ABSTRACT:

Window diagram theory has been described by Purnell and his research team in various publications. In this paper we apply this theory to optimize a separation of complex mixture containing propylene oxide, 1-hexene, cyclohexene, tert. amylmethyl wther, 4-octene, 1-octyne, 1-nonene, p-xylene and n-decane by using two different polarity serial columns; squalane (SQ) as a non-polar solvent and Diisobutyl phthalate (DBP) as a polar solvent. A baseline separation of all mixture components is achieved following window analysis that defined the necessary relative and total column lengths. Identical chromatograms for both options: (1) SQ = front, (2) DBP=front are successfully obtained.
INTRODUCTION

The partition coefficient of any sample component, $K_R$, in multi-component substrates is defined by Purnell and his co-workers in the theory called microscopic partitions (MP) [1-4] which is based upon the linear equation:

$$K_R = \phi_K K_{R(A)}^0 + \phi_S K_{R(S)}^0 \quad \text{(for a binary (A+S) liquid phase)} \quad (1)$$

where $K_R$ is the solute liquid vapor partition coefficient with a binary stationary phase composed of A, of volume fraction, and $K_{R(A)}^0$ and $K_{R(S)}^0$ pertain to each of the pure liquid phases.

For any pair of sample components ($1$ and $2$) equation 1 can be written:

$$K_{R_2} = \frac{\phi_A K_{R(A)_2}^0 + \phi_S K_{R(S)_2}^0}{\phi_A K_{R(A)_1}^0 + \phi_S K_{R(S)_1}^0} \quad (2)$$

from which $\alpha_2/1$ values of all solute with respect to all other solutes may be calculated as function of $\phi_A$.

The windows diagram procedure has been defined in 1975 by Laub and Purnell [5]. We present here experimental results that apply the theory for different polarity columns in Gas-liquid chromatography.

Theory:

In order to facilitate understanding of the analysis of the experimental information cited later, the practically important elements of window diagram theory [6] are presented here.

The total retention of a given solute eluted through a serial pair of columns of any type is the sum of the retentions ($t_R$) in the individual sections, so for two columns labelled front (F) abd back (B),

$$t_R = t_{RF} + t_{FR} = t_{dF}(1 + k_F') + t_{dB}(1 + k_B') \quad (3)$$

where $t_d$ represents dead time ($k' = 0$) and $k'$ represents a capacity factor. It then follows, as a perfectly general results, that

$$k' = \frac{PK_F' + k_B}{P + 1} \quad (5)$$

This is true for binary serial systems of any kind of column and, being independent of assumption is the most useful form of the basic equation for serial retention.

The dependence of $k'$ and thus of relative retention $\alpha$, on column sequence FB or BF and on $k_F'$ and $k_B'$ is totally described by eqn. 5, and given that we know $k_F'$, $k_B'$ and P, there is no problem in calculating either absolute or relative retentions in serial systems. The determination of $k_F'$ and $k_B'$ is straightforward but that of P is not, since we require to know not only the values of the inlet $p_i$ and outlet $p_o$ pressures, but of the junction pressure $P$, as shown below.

Hilderbrand and Reilley [7] introduced the concept of a resistance to gas flow function $R_F$ defined in terms of average carrier velocity, $u$, by

$$R_F = \frac{(p_i^2 - p_o^2)}{pu} \quad (6)$$

and it is a simple matter then to show [6, 7] that $t_d$ is given by

$$t_d = \left[ \frac{2LR_F}{3} \right] \left( \frac{p_i^3 - p_o^3}{(p_i^2 - p_o^2)^2} \right) \quad (7)$$

where L is column length. Both eqns. 6 and 7 are, again perfectly general, applying to both packed and open tube columns. Thus, for an open tube column (Poiseuille's law),

$$R_F = 32L\eta/3r^2$$

where $r$ is the radius and $\eta$ the carrier gas viscosity. For a packed column (D'Arcy's law), corresponding [7],

$$R_F = 2\eta\epsilon L/B_o$$

where $\epsilon$ is the total porosity of the column packing and $B_o$ is its specific permeability.

$R_F$ is, thus, very readily measured experimentally for any column by determining $t_d$ as a function of $p_i$ and evaluating $2LR_F/3$ as the slope of a plot of $t_d$ against $(p_i^3 - p_o^3)/(p_i^2 - p_o^2)$ [2].

