LVIII. *On the Colour of the Sea.* *By* K. R. RAMANATHAN, *M.A., Assistant Lecturer in Physics, University College, Rangoon, Burma* *.

1. *Introduction.*

IN a recent paper †, Prof. C. V. Raman has put forward the theory that the deep blue colour characteristic of the larger part of ocean waters is due to the molecular scattering of light in water, and supported it by calculations of the intensity and quality of the light returned from deep water. He has shown that pure, dust-free water scatters light in accordance with a formula originally deduced by Einstein for the critical opalescence of fluids, and that molecular scattering by itself without the aid of any extraneous agency is sufficient to account for the return of a part of the incident light. The following investigation was undertaken in order to test how far actual sea-water comes up to the ideal dust-free condition, and to find how the waters in seas showing different colours vary from one another.

2. *Theoretical Discussion.*

Preliminarily, it is useful to consider what intensity and colour we should expect from a *perfectly absorptionless* dust-free ocean of infinite depth. In such a case, the diminution of intensity of light in its passage through the medium would be wholly accounted for by molecular scattering. Since there is no transformation of the incident energy, it would be entirely thrown back, and the returned light would be of the same quality as the incident ‡. Since the scattering coefficient varies inversely as the fourth-power of the wave-length, the depth of the medium responsible for the return of a certain percentage of blue light would be smaller than that responsible for the return of the same

* Communicated by Prof. C. V. Raman, M.A., D.Sc.

† C. V. Raman, Proc. Roy. Soc. A, vol. ci. p. 64 (1922). See also 'Molecular Diffraction of Light,' Calcutta University Press, 1922, chapter v.

‡ *Vide* Schuster, 'Theory of Optics,' Second Edition, p. 271.

percentage of red light. Selective absorption, however, would modify the condition of affairs. The light of those wave-lengths for which the medium exercises a selective absorption would be gradually diminished in intensity as the light penetrates into the medium, and if the absorption is at all considerable, there would be very little of these radiations returned. Now, water is known to exercise a selective absorption in the red which gradually decreases as we proceed into the region of shorter wave-lengths. The most extensive measurements of absorption coefficients for water that we possess are those of Count Aufsess * between wave-lengths 658 $\mu\mu$ and 494 $\mu\mu$. Recently, W. H. Martin † has measured the absorption coefficients of water repeatedly distilled *in vacuo* for the mercury lines 578 $\mu\mu$, 546·1 $\mu\mu$, and 435·8 $\mu\mu$. As has been pointed out by Martin, there is an error in Aufsess's measurements, as he neglected to take into account the loss of light on reflexion at the glass surfaces at the ends of the absorption-tube. However, considering the length of tube which Aufsess employed (5·5 metres), the relative error involved is not large in the region of the red where the absorption is large. We shall therefore adopt Aufsess's values for the absorption coefficients in the red. In Table I. are shown the experimental values of the extinction coefficient γ, defined by $I=I_0e^{-\gamma x}$, where I_0 is the intensity of a parallel beam of incident light, and I is the intensity after traversing a thickness x of water. In the fourth column are shown the values of the extinction coefficients, if the extinction were due *solely* to molecular scattering. These are calculated according to the formula

$$\alpha=\frac{8\pi^3}{27}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2\ \ddagger.$$

* Count Aufsess, *Ann. der Physik*, vol. xiii. (1904).

† W. H. Martin, Journ. Phys. Chem. xxvi. p. 471 (1922).

‡ *Vide* C. V. Raman, *loc. cit.* and 'Molecular Diffraction of Light,' chapter iv. p. 52.

This is derived on the assumption that the light scattered in a direction perpendicular to the incident beam is perfectly polarized. As a matter of fact, the transversely scattered light shows a defect in polarization. In addition to the polarized "Einstein scattering," there is an additional scattering due to the anisotropy of the molecules, which for the most part is unpolarized. If we take the latter also into account, the formula for the coefficient of extinction becomes

$$\alpha=\frac{2\pi^3}{9}\frac{R'T\beta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2\left\{\frac{4}{3}+\frac{r}{1-r}\right\},$$

where r is the ratio of the weak component to the strong in the transversely scattered light, and the values of the extinction coefficients come out to be $8{\cdot}2\times10^{-6}$, $1{\cdot}08\times10^{-5}$, $1{\cdot}38\times10^{-5}$, $1{\cdot}76\times10^{-5}$, and $5{\cdot}0\times10^{-5}$ for the wave-lengths given above.

