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Retention Time in Nonlinear Gas–Liquid Chromatography. Influence of the Sample Size. Part II. Case of a Nonlinear Isotherm

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Summary

The effect of the sample size on the retention time is studied both experimentally and theoretically. It has already been shown that the deviation of the retention time from its value at infinite dilution is a consequence of a nonlinearity in the basic transfer relations. The previous approach is extended to systems for which the equilibrium isotherm is no longer linear. The relative deviation is either positive or negative according to the curvature of the isotherm. A good agreement between predicted and experimental values is obtained.

INTRODUCTION

Porter et al. (*1*) and Conder and Purnell (*2*) have presented experimental results which show the deviation of the retention time from its value at infinite dilution when a large amount of solute is injected. These deviations appear to be caused by a variable partition coefficient along the column and by a variable solute partial pressure. Even when the partition coefficient remains constant, the retention time varies with the sample size. For this case a theoretical approach has been presented in a previous paper (*3*), which will hereunder be referred to as Part I.

In what follows, this previous approach is extended to take into account the effect of a variable partition coefficient.

EXPERIMENTAL PROCEDURE

The apparatus used was described in Part I. The chromatograph is equipped with thermal conductivity detectors which enable the input impulse as well as the response impulse to be known. The retention time is measured by taking the difference between the average times corresponding to the two impulses. The flow rate of the carrier gas (helium) is regulated by needle valves and measured by a soap-bubble flowmeter at atmospheric pressure. The volume of pure solute injected is determined by measuring the peak area at the end of the column. Different columns of various lengths (from 0.5 to 2 m) and various diameters ($\frac{1}{8}$ or $\frac{1}{4}$ in.) are used. They are immersed in a liquid bath at 25 ± 0.1°C and packed with Fluoropak. Other experimental procedure details are given elsewhere (*4*, *5*).

REVIEW OF PREVIOUS RESEARCH

Bosanquet and Morgan (*6*, *7*), and Haarhoff and Van Der Linde (*6*) first pointed out the importance of a solute concentration. Experimental results were reported by Pollard and Hardy and others (*1*, *9–11*). Conder and Purnell (*2*, *12*), following these earlier works, were able to calculate the retention time in the case of a finite solute vapor concentration, but with a linear isotherm and an instantaneous equilibrium. An important result is that finite vapor concentration causes retention volumes to decrease with an increase in sample size.

The effect of a nonlinear isotherm has also been considered (*1*, *13*). De Vault (*14*) was the first to take this effect into account by considering the first-order conservation equation. This equation was taken as a basis for other developments. Weiss (*15*) studied the effect of the Langmuir and Freundlich isotherms, and Glueckauf (*16*) that of sigmoid isotherms. Helfferich (*17*) and Stalkup (*18*) tried to predict nonlinear isotherms from retention volumes. All these models are based on the assumption of instantaneous equilibrium. Actually, the rate of sorption on gas–liquid chromatography is an essential cause of zone spreading (*19*, *20*).

PREDICTION OF RETENTION TIME

The basic relations are the same as in Part I. The gas-phase concentration of Component A which is injected in the column will be represented either by the mole fraction C_g (moles of A/moles of carrier gas + moles of A) or by C_g' (moles of A/moles of carrier gas alone).

The differential equations relating C_g or C_g' and the liquid-phase mole fraction C_l to the distance z along the axis of the column and to the time t are obtained by a material balance on A around an element dz.

$$\frac{\partial}{\partial z}(vC_g') + \frac{\epsilon H}{V}\frac{\partial}{\partial t}C_g + Ka\left(\frac{C_g}{m} - C_l\right) = 0 \qquad (1)$$

$$\frac{\epsilon(1-H)'}{V}\frac{\partial}{\partial t}C_l - Ka\left(\frac{C_g}{m} - C_l\right) = 0 \qquad (2)$$

The boundary conditions at $t = 0$ are

$$C_g' = C_l = 0 \qquad (3)$$

and at $z = 0$

$$C_g'(t) = C_{g_e}'(t) \qquad (4)$$

In these equations it is assumed that total pressure may be considered as constant along the column and that the mass transfer rate between the two phases is controlled by a liquid-phase resistance. For such a case the mass transfer driving force is $(C_g/m) - C_l$ and, although the partition coefficient m varies with C_g, the mass transfer coefficient K remains constant (*21*). Equation (1) is somewhat more general than the corresponding equation of Part I since the carrier gas flow rate is no longer assumed to be constant. It will be shown that this modification generally causes only a slight correction in the results.

