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Studies on Salt Solution Aerosols. IV.[1] Droplet Size Determination of Aqueous Sodium Chloride Solution Aerosols by Chemical Spot Method

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Droplets of aqueous NaCl solution aerosols generated by atomization were collected on an $AgNO_3$ containing film, by measuring microscopically the sizes of the AgCl spots formed on the film, the diameters of the droplets were determined with the aid of the calibration curve between the spot and droplet diameters. It was found that the calibration curve can be expressed by a relation $D_d^3 = Kd_s^2$, where D_d is the volume average diameter of the droplets, d_s the surface average diameter of the spots and K a constant. The meaning of K was considered.

For aerosol investigation it is essential to measure the particle size distribution. This is one of the main tasks of aerosol studies, but it is very difficult to size and count the droplets of volatile aqueous solution that evaporate appreciably during sampling and measurement.

The oil method,[2] in which the collected droplets are suspended in an oil film on a glass slide and observed under a microscope is most frequently used.

There are other methods such as ultramicroscopical measurement of the sedimentation rate of droplets or of their mobility in electric field. Recently photoelectric counters have been available for use, but these are not always applicable for aerosols of volatile droplets as complete elimination of evaporation is very difficult.

As one technique for measuring droplet size with an optical microscope we deal with their spots impressed on a support. Soot-[3] or magnesium oxide-[4] coated glass slides have been utilized widely, though they cannot register spots less than 10 μ in diameter owing to their poor impressions. Because of fragile soot or oxide coating, use of films containing a dye or special reagents

1) Part III: I. Sano, S. Hikita, and Y. Ueno, Nippon Kagaku Zasshi, **90**, 876 (1969).

2) F. Albrecht, *Physik Z.*, **32**, 48 (1931); H. K. Weikmann and H. J. aufm Kampe, *J. Meteor.*, **10**, 204 (1953).

3) L. Strazhevsky, *Tech. Phys. (U. S. S. R.)*, **4**, 978 (1938); R. L. Stoker, *J. Appl. Phys.*, **17**, 243 (1946).

4) K. R. May, *J. Sci. Instr.*, **22**, 187 (1945); H. Maruyama and K. Hama, *J. Meteor. Soc. Japan*, **32**, 49 (1954); E. Uchida, *ibid.*, **44**, 234 (1966).

in gelatine, polyvinyl alcohol, ethyl hydroxycellulose and so on has been introduced.[5] However, these is little information for physicochemical studies both of the spots of aqueous salt solution droplets on these films and of the application to the droplet size measurement, except a few reports on the solid particles of sodium chloride.[6]

Employing an Hg_2SiF_6 or $HgNO_3$ containing gelatine film, Sano *et al.*[7] measured the particle size of NaCl aerosols having an average diameter less than 0.5 μ (prepared by condensation method) and one less than 8 μ (prepared by dispersion method). They assumed the spot of HgCl formed to be hemispherical and found a good agreement between the calculated and observed sizes. Farlow[8] developed a technique making use of an $Ag_2Cr_2O_7$ containing gelatine film. The NaCl particles collected on the film, and dissolved by keeping the film in moist air, reacted with the dichromate to produce the spots of AgCl, which were apparently clear. Assuming that they are cylindrical, he found that the relation $w=0.54\ d^{2/3}$ ($w>20\ \mu$) holds, where w is the particle size represented by the width of one crystal face of a cubic NaCl particle and d the diameter of the spot on the film. This paper will present information on the droplet size determination of aqueous NaCl aerosols.

Experimental

Materials. C_2H_5OH, HNO_3, and $AgNO_3$ used were of the extra pure grade. Polyvinyl alcohol obtained from the Kurashiki Rayon Co. was 1700 in polymerization degree and 85% in saponification.

Preparation of the Reagent Film. An aqueous solution containing 4% by weight of PVA was made by stirring the dry powder into distilled water with strong agitation at room temperature. To 100 g of the solution, 200 m*l* of C_2H_5OH and 1.5 m*l* of 1 N HNO_3 were mixed and further, (a) 2 m*l*, (b) 3 m*l*, (c) 5 m*l*, or (d) 7 m*l* of an aqueous 40% $AgNO_3$ solution was added to obtain four NaCl-detecting reagents of different concentrations. The $AgNO_3$ containing PVA solutions so prepared retained their properties for an extended time at room teperature in the dark.

