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THE SIZE DISTRIBUTION OF SEA-SALT NUCLEI AND ITS CONTRIBUTION TO VISIBILITY

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1. Introduction.

Sea-salt nuclei in the atmosphere are important in meteorology on the formation of cloud and rain and also on visibility. Therefore not a few papers on the nature and the number of these nuclei have been published by many investigators. KÖHLER⁶⁾ made observations of the size of cloud particles and made chemical analysis of the rime formed from them and in 1922 expressed the conclusion that cloud particles formed on the nuclei were consisting of $1.847 \times 10^{-14}g$ of sea-salt. In 1940 WRIGHT¹⁴⁾ published a paper on atmospheric opacity in which he showed that the variation of visibility with relative humidity at Valentia could be explained by the presence of a certain number of sea-salt nuclei. Against WRIGHT's opinion SIMPSON¹⁰⁾ considered that the shape of WRIGHT's curve of the opacity at Valentia proved that the nuclei were more likely to be of the nature of an acid than of sea-salt. However neither WRIGHT nor SIMPSON studied the relation between relative humidity and visibility by sampling the atmospheric nuclei.

Recently, direct sampling of atmospheric nuclei has been made by many investigators. In 1948 WOODCOCK¹²⁾ *etc.* observed atmospheric nuclei on the coast of Woods Hole and found that their number was about 10 per cc and that most of them contained between

$10^{-9}g$ and $10^{-15}g$ of sea-salt. However he did not refer to the relation between sea-salt nuclei and visibility.

On July 26, 1950 we made observations on atmospheric nuclei at Yuriage on the Pacific coast of Northern Honshû (Fig. 1) by the spiders' threads method which was used by DESSENS^{1, 2)} in 1947, and found that these nuclei contained sea-salt and that their size distribution was given by a simple formula. Using the above formula and the empirical formula which expresses the saturation water vapour pressure on the sea water surface in terms of the concentration of dissolved sea-salt, we obtained a new formula which gives visibility in relation to the relative humidity of the atmosphere. Furthermore it was found that the result of observation at Valentia could be well explained by the new formula.

2. Method of Observations.

Observations were consisted of two parts, one of them was the observation of the number and the size of nuclei and another was that of



Fig. 1.

their nature. To observe the number and the size of nuclei we used a net of spiders' threads which was made on a square frame (Fig. 2).

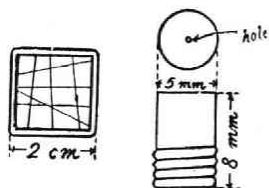


Fig. 2. Frame (left) and Träger (right).

(Fig. 2) is a sample holder which is used for supporting samples when observed by electron-microscope. On the hole in the center of the upper surface of Träger thin collodion film was coated. The diameter of the hole was 0.1 mm.

In order to capture nuclei on the threads and the collodion film, the frame and Träger

The length of each side of the frame was 2 cm and the diameter of threads was from 0.03 to 0.3 μ . We used "Träger" to observe the nature of nuclei. Träger

were exposed in the atmosphere with their surfaces normal to the wind. After a suitable time of exposure we observed the number and the size of nuclei captured on the threads by the optical microscope whose magnification was 900. The radius of the smallest nucleus which could be measured by the microscope was about 0.2 μ . The form of nuclei captured on the collodion film was observed by electron-microscope (type HU 6 made by Hitachi Ltd.). Observations were made on the coast 80 m apart from the sea shore and 2.5 m higher than the sea surface.

Two observations were made, one of them from 0809 to 0928 (a.m.) and another from 1225 to 1255 (p.m.). During the observation sea breezes between S and SE prevailed and the relative humidities were from 81 to 87 %. The meteorological conditions during the observations are shown in Table 1.

Table 1.

