

CRITICAL EXAMINATION OF THE ISOPIESTIC METHOD FOR THE MEASUREMENT OF SEA-SALT NUCLEI MASSES

By

Yoshiaki TOBA

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Abstract

Causes of errors in the isopiestic method for the measurement of sea-salt nuclei masses, are precisely investigated by following up changes in the shape, size and volume of a salt droplet, when the vapor-pressure-control solutions of various concentrations are introduced, one after another, in a control chamber. It is found that a very large error is caused by the fact that dependence of the equilibrium vapor pressure of sea salt solution on the temperature is much greater than on the salinity, and also by the relation between the change in the salinity and that in the volume of a droplet, especially when the relative humidity in the control chamber is high. If a control solution which keeps the droplet in a near-saturation concentration with, say, a salinity of 25%, is used, and the effect of the illumination is minimized, the error may be kept within 4 or 5 percent. The effect of the hysteresis of the contact angle should also be kept in mind.

1. Introduction

Since its intensive application by Woodcock (Woodcock and Gifford [1949], etc.), the "isopiestic" or equal pressure method has been one of the effective techniques for determining the mass of individual sea-salt nuclei¹ in the atmosphere. The isopiestic method consists of the following procedures. Sea-salt particles are collected on a hydrophobic surface, and placed in a control chamber made of transparent material, which contains, on the bottom, some control solution for controlling water vapor pressure in the chamber after it is sealed. When the particles attain their equilibrium sizes in the chamber, the salinity of the particles is assumed to have a value such that the equilibrium vapor pressure is equal to that of the control solution. The mass of the nuclei is then determined through the measurement of the volume of the particles. Woodcock and Gifford described a box, which contained a microscope, the control chamber, and accessory equipment, and in which the temperature was thermostatically controlled. However, it seems

¹ In this article, sea-salt particles in the crystalline phase are termed sea-salt nuclei.

that the control chamber is used in a more simple way by other people, i. e., under a microscope at room temperature.

When the isopiestic method is applied for determining the relation between the diameter of the white halo which was developed on a film chemically treated by Farlow's method, and the chloride content of the particle producing the halo (Toba and Tanaka [1965]), a problem arose which was hard to solve and which led to the present study. Droplets of the NaCl solution were sprayed on a hydrophobic surface, and after a microphotograph had been taken at the state of equilibrium in the control chamber, the particles were dried out and then transferred to Farlow's film by bringing it into contact with the hydrophobic film, and another microphotograph was taken of the halos developed in the same pattern on the film; thus a one-to-one correspondence between the mass of chloride and the diameter of the halo was obtained. However, a systematic deviation appeared when different concentrations of the control solution were used. The deviation was larger when lower concentrations were used, namely, when the humidity in the chamber was lower.

Durbin and White [1961] seem to have observed the same tendency: their calibration curves for Vittori's film for measuring sea-salt nuclei differed according to the relative humidity, and the deviation was larger when the relative humidity was lower. However, they did not give any further explanation.

At this point, a report on the error of the isopiestic method made by Crozier [1952] may be recalled. He reported the existence of an error (underestimated) of about 20% at 93% relative humidity, and about 35% at 96% relative humidity in the measurement of the mass of NaCl nuclei, while the error was within a few percent at 81.1% relative humidity. He stated that "no satisfactory explanation has been found for the apparent difference in vapor pressure behavior between the solution in small hemispherical droplets and larger, more or less plane, areas." All of these investigations consistently disclose the same problem for elucidation.

In his experiment, Crozier assumed that the contact angle of salt water with the hydrophobic surface was 90°, consequently that the droplets were practically hemispherical, and he measured the diameters of the droplets only from above. Allowing the possibility that the hysteresis of wetting may be related to the above-mentioned phenomenon, a control chamber has been constructed in the present study such that control solutions of various concentrations can be exchanged, one after another, with the chamber closed, and an exact examination of the phenomenon has been performed by taking microphotographs of the side view of the particles.

