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Light Absorption Measurements on Turbid Solutions

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In a previously published paper[1], one of the authors described a simple and rapid method of measuring the turbidity of a suspension. The method is insensitive to large variations in the color of the continuous phase. One of the commercially available photoelectric colorimeters can be used without any alterations.

It is often of interest to measure the absorption of a more or less turbid or opalescent liquid photoelectrically. Usually the problem is solved by removing the turbidity by filtration or centrifugation. In special cases, however, these methods are not applicable, or at least difficult to perform.

A rational solution of the problem of how to make colorimetric measurements on turbid solutions is the use of an integrating sphere. Dognon[2,3] describes an instrument consisting of a light source surrounded by the solution to be studied contained in a sample holder shaped as nearly as possible like a spherical shell, the whole being placed in the center of an integrating sphere. The principle is evidently sound, but due to the difficulties in realizing the theoretical requirements of the construction, Dognon was only able to use his instrument for relative measurements.

We propose to show how the problem can be solved with the aid of a photoelectric colorimeter provided with ample space for the sample holders.

THEORY

We assume that a beam of parallel light enters a suspension in a plane parallel sample holder at right angles. The continuous phase is light-absorbing. The light is received by a photocell on the other side.

The notations used are:

I_0 = intensity of light entering the suspension
I = intensity of transmitted (undeviated) light
I_s = total intensity of scattered light
aI_s = fraction of scattered light, striking the photocell
I_a = intensity of absorbed light
x = distance between suspension and photocell
d = length of light path through suspension
T_x = intensity of light received by the photocell when the distance from the suspension is x.

We can consider the sample holder as being divided into two compartments, each having the same thickness as the original one. The first is filled with the coloring matter, the second with the light scattering particles. This means that we tacitly assume the turbidity to be so low, that the average distance covered by a light ray in the colored and turbid medium is not appreciably increased.

After having passed through the first compartment, the light intensity is reduced to:

$$I_0 - I_a = I_0 \, e^{-k'c'd} \tag{1}$$

(k' = extinction coefficient and c' = concentration of the coloring matter). The problem is to determine either k' or c' when the other is known.

Part of the light intensity ($I_0 - I_a$) is scattered in the second compartment. If Lambert's law is valid, we have

$$I_t = (I_0 - I_a) \, e^{-\varkappa d} = I_0 \, e^{-(\varkappa + k'c')d} \tag{2}$$

($\varkappa$ = extinction coefficient for the turbid medium).

The intensity of light received by the photocell, when the sample holder is in position x_1 (close to the photocell) is

$$T_{x_1} = I_t + a_1(I_0 - I_a - I_t) \tag{3}$$

or rearranged

$$I_a = I_0 - \frac{1}{a_1}\left[T_{x_1} - I_t \, (1 - a_1)\right] \tag{4}$$

By making measurements with the sample holder filled first with distilled water and then with the colored and turbid medium, relative values of the light intensities I_0 and T_{x_1} are obtained directly. By measuring T_x for increasing distances between sample holder and photocell and extrapolating to infinity, I_t may also be calculated (see previous paper). Only if α_1 is known in advance, can I_a be calculated from (4) and introduced into (1). It is seen that the result is quite independent of the validity of (2). In other words it does not matter if the scattering follows Lambert's law.

The possibilities of determining α_1 will be discussed in detail. For convenience this quantity is, in the following, sometimes called "scattering coefficient". The value of α_1, *i. e.* the relative amount of the scattered light which strikes the photocell when the sample holder is in position x_1 close to the photocell, depends firstly on the experimental arrangements, especially on the solid angle through which the photocell is seen from the turbid solution. Secondly, the character of the suspension, especially the size and shape of the scattering particles, determines the intensity of the scattered light in different directions (see *e. g.* ref. 4—7). Thirdly, it will be seen, that α_1 also depends on the concentration of scattering substance, probably because the secondary scattering increases with the concentration.

