

## Chapter I

# Optical Properties of Pure Water and Pure Sea Water

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## I. INTRODUCTION

An optically pure medium is defined as a medium which is totally exempt from any suspended particles. This definition does not imply that the medium is a chemically pure compound, it can be a mixture or a solution as well. This definition only implies that the optical properties, especially scattering and absorption, are only determined by molecules or ions.

Though the problems of scattering and absorption of pure water belongs to physical chemistry, it is also of interest in optical oceanography. As is well known, the waters of the open ocean, particularly the deep waters, are of great purity. Consequently the water itself plays an important part in the observed scattering process. Moreover hypothetically pure sea water forms the "blank" for various optical measurements. Scattering by pure water must be subtracted from the observed scattering to estimate the role played by the particles. A similar subtraction yields the absorption by dissolved matter.

The Committee on Radiant Energy in the Sea (IAPO) set forth definitions for attenuation, absorption and scattering. These concepts

are also applicable for an optically pure medium. The subsequent definition, as recalled by Jerlov (1968) are used, with the following relations:

$$c = a + b \quad (1)$$

$$b = \iint_{4\pi} \beta(\theta) d\Omega = 2\pi \int_0^\pi \beta(\theta) \sin \theta d\theta \quad (2)$$

between the attenuation coefficient  $c$ , the absorption coefficient  $a$ , the total scattering coefficient  $b$ , and the volume scattering function  $\beta(\theta)$ . Nevertheless, in the theoretical discussion, in accordance with the physical chemical literature, the Rayleigh ratio  $R$  will be used instead of the volume scattering function at right angle  $\beta(90^\circ)$ . These quantities have the same definition.

Since scattering is a part of attenuation, it will be examined first. Absorption should be considered in the same manner but, this property lends itself with difficulty to experimentation and, in general, is found from eq. (1).

For this reason, it is not examined separately.

## II. SCATTERING

### A. THEORY

The theory of the scattering dipole, developed by Lord Rayleigh (1871), was historically, the first interpretation of the phenomenon of light scattering. In the case of dust free gas, Rayleigh assumed (1899) that the dipoles must be the molecules themselves; in other words, that the optically pure medium scattered because of the discontinuous structure of matter. This theory is successfully applied to isotropic particles small in comparison to the wavelength (the colloidal particles in silica sols, for example). The theory was modified by Rayleigh (1920) and Cabannes (1920) to take into account the anisotropy of molecules. This form is applicable to gases, however, it is not satisfactory for dense media such as liquids.

Paradoxically, scattering by liquids, although more intense than that of gases (having equal volume, but not equal mass), was clearly demonstrated some years later (Martin, 1913). The difficulty of preparing optically pure liquids exempt from fluorescence rendered previous observations questionable.

Smoluchowski (1908) and Einstein (1910) formulated a completely different theoretical approach from statistical thermodynamics. Initially this work was initiated to explain the phenomenon of critical opalescence. This theory also applies to density fluctuations of smaller

amplitudes such as those present in a fluid in the ordinary state. Critical opalescence and scattering would thus be phenomena of the same nature differing only in their intensity.

Although the Rayleigh theory is not applicable to liquids, a number of the results obtained from it remain valid in the theory of fluctuations. For this reason it is useful to come back to Rayleigh theory.

### (1) *Rayleigh theory*

A particle of any form whatever placed in an electrical field  $E$  behaves like a dipole whose induced moment  $P$  is given by the electrostatic formula:  $P = pE$ , where  $p$  is the polarizability of the particle. The particle should be small compared to the wavelength so that the applied field  $E$  can be considered to be homogeneous. The scattering is then assumed to result from the oscillation of this dipole at the frequency imposed by the exciting radiation.

Given that  $I_o$  is the intensity of the incident beam (parallel monochromatic and unpolarized light),  $d$  the distance between the observation point and the particle,  $\theta$  the angle between the direction of propagation of the incident beam and the direction of observation, the scattered intensity  $I(\theta)$  in that direction is expressed by:

$$I(\theta) = \frac{I_o}{2 d^2} k^4 p^2 (1 + \cos^2 \theta) \quad (3)$$

where  $k$  is the wave number defined by  $k = 2\pi/\lambda$ ,  $\lambda$  being the wavelength. This formula corresponds to the case in which the particle is isotropic, i.e. the polarizability is a scalar. **The first well known result of this theory is the wavelength dependence of the scattering according to a  $\lambda^{-4}$  law. The second result is the symmetrical shape of the scattering diagram with respect to the direction perpendicular to the incident beam ( $\theta = 90^\circ$ ).**

The incident light being natural, the scattered light is polarized and the polarization depends on  $\theta$ . The dimensionless functions of intensity,  $i_1$  and  $i_2$ , correspond to the two polarized components respectively perpendicular and parallel to the plane defined by the directions of propagation and of observation ( $i_1$  and  $i_2$  are also called, respectively, vertical and horizontal components).  $i_1$  and  $i_2$  are related to the total intensity  $I$  by:

$$I(\theta) = \frac{I_o}{2k^2 d^2} [i_1(\theta) + i_2(\theta)]$$

and we have:

$$\begin{vmatrix} i_1 \\ i_2 \end{vmatrix} = k^6 p^2 \begin{vmatrix} 1 \\ \cos^2 \theta \end{vmatrix}$$

Component  $i_1$  is constant, while component  $i_2$  varies with  $\cos^2 \theta$ . At right angle the scattered light is totally polarized ( $i_2 = 0$ ), and totally depolarized ( $i_1 = i_2$ ) at  $0^\circ$  and  $180^\circ$ .

If we consider a unit of volume containing  $N$  particles and if the intensities scattered by the particles are considered to be additive, the Rayleigh ratio  $R$  (or the volume scattering function at  $90^\circ$ ,  $\beta_{90}$ , defined in the same manner) is:

$$R(= \beta_{90}) = N \frac{I_{90}}{I_0} d^2 \quad (4)$$

$$= \frac{1}{2} N k^4 p^2 = N \frac{8\pi^4}{\lambda^4} p^2 \quad (5)$$

$p$  has the dimensions of  $L^3$ ,  $N$  those of  $L^{-3}$ . If  $I(\theta)$  replaces  $I_{90}$  in eq. (4), we obtain  $\beta(\theta)$  which is expressed by combining (3) and (4) by:

$$\beta(\theta) = \beta_{90}(1 + \cos^2 \theta) \quad (6)$$

Eq. (3) corresponds to isotropic particles. If they are spherical, the polarizability is given by the Lorentz-Lorenz formula:

$$p = \frac{n^2 - 1}{n^2 + 2} r^3$$

where  $r$  is the radius of the sphere and  $n$  the refractive index. The eq. (5) becomes:

$$R = N \frac{8\pi^4}{\lambda^4} r^6 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (7)$$

