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THEORY OF CAPILLARY CHROMATOGRAPHY

EFFECT OF COILING AND INTERPHASE MASS TRANSFER

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SUMMARY

A satisfactory mathematical description of gas-liquid partition capillary chromatography is desirable for design and optimization of separation processes, as well as for determination of physical properties. A mathematical model is presented that includes the effects of mass transport in the mobile and stationary phases, assumes equilibrium at the gas-liquid interface, and accounts for axial dispersion of solute. Interphase mass transfer is included, and is found to be a significant contribution to band-spreading. To account for the effect of coiling on axial dispersion, an empirical coefficient Θ is introduced in the expression for the effective axial dispersion coefficient, since a complete theory for this phenomenon does not exist. Attempts to correlate experimental Θ values with molecular weight of solutes, kinematic viscosity of carrier gases, film thickness, and temperature are described. A criterion is established for the improvement in resolution due to coiling.

INTRODUCTION

Separation in gas-liquid partition capillary chromatography occurs because of different solubilities of different gaseous solutes in the liquid layer coating the inside of the column. The separation is hindered by mass transfer phenomena, including diffusion within the liquid layer, mass transfer resistance between gas and liquid phases, and longitudinal (axial) dispersion in the mobile gas phase. These processes cause band-spreading and may cause output peaks to overlap, reducing separation resolution. Capillary columns are usually very long and are therefore coiled. This coiling has a significant effect on axial dispersion, as we will show, and thus can strongly influence the resolving power of capillary columns.

The Golay¹ model of capillary chromatography includes axial dispersion but ignores the effect of coiling. Golay also treated the interphase mass transfer resistance in an approximate manner and approximated radial diffusion in the liquid film with a rectangular film model. Aris² extended the Golay model by accounting

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for possible non-equilibrium at the gas-liquid interface and by including longitudinal diffusion in the liquid film. This latter effect is simply of the order of the liquid-phase diffusion coefficient and is negligible compared with the gas-phase diffusion. Khan³ also attempted to account for interfacial non-equilibrium at the gas-liquid interface; but based on the pertinent discussions³⁻⁵, we conclude that it will be entirely negligible in typical capillary chromatography.

Subramanian⁶ studied capillary chromatography using the method developed with Gill⁷. A special term, which is essentially unrelated to the conventional mass transfer coefficient k_g , came out of the theory to describe interphase transfer of solute. The theory did not include the effect of coiling, nor diffusion in the liquid, and was not compared with experimental data.

Hazeldean and Scott⁴ have considered the possibility that adsorption at the liquid-solid interface can contribute to band-spreading. They performed experiments with columns stripped of the liquid layer, and found adsorption sufficiently strong to cause asymmetric output peaks. For the experimental data⁸⁻¹⁰ considered herein, output peaks were symmetric and showed no indication of adsorption. Therefore, in the present theory we ignore adsorption at the liquid-solid and at the gas-liquid interfaces.

A number of investigators have studied the effect of coiling on axial dispersion in uncoated tubes¹¹⁻¹⁵. Giddings¹⁶ asserts that even a single 90° bend can destroy resolution in packed columns. Tijssen^{17,18} is apparently alone in examining how coiling might affect axial dispersion in coated capillary tubes. His theory predicts that secondary flows produced by coiling can have either a positive or negative effect on resolution, depending on the (assumed) shape of the velocity profile of the mobile phase and the ratio of column diameter to helix diameter. Tijssen and Wittebrood's theory¹⁸ is based on assumed velocity profiles and was not compared with experimental data.

The objective of the present work is to attempt to determine quantitatively the influence of the approximations mentioned above. Accordingly, we present an improved model for capillary chromatography which includes accurate estimates for interphase mass transfer coefficients, liquid diffusion in the cylindrical film, and the effect of coiling on axial dispersion. Our treatment of the coiling effect is semi-empirical. We have compared our model with available experimental data in the literature. We find that interphase mass transfer resistance is not negligible, but, in fact, can be a major contribution for columns with thicker liquid films. We find that the rectangular-coordinate representation of radial liquid-phase diffusion is accurate. An important correction to the Golay¹ theory is found to be the coiling effect. We discuss how coiling influences resolution and optimization in capillary chromatography. We follow the general method used by Carbonell and McCoy¹⁹ in their study of resolution and optimization in adsorption chromatography and gel permeation chromatography.

THEORY

Other models^{1-3,6,18} of capillary chromatography begin with the point, differential mass balance equation for concentration in the mobile phase, $C(t,r,z)$, and average the equation over the tube cross-section to obtain an equation for the area-averaged concentration, $c(t,z)$. This approach yields an expression for the axial dis-

persion coefficient D_0 . Our procedure is to begin with the equation for $c(t,z)$, and adopt an expression for D_0 that includes all the effects studied by Golay¹, in addition to an empirical parameter to account for the coiling effect. Accordingly, we write

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} + \frac{2}{R'} k_g (c - c_s) - D_0 \frac{\partial^2 c}{\partial z^2} = 0 \quad (1)$$

where we have written the driving force for interphase mass transfer as $(c - c_s)$ instead of the more usual difference between bulk-average concentration and surface concentration²⁰. This approximation will be satisfactory when the rate of mass transfer to the liquid is small, resulting in small radial gradients in concentration.

