New Approximate Model for Diffusion and Reaction in a Porous Catalyst

Mirosław K. Szukiewicz
Dept. of Chemical Engineering and Process Control, Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Fixed-bed reactors are commonly used in industry for heterogeneous catalytic processes. There are two groups of models applied in modeling of this type of apparatus: (1) pseudohomogeneous models assume the same temperature and component concentrations in the fluid bulk and catalyst particles. Because of this assumption, the model is described by a PDE only for the fluid phase. Despite their low accuracy in most cases, pseudohomogeneous models are relatively easy to solve and they are commonly used to describe reactors. (2) Heterogeneous models, in contrast to pseudohomogeneous ones, give results with quite good accuracy. They are described by PDEs, both for the fluid and for the catalyst pellets, but they are difficult to solve. The widely reported way to avoid this drawback is to use an effectiveness-factor concept. This concept reduces the equation set of the heterogeneous model and makes the solution much easier to obtain. Unfortunately, for most cases, finding the proper value of the mentioned factor is a difficult and/or lengthy task (see also Szukiewicz et al., 1998) limiting the application of heterogeneous models.

Another way to simplify the mathematical model is widely reported for the diffusion and adsorption processes. In this approach the PDE for the mass balance in a pellet is replaced by a proper ODE (the so-called ''approximate model''), simplifying greatly the model solution with the same or only slightly poorer accuracy. As a result, a number of approximate models have been developed. These models differ from one another with respect to accuracy and validity ranges. One can find more information, for example in the papers by Goto and Hirose (1993), or Zhang and Ritter (1997). Here, only the linear driving-force approximation proposed by Glueckauf (1955) is presented. In dimensionless form this approximation can be written as:

$$\frac{\partial c_{av}}{\partial \tau} = 15 \cdot (c_s - c_{av}). \qquad (1)$$

This formula is distinguished from other models by its simplicity and its validity. It is almost classic (one can say ''standard''), and is the approximation formula cited most often. It has been used, for example, in the analysis of chromatographic processes (Raghavan and Ruthven, 1985), packed-bed adsorption (Morbidelli et al., 1982; Doong and Yang, 1987), and, recently, in nonlinear multicomponent chromatography (Kaczmarski, 1996; Kaczmarski and Antos, 1996).

To make use of this idea of model approximation for diffusion and chemical reaction processes, other models should be developed. Some approaches that approximate a mass balance in a porous particle have been advanced. Kim (1989) has proposed two linear driving-force formulas. The accuracy of the better of them is good, but it first requires calculation of as many as three coefficients, and second computation of surface-concentration derivatives. Finding the derivative is difficult if the surface concentration cannot be described by an analytical function, which is not uncommon in practice. Moreover the individual terms of the model—accumulation, rate of mass transfer, and reaction rate—no longer have their physical meaning. In the initial basis equation one can find the terms given previously without any problem, whereas in Kim's model it is difficult if not impossible. Goto and Hirose (1993) have presented a number of approximate models that are free of the disadvantages cited. Unfortunately, even in their own opinion, the accuracy of the proposed formulas for diffusion and reaction processes are unsatisfactory. The formulas are not valid for larger values of the Thiele modulus. Note that all models mentioned are analogous to Glueckauf's formula for diffusion processes.

In the present work an approximate model is developed that is valid for diffusion−reaction processes and that is free of the drawbacks of earlier models. The approximate, linear driving-force (LDF) formula, which is also analogous to Gluackauf's formula, has been derived. The accuracy of the developed model is very high. Moreover, the method applied here for derivation of the approximate model can be useful not only for diffusion and reaction process in porous catalysts, but also for any process that takes into account internal diffusion, adsorption, and the like.

