

INDUSTRIAL PHOTOCHEMISTRY VIII: LIGHT REPARTITION IN HETEROGENEOUS CYLINDRICAL PHOTOREACTORS

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Summary

Several models of light repartition in homogeneous absorbing media have already been proposed in the literature. They are based on the general assumption that the light path is a straight line. However, for systems which both scatter and partially absorb light, this principle of optics is no longer realistic. As the scattering by a particle cannot be expressed by an analytical relationship, we have treated the modelling of light repartition in a scattering and absorbing medium using a Monte Carlo method. It is shown that the model is in satisfactory agreement with experimental results.

In particular, we show that a very simple analytical relationship can be proposed for the light repartition in a reactor of cylindrical symmetry, a relationship in which scattering and absorbing effects are separated.

1. Introduction

Although many fundamental research papers have appeared over the past ten years which are concerned with photoreactions which are either catalysed by solid catalysts or assisted by photosensitizers and are related in particular to the use of solar energy (see ref. 1 and references cited therein), there are very few examples of industrial photoreactions that are truly heterogeneous in nature. Such reactions are, for example, photochemical chlorination [2 - 6], nitrosation [7] and sulphoxidation [8]. For the last reaction, the system is a multiphase liquid stirred by a gas and this leads to complications.

In order to develop photochemical reactors and reactions in the laboratory using semiconductor particles and to get a better understanding of light repartition in industrial heterogeneous reactors, we have studied the influence of light-scattering solid particles on the irradiation light absorption profile. Knowledge of this profile is most essential for the design of photo-

reactors on both the laboratory and the industrial scale [9 - 12]. Most of the systems are commercial cylindrical lamps and this leads to the use of cylindrical reactors. This allows a reduction in the number of parameters which are required to describe the light separation in the experiments and the models to a single space parameter, the radius ρ .

In a previous paper [13] we proposed a methodology for studying a plane reactor filled with a single scattering medium. Starting from the results and the basic methods developed in this paper, we have been able to carry out a study of the light repartition $S(\rho)$ in a cylindrical photoreactor in which the medium both scatters and absorbs light.

The theoretical and experimental study reported in this paper shows that, under our optical conditions, the absorption follows a very simple law which is nearly exponential. Moreover, the parameter which expresses the flux decrease varies linearly with the concentrations of the scattering agent and the absorbing substance.

2. Monte Carlo simulation of the light distribution in a scattering and absorbing medium

When the system reaches a certain volume (determined by the scattering efficiency and the concentration of the particles), multiple scattering occurs [14] which leads to "re-emissions" which differ markedly from those observed for isolated particles. The main effects of the multiple scattering are complete scrambling of the scattering diagrams and a noticeable increase in backscattering [15].

Assuming that in an elementary volume dv the particle concentration is such that the emission from this volume can be considered as isotropic, we carried out a simulation of the light repartition for a reactor (shown in Fig. 1) in which the light enters the reactor in the plane defined by the lamp axis and the angle α_0 (owing to the cylindrical symmetry, α_0 can be taken as zero).

The initial direction for a mercury lamp of practically negligible radius can be expressed by the Lambert law [16] (*cf.* Fig. 1)

$$P(\varphi_0) = \cos \varphi_0$$

Photons travelling in the reactor along a direction characterized by the angles θ and φ continue in this direction unless they meet a scattering particle; they then travel along a new direction characterized by the new angles θ' and φ' and this process is repeated until they are absorbed.

2.1. Case of a non-absorbing scattering solution

Let us define the probability p ($0 < p < 1$) for a photon to be scattered along a distance Δr taken as an elementary path inside the reactor. Initially, a photon enters the reactor perpendicularly to the entrance window. For each step Δr a random number x ($0 < x < 1$) is taken and compared with p

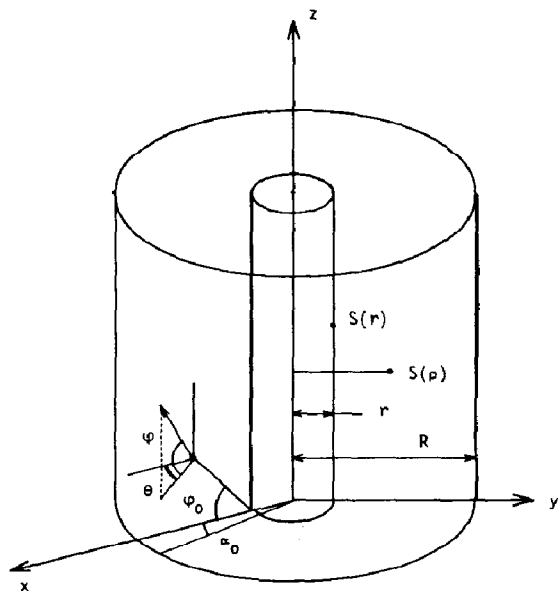


Fig. 1. Light repartition in a cylindrical reactor.

(Monte Carlo method). If $p < x$ the direction is conserved, but if $p > x$ the new direction is given by angles θ' and φ' . If the photon leaves the reactor it is considered as lost and a new assay is carried out.

We consider that a photon which reaches the distance $R = 200 \Delta r$ has a negligible probability of coming back into the zone of interest ($0 - 30 \Delta r$). Further calculations have been carried out using different maximum distances ($R = 150 \Delta r$ and $R = 250 \Delta r$) and these show that R has a very small influence on the variation in the light intensity $S(\rho)$ with the distance ρ to the entrance window of the cylindrical reactor.

