

# New approach for evaluation of capillary column inverse gas chromatography

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## 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  $\beta$  and  $\gamma$ . Taylor dispersion effect causes more spread in the longitudinal direction and the peaks become broader. Taylor dispersion becomes more significant as  $\beta$  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  $t \gg R^2/(3.8)^2D$ . He also showed that the effective axial diffusion coefficient under these conditions is given by

$D_{ax} = R^2\bar{u}^2/48D$ . 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  $\gamma$  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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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 Peclet number  $Pe$  is made very small, Taylor dispersion effect becomes significant and should be included in the analysis. The Peclet 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

$$\begin{aligned} y &= \frac{cL}{c_0\bar{u}}, & x &= \frac{z}{L}, & \eta &= \frac{(r-R)}{\tau} \\ \theta &= \frac{\bar{u}t}{L}, & q &= \frac{c'L}{c_0K\bar{u}}, & \zeta &= \frac{r}{R} \end{aligned} \quad (4)$$

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 re-written 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

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

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

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

where

$$\alpha = \frac{R}{K\tau} \quad (15)$$

The new quantity  $\overline{(\tilde{u}\tilde{y})}$  is the additional contribution to dispersion caused by velocity fluctuation from the plug flow model. It is the axial component of the dispersion that represents the flux associated with the correlation between the fluctuations in velocity,  $\tilde{u}$ , and concentration,  $\tilde{y}$ , relative to their depth-averaged values. This additional term was neglected in the usual IGC models due to the radial uniformity assumption. The next step is to obtain an expression for  $\tilde{y}$  in terms of  $\bar{y}$  and calculate  $\overline{(\tilde{u}\tilde{y})}$ .

Subtracting Eq. (14) from Eq. (12), yields

$$\begin{aligned} \frac{\partial \tilde{y}}{\partial \theta} + \tilde{u} \frac{\partial \tilde{y}}{\partial x} &= \gamma \frac{\partial^2 \tilde{y}}{\partial x^2} + \gamma \left( \frac{L}{R} \right)^2 \left[ \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \left( \zeta \frac{\partial \tilde{y}}{\partial \zeta} \right) \right] \\ &+ \frac{\partial}{\partial x} [\overline{(\tilde{u}\tilde{y})} - u\tilde{y}] - \tilde{u} \frac{\partial \tilde{y}}{\partial x} - \frac{2}{\alpha\beta^2} \frac{\partial q(0)}{\partial \eta} \end{aligned} \quad (16)$$

It is convenient to transform (16) to a new coordinate system,  $x_1 = x - \tilde{u}\theta$ , moving with the average flow velocity. In terms of the new coordinate system, Eq. (16) is written as

$$\begin{aligned} \frac{\partial \tilde{y}}{\partial \theta} &= \gamma \frac{\partial^2 \tilde{y}}{\partial x_1^2} + \underbrace{\gamma \left( \frac{L}{R} \right)^2 \left[ \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \left( \zeta \frac{\partial \tilde{y}}{\partial \zeta} \right) \right]}_I + \underbrace{\frac{\partial}{\partial x_1} [\overline{(\tilde{u}\tilde{y})} - \tilde{u}\tilde{y}]}_II \\ &- \underbrace{\tilde{u} \frac{\partial \tilde{y}}{\partial x_1}}_{III} - \frac{2}{\alpha\beta^2} \frac{\partial q(0)}{\partial \eta} \end{aligned} \quad (17)$$

In his study for dispersion of solute in solvent through a tube, Taylor [1] concluded that provided a sufficiently long time has elapsed after solute injection, the rate at which perturbations in concentration profile are created is mainly controlled by the balance between perturbations in concentration profiles created by differential advection, term III, and the dissipation of the perturbations by lateral diffusion, term I. However, during the early stages of dispersion, the mean concentration gradients are very large and term II becomes important. At a relatively large time, the term II becomes small and is neglected. In this case, Eq. (17) can be re-written as

$$\frac{\partial \tilde{y}}{\partial \theta} = \gamma \frac{\partial^2 \tilde{y}}{\partial x_1^2} + \gamma \left( \frac{L}{R} \right)^2 \left[ \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \left( \zeta \frac{\partial \tilde{y}}{\partial \zeta} \right) \right] + g(x_1, \theta, \zeta) \quad (18)$$

where

$$g(x_1, \theta, \zeta) = -\tilde{u} \frac{\partial \tilde{y}}{\partial x_1} - \frac{2}{\alpha\beta^2} \frac{\partial q(0)}{\partial \eta} \quad (19)$$

Eq. (18) is solved using the integral transform technique [6]. Using the integral transform pair

$$\bar{T} = \int_0^1 \zeta J_0(\beta_m, \zeta) \tilde{y} d\zeta \quad (20)$$

$$\tilde{y} = \sum_{m=1}^{\infty} \frac{J_0(\beta_m, \zeta)}{N(\beta_m)} \bar{T} \quad (21)$$