As the hydrophobic surface, a polished glass slide, coated with Toshiba Silicone TSF-451 and treated at 200°C for two hours, is used. Droplets of NaCl solution

containing about 3×10^{-4} gm of NaCl are examined. In this case, the effect of curvature on the vapor pressure as well as the effect of gravity on the shape of the droplets may be disregarded. As the control solution, NaCl solution is used for the sake of the self-compensation of temperature effect: if temperatures of the droplets and of the control solution are kept equal to each other, the salt concentration of the droplets is theoretically unaltered even if the absolute temperature changes. The reason for using NaCl solution instead of sea-salt solution as droplets and as the control solution is to make the system concerned simple.

The volume, V , of a droplet is obtained by measuring the height, b , and the radius of the bottom, a , of the droplet on a microphotograph, and through simple calculation, by assuming the droplet to be part of a sphere of the radius, r , by

$$V = \pi b^2 \left(r - \frac{b}{3} \right) = \pi b^2 \left(\frac{a^2}{2} + \frac{b^2}{6} \right). \quad (1)$$

The mass of salt, m , is then obtained by

$$m = SV, \quad (2)$$

where S is the concentration of salt expressed in grams per 1 cc of the solution, and is related to the weight concentration of salt expressed in grams per 1 gm of the solution, S , by

$$S = \rho S, \quad (3)$$

where ρ is the density of the solution.

2. Effect of the hysteresis of wetting

The contact angle made by a droplet resting on a solid surface is larger after the volume of the droplet has increased (advancing contact angle), and smaller after it has decreased (receding contact angle). This phenomenon is called the hysteresis of the contact angle or the hysteresis of wetting. A few theories on this phenomenon have been proposed so far, but there seems to be no definitive theory (Bikerman [1958]).

In the upper picture of Fig. 1 is shown the shape of a droplet of NaCl solution when the equilibrium volume in the control chamber is larger than its early volume, and in the lower picture is shown the opposite case, the concentration of the control solution be-

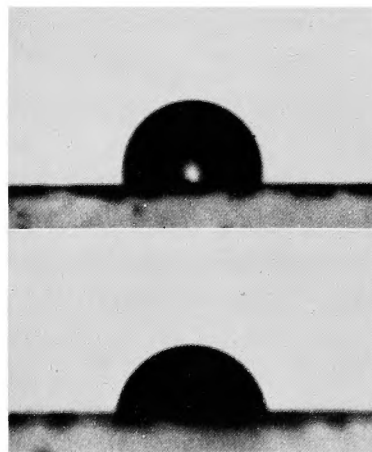


Fig. 1. Two cases of the shape of a droplet of NaCl solution on a hydrophobic surface. Upper: Case of the advancing contact angle. Lower: Case of the receding contact angle.

ing the same for both cases. The shape does not show a marked change for a long time after the equilibrium volume has been attained.

Tests have been made many times to ascertain whether or not the equilibrium volume of a droplet differs according to whether the contact angle is advancing or receding. Results have shown that there is no significant difference, if we compare the difference with such a fluctuation of the volume as will be described in the succeeding sections, although there is a slight tendency for the volume to be larger when the contact angle is receding than when it is advancing, even after allowing a sufficiently long time for the droplet to reach equilibrium.

3. Effect of the illumination

The illumination necessary for taking the microphotograph causes a tempera-

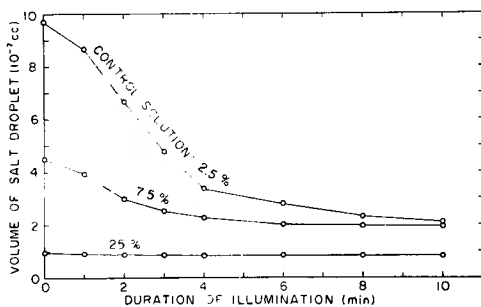


Fig. 2. Volume change of the droplet caused by illumination.

ture change, leading to a volume change, in the droplets. The volume change of a droplet in a state of equilibrium is followed up for 10 minutes after the beginning of illumination. As is shown in Fig. 2, the effect of illumination is very large for low concentrations of the control solution, and very small for a near saturation concentration. The explanation will clearly be given in section 5.

