R & D NOTES

The Radial Light Intensity Profile in Cylindrical Photoreactors

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The distribution of light intensity within elliptical-reflector photoreactors remains a subject of theoretical and practical interest to those concerned with their application to photochemical kinetic studies.

A theoretical light intensity distribution model was proposed by Matsuura and Smith (1970) and subsequently modified by Roger and Villermaux (1975). This model portrays the incident light as arriving at the reactor surface in bands which are perpendicular to the longitudinal axis of the tubular reactor. The model contains an adjustable parameter, the band width, which can vary from zero up to the width of the reactor diameter. At a band width of zero, the Matsuura and Smith model reduces to the radially incident model in which all radiation travels through the radial center of the reactor. As a consequence, an infinite intensity is predicted at the radial center regardless of the optical density of the absorbing medium within the reactor. A fully diffuse model is obtained at a band width equal to the reactor diameter. This model predicts a uniform light intensity profile within a transparent reactor and a minimum intensity at the radial center in the case of an absorbing reactor medium.

Cerdá, Irazoqui, and Cassano (1973) presented an extense model of the elliptical-reflector reactor light distribution which accounts for the geometric properties of lamp, reflector, and reactor. The radiation arriving at any point within the reactor is traced back to the lamp surface, either via a direct path or by means of a single reflection at the elliptical-reflector surface. While the extense model does not require the selection of arbitrary parameters in order to compute the intensity within the reactor, it does lack the ease of application associated with the Matsuura and Smith model.

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Zolner and Williams (1971) proposed a three-dimensional light intensity distribution model based on an external, cylindrical sleeve radiation source, within which the reactor is centered. This model contains an adjustable parameter which is the location of the source relative to the reactor. If the emitting source is placed exactly at the reactor surface, then the model predicts an infinite radiation flux at that point.

While theoretical light intensity distribution models abound, there is a scarcity of experimental data with which to test these models. In this regard it is of interest to briefly review the methods by which the models can be tested. These methods are conveniently classified as either integral or point intensity comparisons of model predictions with experimental data.

MODEL TESTING METHODS

The integral test consists of determining photoreaction rates under conditions where the incident light intensity is known or has been inferred from knowledge of the spatially averaged light intensity within the reactor. Experimental reaction rates are then compared with corresponding rates predicted by the application of a light intensity distribution model in conjunction with a suitable kinetic rate model. This testing method suffers the defect of excessive smoothing of data through integration of the models. For example, while the radial model predicts an infinite intensity at the radial center and the fully diffuse model predicts an intensity of only πI_w at the same point in a transparent reactor, their respective spatially averaged intensities, when expressed as a ratio, differ only by a factor of $4/\pi$.

Furthermore, at sufficiently large optical densities of the absorbing solution, nearly all incident radiation will be absorbed regardless of the orientation of the incident flux. For reactions which are first-order with respect to the volumetric rate of light absorption, all distribution models will tend to predict nearly the same reaction rate if the contents are well mixed in the radial cross section of the reactor. For the above reasons, the point determination of the light intensity within the reactor is to be preferred over the integral testing method as a means of discriminating among competitive models.

A point determination of light intensity within an elliptical-reflector reactor has been reported by Jacob and Dranoff (1969). A selenium-barrier photocell, whose characteristic linear dimension was about 14% of the reactor diameter, was used in their work. These measurements were reported as relative, rather than absolute, intensities. In addition, their photocell was limited to the reception of incident radiation over a solid angle of 2π, while in practice one would expect to receive radiation over an angle of 4π. Nonetheless, Cerdá, Irazoqui, and Cassano (1973) showed, through application of their extense model, that reasonably fair agreement is achieved between theory and experimental relative intensities. Theoretical intensity distribution models and point intensity data are best compared on an absolute basis in order to eliminate the possibility of different models predicting the same relative shape of the intensity distribution while, in fact, the absolute intensity values differ.

This work reports an experimental method for determining absolute intensities within the reactor. The method is based on the use of a chemical actinometer probe which receives incident radiation over a solid angle of nearly 4π.