The integral transform of Eq. (18) is

$$\frac{\partial \bar{T}}{\partial \theta} + \lambda \bar{T} - \gamma \frac{\partial^2 \bar{T}}{\partial x_1^2} = \bar{g}(x_1, \theta, \zeta) \quad (22)$$

where

$$\lambda = \gamma \left( \beta_m \frac{L}{R} \right)^2, \quad \bar{g}(x_1, \theta) = -\frac{\partial \tilde{y}}{\partial x_1} \int_0^1 \zeta J_0(\beta_m, \zeta) \tilde{u} d\zeta \quad (23)$$

The solution of Eq. (22) is given in [6] as

$$\begin{aligned} \bar{T} &= \int_{t'=0}^{\theta} \int_{\omega=-\infty}^{\infty} \frac{\bar{g}(x_1, \theta, \zeta)}{[4\pi\gamma(\theta-t')]^{1/2}} \exp(\lambda\theta) \\ &\times \exp \left[ -\frac{(x_1 - w)^2}{4\gamma(\theta-t')} \right] dw dt' \end{aligned} \quad (24)$$

Following [7], the integral can be approximated by expanding  $\bar{g}(x_1, \theta, \zeta)$  around  $w = x_1$  and  $t = \theta$  and retaining only first order terms in  $(w - x_1)$  and  $(t - \theta)$  to yield

$$\bar{T} = \bar{g} \left( \frac{1 - e^{-\lambda\theta}}{\lambda} \right) - \left( \frac{\partial \bar{g}}{\partial \theta} - \gamma \frac{\partial^2 \bar{g}}{\partial x_1^2} \right) \left( \frac{1 - (1 + \lambda\theta)e^{-\lambda\theta}}{\lambda^2} \right) \quad (25)$$

Using Eq. (21), one can find

$$\overline{(\tilde{u}\tilde{y})} = \sum_{m=1}^{\infty} \frac{\overline{\tilde{u}J_0(\beta_m, \zeta)}}{N(\beta_m)} \bar{T} \quad (26)$$

Substituting Eq. (26) into Eq. (14) yields the final mean solute concentration equation

$$\begin{aligned} \frac{\partial \bar{y}}{\partial \theta} &- \left( \sum_{m=1}^{\infty} \frac{\overline{\tilde{u}J_0(\beta_m, \zeta)}}{N(\beta_m)} \left( \frac{1 - e^{-\lambda\theta}}{\lambda} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \tilde{u} d\zeta \right) \\ &\times \frac{\partial^2 \bar{y}}{\partial x_1^2} + \left( \sum_{m=1}^{\infty} \frac{\overline{\tilde{u}J_0(\beta_m, \zeta)}}{N(\beta_m)} \left( \frac{1 - (1 + \lambda\theta)e^{-\lambda\theta}}{\lambda^2} \right) \right) \\ &\times \int_0^1 \zeta J_0(\beta_m, \zeta) \tilde{u} d\zeta \frac{\partial^3 \bar{y}}{\partial x_1^2 \partial \theta} - \left( \sum_{m=1}^{\infty} \gamma \frac{\overline{\tilde{u}J_0(\beta_m, \zeta)}}{N(\beta_m)} \right) \\ &\times \left( \frac{1 - (1 + \lambda\theta)e^{-\lambda\theta}}{\lambda^2} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \tilde{u} d\zeta \frac{\partial^4 \bar{y}}{\partial x_1^4} \\ &= \gamma \frac{\partial^2 \bar{y}}{\partial x_1^2} + \frac{2}{\alpha\beta^2} \frac{\partial q(0)}{\partial \eta} \end{aligned} \quad (27)$$

For large time analysis, Eq. (27) reduces to

$$\begin{aligned} \frac{\partial \bar{y}}{\partial \theta} &- \left( \sum_{m=1}^{\infty} \frac{\bar{u} J_0(\beta_m, \zeta)}{N(\beta_m)} \left( \frac{1}{\lambda} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \bar{u} d\zeta \right) \frac{\partial^2 \bar{y}}{\partial x_1^2} \\ &+ \left( \sum_{m=1}^{\infty} \frac{\bar{u} J_0(\beta_m, \zeta)}{N(\beta_m)} \left( \frac{1}{\lambda^2} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \bar{u} d\zeta \right) \frac{\partial^3 \bar{y}}{\partial x_1^2 \partial \theta} \\ &- \left( \sum_{m=1}^{\infty} \gamma \frac{\bar{u} J_0(\beta_m, \zeta)}{N(\beta_m)} \left( \frac{1}{\lambda^2} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \bar{u} d\zeta \right) \frac{\partial^4 \bar{y}}{\partial x_1^4} \\ &= \gamma \frac{\partial^2 \bar{y}}{\partial x_1^2} + \frac{2}{\alpha \beta^2} \frac{\partial q(0)}{\partial \eta} \end{aligned} \quad (28)$$