The integral over all directions which yields the total scattering coefficient  $b$ , according to eq. (2), has, when  $\beta(\theta)$  is expressed by eq. (6), the following value:

$$b = \frac{16\pi}{3} \beta_{90} \quad (8)$$

which combined with (7) gives:

$$b = \frac{16\pi}{3} 8N \frac{\pi^4}{\lambda^4} r^6 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2$$

Experiment has shown that even in the case of gases (Strutt, 1918), polarization is not total at right angle. Lord Rayleigh (1920) explained depolarization by the anisotropy of molecules and related the depolarization ratio  $\delta = i_2(90)/i_1(90)$  to the three components of the polarizability vector. Cabannes (1920) showed in addition that anisotropy brought about an increase of scattering which he expressed in function

of  $\delta$ . Given that the isotropic part of the Rayleigh ratio,  $R_{\text{iso}}$ , has the value expressed by eq. (7), the total Rayleigh ratio,  $R_{\text{tot}}$ , is:

$$R_{\text{tot}} = R_{\text{iso}} \frac{6+6\delta}{6-7\delta} \quad (9)$$

$6+6\delta/6-7\delta$  is the so called Cabannes factor.

Eq. (6) and (8) are also modified:

$$\beta(\theta) = \beta(90) \left( 1 + \frac{1-\delta}{1+\delta} \cos^2 \theta \right) \quad (10)$$

$$b = \frac{8\pi}{3} \beta(90) \frac{2+\delta}{1+\delta} \quad (11)$$

$\beta_{90}$  takes the value of  $R_{\text{tot}}$  (and no longer  $R_{\text{iso}}$ )

$$\frac{1-\delta}{1+\delta} = \frac{i_1 - i_2}{i_1 + i_2} \text{ is the degree of polarization.}$$

A more complete description of the polarization state is given by the Krishnan relations which correspond experimentally to the different combinations of orientation of the polarizer and the analyzer. The capital letters refer to the components analyzed in the scattered beam, the subscripts designate the state of polarization of the incident beam ( $v$  for vertically,  $h$  horizontally,  $u$  unpolarized). Whatever the angle  $\theta$  may be, we have:

$$\begin{aligned} V_u + H_u &= U_v + U_h = \frac{1}{2}(V_v + V_h + H_v + H_h) \\ &= R_{\text{tot}} \quad \text{if } \theta = 90^\circ \end{aligned}$$

The angular dependence for each term is expressed by:

$$\begin{aligned} V_v(\theta) &= \text{const.} \\ V_h(\theta) &= H_v(\theta) = \text{const.} \quad (= 0 \text{ for isotropic particles}) \\ H_h(\theta) &= H_v \sin^2 \theta + V_v \cos^2 \theta \end{aligned} \quad (12A)$$

hence, at  $90^\circ$ :  $H_h = H_v$ .

The depolarization ratio  $\delta$  can be measured with a polarizer in the incident beam or an analyzer in the scattered beam (or with a combination of both) according to:

$$\delta = \frac{H_v + H_h}{V_v + V_h} = \frac{V_h + H_h}{V_v + H_v} = \frac{H_u}{V_u} = \frac{U_h}{U_v} \quad (12B)$$

If the polarizer is put in the incident beam, the components of the scattered beam are expressed by:

$$\begin{aligned} U_v(\theta) &= U_v(90) \\ U_h(\theta) &= U_v[\delta + (1-\delta) \cos^2 \theta] \end{aligned} \quad (12C)$$

(2) *Fluctuation theory*

Experience has shown that a given mass of a fluid scatters much more in a gaseous state than in a liquid state which is not consistent with Rayleigh's "molecular" theory. The latter applies to independently scattering particles but cannot apply to liquid because of the strong interaction effects between molecules. However, for the wavelength dependence, the symmetry of the scattering diagram, and the polarization the results so obtained continue to exist in the theory of fluctuations. Mainly this theory gives a new expression for intensity (more precisely, for the isotropic part  $R_{\text{iso}}$ ) which can apply to dense media.

In the Einstein-Smoluchowski theory, scattering is considered to be caused by the random motion of molecules which in a sufficiently small volume causes fluctuations of density and, therefore, of the dielectric constant. The fluctuations to be considered are those whose frequencies are optical frequencies. In this theory, the isotropic part of the Rayleigh ratio is given by:

$$R_{\text{iso}} = \frac{\pi^2}{2\lambda_0^4} \Delta V \langle \overline{\Delta\epsilon} \rangle^2 \quad (13)$$

$\langle \overline{\Delta\epsilon} \rangle^2$  is the mean square of fluctuations in the dielectric constant in a small volume element  $\Delta V$  of the medium, and  $\lambda_0$  is the wavelength *in vacuo*. The fluctuations of  $\epsilon$  are assumed to be the result of the density fluctuations, so that

$$\langle \overline{\Delta\epsilon} \rangle^2 = \left( \frac{d\epsilon}{d\rho} \right)^2 \langle \overline{\Delta\rho} \rangle^2$$

where  $\langle \overline{\Delta\rho} \rangle^2$  is the mean square of the density fluctuation. These fluctuations are related to the probability of the occurrence of change in the average number of molecules in the volume  $\Delta V$ .  $\Delta V$  should be small in comparison to the wavelength, but large enough to obey the laws of statistical thermodynamics. From this theory, an expression of  $\Delta V \langle \overline{\Delta\rho} \rangle^2$  is obtained which leads to:

$$R_{\text{iso}} = \frac{\pi^2}{2\lambda_0^4} K T \beta_T \rho^2 \left( \frac{d\epsilon}{d\rho} \right)^2$$

or

$$R_{\text{iso}} = \frac{2\pi^2}{\lambda_0^4} K T \beta_T \left( \rho n \frac{dn}{d\rho} \right)^2 \quad (14)$$

here  $K$  is the Boltzmann constant,  $T$  the absolute temperature,  $\beta_T$  the isothermal compressibility, and  $\epsilon$  is replaced by  $n^2$ .