TABLE I.

Wave-length.	Absorption coefficient.	Author.	Extinction coefficient due to scattering alone.
658.....	$3{\cdot}2 \times 10^{-3}$	Aufsess.	$7{\cdot}5 \times 10^{-6}$
612.....	$2{\cdot}33 \times 10^{-3}$	Aufsess.	$9{\cdot}9 \times 10^{-6}$
578.....	$6{\cdot}4 \times 10^{-4}$	Martin.	$1{\cdot}3 \times 10^{-5}$
546·1	$3{\cdot}4 \times 10^{-4}$	Martin.	$1{\cdot}6 \times 10^{-5}$
435·8	$1{\cdot}2 \times 10^{-4}$	Martin.	$4{\cdot}3 \times 10^{-5}$

In the red, yellow, and green, up to 546 $\mu\mu$, practically the whole of the extinction is due to absorption, while in the blue and the violet, scattering takes away an appreciable part. The intensity of the incident radiation is reduced to one-half at a depth of approximately 2 metres for 658 $\mu\mu$, 10 metres for 578 $\mu\mu$, 20 metres for 546 $\mu\mu$, and 60 metres for 435·8 $\mu\mu$. Taking primary scattering alone into account and considering the directions of incidence and observation to be vertical, the total observed brightness due to an infinite depth of water can be easily shown to be $B/\gamma\lambda^4$ *, where the scattering coefficient in a transverse direction has the value

$$B = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (\mu^2-1)^2 (\mu^2+2)^2.$$

We can now see why the returned light should be specially deficient in the red, yellow, and green. The increase in absorption goes hand in hand with the decrease in scattering, and the two together serve practically to eliminate the longer wave-lengths. The following Table gives the course of values of $B/\gamma\lambda^4$:—

λ in $\mu\mu$.	658.	612.	578.	546.	436.
$B/\gamma\lambda^4$.....	$1{\cdot}4 \times 10^{-4}$	$2{\cdot}5 \times 10^{-4}$	$1{\cdot}2 \times 10^{-3}$	$2{\cdot}8 \times 10^{-3}$	$2{\cdot}1 \times 10^{-2}$

In order to obtain the resultant colour of the sea, we have only to compound the effects of different wave-lengths in their proper proportions. The intensities for the different wave-lengths throughout the visible spectrum can be obtained

* C. V. Raman. *loc. cit.* If the anisotropic scattering is also taken into account this would become $B(1+r)/\gamma\lambda^4$.

by the above formula, and their colour effects expressed in terms of the spectrum colours 630·2 $\mu\mu$, 538·1 $\mu\mu$, and 456·9 $\mu\mu$, using the values given by the late Lord Rayleigh in his paper on "The Colours of Thin Plates"*. The resultant colour is found to have the composition $1{\cdot}56 \times 10^{-3}$ red, $2{\cdot}49 \times 10^{-2}$ green, and $9{\cdot}53 \times 10^{-2}$ violet, and approaches the spectrum colour 475·0 $\mu\mu$, being very near the indigo of the second order in the colours of thin plates. The inclusion of secondary scattering would reduce the effective depth of the sea from which the scattered light returns; it would also serve to further diminish the intensities of the red and yellow, for which the absorption is strong.

It is obvious that the presence of any dissolved matter giving rise to extra absorption in any particular region of the spectrum would cause a corresponding diminution of the intensity of the returning light in that region of the spectrum.

Let us now consider the effect of suspended matter. It would give rise to an additional scattering, and hence the depth to which the light would penetrate would get reduced. If the particles are small in comparison with the wave-length, the scattering would still be proportional to λ^{-4}. If present in small quautities, there would be little effect on the characters of the returned light, but if present in larger quantities, there would be less chance for the absorptive properties of the medium to have their full play, and as a consequence, the light would be more mixed with the longer wave-lengths, and the blue colour of the sea would tend to get less saturated. As the particles get larger in comparison with the wave-length, the scattering in the direction of primary propagation will be specially favoured, and also, instead of being proportional to, it would tend to be independent of the wave-length. Since the light of longer wave-lengths can return by other means than molecular scattering, their relative proportion in the light returned would increase more and more as the quantity of suspended matter increased, and the sea would get greenish blue, green, whitish green, and finally white. However, as we shall see, when the quantity of matter is not large, the light scattered against the direction of the incident light is but an insignificant fraction of that scattered in the direction of the incident light.

