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The influence of nonuniform coating and taylor dispersion on the evaluation of capillary column inverse gas chromatography

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Abstract

A mathematical model which takes into account the combined effect of Taylor dispersion and film eccentricity on the elution profiles has been developed for the analysis of a capillary column inverse gas chromatography (CCIGC) experiment. In this paper, we present an additional improvement on the model presented by Hamdan et al. [E. Hamdan, J.F. Milthorpe, J.C.S. Lai, J. Chromatogr. A, 1078 (2005) 144] to include the effect of coating nonuniformity. The new model shows that while Taylor dispersion effect has a very significant effect on the elution profiles at low values of β and γ, the general effect of film asymmetry is to reduce this effect. At sufficiently large γ and/or β values, Taylor dispersion effect becomes negligible and the elution profiles will be mainly affected by film asymmetry. The inclusion of Taylor dispersion effect will increase the variance of the elution curves which could significantly affect the estimated value of the diffusivity D_p. The error in the estimated D_p values obtained using the Pawlisch et al. [C.A. Pawlisch, J.R. Bric, R.L. Laurence, Macromolecules 21 (1988) 1685] nonuniform model increases as γ and/or β are reduced and when the coated polymer exhibits less deviation from uniform films.
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1. Introduction

Inverse gas chromatography (IGC) has been used extensively for the measurement of polymer phase diffusion coefficients in polymer–solvent systems. Information on the migration and partitioning of small molecules in various polymers is of primary interest in many practical applications: devolatilization, coating, painting, membrane separation and so forth. The principle behind IGC is based on the distribution of volatile solvent molecules between a mobile gas phase and a stationary polymeric phase. The polymer transfer resistance can have a significant effect on broadening and distortion of the chromatographic peak. This effect has been used in IGC to estimate the solubility and diffusivity in the stationary phase. The model being extensively used to analyze the response for capillary column inverse gas chromatography (CCIGC)

under conditions of uniform polymer coating and a negligible Taylor dispersion effect was presented by Pawlisch et al. [3]. However, the model presented in [3] loses its sensitivity to analyze IGC data at high β values (i.e., $\beta > 5.0$) according to Surana et al. [4]. Vrentas et al. [5] presented a modified IGC model to be used at very low polymer phase diffusion coefficients when β exceeds the upper limit of 5.0 and the sensitivity of the usual IGC model is lost [4]. The stationary phase can be made quite uniform by filling the column with a predetermined concentration of a degassed solution, and finally recovering the polymer by vacuum removal of the volatile solvents. However, the coating procedure may produce a small eccentricity as a result of deformation of the liquid/vapor meniscus by gravitational forces. Pawlisch et al. [2] observed, based on scanning electron microscopy analysis, that the coating film thickness varied only about the circumference of the column while the uniformity in the axial direction was still retained. Pawlisch et al. [2] presented improvements on their earlier model in [3] to account for nonuniform polymer

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film thickness (eccentricity). It was found that when the film exhibits more deviations, this will increase the variance of the elution curve and the distribution skewed more sharply. In this case, the nonuniform model will capture the distortion of the elution profile rather well, Pawlisch et al. [2] and Romdhane et al. [6]. Using the uniform version of CCIGC for a nonuniform coating will result in underestimated D_p values. Despite this finding, most researchers in the field of IGC have used the model proposed by Pawlisch et al. [3] by assuming a negligible Taylor dispersion effect and the coating to be very uniform. To overcome the problem of nonuniform coating, Huang et al. [7] proposed using a rectantangular thin channel column for inverse gas chromatography. The column consists of two plates and a thin flat membrane which forms the stationary phase is sandwiched by the two plates. The preparation of the thin membrane is expected to produce a very uniform coating and the simple geometry allows for repeated use of the column. In previous models [2,3,7], Taylor dispersion effect was neglected in the analysis. The problem of solute dispersion in a capillary tube was first studied by Taylor [8]. 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 whole system co-ordinate moving with a velocity equal 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 $D_{ax} = R^2 \bar{u}^2/48D$. Later on, Aris [9] 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 the molecular diffusion coefficient D and the Taylor's effective axial diffusion coefficient (i.e., $D + R^2\bar{u}^2/48D$). Therefore, the usual IGC models [2,3,7] assumption that the gas-phase axial dispersion is independent of flow velocity is highly questionable. Hamdan et al. [1] introduced improvements to the uniform model of Pawlisch et al. [3] by including Taylor dispersion effect which was found to have a significant effect on the elution profiles at low values of γ and β.