By introducing Laplace transforms, Eqs. (1) and (2) become

$$\frac{d}{dz}(\overline{vC_g'}) + \frac{\epsilon H}{V}p\overline{C_g} + Ka\left[\left(\overline{\frac{C_g}{m}}\right) - \overline{C_l}\right] = 0 \qquad (5)$$

$$\frac{\epsilon(1-H)'}{V}p\overline{C_l} - Ka\left[\left(\overline{\frac{C_g}{m}}\right) - \overline{C_l}\right] = 0 \qquad (6)$$

Instead of trying to solve these equations in terms of Laplace transforms and then calculating the moments of the response impulse, it is possible to derive equations in which the moments are the main variables.

By taking $p = 0$, Eq. (6) leads to a relation between the zero-order moments:

$$C_{1_0} = \left(\frac{C_g}{m}\right)_0 \tag{7}$$

De Vault's first-order conservation equation, written in terms of Laplace transform variables, may be deduced from Eqs. (5) and (6):

$$\frac{d}{dz}\,(\overline{vC_g'}) + \frac{p}{V}\,[\epsilon H\overline{C_g} + \epsilon(1 - H)'\overline{C_1}] = 0 \tag{8}$$

Taking the first moment of Eq. (8), it is found that

$$\frac{d}{dz}\,(vC_g')_1 + \frac{1}{V}\,[\epsilon HC_{g_0} + \epsilon(1 - H)'C_{1_0}] = 0 \tag{9}$$

In the case of an infinite dilution, $m = m_\infty$, $v = v_0$, and C_g' is equivalent to C_g.

Replacing C_{1_0} in Eq. (9) by its value C_{g_0}/m_∞ given by relation (7), it follows that

$$t_{R_l} = \left(\frac{C_{g_1}}{C_{g_0}}\right)_{z=L} = \frac{L}{Vv_0}\left[\epsilon H + \epsilon(1 - H)'\,\frac{1}{m_\infty}\right] \tag{10}$$

In the general case m varies with C_g and can be expressed by an expansion in series:

$$\frac{1}{m} = \frac{1}{m_\infty}\left(\sum_{k=1}^{\infty} \alpha_{k+1}C_g{}^k\right) \qquad \text{with } \alpha_1 = 1 \tag{11}$$

In general, it is possible to express the variation of m with C_g by considering only a few terms of expansion (11).

The relation (7) becomes

$$C_{1_0} = \frac{1}{m_\infty}\sum_{k=1}^{\infty} \alpha_k(C_g{}^k)_0 \tag{12}$$

Replacing C_{1_0} in Eq. (9), it follows that

$$(vC_g')_1 = \sum_{k=1}^{\infty} \beta_k\left[\int_0^L (C_g{}^k)_0\,dz\right] \tag{13}$$

with

$$\beta_1 = \frac{1}{V}\left[\epsilon H + \epsilon(1 - H)'\frac{1}{m_\infty}\right] = t_{R_l}\frac{v_0}{L} \tag{14}$$

and for $k \geq 2$

$$\beta_k = \frac{\epsilon(1 - H)'}{V}\frac{\alpha_k}{m_\infty} = (t_{R_l} - t_m)\frac{v_0}{L}\alpha_k \tag{15}$$

The problem now is to evaluate the integrals

$$\lambda_k = \int_0^L (C_g{}^k)_0\,dz = \int_0^L\int_{-\infty}^{+\infty}\left(\frac{C_g'}{1 + C_g'}\right)^k dz\,dt \tag{16}$$

One way of doing this is to replace C_g' by its Gaussian linear approximation value:

$$C_g' = \frac{C_{g0}'}{\sigma(2\pi)^{1/2}}\exp - \frac{1}{2}\left(\frac{t - t_R}{\sigma}\right)^2 \tag{17}$$