By dropping 10 μl of the $AgNO_3$ containing PVA solution upon a diameter of around 2.1 cm is obtained and the solvent alcohol and water, rapidly evaporate off. The film formed is photosensitive and must be stored in a closed container in the dark.

The glass side used as PVA film carrier was first immersed in chromic acid mixture to remove greasy material and then, thoroughly washed in running water and finally in distilled water. The slides were kept in a desiccator, hanging in a vertical position.

Generation of the Droplets and the Measurement of their Size Distribution. Droplets were generated by using an atomizer filled with an aqueous 5% NaCl solution and introduced into a chamber, where they were dispersed homogeneously and subjected to aging with constant stirring. The chamber is a cylindrical plastic vessel of about 0.23 m^3, the inside of which had been saturated, previous to introduction of the droplets, with water vapor by putting an aqueous 5% NaCl solution on the bottom.

The film carrying glass slides were inserted horizontally, at chamber, the droplets collected on them impressing the spots. In order to know the size of the droplets corresponding to the spots impressed, the oil film technique was applied at the same time, employing glass slides coated on one slide with silicone or the like. Their microphotographs were enlarged and the size reading of both the spots and droplets were made with care, the droplets examined being in the size range of a few tenths of a micron and greater in diameter.

Results

Spots on the Reagent Film. Typical spots impressed on the film are shown in Fig. 1. Influence of the concentration of reagent as well as the exposure to ultraviolet light upon the spot formation is shown in Fig. 2. We see that the smaller spots exhibit more distinct and clear-cut outlines after a 30 min exposure at 10 cm distance from a mercury lamp, the mechanism possibly being that, by photochemical reduction of precipitated AgCl to colloidal silver, spots are given sharp contrast in color, the spots not subjected to the exposure being of somewhat ambiguous image so that they could be observed only when they were of the size above 1 μ in diameter, under a phase-contrast microscope. Figure 3 indicates the microphotographs of the droplets in the oil film.

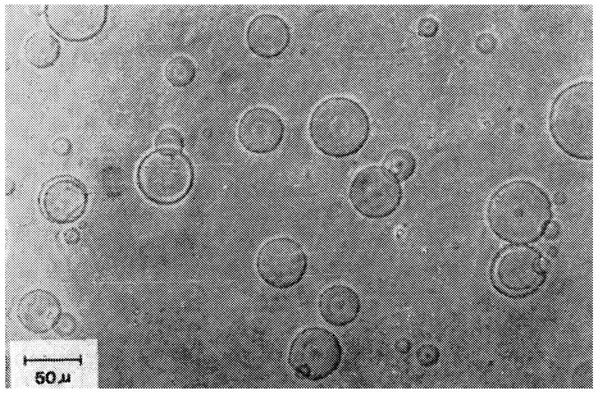

Fig. 1. Spots of 5% NaCl solution droplets (viewed under phase-contrast microscope) on a 5 m*l* $AgNO_3$ solution film.

Construction of the Calibration Curve. The droplets suspending in the oil film and their spots impressed on the reagent film have both their own size distributions, and therefore, taking the volume average diameter (D_d) for the former and the surface average diameter (d_s) for the latter, the calibration curve was drawn for each of the four films, (a), (b), (c), and (d) having different concentrations with respect to the reagent, $AgNO_3$ (Fig. 4). From the figure, it is evident that the spot diameter increases more rapidly than the droplet diameter and that it gets smaller as the reagent concentration in film increases.

Discussion

It has been referred to above that the circular film

5) H. F. Liddel and N. W. Wotten, *Quart. J. Meteor. Soc.*, **83**, 263 (1957); T. Okita, *J. Meteor. Soc. Japan*, **36**, 42 (1958).