Time (JST)	T_{dry} °C	T_{wet} °C	Water Vapour Pressure mb	R. H. %	Wind Velocity and Direction m/sec	Cloud Amount and Form
0800	26.3	23.7	27.6	81	0.2 NW	4 St
0821					0.2 NW	
0831					0.1 ESE	
0843					0.1 ESE	
0855	26.7	24.3	28.8	82	2.3 ESE	4 Cu, St
0918					2.8 SE	
0935						
1215	26.3	24.0	28.3	83		4 Ac, Cu, St
1229	26.9	25.0	30.4	86		9 Ci, Cu, Cb, Ac
1255	26.7	24.9	30.3	87	6.6 S	9 Ci, Cb, Cu
1310					7.4 S	

3. Size Distribution of Sea-Salt Nuclei.

Nuclei captured on the collodion film were spherical drops when observed by optical microscope, but all of them became crystalline in the vacuous space of electron-microscope. The photograph of one of these crystals is shown in Fig. 3. It is apparent from the figure that these crystals are the aggregates of small crystals. On the other hand

we studied the forms of small sea-salt, sodium chloride and calcium sulphate crystals by electron-microscope by spraying their solutions. The sea-salt crystals are the aggregates of finely separated crystals of each component as shown in Fig. 4. The largest mass in each group of separated crystals in the photograph seems to be sodium chloride crystal. On the other hand crystals of sodium chloride and calcium sulphate are more simple as shown in

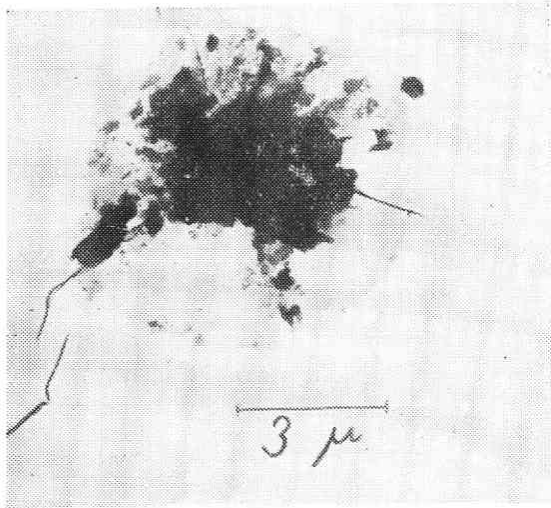


Fig. 3. Crystal Obtained on the Coast
(Photo. by Electron-microscope).

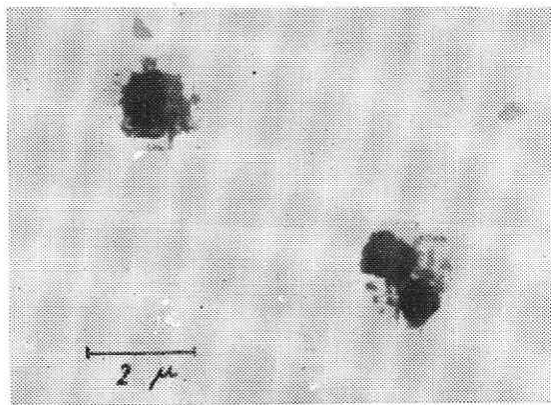


Fig. 4. Sea-salt Crystals
(Photo. by Electron-microscope).

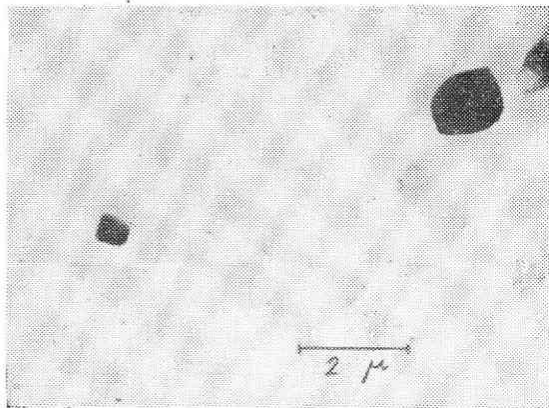


Fig. 5. Sodium Chloride Crystals
(Photo. by Electron-microscope).

Fig. 5. The crystals obtained on the coast have nearly the same form as sea-salt crystals. Therefore the nuclei captured on the coast may be supposed to be sea-salt nuclei.

Recently WOODCOCK¹²⁾ *etc.* observed the atmospheric nuclei captured on the glass slide coated with Dry-film on the coast of Woods Hole and found that they were consisted of sea-salt.

From reasons above mentioned it is concluded that except near the industrial area atmospheric nuclei over the sea are consisted of sea-salt.

