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EFFECTS OF THE COLUMN LENGTH ON THE HETP IN GAS CHROMATOGRAPHY

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SUMMARY

The effects of varying the length of a gas chromatography column operated under laminar flow conditions on the course of the HETP *versus* flow velocity curve have been discussed in terms of the mean absolute column pressure. Systems have been considered with both high and low liquid load packings, operated at either a constant outlet and variable inlet pressures or *vice versa*. An account has been given of the effects of varying the absolute mean column pressure at a constant column length.

The application of Van Deemter's equation[1,2] in gas chromatography presents certain problems stemming from the compressibility of the mobile phase. A rational approach to these problems was the concept of a local HETP[3-5], which led to the formulation of equations expressing the apparent HETP in the original Van Deemter terms corrected for the compressibility effects. Though it can be inferred from a number of fundamental studies[3,6-12] and has also been stated explicitly by some authors[5,13-16], it is pertinent to point out that the variables occurring in the HETP–carrier gas velocity dependence are interdependent, each having a specific influence on the shape and position of the respective curve. For instance, although the effect of a mere pressure drop across the column has been found insignificant[5,13,14], the changes of the absolute column pressure incident to the pressure drop changes may essentially influence the course of the HETP–carrier gas velocity curve. The same obviously holds for the absolute column pressure changes brought about by the changes in the column length, other permeability parameters, and either the column outlet or inlet pressures. However, the above effects are rather small under current conditions and may be accurately perceived only upon very careful measurements. The results of such measurements have shown[17,18] that the problem is still open.

The aim of the present paper is to show that simple concepts based on appreciating the effects of the mean absolute column pressure may render a consistent view on the interrelations between the course of an HETP–carrier gas velocity curve and the column length as well as the other permeability characteristics, taking into account the degree of the stationary phase load and the method of accomplishing the carrier gas flow. A case of streamlined carrier gas flow will be considered.

Owing to the secondary influence of the pressure gradient alone on the HETP as well as with regard to other approximations further introduced, the corrections for the decompression effects[3-5] will be neglected in this treatment. A chromatographic zone having passed under the actual conditions through the column will be looked upon as if it had passed under the average carrier gas velocity ($\bar{u}$) and the mean absolute pressure ($\bar{P}$) in the column. Since $\bar{P}\bar{D}_m = P'D'_m$ where $\bar{D}_m$ and D'_m are the solute diffusion coefficients in the mobile phase at the mean pressure in the column and at a unit pressure (P'), respectively, the apparent HETP ($\bar{H}$) can be immediately expressed by

$$\bar{H} = A + B_s/\bar{u} + B_m/\bar{P}\bar{u} + C_m\bar{P}\bar{u} + C_s\bar{u} \tag{1}$$

where the constants A–C_s should be independent of pressure. Besides the usual terms, a term $B_s/\bar{u}$ has been introduced in the equation to allow for longitudinal diffusion in the stationary phase[10]; this term may become comparable with $B_m/\bar{P}\bar{u}$ at higher absolute column pressures. This holds for the mean (time average) carrier gas velocity $\bar{u} = u_o(P_o/\bar{P}) = u_oj$ where u_o and P_o are the velocity and pressure at the column outlet and j is the well-known James–Martin correction factor. Apart from the term $B_s/\bar{u}$, eqn. 1 is one of the most used forms of expressing the Van Deemter equation in gas chromatography[11,16].

As the dependences of the diffusion coefficient and carrier gas velocity are the same, the contributions of the B_m and C_m terms to the HETP are constant throughout the given column (*cf.* refs. 3, 14). However, this invariability only applies to a position in the column under given conditions. In fact, it is just the above terms that render the $\bar{H}$ generally dependent on the absolute column pressure, regardless whether the $\bar{H}$ has been expressed as a function of $\bar{u}$ or u_o.

It can be derived from Darcy's law that the mean column pressure is related to the average velocity and the other quantities involved by

$$\bar{u} = (K/\eta L)\,(P_i^2 - P_o^2)/2\bar{P} \tag{2}$$

where K, η, and L are the column permeability constant, carrier gas dynamic viscosity, and column length, P_i and P_o stand for the column inlet and outlet pressures, respectively. The pressure term can be expressed in the form $(P_i + P_o)\,(P_i - P_o)/2\bar{P}$ where, at moderate pressure drops, $(P_i + P_o)/2\bar{P}$ is close to unity, and the $\bar{P}$ can be expressed approximately by either $\bar{P} \simeq P_o + (P_i - P_o)/2$ or $\bar{P} \simeq P_i - (P_i - P_o)/2$. Thus, one can write

$$\bar{u} \simeq (K/\eta L)\,(P_i - P_o) \simeq (2K/\eta L)\,(\bar{P} - P_o) = (2K/\eta L)\,(P_i - \bar{P}) \tag{3}$$

which yields, upon rearranging,

$$\bar{P} \simeq P_o + \eta L\bar{u}/2K = P_i - \eta L\bar{u}/2K \tag{4}$$

The combination of eqns. 1 and 4 renders an illustrative picture of the effects of varying the column length on the separation efficiency at either a constant outlet pressure and variable inlet pressures or *vice versa*. Thus, one can obtain by substituting for $\bar{P}$ in eqn. 1 from eqn. 4 either