According to the linear approximation, σ will be assumed to be pro-

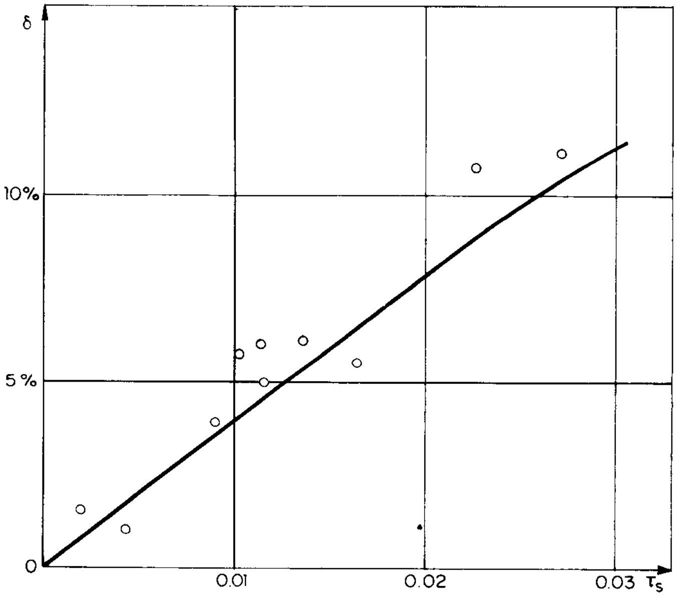

FIG. 1. Relative deviation δ vs. parameter τ_s for the benzene–dimethylsulfoxide system: (○) experimental vaules, (—) predicted values (Eq. 23).

portional to $\sqrt{z}$ and C_{g_0}' to be equal to I_m/v_0, with I_m being the number of moles of A injected at the entry of the column and v_0 the molar flow rate of the carrier gas at the entry. Integration is done first on z and then on t. If the input impulse is considered to be instantaneous (Dirac impulse), the integrals λ_k are found to depend on a single dimensionless parameter τ_s defined as

$$\tau_s = C_{g_0}'/(2\pi)^{1/2}\sigma_s \tag{18}$$

Integrals λ_k are expressed as

$$\lambda_k = [I_{k-2}(\tau_s) - 2I_{k-1}(\tau_s) + I_k(\tau_s)]LC_{g_0}' \tag{19}$$

with

$$I_{-1} = 1 + \sqrt{2}\,\tau_s$$

$$I_0 = \sqrt{2}\,\tau_s$$

$$I_1 = 2\left[\sum_{n=1}^{\infty} (-1)^{n+1}\frac{1}{n}\,\frac{1}{(n+3)^{1/2}}\,\tau_s^{\,n+2} - \frac{1}{\sqrt{3}}\,\tau_s^{\,2}\ln\tau_s + \frac{1}{\sigma\sqrt{3}}\,\tau_s^{\,2}\right]$$

$$I_k = \frac{2}{1-k}\left[\sum_{n=0}^{\infty} (-1)^n\,\frac{(n+k-2)!}{(k-2)!\,n!}\,\frac{1}{(n+k+2)^{1/2}}\,\tau_s^{\,n+k+1} - \frac{\tau_s^{\,2}}{\sqrt{3}}\right]$$

$$k \geq 2 \tag{20}$$

Furthermore, it is shown (see Appendix) that the variation of v along the column introduces a correction term such as in the case of a Dirac input impulse:

$$(vC_g')_1 = v_0\left[(C_g')_{1_{z=L}} - t_m C_{g_0}'\,\frac{\tau_s}{\sqrt{2}}\right] \tag{21}$$

Therefore

$$t_R = t_{R1}\left[1 + \delta(\tau_s)\right] = t_{R1}\left[\lambda_1 + \frac{t_{R1} - t_m}{t_{R1}}\sum_{k=2}^{\infty}\alpha_k\lambda_k + \frac{t_m}{t_{R1}}\,\frac{\tau_s}{\sqrt{2}}\right] \tag{22}$$

By observing that the retention time at infinite dilution is proportional to the square of the variance, it follows that, for a finite spreading of the entry impulse:

$$t_R = t_{R1}\left\{1 + \frac{1}{\sigma_s^2 - \sigma_e^2}\left[\sigma_s^2\delta(\tau_s) - \sigma_e^2\delta(\tau_e)\right]\right\} \tag{23}$$