Nuclei captured on the threads were also spherical drops when observed by optical microscope. We shall compute the number of sea-salt nuclei in 1 cc of the atmosphere from their number captured on the spiders' threads. We assume that any nucleus whose centre enters into the range within r from the thread is captured by the thread, that is to say, the rate of capture by the thread is assumed to be equal to unity, where r is the radius of nuclei captured. Then the number n_1 of nuclei with radius $r \mu$ in 1 cc of the atmosphere is given by

$$n_1 = \frac{n'}{2rvt},$$

where n' is the number of nuclei captured on the thread of 100μ long, v is the wind velocity in m/sec and t is the duration of exposure of threads in the atmosphere in sec.

Radii of the largest and the smallest nucleus observed by optical microscope were about 9 and 0.2μ respectively, and the number of nuclei was counted for each about one micron interval of their radii. Total numbers of the observed nuclei were obtained by summing up n_1 and they were about 10 (a.m.) and 3 (p.m.). However as will be described at the end of the paper we underestimated the number of nuclei in the atmosphere. Therefore the number of nuclei in 1 cc of the atmosphere

will be more than those computed above.

We shall compute the size distribution of sea-salt nuclei, where the size of nuclei means their size when they are crystalline. For convenience of computation we shall assume that the form of sea-salt crystals is spherical. Then the radius of the sea-salt crystals will be computed by the following procedure. The relative humidity in equilibrium with sea water for different concentrations of dissolved sea-salt is shown in Fig. 6^d.

$$r_0 = \left(\frac{3w}{4\pi\rho_0} \right)^{1/3}$$

where ρ_0 is the density of sea-salt (about 2.2).

Curvature effect upon water vapour pressure over the drop is not generally significant in our case. This is due to the fact that the increase in vapour pressure due to surface tension over the observed smallest drop with radius 0.2μ is only 0.45% and this small increase is readily balanced by the decrease in vapour pressure produced by the small increase in the salt concentration.

The size distributions of sea-salt nuclei

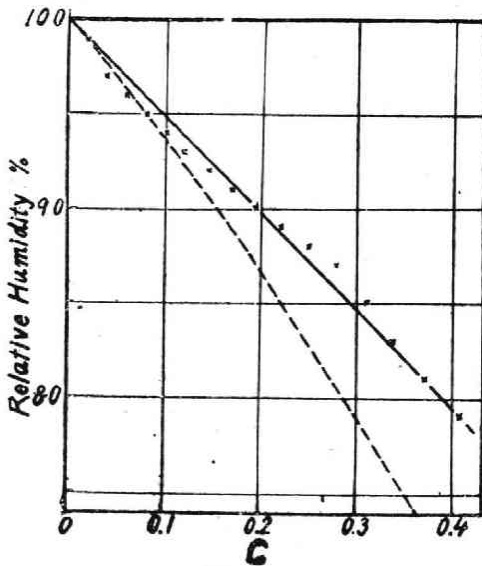


Fig. 6. Equilibrium Relative Humidity on the Surface of Solution in Terms of Concentration.

- c Ratio of Mass of Dissolved Salt to That of Water.
- \times Observed Value (Sea Water at 25°C).
- $H=1-0.52c$.
- Observed Value (Sodium Chloride Solution at 20°C).

The concentration of dissolved sea-salt in each drop is read from the figure for each relative humidity and the mass w of sea-salt in each drop is deduced from the concentration and the radius of the drop. Then the radius r_0 of the sea-salt crystal is given by