Turning now to the situation where two columns are serially linked with pressure drop $p_i - p$ in column F and of $p - p_o$ in
column B, it is a straight forward matter to show\(^8\) that, on account of conservation of mass,

\[
\frac{V_{MF}}{L_F R_{IF}} (p^2 - p^2) = \frac{V_{MB}}{L_B R_{IB}} (p^2 - p_0^2)
\]  

whence,

\[
p^2 = \frac{\left[ p_i^2 - 1 - \left( \frac{p_i^2 - (V_{MB} \tilde{R}_{IF} / V_{MF} \tilde{R}_{IF}) p_0^2}{1 - \left( \frac{V_{MB} \tilde{R}_{IF} / V_{MF} \tilde{R}_{IF}}{V_{MB} \tilde{R}_{IB} / V_{MF} \tilde{R}_{IB}} \right)^2} \right] \right]^{\frac{1}{2}}}{1 - \tilde{I}_F}
\]

where \(V_{MF}\) and \(V_{MB}\) are the mobile phase (void) volumes of columns F and B and \(L_F = L_B \) is the length fraction, \(L_F / (L_F + L_B)\), note also \(I_F + I_B = 1\). \(V_{MF}\) and \(V_{MB}\) are easily measured directly via the usual relationship.

\(V_{MF} = jF_{td}\)

Where \(j\) is the James-Martin compressibility correction and \(F_{td}\) is the temperature corrected column flow-rate. Hence, \(p\) is readily evaluated for any \(I_F\) or pressures.

Eqns. 7 and 9 now allows us to calculate \(P\) since \(\tilde{I}_F\)

\[
P = t_{df} / t_{db} = \frac{L_B R_{IB}}{L_F R_{IF}} \left[ \frac{V_{MB}}{V_{MF}} \right] \left( \frac{p_i^2 - p_0^2}{p^2 - p_0^2} \right)
\]

All the quantities needed to evaluate \(P\) can be determined experimentally. We can subsequently, via eqn. 5, calculate \(k'\) for any column combination and any \(p_i\) and \(p_0\) and, hence, \(\alpha\) for solute pairs.

**Calculating Column Lenghts for Optimizing Separations.** Purnell and Williams\([8]\) optimisation theory starts by defining a function, \(f_F\), corresponding to some true length fraction, \(l_F\) such that

\[
k' = f_F k' + f_B k' = (P k' + k') / (P + 1)
\]

where \(f_F + f_B = 1\)

From above, \(f_F = P / (P + 1)\) or \(P = f_F / (1 - f_F)\).

Rearranging eq (10) then gives us

\[
p^3 = \frac{p_i^3 + P p_0^3}{1 + P \gamma}
\]

where

\[
\gamma = \frac{L_F R_{IF}}{L_B R_{IB}} \left[ \frac{V_{MB}}{V_{MF}} \right]^2 = \frac{R_{IF}}{R_{IB}} \left[ \frac{V_{MB}}{V_{MF}} \right]^2
\]

where \(R_{IF}\) and \(V_{MB}\) are the respective quantities per unit length for each column and are, ideally, constants. It follows, therefore, that \(\gamma\) is also a constant, being independent of the individual column lengths comprising any whole column.

Substituting for \(P(f_F / (1 - f_F))\) in the equation for \(p^3\) leads to

\[
p^3 = \frac{p_i^3 - f_F (p_i^3 - \gamma p_0^3)}{1 - f_F (1 - \gamma)}
\]

Finally, rearranging the equation for \(p^2\), we get the length fraction corresponding to \(F\) at fixed \(p_i\) and \(p_0\) via rearrangement of equation (8) as

\[
I_F = \left[ \frac{R_{IF} V_{MB}}{R_{IF} V_{MF}} \left( \frac{p^2 - p_0^2}{p_i^2 - p_0^2} \right) + 1 \right]^{-1}
\]

and \(P\) can now be calculated for any \(F\) so as to yield the corresponding value of \(I_F\).

Knowing the \(\alpha_{min}\) (at the maximum window), we identify the corresponding optimum solvent composition, and knowing \(\alpha_{min}\) for baseline resolution of all components of the mixture, the number of plates can be calculated from\([9]\)

\[
N_{req} = 36 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{k + 1}{k} \right)^2
\]

where \(k\) is the capacity factor of the second component of the most difficult to separate pair.

**Experimental Section:**

Squalane (SQ), Diisobutyl phthalate (DBP) and 60-80 mesh Chromosorb-G (AW-DMCS) were procured from phase
separations (Queensferry, U.K.) and used as received. Sample components were of Laboratory grade. Columns of both SQ and DBP were made up in 270 cm and 300 cm lengths, respectively, of 3.2 mm O.D. Stainless-steel tube, the liquid substrates being deposited on the Chromosorb by standard means. Swagelock fittings, to which packing was added if possible, minimized extraneous or coupling dead volumes. When used either alone or serially, columns, irrespective of mode, were always used with flow in the same direction to avoid void creation, which can occur on reversal of packed columns.

