configuration of a multibranch star polymer. Such behavior is not observed in the range studied; presumably the approach is much slower when the side chains are in an unfavorable environment and the backbone expanded than when the reverse occurs as in cyclohexane.

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Effect of Diffusional Resistance upon Gas Chromatography in Capillary Columns

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ABSTRACT: A theoretical investigation indicates the effect stationary-phase mass-transfer resistance has on thermodynamic properties as obtained from chromatographic measurements utilizing open-tubular columns. The model applies to a wide range of experimental conditions. Parameters for the system are: carrier-gas flow rate, column length, solute diffusivity, absorbent layer thickness, ratio of tube radius to absorbing layer thickness, and the true Henry's constant. A plot has been developed which allows simple determination of the true Henry's constant from the experimentally observed Henry's constant. The analysis predicts lower true Henry's constants than those predicted by previously presented reduction methods. As a result, Flory's χ parameters determined by packed and by capillary columns for the benzene– and cyclohexane–polyisobutylene systems are brought into better mutual agreement. The analysis indicates that both the diffusivity and the true Henry's constant for a given solute–solvent system may be determined from a single set of chromatographic experiments.

Gas–liquid chromatography (GLC) has long been recognized as a useful tool for the separation and identification of the components constituting a chemical sample. In recent years, however, GLC has also gained acceptance as a technique for the accurate determination of the solubility of vapors in a liquid phase.[1,2] This method is especially well-suited to polymeric solvents, where the time for a single measurement by conventional bulk-equilibration methods may be several days, in contrast to only minutes by chromatography. In addition, GLC offers the advantage of allowing solubility measurements at much lower concentrations than can be achieved in the static method. As a result, measurements reflect the properties of a system more closely resembling the conventional thermodynamic standard state, infinite dilution.

The solubility (or Henry's constant) of the solute is determined by measuring the net retention time for a solute "probe" passing through a column which contains the stationary liquid (or polymeric) phase. Experimentally determined solubilities have, however, been found to be dependent on the carrier-gas flow rate,[3,4] film thickness,[5] and the temperature of the system relative to the glass-transition temperature of the polymer.[6,7] This implies that a kinetic or transport effect exists in such measurements. The chromatographic measurements must be extrapolated to the value where the flow-rate effect no longer exists in order to determine purely thermodynamic properties.

It has been recognized from the earliest theories of chromatography that one of the causes of departure from the ideal of instantaneous equilibrium of gas and stationary phases is the diffusional resistance of the solute through the stationary phase. This effect is usually relatively minor in the case of a liquid absorption layer. However, in the case of a polymeric absorption phase, this phenomenon is magnified as a result of the greatly reduced solute diffusion in the solvent.

Effect of Equilibrium. The fundamental principle of gas chromatography is that solutes are selectively absorbed by the liquid or, as in this work, the polymer phase:

$$u_{\mathrm{sp}} = uf + u_{\mathrm{p}}(1 - f) \tag{1}$$

where u is the linear velocity of the carrier gas (cm/s), f is the fractional time that the solute spends in the gas phase, subscript sp signifies *solute peak,* and subscript p signifies *polymer phase.* From ensemble theory, for a large number of molecules, f also represents the fraction of solute molecules in the gas phase at any given time.

In gas–liquid chromatography, the linear velocity of the polymer phase is zero, and eq 1 may be simplified to

$$u_{\mathrm{sp}} = uf \tag{2}$$

Due to the difference in these two velocities, u and u_{sp}, a sample of solute will elute from the column at a longer time, t_{R}, than the retention time of the pure carrier gas, t_{G}.

A solute probe, passing through a column under the conditions of instantaneous equilibration, is represented in Figure 1. The carrier gas and solvent probe proceeded down the column with velocities of u and u_{sp}, respectively. The solute in

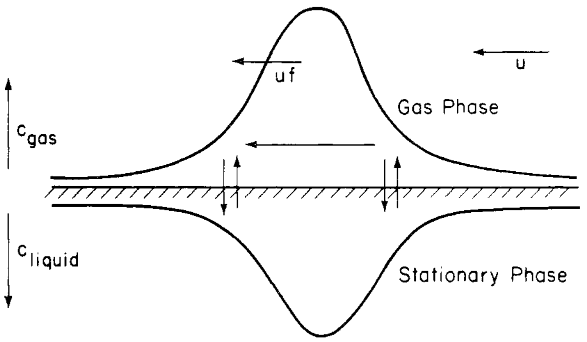

Figure 1. Gas–liquid chromatography with instantaneous equilibration.

the gas and stationary phases is in equilibrium, and as a result, the maximum of solute–species concentration in each of the phases occurs concurrently.

