Effect of Nonlinear Equilibrium on Zero Length Column Experiments in Mesoporous or Macroporous Sorbents: Limiting Analytical Asymptotic Forms

by

Kevin F. Loughlin

Department of Chemical Engineering

King Fahd University of Petroleum & Minerals

Dhahran-31261, Saudi Arabia.

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* to whom all correspondence should be addressed

Department of Chemical Engineering

KFUPM, Dhahran-31261

Saudi Arabia

EMAIL: loughkf@dpc.kfupm.edu.sa

FAX: (966) (3) 860-4234

ABSTRACT

Brandani has derived a solution for nonlinear equilibrium on a homogeneous surface using the Langmuir isotherm for micropore controlled particles. In this paper a family of solutions for heterogeneous surfaces is derived using the Toth isotherm which has a heterogeneity parameter t in it. The solution of Brandani when t = 1 is a particular member of the family of solutions

The project novelty is the extension of the literature work of Brandani which covered homogeneous surfaces to all surfaces which basically are heterogeneous in nature. Brandani showed that ZLC experiments for homogeneous surfaces provide satisfactory diffusivities in the long time region of the experiment but that the equilibrium parameters are difficult to determine accurately. In this paper, in determining both the diffusivity and equilibrium parameters for heterogeneous surfaces due caution should be observed. In fact for the heterogeneity parameter t less than 0.5, it is very difficult to determine either diffusivity or equilibrium parameters just using the long time region of the experimental curve.

KEYWORDS: nonlinear equilibrium, zero length column, mesopore, macropore

INTRODUCTION

The zero length column (ZLC) was introduced to measure the intracrystalline diffusivity, by Eic and Ruthven in 1988. Since that time, over 127 papers have been published on the technique, and a review was published in 2000 by Ruthven and Brandani. The technique has been applied to the diffusion of gases in microporous [Ruthven and Eic 1989, Ruthven and Xu 1993, Hufton and Ruthven 1993, Jiang and Eic 2003, Grande et al 2002], mesoporous [Cavalcante et al 2003, Thang et al 2003, Qiao and Bhatia 2005] and macroporous materials [Ruthven and Brandani 2000, Brandani 1996a,1996b, Silva and Rodrigues 1996, Silva et al 1999, Silva and Rodrigues 1996, Jiang and Eic 2003, Da Silva et al 1999, Grande et al 2002]. The method has been extended to include self-diffusion [Hufton et al 1994, Brandani and Ruthven 1996d, Brandani et al. 1995a, 1995b.], counter-diffusion [Jiang and Eic 2003, Brandani, et al. 2000], equilibrium studies [Brandani et al. 2003, Brandani and Ruthven 2003] and diffusion in liquids [Brandani and Ruthven 1995]. Diffusivities have been extracted from the short time solution [Brandani and Ruthven 1996c, Hufton and Ruthven 1993, Han et al 1999], intermediate time solution [Hufton et al. (1994)], long time solution [Eic and Ruthven 1987, Hufton and Ruthven 1993, Han et al. 1999] and using the full time solution of the desorption curve. The primary emphasis has been on extracting the diffusivity and equilibrium constants using the slope and intercept of the long time region of the desorption curve [Brandani and Ruthven 1996c]. The method was originally developed for the linear equilibrium region [Eic. and Ruthven1988] but has been expanded to the nonlinear region [Brandani 1998a, 1998b]. Criteria have been developed for apparatus limitations [Karger and Ruthven 1992], purge gas flow rate [Brandani and Ruthven 1996d], equilibrium control [Ruthven and Brandani 1996c], fluid phase holdup [Brandani and Ruthven 1996c, Brandani and Ruthven 1995], external mass transfer [Ruthven and Eic (1989)], surface resistance control [Brandani and Ruthven 1996e, Ruthven and Brandani 2005], equilibration time [Ruthven and Eic (1989)], particle size distribution [Duncan and Moeller 2002] and heat effects [Brandani et al (1998)].

This manuscript is concerned with non-linear equilibrium effects in ZLC analysis. Brandani in 1998 examined this topic in detail for non-linear Langmuir desorption for microporous systems. His basic conclusion was that the long time analysis produced little error in determining the diffusivity results similar to the linear case but that larger errors could arise in the equilibrium constant determination. This analysis is extended to macroporous/mesoporous systems involving a heterogeneous adsorption isotherm.

THEORETICAL MODEL

The cell mass balance for a desorption experiment is given by

$$V_P(1-\varepsilon)\frac{d\bar{q}}{dt}+Fc=0 \tag{1}$$

where V_P is the volume of the pellet, ε is the pellet voidage, $\bar{q}$ is the average concentration inside the particles and c is the composition in the fluid phase. For the solid phase mass balance, assuming spherical particles with a constant pore diffusivity

$$\varepsilon\frac{\partial c_P}{\partial t}+(1-\varepsilon)\frac{\partial q}{\partial t}=-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2N\right) \tag{2}$$

where

$$N=-\varepsilon D_P\frac{\partial c_P}{\partial r} \tag{3}$$

where D_P is the pore diffusivity.
A general nonlinear isotherm equation is

$$q=f(c) \tag{4}$$

Since

$$\frac{\partial q}{\partial r}=f'(c)\frac{\partial c_P}{\partial r} \tag{5}$$

the molar flux may be expressed in terms of the adsorbate loading as

$$N=-\frac{\varepsilon D_P}{f'(c)}\frac{\partial q}{\partial r} \tag{6}$$

Assuming for a gas that term $\partial c_P/\partial t << \partial q/\partial t$, and incorporating Equation 6 for the flux expression, Equation 2 may be rewritten as

$$\frac{\partial q}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\varepsilon}{(1-\varepsilon)}\frac{D_P}{f'(c)}\frac{\partial q}{\partial r}\right) \tag{7}$$