The capillary column investigated by Taylor [1] is different from that used in the IGC where a thin polymer film is coated on the inner wall. Since Taylor assumed that the transfer of solute along the tube by molecular diffusion is small compared with that produced by convection, the first term on the RHS of Eq. (28) was neglected. As there is no polymer in Taylor's case, there is no second term on the RHS of Eq. (28). Hence, Taylor's case is a special case of the general Eq. (28) containing only the first two terms on the LHS. Taking the Laplace transform of Eq. (28) and neglecting the fourth term (see criterion Eq. (40)) yields in terms of a fixed co-ordinate system

$$-A_0 \frac{\partial^2 \bar{y}^0}{\partial x^2} + \bar{u} \frac{\partial \bar{y}^0}{\partial x} + G(s) \bar{y}^0 = \delta(x) \quad (29)$$

where

$$\bar{u} = 1 \quad (30)$$

$$\begin{aligned} A_0 &= \left( \sum_{m=1}^{\infty} \frac{\bar{u} J_0(\beta_m, \zeta)}{N(\beta_m)} \left( \frac{1}{\lambda} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \bar{u} d\zeta \right) \\ &- \left( \sum_{m=1}^{\infty} \frac{\bar{u} J_0(\beta_m, \zeta)}{N(\beta_m)} \left( \frac{1}{\lambda^2} \right) \int_0^1 \zeta J_0(\beta_m, \zeta) \bar{u} d\zeta \right) s + \gamma \end{aligned} \quad (31)$$

and

$$G(s) = s + \frac{2\sqrt{s}}{\alpha\beta} \tan h(\beta\sqrt{s}) \quad (32)$$

Evaluating the terms between brackets in Eq. (31) gives

$$A_0 = b_0 - b_1 s + \gamma \quad (33)$$

where

$$b_0 = \frac{1}{48\gamma(L/R)^2} \quad (34)$$

and

$$b_1 = \frac{1}{720\gamma^2(L/R)^4} \quad (35)$$

Following [6], the general solution of Eq. (29) at  $x = 1$  is

$$\bar{y}^0 = \frac{\exp(1/2A_0) \exp[-(1/2A_0)(1 + 4A_0G(s))^{1/2}]}{(1 + 4A_0G(s))^{1/2}} \quad (36)$$

The value of the constant  $1/48$  in  $b_0$  (Eq. (34)) is equivalent to that obtained by Taylor in [1]. Thus, the present model retains the Taylor dispersion effect which is made negligible in the usual IGC models.

The case where Taylor dispersion effect is neglected, can be retained from Eq. (25) by using Taylor expansion of the exponential function and setting  $\lambda = 0$ . In this case, Eq. (25) yields

$$\bar{T} = \theta \bar{g} - \frac{1}{2} \theta^2 \left( \frac{\partial \bar{g}}{\partial \theta} - \gamma \frac{\partial^2 \bar{g}}{\partial x^2} \right) \quad (37)$$

Substituting Eq. (37) into Eqs. (26) and (27) and taking the Laplace transform of the resulting equation yields  $A_0 = \gamma$ . Clearly, setting  $A_0 = \gamma$  in Eq. (36) yields the Laplace solution of the usual IGC model. Eq. (28) can be re-written in terms of the fixed coordinate system as

$$\begin{aligned} \frac{\partial}{\partial \theta} \underbrace{\left( \bar{y} + b_1 \frac{\partial^2 \bar{y}}{\partial x^2} \right)}_{\text{IV}} - b_0 \frac{\partial^2}{\partial x^2} \underbrace{\left( \bar{y} + \frac{\gamma}{\lambda} \frac{\partial^2 \bar{y}}{\partial x^2} \right)}_{\text{V}} + \frac{\partial \bar{y}}{\partial x} \\ = \gamma \frac{\partial^2 \bar{y}}{\partial x^2} + \frac{2}{\alpha \beta^2} \frac{\partial q(0)}{\partial \eta} \end{aligned} \quad (38)$$

By examining the order of magnitudes of the terms in Eq. (38), it is clear that the second term in IV is small compared with the first term when

$$720(\gamma L^*)^2 \left( \frac{L}{R} \right)^4 \gg 1 \quad (39)$$

and the second term in V is small compared with the first term when

$$L^*{}^2 \left( \beta_m \frac{L}{R} \right)^2 \gg 1 \quad (40)$$

where  $L^*$  is the length of the capillary column between points where the concentration of the solute is 1% and 99% of the full concentration, normalized by the length of the column [8]. Criterion Eq. (40) is much easier to meet than criterion Eq. (39). In most practical cases, criteria Eqs. (39) and (40) are both satisfied so that Eq. (38) can be reduced to

$$\frac{\partial \bar{y}}{\partial \theta} + \frac{\partial \bar{y}}{\partial x} - \gamma^* \frac{\partial^2 \bar{y}}{\partial x^2} = \frac{2}{\alpha \beta^2} \frac{\partial q(0)}{\partial \eta} \quad (41)$$

where

$$\gamma^* = b_0 + \gamma = A_0 + b_1 s \quad (42)$$

is the effective axial diffusion coefficient in the gas phase.