If $\rho < r$, light enters the source. We then calculate the point at which the light beam crosses the cylinder which forms the irradiation system. The angle between the line and the horizontal half-line passing through the z axis and the beam-lamp crossing point define a θ value; φ is unchanged (except for the sign) and, through an axis rotation, we start again with $x_0 = r$ and $y_0 = z_0 = 0$.

By following the flow chart shown in Fig. 2, it is possible to determine the variations in $S(\rho)$ if the scattering law is known. We have chosen for this law a secondary emission around a grain, independent of the incident direction. The corresponding variations in $\rho S(\rho)$ vs. ρ are represented in Fig. 3. Light confinement inside the reactor leads to an increase in $S(\rho)$, and this is contrary to what happens in a transparent medium in which $S(\rho)$ is constant. This simulation enables us to show that the product $S(\rho)$ can be expressed in the region of interest by a simple law such as

$$\rho S(\rho) = A_0 + B_0 \exp\left(-\frac{\rho}{c_0}\right)$$

(see Fig. 3).

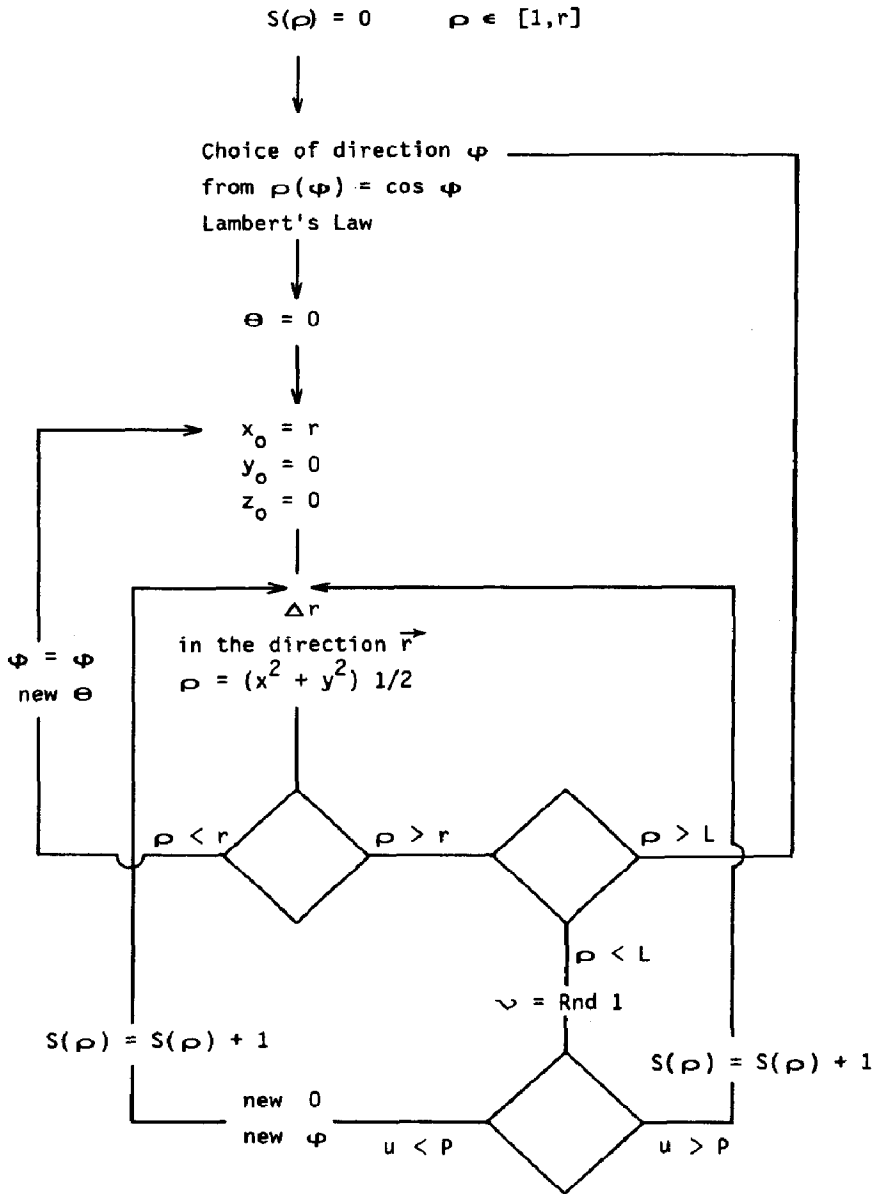


Fig. 2. Flow chart for the Monte Carlo program (p , diffusion probability).

2.2. Case of a scattering and absorbing medium

It is possible to include in the procedure a number p' between 0 and $(1 - p)$ which defines the probability for the photon to be absorbed by a layer of liquid of thickness Δr .

The program runs as described above except that the decision step related to a random number is now as follows: if $0 < x < p$ there is scattering; if $p < r < 1 - p'$ there is no scattering; if $1 - p' < x < 1$ the photon is absorbed and a new assay is started.