The illumination in the case of Fig. 2 is so intense as to yield 1/10 second shutter speed for a Minicopy film of ASA 32.

4. Stability of the droplet size in the control chamber

The change in the volume of a droplet is followed up for many hours after a control solution has been exchanged in the control chamber. In this case, of course, the effect of illumination is avoided as much as possible. We do not have a temperature control system as described by Woodcock and Gifford [1949], but a rapid change in room temperature is avoided by closing the windows. The room temperature ranged between 21.5 C and 25.0 C through the course of the experiment.

Some examples of the results are shown in Fig. 3. The equilibrium sizes seem to be reached within one hour after the control solution has been exchanged; however the droplet size is not stable but shows a slow variation. The variation is very small when the control solution is near saturation, and large when

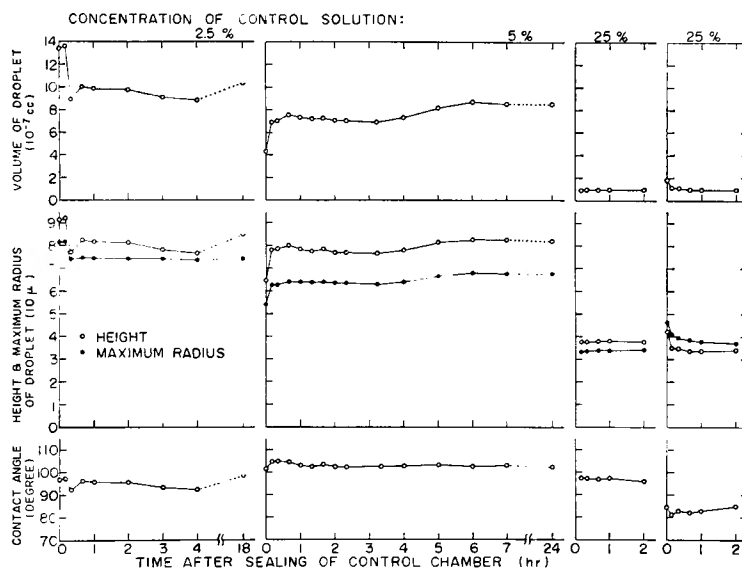


Fig. 3. Change of volume, size and contact angle of a droplet after the control solution has been exchanged. Cases of 2.5% and 25% of the concentration of NaCl solution show the same droplet as that in Fig. 6. Cases of 2.5% and the second 25% are of the receding contact angle, the others are of the advancing contact angle.

the concentration of the solution is low. It is considered that this instability of the droplet volume at a low concentration is the main source of the error. The explanation of this instability will be clearly given in the next section.

5. Dependence of equilibrium vapor pressure on salinity and temperature

The measurement of the equilibrium vapor pressure or the vapor pressure lowering of NaCl solution has been carried out by many people over several decades (International Critical Tables [1928]), and the values for sea-salt solution were measured by Higashi *et al.* [1931], Shiba and Saino [1954], and Arons and Kientzler [1954]. For discussing the general trend, either data for NaCl solution or sea-salt solution may be used, since the difference between them is not very great.

In a tabulation in the form of vapor pressure lowering, the essential point is apt to be overlooked, and further, in the form of relative humidity, the temperature dependence almost disappears: the equilibrium relative humidity on sea-salt solution is, as a first approximation, a function of salinity (Toba [1965]). However, the equilibrium vapor pressure itself is much more temperature dependent than it is salinity dependent, as is shown in the inset of Fig. 4. The change in the vapor pressure, when the temperature increases or decreases by 0.2°C and by 0.5°C from 20°C , is seen in Fig. 4, as a function of salinity. The