Theory

A mass-balance equation for unsteady-state diffusion and first-order reaction in a porous spherical particle can be described by

$$\frac{\partial c_A}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{\mathrm{ef},A}\cdot r^2\cdot\frac{\partial c_A}{\partial r}\right) - k_1\cdot c_A, \tag{2}$$

with

$$\begin{aligned} &\text{IC:} \quad t=0 \quad c_A(0,r) = c_{A,\mathrm{in}} && (3)\\ &\text{BC:} \quad t>0 \quad c_A(t,0) = \text{extremum} && \\ &\qquad\qquad \left(\text{it is equivalent to } \left.\frac{\partial c_A}{\partial r}\right|_{r=0} = 0\right) && (4)\\ &\qquad\qquad c_A(t,R) = c_{A,s}(t). && (5) \end{aligned}$$

Equation 2 can be rearranged to a dimensionless form:

$$\frac{\partial c}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\cdot\frac{\partial c}{\partial x}\right) - \Phi^2\cdot c \tag{6}$$

$$\begin{aligned} &\text{IC:} \quad \tau=0 \quad c(0,x) = c_{\mathrm{in}} && (7)\\ &\text{BC:} \quad \tau>0 \quad c(\tau,0) = \text{extremum} && (8)\\ &\qquad\qquad c(\tau,1) = c_s(\tau), && (9) \end{aligned}$$

where

$$x = \frac{r}{R} \qquad c = \frac{c_A}{c_{A,\max}} \qquad \tau = \frac{D_{\mathrm{ef},A}}{R^2}\cdot t$$

$$\Phi = R\sqrt{\frac{k_1}{D_{\mathrm{ef},A}}}.$$

The LDF formula will be searched in the following form:

$$\frac{\partial c_{\mathrm{av}}}{\partial \tau} = \alpha\cdot(c_s - c_{av}) - \Phi^2\cdot c_{av}. \tag{10}$$

Generally α varies with time, but it is commonly treated as a constant value in approximated formulas. The volume-averaged concentration c_{av} can be calculated as

$$c_{\mathrm{av}} = 3\cdot\int_0^1 c\cdot x^2\cdot dx. \tag{11}$$

The substitution

$$q(\tau,x) = x\cdot c(\tau,x) \tag{12}$$

converts Eq. 6 to

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial x^2} - \Phi^2\cdot q \tag{13}$$

$$\begin{aligned} &\text{IC:} \quad \tau=0 \quad q(0,x) = x\cdot c_{\mathrm{in}} && (14)\\ &\text{BC:} \quad t>0 \quad q(\tau,0) = 0 && (15)\\ &\qquad\qquad q(\tau,1) = 1\cdot c_s(\tau) = c_s(\tau). && (16) \end{aligned}$$

If one now defines

$$Q(p,x) = p\cdot\int_0^\infty e^{-p\tau}\cdot q(\tau,x)\cdot d\tau$$

$$\text{(Laplace-Carson transform).} \tag{17}$$

In the text below, capital letters are used to describe the complex functions corresponding to the real functions. In the Laplace-Carson transform, defined analogously as Eq. 17, one can obtain

$$p\cdot Q - p\cdot x\cdot c_{\mathrm{in}} = \frac{\partial^2 Q}{\partial x^2} - \Phi^2\cdot Q \tag{18}$$

$$\begin{aligned} &\text{BC:} \quad Q(p,0) = 0 && (19)\\ &\qquad\quad Q(p,1) = C_s(p). && (20) \end{aligned}$$

The solution of Eq. 18 with its conditions (Eqs. 19 and 20) presents

$$Q = \left(C_s - \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p}\right)\cdot\frac{\sinh\left(\sqrt{\Phi^2+p}\cdot x\right)}{\sinh\left(\sqrt{\Phi^2+p}\right)} + \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p}\cdot x. \tag{21}$$

According to Eq. 11, C_{av} can be described as

$$C_{\mathrm{av}} = 3\cdot\int_0^1 C\cdot x^2\cdot dx = 3\cdot\int_0^1 Q\cdot x\cdot dx. \tag{22}$$