CHEMICAL ACTINOMETER PROBE

The probe consists of a 1.0 mm ID quartz tube carefully positioned in the radial cross section of a 25 mm diameter reactor tube. Thus, the characteristic linear dimension of the probe was only 4% of the corresponding dimension of the reactor. The external surface of the probe was painted black except for a 10 cm portion. This window area was positioned symmetrically with respect to the reactor tube length which was 61.4 cm. The construction details of the elliptical-reflector photoreactor used in this work have been discussed by Ragonese and Williams (1971). A solution of 0.08 molar potassium ferric oxalate in 0.1 normal sulfuric acid was circulated, in a closed system, through the probe for a period of 5 min. The radiation arriving at the radial position occupied by the probe was partially absorbed in passing through the probe window area and, as a result, produced ferrous ions which were detected via the method of Baxendale and Bridge (1955). The known quantum yield of the reaction was used to determine the volumetric rate of light absorption according to Equation (1):

$$I_a = \frac{[Fe^{+2}]\, V_s}{\Phi V_p\, t} \tag{1}$$

The spatially averaged intensity within the probe $\bar{I}$ can be found from the volumetric rate of light absorption I_a by means of Equation (2) in which the attenuation coefficient μ_λ is evaluated at the principal wavelength of the source. In this particular case, $\mu_\lambda = 2.384\ cm^{-1}$ at the principal wavelength of 253.7 nm:

$$\bar{I} = \frac{I_a}{\mu_\lambda} \tag{2}$$

The spatially averaged intensity $\bar{I}$ obtained from Equation (2) represents a lower limit estimate of the actual intensity at the radial position of the probe. There are several reasons for this fact. First, the viewing angle of the probe is somewhat less than 4π owing to the opaque ends of the probe tube. Second, some radiation is lost by reflection from the surface of the quartz probe and by absorption in passing through the probe wall. Third, the radiation incident upon the probe is partially attenuated in passing through the actinometer solution. This is the most important reason for the fact that the measured intensity must necessarily be less than the actual intensity at the probe location.

The intensity distribution was determined in an empty quartz reactor tube so that the data would be representative of a transparent reactor. Light intensities predicted from theoretical models display the greatest divergence under these conditions. The probe was sequentially located at radial positions of 0, 2.58, 5.75, 8.91, and 11.5 mm. Multiple, reproducible determinations were made of the amount of ferrous ions produced at each location. Equations (1) and (2) were utilized to compute $\bar{I}$, and the results were expressed as the ratio of average probe intensity to the incident reactor wall intensity $\bar{I}/I_w$. The reactor wall intensity, previously determined by Williams and Yen (1973), was found to be 3.00×10^{-7} keinsteins $\cdot\ m^{-2} \cdot s^{-1}$ for a transparent reactor.

THEORETICAL MODELS

Experimental values of the point intensity were compared with theoretical predictions obtained from the following models:

Radial model:

$$(I/I_w)_{\text{radial}} = \frac{2R}{r} \tag{3}$$

Diffuse model:

$$(I/I_w)_{\text{diffuse}} = 3.14, \quad \text{for all } r \tag{4}$$

Cylindrical source model:

$$(I/I_w)_{\text{cylinder}} = \int_o^{z'} \int_o^{2\pi} \frac{R d\psi\, dz}{R^2 + r^2 + z^2 - 2Rr\cos\psi} + \int_o^{L-z'} \int_o^{2\pi} \frac{R\, d\psi\, dz}{R^2 + r^2 + z^2 - 2Rr\cos\psi} \quad (5)$$

Equation (5) represents a special case of the cylindrical source model which has been presented in detail elsewhere (Zolner and Williams, 1971). The distinctive feature of the model in this instance is the location of a directionally independent emitting source at the surface of the transparent reactor $r = R$. The radiation flux can be computed at any radial r and axial z' position within the transparent reactor by integration of Equation (5). An analytic solution of Equation (5) is available for all values of z' at the radial position, $r = 0$:

$$(I/I_w)_{\text{cylinder}} = 2\pi \left[\arctan \frac{z'}{R} + \arctan \frac{L - z'}{R} \right] \quad (6)$$