Eqn. 1 is coupled to the mass balance for the solute in the stationary (liquid) phase,

$$\frac{\partial c_L}{\partial t} = D_L \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_L}{\partial r} \right) \quad (2)$$

where we have ignored longitudinal molecular diffusion². The initial conditions for eqns. 1 and 2 are

$$c(z, t = 0) = 0 \quad (3)$$

$$c_L(r, t = 0) = 0 \quad (4)$$

The boundary conditions for the z coordinate are

$$c(z = 0, t) = c_0(t) \quad (5)$$

$$c(z \rightarrow \infty, t) = 0 \quad (6)$$

When instantaneous equilibrium at the surface is assumed to be established, we have

$$c_L(R') = Kc_s \quad (7)$$

where K is the partition coefficient of solute in liquid, *i.e.*, the Henry's law equilibrium constant at the gas-liquid interface. Continuity of flux at the interface serves as a boundary condition that couples eqns. 1 and 2,

$$k_g (c - c_s) = -D_L \frac{\partial c_L}{\partial r} (r = R') \quad (8)$$

Finally, since there is no flux through the column wall,

$$\frac{\partial c_L}{\partial r} (r = R) = 0 \quad (9)$$

Golay¹ and Aris² used the boundary condition

$$D_g \frac{\partial C}{\partial r} (r=R') = D_L \frac{\partial c_L}{\partial r} (r=R') \quad (10)$$

instead of eqn. 8. They then evaluated the gradient of C at $r = R'$ using an approximate solution for the concentration profile in the gas phase. Our approach allows us to use mass transfer coefficients k_g obtained from exact solutions, and at the same time express the flux of solute to the wall as a linear function of the area averaged concentration. This is particularly convenient when the moments of eqn. 1 with respect to time are to be calculated.

In his theoretical treatment of coated capillary columns without coiling, Golay¹ made approximations similar to those made by Taylor²¹ and derived an expression for the effective axial dispersion coefficient. Aris generalized Golay's result and obtained,

$$D_0 = D_g + \frac{R^2 v^2}{D_g} \mathcal{L} \quad (11)$$

where

$$\mathcal{L} = (11 - 16\bar{R} + 6\bar{R}^2)/48 \quad (12)$$

in terms of

$$\bar{R} = 1/[1 + K((R/R')^2 - 1)] \quad (13)$$

For very thin liquid films

$$\bar{R} \approx 1/(1 + K') \quad (14)$$

and therefore,

$$\mathcal{L} \approx (1 + 6K' + 11K'^2)/48(1 + K')^2 \quad (15)$$

which is the expression derived by Golay¹.

As for coated coiled tubes Tijssen and Wittebrood¹⁸ pointed out that \mathcal{L} is very sensitive to the exact shape of the velocity profile. Recognizing that secondary flows induced by a coiled tube will alter the velocity profile, they calculated values of \mathcal{L} for different assumed profiles $v(r)$. Tijssen and Wittebrood's¹⁸ treatment of interphase mass transfer is like Golay's¹. Thus the essential difference in Tijssen's theory as compared with the Golay theory¹ is the attempt to include the coiling effect. For example, for a linear profile Tijssen and Wittebrood¹⁸ found

$$\mathcal{L} = (4 + 11K' + 17K'^2)/80(1 + K')^2 \quad (16)$$

Taking the ratio of eqn. 16 to eqn. 15, we have an expression which provides a measure of the coiling effect:

$$\mathcal{R} = \frac{48}{80} \left(\frac{4 + 11K' + 17K'^2}{1 + 6K' + 11K'^2} \right) \quad (17)$$

As K' varies from 0 to ∞ , \mathcal{R} varies from 2.4 to 0.93. Physical values of K' may range from 10^{-3} to 20. Therefore, this model predicts axial dispersion will increase in coiled

tubes with absorption in the thin liquid film, unless K' is greater than 1.75. We emphasize that Tijssen and Wittebrood's¹⁸ theory is based on an arbitrary velocity profile, and predicted trends were not compared with experimental data in that work.

Because the gas flow-rate is very low in capillary chromatography, the departure from a Poiseuille profile should be small. Thus, the present approach is to adopt the form of Golay's expression for ℓ and substitute an empirical coefficient for 48 in eqn. 12. The proposed expression is

$$\ell = (11 - 16\bar{R} + 6\bar{R}^2)/\Theta \quad (18)$$

where Θ accounts for the coiling effect on axial dispersion. In a straight tube Θ is equal to 48. Values of Θ determined empirically will enable us to make certain generalizations concerning the dependence of Θ on system parameters.

It is impossible to solve analytically the system of differential equations 1-9. However, chromatographic peaks can be characterized by normalized absolute and central moments. The moments are related to limits of derivatives of the Laplace-transformed concentration,

$$m_n(z) = (-1)^n \lim_{s \rightarrow 0} \frac{d^n \bar{c}(z,s)}{ds^n}, \quad n = 0, 1, 2, \dots \quad (19)$$

where

$$m_n(z) = \int_0^\infty c(z,t) t^n dt \quad (20)$$

Since the zero moment m_0 is a constant, we normalize the absolute moments as

$$\mu_i(z) = m_i(z)/m_0, \quad i = 1, 2, \dots \quad (21)$$

The normalized second central moment is

$$\mu_2(z) = \mu_2'(z) - [\mu_1'(z)]^2 \quad (22)$$

In the Appendix we show details in the derivation of the moment expressions, which are

$$\mu_1'(z) = \mu_1'(0) + \xi_1 z \quad (23)$$

where

$$\xi_1 = \left[1 + \frac{\delta K}{R'} (1 + R/R') \right] / v \quad (24)$$

and

$$\mu_2(z) = \mu_2(0) + 2\Gamma z / v \quad (25)$$

where

$$\Gamma = x/v^2 + y \quad (26)$$

with

$$x = D_0 \delta_0^2 \quad (27)$$

$$\delta_0 = 1 + \frac{\delta K}{R'} (1 + R/R') \quad (28)$$

and

$$y = \frac{\delta K}{R'} (1 + R/R') \mathcal{A} \quad (29)$$

where \mathcal{A} is given by eqn. A-18 of the Appendix.

