ESTIMATION OF PARAMETERS USED IN A LIGHT SCATTERING MODEL FOR A SOLID-LIQUID PHOTOREACTION SYSTEM

TOSHIYUKI YOKOTA, YASUYUKI TAKAHATA, YUKIO OHTO AND KOJI TAKAHASHI
Department of Chemical Engineering, Yamagata University, Yonezawa 992

***Key Words*:** Heterogeneous Photoreaction, Light Scattering, Random Walk Model, Monte Carlo Method, Photoreactor

Introduction

The statistical approach is one of the most useful techniques for assessing the light absorption rate in a heterogeneous photoreacting system. Spadoni *et al.*[2] solved a radiant energy balance equation using the Monte Carlo method to obtain the local light absorption rate, and Koizumi *et al.*[1] extended the method for evaluation of the radiant energy absorption rate in a fermentor of photosynthetic bacteria. We have also proposed a statistical random-walk model to predict the radiation energy distribution in a heterogeneous solid-liquid photoreactor.[3] The model assumed that scattering light rays would

Received November 4, 1988. Correspondence concerning this article should be addressed to T. Yokota.

travel along one of the six Cartesian coordinate directions randomly (see **Fig. 1(a)**); p_f was the probability for forward travel of a ray after collision, whereas the probability for each of the other directions was simplified to be $1/5(1-p_f)$ (see Fig. 1(b)). Another parameter τ represented light intensity decrease after collision (see Fig. 1(c)). By the restriction of tavel directions the simulation program for light scattering became very simple and easy to apply for a reactor with any boundaries. The model could express nonisotropic scattering by the model parameter p_f and the light absorption according to particles by the parameter τ. Details of the model developed were described elsewhere.[3]

In this study we related quantitatively the two model parameters to optical properties of solid particles, by investigating the relationship between the parameter p_f and the relative refraction of liquid to solid, and the relationship between the parameter τ and the diffuse reflectance of solid particles. The solid particles considered here were transprent or translucent ones. In heterogeneous photosensitizing reactions such solid particles are often used as supporting particles for the dye sensitizer, and therefore are of practical importance. Particles coated by the dyes, which could be utilized as sensitizer, were also examined to assess the model parameters.

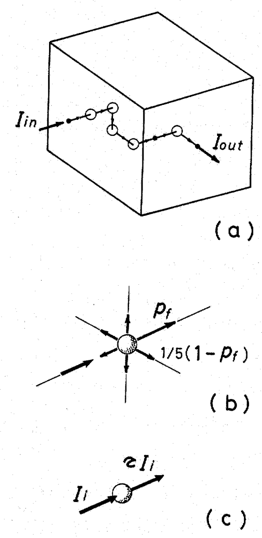

Fig. 1. Random-walk model and model parameters

1. Experimental

We adopted a relative refractive index and a diffuse reflectance as measurable optical porperties of particles. The solid-liquid systems examined first were silica gel particle—carbon tetrachloride and acrylic resin bead—benzene, which are popular pairs used for photosensitized reactions. These systems took certain values of relative refractive index defined as

$$N = n_l / n_s \tag{1}$$

To get other values of relative refractive index, we used pairs of resin bead and water-ethanol mixture or benzen-phenol mixture; of silica gel particles and water, benzene or carbon disulfide; and other combinations such as glass particles in aqueous solutions of zinc chloride. The solid refractive index was measured by the immersion method and the liquid refractive index by Abbe's refractometer. The relative refractive index ranged from 0.85 to 1.15.

To obtain colored particles we impregnated solid particles (resin bead and silica gel particles) with a dye solution (rose bengal, eosin yellow and methylene blue dye solution) for several hours in a rotavapor at room temperature. Supported dye quantity was determined by colorimetric analysis of the mother liquids. The diffuse reflectance of the colored particles R_λ was measured at each wave length using an integrating sphere photometer. Because an incident light energy spectrum must be considered, the average reflectance over a wave length range was defined as

$$R = \sum_{\lambda} R_\lambda (F_\lambda / F_t) \tag{2}$$

The value of R could be changed by controlling the quantity of dye coated on solid particles.