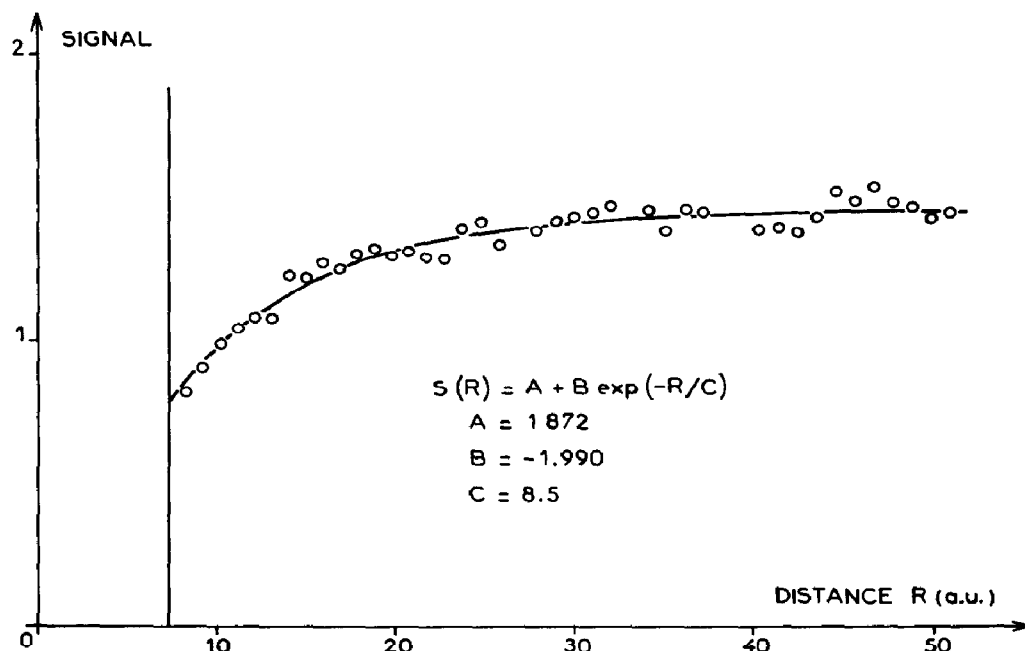


Fig. 3. Monte Carlo simulation of the variations in $\rho S(\rho)$ vs. ρ ($p' = 0.1$).

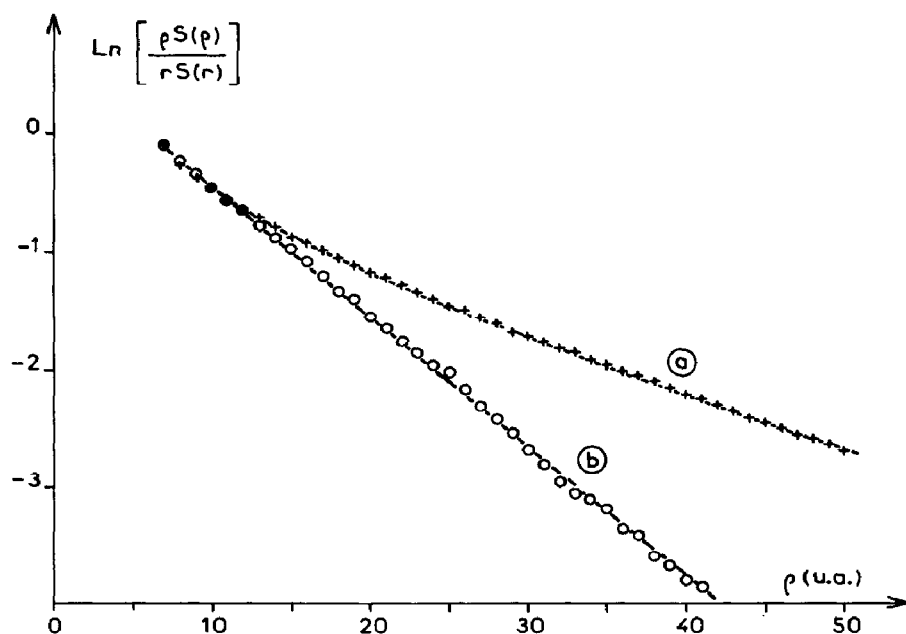


Fig. 4. $\ln\{\rho S(\rho)/r S(r)\}$ vs. ρ for a scattering and absorbing medium with $p' = 0.04$; curve a, $p = 0$; curve b, $p = 0.1$.

Figure 4 shows the results of a few simulations corresponding to different values of p' . Contrary to the case where no absorption occurs, it appears possible to represent approximately the light repartition in the medium by an exponential law such as

$$\ln \left\{ \frac{\rho S(\rho)}{r S(r)} \right\} = -A(\rho - r)$$

where A is a parameter characteristic of the absorbing and scattering substance.

Figure 4 also shows the effect of scattering by particles which, by increasing the light path in the medium, leads to an absorption larger than would be expected from the Beer-Lambert classical absorption law.

2.2.1. Variations in A with the optical parameters

By carrying out different assays for various values of p and p' , we can study the influence of the scattering particles on the value of A , the important parameter which defines the light repartition in a cylindrical reactor. Figure 5 shows the variations in A vs. p and p' . As soon as the medium is slightly absorbing ($p' > 10^{-2}$), A varies linearly with p' . There are in fact two distinct domains of light repartition corresponding to two distinct laws: that where p' is practically zero and where $\rho S(\rho)$ does not vary linearly with ρ

