New approach for evaluation of capillary column inverse gas chromatography

E. Hamdan *, J.F. Milthorpe, J.C.S. Lai

*School of Aerospace, Civil and Mechanical Engineering, University College, University of New South Wales,
Australian Defense Force Academy, Canberra 2600, Australia*

Abstract

A mathematical model has been developed for the analysis of a capillary column IGC experiment. An important feature in the derivation of the model is the inclusion of Taylor dispersion effect. The model shows that Taylor dispersion effect has a very significant effect on elution profiles at low values of β and γ. Taylor dispersion effect causes more spread in the longitudinal direction and the peaks become broader. Taylor dispersion becomes more significant as β becomes smaller. The model presented in this paper is more general than the usual IGC models and sets criteria equations to determine under what conditions the Taylor dispersion effect can be made negligible. A comparison between the present and usual IGC models above and near the glass temperature of the polymer is conducted. The analysis also describes the effect of kurtosis on pulse dispersion at extremely low diffusivities.
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1. Introduction

Inverse gas chromatography is the most widely used technique for accurate measurement of polymer phase diffusion coefficients in polymer–solvent systems. Although extensive studies on inverse gas chromatography exist in the literature, none of these investigated the effect of Taylor dispersion on the elution profiles. In all previous IGC models, the effective axial dispersion coefficient was assumed to be independent of the carrier gas velocity. The problem of solute dispersion in a capillary tube was first studied by Taylor [1]. He outlined that under certain conditions, the solute is dispersed along the pipe in a manner similar to diffusion from a plane source, but with the system co-ordinate moving with a velocity equals to the mean velocity of the flow. The criteria under which Taylor analysis was valid could be expressed as $\bar{u} \gg 7D/R$ and $t \gg R^2/(3.8)^2 D$. He also showed that the effective axial diffusion coefficient under these conditions is given by

$D_{\mathrm{ax}} = R^2 \bar{u}^2 / 48D$. Later on, Aris [2] gave a new treatment and removed the restriction imposed by Taylor and showed that the effective axial diffusion coefficient is equal to the sum of molecular diffusion coefficient D and the Taylor's effective axial diffusion coefficient. Therefore, the IGC model assumption that the gas-phase axial dispersion is independent of flow velocity is highly questionable. However, this assumption has been used earlier by Pawlisch and coworkers [3] to derive a mathematical model applicable for analyzing IGC experiments. Most of the subsequent researchers interested in IGC have used the same model. Pawlisch and coworkers [4] have presented improvements on their earlier model [3] to account for a nonuniform polymer film thickness (eccentricity). By using the model developed in [3], Vrentas and coworkers [5] derived a simple equation for IGC data analysis at very low polymer phase diffusion coefficients D_{p}. In their modified model, since γ is typically small, it was assumed that the axial diffusion in the gas phase has a negligible effect on the dispersion process. The reason for neglecting axial diffusion effect at very low polymer phase diffusion coefficients is because the solute molecules will spend most of the time

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* Corresponding author. Tel.: +61 2 62686057; fax: +61 2 62688276.
  E-mail address: e.hamdan@student.adfa.edu.au (E. Hamdan).

diffusing slowly in the stationary phase and therefore, the results are not sensitive to the gas phase diffusion coefficient D_g. However, neglecting the effect of molecular diffusion would mean that the whole of the longitudinal mass transfer is due to convection and unless the Peclect number Pe is made very small, Taylor dispersion effect becomes significant and should be included in the analysis. The Peclect number can be made small by reducing column radius R, carrier gas velocity $\bar{u}$ or increasing the diffusion coefficient of the solute in the gas phase D_g. However, there are limits imposed on these parameters in order to conduct experiments within reasonably short times and to avoid peak broadening. The purpose of this work is to derive a mathematical model for analysing IGC experiments which takes into consideration the dependence of the gas-phase dispersion on the carrier gas velocity. The model could be used to assess the validity of assuming negligible Taylor dispersion effect as done previously in the usual IGC models.