Also, from an overall mass balance on the solid the following relationship holds

$$\frac{d\bar{q}}{dt}=\frac{.3}{R}\left(\frac{\varepsilon}{(1-\varepsilon)}\frac{D_P}{f'(c)}\frac{\partial q}{\partial r}\right)_{r=R} \tag{8}$$

To evaluate $f'(c)$ the type of isotherms need to be selected. The isotherms selected are the Langmuir isotherm representing a homogeneous surface and the Toth isotherm representing a heterogeneous surface. The parameters of the isotherms are presented in Table 1. The following argument is derived based on the Toth isotherm; the Langmuir results may simply be found by setting n = 1 in the Toth formulation.

Table 1 Isotherm Forms

Type	*Name*	*Isotherm*	$f'(c)$	$f'(c)$ *Normalized*
1	Langmuir	$\frac{q}{q_s}=\frac{bc}{1+bc}$	$bq_s\left[1-\frac{q}{q_s}\right]^2$	$K(1-\lambda Q)^2$

2	Toth	$\dfrac{q}{q_S} = \dfrac{c}{\left[b + c^n\right]^{1/n}}$	$q_s b^{-1/n}\left[1 - \left(\dfrac{q}{q_s}\right)^n\right]^{n+1/n}$	$K\left[1 - (\lambda Q)^n\right]^{1/n}$
$Q = q/q_o; \quad \lambda = q_o/q_s; \quad K = bq_s\ (Langmuir) = b^{-1/n} q_s\ (Toth)$				

Defining the following dimensionless variables:

$$Q = \frac{q}{q_\infty}; \quad C = \frac{c}{c_o}; \quad \tau = \frac{\varepsilon}{(1-\varepsilon)}\frac{D_P t}{KR^2} = \frac{D_{eff} t}{R^2}; \quad \eta = \frac{r}{R} \tag{9}$$

and dimensionless parameters

$$L = \frac{1}{3}\frac{(1-\varepsilon)}{\varepsilon}\frac{FR^2 K}{V_S K D_P} = \frac{1}{3}\frac{FR^2}{VKD_{eff}}; \quad \lambda = \frac{q_o}{q_s} \tag{10}$$

where the Henry constant K is defined in Table 1.

Note that the effective diffusivity in this formulation is defined as

$$D_{eff} = \frac{\varepsilon D_P}{(1-\varepsilon)K} \tag{11}$$

whereas for the linear adsorption case, the analogous equation is [ ]

$$D_{eff} = \frac{\varepsilon D_P}{\varepsilon + (1-\varepsilon)K} \tag{12}$$

For high values of K, these two equations are intrinsically similar giving identical effective diffusivity values. Also Equation 10 for the parameter L can be written canceling the K values as follows

$$L = \frac{1}{3}\frac{FR^2}{V_S \varepsilon D_P} \tag{13}$$

This is quite easy to evaluate for a given flowrate F and D_P for a mesoporous or macroporous sorbent.

The normalized equations are

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left[\frac{\eta^2}{\left(1 - \langle \lambda Q \rangle^n\right)^{n+1/n}}\frac{\partial Q}{\partial \eta}\right] \tag{14}$$

$$Q(1,\tau) = \frac{C}{\left[1 - \lambda^n + (\lambda C)^n\right]^{1/n}} \tag{15}$$

$$\left(\frac{\partial Q}{\partial \eta}\right)_{\eta=0} = 0 \tag{16}$$

$$\left(1 - \lambda^n + (\lambda C)^n\right)^{1/n}\left.\frac{\partial Q}{\partial \eta}\right|_{\eta=1} + LC = 0 \tag{17}$$

In the limit of infinite dilution $(\lambda = 0)$, the proposed model becomes linear and an analytical solution is available (Crank, 1975)

$$C = \sum_{n=1}^{\infty}\frac{2L\exp\left(-\beta_n^2 \tau\right)}{\beta_n^2 + L(L-1))} \tag{18}$$

with the eigenvalues for the system given by

$$\beta_n Cot\beta_n + L - 1 = 0 \tag{19}$$

This solution has a linear asymptote in the long time (LT) region

$$\ln C = \ln\left(\frac{2L}{\beta_1^2 + L(L-1)}\right) - \beta_1^2\tau \qquad (20)$$

For the case of L small, $\beta_1^2 \approx 3L$ and Equation 20 further reduces to

$$\ln C \approx \ln\left(\frac{2}{2+L}\right) - 3L\tau \qquad (21)$$

For the case of L large, [L $\geq$ 20], Equation 20 reduces to

$$\ln C \approx \ln\left(\frac{2}{L}\right) - \beta_1^2\tau \qquad (22)$$

providing a rapid means of estimating the intercept in the LT region.