$$\bar{H} = A + \frac{B_s}{\bar{u}} + \frac{B_m}{\bar{u}P_o + (\eta L/2K)\bar{u}^2} + C_m P_o \bar{u} + C_m(\eta L/2K)\bar{u}^2 + C_s \bar{u} \tag{5}$$

or

$$\bar{H} = A + \frac{B_s}{\bar{u}} + \frac{B_m}{\bar{u}P_i - (\eta L/2K)\bar{u}^2} + C_m P_i \bar{u} - C_m(\eta L/2K)\bar{u}^2 + C_s \bar{u} \tag{6}$$

It is interesting to note the presence of the terms with $\bar{u}^2$ in eqns. 5 and 6. This justifies HALÁSZ's presumption that the Van Deemter equation in its usual form should be regarded as "no more than a short McLaurin series"[16]; the terms with $\bar{u}^2$ correspond with those suggested by PAPENDICK[20]. It is worth emphasizing that the above terms may acquire either positive or negative signs.

With regard to eqn. 1, it can be derived for the optimum $\bar{u}$ ($\bar{u}_{\text{opt}}$) and the corresponding $\bar{H}$ ($\bar{H}_{\text{opt}}$) that

$$\bar{u}_{\text{opt}} = \{[(B_m/\bar{P}_{\text{opt}}) + B_s]/(C_m\bar{P}_{\text{opt}} + C_s)\}^{\frac{1}{2}} \tag{7}$$

and

$$\bar{H}_{\text{opt}} = A + 2\,\{[(B_m/\bar{P}_{\text{opt}}) + B_s]\,(C_m\bar{P}_{\text{opt}} + C_s)\}^{\frac{1}{2}} \tag{8}$$

However, $\bar{P}_{\text{opt}}$ is also a function of $\bar{u}_{\text{opt}}$ (*cf.* eqn. 4) so that eqns. 7 and 8 are not very illustrative; the explicit expression of $\bar{u}_{\text{opt}}$ and $\bar{H}_{\text{opt}}$ implies the solving of biquadratic equations, which is tedious and yields cumbrous relations. Therefore, in conformity with the procedures used by other authors[13,15,16], we shall consider only two limiting cases characterized by either $(B_m/\bar{P}) \gg B_s$ and $C_m\bar{P} \gg C_s$ or $(B_m/\bar{P}) \gg B_s$ and $C_s \gg C_m\bar{P}$, so that eqns. 7 and 8 will be reduced to either

$$\bar{u}_{\text{opt}} = (1/\bar{P}_{\text{opt}})\,(B_m/C_m)^{\frac{1}{2}} \tag{9}$$

and

$$\bar{H}_{\text{opt}} = A + 2(B_m C_m)^{\frac{1}{2}} \tag{10}$$

or

$$\bar{u}_{\text{opt}} = [(1/\bar{P}_{\text{opt}})\,(B_m/C_s)]^{\frac{1}{2}} \tag{11}$$

and

$$\bar{H}_{\text{opt}} = A + 2(B_m C_s/\bar{P}_{\text{opt}})^{\frac{1}{2}} \tag{12}$$

respectively. It is possible to assess from eqns. 9–12 the direction and limits in which $\bar{u}_{\text{opt}}$ and $\bar{H}_{\text{opt}}$ will vary upon changing the column length. Thus, in the work at a constant outlet pressure, both $\bar{u}_{\text{opt}}$ and $\bar{H}_{\text{opt}}$ will decrease on increasing the column length. As for the $\bar{u}_{\text{opt}}$, the extent of the decrease rises with decreasing importance of the C_s term, whereas the decrease of the $\bar{H}_{\text{opt}}$ slackens under the same circumstances; if $C_s \ll C_m\bar{P}$, the $\bar{H}_{\text{opt}}$ tends to be independent of the column length. In the case of work at a constant inlet pressure and variable outlet pressure, the situation is converse as to the direction of the shifts, but the same as to their extent. Combining eqns. 9 and 11 with the appropriate form of eqn. 4 and solving the resulting equations, one obtains

$$\bar{u}_{\text{opt}} = (K/\eta L)\ \{[P_o^2 + (2\eta L/K)\ (B_m/C_m)^{\frac{1}{2}}]^{\frac{1}{2}} - P_o\} \tag{13}$$

and

$$\bar{u}_{\text{opt}} = (K/\eta L)\ \{P_i - [P_i^2 - (2\eta L/K)\ (B_m/C_m)^{\frac{1}{2}}]^{\frac{1}{2}}\} \tag{14}$$

for the case described by eqn. 9 and for a constant outlet pressure and a constant inlet pressure, respectively. The situation corresponding analogously to eqn. 11 is characterized by

$$\bar{u}_{\text{opt}} = -a + [b - a^3 + (b^2 - 2ba^3)^{\frac{1}{2}}]^{\frac{1}{3}} + [b - a^3 - (b^2 - 2ba^3)^{\frac{1}{2}}]^{\frac{1}{3}} \tag{15}$$

where

where $a = (2P_o/3)\ (K/\eta L)$ and $b = (B_m/C_s)\ (K/\eta L)$, and

$$\bar{u}_{\text{opt}} = a + [a^3 - b + (b^2 - 2ba^3)^{\frac{1}{2}}]^{\frac{1}{3}} + [a^3 - b - (b^2 - 2ba^3)^{\frac{1}{2}}]^{\frac{1}{3}} \tag{16}$$

where $a = (2P_i/3)\ (K/\eta L)$ and b is the same as in eqn. 15.