Substitution for Q and integrating results in the following equation:

$$\begin{aligned} C_{\mathrm{av}} = {} & 3\cdot\left(C_s - \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p}\right)\cdot\frac{1}{\Phi^2+p}\\ & \cdot\frac{\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right) - \sinh\left(\sqrt{\Phi^2+p}\right)}{\sinh\left(\sqrt{\Phi^2+p}\right)} + \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p}, \end{aligned} \tag{23}$$

which can be easily rearranged to

$$\begin{aligned} & \frac{1}{3}\cdot\left(C_{\mathrm{av}} - \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p}\right)\\ & \quad\cdot\frac{(\Phi^2+p)\cdot\sinh\left(\sqrt{\Phi^2+p}\right)}{\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right) - \sinh\left(\sqrt{\Phi^2+p}\right)}\\ & \quad + \frac{p\cdot c_{\mathrm{in}}}{\Phi^2+p} = C_s. \end{aligned} \tag{24}$$

And now successively
- Subtracting C_{av};
- Multiplying by

$$3\cdot\frac{\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right) - \sinh\left(\sqrt{\Phi^2+p}\right)}{(\Phi^2+p)\cdot\sinh\left(\sqrt{\Phi^2+p}\right)};$$

- Multiplying by

$$(\Phi^2+p)\cdot\left[1-3\frac{\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right)-\sinh\left(\sqrt{\Phi^2+p}\right)}{(\Phi^2+p)\cdot\sinh\left(\sqrt{\Phi^2+p}\right)}\right]^{-1};$$

- And finally subtracting $\Phi^2\cdot C_{\text{av}}$ to both sides of Eq. 24, one can obtain

$$p\cdot C_{\text{av}}-pc_{\text{in}}=3\cdot\frac{(\Phi^2+p)\cdot\left[\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right)-\sinh\left(\sqrt{\Phi^2+p}\right)\right]}{(\Phi^2+p)\cdot\sinh\left(\sqrt{\Phi^2+p}\right)-3\cdot\left[\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right)-\sinh\left(\sqrt{\Phi^2+p}\right)\right]}\cdot(C_s-C_{\text{av}})-\Phi^2\cdot C_{\text{av}}. \quad (25)$$

Although a time-dependent form of coefficient α in Eq. 10 is not known, Eq. 25 can be considered as the Laplace-Carson transform of Eq. 10. The analysis of these equations leads to the conclusion that defining the coefficient α in the real domain on the basis of Eq. 25 is easy when α is constant. Thus, if it is assumed that $\lim_{t\to\infty}\alpha$ is finite ($\alpha=$ const. as τ approaches infinity), it can be calculated as

$$\lim_{t\to\infty}\alpha=\lim_{p\to 0}\frac{3\cdot(\Phi^2+p)\cdot\left[\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right)-\sinh\left(\sqrt{\Phi^2+p}\right)\right]}{(\Phi^2+p)\cdot\sinh\left(\sqrt{\Phi^2+p}\right)-3\cdot\left[\sqrt{\Phi^2+p}\cdot\cosh\left(\sqrt{\Phi^2+p}\right)-\sinh\left(\sqrt{\Phi^2+p}\right)\right]}$$

$$=3\cdot\frac{\Phi^2\cdot(\Phi\cdot\cosh\Phi-\sinh\Phi)}{\Phi^2\cdot\sinh\Phi-3\cdot(\Phi\cdot\cosh\Phi-\sinh\Phi)}. \quad (26)$$

Denoted as

$$\Psi=\frac{\Phi^2\cdot(\Phi\cdot\cosh\Phi-\sinh\Phi)}{\Phi^2\cdot\sinh\Phi-3\cdot(\Phi\cdot\cosh\Phi-\sinh\Phi)}, \quad (27)$$

Eq. 25 can be written as

$$p\cdot C_{\text{av}}-p\cdot c_{\text{in}}=3\cdot\Psi\cdot(C_s-C_{\text{av}})-\Phi^2\cdot C_{\text{av}}. \quad (28)$$

The inverse transform of this equation is

$$\frac{\partial c_{\text{av}}}{\partial\tau}=3\cdot\Psi\cdot(c_s-c_{\text{av}})-\Phi^2\cdot c_{\text{av}} \quad (29)$$

$$\text{IC:}\quad \tau=0 \qquad c_{\text{av}}=c_{\text{in}}. \quad (30)$$

It is easy to show that the initial condition denoted as Eq. 30 corresponds to the initial condition denoted as Eq. 7.

