

A NEW EQUATION FOR THE HEIGHT EQUIVALENT TO A THEORETICAL PLATE

TOMIHITO KAMBARA, KUNIO OHZEKI AND KOICHI SAITOH

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo (Japan)

(Received June 14th, 1966)

INTRODUCTION

A fundamental system of differential equations for the mass transfer in a continuous column, under the assumption of a uniform fluid velocity, has been proposed and solved by LAPIDUS AND AMUNDSON¹. VAN DEEMTER *et al.*² convert the solution into the familiar form of Gaussian distribution. The concept of HETP introduced from the plate theory³, is also dealt with by VAN DEEMTER *et al.*² to explain the band broadening and the column efficiency. They derive the following famous equation:

$$H = A + \frac{B}{u} + Cu \quad (1)$$

Here H is HETP, u the linear velocity of carrier gas and A , B and C are constants.

It is well known that the linear velocity of carrier gas varies with pressure gradient along the column and that the diffusion coefficient of gas is inversely proportional to the pressure. KAMBARA AND OHZEKI⁴ proposed a mathematical theory for the column, in which the kinetic role of pressure drop⁵ and diffusion are considered, and derived the solution in a form of Gaussian distribution.

THEORETICAL CONSIDERATIONS

The expression for the outlet concentration of solute in gas chromatography derived by KAMBARA AND OHZEKI⁴ is shown by:

$$C(l, t) = \frac{p_0 C_0 t_0}{p_l \sqrt{2\pi\sigma^2}} \exp \left\{ -\frac{(t - t_R)^2}{2\sigma^2} \right\} \quad (2)$$

with

$$\sigma^2 = \sigma_D^2 + \sigma_\alpha^2 \quad (3)$$

$$\sigma_D^2 = \frac{D^* l}{\beta^2 u_0^3 p_0} \left(\frac{p_l^2 + p_0^2}{p_0^2} \right) \quad (4)$$

$$\sigma_\alpha^2 = \frac{2F_s^2 T_l}{\alpha F K^2} \quad (5)$$

$$t_R = \frac{T_l}{\beta} \quad (6)$$

$$T_l = \frac{4l^2(p_i^3 - p_o^3)}{3w(p_i^2 - p_o^2)^2} \quad (7)$$

and

$$v = qu\phi F = \frac{wqF(p_i^2 - p_o^2)}{2l} \quad (8)$$

The significance of the symbols is summarized in Table I.

TABLE I
LIST OF SYMBOLS

Symbol	Significance	Unit or dimension
C	concentration in gas phase	mole cm^{-3}
C_S	same in stationary phase	mole cm^{-3}
C_0	initial concentration injected	mole cm^{-3}
D^*	diffusion constant under the unit atmosphere	$\text{cm}^2 \text{sec}^{-1} \text{atm}$
F	fraction by volume occupied by mobile phase	dimensionless
F_S	fraction by volume occupied by stationary phase	dimensionless
H	height equivalent to a theoretical plate, HETP	cm
K	distribution coefficient ($= C/C_S$ at equilibrium)	dimensionless
l	length of packing	cm
n	number of theoretical plates	dimensionless
p_i	pressure of carrier gas at column inlet	atm $[\text{ML}^{-1} \text{T}^{-2}]$
p_o	pressure of carrier gas at column outlet	atm $[\text{ML}^{-1} \text{T}^{-2}]$
q	proportionality factor in eqn. (8)	$\text{atm}^{-1} \text{mole cm}^{-3}$
t_0	duration of concentration pulse injected	sec
t_R	retention time of sample component	sec
T_l	passing time of carrier gas through the whole column length l	sec
u	linear gas velocity	cm sec^{-1}
u_o	linear gas velocity at column outlet	cm sec^{-1}
v	gas flow rate per unit cross section of column	$\text{mole cm}^{-2} \text{sec}^{-1}$
w	permeability coefficient	$\text{cm}^2 \text{sec}^{-1} \text{atm}^{-1}$
α	rate constant of dissolution or adsorption	sec^{-1}
β	$1 + (F_S/KF)$	dimensionless
σ^2	variance of peak	sec^2
σ_D^2	contribution of diffusion term to variance	sec^2
σ_α^2	contribution of adsorption rate term to variance	sec^2

The HETP is given by:

$$H = \frac{l}{n} = l \cdot \frac{\sigma^2}{t_R^2} \quad (9)$$

Hence, it can easily be derived that

$$H = \frac{9D^*l(p_i^4 - p_o^4)}{2w(p_i^3 - p_o^2)^3} + \frac{3wF_S^2\beta^2(p_i^2 - p_o^2)^2}{2\alpha FK^2l(p_i^3 - p_o^3)} \quad (10)$$