* Lord Rayleigh, 'Scientific Papers,' vol. ii. table i. p. 503.

III. *Examination of Light scattered by Sea-water.*

Samples of sea-water were collected in carefully cleaned stoppered bottles from the Bay of Bengal in two voyages between Calcutta and Rangoon from places where the sea exhibited different colours varying from deep indigo to green. The bottles were securely placed in a galvanized-iron wire cage tied to the end of a wire, and the cage was thrown into the sea from the lower deck of the ship near the bow. The bottles were rinsed out with the sea-water five or six times before each sample was finally collected. The colour of the sea at the time was also noted. In observing the proper colour of the sea, a nicol is helpful in abolishing sky-reflexion, as has been pointed out by Raman.

The scattering of light by the different specimens was examined by concentrating a beam of sunlight at the centre of each bottle in a dark room. The back surfaces of the bottles were painted black, in order to be better able to see the tracks. Table II. gives the details regarding the scattering in different specimens. The intensities of the transversely scattered light given in the last column are expressed in terms of that in dust-free distilled water.

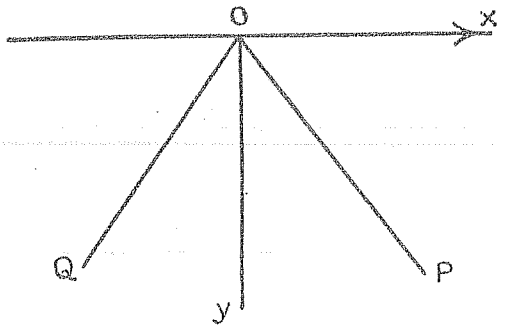
TABLE II.

Specimen No.	Date and time of collection.	Approximate position of ship at time of collection.	Colour of Sea.	Appearance of transversely scattered light.	Intensity of transversely scattered light.
A	1.10.22. 10.30 A.M.	...	Indigo.	Indigo with visible particles.	1·68
B	4.11.22. 8 A.M.	Lat. 19° 40′ N. Long. 90° E.	Greenish blue.	Blue—Few visible particles.	1·4
C	4.11.22. 11.15 A.M.	Lat. 19° 10′ N. Long. 90° 30′ E.	Deep blue.	Indigo—A few large particles.	1·5
D	4.11.22. 4 P.M.	Lat. 18° 30′ N. Long. 91° E.	Indigo.	Indigo—A few large particles.	1·5
E	5.11.22. 7.30 A.M	...	Greenish.	Blue with large thin flakes of something floating.	1·65
F	5.11.22. 11.40 A.M.	Lat. 15° 30′ N. Long. 94° 15′ E.	Green.	Bluish white—Motes visible.	1·6 Blue. 2·0 Red.

The colour of the transversely scattered light in specimens A, C, and D approached that of dust-free distilled water. The intensity of the transversely scattered light from A was compared with that from dust-free distilled water, by sending a concentrated beam of light through the two bottles in succession and making use of an Abney rotating disk-photometer for equalizing the intensities. Correction was made for the loss of light on reflexion at the glass surfaces. In the case of the other specimens, the comparisons were made by inserting perpendicularly in the path of the stronger beam a number of thin, selected microscope slides, so as to equalize the apparent brightnesses.

When the direction of observation was OP instead of Oy, the suspended particles were much more in evidence

Fig. 1.