Reverting to dimensional variables, we obtain:

$$\frac{\partial c_{A,\text{av}}}{\partial t}=\frac{3D_{\text{ef},A}}{R^2}\cdot\Psi\cdot(c_{A,s}-c_{A,\text{av}})-k_1\cdot c_{A,\text{av}}. \quad (31)$$

Equations 29 and 31, where Ψ is given by Eq. 27, are long time approximations for diffusion with chemical reaction processes. If the chemical reaction is negligible ($\Phi\to 0$), Eq. 29 becomes Glueckauf's formula, Eq. 1, because

$$\lim_{\Phi\to 0}\Psi=5$$

$$\text{(it can be calculated applying l'Hospital's rule)}. \quad (32)$$

Results and Discussion

At the beginning of this part of the article the analytic solution of Eq. 6 with its conditions (Eqs. 7–9) is presented. It is additionally assumed that

$$c_{\text{in}}=0. \quad (33)$$

Then (according to Kim (1989))

$$c(\tau,x)=\frac{2}{x}\cdot\sum_{n=1}^{\infty}(-1)^{n+1}\cdot n\pi\cdot\sin(n\pi x)\cdot e^{-\lambda_n\tau}\cdot\int_0^{\tau}e^{\lambda_n\xi}\cdot c_s(\xi)\cdot d\xi, \quad (34)$$

where

$$\lambda_n=\Phi^2+n^2\pi^2. \quad (35)$$

The volume-averaged fluid phase concentration is (according to Eq. 11)

$$c_{\text{av}}=6\cdot\sum_{n=1}^{\infty}e^{-\lambda_n\tau}\cdot\int_0^{\tau}e^{\lambda_n\tau}\cdot c_s(\xi)\cdot d\xi. \quad (36)$$

The accuracy of the LDF formulas proposed earlier was tested in two steps for a wide range of Thiele modulus values (the c_{in} value was taken according to Eq. 33):

1. For the unit step change in surface concentration

$$c_s(\tau)=1. \quad (37)$$

This is, one can say, the standard test for approximated equations.

2. For a time-dependent surface concentration

$$c_s(\tau)=c_0+A\cdot\sin(\omega\tau) \qquad \text{(harmonic function)}. \quad (38)$$

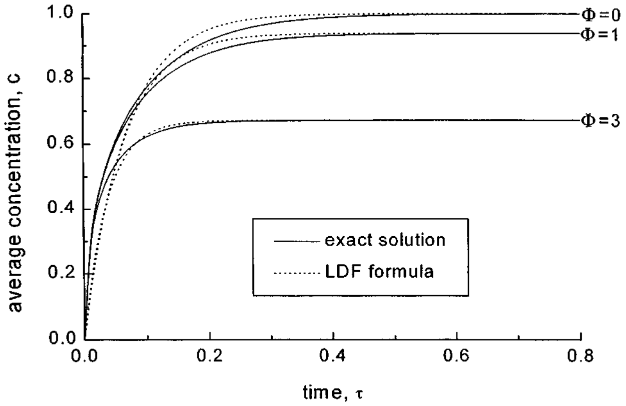

Figure 1. Exact solution vs. LDF formula for unit step change in the surface concentration for smaller Φ values.

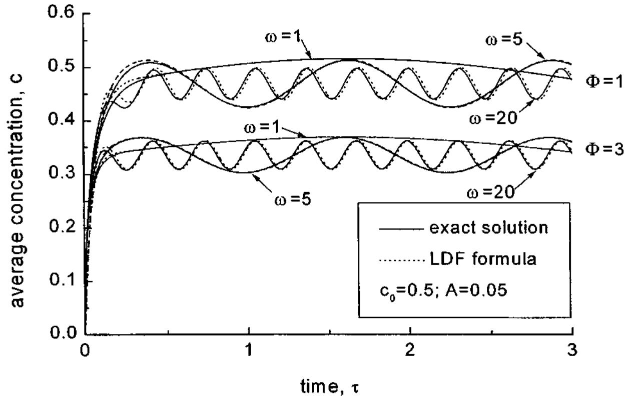

Figure 3. Exact solution vs. LDF formula for sinusoidal changes in the surface concentration for smaller values of Thiele modulus; the effect of frequency for small amplitude.