One can notice that even with these assumptions, the resulting Eq. (41), still contains the Taylor dispersion term,  $b_0$ , which is made negligible in the usual IGC models. As shown

in [3], the first and second moments of ditribution obtained using the transform solution Eq. (36) are

$$\mu_1 = \left(1 + \frac{\tau K}{R}\right) t_c \quad (43)$$

$$\mu_2 = \left(\frac{4K\tau^3}{3RD_p t_c} + 2\gamma^* \left(1 + \frac{\tau K}{R}\right)^2\right) t_c^2 \quad (44)$$

An alternative approach to deriving Eq. (41) is to use Taylor’s assumptions in [1]. In this case, Eq. (17) can be written as

$$\tilde{u} \frac{\partial \bar{y}}{\partial x_1} = \gamma \left(\frac{L}{R}\right)^2 \left[ \frac{1}{\zeta} \frac{\partial}{\partial \zeta} \left( \zeta \frac{\partial \bar{y}}{\partial \zeta} \right) \right] - \frac{2}{\alpha \beta^2} \frac{\partial q(0)}{\partial \eta} \quad (45)$$

Integrating (46) and making use of boundary condition  $\partial \bar{y} / \partial \zeta |_{\partial=0} = 0$ ,  $\bar{y}$  can be expressed in terms of  $\bar{y}$  as

$$\bar{y} = \frac{1}{\gamma(L/R)^2} \frac{\partial \bar{y}}{\partial x_1} \left\{ \int_0^{\zeta'} \frac{1}{\zeta'} \left[ \int_0^{\zeta} \zeta \tilde{u} d\zeta \right] d\zeta' \right\} \quad (46)$$

Since we are only interested in evaluating the term  $\partial / \partial x_1 (\tilde{u} \bar{y})$ , the constant of integration and the second term to the right hand side of Eq. (45) are independent of  $x_1$  and, therefore, were neglected in the analysis. Using Eq. (46),

$\partial / \partial x_1 (\tilde{u} \bar{y})$  can be evaluated easily and the final result is

$$\frac{\partial}{\partial x_1} (\tilde{u} \bar{y}) = \frac{1}{48\gamma(L/R)^2} \frac{\partial \bar{y}}{\partial x_1} \quad (47)$$

Substiuting Eq. (47) into Eq. (14), yields Eq. (41).

### 3. Results and discussion

The results presented in this study are the solutions of Eq. (41) with criteria Eqs. (39) and (40) being both satisfied. The values of  $\alpha$  (0.52) and  $\beta$  (0.01–10) are the same as those used by Surana and coworkers [9] while the effect of reducing the gas phase diffusion coefficient  $\gamma$  from  $2.8e-5$  to  $2.8e-8$  is examined. When  $\gamma$  is sufficiently high such as  $\gamma = 2.8e-5$  in Fig. 1a, convective diffusion is so slow that molecular diffusion controls dispersion and Taylor dispersion effect is negligible. Reducing  $\gamma$  to  $2.8e-6$ , as shown in Fig. 1b, increases the effect of Taylor dispersion on solute dispersal and its effect becomes more pronounced as  $D_p$  becomes larger or  $\beta$  becomes smaller such as  $\beta = 0.01$ . Although the value of  $\beta = 0.01$  is below the range 0.03–5 recommended by Surana et al [9], it was used here to show that Taylor dispersion could affect the elution profiles when  $\beta$  is sufficiently