It can be inferred from eqns. 5 and 6 that the column length also essentially influences the slope of the ascending branch of the $\bar{H}$ *vs.* $\bar{u}$ curve. In the case of higher velocities (*cf.* eqn. 1) it holds that

$$\frac{\mathrm{d}\bar{H}}{\mathrm{d}\bar{u}} = \frac{\mathrm{d}(C_m\bar{P} + C_s)}{\mathrm{d}\bar{u}} = C_s + C_m\left(\frac{\mathrm{d}\bar{P}}{\mathrm{d}\bar{u}}\,\bar{u} + \bar{P}\right) \tag{17}$$

which, on combining with eqn. 4 results in

$$\frac{\mathrm{d}\bar{H}}{\mathrm{d}\bar{u}} = C_s + C_m\left(\frac{\eta L}{K}\,\bar{u} + P_o\right) \tag{18}$$

and

$$\frac{\mathrm{d}\bar{H}}{\mathrm{d}\bar{u}} = C_s + C_m\left(P_i - \frac{\eta L}{K}\,\bar{u}\right) \tag{19}$$

It is evident from the above relations that the column elongation will generally enhance the dependence of the slope on the carrier gas velocity and, consequently, the curvature of the slope. Thus, when working at a constant outlet pressure, the $\bar{H}$ *vs.* $\bar{u}$ curve measured on a longer column will display a steeper ascending branch, which leads to higher $\bar{H}$ values on longer columns at a higher velocity. However, in the work at a constant inlet pressure, the column elongation will cause a more gentle slope of the ascending branch, as the velocity-dependent component of the slope is negative. This obviously results in lower $\bar{H}$ values measured on longer columns at a higher velocity. The negative contribution of the term $C_m\eta L\bar{u}/K$ causes the ascending part of the $\bar{H}$ *vs.* $\bar{u}$ curve to become concave at higher velocities when measured at a constant inlet pressure.

It readily occurs that what has been said about the effects of the column length actually applies to the whole expression $\eta L/K$, which substantially extends the applicability of the above relations. The possibility of assessing the effects of varying parametrically the outlet pressure at a constant inlet pressure and *vice versa* represents another important feature. Hence, the question what effect will the column elongation have on the apparent HETP is quite indefinite without quoting the conditions. The results may be summarized as follows:

(1) Column operated at a constant outlet pressure. An increase of the parameter $\eta L/K$ results in a decrease in both the $\bar{u}_{\text{opt}}$ and $\bar{H}_{\text{opt}}$ when employing a high liquid load packing, and in a more pronounced decrease of the $\bar{u}_{\text{opt}}$ and no change of the $\bar{H}_{\text{opt}}$ in the case of a low liquid load packing. The ascending branch of an $\bar{H}$ *vs.* $\bar{u}$ curve grows steeper on increasing $\eta L/K$, which renders higher $\bar{H}$ values at a given velocity in the respective region; the branch is always convex, provided the C_s and C_m are really constants, and the increase of the slope upon raising the $\eta L/K$ is given by the product $C_m\bar{u}$. The consequences of varying the column outlet pressure as a parameter are similar to those incidental to varying the $\eta L/K$; the increase of the slope upon increasing the P_o is given by the C_m itself.

(2) Column operated at a constant inlet pressure. The situation is opposite in all aspects mentioned in the preceding case, the functions of $C_m\bar{u}$ and C_m in connection with increasing the $\eta L/K$ and decreasing the P_i, respectively, being negative in this case. In the region of higher velocities, the ascending part of the curve becomes concave.

If one increases the inlet pressure while decreasing the outlet pressure so as to keep the $\bar{P}$ constant, one should obtain an ideal Van Deemter curve, with its shape and position practically independent of varying the $\eta L/K$ and with the ascending branch approaching a straight line ($d\bar{P}/d\bar{u} = 0$, eqn. 17) at high velocities.

It may be concluded that the minimum attainable HETP in a system operated at a constant outlet pressure may be either lowered or unchanged upon elongating the column, provided no sources of extra-column zone broadening have been introduced by coupling the columns. In the constant inlet pressure operation, the minimum HETP either rises or remains practically unchanged upon elongating the column. A number of excellent examples for both the constant outlet pressure operation[9–11] and inlet pressure operation[3,21] as well as for measurement at a constant mean column pressure[8] may be found in the literature to corroborate the consistency of the above account.

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