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Actinometric and spectrophotometric study of the light interaction with aqueous suspensions of various solids

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Abstract

Light scattered by aqueous suspensions of various polycrystalline solids (quartz sand, calcium carbonate, kaolin and titanium dioxide) in a concentration range of three orders of magnitude (0.003–6 g dm^{-3}) was evaluated by means of a special actinometric device and with a UV–Vis spectrophotometer equipped with an integrating sphere. Spectrophotometric measurements of transmittance, turbidity and diffuse reflectance were performed in the spectral range 250–800 nm. On the other hand, monochromatic light ($\lambda = 365$ nm) scattered at various angles was evaluated using a special arrangement for ferrioxalate actinometries. A good correlation was obtained between physical parameters and chemical activities. Moreover, a maximum can be observed in the light intensity laterally scattered when the concentration changes. The position of this maximum depends on the nature of the suspended matter. The empirical exponential dependence analogous to Lambert–Beer law which has been proposed elsewhere is only valid for low scattering suspensions.

Keywords: Aqueous suspensions; Titanium dioxide; Light scattering; Chemical actinometry; Diffuse reflectance

1. Introduction

A major problem in the research area of photochemistry of heterogeneous systems is the determination of the quantity of photons absorbed by suspensions of polycrystalline solids. Knowledge of this parameter is of a great importance because the efficiency of photochemical processes must be evaluated on the basis of the absorbed photons and not, as sometimes done, on the basis of the total photon flow entering the photoreactor. Indeed, the amount of emitted photons is clearly independent of the specific features of the photoreacting system and therefore it can not be used in place of the photon absorption rate.

Palmisano et al. [1,2] proposed a simple experimental method for evaluation of the absorbed photon flow. It was based on an actinometric measurement of the photon flow transmitted by a suspension for different photoreactor thickness and various concentrations of the solid. They found an empirical exponential dependence analogous to the Lambert–Beer law. This fact was employed to extrapolate a limit value at zero concentration and so to estimate the backward-reflected photon flow.

The aim of the present work is to correlate physical parameters, namely transmittance, turbidity and diffuse reflectance, with chemical actinometries, and to study the influence of concentration of the suspension on scattered light (laterally, backwards and forwards) for various absorbing and non-absorbing solids in aqueous suspension. The validity of the empirical exponential law previously proposed for suspensions is discussed.

2. Experimental details

2.1. Reactants and suspensions

Four substances were studied in aqueous suspensions:

- titanium dioxide, Degussa P25
- calcium carbonate, < 5 μm, Prolabo (Rhône-Poulenc)
- kaolin, Fluka
- sand Fontainebleau, ground and sieved in order to keep < 50 μm.

A stock suspension of each solid (6 g dm^{-3}) was prepared and then diluted by 2, 4, 8, ···, 2^n ($n \leq 11$). These suspensions were employed to measure transmittance, reflectance, turbidity and chemical actinometries.

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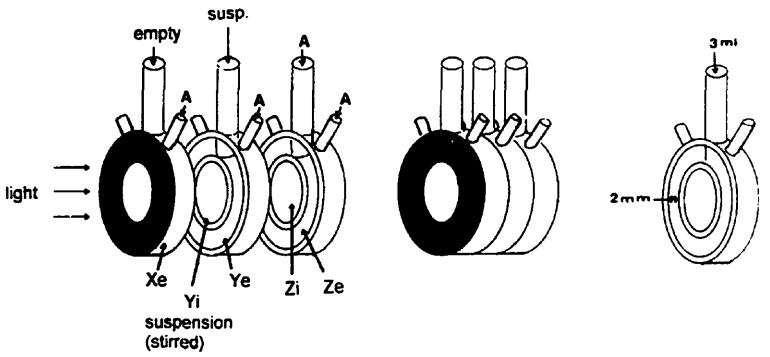

Fig. 1. Device for the chemical actinometry measurements.

2.2. Actinometries

The device used for chemical actinometry measurements consists of three cylindrical quartz cells with cooling space around as represented in Fig. 1. The outside compartment of each (X_e, Y_e, Z_e) and the central compartment of the last (Z_i) were filled with ferrioxalate actinometer. The central compartment of the intermediate cell (Y_i) was filled with the aqueous suspension, magnetically stirred and monochromatically irradiated in a homogeneous parallel beam at 365 nm. After irradiation, an aliquot volume of each compartment containing actinometer was sampled to evaluate the photon flow received by this compartment.