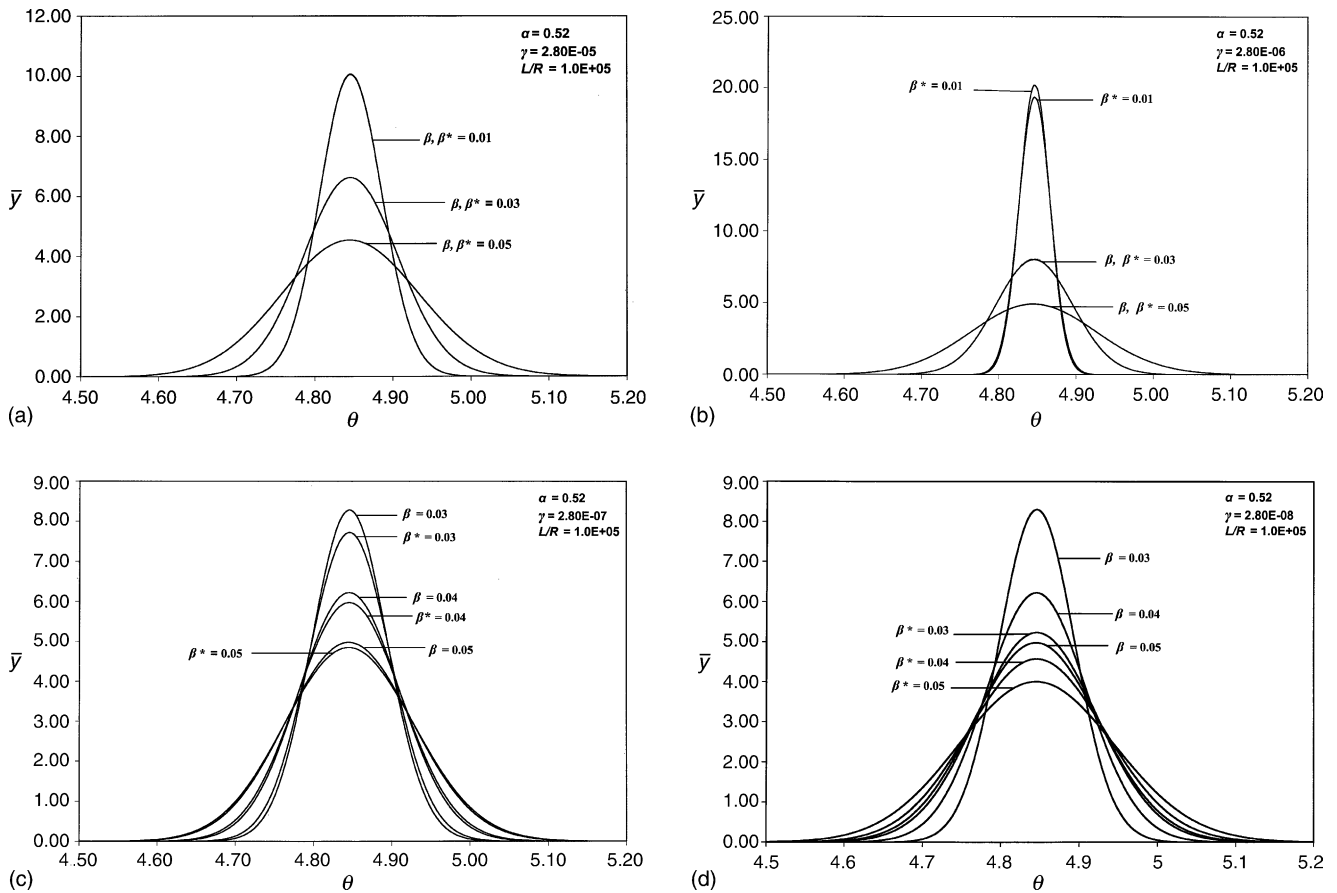


Fig. 1. Comparison of the elution profiles of the present (\*) model and the usual IGC models for  $\alpha = 0.52$ ,  $L/R = 100,000$  and various  $\beta$  values as  $\gamma$  is reduced: (a)  $\gamma = 2.8e-5$ ; (b)  $\gamma = 2.8e-6$ ; (c)  $\gamma = 2.8e-7$ ; and (d)  $\gamma = 2.8e-8$ .

small and  $\gamma$  is within the range  $10^{-5}$ – $10^{-7}$  usually used in IGC experiments. When  $\gamma$  is reduced further to  $2.8\text{e-}7$  in Fig. 1c and to  $2.8\text{e-}8$  in Fig. 1d, Taylor dispersion effect becomes more significant over a wide range of low  $\beta$  values (0.03–0.05) and a significant difference is observed between the present and usual IGC model solutions. In this case, the dispersion process is controlled by the combination of molecular diffusion and Taylor dispersion effect. Fig. 1c and d also show the effect of varying  $\beta$  on the elution profiles. Assigning higher values for  $\beta$  tend to broaden the elution profile while the symmetry and peak maximum position are unaffected. These results also show that for the same  $\beta$  value, the effect of Taylor dispersion becomes significant as  $\gamma$  is reduced, causing more dispersion in the axial direction and broader peaks. For a given  $\gamma$ , as  $\beta$  becomes smaller, Taylor dispersion effect on the elution profiles increases and peaks become broader.

The influence of  $L/R$  ratio on the Taylor dispersion effect and the elution profiles can be seen by comparing Fig. 1c for  $L/R = 100,000$  and Fig. 2 for  $L/R = 500,000$ . It is quite clear from Fig. 1c and Fig. 2 that increasing  $L/R$  reduces Taylor dispersion effect and the elution profiles obtained by the present model approach those obtained using the IGC model developed in [3]. Results from Figs. 1 and 2 indicate that the effect of Taylor dispersion depends on the time the solute spends in the stationary phase relative to the time it spends in the mobile phase. Large values of  $\beta$  (very low  $D_p$ ) means more time spent by the solute in the stationary phase and therefore, the effect of Taylor dispersion on the elution profiles is less. The partition coefficient  $K$  is proportional to the solute residence time in the stationary phase. Increasing the value of  $K$  will increase solute residence time in the stationary phase relative to the time it spends in the gas phase and therefore, this will decrease the effect of Taylor dispersion. For a given solute and stationary phase, a change in the column temperature or column diameter  $2R$  and/or film thickness  $\tau$  will cause a change in the retention time of the solute and thus the value of  $K$  [10].