6) B. Seely, *Anal. Chem.*, **24**, 576 (1952); N. H. Farlow and F. A. French, *J. Colloid Sci.*, **11**, 184 (1956).

7) I. Sano, Y. Fujitani and T. Sugiyama, Nippon Kagaku Zasshi, **76**, 466 (1955).

8) N. W. Farlow, *Anal. Chem.*, **29**, 883 (1957).

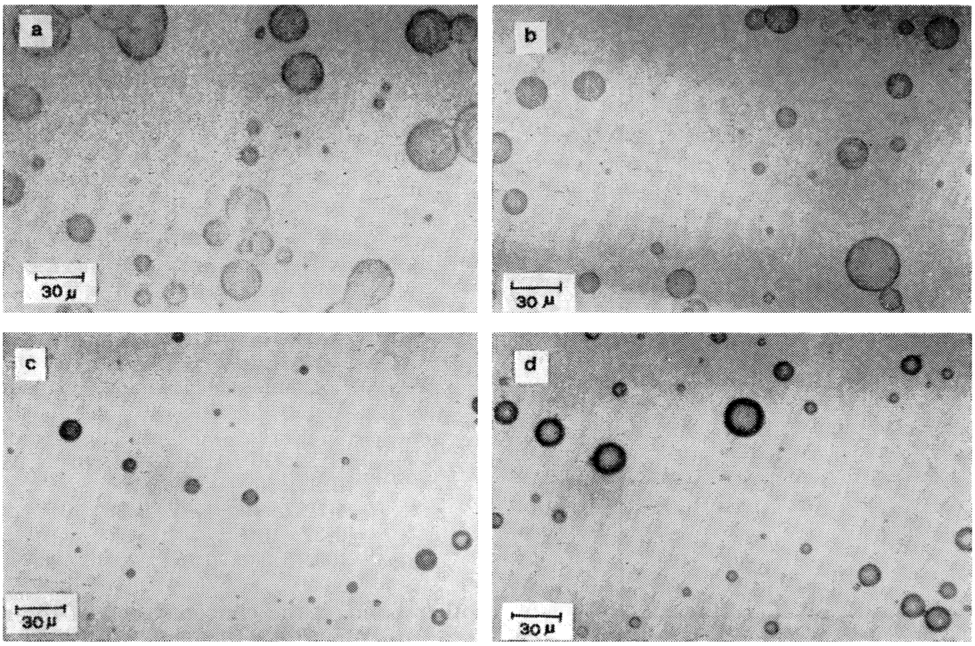

Fig. 2. Spots of 5% NaCl solution droplets after 10 min exposure to ultraviolet light (viewed with ordinary microscope).
(a) on a 2 m*l* $AgNO_3$ solution film (b) on a 3 m*l* $AgNO_3$ solution film
(c) on a 5 m*l* $AgNO_3$ solution film (d) on a 7 m*l* $AgNO_3$ solution film

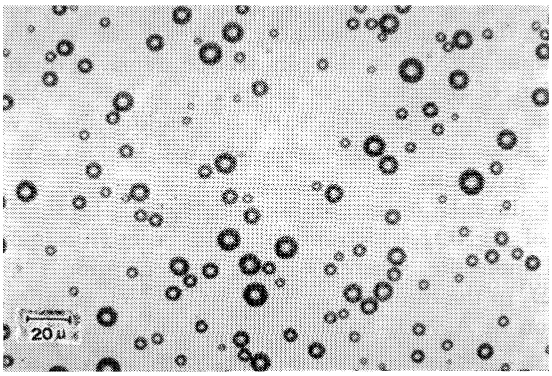

Fig. 3. 5% NaCl solution droplets in oil (viewed under microscope).