The second moment, a measure of band-spreading, leads to a definition of height equivalent to a theoretical plate,

$$H = L\mu_2(L)/[\mu_1(L) - \mu_1(0)]^2 \quad (30)$$

Substituting eqns. 23 and 25 into 30, one finds

$$H = \frac{\mu_2(0)v^2}{L \delta_0^2} + \frac{2D_0}{v} + \frac{2y}{\delta_0^2} v \quad (31)$$

Substituting eqn. 29 for y and the expression for D_0 as a function of v , eqn. 11 with 18, one can express H in the form of the well-known equation:

$$H = A + B/v + Cv \quad (32)$$

where

$$A = \mu_2(0)v^2/L\delta_0^2 - \left(\frac{S}{\pi R'^2}\right)^2 / 12L\delta_0^2 \quad (33)$$

$$B = 2D_0 \quad (34)$$

$$C = C_g + C_i + C_L \quad (35)$$

$$C_g = \frac{2R^2}{\Theta D_0} (11 - 16\tilde{R} + 6\tilde{R}^2) \quad (36)$$

$$C_i = \frac{2K^2\delta^2(R + R')^2}{\delta_0^2 R'^3 k_g} \quad (37)$$

and

$$C_L \approx \frac{2}{3} \frac{K'}{(1 + K')^2} \frac{\delta^2}{D_L} \text{ for } \delta/R \ll 1 \text{ (see Appendix, eqn. A-22)} \quad (38)$$

Eqn. 32 may be directly compared with an equation of the same form derived by Golay¹. We find that Golay's theory omits the A term, which is negligible when the sample volume S is very small, the usual case in capillary chromatography. The

B term is identical in the two theories. Our C_g term contains Θ , which is equal to 48 in Golay's theory. The C_i term is absent in Golay's model, a result of his technique for evaluating the flux of solute to the capillary wall. Our C_L term, eqn. A-22, is exact for cylindrical films; for $\delta/R \ll 1$ we obtain eqn. 38, identical to Golay's rectangular-coordinate treatment of the liquid-phase diffusion.

DISCUSSION

The experimental data used in this work are from Desty and Goldup⁸, Hazeldean and Scott⁹, and Halasz and Horvath¹⁰. They experimentally studied the relationships between the plate height and velocity in great detail. The output peaks obtained in these experiments were sharp and sufficiently close to Gaussian that first and second moments adequately describe their position and shape. Desty and Goldup⁸ stated that coiled glass capillary columns were employed. Hazeldean and Scott⁹ did not mention whether their nylon tubing was coiled, but in their later work⁴ they stated that the nylon capillary was wound on to a brass cylinder.

Because of secondary flows, mass transfer at the surface of coiled tubes is enhanced compared with mass transfer in straight tubes²². To determine whether this enhancement is significant in the present capillary columns, we estimated the coil to tube diameter ratio to be 100 and the velocity to have an upper limit of 100 cm/sec. With the values of physical parameters appropriate to the experiments, we find the Schmidt number to be less than 4. Therefore, the average mass transfer Nusselt number is very nearly the same as for a straight tube²². Accordingly, we express the mass transfer coefficient for the very long capillary columns as

$$k_g = 3.657 D_g/d \quad (39)$$

The experimental papers⁸⁻¹⁰ used the Gilliland²³ correlation to estimate gas diffusion coefficients, D_g . By means of the more accurate Chapman-Enskog formula²⁴ we have re-evaluated D_g in this work. The difference between the two formulae for D_g varies from 1 to 20%, and helps somewhat in bringing theory into accord with experiment at the lower velocities.

Values of Θ were determined empirically so that eqn. 32 had the same slope at higher velocities as did the experimental plots of H vs. v . The results for n -propane through n -nonane are shown in Table I. We found Θ to range from 0.7 to 197, which encompasses the range of 20 to 52 determined from Tijssen and Wittebrood's¹⁸ approximate theory, eqn. 16.

Typical plots of H vs. v are shown in Figs. 1-4. These figures are representative of the results obtained with the n -alkanes and the values of Θ shown in Table I. The worst agreement obtained between model and experiment for any of the n -alkanes is shown in Figs. 1 and 3. Fig. 2 shows an agreement typical of most comparisons made with experiment. Fig. 4 shows a case where the agreement is very good, but not the best obtained. For all the data Golay's¹ theory decidedly underestimated H in the higher velocity range, where interphase mass transfer and the coiling effect on axial dispersion are important. The ranges of C_g , C_L , and C_i are $2.0 \cdot 10^{-4}$ to $3.5 \cdot 10^{-3}$ sec, $2.0 \cdot 10^{-6}$ to $1.2 \cdot 10^{-3}$ sec, and $6.0 \cdot 10^{-7}$ to $2.2 \cdot 10^{-3}$ sec, respectively. Since C_i increases as δ^2 , eqn. 37, for the columns with thicker liquid films the increased interphase mass transfer can be the major contribution to C . Numerical results showed

TABLE I
VALUES OF θ CALCULATED FROM EXPERIMENTAL DATA FOR *n*-ALKANES

Carrier gas	Temperature (°C)	Column	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	Ref.
Nitrogen	25	1		9.27	9.14	10.0	17.2			8
Nitrogen	25	2	5.28	6.08	9.00	16.5	32.5			8
Nitrogen	25	3		3.81	7.70	14.2	32.8			8
Nitrogen	25	4		4.50	3.50	5.70	7.09			8
Nitrogen	25	5		2.50	5.13	6.65	9.24			8
Nitrogen	25	6		11.5	12.5	10.2	14.5			8
Nitrogen	50	2		15.6	12.0	17.8	25.5	35.7		8
Nitrogen	75	2			9.0	9.5	20.0	33.9	55.1	8
Hydrogen	25	2	2.30	1.43						8
Hydrogen	80	C			0.7		1.5			10
Hydrogen	80	D			2.8		4.5			10
Argon	25	2		7.0						8
Argon	21	7			37.4	80.0	88.2	197.0		9
Argon	21	8					27.5			9
Argon	21	9					25.6			9