The first way of expressing the density derivative of  $\epsilon$  is to use a direct relationship between  $\epsilon$  (or  $n$ , the refractive index, with  $\epsilon = n^2$ ) and  $\rho$ . Many overly empirical theoretical equations have been proposed. That of Lorentz–Lorenz, for example:

$$\frac{n^2-1}{n^2+2} \frac{1}{\rho} = \text{const.}$$

the derivative of which gives:

$$\rho \left( \frac{d\epsilon}{d\rho} \right) = \frac{I}{3} (n^2-1)(n^2+2)$$

and leads to the expression given by Einstein:

$$R_{\text{iso}} = \frac{\pi^2}{2\lambda_0^4} K T \beta_T \frac{(n^2-1)^2(n^2+2)^2}{9} \quad (15)$$

The use of the Sellmeier formula (Laplace)  $(n^2-1)/\rho = \text{const.}$ , from which  $\rho \frac{d\epsilon}{d\rho} = n^2-1$ , leads to an alternative expression of  $R_{\text{iso}}$  given by King (1923) and Rocard (1925). The Gladstone–Dale empirical formula  $(n-1)/\rho = \text{const.}$ , from which  $\rho \frac{d\epsilon}{d\rho} = 2n(n-1)$ , was also proposed.

It should be observed that in the case of liquids, by combining the Lorentz–Lorenz equation or the others with the density-temperature relation the values of  $dn/dT$  obtained do not match the experiments. **Furthermore, the relationship between  $n$  and  $\rho$ , should be independent of the pressure and temperature. This has not been found.** It is mainly these reasons that have led to abandoning the initial formula of Einstein, or of Vessot–King, in favour of formulas which make direct use of the experimental values  $(\partial n/\partial T)_P$  or  $(\partial n/\partial P)_T$ .

The derivative  $d\epsilon/d\rho$  is replaced by the partial derivatives  $\left( \frac{\partial \epsilon}{\partial P} \right)_T$  or  $\left( \frac{\partial \epsilon}{\partial T} \right)_P$  according to the choice which has been made between  $T$  or  $P$  to describe the thermodynamic state:

in the first case

$$\rho \frac{d\epsilon}{d\rho} = \frac{1}{\beta_T} \left( \frac{\partial \epsilon}{\partial P} \right)_T = \frac{2n}{\beta_T} \left( \frac{\partial n}{\partial P} \right)_T$$

and replaced in (13):

$$R_{\text{iso}} = \frac{2\pi^2}{\lambda_0^4} K T n^2 \frac{1}{\beta_T} \left( \frac{\partial n}{\partial P} \right)_T^2 \quad (16)$$

In the second case:

$$\rho \frac{d\epsilon}{d\rho} = -\frac{1}{\alpha_P} \left( \frac{\partial \epsilon}{\partial T} \right)_P = -\frac{2n}{\alpha_P} \left( \frac{\partial n}{\partial T} \right)_P$$

$\alpha_P$  being the volume expansion coefficient, which leads to:

$$R_{\text{iso}} = \frac{2\pi^2}{\lambda_0^4} K T n^2 \frac{\beta_T}{\alpha_P} \left( \frac{\partial n}{\partial T} \right)_P^2 \quad (17)$$

Coumou *et al.* (1964) gave a complete description involving both partial derivatives. However, the conclusion is that formula (16) is the best approximation, since the corrective term introduced by temperature fluctuations is negligible, particularly in the case of water, complete formulas are useless (Kratohvil *et al.*, 1965; Deželić, 1966). With this equation the isotropic part of the Rayleigh ratio can be determined from physical constants and from experimental values of  $\beta_T$  and  $(\partial n / \partial P)_T$ .

In the theory of fluctuation, the depolarization or the anisotropic scattering is considered as an effect of fluctuation in the orientation of anisotropic molecules. The theory is not as simple as in the case of the modified Rayleigh theory for an individual anisotropic particle. The anisotropic part of the Rayleigh ratio has been related to other physical quantities dependent on optical isotropy (electric and magnetic birefringence). Cabannes (1929), Prinz and Prinz (1956), Benoit and Stockmayer (1956) indicate that eq. (9) remains valid for liquids and Coumou *et al.* (1964) confirm it experimentally.

Finally, combining (9) and (16) the following is obtained:

$$R_{\text{tot}} = \frac{2\pi^2}{\lambda_0^4} K T n^2 \frac{1}{\beta_T} \left( \frac{\partial n}{\partial P} \right)_T^2 \frac{6+6\delta}{6-7\delta} \quad (18)$$

Eq. (12), which express the angular dependence of different polarized components, can be considered exact for dense media according to experiments and discussion by Deželić and Vavra (1966).

### (3) Electrolyte solutions

In the case of a solution, the theory of fluctuations remains formally unchanged, but the evaluation of  $\langle \Delta \epsilon \rangle^2$  requires, in addition to the previous variables, new thermodynamic variables characteristic to the solution. A complete formula, as written by Stockmayer (1950) for a multicomponent system, involves all the partial derivatives related to each compound, such as:

$$\left( \frac{\partial \epsilon}{\partial m_i} \right)_{T,P,m} \quad \text{and} \quad \left( \frac{\partial m_i}{\partial \mu_j} \right)_{T,P,\mu}$$



where  $m$  is the molality,  $\mu$  the chemical potential, and the subscripts  $i$  and  $j$  stand for the components  $i$  and  $j$ . It is possible to imagine the phenomenon as being the result of two different effects:

- (a) Addition of a new term due to concentration fluctuation in the volume element.
- (b) Modification of the density fluctuation term when pure solvent is replaced by solution.

The concentration fluctuation term:

The complete formula is considerably simplified for a two-component system (Debye, 1944; Oster, 1948). The additional term, due to the concentration fluctuation  $R_{cf}$ , is expressed in the case of an electrolyte solution by:

$$R_{cf} = H \frac{M}{\nu} C \frac{1}{-\partial(\ln a_0)/\partial C_{P,T}} \quad (19)$$

$M$  is the molecular weight of the electrolyte,  $\nu$  the number of ions,  $C$  the concentration of the solute (in g/g), and  $a_0$  the activity of the solvent. The factor  $H$  is given by:

$$H = \frac{2\pi^2}{\lambda_0^4} \frac{n_0^2}{N_A} \left( \frac{\partial n}{\partial C} \right)_{P,T}^2 \quad (20)$$

$n_0$  is the refractive index of the pure solvent and  $N_A$  is the Avogadro number.  $H$  can be regarded as a constant as long as  $\partial n/\partial C$  does not depend on  $C$ , which is correct in the case of diluted solutions. In addition, if the solution is ideal, eq. (19) becomes simpler:

$$R_{cf} = H \frac{M}{\nu} C \quad (21)$$

The density fluctuation term:

Modification of the density fluctuation term can be anticipated with eq. (14) giving the isotropic part of the Rayleigh ratio. The introduction of a solute changes the terms  $n$ ,  $\beta_T$ , and  $\rho$ , and the modified ratio can be written:

$$(R_{iso})_{mod} = R_{iso} \times F$$

with

$$F = \frac{\beta}{\beta_0} \left( \frac{\rho n (\partial n / \partial \rho)}{\rho_0 n_0 (\partial n_0 / \partial \rho)} \right)^2$$

the subscript  $o$  stands for pure solvent.