It is not possible to calculate the value of the scattering coefficient theoretically, not even at infinite dilution. If the scattering followed Rayleigh's classical law, this might be possible, but Rayleigh had to presuppose that the scattering particles were small compared with the wavelength of the light. This condition is seldom fulfilled and although much work has been devoted, especially by Debye and by Mark and co-workers (for reviews see ref. 5—7), towards extending the theory to larger scattering particles, the theoretical approaches are far too complicated to be of any use in the cases considered here.

Values of α_1 are determined from an evaluation curve calculated by means of eq. (9) in the previous publication. It is necessary to have available suspensions of different turbidity (including a clear solution), either colorless or with a constant light absorption. In the actual absorption measurements the amount of scattering substance in grams per liter will seldom be known and is, moreover, without interest. It is therefore recommended that the scattering coefficient be plotted against I_s/I_0 instead. As the value of I_s cannot be calculated until I_a is known, the correct value of α_1 to be put into (4) must be determined by successive approximations.

In cases where an evaluation curve of the type described cannot be made, it may be possible to measure the scattering coefficient separately on the same suspension, the absorption of which should be determined, simply by changing the light filter to a wavelength with no appreciable light absorption. Although the amount of scattered light of course varies strongly with the wavelength as predicted by Rayleigh's law, measurements described below indicate that the variation in α_1 is much smaller.

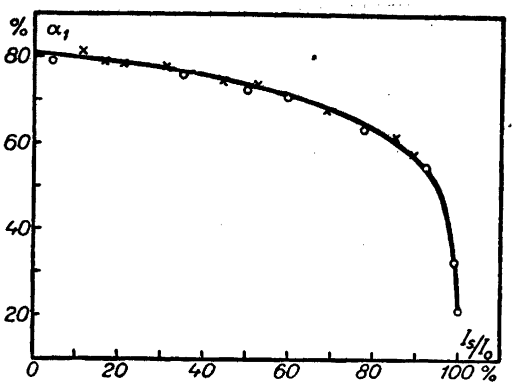

Fig. 1. The scattering coefficient α_1 *as a function of the relative intensity of scattered light* I_s/I_0 *for dilute rubber latex and turbidity standard suspensions. Calculated from Figs. 3 and 6 in previously published paper.*
× *rubber latex* ○ *turbidity standard*

Should none of the possibilities described above be practicable it is still feasible to determine acceptable values of the scattering coefficient on suspensions similar to the ones used in the absorption measurements.

The model experiments to be described show that formula (4) gives correct values as long as the turbidity is not too large. When the turbidity exceeds a certain limit, the values of I_a found from (4) tend to increase, *i. e.* the correction for turbidity is too small. An explanation is easily found. In deriving the formulas above we have assumed the turbidity to be so low, that the distance covered by a light ray in the sample holder is not increased by the turbidity. Due to the scattering, this distance must increase with the turbidity, which means that more light is absorbed.

It is outside the scope of this investigation to attempt a theoretical calculation of the effect. A semi-empirical correction can, however, be applied by assuming that in the formal division of the sample holder into two parts, the one filled with the coloring matter has a light path $(d + \Delta d)$ instead of d.

Formula (4) still gives the true amount of light absorption for the colored and turbid medium. For the light absorption corresponding to the light path d we get

$$I_a = I_0 - \frac{e^{k'c'\Delta d}}{\alpha_1}\left[T_{x_1} - I_t\,(1 - \alpha_1)\right] \qquad (5)$$

which is identical with (4) when $\Delta d = 0$.

EXPERIMENTS

In Fig. 1, values of the scattering coefficient for rubber latex and turbidity standard suspensions taken from the previous publication have been plotted against I_s/I_0. Although these types of suspensions are distinctly different with

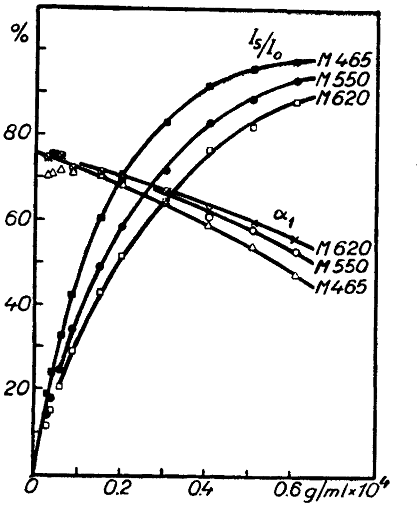

Fig. 2. Intensity of scattered light and scattering coefficient as a function of latex concentration for different light filters.