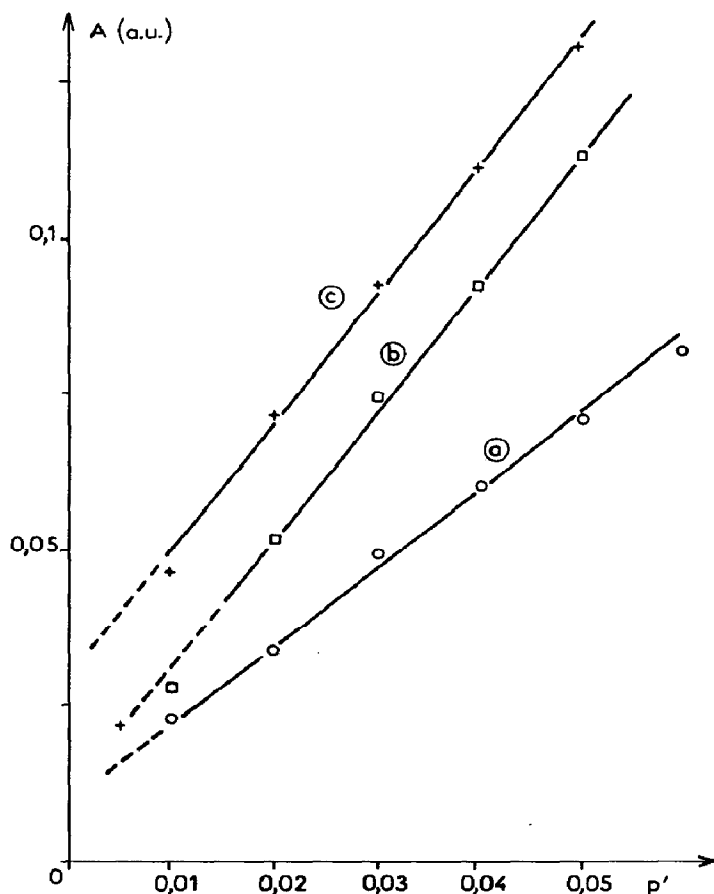


Fig. 5. A vs. p' for various values of p : curve a, $p = 0$; curve b, $p = 0.05$; curve c, $p = 0.1$.

and that where $p' > 0.01$ where $\rho S(\rho)$ varies exponentially with the distance to the lamp axis. Thus an intermediate domain can be found which is difficult to describe. However, this description is not fundamental as experimental conditions corresponding to very low absorption ($p' < 0.01$) are actually outside the range of conditions usually employed in industrial photochemistry.

Figure 5 shows that there is a difference in behaviour whether the medium is scattering or not. In particular, the larger the value of p , the larger is A , which is easily understood considering the corresponding increase in the optical path in the reaction medium. As soon as the medium is scattering, the variations in A with p' are identical; this can be expressed in the modelling by allowing p and p' to influence A independently. This means that A can be expressed by a relationship such as

$$A \approx f_1(p) + f_2(p')$$

f_1 and f_2 may correspond to linear relationships.

The aim of the experiments described below is to show the validity of the modelling given above.

3. Experimental testing of the model

3.1. Experimental set-up

3.1.1. Light detector

In an absorbing and scattering medium the light intensity at a given distance ρ from the reactor axis can be decomposed into two components, one corresponding to incident light that has been neither scattered nor absorbed, and one corresponding to scattered light coming from all directions. The light detector used in the work described in ref. 16 is designed to carry out an oriented detection and cannot be used in this instance because of the large number of measurements which would have to be taken (an integration over θ , φ and ρ). Moreover, it would be physically impossible to use this detector under some conditions, especially for values of φ greater than $\pi/2$.

To design a photoreactor in such a medium, it is vital to know the number of photons absorbed in an elementary volume, and this is proportional to the light repartition. Thus we used a detector with an integrating sphere (this has been described previously in ref. 13). This detector uses a scattering sphere of diameter 3 mm which simultaneously measures both the direct and the scattered light with the same sensitivity (*cf.* Fig. 6). The sphere is fixed at one end of a fibreglass rod. The other end contains a light-dispersing device which allows the wavelength of interest to be selected (*cf.* Fig. 7).

3.1.2. Heterogeneous photochemical reactor

The light emitted by the mercury lamp (a tube of diameter 6 mm and length 150 mm) reaches the detector and this transmits it through a glass fibre to a monochromator which selects the wavelength of interest and

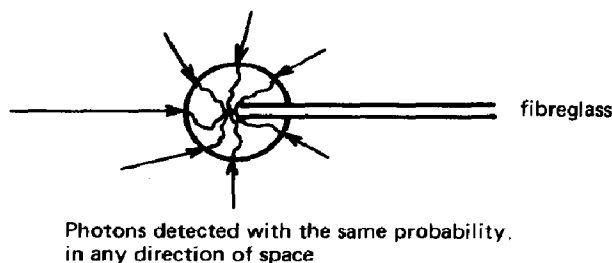
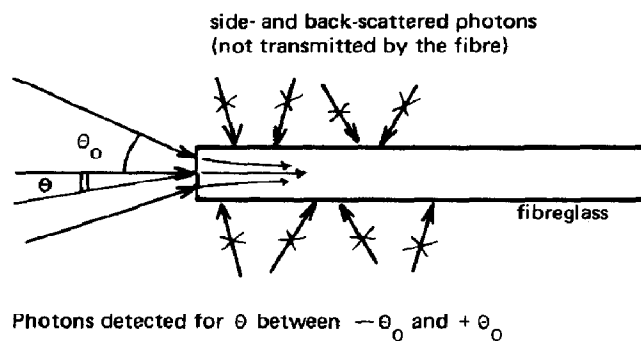


Fig. 6. Comparison of the two types of light detector.

passes it to a photomultiplier whose output signal feeds an amplifier and a recorder.

The scattering and absorbing medium was an aqueous suspension of titanium oxide (scattering TiO_2 crystal) and a solution of sodium dichromate (absorbing $\text{Na}_2\text{Cr}_2\text{O}_7$ salt). Problems which arise when preparing the TiO_2 suspension have been reported previously in ref. 13.

The reaction vessel was a cylindrical tank of equal diameter and height (25 cm).