The HETP is also related to u_0 , the linear velocity of carrier gas at the column outlet, according to:

$$H = \frac{18D^*l^2}{w^3} \times \frac{u_0 p_0 (lu_0 p_0 + wp_0^2)}{\left\{ \left(\frac{2lu_0 p_0}{w} + p_0^2 \right)^{3/2} - p_0^3 \right\}^2} + \frac{6F_s^2 \beta^2 l}{\alpha FK^2 w} \times \frac{(u_0 p_0)^2}{\left\{ \left(\frac{2lu_0 p_0}{w} + p_0^2 \right)^{3/2} - p_0^3 \right\}} \quad (11)$$

If the condition:

$$p_l^2 \gg p_0^2 \quad (12)$$

holds, one has:

$$H = \frac{9D^*}{4u_0 p_0} + \frac{3wF_s^2 \beta^2}{2\alpha FK^2 l} \sqrt{\frac{2u_0 p_0 l}{w}} \quad (13)$$

Thus, in the case where the carrier gas flow rate is very high, the simplified form for HETP is shown by:

$$H = \frac{B}{u_0} + C\sqrt{u_0} \quad (14)$$

or

$$H = \frac{B'}{v} + C'\sqrt{v} \quad (15)$$

EXPERIMENTAL

The gas chromatograph used was a Hitachi product, type KGL-2A, equipped with a thermal conductivity detector. The column, 2 m in length and 0.4 cm in diameter, was a copper tube packed with a stationary phase of 25% DNP on 60-80 mesh Shimalite W. The difference between the inlet and outlet pressures was measured by means of a pressure gauge and it was confirmed that under the conditions of operation the outlet pressure was always kept constant at atmospheric within $ca. \pm 1\%$, as shown in Table II. Helium carrier gas flow rate was measured with a soap film meter and corrected for the saturated water vapour pressure. The column temperature was maintained at $77 \pm 0.1^\circ$, at which temperature the chromatogram of benzene can be considered to obey approximately the normal distribution law. The number of plates and the HETP for benzene were found to be independent of the sample size with amounts smaller than 0.8 μ l and so they were determined for 0.6 μ l samples.

RESULTS AND DISCUSSION

Values of the flow rate and the HETP obtained from chromatograms of benzene under varying inlet pressures are summarized in Table II.

The flow rate v , expressed in mole $\text{sec}^{-1} \text{cm}^{-2}$, is plotted against $(p_i^2 - p_o^2)$ in Fig. 1. The results shows a good agreement with eqn. (8).

TABLE II

VARIATIONS OF CARRIER GAS FLOW RATE AND HETP WITH PRESSURE DIFFERENCE

Pressure difference, $p_i - p_o$ (atm)	Outlet pressure, p_o (atm)	Carrier gas flow rate (10^{-5} mole $\text{cm}^{-2} \text{sec}^{-1}$)	HETP (mm)
0.39	0.990	0.65	1.32
0.59	0.992	1.09	0.98
0.78	0.990	1.54	0.88
0.97	0.988	2.07	0.85
1.17	0.988	2.64	0.87
1.36	0.983	3.24	0.88
1.55	0.983	3.96	0.94
1.75	0.980	4.68	0.99
1.94	0.980	5.41	1.06
2.14	0.979	6.34	1.15
2.33	0.982	7.18	1.21
2.52	0.986	8.17	1.30
2.72	0.979	9.12	1.38
2.91	0.975	10.21	1.44

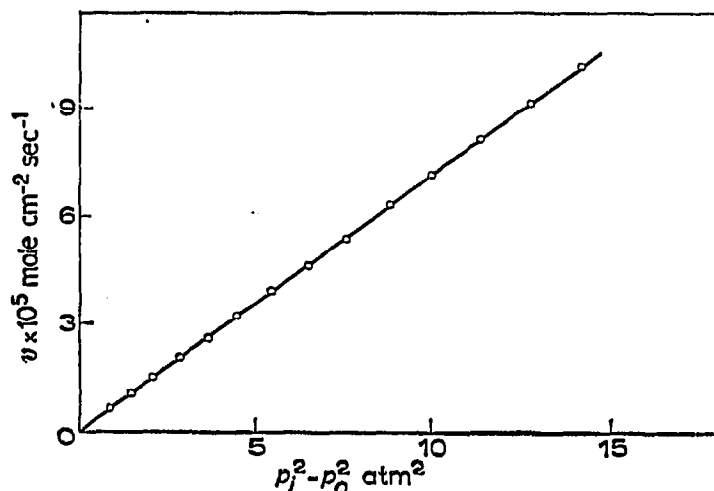


Fig. 1. The absolute flow rate of the helium carrier gas plotted against the difference between the squares of inlet and outlet pressures as shown by eqn. (8).

