detector, a visual display unit (VDU), and capable of VDU readout and gauge readout of carrier gas flow rate and pressure respectively.

Determination of retention times were made using a 98.5 cm steel column with a 1.5 mm bore and packed with Fluoropak 80, 40/60 mesh, as solid support and 5% squalane as stationary phase. Determinations were made by injecting 0.1 μ l of the neat liquid sample after the column has sufficiently conditioned. Determination were made at 80°C isothermal column temperature. The injection port and the detectors were maintained at 100°C and 120°C respectively. Retention time determinations were made in quadruplicate.

TABLE 1: Values at t_R^1 at different flow rates for benzene.

μ (ml/min)	Pressure (mmHg)	t_R^1 (min)	V_R^1 (min)
8	300,025	1,990	15,920
12	450,037	1,510	18,120
18	600,049	1,135	19,295
22	770,07	0,910	20,020
30	900,074	0,745	22,350
37	1125,093	0,620	22,940
40	1200,099	0,585	23,400
45	1350,111	0,555	24,475
50	1425,117	0,510	25,500
55	1485,122	0,495	27,225
60	1552,627	0,460	27,600

TABLE 2: Values of t_R^1 at different flow rates for acetonitrile.

μ (ml/min)	Pressure (mmHg)	t_R^1 (min)	V_R^1 (ml)
12	450,037	0,310	3,720
17	675,056	0,230	3,010
22	770,070	0,201	4,422
26	900,074	0,185	4,810
30	937,557	0,170	5,100
34	1050,086	0,150	5,100
37	1125,093	0,145	5,365
40	1200,099	0,140	5,600
45	1275,105	0,135	6,075
50	1350,111	0,127	6,334
55	1485,122	0,115	6,325
60	1500,123	0,110	6,600
70	1687,693	0,105	7,350

TABLE 3: Values of t_R^1 at different flow rates for pentane

μ (ml/min)	Pressure (mm Hg)m	t_R^1 (min)	V_R^1 (min)
10	300,025	0,650	6,500
15	600,049	0,440	6,600
20	750,062	0,350	7,000
22	787,565	0,320	7,040
25	900,074	0,290	7,250
30	1050,086	0,250	7,500
35	1125,093	0,190	8,050
40	1200,099	0,21	8,400

RESULTS AND DISCUSSION

Tables 1 to 3 show that retention times obtained for benzene, acetonitrile and n-pentane respectively, while values of V_R^1 are plotted against U in figure 1 to 3. Figures 1 to 3 show that contrary to the predictions of equ 9 above, V_R^1 increases in a step wise fashion with increase in flow rate. The effect is more pronounced with the more polar acetonitrile (Fig. 3). The only parameter that can vary in equ 9 is n . These results suggest n is a function of flow rate. Below we discuss a possible kinetic model to account for the observed results.

Proposed Kinetic Model

If we assume the analyte-stationary phase interaction occurs at adsorbant sites on the stationary phase, then the elementary reaction at these sites may be modelled as follows:

Where x is the analyte molecule and s represents the active (adsorbant) site. If we let Q be the total number of adsorbant/active sites, and n be the number of active sites recognised by a single analyte molecule during its passage through the chromatographic column, then for a single analyte molecule we have.

$$k_1[X][s] = k_{-1}[x-s] \quad (11)$$

Where the brackets denote number density.

For $[x] = 1$, we have

$$k_1(Q-n) = k_{-1}n$$

$$\text{or } n = \frac{k_1 Q}{k_{-1} + k_1} \quad (12)$$

Both k_1 and k_{-1} are functions of the average carrier gas pressure, P , or flow rate, u , and we may write

$$k_1 = f_1(u)$$

$$k_{-1} = f_2(u)$$

$$\text{When } k_1 \gg k_{-1}, \quad n = Q, \quad (13)$$

$$\text{and when } k_{-1} \gg k_1 \quad n = \frac{k_1 Q}{k_{-1}} \quad (14)$$

suggesting that in equation 9 n is not a constant but has a value which is dependent on flow rate and $(k_1/k_{-1})Q \leq n \leq Q$

Fig.1: V_R^1 vs u curve for benzene

The step wise nature of the V_R^1 vs u curves in figures 1 to 3 suggests that several types of adsorbant/active sites are involved. In each step $k_1 > k_{-1}$ at high flow rates, while $k_{-1} > k_1$ at low flow rates, so that in each step n is initially given by equation 14 then increases as k_1 increases with increase in flow rate, until $n = Q$, a constant, according to equation 13.

Fig. 2: V_R vs u curve for pentane Fig. 3: V_R vs u curve for acetonitrile

Equation 9 should be amended to reflect the existence of several types of adsorbant/active sites on the column thus

$$V_R^1 = \frac{R.L.T.c}{\gamma p^0} (n_1 + n_2 + n_3 + \dots) \quad (15)$$

where n_1 , n_2 , n_3 , etc are the number densities of the different active sites on the column. Major molecular interactions commonly recognised in chromatography include dispersion or London force interactions, dipole-dipole interactions, hydrogen bonding and ionic interactions (2). n_1 , n_2 , n_3 , etc, can be identified with the sites on the column at which these different types of intermolecular interactions can occur.

Relationship between k_1 , k_{-1} and the partition coefficient, K .

If the total number of solute molecules being eluted is q and the number solute molecules adsorbed is x , then equation 11. becomes

$$K_1 [(q) - (x)] [s] = k_{-1} [x-s] \quad (16)$$

and the partition coefficient, of the salute between the stationary phase and the mobile phase is given by

$$\begin{aligned} K &= \frac{[x-s]}{[(q) - (x)]} \\ &= k_1 \frac{[s]}{k_{-1}} \end{aligned} \quad (17)$$

i.e the partition coefficient of a solute between the stationary phase and the mobile phase in gas liquid chromatography is a function of the total number of active sites, s , on the column and of the ratio k_1/k_{-1} . From the discussion above K_1/k_{-1} increases with increase in flow rate or carrier gas pressure. Thus K should be a function flow rate. This conclusion should not be surprising, since the solubility of a gas in a liquid (e.g in gas liquid chromatography) or the adsorption of a gas at a surface (as in gas solid chromatography) increases with pressure.

CONCLUSION

From the data presented above we conclude that V_R^1 increases with increase in carrier gas flow rate in gas liquid chromatography, and that this phenomenon can be explained in terms of a model based on the kinetics of adsorption of gases at surfaces and which takes into account the existence of different type of solute-stationary phase interaction sites on the column.

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