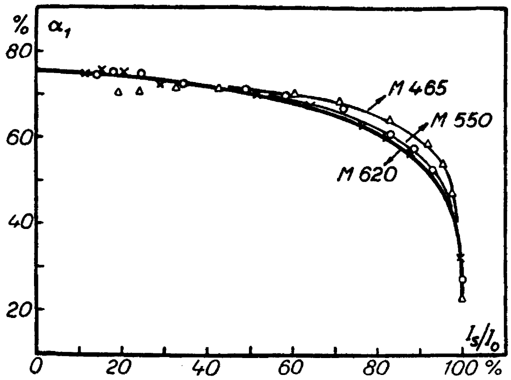

Fig. 3. Scattering coefficient plotted against relative intensity of scattered light. See Fig. 2.

regard to scattering properties, the values of α_1 practically coincide. The explanation probably lies in the very pronounced forward scattering, giving values of α_1 as high as 80 %. In the position x_1, close to the photocell, most of the scattered light is received by the photocell in any case. Differences in the intensity distribution begin to become appreciable at larger distances between the photocell and sample holder.

Figs. 2 and 3 show on dilute latex suspensions how I_s/I_0 and α_1 vary with the wavelength. When plotted against concentration, the variation of the scattering coefficient is much smaller than the variation of the percentage of scattered light. When α_1 is plotted against I_s/I_0 the differences almost disappear. It should be noted that the experimental errors in the determination of α_1 are largest at small turbidities.

In order to test eq. (4) model experiments were made on solutions of copper sulphate in ammonia with and without addition of rubber latex suspension. The copperammine complex has a distinct absorption maximum around 620 mμ [8]. Three different copper concentrations were chosen: 40, 160 and 400 ppm. Values of α_1 at different latex concentrations (Fig. 4) were found to be almost independent of the copper concentration between 0 and 160 ppm but slightly lower at 400 ppm. It seems therefore advisable to investigate the possible color dependence of α_1 in cases where large variations in absorption are expected.

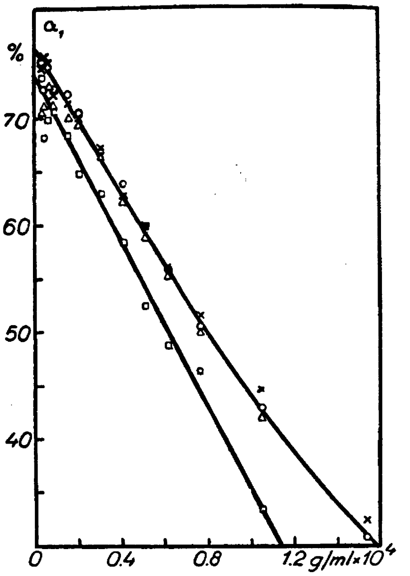

Fig. 4. Comparison between values of scattering coefficient for different copper concentrations. × = *0 ppm* Cu^{++}. ○ = *40 ppm* Cu^{++}. △=*160 ppm* Cu^{++}. □=*400 ppm* Cu^{++}.

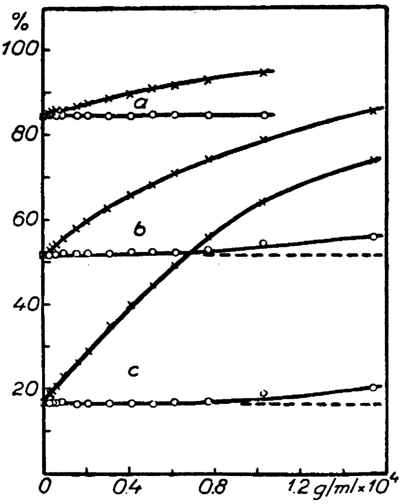

Fig. 5. Relative light absorption as function of latex turbidity. a: 400 ppm Cu^{++}; *b: 160 ppm* Cu^{++}; *c: 40 ppm* Cu^{++}. *Filter M 620.* × *apparent value of absorption, the turbidity being neglected.* ○ *absorption* I_a *in percent calculated from (4).*