The plot of HETP against v is shown in Fig. 2. As the flow rate increases, the plot becomes slightly convex as it curves upwards and deviates from the linearity predicted by the original VAN DEEMTER theory. Such a tendency has also been observed recently by LITTLEWOOD⁶.

The plot shown in Fig. 3 forcibly demonstrates the theoretical prediction derived from eqn. (10), which holds generally for a wide interval of pressure difference.

Next, the plot of $\log H$ against $\log v$, shown in Fig. 4, indicates most clearly and definitely the essential validity of the present theory at higher flow rates. The slope of this straight line, which is evidently 0.5, reveals that HETP is proportional to \sqrt{v} or $\sqrt{u_0}$ in this range and not to v or u_0 itself.

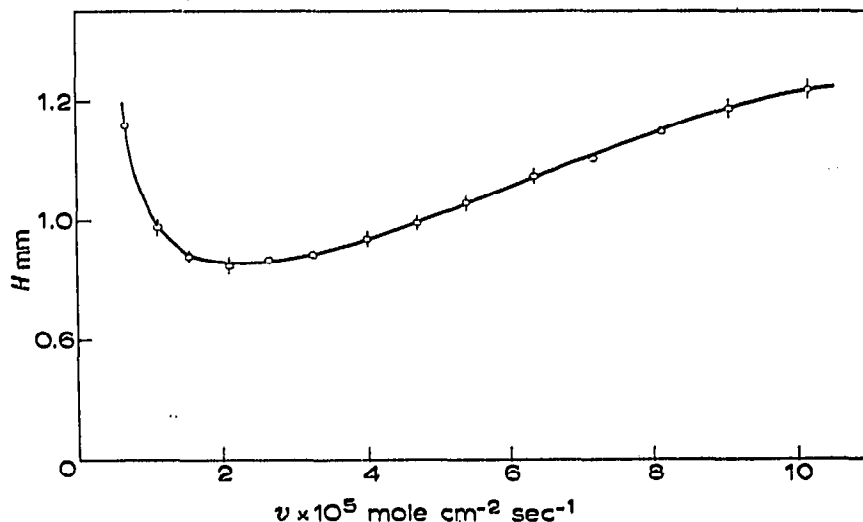


Fig. 2. The HETP plotted against the absolute flow rate of the carrier gas. Sample: benzene. Column: 2 m long, 0.4 cm diam., 25% DNP on 60-80 mesh Shimalite W at 77°. The vertical lines denote the 95% confidence interval.

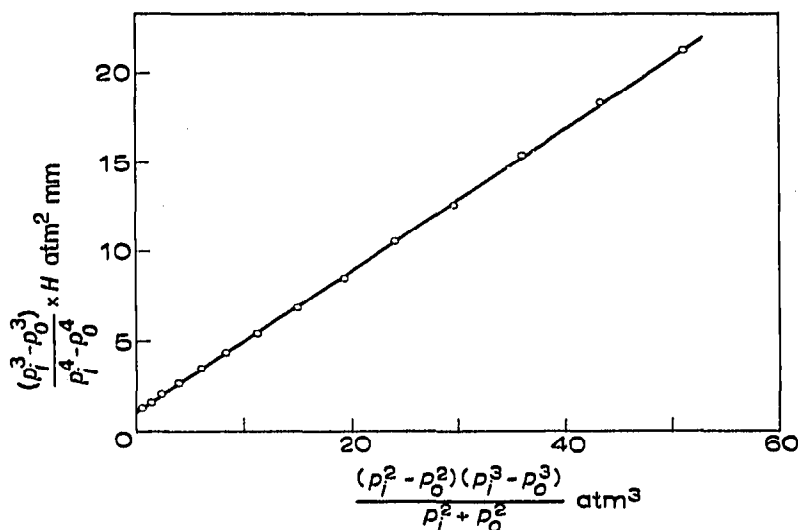


Fig. 3. Verification of the inlet and outlet pressure dependencies of the HETP as shown by eqn. (10).