The purpose of this work is to expand the model presented by Hamdan et al. [1] to include the effect of the polymer coating nonuniformity on the elution profiles. This model will be more general than the one presented in [1,2] and allows researchers to investigate the combined effect of film nonuniformity and Taylor dispersion on the theoretical profiles used to analyze experimental IGC data. The model could also be used to assess the validity of assuming a negligible Taylor dispersion effect, as previously done by Pawlisch et al. [2], when the coated film exhibits eccentricity.

2. Capillary column model for nonuniform coating

With the exception of including Taylor dispersion effect, the main assumptions and the transport equations for IGC are the same as those used in the early study of Pawlisch et al. [2]. 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 Pawlisch et al. [2] as

$$
\begin{array}{ll}
c' = c' = 0 & t = 0 \\
\dfrac{\partial c'}{\partial r} = 0 & r = R + \tau(\phi) \\
c(r, z, t) = \delta(t)c_0 & z = 0 \\
c(r, z, t) = \dfrac{c'(r, z, t)}{K} & r = R \\
D_g\dfrac{\partial c}{\partial r} = D_p\dfrac{\partial c'}{\partial r} & r = R \\
\dfrac{\partial c}{\partial r} = 0 & r = 0
\end{array}
\quad (3)
$$

The film thickness depends only on the azimuthal angle ϕ (cf. Fig. 1). The following non-dimensional variables [2] are introduced.

$$y = \frac{cL}{c_0\bar{u}}, \quad x = \frac{z}{L}, \quad \eta = \frac{r - R}{\tau_m}, \quad \theta = \frac{\bar{u}t}{L},$$

$$q = \frac{c'L}{c_0K\bar{u}}, \quad \zeta = \frac{r}{R}, \quad W(\phi) = \frac{\tau(\phi)}{\tau_m} \quad (4)$$

where τ_m is the mean of $\tau(\phi)$, and $W(\phi)$ is the dimensionless film thickness. Following Pawlisch et al. [2], the choice of
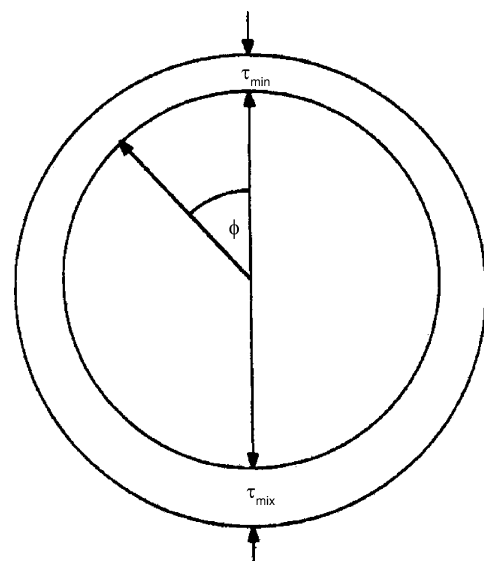

Fig. 1. Cross sectional view of a nonuniform film.

film distribution was based on examination of column samples and $W(\phi)$ in the simplest kind of nonuniform coating is represented as

$$W(\phi) = a + b|\phi| \tag{5}$$

$$Q = \frac{\tau_{min}}{\tau_{max}}, \quad a = \frac{2Q}{1+Q}, \quad b = \frac{2(1-Q)}{\pi(1+Q)} \tag{6}$$

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

$$\frac{\partial y}{\partial \theta} + u(\zeta)\frac{\partial y}{\partial x} = \gamma \frac{\partial^2 y}{\partial x^2} + \gamma \left(\frac{L}{R}\right)^2 \left[\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\left(\zeta \frac{\partial y}{\partial \zeta}\right)\right] \tag{7}$$

$$\frac{\partial q}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial^2 q}{\partial \eta^2} \tag{8}$$

where

$$\gamma = \frac{D_g}{\bar{u}L}, \beta^2 = \frac{\bar{u}\tau^2}{LD_p} \tag{9}$$

$$u(\zeta) = 2(1 - \zeta^2) \tag{10}$$

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

$$
\begin{aligned}
y &= \delta(\theta) & x &= 0 \\
y &= q & \eta &= 0 \\
\left(\frac{\partial y}{\partial \zeta}\right)_{\zeta=1} &= \varepsilon\left(\frac{\partial q}{\partial \eta}\right)_{\eta=0} & & \\
q &= y = 0 & \theta &= 0, \, x > 0 \\
\frac{\partial q}{\partial \eta} &= 0 & \eta &= W(\phi) \\
\frac{\partial y}{\partial \zeta} &= 0 & \zeta &= 0
\end{aligned}
\tag{11}
$$