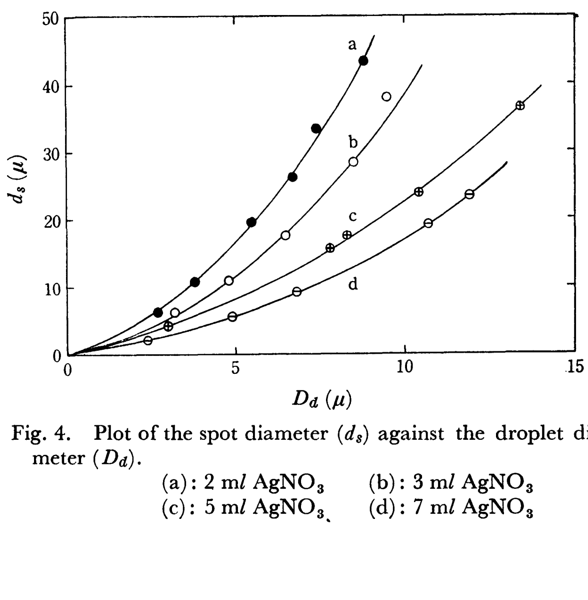

Fig. 4. Plot of the spot diameter (d_s) against the droplet diameter (D_d).
(a): 2 m*l* $AgNO_3$ (b): 3 m*l* $AgNO_3$
(c): 5 m*l* $AgNO_3$ (d): 7 m*l* $AgNO_3$

of PVA–$AgNO_3$ mixture formed on a glass slide is of a constant diameter (2.1 cm) within experimental error, regardless of the reagent concentration in the film. Let us assume as follows:

1) The circular film has a uniform thickness and consists of solid PVA and $AgNO_3$, with a density corresponding to the mixing ratio, 2) the reagent, $AgNO_3$, is distributed homogeneously throughout the film, 3) all the chloride ions in a droplet collected on the film react with silver ions in the film to yield silver chloride, 4) the spots are cylinders which are microscopically viewed and whose heights are equal to the film thickness.

On the basis of these assumptions we obtain the expression

$$D_d^3 = 3/2\rho[\text{Film}]C[\text{AgNO}_3]M[\text{NaCl}]/\rho[\text{NaCl}]C[\text{NaCl}]M[\text{AgNO}_3]Hd_s^2 \quad (1)$$

ρ[Film]: density of film
ρ[NaCl]: density of aqueous NaCl solution
C[NaCl]: concentration of aqueous NaCl solution (wt%)
$C[AgNO_3]$: concentration of $AgNO_3$ in film (wt%)
M[NaCl]: molecular weight of NaCl
$M[AgNO_3]$: molecular weight of $AgNO_3$
H: thickness of film

Since the concentration of the NaCl solution used is constant throughout the whole range of distribution, we get, in place of Eq. (1),

$$D_d^3 = Kd_s^2 \quad (2)$$

K being a constant which is given by $K=10.0\ \rho$[Film] $HC[AgNO_3]$.[9] According to Eq. (2), a plot of log D_d

9) For the values of ρ_{Film}, H and C_{AgNO_3}, *cf.* Table 1. The concentration of the dispersing solution is 5% by weight of NaCl. The term corresponding to $3/2\cdot M_{NaCl}/(\rho_{Film}\cdot C_{AgNO_3}\cdot M_{AgNO_3})$ is then.

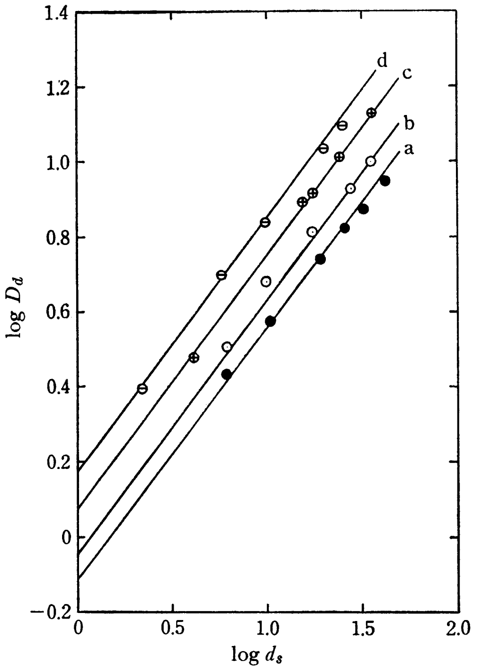

Fig. 5. Plot of log D_d (droplet diameter) against log d_s (spot diameter).
(a): 2 m*l* $AgNO_3$ (b): 3 m*l* $AgNO_3$
(c): 5 m*l* $AgNO_3$ (d): 7 m*l* $AgNO_3$

against log d_s should be linear, and this is found to be actually the case, as is shown in Fig. 5, where the experimental values depicted in Fig. 4 are reproduced as the relation between log D_d and log d_s; these plots are all straight lines parallel with one another and have a slope of 2/3 that might be expected of Eq. (2).