In Fig. 5, the product Hv is plotted against $v^{3/2}$. The linear relationship at higher flow rates also proves the correctness of the present new HETP equation.

The constant term A in the original VAN DEEMTER equation (1) has been introduced under the assumption that the effective diffusion coefficient is an algebraic sum

of the true diffusion coefficient multiplied by the labyrinth factor and the eddy diffusivity. If one regards that the former is independent of the linear velocity, while the latter is proportional to it, the term A appears in the HETP equation. In some earlier investigations, *e.g.* by BOHEMEN AND PURNELL⁷, it was, however, reported that the term A showed negative values indicating the weakness of the above assumption.

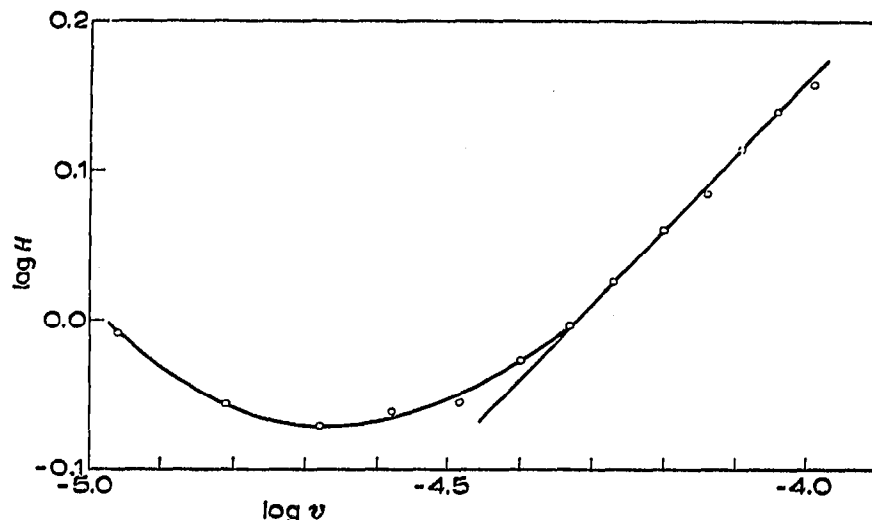


Fig. 4. Double-logarithmic plot of HETP against the absolute flow rate of carrier gas. The slope of the linear part in the higher flow rate region clearly shows the correctness of the revised HETP expression given by eqns. (14) and (15).

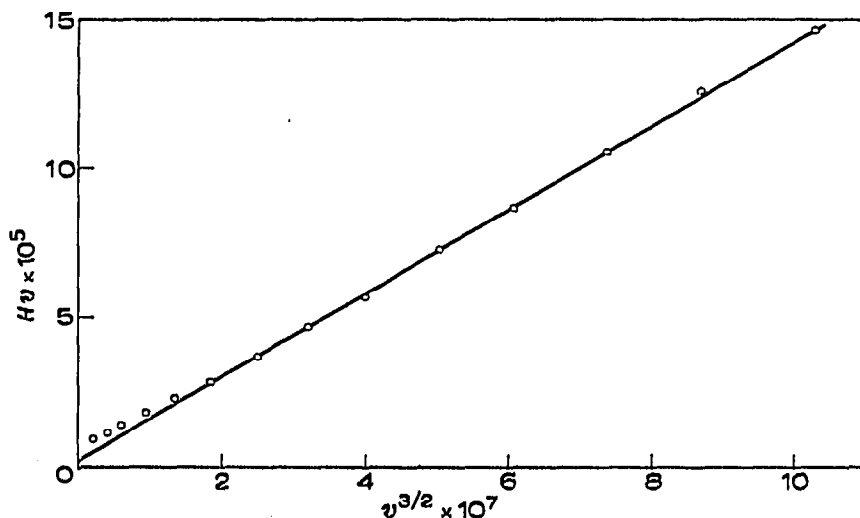


Fig. 5. Plot of the product of HETP and the absolute flow rate v of carrier gas against $v^{3/2}$ as predicted by the revised eqn. (15) for HETP.

SUMMARY

On the basis of our previous kinetic theory, in which the pressure dependencies of the diffusion coefficient in the gas phase and the linear velocity distribution along

the column are taken into account, a new expression for the gas chromatographic HETP is derived theoretically. Experimental results definitely confirm the essential validity of the present revised equation for HETP. It is concluded that in the VAN DEEMTER equation the constant term A should disappear and the term Cu_0 should be proportional not to the linear velocity u_0 but to the square root of it.

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