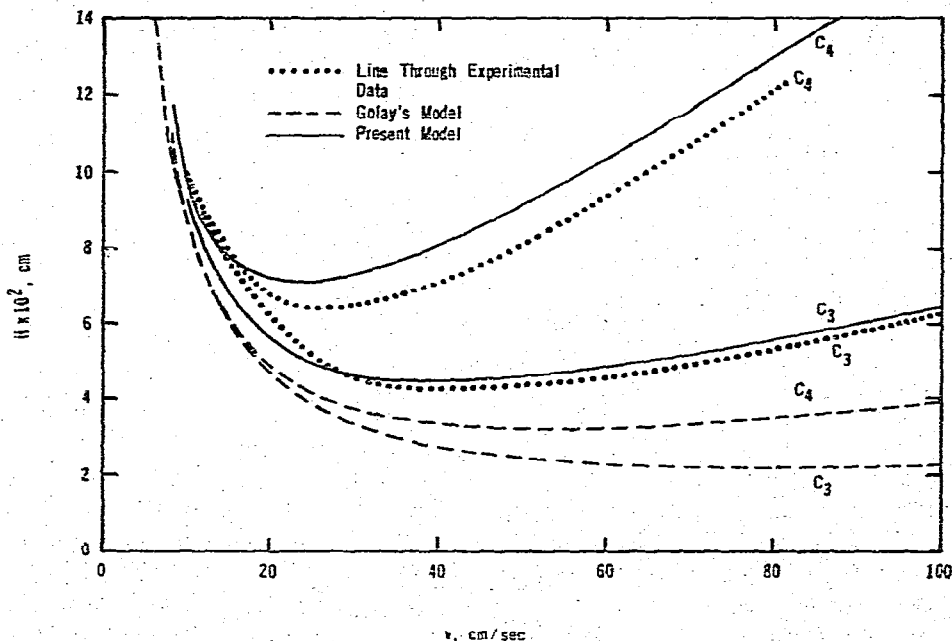


Fig. 1. Comparison of the relation H vs. v for this model and Golay's model with experimental data: *n*-alkanes eluted by hydrogen at 25° from column 2 of ref. 8.

that the difference between the cylindrical- and rectangular-coordinate treatments of C_L , eqns. A-21 and 38, was negligible for these films.

To find the dependence of θ on the molecular weight of the solutes, the values of $\log \theta$ were plotted against the values of \log molecular weight of solute. As Fig. 5

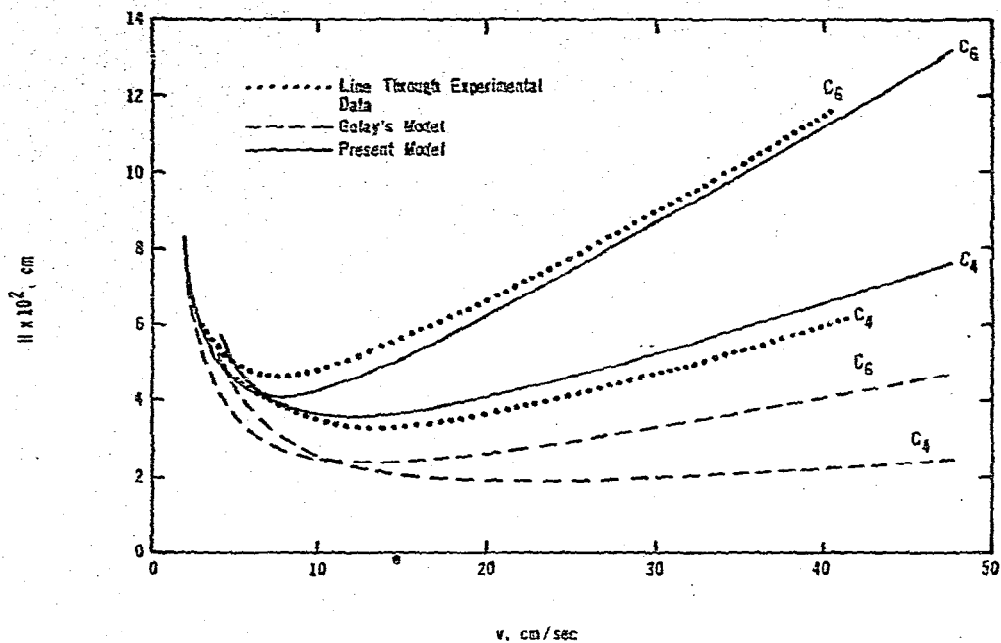


Fig. 2. Comparison of the relation H vs. v for this model and Golay's model with experimental data: n -alkanes eluted by nitrogen at 25° from column 2 of ref. 8.

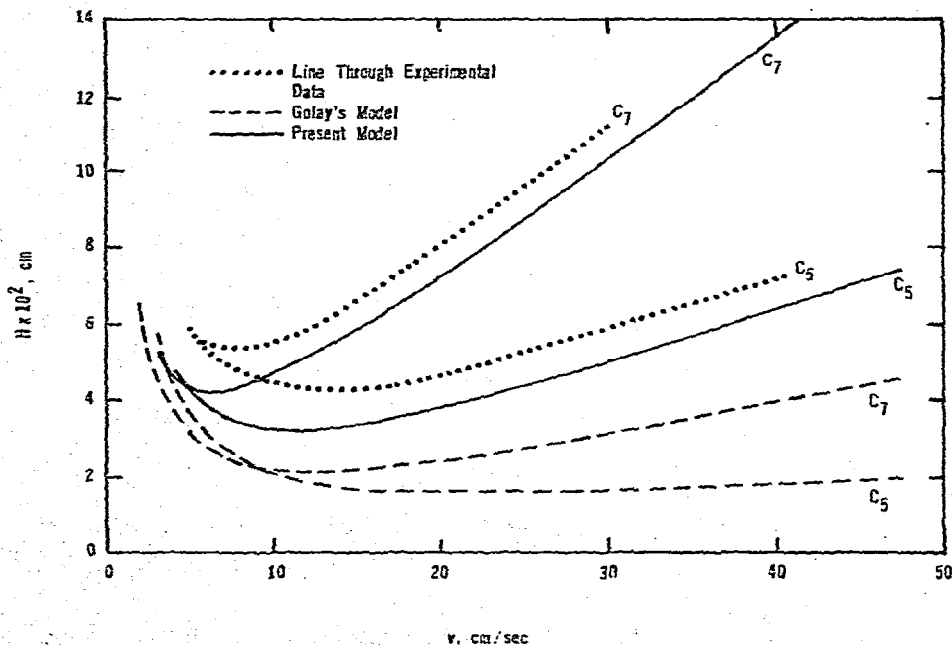


Fig. 3. Comparison of the relation H vs. v for this model and Golay's model with experimental data: n -alkanes eluted by nitrogen at 25° from column 1 of ref. 8.