Figure 2 illustrates qualitatively the effect diffusional resistance has on the behavior of the column. Since the solute molecules encounter diffusional resistance into the stationary phase, instantaneous equilibrium is no longer attained. As a result, at any given time the total number of solute molecules in the gas phase is greater than that expected from purely thermodynamic considerations. The values of f and u_{sp} shown in eq 2 are then increased. The elution time of the peak is shortened, and the experimentally determined solubility of the solute is less than the true thermodynamic value.

The second observable effect due to polymer-phase diffusional resistance is tailing of the eluted solute peak, a consequence of the finite rate at which the small amount of dissolved solute leaves the stationary phase.

Background. Nonideality of real columns is manifested to a much larger degree in the dispersion of the solute peak rather than in the shift in the peak maximum. Thus, it was not until chromatography was recognized as an experiment yielding thermodynamic data that the difference between the elution time of the solute peak in a real column and in an ideal column (with instantaneous equilibration) warranted more detailed investigation.

In light of the early concern with separation efficiency, the early rate theories[8–10] were constructed such that the behavior of the peak maximum as a function of time was not expressly given, but rather the peak width. Investigations concerned explicitly with the effect of mass transfer on elution times have been undertaken only recently by Gray and Guillet[11] and by Wičar et al.[12] Although these latter theories describe the solute concentrations in a quantitative form as a function of time, the model of interphase mass transfer is not realistic for some commonly encountered chromatographic conditions. The interphase mass-transfer rate is taken to be simply proportional to the difference between the actual solute concentration in the polymer phase and that solute concentration when the polymer is in equilibrium with the gas phase. It is shown later that this underestimates the flux at the surface leading to inaccurate predictions of the solute elution times. Recent work[13,14] on the analysis of GLC peak shapes by sophisticated numerical techniques also uses this approximate form to describe the interfacial mass transfer.

More refined theories (such as Golay's theory of the capillary column,[15] or Giddings' generalized nonequilibrium theory[16]) recognized the deficiency of the mass-transfer expression but were directed at predicting the column separation efficiency.

It has been proposed,[3,17,18] based on experimental observations, that there is a linear relationship between the observed elution times and the carrier-gas flow rate. Lichtenthaler et al.,[4] on the other hand, reasoning that this dependence should vanish at some sufficiently low nonzero flow rate, have presented empirical equations to describe this effect.

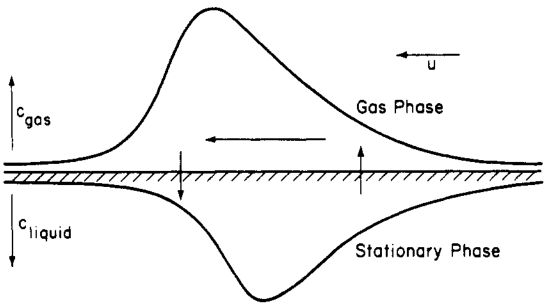

Figure 2. Gas–liquid chromatography with diffusional resistance.

Due to the uncertainties of the work cited above, this paper investigates, on a theoretical basis, the behavior of elution time (and resulting Henry's constant) as experimentally determined in capillary columns. Moreover, results are presented which provide information for sound design of experiments and for simple interpretation of experimental data.

Although presented for gas chromatography, the results have significance in other absorption techniques, such as ion exchange. The model is constructed in such a manner that additional considerations encountered in gas chromatography may be easily added in the future. These include axial diffusion, mass-transfer resistance in the gas phase, and other geometries of the sorbent.

Mathematical Model

The open-tubular gas-chromatographic column is modeled as a capillary column of circular cross section, having a polymer film of thickness τ coated on the inner wall. The polymer–gas interface is at a distance r_i from the center of the column.

The following assumptions are made:

(1) The polymeric stationary phase is homogeneous. (2) The polymeric film is of constant thickness the entire length of the column. (3) Axial molecular diffusion in both the gas and stationary phases is negligible. (4) The carrier gas is insoluble in the stationary phase. (5) The partition of solute between gas and stationary phases is described by Henry's law. (6) No accumulation of solute occurs at the gas–polymer interface.

Under these assumptions, the continuity equations may be written for the solute species in both the gas and stationary phases:

$$\frac{\partial c}{\partial t} + u_z \frac{\partial c}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_G \frac{\partial c}{\partial r}\right) \tag{3}$$

$$\frac{\partial c'}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_S \frac{\partial c'}{\partial r}\right) \tag{4}$$

where c is the gas-phase solute concentration (mol/cm^3), c' is the stationary-phase solute concentration, D_G signifies gas-phase diffusivity of solute (cm^2/s), D_S is stationary-phase diffusivity of solute, and z represents the longitudinal distance (cm).