From Eq. (2), we write as follows.

$$D_d{}^3{}_{\text{theor.}} = K_{\text{theor.}} d_s{}^2{}_{\text{theor.}} \tag{3}$$

$$D_d{}^3{}_{\text{exptl.}} = K_{\text{exptl.}} d_s{}^2{}_{\text{exptl.}} \tag{4}$$

It follows from Eqs. (3) and (4), on equating $D_{d\text{exptl.}} = D_{d\text{theor.}}$ that

$$d_{s\ \text{theor.}}/d_{s\ \text{exptl.}} = (K_{\text{exptl.}}/K_{\text{theor.}})^{1/2} = \varepsilon \tag{5}$$

It is to be noted that K's of Eq. (5) can be evaluated either theoretically from Eq. (2) with the known values of ρ[Film], H, and $C[AgNO_3]$ or experimentally as the intercept on the $\log D_d$ axis in Fig. 5. Denote the square root of their ratio by ε. It will give us a measure of a theoretical size of a spot relative to a experimental one. The value of ε thus found is represented in Table 1 and it might be considered from the table that ε increases with the increase in the reagent concentration.

If the above assumptions be valid, we should obtain a value of unity for ε. However, this is not the case actually. First, if the concentration of the reagent is small as in the films (a) and (b), a greater part might have been protected by PVA for it to be of lower reactivity, and consequently, the droplets collected would spread to yield larger spots, giving ε values less than unity. In these cases, we have portion of the reagent remaining unreacted in the spot, and in line with this, we have occasionally found a smaller forming on a larger one with the cases of the droplets collected on the film (c) and (d) which contain $AgNO_3$ thickly. On the other hand, if the concentration of the reagent is large as in the films (c) and (d), a greater part would possess reactivity and we will obtain ε values close to unity; for the films of highest concentrations of reagent, it might be very likely that the precipitate of AgCl is formed densely, preventing the NaCl molecules in the droplet from diffusing to react upon $AgNO_3$ molecules outside the spot; in this case, we would have ε values higher than unity. Secondly, there is the possibility that some $AgNO_3$ in the film will be deprived owing to location, of the chance of meeting with NaCl collected on the film; this will vary, depending upon what shape is assumed by the spot, and will lead to ε values other than unity.

TABLE 1. THE ESTIMATED VALUES OF ρ_{Film}, H, AND C_{AgNO_3} AND THE EXPERIMENTAL VALUE OF ε

Film	ρ_{Film} (g/cc)$^{a)}$	H (μ)$^{b)}$	C_{AgNO} (%)$^{c)}$	ε
(a)	1.56	0.32	22.7	0.60_6
(b)	1.67	0.33	30.6	0.56_9
(c)	1.86	0.35	42.4	0.80_6
(d)	2.03	0.37	50.7	0.93_0

a), b), c) The values of ρ_{Film}, H, and C_{AgNO_3} are obtained, by the relations:

$\rho_{\text{Film}}=(W_{PVA}/\rho_{PVA}+W_{AgNO_3}/\rho_{AgNO_3})/(W_{PVA}+W_{AgNO_3})$

$H=4(W_{PVA}/\rho_{PVA}+W_{AgNO_3}/\rho_{AgNO_3})/\pi D^2$

$C_{AgNO_3}=100\, W_{AgNO_3}/(W_{PVA}+W_{AgNO_3})$

where W and ρ are the weight and density of solid PVA or $AgNO_3$, and D the diameter of the film (2.1 cm). For example, in the case of the reagent concentration of (a),