Following the argument of Brandani (1998), and Brandani and Ruthven (1997), the L parameter can be viewed as the ratio of two time constants or as the initial dimensionless flux at the surface of the solid at time zero. This is true also for the nonlinear case, since at time zero $C = 1$ and from Equation 17

$$\left.\frac{\partial Q}{\partial \eta}\right|_{\eta=1} = -L \qquad (23)$$

Therefore when the L parameter is small the dimensionless concentration profile inside the particle is independent of position and essentially flat. Under these conditions the system is in the equilibrium control range, and the column mass balance may be rewritten as

$$\frac{1}{3}\frac{d\overline{Q}}{dL\tau} + \frac{C}{\left(1-\lambda^n\right)^{1/n}} = 0 \qquad (24)$$

For the Toth isotherm

$$\overline{Q} = \frac{C}{\left(1-\lambda^n + [\lambda C]^n\right)^{1/n}} \qquad (25)$$

Substituting into Equation 22 gives

$$-3dL\tau = \frac{dC}{C\left[1+\left(\frac{\lambda^n}{1-\lambda^n}\right)C^n\right]^{\frac{n+1}{n}}} \qquad (26)$$

Solution of Equation 26 for $\left(\frac{n+1}{n}\right)$ integer {i.e., $n = 1/2, 1/3, 1/4\ etc$) is

$$3L\tau = \frac{1}{n}\left\langle \sum_{m=1}^{\frac{1}{n}}\frac{1}{m}\left(1-\lambda^n\right)^m - \ln\left[\frac{C^n}{1-\lambda^n+(\lambda C)^n}\right] - \sum_{m=1}^{\frac{1}{n}}\frac{1}{m}\left[\frac{1-\lambda^n}{1-\lambda^n+(\lambda C)^n}\right]^m \right\rangle \qquad (27)$$

For the long time region this expression may be reduced to a linear asymptote in a semilog plot

$$\ln C = \frac{1}{n}\left\langle \sum_{m=1}^{\frac{1}{n}}\frac{1}{m}\left(1-\lambda^n\right)^m + \ln\left(1-\lambda^n\right) - \sum_{m=1}^{\frac{1}{n}}\frac{1}{m} - 3nL\tau \right\rangle \qquad (28)$$

with slope -3L and intercept $\left\langle \sum_{m=1}^{\frac{1}{n}}\frac{1}{m}\left(1-\lambda^n\right)^m + \ln\left(1-\lambda^n\right) - \sum_{m=1}^{\frac{1}{n}}\frac{1}{m} \right\rangle$.

Table 2. Summary of 3Lτ Solutions

n	*Solution*
n	$n\left\langle \sum_{1}^{m}\frac{1}{m}\left(1-\lambda^{1/n}\right)^{m}-\ln\left[\frac{C^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]-\sum_{1}^{m}\frac{1}{m}\left[\frac{1-\lambda^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]^{m}\right\rangle$
1	$(1-\lambda)-\ln\left[\frac{C}{1-\lambda+\lambda C}\right]-\frac{1-\lambda}{1-\lambda+\lambda C}$
2	$2\left\langle\left(1-\lambda^{1/2}\right)+\frac{1}{2}\left(1-\lambda^{1/}\right)^{2}-\ln\left[\frac{C^{1/2}}{1-\lambda^{1/2}+(\lambda C)^{1/2}}\right]-\left[\frac{1-\lambda^{1/2}}{1-\lambda^{1/2}+(\lambda C)^{1/2}}\right]-\frac{1}{2}\left[\frac{1-\lambda^{1/2}}{1-\lambda^{1/2}+(\lambda C)^{1/2}}\right]^{2}\right\rangle$
3	$3\left\langle\left(1-\lambda^{1/3}\right)+\frac{1}{2}\left(1-\lambda^{1/3}\right)^{2}+\frac{1}{3}\left(1-\lambda^{1/3}\right)^{3}-\ln\left[\frac{C^{1/3}}{1-\lambda^{1/3}+(\lambda C)^{1/3}}\right]-\left[\frac{1-\lambda^{1/3}}{1-\lambda^{1/3}+(\lambda C)^{1/5}}\right]-\frac{1}{2}\left[\frac{1-\lambda^{1/3}}{1-\lambda^{1/3}+(\lambda C)^{1/5}}\right]^{2}-\frac{1}{3}\left[\frac{1-\lambda^{1/3}}{1-\lambda^{1/3}+(\lambda C)^{1/3}}\right]^{3}\right\rangle$
4	$4\left\langle\left(1-\lambda^{1/4}\right)+\frac{1}{2}\left(1-\lambda^{1/4}\right)^{2}+\frac{1}{3}\left(1-\lambda^{1/4}\right)^{3}+\frac{1}{4}\left(1-\lambda^{1/4}\right)^{4}-\ln\left[\frac{C^{1/4}}{1-\lambda^{1/4}+(\lambda C)^{1/4}}\right]-\left[\frac{1-\lambda^{1/4}}{1-\lambda^{1/4}+(\lambda C)^{1/4}}\right]-\frac{1}{2}\left[\frac{1-\lambda^{1/4}}{1-\lambda^{1/4}+(\lambda C)^{1/4}}\right]^{2}-\frac{1}{3}\left[\frac{1-\lambda^{1/4}}{1-\lambda^{1/4}+(\lambda C)^{1/4}}\right]^{4}-\frac{1}{4}\left[\frac{1-\lambda^{1/4}}{1-\lambda^{1/4}+(\lambda C)^{1/4}}\right]^{4}\right\rangle$
⋮	⋮
n	$n\left\langle\left(1-\lambda^{1/n}\right)+\frac{1}{2}\left(1-\lambda^{1/n}\right)^{2}+\cdots+\frac{1}{n}\left(1-\lambda^{1/n}\right)^{n}-\ln\left[\frac{C^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]-\left[\frac{1-\lambda^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]-\frac{1}{2}\left[\frac{1-\lambda^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]^{2}-\cdots-\frac{1}{n}\left[\frac{1-\lambda^{1/n}}{1-\lambda^{1/n}+(\lambda C)^{1/n}}\right]^{n}\right\rangle$