2.3. Spectrophotometry

Spectrophotometric measurements of the aqueous suspensions were performed on a Shimadzu UV–Vis Scanning Spectrophotometer UV-210PC equipped with integrating sphere (IRS 260). According to the cell position, transmittance, diffuse reflectance and turbidity can be measured with the same device (scheme on Fig. 2). The suspension is set in 'As' for transmittance, in 'Bs' for diffuse reflectance and in both 'Ar' and 'As' for turbidity measurements ('Bs' being open). A magnetic stirrer, Hellma CUV-O-STIR Model 333, was employed in the cases of transmittance and turbidity measurements when standard 1 cm spectroscopic cuvettes were used. For diffuse reflectance measurements, a cylindrical cell of the actinometric device described above without stirring was utilized (sedimentation of the solid during measurement was neglected). Before recording a spectrum, the corresponding numerical value at the wavelength 365 nm was read from the display. After recording the spectrum from 800 to 250 nm with the maximal speed for the data interval 0.5 nm and the slit 5 nm, the value on 365 nm was controlled once more. Differences between the first and second value were found to be negligible (maximum 2–3%). The turbidity measurement was not possible for the highest concentrations of titanium dioxide because of an excessive noise. No data for these concentrations were taken into account for the multiple regression analysis described below.

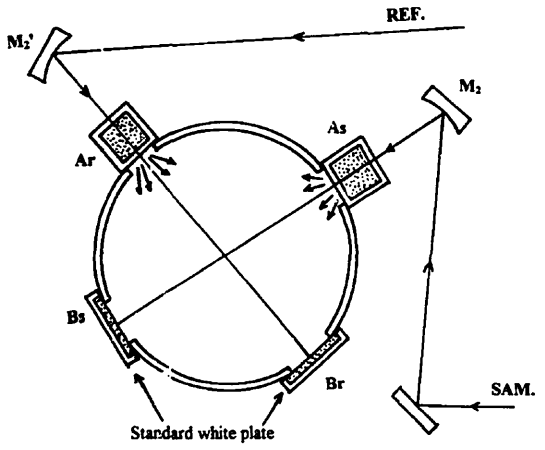

Fig. 2. Scheme of the integration sphere assembly.

3. Results

3.1. Chemical actinometries

As results of actinometric measurements, light intensities (numbers of photons absorbed per second in one milliliter of ferrioxalate solution) in each compartment (X_e, X_e, Z_e and Z_i) as a function of concentration for all the investigated solids (calcium carbonate, kaolin, titanium dioxide and quartz sand) and irradiation wavelength 365 nm were calculated. These numerical values (of an order of magnitude of 10^{15} photons $cm^{-3} s^{-1}$) for suspensions were divided by a sum of light intensities in compartments X_e, Y_e, Z_e and Z_i obtained for pure water so that relative values were obtained. These relative light intensities (multiplied by hundred to be percentages) are represented in the figures and were employed for the statistical treatment described below.

Experimental values of the relative light intensities in each compartment as a function of concentration are reviewed as

large open symbols in Figs. 3–6 for calcium carbonate, kaolin, titanium dioxide and quartz sand, respectively.

3.2. Physical photometric measurements

Numerical values of transmittance, turbidity and diffuse reflectance (in percentages) at 365 nm, as functions of concentration of investigated solids, were obtained as indicated in Section 2.3. These quantities characterize suspensions concerning light scattering. It can be assumed that there exists a direct relation between actinometric and photometric data because these both describe the same properties of an aqueous suspension. A statistical treatment of multiple regression was applied using both actinometric (relative light intensity as a dependent variable) and photometric (transmittance, turbidity and reflectance as independent variables) data to find parameters a, b_1, b_2 and b_3 of the equation

$$\text{light intensity} = a + b_1 \cdot \text{transmittance} + b_2 \cdot \text{turbidity} + b_3 \cdot \text{reflectance} \quad (1)$$

as a linear least-squares fit.

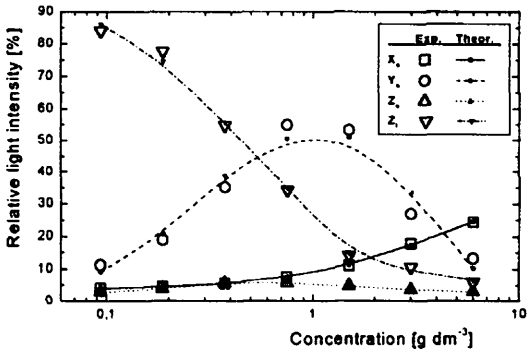

Fig. 3. Relative light intensities in particular compartments of the actinometric device as a function of concentration of aqueous suspension of calcium carbonate.

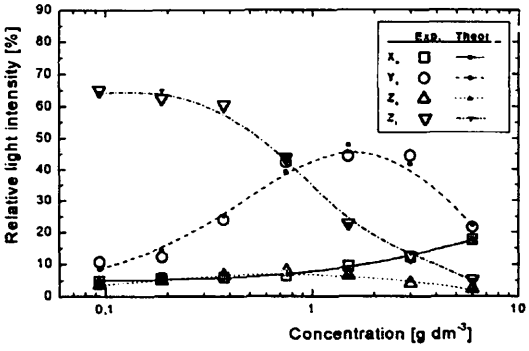

Fig. 4. Relative light intensities in particular compartments of the actinometric device as a function of concentration of aqueous suspension of kaolin.