The gas-phase concentration may be averaged over the radial direction

$$\bar{c} = \frac{\int_0^{r_i} 2\pi rc \, dr}{\int_0^{r_i} 2\pi r \, dr} \tag{5}$$

This is the gas-phase concentration of most interest (reflecting the inherent averaging of the chromatographic detector).

Equation 3 may now be rewritten, assuming u_z is the apparent linear velocity, u, as

$$\frac{\partial \bar{c}}{\partial t} + u\frac{\partial \bar{c}}{\partial z} = \frac{2}{r_i} D_G \left.\frac{\partial c}{\partial r}\right|_{r_i} \tag{6}$$

The initial conditions are

$$\bar{c} = c' = 0 \quad \text{at} \quad t = 0 \tag{7}$$

and

$$\bar{c} = \delta(z) \tag{8}$$

the Dirac δ function, at $t = 0$. The boundary conditions are

$$\bar{c} = Kc' \quad \text{at} \quad r = r_i \tag{9}$$

$$D_S \left.\frac{\partial c'}{\partial r}\right|_{r_i} = D_G \left.\frac{\partial c}{\partial r}\right|_{r_i} \tag{10}$$

and

$$\frac{\partial c'}{\partial r} = 0 \quad \text{at} \quad r = r_i + \tau \tag{11}$$

The first boundary condition expresses Henry's law. For very dilute solute concentrations in the stationary phase, the partition coefficient, K, is

$$K = HM_1/RT\rho_2 \tag{12}$$

where H is weight-fraction Henry's constant,

$$H = \lim_{w_1 \to 0} (f_1/w_1)$$

f_1 is the fugacity of the solute, w_1 is the solute weight fraction, M_1 is the molecular weight of solute (g/mol), and ρ_2 represents density of polymer (g/cm^3). A mass balance at the gas–polymer interface, reflecting no surface adsorption, constitutes the second condition. Lastly, eq 11 indicates that the outer wall of the column is impermeable.

To introduce a greater amount of generality into our analysis, and to reduce the number of adjustable parameters, we use the following dimensionless variables:

$$\theta = ut/L$$

$$\zeta = z/L$$

$$\lambda = r/\tau$$

$$\eta = r_i/\tau$$

$$\beta = \tau^2 u/D_S L$$

where L is the total length of the column.

We may now rewrite eq 4 to 11:

$$\frac{\partial \bar{c}}{\partial \theta} + \frac{\partial \bar{c}}{\partial \zeta} = \frac{2}{\eta\beta}\left.\frac{\partial c'}{\partial \lambda}\right|_{\eta} \tag{13}$$

$$\frac{\partial c'}{\partial \theta} = \frac{1}{\beta}\left(\frac{\partial^2 c'}{\partial \lambda^2} + \frac{1}{\lambda}\frac{\partial c'}{\partial \lambda}\right) \tag{14}$$

$$\bar{c} = c' = 0 \quad \text{at} \quad \theta = 0 \tag{15}$$

$$\bar{c} = (1/L)\delta(\zeta) \quad \text{at} \quad \theta = 0 \tag{16}$$

$$\bar{c} = Kc' \quad \text{at} \quad \lambda = \eta \tag{17}$$

$$\partial c'/\partial \lambda = 0 \quad \text{at} \quad \lambda = \eta + 1 \tag{18}$$

These equations constitute a set of two simultaneous, coupled, partial-differential equations. We note, however, that the system of equations may be simplified by finding an expression for $(\partial c'/\partial \lambda)\,|_\eta$. Utilization of this solution, together with the coupling condition (eq 17), results in eq 13 becoming a partial integrodifferential equation with a single dependent variable, $\bar{c}$.

Solving for $(\partial c'/\partial \lambda)\,|_\eta$ as given by eq 14, we make use of Duhamel's theorem (the superposition integral). If the solution of the differential equation for a unit step change in interfacial concentration is

$$\left.\frac{\partial c'}{\partial \lambda}\right|_{\eta} = j(\theta)$$

then the solution for the time-dependent boundary condition

$$c'|_\eta = \bar{c}(\theta)/K$$

is

$$\left.\frac{\partial c'}{\partial \lambda}\right|_{\eta} = \frac{1}{K}\int_0^{\theta} \left.\frac{\partial \bar{c}}{\partial \sigma}\right|_{\sigma=\theta} j(\theta - \sigma)\, d\sigma \tag{19}$$

For the unit-step change in interfacial concentration, the solution of eq 14, as expressed in Laplace transform space, is

$$J(s) = \frac{q}{s}\frac{K_1[q(\eta+1)]I_1(q\eta) - I_1[q(\eta+1)]K_1(q\eta)}{I_0(q\eta)K_1[q(\eta+1)] + I_1[q(\eta+1)]K_0(q\eta)} \tag{20}$$

where $q = (s\mathrm{B})^{1/2}$ and I_i and K_i are the ith order modified Bessel functions of the first and second kind, respectively.