The probe window area lies in the range 25.7 cm $\leq z' \leq$ 35.7 cm, and it can be easily shown that the axial variation of radiation flux at $r = 0$ is less than 0.08% in that range. Therefore, the radial distribution of the point intensity for this situation can be well represented by values at the axial center of the reactor where $z' = L/2$, or in this case 30.7 cm. For $z' = L/2$, Villermaux and Roger (1977) have shown that Equation (5) can be transformed into an elliptic integral of the first kind and expressed as

$$(I/I_w)_{\text{cylinder}} = \int_o^{\tau_o} \frac{du_o}{(1 - k_o^2 \sin^2 u_o)^{1/2}} \quad (7)$$

EXPERIMENTAL RESULTS

Experimental and theoretical values of I/I_w are presented in Table 1. The experimental results are not satisfactorily explained by any of the three models. The radial model exhibits a declining intensity profile from the radial center but greatly underestimates the intensity at all positions other than the radial center. The diffuse model severely underestimates the magnitude of the interior intensities and does not predict the intensity decline toward the wall. The cylindrical source model incorrectly predicts that the intensity increases from the radial center to the wall, but absolute magnitudes are much better predicted than in the case of either the radial or diffuse model.

Some conclusions, based on the experimental data, are evident. The diffuse model underestimates the interior intensities by nearly an order of magnitude and can not possibly represent the mechanism by which radiation is transmitted through the reactor. The experimental intensities show a decline near the wall which is qualitatively consistent with a radial model. As a consequence, it is likely that the incident flux possesses a strong, radial directed component. This is not surprising, since the reflector consists of an elliptically shaped, Alzak aluminum surface designed to specularly reflect light which originates from the lamp, radially into the reactor.

Table 1. Experimental and Theoretical Radial Intensity Distribution for a Transparent Reactor

Probe location radius, mm	Experimental	I/I_w Radial	Diffuse	Cylindrical
0	26.54	∞	3.14	19.23
2.58	26.17	9.61	3.14	19.44
5.75	20.32	4.31	3.14	20.42
8.91	16.70	2.79	3.14	22.87
11.5	14.70	2.17	3.14	29.36
12.5	—	2.00	3.14	∞

The fact that observed intensities exceed intensities computed from the two-dimensional models indicates that a given interior point in the reactor cross section receives radiation from the entire surface of the reactor tube. This conclusion is supported by the fact that the cylindrical source model is superior in its ability to predict the magnitude of interior intensities.

These results strongly suggest that photoreactions conducted under conditions of low optical density, such as gas phase reactions, can not be accurately described in terms of the two-dimensional light intensity distribution models. Differences of predicted intensity among models are expected to be much less for strongly absorbing solutions than they are for a transparent reactor. In absorbing solutions, an interior point, near the radial center of the reactor, can effectively see only a very narrow region of the reactor wall. Thus, two-dimensional models will tend to correctly predict the relative shape of the intensity profile near the radial center. In addition, these models, which direct the incident flux along the shortest path to deeply placed interior positions, will tend to overestimate the absolute intensities at such points. Speculation on this point is supported by the work of Williams (1976) in which the application of two-dimensional models was found to predict higher conversions than were experimentally observed in the subject reactor.

In conclusion, it is expected that the application of a two-dimensional incident model will underestimate true reaction rates at low optical densities and overestimate them at medium to high optical densities. Clearly, intermediate optical densities exist such that the predictive capabilities of two-dimensional models will be quite good when applied under fortuitous conditions.