As pointed out by Lohet (1953), using the Einstein eq. (15),  $F$  remains very close to 1 in the case of aqueous electrolyte solutions.

The reason lies in the contradictory influence of the electrolyte on  $\beta_T$  and  $n$ . In general, for water,  $n$  increases and  $\beta_T$  decreases when a solute is added (for the small ions acting weakly on  $n$ ,  $F$  is slightly smaller than 1). Numerically, it seems that modification of the density fluctuation term is very small and practically negligible compared to the additional term due to concentration fluctuation.

The depolarization factors:

It seems plausible that if the electrolyte gives small isotropic ions (as  $\text{Cl}^-$ ,  $\text{Na}^+$ ) the concentration fluctuation term is an isotropic contribution. Thus, the depolarization factor should decrease in the case of a solution. Pethica and Smart (1966) confirmed experimentally this decrease. But the effect is less important than theoretically foreseen because the increase of anisotropy of water molecules attracted by the ions increases the anisotropic part of the Rayleigh Ratio (Rousset-Lochet, 1955).

## B. RESULTS AND DISCUSSION

### (1) *Experimental*

Experimental determination of scattering constants for optically pure water raises some very difficult problems that can be separated into three categories:

- (a) The problem of the absolute calibration of the scattering meter (which exists for all liquids). In essence it is a question of accurately measuring a ratio in the order of  $10^{-6}$  between the scattered flux and the incident flux.
- (b) The presence of stray light (difficult to eliminate or even to evaluate). This problem is particularly difficult since the water scatters very weakly (approximately 15 times less than benzene).
- (c) Purification, which is more difficult to accomplish for water than for other liquids, as noticed at the time of the first experiments.

Without going into details on problem (a) it must be said that in the case of water, measurements have been made with reference to a standard, either a standard opal diffusor (see for example Brice *et al.*, 1950) or a standard formed by an optically pure liquid such as benzene or carbon tetrachloride (problems (b) and (c) are less critical for these liquids). The absolute calibration of the instrument can be checked by measuring scattering by an almost monodisperse suspension (polystyrene latexes) and by comparing with the computed Mie intensity functions, or by determining the molecular weight (by eq. (21)) of a known compound (Kratohvil *et al.*, 1965). The use of benzene as a

standard has created several problems because of the controversy over the absolute values to be attributed to this liquid. This controversy was raised by Carr and Zimm (1950) but seems to be closed now (Deželić, 1966) with the confirmation of "high values". When the measurement is made relative to a standard liquid, a geometrical-optical correction should be introduced to take into account the change of refractive index (known as the " $n^2$  correction").

Stray light is particularly due to reflection and to scattering by the glass of the cell. Practical solutions to eliminate it include the use of semi-octagonal black painted cells with narrow apertures. It seems that a better solution is to place the (cylindrical) cell in a tank of benzene, the equality of indexes practically eliminates any reflection.

To prepare dust free water different methods have been proposed: ultracentrifuging, envelopment by various precipitates (Sweitzer, 1927), distillation *in vacuo* without ebullition (Martin, 1920), ultra-filtration and filtration through millipore filters (pore sizes 0.1 or 0.22  $\mu\text{m}$ ). The latter is simple, efficient, and is used now. All the results to be presented have been obtained by this latter method, except those of Morel (1966) who used the old method of distillation *in vacuo*, and upon comparison, the millipore filtration was found to be slightly less efficient (scattering was 3% greater on the average). It has often been noticed that adding a very small amount of electrolyte, drastically lowering resistivity, makes purification by filtration more efficient. Finally, we must remember that filtration or distillation should be repeated in order to ensure proper cleaning of both the water and cell.

Optical purity may be tested with an intense light beam by viewing at small scattering angles, but it is more reliable to check if the intensities scattered at two symmetrical angles ( $30^\circ$  and  $150^\circ$  for example) are equal, as the theory anticipates. However, this criterion is revealed to be insufficient because the very small particles remaining do not exhibit a very dissymmetric scattering function. For these particles polarization at  $90^\circ$  is almost total which decreases the measured value of the depolarization factor and modifies the curves derived from eq. (12C) without destroying their symmetry. This is probably the most sensitive criterion.

It must also be pointed out that, for water, light emitted by fluorescence or by Raman effect is not negligible in comparison with scattered light. The precaution must be taken, especially for measurements at short wavelength, of placing monochromatic filters on the incident beam and on the scattered beam (light emitted by fluorescence is not polarized, its presence can be detected by the increase of  $\delta$ ).

TABLE 1. The literature values of  $R_{\text{tot}} (= \beta_{90})$  for pure water expressed in  $10^{-4} \text{ m}^{-1}$ , and of the corresponding  $\delta$  (number in parentheses). The temperature ranges from  $18^\circ\text{C}$  to  $25^\circ\text{C}$ .

$\lambda(\text{nm})$	(1)	(2)*	(3)	(4)	(5)	(6)	(7)	(8)	(9)
366	6.80					4.53			
405	4.05					2.90			
436	2.89 (0.083)	2.95	2.86	2.45 (0.100)	2.32 (0.087)	2.12 (0.09)	2.54 (0.091)		2.82 (0.10)
546	1.05	1.13	1.07	1.08 (0.116)	0.86 (0.076)	0.83 (0.09)	1.08 (0.109)	1.10 (0.05)	1.16 (0.15)
578						0.66			

(1) Kraut-Dandliker, 1955; (2) Mysels-Princen, 1959; (3) Huisman, 1964; (4) Kratochvil *et al.*, 1965; (5) Cohen-Eisenberg, 1965; (6) Morel, 1966-1968; (7) Pethica-Smart, 1966; (8) Lanshina-Shakhparonov, 1966; (9) Parfitt-Wood, 1968.

Data reported as total coefficient  $b$ :  $R_{\text{tot}}$  is computed using  $\delta = 0.09$  in eq. (11).

(1) *Pure water*

In Table 1, most of the data for  $R_{\text{tot}}$  and  $\delta$ , obtained since 1954 are presented. The older determinations are not recalled for various reasons, such as inadequate knowledge of the geometrical optical correction factor and the wavelength.