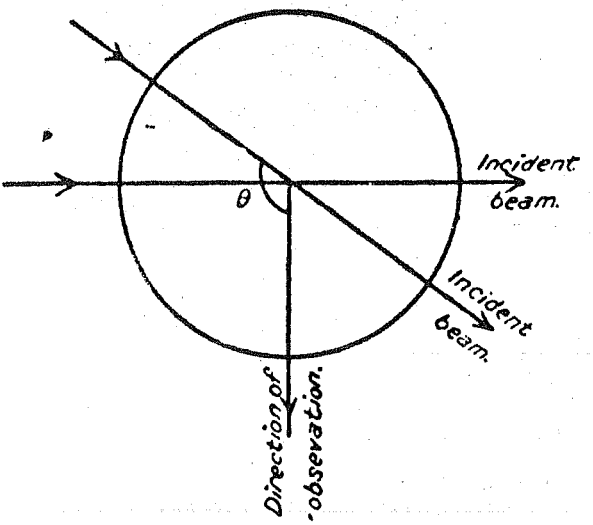


and the colour was more reddish. On the other hand, in the direction OQ, the particles were less conspicuous and the colour even more saturated than along Oy. This is what we should expect if the particles are large in comparison with the wave-length. Since, in the case of the sea, we are primarily concerned with the light proceeding backward, we should consider the intensity of the scattered beam in a direction against that of the incident beam. Comparisons of the intensity of scattering in different directions were made by the method indicated below (fig. 2).

Two beams of sunlight were concentrated one above the other at the centre of the bottle by two lenses of the same focal length (nearly 100 cm. and achromatic) in directions making a definite angle with each other. The scattering was observed in a direction at right angles to one of the beams, and the apertures of the lenses were adjusted by suitable shutters so that the tracks appeared of equal intensity. The inverse ratio of the areas of the apertures

gives the ratio of the intensities scattered in the two directions. Since the depth of layer contributing to the luminosity is different in the two cases, being proportional to cosec θ, where θ is the angle indicated in the figure, the

Fig. 2.



luminosity observed in the direction θ was multiplied by sin θ in order to get the effect due to the same thickness of radiating column. Table III. gives the relative intensities of scattering in different directions in specimen A :—

TABLE III.

S_θ = Scattering in specimen in direction θ.

σ_θ = Scattering in dust-free distilled water in direction θ.

θ.	$S_\theta/S_{90°}$.	$S_\theta/\sigma_{90°}$.	$\sigma_\theta/\sigma_{90°}$.
30°	1·12	1·88	1·60
45°	0·91	1·53	1·40
60°	0·87	1·46	1·20
90°	1·00	1·68	1·00
120°	2·54	4·26	1·20
150°	5·5	9·2	1·60

The values in the fourth column are calculated on the assumption that the scattering by a pure, dust-free liquid in a direction θ is given by $\sigma\left(1+\frac{1-r}{1+r}\cos^2\theta\right)$, where σ is the scattering in a direction perpendicular to the incident beam. It will be seen that in the particular specimen of sea-water, when θ is greater than 90°, the scattering increases with

increasing values of θ at a much more rapid rate than in dust-free water, and that although the transverse scattering is 1·68 times that of dust-free water, the values of the scattering in directions 30° and 45° are not appreciably different from those of pure water. From the progress of values, we may expect that with smaller values of θ, the scattering will be practically the same as for dust-free water.

This result is of great importance in its bearing on the colour of the sea. Suspended matter, when present in small quantities, although it considerably increases the total scattering, contributes but little to the scattering against the direction of the incident light. The increase in the total scattering would reduce the transparency of the medium, but so long as the defect of transparency due to this cause is small compared with the absorption proper, the quality and intensity of the returned light would not be much affected by the presence of such matter.

Table IV. gives similar data for specimens B, C, and F. With a view to bringing out the difference in the distribution of scattered light for red and blue, comparisons were made after introducing ruby-red and deep-blue glasses respectively in the paths of the scattered beams.

TABLE IV.

θ.	$S_\theta/S_{90°}$.					
	B.		C.		F.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.
30°	1·01	1·22	1·06	1·13	0·88	1·03
45°	1·10	1·05	1·13	1·13	0·95	1·02
60°	0·90	1·00	0·97	0·97	0·83	0·95
90°	1·00	1·00	1·00	1·00	1·60	1·00
120°	1·65	1·52	1·55	1·60	2·09	1·63
135°	3·92	2·45	3·18	2·76	5·05	3·98
150°	9·0	6·0	8·3	6·3	16	9·4

It will be observed that in all cases the red gets more and more prominent as θ increases.

