Analysis of Inverse Gas Chromatography Experiments

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Introduction

The inverse gas chromatography (IGC) experiment provides a valuable method of obtaining solubility and diffusivity data for polymer–penetrant systems. The data obtained from IGC experiments are useful in the design of certain polymer processing operations, such as a devolatilization process. Furthermore, these data can be used to evaluate theories for polymer–solvent transport, such as the free-volume theory of diffusion. Several very extensive and very thorough investigations[1-4] have contributed significantly to the refinement of this technique, particularly for the measurement of diffusion coefficients. The major purpose of this paper is to derive two simple equations which can be used in the data analysis for IGC experiments under certain conditions. In addition, the role of axial diffusion in the gas phase is reexamined.

Formulation of Equations

The basic assumptions and equations for the analysis of a capillary column inverse gas chromatography experiment have been presented in previous investigations.[1-4] It can be assumed that the capillary column extends axially from $z = -\infty$ to $z = +\infty$ and that the penetrant sample is injected as a narrow pulse at $z = 0$. The pertinent equations[1] describing the transport processes for this system can be written as follows:

$$\frac{\partial y}{\partial \theta} + \frac{\partial y}{\partial x} = \gamma \frac{\partial^2 y}{\partial x^2} + \frac{2}{\alpha \beta^2}\left(\frac{\partial q}{\partial \eta}\right)_{\eta=0} \tag{1}$$

$$\frac{\partial q}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial^2 q}{\partial \eta^2} \tag{2}$$

$$y(-\infty,\theta) = 0 \tag{3}$$

$$y(+\infty,\theta) = 0 \tag{4}$$

$$y = \delta(x), \quad \theta = 0, \quad -\infty < x < \infty \tag{5}$$

$$\partial q/\partial \eta = 0, \quad \eta = 1 \tag{6}$$

$$q = 0, \quad \theta = 0, \quad 0 < \eta \leq 1 \tag{7}$$

$$q = y, \quad \eta = 0 \tag{8}$$

$$\alpha = R/K\tau \tag{9}$$

$$\beta^2 = V\tau^2/D_p L \tag{10}$$

$$\gamma = D_g/VL \tag{11}$$

$$y = C_a L/C_0 V \tag{12}$$

$$x = z/L \tag{13}$$

$$\eta = (r - R)/\tau \tag{14}$$

$$\theta = Vt/L \tag{15}$$

$$q = \bar{C}L/C_0 KV \tag{16}$$

In these equations, z and r are the axial and radial coordinates, t is time, V is the average velocity in the gas phase, R is the radius of the polymer–gas interface, $\delta(x)$ is a Dirac delta function, and L is the length of the column from the injection point to the position at which the detector is located. Also, D_g and D_p are the gas phase and polymer phase mutual diffusion coefficients, K is the partition coefficient for the penetrant between the gas and polymer phases, τ is the thickness of the polymer film, and C_0 is the strength of the input pulse. Finally, C_a is the average concentration of the penetrant in the gas phase, and $\bar{C}$ is the penetrant concentration in the polymer phase.

There is one very important difference between the above set of equations and the equation set formulated in a previous investigation.[1] Here, we follow the usual practice in dispersion theory[5-7] and introduce the concentrated injection of solute as an initial condition for the parabolic partial differential equation for y. Boundary conditions for this equation are then imposed at $x = \pm\infty$ by simply noting the absence of solute at these infinte positions. On the other hand, in the previous study,[1] the injection of solute was introduced as a boundary condition at $x = 0$ with the assumption that it was somehow possible to control the solute concentration at this point during the entire experiment. However, in the presence of axial diffusion, it is not possible to set the concentration of solute at $x = 0$, which is an interior point of the diffusion field, since the action of axial diffusion will necessarily change the solute concentration at $x = 0$ during the experiment. Therefore, we believe the present equation set is more realistic and more closely describes the physics of the transport process in the gas phase.

Introduction of the Laplace transform produces the following ordinary differential equation and boundary conditions for $Y(x,p)$, the Laplace transform of the solute gas phase concentration:

$$-\gamma \frac{d^2Y}{dx^2} + \frac{dY}{dx} + YG = \delta(x) \tag{17}$$

$$Y(-\infty) = 0 \tag{18}$$

$$Y(+\infty) = 0 \tag{19}$$

$$G = p + \frac{2p^{1/2}}{\alpha\beta}\tanh \beta p^{1/2} \tag{20}$$

The solution to this distributional differential equation can be written as follows:

$$Y(x,p) = \frac{\exp\left[\left\{\frac{1}{2\gamma} + \frac{(1+4G\gamma)^{1/2}}{2\gamma}\right\}x\right]}{(1+4G\gamma)^{1/2}} \qquad x < 0 \tag{21}$$

$$Y(x,p) = \frac{\exp\left[\left\{\frac{1}{2\gamma} - \frac{(1+4G\gamma)^{1/2}}{2\gamma}\right\}x\right]}{(1+4G\gamma)^{1/2}} \qquad x > 0 \tag{22}$$