Table 3. Summary of ln C Long Time Solutions

n	*Solution*
n	$\mathrm{n}\left\langle \sum_{1}^{m} \frac{1}{m}\left(1-\lambda^{1/n}\right)^{m} + \ln\left(1-\lambda^{1/n}\right) - \sum_{1}^{m}\frac{1}{m} - \frac{3}{n}L\tau \right\rangle$
1	$(1-\lambda)+\ln[1-\lambda]-1-3L\tau$
2	$2\left\langle \left(1-\lambda^{1/2}\right)+\frac{1}{2}\left(1-\lambda^{1/2}\right)^{2}+\ln\left[1-\lambda^{1/2}\right]-1-\frac{1}{2}-\frac{3}{2}L\tau \right\rangle$
3	$3\left\langle \left(1-\lambda^{1/3}\right)+\frac{1}{2}\left(1-\lambda^{1/3}\right)^{2}+\frac{1}{3}\left(1-\lambda^{1/3}\right)^{3}-\ln\left[1-\lambda^{1/3}\right]-1-\frac{1}{2}-\frac{1}{3}-\frac{3}{3}L\tau \right\rangle$
4	$4\left\langle \left(1-\lambda^{1/4}\right)+\frac{1}{2}\left(1-\lambda^{1/4}\right)^{2}+\frac{1}{3}\left(1-\lambda^{1/4}\right)^{3}+\frac{1}{4}\left(1-\lambda^{1/4}\right)^{4}+\ln\left[1-\lambda^{1/4}\right]-1-\frac{1}{2}-\frac{1}{3}-\frac{1}{4}-\frac{3}{4}L\tau \right\rangle$
⋮	⋮
n	$n\left\langle \left(1-\lambda^{1/n}\right)+\frac{1}{2}\left(1-\lambda^{1/n}\right)^{2}+\cdots+\frac{1}{n}\left(1-\lambda^{1/n}\right)^{n}+\ln\left[1-\lambda^{1/n}\right]-1-\frac{1}{2}-\cdots-\frac{1}{n}-\frac{3}{n}L\tau \right\rangle$

The family of solutions for Equations 27 and 28 are presented in Tables 2 and 3 respectively, and in particular for the cases n=1,2,3,4 and n.

Both solutions for n = 1 in Tables 2 and 3 were earlier derived by Brandani (1998) for the Langmuir isotherm. As the Toth isotherm reduces to the Langmuir isotherm when n = 1, this is expected. However the case n = 1 is only one particular solution in the family of solutions.

The reader is referred to the article by Brandani (1998) for an expanded discussion on these limiting forms of the equation. Succinctly, he proves that the limiting form for a microporous solid with nonlinear Langmuir equilibrium is the average involving Equations 17, 26 and an Equation for the limiting form of the tracer diffusivity.

The interesting result is that the limiting form, Equation 26, for the nonlinear Langmuir Equation is applicable to microporous, mesoporous and macroporous materials, with the same slope of -3L in all three cases Further, the limiting slope at long time is identical for the Toth isotherm having a heterogeneity parameter of n = ½ for the mesoporous and macroporous materials. This suggests that the limiting slope is -3L for all values of n but this will need a simulation to establish. The only difference between the microporous and both the mesoporous and macroporous materials is that the diffusivity observed is D_o the diffusivity at infinite dilution in the Darken expression in microporous materials and the effective diffusivity D_{eff} at infinite dilution in mesoporous/macroporous materials, In fact the zero length column (ZLC) produces the zero loading diffusivity (ZLD) when measured in the long time region.

MODELING RESULTS and APPLICATION TO DATA

This is presently being revised. Figures for different L's must be included. Will be resubmitted within the next 10 days.

CONCLUSIONS

ACKNOWLEDGMENTS

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NOMENCLATURE

b	Equilibrium parameter, ccm./mol [Langmuir isotherm]
b	Toth parameter, $[mol/ccm.]^n$
c_P	pore gas phase concentration, mol/ccm
c	cell concentration, mol/ccm.
c_o	initial cell concentration, mol/ccm.
C	dimensionless gas concentration $[=c/c_o]$
D_P	pore diffusion coefficient, cm^2/s
F	Cell flowrate, ccm/s.
K	Henrys' constant defined in Table 1.
L	dimensionless parameter defined in Eq. 10.
N	molar flux, mol/s.
n	Toth parameter
q	solid phase concentration, mol/ccm.
$\overline{q}$	average solid phase concentration, mol/ccm.
q_s	saturated solid phase concentration, mol/ccm.
q_o	initial solid phase concentration, mol/ccm.
Q	dimensionless solid phase concentration, defined in Eq. 9.
r	radial coordinate, cm.
t	time, s.
V_P	pellet volume, ccm.

Greek Letters

ε	pellet voidage
λ	nonlinearity parameter.
τ	dimensionless time, defined in Eq. 9.
η	dimensionless radial coordinate, defined in Eq. 9.