The solution for the averaged gas-phase concentration resulting from eq 13, as given in Laplace transform space, is:

$$L\overline{C}(s) = \exp\left\{-s\zeta\left[1 - \frac{2}{\eta K\beta}J(s)\right]\right\} \tag{21}$$

where $J(s)$ is given above.

Our interest, however, lies not in the behavior of the solute concentration in Laplace transform space but in the concentration in dimensionless time, θ, space. Due to the complexity of eq 21, an analytic inversion was impossible to obtain. As a result, a numerical technique was employed for inverting the Laplace transform.

The technique is based on the approximation of the Laplace transform integral

$$\overline{C}(s) = \int_0^{\infty} e^{-s\theta}\bar{c}(\theta)\, d\theta \tag{22}$$

by the method of Gaussian quadrature.[19] Introducing a new variable of integration, $x = e^{-\theta}$, eq 22 may be written as

$$\overline{C}(s) = \int_0^1 x^{s-1}g(x)\, dx \tag{23}$$

where $g(x) = \bar{c}(-\ln x)$. Applying the quadrature formula, eq 23 may be approximated by

$$\overline{C}(s) = \sum_{i=1}^{N} \hat{w}_i x_i^{s-1} g(x_i) \tag{24}$$

The appropriate values of $\hat{w}_i$, the weighting factors, based on the zeros of the Legendre polynomial of degree N, x_i, have been evaluated by Bellman et al.[19] Letting s assume N different values yields a linear system of N equations in the N unknowns, $g(x_i)$. This system of equations may then be solved for $g(x_i)$ by conventional matrix techniques. For our case, $g(x_i)$ represents the gas-phase concentration at the dimensionless time, $\theta_i = -\ln x_i$.

Utilizing the discrete data generated by the Legendre–Gaussian quadrature technique, curves were obtained which simulated the behavior of the gas chromatograph as a function of time and axial position.

Results

First, we examine the elution time for a solute peak passing through a chromatographic column with instantaneous equilibration. This allows us to describe quantitatively the effect of mass-transfer resistance later in our discussion.

The total length of the column, L, may be expressed in terms of the elution times and velocities of the solute peak and

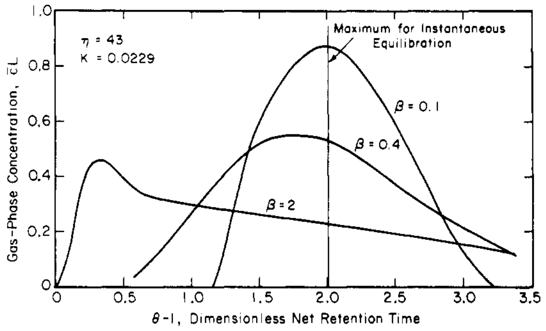

Figure 3. Computer-generated chromatograms.

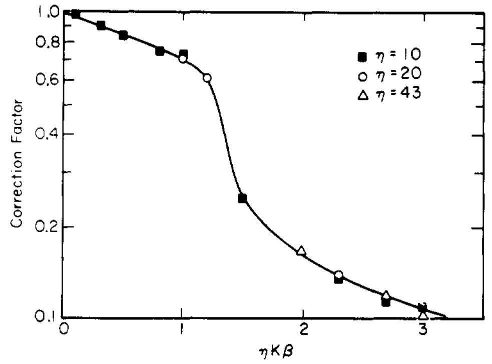

Figure 4. Correction factor for gas chromatography with the dependence on the thermodynamic partition coefficient.

carrier gas:

$$L = u_{\text{sp}}t_{\text{R}} = ut_{\text{G}} \tag{25}$$

The fractional time, f, the solute spends in the gas phase is

$$f = \frac{VKc'}{V_{\text{S}}c' + VKc'} \tag{26}$$

where V and V_{S} are the total volumes of the gas and stationary phases, respectively. Combining these equations with eq 2, we find that the solute-peak maximum should elute at

$$t_{\text{R}} - t_{\text{G}} = \frac{\tau^2 + 2\tau r_{\text{i}}}{Kr_{\text{i}}^2}t_{\text{G}} \tag{27}$$

in a column with instantaneous equilibration. In terms of the dimensionless variables, the maximum under ideal conditions occurs at:

$$\theta_{\text{ideal}} - 1 = \frac{2}{\eta K} + \frac{1}{K\eta^2} \tag{28}$$

Figure 3 presents chromatograms resulting from the numerical inversion technique for various values of β. The position of the ideal peak maximum for the appropriate values of η and K is indicated. The peaks exhibit the behavior characteristic of mass-transfer resistance (shorter elution times and increased tailing) as the kinetic factor, β, is increased.