We determined the model parameters p_f and τ by measuring intensities of light rays which escaped from the rear face and a side face of an irradiated cubic cell (20 mm × 20 mm × 20 mm) containing a solid-particle suspension. The experimental apparatus was almost the same as that used in the previous study.[3] The light intensity was measured by a selenium photocell with white diffuse plate instead of the chemical actinometer used in the previous experiments.[3] The validity of this physical measurement was assessed in advance by comparison with the results from chemical actinometric measurement. The procedure of parameter estimation was the same as described before.[3]

2. Results and Discussion

The parameter p_f, which represents a directional index for light scattering, is related to the relative refraction index of liquid-solid phase. **Figure 2** shows the results. All kinds of particles show the same property except acrylic resin particles (Amberlite XAD-7). Amberlite XAD-7 particles sucked liquid into micropores and swelled. When it was suspended in a liquid with low refractive index, many refraction surfaces were formed inside the particle. Then a light beam passed into the particle was refracted and reflected many times at the inside surfaces, thus giving an opaque appearance to the particle. Therefore, the data for Amberlite XAD-7 were differerent from those for other transparent particles in a region of low

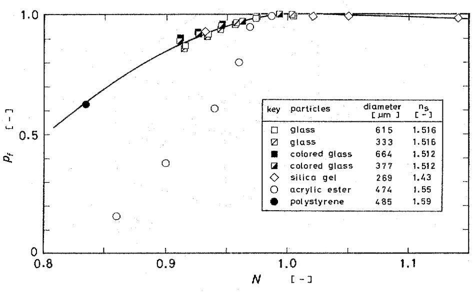

Fig. 2. Relationship between parameter p_f and relative refractive index

relative refraction index. The data for polystyrene particle-water suspension given in the previous work[3] are also shown in Fig. 2. The solid curve in the figure is the result of data fitting except for the data of XAD-7. It can be expressed by the following two equations.

$$p_f = 1 - 7.8(1-N)^{1.7} \quad \text{for} \quad N<1 \tag{3}$$

$$p_f = 1 - 0.5(N-1)^{1.7} \quad \text{for} \quad N>1 \tag{4}$$

Figures 3(a), (b) and **(c)** show relationships between the light intensity decrease parameter τ and diffuse reflectance of particles. Here the value of τ was determined using the value of p_f for each solid-liquid system shown in Fig. 2 (p_f for no dye-coated particles).

When a light beam with intensity I_o irradiated particles coated by dye, a following equation holds.

$$I_o = I_a + I_r + I_t \tag{5}$$

Here I_a is intensity of light absorbed, and I_r and I_t are respectively the intensities of light reflected and transmitted through the particles layer.

Then

$$R = I_r/I_o$$
$$= 1 - (I_a/I_o + I_t/I_o) \tag{6}$$

For supporting particles with no dye coating the portion of light absorption is very small compared to those of light reflection and transmission.

$$R_o = 1 - I_t^o/I_o \tag{7}$$

Here we assume that light absorption by colored particles has the following relation to the model parameter τ:

$$I_a/I_o = (1-\tau)^m \tag{8}$$

and that of light transmission is:

$$I_t/I_o = \tau(I_t^o/I_o) \tag{9}$$

Consequently, we obtain an equation from Eqs. (6), (7), (8), (9)

$$(1-R) = (1-\tau)^m + \tau(1-R_o) \tag{10}$$

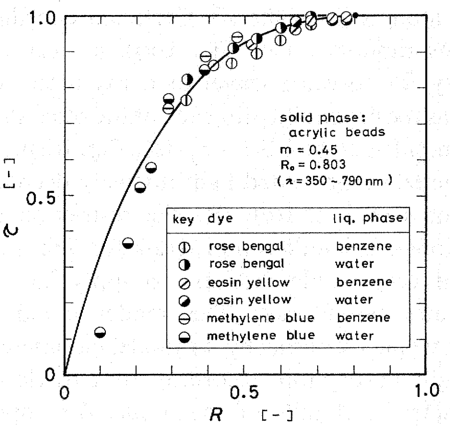

Fig. 3(a). Relationship between parameter τ and diffuse reflectance for acrylic beads