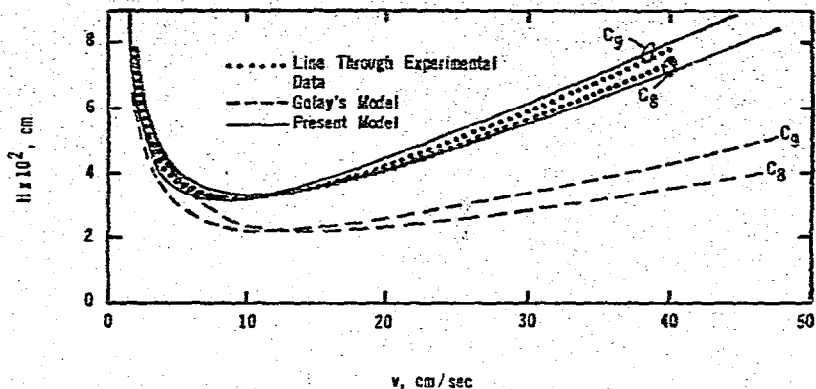


Fig. 4. Comparison of the relation H vs. ν for this model and Golay's model with experimental data: n -alkanes eluted by nitrogen at 75° from column 2 of ref. 8.

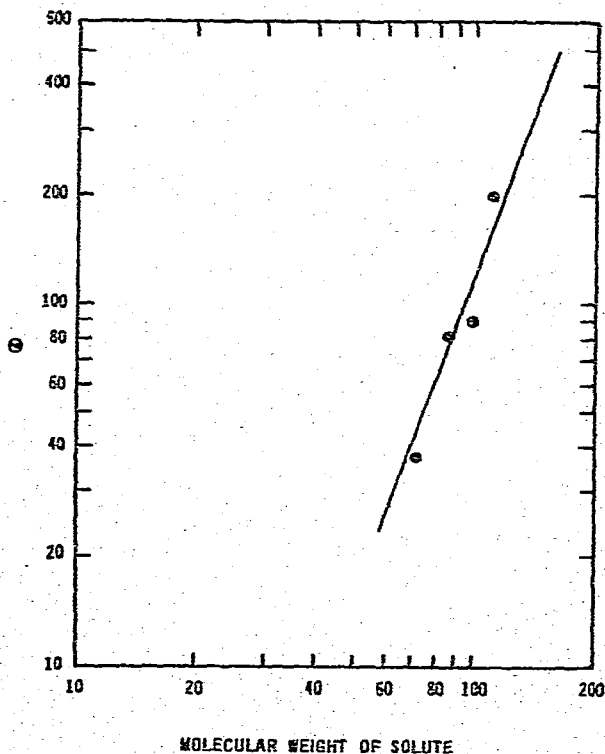


Fig. 5. Log-log plot of Θ vs. molecular weight of solute for experiments of ref. 9 with argon as carrier gas.

shows, for example, a set of lines with slope equal to 3.0 is obtained. Thus, Θ is proportional to the third power of solute molecular weight.

The log-log plot of Θ vs. kinematic viscosity ν of carrier gas is shown in Fig. 6.

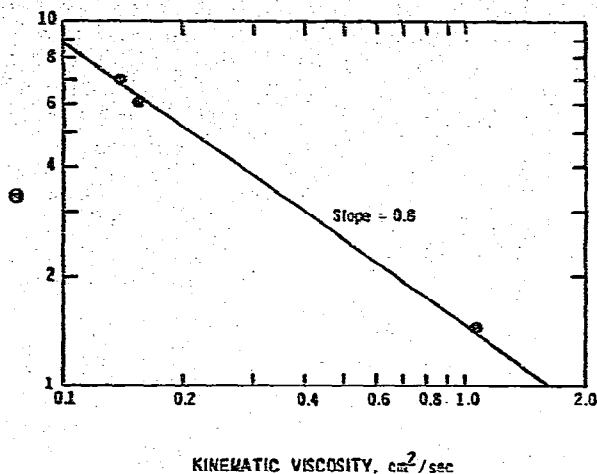


Fig. 6. Log-log plot of Θ vs. kinematic viscosity of carrier gas for experiments of ref. 8 with column 2.

We conclude that Θ is inversely proportional to the 4/5 power of kinematic viscosity of carrier gas.

Plots of Θ vs. film thickness or temperature are less definitive, but optimum conditions which maximize Θ and thereby minimize axial dispersion appear to exist. There are presently insufficient data for finding the dependence of Θ on the radius, radius of the helix into which the column is wound, film thickness, and physical properties of the stationary phase.

RESOLUTION AND OPTIMIZATION

The extent of separation of two Gaussian peaks for solutes A and B may be quantified by defining the resolution¹⁹,

$$R_s = \frac{\mu'_{1B} - \mu'_{1A}}{\mu'_{2B} + \mu'_{2A}} \quad (40)$$

In practical work it is often desirable to estimate the required column length for the separation of a given solute pair. By substituting the expressions for moments, eqns. 23 and 25, into eqn. 40, and squaring the resulting equation twice, one can solve for the column length,

$$L = 2v \left(\frac{R_s}{a} \right)^2 \left\{ \Gamma_A + \Gamma_B + \left[4\Gamma_A\Gamma_B + \mu_2(0) \left(\frac{a}{R_s} \right)^2 \right]^{\frac{1}{2}} \right\} \quad (41)$$

where $a = \delta_{0A} - \delta_{0B}$. In obtaining eqn. 41, the input pulse is assumed to be a homogeneous mixture which satisfies

$$\mu'_{1A}(0) = \mu'_{1B}(0) = \mu'_1(0) \quad (42)$$

and

$$\mu'_{2A}(0) = \mu'_{2B}(0) = \mu'_2(0) \quad (43)$$

If $\mu_2(0)$ is negligible, we find

$$L = 2v \left(\frac{R_s}{a} \right)^2 \left[\Gamma_A^{\pm} + \Gamma_B^{\pm} \right]^2 \quad (44)$$

so that resolution increases as the square root of column length, in agreement with other analyses¹⁹.