If t_{R} and t_{G} can be determined either experimentally or theoretically, we may define a net specific retention volume

$$V_{\text{g}}^0 = \frac{(t_{\text{R}} - t_{\text{G}})273.15Q}{TW_2} \tag{29}$$

$$= \frac{273.15R}{HM_1} \tag{30}$$

where $t_{\text{R}} - t_{\text{G}}$ is the net retention time (s), Q is carrier-gas volumetric flow rate (cm^3/s), and W_2 specifies the total weight of polymer phase (g).

Upon examining eq 12, 29, and 30, we see that H, K, $1/V_{\text{g}}^0$, and $1/(t_{\text{R}} - t_{\text{G}})$ are proportional to each other. Thus, the ratio of the observed quantity and that obtained with instantaneous equilibration should have the identical value when expressed in terms of any of the given parameters. The correction for the kinetic behavior mass-transfer resistance on gas chromatography is given quantitatively in terms of this ratio, the *correction factor*.

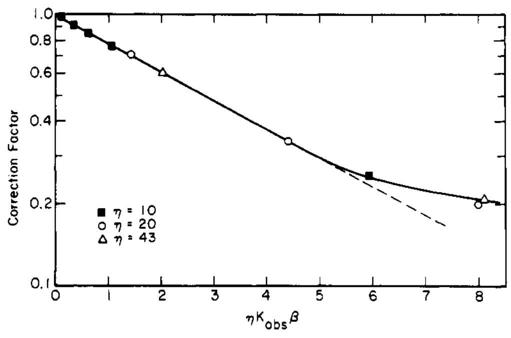

Figure 5. Correction factor for gas chromatography with the dependence on the observed partition coefficient.

Figure 4 gives the correction factor as a function of the dimensionless variable $\eta K\beta$ for the range of η commonly encountered in capillary columns.

Figure 4, however, requires a knowledge of the "true" thermodynamic quantity, K or H. In most applications, this is the property we are trying to evaluate. Recognizing the two simultaneous sets of conditions imposed by (1) the results of the numerical simulation and (2) that $K_{\text{true}}/K_{\text{obsd}}$ = correction factor, we may express the correction factor in terms of K_{obsd}. This revised plot is shown in Figure 5.

Upon examining this figure, one sees that the curve may be expressed as

$$\ln \frac{V_{\text{g}}{}^0{}_{\text{obsd}}}{V_{\text{g}}{}^0{}_{\text{ideal}}} = a\eta K_{\text{obsd}}\beta \tag{31}$$

where a (= −0.243) is the slope of the line at lower values of $\eta K_{\text{obsd}}\beta$. Equivalently,

$$\ln V_{\text{g}}{}^0{}_{\text{obsd}} = \ln V_{\text{g}}{}^0{}_{\text{ideal}} + a'\frac{Q}{V_{\text{g}}{}^0{}_{\text{obsd}}} \tag{32}$$

where

$$a' = a273.15/\pi\eta LD_{\text{S}}T$$

This leads to a remarkable result. From one isothermal data set of observed specific retention volume as a function of carrier-gas flow rate, we may not only obtain the ideal specific retention volume (and thus the true Henry's constant) but also the diffusivity of the solute in the polymer phase.

Discussion

The primary problem in constructing a mathematical model of the gas chromatograph to investigate the kinetic, or transport, effects is to choose an expression for the flux of the solute across the gas–polymer interface which, while allowing a simple solution for the solute concentration in the gas phase, still accurately describes the exact behavior of the flux. We now compare the behavior of the flux expression chosen for this work with other possible choices.

The flux at the gas–polymer interface (for large η) can be described by

$$N = -\frac{D_{\text{S}}}{\tau}\left.\frac{\partial c'}{\partial \lambda}\right|_{\eta} \tag{33}$$

The solution of eq 14 for $\partial c'/\partial\lambda$ may be expressed in two different forms, one appropriate for long times and the other for short times. The "long-time approximation" for the flux is the first term of a series solution for eq 14.[20] The short time expression is obtained by expanding the modified Bessel function solution shown in eq 20 suitable for large values of s.

These two approximations for the solute flux at the gas–polymer interface due to a unit step change in surface concentration are shown in Figure 6 together with the exact solution obtained from the numerical inversion technique.

The short-time approximation, while agreeing well with the exact solution at small θ/β, predicts a flux that is too large at greater values, resulting in an elevated estimate of the solute concentration in the polymer phase. If this expression is used in the model rather than eq 20, correction factors greater than unity are obtained for small values of $\eta K\beta$ in Figure 4.