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 ($\tilde{y}$ and $\tilde{u}$) from the area averages as

$$y = \bar{y} + \tilde{y} \tag{12}$$

$$u = \bar{u} + \tilde{u} \tag{13}$$

Substituting Eq. (12) into Eq. (7) gives

$$\frac{\partial \bar{y}}{\partial \theta} + \frac{\partial \tilde{y}}{\partial \theta} + u\frac{\partial \bar{y}}{\partial x} + u\frac{\partial \tilde{y}}{\partial x} = \gamma\left(\frac{\partial^2 \bar{y}}{\partial x^2} + \frac{\partial^2 \tilde{y}}{\partial x^2}\right) + \gamma\left(\frac{L}{R}\right)^2\left[\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\left(\zeta\frac{\partial \tilde{y}}{\partial \zeta}\right)\right] \tag{14}$$

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. (14) and making use of the boundary conditions in Eq. (10) and the property of spatial averaged fluctuations

$$\bar{\bar{y}} = \bar{\tilde{u}} = 0 \tag{15}$$

yields

$$\frac{\partial \bar{y}}{\partial \theta} + \bar{u}\frac{\partial \bar{y}}{\partial x} = \gamma\frac{\partial^2 \bar{y}}{\partial x^2} - \frac{\partial}{\partial x}\overline{(\tilde{u}\tilde{y})} + \frac{2}{\alpha\beta^2}\frac{\partial q(0)}{\partial \eta} \tag{16}$$

where

$$\alpha = \frac{R}{K\tau} \tag{17}$$

The new quantity $\overline{(\tilde{u}\tilde{y})}$ is the additional contribution to dispersion caused by the 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 [2,3] due to the radial uniformity assumption in the concentration profile. Hamdan et al. [1] obtained an expression for $\tilde{y}$ in terms of $\bar{y}$ and evaluated $\overline{(\tilde{u}\tilde{y})}$. The final mean solute concentration equation becomes

$$
\begin{aligned}
&\frac{\partial \bar{y}}{\partial \theta} - \left(\sum_{m=1}^{\infty}\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1-e^{-\lambda\theta}}{\lambda}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^2 \bar{y}}{\partial x_1^2} \\
&+ \left(\sum_{m=1}^{\infty}\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1-(1+\lambda\theta)e^{-\lambda\theta}}{\lambda^2}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^3 \bar{y}}{\partial x_1^2 \partial\theta} \\
&- \left(\sum_{m=1}^{\infty}\gamma\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1-(1+\lambda\theta)e^{-\lambda\theta}}{\lambda^2}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^4 \bar{y}}{\partial x_1^4} = \gamma\frac{\partial^2 \bar{y}}{\partial x_1^2} + \frac{2}{\alpha\beta^2}\frac{\partial q(0)}{\partial \eta}
\end{aligned}
\tag{18}
$$

For large time analysis, Eq. (18) reduces to

$$
\begin{aligned}
&\frac{\partial \bar{y}}{\partial \theta} - \left(\sum_{m=1}^{\infty}\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1}{\lambda}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^2 \bar{y}}{\partial x_1^2} + \left(\sum_{m=1}^{\infty}\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1}{\lambda^2}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^3 \bar{y}}{\partial x_1^2 \partial\theta} \\
&- \left(\sum_{m=1}^{\infty}\gamma\frac{\overline{\tilde{u}J_0(\beta_m,\zeta)}}{N(\beta_m)}\left(\frac{1}{\lambda^2}\right)\int_0^1 \zeta J_0(\beta_m,\zeta)\tilde{u}\,d\zeta\right)\frac{\partial^4 \bar{y}}{\partial x_1^4} = \gamma\frac{\partial^2 \bar{y}}{\partial x_1^2} + \frac{2}{\alpha\beta^2}\frac{\partial q(0)}{\partial \eta}
\end{aligned}
\tag{19}
$$

Taking the Laplace transform of Eq. (19) and neglecting the fourth term [1], Eq. (19) with the conditions in Eq. (3), may be solved in terms of a fixed co-ordinate system to obtain [2]

$$\bar{y}^0 = \exp\left(\frac{1}{2A_0}\right)\exp\left[-\left(\frac{1}{2A_0}\right)(1 + 4A_0 G(s))^{1/2}\right] \quad (20)$$

where

$$G(s) = s + \left(\frac{2}{\alpha\beta^2\pi b}\right)\log\left[\frac{\cosh[\beta s^{1/2}(a + b\pi)]}{\cosh[\beta s^{1/2}a]}\right] \quad (21)$$

and

$$A_0 = b_0 - b_1 s + \gamma \quad (22)$$

where

$$b_0 = \frac{1}{48\gamma(L/R)^2} \quad (23)$$

and

$$b_1 = \frac{1}{720\gamma^2(L/R)^4} \quad (24)$$

In most practical cases, the third term in Eq. (19) also could be neglected [1]. In this case, Eq. (19) can be reduced to

$$\frac{\partial\bar{y}}{\partial\theta} + \frac{\partial\bar{y}}{\partial x} - \gamma^*\frac{\partial^2\bar{y}}{\partial x^2} = \frac{2}{\alpha\beta^2}\frac{\partial q(0)}{\partial\eta} \quad (25)$$

where

$$\gamma^* = b_0 + \gamma \quad (26)$$

is the effective axial diffusion coefficient in the gas phase.