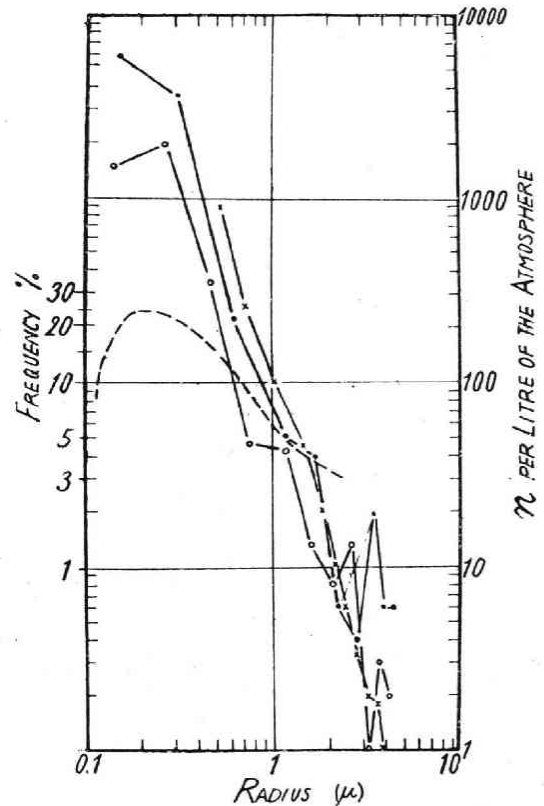


Fig. 7. Size Distributions of Sea-salt Nuclei and Sand Stone Dusts Produced by Grinding.

- n Number of Sea-salt Nuclei.
- \bullet a. m., \circ p. m., \times WOODCOCK.
- Size Frequency Curve of Sand Stone Dusts.

thus obtained are shown in Fig. 7. In the figure WOODCOCK's result is also shown together with our results, and it will be easily seen that these three distributions resemble fairly well with each other. For the comparison with the above results the size distribution¹⁰⁾ of sand stone dusts which were artificially produced by grinding is also shown in the figure.

The size distributions of sea-salt nuclei in Fig. 7 are expressed by

$$\begin{aligned} \text{(a.m.)} \quad n &= 2.8 \times 10^{-9} r_0^{-3.24} \\ \text{(p.m.)} \quad n &= 5.4 \times 10^{-9} r_0^{-3.09} \\ \text{WOODCOCK} \quad n &= 7.1 \times 10^{-9} r_0^{-2.9} \end{aligned} \quad (1)$$

respectively, where $n \Delta r_0$ is the number of nuclei in 1 cc of the atmosphere with radii from $(r_0 - \frac{\Delta r_0}{2})$ to $(r_0 + \frac{\Delta r_0}{2})$ and Δr_0 is taken to be 0.58μ (a. m.), 0.54μ (p. m.) and 0.34μ (WOODCOCK) respectively. (In Fig. 7, for nuclei with radii smaller than 0.6μ the width of interval is from 0.25 to 0.1μ). Two formulae from the beginning hold for nuclei with radii from 0.1 to 2.5μ and the last one for nuclei from 0.5 to 5μ .

These three distributions may be approximately expressed by the simple formula

$$nr_0^3 = C. \quad (2)$$

This is the new formula expressing the size distribution of sea-salt nuclei, in which C depends on the meteorological conditions and the geographical situation.

We could not determine the distribution of the nuclei with radii between 2.5 and 5μ , because only a small number of them were observed. However as described above the number of nuclei in this range observed by WOODCOCK can be approximately expressed by (2). Therefore it may be presume that also in our case there were as many nuclei in this range of radius suspended in the atmosphere as were given by (2). Very few nuclei with radii larger than 5μ were found in our observation and also in WOODCOCK's one. Therefore

we may assume that the radius of the largest nuclei is about 5μ .

Although the formula (2) holds for about 0.5μ interval of the radii of nuclei, for convenience of computation, we shall assume that (2) also holds for infinitesimal interval of the radii of nuclei. Then the total mass W of sea-salt contained in 1 cc of the atmosphere is given by $W = \int_{r_{01}}^{r_{02}} 4\pi r_0^2 n dr_0 = \frac{4\pi \rho_0 C}{3} (r_{02} - r_{01})$, where r_{01} and r_{02} are the radii of the smallest and the largest nucleus respectively. Usually $r_{02} \gg r_{01}$ and as described above r_{02} is approximately equal to 5μ , W is expressed by the simple formula

$$W = 4.6 C \times 10^{-3} \text{g.} \quad (3)$$

The mean value of C obtained from our observation and that of WOODCOCK is equal to about 5×10^{-9} , then W is found to be 2.3×10^{-11} g/cc. In spite of our underestimation of the number of nuclei, this value of W is the same order of magnitude as those obtained by chemical analysis¹⁴⁾.

4. New Formula of Opacity in Terms of Relative Humidity.

HIGASHI's result shown in Fig. 6 can be expressed by the empirical formula

$$H = 1 - 0.52 c$$

for the range of relative humidity from 79 to 100%, where H is the relative humidity over sea-salt drop and c is the ratio of the mass of dissolved sea-salt to that of water in the sea-salt drop.