On the other hand, the long-time approximation agrees well with the exact solution at higher values of θ/β, but underestimates the flux at the lesser values. As shown in the Appendix, this approximation is equivalent to the mass flux expression used in the work of Gray and Guillet[11] and of Wičar et al.[12]

The flux to a region having zero initial concentration must be infinite during the first infinitesimal increment of time. For a single contact step, the amount of error due to the use of the long-time approximation is small in relation to the total flux for large values of θ/β. However, in a mathematical model, where there are a large number of contact steps, this small error accumulates until, at large values of $\eta K\beta$, the predicted net retention time is less than that which would be observed experimentally. This follows from underestimation of the interfacial flux that results in an overestimation of f in eq 2.

A fundamental assumption in the model is that the mass-transfer resistance exists only in the polymer phase, that is, there is no radial concentration gradient in the gas phase. For a solute diffusing into a finite solvent layer of thickness x_i, the time-dependent concentration would be expressed in terms of a characteristic time x_i^2/D_S. Typical values of the ratio of the characteristic time for the gas phase (r_i^2/D_G) to the characteristic time for the polymer phase (τ^2/D_S) result in values of $\sim 1 \times 10^{-3}$ for typical open-tubular columns. Due to the small value of this ratio, any resistance to mass transfer in the gas phase is small compared to that of the polymer-phase resistance. However, gas-phase resistance could be included in the framework of the model.

An additional assumption is that molecular diffusion in the axial direction is negligible. If an initially symmetric peak could be observed during its passage through a column with ideal absorption, one would observe that axial diffusion causes the peak simply to broaden, not altering the symmetric character of the peak. Thus, the relative position of the peak maximum will remain constant. However, experimentally observed peaks do have a skewed shape because they are observed as a function of time by a detector at a fixed position, rather than by observing the whole peak profile at a fixed time. In the case where the carrier gas flow rate is very low, the trailing portions of the peak (still residing in the absorption area of the column) have a longer time to diffuse in the axial direction than the leading portions (already recorded by the detector), resulting in a skewed *observed* peak and a net retention time less than that determined ideally. Wičar et al.[12] have investigated this variation of net retention time due to axial diffusion at low carrier-gas flow rates. Using their analysis we find that, for axial diffusion to cause 1% or more deviation in the reported peak maximum in typical capillary columns (2000 cm length), flow rates of less than 1.3×10^{-2} cm^3/min would be required, a value far less than is commonly used.

It is now appropriate to examine the significance of the dimensionless group

$$\eta K B = r_i \tau^2 uK/\tau L D_S \qquad (34)$$

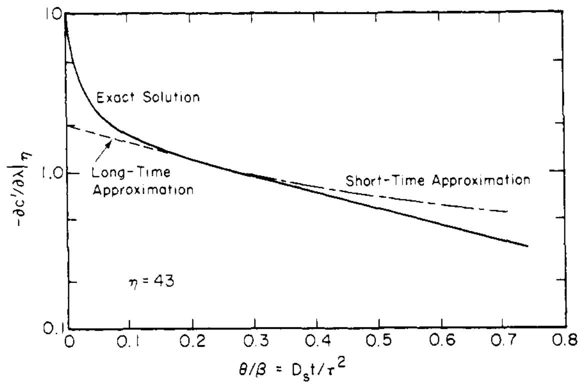

Figure 6. Mass flux at the gas–polymer interface due to a unit step change in the surface concentration.

For a thin film, the fraction of time the solute spends in the polymer phase $(1 - f)$ is $2/\eta K$ (see eq 28). Thus $\eta K\beta$ represents the ratio of the characteristic time for diffusion in the polymer phase (τ^2/D_S) to the total time the solute spent in the polymer phase during its passage down the column ($L/\eta K u$).

The dimensionless group $\eta K\beta$ is first order in all variables, in contrast to the analysis of Gray and Guillet,[11] which indicated a second-order dependence on the polymer film thickness, τ. To our knowledge, there has been no experimental investigation in which the film thickness in capillary columns has been varied enough to distinguish the dependence on film thickness from the experimental error.

The kinetic parameter, β, also depends on the length of the chromatographic column, L. As the solute peak travels down the column, it spreads due to a nonequilibrium condition resulting from the mass-transfer resistance of the polymer phase. As the peak spreads, the solute is in contact with the polymer for a long enough time for equilibrium to be approached.

Figure 4 shows two asymptotic limits of the correction factor curves: One limit is that of instantaneous equilibration (that region in which the column's behavior is solely controlled by the partition of the solute between the two phases) which occurs at small values of $\eta K\beta$. In contrast is the asymptote, occurring at large values of $\eta K\beta$, determined by kinetic considerations (that limit in which the solubility is reduced effectively to zero by the mass-transfer resistance and, as a result, the solute peak is eluted at a velocity equal to that of the carrier gas).