One can notice that the resulting Eq. (25) contains the Taylor dispersion term, b_0, which is made negligible in the nonuniform model presented by Pawlisch et al. [2]. As shown in [2], the analytic expression for the mean and variance of the elution curve for the nonuniform model and when Taylor dispersion effect is neglected, can be presented as

$$\mu_{1(nu)} = \left(1 + \frac{2}{\alpha}\right)t_c \quad (27)$$

$$\mu_{2(nu)} = \left(\frac{4\beta^2}{3\alpha}\frac{2(1 + Q^2)}{(1 + Q)^2} + 2\gamma\left(1 + \frac{2}{\alpha}\right)^2\right)t_c^2 \quad (28)$$

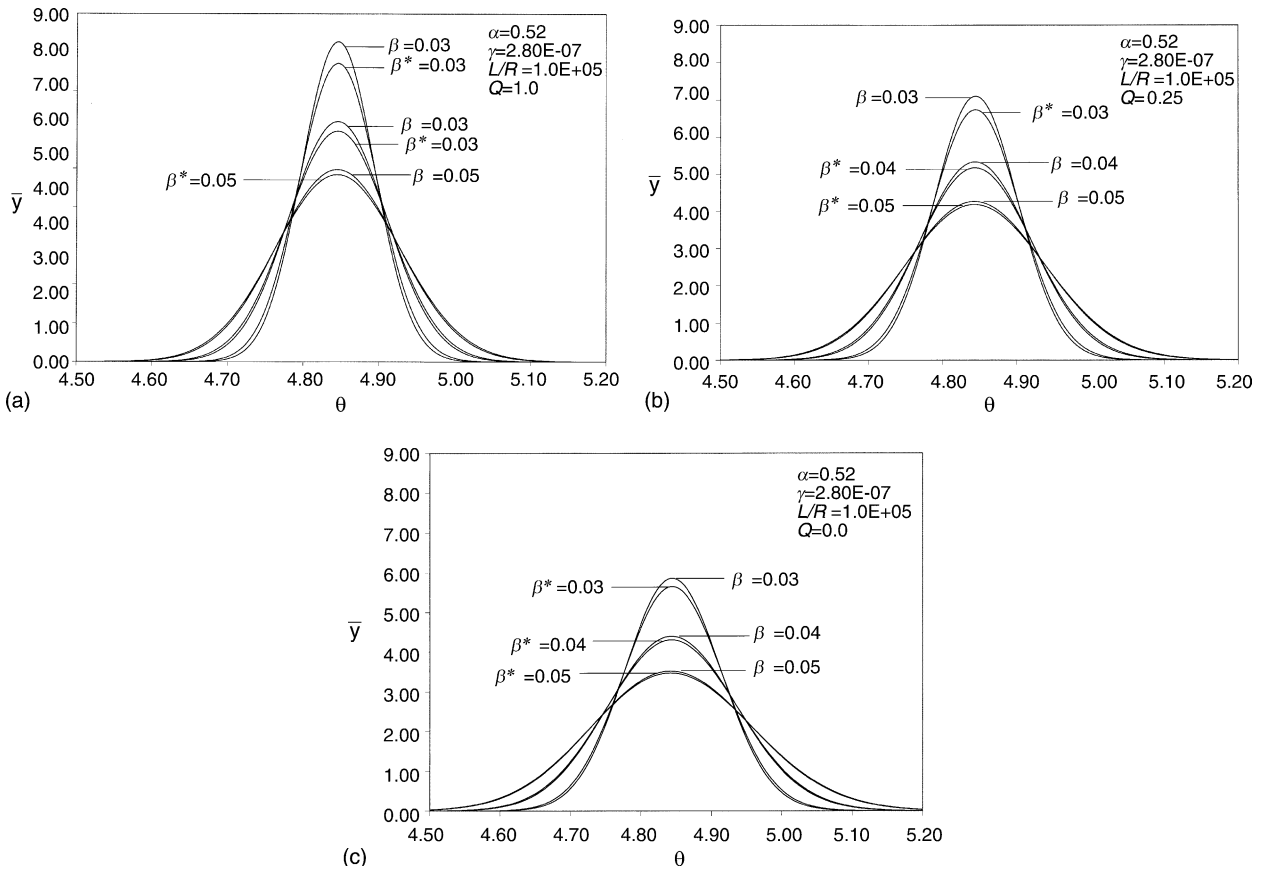Fig. 2. Comparison of the elution profiles of the present (*) and Pawlisch [2] nonuniform models for $\alpha = 0.52$; $L/R = 100{,}000$; $\gamma = 2.8e-7$ and various β values as Q is reduced: (a) $Q = 1.0$; (b) $Q = 0.25$; (c) $Q = 0.0$.