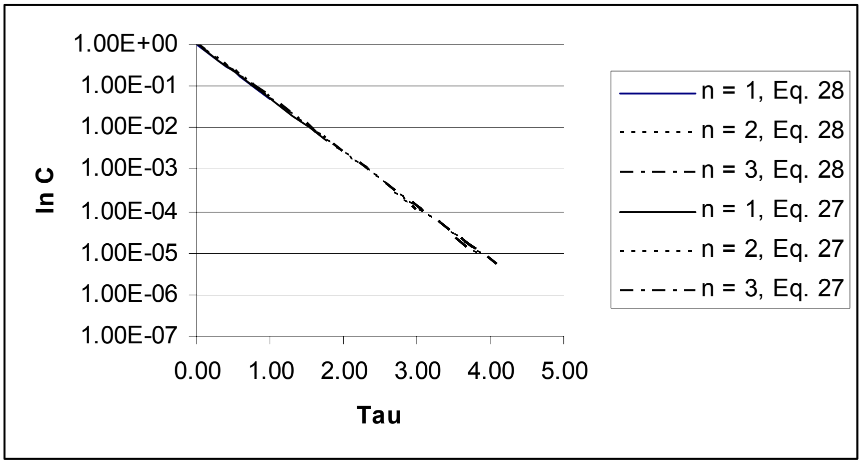

Figure 1. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [$\lambda = 0$, L = 1]

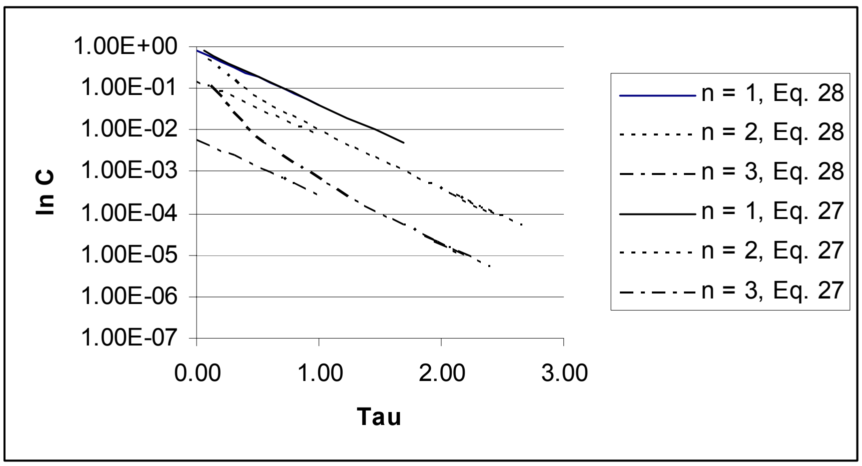

Figure 2. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [$\lambda = 0.1$, L = 1]

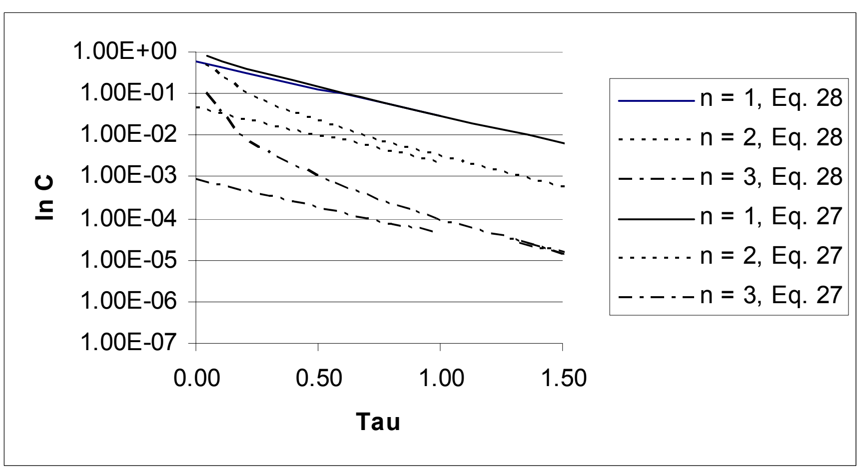

Figure 3. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [$\lambda = 0.25$, L = 1]

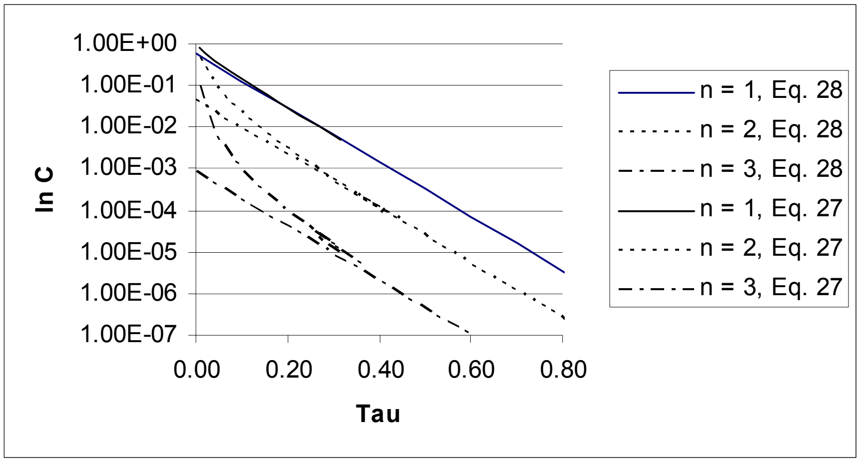

Figure 4. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.25, L = 5]