If in the preceding formula the ratio A/c_0 is small, it can simulate oscillation of a substrate concentration in a reactor inlet; if it is large, it can simulate a substrate concentration change inside a reactor. From the engineer's point of view, the accuracy of the approximate model in the first test plays a major role. Nevertheless, the second test is useful for a better understanding of the constraints of the approximate model.

Results obtained by using Eq. 29 were compared with the exact (analytic) solution, Eq. 36. The case of no reaction process ($\Phi = 0$) is also presented.

The results obtained for point number 1 are presented in Figures 1 and 2. The average concentration approaches the steady-state value as time passes. The accuracy of calculations using the LDF formula proposed here is excellent over the entire range of Φ at steady state. At small values of τ differences between the exact solution and the LDF formula are larger, as expected, but they are smaller at larger Φ values. Moreover, satisfactory compatibility of results is obtained for the smaller times, when the Thiele modulus rises. For $\Phi = 50$ the LDF formula and analytic solution give the same responses for even very short times (see Figure 2). The results presented confirm that the LDF formula obtained approximates very well the exact solution for "long times." For practical purposes for all τ determined by the relation

$$\tau \geq \frac{5}{3\Psi + \Phi^2}, \tag{39}$$

the exact model and the approximate one give the same results (error about 1%). This outcome clearly explains why the larger the value of Φ, the better is the approximation.

Results obtained in point number 2 for the chosen values of the parameters of the harmonic function (Eq. 38) are presented in Figures 3 and 4. The proposed LDF approximation also very accurately gives the average concentration changes for the time-dependent surface concentration case. Only for small values of Φ and the highest tested frequency ($\omega = 20$) does the calculation precision become slightly less satisfactory. This confirms previous observations that the higher the value of the Thiele modulus, the higher the accuracy of the LDF formula.

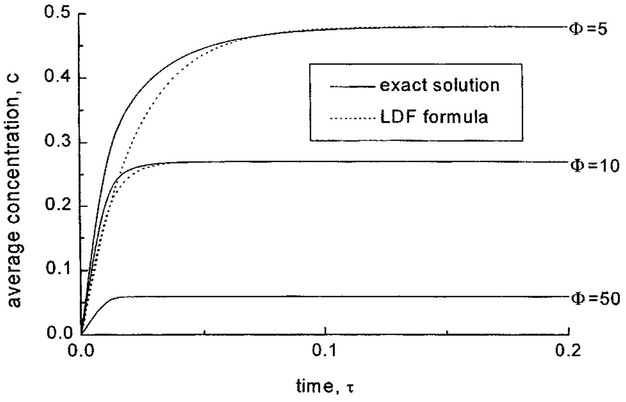

Figure 2. Exact solution vs. LDF formula for unit step change in the surface concentration for larger Φ values.

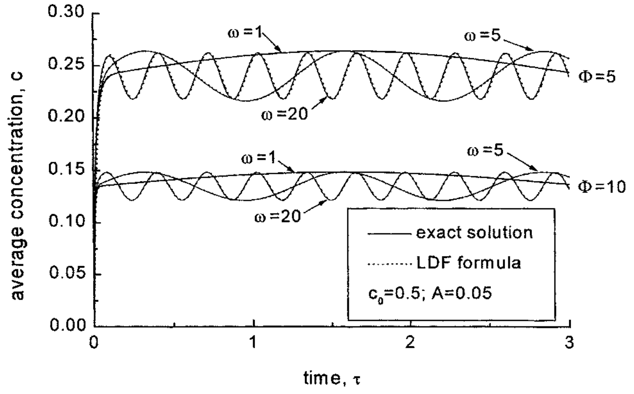

Figure 4. Exact solution vs. LDF formula for sinusoidal changes in the surface concentration for larger values of Thiele modulus; the effect of frequency for small amplitude.