TABLE 2. Calculated values of  $R_{\text{iso}}$  and  $R_{\text{tot}} (= \beta_{90})$  for water, expressed in  $10^{-4} \text{ m}^{-1}$ ,  $T = 20^\circ\text{C}$ .

$\lambda(\text{nm})$	$R_{\text{iso}}$	$R_{\text{tot}}$		
		$\delta = 0.06$	$\delta = 0.09$	$\delta = 0.11$
366	4.36	4.97	5.32	5.55
405	2.80	3.19	3.42	3.57
436	2.04	2.33	2.49	2.59
546	0.78	0.88 <sub>4</sub>	0.94 <sub>7</sub>	0.99
578	0.60	0.68 <sub>4</sub>	0.73 <sub>2</sub>	0.76

Presented in Table 2 are the theoretical values of  $R_{\text{iso}}$  computed according to eq. (16) with the values chosen from the literature by Kratochvil *et al.* (1965) for the physical quantities  $\beta_T$ ,  $n$ , and  $(\partial n/\partial P)_T$  and for  $T = 20^\circ\text{C}$ . These quantities are sufficiently accurate (except perhaps  $\partial n/\partial P$ ) and the different computations (Mysels, 1964), (Parfitt-Wood, 1968) give very similar results (within 2–3%). They are, on the other hand, different from the previously proposed theoretical values (Dawson-Hulburt, 1937) (Le Grand, 1939), calculated with the Einstein or Vessot-King equation using a different value for  $\beta_T$ .  $R_{\text{tot}}$  is then computed with eq. (9) for three different values of  $\delta$  occurring in the Cabannes factor. We see that the influence of this experimental term on the “theoretical” value is great.

As written by Mysels (1964), “because of the problems of stray light and of contaminating dust . . . all the normally expected errors are positive”. This remark tends to confirm the lowest values. But the experimental values form two groups: one of low values (columns 5 and 6, Table 1) obtained with the same apparatus (SOFICA) and another of high values generally obtained with the Brice-Phoenix apparatus. Consequently, the preceding remark should be interpreted with care. The differences of purification cannot account for this discrepancy. If, according to the scattering diagrams, water can be considered as optically pure in the experiments by Cohen-Eisenberg and Morel (low values), it can also be considered so in the case of certain high values.

Kratohvil *et al.*, Pethica and Smart observe an apparent  $45^\circ/135^\circ$  dissymmetry very close to 1 or even equal to 1.0. Most probably the differences between the calibration methods should be put forward to explain the differences in the data.

The experimental values of  $\delta$  are also quite variable. Nevertheless, it seems that the 0.09 value, which represents an average, can be adopted. This value inserted in the calculation leads to the values of  $R_{\text{tot}}$  in column 4 (Table 2). In relation to the values of  $R_{\text{tot}}$ , the "high" experimental values are 10% to 20% higher\*, Morel's values systematically ranging from 10% to 15% (at 366 nm) lower. The Cohen-Eisenberg values are also lower, but closer to the theoretical values (especially if they are computed with the observed values of  $\delta$ ).

In conclusion, the experimental values are in reasonable agreement with the values prescribed by the theory (it can be noted that agreement is better for liquids other than water). Since there is no decisive argument for choosing between the experimental values, the theoretical values can thus be considered reliable.

The other aspects of the theory were well checked experimentally (particularly by experiments based on relative measurements). Thus, after purification by distillation *in vacuo*, Morel observed scattering functions which agree well with the theoretical curves (Fig. 1). Wavelength selectivity of scattering was demonstrated experimentally by

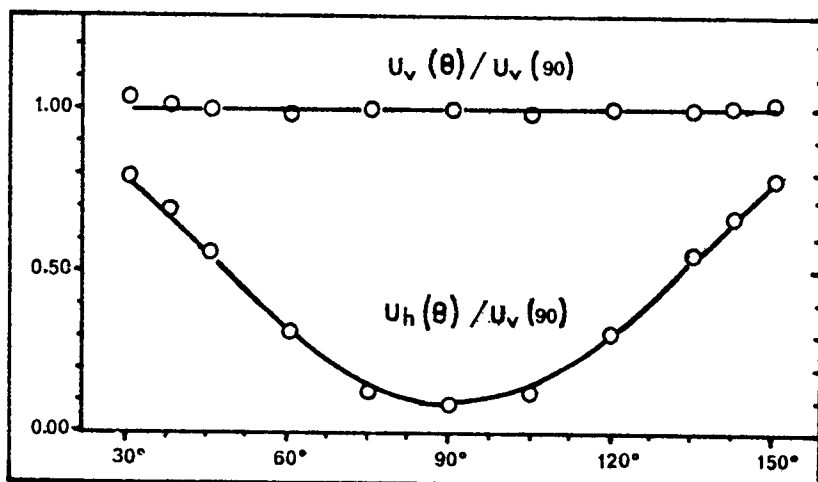


Fig. 1. Curves are theoretical and derived from equations (12C) using  $\delta = 0.09$ . Dots are experimental (Morel, 1966) and concern water purified by distillation without ebullition *in vacuo*.

\* Mysels (1964) had attributed this excess to fluctuations of the degree of association between the water molecules. This excess scattering has been estimated by Litan (1968) and found within the range of experimental error in accordance with the opinions of Kratochvil *et al.* or Cohen-Eisenberg.

Hulburt (1934) who showed that it roughly obeyed a  $\lambda^{-4}$  law. In fact, there is dispersion of  $n$  and  $\partial n/\partial P$  (in addition to that of the term  $\lambda^{-4}$ ) which reinforces selectivity. Table 3, compiled from Tables 1 and 2, shows a good agreement between the computed and observed values. If the wavelength dependence is expressed in terms of a power law, the best exponent is  $-4.32$ .

TABLE 3. Wavelength selectivity of scattering.

$\lambda$ (nm)	Computed from table 2	Experimental $R_{\text{tot}}(\lambda)/R_{\text{tot}}(546)$					Pure sea water
	$\frac{R_{\text{iso}}(\lambda)}{R_{\text{iso}}(546)}$	Pure water					
		(1)*	(4)*	(5)*	(6)*	(7)*	(6)*
366	5.60	6.49			5.43		5.43
405	3.59	3.96			3.48		3.56
436	2.62	2.75	2.27	2.70	2.54	2.36	2.57
546	1.0	1.0	1.0	1.0	1.0	1.0	1.0
578	0.77				0.79		0.79

\* The numbers in parentheses correspond to the references listed in Table 1.