It has been considered that sea-salt drops become crystalline at the relative humidity of about 70%. WOODCOCK,¹²⁾ however, observed that they do not crystallize for humidity as low as above 30% and DESSENS^{1,2)} also found that the drops of sodium chloride solution remain in equilibrium with the atmosphere at the humidities from 100 to 40%. Further it may be supposed that it will take

a long time for the sea-salt drops to become crystalline. Therefore we can assume that sea-salt drops do not crystallize for the humidities at least above 50% and that the above formula holds for these humidities.

The sea-salt concentration c and the density ρ of the drop are given by $c = r_0^3 \rho_0 / (r^3 \rho - r_0^3 \rho_0)$ and $\rho = (1+c) / (1 + \frac{c}{\rho_0})$ respectively, where r and r_0 are the radius of the drop and that of dissolved salt crystal respectively. Then the ratio of the radius of sea-salt drop to that of dissolved sea-salt crystal is given by

$$\frac{r}{r_0} = \left\{ \frac{0.52 \rho_0 + (1-H)}{1-H} \right\}^{1/3} \quad (4)$$

The values of r/r_0 for several different humidities are shown in Table 2, in which ρ_0 is taken as equal to 2.2.

Table 2.

H	90	80	70	60	50
r/r_0	2.31	1.89	1.69	1.57	1.49

Next we shall obtain the relation between visibility or opacity and the relative humidity using the above result. KOSCHMIEDER⁷⁾ obtained a relation expressing visibility V in terms of extinction coefficient due to suspensoids in the atmosphere. We shall use opacity χ nebule/km in place of extinction coefficient where nebule is the unit proposed by GOLD⁸⁾. Then the above relation is given by $\chi V = 57$, where V is expressed in km.

Opacity χ is composed of three components: that is,

$$\chi = \chi_N + \chi_P + \chi_M, \quad (5)$$

where χ_N , χ_P and χ_M denote the opacity due to scattering and absorption of light by hygroscopic particles, non-hygroscopic particles and molecules of the air respectively, the last being equal to 0.23 neb/km.

STRATTON and HOUGHTON¹¹⁾ computed the

opacity due to water drops and obtained the following expression

$$\chi_N = 1.45 \pi k(\beta) N r^2 \cdot 10^6, \quad (6)$$

where N is the number of water drops in 1 cc of the atmosphere, r is their radius (cm) and k is a factor depending on the ratio of r to the wave length λ of the light. In Fig. 8 the values of k computed by HOUGHTON¹¹⁾ *etc.* are shown in terms of $\beta = 2\pi r/\lambda$. For β larger than 50 k is approximately equal to 2.

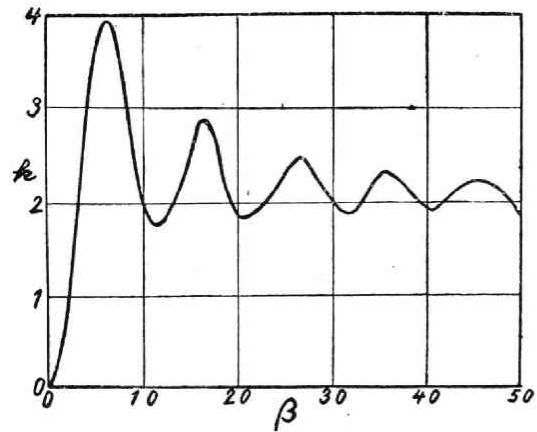


Fig. 8. k in Terms of β .

It will be unreasonable to assume that equation (6) will hold also for sea-salt nuclei. Then if the size distribution of nuclei is taken into consideration the opacity χ_N due to sea-salt nuclei is given by

$$\chi_N = 1.45 \pi \left\{ \int n k(\beta) r^2 dr_0 \right\} \cdot 10^6. \quad (7)$$

By combining (2) and (4) with (7) we obtain

$$\chi_N = 1.45 \pi C \left\{ \frac{0.52 \rho_0 + (1-H)}{1-H} \right\}^{2/3} \left\{ \int \frac{k}{r_0} dr_0 \right\} \cdot 10^6. \quad (8)$$

As the formula (2) holds for nuclei with radii r_0 between 0.1 and 5 μ , (8) holds also for these nuclei and so the upper limit of integration is equal to 5 μ . The size of nuclei smaller than 0.1 μ was so small that we

could not estimate their number. However for these nuclei k is so small and their number is presumed to decrease so rapidly as their radii decrease as in the case of sand stone dusts shown in Fig. 7 that the contribution of these small nuclei to opacity may be regarded as negligible. Therefore the lower limit of integration may be taken to be 0.