At the detector, which is at $x = 1$, we have the following expression:

$$Y(1,p) = \frac{\exp\left[\frac{1-(1+4G\gamma)^{1/2}}{2\gamma}\right]}{(1+4G\gamma)^{1/2}} \tag{23}$$

It appears to us that eq 23 is the appropriate equation for assessing the importance of axial diffusion effects on the dispersion process in the capillary column. Since γ is typically less than 10^{-4}, it is quite likely that axial diffusion of the solute in the gas phase will generally have a negligible influence on the dispersion process. Pawlisch[3] concluded

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previously that axial diffusion has a small effect on the dispersion processes in the capillary column. This conclusion was based on the flow dependence of the moment data and on a theoretical analysis based on using a boundary condition at $x = 0$. Equation 23 should provide a definitive theoretical assessment of the importance of axial diffusion for a particular set of conditions, and conclusions on the significance of axial diffusion should be based on the utilization of this equation. As $\gamma \to 0$, eq 23 reduces to

$$Y(1,p) = \exp[-G] \tag{24}$$

and this is the equation which will be used in the next section to derive two simple equations for the analysis of elution curves.

Derivation of Simple Equations

When axial diffusion in the gas phase is negligible, analysis of the elution curve is based on eq 24. Analytical inversion of eq 24 is difficult, so the analysis of experimental chromatographic data has been based on numerical inversion of the transform or on the utilization of a moment analysis of the elution profile.[1-4] Arnould[4] has noted that difficulties appear in the data analysis when $\beta > 1$ for $\alpha = 4$, $\beta > 2$ for $\alpha = 1$, and $\beta > 5$ for $\alpha = 0.2$. These problems are a result of the difficulty in making precise measurements of the tails of highly skewed peaks. The purpose of this study is to derive two simple analytical expressions which can be used in an analysis of the chromatographic data for sufficiently large β. These should be useful since difficulties appear in the standard data analyses as β increases.

From eqs 20 and 24, it is possible to use expansions in terms of negative exponentials to show that eq 24 takes the following limiting form for large β:

$$Y(1,p) = \exp[-p] \exp\left[-\frac{2p^{1/2}}{\alpha\beta}\right] \tag{25}$$

Inversion of this result gives

$$y = 0, \quad 0 < \theta < 1 \tag{26}$$

$$y = \frac{1}{\alpha\beta\pi^{1/2}(\theta-1)^{3/2}} \exp\left[-\frac{1}{\alpha^2\beta^2(\theta-1)}\right], \quad \theta > 1 \tag{27}$$

From this equation, it can be shown that the maximum value of y in the elution curve, y_m, and the time at which the maximum occurs, θ_m, are given by the following expressions:

$$y_m = \frac{\alpha^2\beta^2}{\pi^{1/2}}\left(\frac{3}{2}\right)^{3/2} \exp\left[-\frac{3}{2}\right] \tag{28}$$

$$\theta_m = 1 + 2/3\alpha^2\beta^2 \tag{29}$$

$$y_m = (C_a)_m L/C_0 V \tag{30}$$

$$\theta_m = Vt_m/L \tag{31}$$

Here, t_m is the actual time at which the maximum in the elution curve occurs and $(C_a)_m$ is the actual maximum average concentration. It is evident that eqs 29 and 31 can be used to determine the quantity $\alpha^2\beta^2$ from the measured value of t_m since V and L are of course known. Similarly, eqs 28 and 30 could be used to determine $\alpha^2\beta^2$ from the measured maximum average concentration if the quantity C_0 were available. It is usually possible to obtain a good estimate of C_0 using the following equation:

$$\int_0^\infty C_a(1,t)\, dt = C_0 \tag{32}$$

Consequently, eqs 28 and 29 provide two very simple expressions for the determination of the quantity $\alpha^2\beta^2$ for large values of β and small values of γ (negligible axial diffusion).