Influences of pressure and temperature on scattering can be predicted from eq. (14). The values of the partial derivatives at high pressure are questionable. However opposite variations of compressibility (which decreases when pressure increases) and of density (which increases when pressure increases) lead us to believe that the scattering value will remain almost unchanged. On the other hand, temperature dependence can be evaluated with greater certainty. Cohen and Eisenberg (1965) showed theoretically and experimentally that the variation was small. The Rayleigh ratio theoretically has a minimum at about 22°C (explained by the multiplication of  $\beta_T$  which has a minimum at about 45°C, by the absolute temperature). At 5°C and 45°C, the increase is only 2% of the minimum value. This variation is hardly detectable within experimental error.

### (3) *Pure solutions and pure sea water*

The experimental study of scattering by electrolyte solutions was first made by Sweitzer (1927) then by Lohet (1953). Increase in scattering is measurable. Since modification of the density fluctuation term can be neglected, the increase, due only to the concentration fluctuation term, is proportional to the concentration and molecular

weight of the electrolyte (only absolutely true if eq. (21) can be applied, i.e. at infinite dilution). Lochet experimentally confirmed this conclusion. By extrapolating his results to zero concentration, he found molecular weights which were in agreement with the formula weights of the electrolytes. Sweitzer's results concerning sodium chloride solutions are presented in Fig. 2 with those of Morel (1966) who used these measurements as a first step in his study of sea water. The results of Pethica and Smart (1966) dealing with potassium chloride solutions are also presented. The Rayleigh ratios of purified solutions are divided by the Rayleigh ratio of similarly purified water. Thus the relative increase is plotted as a function of concentration. Eqs. (20) and (21) enable the calculation of  $R_{cf}/c$  which, divided by the value of  $R_{tot}$  at the same wavelength (Table 2, 4th column), gives the slope of the theoretical lines. These linear relationships are only valid when approaching zero concentration. It must be noted that the calculated slope is not affected by the wavelength as  $R_{cf}$ , like  $R_{tot}$ , varies with  $n_0^2\lambda^{-4}$ .

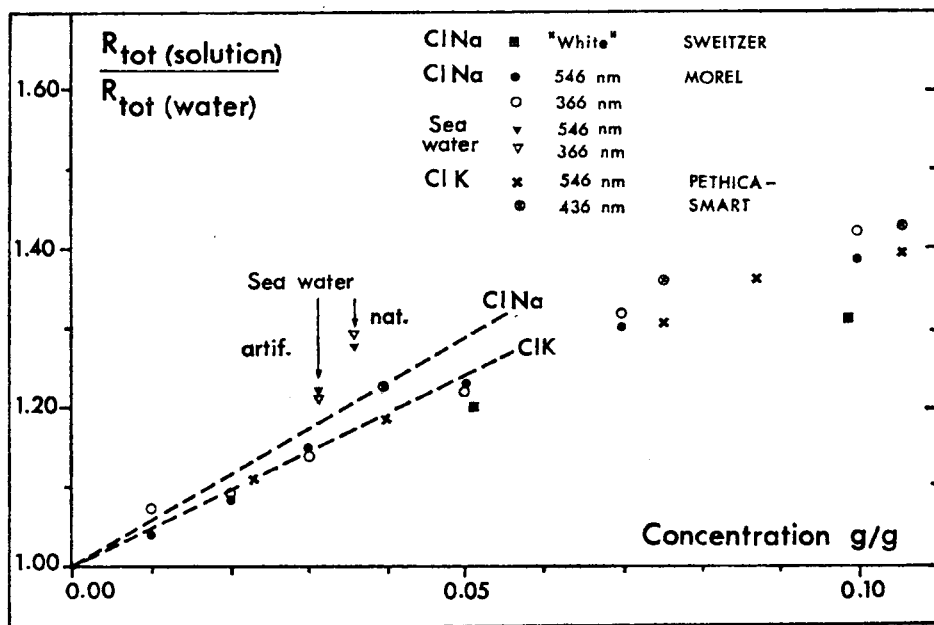


FIG. 2. Relative increase of the Rayleigh ratio for solutions as a function of concentration.

The experimental results of different authors are good verification of the theoretical predictions. At a greater concentration, the evaluation of  $R_{cf}$  through eq. (19) rather than through (21) leads to lower values. (Furthermore;  $\partial n/\partial c$  is not constant, but decreases as concentration increases). We find that a NaCl solution of 0.035 g/g, which has approximately the same concentration in  $\text{Cl}^-$  ions as sea water of 38‰ salinity,



**TABLE 4.** Volume scattering function at  $90^\circ$  and total scattering coefficient for pure water and sea water as a function of the wavelength.

$\lambda(\text{nm})$	350	375	400	425	450	475	500	525	550	575	600	
$\beta_{90}(10^{-4} \text{ m}^{-1})$	6.47	4.80	3.63	2.80	2.18	1.73	1.38	1.12	0.93	0.78	0.68	Pure water
$b^*(10^{-4} \text{ m}^{-1})$	103.5	76.8	58.1	44.7	34.9	27.6	22.2	17.9	14.9	12.5	10.9	
$\beta_{90}(10^{-4} \text{ m}^{-1})$	8.41	6.24	4.72	3.63	2.84	2.25	1.80	1.46	1.21	1.01	0.88	Pure sea water
$b^*(10^{-4} \text{ m}^{-1})$	134.5	99.8	75.5	58.1	45.4	35.9	28.8	23.3	19.3	16.2	14.1	( $S = 35\text{--}39\%$ )

\* Computed according to eq. (11) with  $\delta = 0.09$  which leads to  $b = 16.0 \times \beta(90)$ .

u36

546

366

scatters 1.18–1.20 times as much light as pure water. In the same figure are results (Morel, 1966) for artificial ( $S = 34.3\text{‰}$ ) and natural ( $S = 38.4\text{‰}$ ) sea water purified in the same manner (millipore filtration). They, though having the same  $\text{Cl}^-$  ion concentration as the NaCl solutions, scatter more than said solutions. Without making use of the theory for a multicomponent system, this result can nevertheless be explained by the diversity of the cations present and, in addition, by the fact that anions, other than  $\text{Cl}^-$ , are also present. A very approximate calculation can be made: assuming that sea water is an ideal solution of a hypothetically unique salt having a molecular weight of 70 and by taking the sea water value, 0.20 for  $\partial n/\partial C$ , the increase of scattering is found to be on the order of 34% for a salinity of 35‰.