The *n*-pentane and *n*-hexane data of Desty and Goldup⁸ and Hazeldean and Scott⁹ are used to evaluate the column length by eqn. 43 for values of R_s from 1.0 to 4.0. Plots of L vs. v are shown in Figs. 7 and 8 for the coiled tube and for the straight tube, where $\Theta = 48$. The length of the column increases with increasing resolution, and the optimum velocity is independent of the desired resolution. In the coiled tube the optimum velocity is 8.0 cm/sec for the Desty and Goldup⁸ data and 9.5 cm/sec for the Hazeldean and Scott⁹ data. As for the straight tube, the optimum velocity shifts to 11 cm/sec and 9.0 cm/sec, respectively. The results confirm that coiling a column may have an improving or worsening effect, depending on operating conditions and properties of the column.

A criterion can be established for determining when coiling is beneficial or detrimental. By substituting eqn. 25 into 40 one finds an equation for L in terms of

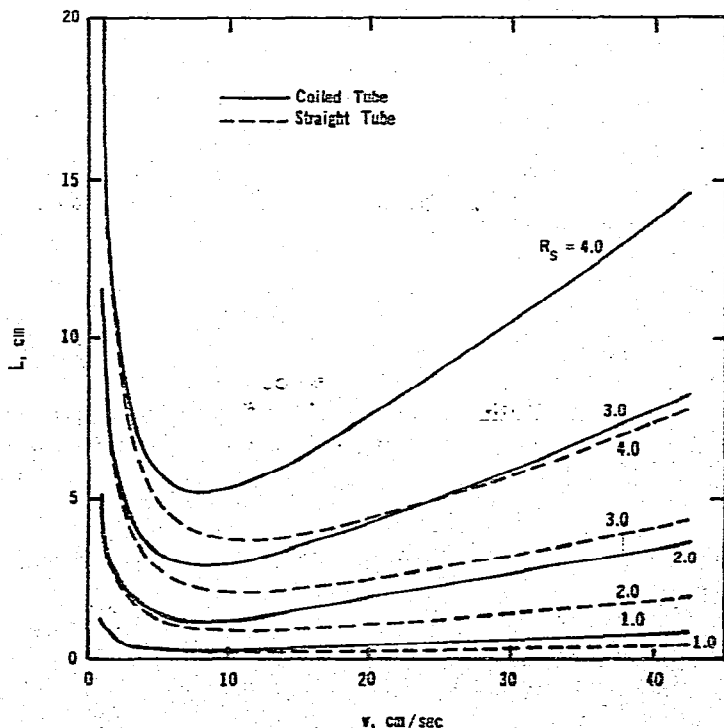


Fig. 7. Effect of velocity and resolution on column length for *n*-pentane and *n*-hexane separation: data are from ref. 8 for nitrogen carrier gas.

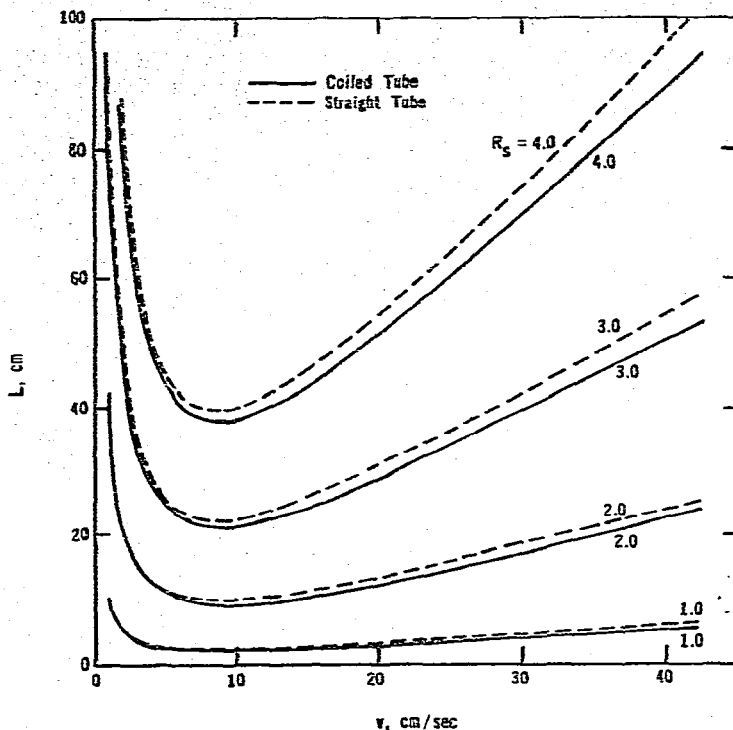


Fig. 8. Effect of velocity and resolution on column length for *n*-pentane and *n*-hexane separation: data are from ref. 9 for argon carrier gas.

v. The same equation for the length of a straight column, L' , is written by replacing Θ_A and Θ_B by 48. The two equations for L are subtracted to give

$$L - L' = 2 \left(\frac{R_s}{a} \right)^2 v [(\alpha + \beta)^2 - (\alpha' + \beta')^2] \quad (45)$$

where

$$\alpha = \frac{(11 - 16\bar{R}_A + 6\bar{R}_A^2)R^2 \delta_{0A}^2}{\Theta_A D_{gA}} + y_A \quad (46)$$

and

$$\beta = \frac{(11 - 16\bar{R}_B + 6\bar{R}_B^2)R^2 \delta_{0B}^2}{\Theta_B D_{gB}} + y_B \quad (47)$$