Macroscopic homogeneity was achieved using a bladed propeller to stir the medium. A monitored resistance maintained the medium at a constant temperature of about 50°C which ensured that the emission of the lamp was intense and stable.

The position of the detector in the medium can be adjusted using the mechanical device reported in refs. 9 - 11 and 13 which allows translation along the three space axes.

3.1.3. Experimental conditions

For each solution we measured the flux of light from the lamp by moving the detector away from the source to up to a distance of 30 - 60 mm depending on the absorption conditions (*i.e.* until the flux can be no longer measured with satisfactory precision).

All the measurements made in this study were carried out at a wavelength of 436 nm.

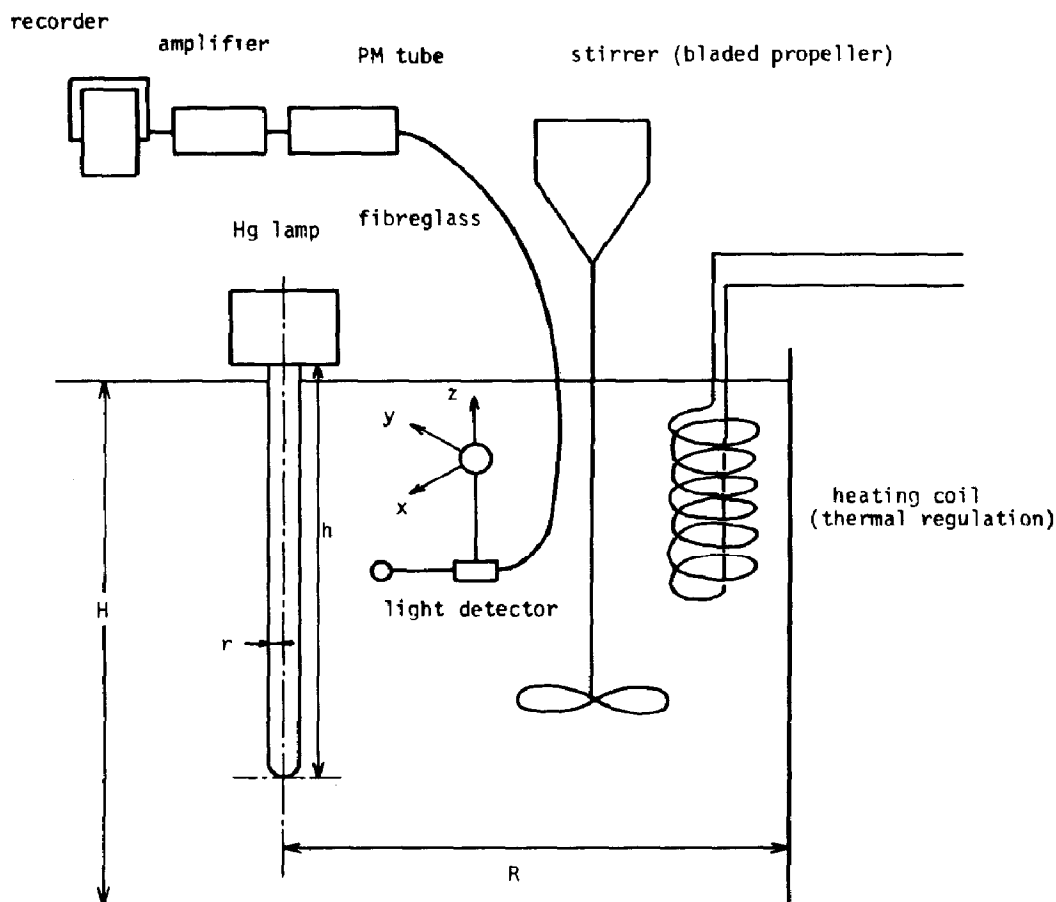


Fig. 7. Experimental set-up.

3.2. Experimental results

The signal $S(\rho)$ of the recorder, for each point in the medium at a distance ρ from the lamp axis, is proportional to the light flux (in einsteins per square metre per second) transmitted by the detector to the fibreglass, to the transmission of the monochromator and to the sensitivity of the light transducer and the amplifier. Taking into account the cylindrical symmetry of the system, the light intensity (i.e. the number of photons which reach the surface of a fictitious cylinder of radius ρ coaxial with the lamp, per unit of time, in einsteins per second) is proportional to the product $\rho S(\rho)$; this light intensity is the only parameter of interest, especially for photochemical applications, so all the results given below are expressed in terms of the variations in $\rho S(\rho)$ with ρ .

3.2.1. Medium which only scatters light (pure TiO_2)

We have shown through Monte Carlo simulation that $S(\rho)$ can be expressed by the equation

$$\rho S(\rho) = A_0 + B_0 \exp\left(-\frac{\rho}{C_0}\right)$$

where A_0 , B_0 and C_0 are constants of the system.

Now, as shown in Fig. 8 which gives the result of experimental measurements of light distribution in a scattering medium containing TiO_2 , $\rho S(\rho)$ agrees very well with the theoretical model.