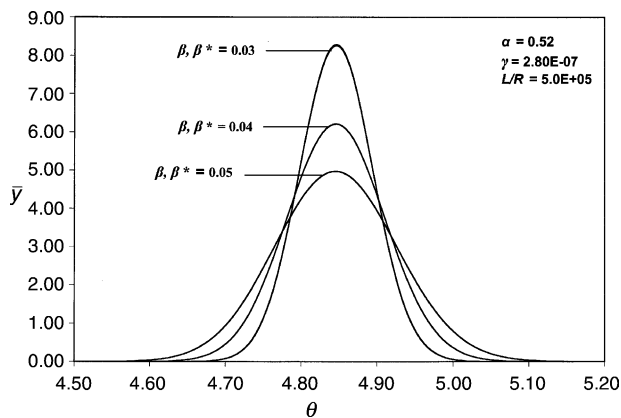


Fig. 2. Comparison of the elution profiles of the present (\*) model and the usual IGC models for  $\alpha = 0.52$ ,  $\gamma = 2.8\text{e-}5$ ,  $L/R = 500,000$  and various  $\beta$  values.

In the case of low polymer phase diffusion coefficients (i.e., high  $\beta$ ) as encountered near the glass temperature of the polymer, reducing  $\gamma$  does not affect the results to a large extent, as shown in Fig. 3a for  $\gamma = 2.8\text{e-}5$  and in Fig. 3b for  $\gamma = 2.8\text{e-}7$ , with  $\beta = 3, 5$  and  $10$ . At very low polymer and gas diffusivities, Taylor dispersion effect becomes very significant and neglecting it will lead to overestimated values for polymer phase diffusion coefficients. Vrentas and coworkers [5] proposed a modified IGC model to be used at very low polymer phase diffusion coefficients when  $\beta$  exceeds the upper limit of 5 and the sensitivity of the usual IGC model is lost [9]. Fig. 4a shows a comparison between the present model solutions at different values of  $\gamma^*$  and those obtained using Vrentas [5] modified model where the axial diffusion in the gas phase is neglected. In the early model developed by Pawlisch and coworkers [3] and the modified model proposed by Vrentas [5], Taylor dispersion effect was not taken into consideration (i.e.,  $\gamma^* = \gamma$  in [3] and  $\gamma^* = \gamma = 0$  in [5]). In the present model,  $\gamma^*$  is equal to the sum of the non-dimensional axial molecular diffusion  $\gamma$  and Taylor dispersion coefficient  $b_0$ . As  $\gamma^*$  decreases, the theoretical curves obtained using the present model approach those of Vrentas [5] modified model (cf. Fig. 4a). To use the modification proposed by Vrentas [5], Taylor dispersion should be made small or negligible. Taylor

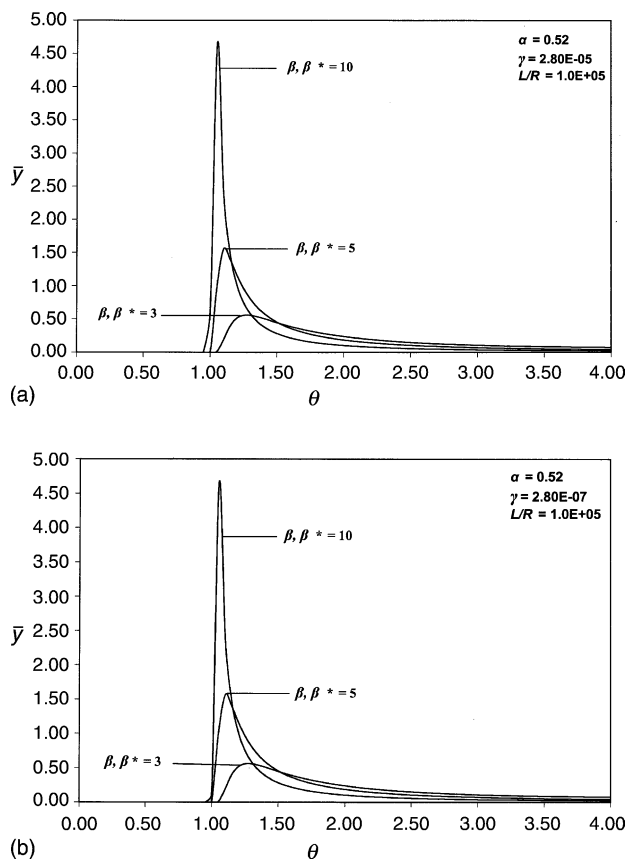


Fig. 3. Comparison of the elution profiles of the present (\*) model and the usual IGC models at very low polymer-phase diffusion coefficients (i.e., large  $\beta$ ) for  $\alpha = 0.52$ ,  $L/R = 100,000$  as  $\gamma$  is reduced: (a)  $\gamma = 2.8\text{e-}5$ ; and (b)  $\gamma = 2.8\text{e-}7$ .