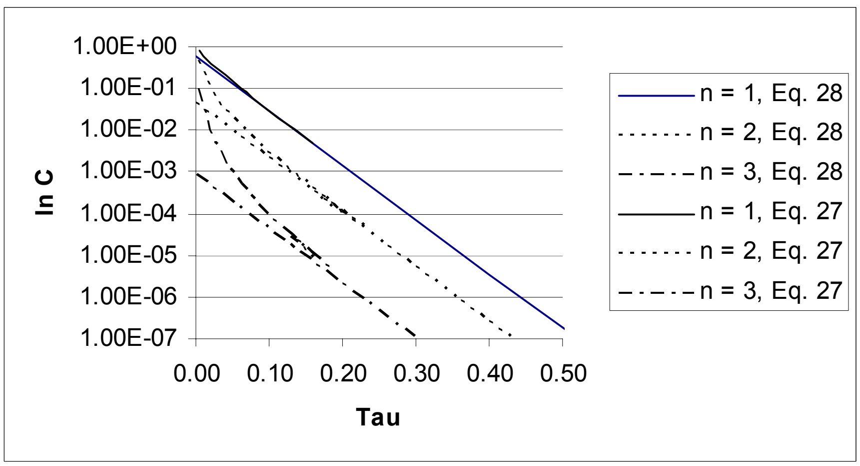

Figure 4. Plot of Limiting Asymptotic Solutions for Eqts. 27 and 28 [λ = 0.25, L = 10]

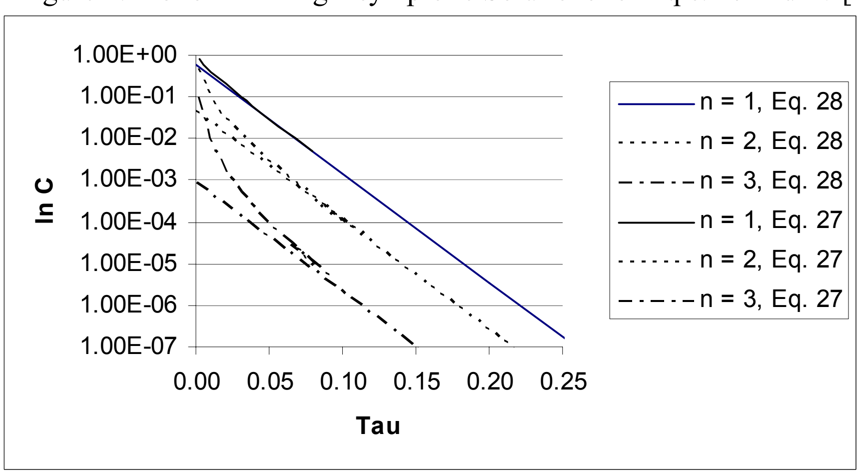

Figure 4. Plot of Limiting Asymptotic Solutions for Eqts. 27 and 28 [λ = 0.25, L = 20]

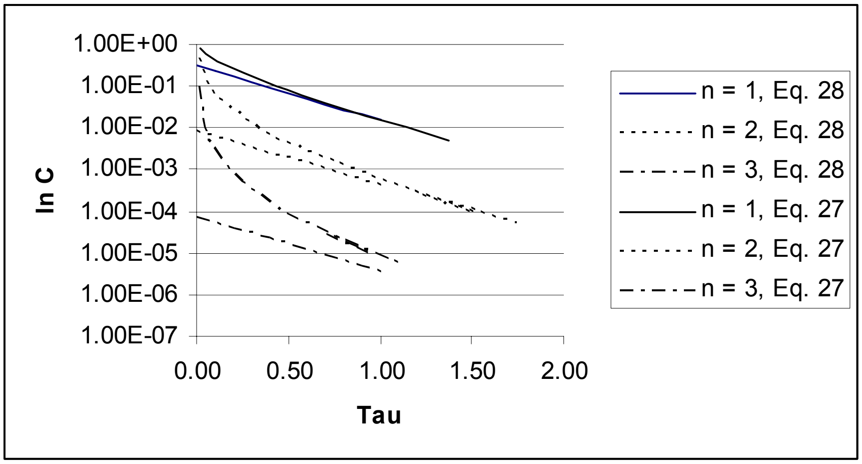

Figure 5. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.5, L = 1]

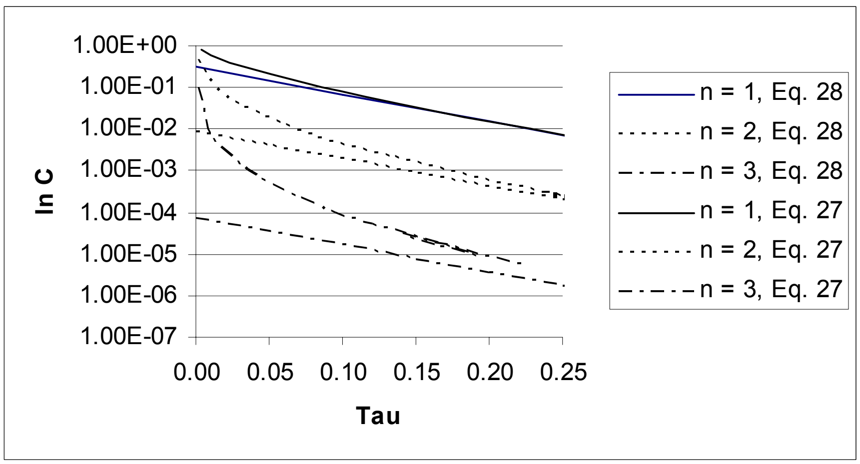

Figure 6. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.5, L = 1]