We shall now examine whether we can find in the varying amount of suspended matter a sufficient cause for the difference in the colour of the seas. For example, the specimen C was collected from a deep blue sea, while specimen B was from a sea which showed greenish blue,

and F from a place where the sea was green. Compared with C, the intensity of scattering in F, although nearly equal for the blue in a transverse direction, is greater by 30 per cent. in the red, and the asymmetry of scattering also is greater. Thus the total scattering of unit volume of specimen F is greater than that of C, and the colour is also much less blue. Both these causes would contribute to a less deep penetration of the light into the medium (relatively more so for longer wave-lengths), and thus the absorption would have less chance of playing its full role, so that the blue, indigo, and violet would be mixed up with a greater proportion of the longer wave-lengths. We should therefore expect the sea to be brighter and of a less saturated blue, but not the distinct green that it actually was. We have therefore to look for some other cause for the green colour. The point is even clearer if we compare the behaviour of B and C. B scatters actually less than C in a transverse direction (nearly 10 per cent. less); and although its track was not indigo like that of C, the asymmetry of scattering was of practically the same order of quantities, and yet the colour of the sea from which it was collected was *greenish blue*.

IV. *Fluorescence of Sea-Water.*

The reason for the difference was found on examining the transversely scattered light from a horizontal track for polarization by means of a double-image prism. When the double-image prism is so oriented as to transmit vertical and horizontal vibrations, the light corresponding to the horizontal vibrations does not actually vanish even in the case of dust-free distilled water * ; but in this case the two beams are of practically the same colour, while in the case of specimens B and F the weaker component was found to be distinctly greenish. The contrast came out sharper when the two beams were equalized for brightness by means of a suitably oriented nicol placed behind the double-image prism, and a double thickness of blue glass was introduced in the path of the incident beam. The green was now much brighter than the blue and the colour contrast sharper. This was evidently a case of *fluorescence*.

To make quite sure, the following arrangement was adopted :—In the path of the incident beam were placed a double thickness of cobalt-blue glass with an absorption cell.

* W. H. Martin, Journ. Phys. Chem. vol. xxiv. p. 478 (1920). C. V. Raman, 'Molecular Diffraction of Light,' chap. iv.

of a solution of potassium permanganate which cut off everything except the extreme blue and violet and a patch in the extreme red. The light was then passed through the sea-water, and the track therein was examined through a prism with its refracting edge horizontal. In addition to the blue and violet, the green was also conspicuously present. Yellow and red were present, but were very faint. Specimen F showed the effect best, B and E came next, and then C and D. The fluorescence was certainly present even in the last two specimens, though it was very weak.

Since the incident light did not contain any ultra-violet, the fluorescence should be excited by the blue and violet. This implies an extra absorption of the blue and the violet. A sea whose water shows the fluorescence would thus appear green, not only because there is a return of green light due to fluorescence, but also as there would be less of the blue and violet returning. As we have seen, that water looks most green which shows the most intense fluorescence, and the water gets more and more towards indigo as the fluorescent material gets less and less.

The transition from the indigo of the deep sea far from land to blue and green may thus be due either to the increase in the amount of suspended matter present, or to the presence of some fluorescent material (most probably organic) which not only causes a return of the green and longer wave-lengths, but also produces a greater absorption of the blue and the violet. The second cause is apparently the more important.

V. *Summary.*

The paper contains a discussion of Raman's theory of the colour of the sea with observations on the scattering of light by different specimens of sea-water from the Bay of Bengal.

(i.) It is shown that an ocean of pure dust-free water would, owing to the effects of molecular scattering and absorption, return light of an indigo-blue colour. The presence of *small* quantities of suspended matter would not appreciably affect the colour. With increasing quantities of suspended matter the colour would change to bluish, green, greenish white, and white.

(ii.) The transverse scattering from different specimens of sea-water has been compared with that of dust-free vacuum-distilled water. The water from the deep blue sea scatters light of nearly the same colour as dust-free water, and the intensity of the transversely scattered light is also of the same order.

(iii.) The intensity of scattering in different directions from different specimens of sea-water has been studied. The effect of dust is negligible so far as scattering against the direction of the incident light is concerned.

(iv). The variation of the dust-content is found to be insufficient to explain the changes of the colour of the sea from place to place. An important reason for the colour changes has been traced to the presence of varying amounts of some fluorescent material present in the sea. It is pointed out that this fluorescence also implies a greater absorption in the blue and violet involving a diminution of intensity at this end of the spectrum in the light returned from the sea.

In conclusion, I would express my most sincere thanks to Professor C. V. Raman for his stimulating interest in the work.

Rangoon,
Feb. 10, 1923.