and using the present model, the variance is expressed as

$$\mu_{2(\text{nu})}^* = \left(\frac{4\beta^2}{3\alpha} \frac{2(1+Q^2)}{(1+Q)^2} + 2\gamma^* \left(1 + \frac{2}{\alpha}\right)^2 \right) t_c^2 \quad (29)$$

where μ_2^* is the variance of the elution profiles obtained when Taylor dispersion effect is taken into account. Using Eq. (29), Pawlisch et al. [2] have developed a relationship between the variances of the elution curves obtained using the unifom [3] and nonuniform [2] models. Neglecting Taylor dispersion effect and after simplification, the relation is expressed as

$$\mu_{2(\text{u})} = \mu_{2(\text{nu})} \frac{(1+Q)^2}{2(1+Q^2)} \quad (30)$$

When Taylor dispersion effect is considered, the relation between the variances of the elution curves obtained using the unifom [1] and the present nonuniform models can be expressed as

$$\mu_{2(\text{u})}^*$$
$$= \mu_{2(\text{nu})}^* \left[\frac{(4\beta^2/3\alpha) + 2\gamma^*(1+(2/\alpha))^2}{(4\beta^2/3\alpha)(2(1+Q^2)/(1+Q)^2) + 2\gamma^*(1+(2/\alpha))^2} \right] \quad (31)$$

Comparing the variances of the elution profiles using the present and Pawlisch et al. [2] nonuniform models give an indication to t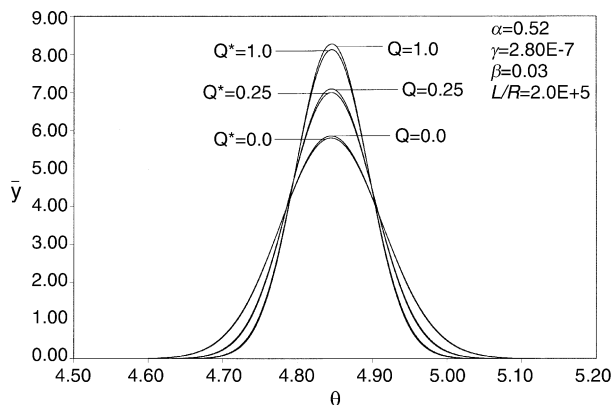he error expected in the estimated diffusivity value D_p when neglecting Taylor dispersion effect. The relation between the two models (present and Pawlisch et al. [2]) variances can be expressed as

$$\mu_{2(\text{nu})}$$
$$= \mu_{2(\text{nu})}^* \left[\frac{(4\beta^2/3\alpha)(2(1+Q^2)/(1+Q)^2) + 2\gamma(1+(2/\alpha))^2}{(4\beta^2/3\alpha)(2(1+Q^2)/(1+Q)^2) + 2\gamma^*(1+(2/\alpha))^2} \right] \quad (32)$$

Fig. 4. Comparison of the elution profiles of the present (*) and Pawlisch [2] nonuniform models for $\alpha = 0.52$; $\beta = 0.03$; $L/R = 200,000$; $\gamma = 2.8\text{e}-7$ and various Q values.
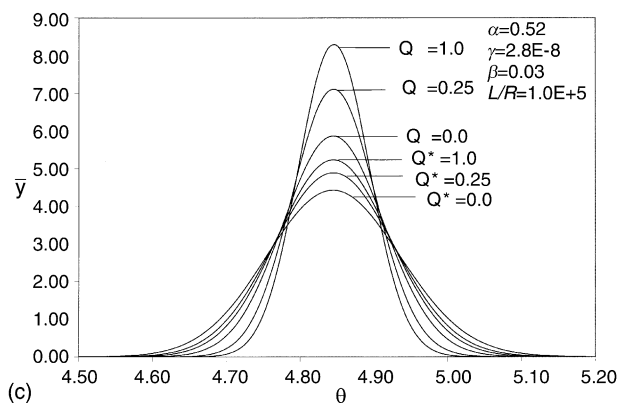