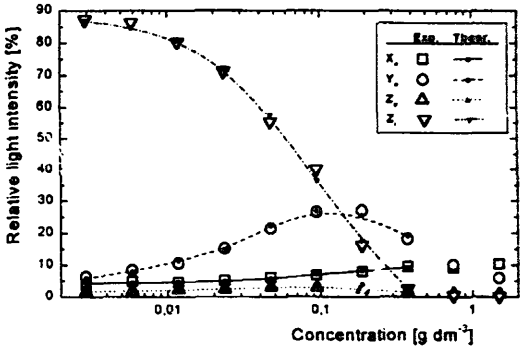

Fig. 5. Relative light intensities in particular compartments of the actinometric device as a function of concentration of aqueous suspension of titanium dioxide.

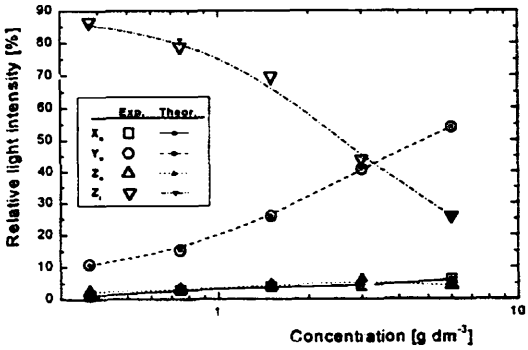

Fig. 6. Relative light intensities in particular compartments of the actinometric device as a function of concentration of aqueous suspension of quartz sand.

This procedure was applied first to treat data of each compartment, X_c, Y_c, Z_c and Z_i, for each solid separately. In this way, various sets of parameters a, b_1, b_2 and b_3 were obtained for each compartment and each solid which are given in Table 1. The goodness of fits is expressed by multiple correlation coefficients R-square. Employing these sets of parameters a, b_1, b_2 and b_3 and Fq. (1), theoretical values of the relative light intensities for each compartment and each solid were calculated as functions of concentration. They are shown as small solid symbols in Figs. 3–6. The connecting curves are B-splines which should only visualize dependencies of the light intensities on concentration. A good agreement between the theoretical and experimental points can be taken as an evidence that the assumption about a direct relation between the actinometric and photometric data has been fulfilled. Moreover, this procedure can be utilized for calculation of estimates of light intensities without performing difficult actinometric measurements, following only the spectrometric data which are easy to obtain.

The same statistical procedure was also applied to data of each compartment X_c, Y_c, Z_c, and Z_i for all solids to see if

Table 1
Parameters (a, b_1, b_2 and b_3) and correlation coefficient (R-square) of multiple regression analysis of actinometric and photometric data of the light interaction with aqueous suspensions of various solids

Sort of solid	Compartment	a	b_1	b_2	b_3	R-square
$CaCO_3$	X_c	5.74903	−0.05282	−0.01383	0.43841	0.99908
$CaCO_3$	Y_c	71.69246	−0.57587	0.13805	−1.56266	0.94938
$CaCO_3$	Z_c	−8.49800	0.10934	0.12828	−0.01512	0.99164
$CaCO_3$	Z_t	−36.62890	1.28927	0.35390	0.13902	0.99717
Kaolin	X_c	4.28933	−0.02622	−0.00123	0.36281	0.99591
Kaolin	Y_c	91.97110	−0.75702	0.02025	−1.85291	0.97023
Kaolin	Z_c	2.16060	0.00243	0.07818	−0.21762	0.93790
Kaolin	Z_t	−30.98352	0.91225	0.35728	−0.09073	0.99731
TiO_2	X_c	3.11924	−0.01517	0.00114	0.26796	0.96939
TiO_2	Y_c	63.77927	−0.39167	0.10148	−2.39813	0.98872
TiO_2	Z_c	9.77561	−0.05011	0.00103	−0.38047	0.97199
TiO_2	Z_t	13.15134	0.96464	0.46629	−2.37446	0.99689
Sand	X_c	−29.54839	0.14032	0.14961	1.42017	0.99999
Sand	Y_c	85.52966	−0.74165	−0.09351	−0.59737	0.99982
Sand	Z_c	25.49468	−0.13789	−0.03058	−1.15886	0.99966
Sand	Z_t	−58.13292	1.26991	0.34003	2.01368	0.99609
All four	X_c	−0.70224	0.00076	0.01191	0.50129	0.92584
All four	Y_c	43.91171	−0.34316	0.23979	−1.20990	0.74681
All four	Z_c	−1.95426	0.03622	0.07396	−0.06970	0.60558
All four	Z_t	32.93801	0.64717	−0.14972	−0.43171	0.95661

there exists a general relation between the actinometric and photometric data independently of the nature of the solid. The results are represented in Table 1. Not such good agreement compared to the previous case of each solid treated separately means that some features of the light scattering are transferred into actinometric and photometric data in a different way for various solids. Nevertheless, a qualitative agreement seems to be without doubt.