2. Capillary column model

The main assumptions and the transport equations for IGC are the same as those used in the early study of Pawlisch and coworkers [3]. The transport equations for the concentration of the solute in the gas phase c and in the polymer phase c' can be written as

$$\frac{\partial c}{\partial t} + 2\bar{u}\left(1 - \left(\frac{r}{R}\right)^2\right)\frac{\partial c}{\partial z} = D_g\left[\frac{\partial^2 c}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right] \quad (1)$$

$$\frac{\partial c'}{\partial t} = D_p\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c'}{\partial r}\right)\right] \quad (2)$$

The initial and boundary conditions are given by Vrentas [5] as

$$
\begin{aligned}
&c(r, \infty, t) = c(r, -\infty, t) = 0 \\
&c' = 0, && t = 0 \\
&\frac{\partial q}{\partial r} = 0, && r = R + \tau \\
&c(r, z, t) = \delta(z)c_0, && t = 0 \\
&c(r, z, t) = \frac{c'(r, z, t)}{K}, && r = R \\
&D_g\frac{\partial c}{\partial r} = D_p\frac{\partial c'}{\partial r}, && r = R \\
&\frac{\partial c}{\partial r} = 0, && r = 0
\end{aligned}
\quad (3)
$$

By introducing the following non-dimensional variables

$$y = \frac{cL}{c_0\bar{u}}, \quad x = \frac{z}{L}, \quad \eta = \frac{(r - R)}{\tau}$$

$$\theta = \frac{\bar{u}t}{L}, \quad q = \frac{c'L}{c_0 K\bar{u}}, \quad \zeta = \frac{r}{R} \quad (4)$$

Eqs. (1) and (2) can be written in non-dimensional form as

$$\frac{\partial y}{\partial \theta} + u(\zeta)\frac{\partial y}{\partial x} = \gamma\frac{\partial^2 y}{\partial x^2} + \gamma\left(\frac{L}{R}\right)^2\left[\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\left(\zeta\frac{\partial y}{\partial \zeta}\right)\right] \quad (5)$$

$$\frac{\partial q}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial^2 q}{\partial \eta^2} \quad (6)$$

where

$$\gamma = \frac{D_g}{\bar{u}L}, \quad \beta^2 = \frac{\bar{u}\tau^2}{LD_p} \quad (7)$$

$$u(\zeta) = 2(1 - \zeta^2) \quad (8)$$

The initial and boundary conditions in Eq. (3) can be rewritten in dimensionless form as

$$
\begin{aligned}
&y(-\infty, \theta) = y(\infty, \theta) = 0 \\
&y = \delta(x), && \theta = 0 \\
&y = q, && \eta = 0 \\
&\left(\frac{\partial y}{\partial \zeta}\right)_{\zeta=1} = \varepsilon\left(\frac{\partial q}{\partial \eta}\right)_{\eta=0} \\
&q = 0, && \theta = 0 \\
&\frac{\partial q}{\partial \eta} = 0, && \eta = 1 \\
&\frac{\partial y}{\partial \zeta} = 0, && \zeta = 0
\end{aligned}
\quad (9)
$$

The concentration of the solute in the gas phase y and the axial flow velocity u can be expressed in terms of their area averaged values ($\bar{y}$ and $\bar{u}$) and fluctuations from the area averages ($\tilde{y}$ and $\tilde{u}$) as

$$y = \bar{y} + \tilde{y} \quad (10)$$

$$u = \bar{u} + \tilde{u} \quad (11)$$

Substituting (10) into (5) gives

$$\frac{\partial \bar{y}}{\partial \theta} + \frac{\partial \tilde{y}}{\partial \theta} + u\frac{\partial \bar{y}}{\partial x} + u\frac{\partial \tilde{y}}{\partial x} = \gamma\left(\frac{\partial^2 \bar{y}}{\partial x^2} + \frac{\partial^2 \tilde{y}}{\partial x^2}\right)$$
$$+ \gamma\left(\frac{L}{R}\right)^2\left[\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\left(\zeta\frac{\partial \tilde{y}}{\partial \zeta}\right)\right] \quad (12)$$

In the usual IGC models, the radial variation in the gas phase concentration y is assumed to be so small such that $\tilde{y} \ll \bar{y}$. In this case, $y = \bar{y}$ is used as an approximation which yields the plug flow model [3]. Taking spatial average of Eq. (12) and making use of the boundary conditions in Eq. (9) and the property of spatial averaged fluctuations

$$\bar{\tilde{y}} = \bar{\tilde{u}} = 0 \quad (13)$$

yields

$$\frac{\partial \bar{y}}{\partial \theta} + \bar{u}\frac{\partial \bar{y}}{\partial x} = \gamma\frac{\partial^2 \bar{y}}{\partial x^2} - \frac{\partial}{\partial x}(\overline{\tilde{u}\tilde{y}}) + \frac{2}{\alpha\beta^2}\frac{\partial q(0)}{\partial \eta} \quad (14)$$