$\rho_{\text{Film}}=(1.32\times10^{-4}/1.31+3.88\times10^{-5}/4.35)/(1.32\times10^{-4}+3.88\times10^{-5})=1.56$

$H=4(1.32\times10^{-4}/1.31+3.88\times10^{-5}/4.35)/3.14\times2.1^2=0.32\times10^{-4}$

$C_{AgNO_3}=100\times3.88\times10^{-5}/(1.32\times10^{-4}+3.88\times10^{-5})=22.7$

For the sake of formulation, let $1-f(C)$ be the fraction of $AgNO_3$ which might hold reactivity upon a NaCl molecule, where C is the concentration (%) of $AgNO_3$ in the film. Concerning $f(C)$ which signifies the fraction of $AgNO_3$ having no reactivity, we have

$$f(C+\mathrm{d}C) = f(C)\cdot(1-\beta\mathrm{d}C)$$

where βdC is the reactivity of an $AgNO_3$ molecule in the range of concentration of dC. It follows that

$$\mathrm{d}f(C) = -f(C)\cdot\beta\mathrm{d}C$$

which, on integrating under the assumption of β being independent of concentration, gives

TABLE 2. APPLICABILITY OF Eq. (7), $\varepsilon=K\,(1-\alpha\,\mathrm{e}^{-\beta C})$

C	$\varepsilon_{\text{obsd}}$$^{a)}$	$\varepsilon_{\text{calcd}}$ $K=2.0^{b)}$	$\varepsilon_{\text{calcd}}$ $K=5.0^{c)}$	$\varepsilon_{\text{calcd}}$ $K=10.0^{d)}$
0.0	—	0.094	0.18	0.19
22.7	0.61	0.52	0.53	0.54
30.6	0.57	0.65	0.64	0.65
42.4	0.81	0.82	0.81	0.83
50.7	0.93	0.92	0.93	0.94
100.0	—	1.38	1.54	1.62

a) *cf.* Table 1.
b) $\alpha=0.95_3$, $\beta=0.011_2$
c) $\alpha=0.96_4$, $\beta=0.0033_2$
d) $\alpha=0.98_1$, $\beta=0.0015_7$

$$f(C) = \alpha e^{-\beta C} \qquad (6)$$

where α is a constant determinable by the condition that, $f(C)$ has at $C=100\%$, a value γ, differing from zero since it is probable for some $AgNO_3$ to remain unreacted, so that $\alpha=\gamma\, e^{100 \cdot \beta}$. Supposing that the quantity $1/\varepsilon$, which represents the ratio of d_{exptl} to d_{theor} is inversely proportional to the reactivity $1-f(C)$, and is affected by diffusivity composed of lateral (surface) and longitudinal (bulk) components, we obtain

$$\varepsilon = d_{\mathrm{theor}}/d_{\mathrm{exptl}} = k(1-\alpha e^{-\beta C}) \qquad (7)$$

where k is a constant relating to diffusivity.

Table 2 indicates the applicability of Eq. (7). We could not carry out experiments for concentrations lower than 20%, because of the difficulty in finding the spots with sharp impression, or for those higher than 60% owing to production of a film with coarse $AgNO_3$ particles deposited, probably due to its decreasing solubility in drying PVA solution.

For a number of years we have been conducting the research on salt solution aerosol droplets and have here reported the size measurement of chloride containing droplets.[10] Extending the technique, we are now making experiments[11] on sulfate containing droplets whose details will be given in near future.

10) I. Sano and Y. Ueno, *Nippon Kagaku Zasshi*, **89**, 102 (1968); *ibid.*, **90**, 47 (1969); I. Sano, S. Hikita, and Y. Ueno, *ibid.*, **90**, 876 (1969).

11) Presented at the 22nd symposium on Colloid- and Interface Chemistry held at Sendai, Japan, on Nov. 11, 1969, under the auspices of the Chem. Soc. of Japan; read before the spring meeting on Cloud Physics held at Nagoya, Japan, on March 6, 1970, under the auspices of the Meteorol Soc. of Japan.