Thus we have

$$\chi_N = 1.45 \pi C \left\{ \frac{0.52 \rho_0 + (1-H)}{1-H} \right\}^{2/3} \times \left\{ \int_0^{5 \times 10^{-4}} \frac{k dr_0}{r_0} \right\} \cdot 10^6. \quad (9)$$

Computing the integral numerically we obtain

$$\int_0^{5 \times 10^{-4}} \frac{k dr_0}{r_0} = A (1 - 0.3(1-H)), \quad (10)$$

where A is a numerical factor depending on the wave length of the light and is approximately equal to 9.5. The deviation of A for the wave length of 0.5 and 0.7 μ from the mean value 9.5 are both below 3%.

By combining (5) and (9) with (10) opacity is expressed by

$$\chi = 1.45 \pi A C \left\{ \frac{0.52 \rho_0 + (1-H)}{1-H} \right\}^{2/3} \times \{1 - 0.3(1-H)\} \cdot 10^6 + \chi_P + 0.23. \quad (11)$$

This is the new formula expressing opacity in terms of relative humidity.

In the case of $A=9.5$ and $\chi_P=0$, the relation between opacity and relative humidity for several different mass W of sea-salt in 1 cc of the atmosphere is shown in Fig. 9. The relation between W and C is given by equation (3). The assumption $\chi_P=0$ was adopted by WRIGHT to explain the visibility at Valentia.

5. Explanation of the Variation of Opacity with Relative Humidity at Valentia.

WRIGHT¹⁰ investigated the variation of opacity with relative humidity at Valentia and concluded that it could be explained by the presence of a certain number of sea-salt nuclei in the atmosphere. He found that the mean mass of salt dissolved in each nucleus was $1.1 \times 10^{-15}g$ and the number of these nuclei contained in 1 cc of the atmosphere was 63. To deduce these mass and number of salt he used the saturated water vapour pressure on the surface of sodium chloride solution in place of that on the sea water at the same concentration. However the former differs considerably from the latter at low humidities as shown in Fig. 6. Furthermore, although his computed value agrees well with observed value for high humidities, for low humidities it deviates considerably from the observed value as shown in Fig. 10. He attributed its discrepancy to the fact that when the humidity is below 70% the sea-salt drops crystallize and that the opacity remains unchanged for lower humidities.

SIMPSON¹⁰, however, pointed out that if the sea-salt drops crystallize at the humidity

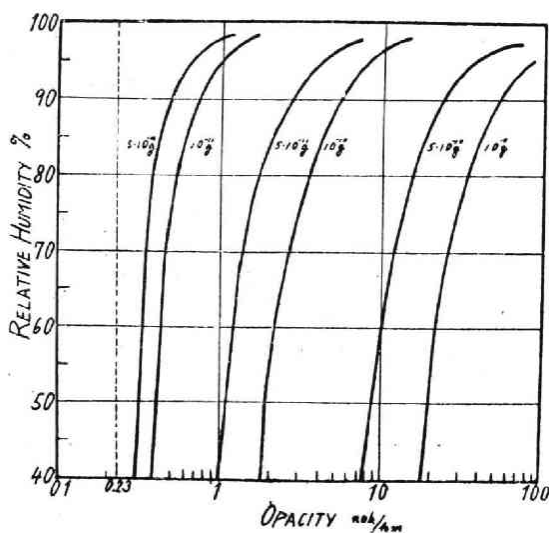


Fig. 9. Relation between Opacity and Relative Humidity for Several Amounts of Sea-salt in 1 cc of the Atmosphere.