The quantity α' is the same as eqn. 46 except Θ_A is replaced by 48; β' is the same as eqn. 47 except Θ_B is replaced by 48. One can express the coiling criterion as

$$(\alpha + \beta)^2 - (\alpha' + \beta')^2 \begin{cases} > 0 \text{ for } L > L' \\ < 0 \text{ for } L < L' \end{cases} \quad (48)$$

It is not difficult to follow the earlier work of Carbonell and McCoy¹⁹ to analyze the economic optimization of capillary chromatography. One expresses the net income as the difference between the product income and the coating replacement and pumping costs. Plots of net income vs. operating velocity show maxima for different values of resolution R_s . The optimum velocity decreases with increasing resolution. An increase or decrease in the maximum income for a coiled tube depends on the values of Θ , which vary with film thickness, temperature, molecular weight of solute, and other properties of the system.

A more detailed presentation of the matters discussed in this paper may be found in ref. 25.

CONCLUSIONS

Interphase mass transfer resistance and column coiling are likely to contribute significantly to the calculation of the height of a theoretical plate in capillary chromatographic columns. Empirical values of the axial dispersion coiling coefficient Θ fall in the range of the theoretical values predicted by Tijssen and Wittebrood¹⁸ for a linear velocity profile. Coiling can either improve or impair the resolution obtained between two components in a straight capillary chromatographic column, according to the criterion expressed in eqn. 48. Although large scale preparative capillary chromatography may presently be economically impracticable, an understanding of the transport phenomena in such systems will be helpful to develop more accurate theories of other chromatographic processes.

LIST OF SYMBOLS

A and B	= Subscripts denoting chemical species
A	= Term defined by eqns. 32 and 33 (cm)
\mathcal{A}	= Term defined by eqn. A-18
a	= $\delta_{0A} - \delta_{0B}$
B	= Term defined by eqns. 32 and 34 (cm ² /sec)
$C(t,r,z)$	= Concentration of solute (g/cm ³)
C	= Term defined by eqns. 32 and 35 (sec)
C_g	= Term defined by eqns. 35 and 36 (sec)
C_l	= Term defined by eqns. 35 and 37 (sec)
C_L	= Term defined by eqns. 35 and A-22 (sec)
$c(t,z)$	= Concentration of solute, averaged over cross-section of column (g/cm ³)
$c_L(t,r)$	= Concentration of solute in liquid film (g/cm ³)
$c_0(t)$	= Concentration of solute at column inlet (g/cm ³)
$c_s(t)$	= Concentration of solute in gas at liquid surface (g/cm ³)
\bar{c}	= Laplace transform of concentration
D_g	= Diffusion coefficient of solute in carrier gas (cm ² /sec)
D_L	= Diffusion coefficient of solute in liquid (cm ² /sec)
D_0	= Axial dispersion coefficient for solute in carrier gas (cm ² /sec)
d	= $2R$, column diameter (cm)
H	= Height equivalent to a theoretical plate (cm)
I_0, I_1	= Modified Bessel functions of first kind

\mathcal{J}	= Term defined by eqn. A-9
K_0, K_1	= Modified Bessel functions of second kind
K	= Partition coefficient
K'	= $2K\delta/R$
\mathcal{K}	= Term defined by eqn. A-11
\mathcal{L}	= Term defined by eqn. 11
k_g	= Mass transfer coefficient (cm/sec)
L	= Length of column (cm)
L'	= Uncoiled column length (cm)
$m_n(z)$	= Unnormalized moment defined by eqn. 20
R	= Column radius (cm)
R'	= $R - \delta$ (cm)
R_s	= Resolution defined by eqn. 40
\bar{R}	= Term defined by eqn. 13
\mathcal{R}	= Term defined by eqn. 17
r	= Radial coordinate (cm)
S	= Input sample volume (cm ³)
s	= Laplace transform variable of time (sec ⁻¹)
t	= Time (sec)
v	= Column cross-sectional average velocity (cm/sec)
x	= Term defined by eqns. 26 and 27
y	= Term defined by eqns. 26 and 29
z	= Axial coordinate (cm)
α	= Term defined by eqn. 46
α'	= Term defined by eqn. 46 with Θ_A replaced by 48
β	= Term defined by eqn. 47
β'	= Term defined by eqn. 47 with Θ_B replaced by 48
Γ	= Coefficient defined by eqns. 25 and 26
δ	= Liquid film thickness (cm)
δ_0	= Quantity defined by eqn. 28
Θ	= Coefficient defined by eqn. 18
$\mu'_n(z)$	= Normalized n th absolute moment (sec)
$\mu_2(z)$	= Normalized second central moment (sec ²)
ν	= Kinematic viscosity (cm ² /sec)
ξ_1	= Quantity defined by eqn. 24
ξ_2	= Quantity defined by eqns. A-16 and A-17

APPENDIX

The Laplace-transformed set of equations 1-9 for $\bar{c}(s,z)$ and $\bar{c}_L(s,r)$ become

$$D_0 \frac{d^2 \bar{c}}{dz^2} - v \frac{d\bar{c}}{dz} - s\bar{c} - \frac{2}{r'} k_g (\bar{c} - \bar{c}_s) = 0 \quad (\text{A-1})$$

$$\frac{d^2 \bar{c}_L}{dr^2} + \frac{1}{r} \frac{d\bar{c}_L}{dr} - \frac{s}{D_L} \bar{c}_L = 0 \quad (\text{A-2})$$

$$\bar{c} = \bar{c}_0, \text{ at } z = 0 \quad (\text{A-3})$$

$$\bar{c} = 0, \text{ at } z \rightarrow \infty \quad (\text{A-4})$$

$$\bar{c}_L = K\bar{c}_s, \text{ at } r = R' \quad (\text{A-5})$$

$$k_g(\bar{c} - \bar{c}_s) = -D_L \frac{d\bar{c}_L}{dr}, \text{ at } r = R' \quad (\text{A-6})$$