Fig. 3. Comparison of the elution profiles of the present (*) and Pawlisch [2] nonuniform models for $\alpha = 0.52$, $\beta = 0.03$, $L/R = 100,000$ and various Q values: (a) $\gamma = 2.8\text{e}-6$; (b) $\gamma = 2.8\text{e}-7$; (c) $\gamma = 2.8\text{e}-8$.
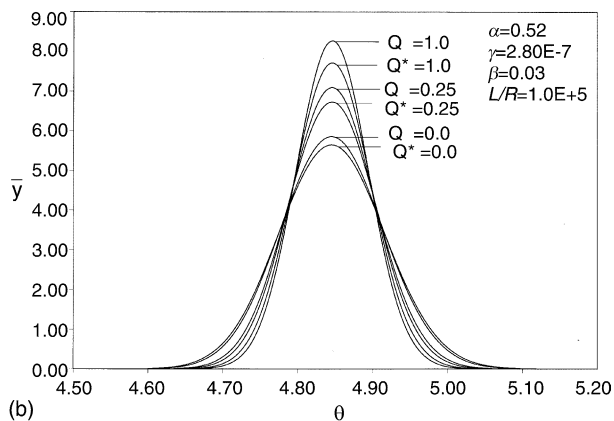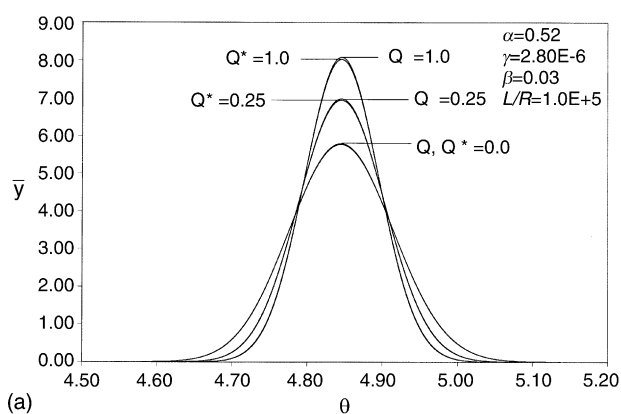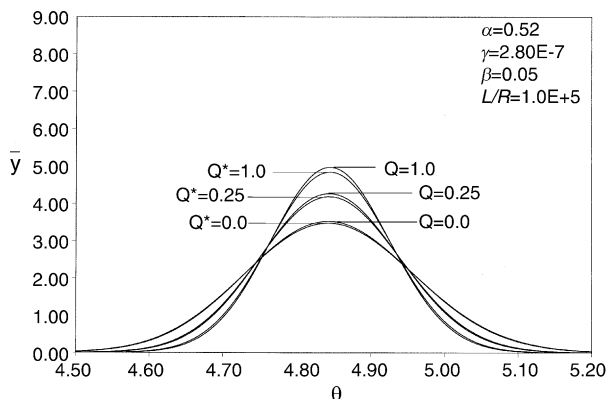
Fig. 5. Comparison of the elution profiles of the present (*) and Pawlisch [2] nonuniform models for $\alpha = 0.52$; $\beta = 0.05$; $L/R = 100{,}000$; $\gamma = 2.8\mathrm{e}-7$ and various values of Q.

3. Results and discussion

The results presented in this study are the solutions of Eq. (20) using the effective axial dispersion coefficient in Eq. (26) and with the same values of α (0.52), β (0.01–10) and γ (2.8e−5, 2.8e−6, 2.8e−7 and 2.8e−8) used by Hamdan et al. [1] while the film changes from uniform ($Q = 1.0$) to nonuniform (i.e., $Q < 1.0$). For uniform polymer coating ($Q = 1.0$) and when γ is sufficiently small, Taylor dispersion