Concluding we can reasonably admit that pure sea water of 35–38‰ salinity scatters 1.30 times more than pure water. This value is used in Table 4 to compute theoretical scattering of pure sea water according

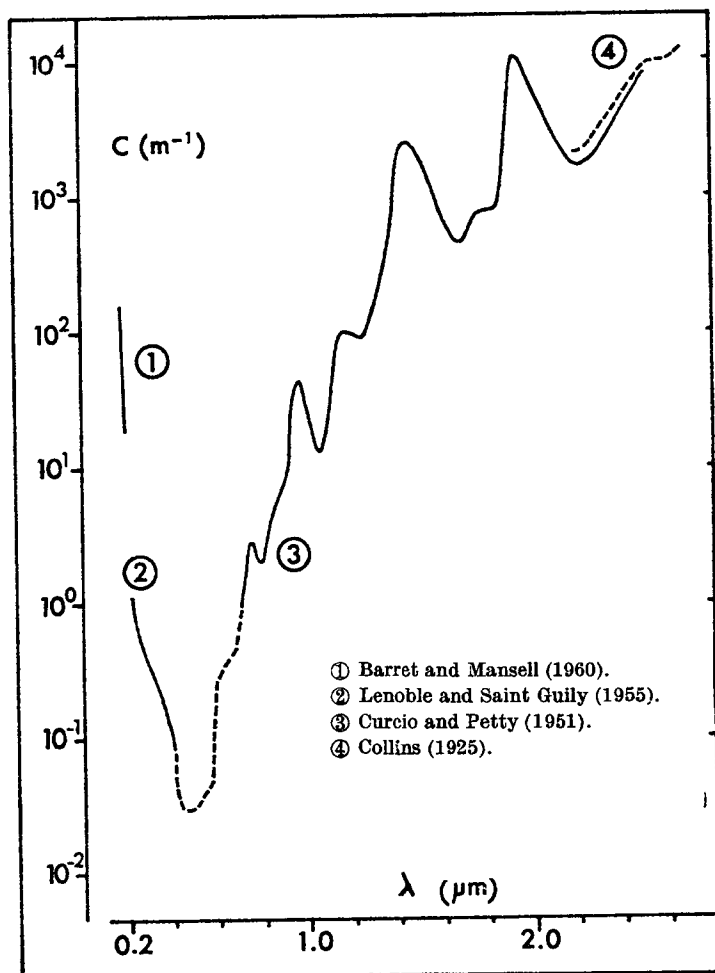


Fig. 3. Attenuation curve for water between 0.2 and 2.8  $\mu\text{m}$ .

to the theoretical values concerning pure water given in Table 2 (for  $\delta = 0.09$ ).

### III. ATTENUATION

Jerlov (1968) reviewed the work concerning attenuation and observed that "progress in the investigation of this factor has been relatively slow". After this review there are only a few details to add for it does not seem that the problem has been fundamentally reinvestigated.

As Fig. 3 shows, a very acute minimum for attenuation lies in the visible part of the spectrum. On both sides of this transmission "window", i.e. in ultraviolet, below 200 nm, and in the infrared, above

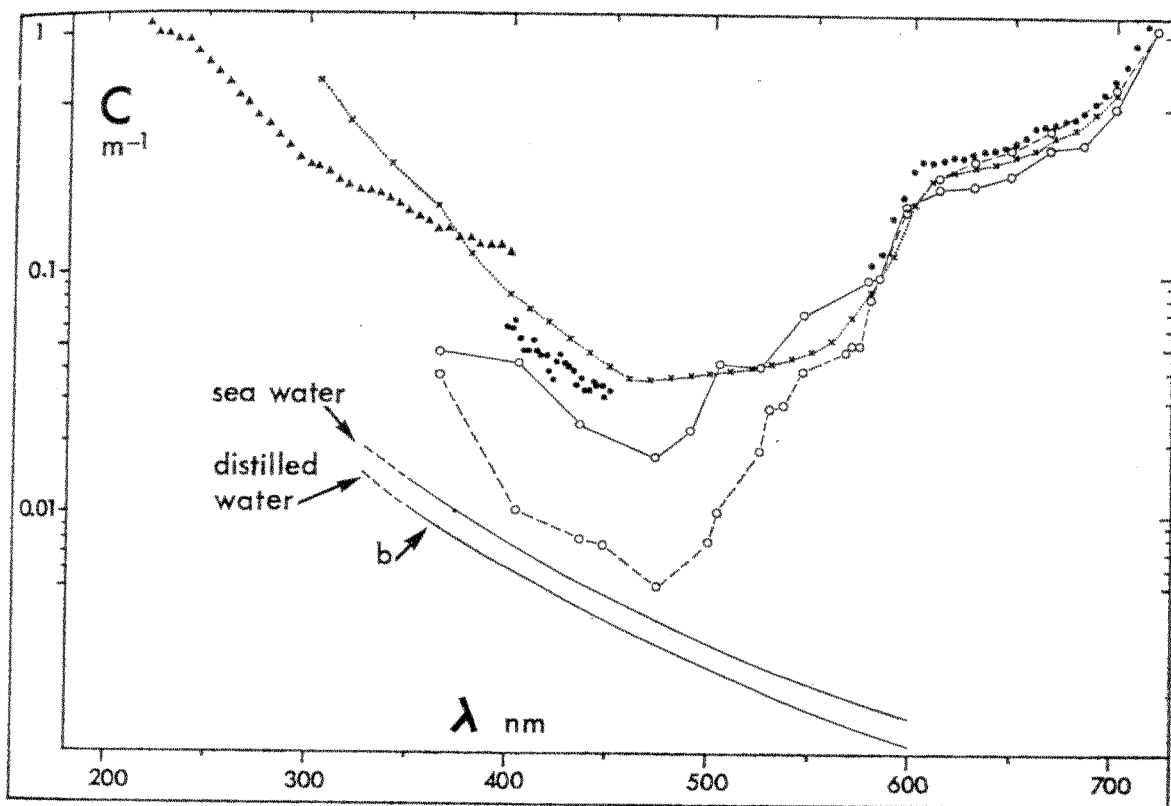


Fig. 4. Attenuation curves in the near ultraviolet and in the visible part of the spectrum.

- ▲ Lenoble-Saint Guily (1955), path length: 400 cm;
- × · · Hulburt (1934) (1945), path length: 364 cm;
- Sullivan (1963), path length: 132 cm;
- — Clarke-James (1939), path length: 97 cm (Ceresin lined tube);
- - - - James-Birge (1938), path length: 97 cm (Silver lined tube).

Total scattering coefficient for pure water and pure sea water as a function of wavelength, according to Table 4.