The two column packings each contained 5% (W/W) solvent and elution was by nitrogen. A Perkin-Elmer (Beaconsfield, U.K.) F.33 system equipped with flame ionisation detection (FID) and modified precision pressure gauges were used, and all experiments cited were conducted at 90°C. Since FID was used, dead-volumes were measured by methane injection, data quoted are the means of numerous measurements.

Table 1:

<table>
<thead>
<tr>
<th>No.</th>
<th>Components</th>
<th>SQ Column k'</th>
<th>DBP Column k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propylene oxide</td>
<td>1.35</td>
<td>0.850</td>
</tr>
<tr>
<td>2</td>
<td>1-Hexene</td>
<td>1.35</td>
<td>2.41</td>
</tr>
<tr>
<td>3</td>
<td>Cyclo-hexane</td>
<td>2.22</td>
<td>4.78</td>
</tr>
<tr>
<td>4</td>
<td>Tert-amyl methyl ether</td>
<td>3.09</td>
<td>4.78</td>
</tr>
<tr>
<td>5</td>
<td>4-Octene</td>
<td>5.55</td>
<td>12.0</td>
</tr>
<tr>
<td>6</td>
<td>1-Octyne</td>
<td>10.2</td>
<td>12.6</td>
</tr>
<tr>
<td>7</td>
<td>1-Nonene</td>
<td>11.3</td>
<td>26.3</td>
</tr>
<tr>
<td>8</td>
<td>p-Xylene</td>
<td>18.1</td>
<td>22.5</td>
</tr>
<tr>
<td>9</td>
<td>n-Decane</td>
<td>21.2</td>
<td>65.1</td>
</tr>
</tbody>
</table>

Having established capacity factor data for the columns we now go on to determine the flow parameters of the test columns. Flow rates were determined at 10 psi intervals form 10 psig for both columns with one extra measurement a 5 psig for the SQ column as shown in Table 2.

Table 2:

<table>
<thead>
<tr>
<th>p(psi)</th>
<th>SQ H(cm)</th>
<th>u(cms⁻¹)</th>
<th>DBP H(cm)</th>
<th>u(cms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.255</td>
<td>2.00</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>10</td>
<td>0.210</td>
<td>4.02</td>
<td>10</td>
<td>0.320</td>
</tr>
<tr>
<td>20</td>
<td>1.05</td>
<td>8.3</td>
<td>20</td>
<td>0.220</td>
</tr>
<tr>
<td>30</td>
<td>1.32</td>
<td>10.0</td>
<td>30</td>
<td>0.144</td>
</tr>
<tr>
<td>40</td>
<td>2.78</td>
<td>15.0</td>
<td>40</td>
<td>0.228</td>
</tr>
</tbody>
</table>

In Table 3 we list the measured values of t₀, Vₘ, and f(p) where this is defined as:

\[ f(p) = \frac{p_1^3 - p_o^3}{(p_l^2 - p_o^2)^2} \]

Table 3:

<table>
<thead>
<tr>
<th>p</th>
<th>t₀</th>
<th>Vₘ</th>
<th>10⁶f(p)</th>
<th>t₀</th>
<th>Vₘ</th>
<th>10⁶f(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(psi)</td>
<td>(sec)</td>
<td>(ml)</td>
<td>(m² IV⁻¹)</td>
<td>(sec)</td>
<td>(ml)</td>
<td>(m² IV⁻¹)</td>
</tr>
<tr>
<td>10</td>
<td>70.7</td>
<td>7.50</td>
<td>11.2</td>
<td>78.0</td>
<td>7.33</td>
<td>11.1</td>
</tr>
<tr>
<td>15</td>
<td>48.2</td>
<td>7.46</td>
<td>7.5</td>
<td>53.2</td>
<td>7.76</td>
<td>7.5</td>
</tr>
<tr>
<td>20</td>
<td>35.8</td>
<td>7.14</td>
<td>5.8</td>
<td>42.0</td>
<td>7.63</td>
<td>5.8</td>
</tr>
<tr>
<td>25</td>
<td>29.8</td>
<td>7.17</td>
<td>4.6</td>
<td>35.2</td>
<td>7.94</td>
<td>4.6</td>
</tr>
<tr>
<td>30</td>
<td>26.1</td>
<td>7.59</td>
<td>3.9</td>
<td>29.6</td>
<td>7.94</td>
<td>3.9</td>
</tr>
<tr>
<td>35</td>
<td>22.6</td>
<td>7.59</td>
<td>3.5</td>
<td>26.2</td>
<td>7.91</td>
<td>3.5</td>
</tr>
<tr>
<td>40</td>
<td>20.1</td>
<td>7.41</td>
<td>3.0</td>
<td>22.5</td>
<td>7.91</td>
<td>3.0</td>
</tr>
</tbody>
</table>