effect becomes significant over a wide range of low β values (0.03–0.05) as shown in Fig. 2a. Fig. 2a–c show the effect of asymmetry on Taylor dispersion. The general effect of film asymmetry is to reduce Taylor dispersion (see, $\beta = 0.03$, $Q = 0.25$ in Fig. 2b and $\beta = 0.03$, $Q = 0.0$ in Fig. 2c) and this effect becomes less pronounced when β is assinged larger values. Increasing β means increasing the solute residence time and therefore, Taylor dispersion effect becomes less significant. The effect of γ and film asymmetry on the elution profiles is shown in Fig. 3a–c for $\gamma = 2.8\mathrm{e}-6$, 2.8e−7 and 2.8e−8, respectively. For all values of γ, the results show that when the film asymmetry increases, Taylor dispersion reduces and so the variance of the elution curve. Fig. 3a–c also show that reducing γ (i.e., from $\gamma = 2.8\mathrm{e}-6$ to 2.8e−7 and 2.8e−8) increases significantly Taylor dispersion effect on solute dispersal and its effect becomes more pronounced when the polymer film exhibits less deviations from uniform coating (i.e., Q increases from 0.0 to 1.0). Therefore, the difference between the elution profiles obtained using the present model and those obtained using Pawlisch et al. [2] nonuniform model is expected to increase with decreasing γ, β and film asymmetry. It is worth noting that for films exhibiting eccentricity and when γ and/or β are sufficiently large (negligible Taylor dispersion effect), the elution profiles will be mainly affected by film asymmetry as shown in Fig. 3a. The influence of varying L/R ratio on Taylor dispersion and
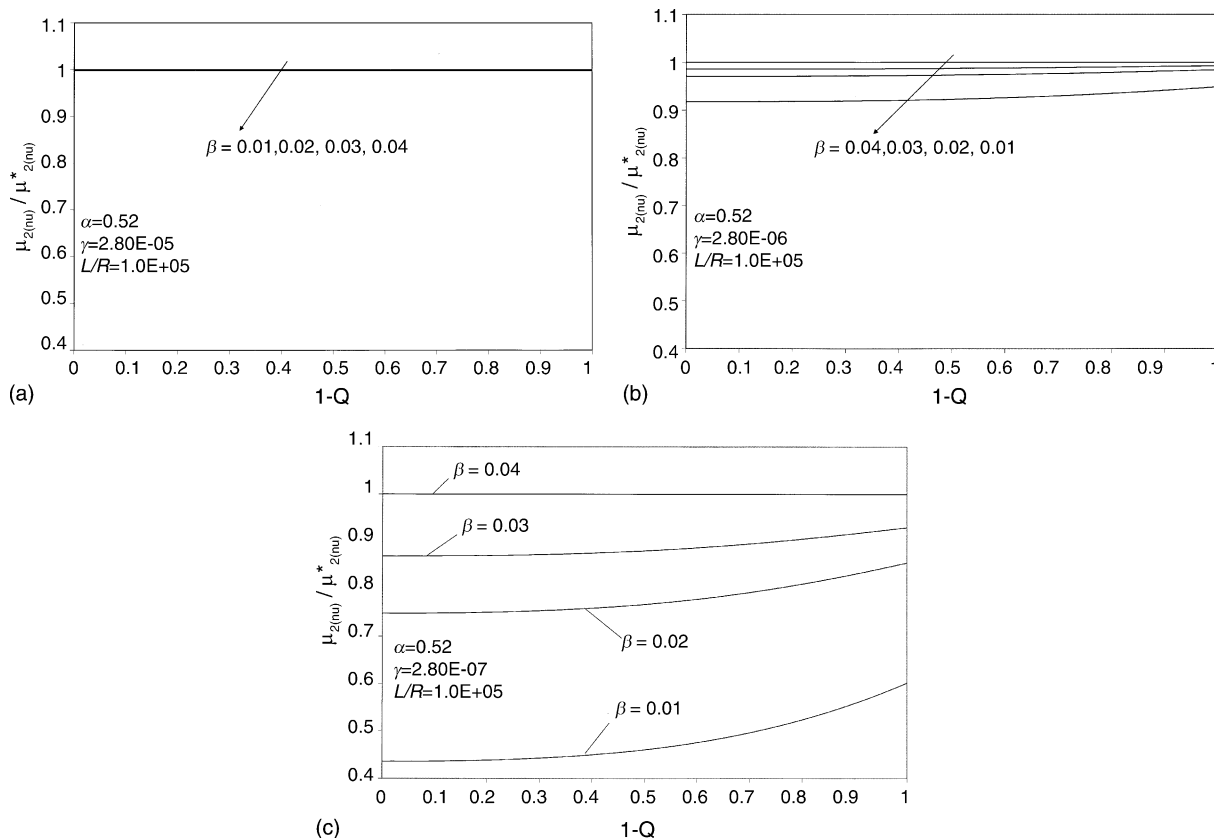

Fig. 6. The error in the estimated D_p value using Pawlisch [2] nonuniform model with a negligible Taylor dispersion effect. Error curves obtained for $\alpha = 0.52$; $L/R = 100{,}000$; $\beta = 0.01$, 0.02, 0.03, 0.04 and Q decreases from 1.0 to 0.0: (a) $\gamma = 2.8\mathrm{e}-6$; (b) $\gamma = 2.8\mathrm{e}-7$; (c) $\gamma = 2.8\mathrm{e}-8$.