COMPARISON WITH EXPERIMENTAL RESULTS

The relative deviation δ of the retention time was measured for three binary systems which are far from thermodynamic ideality. Coefficients

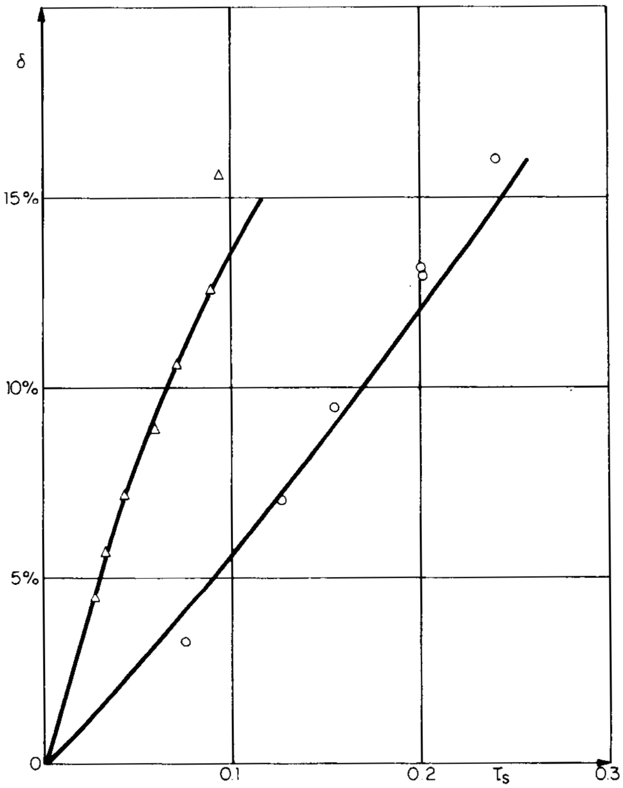

FIG. 2. Relative deviation δ vs. parameter τ_s for the hexane–nitrobenzene system: Column 1, (○) experimental values, (—) predicted values (Eq. 23); Column 2, (△) experimental values, (—) predicted values (Eq. 23).

α_k appearing in Eq. (22) are obtained from liquid–vapor equilibrium measurements (*22, 23*). Three coefficients were used in every case.

Experimental and calculated values of δ are plotted in Figs. 1, 2, and 3 versus the dimensionless parameter τ_s. The agreement between these values is satisfactory.

Deviations δ are positive for both benzene–dimethylsulfoxide and hexane–nitrobenzene systems but are negative for the sulfur dioxide–tributylphosphate system. Equation (22) shows that the qualitative behavior of δ essentially depends on the parameter α_1, which represents the curvature of the isotherm at infinite dilution. The deviations are extensive for the benzene–dimethylsulfoxide system, even for low values of τ_s, as the result of a high value of α_1. In the case of a linear isotherm,

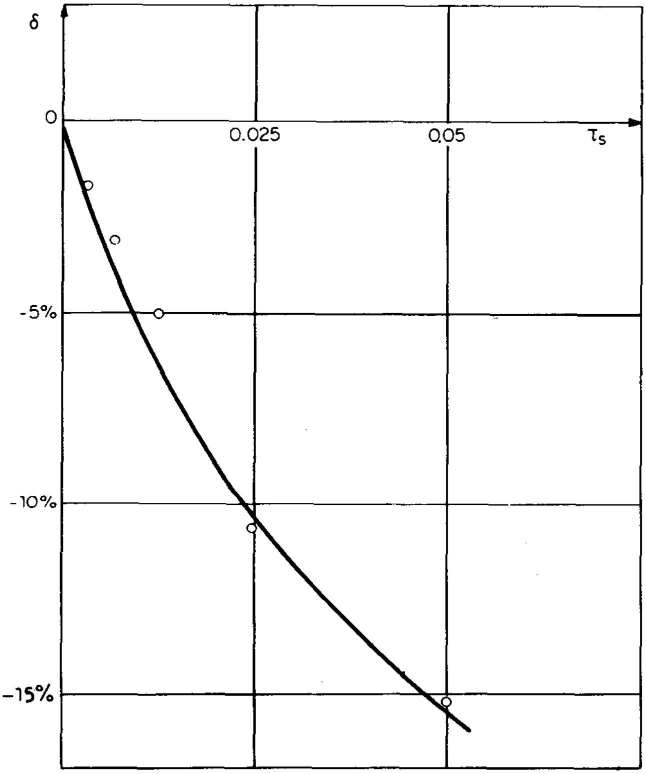

FIG. 3. Relative deviation δ vs. parameter τ_s for the sulfur dioxide–tributylphosphate system: (O) experimental values, (—) predicted values (Eq. 23). Experimental α_k obtained by P. Renault.