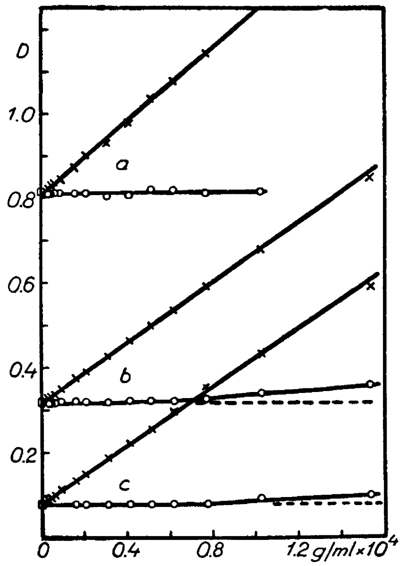

Fig. 6. Extinction as a function of latex turbidity (see Fig. 5).

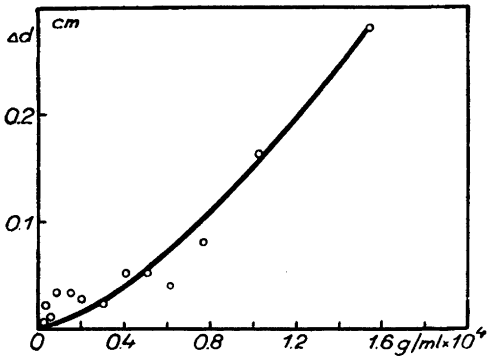

Fig. 7. Δd *calculated from eq. (5) as a function of latex concentration. Copper concentration 160 ppm.*

In Fig. 5, the values of $(I_0—T_{x_1})$, that is, the uncorrected values of the light absorption, are compared with I_a calculated according to (4). Fig. 6 gives the corresponding extinction values D. Eq. (4) is valid up to latex concentrations of $0.6—0.8 \cdot 10^{-4}$ g/ml, which corresponds to values of $I_s/(I_0—I_a)$ of around 90 %, a considerable turbidity.

For higher values of the turbidity the use of eq. (4) still gives fairly good values for the light absorption. By means of eq. (5) values of Δd have been calculated for one of the three copper concentrations used (Fig. 7).

DETAILS OF THE MEASUREMENTS

The instrument used was a Lumetron Photoelectric Colorimeter, Model 402 E (from Photovolt Corp., New York, USA).

Length of light path through the sample holder 2 cm. in all experiments.

The spectral transmittance of the light filters used was measured with a Beckman spectrophotometer.

Filter	Transmission range
M 465	435—480 mμ
M 550	530—570 mμ
M 620	610—640 mμ

The rubber latex (from Trelleborgs Gummifabriks AB) had a solids content of 61.5 % (drying 3 hours at 105° C) and was diluted with ammonia (approx. 5 %). Solutions of copper sulphate were also made with 5 % ammonia.

The extrapolation of the transmission readings to infinite distance between sample and photocell was made as previously described.

SUMMARY

When light absorption measurements are made with photoelectric colorimeters on turbid solutions, the values obtained will be too high due to the scattering. A way to overcome this difficulty is described. It is necessary to know a quantity, for convenience called "scattering coefficient", which gives the percentage of scattered light reaching the photocell when the sample holder is placed close to it. The possibilities of measuring the scattering coefficient are discussed in detail. Model experiments have been made on solutions of copper sulphate in ammonia with varying amounts of rubber latex added. Correct values of the light absorption are obtained up to turbidities corresponding to 90 % scattering of the non-absorbed light. At higher turbidities a moderate deviation is found. A possible explanation for this is given and a semi-empirical correction formula suggested.

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