Since

$$\alpha^2\beta^2 = R^2V/K^2D_pL \tag{33}$$

either of the above equations yields only a value for K^2D_p, and the proposed data analysis does not provide a method of separating the partition coefficient from the mutual diffusion coefficient. The principal advantage of the capillary column inverse gas chromatography experiment is its ability to measure infinite dilution diffusion coefficients over significant temperature ranges in relatively short periods of times. It is difficult to obtain diffusivity data at very low solute concentrations using a vapor sorption experiment. On the other hand, thermodynamic data can be obtained using vapor sorption experiments, and the K deduced from such measurements can be combined with the capillary column IGC experiment to deduce D_p from measured values of $\alpha^2\beta^2$. In addition, the two simple equations for determining $\alpha^2\beta^2$ can be useful for evaluating D_p at low temperatures. At the higher temperatures of a temperature interval, β and α (and hence D_p and K) can be determined separately from numerical inversion or a moment analysis since β can be made reasonably small for a capillary column IGC experiment. As the temperature is lowered, the diffusion coefficient drops quickly, and high values of β can be obtained. The present analysis (either eq 28 or eq 29) can thus be used to determine $\alpha^2\beta^2$. The diffusivity D_p can then be evaluated by using the high-temperature thermodynamic data to estimate K at the low temperatures. For example, suppose that the thermodynamic characteristics of the polymer–solvent system are adequately described by the Flory–Huggins theory[8] above the glass transition temperature of the polymer. At infinite solvent dilution, the thermodynamic behavior of the polymer–solvent system is then described by the expression

$$\frac{1}{K} = \frac{M_1 p_1^0 \hat{V}_1}{\bar{R}T} \exp[1 + \chi] \tag{34}$$

where χ is the interaction parameter, M_1 is the solvent molecular weight, T is temperature, p_1^0 is the vapor pressure of the solvent, $\hat{V}_1$ is the partial specific volume of the solvent at infinite solvent dilution, and $\bar{R}$ is the gas constant per mole. It is evident that χ can be evaluated from high-temperature data using eq 34. Then, since χ is generally not a strong function of temperature, this value of χ can be substituted in eq 34 to obtain an estimate for K at low temperatures. The chromatographic data and either eq 28 or eq 29 can then be used to determine D_p. It should be noted that Pawlisch[3] concluded that χ for three polystyrene–solvent systems was effectively constant over the temperature range 110–140 °C.

It remains to establish the range of validity of the analytical expressions for y_m and θ_m (eqs 28 and 29). This is done here by comparing the predictions of these two equations with computations for y_m and θ_m based on numerical inversion of eq 24. These comparisons are presented in Table I for three values of α. This table shows that the limiting analytical expressions give acceptable predictions for $\beta^2 > 1.5$ when $\alpha = 1$, $\beta^2 > 1$ when $\alpha = 4$, and $\beta^2 > 8$ when $\alpha = 0.2$. As stated above, Arnould[4] has noted that problems exist in the standard data analyses when $\beta^2 > 4$ when $\alpha = 1$, $\beta^2 > 1$ when $\alpha = 4$, and $\beta^2 > 25$ when $\alpha = 0.2$. Clearly, the present analysis is capable of providing accurate values of $\alpha^2\beta^2$ in this range and hence

Table I. Comparison of Exact and Limiting Solutions

		y_m		θ_m	
α	β^2	eq 28	exact	eq 29	exact
1	1	0.231	0.386	1.67	2.35
1	1.5	0.347	0.353	1.44	1.50
1	2	0.463	0.463	1.33	1.33
1	5	1.16	1.16	1.13	1.13
1	10	2.31	2.31	1.067	1.067
4	1	3.70	3.66	1.042	1.043
0.2	6	0.0555	0.0726	3.78	6.96
0.2	8	0.0740	0.0746	3.08	3.18
0.2	10	0.0925	0.0925	2.67	2.67

serves to complement the numerical inversion or moment analysis procedures. Consequently, it is fair to conclude that the two simplified equations derived here can provide a method of analyzing capillary column IGC experiments for low diffusivities (large β) when the other methods can lead to significant errors for α and β.

The proposed procedure has been tested on simulated data which are the theoretical real-time concentration profiles generated from a numerical inversion of eq 24. This equation is valid in the limit $\gamma = 0$, so axial diffusion is of course completely absent. However, it is easy to show that the two simplified equations also describe concentration profiles for small, nonzero values of γ. For $\beta^2 > 1$, numerical inversion of eq 23 for $\gamma < 10^{-4}$ (the usual range) leads to concentration profiles which are essentially identical to those obtained from eq 24 with $\gamma = 0$. Hence, the proposed equations can be applied to situations where there is a small axial diffusion effect. Finally, we note that Hattam and Munk[9] have carried out a numerical simulation of inverse gas chromatography in a packed column. From their numerical solution, they obtained an equation for the time at which the maximum occurs. This equation is simply a curve fit of the numerical data. Although this empirical equation is similar to our eq 29, the form of the dependence of the maximum time on the appropriate dimensionless groups is different.

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