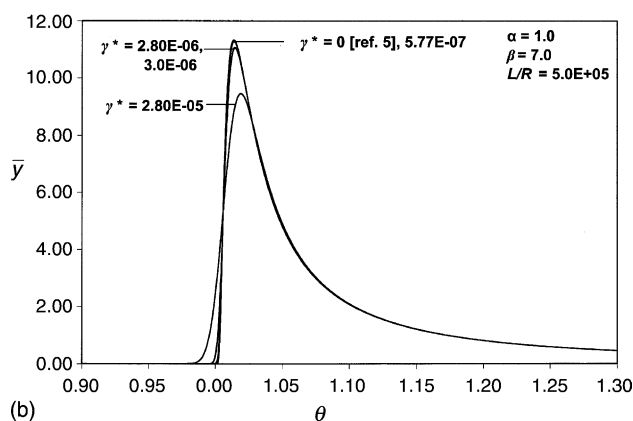
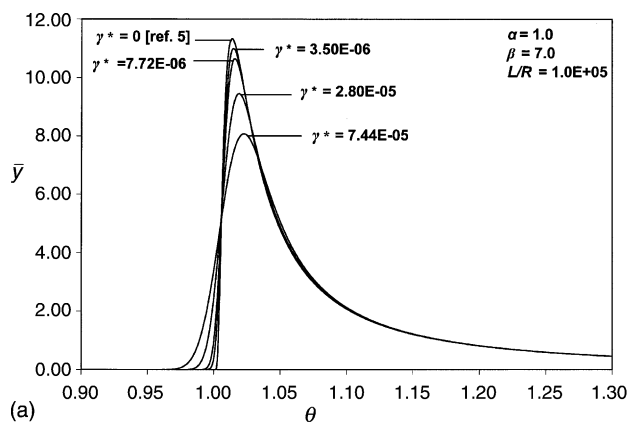


Fig. 4. Comparison of the elution profiles of the present (\*) model at very low polymer-phase diffusion coefficients (i.e., large  $\beta$ ) for  $\alpha = 1$ ,  $\beta = 7$ , and various values of  $\gamma^*$  with the modified model [5] for  $\gamma^* = 0$ : (a)  $L/R = 100,000$ ; and (b)  $L/R = 500,000$ .

dispersion may significantly affect the elution profiles at large  $\beta$  and small  $\gamma$  values. Increasing the  $L/R$  ratio from 100,000 in Fig. 4a to 500,000 in Fig. 4b reduces Taylor dispersion effect and Vrentas [5] modified model becomes applicable over a wider range of  $\gamma^*$  values. The results in Fig. 4 clearly demonstrate the effect of Taylor dispersion on the range of applicability of Vrentas [5] modified model which is usually used when  $\beta$  is large.

### 3.1. Kurtosis effect

In the usual IGC experiment,  $\gamma$  lies in the range  $10^{-5}$ – $10^{-7}$  or in special cases could be set to the order  $10^{-8}$  (for example, nitrogen as a carrier gas with Butane as a solute). Therefore, in most practical cases in IGC, criterion Eq. (39) is met. To the best of the authors knowledge, cases of extremely low gas phase diffusivities below the practical range of IGC ( $10^{-5}$ – $10^{-7}$ ) has not been studied as such cases could be rare or do not exist. Mathematically speaking, at extremely low values of  $\gamma$  and when criterion Eq. (39) is not met, the contribution from the second term in bracket IV of Eq. (38) becomes significant. As expected from Eq. (35), extremely low diffusivities will increase the value of  $b_1$  and in turn, will reduce the value of the effective axial diffusion coefficient  $A_0$  in Eq.

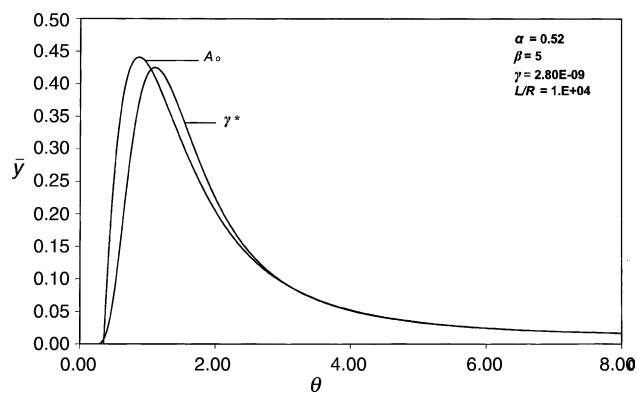


Fig. 5. Effect of Kurtosis on the elution profiles at extremely low diffusivities for  $\alpha = 0.52$ ,  $L/R = 10,000$ ,  $\gamma = 2.8e-9$  and  $\beta = 5$ .