$\alpha_1 = 0$ and δ is negative. Thus, the results of Part I appear as a particular case.

CONCLUSION

The deviation of the retention time from its ideal value at infinite dilution, when large samples are injected, is shown to be the consequence of a nonlinearity in the basic transfer relations. This nonlinearity is the result of a finite vapor concentration, as analyzed in Part I, and of a variable partition coefficient along the column.

The theoretical approach proposed in this paper is entirely predictive. Calculated and experimental values are in good agreement.

APPENDIX

Calculation of v at $z = L$

By considering a material balance on the moles of carrier gas, the following conservation equation is obtained:

$$\frac{\partial}{\partial z} v + \frac{\epsilon H}{V} \frac{\partial}{\partial t} (1 - C_g) = 0 \qquad \text{(A-1)}$$

This equation leads to the relation

$$v = v_0 \left[1 + \frac{t_m}{L} \int_0^L \frac{\partial}{\partial t} C_g \, dz \right] \qquad \text{(A-2)}$$

In order to calculate the moment $(vC_g')_1$, only the value of v at $z = L$ is needed. This value deviates from v_0 only when the impulse is passing through the section located at $z = L$. Therefore, if the column is long enough, it can be assumed that C_g is given by

$$C_g(L,t) \simeq C_g'(L,t) \simeq \frac{C_{g0}'}{\sigma_s \sqrt{2\pi}} \exp \left[- \frac{(t - \chi z)^2}{2\sigma_s^2} \right] \qquad \text{(A-3)}$$

Equation (A-2) becomes

$$v_{z=L} = v_0 - \frac{t_m}{t_{R_{z=L}}} v_0 C_g'(L,t) \qquad \text{(A-4)}$$

The moment $(vC_g')_1$ is then obtained

$$(vC_g')_{1_{z=L}} = v_0(C_g')_{1_{z=L}} - \frac{t_m}{t_{R_{z=L}}} v_0 \int_{-0}^{+\infty} tC_g'^2(L,t)\,dt \qquad \text{(A-5)}$$

Finally

$$(vC_g')_{1_{z=L}} = v_0 \left[(C_g')_{1_{z=L}} - t_m C_{g0}' \frac{\tau_s}{\sqrt{2}} \right] \qquad \text{(A-6)}$$

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SYMBOLS

a	liquid–gas interfacial area per unit volume
C_g	mole fraction of solute in the gas phase
C_1	mole fraction of solute in the liquid phase
C_g'	mole fraction on a solute free basis
$C_{ge}'(t)$	imput impulse curve
C_{g0}'	time integral of the impulse curve
H	vacuum fraction of the column occupied by the gas phase
$(1 - H)'$	$= (1 - H)V/V'$
I_m	injected moles of the sample
K	transfer coefficient
L	length of the column
m	equilibrium constant of the solute
m_∞	equilibrium constant of the solute at infinite dilution
p	Laplace operator
Q	flow rate at the inlet to the column
t_R	retention time
t_{R1}	retention time at infinite dilution
t_m	dead time
v	flow rate per unit section
v_0	flow rate per unit section at the inlet to the column
V	molar volume of mobile phase
V'	molar liquid volume of the solute

Greek Letters

α_k	coefficients in the development of m
β_k	coefficients
δ	relative deviation of the retention time
ϵ	porosity of the solids
λ_k	integrals
σ	variance of the impulse at z
τ	$= C_{g_0}'/\sqrt{2}\pi\sigma$ dimensionless parameter
χ	$= t_R/Z$

Subscripts

0	a zero-order moment
1	a first-order moment
e	concerning entry of column
s	concerning end of column

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