and

$$\frac{d\bar{c}_L}{dr} = 0, \text{ at } r = R \quad (\text{A-7})$$

The solution of eqn. A-2 with boundary conditions A-6 and A-7 is expressed in terms of Bessel functions I_0 , I_1 , K_0 and K_1 ,

$$\bar{c}_L(r) = \frac{k_g(\bar{c} - \bar{c}_s)}{\sqrt{D_L s} \mathcal{J}} \left[I_0(r\sqrt{s/D_L}) + \frac{I_1(R\sqrt{s/D_L})}{K_1(R\sqrt{s/D_L})} K_0(r\sqrt{s/D_L}) \right] \quad (\text{A-8})$$

where

$$\mathcal{J} = -I_1(R'\sqrt{s/D_L}) + I_1(R\sqrt{s/D_L}) K_1(R'\sqrt{s/D_L}) / K_1(R\sqrt{s/D_L}) \quad (\text{A-9})$$

By use of eqn. A-5 the flux at the interface becomes

$$k_g(\bar{c} - \bar{c}_s) = k_g \bar{c} \sqrt{D_L s} \mathcal{J} / [k_g \mathcal{K} / K + \sqrt{D_L s} \mathcal{J}] \quad (\text{A-10})$$

where

$$\mathcal{K} = I_0(R'\sqrt{s/D_L}) + I_1(R\sqrt{s/D_L}) K_0(R'\sqrt{s/D_L}) / K_1(R\sqrt{s/D_L}) \quad (\text{A-11})$$

Substituting eqn. A-11 into eqn. A-1 gives the differential equation

$$\frac{d^2 \bar{c}}{dz^2} - \frac{v}{D_0} \frac{d\bar{c}}{dz} - \frac{h}{D_0} \bar{c} = 0 \quad (\text{A-12})$$

where

$$h = s + \frac{2k_g}{R'(1 + k_g T/K)} \quad (\text{A-13})$$

with

$$T = \frac{1}{\sqrt{s D_L}} \frac{\mathcal{K}}{\mathcal{J}} \quad (\text{A-14})$$

The solution of eqn. A-12 with boundary conditions A-3 and A-4 is

$$\bar{c}(z, s) = \bar{c}_0(s) e^{\lambda z} \quad (\text{A-15})$$

where

$$\lambda = \frac{v}{2D_0} [1 - \sqrt{1 + 4hD_0/v^2}] \approx s \xi_1 + s^2 \xi_2 \text{ (for small } s) \quad (\text{A-16})$$

with ξ_1 defined in eqn. 23 and

$$\xi_2 = \frac{D_0}{v^2} \left[1 + \frac{\delta K}{R'} (1 + R/R') \right]^2 + \frac{\mathcal{A} \delta K}{R' v} (1 + R/R') \quad (\text{A-17})$$

in terms of

$$\begin{aligned} \mathcal{A} = & \frac{K\delta(R+R')}{2R'k_g} - \frac{2RR'}{\delta(R+R')} \left[\frac{RR'}{4D_L} \ln \left(1 - \frac{\delta}{R} \right) \right. \\ & + \frac{R^2}{16D_L} \left(1 + \frac{\delta}{R'} \right) - \frac{R'^2}{16D_L} \left(1 - \frac{\delta}{R} \right) \left. \right] + \frac{R^2}{2D_L} \ln \left(1 + \frac{\delta}{R'} \right) \\ & - \frac{R^2}{4D_L} + \frac{RR'}{4D_L} \left[1 - \frac{\delta}{R} \right] \quad (\text{A-18}) \end{aligned}$$

Substitution of eqn. A-16 into eqn. A-15 evaluated at $z = L$ yields after expanding $\bar{c}_0(s)$ and the exponential,

$$\begin{aligned} \bar{c}(L,s) \approx & \left[\bar{c}_0(s=0) + s \frac{d\bar{c}_0}{ds}(s=0) + \frac{s^2}{2} \frac{d^2\bar{c}_0}{ds^2}(s=0) \right] \\ & \left[1 + s\xi_1 L + s^2 \left(\frac{1}{2} \xi_1^2 L^2 + \xi_2 L \right) \right] \quad (\text{A-19}) \end{aligned}$$

Dividing eqn. A-19 by

$$m_0 = \bar{c}_0(s=0) \quad (\text{A-20})$$

and re-arranging gives the Taylor series expansion

$$\bar{c}(L,s)/m_0 \approx 1 - s\mu'_1(L) + \frac{1}{2} s^2 \mu'_2(L) \quad (\text{A-21})$$

which with eqns. 19-22 yields the moment equations 23-29.

When one carries out the operations to calculate the height equivalent to a theoretical plate based on the definition eqn. 30, one obtains eqns. 32-37 and

$$\begin{aligned} C_L = & \frac{2\delta K}{\delta_0^2 R'} \left(1 + \frac{R}{R'} \right) \left\{ - \frac{2RR'}{(R+R')\delta} \left[\frac{RR'}{4D_L} \ln \left(1 - \frac{\delta}{R} \right) \right. \right. \\ & + \frac{R^2}{16D_L} \left(1 + \frac{\delta}{R'} \right) - \frac{R'^2}{16D_L} \left(1 - \frac{\delta}{R} \right) \left. \right] + \frac{R^2}{2D_L} \ln \left(1 + \frac{\delta}{R'} \right) \\ & \left. - \frac{R^2}{4D_L} + \frac{RR'}{4D_L} \left(1 - \frac{\delta}{R} \right) \right\} \quad (\text{A-22}) \end{aligned}$$

When $\delta/R \ll 1$ one can expand the functions $\ln(1 \pm \delta/R)$ and $1/(1 \pm \delta/R)$ up to terms of order $(\delta/R)^3$, and show that eqn. 38, identical to Golay's¹ expression, is the result.

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