(33). For  $\alpha = 0.52$ ,  $L/R = 10,000$ ,  $\gamma = 2.8e-9$ ,  $\beta = 5$  and with  $L^*$  being less than 1, criterion Eq. (39) is not satisfied. The two elution profiles calculated under this condition by using  $A_0$  (Eq. (33)) and  $\gamma^*$  (Eq. (42)) are shown in Fig. 5. It is clear that there is a significant error in the elution profile calculated using  $\gamma^*$  when criterion Eq. (39) is not met. This result can be explained by considering the moments of concentration distribution. Without going into details of moment analysis, it is quiet clear that the contribution of the term  $b_1 \partial^3 \bar{y} / \partial x_1^2 \partial \theta$  will only appear when considering the fourth moment ('Kurtosis'), i.e.  $(\partial / \partial \theta) \int_{-\infty}^{+\infty} x_1^n (\partial^2 \bar{y} / \partial^2 x_1) = 0$ ;  $n < 4$ ). As shown by Chatwin [11], the eventual decay of the skewness in the case of dispersion in Poiseuille pipe flow is at a rate  $t^{-1/2}$ . Therefore at large times, it is expected that the significant difference between elution curves at extremely low diffusivities is mainly attributed to kurtosis effect.

## 4. Conclusion

A general model has been developed which takes into account the effect of Taylor dispersion on pulse dispersal in a typical IGC experiment. It can be used effectively to check the validity of assuming solute dispersion to be independent of carrier gas velocity. The present model shows that near the glass temperature of polymers, Taylor dispersion has a negligible effect over a wide range of  $\gamma$ . At extremely low diffusivities and when criterion Eq. (39) is not satisfied, kurtosis effect becomes significant and the axial diffusion term given by Eq. (33) should be used. In general, for high values of  $D_p$  (low  $\beta$ ), larger  $L/R$  ratios than previously anticipated should be used to make Taylor dispersion effect negligible.

## 5. Nomenclature

- $A_0$  effective axial diffusion coefficient defined in (33)  
 $b_0$  a parameter defined in (34)

$b_1$	a parameter defined in (35)
$c$	concentration of the solute in the gas phase
$c'$	concentration of the solute in the polymer phase
$c_0$	strength of input pulse
$D$	molecular diffusion coefficient
$D_{ax}$	Taylor's effective axial diffusion coefficient
$D_g$	diffusion coefficient of the solute in the gas phase
$D_p$	diffusion coefficient of the solute in the polymer phase
$g$	a term defined in (19)
$\bar{g}$	a term defined in (23)
$J_0$	Bessel function of the zero kind
$J_1$	Bessel function of the first kind
$K$	partition coefficient
$L$	column length
$L^*$	dimensionless characteristic length defined by Taylor [8]
$N(\beta_m)$	$[= 2/J_0^2(\beta_m)]$
$Pe$	Peclet number ( $= R\bar{u}/D_g$ )
$q$	dimensionless concentration of the penetrant in polymer phase
$r$	radial co-ordinate
$R$	capillary radius
$s$	Laplace variable
$t$	time
$t_c$	residence time of the carrier gas ( $= L/\bar{u}$ )
$t'$	dummy variable of integration
$\bar{T}$	integral transform defined in Eq. (20)
$u$	dimensionless axial fluid velocity
$\bar{u}$	dimensionless mean axial velocity
$\tilde{u}$	dimensionless axial velocity fluctuation
$w$	dummy variable of integration
$x$	dimensionless axial co-ordinate
$x_1$	dimensionless axial co-ordinate moving with the mean flow velocity $\bar{u}$
$y$	dimensionless concentration of solute
$\bar{y}$	dimensionless average concentration of solute

$\tilde{y}$	dimensionless fluctuation of solute concentration
$\bar{y}^0$	Laplace transform of $\bar{y}$
$z$	axial coordinate

#### Greek symbols

$\alpha$	dimensionless group defined in Eq. (15)
$\beta$	dimensionless group defined in Eq. (7)
$\beta_m$	eigenvalues of $J_1(\beta_m) = 0$
$\delta$	dirac delta function
$\varepsilon$	dimensionless group ( $KRD_p/\tau D_g$ )
$\gamma$	dimensionless group (gas phase diffusion coefficient) defined in Eq. (7)
$\gamma^*$	effective axial diffusion coefficient defined in Eq. (42)
$\eta$	dimensionless radial group defined in Eq. (4)
$\lambda$	dimensionless variable defined in Eq. (23)
$\zeta$	dimensionless radial co-ordinate in Eq. (4)

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