Conclusions

The linear driving-force formula, which approximates diffusion with the chemical reaction processes (such as heterogeneous catalysis), is distinguished by the high accuracy of its calculations and the simplicity of its form. The simplicity of the form is important because it makes it possible to extend the validity of the LDF formula, for example, to another type of kinetic equation, in a relatively easy way. The formula has been derived as a ''long time'' approximation, and its accuracy rises for longer times, as expected. A simple relation that defines the validity range of the approximate model was presented. It was shown, that the higher the value of the Thiele modulus, the greater the accuracy of the calculations for shorter times. This means that the proposed approximation can be used for higher Thiele modulus values for almost the entire time scale.

The LDF formula presented was derived for first-order reactions. It also can be useful for an analysis of reactions not in this category, provided that the nonlinear model is linearized (such as by using Taylor series expansion and truncating with first-order terms) and variables are interpreted as deviations from the steady state. Such a method of model analysis is commonly applied in the process control field.

Notation

A = coefficient in Eq. 38
c, c_A = concentration of component A
c_{av}, $c_{A,av}$ = volume-averaged concentration of component A
c_{in}, $c_{A,in}$ = initial concentration of component A
c_0 = coefficient in Eq. 38
c_s, $c_{A,s}$ = surface concentration of component A
$D_{ef,A}$ = effective diffusivity of component A
k_1 = reaction rate constant
p = complex variable
q = function defined by Eq. 12
r = position in a pellet
R = radius of a pellet
t = time
x = dimensionless position in a pellet
α = coefficient in Eq. 10
τ = dimensionless time
ξ = variable
ω = coefficient in Eq. 38
Φ = Thiele modulus
Ψ = coefficient defined by Eq. 27

The complex functions corresponding to the real functions in the Laplace-Carson transform are described by capital letters.

Literature Cited

Doong, S. J., and R. T. Yang, ''Bidisperse Pore Diffusion Model for Zeolite Pressure Swing Adsorption,'' *AIChE J.*, **33**, 1045 (1987).

Glueckauf, E., ''Theory of Chromatography 10: Formula for Diffusion into Spheres and Their Application to Chromatography,'' *Trans. Faraday Soc.*, **51**, 1540 (1955).

Goto, M., and T. Hirose, ''Approximate Rate Equation for Intraparticle Diffusion With or Without Reaction,'' *Chem. Eng. Sci.*, **48**, 1912 (1993).

Kaczmarski, K., ''Use of Orthogonal Collocation on Finite Elements with Moving Boundaries in the Simulation of Non-Linear Multicomponent Chromatography. Influence of Fluid Velocity Variation on Retention Time in LC and HPLC,'' *Comput. Chem. Eng.*, **20**, 49 (1996).

Kaczmarski, K., and A. Antos, ''Modified Rouchon and Rouchon-Like Algorithms for Solving Different Models of Multicomponent Preparative Chromatography,'' *J. Chromatogr. A*, **756**, 73 (1996).

Kim, D. H., ''Linear Driving Force Formulas for Diffusion and Reaction in Porous Catalysts,'' *AIChE J.*, **35**, 343 (1989).

Morbidelli, M., A. Servida, G. Storti, and S. Carra, ''Simulation of Multicomponent Adsorption Bed. Model Analysis and Numerical Solution,'' *Ind. Eng. Chem. Fundam.*, **21**, 123 (1982).

Raghavan, N. S., and D. M. Ruthven, ''Simulation of Chromatographic Responses in Columns Packed with Bidisperse Structured Particles,'' *Chem. Eng. Sci.*, **40**, 699 (1985).

Szukiewicz, M. K., K. Kaczmarski, and R. Petrus, ''Modelling of Fixed-Bed Reactor: Two Models of Industrial Reactor for Selective Hydrogenation of Acetylene,'' *Chem. Eng. Sci.*, **53**, 149 (1998).

Zhang, R., and J. A. Ritter, ''New Approximate Model for Nonlinear Adsorption and Diffusion in a Single Particle,'' *Chem. Eng. Sci.*, **52**, 3161 (1997).

Manuscript received Mar. 18, 1999, and revision received Oct. 12, 1999.