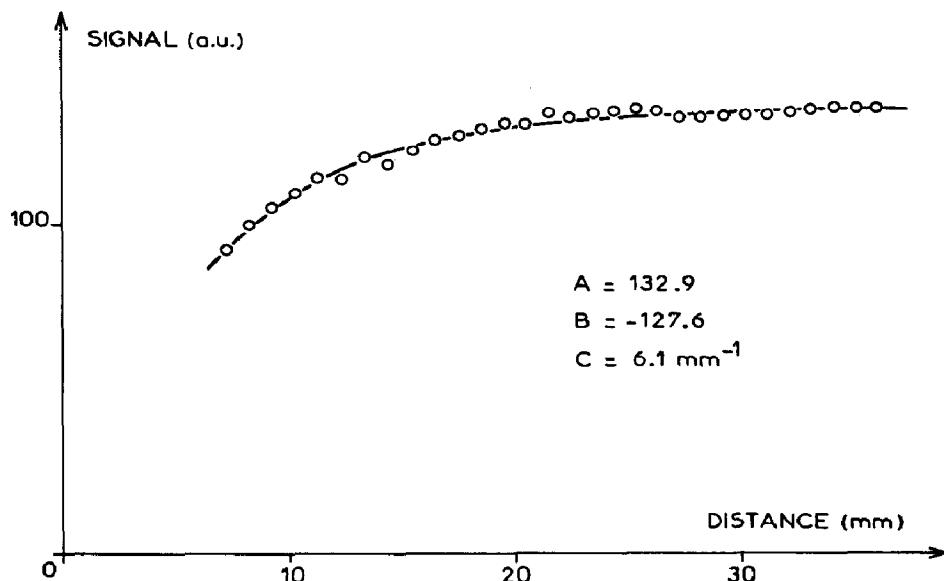


Fig. 8. $\rho S(\rho)$ vs. ρ for $\lambda = 436 \text{ nm}$ and $[\text{TiO}_2] = 2.70 \text{ g l}^{-1}$.

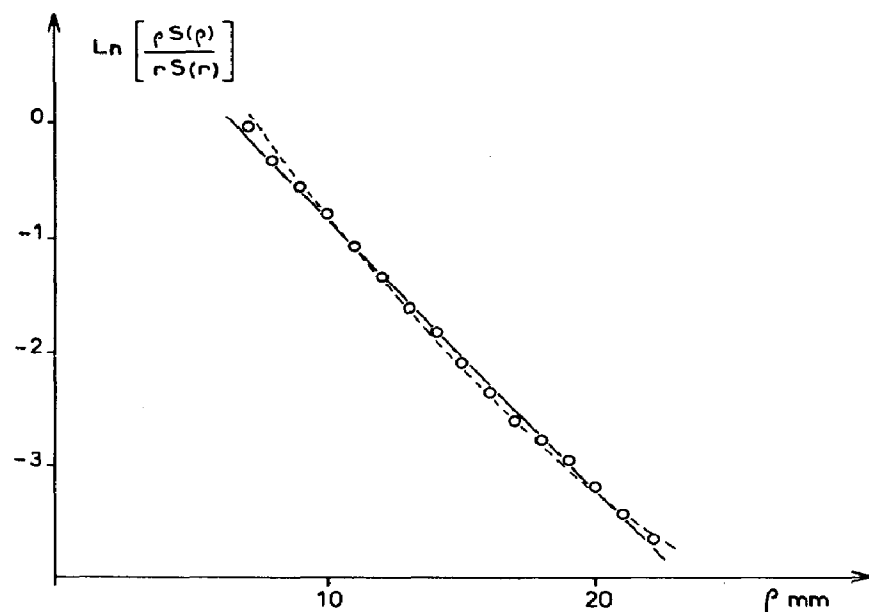


Fig. 9. $\text{Ln}\{\rho S(\rho)/r S(r)\}$ vs. ρ for an absorbing medium (optical density at excitation wavelength, 1). The straight line is the linear relationship.

However, an extended analysis of the measurements concerning the case of light scattering alone is not the main object of this work as no light is absorbed. The main aim of such measurements is to show the agreement between model and experiment.

3.2.2. Medium which only absorbs light

Although we have shown in ref. 9 that $\rho S(\rho)$ vs. ρ does not follow a truly exponential law, Fig. 9 shows that $\ln\{\rho S(\rho)\}$ vs. ρ can be satisfactorily represented by a straight line.

The results shown here are in agreement with those previously reported in ref. 17.

3.2.3. Medium which both absorbs and scatters light

In agreement with the models given in Section 2, $\ln\{\rho S(\rho)/rS(r)\}$ vs. ρ can be represented by a linear relationship as shown by the experimental data plotted in Fig. 10.

3.3. Interpretation of the experimental results and discussion

The models described in Section 2 correspond very well to reality, as shown by the variations in $\ln\{\rho S(\rho)/rS(r)\}$ vs. ρ in an absorbing medium;