the resulting elution profiles can be seen by comparing Fig. 3b for $L/R = 100,000$ and Fig. 4 for $L/R = 200,000$ at various values of Q. It is quite clear that increasing L/R ratio reduces Taylor dispersion effect and the elution profiles obtained by the present model approach those obtained using Pawlisch et al. [2] nonuniform model. Figs. 3b and 5 show that assigning higher values for β (i.e., increasing the solute residence time in the stationary phase) reduces Taylor dispersion effect and inturn, the present model solution approaches those obtained by Pawlisch et al. [2]. The relationship presented by Pawlisch et al. [2] between the estimated diffusivity value D_p using the unifom model in [3] and that obtained using the nonuniform model in [2] (Eq. (30)) is only a function of film nonuniformity Q and is insensitive to γ and β. Pawlisch et al. [2] argued that the second term of Eq. (28) is always small when compared to the first term and therefore, can be neglected. However, the variance of the elution profile obtained using the present model (Eq. (28)), increases as γ is reduced. This is because the Taylor dispersion term, b_0, is inversely proportional to γ and therefore, a significant error will result in the estimated D_p value when γ is sufficiently small and the second term in Eq. (28) is neglected. This error is expected to be less when γ and/or β is assigned larger values. Fig. 6a–c are the plots of Eq. (32) which show the error that results from using Pawlisch et al. [2] nonuniform model to estimate D_p. When γ is sufficiently large (i.e., $\gamma = 2.8e-5$ in Fig. 6a), Taylor dispersion effect bcomes very small and has a neglegible effect on the elution profiles. In this case, using Pawlisch et al. [2] nonuniform model will not lead to a significant error in the estimated value of D_p. As γ decreases to $2.8e-6$ in Fig. 6b and to $2.8e-7$ in Fig. 6c, Taylor dispersion effect becomes more pronounced and the estimated value of the diffusivity D_p using Pawlisch et al. [2] nonuniform model will be lower than that obtained using the present model. It is apparent from Fig. 6a–c, that the error in the estimated D_p value increases as γ and β are reduced and reaches its maximum when the film is nearly uniform ($Q = 1.0$). The error could be quite large reaching up to 60% (Fig. 6c) and is expected to increase as γ and/or β is reduced further. As the film eccentricity increases, Taylor dispersion effect becomes less and the present model solutions approaches more Pawlisch et al. [2] nonuniform model solution. However, the effect of reducing γ and β on Taylor dispersion is more significant than the deviations in the polymer film and causes the major error in the estimated D_p value when using Pawlisch et al. [2] nonuniform model.

4. Conclusion

A general model has been developed which takes into account the combined effect of Taylor dispersion and film asymmetry on the elution profiles used to analyze experimental IGC data. The model should be used specially at low γ and β values where Taylor dispersion effect has a very significant effect on the elution profiles. The model clearly shows that while reducing γ, β and L/R have a major impact on increas-

ing the effect of Taylor dispersion, the general effect of film asymmetry is to reduce it. As long as γ and β are sufficiently large, the effect of film asymetry on Taylor dispersion is negligible and using Pawlisch et al. [2] nonuniform model will not result in a significant error in the estimated D_p values. The effect of film asymmetry on Taylor dispersion becomes more pronounce at low γ and β values and in this case, the present model should be used for IGC data analysis.

5. Nomenclature

A_0	effective axial diffusion coefficient defined in Eq. (22)
b_0	a parameter defined in Eq. (23)
b_1	a parameter defined in Eq. (24)
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
J_0	Bessel function of the zero kind
J_1	Bessel function of the first kind
K	partition coefficient
L	column length
$N(\beta_m)$	$[= 2/J_0^2(\beta_m)]$
q	dimensionless concentration of the penetrant in polymer phase
Q	film nonuniformity parameter defined in Eq. (6)
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
u	dimensionless axial fluid velocity
$\bar{u}$	dimensionless mean axial velocity
$\tilde{u}$	dimensionless axial velocity fluctuation
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

α	dimensionless group defined in Eq. (17)
β	dimensionless group defined in Eq. (9)
β_m	eigenvalues of $J_1(\beta_m) = 0$
δ	dirac delta function
ε	dimensionless group ($KRD_p/\tau D_g$)

γ^{*} effective axial diffusion coefficient defined in Eq. (26)

γ dimensionless group (gas phase θ dimensionless time

η dimensionless radial group defined in Eq. (4)

$\mu_{2(u)}$ the variance of the elution profile obtained using the uniform model in [3]

$\mu_{2(nu)}$ the variance of the elution profile obtained using the nonuniform model in [2]

$\mu_{2(u)}^{*}$ the variance of the elution profile obtained using the uniform model in [1]

$\mu_{2(nu)}^{*}$ the variance of the elution profile obtained using the present nonuniform model

τ polymer film thickness diffusion coefficient) defined in Eq. (9)

ζ dimensionless radial co-ordinate in Eq. (4).

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