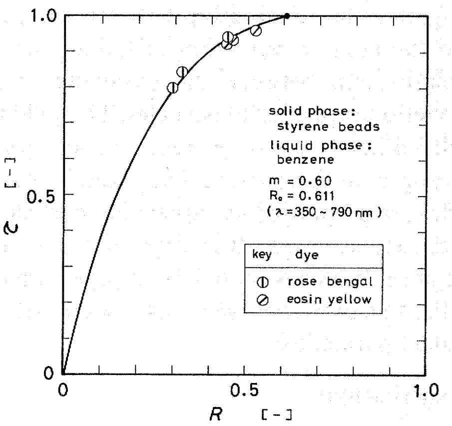

Fig. 3(b). Relationship between parameter τ and diffuse reflectance for styrene beads

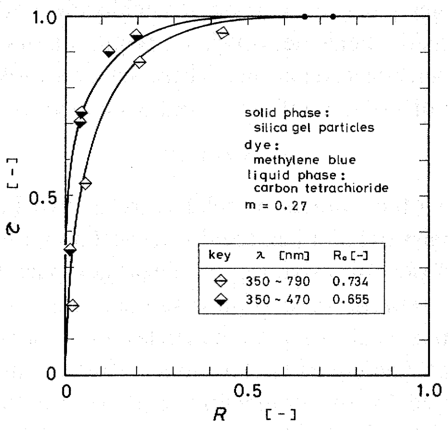

Fig. 3(c). Relationship between parameter τ and diffuse reflectance for silica gel particles

Here, m is a constant for particles without dye coating.

Equation (10) gave the solid curves in Figs. 3(a), (b) and (c). The constant m shown in each figure was determined to fit the experimental points, and R_o in the figure was the value measured for each supporting particle. The exponent m differed with particle quality: $m=0.45$ for acrylic resin particles XAD-7, $m=0.60$

for styrene resin particles XAD-4, and for silica gel particles $m=0.27$. In Fig. 3(c) the effect of the incident light spectrum is also shown. The half-closed points show the results for incident light in the 350–470 nm wave length range. The solid line for these points in Fig. 3(c) shows values predicted by Eq. 10, in which R_o was 0.655, measured in the narrow spectrum range and m was 0.27, obtained previously from the other data.

From the results above we conclud that Eqs. (3), (4) and (10) are useful in predicting the random-walk parameters for transparent or translucent particles from the optical properties of solid particles.

Nomenclature

F_λ/F_t	= spectral energy distribution of incident light	[—]
I_a	= absorbed light intensity	$[J \cdot m^{-2} \cdot s^{-1}]$
I_o	= incident light intensity	$[J \cdot m^{-2} \cdot s^{-1}]$
I_r	= reflected light intensity	$[J \cdot m^{-2} \cdot s^{-1}]$
I_t	= transmitted light intensity	$[J \cdot m^{-2} \cdot s^{-1}]$
I_t^o	= transmitted light intensity through supporting particles	$[J \cdot m^{-2} \cdot s^{-1}]$
m	= exponent used in Eq. (10)	[—]
N	= relative refractive index	[—]
n_l	= refractive index of liquid phase	[—]
n_s	= refractive index of solid phase	[—]
p_f	= probability of forward scattering	[—]
R	= reflectance averaged over a wave length range	[—]
R_o	= reflectance of supporting particles	[—]
R_λ	= reflectance at wave length λ	[—]
τ	= light intensity decrease parameter	[—]

Literature Cited

1) Koizumi, J., I. Yabe and S. Aiba: *Kagaku Kogaku Ronbunshu*, **5**, 644 (1979).
2) Spandoni, G., E. Bandini and F. Santarelli: *Chem. Eng. Science*, **33**, 517 (1978).
3) Yokota, T., Y. Takahata, H. Nanjo and K. Takahashi: *J. Chem. Eng. Japan*, **22**, 537 (1989).