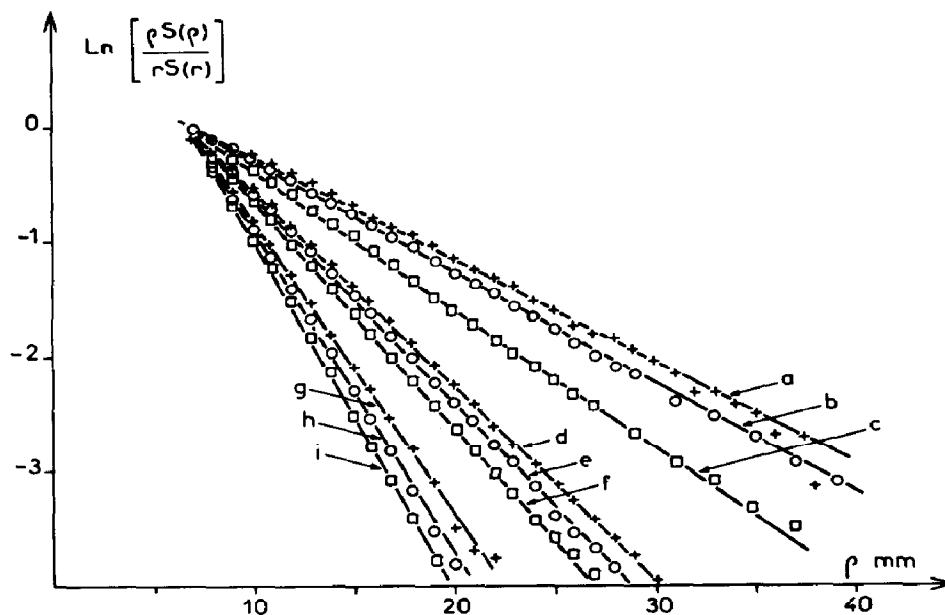


Fig. 10. $\ln\{\rho S(\rho)/rS(r)\}$ vs. ρ in an absorbing and scattering medium. Absorption: curves a, b and c, $OD_{\text{Na}_2\text{Cr}_2\text{O}_7} = 0.3$; curves d, e and f, $OD_{\text{Na}_2\text{Cr}_2\text{O}_7} = 0.6$; curves g, h and i, $OD_{\text{Na}_2\text{Cr}_2\text{O}_7} = 1$. Scattering: curves a, d and g, $[\text{TiO}_2] = 0.061 \text{ g l}^{-1}$; curves b, e and h, $[\text{TiO}_2] = 0.145 \text{ g l}^{-1}$; curves c, f and i, $[\text{TiO}_2] = 0.272 \text{ g l}^{-1}$. ($[\text{TiO}_2] = 0.272 \text{ g l}^{-1}$ corresponds to an apparent absorbance of unity measured at 350 nm.)

the relationship

$$\ln \left\{ \frac{\rho S(\rho)}{r S(r)} \right\} = -A(\rho - r)$$

is obeyed, where A is a constant which depends on the concentration of both the scattering and the absorbing substances.

A has been determined for several concentrations of titanium oxide particles and for several concentrations of potassium dichromate. The results

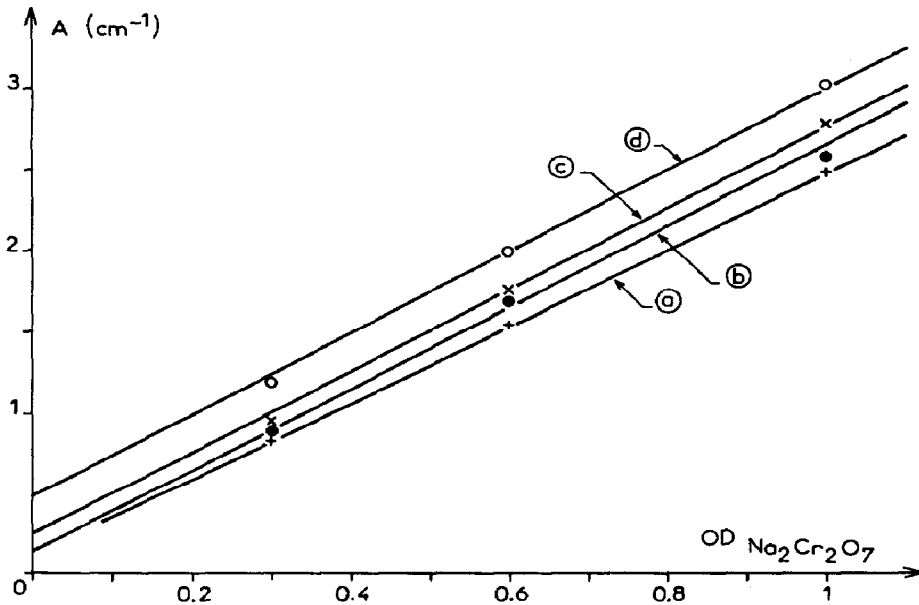


Fig. 11. A vs. the absorbance OD for various concentrations of TiO_2 : curve a, $[\text{TiO}_2] = 0$; curve b, $[\text{TiO}_2] = 0.061 \text{ g l}^{-1}$; curve c, $[\text{TiO}_2] = 0.145 \text{ g l}^{-1}$; curve d, $[\text{TiO}_2] = 0.272 \text{ g l}^{-1}$.

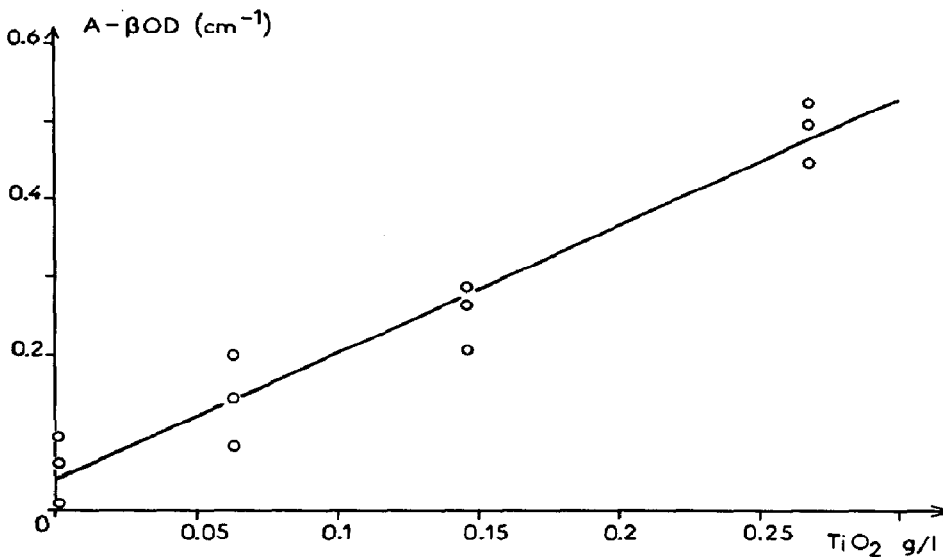


Fig. 12. $(A - \beta\text{OD})$ vs. $[\text{TiO}_2]$.

obtained are gathered in Fig. 11; they show that, within experimental error, there is a linear relationship between A and the absorbance OD.