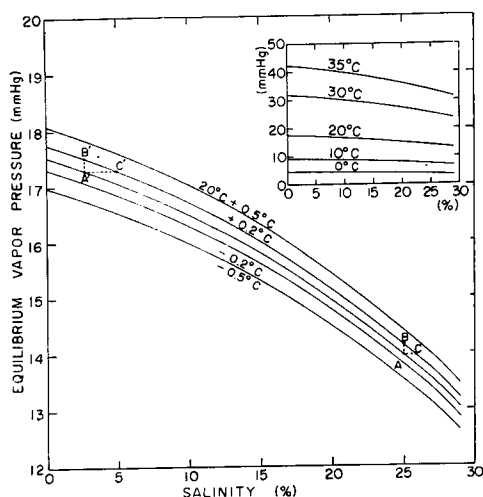


Fig. 4. Equilibrium vapor pressure of sea-salt solution (see the context).

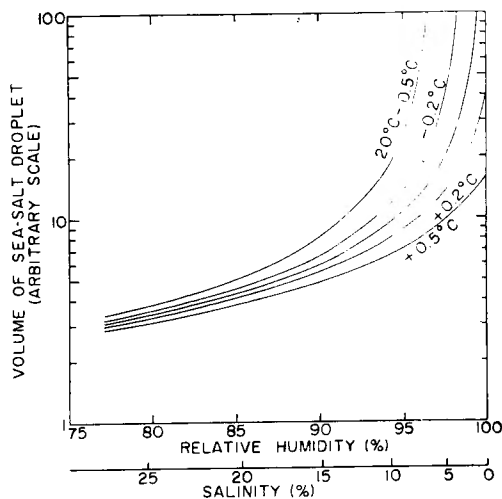


Fig. 5. Volume change of a droplet of sea-salt solution when the temperature of the control solution is 20°C and that of the droplet deviates by $\pm 0.2^\circ\text{C}$ and by $\pm 0.5^\circ\text{C}$.

values are shown for sea-salt solution.

Taking into account the fact that small droplets are more sensitive to temperature change than the control solution of a larger volume, consider a case where the temperature of a droplet becomes higher relatively to that of the control solution, owing to a change in the room temperature or to the illumination, say by 0.2°C . Then the equilibrium vapor pressure of the droplet becomes higher (point B in Fig. 4) than the vapor pressure in the control chamber (point A), and the droplet will evaporate and become smaller until the concentration assumes a slightly higher value (point C) at which the equilibrium vapor pressure at 20.2°C is equal to the vapor pressure in the control chamber.

This effect on the volume change is small for higher concentrations, but becomes extremely large for a low concentration as may be seen from points A', B' and C'. This is more clearly shown in Fig. 5, where the volume change of a droplet is seen, when the temperature of the control solution is 20°C and that of the droplet deviates by $\pm 0.2^\circ\text{C}$ and by $\pm 0.5^\circ\text{C}$, respectively. When the salinity of the control solution is 25% (the relative humidity, $\text{RH}=79.7\%$), the volume change is about 4% for the temperature deviation of $+0.2^\circ\text{C}$, and when the salinity is 10% ($\text{RH}=94.2\%$), the volume change is about 16%, but when the salinity is 3.5% of sea water ($\text{RH}=98.2\%$), the volume change amounts to about 40%. This volume change directly affects the determination of mass of the nuclei, as is seen from the equation (2).

It is also seen that slow volume change in Fig. 3 may be caused by a temperature deviation of 0.2°C or less.

In Fig. 6 are shown some results of the measurement of the equilibrium volume of a specific NaCl droplet for different concentrations of the control solution. First, the particle starts from the crystalline phase. The control solution of 25% is introduced, the equilibrium state of the droplet is photographed, then the control solution is exchanged, with solutions of 20%, 15%, 10%, 7.5%, 5%, 2.5% and 1%, in successive order, and the measured volume in this series is indicated by open circles in Fig. 6. Then the solution is succes-

sively exchanged, in the opposite order down to 25%. The measured volume in this series is indicated by black circles. Two equal circles at one concentration represent an example of the volume fluctuation. The line shows the theoretical volume change at the mean temperature at which the experiment was carried out. Although there is a slight tendency for open circles to show lower values than black circles, it is seen that most of the points lie within errors caused by the temperature deviation of $\pm 0.2^{\circ}\text{C}$.