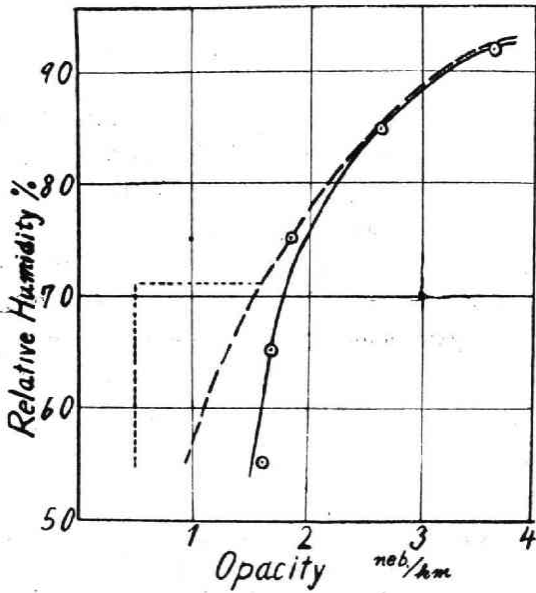


Fig. 10. Relation between Opacity and Relative Humidity at Valentia.

- Observed Value.
- Computed Value from (11).
- - - WRIGHT.
- · · · · SIMPSON.

of about 70% the size of drops decreases rapidly there, then opacity would decrease discontinuously at this humidity and its variation would be shown by the dotted line in Fig. 10. He then concluded that the nuclei suspended in the atmosphere are more likely to be of the nature of an acid than of sea-salt.

Our treatment differs from both WRIGHT and SIMPSON in following respects. First we used the saturation water vapour pressure on the sea water surface as equilibrium vapour pressure on the sea-salt nucleus. Secondary we used the size distribution of sea-salt nuclei which was obtained in § 3, and lastly we assumed that sea-salt drops do not crystallize at least above 50% relative humidity. If we put 1.21×10^{-7} and 0.15 neb.km for AC and χ_P in (11) respectively the opacities obtained from (11) come very close to the observed values at Valentia

as shown in Fig. 10. Thus formula (11) well explains the result of observation without assuming that the nuclei are of the nature of an acid.

That the values of AC and χ_P assumed above are reasonable will be understood by the following explanations. If A is given by 9.5 C becomes 1.3×10^{-8} from the above assumption. The amount of sea-salt contained in 1 cc of the atmosphere is estimated from (3) and is found to be 6.0×10^{-14} g/cc, which is the reasonable value¹⁴⁾ in the atmosphere. The opacity χ_P due to non-hygroscopic particles has not been studied in detail. However it may be assumed that the similar expression to (6) would hold for χ_P , then $\chi_P = 1.45 \pi k' \times N' r'^2 \cdot 10^6$, where r' is the radius of particles in cm, N' the number of particles per cc of the atmosphere and k' is a numerical factor. It may be supposed that the value of k' has the same order of magnitude as that for water drops. If we assume that the mean radius r' of particles is equal to 0.15μ and that the wave length of the light is 0.5μ , k' becomes 0.5 from Fig. 8. Then in the case of $\chi_P = 0.15$ neb/km the number of particles is found to be 290 per cc of the atmosphere. Since the number of nuclei observed over the sea by AITKEN's dust counter has the same order of number as that obtained above, the value of χ_P assumed above also may be regarded as reasonable.

6. Summary.

We made observations of the atmospheric nuclei on the coast and found that these nuclei contained sea-salt and that their size distribution was expressed by $n r_0^3 = C$. From the above formula and the empirical formula which expresses the saturated water vapour pressure on the sea water surface in terms of the concentration of dissolved salt we obtained a new formula expressing opacity as a function of relative humidity, that is

$$\chi = 1.45 \pi A C \left\{ \frac{0.52 \rho_0 + (1-H)}{1-H} \right\}^{2.5} \\ \times \{1 - 0.3(1-H)\} \cdot 10^6 + \chi_P + 0.23.$$

Furthermore it was found that by inserting reasonable values for χ_P and C the result of observation at Valentia could be well explained by the above formula.

The opacities computed from the numbers of observed nuclei are only about one-fourth (a.m.) and one-tenth (p.m.) of that of WRIGHT. However during our observation the wind was so gusty that the wind direction was not

always normal to the surface of *Träger* and frame, therefore the total numbers of observed nuclei are not reliable one. In addition, as there was no suitable landmarks, to our regret, we could not examine our new formula directly from the observation of visibility.

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