We have also shown that the variations in A with the absorbance OD for different concentrations of scattering substance correspond, in agreement with the model simulations shown in Fig. 5, to nearly parallel straight lines, that is

$$A = f([\text{TiO}_2]) + \beta\text{OD}$$

where the parameter β and the function f are associated with the system, β being independent of the TiO_2 concentrations.

Not only has it been shown that the effects of absorption and scattering on A are independent, as predicted by the Monte Carlo simulation, but also that it is possible to express the variations in $(A - \beta\text{OD})$ for various values of OD and A . The results shown in Fig. 12 show that, within experimental error, $f([\text{TiO}_2])$ is a linear relationship. A can then be expressed by the simple law

$$A = \alpha_0 + \alpha_1[\text{TiO}_2] + \beta\text{OD}$$

with the following parameters obtained by least squares fitting: $\alpha_0 = 0.397 \times 10^{-3} \text{ cm}^{-1}$; $\alpha_1 = 1.635 \text{ cm}^{-1} \text{ l g}^{-1}$; $\beta = 2.48 \text{ cm}^{-1}$ (instead of 2.3 for the Beer-Lambert law [17]).

This law, which had been predicted by the modelling, clearly indicates the independence of the effects of $[\text{TiO}_2]$ and OD, the scattering and absorbing effects, on the value of A . This statement means in particular that there is no interaction (at least on the basis of the observed phenomena) between the scattering and the absorbing agents.

4. Conclusions

The experimental measurement of the light repartition in both absorbing and scattering media, together with the Monte Carlo models, show that it is possible to separate the effects of the absorption and the scattering of light on the absorption profile of the light in a cylindrical photochemical reactor. This absorption profile $S(\rho)$ can be represented by the following law:

$$\ln \left\{ \frac{\rho S(\rho)}{r S(r)} \right\} = -A(\rho - r)$$

with

$$A = \alpha_0 + \alpha_1[\text{TiO}_2] + \beta\text{OD}$$

where α_0 , α_1 and β are constants which probably depend on the actual reactor itself.

The study reported in this paper will enable us to design cylindrical photochemical reactors filled with heterogeneous media.

References

- 1 P. L. Yue, Studies of photoreactions in heterogeneous photoreactors, in M. Schiavello (ed.), *Photoelectrochemistry, Photocatalysis and Photoreactors*, Reidel, Dordrecht, 1985, pp. 575 - 585.
- 2 H. J. Schumacher, *Angew. Chem.*, 49 (1936) 613.
- 3 L. J. Governale and J. T. Clarke, *Chem. Eng. Progr.*, 52 (1956) 281.
- 4 G. Book and J. Eggert, *Z. Elektrochem.*, 29 (1923) 521.
- 5 W. H. Shearon, Jr., H. E. Hall and J. E. Stevens, Jr., *Ind. Eng. Chem.*, 41 (1949) 1812.
- 6 A. Tournier, *Ph.D. Thesis*, University of Nancy, 1982.
J. C. Andre, M. Niclause, A. Tournier and X. Deglise, *J. Photochem.*, 18 (1981) 57, and references cited therein.
- 7 B. B. Brown, Photochemical preparation of oximes, *U.S. Patent 2,719,116* (September 27, 1955).
Y. Ito, *Bull. Chem. Soc. Jpn.*, 29 (1956) 227.
- 8 N. Dellerio-Saint-Jean, *Diplôme d'Etudes Approfondies*, Institut National Polytechnique de Lorraine, Nancy, 1982.
- 9 A. Tournier, X. Deglise, J. C. Andre and M. Niclause, *AIChEJ.*, 28 (1982) 156.
- 10 J. C. Andre, M. L. Viriot, J. Villermaux and A. Tournier, *Entropie*, 107 - 108 (1982) 62.
- 11 J. Villermaux, J. C. Andre and M. Roger, *Prospectives en Photochimie Industrielle, January 5, 1984, Nancy*, in *Entropie*, 127 (1986) 4 - 7.
- 12 F. Cardon, W. P. Gomes and W. Oekeyser, *Photovoltaic and Photoelectrochemical Energy Conversion*, Plenum, New York, 1981.
M. Grätzel and V. H. Houlding, *J. Am. Chem. Soc.*, 105 (1983) 5695.
H. S. Wrighton, *Acc. Chem. Res.*, 12 (1979) 300.
K. Honda, A. Fujishima and T. Miyasaka, *Kagaku Zakan (Kyoto)*, 86 (1980) 23.
- 13 C. Braun and J. C. Andre, *J. Photochem.*, 28 (1985) 13.
- 14 J. C. Andre, C. Braun, J. F. D'Allest and F. Baros, *Symp. on Applied Modelling and Simulation, Nice, June 19 - 21, 1984*, Acta Press, Anaheim, 1984, p. 140.
- 15 M. C. van de Hulst, *Multiple Light Scattering*, Academic Press, New York, 1980.
- 16 J. C. Andre, M. Roger and J. Villermaux, *Chem. Eng. J.*, 31 (1985) 199 - 208.
- 17 J. C. Andre, A. Tournier, M. Niclause and X. Deglise, *J. Photochem.*, 18 (1981) 47.