Besides the measurement of photometric quantities on a separate wavelength of 365 nm, spectra of transmittance, turbidity and diffuse reflectance in the spectral range from 800 to 250 nm for all investigated suspensions were also recorded. These spectra give comprehensive information about properties of suspensions of the particular solids and allow one to compare each solid with the others. As an example, spectra of the diffuse reflectance of aqueous suspensions (6 g dm^{-3}) of calcium carbonate, kaolin, titanium dioxide and sand are shown in Fig. 7. There is a marked difference between absorbing (titanium dioxide) and non-absorbing (calcium carbonate, kaolin and quartz sand) materials.

A semi-logarithmic plot of the light intensities in the compartment Z_t as a function of concentration of calcium carbonate, kaolin, titanium dioxide and quartz sand, respectively, together with corresponding exponential fits is represented in Fig. 8. The discrepancy between experimental points and exponential fit can be correlated to scattering properties of

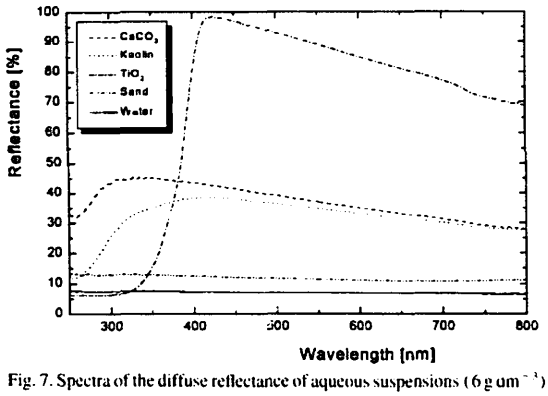

Fig. 7. Spectra of the diffuse reflectance of aqueous suspensions (6 g dm^{-3}) of calcium carbonate, kaolin, titanium dioxide and quartz sand.

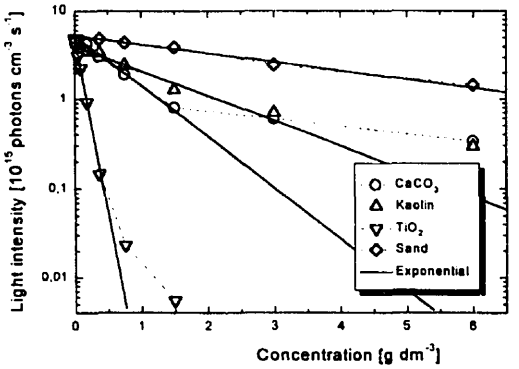

Fig. 8. A semi-logarithmic plot of the light intensities in compartment Z_t of the actinometric device as a function of concentration of calcium carbonate, kaolin, titanium dioxide and quartz sand, respectively, together with corresponding exponential fits.

solids. A good agreement was observed with quartz and titanium dioxide which scatter laterally only a low proportion of incident light (see Figs. 5 and 6). In contrast, the discrepancy is evident with calcium carbonate and kaolin which are highly scattering as it appears in Figs. 3 and 4.

4. Discussion and conclusion

Besides looking for the correlation between actinometric and photometric data, investigation of the light scattered by suspensions of various solids brings about general information concerning this phenomenon. The following findings can be mentioned.

- Light scattering is not negligible even in the case of suspensions of strongly absorbing and highly concentrated solids (i.e. for a suspension of 1.5 g of titanium dioxide per liter of water, about 10% of irradiation light is scattered into compartment X_c, 6% into Y_c, less then 1% into Z_c, less then 0.1% into Z_i and only about 83% together is scattered backwards and absorbed).
- Dependence of the intensity of laterally scattered light on the solid concentration goes through a maximum which is reached sooner for smaller (compartment X_c) than for larger (compartment Z_c) scattering angles and sooner for absorbing (titanium dioxide) than for non-absorbing (quartz sand) solids.
- The last comment concerns the findings of Augugliaro et al. [2] that there exists an exponential dependence of the transmitted light on the concentration of titanium dioxide in aqueous suspension, which enables an estimation of the backwards scattered light as an extrapolated value to the zero concentration. In our case of solids and concentrations, only quartz sand and titanium dioxide fulfil the exponential dependence. Calcium carbonate and kaolin exhibit considerable positive deviation for higher concentrations (higher light intensities in compartment Z_i were found as it would be expected according to the exponential law).

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[2] V. Augugliaro, L. Palmisano, M. Schiavello, AIChE J. 37(7) (1991) 1096.