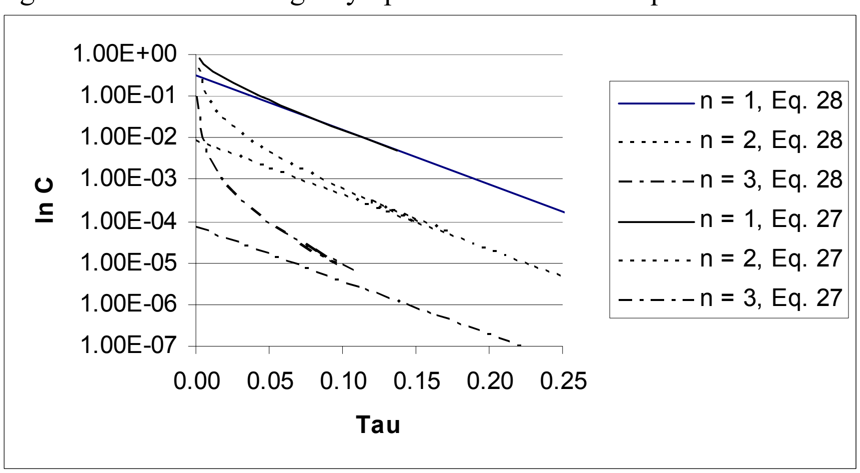

Figure 7. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.5, L = 10]

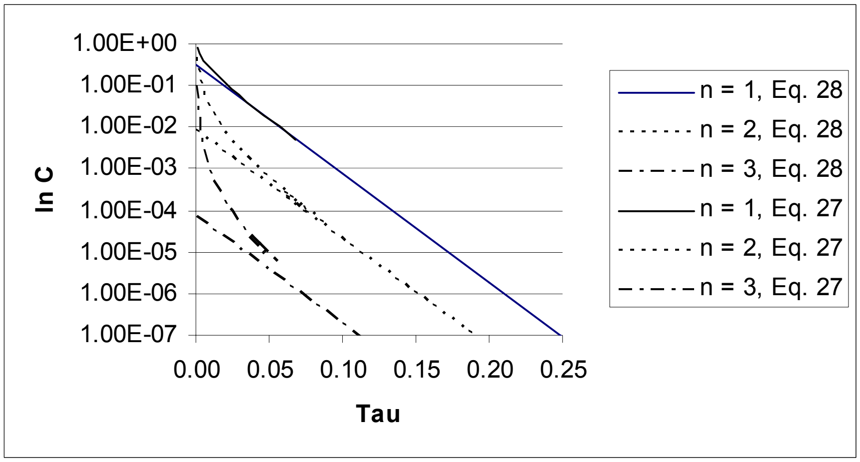

Figure 8. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.5, L = 20]

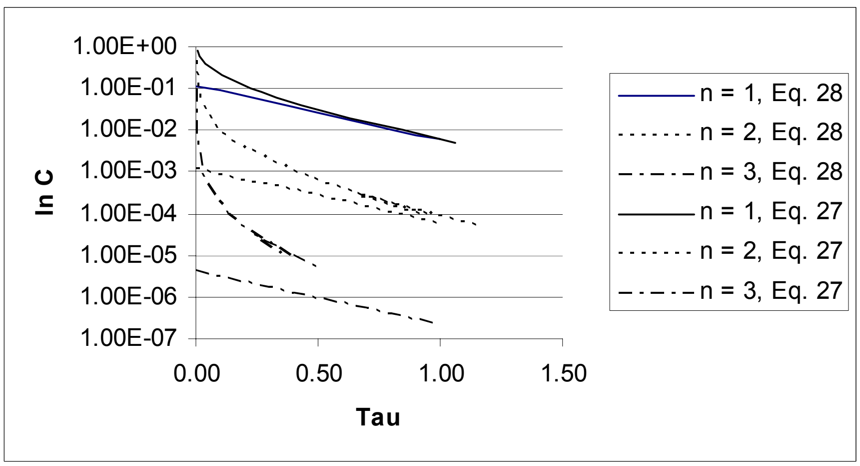

Figure 9. Plot of Limiting Asymptotic Solutions for Equations 27 and 28 [λ = 0.75, L = 1]