700 nm, absorption increases strongly. No theory for remnant absorption between these two limits (200–700 nm) is postulated. Moreover, it must be noted that this residual absorption is  $10^4$  or  $10^6$  times weaker than absorption outside the limits.

Regions of high absorption have been studied extensively and the existence of bands explained. Absorption at high frequency (in the far ultraviolet) is related to electron transitions, the bands at lower frequency (in the infrared and distant infrared) are connected with different intramolecular and intermolecular motions. These motions depend on the structure of water, which remains temperature dependent. Consequently, the influence of temperature on certain absorption bands in the infrared (or on the Raman bands which correspond to the same vibrational motions) has been studied extensively (for example, see Walrafen, 1967).

The relatively high transparency of water in the visible and near ultraviolet part of the spectrum varies with wavelength. It is well known that the attenuation coefficient is at a minimum in the blue region (450–500 nm). The curve showing the spectral dependence of  $c$ , between 200 and 700 nm, is roughly symmetrical with respect to this minimum (Fig. 4). Rapid increase of  $c$  is noted between 570 and 600 nm, followed by further increase from 700 to 760 nm. This wavelength corresponds to the first absorption band in the infrared (Curcio-Petty, 1951).

## A. RESULTS AND DISCUSSION

### (1) *Experimental*

The problem of experimentally determining attenuation coefficients of pure water and of pure sea water has much in common with the problem of scattering measurements. There is also:

- a radiometrical problem due here to the fact that the fluxes to be compared (the transmitted flux and the incident flux) are almost the same and that the coefficient  $c$  to be measured is very small.
- a geometrical problem. The measurement should be made under conditions specified by the definition of the coefficient itself. Practically it becomes a problem of stray light. The incident beam must be freed of divergent rays, the detection beam must be freed of stray light reflected by the cell (tube) and of scattered light travelling around the beam.
- a purification problem which is *a priori* more critical than in the case of scattering measurements, firstly, the necessary

volumes are greater and, secondly, because the non eliminated particles can, according to their size, change the total scattering coefficient  $b$  much more than the coefficient  $\beta$  (90).

For the most penetrating radiations, the decrease of flux by attenuation is only a few percents for an optical path of one meter, a minimal length allowing the measurement to be made with sufficient precision.

Greater lengths have been used (see Fig. 4, legend) but the solution that proposes increasing the length of the path has the disadvantage of making the second and third problems more difficult to solve. It is also possible to make the beam cross the tube several times by reflection (4 times 488 cm for the Drummeter and Knestrick measurements, 1967).

The problem of obtaining a high collimation, whatever the wavelength, for both the incident beam and the perfectly centered detection beam, can only be partially resolved in practice. The errors due to not respecting the theoretical conditions have been discussed (see references in Jerlov, 1968, page 48).

Purification has always been obtained by distillation often followed by filtration through a fritted glass filter. Millipore filtration apparently was not used, possibly because it may cause an organic contamination that would modify the values in the ultraviolet part of spectrum. To check optical purity, it would be advisable to obtain simultaneous scattering measurements, since the scattering values are better known.

## (2) *Pure water*

The results of James and Birge (1938) and the results of subsequent work are presented in Fig. 4. Findings prior to 1938 have been collected and discussed by James and Birge.

Agreement between the different measurements presented is reasonable for wavelengths greater than 550 nm, but is considerably less adequate for the region of the attenuation minimum where, of course, the measurements are the most difficult. Furthermore, in the violet and ultraviolet part of the spectrum (350–400 nm) the junction of the curves is questionable. The lowest values for  $c$  (with a minimum at 473 nm) were obtained with the same apparatus: (James–Birge, 1938) (Clarke–James, 1939). The only difference between the two series of measurements is the cell: a silver lined tube was used in 1938, leading to the lowest values (low curve), while in 1939 a ceresin lined tube was used.

We might think that the sources of discrepancy in these measurements are more often located in the experimental devices than in the purity of water. Moreover, the lowest values are not necessarily the

best because of the possibility that the forward scattered light entered the detector. There is no sound basis for choosing between these measurements. Those of Clarke and James are used most frequently.

The search for fine structure (narrow light transmittance region or absorption bands which should be higher harmonics of infrared bands) is the basis of works done by Sullivan (1963) and, more recently (1967) by Drummeter and Knestrick. These two authors approached the problem differently by limiting themselves to relative measurements performed by photographic densitometry. The value of  $c$  is unknown but very slight variations of  $c$  ( $1 \times 10^{-3} \text{ m}^{-1}$ ) can be detected for adjacent wavelengths. Three very weak absorption bands were detected at 470 nm, 515 nm and 550 nm. They are 5–10 nm wide.

### (3) *Pure sea water*

The authors who studied distilled water and filtered sea water with the same apparatus did not find any difference exceeding the precision of the measurements. While studying filtered sea water with a Berkefeld filter, Clarke and James (1939) found slightly lower values than those they obtained with distilled water (in the region of maximum transmission). These measurements tend to confirm the values of James and Birge (1938). The Sullivan (1963) measurements (between 790 and 580 nm) for artificial sea water are perfectly indistinguishable from the measurements concerning distilled water if we plot them on Fig. 4. The ions, at the concentration of sea water, do not have an absorbing action in the visible spectrum, but they do in the ultraviolet, according to Lenoble (1956). Absorption due to said ions would range from  $0.05 \text{ m}^{-1}$  (at 360 nm) to  $0.51 \text{ m}^{-1}$  (at 250 nm). Lenoble insists on the difficulty of obtaining reproducible measurements with the salts employed, despite their high purity. Lower values for  $c$  were obtained by Copin-Montegut *et al.* (1971) with natural sea water filtered on a Whatman filter and subsequently irradiated with a u.v. lamp to destroy the organic matter in solution.

Sea water behaves very differently from distilled water at wavelengths smaller than 250 nm. The bromide ion induces strong absorption (Ogura-Hanya, 1966). Nitrate (Armstrong, 1963) and dissolved oxygen (Copin-Montegut *et al.*, 1971) also produce an absorption but slight in comparison to that of bromide. Organic matter dissolved in natural sea water absorbs in the ultraviolet. The practical interest of the preceding studies was renewed by the recent search for quantitative methods for evaluating dissolved organic matter.

The word absorption has often been used instead of attenuation. This is justified because scattering is negligible compared to absorption

everywhere else in the spectrum, except in the region 400–500 nm where absorption is minimal. Curves corresponding to the total scattering coefficient  $b$  for pure water and for pure sea water from Table 4, have been plotted on Fig. 4. The lack of reliable values for the minimum prevent determining the true role of scattering in the attenuation process, when it is not negligible.

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