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NOTATION

$[Fe^{+2}]$ = molar concentration of ferrous ions in exposed actinometer solution, kmole · m^{-3}
I_a = volumetric rate of light absorption, keinsteins · $m^{-3} \cdot s^{-1}$
$\bar{I}$ = average light intensity in cross section of probe, keinsteins · $m^{-2} \cdot s^{-1}$
I_w = incident wall intensity, keinsteins · $m^{-2} \cdot s^{-1}$
k_o^2 = $4Rr/(R + r)^2$
L = length of photoreactor, m
r = radial position in reactor cross section, m
R = radius of reactor, m
t = exposure time, s
u_o = arctan $(z/R - r)$
V_p = volume of solution within exposed probe window, m^3
V_s = volume of actinometer solution maintained in closed loop circulation system, m^3
Φ = quantum yield of actinometer, kmole · $keinsteins^{-1}$
τ_o = arctan $[L/2(R - r)]$

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Mass Transfer in Laminar Flow With Linear Wall Resistance—Entrance Region Solutions

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Numerous workers (Colton et al., 1971; Kooijman, 1973; Davis, 1973; Cooney et al., 1974; Walker and Davies, 1974) have analyzed the problem in which a fully developed laminar flow, between parallel plates or in a tube, encounters a mass transfer section where the flux to the wall is proportional to the wall concentration. For constant properties, low transfer rates, and negligible axial diffusion, the concentration profile is governed by

$$v_\xi^*(\eta)\frac{\partial\theta}{\partial x} = (\nabla^2\theta)_\eta \tag{1}$$

with

$$\theta = 1 \quad @ \quad x \leqq 0, \quad \text{all } \eta \tag{2}$$

$$\frac{\partial\theta}{\partial\eta} = 0 \quad @ \quad \eta = 0, \quad \text{all } x \tag{3}$$

and

$$\theta = -\epsilon\frac{\partial\theta}{\partial\eta} \quad @ \quad \eta = \pm 1, \quad x \geqq 0 \tag{4}$$

where

$$x = \frac{(\xi/h)}{Pe} \tag{5}$$

The dimensionless axial velocity $v_\xi^*(\eta)$ is parabolic in η. The parameter ϵ is defined as

$$\epsilon = D/kh = 1/Sh_w \tag{6}$$

The Peclet number is defined here as $Pe = [h < v_\xi > /D]$ for parallel plates and as $Pe = [4h < v_\xi > /3D]$ for cylindrical tubes.

In the exact solution, many eigenfunctions are required for accuracy at small x. For example, Walker and Davies' solution, with six eigenfunctions, is not adequate for $x < 0.05$. Accordingly, several workers (Colton, 1971; Pancharatnam and Homsy, 1972; Friedman, 1976) have derived entrance-region solutions. These Lévêque types of solutions may be accurate only for $x < 0.01$, as found by Newman (1969) for the cylindrical case with $\epsilon = 0$. We present here an extended entrance-region solution for x up to 0.1 and significant wall resistance ($\epsilon > 1$).

ENTRANCE-REGION SOLUTIONS

In the mass transfer entrance region, the velocity profile is linear within the diffusion layer, and curvature may be neglected. The approximate differential equation for small x becomes

$$3y\frac{\partial\theta}{\partial\bar{x}} = \frac{\partial^2\theta}{\partial y^2} \tag{7}$$

where

$$y = (1-\eta)/\epsilon \tag{8}$$

and

$$\bar{x} = x/\epsilon^3 \tag{9}$$

Boundary conditions (2) and (4) become

$$\theta = 1 \quad @ \quad \bar{x} = 0 \tag{10}$$

and

$$\frac{\partial\theta}{\partial y} = \theta \quad @ \quad y = 0 \tag{11}$$

The third boundary condition, Equation (3), is approximated by

$$\theta \to 1 \quad \text{at} \quad y \to \infty \tag{12}$$

The solution of this problem may be obtained by Laplace transformation. The wall concentration resulting from inversion is

$$\theta_w(\bar{x}) = \frac{b\sqrt{3}}{2\pi}\int_0^\infty \frac{r^{-2/3}e^{-\bar{x}r}dr}{r^{2/3} + br^{1/3} + b^2} \tag{13}$$

where $b = 0.95109834$. We have evaluated this integral by Romberg integration, and the result is plotted in Figure 1.