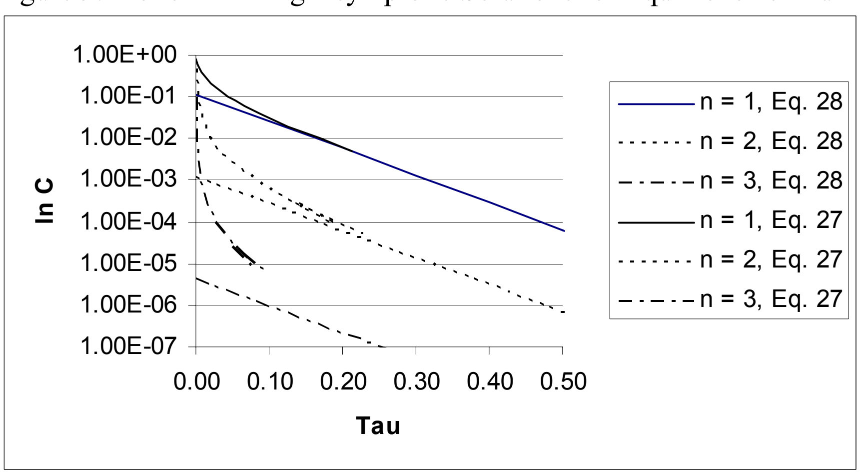

Figure 10. Plot of Limiting Asymptotic Solutions for Eqts. 27 and 28 [λ = 0.75, L = 5]

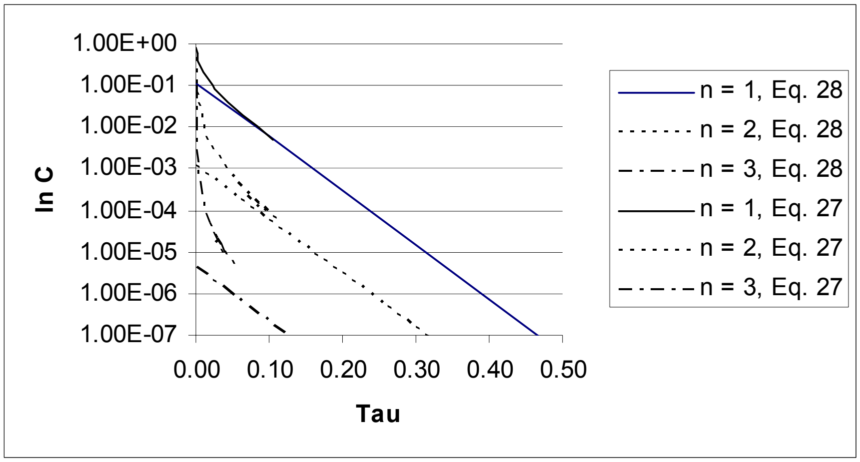

Figure 10. Plot of Limiting Asymptotic Solutions for Eqts. 27 and 28 [λ = 0.75, L = 10]

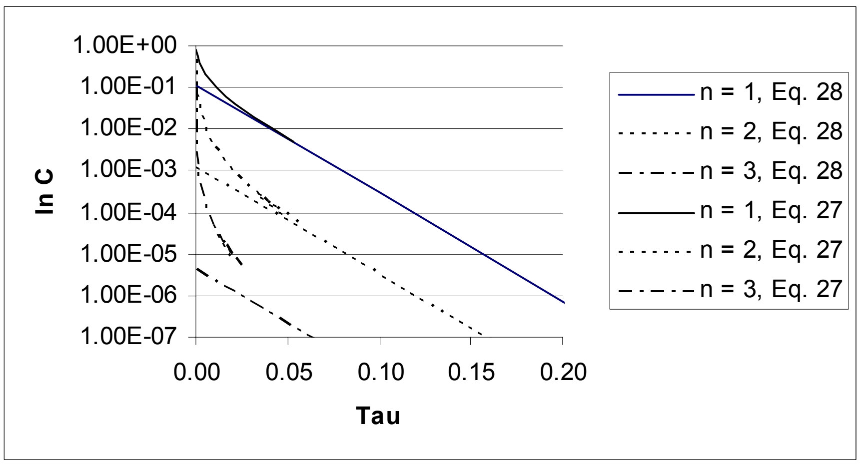

Figure 10. Plot of Limiting Asymptotic Solutions for Eqts. 27 and 28 [λ = 0.75, L = 20]

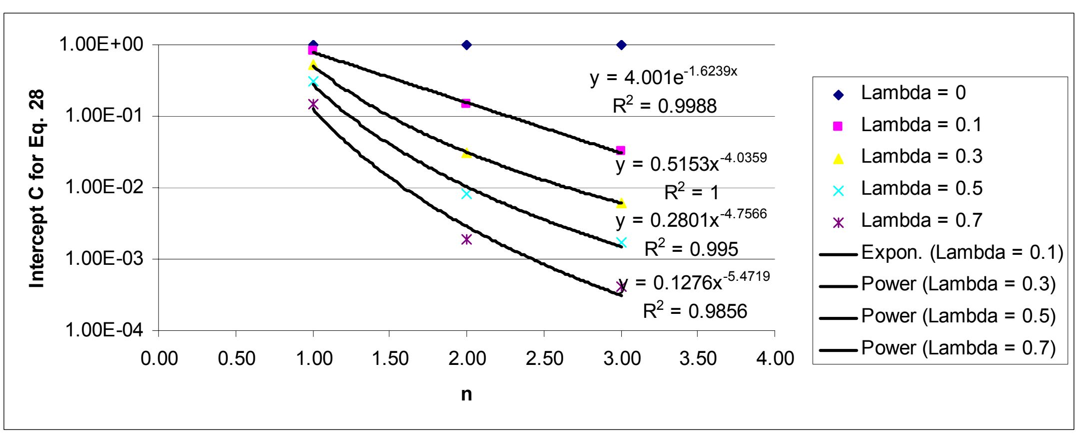

Figure 7. Variation of Intercept C [Eq. 28] as a function of λ and n with calculated Regression Equations.

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