In the case where some other kind of control solution such as sulphuric acid and water is used, the above conclusion holds as well, provided that the temperature of the control solution remains unaltered and that of the droplet deviates.

Also, the fact that a slight change in the equilibrium vapor pressure does not largely affect the volume of a droplet for higher concentrations, applies as well to the change in equilibrium vapor pressure caused by the effect of curvature for smaller droplets.

6. Substituting NaCl solution for sea-salt solution as the control solution for measuring sea-salt nuclei

When a salt solution of the same composition as the droplets to be measured is used as the control solution, the concentration of the droplets is equal to that

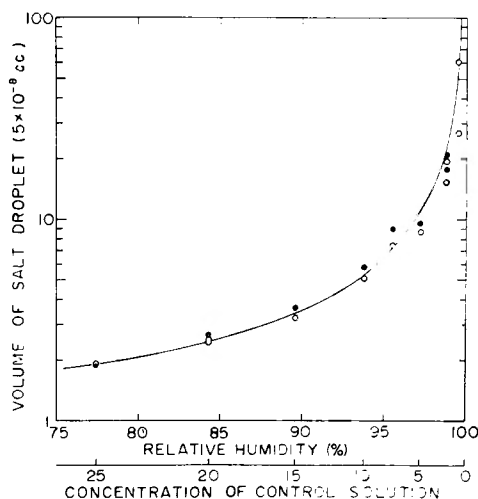


Fig. 6. Measurements of equilibrium volume of an NaCl droplet for different concentrations of the control solution. Open circles show cases for the advancing contact angle, and black circles show those for the receding contact angle. The line shows the theoretical curve.

of the control solution, provided that the temperature of the droplet is equal to that of the control solution. So, in this case, it is not necessary to measure precisely the temperature itself, partly because the density of the solution appearing in equation (3) changes only slightly with the temperature.

Temperature dependences of the equilibrium vapor pressure of NaCl solution and of sea-salt solution are very similar to each other. The concentration of NaCl solution, S (%), of which the equilibrium vapor pressure is equal to that of sea-salt solution of the salinity of 25%, is approximately given, in a range of ordinary room temperature, T , by

$$S = 22.2 + 0.063T. \quad (4)$$

Since it is not so easy to obtain sea-salt solution of the salinity of 25%, it is proposed for practical convenience to substitute NaCl solution of the concentration given by the equation (4) for sea-salt solution of the salinity of 25% as the control solution. Even though the temperature of the control solution changes by 10°C , the error caused by the substitution is found to be comparable with that caused by the temperature deviation of 0.2°C of the droplets from the control solution.

7. Conclusion

(1) When the isopiestic method for the measurement of sea-salt nuclei masses is used at room temperature without the use of a complicated system for temperature control, a very large error is caused by the fact that dependence of the equilibrium vapor pressure of sea-salt solution on the temperature is much greater than on the salinity, and also by the relation between the change in the salinity and that in the volume of a droplet, especially when a control solution of low concentration is used. If a control solution of the concentration of near saturation, say 25%, is used, the error may be kept within 4 or 5 percent.

(2) The effect of illumination considerably reduces the volume of a droplet. The duration of the illumination should be minimized.

(3) The effect of the hysteresis of the contact angle causes a change in the shape of a droplet, according as the droplet has grown or receded to reach the equilibrium volume. So the history of the volume should also be controlled to calculate the volume. However, the hysteresis of the contact angle itself does not seem to affect significantly the equilibrium volume of a droplet.

(4) It is suggested that NaCl solution of a concentration given by the equation (4) be substituted for sea-salt solution of the salinity of 25%, as the control solution for measuring sea-salt nuclei.

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