The final result of this work is the new data reduction scheme expressed in eq 32. Two different extrapolation techniques have been proposed in the literature: the method of Cruickshank et al.[17] proposes that $V_g{}^0{}_{\text{obsd}}$ is a function of Q and Lichtenthaler et al.[4] hypothesize that ln $V_g{}^0{}_{\text{obsd}}$ is a function of Q^2, with $V_g{}^0{}_{\text{obsd}}$ approaching a constant value as Q approaches zero.

The correction factor, presented in terms of $V_g{}^0$, is plotted on linear scales in Figure 7. At small values of $\eta K\beta$, the plot assumes a linear character as hypothesized by Cruickshank et al. However, at a value of approximately unity, the curve exhibits some concave-downward behavior (not unlike the parabolic curve hypothesized by Lichtenthaler et al.) before becoming concave upward to approach an asymptotic limit.

Applications

The model may be utilized in two fashions in the determination of Henry's constants by gas–liquid chromatography. The first application is during the initial experimental design, and the second is during the reduction of the experimentally obtained data.

Figure 4 is used in the scientific design of an experiment to

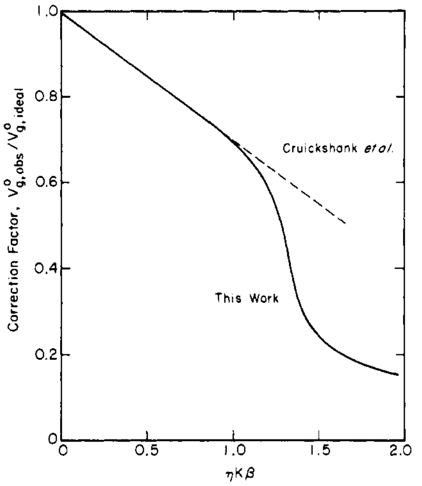

Figure 7. Correction factor for capillary-column gas chromatography, plotted on linear scales.

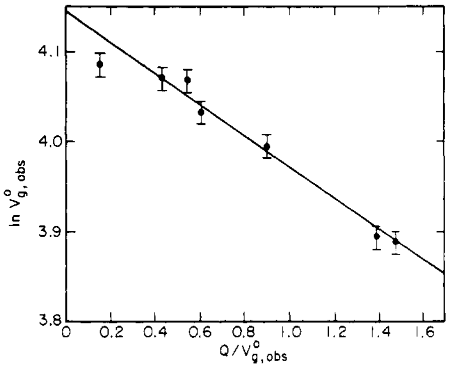

Figure 8. Data reduction of cyclohexane–polyisobutylene system at 75 °C, based on the measurements of Lichtenthaler et al.

optimize values of the adjustable experimental variables: column length, polymer film thickness, and carrier-gas flow rates. Use of this graph requires an estimate of the Henry's constant (or the partition coefficient) and the diffusivity of the solute through the polymer for the system of interest. Acceptable estimates of these parameters, however, are easily obtained from existing correlations. Once such estimates are made, Figure 4 yields such information as how close the column will be to ideality and how critically the thermodynamic measurement depends on the independent experimental variables.

More importantly, however, the model corrects observed measurement for the kinetic nonidealities of the column. As an example, we examine experimental data presented by Lichtenthaler et al.[4]

In their work, the wall of a 0.0375 cm radius column of 2000 cm length was coated with a 10^4 to 10^5 Å layer of polymer and used to examine the retention behavior of various solutes. (The thickness of the polymer in these capillary columns is thicker than that commonly encountered in packed columns, where thicknesses of only about 10^2 to 10^3 Å are commonly used.)

Figure 8 presents their data for the cyclohexane–polyisobutylene system at 75 °C in terms of the new reduction procedure proposed above. The data do, within experimental error, assume a linear character.

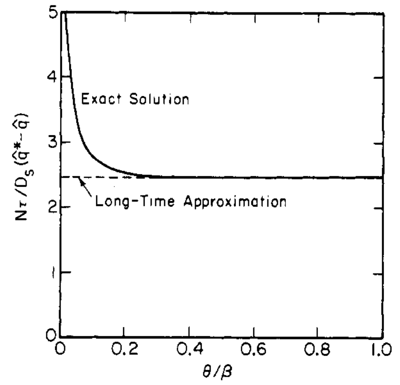

Figure 9. Time dependence of mass-transfer coefficient.

Table I
Comparison of Physical Properties Obtained by GLC for Hydrocarbon–Polyisobutylene Systems at 75 °C

	Capillary column		Packed column
	This work	Lichtenthaler et al.	Lichtenthaler et al.
Henry's constants, atm			
Cyclohexane	4.23	4.41	3.98
Benzene	5.21	5.44	5.11
			Van Krevelan
Diffusivity, cm^2/s			
Cyclohexane	5.4×10^{-9}	*a*	1.8×10^{-8}
Benzene	9.0×10^{-9}		4.7×10^{-9}

[a] Not available from given reduction scheme.