In figure 3 we show plots of H against u for the two columns to determine lowest H value by the curves.
In plots of $t_F$ against $(p_{ii} - p_{oi})^2$ for the two columns which are evidently, of excellent linearity and provide the values of $R_f$ for SQ and DBP listed in Table 4, values of $V_M$ for the two columns, predicted from plots of $1/\alpha$ against $f$, are cited in Table 4.

Table 4
Values of $R_f$ and $V_M$ for the row columns at 90° C.

<table>
<thead>
<tr>
<th>Column</th>
<th>$10^3 R_f$ (Nsm⁻¹)</th>
<th>$V_M$ (ml m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBP</td>
<td>1.18 ± 0.25</td>
<td>2.591 ± 0.08</td>
</tr>
<tr>
<td>SQ</td>
<td>1.296 ± 0.19</td>
<td>2.74 ± 0.07</td>
</tr>
</tbody>
</table>

Having established the necessary data we can now proceed to construct a plot of $k'$ against $f$ for the solvent pair for all solutes. All this involves is plotting the $k'$ values for a solute on each side of the diagram and connecting the pairs for each solute with a straight line. The relevant plot is shown in Figure 4 where represents the front columns ($f_F$). Figure 5 illustrates the window diagram for this combination in the same mode (DBP = Front), the relevant values of $\alpha$ having been calculated in steps of $f_F$ ver the range 0-1. This reveals a best $\alpha$ of 1.325 at $f_F = 0.818$.

Using equations (12, 13, 15) we can calculate $t_F$ corresponding to the optimum $f_F$ derived from the best window. These calculations produce the following results to provide baseline separation at the $\alpha_{\text{min}}$ corresponding to the top of the window ($L = N_{\text{req}} H_{\text{min}}$).

Mode A : SQ(F) / DBP (B) : $t_F = 0.11$, $L = 3.45$ m  
so $L_{SQ} = 0.37$ m and $L_{DBP} = 3.08$ m  
Mode B : DBP (F) / SQ (B) : $t_F = 0.735$, $L = 3.45$ m  
so $L_{DBP} = 2.53$ m and $L_{SQ} = 0.92$ m

Figure 6 shows the chromatograms obtained from the column systems (A/B) as predicted above. These are very successful because baseline resolution is to all intents and purposes achieved. As theory demands, the chromatograms are identical and a reasonable agreement between the experimental and calculated values of $k'$, as shown in table 5. It is notable that despite the column length, total analysis time is only 16 minutes.

Operating conditions : 90 °C, 30 p. s. i. g. $N_2$; columns as in text.
## Table 5
Comparison of experimental and calculated values of k’ for Column Combination of SQ and DBP at optimum lengths.

<table>
<thead>
<tr>
<th>Cols. Comb.</th>
<th>SQ / DBP</th>
<th>DBP / SQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. No.</td>
<td>K’cal.</td>
<td>k’Exp. k’Exp. / k’Cal</td>
</tr>
<tr>
<td>1</td>
<td>1.27</td>
<td>1.21 0.953</td>
</tr>
<tr>
<td>2</td>
<td>1.51</td>
<td>1.53 1.01</td>
</tr>
<tr>
<td>3</td>
<td>2.62</td>
<td>2.64 1.01</td>
</tr>
<tr>
<td>4</td>
<td>3.36</td>
<td>3.43 1.02</td>
</tr>
<tr>
<td>5</td>
<td>6.56</td>
<td>6.59 1.01</td>
</tr>
<tr>
<td>6</td>
<td>10.6</td>
<td>11.0 1.04</td>
</tr>
<tr>
<td>7</td>
<td>13.6</td>
<td>14.1 1.03</td>
</tr>
<tr>
<td>8</td>
<td>18.8</td>
<td>19.7 1.05</td>
</tr>
<tr>
<td>9</td>
<td>28</td>
<td>28.9 1.03</td>
</tr>
</tbody>
</table>

Mean 1.02 ± 0.028

Mean 1.00 ± 0.025

REFERENCES:


Received 20 April, 1996