Physical parameters obtained at 75 °C from the capillary column data of Lichtenthaler et al. for the cyclohexane–polyisobutylene and benzene–polyisobutylene systems are shown in Table I. The Henry's constants as obtained using their data reduction scheme, and our reduction scheme, are compared to values for the same system obtained by the same authors using conventional packed columns. Thus the present model, through the proposed reduction technique, brings thermodynamic measurements, as obtained from packed and capillary gas–liquid chromatographic columns, into agreement within experimental accuracy.

A correlation, as proposed by Van Krevelan,[21] was used for the estimation of the diffusivities of the solutes through the polymer. These are compared in Table I with measured values derived from eq 32 and the slope of graphs like Figure 8. Due to the many orders of magnitude that solute diffusivities may vary depending on the system, the agreement is certainly satisfactory. Thus, the variation of net retention time of a solute peak as a function of carrier-gas flow rate appears to be a valid technique for determination of solute diffusivities.

The kinetic-effect correction resulting from the model also has ramifications in other thermodynamic quantities commonly determined by gas–liquid chromatography. The fugacity of the solute in the polymer phase at infinite dilution may be expressed in either the Henry's law form or the Raoult's law form:

$$f_1^{P} = w_i \Omega_i^{\infty} P_1^{sat} = w_i H_{1,2} \qquad (35)$$

where Ω_i^{∞} is an infinite-dilution activity coefficient and P_1^{sat} is the vapor pressure of the pure solute. Patterson and coworkers[22] have proposed that the nonidealities in a polymer solution may be expressed as an interaction parameter χ, where

$$\chi = \ln \Omega_1^{\infty} - [\ln v_1^*/v_2^*] + 1 \qquad (36)$$

and v_1^* and v_2^* represent the hard-core volumes of the solute and polymer, respectively.

Table II
Flory χ Parameters for Hydrocarbon–Polyisobutylene Systems from GLC and from Static Measurements at 65 °C

	GLC packed column		GLC capillary column[a]		Static
Solute	Lichtenthaler et al.[a]	Ref 24	This work	Lichtenthaler et al.	Ref 23
Benzene	0.87	0.75	0.89	0.95	0.94
Cyclohexane	0.50	0.56	0.56	0.62	0.64

[a] Extrapolated values on ln H vs. $1/T$ plot.

Table II presents χ values obtained by various techniques for the polyisobutylene systems at 65 °C. The introduction of the correction for the kinetic effects of mass-transfer resistance within the column results in better agreement of values obtained from packed columns and capillary columns. The two values are probably within experimental error of each other.

Although correction for the effect of finite interfacial mass-transfer results is in better agreement for values from packed and capillary columns, the disagreement of the χ values obtained from GLC and static methods cannot be explained within the scope of this work.

Summary

A model has been formulated which allows the prediction of the effect of nonidealities due to mass-transfer resistance on thermodynamic properties determined by gas chromatography using open-tubular capillary columns. Moreover, the model is valid when desired experimental parameters (thickness of polymer film; carrier-gas flow rate; and diffusivity of solute through polymer, resulting from system temperature) mandate conditions far removed from the ideal of instantaneous equilibrium.

A new data reduction scheme has been proposed which yields corrected values for experimentally observed Henry's constants and, simultaneously, the determination of the diffusivity of a solute through a polymeric matrix.

The correction factor results in closer agreement between thermodynamic measurements obtained from packed and capillary gas–liquid chromatographic columns.

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Appendix

In previous work modeling the open-tubular chromatographic column, the commonly adopted expression for the flux of the solute across the gas-polymer interface is

$$N = k(\hat{q}^* - \hat{q}) \tag{A1}$$

where k is a mass-transfer coefficient and $\hat{q}^* - \hat{q}$ is the difference between that *average* solute concentration which exists when the polymer is in equilibrium with the gas phase and the *average* concentration of the solute in the polymer phase.

Figure 9 represents the ratio of the interphase flux and the difference of average concentration for a unit step change in surface concentration as a function of time. The average concentration is defined as

$$\hat{q} = \frac{\int_{\eta}^{\eta+1} 2\pi\lambda c' \, d\lambda}{\int_{\eta}^{\eta+1} 2\pi\lambda \, d\lambda} \tag{A2}$$

where c' is the solution of eq 14.

The exact solution indicates that the mass-transfer coefficient has a strong dependence on time, particularly at small values of θ/β. On the other hand, using the long-time approximation results in a time-independent value for the mass-transfer coefficient, the same behavior indicated by eq A1. Thus the adoption of eq A1 to describe the mass flux is equivalent to using the long-time approximation of Figure 6.

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